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**Physical and
Chemical
Reference Data**

Monograph No. 9

NIST-JANAF Thermochemical Tables
Fourth Edition
Part I, Al-Co

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National Institute of Standards and Technology
Gaithersburg, Maryland 20899-0001







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Foreword

The Journal of Physical and Chemical Reference Data is published jointly by the American Institute of Physics and the American Chemical Society for the National Institute of Standards and Technology. Its objective is to provide critically evaluated physical and chemical property data, fully documented as to the original sources and the criteria used for evaluation. One of the principal sources of material for the journal is the National Standard Reference Data System (NSRDS), a program coordinated by NIST for the purpose of promoting the compilation and critical evaluation of property data.

The regular issues of the Journal of Physical and Chemical Reference Data are published bimonthly and contain compilations and critical data reviews of moderate length. Longer works, volumes of collected tables, and other material unsuited to a periodical format have previously been published as Supplements to the Journal. In 1989 the generic title of these works was changed to Monograph, reflecting their character as independent publications.

This volume, the Fourth Edition of the NIST-JANAF Thermochemical Tables, is Monograph No. 9 in the current series. Its predecessor, the Third Edition, was referred to as a Supplement. Of the over 500 titles published in the last 25 years, the articles dealing with the JANAF Thermochemical Tables have been the most widely distributed and used.

The Journal of Physical and Chemical Reference Data is therefore pleased to be able to publish this Fourth Edition of the NIST-JANAF Thermochemical Tables. There are two important features of this edition. First, the acronym NIST has been added to the title of this activity. This is due to the fact that during the past 10 years, NIST has been the leading financial supporter for this effort. Additionally, this project is now housed within the Physical and Chemical Properties Division at NIST. Second, the Fourth Edition contains additional species not included in the Third Edition. A number of typographical errors have also been corrected.

Malcolm W. Chase, Jr., Editor
Journal of Physical and Chemical Reference Data

Preface to the First Edition

Beginning in the mid-1950s, when elements other that the conventional carbon, hydrogen, oxygen, nitrogen, chlorine, and fluorine came into consideration as rocket propellant ingredients, formidable difficulties were encountered in conducting rigorous theoretical performance calculations for these new propellants. The first major problem was the calculational technique. The second was the lack of accurate thermodynamic data.

By the end of 1959, the calculational technique problem had been substantially resolved by applying the method of minimization of free energy to large, high speed digital computers. At this point the calculations became as accurate as the thermodynamic data upon which they were based. However, serious gaps were present in the available data. For propellant ingredients, only the standard heat of formation is required to conduct a performance calculation. However, this must be known to a high degree of accuracy. For combustion products, the enthalpy and entropy must be known, as a function of temperature, in addition to the standard heat of formation.

In order to resolve the problem, a substantial experimental thermodynamic research program was initiated under the sponsorship and technical direction of Project PRINCIPIA of the Advanced Research Projects Agency. Simultaneously, a project was initiated to critically evaluate and compile consistent tables of thermodynamic properties of propellant combustion products for use by the aerospace industry. This project, known as the JANAF Thermochemical Tables, was undertaken by the Dow Chemical Company. Since the objective of the project was to have one single source of best available data prepared for use by the entire industry, the JANAF Thermochemical Panel undertook the task of furnishing a critical review of the Tables prior to their publication and distribution. This approach was designed to ensure that the Tables be of the highest possible quality.

Washington, DC
July 1964

C. V. Mock
Advance Research Projects Agency

Preface to the Second Edition

It is appropriate to call attention to some of the reasons for the phenomenal success of the JANAF Thermochemical Tables in achieving, first, the initial limited objective of providing the standard data for the chemical rocket propulsion industry, and later, upon publication, worldwide recognition as thermodynamic reference data of the highest quality and timeliness.

First, and most obvious, there was the selection and continued support of a highly competent evaluation team, themselves engaged in a broad spectrum of thermodynamic research. The personnel of the Thermal Research Laboratory of the Dow Chemical Company, under the direction of Dr. D. R. Stull and Dr. H. Prophet, have filled this role to a degree of excellence not likely to be exceeded anywhere. Moreover, the group has heroically remained productive in spite of many battles to retain continuing support, and the actual sharp reduction of funding over the past two years to a less-than-viable level.

A second important factor is the unusual approach to format, evaluation, and distribution of the Tables, as it has been followed since their inception. The primary distribution is in frequently issued loose-leaf supplements. Each previously issued table may thus be revised as often as necessary to take account of improved data. Each loose-leaf table is accompanied on its reverse side by a complete explanation of the selection of the key data, together with all references.

The third vital distinction of these tables has been the existence of a continuing cognizant working group composed of technological users of data, thermodynamicists, and government sponsors of both research and development. Independent prepublication review of the Tables has been an important contribution of some of the members of this group; but its annual technical meetings have resulted in even more far-reaching benefits. Together, the users and generators of data have been able to establish realistic priorities for the species to be included in the Tables; at the same time the course of experimental research has been guided by the demonstration of absence or inadequacy of needed data. Although the working group no longer enjoys official recognition, the members and participants have enthusiastically volunteered to continue meeting in this important work.

Special words of appreciation are due to Dr. Charles W. Beckett, who has lined up all the technical presentations at the last six annual meetings of the working group; and to Mr. Curtis C. Selph who has served with wisdom and insight as the Air Force project monitor for the JANAF Thermochemical Tables contracts.

Arlington, Virginia
October 1970

Joseph F. Masi
Air Force Office of Scientifc Research

Preface to the Third Edition

The United States Air Force (USAF) for more than 20 years has supported, and continues to support, the preparation of the JANAF Thermochemical Tables. The Tables, funded through Air Force Office of Scientific Research (AFOSR), were intended originally for calculating performance of thermochemical reactors, such as rocket engines. The computation of such performance figures as thrust and exhaust temperature for a rocket require data such as those in these tables.

The Department of Energy (DOE) [and predecessor agencies Energy Research and Development Administration (ERDA), Office of Coal Research, and Bureau of Mines] became interested in the JANAF Thermochemical Tables because the tables had become *the* benchmark for thermochemical data for performance calculations. However, reactors and reagents of interest to DOE are different from those of the USAF.

The Department of Energy needs performance calculations for several types of reactors that are of interest in fossil fuel research. These reactors include air pollution control equipment, automotive internal combustion engines, coal gasifiers and furnaces, fuel cells, liquefaction reactors and their catalyst structures, and magnetohydrodynamic generators. For example, researchers might wish to calculate the first-law efficiency of an electrical power plant, or the exhaust concentration of a pollutant such as sulfur dioxide or mercury.

The calculations needed for DOE interests have as their basis the same mathematics and physical chemistry as required for the performance calculations of USAF interest, but DOE needs tables for more and different chemicals. For example, a rocket fuel probably would not be formulated to include silicon or sulfur, but all known coals contain both these elements. Silicon and sulfur are two distinguishing elements accounting for many peculiarities of coal utilization chemistry (which include the chemistries of all the polysulfides, thiosulfates, alums, etc., and of the many glasses and mixed silicates).

For more than six years (1975-1982), Dow Chemical has worked on separate but complementary contracts to satisfy the thermochemical tables' needs of USAF and DOE. This Third Edition of the JANAF Thermochemical Tables presents the results of these efforts, along with reformatted versions of previous tables, to provide an extensive set of tables of wide utility that are consistent with each other and with the requirements of thermodynamic theory.

There remain open questions about calculation methods for equilibrium problems. I mention this because the foreword for the First Edition endorses free-energy-minimization as if it solved all problems of numerical instability. I would remove this apparent endorsement as confusing, inappropriate, and uninformative for users of these tables. For example, the paper of White, Johnson, and Dantzig [J. Phys. Chem. 28, 751 (1958)] does not address numeric stability in any way. Removing this endorsement would not diminish Dow's JANAF work.

I want to thank several people. All the Dow personnel did outstanding work, and several fellow federal employees helped with orchestrating the various contracts to nourish this finished product. In AFOSR, Joseph Masi, Robert Sperlein, and Leonard Caveny were always encouraging. Within the Bureau of Mines, then in ERDA, and finally in DOE, I was helped and encouraged by Daniel Bienstock, Irving Wender, Jim Hendrie, Alex Mills, Kermit Woodcock, and Mike Hogan.

Pittsburgh, Pennsylvania
April 1984

Francis E. Spencer, Jr.
Pittsburgh Energy Technology Center
Department of Energy

Preface to the Fourth Edition

As the Standard Reference Data Program at the National Institute of Standards and Technology approaches its thirtieth year, the release of the fourth edition of the NIST-JANAF Thermochemical Tables provides not only a major update to this important reference work, but also a symbol of the long-term dedication of NIST and its scientists to improving the quality and accessibility of scientific data.

First, let us address the importance of the NIST-JANAF Thermochemical Tables. This fourth edition continues to serve its original community, that is, the scientists and engineers who design rocket propellants. For this use, the updated tables offer additional species and in some cases, corrected data for older species. The use of the NIST-JANAF Thermochemical Tables, however, now far transcends the original need. Today, as modeling of complex chemical processes is becoming routine, NIST-JANAF information is an invaluable resource for reliable thermochemical data. Care of preparation and critical evaluation still form the essence of the compilation. New users are demanding new species, and the tables are being responsive to those demands. There is no other comprehensive source of temperature dependent thermochemical data for inorganic species, certainly none of such high quality.

From another perspective, this edition is an important milestone, for this publication again demonstrates the long-term commitment by NIST to providing evaluated scientific and technical data through its Standard Reference Data Program. Established by the Standard Reference Data Act of 1968, the program today operates data evaluation activities in most areas of NIST's scientific and engineering work.

The Physical and Chemical Properties Division of the NIST Chemical Science and Technology Laboratory (and its predecessors) has for many decades been committed to providing critically evaluated thermochemical data. The "International Critical Tables," "The NIST Tables of Chemical Thermodynamic Properties; Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units," and now the "NIST-JANAF Thermochemical Tables" are prime examples of the fruit of this commitment.

The scientific effort required to produce critically evaluated data is difficult for the non-specialist to appreciate. Even though many thermochemical, experimental, and theoretical techniques are well-developed, rarely does one individual measurement or calculation provide "property data." Instead most properties of substances come from repeated measurements, done over time and by different groups, and it is the job of the data evaluator to reconcile conflicting information and extract standard reference data of the type presented in the NIST-JANAF Thermochemical Tables. Malcolm W. Chase was the responsible scientist for the third and fourth editions, and the high quality of data contained in this latest edition is a tribute to his experience and skills as an evaluator.

Finally, it should be noted that the change of name to the NIST-JANAF Thermochemical Tables is the result of greater involvement by NIST in supporting the new edition. Data work at NIST is a team effort, in this case, of the Physical and Chemical Properties Division and the Standard Reference Data Program. The NIST-JANAF Thermochemical Tables represent a renewed dedication on the part of both organizations to make sure that scientists and engineers in industry, government, and academe have access to numeric recommendations of known reliability, for use in research, development, and related technical activities. NIST is proud to present this data compilation to the technical community.

Gaithersburg, Maryland
January 1998

Richard F. Kayser
Chief, Physical and Chemical Properties Division
and
John R. Rumble
Chief, Standard Reference Data Program

Contents

Foreword III
Preface to the First Edition V
Preface to the Second Edition VII
Preface to the Third Edition IX
Preface to the Fourth Edition XI
1. Introduction 3
2. History of the JANAF Thermochemical Tables 3
2.1. JANAF Panel Members and Reviewers 4
2.2. Project Personnel 5
3. Notation and Terminology 5
3.1. Definition of the Standard State 6
3.2. Symbols 6
3.3. Relative Atomic Masses and Natural Isotopic Composition of the Elements 8
3.4. Fundamental Constants and Conversion Factors 10
3.5. Temperature Scale 10
4. Reference States and Conversions 11
4.1. Reference State 11
4.2. Single-Phase and Multiphase Tables 11
4.3. Conversion to SI Units and the Standard-State Pressure 12
4.4. Boiling Temperature and the Standard-State Pressure 13
5. Evaluation of Thermodynamic Data 13
5.1. General Evaluation Techniques 14
6. Construction of the Tables 16
6.1. Calculational Methods 17
6.1.1. Ideal Monatomic Gas 17
6.1.2. Ideal Diatomic Gas 18
6.1.3. Linear Polyatomic Molecule 18
6.1.4. Nonlinear Polyatomic Molecule 18
6.2. Dates 19
7. Additions, Revisions, and Corrections 19
8. Acknowledgments 19
9. References 20
10. Indices to the Tables 21
10.1. Description of the Chemical Formula Index to the NIST-JANAF Thermochemical Tables 21
10.2. Description of the Chemical Name Index to the NIST-JANAF Thermochemical Tables 21
10.3. Chemical Formula Index 23
10.4. Chemical Name Index 41
11. NIST-JANAF Thermochemical Tables (Arranged as in Chemical Formula Index) 59

The Table of Contents is a cumulative listing of Parts I and II.
Part I contains pp. I–XI and 1–957 (Tables for Al-Co), and
Part II contains pp. 959–1951 (Tables for Cr-Zr).

1. Introduction

The Fourth Edition to the NIST-JANAF Thermochemical Tables has been assembled under the sponsorship of the Standard Reference Data Program at the National Institute of Standards and Technology. It contains tables of recommended temperature-dependent values for the standard enthalpy of formation, Gibbs (free) energy of formation, the logarithm of the equilibrium constant of formation, the heat capacity, entropy, enthalpy, and Gibbs energy function for 48 elements and many of their compounds. This publication is a current collection of all tables issued through 1997 under contracts with the U.S. Department of Energy and the U.S. Air Force Office of Scientific Research, NASA, the JANNAF Combustion Subcommittee, and the Standard Reference Data Program. It supersedes the Third Edition,[1] which, in turn, superseded the Second Edition,[2] and the four supplemental updates published in the Journal of Physical and Chemical Reference Data.[3–6]

Numerous new and revised thermochemical tables are included in this collection. [Refer to Sec. 7] Unlike the Third Edition of these tables, the Fourth Edition is not a rewriting and a recalculation of all the tables; no attempt has been made to reanalyze the data for all tables. A continued effort was made to correct all typographical errors from previous publications and to force an increasingly consistent style and format. The tables adhere more closely to the current IUPAC recommendations on symbols and notation. The tables, as published in the previous Third Edition, are all based on the 1981 IUPAC[7a] and 1973 CODATA[8a] recommendations for relative molecular masses and fundamental constants. As a result, a comparison of a table in the Fourth and Third Editions and their previously published form (i.e., same revision date) will reveal differences; however, these result from the adjustments mentioned above rather than from a reanalysis of the data. For tables issued since the Third Edition, values of the fundamental constants and relative molecular masses are based on the 1993 IUPAC[7b] and 1986 CODATA[8b] recommendations. It should be noted that there is a revised set of recommendations for the fundamental constants due in late 1998. Also, it should be remembered that the relative molecular masses are reassessed and updated every two years. The effects of these changes will be discussed later.

All thermal functions have been calculated using the same auxiliary data. Following a similar procedure for the formation properties has introduced slight inconsistencies in those tables for which the formation properties were derived from the previous thermal functions.

2. History of the JANAF Thermochemical Tables

Between 1955 and 1958, severe difficulties were encountered by individuals attempting to conduct rigorous performance calculations for propellant systems that gave multiphase combustion products characterized by complex chemical and thermal equilibria. Several of these individuals approached the Armed Services requesting that a group be assembled to assess the validity of the calculation methods and thermochemical data which were being employed at that time.

January 1958, the Armed Services jointly instructed the Solid Propellant Information Agency to organize the Joint Army-Navy-Air Force Ad Hoc Panel on Performance Calculation Methods and Thermodynamic Data. This panel, which consisted of 38 representatives of military facilities, defense contractors, and research organizations, terminated its operations in June 1959, with a recommendation that future activities under its purview could more appropriately be handled by a smaller working group. An additional recommendation included in the panel's final report was that this working group initiate the establishment of a thermochemical data compilation, evaluation, and dissemination program utilizing the available personnel and facilities of the Dow Chemical Company.

On 1 September 1959, the Joint Army-Navy-Air Force Thermochemical Panel was formed under the sponsorship of the Bureau of Naval Weapons, Department of the Navy; Office, Chief of Ordnance, Department of the Army; Air Research and Development Command, Department of the Air Force; and the Advanced Research Projects Agency, Department of Defense. The panel operated in accordance with the Rules of Operations of Solid Propellant Panels as adopted by representatives of the above offices on 1 September 1959.

The JANAF Thermochemical Panel Membership, which consisted originally of approximately 15 individuals with special experience in the technological subject under panel purview, met at the Pentagon on 16 November 1959, at which time plans for the thermochemical compilation project were reviewed and the project formally initiated.

Urgency required that a large set of consistent tables be assembled as quickly as possible. Computer programs had to be developed, and at first it was not possible to adequately assess the input information for every table. When the original data were evaluated, the table was printed on white paper; otherwise, the table was printed on gray paper. By the end of 1960, the first set was ready for distribution to some 1000 qualified recipients. For a number of years, at the end of each quarter, a supplement was issued which contained additional tables and revised tables. Some of the gray tables were revised to white tables.

The distribution of quarterly supplements continued through 31 December 1967, at which time the distribution shifted to semiannual supplements. Simultaneously, the tables were prepared under the auspices of the Interagency Chemical Rocket Propulsion Group, Working Group on Thermochemistry. On 31 December 1970, the working group became the Ad Hoc Working Group on Thermochemistry. By 30 June 1971, the tables project was sponsored by the U. S. Air Force Office of Scientific Research (AFOSR) and prepared under the advice and assistance of a thermochemistry group, referred to as reviewers. In late 1976, the U.S. Energy Research and Development Administration (now reorganized to be the U.S. Department of Energy) joined in sponsoring the tables.

The distribution reverted to a quarterly schedule with an expanded list of reviewers. AFOSR and DOE jointly funded this activity until late 1982. AFOSR continued as the sole sponsor until 1986.

From 1967 through 1985, the JANAF Thermochemical Tables have been sponsored by the U.S. Air Force Office of Scientific Research and the U.S. Department of Energy under the following contracts:

Air Force Contracts	Department of Energy Contracts
F04611-67-C-0009	DE AC22-76ET10637
F04611-70-C-0028	DE AC22-81PC41514
F44620-70-C-0104	
F44620-75-C-0048	
F49620-82-C-0016	

In addition, there was an interagency transfer of funds, from AFOSR to DOE, in the period 1976-1981.

In 1970 the output of the JANAF project was incorporated into the National Standard Reference Data System, a national program on evaluated physical and chemical data which is coordinated by the National Institute of Standards and Technology. Since that time the JANAF Thermochemical Tables have been disseminated as part of the Journal of Physical and Chemical Reference Data. Loose-leaf supplements were terminated with the publication of the Third Edition.

In January 1986, the JANAF Thermochemical Tables project transferred from the Dow Chemical Company to the National Institute of Standards and Technology. Funding since 1986 has come in large part from the Standard Reference Data Program, with additional contracts with NASA, JANNAF Combustion Subcommittee, and the U. S. Army. Updates to this Fourth Edition are being made in separate articles, many of which (but not all) are to be published in the Journal of Physical and Chemical Reference Data.

2.1. Members of the JANAF Thermochemical Panel (1959-1961) and the JANAF Thermochemical Working Group (1961-1964)

T. O. Dobbins, Advanced Research Projects Agency (Past Chairman)

W. H. Jones, Institute for Defense Analyses; Aerospace Corporation (Past Chairman)

W. G. May, Institute for Defense Analyses; Esso Research and Engineering Company (Past Chairman)

C. W. Beckett, National Bureau of Standards (Vice Chairman)

G. W. Avery, Chemical Propulsion Information Agency (Past Secretary)

B. K. Farris, Chemical Propulsion Information Agency (Past Secretary)

T. L. Reedy, Chemical Propulsion Information Agency (Secretary)

B. J. Alley, Army Materiel Command

P. W. Bender, University of Wisconsin

W. A. Bernett, Bureau of Naval Weapons

B. Brown, Hercules Powder Company

C. L. Funk, Jet Propulsion Laboratory

J. S. Gordon, Thiokol Chemical Corporation

L. J. Gordon, Aerojet-General Corporation

S. A. Greene, North American Aviation

C. B. Henderson, Atlantic Research Corporation

D. L. Hildenbrand, Philco Corporation

J. L. Margrave, University of Wisconsin

J. P. McCullough, U.S. Bureau of Mines

P. L. Nichols, Jr., Jet Propulsion Laboratory

C. C. Selph, Air Force Systems Command

D. R. Stull, Dow Chemical Company

The Thermochemical Working Group of the Interagency Chemical Rocket Propulsion Group (ICRPG) has consisted of the following at various times during its existence (1964-1969).

Members

J. F. Masi, Air Force Office of Scientific Research (Chairman)

C. W. Beckett, National Bureau of Standards (Vice Chairman)

T. O. Dobbins, Advanced Research Projects Agency

S. Gordon, National Aeronautics and Space Administration

R. Jackel, Office of Naval Research

J. Murrin, Naval Ordnance Systems Command

R. Odom, Army Materiel Command

C. C. Selph, Air Force Rocket Propulsion Laboratory

D. Squire, Army Research Office

Participants

G. S. Bahn, Marquardt Corporation

B. Brown, Hercules, Inc.

H. F. Calcote, AeroChem Research Laboratories

J. P. Coughlin, Aerojet-General Corporation

J. S. Gordon, Atlantic Research Corporation

D. R. Douslin, U.S. Bureau of Mines

M. Farber, Space Sciences, Inc.

R. M. Fristrom, Applied Physics Laboratory

C. B. Henderson, Atlantic Research Corporation

D. L. Hildenbrand, Douglas Aircraft Company

J. L. Margrave, Rice University

W. G. May, Esso Research and Engineering Company

W. Mitchell, Thiokol Chemical Corporation

C. F. Robillard, Jet Propulsion Laboratory

L. Schieler, Aerospace Corporation

C. H. Shomate, Naval Weapons Center

D. R. Stull, Dow Chemical Company

M. Zimmer, Naval Ordnance Station

Secretariat (Chemical Propulsion Information Agency)

T. Gilliland

M. McCormack

T. L. Reedy

In the period 1969-1984, various scientists donated their time to critique the loose-leaf supplements to the JANAF

Thermochemical Tables prior to their distribution. Their efforts certainly increased the quality of the tables. As of January 1982 the reviewers of the JANAF Thermochemical Tables were:

DOE Reviewers

Francis E. Spencer, Jr., DOE/PETC Combustion Technical Division

Joseph W. Martin, DOE/METC, Coal Projects Management Division

Thomas C. Ehlert, Marquette University

R. Howald, Montana State University

Fred C. Fehsenfeld, NOAA Environmental Research Laboratory

Gerd Rosenblatt, Los Alamos National Laboratory

Martin Steinberg, University of California, Santa Barbara

C. B. Alcock, University of Toronto

J. Brian Pedley, University of Sussex

Malcolm H. Rand, AERE Harwell.

AFOSR Reviewers

David White, University of Pennsylvania

W. L. Worrell, University of Pennsylvania

Stanley Abramowitz, U.S. National Bureau of Standards

David A. Ditmars, U.S. National Bureau of Standards

H. M. Rosenstock, U.S. National Bureau of Standards

Leonard Caveny, AFOSR/NA, Bolling AFB

John L. Haas, Jr., U.S. Geological Survey

John S. Gordon, TRW Energy Systems

Joseph F. Masi, AFOSR (retired)

Sanford Gordon, NASA Lewis Research Center

Edgar F. Westrum, Jr., University of Michigan

William D. Good, DOE/BETC

R. H. Hauge, Rice University

John L. Margrave, Rice University

Milton Farber, Space Sciences, Inc.

Curtis C. Selph, AFRPL/LKDH

Donald L. Hildenbrand, SRI International

Leo Brewer, University of California

James P. Coughlin, Aerojet Tactical Systems Co.

N. A. Gokcen, U.S. Bureau of Mines, AMRC

2.2. Project Personnel

The Tables began under the direction of Daniel R. Stull in 1959. Major contributions in the first two years were made by Thomas E. Dergazarian, Samuel Levine, and Louis A. DuPlessis. In 1969 Harold Prophet succeeded Daniel R. Stull as project director and continued in that position until his untimely death in late 1972. Malcolm W. Chase has been project director since late 1972.

The following professional personnel of the Dow Chemical Company have been involved in the preparation of the JANAF Thermochemical Tables:

Project Director, D. R. Stull	1959-1969
Project Director, H. Prophet	1969-1972
Project Director, M. W. Chase	1972-1985
P. A. Andreozzi	1980-83
J. Chao	1961-69
J. L. Curnutt	1969-79
T. E. Dergazarian	1959-63
C. A. Davies	1980-85
J. R. Downey, Jr.	1976-85
L. A. DuPlessis	1960-61
D. J. Frurip	1983-85
S. T. Hadden	1962
A. T. Hu	1965-70
B. H. Justice	1964
G. C. Karris	1965-68
S. Levine	1960-61
R. A. McDonald	1971-85
F. L. Oetting	1961
R. S. Orehotsky	1963-64
R. V. Petrella	1961-62
E. W. Phillips	1963-66
J. A. Rizos	1962-63
G. C. Sinke	1962,65,69,70
A. C. Swanson	1962-64
A. N. Syverud	1963-84
H. K. Unger	1963-64
E. A. Valenzuela	1975-81
L. C. Walker	1971-73
D. U. Webb	1967-68
S. K. Wollert	1963-65

We also wish to mention the valuable assistance in the typing of these Tables of Norma Dumont, 1959-64; Viola E. Harrington, 1964-66; Carol S. Scheffier, 1966-67; Wildene B. Harris, 1967-68; Mary J. Walter, 1968-71; and for the time period of 1971-78 of Joan Weldon, Cheri Snow, Barbara Boman, Sheila Knoerr, Patricia Grochowski, and Lisa Ittner. For the years 1978–1985 Betty Clark, Jan Crouch, and Rhoda Toth have typed the tables. Isabel Carr provided valuable services to the group in abstracting, searching and ordering documents, and proofreading the Tables for the Second Edition. For the period 1978–1985 Dana Donley, Debbie Simpson, Marge Sheets, Barbara Meier, Diana Scribner, and Anne Schmidt have provided similar assistance. Milton D. Marks was very instrumental in all computer aspects of this project in the 1980's.

In the time period of 1985 to 1998, technical contributions have been made by Stanley Abramowitz and David Neumann. Additional help in literature searching, data collection, and data entry has been provided by Cindy Jackson, Rhoda Levin, and Sabina Crisen.

3. Notation and Terminology

The symbols and terminology for physicochemical quantities and units are those recommended by IUPAC through its Physical Chemistry Division.[9,10] For the thermodynamic notation needed but not specified by these two sources, the recom-

mendations of the Bulletin of Chemical Thermodynamics[11] are used. Similarly, for spectroscopic nomenclature, the common practice of Moore[12] and Herzberg[13–16] is followed.

3.1. Definition of the Standard State

This description of the standard state is an abbreviated version of that given by the IUPAC Physical Chemistry Division.[10]

Absolute values of some thermodynamic quantities are unknown. Only changes in values caused by changes in parameters such as temperature and pressure can be determined. It is therefore important to define a base line for substances, to which the effect of such variations may be referred. The standard state is such a base line. The properties of these standard states are indicated by use of the symbol°. For a pure substance the concept of standard state applies to the substance in a well-defined state of aggregation at a well-defined but arbitrarily chosen standard pressure.

Historically, the defined pressure for the standard state, i.e., the standard-state pressure, had been one standard atmosphere (101 325 Pa). With the growing use of SI units, continued use of the atmosphere is inconvenient. IUPAC has recommended that the thermodynamic data should be reported for a defined standard-state pressure of 100 000 Pa. The standard-state pressure in general is symbolized as $p°$. Previously all JANAF thermochemical publications prior to the Third Edition, $p°$ was taken as 1 atm. Beginning with the Third Edition of the JANAF Thermochemical Tables, $p°$ is taken as 100 000 Pa (1 bar). It should be understood that the present change in the standard-state pressure carries no implication for "standard pressures" used in other contexts, e.g., the convention that "normal boiling points" refer to a pressure of 101 325 Pa (1 atm).

The change of the customary value of $p°$ from 1 atm (101 325 Pa) to 1 bar (100 000 Pa) results in small alterations in standard values of some thermodynamic quantities for all substances. For condensed phases the magnitude of these alterations is nearly always negligible in comparison with the uncertainty of current data. However, the alterations in values of entropy and the Gibbs energy function for a pure gaseous substance and of the Gibbs energy of reaction for a reaction involving gaseous species may not be negligible. This will be discussed in detail later (Sec. 4.3).

Hence, in all the tables appearing in this publication the standard state for a pure gaseous substance is that of the substance as an (hypothetical) ideal gas at 1 bar; the standard state for a pure liquid substance is that of the pure liquid under a pressure of 1 bar; the standard state for a pure solid substance is that of the pure crystalline substance under a pressure of 1 bar.

Since an enthalpy measurement is made as a difference between an initial and a final state, the reference temperature for enthalpy must be arbitrarily chosen. It is taken to be 298.15 K in all tables. Refer to the discussion of types of thermochemical tables for further details (Secs. 4.2 and 6).

3.2. Symbols

States of aggregation

The symbols and their corresponding descriptions for the states of aggregation are exactly those given by IUPAC.[9,10] They are rewritten here for the convenience of the reader.

Single letters are used to denote the three basic states of aggregation, gas, liquid, and solid, while combinations of letters are used for more subtle descriptions of states.

g	gas or a vapor
l	liquid
s	solid
cd	condensed phase (i.e., either the solid or the liquid state)
fl	fluid (i.e., either the gaseous or the liquid state)
cr	crystalline solid; where polymorphism occurs, it may be necessary to augment the symbol cr with a descriptor for the crystal modification under discussion; the preferred descriptors are Roman numerals, with textual definition of the crystallographic significance of the numerals used
am	amorphous solid
vit	vitreous substance (a glass)
mon	monomeric form
pol	polymeric form (in many cases the monomeric or polymeric character of the entity will be clear from the context without the symbol and the symbol should be used only in cases where ambiguity might result)
sln	solution; in many contexts it will be clear whether a liquid solution or a solid solution is meant, but where this is unclear it must be made clear by supplemental notation
aq	solution in which water is the solvent (an aqueous solution); in the past this symbol has sometimes been used to denote an infinitely dilute aqueous solution, but infinite dilution should henceforward be denoted by the extra symbol ∞.
sat	saturated; the state of equilibrium between phases, whether of a pure substance or a system of more than one component.

Processes

The symbols and their corresponding descriptions for processes are exactly those given by IUPAC.[9,10] The remaining six processes are denoted by the symbols recommended by the Bulletin of Chemical Thermodynamics.[11] The use of special symbols to denote a process are as follows:

vap	vaporization (evaporation) of a liquid
sub	sublimation (evaporation) of a solid
fus	melting (fusion) of a solid
trs	transition of one solid phase to another
mix	the mixing of fluids
sol	the process of solution (dissolution)
r	chemical reaction in general

c	combustion reaction; also can denote critical properties
f	a reaction in which a compound is formed from its elements (formation)
at	a process in which a substance is separated into its constituent gaseous atoms (atomization)
dcm	a process in which a substance decomposes (not given by IUPAC)
dso	a process in which a substance dissociates (not given by IUPAC)
dim	a process in which a substance dimerizes (not given by IUPAC)
dil	the dilution of a solution
gt	glass transition (not given by IUPAC)
hyd	hydrolysis (not given by IUPAC)
ion	ionization (not given by IUPAC)

Fundamental Constants

c	speed of light in vacuum
h	Planck constant
N_A	Avogadro constant
e	elementary charge
F	Faraday constant
R	gas constant
T_0	absolute temperature of "ice point"
k	Boltzmann constant
c_2	second radiation constant

Units

cal	calorie
eV	electron volt
g-atom	a mole of atoms
J	joule
K	kelvin
kcal	kilocalorie
kJ	kilojoule
mol	mole
L	liter

Mathematical Quantities

ln logarithm to the base e
lg logarithm to the base 10 (log)

Spectroscopic Quantities

The spectroscopic symbols, use, and description follow the well-established practices of Moore[12] and Herzberg.[13–16] These sources provide more extensive discussion as to the meaning and use of the various spectroscopic quantities.

The measured quantities often are reported in the literature for a specific isotopic molecule. The thermochemical tables in this publication normally use spectroscopic information for a natural isotopic abundance "molecule." Care should be exercised in noting to which molecule the spectroscopic data pertains.

Å	Angstrom
AP	appearance potential
B_0, B_e	rotational constant
D	centrifugal distortion constant
D_0°	dissociation energy is defined as the enthalpy of the ground-state products relative to the lowest existing level of the molecule; $D_0^\circ = \Delta_{at}H^\circ$ (0 K).
E_i	ionization energy (IP)
E_{ea}	electron affinity (EA)
g_i	quantum (or statistical) weight of the ith electronic state; quantity is the product of the spin multiplicity and state degeneracy of the electronic level under consideration
I_A, I_B, I_C	principal moments of inertia of a molecule
k	Hooke's law force constant
n	number of potential maxima in an internal rotation; also refers to principal quantum number in describing energy levels of atoms
N	number of atoms in molecule
r_e	internuclear distance (for the "equilibrium" structure of the molecule)
V_0	potential barrier to internal rotation
α_e	first-order rotation-vibration interaction constant
ϵ_i	ith electronic energy level
σ	symmetry number
μ	reduced mass of the molecule
ν	observed vibrational fundamental
ω_e	vibrational fundamental for infinitesimal amplitude
$\omega_e x_e$, $\omega_e y_e$	vibrational anharmonicity constants

Thermodynamic and Other Quantities

A_r	relative atomic mass (atomic weight)
C_p	molar heat capacity at constant pressure
C_s	molar heat capacity at saturation
ΔU	change in internal energy
ΔG	change in Gibbs energy, $G = H - TS = U + PV - TS$
ΔH	change in enthalpy, $H = U + PV$
K	equilibrium constant
M_r	relative molecular mass (molecular weight)
p	pressure
T	temperature, in kelvin
t	temperature, in degrees Celsius (°C)
V	volume
Δ	indicates the increment in a given property for a given process or reaction, taken as the value for the final state (or sum for the products) less that for the initial state (or sum for reactants).
$\Delta_f H^\circ$	represents the standard enthalpy of formation, which is the increment in enthalpy associated with the reaction of forming the given compound from its elements in their reference states, with each substance in its thermodynamic standard state at the given temperature.

Experimental Method Techniques

dsc	differential scanning calorimetry
dta	differential thermal analysis
emf	electromotive force
esr	electron spin resonance
glc	gas-liquid chromatography
gpc	gel permeation chromatography
ir	infrared spectroscopy
nmr	nuclear magnetic resonance
tga	thermogravimetric analysis
LLE	liquid-liquid equilibria
VLE	vapor-liquid equilibria
VP/xxxx	vapor pressure/experimental technique
/ebul	= ebulliometric
/Knud	= Knudsen effusion
/stat	= static
/Kems	= Knudsen effusion-mass spectrometry
/Kete	= Knudsen effusion-torsion effusion
/tran	= transpiration
/Lang	= Langmuir free evaporation
/Lams	= Langmuir-mass spectrometry

3.3. Relative Atomic Masses and Natural Isotopic Composition of the Elements

The Table of Atomic Weights of the Elements 1981[7a] is reprinted below. Added to this list are the relative atomic masses for the electron (e-) and deuterium (D). The relative atomic mass for the electron is given by Cohen and Taylor.[8a]

The 1981 report on atomic weights[17] includes a complete review of the natural isotopic composition of the elements and also tabulates the relative atomic masses for selected radioisotopes. This information is required for the conversion of spectroscopic data from that corresponding to specific isotopes to the naturally occurring isotopic abundance. For tabulations issued with dates later than 1985, more recent values are used.

As in the IUPAC report, values in parentheses are used for radioactive elements whose relative masses cannot be quoted exactly without knowledge of the origin of the elements; the value given is the atomic mass number of the isotope of that element of longest known half life. Alternatively, the relative atomic mass of the isotope with the longest known half life or that of a commonly used isotope could be listed, since the relative atomic masses of the individual isotopes are accurately known.

As mentioned in the Introduction (Sec. 1), for tables issued since the Third Edition, values of the molecular masses are based on the 1993 IUPAC recommendations.

Table of relative atomic masses of the elements, 1981
[Pure Appl. Chem. **55**, 1101 (1983), alphabetical order, based on the relative atomic mass, $A_r(^{12}C) = 12$]

Name	Symbol	atomic number	Relative atomic mass
Actinium	Ac	89	227.0278
Aluminum	Al	13	26.98154
Americium	Am	95	(243)
Antimony (Stibium)	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.9216
Astatine	At	85	(210)
Barium	Ba	56	137.33
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01218
Bismuth	Bi	83	208.9804
Boron	B	5	10.81
Bromine	Br	35	3579.904
Cadmium	Cd	48	112.418
Caesium	Cs	55	132.9054
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C		12.011
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.9312
Copper	Cu	29	63.546
Curium	Cm	96	(247)
Deuterium	D	1	2.014102
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Electron	e-		0.000 548 58
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257)
Fluorine	F	9	18.998403
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.9665
Hafnium	Hf	72	178.49
Helium	He	2	4.00260
Holmium	Ho	67	164.9304
Hydrogen	H	1	1.00794
Indium	In	49	114.82
Iodine	I	53	126.9045
Iridium	Ir	77	192.22
Iron	Fe	26	55.847
Krypton	Kr	36	83.80
Lanthanum	La	57	138.9055
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.2
Lithium	Li	3	6.941
Lutetium	Lu	71	174.967
Magnesium	Mg	12	24.305
Manganese	Mn	25	54.9380
Medelevium	Md	101	(258)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.179
Neptunium	Np	93	237.0482
Nickel	Ni	28	58.69
Niobium	Nb	41	92.9064
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.42
Phosphorus	P	15	30.97376
Platinum	Pt	78	195.0
Plutonium	Pu	94	(244)
Polonium	Po	84	(209)
Potassium (Kalium)	K	19	39.0983
Praseodymium	Pr	59	140.9077
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.0359
Radium	Ra	88	226.0254
Radon	Rn	86	(222)
Rhenium	Re	75	186.207
Rhodium	Rh	45	102.9055
Rubidium	Rb	37	85.4678
Ruthenium	Ru	44	101.07
Samarium	Sm	62	150.36
Scandium	Sc	21	44.9559
Selenium	Se	34	78.96
Silicon	Si	14	28.0855
Silver	Ag	47	107.8682
Sodium (Natrium)	Na	11	22.98977
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.9479
Technetium	Tc	43	(98)
Tellurium	Te	52	127.60
Terbium	Th	65	158.9254
Thallium	Ti	81	204.383
Thorium	Th	90	232.0381
Thulium	Tm	69	168.9342
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten (Wolfram)	W	74	183.85
(Unnilhexium)	(Unh)	106	(263)
(Unnilpentium)	(Unp)	105	(262)
(Unnilquadium)	(Unq)	104	(261)
Uranium	U	92	238.0289
Vanadium	V	23	50.9415
Xenon	Xe	54	131.29
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.9059
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

3.4 Fundamental Constants and Conversion Factors

The numerical values of the fundamental constants used in our calculations are those obtained by Cohen and Taylor[8a] based on a least-squares adjustment of data existing in 1973. These values have been adopted by CODATA.[8a]

As mentioned in the Introduction (Sec.1), for tables issued since the Third Edition, values of the fundamental constants are based on the 1986 CODATA recommendations.[8b]

Fundamental constants

Quantity	Symbol	Value[a]
Speed of light in vacuum	c	299 792 458(1.2) m s^{-1}
Planck constant	h	6.626 176(36) × 10^{-34} J s
	$h/2\pi$	1.054 588 7(57) × 10^{-34} J s
Avogadro constant	N_A	6.022 045(31) × 10^{23} mol^{-1}
Elementary charge	e	1.602 189 2(46) × 10^{-19} C
Faraday constant, N_Ae	F	9.648 456(27) × 10^4 C mol^{-1}
Absolute temperature of "ice point," O °C	T_O	273.150 0 K
Molar gas constant	R	8.314 41(26) J mol-1 K^{-1}
Boltzmann constant, RN_A^{-1}	k	1.380 662(44) × 10^{-23} J K^{-1}
Second radiation constant, hck^{-1}	c_2	1.438 786(45) × 10^{-2} m K

[a]Numbers in parentheses are the one standard deviation uncertainties in the last digits of the quoted value.

Conversion factors for energy-related units. 1973 CODATA constants

	kJ mol^{-1}	kcal mol^{-1}	eV (per molecule)	cm^{-1}	MHz
1 kJ mol^{-1}	1	0.239 005 7	0.010 364 35	83.593 47	2.506 069 × 10^6
1 kcal mol^{-1}	4.184	1	0.043 364 45	349.755 1	1.048 539 × 10^7
1 eV (per molecule)	96.4846	23.06036	1	8065.479	2.417 970 × 10^8
1 MHz	3.990 313 × 10^{-1}	9.537 077 × 10^{-8}	4.135 701 × 10^{-9}	3.335 641 × 10^{-5}	1
1 cm^{-1}	0.011 962 66	2.859 144 × 10^{-3}	1.239 852 × 10^{-4}	1	2.997 924 × 10^4
1 K (degree)	8.314 41 × 10^{-3}	1.987 19 × 10^{-3}	8.617 349 × 10^{-5}	0.695 030 4[a]	2.083 649 × 10^4
1 hartree	2625.500	627.509 5	27.211 606	2.194 746 × 10^5	6.579 684 × 10^9
1 rydberg	1312.750	313.754 7	13.605 803	1.097 373 × 10^5	3.289 842 × 10^9

[a]This value is inverse of the second radiation constant c_2; $(hc/k)^{-1} = c_2^{-1} = 0.695\ 030\ 4$.

3.5. Temperature Scale

Since the NIST-JANAF Thermochemical Tables deal with properties that vary with temperature, the temperature scale is of significance. The International Temperature Scales are devised to approximate, as closely as possible, the absolute thermodynamic (kelvin) temperature suggested by W. Thomson (Lord Kelvin) in 1854. The International Temperature Scale is established by the Comité International des Poids et Mesures (International Committee of Weights and Measures).

There have been four international temperature scales: The International Temperature Scale of 1927,[18] The International Temperature Scale of 1948 which was renamed the International Practical Temperature Scale of 1948 (IPTS-48) in 1960,[19-20] The International Practical Temperature Scale of 1968 (IPTS-68)[21] and The International Temperature Scale of 1990 (ITS-90).[22]

Our concern in the preparation of the NIST-JANAF Thermochemical Tables is to adjust any experimental measurements to the thermodynamic scale. In practice, this means converting to the ITS-90 scale since it is the currently accepted closest approximation to the thermodynamic scale.

To facilitate temperature adjustments, the article by Corruceini[19] was used for the 1927 to 1948 conversions and the article by Douglas[23] for the 1948 to 1968 conversion. Guildner and Edsinger[24] included a plot showing the deviation of IPTS-69 from the thermodynamic temperatures from 273.16 to 730 K. For conversions to the current scale (ITS-90), there are numerous articles which discuss the conversion of experimental data or smoothed results to the new temperature scale.

Ideal-gas tables of thermodynamic properties derived from statistical mechanics are based on the thermodynamic temperatures (as well as on the values of the physical constants used) and are hence independent of any practical temperature scale. The enthalpy of formation, Gibbs energy of formation, and logarithm of the equilibrium constant might depend on temperature-adjusted data.

For condensed phase tables, the temperature scale conversion is often not necessary and is not made since the correction would be small compared with the uncertainty in the data.

4. Reference States and Conversions

There are three types of tables included in this publication: single-phase, multiphase, and reference state tables. The tables are clearly labeled as to the type at the top of each page and by the state designations associated with the chemical formula. The reference state can involve a single phase or multiphases. The major difference between a multiphase table and a single-phase table is the existence of a discontinuity in each function (or in its first derivative) at a first-order transition temperature.

4.1. Reference State

A related set of thermodynamic property tables requires that there be a reference table of the thermodynamic properties for each element to which all other forms of that element or any compound involving that element may be referred. If the temperature range of interest (0 K to 6000 K herein) can be represented by a single phase for that material (say hydrogen) the tabulated values in the reference table will be smooth and regular. If the temperature range of interest includes more than one phase (say magnesium), there will be a solid phase (from 0 K to 923 K, the melting temperature), a liquid phase (923 K to 1378 K, where the vapor pressure reaches 1 bar), and a gas phase (1378 K to 6000 K), and the tabulated values in the reference table will be discontinuous at these temperatures or phase boundaries. Practical usage dictates that in so far as possible the phase most stable at 1 bar pressure be selected. This practice is followed in these tables, and does lead to discontinuities in the thermodynamic functions. Attention is called to these discontinuities in the reference state tables by insertion of a comment as to the type of transition at the temperature of the phase transition.

Since these tables deal with ideal gases, the pressure is really the fugacity. Calculating a boiling temperature as the temperature at which $\Delta_{vap}G^\circ = 0$ for the process Mg(l)→Mg(g) corresponds to an (ideal) fugacity of 1 bar. This will differ from the real (observed) boiling point at 1 bar which is also different from the real (observed) boiling point at 1 atm. Each of these "three boiling points" corresponds to a different $\Delta_{vap}G^\circ$ value.

With the use of f and °, as in $\Delta_f H^\circ$, the implication is that both the compound in question and its constituent elements are in standard states and that the elements, moreover, are in their reference states; for any given temperature the reference states of the elements will normally be those that are stable at the chosen standard-state pressure and at that temperature. A resulting feature of tabulations of $\Delta_f H^\circ$ and $\Delta_f G^\circ$ as functions of temperature for compounds is that discontinuous changes are sometimes to be seen; these correspond to changes in the stable reference states of the elements, as phase-transition temperatures are passed. Thus, values of $\Delta_f H^\circ$ (SO_2Cl_2,g) would show discontinuous changes at three temperatures corresponding to the transitions S(cr,I)→S(cr,II), S(cr,II)→S(l), and S(l)→1/2 S_2(g), where I refers to rhombic and II to monoclinic crystal forms.

4.2. Single-Phase and Multiphase Tables

A multiphase table contains the data for two or more phases of a pure substance. Each phase is limited to the temperature range in which it is more stable (i.e., has a lower $\Delta_f G^\circ$ than the other phases in the table). There are discontinuities in the properties C_p°, S°, and H° at the temperatures where each phase transforms ($\Delta G^\circ = 0$) to the next phase. Alternatively, the properties of a pure substance can be given in a series of tables where each table is devoted to a single phase. Single-phase tables do not have discontinuities in the properties C_p°, S°, and H° at transition temperatures. Moreover, the properties are extrapolated beyond the transition temperatures into regions where that phase is less stable than its other phases. These characteristics of continuity and extrapolation of properties lead directly to the advantages and problems of single-phase tables. The enthalpy of formation and Gibbs energy of formation may have discontinuities, even in single-phase tables, corresponding to transitions in the reference states.

Single-phase tables are more convenient than multiphase tables in certain computer applications. Interpolation and approximation (curve fitting) apply directly to the continuous properties in a single-phase table. Multiphase tables must first be divided into segments using the stored values of the transition temperatures; then interpolation and approximation must be limited to the temperatures in the pertinent segment.

Single-phase tables are essential in uses that involve unstable phases. This includes phases that persist in a metastable region or those that are unstable at all temperatures. [Such cases abound in the real world.] Single-phase tables are often applied to solid-solid or solid-liquid equilibrium in mixtures, where an unstable phase is "stabilized" in the presence of other components. Analysis of such equilibria often requires liquid or solid properties that are many hundreds of degrees into the metastable region of each pure phase. Single-phase tables are designed to supply these properties, but their preparation is not trivial.

The NIST-JANAF Thermochemical Tables often include estimated glass transitions in the liquid tables. The glass temperature is usually assumed to be ~0.7 times the melting temperature. The heat capacity of the glass is usually assumed to be equal to that of the stable crystalline phase, since existing glass data show a decrease in C_p° to values near those of the crystal. Such tables are, in fact, not single-phase tables but two-phase glass-liquid tables.

The glass transition is of practical concern when thermochemical tables are used near the glass transition temperature of any of the pure liquids. Although the ratio of the glass temperature to the melting temperature can vary from perhaps 0.35 to >0.8, it often is ~0.7. Temperatures this low are not uncommon when tables for liquids are used in the analysis of binary or multicomponent phase diagrams.

It is important to ask whether glass transitions should be included in liquid tables intended for such use. Estimated glass transitions are included for two reasons: the transition is usually observed in supercooled liquids and its inclusion avoids an entropy paradox. The first reason presumes that

glass transitions do occur but cannot be observed in liquids that readily crystallize. The more compelling reason is the avoidance of the paradox in which the entropy of the supercooled liquid (a disordered state) becomes less than that of the stable crystalline state.

The choice remains as to what temperature and what phase should be used as the reference point for enthalpy in the extrapolated single-phase tables. Since 298.15 K was adopted as the reference temperature for multiphase and reference state tables, there is strong incentive for retention of that temperature in single-phase tables. The choice has been made to have the reference at the same arbitrary point in each phase. Thus, the JANAF Thermochemical Tables use a reference temperature of 298.15 K in the table for the high-temperature phase even when that phase is not stable at 298.15 K.

Enthalpies at all temperatures depend on the arbitrary extrapolations needed to relate the observed data to the reference temperature. Each single-phase table has a different reference $\Delta_f H°$ dependent on an arbitrary extrapolation of enthalpy.

For the reference temperature of 298.15 K, the enthalpy at $T \rightarrow 0$ is always negative. This means that the function $-(G° - H)/T$ approaches positive ∞ at $T \rightarrow 0$ and is therefore difficult to interpolate near $T \rightarrow 0$.

4.3. Conversion to SI Units and the Standard-State Pressure

In all previous JANAF Thermochemical Tables, the standard-state pressure was one atmosphere (101 325 Pa) and the unit of energy was the thermochemical calorie (4.184 J). For this publication, the standard-state pressure is changed to one bar (100 000 Pa) and the energy unit to the joule. The values from previous JANAF tabulations have been converted as described below. This information is provided not only to make clear the correspondence between this publication and previous JANAF Thermochemical Tables but also to assist the reader in making comparisons with other tables. This information is the same as that provided in "The NBS Tables of Chemical Thermodynamic Properties."[6]

Conversion of Values in Calories to Joules

For the energy units the defined conversion factor of 4.184 $J \cdot cal^{-1}$ is used.

Conversion for Change in Pressure

The following expressions define the effect of pressure on the properties of all substances.

$$(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p = V(1 - \alpha T),$$
$$(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2),$$
$$(\partial S/\partial p)_T = -V\alpha = -(\partial V/\partial T)_p,$$
$$(\partial G/\partial p)_T = V,$$
$$\alpha \equiv (1/V)(\partial V/\partial T)_p$$

For the small pressure change from 1 atm to 1 bar, the pressure coefficients may be taken as constants for condensed phases. There are no condensed phase cases in this publication for which the pressure coefficients are large enough to affect the tabulated values. Typical values of α for solids are 10^{-5} to 2×10^{-4} K^{-1} and $V < 10^{-3}$ m^3 mol^{-1}. For ideal gases, $V = RT/p$ and $\alpha = R/pV = 1/T$. The pressure coefficients for gases are large enough to affect high-accuracy data. In practice the only properties tabulated here that are affected are $S°(T)$ and $-(G°(T) - H°[298.15\ K])/T$ for all gases, and $\Delta_f G°(T)$ and lg K_f for any substance whenever gases are involved.

The conversion equations used for the change in standard-state pressure are listed below together with some that apply to thermal functions. Superscripts ° and * denote values at 1 bar and 1 atm, respectively. These equations apply to the small change in pressure from 1 atm to 1 bar.

For all substances, exactly for ideal gases and within the limit of experimental inaccuracy for all other phases:

$$\Delta_f H°(T) - \Delta_f H*(T) = 0,$$
$$[H°(T) - H°(T_1)] = [H*(T) - H*(T_1)] = 0,$$
$$C_p°(T) - C_p*(T) = 0,$$

where T_1 is a reference temperature.

For condensed phases, within the limit of experimental inaccuracy:

$$S°(T) - S*(T) = 0$$
$$G°(T) - G*(T) = 0$$

For substances that are gaseous:

$$S°(T) - S*(T) = R \ln p*/p°$$
$$= R \ln \frac{101325}{100\,000} = 0.109\ 444\ J \cdot K^{-1}\ mol^{-1}.$$

For substances that are gaseous at T but may or may not be gaseous at T_1:

$$-[G°(T) - H°(T_1)]/T + [G*(T) - H*(T_1)]/T = R \ln p*/p° \text{ as for } S.$$

$$[G°(T) - G°(T_1)] - [G*(T) - G*(T_1)] = R(T - T_j)\ln p*/p°,$$

where $T > T_j \geq T_1$ and T_j is the temperature at which the function begins to apply to the ideal gas, usually the boiling temperature at 1 bar.

For each substance with gases in its formation reaction:

$$\Delta_f G°(T) - \Delta_f G*(T) = -\delta RT \ln 1.013\ 25 = -0.032\ 63\ \delta\ kJ\ mol^{-1} \text{ at } 298.15\ K.$$

where δ is the net increase in the number of moles of gas in the formation reaction.

Conversions for Entropies of Gases

To convert from:	$S°$(g,0.1 MPa) / J·K^{-1} mol^{-1}	$S*$(g,1 atm) / cal·K^{-1} mol^{-1}	$S^{\dagger}$ (g,1 atm) / J·K^{-1} mol^{-1}
To:	Use		
$S°$(g,0.1 MPa) / J·K^{-1} mol^{-1}	$= S°$	$4.184(S* + 0.026\ 157)$	$S^{\dagger} + 0.109\ 442$
$S^{\dagger}$ (g,1 atm) / J·K^{-1} mol^{-1}	$= S° - 0.109\ 442$	$4.184\ S*$	$S^{\dagger}$
S(g,0.1 MPa) / cal·K^{-1} mol^{-1}	$= S°/4.184$	$S* + 0.026\ 157$	$(S^{\dagger} + 0.109\ 442)/4.184$
$S*$(g,1 atm) / cal·K^{-1} mol^{-1}	$= (S° - 0.109\ 442)/4.184$	$S*$	$S^{\dagger}/4.184$

$S°$ entropy for a gas at 0.1 MPa in J·K^{-1} mol^{-1}.
$S*$ entropy for a gas at 1 atm in cal·K^{-1} mol^{-1}.
$S^{\dagger}$ entropy for a gas at 1 atm in J·K^{-1} mol^{-1}.

4.4. Boiling Temperature and the Standard-State Pressure

In these tables, the defined pressure for the standard state is 1 bar (100 000 Pa). As stated by IUPAC,[9] the present recommended change in the standard-state pressure carries no implication for "standard pressures" used in other contexts, e.g., the convention that "normal boiling points" refer to a pressure of 1 atm (101 325 Pa). Instances may occur where it is desirable to adopt yet other values for $p°$ and so all authors must clearly state the value adopted.

In these tables, the temperature at which $\Delta_r G° = 0$ for the process liquid to gas, refers to a fugacity of 1 bar. Typically the real (i.e., observed) boiling point (corresponding to a nonideal gas) is slightly higher. In many cases the experimental uncertainties in measuring a boiling point (at 1 bar) and the uncertainties in the calculated value due to uncertainties in the thermal functions make this difference meaningless. Such a situation exists whether the standard-state pressure is 1 bar or 1 atm.

The phrase "boiling point" must be used carefully for other reasons. Care must be exercised such that the boiling process is indeed defined. Two examples which illustrate this point are MgO and LiF. Magnesium oxide does not vaporize congruently (so that the total vapor pressure depends on the ambient oxygen potential), whereas LiF vaporizes congruently but monomer, dimer, and trimer species exist in the vapor.

5. Evaluation of Thermodynamic Data

Interconsistency

The basic aim of these thermodynamic property tables is to provide a related and consistent set of enthalpies of formation and Gibbs energies of formation. This allows the prediction of the enthalpy and Gibbs energy changes and the equilibrium constants for any reaction among the constituents of the tables.

The enthalpy of formation and Gibbs energy of formation are related to each other through the entropy of formation of the substance. Self-consistency can be assured by use of this constraint to derive any one property from selected values of the other two. The entropy, which is an absolute quantity in thermochemical calculations, is suitable for one of the selected properties. The enthalpy of formation is convenient for the other, since enthalpy of reaction is the most commonly measured link between different substances.

Enthalpy changes are relative quantities, so it is important to relate each substance to a consistent base. This is done by referring each enthalpy of formation to the chemical elements in their standard reference states. By convention, the enthalpy of formation of an element in its standard reference state is zero at all temperatures.

The reference state table may involve a single phase or several phases and examples of both kinds are found in this compilation. For elements which are solid at room temperature, the reference state is normally the stable solid state(s) up to the melting point, the liquid up to the boiling point at 1 bar, and thereafter the gas phase which may be monatomic or diatomic. For other elements, the choices for the reference states are:

(1) the ideal monatomic gas for the inert rare gases and the electron gas He, Ne, Ar, Kr, Xe, Rn, and e^-. The classical statistical mechanical values are assumed for $H°(T) - H°(0)$ for the electron.

(2) the ideal diatomic gas for the following gases: H_2, D_2, N_2, O_2, F_2, and Cl_2.

(3) crystalline white phosphorus and the ideal diatomic gas, $\frac{1}{2}P_2(g)$. The early JANAF publications used red phosphorus as the reference state. Although red phosphorus is the more stable form, it is less well characterized and its properties are less reproducible.

(4) the ideal diatomic gas combined with the appropriate condensed phases for Br_2, I_2, and S; for sulfur, the gaseous portion of the reference state is $\frac{1}{2}S_2(g)$.

(5) graphite (Acheson-spectroscopic grade) for carbon at all temperatures.

These choices are arbitrary and vary in different compilations. Enthalpies or Gibbs energies of formation taken from different sources should be converted to common reference states before use.

The establishment of reference states is the first step in any scheme for interconsistency. The next step, ideally, would be to solve simultaneously for all $\Delta_f H°$, $\Delta_f G°$, $S°$ using all the suitable data for $\Delta_r H°$, $\Delta_r G°$, $\Delta_r S°$, and $S°$. This would provide values for enthalpies, Gibbs energies, and entropies which, when combined, would yield the minimum overall deviations from the measured values. Simultaneous solution is limited in practice to small groups of interrelated substances.

We have used this simultaneous approach in a limited way for treating groups of interrelated fluorides. Dr. John L. Haas, Jr. (U.S. Geological Survey) has treated, simultaneously, the data for some geologically important systems as a function of temperature and pressure.[25] Dr. J. Brian Pedley (University of Sussex) has treated $\Delta_r H°$ data for several systems, the most pertinent involving all the diatomic oxides.[26] Dr. Vivian Parker and Dr. David Garvin (NBS) have refined the latter method and applied it to some species that were adopted by CODATA.[27] JANAF policy is to use the results of these treatments.

Since simultaneous solution has not been attempted for all substances it is necessary to fix, simultaneously when possible, certain key values for common substances. These are then used in the usual sequential way to help fix other substances. JANAF policy is to adopt the key values recommended by the CODATA Task Group for Key Values in Chemical Thermodynamics.[28] Exceptions to this policy only occur when additional recent data are available.

Because of the many revisions of these tables, perfect interconsistency is not always attained. However, any inconsistency of the tables is a prime concern and is a cause for revision if the effects are of the same order of magnitude as the stated uncertainties.

An approximate type of consistency relates to trends in properties within families in the periodic table. Expected trends can aid both in estimation of missing data and in evaluation of observed data, for example, in a series from fluoride to iodide or from polyhalide to monohalide.

5.1. General Evaluation Techniques

Heat Capacities and Enthalpy Difference

The evaluation of reported values is a judgmental process, but the analysis should be as objective as possible and therefore certain ground rules must be established. The first step involves the examination of a plot of all information so that a general idea of the agreement can be visually obtained. If certain data sets differ from the majority, they are examined for possible causes of the difference. Calibration data, sample purity, and experimental scatter are checked. If the source of error can be located, the data are given appropriately less weight. Otherwise all data of equal reliability are considered equal, even if they disagree. Such data are then smoothed by a weighted least-squares curve fit. Enthalpy data are smoothed similarly and heat capacities are derived exactly from the differentiated polynomial. The smoothing of enthalpy data often requires constraining the fit so that it passes through zero at the reference temperature. Additional constraints are often used to fix the heat capacity at 298.15 K or to join enthalpy data smoothly with low-temperature heat capacities.

Transitions

The evaluation of solid-state transitions involves first the recognition of the type of transition, which may not always be obvious. A first-order transition such as fusion involves a discontinuous change of enthalpy and entropy at the transition point, whereas second-order transitions involve only discontinuities in heat capacity. Because of impurities and other factors, first-order transitions often do not occur sharply at one temperature; instead, they spread a little on either side and are sometimes difficult to distinguish from λ-type second-order transitions.

Many enthalpies of fusion and enthalpies of solid-state transitions are obtained from enthalpy measurements. Here the enthalpies are given directly by the difference in enthalpy at the transition temperature. Normally, the enthalpy above and below can be smoothly extended to the temperature of transition, although the transition temperature may not be clearly obtainable from the enthalpy data.

The enthalpies of the transitions involving vaporization and sublimation are evaluated from equilibrium data by the second- and third-law methods. When reliable calorimetric measurements are available, the adopted enthalpy of transition is usually based on them.

Equilibrium

Perhaps the most significant facts to be established in evaluating equilibrium data are whether equilibrium was attained and whether the process was properly described. For example, in a sublimation process the most accurate measurements are valueless if the vapor phase is not uniquely defined. If polymerization or breakdown might have occurred, it is important to establish the exact reaction first. Because mass spectroscopy has shown that vapor phases are often extremely complex, it is almost a requirement that the vapor composition be established by a mass spectrometer before equilibrium data can be accepted. Some methods of measurement are less accurate than others and should be given less weight. For example, equilibria determined in a mass spectrometer may have significant uncertainty because of the approximations involved in obtaining absolute pressures. On the other hand, measurements of the electromotive force of reversible cells can have great accuracy. Mass spectra provide identification

of the vapor species while a very precise emf measurement tells nothing as to the reaction which is occurring. Each method has inherent limitations; these may be more critical in some uses than in other uses. Clues to the existence of these limitations often appear in the second- and third-law analyses.

The Second-Law Method

Starting from the equation $\Delta G^\circ = -RT \ln K$, by differentiation with respect to T and substitution of $d(\Delta G^\circ)/dT = -\Delta S^\circ$, we obtain $\Delta H^\circ = RT^2 d(\ln K)/dT$, the well-known van't Hoff equation. By substituting $dT = -T^2 d(1/T)$, one obtains $\Delta H^\circ = -R\, d(\ln K)/d(1/T)$; thus, the slope of ln K versus $1/T$ plot is $-\Delta H^\circ/R$. If ΔH° is constant, then the slope is constant and the plot is a straight line. Since the variation of ΔH° with temperature is often quite small, it is customary to assume a straight-line relationship. This method of obtaining enthalpies of reaction from equilibrium measurements is known as a "second-law" calculation. For greatest accuracy the equilibrium measurements should extend over a wide range of temperature, and in this case ΔH° is usually not constant.

Curvature corrections can be applied by assuming a specific form for the variation of ΔH° with temperature. In this manner we can calculate $\Delta_r H^\circ$ (298.15 K) from $\Delta_r H^\circ$ (T). The effects of such corrections may be of significance. It should be noted that the second law cannot be applied to a single observation, but the third-law method, which is described below, can be so used. The second-law method also can be applied when only relative values of the equilibrium constant are available, for example, from mass-spectroscopic intensity measurements.

The Third-Law Method

The "third-law" method is based on a knowledge of the absolute entropy of the reactants and products. It allows the calculation of a reaction enthalpy from each data point when the change in the Gibbs energy function for the reaction is known. The Gibbs energy function used here is defined as

$$\text{gef}(T) = [G^\circ(T) - H^\circ(298.15\ \text{K})]/T$$

and is easily calculated from the relation

$$\begin{aligned} S^\circ/(T) &= -[G^\circ(T) - H^\circ(T)]/T \\ &= [H^\circ(T) - H^\circ(298.15\ \text{K})]/T \\ &\quad - [G^\circ(T) - H^\circ(298.15\ \text{K})]/T \end{aligned}$$

thus,

$$\text{gef}(T) = -S^\circ(T) + [H^\circ(T) - H^\circ(298.15\ \text{K})]/T$$

From the definition we can write for the change in a reaction

$$\Delta G^\circ/T = \text{gef}(T) + \Delta H^\circ(298.15\ \text{K})/T = -R \ln K,$$

thus,

$$\Delta H^\circ(298.15\ \text{K})/T = -R \ln K - \Delta\text{gef}(T),$$

where Δgef signifies gef(products) − gef(reactants).

In the NIST-JANAF Thermochemical Tables, Gibbs energy functions are based on an enthalpy reference temperature of 298.15 K and thus yield enthalpy changes at 298.15 K regardless of the temperature of the reaction. It should be noted that the Gibbs energy function in a single-phase table is based on the enthalpy of that phase at 298.15 K even though the phase may not be stable at 298.15 K. This differs from the usual convention of combining all condensed phases into one multiphase table such that the enthalpy of reaction refers to the phase stable at the reference temperature. In the JANAF tables the functions always refer to the designated phase for 298.15 K regardless of its stability. For example, if the vapor pressure over liquid copper is analyzed using Cu(l) Gibbs energy functions, the result is the enthalpy of vaporization of the liquid at 298.15 K. To calculate the enthalpy of sublimation of Cu(cr) it is necessary to add the enthalpy of fusion at 298.15 K, which is the difference in the enthalpy of formation of Cu(l) and Cu(cr) at 298.15 K. It should also be noted that Gibbs energy functions are always negative, thus the negative of the function is usually tabulated and the proper sign must be remembered when using these functions.

The analysis of data by the third-law method is generally considered superior to the second-law analysis. It is definitely superior if the Gibbs energy functions are accurately known because each equilibrium point yields one value for the enthalpy change. These values will often reveal trends that indicate nonequilibrium or erroneous values in the equilibrium constants of a set of data. If the data are good, the second-law value should agree. When the Gibbs energy functions are estimated, the third-law values derived from them must be handled carefully. Values that are constant and that agree with the second-law enthalpy indicate that the Gibbs energy functions and equilibrium data are mutually consistent. A drift with temperature of the third-law values indicates errors in either the data or the functions. The magnitude of such drifts is often given in the table write-up and represents the entropy change required to bring the second- and third-law values into agreement. If the drift is within the uncertainty of the experimental entropy, then the data are acceptable. Drifts that are much larger than reasonable entropy errors generally indicate failure to attain equilibrium or improperly estimated Gibbs energy functions.

We have found a combination of the two methods to be so valuable that a third-law calculation is always accompanied by a second-law treatment of the same data. The calculation is done in ascending temperature order to give $\Delta_r H^\circ$(298.15 K) and its deviation from the mean along with the calculated log K and its deviation from the least-square line. Third-law analysis enables bad points to be seen as deviations from the general trend of the differences; thus the method can be used even when the Gibbs energy functions are estimated. If these bad points are located on the ends of the data set, the second-law line often fits them quite well and by itself does not arouse suspicion. But the dropping of such points can bring widely discordant ΔH° values into agreement with each other and often with the third-law values.

In our analysis of equilibrium data, tabulations for both the second- and third-law results are normally given. In addition, we often list values for the drift of δS, as defined by

$$- \text{drift} = \delta S = \Delta_r S^\circ \text{ (2nd law, 298.15 K)} - \Delta_r S^\circ \text{ (3rd law, 298.15 K)}$$

δS previously called a drift (in $\Delta_r H^\circ$), gives a direct comparison of the deviation of the calculated second-law entropies from our adopted functions. The current policy is to use δS rather than drift. $\Delta_r S^\circ$ (2nd law, 298.15 K) is not calculated, however, via the usual second-law method or the method.[29,31] It is instead derived from the slope of the assumed linear temperature dependence of the deviations from the mean of the third-law enthalpies of reaction. Our experience indicates that this method agrees closely, but not exactly, with the method.

6. Construction of the Tables

The NIST-JANAF Thermochemical Tables consist of thermal functions and formation functions, both of which are temperature dependent. The thermal functions consist of heat capacity, enthalpy increments, entropy, and Gibbs energy function. The normal relationships hold between thermal functions:

$$H^\circ(T) = \int_0^T C_p^\circ(T)\mathrm{d}T,$$

$$S^\circ(T) = \int_0^T [C_p^\circ(T)/T]\mathrm{d}T,$$

$$[G^\circ(T) - H^\circ(298.15\text{ K})]/T = -S^\circ(T) + [H^\circ(T) - H^\circ(298.15\text{ K})]/T.$$

The formation functions consist of enthalpy of formation, Gibbs energy of formation, and the logarithm of the equilibrium constant of formation. Enthalpies of formation at temperatures other than 298.15 K require a knowledge of enthalpies of the reference elements:

$$\Delta_f H^\circ(T) = \Delta_f H^\circ(298.15\text{ K}) + [H^\circ(T) - H^\circ(298.15\text{ K})]_{\text{compound}} - \Sigma[H^\circ(T) - H^\circ(298.15\text{ K})]_{\text{elements}}.$$

The Gibbs energy of formation is readily calculated from the enthalpy of formation when the entropies of the elements are known. Thus

$$\Delta_f G^\circ(T) = \Delta_f H^\circ(T) - T\{S^\circ(T)_{\text{compound}} - \Sigma S^\circ(T)_{\text{elements}}\}.$$

The logarithm of the equilibrium constant of formation is then found from the relation $\Delta_f G^\circ(T) = -RT \ln K_f$.

Solid Phase Thermal Functions

The solid phase thermal functions are derived from recommended heat capacity and/or enthalpy increment values. Although the NIST-JANAF Thermochemical Tables place more emphasis on high temperatures ($T > 298.15$ K), it is desirable have data in the temperature range of $T \rightarrow 0$ to 298.15 K. There is no basic difference in evaluating low-temperature data, but many more heat capacity points are needed to describe fully the large curvature in the temperature dependence of the heat capacity. In order to evaluate the enthalpy increment it is necessary to start with the temperature $T = 0$ and integrate up to 298.15 K; then the value at 298.15 K is subtracted from the intermediate values, giving negative values for the enthalpy below 298.15 K.

The tables extend to well above the normal melting point to provide data in a metastable region which in this case is a superheated region. Explanations are inserted in the tabulations to indicate the end of the phase stability and any solid-state transitions.

Liquid Phase Thermal Functions

The construction of the liquid single-phase thermal functions is identical with that used for the solid phase; however, the required data at 298.15 K are not usually readily available. The data are obtained by calculating a preliminary table using the chosen heat capacities with zero values for $\Delta_f H^\circ$ (298.15 K) and S° (298.15 K). The correct starting values are then determined by comparing the values from the tables of crystal and liquid, using the following equations:

$$\Delta_{\text{fus}} H^\circ = \Delta_f H^\circ(T_{\text{fus}},\text{l}) - \Delta_f H^\circ(T_{\text{fus}},\text{cr}),$$

$$\Delta_{\text{fus}} S^\circ = \Delta_{\text{fus}} H^\circ / T_{\text{fus}} = S^\circ(T_{\text{fus}},\text{l}) - S^\circ(T_{\text{fus}},\text{cr}).$$

The correct values at 298.15 K may be obtained from the above relations. A typical liquid table is extrapolated both below the melting point (if the melting point is above 298.15 K) and above the boiling point to facilitate interpolation and to provide data in the metastable regions, both in the supercooled and superheated regions. A glass transition may be included in which case the tabulation becomes a multiphase table.

Gas Phase Thermal Functions

The gas phase thermal functions are generated using statistical mechanical relationships. Minimal data required for the various types of molecules are summarized below. Some of the equations used are given in Sec. 6.1 on Calculational Methods. The relative molecular mass is required for all molecules. Minimum information required is:

Monatomic species:
- Low-lying atomic energy levels and their statistical weights.

Diatomic species:
- Spectroscopic parameters such as the vibrational-rotational constants, symmetry number, and low-lying electronic energy levels.

Linear polyatomic species:
- Rotational constant, symmetry number, vibrational frequencies, and low-lying electronic levels.

Nonlinear polyatomic species:
- Principal moments of inertia, symmetry number, vibrational frequencies, and low-lying electronic levels.

Multiphase Tables

Tables which show only values for the stable phases at 1 bar pressure are multiphase tables. Multiphase tables can always be recognized by the presence of solid lines, indicating phase transitions, on the table. They are prepared in a manner similar to tables for condensed phases. The functions are evaluated in the same manner as for a solid up to the first transition point; then the enthalpy and entropy of transition are added and the integration is continued using the heat capacities of the next phase. At each transition, the above process is repeated.

6.1. Calculational Methods

The calculation of the temperature-dependent values of the thermal function is performed using a variety of procedures. Some of these procedures were developed internally while others were developed at other locations. A general description of the traditional equations used in the JANAF project follows. Numerous higher order calculational schemes are used whenever the data are sufficient. These procedures are detailed on the appropriate tables.

In gas phase calculations, all thermodynamic variables are calculated in dimensionless form, e.g., C_p/R to at least seven significant figures. This is an arbitrary choice since most data do not warrant this accuracy. This has been done to permit the calculation of the crossover temperatures and enthalpies between single-phase tables accurately and to permit conversion to the desired units without loss of accuracy. The printed tables, however, will only contain three decimal places. Condensed phase tables do not depend directly on R (the gas constant) and they are not calculated in dimensionless form, but are calculated to five decimal places for units conversion.

Condensed Phase Species

Thermodynamic data for condensed states are derived from either measured or estimated information. The thermochemical table is obtained normally by the appropriate integration of heat capacity data. At the. appropriate temperatures, transition enthalpies are added to the enthalpy total, while the quotient of the transition enthalpy divided by the thermodynamic temperature is added to the entropy total.

Gaseous Species

Calculation of the contributions of rotation and translation involves the use of quantum statistics, but to obtain a numerical solution, the quantum statistics are usually replaced by classical statistics at temperatures above about 10 K; below 10 K this classical approximation no longer holds. For this reason the equations presented here fail in the vicinity of $T \rightarrow 0$. In agreement with the third-law concept, C_p° and S° are zero at $T \rightarrow 0$. For a reference element, $\log K_f$ is zero at $T \rightarrow 0$, while for compounds the absolute values of the Gibbs energy function and $\log K_f$, become infinite at $T \rightarrow 0$, for the choice of the enthalpy reference temperature of 298.15 K.

In addition, classical statistics can sometimes lead to erroneous results at high temperatures. For example, the classical approximation could give abnormally high C_p° values for a diatomic molecule having a shallow potential energy curve.

The functions calculated for gases are obtained, in general, from molecular constants that have been adjusted to the natural isotopic abundance. Normally, the approximation of adjusting the molecular parameters by a weighting according to a weighted natural isotopic abundance can be made. The proper correction (which is used for all reference states) is based on a weighted isotopic average of the tabulations.

An electronic term of unit statistical weight lying at 30 000 cm^{-1} and above contributes a negligible amount to the thermodynamic functions at temperatures of 6000 K and below. On the other hand, a number of such terms cannot be neglected. In these cases, the number of terms and their values have been summed and their contribution included.

Some fundamental vibrational frequencies have been estimated by analogy with related molecules. Occasionally, two or more fundamentals are estimated at the same value. This is not to be confused with a true degeneracy which is indicated by placing the degeneracy value in parentheses following the frequency. However, when the information has been taken from another compilation, the degeneracies indicated by the compiler have been retained.

The method used in generating the thermal functions depends not only on the quality/quantity of information available but also on the specifics of the nature of the information (e.g., split ground state, shallow potential wells, etc.). The gas phase tables are generated using the following relationships unless stated otherwise. These relationships are given in Mayer and Mayer[30] and Pitzer and Brewer.[31]

Use of a more sophisticated approach will always be noted and details given on the appropriate tables. The more common alternative approaches are given by McBride and Gordon[32] and McDowell[33] for monatomic and polyatomic gases. For many diatomic gaseous molecules (the alkali metal dimers, the alkaline earth metal dimers, the halogens, hydrogen, deuterium, nitrogen, oxygen, sulfur), a direct summation technique has been used. This technique, stated explicitly on the individual tables, involves a summation over the individual rotation-vibrational energy levels for each electronic state in the partition function expression. In addition, the summation is terminated at the dissociation energy for a particular electronic state of the diatomic molecule; although in some cases, the metastable states (above the dissociation energy) are included in the summation.

6.1.1. Ideal Monatomic Gas

(a) Translation

$$C_p^\circ/R = 5/2,$$

$$[H^\circ(T) - H^\circ(0\,\mathrm{K})]/RT = 5/2$$

$$S^\circ/R = 3/2 \ln M_r + 5/2 \ln T + 5/2 + \ln \frac{k}{p^\circ}\left(\frac{2\pi k}{Nh^2}\right)^{3/2},$$

$$-[G^\circ(T) - H^\circ(0\,\mathrm{K})]/RT = 3/2 \ln M_r + 5/2 \ln T + \ln \frac{k}{p^\circ}\left(\frac{2\pi k}{Nh^2}\right)^{3/2}.$$

(b) Electronic

$$C_p^\circ/R = T^2 \frac{d^2 \ln Q}{dT^2} + 2T \frac{d \ln Q}{dT}$$

$$[H^\circ(T) - H^\circ(0\,K)]/RT = T \frac{d \ln Q}{dT^2},$$

$$S^\circ/R = T \frac{d \ln Q}{dT^2} + \ln Q,$$

$$-[G^\circ(T) - H^\circ(0\,K)]/RT = \ln Q,$$

where

$$Q = \sum_i g_i \exp(-c_2\epsilon_i/T),$$

where ϵ_i is in cm^{-1} and the electronic levels to be included are discussed on the appropriate gas phase table.

6.1.2. Ideal Diatomic Gas

(a) Translation: Same as in I(a).

(b) Rotation

$$C_p^\circ/R = 1 + (c_2B/T)^2/45,$$

$$[H^\circ(T) - H^\circ(0\,K)]/RT = 1 - (c_2B/T)/3 - (c_2B/T)^2/45.$$

$$S^\circ/R = 1 - \ln(c_2B\sigma/T) - (c_2B/T)/90.$$

$$-[G^\circ(T) - H^\circ(0\,K)]/RT = -\ln(c_2B\sigma/T) + (c_2B/T)/3 + (c_2B/T)^2/90,$$

where

$$B = (B_e - \alpha_e/2);$$

in cm^{-1} when spectroscopic constants are available, or

$$B = h/8\pi^2cI = 2.799\,320 \times 10^{-39}/I;$$

in cm^{-1} when calculated from molecular model, I in $g \cdot cm^2$.

(c) vibration

$$C_p^\circ/R = u^2e^{-u}/(1 - e^{-u})^2,$$

$$[H^\circ(T) - H^\circ(0\,K)]/RT = ue^{-u}/(1 - e^{-u}),$$

$$S^\circ/R = ue^{-u}/(1 - e^{-u}) - \ln(1 - e^{-u}),$$

$$-[G^\circ(T) - H^\circ(0\,K)]/RT = -\ln(1 - e^{-u}),$$

where

$$u = c_2(\omega_e - 2\omega_e x_e)/T;$$

when spectroscopic constants (in cm^{-1}) are available, or

$$u = c_2\omega/T;$$

where ω (in cm^{-1}) is the fundamental frequency of a harmonic oscillator.

(d) Corrections for anharmonic vibrations

$$C_p^\circ/R = \frac{16\gamma}{u} - \frac{\delta u^2 e^e}{(e^u - 1)^2} + \frac{u^2e^u(2\delta e^u - 4Xu - 8x)}{(e^u - 1)^3} + \frac{12Xu^3e^{2-u}}{(e^u - 1)^4},$$

$$[H^\circ(T) - H^\circ(0\,K)]/RT = \frac{8\gamma}{u} + \frac{u(\delta e^u - 2X)}{(e^u - 1)^2} + \frac{4Xu^2e^u}{(e^u - 1)},$$

$$S^\circ/R = \frac{16\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{\delta u e^u}{(e^u - 1)^2} + \frac{4Xu^2e^u}{(e^u - 1)^3},$$

$$-[G^\circ(T) - H^\circ(0\,K)]/RT = \frac{8\gamma}{u} + \frac{\delta}{(e^u - 1)} + \frac{2Xu}{(e^u - 1)^2},$$

where $u = (\omega_e - 2\omega_e x_e)(c_2/T)$, $X = \omega_e x_e/\omega_e$, $\delta = \alpha_e/B_e$, and $\gamma = B_e/\omega_e$; ω_e, $\omega_e x_e$, B_e and α_e are in cm^{-1}.

(e) Electronic

Same as I(b) when the ith-state vibrational partition function, Q_v^i, and the ith-state rotational partition function, Q_r^i, are equal to the respective ground-state partition functions. In this case the partition function

$$Q = Q_tQ_vQ_r^i \sum_i Q_e^i,$$

otherwise all the thermodynamic functions are derived from

$$Q = Q_t[\sum_i Q_e^iQ_v^iQ_r^i,$$

where Q_t is the translational partition function and

$$Q_e^i = g_i \exp(-c_2\epsilon_i/T).$$

6.1.3. Linear Polyatomic Molecule

(a) Translation: Same as in I(a).

(b) Rotation: Same as in II(b).

(c) Vibration: Same as in II(c) for $3N - 5$ vibrational degrees of freedom.

(d) Corrections for anharmonic vibrations: This contribution is normally neglected.

(e) Electronic: Same as II(e) where levels and quantum weights are known.

6.1.4. Nonlinear Polyatomic Molecule (Rigid Rotator, Harmonic Oscillator)

(a) Translation: Same as in I(a).

(b) Rotation:

$$C_p^\circ/R = 3/2,$$

$$[H^\circ(T) - H^\circ(0\,K)]/RT = 3/2,$$

$$S°/R = \frac{3}{2} + \frac{1}{2}\ln(I_A I_B I_C) - \ln\sigma + \frac{3}{2}\ln T + (-\frac{3}{2}\ln\frac{h2}{8R\pi°} + \frac{1}{2}\ln\pi)$$

$$-[G°(T) - H°(0\,K)]/RT = \frac{1}{2}\ln(I_A I_B I_C) - \ln\sigma + \frac{3}{2}\ln T + (-\frac{3}{2}\ln\frac{h2}{8R\pi°} + \frac{1}{2}\ln\pi)$$

(c) Vibration
Same as II(c) for $3N - 6$ vibrational degree of freedom.

(d) Corrections for anharmonic vibrations.
This contribution is normally neglected.

(e) Electronic
Same as II(e) where levels and quantum weight are known.

6.2. Dates

At the bottom of the tabulation side of each table, there are one or two dates. These dates refer to the approximate time at which the evaluation for these tables was completed. The data for the most recent and the preceding evaluation are given. These dates will be at the bottom of the page at the right-hand side and left-hand side, respectively. Previously, all revision dates had been listed. Current practice will limit the dates to two. For the gas phase tables, the standard-state pressure is given in parentheses after the date(s). If the dates are identical, then the difference in this current table and its predecessor lies in the changes due to the standard-state pressure. Contrary to previous practice, the latest issue date of each table is not given in either of the two indices in this publication.

7. Additions, Revisions, and Corrections

In this Fourth Edition there are numerous typographical errors from the Third Edition which have been corrected. However, there are calculation errors in the formation properties for the following compounds: $AlCl_4Na$(cr), BHO_2(cr), BH_2O_2(g), $B_8K_2O_{13}$(l), Be_4O_4(g), Br_3OP(g), Br_3PS(g), CH^+(g), CN(g), CO(g), CTi(cr), C_2H_2(g), C_2Li_2(cr), C_2Mg(cr), CH_3Cl_3Si(g), CH_3F_3Si(g), ClFMg(g), ClH_4N(cr), Cl_4Mo(g), Cl_4Pb(g), Cl_4Ti(cr, l, cr/l), F_2Hg_2(cr), F_2Ti(g), FeH_2O_2(g), HP(g), HS(g), H_2P(g), H_3P(g), Hg^+(g), LiO^-(g), $Mg_3P_2O_8$(cr), OS_2(g), W(g), W^+(g), Zr(g), and Zr^+(g). These also have been corrected.

In addition new tables have been constructed many halogen oxides. These include 5 iodine oxides, 5 bromine oxides, 7 chlorine oxides, and 4 oxygen fluorides.

8. Acknowledgments

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10. Indices to Tables

There are two indices provided with this publication. Both indices are alphabetical, one by chemical name and one by chemical formula. In both cases the state of the compound is given in parentheses after the chemical formula. The tables and discussions are arranged in the same order as given in the chemical formula index.

10.1. Description of the Chemical Formula Index to the NIST-JANAF Thermochemical Tables

The tables included in this publication are ordered as given by the Chemical Formula Index. The modified Hill indexing system [J. Am. Chem. Soc. **22,** 478 (1900)] for chemical compounds, as used by Chemical Abstracts, is employed here to order the tables.

The Hill empirical formula is obtained for a particular compound by placing the elements in their alphabetical order unless C is present, in which case C is placed first, H second, and the remaining elements in alphabetical order. Substances with the same Hill formula are ordered alphabetically by their name. However, tables representing different states of the same species are in the order crystal, liquid, crystal-liquid, and ideal gas.

As examples, BeCl(g) would appear as written, whereas NaCl(g) would be filed under ClNa(g). To expand on the ordering of carbon compounds, the C always comes first, followed immediately by H if hydrogen is present, and then followed by any other elements present in their normal alphabetical order. The number of atoms of the element indexed first also influences the order of indexing the compound; e.g., all formulas with C (one carbon atom only) come before those with C_2 (two carbon atoms), followed by C compounds, and so on. Thus: $CHBF_4O$ (formyl fluoride, compound with BF_3), $CHCl_3$ (chloroform), CH_2F_3P (trifluormethylphosphine), CH_3NO_3 (methyl nitrate), CH_4Cl_2Si (dichloromethylsilane), $CH_{10}N_4O_3$ (hydrazine carbonate), CO (carbon monoxide), CO_2 (carbon dioxide), CO_3Zn (zinc carbonate), CZr (zirconium carbide), C_2Ba (barium acetylide), C_2BrClF_2 (bromochlorodifluoroethylene), C_2Ca (calcium carbide), and so on. See any formula index of Chemical Abstracts for further details and examples.

The electron gas, e^- (ref st), is inserted in the filing order after the deuterium species. Nonstoichiometric compounds are inserted just prior to or just after the corresponding stoichiometric order.

10.2. Description of the Chemical Name Index to the NIST-JANAF Thermochemical Tables

The nomenclature for the chemical species included in this publication does not fully correspond to the current Chemical Abstracts practice. The attempt has been made to use names as easily understandable as possible while not deviating far from the Chemical Abstracts system. Cited are two examples where the Chemical Abstracts nomenclature is followed, $AlBr_3(g)$ and $BBr_3(g)$ are listed as aluminum bromide and tribromoborane, respectively. For historical reasons, we would have preferred to name $BBr_3(g)$ as boron bromide. However, Chemical Abstracts refers to most boron halides as borane derivatives. On the other hand, whereas Al_2Br_6 is called di-μ-bromotetrabromoaluminum in Chemical Abstracts, this publication uses aluminum bromide.

In summary, general comments on the nomenclature are:

(1) The carbon and silicon neutral species follow the Chemical Abstracts organic-type nomenclature in which the name reflects the type of bonding.

(2) The -ium suffix that denotes positive ions is not used. $CH^+(g)$ is named 'methylidyne, ion' whereas Chemical Abstracts uses methyliumylidene.

(3) Salts are not named as an acid, metal salt of. For example, $BaSO_4$ is barium sulfate, not sulfuric acid, barium salt.

(4) Many mineral names are used.

(5) The sometimes confusing nomenclature for bridged structures in dimers is not used. Normally the monomer name is used.

In adopting this modified Chemical Abstracts nomenclature, there are numerous species for which the name will be significantly different from earlier JANAF publications. It is impractical to list all name changes, but in the more severe cases, a comment is made on the tables as to the previously used name.

10.3 Chemical Formula Index

Formula	Table Title	Page
Al_1(ref)	Aluminum (Al)	59
Al_1(cr)	Aluminum (Al)	60
Al_1(l)	Aluminum (Al)	61
Al_1(cr,l)	Aluminum (Al)	62
Al_1(g)	Aluminum (Al)	63
Al_1^+(g)	Aluminum, ion (Al^+)	64
Al_1^-(g)	Aluminum, ion (Al^-)	65
$Al_1B_1O_2$(g)	Aluminum borate ($AlBO_2$)	66
Al_1Br_1(g)	Aluminum bromide (AlBr)	67
Al_1Br_3(cr)	Aluminum bromide ($AlBr_3$)	68
Al_1Br_3(l)	Aluminum bromide ($AlBr_3$)	69
Al_1Br_3(cr,l)	Aluminum bromide ($AlBr_3$)	70
Al_1Br_3(g)	Aluminum bromide ($AlBr_3$)	71
Al_1Cl_1(g)	Aluminum chloride (AlCl)	72
$Al_1Cl_1^+$(g)	Aluminum chloride, ion ($AlCl^+$)	73
$Al_1Cl_1F_1^+$(g)	Aluminum chloride fluoride (AlClF)	74
$Al_1Cl_1F_1$(g)	Aluminum chloride fluoride, ion ($AlClF^+$)	75
$Al_1Cl_1F_2$(g)	Aluminum chloride fluoride ($AlClF_2$)	76
$Al_1Cl_1O_1$(cr)	Aluminum chloride oxide (OAlCl)	77
$Al_1Cl_1O_1$(g)	Aluminum chloride oxide (OAlCl)	78
Al_1Cl_2(g)	Aluminum chloride ($AlCl_2$)	79
$Al_1Cl_2^+$(g)	Aluminum chloride, ion ($AlCl_2^+$)	80
$Al_1Cl_2^-$(g)	Aluminum chloride, ion ($AlCl_2^-$)	81
$Al_1Cl_2F_1$(g)	Aluminum chloride fluoride ($AlCl_2F$)	82
Al_1Cl_3(cr)	Aluminum chloride ($AlCl_3$)	83
Al_1Cl_3(l)	Aluminum chloride ($AlCl_3$)	84
Al_1Cl_3(cr,l)	Aluminum chloride ($AlCl_3$)	85
Al_1Cl_3(g)	Aluminum chloride ($AlCl_3$)	86
$Al_1Cl_4K_1$(cr)	Potassium tetrachloroaluminate ($KAlCl_4$)	87
$Al_1Cl_4Na_1$(cr)	Sodium tetrachloroaluminate ($NaAlCl_4$)	88
$Al_1Cl_6K_3$(cr)	Potassium hexachloroaluminate (K_3AlCl_6)	89
$Al_1Cl_6Na_3$(cr)	Sodium hexachloroaluminate (Na_3AlCl_6)	90
Al_1F_1(g)	Aluminum fluoride (AlF)	91
$Al_1F_1^+$(g)	Aluminum fluoride, ion (AlF^+)	92
$Al_1F_1O_1$(g)	Aluminum fluoride oxide (OAlF)	93
Al_1F_2(g)	Aluminum fluoride (AlF_2)	94
$Al_1F_2^+$(g)	Aluminum fluoride, ion (AlF_2^+)	95
$Al_1F_2^-$(g)	Aluminum fluoride, ion (AlF_2^-)	96
$Al_1F_2O_1$(g)	Aluminum fluoride oxide ($OAlF_2$)	97
$Al_1F_2O_1^-$(g)	Aluminum fluoride oxide, ion ($OAlF_2^-$)	98
Al_1F_3(cr)	Aluminum fluoride (AlF_3)	99
Al_1F_3(l)	Aluminum fluoride (AlF_3)	100
Al_1F_3(cr,l)	Aluminum fluoride (AlF_3)	101
Al_1F_3(g)	Aluminum fluoride (AlF_3)	102
$Al_1F_4^-$(g)	Tetrafluoroaluminate, ion (AlF_4^-)	103
$Al_1F_4Li_1$(g)	Lithium tetrafluoroaluminate ($LiAlF_4$)	104
$Al_1F_4Na_1$(g)	Sodium tetrafluoroaluminate ($NaAlF_4$)	105
$Al_1F_6K_3$(cr)	Potassium hexafluoraluminate (K_3AlF_6)	106
$Al_1F_6Li_3$(cr)	Lithium hexafluoroaluminate (Li_3AlF_6)	107
$Al_1F_6Li_3$(l)	Lithium hexafluoroaluminate (Li_3AlF_6)	108
$Al_1F_6Li_3$(cr,l)	Lithium hexafluoroaluminate (Li_3AlF_6)	109
$Al_1F_6Na_3$(cr)	Cryolite, alpha (Na_3AlF_6)	110
$Al_1F_6Na_3$(cr)	Cryolite, beta (Na_3AlF_6)	111
$Al_1F_6Na_3$(l)	Cryolite (Na_3AlF_6)	112
$Al_1F_6Na_3$(cr,l)	Cryolite (Na_3AlF_6)	113
Al_1H_1(g)	Aluminum hydride (AlH)	114
$Al_1H_1O_1$(g)	Aluminum hydride oxide (OAlH)	115
$Al_1H_1O_1$(g)	Aluminum hydroxide (AlOH)	116
$Al_1H_1O_1^+$(g)	Aluminum hydroxide, ion ($AlOH^+$)	117
$Al_1H_1O_1^-$(g)	Aluminum hydroxide, ion ($AlOH^-$)	118
$Al_1H_1O_2$(g)	Aluminum hydroxide oxide (OAlOH)	119
$Al_1H_4Li_1$(cr)	Lithium tetrahydroaluminate ($LiAlH_4$)	120
Al_1I_1(g)	Aluminum iodide (AlI)	121
Al_1I_3(cr)	Aluminum iodide (AlI_3)	122
Al_1I_3(l)	Aluminum iodide (AlI_3)	123
Al_1I_3(cr,l)	Aluminum iodide (AlI_3)	124
Al_1I_3(g)	Aluminum iodide (AlI_3)	125
$Al_1Li_1O_2$(cr)	Lithium aluminum oxide ($LiAlO_2$)	126
$Al_1Li_1O_2$(l)	Lithium aluminum oxide ($LiAlO_2$)	127
$Al_1Li_1O_2$(cr,l)	Lithium aluminum oxide ($LiAlO_2$)	128
Al_1N_1(cr)	Aluminum nitride (AlN)	129
Al_1N_1(g)	Aluminum nitride (AlN)	130
$Al_1Na_1O_2$(cr)	Sodium aluminum oxide ($NaAlO_2$)	131
Al_1O_1(g)	Aluminum oxide (AlO)	132
$Al_1O_1^+$(g)	Aluminum oxide, ion (AlO^+)	133
$Al_1O_1^-$(g)	Aluminum oxide, ion (AlO^-)	134
Al_1O_2(g)	Aluminum oxide (AlO_2)	135
$Al_1O_2^-$(g)	Aluminum oxide, ion (AlO_2^-)	136
Al_1S_1(g)	Aluminum sulfide (AlS)	137
Al_2(g)	Aluminum (Al_2)	138
$Al_2Be_1O_4$(cr)	Beryllium aluminum oxide ($BeAl_2O_4$)	139
$Al_2Be_1O_4$(l)	Beryllium aluminum oxide ($BeAl_2O_4$)	140
$Al_2Be_1O_4$(cr,l)	Beryllium aluminum oxide ($BeAl_2O_4$)	141
Al_2Br_6(g)	Aluminum bromide ($(AlBr_3)_2$)	142
Al_2Cl_6(g)	Aluminum chloride ($(AlCl_3)_2$)	143
$Al_2Cl_9K_3$(cr)	Potassium aluminum chloride ($K_3Al_2Cl_9$)	144
Al_2F_6(g)	Aluminum fluoride ($(AlF_3)_2$)	145
Al_2I_6(g)	Aluminum iodide ($(AlI_3)_2$)	146
$Al_2Mg_1O_4$(cr)	Magnesium aluminum oxide ($MgAl_2O_4$)	147
$Al_2Mg_1O_4$(l)	Magnesium aluminum oxide ($MgAl_2O_4$)	148
$Al_2Mg_1O_4$(cr,l)	Magnesium aluminum oxide ($MgAl_2O_4$)	149
Al_2O_1(g)	Aluminum oxide (Al_2O)	150
$Al_2O_1^+$(g)	Aluminum oxide, ion (Al_2O^+)	151
Al_2O_2(g)	Aluminum oxide ($(AlO)_2$)	152
$Al_2O_2^+$(g)	Aluminum oxide, ion ($Al_2O_2^+$)	153
Al_2O_3(cr)	Aluminum oxide, alpha (Al_2O_3)	154
Al_2O_3(cr)	Aluminum oxide, delta (Al_2O_3)	155
Al_2O_3(cr)	Aluminum oxide, gamma (Al_2O_3)	156
Al_2O_3(cr)	Aluminum oxide, kappa (Al_2O_3)	157
Al_2O_3(l)	Aluminum oxide (Al_2O_3)	158
Al_2O_3(cr,l)	Aluminum oxide (Al_2O_3)	159
$Al_2O_5Si_1$(cr)	Aluminum silicate, andalusite (Al_2SiO_5)	160
$Al_2O_5Si_1$(cr)	Aluminum silicate, kyanite (Al_2SiO_5)	161
$Al_2O_5Si_1$(cr)	Aluminum silicate, sillimanite (Al_2SiO_5)	162
Al_2S_3(cr)	Aluminum sulfide (Al_2S_3)	163
$Al_3F_{14}Na_5$(cr)	Chiolite ($Na_5Al_3F_{14}$)	164
$Al_3F_{14}Na_5$(l)	Chiolite ($Na_5Al_3F_{14}$)	165
$Al_3F_{14}Na_5$(cr,l)	Chiolite ($Na_5Al_3F_{14}$)	166

Formula	Table Title	Page
$Al_6Be_1O_{10}$(cr)	Beryllium aluminum oxide ($BeAl_6O_{10}$)	167
$Al_6Be_1O_{10}$(l)	Beryllium aluminum oxide ($BeAl_6O_{10}$)	168
$Al_6Be_1O_{10}$(cr,l)	Beryllium aluminum oxide ($BeAl_6O_{10}$)	169
$Al_6O_{13}Si_2$(cr)	Aluminum silicate, mullite ($Al_6Si_2O_{13}$)	170
Ar_1(ref)	Argon (Ar)	175
Ar_1^+(g)	Argon, ion (Ar^+)	176
B_1(ref)	Boron (B)	177
B_1(cr)	Boron, beta-rhombohedral (B)	178
B_1(l)	Boron (B)	179
B_1(cr,l)	Boron (B)	180
B_1(g)	Boron (B)	181
B_1^+(g)	Boron, ion (B^+)	182
B_1^-(g)	Boron, ion (B^-)	183
$B_1Be_1O_2$(g)	Beryllium borate ($BeBO_2$)	184
B_1Br_1(g)	Bromoborane (BBr)	185
$B_1Br_1Cl_1$(g)	Bromochloroborane (BBrCl)	186
$B_1Br_1Cl_2$(g)	Bromodichloroborane ($BBrCl_2$)	187
$B_1Br_1F_1$(g)	Bromofluoroborane (BBrF)	188
$B_1Br_1F_2$(g)	Bromodifluoroborane ($BBrF_2$)	189
$B_1Br_1O_1$(g)	Boron bromide oxide (OBBr)	190
B_1Br_2(g)	Dibromoborane (BBr_2)	191
$B_1Br_2Cl_1$(g)	Dibromochloroborane (BBr_2Cl)	192
$B_1Br_2F_1$(g)	Dibromofluoroborane (BBr_2F)	193
$B_1Br_2H_1$(g)	Dibromoborane ($BHBr_2$)	194
B_1Br_3(l)	Tribromoborane (BBr_3)	195
B_1Br_3(g)	Tribromoborane (BBr_3)	196
B_1Cl_1(g)	Chloroborane (BCl)	197
$B_1Cl_1^+$(g)	Chloroborane, ion (BCl^+)	198
$B_1Cl_1F_1$(g)	Chlorofluoroborane (BClF)	199
$B_1Cl_1F_2$(g)	Chlorodifluoroborane ($BClF_2$)	200
$B_1Cl_1O_1$(g)	Boron chloride oxide (OBCl)	201
B_1Cl_2(g)	Dichloroborane (BCl_2)	202
$B_1Cl_2^+$(g)	Dichloroborane, ion (BCl_2^+)	203
$B_1Cl_2^-$(g)	Dichloroborane, ion (BCl_2^-)	204
$B_1Cl_2F_1$(g)	Dichlorofluoroborane (BCl_2F)	205
$B_1Cl_2H_1$(g)	Dichloroborane ($BHCl_2$)	206
B_1Cl_3(g)	Trichloroborane (BCl_3)	207
B_1F_1(g)	Fluoroborane (BF)	208
$B_1F_1O_1$(g)	Boron fluoride oxide (OBF)	209
B_1F_2(g)	Difluoroborane (BF_2)	210
$B_1F_2^+$(g)	Difluoroborane, ion (BF_2^+)	211
$B_1F_2^-$(g)	Difluoroborane, ion (BF_2^-)	212
$B_1F_2H_1$(g)	Difluoroborane (BHF_2)	213
$B_1F_2H_1O_1$(g)	Difluorohydroxyborane (BF_2OH)	214
$B_1F_2O_1$(g)	Boron fluoride oxide (OBF_2)	215
B_1F_3(g)	Trifluoroborane (BF_3)	216
$B_1F_4K_1$(cr)	Potassium tetrafluoroborate (KBF_4)	217
$B_1F_4K_1$(l)	Potassium tetrafluoroborate (KBF_4)	218
$B_1F_4K_1$(cr,l)	Potassium tetrafluoroborate (KBF_4)	219
$B_1F_4K_1$(g)	Potassium tetrafluoroborate (KBF_4)	220
B_1H_1(g)	Borane (BH)	221
$B_1H_1O_1$(g)	Boron hydride oxide (HBO)	222
$B_1H_1O_1^+$(g)	Boron hydride oxide, ion (HBO^+)	223
$B_1H_1O_1^-$(g)	Boron hydride oxide, ion (HBO^-)	224
$B_1H_1O_2$(cr)	Boric acid (HBO_2)	225
$B_1H_1O_2$(g)	Boric acid (HBO_2)	226
$B_1H_1S_1$(g)	Boron hydride sulfide (HBS)	227
$B_1H_1S_1^+$(g)	Boron hydride sulfide, ion (HBS^+)	228
B_1H_2(g)	Borane (BH_2)	229
$B_1H_2O_2$(g)	Dihydroxyborane ($B(OH)_2$)	230
B_1H_3(g)	Borane (BH_3)	231
$B_1H_3O_3$(cr)	Boric acid (H_3BO_3)	232
$B_1H_3O_3$(g)	Boric acid (H_3BO_3)	233
$B_1H_4K_1$(cr)	Potassium tetrahydroborate (KBH_4)	234
$B_1H_4Li_1$(cr)	Lithium tetrahydroborate ($LiBH_4$)	235
$B_1H_4Na_1$(cr)	Sodium tetrahydroborate ($NaBH_4$)	236
B_1I_1(g)	Iodoborane (BI)	237
B_1I_2(g)	Diiodoborane (BI_2)	238
B_1I_3(g)	Triiodoborane (BI_3)	239
$B_1K_1O_2$(cr)	Potassium borate (KBO_2)	240
$B_1K_1O_2$(l)	Potassium borate (KBO_2)	241
$B_1K_1O_2$(cr,l)	Potassium borate (KBO_2)	242
$B_1K_1O_2$(g)	Potassium borate (KBO_2)	243
$B_1Li_1O_2$(cr)	Lithium borate ($LiBO_2$)	244
$B_1Li_1O_2$(l)	Lithium borate ($LiBO_2$)	245
$B_1Li_1O_2$(cr,l)	Lithium borate ($LiBO_2$)	246
$B_1Li_1O_2$(g)	Lithium borate ($LiBO_2$)	247
B_1N_1(cr)	Boron nitride (BN)	248
B_1N_1(g)	Boron nitride (BN)	249
$B_1Na_1O_2$(cr)	Sodium borate ($NaBO_2$)	250
$B_1Na_1O_2$(l)	Sodium borate ($NaBO_2$)	251
$B_1Na_1O_2$(cr,l)	Sodium borate ($NaBO_2$)	252
$B_1Na_1O_2$(g)	Sodium borate ($NaBO_2$)	253
B_1O_1(g)	Boron oxide (BO)	254
B_1O_2(g)	Boron oxide (BO_2)	255
$B_1O_2^-$(g)	Boron oxide, ion (BO_2^-)	256
B_1S_1(g)	Boron sulfide (BS)	257
B_1Ti_1(cr)	Titanium boride (TiB)	258
B_2(g)	Boron (B_2)	259
$B_2Be_1O_4$(g)	Beryllium borate ($Be(BO_2)_2$)	260
$B_2Be_3O_6$(cr)	Beryllium borate ($Be_3B_2O_6$)	261
B_2Cl_4(g)	Dichloroborane ($(BCl_2)_2$)	262
B_2F_4(g)	Difluoroborane ($(BF_2)_2$)	263
$B_2F_4O_1$(g)	Difluoroborane oxide ($O(BF_2)_2$)	264
$B_2H_4O_4$(cr)	Dihydroxyborane ($(B(OH)_2)_2$)	265
$B_2H_4O_4$(g)	Dihydroxyborane ($(B(OH)_2)_2$)	266
B_2H_6(g)	Diborane (B_2H_6)	267
B_2Mg_1(cr)	Magnesium boride (MgB_2)	268
B_2O_1(g)	Boron oxide (B_2O)	269
B_2O_2(g)	Boron oxide ($(BO)_2$)	270
B_2O_3(cr)	Boron oxide (B_2O_3)	271
B_2O_3(l)	Boron oxide (B_2O_3)	272
B_2O_3(cr,l)	Boron oxide (B_2O_3)	273
B_2O_3(g)	Boron oxide (B_2O_3)	274
$B_2O_4Pb_1$(cr)	Lead borate (PbB_2O_4)	275
B_2Ti_1(cr)	Titanium boride (TiB_2)	276
B_2Ti_1(l)	Titanium boride (TiB_2)	277
B_2Ti_1(cr,l)	Titanium boride (TiB_2)	278
B_2Zr_1(cr)	Zirconium boride (ZrB_2)	279
B_2Zr_1(l)	Zirconium boride (ZrB_2)	280

Formula	Table Title	Page
$B_2Zr_1(cr,l)$	Zirconium boride (ZrB_2)	281
$B_3Cl_3O_3(g)$	Trichloroboroxin ($B_3O_3Cl_3$)	282
$B_3F_1H_2O_3(g)$	Fluoroboroxin ($B_3H_2O_3F$)	283
$B_3F_2H_1O_3(g)$	Difluoroboroxin ($B_3HO_3F_2$)	284
$B_3F_3O_3(cr)$	Trifluoroboroxin ($B_3O_3F_3$)	285
$B_3F_3O_3(g)$	Trifluoroboroxin ($B_3O_3F_3$)	286
$B_3H_3O_3(cr)$	Boroxin ($B_3H_3O_3$)	287
$B_3H_3O_3(g)$	Boroxin ($B_3H_3O_3$)	288
$B_3H_3O_6(g)$	Boric acid ($(HBO_2)_3$)	289
$B_3H_6N_3(g)$	Borazine ($B_3H_6N_3$)	290
$B_4K_2O_7(cr)$	Potassium borate ($K_2B_4O_7$)	291
$B_4K_2O_7(l)$	Potassium borate ($K_2B_4O_7$)	292
$B_4K_2O_7(cr,l)$	Potassium borate ($K_2B_4O_7$)	293
$B_4Li_2O_7(cr)$	Lithium borate ($Li_2B_4O_7$)	294
$B_4Li_2O_7(l)$	Lithium borate ($Li_2B_4O_7$)	295
$B_4Li_2O_7(cr,l)$	Lithium borate ($Li_2B_4O_7$)	296
$B_4Mg_1(cr)$	Magnesium boride (MgB_4)	297
$B_4Na_2O_7(cr)$	Sodium borate ($Na_2B_4O_7$)	298
$B_4Na_2O_7(l)$	Sodium borate ($Na_2B_4O_7$)	299
$B_4Na_2O_7(cr,l)$	Sodium borate ($Na_2B_4O_7$)	300
$B_4O_7Pb_1(cr)$	Lead borate (PbB_4O_7)	301
$B_5H_9(l)$	Pentaborane (B_5H_9)	302
$B_5H_9(g)$	Pentaborane (B_5H_9)	303
$B_6K_2O_{10}(cr)$	Potassium borate ($K_2B_6O_{10}$)	304
$B_6Li_2O_{10}(cr)$	Lithium borate ($Li_2B_6O_{10}$)	305
$B_6Na_2O_{10}(cr)$	Sodium borate ($Na_2B_6O_{10}$)	306
$B_6O_{10}Pb_1(cr)$	Lead borate (PbB_6O_{10})	307
$B_8K_2O_{13}(cr)$	Potassium borate ($K_2B_8O_{13}$)	308
$B_8K_2O_{13}(l)$	Potassium borate ($K_2B_8O_{13}$)	309
$B_8K_2O_{13}(cr,l)$	Potassium borate ($K_2B_8O_{13}$)	310
$B_8Li_2O_{13}(cr)$	Lithium borate ($Li_2B_8O_{13}$)	311
$B_{10}H_{14}(cr)$	Decaborane ($B_{10}H_{14}$)	312
$B_{10}H_{14}(l)$	Decaborane ($B_{10}H_{14}$)	313
$B_{10}H_{14}(cr,l)$	Decaborane ($B_{10}H_{14}$)	314
$B_{10}H_{14}(g)$	Decaborane ($B_{10}H_{14}$)	315
$B_{10}O_{17}Pb_2(cr)$	Lead borate ($Pb_2B_{10}O_{17}$)	316
$Ba_1(ref)$	Barium (Ba)	319
$Ba_1(cr)$	Barium (Ba)	320
$Ba_1(l)$	Barium (Ba)	321
$Ba_1(cr,l)$	Barium (Ba)	322
$Ba_1(g)$	Barium (Ba)	323
$Ba_1^+(g)$	Barium, ion (Ba^+)	324
$Ba_1Br_1(g)$	Barium bromide (BaBr)	325
$Ba_1Br_2(cr)$	Barium bromide ($BaBr_2$)	326
$Ba_1Br_2(l)$	Barium bromide ($BaBr_2$)	327
$Ba_1Br_2(cr,l)$	Barium bromide ($BaBr_2$)	328
$Ba_1Br_2(g)$	Barium bromide ($BaBr_2$)	329
$Ba_1Cl_1(g)$	Barium chloride (BaCl)	330
$Ba_1Cl_2(cr)$	Barium chloride ($BaCl_2$)	331
$Ba_1Cl_2(l)$	Barium chloride ($BaCl_2$)	332
$Ba_1Cl_2(cr,l)$	Barium chloride ($BaCl_2$)	333
$Ba_1Cl_2(g)$	Barium chloride ($BaCl_2$)	334
$Ba_1F_1(g)$	Barium fluoride (BaF)	335
$Ba_1F_1^+(g)$	Barium fluoride, ion (BaF^+)	336
$Ba_1F_2(cr)$	Barium fluoride (BaF_2)	337
$Ba_1F_2(l)$	Barium fluoride (BaF_2)	338
$Ba_1F_2(cr,l)$	Barium fluoride (BaF_2)	339
$Ba_1F_2(g)$	Barium fluoride (BaF_2)	340
$Ba_1H_1O_1(g)$	Barium hydroxide (BaOH)	341
$Ba_1H_1O_1^+(g)$	Barium hydroxide, ion ($BaOH^+$)	342
$Ba_1H_2O_2(cr)$	Barium hydroxide, alpha ($Ba(OH)_2$)	343
$Ba_1H_2O_2(l)$	Barium hydroxide ($Ba(OH)_2$)	344
$Ba_1H_2O_2(cr,l)$	Barium hydroxide ($Ba(OH)_2$)	345
$Ba_1H_2O_2(g)$	Barium hydroxide ($Ba(OH)_2$)	346
$Ba_1I_1(g)$	Barium iodide (BaI)	347
$Ba_1I_2(cr)$	Barium iodide (BaI_2)	348
$Ba_1I_2(l)$	Barium iodide (BaI_2)	349
$Ba_1I_2(cr,l)$	Barium iodide (BaI_2)	350
$Ba_1I_2(g)$	Barium iodide (BaI_2)	351
$Ba_1O_1(cr)$	Barium oxide (BaO)	352
$Ba_1O_1(l)$	Barium oxide (BaO)	353
$Ba_1O_1(cr,l)$	Barium oxide (BaO)	354
$Ba_1O_1(g)$	Barium oxide (BaO)	355
$Ba_1S_1(cr)$	Barium sulfide (BaS)	356
$Ba_1S_1(g)$	Barium sulfide (BaS)	357
$Be_1(ref)$	Beryllium (Be)	361
$Be_1(cr)$	Beryllium (Be)	362
$Be_1(l)$	Beryllium (Be)	363
$Be_1(cr,l)$	Beryllium (Be)	364
$Be_1(g)$	Beryllium (Be)	365
$Be_1^+(g)$	Beryllium, ion (Be^+)	366
$Be_1Br_1(g)$	Beryllium bromide (BeBr)	367
$Be_1Br_2(cr)$	Beryllium bromide ($BeBr_2$)	368
$Be_1Br_2(g)$	Beryllium bromide ($BeBr_2$)	369
$Be_1Cl_1(g)$	Beryllium chloride (BeCl)	370
$Be_1Cl_1^+(g)$	Beryllium chloride, ion ($BeCl^+$)	371
$Be_1Cl_1F_1(g)$	Beryllium chloride fluoride (BeClF)	372
$Be_1Cl_2(cr)$	Beryllium chloride, alpha ($BeCl_2$)	373
$Be_1Cl_2(cr)$	Beryllium chloride, beta ($BeCl_2$)	374
$Be_1Cl_2(l)$	Beryllium chloride ($BeCl_2$)	375
$Be_1Cl_2(cr,l)$	Beryllium chloride ($BeCl_2$)	376
$Be_1Cl_2(g)$	Beryllium chloride ($BeCl_2$)	377
$Be_1F_1(g)$	Beryllium fluoride (BeF)	378
$Be_1F_2(cr)$	Beryllium fluoride (BeF_2)	379
$Be_1F_2(l)$	Beryllium fluoride (BeF_2)	380
$Be_1F_2(cr,l)$	Beryllium fluoride (BeF_2)	381
$Be_1F_2(g)$	Beryllium fluoride (BeF_2)	382
$Be_1F_3Li_1(cr)$	Lithium trifluoroberyllate ($LiBeF_3$)	383
$Be_1F_3Li_1(l)$	Lithium trifluoroberyllate ($LiBeF_3$)	384
$Be_1F_3Li_1(cr,l)$	Lithium trifluoroberyllate ($LiBeF_3$)	385
$Be_1F_3Li_1(g)$	Lithium trifluoroberyllate ($LiBeF_3$)	386
$Be_1F_4Li_2(cr)$	Lithium tetrafluoroberyllate (Li_2BeF_4)	387
$Be_1F_4Li_2(l)$	Lithium tetrafluoroberyllate (Li_2BeF_4)	388
$Be_1F_4Li_2(cr,l)$	Lithium tetrafluoroberyllate (Li_2BeF_4)	389
$Be_1H_1(g)$	Beryllium hydride (BeH)	390
$Be_1H_1^+(g)$	Beryllium hydride, ion (BeH^+)	391
$Be_1H_1O_1(g)$	Beryllium hydroxide (BeOH)	392
$Be_1H_1O_1^+(g)$	Beryllium hydroxide, ion ($BeOH^+$)	393
$Be_1H_2(g)$	Beryllium hydride (BeH_2)	394
$Be_1H_2O_2(cr)$	Beryllium hydroxide, alpha ($Be(OH)_2$)	395

Formula	Table Title	Page
$Be_1H_2O_2$(cr)	Beryllium hydroxide, beta ($Be(OH)_2$)	396
$Be_1H_2O_2$(g)	Beryllium hydroxide ($Be(OH)_2$)	397
Be_1I_1(g)	Beryllium iodide (BeI)	398
Be_1I_2(cr)	Beryllium iodide (BeI_2)	399
Be_1I_2(l)	Beryllium iodide (BeI_2)	400
Be_1I_2(cr,l)	Beryllium iodide (BeI_2)	401
Be_1I_2(g)	Beryllium iodide (BeI_2)	402
Be_1N_1(g)	Beryllium nitride (BeN)	403
Be_1O_1(cr)	Beryllium oxide, alpha (BeO)	404
Be_1O_1(cr)	Beryllium oxide, beta (BeO)	405
Be_1O_1(l)	Beryllium oxide (BeO)	406
Be_1O_1(cr,l)	Beryllium oxide (BeO)	407
Be_1O_1(g)	Beryllium oxide (BeO)	408
$Be_1O_4S_1$(cr)	Beryllium sulfate, alpha ($BeSO_4$)	409
$Be_1O_4S_1$(cr)	Beryllium sulfate, beta ($BeSO_4$)	410
$Be_1O_4S_1$(cr)	Beryllium sulfate, gamma ($BeSO_4$)	411
$Be_1O_4W_1$(cr)	Beryllium tungsten oxide ($BeWO_4$)	412
Be_1S_1(cr)	Beryllium sulfide (BeS)	413
Be_1S_1(g)	Beryllium sulfide (BeS)	414
Be_2(g)	Beryllium (Be_2)	415
Be_2Cl_4(g)	Beryllium chloride ($(BeCl_2)_2$)	416
$Be_2F_2O_1$(g)	Beryllium fluoride oxide ($O(BeF)_2$)	417
Be_2O_1(g)	Beryllium oxide (Be_2O)	418
Be_2O_2(g)	Beryllium oxide ($(BeO)_2$)	419
$Be_2O_4Si_1$(cr)	Beryllium silicate (Be_2SiO_4)	420
Be_3N_2(cr)	Beryllium nitride, alpha (Be_3N_2)	421
Be_3N_2(l)	Beryllium nitride (Be_3N_2)	422
Be_3N_2(cr,l)	Beryllium nitride (Be_3N_2)	423
Be_3O_3(g)	Beryllium oxide ($(BeO)_3$)	424
Be_4O_4(g)	Beryllium oxide ($(BeO)_4$)	425
Be_5O_5(g)	Beryllium oxide ($(BeO)_5$)	426
Be_6O_6(g)	Beryllium oxide ($(BeO)_6$)	427
Br_1(g)	Bromine (Br)	429
Br_1^+(g)	Bromine, ion (Br^+)	430
Br_1^-(g)	Bromine, ion (Br^-)	431
Br_1Ca_1(g)	Calcium bromide (CaBr)	432
Br_1Cl_1(g)	Bromine chloride (BrCl)	433
Br_1F_1(g)	Bromine fluoride (BrF)	434
Br_1F_3(g)	Bromine fluoride (BrF_3)	435
Br_1F_5(g)	Bromine fluoride (BrF_5)	436
$Br_1F_5S_1$(g)	Sulfur bromide fluoride ($SBrF_5$)	437
Br_1H_1(g)	Hydrogen bromide (HBr)	438
$Br_1H_3Si_1$(g)	Bromosilane (SiH_3Br)	439
$Br_1H_4N_1$(cr)	Ammonium bromide (NH_4Br)	440
Br_1Hg_1(g)	Mercury bromide (HgBr)	441
Br_1I_1(g)	Iodine bromide (IBr)	442
Br_1K_1(cr)	Potassium bromide (KBr)	443
Br_1K_1(l)	Potassium bromide (KBr)	444
Br_1K_1(cr,l)	Potassium bromide (KBr)	445
Br_1K_1(g)	Potassium bromide (KBr)	446
Br_1Li_1(cr)	Lithium bromide (LiBr)	447
Br_1Li_1(l)	Lithium bromide (LiBr)	448
Br_1Li_1(cr,l)	Lithium bromide (LiBr)	449
Br_1Li_1(g)	Lithium bromide (LiBr)	450
Br_1Mg_1(g)	Magnesium bromide (MgBr)	451
Br_1Mo_1(g)	Molybdenum bromide (MoBr)	452
Br_1N_1(g)	Bromoimidogen (NBr)	453
$Br_1N_1O_1$(g)	Nitrosyl bromide (ONBr)	454
Br_1Na_1(cr)	Sodium bromide (NaBr)	455
Br_1Na_1(l)	Sodium bromide (NaBr)	456
Br_1Na_1(cr,l)	Sodium bromide (NaBr)	457
Br_1Na_1(g)	Sodium bromide (NaBr)	458
Br_1O_1(g)	Bromine oxide (BrO)	459
Br_1O_2(g)	Bromine oxide (OBrO)	460
Br_1O_2(g)	Bromine oxide (BrOO)	461
Br_1O_3(g)	Bromine oxide (BrO_3)	462
Br_1P_1(g)	Phosphorus bromide (PBr)	463
Br_1Pb_1(g)	Lead bromide (PbBr)	464
Br_1Si_1(g)	Bromosilylidyne (SiBr)	465
Br_1Sr_1(g)	Strontium bromide (SrBr)	466
Br_1Ti_1(g)	Titanium bromide (TiBr)	467
Br_1W_1(g)	Tungsten bromide (WBr)	468
Br_1Zr_1(g)	Zirconium bromide (ZrBr)	469
Br_2(ref)	Bromine (Br_2)	470
Br_2(cr,l)	Bromine (Br_2)	471
Br_2(g)	Bromine (Br_2)	472
Br_2Ca_1(cr)	Calcium bromide ($CaBr_2$)	473
Br_2Ca_1(l)	Calcium bromide ($CaBr_2$)	474
Br_2Ca_1(cr,l)	Calcium bromide ($CaBr_2$)	475
Br_2Ca_1(g)	Calcium bromide ($CaBr_2$)	476
Br_2Fe_1(cr)	Iron bromide ($FeBr_2$)	477
Br_2Fe_1(l)	Iron bromide ($FeBr_2$)	478
Br_2Fe_1(cr,l)	Iron bromide ($FeBr_2$)	479
Br_2Fe_1(g)	Iron bromide ($FeBr_2$)	480
$Br_2H_2Si_1$(g)	Dibromosilane (SiH_2Br_2)	481
Br_2Hg_1(cr)	Mercury bromide ($HgBr_2$)	482
Br_2Hg_1(l)	Mercury bromide ($HgBr_2$)	483
Br_2Hg_1(cr,l)	Mercury bromide ($HgBr_2$)	484
Br_2Hg_1(g)	Mercury bromide ($HgBr_2$)	485
Br_2Hg_2(cr)	Mercury bromide (Hg_2Br_2)	486
Br_2K_2(g)	Potassium bromide ($(KBr)_2$)	487
Br_2Li_2(g)	Lithium bromide ($(LiBr)_2$)	488
Br_2Mg_1(cr)	Magnesium bromide ($MgBr_2$)	489
Br_2Mg_1(l)	Magnesium bromide ($MgBr_2$)	490
Br_2Mg_1(cr,l)	Magnesium bromide ($MgBr_2$)	491
Br_2Mg_1(g)	Magnesium bromide ($MgBr_2$)	492
$Br_2Mg_1^+$(g)	Magnesium bromide, ion ($MgBr_2^+$)	493
Br_2Mo_1(cr)	Molybdenum bromide ($MoBr_2$)	494
Br_2Mo_1(g)	Molybdenum bromide ($MoBr_2$)	495
Br_2Na_2(g)	Sodium bromide ($(NaBr)_2$)	496
Br_2O_1(g)	Bromine oxide (BrOBr)	497
Br_2O_1(g)	Bromine oxide (BrBrO)	498
Br_2Pb_1(cr)	Lead bromide ($PbBr_2$)	499
Br_2Pb_1(l)	Lead bromide ($PbBr_2$)	500
Br_2Pb_1(cr,l)	Lead bromide ($PbBr_2$)	501
Br_2Pb_1(g)	Lead bromide ($PbBr_2$)	502
Br_2Si_1(g)	Dibromosilylene ($SiBr_2$)	503
Br_2Sr_1(cr)	Strontium bromide ($SrBr_2$)	504
Br_2Sr_1(l)	Strontium bromide ($SrBr_2$)	505
Br_2Sr_1(cr,l)	Strontium bromide ($SrBr_2$)	506
Br_2Sr_1(g)	Strontium bromide ($SrBr_2$)	507

Formula	Table Title	Page
$Br_2Ti_1(cr)$	Titanium bromide ($TiBr_2$)	508
$Br_2Ti_1(g)$	Titanium bromide ($TiBr_2$)	509
$Br_2Zr_1(cr)$	Zirconium bromide ($ZrBr_2$)	510
$Br_2Zr_1(l)$	Zirconium bromide ($ZrBr_2$)	511
$Br_2Zr_1(cr,l)$	Zirconium bromide ($ZrBr_2$)	512
$Br_2Zr_1(g)$	Zirconium bromide ($ZrBr_2$)	513
$Br_3H_1Si_1(g)$	Tribromosilane ($SiHBr_3$)	514
$Br_3Mo_1(cr)$	Molybdenum bromide ($MoBr_3$)	515
$Br_3Mo_1(g)$	Molybdenum bromide ($MoBr_3$)	516
$Br_3O_1P_1(g)$	Phosphoryl bromide ($POBr_3$)	517
$Br_3P_1(g)$	Phosphorus bromide (PBr_3)	518
$Br_3P_1S_1(g)$	Thiophosphoryl bromide ($PSBr_3$)	519
$Br_3Si_1(g)$	Tribromosilyl ($SiBr_3$)	520
$Br_3Ti_1(cr)$	Titanium bromide ($TiBr_3$)	521
$Br_3Ti_1(g)$	Titanium bromide ($TiBr_3$)	522
$Br_3Zr_1(cr)$	Zirconium bromide ($ZrBr_3$)	523
$Br_3Zr_1(g)$	Zirconium bromide ($ZrBr_3$)	524
$Br_4Fe_2(g)$	Iron bromide ($(FeBr_2)_2$)	525
$Br_4Mg_2(g)$	Magnesium bromide ($(MgBr_2)_2$)	526
$Br_4Mo_1(cr)$	Molybdenum bromide ($MoBr_4$)	527
$Br_4Mo_1(g)$	Molybdenum bromide ($MoBr_4$)	528
$Br_4Pb_1(g)$	Lead bromide ($PbBr_4$)	529
$Br_4Si_1(l)$	Tetrabromosilane ($SiBr_4$)	530
$Br_4Si_1(g)$	Tetrabromosilane ($SiBr_4$)	531
$Br_4Ti_1(cr)$	Titanium bromide ($TiBr_4$)	532
$Br_4Ti_1(l)$	Titanium bromide ($TiBr_4$)	533
$Br_4Ti_1(cr,l)$	Titanium bromide ($TiBr_4$)	534
$Br_4Ti_1(g)$	Titanium bromide ($TiBr_4$)	535
$Br_4Zr_1(cr)$	Zirconium bromide ($ZrBr_4$)	536
$Br_4Zr_1(g)$	Zirconium bromide ($ZrBr_4$)	537
$Br_5Nb_1(cr)$	Niobium bromide ($NbBr_5$)	538
$Br_5Nb_1(l)$	Niobium bromide ($NbBr_5$)	539
$Br_5Nb_1(cr,l)$	Niobium bromide ($NbBr_5$)	540
$Br_5Nb_1(g)$	Niobium bromide ($NbBr_5$)	541
$Br_5W_1(cr)$	Tungsten bromide (WBr_5)	542
$Br_5W_1(l)$	Tungsten bromide (WBr_5)	543
$Br_5W_1(cr,l)$	Tungsten bromide (WBr_5)	544
$Br_5W_1(g)$	Tungsten bromide (WBr_5)	545
$Br_6W_1(cr)$	Tungsten bromide (WBr_6)	546
$Br_6W_1(g)$	Tungsten bromide (WBr_6)	547
$C_{0.98}Nb_1(cr)$	Niobium carbide ($NbC_{0.98}$)	549
C_1(ref)	Carbon (C)	550
$C_1(g)$	Carbon (C)	551
$C_1^+(g)$	Carbon, ion (C^+)	552
$C_1^-(g)$	Carbon, ion (C^-)	553
$C_1Al_1(g)$	Aluminum carbide (AlC)	554
$C_1B_1(g)$	Boron carbide (BC)	555
$C_1B_4(cr)$	Boron carbide (B_4C)	556
$C_1B_4(l)$	Boron carbide (B_4C)	557
$C_1B_4(cr,l)$	Boron carbide (B_4C)	558
$C_1Be_2(cr)$	Beryllium carbide (Be_2C)	559
$C_1Be_2(l)$	Beryllium carbide (Be_2C)	560
$C_1Be_2(cr,l)$	Beryllium carbide (Be_2C)	561
$C_1Br_1(g)$	Bromomethylidyne (CBr)	562
$C_1Br_1F_3(g)$	Bromotrifluoromethane ($CBrF_3$)	563
$C_1Br_1N_1(g)$	Cyanogen bromide (BrCN)	564
$C_1Br_4(g)$	Tetrabromomethane (CBr_4)	565
$C_1Cl_1(g)$	Chloromethylidyne (CCl)	566
$C_1Cl_1F_1O_1(g)$	Carbonic chloride fluoride (COClF)	567
$C_1Cl_1F_3(g)$	Chlorotrifluoromethane ($CClF_3$)	568
$C_1Cl_1N_1(g)$	Cyanogen chloride (ClCN)	569
$C_1Cl_1O_1(g)$	Carbonyl chloride (COCl)	570
$C_1Cl_2(g)$	Dichloromethylene (CCl_2)	571
$C_1Cl_2F_2(g)$	Dichlorodifluoromethane (CCl_2F_2)	572
$C_1Cl_2O_1(g)$	Carbonic dichloride ($COCl_2$)	573
$C_1Cl_3(g)$	Trichloromethyl (CCl_3)	574
$C_1Cl_3F_1(g)$	Trichlorofluoromethane (CCl_3F)	575
$C_1Cl_4(g)$	Tetrachloromethane (CCl_4)	576
$C_1Cu_1N_1(cr)$	Copper cyanide (CuCN)	577
$C_1F_1(g)$	Fluoromethylidyne (CF)	578
$C_1F_1^+(g)$	Fluoromethylidyne, ion (CF^+)	579
$C_1F_1N_1(g)$	Cyanogen fluoride (FCN)	580
$C_1F_1O_1(g)$	Carbonyl fluoride (COF)	581
$C_1F_2(g)$	Difluoromethylene (CF_2)	582
$C_1F_2^+(g)$	Difluoromethylene, ion (CF_2^+)	583
$C_1F_2O_1(g)$	Carbonic difluoride (COF_2)	584
$C_1F_3(g)$	Trifluoromethyl (CF_3)	585
$C_1F_3^+(g)$	Trifluoromethyl, ion (CF_3^+)	586
$C_1F_3I_1(g)$	Trifluoriodomethane (CIF_3)	587
$C_1F_4(g)$	Tetrafluoromethane (CF_4)	588
$C_1F_4O_1(g)$	Trifluoromethyl hypofluorite (CF_3OF)	589
$C_1F_8S_1(g)$	Pentafluoro(trifluoromethyl)sulfur (CF_3SF_5)	590
$C_1H_1(g)$	Methylidyne (CH)	591
$C_1H_1^+(g)$	Methylidyne, ion (CH^+)	592
$C_1H_1Cl_1(g)$	Chloromethylene (CHCl)	593
$C_1H_1Cl_1F_2(g)$	Chlorodifluoromethane ($CHClF_2$)	594
$C_1H_1Cl_2F_1(g)$	Dichlorofluoromethane ($CHCl_2F$)	595
$C_1H_1Cl_3(g)$	Trichloromethane ($CHCl_3$)	596
$C_1H_1F_1(g)$	Fluoromethylene (CHF)	597
$C_1H_1F_1O_1(g)$	Formyl fluoride (HCOF)	598
$C_1H_1F_3(g)$	Trifluoromethane (CHF_3)	599
$C_1H_1N_1(g)$	Hydrogen cyanide (HCN)	600
$C_1H_1N_1O_1(g)$	Hydrogen isocyanate (HNCO)	601
$C_1H_1O_1(g)$	Formyl (HCO)	602
$C_1H_1O_1^+(g)$	Formyl, ion (HCO^+)	603
$C_1H_1P_1(g)$	Methinophosphide (CHP)	604
$C_1H_2(g)$	Methylene (CH_2)	605
$C_1H_2Cl_1F_1(g)$	Chlorofluoromethane (CH_2ClF)	606
$C_1H_2Cl_2(g)$	Dichloromethane (CH_2Cl_2)	607
$C_1H_2F_2(g)$	Difluoromethane (CH_2F_2)	608
$C_1H_2O_1(g)$	Formaldehyde (H_2CO)	609
$C_1H_3(g)$	Methyl (CH_3)	610
$C_1H_3Cl_1(g)$	Chloromethane (CH_3Cl)	611
$C_1H_3Cl_3Si_1(g)$	Trichloromethylsilane ($SiCH_3Cl_3$)	612
$C_1H_3F_1(g)$	Fluoromethane (CH_3F)	613
$C_1H_3F_3Si_1(g)$	Trifluoromethylsilane ($SiCH_3F_3$)	614
$C_1H_4(g)$	Methane (CH_4)	615
$C_1I_1N_1(g)$	Cyanogen iodide (CNI)	616
$C_1K_1N_1(cr)$	Potassium cyanide (KCN)	617
$C_1K_1N_1(l)$	Potassium cyanide (KCN)	618
$C_1K_1N_1(cr,l)$	Potassium cyanide (KCN)	619

Formula	Table Title	Page
$C_1K_1N_1(g)$	Potassium cyanide (KCN)	620
$C_1K_2O_3(cr)$	Potassium carbonate (K_2CO_3)	621
$C_1K_2O_3(l)$	Potassium carbonate (K_2CO_3)	622
$C_1K_2O_3(cr,l)$	Potassium carbonate (K_2CO_3)	623
$C_1Li_2O_3(cr)$	Lithium carbonate (Li_2CO_3)	624
$C_1Li_2O_3(l)$	Lithium carbonate (Li_2CO_3)	625
$C_1Li_2O_3(cr,l)$	Lithium carbonate (Li_2CO_3)	626
$C_1Mg_1O_3(cr)$	Magnesium carbonate ($MgCO_3$)	627
$C_1N_1(g)$	Cyanogen (CN)	628
$C_1N_1^+(g)$	Cyanogen, ion (CN^+)	629
$C_1N_1^-(g)$	Cyanide (CN^-)	630
$C_1N_1Na_1(cr)$	Sodium cyanide (NaCN)	631
$C_1N_1Na_1(l)$	Sodium cyanide (NaCN)	632
$C_1N_1Na_1(cr,l)$	Sodium cyanide (NaCN)	633
$C_1N_1Na_1(g)$	Sodium cyanide (NaCN)	634
$C_1N_1O_1(g)$	NCO radical (NCO)	635
$C_1N_2(g)$	CNN radical (CNN)	636
$C_1N_2(g)$	NCN radical (NCN)	637
$C_1Na_2O_3(cr)$	Sodium carbonate (Na_2CO_3)	638
$C_1Na_2O_3(l)$	Sodium carbonate (Na_2CO_3)	639
$C_1Na_2O_3(cr,l)$	Sodium carbonate (Na_2CO_3)	640
$C_1O_1(g)$	Carbon monoxide (CO)	641
$C_1O_1S_1(g)$	Carbon oxide sulfide (COS)	642
$C_1O_2(g)$	Carbon dioxide (CO_2)	643
$C_1O_2^-(g)$	Carbon dioxide, ion (CO_2^-)	644
$C_1P_1(g)$	Carbon phosphide (CP)	645
$C_1S_1(g)$	Carbon sulfide (CS)	646
$C_1S_2(g)$	Carbon disulfide (CS_2)	647
$C_1Si_1(cr)$	Silicon carbide, alpha (SiC)	648
$C_1Si_1(cr)$	Silicon carbide, beta (SiC)	649
$C_1Si_1(g)$	Silicon carbide (SiC)	650
$C_1Si_2(g)$	Silicon carbide (Si_2C)	651
$C_1Ta_1(cr)$	Tantalum carbide (TaC)	652
$C_1Ta_1(l)$	Tantalum carbide (TaC)	653
$C_1Ta_1(cr,l)$	Tantalum carbide (TaC)	654
$C_1Ti_1(cr)$	Titanium carbide (TiC)	655
$C_1Ti_1(l)$	Titanium carbide (TiC)	656
$C_1Ti_1(cr,l)$	Titanium carbide (TiC)	657
$C_1Zr_1(cr)$	Zirconium carbide (ZrC)	658
$C_1Zr_1(l)$	Zirconium carbide (ZrC)	659
$C_1Zr_1(cr,l)$	Zirconium carbide (ZrC)	660
$C_2(g)$	Carbon (C_2)	661
$C_2^-(g)$	Carbon, ion (C_2^-)	662
$C_2Be_1(g)$	Beryllium carbide (BeC_2)	663
$C_2Cl_2(g)$	Dichloroethyne (C_2Cl_2)	664
$C_2Cl_4(g)$	Tetrachloroethene (C_2Cl_4)	665
$C_2Cl_6(g)$	Hexachloroethane (C_2Cl_6)	666
$C_2Cr_3(cr)$	Chromium carbide (Cr_3C_2)	667
$C_2F_2(g)$	Difluoroethyne (C_2F_2)	668
$C_2F_3N_1(g)$	Trifluoroacetonitrile (CF_3CN)	669
$C_2F_4(g)$	Tetrafluoroethene (C_2F_4)	670
$C_2F_6(g)$	Hexafluoroethane (C_2F_6)	671
$C_2H_1(g)$	Ethynyl (C_2H)	672
$C_2H_1Cl_1(g)$	Chloroethyne (C_2HCl)	673
$C_2H_1F_1(g)$	Fluoroethyne (C_2HF)	674
$C_2H_2(g)$	Ethyne (C_2H_2)	675
$C_2H_4(g)$	Ethene (C_2H_4)	676
$C_2H_4O_1(g)$	Oxirane (C_2H_4O)	677
$C_2K_2N_2(g)$	Potassium cyanide ($(KCN)_2$)	678
$C_2Li_2(cr)$	Lithium carbide (Li_2C_2)	679
$C_2Mg_1(cr)$	Magnesium carbide (MgC_2)	680
$C_2N_1(g)$	CNC radical (C_2N)	681
$C_2N_2(g)$	Ethanedinitrile ($(CN)_2$)	682
$C_2N_2Na_2(g)$	Sodium cyanide ($(NaCN)_2$)	683
$C_2O_1(g)$	CCO radical (C_2O)	684
$C_2Si_1(g)$	Silicon carbide (SiC_2)	685
$C_3(g)$	Carbon (C_3)	686
$C_3Al_4(cr)$	Aluminum carbide (Al_4C_3)	687
$C_3Cr_7(cr)$	Chromium carbide (Cr_7C_3)	688
$C_3Mg_2(cr)$	Magnesium carbide (Mg_2C_3)	689
$C_3O_2(g)$	Carbon suboxide (C_3O_2)	690
$C_4(g)$	Carbon (C_4)	691
$C_4H_{12}Si_1(g)$	Tetramethylsilane ($Si(CH_3)_4$)	692
$C_4N_2(g)$	2−Butynedinitrile (C_4N_2)	693
$C_4Ni_1O_4(l)$	Nickel carbonyl ($Ni(CO)_4$)	694
$C_4Ni_1O_4(g)$	Nickel carbonyl ($Ni(CO)_4$)	695
$C_5(g)$	Carbon (C_5)	696
$C_5Fe_1O_5(l)$	Iron carbonyl ($Fe(CO)_5$)	697
$C_5Fe_1O_5(g)$	Iron carbonyl ($Fe(CO)_5$)	698
$C_6Cr_{23}(cr)$	Chromium carbide ($Cr_{23}C_6$)	699
$Ca_1(ref)$	Calcium (Ca)	703
$Ca_1(cr)$	Calcium, alpha (Ca)	704
$Ca_1(cr)$	Calcium, beta (Ca)	705
$Ca_1(l)$	Calcium (Ca)	706
$Ca_1(cr,l)$	Calcium (Ca)	707
$Ca_1(g)$	Calcium (Ca)	708
$Ca_1^+(g)$	Calcium, ion (Ca^+)	709
$Ca_1Cl_1(g)$	Calcium chloride (CaCl)	710
$Ca_1Cl_2(cr)$	Calcium chloride ($CaCl_2$)	711
$Ca_1Cl_2(l)$	Calcium chloride ($CaCl_2$)	712
$Ca_1Cl_2(cr,l)$	Calcium chloride ($CaCl_2$)	713
$Ca_1Cl_2(g)$	Calcium chloride ($CaCl_2$)	714
$Ca_1F_1(g)$	Calcium fluoride (CaF)	715
$Ca_1F_2(cr)$	Calcium fluoride (CaF_2)	716
$Ca_1F_2(l)$	Calcium fluoride (CaF_2)	717
$Ca_1F_2(cr,l)$	Calcium fluoride (CaF_2)	718
$Ca_1F_2(g)$	Calcium fluoride (CaF_2)	719
$Ca_1H_1O_1(g)$	Calcium hydroxide (CaOH)	720
$Ca_1H_1O_1^+(g)$	Calcium hydroxide, ion ($CaOH^+$)	721
$Ca_1H_2O_2(cr)$	Calcium hydroxide ($Ca(OH)_2$)	722
$Ca_1H_2O_2(g)$	Calcium hydroxide ($Ca(OH)_2$)	723
$Ca_1I_1(g)$	Calcium iodide (CaI)	724
$Ca_1I_2(cr)$	Calcium iodide (CaI_2)	725
$Ca_1I_2(l)$	Calcium iodide (CaI_2)	726
$Ca_1I_2(cr,l)$	Calcium iodide (CaI_2)	727
$Ca_1I_2(g)$	Calcium iodide (CaI_2)	728
$Ca_1O_1(cr)$	Calcium oxide (CaO)	729
$Ca_1O_1(l)$	Calcium oxide (CaO)	730
$Ca_1O_1(cr,l)$	Calcium oxide (CaO)	731
$Ca_1O_1(g)$	Calcium oxide (CaO)	732
$Ca_1S_1(cr)$	Calcium sulfide (CaS)	733

Formula	Table Title	Page
$Ca_1S_1(g)$	Calcium sulfide (CaS)	734
$Ca_2(g)$	Calcium (Ca_2)	735
$Cl_1(g)$	Chlorine (Cl)	737
$Cl_1^+(g)$	Chlorine, ion (Cl^+)	738
$Cl_1^-(g)$	Chlorine, ion (Cl^-)	739
$Cl_1Co_1(g)$	Cobalt chloride (CoCl)	740
$Cl_1Cs_1(cr)$	Cesium chloride (CsCl)	741
$Cl_1Cs_1(l)$	Cesium chloride (CsCl)	742
$Cl_1Cs_1(cr,l)$	Cesium chloride (CsCl)	743
$Cl_1Cs_1(g)$	Cesium chloride (CsCl)	744
$Cl_1Cu_1(cr)$	Copper chloride (CuCl)	745
$Cl_1Cu_1(l)$	Copper chloride (CuCl)	746
$Cl_1Cu_1(cr,l)$	Copper chloride (CuCl)	747
$Cl_1Cu_1(g)$	Copper chloride (CuCl)	748
$Cl_1D_1(g)$	Hydrochloric acid−d (DCl)	749
$Cl_1D_1O_1(g)$	Hypochlorous acid−d (DOCl)	750
$Cl_1F_1(g)$	Chlorine fluoride (ClF)	751
$Cl_1F_1Li_2(g)$	Lithium chloride fluoride (Li_2ClF)	752
$Cl_1F_1Mg_1(g)$	Magnesium chloride fluoride (MgClF)	753
$Cl_1F_1O_2S_1(g)$	Sulfuryl chloride fluoride (SO_2ClF)	754
$Cl_1F_1O_3(g)$	Perchloryl fluoride (ClO_3F)	755
$Cl_1F_2O_1P_1(g)$	Phosphoryl chloride fluoride ($POClF_2$)	756
$Cl_1F_3(g)$	Chlorine fluoride (ClF_3)	757
$Cl_1F_3Si_1(g)$	Chlorotrifluorosilane ($SiClF_3$)	758
$Cl_1F_5(g)$	Chlorine fluoride (ClF_5)	759
$Cl_1F_5S_1(g)$	Sulfur chloride fluoride ($SClF_5$)	760
$Cl_1Fe_1(g)$	Iron chloride (FeCl)	761
$Cl_1H_1(g)$	Hydrogen chloride (HCl)	762
$Cl_1H_1O_1(g)$	Hypochlorous acid (HOCl)	763
$Cl_1H_3Si_1(g)$	Chlorosilane (SiH_3Cl)	764
$Cl_1H_4N_1(cr)$	Ammonium chloride (NH_4Cl)	765
$Cl_1H_4N_1O_4(cr)$	Ammonium perchlorate (NH_4ClO_4)	766
$Cl_1Hg_1(g)$	Mercury chloride (HgCl)	767
$Cl_1I_1(cr)$	Iodine chloride (ICl)	768
$Cl_1I_1(l)$	Iodine chloride (ICl)	769
$Cl_1I_1(cr,l)$	Iodine chloride (ICl)	770
$Cl_1I_1(g)$	Iodine chloride (ICl)	771
$Cl_1K_1(cr)$	Potassium chloride (KCl)	772
$Cl_1K_1(l)$	Potassium chloride (KCl)	773
$Cl_1K_1(cr,l)$	Potassium chloride (KCl)	774
$Cl_1K_1(g)$	Potassium chloride (KCl)	775
$Cl_1K_1O_4(cr)$	Potassium perchlorate ($KClO_4$)	776
$Cl_1Li_1(cr)$	Lithium chloride (LiCl)	777
$Cl_1Li_1(l)$	Lithium chloride (LiCl)	778
$Cl_1Li_1(cr,l)$	Lithium chloride (LiCl)	779
$Cl_1Li_1(g)$	Lithium chloride (LiCl)	780
$Cl_1Li_1O_1(g)$	Lithium hypochlorite (LiOCl)	781
$Cl_1Li_1O_4(cr)$	Lithium perchlorate ($LiClO_4$)	782
$Cl_1Li_1O_4(l)$	Lithium perchlorate ($LiClO_4$)	783
$Cl_1Li_1O_4(cr,l)$	Lithium perchlorate ($LiClO_4$)	784
$Cl_1Mg_1(g)$	Magnesium chloride (MgCl)	785
$Cl_1Mg_1^+(g)$	Magnesium chloride, ion ($MgCl^+$)	786
$Cl_1N_1O_1(g)$	Nitrosyl chloride (ONCl)	787
$Cl_1N_1O_2(g)$	Nitryl chloride (NO_2Cl)	788
$Cl_1Na_1(cr)$	Sodium chloride (NaCl)	789
$Cl_1Na_1(l)$	Sodium chloride (NaCl)	790
$Cl_1Na_1(cr,l)$	Sodium chloride (NaCl)	791
$Cl_1Na_1(g)$	Sodium chloride (NaCl)	792
$Cl_1Na_1O_4(cr)$	Sodium perchlorate ($NaClO_4$)	793
$Cl_1Ni_1(g)$	Nickel chloride (NiCl)	794
$Cl_1O_1(g)$	Chlorine oxide (ClO)	795
$Cl_1O_1Ti_1(g)$	Titanium chloride oxide (OTiCl)	796
$Cl_1O_2(g)$	Chlorine oxide (OClO)	797
$Cl_1O_2(g)$	Chlorine oxide (ClOO)	798
$Cl_1O_3(g)$	Chlorine oxide (ClO_3)	799
$Cl_1P_1(g)$	Phosphorus chloride (PCl)	800
$Cl_1Pb_1(g)$	Lead chloride (PbCl)	801
$Cl_1Pb_1^+(g)$	Lead chloride, ion ($PbCl^+$)	802
$Cl_1S_1(g)$	Sulfur chloride (SCl)	803
$Cl_1S_1^+(g)$	Sulfur chloride, ion (SCl^+)	804
$Cl_1S_2(g)$	Sulfur chloride (S_2Cl)	805
$Cl_1Si_1(g)$	Chlorosilylidyne (SiCl)	806
$Cl_1Sr_1(g)$	Strontium chloride (SrCl)	807
$Cl_1Ti_1(g)$	Titanium chloride (TiCl)	808
$Cl_1W_1(g)$	Tungsten chloride (WCl)	809
$Cl_1Zr_1(g)$	Zirconium chloride (ZrCl)	810
$Cl_2(ref)$	Chlorine (Cl_2)	811
$Cl_2Co_1(cr)$	Cobalt chloride ($CoCl_2$)	812
$Cl_2Co_1(l)$	Cobalt chloride ($CoCl_2$)	813
$Cl_2Co_1(cr,l)$	Cobalt chloride ($CoCl_2$)	814
$Cl_2Co_1(g)$	Cobalt chloride ($CoCl_2$)	815
$Cl_2Cs_2(g)$	Cesium chloride ($(CsCl)_2$)	816
$Cl_2Cu_1(cr)$	Copper chloride ($CuCl_2$)	817
$Cl_2F_1O_1P_1(g)$	Phosphoryl chloride fluoride ($POCl_2F$)	818
$Cl_2Fe_1(cr)$	Iron chloride ($FeCl_2$)	819
$Cl_2Fe_1(l)$	Iron chloride ($FeCl_2$)	820
$Cl_2Fe_1(cr,l)$	Iron chloride ($FeCl_2$)	821
$Cl_2Fe_1(g)$	Iron chloride ($FeCl_2$)	822
$Cl_2H_2Si_1(g)$	Dichlorosilane (SiH_2Cl_2)	823
$Cl_2Hg_1(cr)$	Mercury chloride ($HgCl_2$)	824
$Cl_2Hg_1(l)$	Mercury chloride ($HgCl_2$)	825
$Cl_2Hg_1(cr,l)$	Mercury chloride ($HgCl_2$)	826
$Cl_2Hg_1(g)$	Mercury chloride ($HgCl_2$)	827
$Cl_2Hg_2(cr)$	Mercury chloride (Hg_2Cl_2)	828
$Cl_2K_2(g)$	Potassium chloride ($(KCl)_2$)	829
$Cl_2Li_2(g)$	Lithium chloride ($(LiCl)_2$)	830
$Cl_2Mg_1(cr)$	Magnesium chloride ($MgCl_2$)	831
$Cl_2Mg_1(l)$	Magnesium chloride ($MgCl_2$)	832
$Cl_2Mg_1(cr,l)$	Magnesium chloride ($MgCl_2$)	833
$Cl_2Mg_1(g)$	Magnesium chloride ($MgCl_2$)	834
$Cl_2Mo_1O_2(g)$	Molybdenum chloride oxide (MoO_2Cl_2)	835
$Cl_2Na_2(g)$	Sodium chloride ($(NaCl)_2$)	836
$Cl_2Ni_1(cr)$	Nickel chloride ($NiCl_2$)	837
$Cl_2Ni_1(l)$	Nickel chloride ($NiCl_2$)	838
$Cl_2Ni_1(cr,l)$	Nickel chloride ($NiCl_2$)	839
$Cl_2Ni_1(g)$	Nickel chloride ($NiCl_2$)	840
$Cl_2O_1(g)$	Chlorine oxide (ClOCl)	841
$Cl_2O_1(g)$	Chlorosyl Chloride (ClClO)	842
$Cl_2O_1Ti_1(g)$	Titanium chloride oxide ($TiOCl_2$)	843
$Cl_2O_2(g)$	Chlorine oxide (ClO_2Cl)	844
$Cl_2O_2(g)$	Chloryl Chloride (ClOClO)	845

Formula	Table Title	Page
$Cl_2O_2(g)$	Chlorine chlorite ($ClClO_2$)	846
$Cl_2O_2S_1(g)$	Sulfuryl chloride (SO_2Cl_2)	847
$Cl_2O_2W_1(cr)$	Tungsten chloride oxide (WO_2Cl_2)	848
$Cl_2O_2W_1(g)$	Tungsten chloride oxide (WO_2Cl_2)	849
$Cl_2Pb_1(cr)$	Lead chloride ($PbCl_2$)	850
$Cl_2Pb_1(l)$	Lead chloride ($PbCl_2$)	851
$Cl_2Pb_1(cr,l)$	Lead chloride ($PbCl_2$)	852
$Cl_2Pb_1(g)$	Lead chloride ($PbCl_2$)	853
$Cl_2Pb_1^+(g)$	Lead chloride, ion ($PbCl_2^+$)	854
$Cl_2S_1(l)$	Sulfur chloride (SCl_2)	855
$Cl_2S_1(g)$	Sulfur chloride (SCl_2)	856
$Cl_2S_1^+(g)$	Sulfur chloride, ion (SCl_2^+)	857
$Cl_2S_2(l)$	Sulfur chloride (ClSSCl)	858
$Cl_2S_2(g)$	Sulfur chloride (ClSSCl)	859
$Cl_2Si_1(g)$	Dichlorosilylene ($SiCl_2$)	860
$Cl_2Sr_1(cr)$	Strontium chloride ($SrCl_2$)	861
$Cl_2Sr_1(l)$	Strontium chloride ($SrCl_2$)	862
$Cl_2Sr_1(cr,l)$	Strontium chloride ($SrCl_2$)	863
$Cl_2Sr_1(g)$	Strontium chloride ($SrCl_2$)	864
$Cl_2Ti_1(cr)$	Titanium chloride ($TiCl_2$)	865
$Cl_2Ti_1(g)$	Titanium chloride ($TiCl_2$)	866
$Cl_2W_1(cr)$	Tungsten chloride (WCl_2)	867
$Cl_2W_1(g)$	Tungsten chloride (WCl_2)	868
$Cl_2Zr_1(cr)$	Zirconium chloride ($ZrCl_2$)	869
$Cl_2Zr_1(l)$	Zirconium chloride ($ZrCl_2$)	870
$Cl_2Zr_1(cr,l)$	Zirconium chloride ($ZrCl_2$)	871
$Cl_2Zr_1(g)$	Zirconium chloride ($ZrCl_2$)	872
$Cl_3Co_1(g)$	Cobalt chloride ($CoCl_3$)	873
$Cl_3Cu_3(g)$	Copper chloride ($(CuCl)_3$)	874
$Cl_3F_1Si_1(g)$	Trichlorofluorosilane ($SiCl_3F$)	875
$Cl_3Fe_1(cr)$	Iron chloride ($FeCl_3$)	876
$Cl_3Fe_1(l)$	Iron chloride ($FeCl_3$)	877
$Cl_3Fe_1(cr,l)$	Iron chloride ($FeCl_3$)	878
$Cl_3Fe_1(g)$	Iron chloride ($FeCl_3$)	879
$Cl_3H_1Si_1(g)$	Trichlorosilane ($SiHCl_3$)	880
$Cl_3Li_3(g)$	Lithium chloride ($(LiCl)_3$)	881
$Cl_3O_1P_1(g)$	Phosphoryl chloride ($OPCl_3$)	882
$Cl_3P_1(g)$	Phosphorus chloride (PCl_3)	883
$Cl_3P_1S_1(g)$	Thiophosphoryl chloride ($SPCl_3$)	884
$Cl_3Si_1(g)$	Trichlorosilyl ($SiCl_3$)	885
$Cl_3Ti_1(cr)$	Titanium chloride ($TiCl_3$)	886
$Cl_3Ti_1(g)$	Titanium chloride ($TiCl_3$)	887
$Cl_3Zr_1(cr)$	Zirconium chloride ($ZrCl_3$)	888
$Cl_3Zr_1(g)$	Zirconium chloride ($ZrCl_3$)	889
$Cl_4Co_2(g)$	Cobalt chloride ($(CoCl_2)_2$)	890
$Cl_4Fe_2(g)$	Iron chloride ($(FeCl_2)_2$)	891
$Cl_4Mg_2(g)$	Magnesium chloride ($(MgCl_2)_2$)	892
$Cl_4Mo_1(cr)$	Molybdenum chloride ($MoCl_4$)	893
$Cl_4Mo_1(l)$	Molybdenum chloride ($MoCl_4$)	894
$Cl_4Mo_1(cr,l)$	Molybdenum chloride ($MoCl_4$)	895
$Cl_4Mo_1(g)$	Molybdenum chloride ($MoCl_4$)	896
$Cl_4O_1W_1(cr)$	Tungsten chloride oxide ($OWCl_4$)	897
$Cl_4O_1W_1(l)$	Tungsten chloride oxide ($OWCl_4$)	898
$Cl_4O_1W_1(cr,l)$	Tungsten chloride oxide ($OWCl_4$)	899
$Cl_4O_1W_1(g)$	Tungsten chloride oxide ($OWCl_4$)	900
$Cl_4Pb_1(g)$	Lead chloride ($PbCl_4$)	901
$Cl_4Si_1(g)$	Tetrachlorosilane ($SiCl_4$)	902
$Cl_4Ti_1(cr)$	Titanium chloride ($TiCl_4$)	903
$Cl_4Ti_1(l)$	Titanium chloride ($TiCl_4$)	904
$Cl_4Ti_1(cr,l)$	Titanium chloride ($TiCl_4$)	905
$Cl_4Ti_1(g)$	Titanium chloride ($TiCl_4$)	906
$Cl_4W_1(cr)$	Tungsten chloride (WCl_4)	907
$Cl_4W_1(g)$	Tungsten chloride (WCl_4)	908
$Cl_4Zr_1(cr)$	Zirconium chloride ($ZrCl_4$)	909
$Cl_4Zr_1(g)$	Zirconium chloride ($ZrCl_4$)	910
$Cl_5Mo_1(cr)$	Molybdenum chloride ($MoCl_5$)	911
$Cl_5Mo_1(l)$	Molybdenum chloride ($MoCl_5$)	912
$Cl_5Mo_1(cr,l)$	Molybdenum chloride ($MoCl_5$)	913
$Cl_5Mo_1(g)$	Molybdenum chloride ($MoCl_5$)	914
$Cl_5Nb_1(cr)$	Niobium chloride ($NbCl_5$)	915
$Cl_5Nb_1(l)$	Niobium chloride ($NbCl_5$)	916
$Cl_5Nb_1(cr,l)$	Niobium chloride ($NbCl_5$)	917
$Cl_5Nb_1(g)$	Niobium chloride ($NbCl_5$)	918
$Cl_5P_1(g)$	Phosphorus chloride (PCl_5)	919
$Cl_5Ta_1(cr)$	Tantalum chloride ($TaCl_5$)	920
$Cl_5Ta_1(l)$	Tantalum chloride ($TaCl_5$)	921
$Cl_5Ta_1(cr,l)$	Tantalum chloride ($TaCl_5$)	922
$Cl_5Ta_1(g)$	Tantalum chloride ($TaCl_5$)	923
$Cl_5W_1(cr)$	Tungsten chloride (WCl_5)	924
$Cl_5W_1(l)$	Tungsten chloride (WCl_5)	925
$Cl_5W_1(cr,l)$	Tungsten chloride (WCl_5)	926
$Cl_5W_1(g)$	Tungsten chloride (WCl_5)	927
$Cl_6Fe_2(g)$	Iron chloride ($(FeCl_3)_2$)	928
$Cl_6Mo_1(cr)$	Molybdenum chloride ($MoCl_6$)	929
$Cl_6Mo_1(g)$	Molybdenum chloride ($MoCl_6$)	930
$Cl_6W_1(cr)$	Tungsten chloride, alpha (WCl_6)	931
$Cl_6W_1(cr)$	Tungsten chloride, beta (WCl_6)	932
$Cl_6W_1(l)$	Tungsten chloride (WCl_6)	933
$Cl_6W_1(cr,l)$	Tungsten chloride (WCl_6)	934
$Cl_6W_1(g)$	Tungsten chloride (WCl_6)	935
$Cl_{10}W_2(g)$	Tungsten chloride ($(WCl_5)_2$)	936
$Co_1(ref)$	Cobalt (Co)	943
$Co_1(cr)$	Cobalt (Co)	944
$Co_1(l)$	Cobalt (Co)	945
$Co_1(cr,l)$	Cobalt (Co)	946
$Co_1(g)$	Cobalt (Co)	947
$Co_1^+(g)$	Cobalt, ion (Co^+)	948
$Co_1^-(g)$	Cobalt, ion (Co^-)	949
$Co_1F_2(cr)$	Cobalt fluoride (CoF_2)	950
$Co_1F_2(l)$	Cobalt fluoride (CoF_2)	951
$Co_1F_2(cr,l)$	Cobalt fluoride (CoF_2)	952
$Co_1F_2(g)$	Cobalt fluoride (CoF_2)	953
$Co_1F_3(cr)$	Cobalt fluoride (CoF_3)	954
$Co_1O_1(cr)$	Cobalt oxide (CoO)	955
$Co_1O_4S_1(cr)$	Cobalt sulfate ($CoSO_4$)	956
$Co_3O_4(cr)$	Cobalt oxide (Co_3O_4)	957
$Cr_1(ref)$	Chromium (Cr)	959
$Cr_1(cr)$	Chromium (Cr)	960
$Cr_1(l)$	Chromium (Cr)	961

Formula	Table Title	Page
$Cr_1(cr,l)$	Chromium (Cr)	962
$Cr_1(g)$	Chromium (Cr)	963
$Cr_1^+(g)$	Chromium, ion (Cr^+)	964
$Cr_1^-(g)$	Chromium, ion (Cr^-)	965
$Cr_1N_1(cr)$	Chromium nitride (CrN)	966
$Cr_1N_1(g)$	Chromium nitride (CrN)	967
$Cr_1O_1(g)$	Chromium oxide (CrO)	968
$Cr_1O_2(g)$	Chromium oxide (CrO_2)	969
$Cr_1O_3(g)$	Chromium oxide (CrO_3)	970
$Cr_2N_1(cr)$	Chromium nitride (Cr_2N)	971
$Cr_2O_3(cr)$	Chromium oxide (Cr_2O_3)	972
$Cr_2O_3(l)$	Chromium oxide (Cr_2O_3)	973
$Cr_2O_3(cr,l)$	Chromium oxide (Cr_2O_3)	974
$Cs_1(ref)$	Cesium (Cs)	977
$Cs_1(cr)$	Cesium (Cs)	978
$Cs_1(l)$	Cesium (Cs)	979
$Cs_1(cr,l)$	Cesium (Cs)	980
$Cs_1(g)$	Cesium (Cs)	981
$Cs_1^+(g)$	Cesium, ion (Cs^+)	982
$Cs_1^-(g)$	Cesium, ion (Cs^-)	983
$Cs_1F_1(cr)$	Cesium fluoride (CsF)	984
$Cs_1F_1(l)$	Cesium fluoride (CsF)	985
$Cs_1F_1(cr,l)$	Cesium fluoride (CsF)	986
$Cs_1F_1(g)$	Cesium fluoride (CsF)	987
$Cs_1H_1O_1(cr)$	Cesium hydroxide (CsOH)	988
$Cs_1H_1O_1(l)$	Cesium hydroxide (CsOH)	989
$Cs_1H_1O_1(cr,l)$	Cesium hydroxide (CsOH)	990
$Cs_1H_1O_1(g)$	Cesium hydroxide (CsOH)	991
$Cs_1H_1O_1^+(g)$	Cesium hydroxide, ion ($CsOH^+$)	992
$Cs_1O_1(g)$	Cesium oxide (CsO)	993
$Cs_2(g)$	Cesium (Cs_2)	994
$Cs_2F_2(g)$	Cesium fluoride ($(CsF)_2$)	995
$Cs_2H_2O_2(g)$	Cesium hydroxide ($(CsOH)_2$)	996
$Cs_2O_1(g)$	Cesium oxide (Cs_2O)	997
$Cs_2O_4S_1(cr)$	Cesium sulfate, I (Cs_2SO_4)	998
$Cs_2O_4S_1(cr)$	Cesium sulfate, II (Cs_2SO_4)	999
$Cs_2O_4S_1(l)$	Cesium sulfate (Cs_2SO_4)	1000
$Cs_2O_4S_1(cr,l)$	Cesium sulfate (Cs_2SO_4)	1001
$Cs_2O_4S_1(g)$	Cesium sulfate (Cs_2SO_4)	1002
$Cu_1(ref)$	Copper (Cu)	1005
$Cu_1(cr)$	Copper (Cu)	1006
$Cu_1(l)$	Copper (Cu)	1007
$Cu_1(cr,l)$	Copper (Cu)	1008
$Cu_1(g)$	Copper (Cu)	1009
$Cu_1^+(g)$	Copper, ion (Cu^+)	1010
$Cu_1^-(g)$	Copper, ion (Cu^-)	1011
$Cu_1F_1(cr)$	Copper fluoride (CuF)	1012
$Cu_1F_1(g)$	Copper fluoride (CuF)	1013
$Cu_1F_2(cr)$	Copper fluoride (CuF_2)	1014
$Cu_1F_2(l)$	Copper fluoride (CuF_2)	1015
$Cu_1F_2(cr,l)$	Copper fluoride (CuF_2)	1016
$Cu_1F_2(g)$	Copper fluoride (CuF_2)	1017
$Cu_1H_2O_2(cr)$	Copper hydroxide ($Cu(OH)_2$)	1018
$Cu_1O_1(cr)$	Copper oxide (CuO)	1019
$Cu_1O_1(g)$	Copper oxide (CuO)	1020
$Cu_1O_4S_1(cr)$	Copper sulfate ($CuSO_4$)	1021
$Cu_2(g)$	Copper (Cu_2)	1022
$Cu_2O_1(cr)$	Copper oxide (Cu_2O)	1023
$Cu_2O_1(l)$	Copper oxide (Cu_2O)	1024
$Cu_2O_1(cr,l)$	Copper oxide (Cu_2O)	1025
$Cu_2O_5S_1(cr)$	Copper oxide sulfate ($CuO \cdot CuSO_4$)	1026
$D_1(g)$	Deuterium (D)	1029
$D_1^+(g)$	Deuterium, ion (D^+)	1030
$D_1^-(g)$	Deuterium, ion (D^-)	1031
$D_1F_1(g)$	Hydrofluoric acid−d_1 (DF)	1032
$D_1H_1(g)$	Hydrogen−d_1 (HD)	1033
$D_1H_1^+(g)$	Hydrogen−d_1, ion (HD^+)	1034
$D_1H_1^-(g)$	Hydrogen−d_1, ion (HD^-)	1035
$D_1H_1O_1(g)$	Water−d_1 (HDO)	1036
$D_1N_1(g)$	Imidogen−d_1 (ND)	1037
$D_1O_1(g)$	Hydroxyl−d_1 (OD)	1038
$D_1S_1(g)$	Mercapto−d_1 (SD)	1039
$D_2(ref)$	Deuterium (D_2)	1040
$D_2^+(g)$	Deuterium, ion (D_2^+)	1041
$D_2^-(g)$	Deuterium, ion (D_2^-)	1042
$D_2N_1(g)$	Amidogen−d_2 (ND_2)	1043
$D_2N_2(g)$	Diazene−d_2, cis (DNND)	1044
$D_2O_1(g)$	Water−d_2 (D_2O)	1045
$D_2S_1(g)$	Hydrogen sulfide−d_2 (D_2S)	1046
$D_3N_1(g)$	Ammonia−d_3 (ND_3)	1047
$e_1^-(ref)$	Electron gas (e^-)	1049
$F_1(g)$	Fluorine (F)	1051
$F_1^+(g)$	Fluorine, ion (F^+)	1052
$F_1^-(g)$	Fluorine, ion (F^-)	1053
$F_1Fe_1(g)$	Iron fluoride (FeF)	1054
$F_1H_1(g)$	Hydrogen fluoride (HF)	1055
$F_1H_1O_1(g)$	Hypofluorous acid (HOF)	1056
$F_1H_1O_3S_1(g)$	Fluorosulfuric acid (HSO_3F)	1057
$F_1H_3Si_1(g)$	Fluorosilane (SiH_3F)	1058
$F_1Hg_1(g)$	Mercury fluoride (HgF)	1059
$F_1I_1(g)$	Iodine fluoride (IF)	1060
$F_1K_1(cr)$	Potassium fluoride (KF)	1061
$F_1K_1(l)$	Potassium fluoride (KF)	1062
$F_1K_1(cr,l)$	Potassium fluoride (KF)	1063
$F_1K_1(g)$	Potassium fluoride (KF)	1064
$F_1Li_1(cr)$	Lithium fluoride (LiF)	1065
$F_1Li_1(l)$	Lithium fluoride (LiF)	1066
$F_1Li_1(cr,l)$	Lithium fluoride (LiF)	1067
$F_1Li_1(g)$	Lithium fluoride (LiF)	1068
$F_1Li_1O_1(g)$	Lithium hypofluorite (LiOF)	1069
$F_1Mg_1(g)$	Magnesium fluoride (MgF)	1070
$F_1Mg_1^+(g)$	Magnesium fluoride, ion (MgF^+)	1071
$F_1Mo_1(g)$	Molybdenum fluoride (MoF)	1072
$F_1N_1(g)$	Fluoroimidogen (NF)	1073
$F_1N_1O_1(g)$	Nitrosyl fluoride (ONF)	1074
$F_1N_1O_2(g)$	Nitryl fluoride (NO_2F)	1075
$F_1N_1O_3(g)$	Fluorine nitrate ($FONO_2$)	1076

Formula	Table Title	Page
$F_1Na_1(cr)$	Sodium fluoride (NaF)	1077
$F_1Na_1(l)$	Sodium fluoride (NaF)	1078
$F_1Na_1(cr,l)$	Sodium fluoride (NaF)	1079
$F_1Na_1(g)$	Sodium fluoride (NaF)	1080
$F_1O_1(g)$	Oxygen fluoride (OF)	1081
$F_1O_1Ti_1(g)$	Titanium fluoride oxide (OTiF)	1082
$F_1O_2(g)$	Oxygen fluoride (OFO)	1083
$F_1O_2(g)$	Oxygen fluoride (FOO)	1084
$F_1P_1(g)$	Phosphorus fluoride (PF)	1085
$F_1P_1^+(g)$	Phosphorus fluoride, ion (PF^+)	1086
$F_1P_1^-(g)$	Phosphorus fluoride, ion (PF^-)	1087
$F_1P_1S_1(g)$	Thiophosphoryl fluoride (PSF)	1088
$F_1Pb_1(g)$	Lead fluoride (PbF)	1089
$F_1S_1(g)$	Sulfur fluoride (SF)	1090
$F_1S_1^+(g)$	Sulfur fluoride, ion (SF^+)	1091
$F_1S_1^-(g)$	Sulfur fluoride, ion (SF^-)	1092
$F_1Si_1(g)$	Fluorosilylidyne (SiF)	1093
$F_1Sr_1(g)$	Strontium fluoride (SrF)	1094
$F_1Sr_1^+(g)$	Strontium fluoride, ion (SrF^+)	1095
$F_1Ti_1(g)$	Titanium fluoride (TiF)	1096
$F_1W_1(g)$	Tungsten fluoride (WF)	1097
$F_1Zr_1(g)$	Zirconium fluoride (ZrF)	1098
F_2(ref)	Fluorine (F_2)	1099
$F_2Fe_1(cr)$	Iron fluoride (FeF_2)	1100
$F_2Fe_1(l)$	Iron fluoride (FeF_2)	1101
$F_2Fe_1(cr,l)$	Iron fluoride (FeF_2)	1102
$F_2Fe_1(g)$	Iron fluoride (FeF_2)	1103
$F_2H_1K_1(cr)$	Potassium fluoride ($K(HF_2)$)	1104
$F_2H_1K_1(l)$	Potassium fluoride ($K(HF_2)$)	1105
$F_2H_1K_1(cr,l)$	Potassium fluoride ($K(HF_2)$)	1106
$F_2H_2(g)$	Hydrogen fluoride ($(HF)_2$)	1107
$F_2H_2Si_1(g)$	Difluorosilane (SiH_2F_2)	1108
$F_2Hg_1(cr)$	Mercury fluoride (HgF_2)	1109
$F_2Hg_1(l)$	Mercury fluoride (HgF_2)	1110
$F_2Hg_1(cr,l)$	Mercury fluoride (HgF_2)	1111
$F_2Hg_1(g)$	Mercury fluoride (HgF_2)	1112
$F_2Hg_2(cr)$	Mercury fluoride (Hg_2F_2)	1113
$F_2K_1^-(g)$	Potassium fluoride, ion (KF_2^-)	1114
$F_2K_2(g)$	Potassium fluoride ($(KF)_2$)	1115
$F_2Li_1^-(g)$	Lithium fluoride, ion (LiF_2^-)	1116
$F_2Li_2(g)$	Lithium fluoride ($(LiF)_2$)	1117
$F_2Mg_1(cr)$	Magnesium fluoride (MgF_2)	1118
$F_2Mg_1(l)$	Magnesium fluoride (MgF_2)	1119
$F_2Mg_1(cr,l)$	Magnesium fluoride (MgF_2)	1120
$F_2Mg_1(g)$	Magnesium fluoride (MgF_2)	1121
$F_2Mg_1^+(g)$	Magnesium fluoride, ion (MgF_2^+)	1122
$F_2Mo_1(g)$	Molybdenum fluoride (MoF_2)	1123
$F_2N_1(g)$	Difluoroamidogen (NF_2)	1124
$F_2N_2(g)$	Nitrogen fluoride, cis (FNNF)	1125
$F_2N_2(g)$	Nitrogen fluoride, trans (FNNF)	1126
$F_2Na_1^-(g)$	Sodium fluoride, ion (NaF_2^-)	1127
$F_2Na_2(g)$	Sodium fluoride ($(NaF)_2$)	1128
$F_2O_1(g)$	Oxygen fluoride (FOF)	1129
$F_2O_1S_1(g)$	Thionyl fluoride (OSF_2)	1130
$F_2O_1Si_1(g)$	Difluorooxosilane ($OSiF_2$)	1131
$F_2O_1Ti_1(g)$	Titanium fluoride oxide ($OTiF_2$)	1132
$F_2O_2(g)$	Oxygen fluoride (FOOF)	1133
$F_2O_2S_1(g)$	Sulfuryl fluoride (SO_2F_2)	1134
$F_2P_1(g)$	Phosphorus fluoride (PF_2)	1135
$F_2P_1^+(g)$	Phosphorus fluoride, ion (PF_2^+)	1136
$F_2P_1^-(g)$	Phosphorus fluoride, ion (PF_2^-)	1137
$F_2Pb_1(cr)$	Lead fluoride, alpha (PbF_2)	1138
$F_2Pb_1(cr)$	Lead fluoride, beta (PbF_2)	1139
$F_2Pb_1(l)$	Lead fluoride (PbF_2)	1140
$F_2Pb_1(cr,l)$	Lead fluoride (PbF_2)	1141
$F_2Pb_1(g)$	Lead fluoride (PbF_2)	1142
$F_2S_1(g)$	Sulfur fluoride (SF_2)	1143
$F_2S_1^+(g)$	Sulfur fluoride, ion (SF_2^+)	1144
$F_2S_1^-(g)$	Sulfur fluoride, ion (SF_2^-)	1145
$F_2S_2(g)$	Difluorodisulfane (FSSF)	1146
$F_2S_2(g)$	Thiothionyl fluoride (SSF_2)	1147
$F_2Si_1(g)$	Difluorosilylene (SiF_2)	1148
$F_2Sr_1(cr)$	Strontium fluoride (SrF_2)	1149
$F_2Sr_1(l)$	Strontium fluoride (SrF_2)	1150
$F_2Sr_1(cr,l)$	Strontium fluoride (SrF_2)	1151
$F_2Sr_1(g)$	Strontium fluoride (SrF_2)	1152
$F_2Ti_1(g)$	Titanium fluoride (TiF_2)	1153
$F_2Zr_1(cr)$	Zirconium fluoride (ZrF_2)	1154
$F_2Zr_1(l)$	Zirconium fluoride (ZrF_2)	1155
$F_2Zr_1(cr,l)$	Zirconium fluoride (ZrF_2)	1156
$F_2Zr_1(g)$	Zirconium fluoride (ZrF_2)	1157
$F_3Fe_1(cr)$	Iron fluoride (FeF_3)	1158
$F_3Fe_1(g)$	Iron fluoride (FeF_3)	1159
$F_3H_1Si_1(g)$	Trifluorosilane ($SiHF_3$)	1160
$F_3H_3(g)$	Hydrogen fluoride (H_3F_3)	1161
$F_3Li_3(g)$	Lithium fluoride ($(LiF)_3$)	1162
$F_3Mo_1(g)$	Molybdenum fluoride (MoF_3)	1163
$F_3N_1(g)$	Nitrogen fluoride (NF_3)	1164
$F_3N_1O_1(g)$	Nitrogen fluoride oxide (NF_3O)	1165
$F_3O_1P_1(g)$	Phosphoryl fluoride (POF_3)	1166
$F_3P_1(g)$	Phosphorus fluoride (PF_3)	1167
$F_3P_1S_1(g)$	Thiophosphoryl fluoride (PSF_3)	1168
$F_3S_1(g)$	Sulfur fluoride (SF_3)	1169
$F_3S_1^+(g)$	Sulfur fluoride, ion (SF_3^+)	1170
$F_3S_1^-(g)$	Sulfur fluoride, ion (SF_3^-)	1171
$F_3Si_1(g)$	Trifluorosilyl (SiF_3)	1172
$F_3Ti_1(cr)$	Titanium fluoride (TiF_3)	1173
$F_3Ti_1(g)$	Titanium fluoride (TiF_3)	1174
$F_3Zr_1(cr)$	Zirconium fluoride (ZrF_3)	1175
$F_3Zr_1(g)$	Zirconium fluoride (ZrF_3)	1176
$F_4H_4(g)$	Hydrogen fluoride (H_4F_4)	1177
$F_4Mg_2(g)$	Magnesium fluoride ($(MgF_2)_2$)	1178
$F_4Mo_1(g)$	Molybdenum fluoride (MoF_4)	1179
$F_4Mo_1O_1(g)$	Molybdenum fluoride oxide (MoF_4O)	1180
$F_4N_2(g)$	Tetrafluorohydrazine (N_2F_4)	1181
$F_4O_1W_1(cr)$	Tungsten fluoride oxide (WF_4O)	1182
$F_4O_1W_1(l)$	Tungsten fluoride oxide (WF_4O)	1183
$F_4O_1W_1(cr,l)$	Tungsten fluoride oxide (WF_4O)	1184
$F_4O_1W_1(g)$	Tungsten fluoride oxide (WF_4O)	1185
$F_4Pb_1(g)$	Lead fluoride (PbF_4)	1186
$F_4S_1(g)$	Sulfur fluoride (SF_4)	1187
$F_4S_1^+(g)$	Sulfur fluoride, ion (SF_4^+)	1188

Formula	Table Title	Page
$F_4S_1^-(g)$	Sulfur fluoride, ion (SF_4^-)	1189
$F_4Si_1(g)$	Tetrafluorosilane (SiF_4)	1190
$F_4Ti_1(cr)$	Titanium fluoride (TiF_4)	1191
$F_4Ti_1(g)$	Titanium fluoride (TiF_4)	1192
$F_4Zr_1(cr)$	Zirconium fluoride (ZrF_4)	1193
$F_4Zr_1(g)$	Zirconium fluoride (ZrF_4)	1194
$F_5H_5(g)$	Hydrogen fluoride (H_5F_5)	1195
$F_5I_1(g)$	Iodine fluoride (IF_5)	1196
$F_5Mo_1(g)$	Molybdenum fluoride (MoF_5)	1197
$F_5P_1(g)$	Phosphorus fluoride (PF_5)	1198
$F_5S_1(g)$	Sulfur fluoride (SF_5)	1199
$F_5S_1^+(g)$	Sulfur fluoride, ion (SF_5^+)	1200
$F_5S_1^-(g)$	Sulfur fluoride, ion (SF_5^-)	1201
$F_6H_6(g)$	Hydrogen fluoride (H_6F_6)	1202
$F_6Mo_1(l)$	Molybdenum fluoride (MoF_6)	1203
$F_6Mo_1(g)$	Molybdenum fluoride (MoF_6)	1204
$F_6S_1(g)$	Sulfur fluoride (SF_6)	1205
$F_6S_1^-(g)$	Sulfur fluoride, ion (SF_6^-)	1206
$F_6W_1(l)$	Tungsten fluoride (WF_6)	1207
$F_6W_1(g)$	Tungsten fluoride (WF_6)	1208
$F_7H_7(g)$	Hydrogen fluoride (H_7F_7)	1209
$F_7I_1(g)$	Iodine fluoride (IF_7)	1210
$F_{10}Mo_2(g)$	Molybdenum fluoride ($(MoF_5)_2$)	1211
$F_{10}S_2(g)$	Sulfur fluoride (S_2F_{10})	1212
$F_{15}Mo_3(g)$	Molybdenum fluoride ($(MoF_5)_3$)	1213
$Fe_{0.947}O_1(cr)$	Iron oxide, wüstite ($Fe_{0.947}O$)	1219
$Fe_{0.877}S_1(cr)$	Iron sulfide, pyrrhotite ($Fe_{0.877}S$)	1220
$Fe_1(ref)$	Iron (Fe)	1221
$Fe_1(cr)$	Iron, alpha−delta (Fe)	1222
$Fe_1(cr)$	Iron, gamma (Fe)	1223
$Fe_1(l)$	Iron (Fe)	1224
$Fe_1(cr,l)$	Iron (Fe)	1225
$Fe_1(g)$	Iron (Fe)	1226
$Fe_1^+(g)$	Iron, ion (Fe^+)	1227
$Fe_1^-(g)$	Iron, ion (Fe^-)	1228
$Fe_1H_2O_2(cr)$	Iron hydroxide ($Fe(OH)_2$)	1229
$Fe_1H_2O_2(g)$	Iron hydroxide ($Fe(OH)_2$)	1230
$Fe_1H_3O_3(cr)$	Iron hydroxide ($Fe(OH)_3$)	1231
$Fe_1I_2(cr)$	Iron iodide (FeI_2)	1232
$Fe_1I_2(l)$	Iron iodide (FeI_2)	1233
$Fe_1I_2(cr,l)$	Iron iodide (FeI_2)	1234
$Fe_1I_2(g)$	Iron iodide (FeI_2)	1235
$Fe_1O_1(cr)$	Iron oxide (FeO)	1236
$Fe_1O_1(l)$	Iron oxide (FeO)	1237
$Fe_1O_1(cr,l)$	Iron oxide (FeO)	1238
$Fe_1O_1(g)$	Iron oxide (FeO)	1239
$Fe_1O_4S_1(cr)$	Iron sulfate ($FeSO_4$)	1240
$Fe_1S_1(cr)$	Iron sulfide, troilite (FeS)	1241
$Fe_1S_1(l)$	Iron sulfide (FeS)	1242
$Fe_1S_1(cr,l)$	Iron sulfide, troilite (FeS)	1243
$Fe_1S_1(g)$	Iron sulfide (FeS)	1244
$Fe_1S_2(cr)$	Iron sulfide, marcasite (FeS_2)	1245
$Fe_1S_2(cr)$	Iron sulfide, pyrite (FeS_2)	1246
$Fe_2I_4(g)$	Iron iodide ($(FeI_2)_2$)	1247
$Fe_2O_3(cr)$	Iron oxide, hematite (Fe_2O_3)	1248
$Fe_2O_{12}S_3(cr)$	Iron sulfate ($Fe_2(SO_4)_3$)	1249
$Fe_3O_4(cr)$	Iron oxide, magnetite (Fe_3O_4)	1250
$Ga_1(ref)$	Gallium (Ga)	1253
$Ga_1(cr)$	Gallium (Ga)	1254
$Ga_1(l)$	Gallium (Ga)	1255
$Ga_1(cr,l)$	Gallium (Ga)	1256
$Ga_1(g)$	Gallium (Ga)	1257
$Ga_1^+(g)$	Gallium, ion (Ga^+)	1258
$Ga_1^-(g)$	Gallium, ion (Ga^-)	1259
$H_1(g)$	Hydrogen (H)	1261
$H_1^+(g)$	Hydrogen, ion (H^+)	1262
$H_1^-(g)$	Hydrogen, ion (H^-)	1263
$H_1Hg_1(g)$	Mercury hydride (HgH)	1264
$H_1I_1(g)$	Hydrogen iodide (HI)	1265
$H_1I_3Si_1(g)$	Triiodosilane ($SiHI_3$)	1266
$H_1K_1(cr)$	Potassium hydride (KH)	1267
$H_1K_1(g)$	Potassium hydride (KH)	1268
$H_1K_1O_1(cr)$	Potassium hydroxide (KOH)	1269
$H_1K_1O_1(l)$	Potassium hydroxide (KOH)	1270
$H_1K_1O_1(cr,l)$	Potassium hydroxide (KOH)	1271
$H_1K_1O_1(g)$	Potassium hydroxide (KOH)	1272
$H_1K_1O_1^+(g)$	Potassium hydroxide, ion (KOH^+)	1273
$H_1Li_1(cr)$	Lithium hydride (LiH)	1274
$H_1Li_1(l)$	Lithium hydride (LiH)	1275
$H_1Li_1(cr,l)$	Lithium hydride (LiH)	1276
$H_1Li_1(g)$	Lithium hydride (LiH)	1277
$H_1Li_1O_1(cr)$	Lithium hydroxide (LiOH)	1278
$H_1Li_1O_1(l)$	Lithium hydroxide (LiOH)	1279
$H_1Li_1O_1(cr,l)$	Lithium hydroxide (LiOH)	1280
$H_1Li_1O_1(g)$	Lithium hydroxide (LiOH)	1281
$H_1Li_1O_1^+(g)$	Lithium hydroxide, ion ($LiOH^+$)	1282
$H_1Mg_1(g)$	Magnesium hydride (MgH)	1283
$H_1Mg_1O_1(g)$	Magnesium hydroxide (MgOH)	1284
$H_1Mg_1O_1^+(g)$	Magnesium hydroxide, ion ($MgOH^+$)	1285
$H_1N_1(g)$	Imidogen (NH)	1286
$H_1N_1O_1(g)$	Nitrosyl hydride (HNO)	1287
$H_1N_1O_2(g)$	Nitrous acid, cis (HONO)	1288
$H_1N_1O_2(g)$	Nitrous acid, trans (HONO)	1289
$H_1N_1O_3(g)$	Nitric acid ($HONO_2$)	1290
$H_1Na_1(cr)$	Sodium hydride (NaH)	1291
$H_1Na_1(g)$	Sodium hydride (NaH)	1292
$H_1Na_1O_1(cr)$	Sodium hydroxide (NaOH)	1293
$H_1Na_1O_1(l)$	Sodium hydroxide (NaOH)	1294
$H_1Na_1O_1(cr,l)$	Sodium hydroxide (NaOH)	1295
$H_1Na_1O_1(g)$	Sodium hydroxide (NaOH)	1296
$H_1Na_1O_1^+(g)$	Sodium hydroxide, ion ($NaOH^+$)	1297
$H_1O_1(g)$	Hydroxyl (OH)	1298
$H_1O_1^+(g)$	Hydroxyl, ion (OH^+)	1299
$H_1O_1^-(g)$	Hydroxyl, ion (OH^-)	1300
$H_1O_1Sr_1(g)$	Strontium hydroxide (SrOH)	1301
$H_1O_1Sr_1^+(g)$	Strontium hydroxide, ion ($SrOH^+$)	1302
$H_1O_2(g)$	Hydroperoxo (HOO)	1303
$H_1P_1(g)$	Phosphinidene (PH)	1304
$H_1Pb_1(g)$	Lead hydride (PbH)	1305

Formula	Table Title	Page
$H_1S_1(g)$	Mercapto (HS)	1306
$H_1Si_1(g)$	Silylidyne (SiH)	1307
$H_1Si_1^+(g)$	Silylidyne, ion (SiH^+)	1308
$H_1Zr_1(g)$	Zirconium hydride (ZrH)	1309
H_2(ref)	Hydrogen (H_2)	1310
$H_2^+(g)$	Hydrogen, ion (H_2^+)	1311
$H_2^-(g)$	Hydrogen, ion (H_2^-)	1312
$H_2I_2Si_1(g)$	Diiodosilane (SiH_2I_2)	1313
$H_2K_2O_2(g)$	Potassium hydroxide ($(KOH)_2$)	1314
$H_2Li_2O_2(g)$	Lithium hydroxide ($(LiOH)_2$)	1315
H_2Mg_1(cr)	Magnesium hydride (MgH_2)	1316
$H_2Mg_1O_2$(cr)	Magnesium hydroxide ($Mg(OH)_2$)	1317
$H_2Mg_1O_2(g)$	Magnesium hydroxide ($Mg(OH)_2$)	1318
$H_2Mo_1O_4(g)$	Molybdic acid ($O_2Mo(OH)_2$)	1319
$H_2N_1(g)$	Amidogen (NH_2)	1320
$H_2N_2(g)$	Diazene, cis (HNNH)	1321
$H_2Na_2O_2(g)$	Sodium hydroxide ($(NaOH)_2$)	1322
H_2O_1(l)	Water (H_2O)	1323
$H_2O_1(g)$	Water (H_2O)	1324
H_2O_1(l,g)	Water, 1 bar (H_2O)	1325
H_2O_1(l,g)	Water, 10 bar (H_2O)	1326
H_2O_1(l,g)	Water, 100 bar (H_2O)	1327
H_2O_1(fl)	Water, 500 bar (H_2O)	1328
H_2O_1(fl)	Water, 5000 bar (H_2O)	1329
$H_2O_2(g)$	Hydrogen peroxide (HOOH)	1330
$H_2O_2Sr_1$(cr)	Strontium hydroxide ($Sr(OH)_2$)	1331
$H_2O_2Sr_1$(l)	Strontium hydroxide ($Sr(OH)_2$)	1332
$H_2O_2Sr_1$(cr,l)	Strontium hydroxide ($Sr(OH)_2$)	1333
$H_2O_2Sr_1(g)$	Strontium hydroxide ($Sr(OH)_2$)	1334
$H_2O_4S_1$(cr,l)	Sulfuric acid ($O_2S(OH)_2$)	1335
$H_2O_4S_1(g)$	Sulfuric acid ($O_2S(OH)_2$)	1336
$H_2O_4W_1$(cr)	Tungstic acid ($O_2W(OH)_2$)	1337
$H_2O_4W_1(g)$	Tungstic acid ($O_2W(OH)_2$)	1338
$H_2P_1(g)$	Phosphino (PH_2)	1339
$H_2S_1(g)$	Hydrogen sulfide (H_2S)	1340
H_2Ti_1(cr)	Titanium hydride (TiH_2)	1341
$H_3I_1Si_1(g)$	Iodosilane (SiH_3I)	1342
$H_3N_1(g)$	Ammonia (NH_3)	1343
$H_3O_1^+(g)$	Hydronium, ion (H_3O^+)	1344
$H_3O_4P_1$(cr)	Phosphoric acid (H_3PO_4)	1345
$H_3O_4P_1$(l)	Phosphoric acid (H_3PO_4)	1346
$H_3O_4P_1$(cr,l)	Phosphoric acid (H_3PO_4)	1347
$H_3P_1(g)$	Phosphine (PH_3)	1348
$H_4I_1N_1$(cr)	Ammonium iodide (NH_4I)	1349
H_4N_2(l)	Hydrazine (N_2H_4)	1350
$H_4N_2(g)$	Hydrazine (N_2H_4)	1351
$H_4O_5S_1$(cr,l)	Sulfuric acid, monohydrate ($H_2SO_4 \cdot H_2O$)	1352
$H_4Si_1(g)$	Silane (SiH_4)	1353
$H_6O_6S_1$(cr,l)	Sulfuric acid, dihydrate ($H_2SO_4 \cdot 2H_2O$)	1354
$H_8O_7S_1$(cr,l)	Sulfuric acid, trihydrate ($H_2SO_4 \cdot 3H_2O$)	1355
$H_{10}O_8S_1$(cr,l)	Sulfuric acid, tetrahydrate ($H_2SO_4 \cdot 4H_2O$)	1356
$H_{15}O_{10.5}S_1$(cr,l)	Sulfuric acid, hemihexahydrate ($H_2SO_4 \cdot 6.5H_2O$)	1357
He_1(ref)	Helium (He)	1361
$He_1^+(g)$	Helium, ion (He^+)	1362
Hf_1(ref)	Hafnium (Hf)	1363
Hf_1(cr)	Hafnium, alpha (Hf)	1364
Hf_1(cr)	Hafnium, beta (Hf)	1365
Hf_1(l)	Hafnium (Hf)	1366
Hf_1(cr,l)	Hafnium (Hf)	1367
$Hf_1(g)$	Hafnium (Hf)	1368
$Hf_1^+(g)$	Hafnium, ion (Hf^+)	1369
$Hf_1^-(g)$	Hafnium, ion (Hf^-)	1370
Hg_1(ref)	Mercury (Hg)	1373
Hg_1(cr,l)	Mercury (Hg)	1374
$Hg_1(g)$	Mercury (Hg)	1375
$Hg_1^+(g)$	Mercury, ion (Hg^+)	1376
$Hg_1I_1(g)$	Mercury iodide (HgI)	1377
Hg_1I_2(cr)	Mercury iodide (HgI_2)	1378
Hg_1I_2(l)	Mercury iodide (HgI_2)	1379
Hg_1I_2(cr,l)	Mercury iodide (HgI_2)	1380
$Hg_1I_2(g)$	Mercury iodide (HgI_2)	1381
Hg_1O_1(cr)	Mercury oxide (HgO)	1382
$Hg_1O_1(g)$	Mercury oxide (HgO)	1383
Hg_2I_2(cr)	Mercury iodide (Hg_2I_2)	1384
Hg_2I_2(l)	Mercury iodide (Hg_2I_2)	1385
Hg_2I_2(cr,l)	Mercury iodide (Hg_2I_2)	1386
$I_1(g)$	Iodine (I)	1387
$I_1^+(g)$	Iodine, ion (I^+)	1388
$I_1^-(g)$	Iodine, ion (I^-)	1389
I_1K_1(cr)	Potassium iodide (KI)	1390
I_1K_1(l)	Potassium iodide (KI)	1391
I_1K_1(cr,l)	Potassium iodide (KI)	1392
$I_1K_1(g)$	Potassium iodide (KI)	1393
I_1Li_1(cr)	Lithium iodide (LiI)	1394
I_1Li_1(l)	Lithium iodide (LiI)	1395
I_1Li_1(cr,l)	Lithium iodide (LiI)	1396
$I_1Li_1(g)$	Lithium iodide (LiI)	1397
$I_1Mg_1(g)$	Magnesium iodide (MgI)	1398
$I_1Mo_1(g)$	Molybdenum iodide (MoI)	1399
$I_1N_1O_1(g)$	Nitrosyl iodide (ONI)	1400
I_1Na_1(cr)	Sodium iodide (NaI)	1401
I_1Na_1(l)	Sodium iodide (NaI)	1402
I_1Na_1(cr,l)	Sodium iodide (NaI)	1403
$I_1O_1(g)$	Iodine oxide (IO)	1404
$I_1O_2(g)$	Iodine oxide (OIO)	1405
$I_1O_2(g)$	Iodine oxide (IOO)	1406
$I_1O_3(g)$	Iodine oxide (IO_3)	1407
$I_1Pb_1(g)$	Lead iodide (PbI)	1408
$I_1Si_1(g)$	Iodosilylidyne (SiI)	1409
$I_1Sr_1(g)$	Strontium iodide (SrI)	1410
$I_1Ti_1(g)$	Titanium iodide (TiI)	1411
$I_1Zr_1(g)$	Zirconium iodide (ZrI)	1412
I_2(ref)	Iodine (I_2)	1413
I_2(cr)	Iodine (I_2)	1414
I_2(l)	Iodine (I_2)	1415
I_2(cr,l)	Iodine (I_2)	1416
$I_2(g)$	Iodine (I_2)	1417

Formula	Table Title	Page
$I_2K_2(g)$	Potassium iodide ($(KI)_2$)	1418
$I_2Li_2(g)$	Lithium iodide ($(LiI)_2$)	1419
$I_2Mg_1(cr)$	Magnesium iodide (MgI_2)	1420
$I_2Mg_1(l)$	Magnesium iodide (MgI_2)	1421
$I_2Mg_1(cr,l)$	Magnesium iodide (MgI_2)	1422
$I_2Mg_1(g)$	Magnesium iodide (MgI_2)	1423
$I_2Mo_1(cr)$	Molybdenum iodide, alpha (MoI_2)	1424
$I_2Mo_1(g)$	Molybdenum iodide (MoI_2)	1425
$I_2O_1(g)$	Iodine oxide (IOI)	1426
$I_2O_1(g)$	Iodine oxide (IIO)	1427
$I_2Pb_1(cr)$	Lead iodide (PbI_2)	1428
$I_2Pb_1(l)$	Lead iodide (PbI_2)	1429
$I_2Pb_1(cr,l)$	Lead iodide (PbI_2)	1430
$I_2Pb_1(g)$	Lead iodide (PbI_2)	1431
$I_2Si_1(g)$	Diiodosilylene (SiI_2)	1432
$I_2Sr_1(cr)$	Strontium iodide (SrI_2)	1433
$I_2Sr_1(l)$	Strontium iodide (SrI_2)	1434
$I_2Sr_1(cr,l)$	Strontium iodide (SrI_2)	1435
$I_2Sr_1(g)$	Strontium iodide (SrI_2)	1436
$I_2Ti_1(cr)$	Titanium iodide (TiI_2)	1437
$I_2Ti_1(g)$	Titanium iodide (TiI_2)	1438
$I_2Zr_1(cr)$	Zirconium iodide (ZrI_2)	1439
$I_2Zr_1(l)$	Zirconium iodide (ZrI_2)	1440
$I_2Zr_1(cr,l)$	Zirconium iodide (ZrI_2)	1441
$I_2Zr_1(g)$	Zirconium iodide (ZrI_2)	1442
$I_3Mo_1(cr)$	Molybdenum iodide (MoI_3)	1443
$I_3Mo_1(g)$	Molybdenum iodide (MoI_3)	1444
$I_3Si_1(g)$	Triiodosilyl (SiI_3)	1445
$I_3Ti_1(cr)$	Titanium iodide (TiI_3)	1446
$I_3Ti_1(g)$	Titanium iodide (TiI_3)	1447
$I_3Zr_1(cr)$	Zirconium iodide (ZrI_3)	1448
$I_3Zr_1(g)$	Zirconium iodide (ZrI_3)	1449
$I_4Mo_1(cr)$	Molybdenum iodide (MoI_4)	1450
$I_4Mo_1(g)$	Molybdenum iodide (MoI_4)	1451
$I_4Pb_1(g)$	Lead iodide (PbI_4)	1452
$I_4Si_1(cr)$	Tetraiodosilane (SiI_4)	1453
$I_4Si_1(l)$	Tetraiodosilane (SiI_4)	1454
$I_4Si_1(cr,l)$	Tetraiodosilane (SiI_4)	1455
$I_4Si_1(g)$	Tetraiodosilane (SiI_4)	1456
$I_4Ti_1(cr)$	Titanium iodide (TiI_4)	1457
$I_4Ti_1(l)$	Titanium iodide (TiI_4)	1458
$I_4Ti_1(cr,l)$	Titanium iodide (TiI_4)	1459
$I_4Ti_1(g)$	Titanium iodide (TiI_4)	1460
$I_4Zr_1(cr)$	Zirconium iodide (ZrI_4)	1461
$I_4Zr_1(g)$	Zirconium iodide (ZrI_4)	1462
$K_1(ref)$	Potassium (K)	1465
$K_1(cr)$	Potassium (K)	1466
$K_1(l)$	Potassium (K)	1467
$K_1(cr,l)$	Potassium (K)	1468
$K_1(g)$	Potassium (K)	1469
$K_1^+(g)$	Potassium, ion (K^+)	1470
$K_1^-(g)$	Potassium, ion (K^-)	1471
$K_1O_1(g)$	Potassium oxide (KO)	1472
$K_1O_1^-(g)$	Potassium oxide, ion (KO^-)	1473
$K_1O_2(cr)$	Potassium superoxide (KO_2)	1474
$K_2(g)$	Potassium (K_2)	1475
$K_2O_1(cr)$	Potassium oxide (K_2O)	1476
$K_2O_2(cr)$	Potassium peroxide (K_2O_2)	1477
$K_2O_3Si_1(cr)$	Potassium silicate (K_2SiO_3)	1478
$K_2O_3Si_1(l)$	Potassium silicate (K_2SiO_3)	1479
$K_2O_3Si_1(cr,l)$	Potassium silicate (K_2SiO_3)	1480
$K_2O_4S_1(cr)$	Potassium sulfate, alpha (K_2SO_4)	1481
$K_2O_4S_1(cr)$	Potassium sulfate, beta (K_2SO_4)	1482
$K_2O_4S_1(l)$	Potassium sulfate (K_2SO_4)	1483
$K_2O_4S_1(cr,l)$	Potassium sulfate (K_2SO_4)	1484
$K_2O_4S_1(g)$	Potassium sulfate (K_2SO_4)	1485
$K_2S_1(cr)$	Potassium sulfide (K_2S)	1486
$K_2S_1(l)$	Potassium sulfide (K_2S)	1487
$K_2S_1(cr,l)$	Potassium sulfide (K_2S)	1488
$Kr_1(ref)$	Krypton (Kr)	1491
$Kr_1^+(g)$	Krypton, ion (Kr^+)	1492
$Li_1(ref)$	Lithium (Li)	1493
$Li_1(cr)$	Lithium (Li)	1494
$Li_1(l)$	Lithium (Li)	1495
$Li_1(cr,l)$	Lithium (Li)	1496
$Li_1(g)$	Lithium (Li)	1497
$Li_1^+(g)$	Lithium, ion (Li^+)	1498
$Li_1^-(g)$	Lithium, ion (Li^-)	1499
$Li_1N_1(g)$	Lithium nitride (LiN)	1500
$Li_1N_1O_1(g)$	Lithium oxynitride (LiON)	1501
$Li_1Na_1O_1(g)$	Lithium sodium oxide (LiONa)	1502
$Li_1O_1(g)$	Lithium oxide (LiO)	1503
$Li_1O_1^-(g)$	Lithium oxide, ion (LiO^-)	1504
$Li_2(g)$	Lithium (Li_2)	1505
$Li_2O_1(cr)$	Lithium oxide (Li_2O)	1506
$Li_2O_1(l)$	Lithium oxide (Li_2O)	1507
$Li_2O_1(cr,l)$	Lithium oxide (Li_2O)	1508
$Li_2O_1(g)$	Lithium oxide (Li_2O)	1509
$Li_2O_2(cr)$	Lithium peroxide (Li_2O_2)	1510
$Li_2O_2(g)$	Lithium oxide ($(LiO)_2$)	1511
$Li_2O_3Si_1(cr)$	Lithium silicate (Li_2SiO_3)	1512
$Li_2O_3Si_1(l)$	Lithium silicate (Li_2SiO_3)	1513
$Li_2O_3Si_1(cr,l)$	Lithium silicate (Li_2SiO_3)	1514
$Li_2O_3Ti_1(cr)$	Lithium titanium oxide (Li_2TiO_3)	1515
$Li_2O_3Ti_1(l)$	Lithium titanium oxide (Li_2TiO_3)	1516
$Li_2O_3Ti_1(cr,l)$	Lithium titanium oxide (Li_2TiO_3)	1517
$Li_2O_4S_1(cr)$	Lithium sulfate, alpha (Li_2SO_4)	1518
$Li_2O_4S_1(cr)$	Lithium sulfate, beta (Li_2SO_4)	1519
$Li_2O_4S_1(l)$	Lithium sulfate (Li_2SO_4)	1520
$Li_2O_4S_1(cr,l)$	Lithium sulfate (Li_2SO_4)	1521
$Li_2O_4S_1(g)$	Lithium sulfate (Li_2SO_4)	1522
$Li_2O_5Si_2(cr)$	Lithium silicate ($Li_2Si_2O_5$)	1523
$Li_2O_5Si_2(l)$	Lithium silicate ($Li_2Si_2O_5$)	1524
$Li_2O_5Si_2(cr,l)$	Lithium silicate ($Li_2Si_2O_5$)	1525
$Li_3N_1(cr)$	Lithium nitride (Li_3N)	1526
$Mg_1(ref)$	Magnesium (Mg)	1529
$Mg_1(cr)$	Magnesium (Mg)	1530
$Mg_1(l)$	Magnesium (Mg)	1531

Formula	Table Title	Page
$Mg_1(cr,l)$	Magnesium (Mg)	1532
$Mg_1(g)$	Magnesium (Mg)	1533
$Mg_1^+(g)$	Magnesium, ion (Mg^+)	1534
$Mg_1N_1(g)$	Magnesium nitride (MgN)	1535
$Mg_1O_1(cr)$	Magnesium oxide (MgO)	1536
$Mg_1O_1(l)$	Magnesium oxide (MgO)	1537
$Mg_1O_1(cr,l)$	Magnesium oxide (MgO)	1538
$Mg_1O_1(g)$	Magnesium oxide (MgO)	1539
$Mg_1O_3Si_1(cr)$	Magnesium silicate ($MgSiO_3$)	1540
$Mg_1O_3Si_1(l)$	Magnesium silicate ($MgSiO_3$)	1541
$Mg_1O_3Si_1(cr,l)$	Magnesium silicate ($MgSiO_3$)	1542
$Mg_1O_3Ti_1(cr)$	Magnesium titanium oxide ($MgTiO_3$)	1543
$Mg_1O_3Ti_1(l)$	Magnesium titanium oxide ($MgTiO_3$)	1544
$Mg_1O_3Ti_1(cr,l)$	Magnesium titanium oxide ($MgTiO_3$)	1545
$Mg_1O_4S_1(cr)$	Magnesium sulfate ($MgSO_4$)	1546
$Mg_1O_4S_1(l)$	Magnesium sulfate ($MgSO_4$)	1547
$Mg_1O_4S_1(cr,l)$	Magnesium sulfate ($MgSO_4$)	1548
$Mg_1O_4W_1(cr)$	Magnesium tungsten oxide ($MgWO_4$)	1549
$Mg_1O_5Ti_2(cr)$	Magnesium titanium oxide ($MgTi_2O_5$)	1550
$Mg_1O_5Ti_2(l)$	Magnesium titanium oxide ($MgTi_2O_5$)	1551
$Mg_1O_5Ti_2(cr,l)$	Magnesium titanium oxide ($MgTi_2O_5$)	1552
$Mg_1S_1(cr)$	Magnesium sulfide (MgS)	1553
$Mg_1S_1(g)$	Magnesium sulfide (MgS)	1554
$Mg_2(g)$	Magnesium (Mg_2)	1555
$Mg_2O_4Si_1(cr)$	Magnesium silicate (Mg_2SiO_4)	1556
$Mg_2O_4Si_1(l)$	Magnesium silicate (Mg_2SiO_4)	1557
$Mg_2O_4Si_1(cr,l)$	Magnesium silicate (Mg_2SiO_4)	1558
$Mg_2O_4Ti_1(cr)$	Magnesium titanium oxide (Mg_2TiO_4)	1559
$Mg_2O_4Ti_1(l)$	Magnesium titanium oxide (Mg_2TiO_4)	1560
$Mg_2O_4Ti_1(cr,l)$	Magnesium titanium oxide (Mg_2TiO_4)	1561
$Mg_2Si_1(cr)$	Magnesium silicide (Mg_2Si)	1562
$Mg_2Si_1(l)$	Magnesium silicide (Mg_2Si)	1563
$Mg_2Si_1(cr,l)$	Magnesium silicide (Mg_2Si)	1564
$Mg_3N_2(cr)$	Magnesium nitride (Mg_3N_2)	1565
$Mg_3O_8P_2(cr)$	Magnesium phosphate ($Mg_3P_2O_8$)	1566
$Mg_3O_8P_2(l)$	Magnesium phosphate ($Mg_3P_2O_8$)	1567
$Mg_3O_8P_2(cr,l)$	Magnesium phosphate ($Mg_3P_2O_8$)	1568
$Mn_1(ref)$	Manganese (Mn)	1571
$Mn_1(cr)$	Manganese (Mn)	1572
$Mn_1(l)$	Manganese (Mn)	1573
$Mn_1(cr,l)$	Manganese (Mn)	1574
$Mn_1(g)$	Manganese (Mn)	1575
$Mn_1^+(g)$	Manganese, ion (Mn^+)	1576
$Mo_1(ref)$	Molybdenum (Mo)	1577
$Mo_1(cr)$	Molybdenum (Mo)	1578
$Mo_1(l)$	Molybdenum (Mo)	1579
$Mo_1(cr,l)$	Molybdenum (Mo)	1580
$Mo_1(g)$	Molybdenum (Mo)	1581
$Mo_1^+(g)$	Molybdenum, ion (Mo^+)	1582
$Mo_1^-(g)$	Molybdenum, ion (Mo^-)	1583
$Mo_1O_1(g)$	Molybdenum oxide (MoO)	1584
$Mo_1O_2(cr)$	Molybdenum oxide (MoO_2)	1585
$Mo_1O_2(g)$	Molybdenum oxide (MoO_2)	1586
$Mo_1O_{2.750}(cr)$	Molybdenum oxide ($MoO_{2.750}$)	1587
$Mo_1O_{2.875}(cr)$	Molybdenum oxide ($MoO_{2.875}$)	1588
$Mo_1O_{2.889}(cr)$	Molybdenum oxide ($MoO_{2.889}$)	1589
$Mo_1O_3(cr)$	Molybdenum oxide (MoO_3)	1590
$Mo_1O_3(l)$	Molybdenum oxide (MoO_3)	1591
$Mo_1O_3(cr,l)$	Molybdenum oxide (MoO_3)	1592
$Mo_1O_3(g)$	Molybdenum oxide (MoO_3)	1593
$Mo_1S_2(cr)$	Molybdenum sulfide (MoS_2)	1594
$Mo_2S_3(cr)$	Molybdenum sulfide (Mo_2S_3)	1595
$Mo_2S_3(l)$	Molybdenum sulfide (Mo_2S_3)	1596
$Mo_2S_3(cr,l)$	Molybdenum sulfide (Mo_2S_3)	1597
$N_{0.465}V_1(cr)$	Vanadium nitride ($VN_{0.465}$)	1599
$N_1(g)$	Nitrogen (N)	1600
$N_1^+(g)$	Nitrogen, ion (N^+)	1601
$N_1^-(g)$	Nitrogen, ion (N^-)	1602
$N_1O_1(g)$	Nitrogen oxide (NO)	1603
$N_1O_1^+(g)$	Nitrogen oxide, ion (NO^+)	1604
$N_1O_2(g)$	Nitrogen oxide (NO_2)	1605
$N_1O_2^-(g)$	Nitrogen oxide, ion (ONO^-)	1606
$N_1O_3(g)$	Nitrogen oxide (NO_3)	1607
$N_1P_1(g)$	*Phosphorus nitride* (PN)	1608
$N_1S_1(g)$	Nitrogen sulfide (NS)	1609
$N_1Si_1(g)$	Silicon nitride (SiN)	1610
$N_1Si_2(g)$	Silicon nitride (Si_2N)	1611
$N_1Ti_1(cr)$	Titanium nitride (TiN)	1612
$N_1Ti_1(l)$	Titanium nitride (TiN)	1613
$N_1Ti_1(cr,l)$	Titanium nitride (TiN)	1614
$N_1V_1(cr)$	Vanadium nitride (VN)	1615
$N_1V_1(g)$	Vanadium nitride (VN)	1616
$N_1Zr_1(cr)$	Zirconium nitride (ZrN)	1617
$N_1Zr_1(l)$	Zirconium nitride (ZrN)	1618
$N_1Zr_1(cr,l)$	Zirconium nitride (ZrN)	1619
$N_1Zr_1(g)$	Zirconium nitride (ZrN)	1620
$N_2(ref)$	Nitrogen (N_2)	1621
$N_2^+(g)$	Nitrogen, ion (N_2^+)	1622
$N_2^-(g)$	Nitrogen, ion (N_2^-)	1623
$N_2O_1(g)$	Nitrogen oxide (N_2O)	1624
$N_2O_1^+(g)$	Nitrogen oxide, ion (N_2O^+)	1625
$N_2O_3(g)$	Nitrogen oxide (N_2O_3)	1626
$N_2O_4(cr)$	Nitrogen oxide (N_2O_4)	1627
$N_2O_4(l)$	Nitrogen oxide (N_2O_4)	1628
$N_2O_4(cr,l)$	Nitrogen oxide (N_2O_4)	1629
$N_2O_4(g)$	Nitrogen oxide (N_2O_4)	1630
$N_2O_5(g)$	Nitrogen oxide (N_2O_5)	1631
$N_3(g)$	Azide (N_3)	1632
$N_4Si_3(cr)$	Silicon nitride, alpha (Si_3N_4)	1633
$N_5P_3(cr)$	Phosphorus nitride (P_3N_5)	1634
$Na_1(ref)$	Sodium (Na)	1637
$Na_1(cr)$	Sodium (Na)	1638
$Na_1(l)$	Sodium (Na)	1639
$Na_1(cr,l)$	Sodium (Na)	1640
$Na_1(g)$	Sodium (Na)	1641
$Na_1^+(g)$	Sodium, ion (Na^+)	1642
$Na_1^-(g)$	Sodium, ion (Na^-)	1643
$Na_1O_1(g)$	Sodium oxide (NaO)	1644

Formula	Table Title	Page
$Na_1O_1^-(g)$	Sodium oxide, ion (NaO^-)	1645
$Na_1O_2(cr)$	Sodium superoxide (NaO_2)	1646
$Na_2(g)$	Sodium (Na_2)	1647
$Na_2O_1(cr)$	Sodium oxide (Na_2O)	1648
$Na_2O_1(l)$	Sodium oxide (Na_2O)	1649
$Na_2O_1(cr,l)$	Sodium oxide (Na_2O)	1650
$Na_2O_2(cr)$	Sodium peroxide (Na_2O_2)	1651
$Na_2O_3Si_1(cr)$	Sodium silicate (Na_2SiO_3)	1652
$Na_2O_3Si_1(l)$	Sodium silicate (Na_2SiO_3)	1653
$Na_2O_3Si_1(cr,l)$	Sodium silicate (Na_2SiO_3)	1654
$Na_2O_4S_1(cr)$	Sodium sulfate, delta (Na_2SO_4)	1655
$Na_2O_4S_1(cr)$	Sodium sulfate, I (Na_2SO_4)	1656
$Na_2O_4S_1(cr)$	Sodium sulfate, III (Na_2SO_4)	1657
$Na_2O_4S_1(cr)$	Sodium sulfate, IV (Na_2SO_4)	1658
$Na_2O_4S_1(cr)$	Sodium sulfate, V (Na_2SO_4)	1659
$Na_2O_4S_1(l)$	Sodium sulfate (Na_2SO_4)	1660
$Na_2O_4S_1(cr,l)$	Sodium sulfate (Na_2SO_4)	1661
$Na_2O_4S_1(g)$	Sodium sulfate (Na_2SO_4)	1662
$Na_2O_4W_1(cr)$	Sodium tungsten oxide (Na_2WO_4)	1663
$Na_2O_5Si_2(cr)$	Sodium silicate ($Na_2Si_2O_5$)	1664
$Na_2O_5Si_2(l)$	Sodium silicate ($Na_2Si_2O_5$)	1665
$Na_2O_5Si_2(cr,l)$	Sodium silicate ($Na_2Si_2O_5$)	1666
$Na_2S_1(cr)$	Sodium sulfide (Na_2S)	1667
$Na_2S_1(l)$	Sodium sulfide (Na_2S)	1668
$Na_2S_1(cr,l)$	Sodium sulfide (Na_2S)	1669
$Na_2S_2(cr)$	Sodium sulfide, beta (Na_2S_2)	1670
$Na_2S_2(l)$	Sodium sulfide (Na_2S_2)	1671
$Na_2S_2(cr,l)$	Sodium sulfide (Na_2S_2)	1672
$Nb_1(ref)$	Niobium (Nb)	1675
$Nb_1(cr)$	Niobium (Nb)	1676
$Nb_1(l)$	Niobium (Nb)	1677
$Nb_1(cr,l)$	Niobium (Nb)	1678
$Nb_1(g)$	Niobium (Nb)	1679
$Nb_1^+(g)$	Niobium, ion (Nb^+)	1680
$Nb_1^-(g)$	Niobium, ion (Nb^-)	1681
$Nb_1O_1(cr)$	Niobium oxide (NbO)	1682
$Nb_1O_1(l)$	Niobium oxide (NbO)	1683
$Nb_1O_1(cr,l)$	Niobium oxide (NbO)	1684
$Nb_1O_1(g)$	Niobium oxide (NbO)	1685
$Nb_1O_2(cr)$	Niobium oxide (NbO_2)	1686
$Nb_1O_2(l)$	Niobium oxide (NbO_2)	1687
$Nb_1O_2(cr,l)$	Niobium oxide (NbO_2)	1688
$Nb_1O_2(g)$	Niobium oxide (NbO_2)	1689
$Nb_2O_5(cr)$	Niobium oxide (Nb_2O_5)	1690
$Nb_2O_5(l)$	Niobium oxide (Nb_2O_5)	1691
$Nb_2O_5(cr,l)$	Niobium oxide (Nb_2O_5)	1692
$Ne_1(ref)$	Neon (Ne)	1695
$Ne_1^+(g)$	Neon, ion (Ne^+)	1696
$Ni_1(ref)$	Nickel (Ni)	1697
$Ni_1(cr)$	Nickel (Ni)	1698
$Ni_1(l)$	Nickel (Ni)	1699
$Ni_1(cr,l)$	Nickel (Ni)	1700
$Ni_1(g)$	Nickel (Ni)	1701
$Ni_1^+(g)$	Nickel, ion (Ni^+)	1702
$Ni_1^-(g)$	Nickel, ion (Ni^-)	1703
$Ni_1S_1(cr)$	Nickel sulfide (NiS)	1704
$Ni_1S_1(l)$	Nickel sulfide (NiS)	1705
$Ni_1S_1(cr,l)$	Nickel sulfide (NiS)	1706
$Ni_1S_1(g)$	Nickel sulfide (NiS)	1707
$Ni_1S_2(cr)$	Nickel sulfide (NiS_2)	1708
$Ni_1S_2(l)$	Nickel sulfide (NiS_2)	1709
$Ni_1S_2(cr,l)$	Nickel sulfide (NiS_2)	1710
$Ni_3S_2(cr)$	Nickel sulfide (Ni_3S_2)	1711
$Ni_3S_2(l)$	Nickel sulfide (Ni_3S_2)	1712
$Ni_3S_2(cr,l)$	Nickel sulfide (Ni_3S_2)	1713
$Ni_3S_4(cr)$	Nickel sulfide (Ni_3S_4)	1714
$O_1(g)$	Oxygen (O)	1717
$O_1^+(g)$	Oxygen, ion (O^+)	1718
$O_1^-(g)$	Oxygen, ion (O^-)	1719
$O_1P_1(g)$	Phosphorus oxide (PO)	1720
$O_1Pb_1(cr)$	Lead oxide, red (PbO)	1721
$O_1Pb_1(cr)$	Lead oxide, yellow (PbO)	1722
$O_1Pb_1(l)$	Lead oxide (PbO)	1723
$O_1Pb_1(cr,l)$	Lead oxide (PbO)	1724
$O_1Pb_1(g)$	Lead oxide (PbO)	1725
$O_1S_1(g)$	Sulfur oxide (SO)	1726
$O_1S_2(g)$	Sulfur oxide (SSO)	1727
$O_1Si_1(g)$	Silicon oxide (SiO)	1728
$O_1Sr_1(cr)$	Strontium oxide (SrO)	1729
$O_1Sr_1(l)$	Strontium oxide (SrO)	1730
$O_1Sr_1(cr,l)$	Strontium oxide (SrO)	1731
$O_1Sr_1(g)$	Strontium oxide (SrO)	1732
$O_1Ta_1(g)$	Tantalum oxide (TaO)	1733
$O_1Ti_1(cr)$	Titanium oxide, alpha (TiO)	1734
$O_1Ti_1(cr)$	Titanium oxide, beta (TiO)	1735
$O_1Ti_1(l)$	Titanium oxide (TiO)	1736
$O_1Ti_1(cr,l)$	Titanium oxide (TiO)	1737
$O_1Ti_1(g)$	Titanium oxide (TiO)	1738
$O_1V_1(cr)$	Vanadium oxide (VO)	1739
$O_1V_1(l)$	Vanadium oxide (VO)	1740
$O_1V_1(cr,l)$	Vanadium oxide (VO)	1741
$O_1V_1(g)$	Vanadium oxide (VO)	1742
$O_1W_1(g)$	Tungsten oxide (WO)	1743
$O_1Zr_1(g)$	Zirconium oxide (ZrO)	1744
$O_2(ref)$	Oxygen (O_2)	1745
$O_2^+(g)$	Oxygen, ion (O_2^+)	1746
$O_2^-(g)$	Oxygen, ion (O_2^-)	1747
$O_2P_1(g)$	Phosphorus oxide (PO_2)	1748
$O_2Pb_1(cr)$	Lead oxide (PbO_2)	1749
$O_2S_1(g)$	Sulfur dioxide (SO_2)	1750
$O_2Si_1(cr)$	Silicon oxide, cristobalite, high (SiO_2)	1751
$O_2Si_1(cr)$	Silicon oxide, cristobalite, low (SiO_2)	1752
$O_2Si_1(cr)$	Silicon oxide, quartz (SiO_2)	1753
$O_2Si_1(l)$	Silicon oxide (SiO_2)	1754
$O_2Si_1(cr,l)$	Silicon oxide (SiO_2)	1755
$O_2Si_1(g)$	Silicon oxide (SiO_2)	1756
$O_2Ta_1(g)$	Tantalum oxide (TaO_2)	1757
$O_2Ti_1(cr)$	Titanium oxide, anatase (TiO_2)	1758

Formula	Table Title	Page
$O_2Ti_1(cr)$	Titanium oxide, rutile (TiO_2)	1759
$O_2Ti_1(l)$	Titanium oxide (TiO_2)	1760
$O_2Ti_1(cr,l)$	Titanium oxide (TiO_2)	1761
$O_2Ti_1(g)$	Titanium oxide (TiO_2)	1762
$O_2V_1(g)$	Vanadium oxide (VO_2)	1763
$O_2W_1(cr)$	Tungsten oxide (WO_2)	1764
$O_2W_1(g)$	Tungsten oxide (WO_2)	1765
$O_{2.72}W_1(cr)$	Tungsten oxide ($WO_{2.72}$)	1766
$O_{2.90}W_1(cr)$	Tungsten oxide ($WO_{2.90}$)	1767
$O_{2.96}W_1(cr)$	Tungsten oxide ($WO_{2.96}$)	1768
$O_2Zr_1(cr)$	Zirconium oxide (ZrO_2)	1769
$O_2Zr_1(l)$	Zirconium oxide (ZrO_2)	1770
$O_2Zr_1(cr,l)$	Zirconium oxide (ZrO_2)	1771
$O_2Zr_1(g)$	Zirconium oxide (ZrO_2)	1772
$O_3(g)$	Ozone (O_3)	1773
$O_3Pb_1Si_1(cr)$	Lead silicate ($PbSiO_3$)	1774
$O_3S_1(g)$	Sulfur trioxide (SO_3)	1775
$O_3Ti_2(cr)$	Titanium oxide (Ti_2O_3)	1776
$O_3Ti_2(l)$	Titanium oxide (Ti_2O_3)	1777
$O_3Ti_2(cr,l)$	Titanium oxide (Ti_2O_3)	1778
$O_3V_2(cr)$	Vanadium oxide (V_2O_3)	1779
$O_3V_2(l)$	Vanadium oxide (V_2O_3)	1780
$O_3V_2(cr,l)$	Vanadium oxide (V_2O_3)	1781
$O_3W_1(cr)$	Tungsten oxide (WO_3)	1782
$O_3W_1(l)$	Tungsten oxide (WO_3)	1783
$O_3W_1(cr,l)$	Tungsten oxide (WO_3)	1784
$O_3W_1(g)$	Tungsten oxide (WO_3)	1785
$O_4Pb_2Si_1(cr)$	Lead silicate (Pb_2SiO_4)	1786
$O_4Pb_3(cr)$	Lead oxide (Pb_3O_4)	1787
$O_4S_1Zn_1(cr)$	Zinc sulfate ($ZnSO_4$)	1788
$O_4Si_1Zr_1(cr)$	Zirconium silicate ($ZrSiO_4$)	1789
$O_4V_2(cr)$	Vanadium oxide (V_2O_4)	1790
$O_4V_2(l)$	Vanadium oxide (V_2O_4)	1791
$O_4V_2(cr,l)$	Vanadium oxide (V_2O_4)	1792
$O_5Ta_2(cr)$	Tantalum oxide (Ta_2O_5)	1793
$O_5Ta_2(l)$	Tantalum oxide (Ta_2O_5)	1794
$O_5Ta_2(cr,l)$	Tantalum oxide (Ta_2O_5)	1795
$O_5Ti_3(cr)$	Titanium oxide, alpha (Ti_3O_5)	1796
$O_5Ti_3(cr)$	Titanium oxide, beta (Ti_3O_5)	1797
$O_5Ti_3(l)$	Titanium oxide (Ti_3O_5)	1798
$O_5Ti_3(cr,l)$	Titanium oxide (Ti_3O_5)	1799
$O_5V_2(cr)$	Vanadium oxide (V_2O_5)	1800
$O_5V_2(l)$	Vanadium oxide (V_2O_5)	1801
$O_5V_2(cr,l)$	Vanadium oxide (V_2O_5)	1802
$O_6P_4(g)$	Phosphorus oxide ($(P_2O_3)_2$)	1803
$O_6W_2(g)$	Tungsten oxide ($(WO_3)_2$)	1804
$O_7Ti_4(cr)$	Titanium oxide (Ti_4O_7)	1805
$O_7Ti_4(l)$	Titanium oxide (Ti_4O_7)	1806
$O_7Ti_4(cr,l)$	Titanium oxide (Ti_4O_7)	1807
$O_8W_3(g)$	Tungsten oxide (W_3O_8)	1808
$O_9W_3(g)$	Tungsten oxide ($(WO_3)_3$)	1809
$O_{10}P_4(cr)$	Phosphorus oxide ($(P_2O_5)_2$)	1810
$O_{10}P_4(g)$	Phosphorus oxide ($(P_2O_5)_2$)	1811
$O_{12}W_4(g)$	Tungsten oxide ($(WO_3)_4$)	1812
$P_1(ref)$	Phosphorus (P)	1817
$P_1(cr)$	Phosphorus, black (P)	1818
$P_1(cr)$	Phosphorus, red, IV (P)	1819
$P_1(cr)$	Phosphorus, red, V (P)	1820
$P_1(cr)$	Phosphorus, white (P)	1821
$P_1(l)$	Phosphorus (P)	1822
$P_1(cr,l)$	Phosphorus (P)	1823
$P_1(g)$	Phosphorus (P)	1824
$P_1^+(g)$	Phosphorus, ion (P^+)	1825
$P_1^-(g)$	Phosphorus, ion (P^-)	1826
$P_1S_1(g)$	Phosphorus sulfide (PS)	1827
$P_2(g)$	Phosphorus (P_2)	1828
$P_4(g)$	Phosphorus (P_4)	1829
$P_4S_3(cr)$	Phosphorus sulfide (P_4S_3)	1830
$P_4S_3(l)$	Phosphorus sulfide (P_4S_3)	1831
$P_4S_3(cr,l)$	Phosphorus sulfide (P_4S_3)	1832
$P_4S_3(g)$	Phosphorus sulfide (P_4S_3)	1833
$Pb_1(ref)$	Lead (Pb)	1835
$Pb_1(cr)$	Lead (Pb)	1836
$Pb_1(l)$	Lead (Pb)	1837
$Pb_1(cr,l)$	Lead (Pb)	1838
$Pb_1(g)$	Lead (Pb)	1839
$Pb_1^+(g)$	Lead, ion (Pb^+)	1840
$Pb_1^-(g)$	Lead, ion (Pb^-)	1841
$Pb_1S_1(cr)$	Lead sulfide (PbS)	1842
$Pb_1S_1(l)$	Lead sulfide (PbS)	1843
$Pb_1S_1(cr,l)$	Lead sulfide (PbS)	1844
$Pb_1S_1(g)$	Lead sulfide (PbS)	1845
$Pb_2(g)$	Lead (Pb_2)	1846
$Rb_1(ref)$	Rubidium (Rb)	1849
$Rb_1(cr)$	Rubidium (Rb)	1850
$Rb_1(l)$	Rubidium (Rb)	1851
$Rb_1(cr,l)$	Rubidium (Rb)	1852
$Rb_1(g)$	Rubidium (Rb)	1853
$Rb_1^+(g)$	Rubidium, ion (Rb^+)	1854
$Rb_1^-(g)$	Rubidium, ion (Rb^-)	1855
$Rb_2(g)$	Rubidium (Rb_2)	1856
$Rn_1(ref)$	Radon (Rn)	1857
$Rn_1^+(g)$	Radon, ion (Rn^+)	1858
$S_1(ref)$	Sulfur (S)	1859
$S_1(cr)$	Sulfur, monoclinic (S)	1860
$S_1(cr)$	Sulfur, orthorhombic (S)	1861
$S_1(l)$	Sulfur (S)	1862
$S_1(cr,l)$	Sulfur (S)	1863
$S_1(g)$	Sulfur (S)	1864
$S_1^+(g)$	Sulfur, ion (S^+)	1865
$S_1^-(g)$	Sulfur, ion (S^-)	1866
$S_1Si_1(g)$	Silicon sulfide (SiS)	1867
$S_1Sr_1(cr)$	Strontium sulfide (SrS)	1868
$S_1Sr_1(g)$	Strontium sulfide (SrS)	1869
$S_2(g)$	Sulfur (S_2)	1870
$S_2Si_1(cr)$	Silicon sulfide (SiS_2)	1871
$S_2Si_1(l)$	Silicon sulfide (SiS_2)	1872

Formula	Table Title	Page
$S_2Si_1(cr,l)$	Silicon sulfide (SiS_2)	1873
$S_3(g)$	Sulfur (S_3)	1874
$S_4(g)$	Sulfur (S_4)	1875
$S_5(g)$	Sulfur (S_5)	1876
$S_6(g)$	Sulfur (S_6)	1877
$S_7(g)$	Sulfur (S_7)	1878
$S_8(g)$	Sulfur (S_8)	1879
$Si_1(ref)$	Silicon (Si)	1881
$Si_1(cr)$	Silicon (Si)	1882
$Si_1(l)$	Silicon (Si)	1883
$Si_1(cr,l)$	Silicon (Si)	1884
$Si_1(g)$	Silicon (Si)	1885
$Si_1^+(g)$	Silicon, ion (Si^+)	1886
$Si_1^-(g)$	Silicon, ion (Si^-)	1887
$Si_2(g)$	Silicon (Si_2)	1888
$Si_3(g)$	Silicon (Si_3)	1889
$Sr_1(ref)$	Strontium (Sr)	1891
$Sr_1(cr)$	Strontium, alpha (Sr)	1892
$Sr_1(cr)$	Strontium, beta (Sr)	1893
$Sr_1(l)$	Strontium (Sr)	1894
$Sr_1(cr,l)$	Strontium (Sr)	1895
$Sr_1(g)$	Strontium (Sr)	1896
$Sr_1^+(g)$	Strontium, ion (Sr^+)	1897
$Ta_1(ref)$	Tantalum (Ta)	1899
$Ta_1(cr)$	Tantalum (Ta)	1900
$Ta_1(l)$	Tantalum (Ta)	1901
$Ta_1(cr,l)$	Tantalum (Ta)	1902
$Ta_1(g)$	Tantalum (Ta)	1903
$Ta_1^+(g)$	Tantalum, ion (Ta^+)	1904
$Ta_1^-(g)$	Tantalum, ion (Ta^-)	1905
$Ti_1(ref)$	Titanium (Ti)	1907
$Ti_1(cr)$	Titanium, alpha (Ti)	1908
$Ti_1(cr)$	Titanium, beta (Ti)	1909
$Ti_1(l)$	Titanium (Ti)	1910
$Ti_1(cr,l)$	Titanium (Ti)	1911
$Ti_1(g)$	Titanium (Ti)	1912
$Ti_1^+(g)$	Titanium, ion (Ti^+)	1913
$Ti_1^-(g)$	Titanium, ion (Ti^-)	1914
$V_1(ref)$	Vanadium (V)	1917
$V_1(cr)$	Vanadium (V)	1918
$V_1(l)$	Vanadium (V)	1919
$V_1(cr,l)$	Vanadium (V)	1920
$V_1(g)$	Vanadium (V)	1921
$V_1^+(g)$	Vanadium, ion (V^+)	1922
$V_1^-(g)$	Vanadium, ion (V^-)	1923
$W_1(ref)$	Tungsten (W)	1925
$W_1(cr)$	Tungsten (W)	1926
$W_1(l)$	Tungsten (W)	1927
$W_1(cr,l)$	Tungsten (W)	1928
$W_1(g)$	Tungsten (W)	1929
$W_1^+(g)$	Tungsten, ion (W^+)	1930
$W_1^-(g)$	Tungsten, ion (W^-)	1931
$Xe_1(ref)$	Xenon (Xe)	1933
$Xe_1^+(g)$	Xenon, ion (Xe^+)	1934
$Zn_1(ref)$	Zinc (Zn)	1935
$Zn_1(cr)$	Zinc (Zn)	1936
$Zn_1(l)$	Zinc (Zn)	1937
$Zn_1(cr,l)$	Zinc (Zn)	1938
$Zn_1(g)$	Zinc (Zn)	1939
$Zn_1^+(g)$	Zinc, ion (Zn^+)	1940
$Zn_1^-(g)$	Zinc, ion (Zn^-)	1941
$Zr_1(ref)$	Zirconium (Zr)	1943
$Zr_1(cr)$	Zirconium, alpha (Zr)	1944
$Zr_1(cr)$	Zirconium, beta (Zr)	1945
$Zr_1(l)$	Zirconium (Zr)	1946
$Zr_1(cr,l)$	Zirconium (Zr)	1947
$Zr_1(g)$	Zirconium (Zr)	1948
$Zr_1^+(g)$	Zirconium, ion (Zr^+)	1949
$Zr_1^-(g)$	Zirconium, ion (Zr^-)	1950

10.4 Chemical Name Index

Table Title	Formula	Page
2-Butynedinitrile (C_4N_2)	C_4N_2(g)	693
Aluminum (Al)	Al_1(ref)	59
Aluminum (Al)	Al_1(cr)	60
Aluminum (Al)	Al_1(l)	61
Aluminum (Al)	Al_1(cr,l)	62
Aluminum (Al)	Al_1(g)	63
Aluminum (Al_2)	Al_2(g)	138
Aluminum borate ($AlBO_2$)	$Al_1B_1O_2$(g)	66
Aluminum bromide ($(AlBr_3)_2$)	Al_2Br_6(g)	142
Aluminum bromide (AlBr)	Al_1Br_1(g)	67
Aluminum bromide ($AlBr_3$)	Al_1Br_3(cr)	68
Aluminum bromide ($AlBr_3$)	Al_1Br_3(l)	69
Aluminum bromide ($AlBr_3$)	Al_1Br_3(cr,l)	70
Aluminum bromide ($AlBr_3$)	Al_1Br_3(g)	71
Aluminum carbide (Al_4C_3)	C_3Al_4(cr)	687
Aluminum carbide (AlC)	C_1Al_1(g)	554
Aluminum chloride ($(AlCl_3)_2$)	Al_2Cl_6(g)	143
Aluminum chloride (AlCl)	Al_1Cl_1(g)	72
Aluminum chloride ($AlCl_2$)	Al_1Cl_2(g)	79
Aluminum chloride ($AlCl_3$)	Al_1Cl_3(cr)	83
Aluminum chloride ($AlCl_3$)	Al_1Cl_3(l)	84
Aluminum chloride ($AlCl_3$)	Al_1Cl_3(cr,l)	85
Aluminum chloride ($AlCl_3$)	Al_1Cl_3(g)	86
Aluminum chloride fluoride (AlClF)	$Al_1Cl_1F_1$(g)	74
Aluminum chloride fluoride ($AlClF_2$)	$Al_1Cl_1F_2$(g)	76
Aluminum chloride fluoride ($AlCl_2F$)	$Al_1Cl_2F_1$(g)	82
Aluminum chloride fluoride, ion ($AlClF^+$)	$Al_1Cl_1F_1^+$(g)	75
Aluminum chloride, ion ($AlCl^+$)	$Al_1Cl_1^+$(g)	73
Aluminum chloride, ion ($AlCl_2^+$)	$Al_1Cl_2^+$(g)	80
Aluminum chloride, ion ($AlCl_2^-$)	$Al_1Cl_2^-$(g)	81
Aluminum chloride oxide (OAlCl)	$Al_1Cl_1O_1$(cr)	77
Aluminum chloride oxide (OAlCl)	$Al_1Cl_1O_1$(g)	78
Aluminum fluoride ($(AlF_3)_2$)	Al_2F_6(g)	145
Aluminum fluoride (AlF)	Al_1F_1(g)	91
Aluminum fluoride (AlF_2)	Al_1F_2(g)	94
Aluminum fluoride (AlF_3)	Al_1F_3(cr)	99
Aluminum fluoride (AlF_3)	Al_1F_3(l)	100
Aluminum fluoride (AlF_3)	Al_1F_3(cr,l)	101
Aluminum fluoride (AlF_3)	Al_1F_3(g)	102
Aluminum fluoride, ion (AlF^+)	$Al_1F_1^+$(g)	92
Aluminum fluoride, ion (AlF_2^+)	$Al_1F_2^+$(g)	95
Aluminum fluoride, ion (AlF_2^-)	$Al_1F_2^-$(g)	96
Aluminum fluoride oxide (OAlF)	$Al_1F_1O_1$(g)	93
Aluminum fluoride oxide ($OAlF_2$)	$Al_1F_2O_1$(g)	97
Aluminum fluoride oxide, ion ($OAlF_2^-$)	$Al_1F_2O_1^-$(g)	98
Aluminum hydride (AlH)	Al_1H_1(g)	114
Aluminum hydride oxide (OAlH)	$Al_1H_1O_1$(g)	115
Aluminum hydroxide (AlOH)	$Al_1H_1O_1$(g)	116
Aluminum hydroxide, ion ($AlOH^+$)	$Al_1H_1O_1^+$(g)	117
Aluminum hydroxide, ion ($AlOH^-$)	$Al_1H_1O_1^-$(g)	118
Aluminum hydroxide oxide (OAlOH)	$Al_1H_1O_2$(g)	119
Aluminum iodide ($(AlI_3)_2$)	Al_2I_6(g)	146
Aluminum iodide (AlI)	Al_1I_1(g)	121
Aluminum iodide (AlI_3)	Al_1I_3(cr)	122
Aluminum iodide (AlI_3)	Al_1I_3(l)	123
Aluminum iodide (AlI_3)	Al_1I_3(cr,l)	124
Aluminum iodide (AlI_3)	Al_1I_3(g)	125
Aluminum, ion (Al^+)	Al_1^+(g)	64
Aluminum, ion (Al-)	Al_1^-(g)	65
Aluminum nitride (AlN)	Al_1N_1(cr)	129
Aluminum nitride (AlN)	Al_1N_1(g)	130
Aluminum oxide ($(AlO)_2$)	Al_2O_2(g)	152
Aluminum oxide (Al_2O)	Al_2O_1(g)	150
Aluminum oxide (Al_2O_3)	Al_2O_3(cr,l)	159
Aluminum oxide (Al_2O_3)	Al_2O_3(l)	158
Aluminum oxide (AlO)	Al_1O_1(g)	132
Aluminum oxide (AlO_2)	Al_1O_2(g)	135
Aluminum oxide, alpha (Al_2O_3)	Al_2O_3(cr)	154
Aluminum oxide, delta (Al_2O_3)	Al_2O_3(cr)	155
Aluminum oxide, gamma (Al_2O_3)	Al_2O_3(cr)	156
Aluminum oxide, ion (Al_2O^+)	$Al_2O_1^+$(g)	151
Aluminum oxide, ion ($Al_2O_2^+$)	$Al_2O_2^+$(g)	153
Aluminum oxide, ion (AlO^+)	$Al_1O_1^+$(g)	133
Aluminum oxide, ion (AlO^-)	$Al_1O_1^-$(g)	134
Aluminum oxide, ion (AlO_2^-)	$Al_1O_2^-$(g)	136
Aluminum oxide, kappa (Al_2O_3)	Al_2O_3(cr)	157
Aluminum silicate, andalusite (Al_2SiO_5)	$Al_2O_5Si_1$(cr)	160
Aluminum silicate, kyanite (Al_2SiO_5)	$Al_2O_5Si_1$(cr)	161
Aluminum silicate, mullite ($Al_6Si_2O_{13}$)	$Al_6O_{13}Si_2$(cr)	170
Aluminum silicate, sillimanite (Al_2SiO_5)	$Al_2O_5Si_1$(cr)	162
Aluminum sulfide (Al_2S_3)	Al_2S_3(cr)	163
Aluminum sulfide (AlS)	Al_1S_1(g)	137
Amidogen (NH_2)	H_2N_1(g)	1320
Amidogen−d_2 (ND_2)	D_2N_1(g)	1043
Ammonia (NH_3)	H_3N_1(g)	1343
Ammonia-d_3 (ND_3)	D_3N_1(g)	1047
Ammonium bromide (NH_4Br)	$Br_1H_4N_1$(cr)	440
Ammonium chloride (NH_4Cl)	$Cl_1H_4N_1$(cr)	765
Ammonium iodide (NH_4I)	$H_4I_1N_1$(cr)	1349
Ammonium perchlorate (NH_4ClO_4)	$Cl_1H_4N_1O_4$(cr)	766
Argon (Ar)	Ar_1(ref)	175
Argon, ion (Ar^+)	Ar_1^+(g)	176
Azide (N_3)	N_3(g)	1632
Barium (Ba)	Ba_1(g)	323
Barium (Ba)	Ba_1(cr,l)	322
Barium (Ba)	Ba_1(l)	321
Barium (Ba)	Ba_1(cr)	320
Barium (Ba)	Ba_1(ref)	319
Barium bromide (BaBr)	Ba_1Br_1(g)	325
Barium bromide ($BaBr_2$)	Ba_1Br_2(g)	329
Barium bromide ($BaBr_2$)	Ba_1Br_2(cr,l)	328
Barium bromide ($BaBr_2$)	Ba_1Br_2(l)	327
Barium bromide ($BaBr_2$)	Ba_1Br_2(cr)	326
Barium chloride (BaCl)	Ba_1Cl_1(g)	330
Barium chloride ($BaCl_2$)	Ba_1Cl_2(g)	334
Barium chloride ($BaCl_2$)	Ba_1Cl_2(cr,l)	333
Barium chloride ($BaCl_2$)	Ba_1Cl_2(l)	332

Table Title	Formula	Page
Barium chloride ($BaCl_2$)	Ba_1Cl_2(cr)	331
Barium fluoride (BaF)	Ba_1F_1(g)	335
Barium fluoride (BaF_2)	Ba_1F_2(g)	340
Barium fluoride (BaF_2)	Ba_1F_2(cr,l)	339
Barium fluoride (BaF_2)	Ba_1F_2(l)	338
Barium fluoride (BaF_2)	Ba_1F_2(cr)	337
Barium fluoride, ion (BaF^+)	$Ba_1F_1^+$(g)	336
Barium hydroxide ($Ba(OH)_2$)	$Ba_1H_2O_2$(g)	346
Barium hydroxide ($Ba(OH)_2$)	$Ba_1H_2O_2$(cr,l)	345
Barium hydroxide ($Ba(OH)_2$)	$Ba_1H_2O_2$(l)	344
Barium hydroxide (BaOH)	$Ba_1H_1O_1$(g)	341
Barium hydroxide, alpha ($Ba(OH)_2$)	$Ba_1H_2O_2$(cr)	343
Barium hydroxide, ion ($BaOH^+$)	$Ba_1H_1O_1^+$(g)	342
Barium iodide (BaI)	Ba_1I_1(g)	347
Barium iodide (BaI_2)	Ba_1I_2(g)	351
Barium iodide (BaI_2)	Ba_1I_2(cr,l)	350
Barium iodide (BaI_2)	Ba_1I_2(l)	349
Barium iodide (BaI_2)	Ba_1I_2(cr)	348
Barium, ion (Ba^+)	Ba_1^+(g)	324
Barium oxide (BaO)	Ba_1O_1(g)	355
Barium oxide (BaO)	Ba_1O_1(cr,l)	354
Barium oxide (BaO)	Ba_1O_1(l)	353
Barium oxide (BaO)	Ba_1O_1(cr)	352
Barium sulfide (BaS)	Ba_1S_1(g)	357
Barium sulfide (BaS)	Ba_1S_1(cr)	356
Beryllium (Be)	Be_1(ref)	361
Beryllium (Be)	Be_1(cr)	362
Beryllium (Be)	Be_1(l)	363
Beryllium (Be)	Be_1(cr,l)	364
Beryllium (Be)	Be_1(g)	365
Beryllium (Be_2)	Be_2(g)	415
Beryllium aluminum oxide ($BeAl_2O_4$)	$Al_2Be_1O_4$(cr)	139
Beryllium aluminum oxide ($BeAl_2O_4$)	$Al_2Be_1O_4$(cr,l)	141
Beryllium aluminum oxide ($BeAl_2O_4$)	$Al_2Be_1O_4$(l)	140
Beryllium aluminum oxide ($BeAl_6O_{10}$)	$Al_6Be_1O_{10}$(l)	168
Beryllium aluminum oxide ($BeAl_6O_{10}$)	$Al_6Be_1O_{10}$(cr)	167
Beryllium aluminum oxide ($BeAl_6O_{10}$)	$Al_6Be_1O_{10}$(cr,l)	169
Beryllium borate ($Be(BO_2)_2$)	$B_2Be_1O_4$(g)	260
Beryllium borate ($Be_3B_2O_6$)	$B_2Be_3O_6$(cr)	261
Beryllium borate ($BeBO_2$)	$B_1Be_1O_2$(g)	184
Beryllium bromide (BeBr)	Be_1Br_1(g)	367
Beryllium bromide ($BeBr_2$)	Be_1Br_2(cr)	368
Beryllium bromide ($BeBr_2$)	Be_1Br_2(g)	369
Beryllium carbide (Be_2C)	C_1Be_2(cr,l)	561
Beryllium carbide (Be_2C)	C_1Be_2(l)	560
Beryllium carbide (Be_2C)	C_1Be_2(cr)	559
Beryllium carbide (BeC_2)	C_2Be_1(g)	663
Beryllium chloride ($(BeCl_2)_2$)	Be_2Cl_4(g)	416
Beryllium chloride (BeCl)	Be_1Cl_1(g)	370
Beryllium chloride ($BeCl_2$)	Be_1Cl_2(l)	375
Beryllium chloride ($BeCl_2$)	Be_1Cl_2(g)	377
Beryllium chloride ($BeCl_2$)	Be_1Cl_2(cr,l)	376
Beryllium chloride, alpha ($BeCl_2$)	Be_1Cl_2(cr)	373
Beryllium chloride, beta ($BeCl_2$)	Be_1Cl_2(cr)	374
Beryllium chloride fluoride (BeClF)	$Be_1Cl_1F_1$(g)	372
Beryllium chloride, ion ($BeCl^+$)	$Be_1Cl_1^+$(g)	371
Beryllium fluoride (BeF)	Be_1F_1(g)	378
Beryllium fluoride (BeF_2)	Be_1F_2(g)	382
Beryllium fluoride (BeF_2)	Be_1F_2(cr,l)	381
Beryllium fluoride (BeF_2)	Be_1F_2(l)	380
Beryllium fluoride (BeF_2)	Be_1F_2(cr)	379
Beryllium fluoride oxide ($O(BeF)_2$)	$Be_2F_2O_1$(g)	417
Beryllium hydride (BeH)	Be_1H_1(g)	390
Beryllium hydride (BeH_2)	Be_1H_2(g)	394
Beryllium hydride, ion (BeH^+)	$Be_1H_1^+$(g)	391
Beryllium hydroxide ($Be(OH)_2$)	$Be_1H_2O_2$(g)	397
Beryllium hydroxide (BeOH)	$Be_1H_1O_1$(g)	392
Beryllium hydroxide, alpha ($Be(OH)_2$)	$Be_1H_2O_2$(cr)	395
Beryllium hydroxide, beta ($Be(OH)_2$)	$Be_1H_2O_2$(cr)	396
Beryllium hydroxide, ion ($BeOH^+$)	$Be_1H_1O_1^+$(g)	393
Beryllium iodide (BeI)	Be_1I_1(g)	398
Beryllium iodide (BeI_2)	Be_1I_2(g)	402
Beryllium iodide (BeI_2)	Be_1I_2(cr,l)	401
Beryllium iodide (BeI_2)	Be_1I_2(l)	400
Beryllium iodide (BeI_2)	Be_1I_2(cr)	399
Beryllium, ion (Be^+)	Be_1^+(g)	366
Beryllium nitride (Be_3N_2)	Be_3N_2(cr,l)	423
Beryllium nitride (Be_3N_2)	Be_3N_2(l)	422
Beryllium nitride (BeN)	Be_1N_1(g)	403
Beryllium nitride, alpha (Be_3N_2)	Be_3N_2(cr)	421
Beryllium oxide ($(BeO)_2$)	Be_2O_2(g)	419
Beryllium oxide ($(BeO)_3$)	Be_3O_3(g)	424
Beryllium oxide ($(BeO)_4$)	Be_4O_4(g)	425
Beryllium oxide ($(BeO)_5$)	Be_5O_5(g)	426
Beryllium oxide ($(BeO)_6$)	Be_6O_6(g)	427
Beryllium oxide (Be_2O)	Be_2O_1(g)	418
Beryllium oxide (BeO)	Be_1O_1(g)	408
Beryllium oxide (BeO)	Be_1O_1(cr,l)	407
Beryllium oxide (BeO)	Be_1O_1(l)	406
Beryllium oxide, alpha (BeO)	Be_1O_1(cr)	404
Beryllium oxide, beta (BeO)	Be_1O_1(cr)	405
Beryllium silicate (Be_2SiO_4)	$Be_2O_4Si_1$(cr)	420
Beryllium sulfate, alpha ($BeSO_4$)	$Be_1O_4S_1$(cr)	409
Beryllium sulfate, beta ($BeSO_4$)	$Be_1O_4S_1$(cr)	410
Beryllium sulfate, gamma ($BeSO_4$)	$Be_1O_4S_1$(cr)	411
Beryllium sulfide (BeS)	Be_1S_1(g)	414
Beryllium sulfide (BeS)	Be_1S_1(cr)	413
Beryllium tungsten oxide ($BeWO_4$)	$Be_1O_4W_1$(cr)	412
Borane (BH)	B_1H_1(g)	221
Borane (BH_2)	B_1H_2(g)	229
Borane (BH_3)	B_1H_3(g)	231
Borazine ($B_3H_6N_3$)	$B_3H_6N_3$(g)	290
Boric acid ($(HBO_2)_3$)	$B_3H_3O_6$(g)	289
Boric acid (H_3BO_3)	$B_1H_3O_3$(cr)	232
Boric acid (H_3BO_3)	$B_1H_3O_3$(g)	233
Boric acid (HBO_2)	$B_1H_1O_2$(g)	226
Boric acid (HBO_2)	$B_1H_1O_2$(cr)	225
Boron (B)	B_1(ref)	177
Boron (B)	B_1(l)	179
Boron (B)	B_1(cr,l)	180
Boron (B)	B_1(g)	181
Boron (B_2)	B_2(g)	259

Table Title	Formula	Page
Boron, beta-rhombohedral (B)	B_1(cr)	178
Boron bromide oxide (OBBr)	$B_1Br_1O_1$(g)	190
Boron carbide (B_4C)	C_1B_4(cr)	556
Boron carbide (B_4C)	C_1B_4(l)	557
Boron carbide (B_4C)	C_1B_4(cr,l)	558
Boron carbide (BC)	C_1B_1(g)	555
Boron chloride oxide (OBCl)	$B_1Cl_1O_1$(g)	201
Boron fluoride oxide (OBF)	$B_1F_1O_1$(g)	209
Boron fluoride oxide (OBF_2)	$B_1F_2O_1$(g)	215
Boron hydride oxide (HBO)	$B_1H_1O_1$(g)	222
Boron hydride oxide, ion (HBO^+)	$B_1H_1O_1^+$(g)	223
Boron hydride oxide, ion (HBO^-)	$B_1H_1O_1^-$(g)	224
Boron hydride sulfide (HBS)	$B_1H_1S_1$(g)	227
Boron hydride sulfide, ion (HBS^+)	$B_1H_1S_1^+$(g)	228
Boron, ion (B^+)	B_1^+(g)	182
Boron, ion (B^-)	B_1^-(g)	183
Boron nitride (BN)	B_1N_1(g)	249
Boron nitride (BN)	B_1N_1(cr)	248
Boron oxide ($(BO)_2$)	B_2O_2(g)	270
Boron oxide (B_2O)	B_2O_1(g)	269
Boron oxide (B_2O_3)	B_2O_3(g)	274
Boron oxide (B_2O_3)	B_2O_3(cr,l)	273
Boron oxide (B_2O_3)	B_2O_3(l)	272
Boron oxide (B_2O_3)	B_2O_3(cr)	271
Boron oxide (BO)	B_1O_1(g)	254
Boron oxide (BO_2)	B_1O_2(g)	255
Boron oxide, ion (BO_2^-)	$B_1O_2^-$(g)	256
Boron sulfide (BS)	B_1S_1(g)	257
Boroxin ($B_3H_3O_3$)	$B_3H_3O_3$(cr)	287
Boroxin ($B_3H_3O_3$)	$B_3H_3O_3$(g)	288
Bromine (Br)	Br_1(g)	429
Bromine (Br_2)	Br_2(ref)	470
Bromine (Br_2)	Br_2(cr,l)	471
Bromine (Br_2)	Br_2(g)	472
Bromine chloride (BrCl)	Br_1Cl_1(g)	433
Bromine fluoride (BrF)	Br_1F_1(g)	434
Bromine fluoride (BrF_3)	Br_1F_3(g)	435
Bromine fluoride (BrF_5)	Br_1F_5(g)	436
Bromine, ion (Br^+)	Br_1^+(g)	430
Bromine, ion (Br^-)	Br_1^-(g)	431
Bromine oxide (BrBrO)	Br_2O_1(g)	498
Bromine oxide (BrO)	Br_1O_1(g)	459
Bromine oxide (BrO_3)	Br_1O_3(g)	462
Bromine oxide (BrOBr)	Br_2O_1(g)	497
Bromine oxide (BrOO)	Br_1O_2(g)	461
Bromine oxide (OBrO)	Br_1O_2(g)	460
Bromoborane (BBr)	B_1Br_1(g)	185
Bromochloroborane (BBrCl)	$B_1Br_1Cl_1$(g)	186
Bromodichloroborane ($BBrCl_2$)	$B_1Br_1Cl_2$(g)	187
Bromodifluoroborane ($BBrF_2$)	$B_1Br_1F_2$(g)	189
Bromofluoroborane (BBrF)	$B_1Br_1F_1$(g)	188
Bromoimidogen (NBr)	Br_1N_1(g)	453
Bromomethylidyne (CBr)	C_1Br_1(g)	562
Bromosilane (SiH_3Br)	$Br_1H_3Si_1$(g)	439
Bromosilylidyne (SiBr)	Br_1Si_1(g)	465
Bromotrifluoromethane ($CBrF_3$)	$C_1Br_1F_3$(g)	563
Calcium (Ca)	Ca_1(ref)	703
Calcium (Ca)	Ca_1(l)	706
Calcium (Ca)	Ca_1(cr,l)	707
Calcium (Ca)	Ca_1(g)	708
Calcium (Ca_2)	Ca_2(g)	735
Calcium, alpha (Ca)	Ca_1(cr)	704
Calcium, beta (Ca)	Ca_1(cr)	705
Calcium bromide (CaBr)	Br_1Ca_1(g)	432
Calcium bromide ($CaBr_2$)	Br_2Ca_1(g)	476
Calcium bromide ($CaBr_2$)	Br_2Ca_1(cr,l)	475
Calcium bromide ($CaBr_2$)	Br_2Ca_1(l)	474
Calcium bromide ($CaBr_2$)	Br_2Ca_1(cr)	473
Calcium chloride (CaCl)	Ca_1Cl_1(g)	710
Calcium chloride ($CaCl_2$)	Ca_1Cl_2(cr)	711
Calcium chloride ($CaCl_2$)	Ca_1Cl_2(l)	712
Calcium chloride ($CaCl_2$)	Ca_1Cl_2(cr,l)	713
Calcium chloride ($CaCl_2$)	Ca_1Cl_2(g)	714
Calcium fluoride (CaF)	Ca_1F_1(g)	715
Calcium fluoride (CaF_2)	Ca_1F_2(g)	719
Calcium fluoride (CaF_2)	Ca_1F_2(cr)	716
Calcium fluoride (CaF_2)	Ca_1F_2(l)	717
Calcium fluoride (CaF_2)	Ca_1F_2(cr,l)	718
Calcium hydroxide ($Ca(OH)_2$)	$Ca_1H_2O_2$(g)	723
Calcium hydroxide ($Ca(OH)_2$)	$Ca_1H_2O_2$(cr)	722
Calcium hydroxide (CaOH)	$Ca_1H_1O_1$(g)	720
Calcium hydroxide, ion ($CaOH^+$)	$Ca_1H_1O_1^+$(g)	721
Calcium iodide (CaI)	Ca_1I_1(g)	724
Calcium iodide (CaI_2)	Ca_1I_2(g)	728
Calcium iodide (CaI_2)	Ca_1I_2(cr,l)	727
Calcium iodide (CaI_2)	Ca_1I_2(l)	726
Calcium iodide (CaI_2)	Ca_1I_2(cr)	725
Calcium, ion (Ca+)	Ca_1^+(g)	709
Calcium oxide (CaO)	Ca_1O_1(l)	730
Calcium oxide (CaO)	Ca_1O_1(cr)	729
Calcium oxide (CaO)	Ca_1O_1(cr,l)	731
Calcium oxide (CaO)	Ca_1O_1(g)	732
Calcium sulfide (CaS)	Ca_1S_1(cr)	733
Calcium sulfide (CaS)	Ca_1S_1(g)	734
Carbon (C)	C_1(g)	551
Carbon (C)	C_1(ref)	550
Carbon (C_2)	C_2(g)	661
Carbon (C_3)	C_3(g)	686
Carbon (C_4)	C_4(g)	691
Carbon (C_5)	C_5(g)	696
Carbon dioxide (CO_2)	C_1O_2(g)	643
Carbon dioxide, ion (CO_2^-)	$C_1O_2^-$(g)	644
Carbon disulfide (CS_2)	C_1S_2(g)	647
Carbon, ion (C^+)	C_1^+(g)	552
Carbon, ion (C^-)	C_1^-(g)	553
Carbon, ion (C_2^-)	C_2^-(g)	662
Carbon monoxide (CO)	C_1O_1(g)	641
Carbon oxide sulfide (COS)	$C_1O_1S_1$(g)	642
Carbon phosphide (CP)	C_1P_1(g)	645
Carbon suboxide (C_3O_2)	C_3O_2(g)	690
Carbon sulfide (CS)	C_1S_1(g)	646
Carbonic chloride fluoride (COClF)	$C_1Cl_1F_1O_1$(g)	567

Table Title	Formula	Page
Carbonic dichloride ($COCl_2$)	$C_1Cl_2O_1(g)$	573
Carbonic difluoride (COF_2)	$C_1F_2O_1(g)$	584
Carbonyl chloride (COCl)	$C_1Cl_1O_1(g)$	570
Carbonyl fluoride (COF)	$C_1F_1O_1(g)$	581
CCO radical (C_2O)	$C_2O_1(g)$	684
Cesium (Cs)	$Cs_1(g)$	981
Cesium (Cs)	$Cs_1(cr,l)$	980
Cesium (Cs)	$Cs_1(l)$	979
Cesium (Cs)	$Cs_1(cr)$	978
Cesium (Cs)	$Cs_1(ref)$	977
Cesium (Cs_2)	$Cs_2(g)$	994
Cesium chloride ($(CsCl)_2$)	$Cl_2Cs_2(g)$	816
Cesium chloride (CsCl)	$Cl_1Cs_1(cr)$	741
Cesium chloride (CsCl)	$Cl_1Cs_1(l)$	742
Cesium chloride (CsCl)	$Cl_1Cs_1(g)$	744
Cesium chloride (CsCl)	$Cl_1Cs_1(cr,l)$	743
Cesium fluoride ($(CsF)_2$)	$Cs_2F_2(g)$	995
Cesium fluoride (CsF)	$Cs_1F_1(cr,l)$	986
Cesium fluoride (CsF)	$Cs_1F_1(l)$	985
Cesium fluoride (CsF)	$Cs_1F_1(cr)$	984
Cesium fluoride (CsF)	$Cs_1F_1(g)$	987
Cesium hydroxide ($(CsOH)_2$)	$Cs_2H_2O_2(g)$	996
Cesium hydroxide (CsOH)	$Cs_1H_1O_1(cr)$	988
Cesium hydroxide (CsOH)	$Cs_1H_1O_1(l)$	989
Cesium hydroxide (CsOH)	$Cs_1H_1O_1(cr,l)$	990
Cesium hydroxide (CsOH)	$Cs_1H_1O_1(g)$	991
Cesium hydroxide, ion ($CsOH^+$)	$Cs_1H_1O_1^+(g)$	992
Cesium, ion (Cs^+)	$Cs_1^+(g)$	982
Cesium, ion (Cs^-)	$Cs_1^-(g)$	983
Cesium oxide (Cs_2O)	$Cs_2O_1(g)$	997
Cesium oxide (CsO)	$Cs_1O_1(g)$	993
Cesium sulfate (Cs_2SO_4)	$Cs_2O_4S_1(l)$	1000
Cesium sulfate (Cs_2SO_4)	$Cs_2O_4S_1(cr,l)$	1001
Cesium sulfate (Cs_2SO_4)	$Cs_2O_4S_1(g)$	1002
Cesium sulfate, I (Cs_2SO_4)	$Cs_2O_4S_1(cr)$	998
Cesium sulfate, II (Cs_2SO_4)	$Cs_2O_4S_1(cr)$	999
Chiolite ($Na_5Al_3F_{14}$)	$Al_3F_{14}Na_5(cr)$	164
Chiolite ($Na_5Al_3F_{14}$)	$Al_3F_{14}Na_5(l)$	165
Chiolite ($Na_5Al_3F_{14}$)	$Al_3F_{14}Na_5(cr,l)$	166
Chlorine (Cl)	$Cl_1(g)$	737
Chlorine (Cl_2)	$Cl_2(ref)$	811
Chlorine fluoride (ClF)	$Cl_1F_1(g)$	751
Chlorine fluoride (ClF_3)	$Cl_1F_3(g)$	757
Chlorine fluoride (ClF_5)	$Cl_1F_5(g)$	759
Chlorine, ion (Cl^+)	$Cl_1^+(g)$	738
Chlorine, ion (Cl^-)	$Cl_1^-(g)$	739
Chlorine oxide (ClClO)	$Cl_2O_1(g)$	842
Chlorine oxide ($ClClO_2$)	$Cl_2O_2(g)$	846
Chlorine oxide (ClO)	$Cl_1O_1(g)$	795
Chlorine oxide (ClO_2Cl)	$Cl_2O_2(g)$	845
Chlorine oxide (ClO_3)	$Cl_1O_3(g)$	799
Chlorine oxide (ClOCl)	$Cl_2O_1(g)$	841
Chlorine oxide (ClOO)	$Cl_1O_2(g)$	798
Chlorine oxide (ClOOCl)	$Cl_2O_2(g)$	844
Chlorine oxide (OClO)	$Cl_1O_2(g)$	797
Chloroborane (BCl)	$B_1Cl_1(g)$	197
Chloroborane, ion (BCl^+)	$B_1Cl_1^+(g)$	198
Chlorodifluoroborane ($BClF_2$)	$B_1Cl_1F_2(g)$	200
Chlorodifluoromethane ($CHClF_2$)	$C_1H_1Cl_1F_2(g)$	594
Chloroethyne (C_2HCl)	$C_2H_1Cl_1(g)$	673
Chlorofluoroborane (BClF)	$B_1Cl_1F_1(g)$	199
Chlorofluoromethane (CH_2ClF)	$C_1H_2Cl_1F_1(g)$	606
Chloromethane (CH_3Cl)	$C_1H_3Cl_1(g)$	611
Chloromethylene (CHCl)	$C_1H_1Cl_1(g)$	593
Chloromethylidyne (CCl)	$C_1Cl_1(g)$	566
Chlorosilane (SiH_3Cl)	$Cl_1H_3Si_1(g)$	764
Chlorotrifluoromethane ($CClF_3$)	$C_1Cl_1F_3(g)$	568
Chlorotrifluorosilane ($SiClF_3$)	$Cl_1F_3Si_1(g)$	758
Chromium (Cr)	$Cr_1(g)$	963
Chromium (Cr)	$Cr_1(ref)$	959
Chromium (Cr)	$Cr_1(cr,l)$	962
Chromium (Cr)	$Cr_1(l)$	961
Chromium (Cr)	$Cr_1(cr)$	960
Chromium carbide ($Cr_{23}C_6$)	$C_6Cr_{23}(cr)$	699
Chromium carbide (Cr_3C_2)	$C_2Cr_3(cr)$	667
Chromium carbide (Cr_7C_3)	$C_3Cr_7(cr)$	688
Chromium, ion (Cr^+)	$Cr_1^+(g)$	964
Chromium, ion (Cr^-)	$Cr_1^-(g)$	965
Chromium nitride (Cr_2N)	$Cr_2N_1(cr)$	971
Chromium nitride (CrN)	$Cr_1N_1(g)$	967
Chromium nitride (CrN)	$Cr_1N_1(cr)$	966
Chromium oxide (Cr_2O_3)	$Cr_2O_3(cr)$	972
Chromium oxide (Cr_2O_3)	$Cr_2O_3(cr,l)$	974
Chromium oxide (Cr_2O_3)	$Cr_2O_3(l)$	973
Chromium oxide (CrO)	$Cr_1O_1(g)$	968
Chromium oxide (CrO_2)	$Cr_1O_2(g)$	969
Chromium oxide (CrO_3)	$Cr_1O_3(g)$	970
Chlorosilylidyne (SiCl)	$Cl_1Si_1(g)$	806
CNC radical (C_2N)	$C_2N_1(g)$	681
CNN radical (CNN)	$C_1N_2(g)$	636
Cobalt (Co)	$Co_1(ref)$	943
Cobalt (Co)	$Co_1(cr)$	944
Cobalt (Co)	$Co_1(l)$	945
Cobalt (Co)	$Co_1(cr,l)$	946
Cobalt (Co)	$Co_1(g)$	947
Cobalt chloride ($(CoCl_2)_2$)	$Cl_4Co_2(g)$	890
Cobalt chloride (CoCl)	$Cl_1Co_1(g)$	740
Cobalt chloride ($CoCl_2$)	$Cl_2Co_1(cr)$	812
Cobalt chloride ($CoCl_2$)	$Cl_2Co_1(l)$	813
Cobalt chloride ($CoCl_2$)	$Cl_2Co_1(cr,l)$	814
Cobalt chloride ($CoCl_2$)	$Cl_2Co_1(g)$	815
Cobalt chloride ($CoCl_3$)	$Cl_3Co_1(g)$	873
Cobalt fluoride (CoF_2)	$Co_1F_2(cr,l)$	952
Cobalt fluoride (CoF_2)	$Co_1F_2(l)$	951
Cobalt fluoride (CoF_2)	$Co_1F_2(g)$	953
Cobalt fluoride (CoF_2)	$Co_1F_2(cr)$	950
Cobalt fluoride (CoF_3)	$Co_1F_3(cr)$	994
Cobalt, ion (Co^+)	$Co_1^+(g)$	948
Cobalt, ion (Co^-)	$Co_1^-(g)$	949
Cobalt oxide (Co_3O_4)	$Co_3O_4(cr)$	957
Cobalt oxide (CoO)	$Co_1O_1(cr)$	955
Cobalt sulfate ($CoSO_4$)	$Co_1O_4S_1(cr)$	956

Table Title	Formula	Page
Copper (Cu)	Cu_1(ref)	1005
Copper (Cu)	Cu_1(cr)	1006
Copper (Cu)	Cu_1(l)	1007
Copper (Cu)	Cu_1(cr,l)	1008
Copper (Cu)	Cu_1(g)	1009
Copper (Cu_2)	Cu_2(g)	1022
Copper chloride ($(CuCl)_3$)	Cl_3Cu_3(g)	874
Copper chloride (CuCl)	Cl_1Cu_1(cr)	745
Copper chloride (CuCl)	Cl_1Cu_1(l)	746
Copper chloride (CuCl)	Cl_1Cu_1(cr,l)	747
Copper chloride (CuCl)	Cl_1Cu_1(g)	748
Copper chloride ($CuCl_2$)	Cl_2Cu_1(cr)	817
Copper cyanide (CuCN)	$C_1Cu_1N_1$(cr)	577
Copper fluoride (CuF)	Cu_1F_1(g)	1013
Copper fluoride (CuF)	Cu_1F_1(cr)	1012
Copper fluoride (CuF_2)	Cu_1F_2(g)	1017
Copper fluoride (CuF_2)	Cu_1F_2(cr,l)	1016
Copper fluoride (CuF_2)	Cu_1F_2(l)	1015
Copper fluoride (CuF_2)	Cu_1F_2(cr)	1014
Copper hydroxide ($Cu(OH)_2$)	$Cu_1H_2O_2$(cr)	1018
Copper, ion (Cu^+)	Cu_1^+(g)	1010
Copper, ion (Cu^-)	Cu_1^-(g)	1011
Copper oxide (Cu_2O)	Cu_2O_1(cr,l)	1025
Copper oxide (Cu_2O)	Cu_2O_1(l)	1024
Copper oxide (Cu_2O)	Cu_2O_1(cr)	1023
Copper oxide (CuO)	Cu_1O_1(cr)	1019
Copper oxide (CuO)	Cu_1O_1(g)	1020
Copper oxide sulfate ($CuO \cdot CuSO_4$)	$Cu_2O_5S_1$(cr)	1026
Copper sulfate ($CuSO_4$)	$Cu_1O_4S_1$(cr)	1021
Cryolite (Na_3AlF_6)	$Al_1F_6Na_3$(cr,l)	113
Cryolite (Na_3AlF_6)	$Al_1F_6Na_3$(l)	112
Cryolite, alpha (Na_3AlF_6)	$Al_1F_6Na_3$(cr)	110
Cryolite, beta (Na_3AlF_6)	Al_1F6Na_3(cr)	111
Cyanide (CN^-)	$C_1N_1^-$(g)	630
Cyanogen (CN)	C_1N_1(g)	628
Cyanogen bromide (BrCN)	$C_1Br_1N_1$(g)	564
Cyanogen chloride (ClCN)	$C_1Cl_1N_1$(g)	569
Cyanogen fluoride (FCN)	$C_1F_1N_1$(g)	580
Cyanogen iodide (CNI)	$C_1I_1N_1$(g)	616
Cyanogen, ion (CN^+)	$C_1N_1^+$(g)	629
Decaborane ($B_{10}H_{14}$)	$B_{10}H_{14}$(g)	315
Decaborane ($B_{10}H_{14}$)	$B_{10}H_{14}$(cr,l)	314
Decaborane ($B_{10}H_{14}$)	$B_{10}H_{14}$(l)	313
Decaborane ($B_{10}H_{14}$)	$B_{10}H_{14}$(cr)	312
Deuterium (D)	D_1(g)	1029
Deuterium (D_2)	D_2(ref)	1040
Deuterium, ion (D^+)	D_1^+(g)	1030
Deuterium, ion (D^-)	D_1^-(g)	1031
Deuterium, ion (D_2^+)	D_2^+(g)	1041
Deuterium, ion (D_2^-)	D_2^-(g)	1042
Diazene, cis (HNNH)	H_2N_2(g)	1321
Diazene−d_2, cis (DNND)	D_2N_2(g)	1044
Diborane (B_2H_6)	B_2H_6(g)	267
Dibromoborane (BBr_2)	B_1Br_2(g)	191
Dibromoborane ($BHBr_2$)	$B_1Br_2H_1$(g)	194
Dibromochloroborane (BBr_2Cl)	$B_1Br_2Cl_1$(g)	192
Dibromofluoroborane (BBr_2F)	$B_1Br_2F_1$(g)	193
Dibromosilane (SiH_2Br_2)	$Br_2H_2Si_1$(g)	481
Dibromosilylene ($SiBr_2$)	Br_2Si_1(g)	503
Dichloroborane ($(BCl_2)_2$)	B_2Cl_4(g)	262
Dichloroborane (BCl_2)	B_1Cl_2(g)	202
Dichloroborane ($BHCl_2$)	$B_1Cl_2H_1$(g)	206
Dichloroborane, ion (BCl_2^+)	$B_1Cl_2^+$(g)	203
Dichloroborane, ion (BCl_2^-)	$B_1Cl_2^-$(g)	204
Dichlorodifluoromethane (CCl_2F_2)	$C_1Cl_2F_2$(g)	572
Dichloroethyne (C_2Cl_2)	C_2Cl_2(g)	664
Dichlorofluoroborane (BCl_2F)	$B_1Cl_2F_1$(g)	205
Dichlorofluoromethane ($CHCl_2F$)	$C_1H_1Cl_2F_1$(g)	595
Dichloromethane (CH_2Cl_2)	$C_1H_2Cl_2$(g)	607
Dichloromethylene (CCl_2)	C_1Cl_2(g)	571
Dichlorosilane (SiH_2Cl_2)	$Cl_2H_2Si_1$(g)	823
Dichlorosilylene ($SiCl_2$)	Cl_2Si_1(g)	860
Difluoroamidogen (NF_2)	F_2N_1(g)	1124
Difluoroborane ($(BF_2)_2$)	B_2F_4(g)	263
Difluoroborane (BF_2)	B_1F_2(g)	210
Difluoroborane (BHF_2)	$B_1F_2H_1$(g)	213
Difluoroborane, ion (BF_2^+)	$B_1F_2^+$(g)	211
Difluoroborane, ion (BF_2^-)	$B_1F_2^-$(g)	212
Difluoroborane oxide ($O(BF_2)_2$)	$B_2F_4O_1$(g)	264
Difluoroboroxin ($B_3HO_3F_2$)	$B_3F_2H_1O_3$(g)	284
Difluorodisulfane (FSSF)	F_2S_2(g)	1146
Difluoroethyne (C_2F_2)	C_2F_2(g)	668
Difluorohydroxyborane (BF_2OH)	$B_1F_2H_1O_1$(g)	214
Difluoromethane (CH_2F_2)	$C_1H_2F_2$(g)	608
Difluoromethylene (CF_2)	C_1F_2(g)	582
Difluoromethylene, ion (CF_2^+)	$C_1F_2^+$(g)	583
Difluorooxosilane ($OSiF_2$)	$F_2O_1Si_1$(g)	1131
Difluorosilane (SiH_2F_2)	$F_2H_2Si_1$(g)	1108
Difluorosilylene (SiF_2)	F_2Si_1(g)	1148
Dihydroxyborane ($(B(OH)_2)_2$)	$B_2H_4O_4$(cr)	265
Dihydroxyborane ($(B(OH)_2)_2$)	$B_2H_4O_4$(g)	266
Dihydroxyborane ($B(OH)_2$)	$B_1H_2O_2$(g)	239
Diiodoborane (BI_2)	B_1I_2(g)	238
Diiodosilane (SiH_2I_2)	$H_2I_2Si_1$(g)	1313
Diiodosilylene (SiI_2)	I_2Si_1(g)	1432
Electron gas (e^-)	e_1^-(ref)	1049
Ethanedinitrile ($(CN)_2$)	C_2N_2(g)	682
Ethene (C_2H_4)	C_2H_4(g)	676
Ethyne (C_2H_2)	C_2H_2(g)	675
Ethynyl (C_2H)	C_2H_1(g)	672
Fluorine (F)	F_1(g)	1051
Fluorine (F_2)	F_2(ref)	1099
Fluorine, ion (F^+)	F_1^+(g)	1052
Fluorine, ion (F^-)	F_1^-(g)	1053
Fluorine nitrate ($FONO_2$)	$F_1N_1O_3$(g)	1076
Fluoroborane (BF)	B_1F_1(g)	208
Fluoroboroxin ($B_3H_2O_3F$)	$B_3F_1H_2O_3$(g)	293
Fluoroethyne (C_2HF)	$C_2H_1F_1$(g)	674
Fluoroimidogen (NF)	F_1N_1(g)	1073

Table Title	Formula	Page
Fluoromethane (CH_3F)	$C_1H_3F_1(g)$	613
Fluoromethylene (CHF)	$C_1H_1F_1(g)$	597
Fluoromethylidyne (CF)	$C_1F_1(g)$	578
Fluoromethylidyne, ion (CF^+)	$C_1F_1^+(g)$	579
Fluorosilane (SiH_3F)	$F_1H_3Si_1(g)$	1058
Fluorosilylidyne (SiF)	$F_1Si_1(g)$	1093
Fluorosulfuric acid (HSO_3F)	$F_1H_1O_3S_1(g)$	1057
Formaldehyde (H_2CO)	$C_1H_2O_1(g)$	609
Formyl (HCO)	$C_1H_1O_1(g)$	602
Formyl fluoride (HCOF)	$C_1H_1F_1O_1(g)$	598
Formyl, unipositive ion (HCO^+)	$C_1H_1O_1^+(g)$	603
Gallium (Ga)	Ga_1(ref)	1253
Gallium (Ga)	Ga_1(cr)	1254
Gallium (Ga)	Ga_1(l)	1255
Gallium (Ga)	Ga_1(cr,l)	1256
Gallium (Ga)	$Ga_1(g)$	1257
Gallium, ion (Ga^+)	$Ga_1^+(g)$	1258
Gallium, ion (Ga^-)	$Ga_1^-(g)$	1259
Hafnium (Hf)	Hf_1(ref)	1363
Hafnium (Hf)	$Hf_1(g)$	1368
Hafnium (Hf)	Hf_1(cr,l)	1367
Hafnium (Hf)	Hf_1(l)	1366
Hafnium, alpha (Hf)	Hf_1(cr)	1364
Hafnium, beta (Hf)	Hf_1(cr)	1365
Hafnium, ion (Hf^+)	$Hf_1^+(g)$	1369
Hafnium, ion (Hf^-)	$Hf_1^-(g)$	1370
Helium (He)	He_1(ref)	1361
Helium, ion (He^+)	$He_1^+(g)$	1362
Hexachloroethane (C_2Cl_6)	$C_2Cl_6(g)$	666
Hexafluoroethane (C_2F_6)	$C_2F_6(g)$	671
Hydrazine (N_2H_4)	$H_4N_2(g)$	1351
Hydrazine (N_2H_4)	H_4N_2(l)	1350
Hydrochloric acid−d_1 (DCl)	$Cl_1D_1(g)$	749
Hydrofluoric acid−d_1 (DF)	$D_1F_1(g)$	1032
Hydrogen (H)	$H_1(g)$	1261
Hydrogen (H_2)	H_2(ref)	1310
Hydrogen bromide (HBr)	$Br_1H_1(g)$	438
Hydrogen chloride (HCl)	$Cl_1H_1(g)$	762
Hydrogen cyanide (HCN)	$C_1H_1N_1(g)$	600
Hydrogen−d_1 (HD)	$D_1H_1(g)$	1033
Hydrogen−d_1, ion (HD^+)	$D_1H_1^+(g)$	1034
Hydrogen−d_1, ion (HD^-)	$D_1H_1^-(g)$	1035
Hydrogen fluoride ($(HF)_2$)	$F_2H_2(g)$	1107
Hydrogen fluoride (H_3F_3)	$F_3H_3(g)$	1161
Hydrogen fluoride (H_4F_4)	$F_4H_4(g)$	1177
Hydrogen fluoride (H_5F_5)	$F_5H_5(g)$	1195
Hydrogen fluoride (H_6F_6)	$F_6H_6(g)$	1202
Hydrogen fluoride (H_7F_7)	$F_7H_7(g)$	1209
Hydrogen fluoride (HF)	$F_1H_1(g)$	1055
Hydrogen iodide (HI)	$H_1I_1(g)$	1265
Hydrogen, ion (H^+)	$H_1^+(g)$	1262
Hydrogen, ion (H^-)	$H_1^-(g)$	1263
Hydrogen, ion (H_2^+)	$H_2^+(g)$	1311
Hydrogen, ion (H_2^-)	$H_2^-(g)$	1312

Table Title	Formula	Page
Hydrogen isocyanate (HNCO)	$C_1H_1N_1O_1(g)$	601
Hydrogen peroxide (HOOH)	$H_2O_2(g)$	1330
Hydrogen sulfide (H_2S)	$H_2S_1(g)$	1340
Hydrogen sulfide−d_2 (D_2S)	$D_2S_1(g)$	1046
Hydronium, ion (H_3O^+)	$H_3O_1^+(g)$	1344
Hydroperoxo (HOO)	$H_1O_2(g)$	1303
Hydroxyl (OH)	$H_1O_1(g)$	1298
Hydroxyl−d_1 (OD)	$D_1O_1(g)$	1038
Hydroxyl, ion (OH^+)	$H_1O_1^+(g)$	1299
Hydroxyl, ion (OH^-)	$H_1O_1^-(g)$	1300
Hypochlorous acid (HOCl)	$Cl_1H_1O_1(g)$	763
Hypochlorous acid−d_1 (DOCl)	$Cl_1D_1O_1(g)$	750
Hypofluorous acid (HOF)	$F_1H_1O_1(g)$	1056
Imidogen (NH)	$H_1N_1(g)$	1286
Imidogen−d_1 (ND)	$D_1N_1(g)$	1037
Iodine (I)	$I_1(g)$	1387
Iodine (I_2)	$I_2(g)$	1417
Iodine (I_2)	I_2(cr,l)	1416
Iodine (I_2)	I_2(l)	1415
Iodine (I_2)	I_2(cr)	1414
Iodine (I_2)	I_2(ref)	1413
Iodine bromide (IBr)	$Br_1I_1(g)$	442
Iodine chloride (ICl)	$Cl_1I_1(g)$	771
Iodine chloride (ICl)	Cl_1I_1(cr,l)	770
Iodine chloride (ICl)	Cl_1I_1(l)	769
Iodine chloride (ICl)	Cl_1I_1(cr)	768
Iodine fluoride (IF)	$F_1I_1(g)$	1060
Iodine fluoride (IF_5)	$F_5I_1(g)$	1196
Iodine fluoride (IF_7)	$F7I_1(g)$	1210
Iodine, ion (I^+)	$I_1^+(g)$	1388
Iodine, ion (I^-)	$I_1^-(g)$	1389
Iodine oxide (IIO)	$I_2O_1(g)$	1427
Iodine oxide (IO)	$I_1O_1(g)$	1404
Iodine oxide (IO_3)	$I_1O_3(g)$	1407
Iodine oxide (IOI)	$I_2O_1(g)$	1426
Iodine oxide (IOO)	$I_1O_2(g)$	1406
Iodine oxide (OIO)	$I_1O_2(g)$	1405
Iodoborane (BI)	$B_1I_1(g)$	237
Iodosilane (SiH_3I)	$H_3I_1Si_1(g)$	1342
Iodosilylidyne (SiI)	$I_1Si_1(g)$	1409
Iron (Fe)	Fe_1(ref)	1221
Iron (Fe)	Fe_1(l)	1224
Iron (Fe)	Fe_1(cr,l)	1225
Iron (Fe)	$Fe_1(g)$	1226
Iron, alpha−delta (Fe)	Fe_1(cr)	1222
Iron bromide ($(FeBr_2)_2$)	$Br_4Fe_2(g)$	525
Iron bromide ($FeBr_2$)	Br_2Fe_1(cr)	477
Iron bromide ($FeBr_2$)	Br_2Fe_1(l)	478
Iron bromide ($FeBr_2$)	Br_2Fe_1(cr,l)	479
Iron bromide ($FeBr_2$)	$Br_2Fe_1(g)$	480
Iron carbonyl ($Fe(CO)_5$)	$C_5Fe_1O_5(g)$	680
Iron carbonyl ($Fe(CO)_5$)	$C_5Fe_1O_5$(l)	697
Iron chloride ($(FeCl_2)_2$)	$Cl_4Fe_2(g)$	891
Iron chloride ($(FeCl_3)_2$)	$Cl_6Fe_2(g)$	928
Iron chloride (FeCl)	$Cl_1Fe_1(g)$	

Table Title	Formula	Page
Iron chloride ($FeCl_2$)	Cl_2Fe_1(cr,l)	821
Iron chloride ($FeCl_2$)	Cl_2Fe_1(cr)	819
Iron chloride ($FeCl_2$)	Cl_2Fe_1(l)	820
Iron chloride ($FeCl_2$)	Cl_2Fe_1(g)	822
Iron chloride ($FeCl_3$)	Cl_3Fe_1(g)	879
Iron chloride ($FeCl_3$)	Cl_3Fe_1(cr,l)	878
Iron chloride ($FeCl_3$)	Cl_3Fe_1(l)	877
Iron chloride ($FeCl_3$)	Cl_3Fe_1(cr)	876
Iron fluoride (FeF)	F_1Fe_1(g)	1054
Iron fluoride (FeF_2)	F_2Fe_1(cr)	1100
Iron fluoride (FeF_2)	F_2Fe_1(l)	1101
Iron fluoride (FeF_2)	F_2Fe_1(cr,l)	1102
Iron fluoride (FeF_2)	F_2Fe_1(g)	1103
Iron fluoride (FeF_3)	F_3Fe_1(g)	1159
Iron fluoride (FeF_3)	F_3Fe_1(cr)	1158
Iron, gamma (Fe)	Fe_1(cr)	1223
Iron hydroxide ($Fe(OH)_2$)	$Fe_1H_2O_2$(cr)	1229
Iron hydroxide ($Fe(OH)_2$)	$Fe_1H_2O_2$(g)	1230
Iron hydroxide ($Fe(OH)_3$)	$Fe_1H_3O_3$(cr)	1231
Iron iodide ($(FeI_2)_2$)	Fe_2I_4(g)	1247
Iron iodide (FeI_2)	Fe_1I_2(g)	1235
Iron iodide (FeI_2)	Fe_1I_2(cr,l)	1234
Iron iodide (FeI_2)	Fe_1I_2(l)	1233
Iron iodide (FeI_2)	Fe_1I_2(cr)	1232
Iron, ion (Fe^+)	Fe_1^+(g)	1227
Iron, ion (Fe^-)	Fe_1^-(g)	1228
Iron oxide (FeO)	Fe_1O_1(g)	1239
Iron oxide (FeO)	Fe_1O_1(cr,l)	1238
Iron oxide (FeO)	Fe_1O_1(l)	1237
Iron oxide (FeO)	Fe_1O_1(cr)	1236
Iron oxide, hematite (Fe_2O_3)	Fe_2O_3(cr)	1248
Iron oxide, magnetite (Fe_3O_4)	Fe_3O_4(cr)	1250
Iron oxide, wüstite ($Fe_{0.947}O$)	$Fe_{0.947}O_1$(cr)	1219
Iron sulfate ($Fe_2(SO_4)_3$)	$Fe_2O_{12}S_3$(cr)	1249
Iron sulfate ($FeSO_4$)	$Fe_1O_4S_1$(cr)	1240
Iron sulfide (FeS)	Fe_1S_1(g)	1244
Iron sulfide (FeS)	Fe_1S_1(l)	1242
Iron sulfide, marcasite (FeS_2)	Fe_1S_2(cr)	1245
Iron sulfide, pyrite (FeS_2)	Fe_1S_2(cr)	1246
Iron sulfide, pyrrhotite ($Fe_{0.877}S$)	$Fe_{0.877}S_1$(cr)	1220
Iron sulfide, troilite (FeS)	Fe_1S_1(cr,l)	1243
Iron sulfide, troilite (FeS)	Fe_1S_1(cr)	1241
Krypton (Kr)	Kr_1(ref)	1491
Krypton, ion (Kr^+)	Kr_1^+(g)	1492
Lead (Pb)	Pb_1(g)	1839
Lead (Pb)	Pb_1(cr,l)	1838
Lead (Pb)	Pb_1(l)	1837
Lead (Pb)	Pb_1(cr)	1836
Lead (Pb)	Pb_1(ref)	1835
Lead (Pb_2)	Pb_2(g)	1846
Lead borate ($Pb_2B_{10}O_{17}$)	$B_{10}O_{17}Pb_2$(cr)	316
Lead borate (PbB_2O_4)	$B_2O_4PB_1$(cr)	275
Lead borate (PbB_4O_7)	$B_4O_7Pb_1$(cr)	301
Lead borate (PbB_6O_10)	$B_6O_10Pb_1$(cr)	307
Lead bromide (PbBr)	Br_1Pb_1(g)	464
Lead bromide ($PbBr_2$)	Br_2Pb_1(cr)	499
Lead bromide ($PbBr_2$)	Br_2Pb_1(l)	500
Lead bromide ($PbBr_2$)	Br_2Pb_1(cr,l)	501
Lead bromide ($PbBr_2$)	Br_2Pb_1(g)	502
Lead bromide ($PbBr_4$)	Br_4Pb_1(g)	529
Lead chloride (PbCl)	Cl_1Pb_1(g)	801
Lead chloride ($PbCl_2$)	Cl_2Pb_1(cr)	850
Lead chloride ($PbCl_2$)	Cl_2Pb_1(l)	851
Lead chloride ($PbCl_2$)	Cl_2Pb_1(cr,l)	852
Lead chloride ($PbCl_2$)	Cl_2Pb_1(g)	853
Lead chloride ($PbCl_4$)	Cl_4Pb_1(g)	901
Lead chloride, ion ($PbCl^+$)	$Cl_1Pb_1^+$(g)	802
Lead chloride, ion ($PbCl_2^+$)	$Cl_2Pb_1^+$(g)	854
Lead fluoride (PbF)	F_1Pb_1(g)	1089
Lead fluoride (PbF_2)	F_2Pb_1(g)	1142
Lead fluoride (PbF_2)	F_2Pb_1(cr,l)	1141
Lead fluoride (PbF_2)	F_2Pb_1(l)	1140
Lead fluoride (PbF_4)	F_4Pb_1(g)	1186
Lead fluoride, alpha (PbF_2)	F_2Pb_1(cr)	1138
Lead fluoride, beta (PbF_2)	F_2Pb_1(cr)	1139
Lead hydride (PbH)	H_1Pb_1(g)	1305
Lead iodide (PbI)	I_1Pb_1(g)	1408
Lead iodide (PbI_2)	I_2Pb_1(cr,l)	1430
Lead iodide (PbI_2)	I_2Pb_1(g)	1431
Lead iodide (PbI_2)	I_2Pb_1(l)	1429
Lead iodide (PbI_2)	I_2Pb_1(cr)	1428
Lead iodide (PbI_4)	I_4Pb_1(g)	1452
Lead, ion (Pb^+)	Pb_1^+(g)	1840
Lead, ion (Pb^-)	Pb_1^-(g)	1841
Lead oxide (Pb_3O_4)	O_4Pb_3(cr)	1787
Lead oxide (PbO)	O_1Pb_1(l)	1723
Lead oxide (PbO)	O_1Pb_1(cr,l)	1724
Lead oxide (PbO)	O_1Pb_1(g)	1725
Lead oxide (PbO_2)	O_2Pb_1(cr)	1749
Lead oxide, red (PbO)	O_1Pb_1(cr)	1721
Lead oxide, yellow (PbO)	O_1Pb_1(cr)	1722
Lead silicate (Pb_2SiO_4)	$O_4Pb_2Si_1$(cr)	1786
Lead silicate ($PbSiO_3$)	$O_3Pb_1Si_1$(cr)	1774
Lead sulfide (PbS)	Pb_1S_1(g)	1845
Lead sulfide (PbS)	Pb_1S_1(cr,l)	1844
Lead sulfide (PbS)	Pb_1S_1(l)	1843
Lead sulfide (PbS)	Pb_1S_1(cr)	1842
Lithium (Li)	Li_1(g)	1497
Lithium (Li)	Li_1(cr,l)	1496
Lithium (Li)	Li_1(l)	1495
Lithium (Li)	Li_1(cr)	1494
Lithium (Li)	Li_1(ref)	1493
Lithium (Li_2)	Li_2(g)	1505
Lithium aluminum oxide ($LiAlO_2$)	$Al_1Li_1O_2$(l)	127
Lithium aluminum oxide ($LiAlO_2$)	$Al_1Li_1O_2$(cr,l)	128
Lithium aluminum oxide ($LiAlO_2$)	$Al_1Li_1O_2$(cr)	126
Lithium borate ($Li_2B_4O_7$)	$B_4Li_2O_7$(cr)	294
Lithium borate ($Li_2B_4O_7$)	$B_4Li_2O_7$(l)	295
Lithium borate ($Li_2B_4O_7$)	$B_4Li_2O_7$(cr,l)	296
Lithium borate ($Li_2B_6O_{10}$)	$B_6Li_2O_{10}$(cr)	305

Table Title	Formula	Page
Lithium borate ($Li_2B_8O_{13}$)	$B_8Li_2O_{13}$(cr)	311
Lithium borate ($LiBO_2$)	$B_1Li_1O_2$(g)	247
Lithium borate ($LiBO_2$)	$B_1Li_1O_2$(cr,l)	246
Lithium borate ($LiBO_2$)	$B_1Li_1O_2$(l)	245
Lithium borate ($LiBO_2$)	$B_1Li_1O_2$(cr)	244
Lithium bromide ($(LiBr)_2$)	Br_2Li_2(g)	488
Lithium bromide (LiBr)	Br_1Li_1(cr)	447
Lithium bromide (LiBr)	Br_1Li_1(l)	448
Lithium bromide (LiBr)	Br_1Li_1(cr,l)	449
Lithium bromide (LiBr)	Br_1Li_1(g)	450
Lithium carbide (Li_2C_2)	C_2Li_2(cr)	679
Lithium carbonate (Li_2CO_3)	$C_1Li_2O_3$(cr)	624
Lithium carbonate (Li_2CO_3)	$C_1Li_2O_3$(l)	625
Lithium carbonate (Li_2CO_3)	$C_1Li_2O_3$(cr,l)	626
Lithium chloride ($(LiCl)_2$)	Cl_2Li_2(g)	830
Lithium chloride ($(LiCl)_3$)	Cl_3Li_3(g)	881
Lithium chloride (LiCl)	Cl_1Li_1(g)	780
Lithium chloride (LiCl)	Cl_1Li_1(cr,l)	779
Lithium chloride (LiCl)	Cl_1Li_1(l)	778
Lithium chloride (LiCl)	Cl_1Li_1(cr)	777
Lithium chloride fluoride (Li_2ClF)	$Cl_1F_1Li_2$(g)	752
Lithium fluoride ($(LiF)_2$)	F_2Li_2(g)	1117
Lithium fluoride ($(LiF)_3$)	F_3Li_3(g)	1162
Lithium fluoride (LiF)	F_1Li_1(l)	1066
Lithium fluoride (LiF)	F_1Li_1(cr,l)	1067
Lithium fluoride (LiF)	F_1Li_1(g)	1068
Lithium fluoride (LiF)	F_1Li_1(cr)	1065
Lithium fluoride, ion (LiF_2^-)	$F_2Li_1^-$(g)	1116
Lithium hexafluoroaluminate (Li_3AlF_6)	$Al_1F_6Li_3$(cr)	107
Lithium hexafluoroaluminate (Li_3AlF_6)	$Al_1F_6Li_3$(l)	108
Lithium hexafluoroaluminate (Li_3AlF_6)	$Al_1F_6Li_3$(cr,l)	109
Lithium hydride (LiH)	H_1Li_1(l)	1275
Lithium hydride (LiH)	H_1Li_1(cr,l)	1276
Lithium hydride (LiH)	H_1Li_1(g)	1277
Lithium hydride (LiH)	H_1Li_1(cr)	1274
Lithium hydroxide ($(LiOH)_2$)	$H_2Li_2O_2$(g)	1315
Lithium hydroxide (LiOH)	$H_1Li_1O_1$(cr)	1278
Lithium hydroxide (LiOH)	$H_1Li_1O_1$(l)	1279
Lithium hydroxide (LiOH)	$H_1Li_1O_1$(cr,l)	1280
Lithium hydroxide (LiOH)	$H_1Li_1O_1$(g)	1281
Lithium hydroxide, ion ($LiOH^+$)	$H_1Li_1O_1^+$(g)	1282
Lithium hypochlorite (LiOCl)	$Cl_1Li_1O_1$(g)	781
Lithium hypofluorite (LiOF)	$F_1Li_1O_1$(g)	1069
Lithium iodide ($(LiI)_2$)	I_2Li_2(g)	1419
Lithium iodide (LiI)	I_1Li_1(g)	1397
Lithium iodide (LiI)	I_1Li_1(cr,l)	1396
Lithium iodide (LiI)	I_1Li_1(l)	1395
Lithium iodide (LiI)	I_1Li_1(cr)	1394
Lithium, ion (Li^+)	Li_1^+(g)	1498
Lithium, ion (Li^-)	Li_1^-(g)	1499
Lithium nitride (Li_3N)	Li_3N_1(cr)	1526
Lithium nitride (LiN)	Li_1N_1(g)	1500
Lithium oxide ($(LiO)_2$)	Li_2O_2(g)	1511
Lithium oxide (Li_2O)	Li_2O_1(g)	1509
Lithium oxide (Li_2O)	Li_2O_1(cr,l)	1508
Lithium oxide (Li_2O)	Li_2O_1(l)	1507
Lithium oxide (Li_2O)	Li_2O_1(cr)	1506
Lithium oxide (LiO)	Li_1O_1(g)	1503
Lithium oxide, ion (LiO^-)	$Li_1O_1^-$(g)	1504
Lithium oxynitride (LiON)	$Li_1N_1O_1$(g)	1501
Lithium perchlorate ($LiClO_4$)	$Cl_1Li_1O_4$(cr)	782
Lithium perchlorate ($LiClO_4$)	$Cl_1Li_1O_4$(l)	783
Lithium perchlorate ($LiClO_4$)	$Cl_1Li_1O_4$(cr,l)	784
Lithium peroxide (Li_2O_2)	Li_2O_2(cr)	1510
Lithium silicate ($Li_2Si_2O_5$)	$Li_2O_5Si_2$(cr)	1523
Lithium silicate ($Li_2Si_2O_5$)	$Li_2O_5Si_2$(l)	1524
Lithium silicate ($Li_2Si_2O_5$)	$Li_2O_5Si_2$(cr,l)	1525
Lithium silicate (Li_2SiO_3)	$Li_2O_3Si_1$(l)	1513
Lithium silicate (Li_2SiO_3)	$Li_2O_3Si_1$(cr,l)	1514
Lithium silicate (Li_2SiO_3)	$Li_2O_3Si_1$(cr)	1512
Lithium sodium oxide (LiONa)	$Li_1Na_1O_1$(g)	1502
Lithium sulfate (Li_2SO_4)	$Li_2O_4S_1$(l)	1520
Lithium sulfate (Li_2SO_4)	$Li_2O_4S_1$(cr,l)	1521
Lithium sulfate (Li_2SO_4)	$Li_2O_4S_1$(g)	1522
Lithium sulfate, alpha (Li_2SO_4)	$Li_2O_4S_1$(cr)	1518
Lithium sulfate, beta (Li_2SO_4)	$Li_2O_4S_1$(cr)	1519
Lithium tetrafluoroaluminate ($LiAlF_4$)	$Al_1F_4Li_1$(g)	104
Lithium tetrafluoroberyllate (Li_2BeF_4)	$Be_1F_4Li_2$(cr)	387
Lithium tetrafluoroberyllate (Li_2BeF_4)	$Be_1F_4Li_2$(l)	388
Lithium tetrafluoroberyllate (Li_2BeF_4)	$Be_1F_4Li_2$(cr,l)	389
Lithium tetrahydroaluminate ($LiAlH_4$)	$Al_1H_4Li_1$(cr)	120
Lithium tetrahydroborate ($LiBH_4$)	$B_1H_4Li_1$(cr)	235
Lithium titanium oxide (Li_2TiO_3)	$Li_2O_3Ti_1$(l)	1516
Lithium titanium oxide (Li_2TiO_3)	$Li_2O_3Ti_1$(cr,l)	1517
Lithium titanium oxide (Li_2TiO_3)	$Li_2O_3Ti_1$(cr)	1515
Lithium trifluoroberyllate ($LiBeF_3$)	$Be_1F_3Li_1$(cr)	383
Lithium trifluoroberyllate ($LiBeF_3$)	$Be_1F_3Li_1$(l)	384
Lithium trifluoroberyllate ($LiBeF_3$)	$Be_1F_3Li_1$(cr,l)	385
Lithium trifluoroberyllate ($LiBeF_3$)	$Be_1F_3Li_1$(g)	386
Magnesium (Mg)	Mg_1(cr,l)	1532
Magnesium (Mg)	Mg_1(g)	1533
Magnesium (Mg)	Mg_1(ref)	1529
Magnesium (Mg)	Mg_1(cr)	1530
Magnesium (Mg)	Mg_1(l)	1531
Magnesium (Mg_2)	Mg_2(g)	1555
Magnesium aluminum oxide ($MgAl_2O_4$)	$Al_2Mg_1O_4$(cr)	147
Magnesium aluminum oxide ($MgAl_2O_4$)	$Al_2Mg_1O_4$(l)	148
Magnesium aluminum oxide ($MgAl_2O_4$)	$Al_2Mg_1O_4$(cr,l)	149
Magnesium boride (MgB_2)	B_2Mg_1(cr)	268
Magnesium boride (MgB_4)	B_4Mg_1(cr)	297
Magnesium bromide ($(MgBr_2)_2$)	Br_4Mg_2(g)	526
Magnesium bromide (MgBr)	Br_1Mg_1(g)	451
Magnesium bromide ($MgBr_2$)	Br_2Mg_1(cr)	489
Magnesium bromide ($MgBr_2$)	Br_2Mg_1(l)	490
Magnesium bromide ($MgBr_2$)	Br_2Mg_1(cr,l)	491
Magnesium bromide ($MgBr_2$)	Br_2Mg_1(g)	492
Magnesium bromide, ion ($MgBr_2^+$)	$Br_2Mg_1^+$(g)	493
Magnesium carbide (Mg_2C_3)	C_3Mg_2(cr)	689
Magnesium carbide (MgC_2)	C_2Mg_1(cr)	680
Magnesium carbonate ($MgCO_3$)	$C_1Mg_1O_3$(cr)	627
Magnesium chloride ($(MgCl_2)_2$)	Cl_4Mg_2(g)	892

able Title	Formula	Page
lagnesium chloride (MgCl)	$Cl_1Mg_1(g)$	785
lagnesium chloride ($MgCl_2$)	$Cl_2Mg_1(g)$	834
lagnesium chloride ($MgCl_2$)	$Cl_2Mg_1(cr,l)$	833
lagnesium chloride ($MgCl_2$)	$Cl_2Mg_1(l)$	832
lagnesium chloride ($MgCl_2$)	$Cl_2Mg_1(cr)$	831
lagnesium chloride fluoride (MgClF)	$Cl_1F_1Mg_1(g)$	753
lagnesium chloride, ion ($MgCl^+$)	$Cl_1Mg_1^+(g)$	786
lagnesium fluoride ($(MgF_2)_2$)	$F_4Mg_2(g)$	1178
lagnesium fluoride (MgF)	$F_1Mg_1(g)$	1070
lagnesium fluoride (MgF_2)	$F_2Mg_1(g)$	1121
lagnesium fluoride (MgF_2)	$F_2Mg_1(cr,l)$	1120
lagnesium fluoride (MgF_2)	$F_2Mg_1(l)$	1119
lagnesium fluoride (MgF_2)	$F_2Mg_1(cr)$	1118
lagnesium fluoride, ion (MgF^+)	$F_1Mg_1^+(g)$	1071
lagnesium fluoride, ion (MgF_2^+)	$F_2Mg_1^+(g)$	1122
lagnesium hydride (MgH)	$H_1Mg_1(g)$	1283
lagnesium hydride (MgH_2)	$H_2Mg_1(cr)$	1316
lagnesium hydroxide ($Mg(OH)_2$)	$H_2Mg_1O_2(cr)$	1317
lagnesium hydroxide ($Mg(OH)_2$)	$H_2Mg_1O_2(g)$	1318
lagnesium hydroxide (MgOH)	$H_1Mg_1O_1(g)$	1284
lagnesium hydroxide, ion ($MgOH^+$)	$H_1Mg_1O_1^+(g)$	1285
lagnesium iodide (MgI)	$I_1Mg_1(g)$	1398
lagnesium iodide (MgI_2)	$I_2Mg_1(cr)$	1420
lagnesium iodide (MgI_2)	$I_2Mg_1(l)$	1421
lagnesium iodide (MgI_2)	$I_2Mg_1(g)$	1423
lagnesium iodide (MgI_2)	$I_2Mg_1(cr,l)$	1422
lagnesium, ion (Mg^+)	$Mg_1^+(g)$	1534
lagnesium nitride (Mg_3N_2)	$Mg_3N_2(cr)$	1565
lagnesium nitride (MgN)	$Mg_1N_1(g)$	1535
lagnesium oxide (MgO)	$Mg_1O_1(cr,l)$	1538
lagnesium oxide (MgO)	$Mg_1O_1(l)$	1537
lagnesium oxide (MgO)	$Mg_1O_1(cr)$	1536
lagnesium oxide (MgO)	$Mg_1O_1(g)$	1539
lagnesium phosphate ($Mg_3P_2O_8$)	$Mg_3O_8P_2(cr)$	1566
lagnesium phosphate ($Mg_3P_2O_8$)	$Mg_3O_8P_2(l)$	1567
lagnesium phosphate ($Mg_3P_2O_8$)	$Mg_3O_8P_2(cr,l)$	1568
lagnesium silicate (Mg_2SiO_4)	$Mg_2O_4Si_1(cr)$	1556
lagnesium silicate (Mg_2SiO_4)	$Mg_2O_4Si_1(l)$	1557
lagnesium silicate (Mg_2SiO_4)	$Mg_2O_4Si_1(cr,l)$	1558
lagnesium silicate ($MgSiO_3$)	$Mg_1O_3Si_1(cr,l)$	1542
lagnesium silicate ($MgSiO_3$)	$Mg_1O_3Si_1(l)$	1541
lagnesium silicate ($MgSiO_3$)	$Mg_1O_3Si_1(cr)$	1540
lagnesium silicide (Mg_2Si)	$Mg_2Si_1(cr)$	1562
lagnesium silicide (Mg_2Si)	$Mg_2Si_1(l)$	1563
lagnesium silicide (Mg_2Si)	$Mg_2Si_1(cr,l)$	1564
lagnesium sulfate ($MgSO_4$)	$Mg_1O_4S_1(cr,l)$	1548
lagnesium sulfate ($MgSO_4$)	$Mg_1O_4S_1(l)$	1547
lagnesium sulfate ($MgSO_4$)	$Mg_1O_4S_1(cr)$	1546
lagnesium sulfide (MgS)	$Mg_1S_1(g)$	1554
lagnesium sulfide (MgS)	$Mg_1S_1(cr)$	1553
lagnesium titanium oxide (Mg_2TiO_4)	$Mg_2O_4Ti_1(l)$	1560
lagnesium titanium oxide (Mg_2TiO_4)	$Mg_2O_4Ti_1(cr,l)$	1561
lagnesium titanium oxide (Mg_2TiO_4)	$Mg_2O_4Ti_1(cr)$	1559
lagnesium titanium oxide ($MgTi_2O_5$)	$Mg_1O_5Ti_2(cr)$	1550
lagnesium titanium oxide ($MgTi_2O_5$)	$Mg_1O_5Ti_2(l)$	1551
agnesium titanium oxide ($MgTi_2O_5$)	$Mg_1O_5Ti_2(cr,l)$	1552

Table Title	Formula	Page
Magnesium titanium oxide ($MgTiO_3$)	$Mg_1O_3Ti_1(l)$	1544
Magnesium titanium oxide ($MgTiO_3$)	$Mg_1O_3Ti_1(cr)$	1543
Magnesium titanium oxide ($MgTiO_3$)	$Mg_1O_3Ti_1(cr,l)$	1545
Magnesium tungsten oxide ($MgWO_4$)	$Mg_1O_4W_1(cr)$	1549
Manganese (Mn)	$Mn_1(cr)$	1572
Manganese (Mn)	$Mn_1(ref)$	1571
Manganese (Mn)	$Mn_1(l)$	1573
Manganese (Mn)	$Mn_1(cr,l)$	1574
Manganese (Mn)	$Mn_1(g)$	1575
Manganese, ion (Mn^+)	$Mn_1^+(g)$	1576
Mercapto (HS)	$H_1S_1(g)$	1306
Mercapto−d_1 (SD)	$D_1S_1(g)$	1039
Mercury (Hg)	$Hg_1(g)$	1375
Mercury (Hg)	$Hg_1(cr,l)$	1374
Mercury (Hg)	$Hg_1(ref)$	1373
Mercury bromide (Hg_2Br_2)	$Br_2Hg_2(cr)$	486
Mercury bromide (HgBr)	$Br_1Hg_1(g)$	441
Mercury bromide ($HgBr_2$)	$Br_2Hg_1(g)$	485
Mercury bromide ($HgBr_2$)	$Br_2Hg_1(cr,l)$	484
Mercury bromide ($HgBr_2$)	$Br_2Hg_1(l)$	483
Mercury bromide ($HgBr_2$)	$Br_2Hg_1(cr)$	482
Mercury chloride (Hg_2Cl_2)	$Cl_2Hg_2(cr)$	828
Mercury chloride (HgCl)	$Cl_1Hg_1(g)$	767
Mercury chloride ($HgCl_2$)	$Cl_2Hg_1(cr)$	824
Mercury chloride ($HgCl_2$)	$Cl_2Hg_1(l)$	825
Mercury chloride ($HgCl_2$)	$Cl_2Hg_1(cr,l)$	826
Mercury chloride ($HgCl_2$)	$Cl_2Hg_1(g)$	827
Mercury fluoride (Hg_2F_2)	$F_2Hg_2(cr)$	1113
Mercury fluoride (HgF)	$F_1Hg_1(g)$	1059
Mercury fluoride (HgF_2)	$F_2Hg_1(g)$	1112
Mercury fluoride (HgF_2)	$F_2Hg_1(cr)$	1109
Mercury fluoride (HgF_2)	$F_2Hg_1(l)$	1110
Mercury fluoride (HgF_2)	$F_2Hg_1(cr,l)$	1111
Mercury hydride (HgH)	$H_1Hg_1(g)$	1264
Mercury iodide (Hg_2I_2)	$Hg_2I_2(cr)$	1384
Mercury iodide (Hg_2I_2)	$Hg_2I_2(l)$	1385
Mercury iodide (Hg_2I_2)	$Hg_2I_2(cr,l)$	1386
Mercury iodide (HgI)	$Hg_1I_1(g)$	1377
Mercury iodide (HgI_2)	$Hg_1I_2(g)$	1381
Mercury iodide (HgI_2)	$Hg_1I_2(cr,l)$	1380
Mercury iodide (HgI_2)	$Hg_1I_2(l)$	1379
Mercury iodide (HgI_2)	$Hg_1I_2(cr)$	1378
Mercury, ion (Hg^+)	$Hg_1^+(g)$	1376
Mercury oxide (HgO)	$Hg_1O_1(g)$	1383
Mercury oxide (HgO)	$Hg_1O_1(cr)$	1382
Methane (CH_4)	$C_1H_4(g)$	615
Methinophosphide (CHP)	$C_1H_1P_1(g)$	604
Methyl (CH_3)	$C_1H_3(g)$	610
Methylene (CH_2)	$C_1H_2(g)$	605
Methylidyne (CH)	$C_1H_1(g)$	591
Methylidyne, ion (CH^+)	$C_1H_1^+(g)$	592
Molybdenum (Mo)	$Mo_1(g)$	1581
Molybdenum (Mo)	$Mo_1(cr,l)$	1580
Molybdenum (Mo)	$Mo_1(l)$	1579
Molybdenum (Mo)	$Mo_1(cr)$	1578
Molybdenum (Mo)	$Mo_1(ref)$	1577

Table Title	Formula	Page
Molybdenum bromide (MoBr)	$Br_1Mo_1(g)$	452
Molybdenum bromide ($MoBr_2$)	$Br_2Mo_1(g)$	495
Molybdenum bromide ($MoBr_2$)	$Br_2Mo_1(cr)$	494
Molybdenum bromide ($MoBr_3$)	$Br_3Mo_1(cr)$	515
Molybdenum bromide ($MoBr_3$)	$Br_3Mo_1(g)$	516
Molybdenum bromide ($MoBr_4$)	$Br_4Mo_1(g)$	528
Molybdenum bromide ($MoBr_4$)	$Br_4Mo_1(cr)$	527
Molybdenum chloride ($MoCl_4$)	$Cl_4Mo_1(cr)$	893
Molybdenum chloride ($MoCl_4$)	$Cl_4Mo_1(l)$	894
Molybdenum chloride ($MoCl_4$)	$Cl_4Mo_1(cr,l)$	895
Molybdenum chloride ($MoCl_4$)	$Cl_4Mo_1(g)$	896
Molybdenum chloride ($MoCl_5$)	$Cl_5Mo_1(g)$	914
Molybdenum chloride ($MoCl_5$)	$Cl_5Mo_1(cr)$	911
Molybdenum chloride ($MoCl_5$)	$Cl_5Mo_1(cr,l)$	913
Molybdenum chloride ($MoCl_5$)	$Cl_5Mo_1(l)$	912
Molybdenum chloride ($MoCl_6$)	$Cl_6Mo_1(g)$	930
Molybdenum chloride ($MoCl_6$)	$Cl_6Mo_1(cr)$	929
Molybdenum chloride oxide (MoO_2Cl_2)	$Cl_2Mo_1O_2(g)$	835
Molybdenum fluoride ($(MoF_5)_2$)	$F_{10}Mo_2(g)$	1211
Molybdenum fluoride ($(MoF_5)_3$)	$F_{15}Mo_3(g)$	1213
Molybdenum fluoride (MoF)	$F_1Mo_1(g)$	1072
Molybdenum fluoride (MoF_2)	$F_2Mo_1(g)$	1123
Molybdenum fluoride (MoF_3)	$F_3Mo_1(g)$	1163
Molybdenum fluoride (MoF_4)	$F_4Mo_1(g)$	1179
Molybdenum fluoride (MoF_5)	$F_5Mo_1(g)$	1197
Molybdenum fluoride (MoF_6)	$F_6Mo_1(l)$	1203
Molybdenum fluoride (MoF_6)	$F_6Mo_1(g)$	1204
Molybdenum fluoride oxide (MoF_4O)	$F_4Mo_1O_1(g)$	1180
Molybdenum iodide (MoI)	$I_1Mo_1(g)$	1399
Molybdenum iodide (MoI_2)	$I_2Mo_1(g)$	1425
Molybdenum iodide (MoI_3)	$I_3Mo_1(g)$	1444
Molybdenum iodide (MoI_3)	$I_3Mo_1(cr)$	1443
Molybdenum iodide (MoI_4)	$I_4Mo_1(g)$	1451
Molybdenum iodide (MoI_4)	$I_4Mo_1(cr)$	1450
Molybdenum iodide, alpha (MoI_2)	$I_2Mo_1(cr)$	1424
Molybdenum, ion (Mo^+)	$Mo_1^+(g)$	1582
Molybdenum, ion (Mo^-)	$Mo_1^-(g)$	1583
Molybdenum oxide (MoO)	$Mo_1O_1(g)$	1584
Molybdenum oxide ($MoO_{2.750}$)	$Mo_1O_{2.750}(cr)$	1587
Molybdenum oxide ($MoO_{2.875}$)	$Mo_1O_{2.875}(cr)$	1588
Molybdenum oxide ($MoO_{2.889}$)	$Mo_1O_{2.889}(cr)$	1589
Molybdenum oxide (MoO_2)	$Mo_1O_2(g)$	1586
Molybdenum oxide (MoO_2)	$Mo_1O_2(cr)$	1585
Molybdenum oxide (MoO_3)	$Mo_1O_3(l)$	1591
Molybdenum oxide (MoO_3)	$Mo_1O_3(cr)$	1590
Molybdenum oxide (MoO_3)	$Mo_1O_3(cr,l)$	1592
Molybdenum oxide (MoO_3)	$Mo_1O_3(g)$	1593
Molybdenum sulfide (Mo_2S_3)	$Mo_2S_3(cr,l)$	1597
Molybdenum sulfide (Mo_2S_3)	$Mo_2S_3(l)$	1596
Molybdenum sulfide (Mo_2S_3)	$Mo_2S_3(cr)$	1595
Molybdenum sulfide (MoS_2)	$Mo_1S_2(cr)$	1594
Molybdic acid ($O_2Mo(OH)_2$)	$H_2Mo_1O_4(g)$	1319
NCN radical (NCN)	$C_1N_2(g)$	637
NCO radical (NCO)	$C_1N_1O_1(g)$	635
Neon (Ne)	$Ne_1(ref)$	1695
Neon, ion (Ne^+)	$Ne_1^+(g)$	1696
Nickel (Ni)	$Ni_1(ref)$	1697
Nickel (Ni)	$Ni_1(cr)$	1698
Nickel (Ni)	$Ni_1(l)$	1699
Nickel (Ni)	$Ni_1(cr,l)$	1700
Nickel (Ni)	$Ni_1(g)$	1701
Nickel carbonyl ($Ni(CO)_4$)	$C_4Ni_1O_4(g)$	695
Nickel carbonyl ($Ni(CO)_4$)	$C_4Ni_1O_4(l)$	694
Nickel chloride (NiCl)	$Cl_1Ni_1(g)$	794
Nickel chloride ($NiCl_2$)	$Cl_2Ni_1(g)$	840
Nickel chloride ($NiCl_2$)	$Cl_2Ni_1(cr,l)$	839
Nickel chloride ($NiCl_2$)	$Cl_2Ni_1(l)$	838
Nickel chloride ($NiCl_2$)	$Cl_2Ni_1(cr)$	837
Nickel, ion (Ni^+)	$Ni_1^+(g)$	1702
Nickel, ion (Ni^-)	$Ni_1^-(g)$	1703
Nickel sulfide (Ni_3S_2)	$Ni_3S_2(cr,l)$	1713
Nickel sulfide (Ni_3S_2)	$Ni_3S_2(l)$	1712
Nickel sulfide (Ni_3S_2)	$Ni_3S_2(cr)$	1711
Nickel sulfide (Ni_3S_4)	$Ni_3S_4(cr)$	1714
Nickel sulfide (NiS)	$Ni_1S_1(l)$	1705
Nickel sulfide (NiS)	$Ni_1S_1(cr)$	1704
Nickel sulfide (NiS)	$Ni_1S_1(g)$	1707
Nickel sulfide (NiS)	$Ni_1S_1(cr,l)$	1706
Nickel sulfide (NiS_2)	$Ni_1S_2(cr,l)$	1710
Nickel sulfide (NiS_2)	$Ni_1S_2(l)$	1709
Nickel sulfide (NiS_2)	$Ni_1S_2(cr)$	1708
Niobium (Nb)	$Nb_1(ref)$	1675
Niobium (Nb)	$Nb_1(cr)$	1676
Niobium (Nb)	$Nb_1(l)$	1677
Niobium (Nb)	$Nb_1(cr,l)$	1678
Niobium (Nb)	$Nb_1(g)$	1679
Niobium bromide ($NbBr_5$)	$Br_5Nb_1(cr)$	538
Niobium bromide ($NbBr_5$)	$Br_5Nb_1(l)$	539
Niobium bromide ($NbBr_5$)	$Br_5Nb_1(cr,l)$	540
Niobium bromide ($NbBr_5$)	$Br_5Nb_1(g)$	541
Niobium carbide ($NbC_{0.98}$)	$C_{0.98}Nb_1(cr)$	549
Niobium chloride ($NbCl_5$)	$Cl_5Nb_1(g)$	918
Niobium chloride ($NbCl_5$)	$Cl_5Nb_1(cr,l)$	917
Niobium chloride ($NbCl_5$)	$Cl_5Nb_1(l)$	916
Niobium chloride ($NbCl_5$)	$Cl_5Nb_1(cr)$	915
Niobium, ion (Nb^+)	$Nb_1^+(g)$	1680
Niobium, ion (Nb^-)	$Nb_1^-(g)$	1681
Niobium oxide (Nb_2O_5)	$Nb_2O_5(cr,l)$	1692
Niobium oxide (Nb_2O_5)	$Nb_2O_5(l)$	1691
Niobium oxide (Nb_2O_5)	$Nb_2O_5(cr)$	1690
Niobium oxide (NbO)	$Nb_1O_1(cr)$	1682
Niobium oxide (NbO)	$Nb_1O_1(l)$	1683
Niobium oxide (NbO)	$Nb_1O_1(cr,l)$	1684
Niobium oxide (NbO)	$Nb_1O_1(g)$	1685
Niobium oxide (NbO_2)	$Nb_1O_2(g)$	1689
Niobium oxide (NbO_2)	$Nb_1O_2(cr,l)$	1688
Niobium oxide (NbO_2)	$Nb_1O_2(l)$	1687
Niobium oxide (NbO_2)	$Nb_1O_2(cr)$	1686
Nitric acid ($HONO_2$)	$H_1N_1O_3(g)$	1290
Nitrogen (N)	$N_1(g)$	1600
Nitrogen (N_2)	$N_2(ref)$	1621

Table Title	Formula	Page
Nitrogen fluoride (NF_3)	$F_3N_1(g)$	1164
Nitrogen fluoride, cis (FNNF)	$F_2N_2(g)$	1125
Nitrogen fluoride oxide (NF_3O)	$F_3N_1O_1(g)$	1165
Nitrogen fluoride, trans (FNNF)	$F_2N_2(g)$	1126
Nitrogen, ion (N^+)	$N_1^+(g)$	1601
Nitrogen, ion (N^-)	$N_1^-(g)$	1602
Nitrogen, ion (N_2^+)	$N_2^+(g)$	1622
Nitrogen, ion (N_2^-)	$N_2^-(g)$	1623
Nitrogen oxide (N_2O)	$N_2O_1(g)$	1624
Nitrogen oxide (N_2O_3)	$N_2O_3(g)$	1626
Nitrogen oxide (N_2O_4)	$N_2O_4(cr)$	1627
Nitrogen oxide (N_2O_4)	$N_2O_4(l)$	1628
Nitrogen oxide (N_2O_4)	$N_2O_4(cr,l)$	1629
Nitrogen oxide (N_2O_4)	$N_2O_4(g)$	1630
Nitrogen oxide (N_2O_5)	$N_2O_5(g)$	1631
Nitrogen oxide (NO)	$N_1O_1(g)$	1603
Nitrogen oxide (NO_2)	$N_1O_2(g)$	1605
Nitrogen oxide (NO_3)	$N_1O_3(g)$	1607
Nitrogen oxide, ion (N_2O^+)	$N_2O_1^+(g)$	1625
Nitrogen oxide, ion (NO^+)	$N_1O_1^+(g)$	1604
Nitrogen oxide, ion (ONO^-)	$N_1O_2^-(g)$	1606
Nitrogen sulfide (NS)	$N_1S_1(g)$	1609
Nitrosyl bromide (ONBr)	$Br_1N_1O_1(g)$	454
Nitrosyl chloride (ONCl)	$Cl_1N_1O_1(g)$	787
Nitrosyl fluoride (ONF)	$F_1N_1O_1(g)$	1074
Nitrosyl hydride (HNO)	$H_1N_1O_1(g)$	1287
Nitrosyl iodide (ONI)	$I_1N_1O_1(g)$	1400
Nitrous acid, cis (HONO)	$H_1N_1O_2(g)$	1288
Nitrous acid, trans (HONO)	$H_1N_1O_2(g)$	1289
Nitryl chloride (NO_2Cl)	$Cl_1N_1O_2(g)$	788
Nitryl fluoride (NO_2F)	$F_1N_1O_2(g)$	1075
Oxirane (C_2H_4O)	$C_2H_4O_1(g)$	677
Oxygen (O)	$O_1(g)$	1717
Oxygen (O_2)	$O_2(ref)$	1745
Oxygen fluoride (FOF)	$F_2O_1(g)$	1129
Oxygen fluoride (FOOF)	$F_2O_2(g)$	1133
Oxygen fluoride (OF)	$F_1O_1(g)$	1081
Oxygen fluoride (OFO)	$F_1O_2(g)$	1083
Oxygen fluoride (OOF)	$F_1O_2(g)$	1084
Oxygen, ion (O^+)	$O_1^+(g)$	1718
Oxygen, ion (O^-)	$O_1^-(g)$	1719
Oxygen, ion (O_2^+)	$O_2^+(g)$	1746
Oxygen, ion (O_2^-)	$O_2^-(g)$	1747
Ozone (O_3)	$O_3(g)$	1773
Pentaborane (B_5H_9)	$B_5H_9(l)$	302
Pentaborane (B_5H_9)	$B_5H_9(g)$	303
Pentafluoro(trifluoromethyl) sulfur	$(CF_3SF_5)C_1F_8S_1(g)$	590
Perchloryl fluoride (ClO_3F)	$Cl_1F_1O_3(g)$	755
Phosphine (PH_3)	$H_3P_1(g)$	1348
Phosphinidene (PH)	$H_1P_1(g)$	10
Phosphino (PH_2)	$H_2P_1(g)$	1339
Phosphoric acid (H_3PO_4)	$H_3O_4P_1(cr,l)$	1347
Phosphoric acid (H_3PO_4)	$H_3O_4P_1(cr)$	1345
Phosphoric acid (H_3PO_4)	$H_3O_4P_1(l)$	1346

Table Title	Formula	Page
Phosphorus (P)	$P_1(l)$	1822
Phosphorus (P)	$P_1(ref)$	1817
Phosphorus (P)	$P_1(g)$	1824
Phosphorus (P)	$P_1(cr,l)$	1823
Phosphorus (P_2)	$P_2(g)$	1828
Phosphorus (P_4)	$P_4(g)$	1829
Phosphorus, black (P)	$P_1(cr)$	1818
Phosphorus bromide (PBr)	$Br_1P_1(g)$	463
Phosphorus bromide (PBr_3)	$Br_3P_1(g)$	518
Phosphorus chloride (PCl)	$Cl_1P_1(g)$	800
Phosphorus chloride (PCl_3)	$Cl_3P_1(g)$	883
Phosphorus chloride (PCl_5)	$Cl_5P_1(g)$	919
Phosphorus fluoride (PF)	$F_1P_1(g)$	1085
Phosphorus fluoride (PF_2)	$F_2P_1(g)$	1135
Phosphorus fluoride (PF_3)	$F_3P_1(g)$	1167
Phosphorus fluoride (PF_5)	$F_5P_1(g)$	1198
Phosphorus fluoride, ion (PF^+)	$F_1P_1^+(g)$	1086
Phosphorus fluoride, ion (PF^-)	$F_1P_1^-(g)$	1087
Phosphorus fluoride, ion (PF_2^+)	$F_2P_1^+(g)$	1136
Phosphorus fluoride, ion (PF_2^-)	$F_2P_1^-(g)$	1137
Phosphorus, ion (P^+)	$P_1^+(g)$	1825
Phosphorus, ion (P^-)	$P_1^-(g)$	1826
Phosphorus nitride (P_3N_5)	$N_5P_3(cr)$	1634
Phosphorus nitride (PN)	$N_1P_1(g)$	1608
Phosphorus oxide ($(P_2O_3)_2$)	$O_6P_4(g)$	1803
Phosphorus oxide ($(P_2O_5)_2$)	$O_{10}P_4(g)$	1811
Phosphorus oxide ($(P_2O_5)_2$)	$O_{10}P_4(cr)$	1810
Phosphorus oxide (PO)	$O_1P_1(g)$	1720
Phosphorus oxide (PO_2)	$O_2P_1(g)$	1748
Phosphorus, red, IV (P)	$P_1(cr)$	1819
Phosphorus, red, V (P)	$P_1(cr)$	1820
Phosphorus sulfide (P_4S_3)	$P_4S_3(cr)$	1830
Phosphorus sulfide (P_4S_3)	$P_4S_3(l)$	1831
Phosphorus sulfide (P_4S_3)	$P_4S_3(cr,l)$	1832
Phosphorus sulfide (P_4S_3)	$P_4S_3(g)$	1833
Phosphorus sulfide (PS)	$P_1S_1(g)$	1827
Phosphorus, white (P)	$P_1(cr)$	1821
Phosphoryl bromide ($POBr_3$)	$Br_3O_1P_1(g)$	517
Phosphoryl chloride ($OPCl_3$)	$Cl_3O_1P_1(g)$	882
Phosphoryl chloride fluoride ($POClF_2$)	$Cl_1F_2O_1P_1(g)$	756
Phosphoryl chloride fluoride ($POCl_2F$)	$Cl_2F_1O_1P_1(g)$	818
Phosphoryl fluoride (POF_3)	$F_3O_1P_1(g)$	882
Potassium (K)	$K_1(ref)$	1465
Potassium (K)	$K_1(cr)$	1466
Potassium (K)	$K_1(l)$	1467
Potassium (K)	$K_1(cr,l)$	1468
Potassium (K)	$K_1(g)$	1469
Potassium (K_2)	$K_2(g)$	1475
Potassium aluminum chloride ($K_3Al_2Cl_9$)	$Al_2Cl_9K_3(cr)$	144
Potassium borate ($K_2B_4O_7$)	$B_4K_2O_7(cr)$	291
Potassium borate ($K_2B_4O_7$)	$B_4K_2O_7(l)$	292
Potassium borate ($K_2B_4O_7$)	$B_4K_2O_7(cr,l)$	293
Potassium borate ($K_2B_6O_{10}$)	$B_6K_2O_{10}(cr)$	304
Potassium borate ($K_2B_8O_{13}$)	$B_8K_2O_{13}(cr)$	308
Potassium borate ($K_2B_8O_{13}$)	$B_8K_2O_{13}(l)$	309
Potassium borate ($K_2B_8O_{13}$)	$B_8K_2O_{13}(cr,l)$	310

Table Title	Formula	Page
Potassium borate (KBO_2)	$B_1K_1O_2$(cr)	240
Potassium borate (KBO_2)	$B_1K_1O_2$(l)	241
Potassium borate (KBO_2)	$B_1K_1O_2$(cr,l)	242
Potassium borate (KBO_2)	$B_1K_1O_2$(g)	243
Potassium bromide ($(KBr)_2$)	Br_2K_2(g)	487
Potassium bromide (KBr)	Br_1K_1(cr)	443
Potassium bromide (KBr)	Br_1K_1(l)	444
Potassium bromide (KBr)	Br_1K_1(cr,l)	445
Potassium bromide (KBr)	Br_1K_1(g)	446
Potassium carbonate (K_2CO_3)	$C_1K_2O_3$(cr,l)	623
Potassium carbonate (K_2CO_3)	$C_1K_2O_3$(l)	622
Potassium carbonate (K_2CO_3)	$C_1K_2O_3$(cr)	621
Potassium chloride ($(KCl)_2$)	Cl_2K_2(g)	829
Potassium chloride (KCl)	Cl_1K_1(g)	775
Potassium chloride (KCl)	Cl_1K_1(cr,l)	774
Potassium chloride (KCl)	Cl_1K_1(l)	773
Potassium chloride (KCl)	Cl_1K_1(cr)	772
Potassium cyanide ($(KCN)_2$)	$C_2K_2N_2$(g)	678
Potassium cyanide (KCN)	$C_1K_1N_1$(cr)	617
Potassium cyanide (KCN)	$C_1K_1N_1$(l)	618
Potassium cyanide (KCN)	$C_1K_1N_1$(cr,l)	619
Potassium cyanide (KCN)	$C_1K_1N_1$(g)	620
Potassium fluoride ($(KF)_2$)	F_2K_2(g)	1115
Potassium fluoride ($K(HF_2)$)	$F_2H_1K_1$(cr)	1104
Potassium fluoride ($K(HF_2)$)	$F_2H_1K_1$(l)	1105
Potassium fluoride ($K(HF_2)$)	$F_2H_1K_1$(cr,l)	1106
Potassium fluoride (KF)	F_1K_1(l)	1062
Potassium fluoride (KF)	F_1K_1(cr)	1061
Potassium fluoride (KF)	F_1K_1(cr,l)	1063
Potassium fluoride (KF)	F_1K_1(g)	1064
Potassium fluoride, ion (KF_2^-)	$F_2K_1^-$(g)	1114
Potassium hexachloroaluminate (K_3AlCl_6)	$Al_1Cl_6K_3$(cr)	89
Potassium hexafluoraluminate (K_3AlF_6)	$Al_1F_6K_3$(cr)	106
Potassium hydride (KH)	H_1K_1(cr)	1267
Potassium hydride (KH)	H_1K_1(g)	1268
Potassium hydroxide ($(KOH)_2$)	$H_2K_2O_2$(g)	1314
Potassium hydroxide (KOH)	$H_1K_1O_1$(g)	1272
Potassium hydroxide (KOH)	$H_1K_1O_1$(cr,l)	1271
Potassium hydroxide (KOH)	$H_1K_1O_1$(l)	1270
Potassium hydroxide (KOH)	$H_1K_1O_1$(cr)	1269
Potassium hydroxide, ion (KOH^+)	$H_1K_1O_1^+$(g)	1273
Potassium iodide ($(KI)_2$)	I_2K_2(g)	1418
Potassium iodide (KI)	I_1K_1(g)	1393
Potassium iodide (KI)	I_1K_1(cr,l)	1392
Potassium iodide (KI)	I_1K_1(cr)	1390
Potassium iodide (KI)	I_1K_1(l)	1391
Potassium, ion (K^+)	K_1^+(g)	1470
Potassium, ion (K^-)	K_1^-(g)	1471
Potassium oxide (K_2O)	K_2O_1(cr)	1476
Potassium oxide (KO)	K_1O_1(g)	1472
Potassium oxide, ion (KO^-)	$K_1O_1^-$(g)	1473
Potassium perchlorate ($KClO_4$)	$Cl_1K_1O_4$(cr)	776
Potassium peroxide (K_2O_2)	K_2O_2(cr)	1477
Potassium silicate (K_2SiO_3)	$K_2O_3Si_1$(cr)	1478
Potassium silicate (K_2SiO_3)	$K_2O_3Si_1$(l)	1479
Potassium silicate (K_2SiO_3)	$K_2O_3Si_1$(cr,l)	1480
Potassium sulfate (K_2SO_4)	$K_2O_4S_1$(l)	1483
Potassium sulfate (K_2SO_4)	$K_2O_4S_1$(cr,l)	1484
Potassium sulfate (K_2SO_4)	$K_2O_4S_1$(g)	1485
Potassium sulfate, alpha (K_2SO_4)	$K_2O_4S_1$(cr)	1481
Potassium sulfate, beta (K_2SO_4)	$K_2O_4S_1$(cr)	1482
Potassium sulfide (K_2S)	K_2S_1(cr)	1486
Potassium sulfide (K_2S)	K_2S_1(l)	1487
Potassium sulfide (K_2S)	K_2S_1(cr,l)	1488
Potassium superoxide (KO_2)	K_1O_2(cr)	1474
Potassium tetrachloroaluminate ($KAlCl_4$)	$Al_1Cl_4K_1$(cr)	87
Potassium tetrafluoroborate (KBF_4)	$B_1F_4K_1$(cr)	217
Potassium tetrafluoroborate (KBF_4)	$B_1F_4K_1$(l)	218
Potassium tetrafluoroborate (KBF_4)	$B_1F_4K_1$(cr,l)	219
Potassium tetrafluoroborate (KBF_4)	$B_1F_4K_1$(g)	220
Potassium tetrahydroborate (KBH_4)	$B_1H_4K_1$(cr)	234
Radon (Rn)	Rn_1(ref)	1857
Radon, ion (Rn^+)	Rn_1^+(g)	1858
Rubidium (Rb)	Rb_1(ref)	1849
Rubidium (Rb)	Rb_1(cr)	1850
Rubidium (Rb)	Rb_1(l)	1851
Rubidium (Rb)	Rb_1(cr,l)	1852
Rubidium (Rb)	Rb_1(g)	1853
Rubidium (Rb_2)	Rb_2(g)	1856
Rubidium, ion (Rb^+)	Rb_1^+(g)	1854
Rubidium, ion (Rb^-)	Rb_1^-(g)	1855
Silane (SiH_4)	H_4Si_1(g)	1353
Silicon (Si)	Si_1(ref)	1991
Silicon (Si)	Si_1(cr)	1882
Silicon (Si)	Si_1(l)	1883
Silicon (Si)	Si_1(cr,l)	1884
Silicon (Si)	Si_1(g)	1885
Silicon (Si_2)	Si_2(g)	1888
Silicon (Si_3)	Si_3(g)	1889
Silicon carbide (Si_2C)	C_1Si_2(g)	651
Silicon carbide (SiC)	C_1Si_1(g)	650
Silicon carbide (SiC_2)	C_2Si_1(g)	685
Silicon carbide, alpha (SiC)	C_1Si_1(cr)	648
Silicon carbide, beta (SiC)	C_1Si_1(cr)	649
Silicon, ion (Si^+)	Si_1^+(g)	1886
Silicon, ion (Si^-)	Si_1^-(g)	1887
Silicon nitride (Si_2N)	N_1Si_2(g)	1611
Silicon nitride (SiN)	N_1Si_1(g)	1610
Silicon nitride, alpha (Si_3N_4)	N_4Si_3(cr)	1633
Silicon oxide (SiO)	O_1Si_1(g)	1728
Silicon oxide (SiO_2)	O_2Si_1(g)	1756
Silicon oxide (SiO_2)	O_2Si_1(cr,l)	1755
Silicon oxide (SiO_2)	O_2Si_1(l)	1754
Silicon oxide, cristobalite, high (SiO_2)	O_2Si_1(cr)	1751
Silicon oxide, cristobalite, low (SiO_2)	O_2Si_1(cr)	1752
Silicon oxide, quartz (SiO_2)	O_2Si_1(cr)	1753
Silicon sulfide (SiS)	S_1Si_1(g)	1867
Silicon sulfide (SiS_2)	S_2Si_1(cr,l)	1873
Silicon sulfide (SiS_2)	S_2Si_1(l)	1872
Silicon sulfide (SiS_2)	S_2Si_1(cr)	1871

Table Title	Formula	Page
Silylidyne (SiH)	$H_1Si_1(g)$	1307
Silylidyne, ion (SiH^+)	$H_1Si_1^+(g)$	1308
Sodium (Na)	$Na_1(g)$	1641
Sodium (Na)	$Na_1(cr,l)$	1640
Sodium (Na)	$Na_1(l)$	1639
Sodium (Na)	$Na_1(cr)$	1638
Sodium (Na)	$Na_1(ref)$	1637
Sodium (Na_2)	$Na_2(g)$	1647
Sodium aluminum oxide ($NaAlO_2$)	$Al_1Na_1O_2(cr)$	131
Sodium borate ($Na_2B_4O_7$)	$B_4Na_2O_7(cr)$	298
Sodium borate ($Na_2B_4O_7$)	$B_4Na_2O_7(l)$	299
Sodium borate ($Na_2B_4O_7$)	$B_4Na_2O_7(cr,l)$	300
Sodium borate ($Na_2B_6O_{10}$)	$B_6Na_2O_{10}(cr)$	306
Sodium borate ($NaBO_2$)	$B_1Na_1O_2(cr,l)$	252
Sodium borate ($NaBO_2$)	$B_1Na_1O_2(g)$	253
Sodium borate ($NaBO_2$)	$B_1Na_1O_2(l)$	251
Sodium borate ($NaBO_2$)	$B_1Na_1O_2(cr)$	250
Sodium bromide ($(NaBr)_2$)	$Br_2Na_2(g)$	496
Sodium bromide (NaBr)	$Br_1Na_1(cr)$	455
Sodium bromide (NaBr)	$Br_1Na_1(l)$	456
Sodium bromide (NaBr)	$Br_1Na_1(cr,l)$	457
Sodium bromide (NaBr)	$Br_1Na_1(g)$	458
Sodium carbonate (Na_2CO_3)	$C_1Na_2O_3(cr,l)$	640
Sodium carbonate (Na_2CO_3)	$C_1Na_2O_3(l)$	639
Sodium carbonate (Na_2CO_3)	$C_1Na_2O_3(cr)$	638
Sodium chloride ($(NaCl)_2$)	$Cl_2Na_2(g)$	836
Sodium chloride (NaCl)	$Cl_1Na_1(cr)$	789
Sodium chloride (NaCl)	$Cl_1Na_1(l)$	790
Sodium chloride (NaCl)	$Cl_1Na_1(cr,l)$	791
Sodium chloride (NaCl)	$Cl_1Na_1(g)$	792
Sodium cyanide ($(NaCN)_2$)	$C_2N_2Na_2(g)$	683
Sodium cyanide (NaCN)	$C_1N_1Na_1(g)$	634
Sodium cyanide (NaCN)	$C_1N_1Na_1(cr)$	631
Sodium cyanide (NaCN)	$C_1N_1Na_1(l)$	632
Sodium cyanide (NaCN)	$C_1N_1Na_1(cr,l)$	633
Sodium fluoride ($(NaF)_2$)	$F_2Na_2(g)$	1128
Sodium fluoride (NaF)	$F_1Na_1(g)$	1080
Sodium fluoride (NaF)	$F_1Na_1(cr,l)$	1079
Sodium fluoride (NaF)	$F_1Na_1(l)$	1078
Sodium fluoride (NaF)	$F_1Na_1(cr)$	1077
Sodium fluoride, ion (NaF_2^-)	$F_2Na_1^-(g)$	1127
Sodium hexachloroaluminate (Na_3AlCl_6)	$Al_1Cl_6Na_3(cr)$	90
Sodium hydride (NaH)	$H_1Na_1(cr)$	1291
Sodium hydride (NaH)	$H_1Na_1(g)$	1292
Sodium hydroxide ($(NaOH)_2$)	$H_2Na_2O_2(g)$	1322
Sodium hydroxide (NaOH)	$H_1Na_1O_1(cr)$	1293
Sodium hydroxide (NaOH)	$H_1Na_1O_1(l)$	1294
Sodium hydroxide (NaOH)	$H_1Na_1O_1(cr,l)$	1295
Sodium hydroxide (NaOH)	$H_1Na_1O_1(g)$	1296
Sodium hydroxide, ion ($NaOH^+$)	$H_1Na_1O_1^+(g)$	1297
Sodium iodide (NaI)	$I_1Na_1(cr)$	1401
Sodium iodide (NaI)	$I_1Na_1(l)$	1402
Sodium iodide (NaI)	$I_1Na_1(cr,l)$	1403
Sodium, ion (Na^+)	$Na_1^+(g)$	1642
Sodium, ion (Na^-)	$Na_1^-(g)$	1643
Sodium oxide (Na_2O)	$Na_2O_1(cr)$	1648
Sodium oxide (Na_2O)	$Na_2O_1(l)$	1649
Sodium oxide (Na_2O)	$Na_2O_1(cr,l)$	1650
Sodium oxide (NaO)	$Na_1O_1(g)$	1644
Sodium oxide, ion (NaO^-)	$Na_1O_1^-(g)$	1645
Sodium perchlorate ($NaClO_4$)	$Cl_1Na_1O_4(cr)$	793
Sodium peroxide (Na_2O_2)	$Na_2O_2(cr)$	1651
Sodium silicate ($Na_2Si_2O_5$)	$Na_2O_5Si_2(cr)$	1664
Sodium silicate ($Na_2Si_2O_5$)	$Na_2O_5Si_2(l)$	1665
Sodium silicate ($Na_2Si_2O_5$)	$Na_2O_5Si_2(cr,l)$	1666
Sodium silicate (Na_2SiO_3)	$Na_2O_3Si_1(cr)$	1652
Sodium silicate (Na_2SiO_3)	$Na_2O_3Si_1(l)$	1653
Sodium silicate (Na_2SiO_3)	$Na_2O_3Si_1(cr,l)$	1654
Sodium sulfate (Na_2SO_4)	$Na_2O_4S_1(l)$	1660
Sodium sulfate (Na_2SO_4)	$Na_2O_4S_1(cr,l)$	1661
Sodium sulfate (Na_2SO_4)	$Na_2O_4S_1(g)$	1662
Sodium sulfate, delta (Na_2SO_4)	$Na_2O_4S_1(cr)$	1655
Sodium sulfate, I (Na_2SO_4)	$Na_2O_4S_1(cr)$	1656
Sodium sulfate, III (Na_2SO_4)	$Na_2O_4S_1(cr)$	1657
Sodium sulfate, IV (Na_2SO_4)	$Na_2O_4S_1(cr)$	1658
Sodium sulfate, V (Na_2SO_4)	$Na_2O_4S_1(cr)$	1659
Sodium sulfide (Na_2S)	$Na_2S_1(cr)$	1667
Sodium sulfide (Na_2S)	$Na_2S_1(l)$	1668
Sodium sulfide (Na_2S)	$Na_2S_1(cr,l)$	1669
Sodium sulfide (Na_2S_2)	$Na_2S_2(l)$	1671
Sodium sulfide (Na_2S_2)	$Na_2S_2(cr,l)$	1672
Sodium sulfide, beta (Na_2S_2)	$Na_2S_2(cr)$	1670
Sodium superoxide (NaO_2)	$Na_1O_2(cr)$	1646
Sodium tetrachloroaluminate ($NaAlCl_4$)	$Al_1Cl_4Na_1(cr)$	88
Sodium tetrafluoroaluminate ($NaAlF_4$)	$Al_1F_4Na_1(g)$	105
Sodium tetrahydroborate ($NaBH_4$)	$B_1H_4Na_1(cr)$	236
Sodium tungsten oxide (Na_2WO_4)	$Na_2O_4W_1(cr)$	1663
Strontium (Sr)	$Sr_1(ref)$	1891
Strontium (Sr)	$Sr_1(l)$	1894
Strontium (Sr)	$Sr_1(cr,l)$	1895
Strontium (Sr)	$Sr_1(g)$	1896
Strontium, alpha (Sr)	$Sr_1(cr)$	1892
Strontium, beta (Sr)	$Sr_1(cr)$	1893
Strontium bromide (SrBr)	$Br_1Sr_1(g)$	466
Strontium bromide ($SrBr_2$)	$Br_2Sr_1(cr)$	504
Strontium bromide ($SrBr_2$)	$Br_2Sr_1(l)$	505
Strontium bromide ($SrBr_2$)	$Br_2Sr_1(cr,l)$	506
Strontium bromide ($SrBr_2$)	$Br_2Sr_1(g)$	507
Strontium chloride (SrCl)	$Cl_1Sr_1(g)$	807
Strontium chloride ($SrCl_2$)	$Cl_2Sr_1(cr)$	861
Strontium chloride ($SrCl_2$)	$Cl_2Sr_1(l)$	862
Strontium chloride ($SrCl_2$)	$Cl_2Sr_1(cr,l)$	863
Strontium chloride ($SrCl_2$)	$Cl_2Sr_1(g)$	864
Strontium fluoride (SrF)	$F_1Sr_1(g)$	1094
Strontium fluoride (SrF_2)	$F_2Sr_1(cr)$	1149
Strontium fluoride (SrF_2)	$F_2Sr_1(l)$	1150
Strontium fluoride (SrF_2)	$F_2Sr_1(cr,l)$	1151
Strontium fluoride (SrF_2)	$F_2Sr_1(g)$	1152
Strontium fluoride, ion (SrF^+)	$F_1Sr_1^+(g)$	1095
Strontium hydroxide ($Sr(OH)_2$)	$H_2O_2Sr_1(cr)$	1331
Strontium hydroxide ($Sr(OH)_2$)	$H_2O_2Sr_1(l)$	1332
Strontium hydroxide ($Sr(OH)_2$)	$H_2O_2Sr_1(cr,l)$	1333

Table Title	Formula	Page
Strontium hydroxide ($Sr(OH)_2$)	$H_2O_2Sr_1(g)$	1334
Strontium hydroxide (SrOH)	$H_1O_1Sr_1(g)$	1301
Strontium hydroxide, ion ($SrOH^+$)	$H_1O_1Sr_1^+(g)$	1302
Strontium iodide (SrI)	$I_1Sr_1(g)$	1410
Strontium iodide (SrI_2)	$I_2Sr_1(g)$	1436
Strontium iodide (SrI_2)	$I_2Sr_1(cr,l)$	1435
Strontium iodide (SrI_2)	$I_2Sr_1(l)$	1434
Strontium iodide (SrI_2)	$I_2Sr_1(cr)$	1433
Strontium, ion (Sr^+)	$Sr_1^+(g)$	1897
Strontium oxide (SrO)	$O_1Sr_1(g)$	1732
Strontium oxide (SrO)	$O_1Sr_1(cr,l)$	1731
Strontium oxide (SrO)	$O_1Sr_1(l)$	1730
Strontium oxide (SrO)	$O_1Sr_1(cr)$	1729
Strontium sulfide (SrS)	$S_1Sr_1(cr)$	1868
Strontium sulfide (SrS)	$S_1Sr_1(g)$	1869
Sulfur (S)	$S_1(ref)$	1859
Sulfur (S)	$S_1(l)$	1862
Sulfur (S)	$S_1(cr,l)$	1863
Sulfur (S)	$S_1(g)$	1864
Sulfur (S_2)	$S_2(g)$	1870
Sulfur (S_3)	$S_3(g)$	1874
Sulfur (S_4)	$S_4(g)$	1875
Sulfur (S_5)	$S_5(g)$	1876
Sulfur (S_6)	$S_6(g)$	1877
Sulfur (S_7)	$S_7(g)$	1878
Sulfur (S_8)	$S_8(g)$	1879
Sulfur bromide fluoride ($SBrF_5$)	$Br_1F_5S_1(g)$	437
Sulfur chloride (ClSSCl)	$Cl_2S_2(l)$	858
Sulfur chloride (ClSSCl)	$Cl_2S_2(g)$	859
Sulfur chloride (S_2Cl)	$Cl_1S_2(g)$	805
Sulfur chloride (SCl)	$Cl_1S_1(g)$	803
Sulfur chloride (SCl_2)	$Cl_2S_1(l)$	855
Sulfur chloride (SCl_2)	$Cl_2S_1(g)$	856
Sulfur chloride fluoride ($SClF_5$)	$Cl_1F_5S_1(g)$	760
Sulfur chloride, ion (SCl^+)	$Cl_1S_1^+(g)$	804
Sulfur chloride, ion (SCl_2^+)	$Cl_2S_1^+(g)$	857
Sulfur dioxide (SO_2)	$O_2S_1(g)$	1750
Sulfur fluoride (S_2F_{10})	$F_{10}S_2(g)$	1212
Sulfur fluoride (SF)	$F_1S_1(g)$	1090
Sulfur fluoride (SF_2)	$F_2S_1(g)$	1143
Sulfur fluoride (SF_3)	$F_3S_1(g)$	1169
Sulfur fluoride (SF_4)	$F_4S_1(g)$	1187
Sulfur fluoride (SF_5)	$F_5S_1(g)$	1199
Sulfur fluoride (SF_6)	$F_6S_1(g)$	1205
Sulfur fluoride, ion (SF^+)	$F_1S_1^+(g)$	1091
Sulfur fluoride, ion (SF^-)	$F_1S_1^-(g)$	1092
Sulfur fluoride, ion (SF_2^+)	$F_2S_1^+(g)$	1144
Sulfur fluoride, ion (SF_2^-)	$F_2S_1^-(g)$	1145
Sulfur fluoride, ion (SF_3^+)	$F_3S_1^+(g)$	1170
Sulfur fluoride, ion (SF_3^-)	$F_3S_1^-(g)$	1171
Sulfur fluoride, ion (SF_4^+)	$F_4S_1^+(g)$	1188
Sulfur fluoride, ion (SF_4^-)	$F_4S_1^-(g)$	1189
Sulfur fluoride, ion (SF_5^+)	$F_5S_1^+(g)$	1200
Sulfur fluoride, ion (SF_5^-)	$F_5S_1^-(g)$	1201
Sulfur fluoride, ion (SF_6^-)	$F_6S_1^-(g)$	1206
Sulfur, ion (S^+)	$S_1^+(g)$	1865
Sulfur, ion (S^-)	$S_1^-(g)$	1866
Sulfur, monoclinic (S)	$S_1(cr)$	1860
Sulfur, orthorhombic (S)	$S_1(cr)$	1861
Sulfur oxide (SO)	$O_1S_1(g)$	1726
Sulfur oxide (SSO)	$O_1S_2(g)$	1727
Sulfur trioxide (SO_3)	$O_3S_1(g)$	1775
Sulfuric acid ($O_2S(OH)_2$)	$H_2O_4S_1(cr,l)$	1335
Sulfuric acid ($O_2S(OH)_2$)	$H_2O_4S_1(g)$	1336
Sulfuric acid, dihydrate ($H_2SO_4 \cdot 2H_2O$)	$H_6O_6S_1(cr,l)$	1354
Sulfuric acid, hemihexahydrate ($H_2SO_4 \cdot 6.5H_2O$)	$H_{15}O_{10.5}S_1(cr,l)$	1357
Sulfuric acid, monohydrate ($H_2SO_4 \cdot H_2O$)	$H_4O_5S_1(cr,l)$	1352
Sulfuric acid, tetrahydrate ($H_2SO_4 \cdot 4H_2O$)	$H_{10}O_8S_1(cr,l)$	1356
Sulfuric acid, trihydrate ($H_2SO_4 \cdot 3H_2O$)	$H_8O_7S_1(cr,l)$	1355
Sulfuryl chloride (SO_2Cl_2)	$Cl_2O_2S_1(g)$	847
Sulfuryl chloride fluoride (SO_2ClF)	$Cl_1F_1O_2S_1(g)$	754
Sulfuryl fluoride (SO_2F_2)	$F_2O_2S_1(g)$	1134
Tantalum (Ta)	$Ta_1(cr)$	1900
Tantalum (Ta)	$Ta_1(ref)$	1899
Tantalum (Ta)	$Ta_1(l)$	1901
Tantalum (Ta)	$Ta_1(cr,l)$	1902
Tantalum (Ta)	$Ta_1(g)$	1903
Tantalum carbide (TaC)	$C_1Ta_1(l)$	653
Tantalum carbide (TaC)	$C_1Ta_1(cr)$	652
Tantalum carbide (TaC)	$C_1Ta_1(cr,l)$	654
Tantalum chloride ($TaCl_5$)	$Cl_5Ta_1(cr)$	920
Tantalum chloride ($TaCl_5$)	$Cl_5Ta_1(g)$	923
Tantalum chloride ($TaCl_5$)	$Cl_5Ta_1(l)$	921
Tantalum chloride ($TaCl_5$)	$Cl_5Ta_1(cr,l)$	922
Tantalum, ion (Ta^+)	$Ta_1^+(g)$	1904
Tantalum, ion (Ta^-)	$Ta_1^-(g)$	1905
Tantalum oxide (Ta_2O_5)	$O_5Ta_2(cr)$	1793
Tantalum oxide (Ta_2O_5)	$O_5Ta_2(l)$	1794
Tantalum oxide (Ta_2O_5)	$O_5Ta_2(cr,l)$	1795
Tantalum oxide (TaO)	$O_1Ta_1(g)$	1733
Tantalum oxide (TaO_2)	$O_2Ta_1(g)$	1757
Tetrabromomethane (CBr_4)	$C_1Br_4(g)$	565
Tetrabromosilane ($SiBr_4$)	$Br_4Si_1(g)$	531
Tetrabromosilane ($SiBr_4$)	$Br_4Si_1(l)$	530
Tetrachloroethene (C_2Cl_4)	$C_2Cl_4(g)$	665
Tetrachloromethane (CCl_4)	$C_1Cl_4(g)$	576
Tetrachlorosilane ($SiCl_4$)	$Cl_4Si_1(g)$	902
Tetrafluoroaluminate, ion (AlF_4^-)	$Al_1F_4^-(g)$	103
Tetrafluoroethene (C_2F_4)	$C_2F_4(g)$	670
Tetrafluorohydrazine (N_2F_4)	$F_4N_2(g)$	1181
Tetrafluoromethane (CF_4)	$C_1F_4(g)$	588
Tetrafluorosilane (SiF_4)	$F_4Si_1(g)$	1190
Tetraiodosilane (SiI_4)	$I_4Si_1(cr)$	1453
Tetraiodosilane (SiI_4)	$I_4Si_1(l)$	1554
Tetraiodosilane (SiI_4)	$I_4Si_1(cr,l)$	1455
Tetraiodosilane (SiI_4)	$I_4Si_1(g)$	1456
Tetramethylsilane ($Si(CH_3)_4$)	$C_4H_{12}Si_1(g)$	692
Thionyl fluoride (OSF_2)	$F_2O_1S_1(g)$	1130
Thiophosphoryl bromide ($PSBr_3$)	$Br_3P_1S_1(g)$	519
Thiophosphoryl chloride ($SPCl_3$)	$Cl_3P_1S_1(g)$	884
Thiophosphoryl fluoride (PSF)	$F_1P_1S_1(g)$	1088

Table Title	Formula	Page
Thiophosphoryl fluoride (PSF_3)	$F_3P_1S_1$(g)	1168
Thiothionyl fluoride (SSF_2)	F_2S_2(g)	1147
Titanium (Ti)	Ti_1(l)	1910
Titanium (Ti)	Ti_1(ref)	1907
Titanium (Ti)	Ti_1(cr,l)	1911
Titanium (Ti)	Ti_1(g)	1912
Titanium, alpha (Ti)	Ti_1(cr)	1908
Titanium, beta (Ti)	Ti_1(cr)	1909
Titanium boride (TiB)	B_1Ti_1(cr)	258
Titanium boride (TiB_2)	B_2Ti_1(cr)	276
Titanium boride (TiB_2)	B_2Ti_1(l)	277
Titanium boride (TiB_2)	B_2Ti_1(cr,l)	278
Titanium bromide (TiBr)	Br_1Ti_1(g)	467
Titanium bromide ($TiBr_2$)	Br_2Ti_1(cr)	508
Titanium bromide ($TiBr_2$)	Br_2Ti_1(g)	509
Titanium bromide ($TiBr_3$)	Br_3Ti_1(cr)	521
Titanium bromide ($TiBr_3$)	Br_3Ti_1(g)	522
Titanium bromide ($TiBr_4$)	Br_4Ti_1(cr,l)	534
Titanium bromide ($TiBr_4$)	Br_4Ti_1(cr)	532
Titanium bromide ($TiBr_4$)	Br_4Ti_1(g)	535
Titanium bromide ($TiBr_4$)	Br_4Ti_1(l)	533
Titanium carbide (TiC)	C_1Ti_1(cr)	655
Titanium carbide (TiC)	C_1Ti_1(l)	656
Titanium carbide (TiC)	C_1Ti_1(cr,l)	657
Titanium chloride (TiCl)	Cl_1Ti_1(g)	808
Titanium chloride ($TiCl_2$)	Cl_2Ti_1(cr)	865
Titanium chloride ($TiCl_2$)	Cl_2Ti_1(g)	866
Titanium chloride ($TiCl_3$)	Cl_3Ti_1(cr)	886
Titanium chloride ($TiCl_3$)	Cl_3Ti_1(g)	887
Titanium chloride ($TiCl_4$)	Cl_4Ti_1(g)	906
Titanium chloride ($TiCl_4$)	Cl_4Ti_1(cr,l)	905
Titanium chloride ($TiCl_4$)	Cl_4Ti_1(l)	904
Titanium chloride ($TiCl_4$)	Cl_4Ti_1(cr)	903
Titanium chloride oxide (OTiCl)	$Cl_1O_1Ti_1$(g)	796
Titanium chloride oxide ($TiOCl_2$)	$Cl_2O_1Ti_1$(g)	843
Titanium fluoride (TiF)	F_1Ti_1(g)	1096
Titanium fluoride (TiF_2)	F_2Ti_1(g)	1153
Titanium fluoride (TiF_3)	F_3Ti_1(cr)	1173
Titanium fluoride (TiF_3)	F_3Ti_1(g)	1174
Titanium fluoride (TiF_4)	F_4Ti_1(cr)	1191
Titanium fluoride (TiF_4)	F_4Ti_1(g)	1192
Titanium fluoride oxide (OTiF)	$F_1O_1Ti_1$(g)	1082
Titanium fluoride oxide ($OTiF_2$)	$F_2O_1Ti_1$(g)	1132
Titanium hydride (TiH_2)	H_2Ti_1(cr)	1341
Titanium iodide (TiI)	I_1Ti_1(g)	1411
Titanium iodide (TiI_2)	I_2Ti_1(cr)	1437
Titanium iodide (TiI_2)	I_2Ti_1(g)	1438
Titanium iodide (TiI_3)	I_3Ti_1(cr)	1446
Titanium iodide (TiI_3)	I_3Ti_1(g)	1447
Titanium iodide (TiI_4)	I_4Ti_1(cr)	1457
Titanium iodide (TiI_4)	I_4Ti_1(l)	1458
Titanium iodide (TiI_4)	I_4Ti_1(cr,l)	1459
Titanium iodide (TiI_4)	I_4Ti_1(g)	1460
Titanium, ion (Ti^+)	Ti_1^+(g)	1913
Titanium, ion (Ti^-)	Ti_1^-(g)	1914
Titanium nitride (TiN)	N_1Ti_1(cr,l)	1614
Titanium nitride (TiN)	N_1Ti_1(l)	1613
Titanium nitride (TiN)	N_1Ti_1(cr)	1612
Titanium oxide (Ti_2O_3)	O_3Ti_2(l)	1777
Titanium oxide (Ti_2O_3)	O_3Ti_2(cr)	1776
Titanium oxide (Ti_2O_3)	O_3Ti_2(cr,l)	1778
Titanium oxide (Ti_3O_5)	O_5Ti_3(l)	1798
Titanium oxide (Ti_3O_5)	O_5Ti_3(cr,l)	1799
Titanium oxide (Ti_4O_7)	O_7Ti_4(cr,l)	1807
Titanium oxide (Ti_4O_7)	O_7Ti_4(l)	1806
Titanium oxide (Ti_4O_7)	O_7Ti_4(cr)	1805
Titanium oxide (TiO)	O_1Ti_1(g)	1738
Titanium oxide (TiO)	O_1Ti_1(cr,l)	1737
Titanium oxide (TiO)	O_1Ti_1(l)	1736
Titanium oxide (TiO_2)	O_2Ti_1(g)	1762
Titanium oxide (TiO_2)	O_2Ti_1(cr,l)	1761
Titanium oxide (TiO_2)	O_2Ti_1(l)	1760
Titanium oxide, alpha (Ti_3O_5)	O_5Ti_3(cr)	1796
Titanium oxide, alpha (TiO)	O_1Ti_1(cr)	1734
Titanium oxide, anatase (TiO_2)	O_2Ti_1(cr)	1758
Titanium oxide, beta (Ti_3O_5)	O_5Ti_3(cr)	1797
Titanium oxide, beta (TiO)	O_1Ti_1(cr)	1735
Titanium oxide, rutile (TiO_2)	O_2Ti_1(cr)	1759
Tribromoborane (BBr_3)	B_1Br_3(g)	196
Tribromoborane (BBr_3)	B_1Br_3(l)	295
Tribromosilane ($SiHBr_3$)	$Br_3H_1Si_1$(g)	514
Tribromosilyl ($SiBr_3$)	Br_3Si_1(g)	520
Trichloroborane (BCl_3)	B_1Cl_3(g)	207
Trichloroboroxin ($B_3O_3Cl_3$)	$B_3Cl_3O_3$(g)	232
Trichlorofluorosilane ($SiCl_3F$)	$Cl_3F_1Si_1$(g)	875
Trichloromethane ($CHCl_3$)	$C_1H_1Cl_3$(g)	596
Trichloromethyl (CCl_3)	C_1Cl_3(g)	574
Trichloromethylsilane ($SiCH_3Cl_3$)	$C_1H_3Cl_3Si_1$(g)	612
Trichlorosilane ($SiHCl_3$)	$Cl_3H_1Si_1$(g)	880
Trichlorosilyl ($SiCl_3$)	Cl_3Si_1(g)	885
Trichlorofluoromethane (CCl_3F)	$C_1Cl_3F_1$(g)	575
Trifluoriodomethane (CIF_3)	$C_1F_3I_1$(g)	587
Trifluoroacetonitrile (CF_3CN)	$C_2F_3N_1$(g)	669
Trifluoroborane (BF_3)	B_1F_3(g)	216
Trifluoroboroxin ($B_3O_3F_3$)	$B_3F_3O_3$(g)	286
Trifluoroboroxin ($B_3O_3F_3$)	$B_3F_3O_3$(cr)	285
Trifluoromethane (CHF_3)	$C_1H_1F_3$(g)	599
Trifluoromethyl (CF_3)	C_1F_3(g)	585
Trifluoromethyl hypofluorite (CF_3OF)	$C_1F_4O_1$(g)	589
Trifluoromethyl, ion (CF_3^+)	$C_1F_3^+$(g)	586
Trifluoromethylsilane ($SiCH_3F_3$)	$C_1H_3F_3Si_1$(g)	614
Trifluorosilane ($SiHF_3$)	$F_3H_1Si_1$(g)	1160
Trifluorosilyl (SiF_3)	F_3Si_1(g)	1172
Triiodoborane (BI_3)	B_1I_3(g)	239
Triiodosilane ($SiHI_3$)	$H_1I_3Si_1$(g)	1266
Triiodosilyl (SiI_3)	I_3Si_1(g)	1445
Tungsten (W)	W_1(g)	1929
Tungsten (W)	W_1(cr,l)	1928
Tungsten (W)	W_1(l)	1927
Tungsten (W)	W_1(cr)	1926
Tungsten (W)	W_1(ref)	1925
Tungsten bromide (WBr)	Br_1W_1(g)	468

Table Title	Formula	Page
Tungsten bromide (WBr_5)	Br_5W_1(cr)	542
Tungsten bromide (WBr_5)	Br_5W_1(l)	543
Tungsten bromide (WBr_5)	Br_5W_1(cr,l)	544
Tungsten bromide (WBr_5)	Br_5W_1(g)	545
Tungsten bromide (WBr_6)	Br_6W_1(cr)	546
Tungsten bromide (WBr_6)	Br_6W_1(g)	547
Tungsten chloride ($(WCl_5)_2$)	$Cl_{10}W_2$(g)	936
Tungsten chloride (WCl)	Cl_1W_1(g)	809
Tungsten chloride (WCl_2)	Cl_2W_1(g)	868
Tungsten chloride (WCl_2)	Cl_2W_1(cr)	867
Tungsten chloride (WCl_4)	Cl_4W_1(g)	908
Tungsten chloride (WCl_4)	Cl_4W_1(cr)	907
Tungsten chloride (WCl_5)	Cl_5W_1(cr,l)	926
Tungsten chloride (WCl_5)	Cl_5W_1(g)	927
Tungsten chloride (WCl_5)	Cl_5W_1(l)	925
Tungsten chloride (WCl_5)	Cl_5W_1(cr)	924
Tungsten chloride (WCl_6)	Cl_6W_1(l)	933
Tungsten chloride (WCl_6)	Cl_6W_1(cr,l)	934
Tungsten chloride (WCl_6)	Cl_6W_1(g)	935
Tungsten chloride, alpha (WCl_6)	Cl_6W_1(cr)	931
Tungsten chloride, beta (WCl_6)	Cl_6W_1(cr)	932
Tungsten chloride oxide ($OWCl_4$)	$Cl_4O_1W_1$(g)	900
Tungsten chloride oxide ($OWCl_4$)	$Cl_4O_1W_1$(cr,l)	899
Tungsten chloride oxide ($OWCl_4$)	$Cl_4O_1W_1$(cr)	897
Tungsten chloride oxide ($OWCl_4$)	$Cl_4O_1W_1$(l)	898
Tungsten chloride oxide (WO_2Cl_2)	$Cl_2O_2W_1$(g)	849
Tungsten chloride oxide (WO_2Cl_2)	$Cl_2O_2W_1$(cr)	848
Tungsten fluoride (WF)	F_1W_1(g)	1097
Tungsten fluoride (WF_6)	F_6W_1(l)	1207
Tungsten fluoride (WF_6)	F_6W_1(g)	1208
Tungsten fluoride oxide (WF_4O)	$F_4O_1W_1$(g)	1185
Tungsten fluoride oxide (WF_4O)	$F_4O_1W_1$(l)	1183
Tungsten fluoride oxide (WF_4O)	$F_4O_1W_1$(cr,l)	1184
Tungsten fluoride oxide (WF_4O)	$F_4O_1W_1$(cr)	1182
Tungsten, ion (W^+)	W_1^+(g)	1930
Tungsten, ion (W^-)	W_1^-(g)	1931
Tungsten oxide ($(WO_3)_2$)	O_6W_2(g)	1804
Tungsten oxide ($(WO_3)_3$)	O_9W_3(g)	1809
Tungsten oxide ($(WO_3)_4$)	$O_{12}W_4$(g)	1812
Tungsten oxide (W_3O_8)	O_8W_3(g)	1808
Tungsten oxide (WO)	O_1W_1(g)	1743
Tungsten oxide ($WO_{2.72}$)	$O_{2.72}W_1$(cr)	1766
Tungsten oxide ($WO_{2.90}$)	$O_{2.90}W_1$(cr)	1767
Tungsten oxide ($WO_{2.96}$)	$O_{2.96}W_1$(cr)	1768
Tungsten oxide (WO_2)	O_2W_1(cr	1764
Tungsten oxide (WO_2)	O_2W_1(g)	1765
Tungsten oxide (WO_3)	O_3W_1(g)	1785
Tungsten oxide (WO_3)	O_3W_1(cr)	1782
Tungsten oxide (WO_3)	O_3W_1(cr,l)	1784
Tungsten oxide (WO_3)	O_3W_1(l)	1783
Tungstic acid ($O_2W(OH)_2$)	$H_2O_4W_1$(g)	1338
Tungstic acid ($O_2W(OH)_2$)	$H_2O_4W_1$(cr)	1337
Vanadium (V)	V_1(g)	1921
Vanadium (V)	V_1(cr,l)	1920
Vanadium (V)	V_1(ref)	1917
Vanadium (V)	V_1(cr)	1918
Vanadium (V)	V_1(l)	1919
Vanadium, ion (V^+)	V_1^+(g)	1922
Vanadium, ion (V^-)	V_1^-(g)	1923
Vanadium nitride (VN)	N_1V_1(g)	1616
Vanadium nitride (VN)	N_1V_1(cr)	1615
Vanadium nitride ($VN_{0.465}$)	$N_{0.465}V_1$(cr)	1599
Vanadium oxide (V_2O_3)	O_3V_2(cr)	1779
Vanadium oxide (V_2O_3)	O_3V_2(l)	1780
Vanadium oxide (V_2O_3)	O_3V_2(cr,l)	1781
Vanadium oxide (V_2O_4)	O_4V_2(cr,l)	1792
Vanadium oxide (V_2O_4)	O_4V_2(l)	1791
Vanadium oxide (V_2O_4)	O_4V_2(cr)	1790
Vanadium oxide (V_2O_5)	O_5V_2(cr,l)	1802
Vanadium oxide (V_2O_5)	O_5V_2(l)	1801
Vanadium oxide (V_2O_5)	O_5V_2(cr)	1800
Vanadium oxide (VO)	O_1V_1(g)	1742
Vanadium oxide (VO)	O_1V_1(cr,l)	1741
Vanadium oxide (VO)	O_1V_1(l)	1740
Vanadium oxide (VO)	O_1V_1(cr)	1739
Vanadium oxide (VO_2)	O_2V_1(g)	1763
Water (H_2O)	H_2O_1(g)	1324
Water (H_2O)	H_2O_1(l)	1323
Water, 1 bar (H_2O)	H_2O_1(l,g)	1325
Water, 10 bar (H_2O)	H_2O_1(l,g)	1326
Water, 100 bar (H_2O)	H_2O_1(l,g)	1327
Water, 500 bar (H_2O)	H_2O_1(fl)	1328
Water, 5000 bar (H_2O)	H_2O_1(fl)	1329
Water−d_1 (HDO)	$D_1H_1O_1$(g)	1036
Water−d_2 (D_2O)	D_2O_1(g)	1045
Xenon (Xe)	Xe_1(ref)	1933
Xenon, ion (Xe^+)	Xe_1^+(g)	1934
Zinc (Zn)	Zn_1(g)	1939
Zinc (Zn)	Zn_1(cr,l)	1938
Zinc (Zn)	Zn_1(l)	1937
Zinc (Zn)	Zn_1(cr)	1936
Zinc (Zn)	Zn_1(ref)	1935
Zinc, ion (Zn^+)	Zn_1^+(g)	1940
Zinc, ion (Zn^-)	Zn_1^-(g)	1941
Zinc sulfate ($ZnSO_4$)	$O_4S_1Zn_1$(cr)	1788
Zirconium (Zr)	Zr_1(ref)	1943
Zirconium (Zr)	Zr_1(l)	1946
Zirconium (Zr)	Zr_1(cr,l)	1947
Zirconium (Zr)	Zr_1(g)	1948
Zirconium, alpha (Zr)	Zr_1(cr)	1944
Zirconium, beta (Zr)	Zr_1(cr)	1945
Zirconium boride (ZrB_2)	B_2Zr_1(cr,l)	281
Zirconium boride (ZrB_2)	B_2Zr_1(l)	280
Zirconium boride (ZrB_2)	B_2Zr_1(cr)	279
Zirconium bromide ($ZrBr$)	Br_1Zr_1(g)	469
Zirconium bromide ($ZrBr_2$)	Br_2Zr_1(g)	513
Zirconium bromide ($ZrBr_2$)	Br_2Zr_1(cr,l)	512
Zirconium bromide ($ZrBr_2$)	Br_2Zr_1(l)	511

Table Title	Formula	Page
Zirconium bromide ($ZrBr_2$)	Br_2Zr_1(cr)	510
Zirconium bromide ($ZrBr_3$)	Br_3Zr_1(g)	524
Zirconium bromide ($ZrBr_3$)	Br_3Zr_1(cr)	523
Zirconium bromide ($ZrBr_4$)	Br_4Zr_1(g)	537
Zirconium bromide ($ZrBr_4$)	Br_4Zr_1(cr)	536
Zirconium carbide (ZrC)	C_1Zr_1(cr,l)	660
Zirconium carbide (ZrC)	C_1Zr_1(l)	659
Zirconium carbide (ZrC)	C_1Zr_1(cr)	658
Zirconium chloride (ZrCl)	Cl_1Zr_1(g)	810
Zirconium chloride ($ZrCl_2$)	Cl_2Zr_1(cr)	869
Zirconium chloride ($ZrCl_2$)	Cl_2Zr_1(l)	870
Zirconium chloride ($ZrCl_2$)	Cl_2Zr_1(cr,l)	871
Zirconium chloride ($ZrCl_2$)	Cl_2Zr_1(g)	872
Zirconium chloride ($ZrCl_3$)	Cl_3Zr_1(cr)	888
Zirconium chloride ($ZrCl_3$)	Cl_3Zr_1(g)	889
Zirconium chloride ($ZrCl_4$)	Cl_4Zr_1(cr)	909
Zirconium chloride ($ZrCl_4$)	Cl_4Zr_1(g)	910
Zirconium fluoride (ZrF)	F_1Zr_1(g)	1098
Zirconium fluoride (ZrF_2)	F_2Zr_1(g)	1157
Zirconium fluoride (ZrF_2)	F_2Zr_1(cr,l)	1156
Zirconium fluoride (ZrF_2)	F_2Zr_1(cr)	1154
Zirconium fluoride (ZrF_2)	F_2Zr_1(l)	1155
Zirconium fluoride (ZrF_3)	F_3Zr_1(g)	1176
Zirconium fluoride (ZrF_3)	F_3Zr_1(cr)	1175
Zirconium fluoride (ZrF_4)	F_4Zr_1(g)	1194
Zirconium fluoride (ZrF_4)	F_4Zr_1(cr)	1193
Zirconium hydride (ZrH)	H_1Zr_1(g)	1309
Zirconium iodide (ZrI)	I_1Zr_1(g)	1412
Zirconium iodide (ZrI_2)	I_2Zr_1(g)	1442
Zirconium iodide (ZrI_2)	I_2Zr_1(cr,l)	1441
Zirconium iodide (ZrI_2)	I_2Zr_1(l)	1440
Zirconium iodide (ZrI_2)	I_2Zr_1(cr)	1439
Zirconium iodide (ZrI_3)	I_3Zr_1(g)	1449
Zirconium iodide (ZrI_3)	I_3Zr_1(cr)	1448
Zirconium iodide (ZrI_4)	I_4Zr_1(g)	1462
Zirconium iodide (ZrI_4)	I_4Zr_1(cr)	1461
Zirconium, ion (Zr^+)	Zr_1^+(g)	1949
Zirconium, ion (Zr^-)	Zr_1^-(g)	1950
Zirconium nitride (ZrN)	N_1Zr_1(g)	1620
Zirconium nitride (ZrN)	N_1Zr_1(cr)	1617
Zirconium nitride (ZrN)	N_1Zr_1(l)	1618
Zirconium nitride (ZrN)	N_1Zr_1(cr,l)	1619
Zirconium oxide (ZrO)	O_1Zr_1(g)	1744
Zirconium oxide (ZrO_2)	O_2Zr_1(cr)	1769
Zirconium oxide (ZrO_2)	O_2Zr_1(l)	1770
Zirconium oxide (ZrO_2)	O_2Zr_1(cr,l)	1771
Zirconium oxide (ZrO_2)	O_2Zr_1(g)	1772
Zirconium silicate ($ZrSiO_4$)	$O_4Si_1Zr_1$(cr)	1789

REFERENCE STATE

0	to	933.45 K	crystal
933.45	to	2790.812 K	liquid
above		2790.812 K	*ideal monatomic gas*

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.539	0.	0.	0.
100	12.997	6.987	47.543	−4.056	0.	0.	0.
200	21.338	19.144	30.413	−2.254	0.	0.	0.
250	23.084	24.108	28.668	−1.140	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
400	25.784	35.630	29.248	2.553	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	___ CRYSTAL <--> LIQUID ___		
933.450	31.751	71.213	40.474	28.693	TRANSITION		
1000	31.751	73.400	42.594	30.806	0.	0.	0.
1100	31.751	76.426	45.534	33.981	0.	0.	0.
1200	31.751	79.189	48.225	37.156	0.	0.	0.
1300	31.751	81.730	50.706	40.331	0.	0.	0.
1400	31.751	84.083	53.007	43.506	0.	0.	0.
1500	31.751	86.273	55.153	46.681	0.	0.	0.
1600	31.751	88.323	57.162	49.856	0.	0.	0.
1700	31.751	90.247	59.052	53.031	0.	0.	0.
1800	31.751	92.062	60.836	56.207	0.	0.	0.
1900	31.751	93.779	62.525	59.382	0.	0.	0.
2000	31.751	95.408	64.129	62.557	0.	0.	0.
2100	31.751	96.957	65.656	65.732	0.	0.	0.
2200	31.751	98.434	67.112	68.907	0.	0.	0.
2300	31.751	99.845	68.505	72.082	0.	0.	0.
2400	31.751	101.196	69.839	75.257	0.	0.	0.
2500	31.751	102.493	71.120	78.432	0.	0.	0.
2600	31.751	103.738	72.350	81.607	0.	0.	0.
2700	31.751	104.936	73.535	84.782	0.	0.	0.
2790.812	31.751	105.986	74.574	87.665	___ LIQUID <--> IDEAL GAS ___		
2790.812	20.795	211.333	74.574	381.667	FUGACITY = 1 bar		
2800	20.795	211.401	75.023	381.858	0.	0.	0.
2900	20.796	212.131	79.738	383.938	0.	0.	0.
3000	20.798	212.836	84.163	386.017	0.	0.	0.
3100	20.800	213.518	88.325	388.097	0.	0.	0.
3200	20.804	214.178	92.248	390.178	0.	0.	0.
3300	20.808	214.818	95.952	392.258	0.	0.	0.
3400	20.815	215.440	99.458	394.339	0.	0.	0.
3500	20.823	216.043	102.780	396.421	0.	0.	0.
3600	20.833	216.630	105.934	398.504	0.	0.	0.
3700	20.846	217.201	108.934	400.588	0.	0.	0.
3800	20.862	217.757	111.790	402.673	0.	0.	0.
3900	20.881	218.299	114.515	404.760	0.	0.	0.
4000	20.904	218.828	117.116	406.849	0.	0.	0.
4100	20.932	219.345	119.603	408.941	0.	0.	0.
4200	20.964	219.849	121.984	411.036	0.	0.	0.
4300	21.002	220.343	124.265	413.134	0.	0.	0.
4400	21.046	220.826	126.455	415.236	0.	0.	0.
4500	21.088	221.299	128.557	417.341	0.	0.	0.
4600	21.143	221.763	130.578	419.452	0.	0.	0.
4700	21.206	222.219	132.523	421.570	0.	0.	0.
4800	21.276	222.666	134.396	423.694	0.	0.	0.
4900	21.352	223.105	136.202	425.824	0.	0.	0.
5000	21.439	223.537	137.945	427.964	0.	0.	0.
5100	21.535	223.963	139.627	430.112	0.	0.	0.
5200	21.641	224.382	141.253	432.271	0.	0.	0.
5300	21.757	224.795	142.825	434.441	0.	0.	0.
5400	21.884	225.203	144.347	436.623	0.	0.	0.
5500	22.021	225.606	145.821	438.818	0.	0.	0.
5600	22.170	226.004	147.249	441.027	0.	0.	0.
5700	22.330	226.398	148.634	443.252	0.	0.	0.
5800	22.496	226.787	149.978	445.491	0.	0.	0.
5900	22.680	227.173	151.284	447.749	0.	0.	0.
6000	22.836	227.552	152.551	450.005	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1983 (1 bar)

$S°(298.15\ K) = 28.275 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 933.45 \pm 0.01\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 10.711 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions for Al(cr) are derived from the studies of Giauque and Meads,[1] Berg,[2] Downie and Martin,[3] Takahashi,[4,5] McDonald,[6] Brooks,[7] Pochapsky[8] and Ditmars *et al.*[9] The mathematical and graphical treatment of these eight studies yields a continuous and smooth heat capacity curve. In contrast, CODATA[9] has recommended an $S°(298.15\ K)$ value which is $0.075\ J \cdot K^{-1} \cdot mol^{-1}$ greater than ours. Their result was based on an analysis of the low temperature heat capacity data of Giauque and Meads[1] and Berg.[2] At the time of their analysis, the studies of Downie and Martin[3] and Takahashi[4,5] had not been published. The three more recent studies[3,4,5,8] suggest a lower heat capacity in the vicinity of 298.15 K, thus the lower entropy in comparison with CODATA.[10]

Roberts[11] surveyed the superconductive properties of the elements and recommended a critical temperature of 1.175 ± 0.002 K for Al(cr). Since this temperature is so low, the effects of superconductivity on the thermodynamic functions are not considered. The entropy contribution due to superconductivity will be less than $0.002\ J \cdot K^{-1} \cdot mol^{-1}$. The data of Giauque and Meads[1] and Downie and Martin[3] agree at temperatures up to 150 K but drift apart by $0.2\ J \cdot K^{-1} \cdot mol^{-1}$ at 200 K and $0.17\ J \cdot K^{-1} \cdot mol^{-1}$ at 300 K, with the Downie and Martin study being lower. The Takahashi[4,5] study is even lower at ~298 K. The high temperature heat capacity values are derived from the enthalpy study of Ditmars *et al.*[9] Their curve is intermediate between those derived from previous studies[4,5,6,7,8] and implies a flatter C_p curve near the melting point (in comparison to previous interpretations). Numerous other heat capacity and enthalpy studies are available but were omitted in this analysis. A detailed discussion of the Group IIIA metals (B, Al, and Ga) is in preparation by the JANAF staff.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

There are no sublimation studies for Al(cr). The adopted value of $\Delta_{sub} H°(298.15\ K)$ is the value recommended by CODATA.[10] Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.539	0.	0.	0.
100	12.997	6.987	47.543	−4.056	0.	0.	0.
200	21.338	19.144	30.413	−2.254	0.	0.	0.
250	23.084	24.108	28.668	−1.140	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
350	25.113	32.231	28.574	1.280	0.	0.	0.
400	25.784	35.630	29.248	2.553	0.	0.	0.
450	26.335	38.699	30.130	3.856	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	--- CRYSTAL <--> LIQUID ---		
1000	34.358	62.055	41.834	20.221	−10.585	0.760	−0.040
1100	36.722	65.438	43.827	23.772	−10.209	1.878	−0.089
1200	39.408	68.746	45.766	27.576	−9.580	2.951	−0.128

PREVIOUS: June 1979 CURRENT: June 1983

$S°(298.15\ K) = [39.549]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 933.45 \pm 0.01\ K$

$\Delta_f H°(298.15\ K) = [10.562]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 10.711 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of liquid aluminum is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(933.45\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacity values are derived from the enthalpy study of McDonald.[1] The enthalpy data, ten experimental points in the liquid region (941–1647 K), were measured in crucibles of BN and TiB_2 sealed in a platinum–rhodium capsule. This containment procedure reduced the problem with the reactivity of liquid aluminum. This data suggests a constant liquid heat capacity of 7.589 $cal·K^{-1}·mol^{-1}$ for this 700 K range.

The liquid enthalpy data of Awbery and Griffiths,[2] four points in the liquid region (937–1036 K), agree within 1% with our adopted enthalpy values. The enthalpy studies of Wust *et al.*[3] and Umino[4] are lower by as much as 4% and 12%, respectively. The heat capacity values of Schmidt *et al.*,[5] 17 values in the range 933–1300 K, are not constant but lie 6–11% lower than our adopted values.

Fusion Data

There are numerous enthalpy of fusion studies reported in the literature. Twelve studies [1-3, 5-13] reported values in the range 2.46 to 2.66 $kcal·mol^{-1}$, with a rather isolated value at 2.15 $kcal·mol^{-1}$.[4] We adopt a value 2.560 ± 0.05 $kcal·mol^{-1}$ based on the enthalpy data of McDonald.[1] The chosen value has eliminated uncertainty due to reaction of liquid aluminum and its vessel by use of BN and TiB_2 containers.

The adopted melting temperature, T_{fus} = 933.45 K, is a secondary standard on IPTS–68.[14,15]

Vaporization Data

The vaporization studies are summarized on the Al(g) table. The boiling point (fugacity of one bar), T_{vap} = 2790.812 K, is calculated as the temperature for which $\Delta_f G° = 0$ for Al(l) ≈ Al(g). The difference in the enthalpy of formation of Al(l) and Al(g) at T_{vap} is the enthalpy of vaporization, $\Delta_{vap}H° = 294.001\ kJ·mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	24.209	39.549	39.549	0.	10.562	7.201	−1.262
300	24.247	39.699	39.550	0.045	10.562	7.180	−1.250
350	25.113	43.505	39.848	1.280	10.562	6.617	−0.987
400	25.784	46.904	40.522	2.553	10.562	6.053	−0.790
450	26.335	49.973	41.404	3.856	10.562	5.489	−0.637
500	26.842	52.774	42.403	5.186	10.562	4.926	−0.515
600	27.886	57.759	44.557	7.921	10.562	3.798	−0.331
700	29.100	62.146	46.762	10.769	10.562	2.671	−0.199
720.000	29.371	62.969	47.201	11.353	GLASS <--> LIQUID		
720.000	31.751	62.969	47.201	11.353	TRANSITION		
800	31.751	66.315	48.948	13.893	10.706	1.535	−0.100
900	31.751	70.054	51.089	17.068	10.740	0.384	−0.022
933.450	31.751	71.213	51.790	18.131	--- CRYSTAL <--> LIQUID ---		
1000	31.751	73.400	53.156	20.244	0.	0.	0.
1100	31.751	76.426	55.136	23.419	0.	0.	0.
1200	31.751	79.189	57.027	26.594	0.	0.	0.
1300	31.751	81.730	58.831	29.769	0.	0.	0.
1400	31.751	84.083	60.552	32.944	0.	0.	0.
1500	31.751	86.273	62.194	36.119	0.	0.	0.
1600	31.751	88.323	63.764	39.294	0.	0.	0.
1700	31.751	90.247	65.266	42.469	0.	0.	0.
1800	31.751	92.062	66.704	45.644	0.	0.	0.
1900	31.751	93.779	68.085	48.819	0.	0.	0.
2000	31.751	95.408	69.410	51.994	0.	0.	0.
2100	31.751	96.957	70.686	55.169	0.	0.	0.
2200	31.751	98.434	71.914	58.344	0.	0.	0.
2300	31.751	99.845	73.098	61.519	0.	0.	0.
2400	31.751	101.196	74.240	64.694	0.	0.	0.
2500	31.751	102.493	75.345	67.870	0.	0.	0.
2600	31.751	103.738	76.413	71.045	0.	0.	0.
2700	31.751	104.936	77.447	74.220	0.	0.	0.
2790.812	31.751	105.986	78.359	77.103	---- FUGACITY = 1 bar ----		
2800	31.751	106.091	78.450	77.395	−293.901	0.968	−0.018
2900	31.751	107.205	79.422	80.570	−292.806	11.499	−0.207
3000	31.751	108.281	80.366	83.745	−291.710	21.953	−0.382

PREVIOUS: June 1979 CURRENT: June 1983

CRYSTAL-LIQUID

0	to	933.45 K	crystal
above		933.45 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−4.539	0.	0.	0.
100	12.997	6.987	47.543	−4.056	0.	0.	0.
200	21.338	19.144	30.413	−2.254	0.	0.	0.
250	23.084	24.108	28.668	−1.140	0.	0.	0.
298.15	24.209	28.275	28.275	0.	0.	0.	0.
300	24.247	28.425	28.276	0.045	0.	0.	0.
350	25.113	32.231	28.574	1.280	0.	0.	0.
400	25.784	35.630	29.248	2.553	0.	0.	0.
450	26.335	38.699	30.130	3.856	0.	0.	0.
500	26.842	41.501	31.129	5.186	0.	0.	0.
600	27.886	46.485	33.283	7.921	0.	0.	0.
700	29.100	50.872	35.488	10.769	0.	0.	0.
800	30.562	54.850	37.663	13.749	0.	0.	0.
900	32.308	58.548	39.780	16.890	0.	0.	0.
933.450	32.959	59.738	40.474	17.982	____ CRYSTAL <--> LIQUID TRANSITION ____		
933.450	31.751	71.213	40.474	28.693			
1000	31.751	73.400	42.594	30.806	0.	0.	0.
1100	31.751	76.426	45.534	33.981	0.	0.	0.
1200	31.751	79.189	48.225	37.156	0.	0.	0.
1300	31.751	81.730	50.706	40.331	0.	0.	0.
1400	31.751	84.083	53.007	43.506	0.	0.	0.
1500	31.751	86.273	55.153	46.681	0.	0.	0.
1600	31.751	88.323	57.162	49.856	0.	0.	0.
1700	31.751	90.247	59.052	53.031	0.	0.	0.
1800	31.751	92.062	60.836	56.207	0.	0.	0.
1900	31.751	93.779	62.525	59.382	0.	0.	0.
2000	31.751	95.408	64.129	62.557	0.	0.	0.
2100	31.751	96.957	65.656	65.732	0.	0.	0.
2200	31.751	98.434	67.112	68.907	0.	0.	0.
2300	31.751	99.845	68.505	72.082	0.	0.	0.
2400	31.751	101.196	69.839	75.257	0.	0.	0.
2500	31.751	102.493	71.120	78.432	0.	0.	0.
2600	31.751	103.738	72.350	81.607	0.	0.	0.
2700	31.751	104.936	73.535	84.782	0.	0.	0.
2790.812	31.751	105.986	74.574	87.665	---- FUGACITY = 1 bar ----		
2800	31.751	106.091	74.677	87.957	−293.901	0.968	−0.018
2900	31.751	107.205	75.780	91.132	−292.805	11.479	−0.207
3000	31.751	108.281	76.846	94.307	−291.710	21.953	−0.382

PREVIOUS: CURRENT: June 1983

IP(Al, g) = 48278.37 ± 0.02 cm^{-1}
$S°$(298.15 K) = 164.553 ± 0.03 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 327.3 ± 4.2 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 329.7 ± 4.2 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P°_{1/2}$	0	2
$^2P°_{3/2}$	112.061	4
$^2S_{1/2}$	25347.756	2
.	.	.
.	.	.
$^2D_{5/2}$	48182.	6
IP	48278.37	

Enthalpy of Formation

The enthalpy of formation is derived from the vaporization measurements of Brewer and Searcy (1383–1468 K),[1] Porter *et al.* (932 K),[2] Potter and Hildenbrand (1400–1611 K),[3] Rao and Motzfeld (1556 K),[4] and Johnson *et al.* (1327 K).[5] The adopted value $\Delta_f H°$(Al, g, 298.15 K) = 78.8 ± 1.0 $kcal·mol^{-1}$ is that adopted by CODATA.[6] The difference in $S°$(Al, cr, 298.15 K) between our adopted value and that of CODATA[6] would create a change of only 0.02 $kcal^{-1}·mol^{-1}$in $\Delta_f H°$(Al, g, 298.15 K). Other vaporization studies have been omitted in this analysis: Farkas (1476 K)[7] Baur and Brunner (1734–2237 K),[8] and Priselkov *et al.* (1273–1473 K).[9]

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Martin and Zalubas.[10] Although we list only the ground state, the two lowest excited states, the highest observed excited state (below the ionization limit), and the ionization potential for Al(g), all levels below the ionization limit listed by Martin and Zalubas[10] are used in the calculation. The 105 observed levels below the ionization limit are too numerous to list completely. However, they include contributions from observed levels to n = 35. The contributions are from excitations of the 3p electron in the ground state configuration, $1s^22s^22p^63s^23p$. There is a contribution at ~29000 cm^{-1} due to the excitation of a 3s electron, giving rise to a $1s^22s^22p^63s3p^2$ configuration. Other contributions of this latter type lie above the ionization limit.

The electronic level at 112.061 cm^{-1} has a significant effect on the thermodynamic values at low temperatures. The higher electronic states have an effect on the values above 3000 K. The Gibbs energy function values up to 4000 K are essentially independent of the estimated missing levels (for n < 35), the cut-off procedure, and the inclusion of levels for n > 3.

The thermal functions at 298.15 K agree with recent CODATA recommendations[6] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, an entropy difference of 0.004 $J·K^{-1}·mol^{-1}$ arises due to the use of slightly different values for the fundamental constants.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.919	327.320	327.320	INFINITE
100	25.192	139.619	184.197	−4.458	329.297	316.034	−165.079
200	22.133	155.883	166.528	−2.129	329.824	302.476	−78.999
250	21.650	160.764	164.907	−1.036	329.804	295.639	−61.770
298.15	21.390	164.553	164.553	0.	329.699	289.068	−50.643
300	21.383	164.686	164.554	0.040	329.694	288.816	−50.287
350	21.221	167.969	164.813	1.104	329.524	282.016	−42.089
400	21.117	170.795	165.388	2.163	329.309	275.243	−35.943
450	21.046	173.278	166.130	3.217	329.060	268.499	−31.167
500	20.995	175.492	166.957	4.268	328.781	261.785	−27.348
600	20.930	179.314	168.708	6.363	328.141	248.444	−21.629
700	20.891	182.537	170.460	8.454	327.385	235.219	−17.552
800	20.866	185.325	172.147	10.542	326.492	222.112	−14.502
900	20.849	187.781	173.751	12.628	325.436	209.126	−12.137
1000	20.836	189.977	175.266	14.712	313.605	197.027	−10.292
1100	20.827	191.963	176.695	16.795	312.513	185.422	−8.805
1200	20.821	193.775	178.044	18.877	311.420	173.917	−7.570
1300	20.816	195.441	179.319	20.959	310.327	162.503	−6.529
1400	20.811	196.984	180.526	23.041	309.233	151.172	−5.640
1500	20.808	198.419	181.672	25.122	308.139	139.921	−4.872
1600	20.805	199.762	182.761	27.202	307.045	128.742	−4.203
1700	20.803	201.023	183.798	29.283	305.950	117.631	−3.614
1800	20.801	202.212	184.789	31.363	304.856	106.585	−3.093
1900	20.800	203.337	185.736	33.443	303.760	95.600	−2.628
2000	20.798	204.404	186.643	35.523	302.665	84.673	−2.211
2100	20.797	205.419	187.513	37.603	301.570	73.800	−1.836
2200	20.796	206.386	188.349	39.682	300.475	62.979	−1.495
2300	20.795	207.311	189.153	41.762	299.379	52.209	−1.186
2400	20.795	208.196	189.928	43.841	298.284	41.486	−0.903
2500	20.794	209.044	190.676	45.921	297.188	30.808	−0.644
2600	20.794	209.860	191.398	48.000	296.092	20.175	−0.405
2700	20.794	210.645	192.097	50.080	294.997	9.583	−0.185
2790.812	20.795	211.333	192.712	51.968	---- FUGACITY = 1 bar ----		
2800	20.795	211.401	192.773	52.159	0.	0.	0.
2900	20.796	212.131	193.428	54.239	0.	0.	0.
3000	20.798	212.836	194.063	56.318	0.	0.	0.
3100	20.800	213.518	194.680	58.398	0.	0.	0.
3200	20.804	214.178	195.279	60.478	0.	0.	0.
3300	20.808	214.818	195.861	62.559	0.	0.	0.
3400	20.815	215.440	196.428	64.640	0.	0.	0.
3500	20.823	216.043	196.980	66.722	0.	0.	0.
3600	20.833	216.630	197.518	68.805	0.	0.	0.
3700	20.846	217.201	198.042	70.889	0.	0.	0.
3800	20.862	217.757	198.553	72.974	0.	0.	0.
3900	20.881	218.299	199.053	75.061	0.	0.	0.
4000	20.904	218.828	199.541	77.150	0.	0.	0.
4100	20.932	219.345	200.017	79.242	0.	0.	0.
4200	20.964	219.849	200.484	81.337	0.	0.	0.
4300	21.002	220.343	200.940	83.435	0.	0.	0.
4400	21.046	220.826	201.386	85.537	0.	0.	0.
4500	21.088	221.299	201.823	87.642	0.	0.	0.
4600	21.143	221.763	202.252	89.753	0.	0.	0.
4700	21.206	222.219	202.672	91.870	0.	0.	0.
4800	21.276	222.666	203.084	93.995	0.	0.	0.
4900	21.352	223.105	203.488	96.125	0.	0.	0.
5000	21.439	223.537	203.885	98.264	0.	0.	0.
5100	21.535	223.963	204.274	100.413	0.	0.	0.
5200	21.641	224.382	204.657	102.572	0.	0.	0.
5300	21.757	224.795	205.033	104.742	0.	0.	0.
5400	21.884	225.203	205.403	106.924	0.	0.	0.
5500	22.021	225.606	205.766	109.119	0.	0.	0.
5600	22.170	226.004	206.124	111.328	0.	0.	0.
5700	22.330	226.398	206.476	113.553	0.	0.	0.
5800	22.496	226.787	206.823	115.792	0.	0.	0.
5900	22.680	227.173	207.165	118.050	0.	0.	0.
6000	22.836	227.552	207.501	120.306	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1983 (1 bar)

IP(Al^+, g) = 151862.7 ± 0.4 cm^{-1}
$S°(298.15\ K)$ = 149.950 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 904.86 ± 4.2 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [912.713] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.00	1
$^3P_0$	37393.03	1
$^3P_1$	37453.91	3
$^3P_2$	37577.79	5
$^1P_1$	59852.02	3

Enthalpy of Formation

$\Delta_f H°(Al^+, g, 0\ K)$ is calculated from $\Delta_f H°(Al, g, 0\ K)$[1] using the spectroscopic value of IP(Al) = 48278.37 ± 0.02 cm^{-1}(577.538 ± 0.0002 $kJ·mol^{-1}$) from Martin and Zalubas.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Al^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Al, g, 0\ K)$ by using IP(Al) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Al(g), $Al^+(g)$, and e^-(ref). $\Delta_f H°(Al \rightarrow Al^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Martin and Zalubas,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is 85481.35 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: Al(g), 6–30–83; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	904.858		
100	20.786	127.243	168.431	−4.119			
200	20.786	141.651	151.852	−2.040			
250	20.786	146.289	150.292	−1.001			
298.15	20.786	149.950	149.950	0.	912.713	870.181	−152.452
300	20.786	150.079	149.951	0.038	912.745	869.917	−151.466
350	20.786	153.283	150.204	1.078	913.589	862.712	−128.753
400	20.786	156.059	150.766	2.117	914.394	855.388	−111.702
450	20.786	158.507	151.493	3.156	915.169	847.965	−98.429
500	20.786	160.697	152.306	4.196	915.919	840.458	−87.802
600	20.786	164.487	154.029	6.274	917.340	825.230	−71.843
700	20.786	167.691	155.758	8.353	918.650	809.774	−60.426
800	20.786	170.466	157.427	10.431	919.826	794.138	−51.852
900	20.786	172.915	159.014	12.510	920.843	778.364	−45.175
1000	20.786	175.105	160.516	14.589	911.084	763.246	−39.868
1100	20.786	177.086	161.934	16.667	912.066	748.415	−35.539
1200	20.786	178.894	163.273	18.746	913.049	733.494	−31.928
1300	20.786	180.558	164.539	20.824	914.031	718.492	−28.869
1400	20.786	182.099	165.739	22.903	915.013	703.413	−26.245
1500	20.786	183.533	166.878	24.982	915.995	688.265	−23.968
1600	20.786	184.874	167.961	27.060	916.977	673.051	−21.973
1700	20.786	186.134	168.994	29.139	917.959	657.775	−20.211
1800	20.786	187.322	169.979	31.217	918.941	642.442	−18.643
1900	20.786	188.446	170.922	33.296	919.924	627.054	−17.239
2000	20.786	189.512	171.825	35.375	920.906	611.615	−15.974
2100	20.786	190.527	172.692	37.453	921.888	596.126	−14.828
2200	20.786	191.493	173.524	39.532	922.870	580.590	−13.785
2300	20.786	192.417	174.326	41.610	923.852	565.010	−12.832
2400	20.786	193.302	175.098	43.689	924.834	549.387	−11.957
2500	20.786	194.151	175.844	45.768	925.816	533.723	−11.152
2600	20.786	194.966	176.563	47.846	926.799	518.020	−10.407
2700	20.786	195.750	177.260	49.925	927.781	502.280	−9.717
2800	20.786	196.506	177.934	52.004	634.862	487.470	−9.094
2900	20.786	197.236	178.587	54.082	636.939	482.169	−8.685
3000	20.786	197.940	179.220	56.161	639.017	476.797	−8.302
3100	20.787	198.622	179.835	58.239	641.094	471.355	−7.942
3200	20.787	199.282	180.433	60.318	643.172	465.847	−7.604
3300	20.788	199.922	181.013	62.397	645.248	460.273	−7.286
3400	20.788	200.542	181.579	64.476	647.325	454.637	−6.985
3500	20.790	201.145	182.129	66.555	649.400	448.939	−6.700
3600	20.791	201.730	182.666	68.634	651.475	443.183	−6.430
3700	20.793	202.300	183.189	70.713	653.549	437.368	−6.175
3800	20.796	202.855	183.699	72.792	655.622	431.498	−5.931
3900	20.800	203.395	184.197	74.872	657.693	425.573	−5.700
4000	20.805	203.922	184.684	76.952	659.763	419.594	−5.479
4100	20.811	204.435	185.159	79.033	661.830	413.565	−5.269
4200	20.818	204.937	185.624	81.115	663.896	407.484	−5.068
4300	20.828	205.427	186.079	83.197	665.958	401.355	−4.875
4400	20.839	205.906	186.524	85.280	668.018	395.178	−4.691
4500	20.853	206.374	186.960	87.365	670.077	388.953	−4.515
4600	20.869	206.833	187.387	89.451	672.130	382.684	−4.346
4700	20.888	207.282	187.806	91.539	674.179	376.369	−4.183
4800	20.910	207.722	188.216	93.628	676.223	370.011	−4.027
4900	20.935	208.153	188.618	95.721	678.264	363.610	−3.876
5000	20.965	208.577	189.013	97.816	680.298	357.168	−3.731
5100	20.999	208.992	189.401	99.914	682.326	350.686	−3.592
5200	21.037	209.400	189.782	102.015	684.347	344.163	−3.457
5300	21.079	209.801	190.156	104.121	686.362	337.602	−3.327
5400	21.127	210.196	190.523	106.232	688.369	331.003	−3.202
5500	21.181	210.584	190.884	108.347	690.368	324.366	−3.081
5600	21.240	210.966	191.240	110.468	692.358	317.694	−2.963
5700	21.305	211.342	191.589	112.595	694.339	310.986	−2.850
5800	21.376	211.714	191.933	114.729	696.313	304.243	−2.740
5900	21.453	212.080	192.271	116.870	698.274	297.466	−2.634
6000	21.538	212.441	192.604	119.020	700.247	290.654	−2.530

PREVIOUS: June 1979 (1 atm) CURRENT: June 1983 (1 bar)

EA(Al, g) = 0.441 ± 0.010 eV
$S°$(298.15 K) = 168.135 ± 0.08 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 284.77 ± 5.2 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [280.790] kJ·mol^{-1}

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0	1
$^3P_0$	26	3
$^3P_2$	76	5
$^1D_2$	2678	5

Enthalpy of Formation

$\Delta_f H°(Al^-, g, 0 K)$ is calculated from $\Delta_f H°(Al, g, 0 K)$[1] using the adopted election affinity of EA(Al) = 0.441 ± 0.010 eV (42.550 ± 0.965 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $Al^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Al^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Al, g, 0 K)$ by using EA(Al) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for $Al^-(g)$, Al(g), and e^-(ref). $\Delta_r H°(Al^- \rightarrow Al + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Al^-(g)$ is given by Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6] The fine-structure separation has been calculated via an isoelectronic extrapolation of ratios of fine structure separations[4] and is that recommended by Hotop and Lineberger.[2]

A comparison of the isoelectronic sequence – $Al^-(g)$, Si(g), $P^+(g)$, and $S^{++}(g)$ – would suggest that two states, $^1D_2$ and $^1S_0$, may exist at low wave numbers. Feigirle *et al.*[3] using laser photodetachment electron spectrometry, observed the bound state, $^1D_2$, at 0.332 eV. The $^1S_0$ state would correspond to a metastable state.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.756	284.770		
100	22.297	144.748	186.955	−4.221			
200	21.171	159.730	170.057	−2.065			
250	21.031	164.437	168.480	−1.011			
298.15	20.960	168.135	168.135	0.	280.790	245.345	−42.983
300	20.958	168.265	168.135	0.039	280.745	245.125	−42.680
350	20.921	171.492	168.390	1.086	279.518	239.285	−35.711
400	20.913	174.285	168.957	2.131	278.251	233.624	−30.508
450	20.933	176.749	169.688	3.177	276.954	228.123	−26.480
500	20.983	178.957	170.506	4.225	275.633	222.768	−23.272
600	21.163	182.797	172.244	6.332	272.926	212.448	−18.495
700	21.421	186.078	173.992	8.460	270.129	202.588	−15.117
800	21.715	188.957	175.686	10.617	267.226	193.136	−12.610
900	22.006	191.532	177.306	12.803	264.192	184.055	−10.682
1000	22.270	193.864	178.847	15.017	250.412	176.081	−9.198
1100	22.493	195.998	180.311	17.256	247.397	168.794	−8.015
1200	22.670	197.963	181.701	19.514	244.402	161.780	−7.042
1300	22.804	199.783	183.023	21.788	241.422	155.016	−6.229
1400	22.897	201.477	184.281	24.074	238.454	148.481	−5.540
1500	22.955	203.058	185.481	26.367	235.493	142.157	−4.950
1600	22.985	204.541	186.626	28.664	232.537	136.031	−4.441
1700	22.991	205.935	187.721	30.963	229.582	130.090	−3.997
1800	22.978	207.249	188.770	33.261	226.627	124.323	−3.608
1900	22.950	208.490	189.776	35.558	223.670	118.720	−3.264
2000	22.912	209.666	190.741	37.851	220.709	113.273	−2.958
2100	22.865	210.783	191.669	40.140	217.744	107.974	−2.686
2200	22.812	211.846	192.562	42.424	214.775	102.816	−2.441
2300	22.756	212.859	193.423	44.702	211.799	97.794	−2.221
2400	22.697	213.826	194.253	46.975	208.818	92.901	−2.022
2500	22.636	214.751	195.054	49.241	205.831	88.133	−1.841
2600	22.576	215.638	195.829	51.502	202.838	83.484	−1.677
2700	22.515	216.489	196.579	53.757	199.839	78.950	−1.527
2800	22.455	217.306	197.304	56.005	−97.067	75.496	−1.408
2900	22.397	218.093	198.008	58.248	−98.983	81.692	−1.471
3000	22.340	218.852	198.690	60.485	−100.904	87.955	−1.531
3100	22.285	219.583	199.352	62.716	−102.831	94.282	−1.589
3200	22.231	220.290	199.996	64.942	−104.764	100.672	−1.643
3300	22.180	220.973	200.621	67.162	−106.703	107.121	−1.696
3400	22.130	221.635	201.229	69.378	−108.647	113.630	−1.746
3500	22.082	222.275	201.822	71.588	−110.597	120.196	−1.794
3600	22.036	222.897	202.398	73.794	−112.552	126.818	−1.840
3700	21.992	223.500	202.961	75.996	−114.514	133.494	−1.885
3800	21.950	224.086	203.509	78.193	−116.480	140.223	−1.928
3900	21.910	224.656	204.044	80.386	−118.453	147.004	−1.969
4000	21.871	225.210	204.566	82.575	−120.432	153.836	−2.009
4100	21.834	225.749	205.076	84.760	−122.417	160.717	−2.048
4200	21.799	226.275	205.575	86.942	−124.409	167.647	−2.085
4300	21.765	226.788	206.062	89.120	−126.407	174.624	−2.121
4400	21.733	227.288	206.539	91.295	−128.413	181.648	−2.156
4500	21.702	227.776	207.005	93.466	−130.424	188.717	−2.191
4600	21.672	228.252	207.462	95.635	−132.446	195.832	−2.224
4700	21.644	228.718	207.909	97.801	−134.476	202.990	−2.256
4800	21.617	229.174	208.348	99.964	−136.515	210.192	−2.287
4900	21.591	229.619	208.777	102.124	−138.564	217.436	−2.318
5000	21.566	230.055	209.198	104.282	−140.624	224.722	−2.348
5100	21.543	230.482	209.612	106.438	−142.696	232.050	−2.377
5200	21.520	230.900	210.017	108.591	−144.780	239.418	−2.405
5300	21.498	231.310	210.415	110.742	−146.878	246.826	−2.433
5400	21.477	231.711	210.806	112.890	−148.990	254.275	−2.460
5500	21.457	232.105	211.189	115.037	−151.117	261.762	−2.486
5600	21.438	232.492	211.566	117.182	−153.260	269.288	−2.512
5700	21.419	232.871	211.937	119.325	−155.421	276.853	−2.537
5800	21.401	233.243	212.301	121.466	−157.597	284.455	−2.562
5900	21.384	233.609	212.659	123.605	−159.795	292.096	−2.586
6000	21.368	233.968	213.011	125.743	−161.991	299.771	−2.610

PREVIOUS: June 1979 (1 atm) CURRENT: June 1983 (1 bar)

$S°(298.15\ K) = [269.6 \pm 10]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -539.0 \pm 17\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -541.4 \pm 17\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[2000](1)	[600](1)
[1000](1)	[350](1)
[600](1)	[800](1)

Ground State Quantum Weight: [1] $\sigma = 1$

Point Group: [C_s]

Bond Distances: Al–O = [1.66] Å; O–B = [1.36] Å; B=O = [1.20] Å

Bond Angles: Al–O–B = [145]°; O–B=O = [180]°

Product of the Moments of Inertia: $I_A I_B I_C = [6.527732] \times 10^{-115}\ g^3\ cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(AlBO_2, g, 298.15\ K) = -129.4 \pm 4$ kcal·mol^{-1} is calculated from the enthalpy of reaction, $\Delta_r H°(1500\ K) = -14.7 \pm 3.2$ kcal·mol^{-1} for 1/2 $Al_2O(g)$ + 1/2 $B_2O_3(g)$ = $AlBO_2(g)$ with all JANAF auxiliary data. The value of $\Delta_r H°(1500\ K)$ was obtained from the mass spectrometric determination of ion intensity ratios by Buchler *et al.*[1]

Heat Capacity and Entropy

The bent molecular structure, the bond distances O–B and B=O, and the bond angle O–B–O are assumed to be the same as those in $LiBO_2(g)$. The bond distance Al–O and the bond angle Al–O–(BO) are estimated to be the same as those in $Al_2O(g)$. The principal moments of inertia are $I_A = 0.7404 \times 10^{-39}$, $I_B = 29.3249 \times 10^{-39}$, and $I_C = 30.0653 \times 10^{-39}$ g cm^2.

The vibrational frequencies were estimated by comparison with those in $LiBO_2(g)$, $Al_2O(g)$, $B_2O_3(g)$, and AlCl(g).

Reference

[1]A. Buchler, P. E. Blackburn, and J. L. Stauffer, ARPA Order No. 315–62, Arthur D. Little, Inc., Cambridge, MA.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.008	−538.981	−538.981	INFINITE
100	34.879	223.687	310.212	−8.653	−539.038	−543.346	283.815
200	43.736	250.340	274.120	−4.756	−540.187	−547.246	142.926
250	48.632	260.633	270.413	−2.445	−540.819	−548.937	114.694
298.15	52.833	269.567	269.567	0.	−541.410	−550.447	96.436
300	52.982	269.894	269.568	0.098	−541.432	−550.503	95.851
350	56.680	278.347	270.227	2.842	−542.026	−551.967	82.377
400	59.785	286.124	271.734	5.756	−542.616	−553.347	72.260
450	62.400	293.321	273.738	8.812	−543.207	−554.653	64.382
500	64.622	300.014	276.035	11.989	−543.805	−555.893	58.074
600	68.173	312.125	281.062	18.638	−545.033	−558.196	48.595
700	70.861	322.845	286.280	25.596	−546.332	−560.288	41.809
800	72.936	332.449	291.462	32.790	−547.739	−562.188	36.707
900	74.562	341.137	296.506	40.168	−549.289	−563.902	32.728
1000	75.853	349.062	301.371	47.691	−561.605	−564.675	29.496
1100	76.890	356.342	306.042	55.330	−563.180	−564.906	26.825
1200	77.731	363.070	310.518	63.062	−564.761	−564.993	24.594
1300	78.420	369.320	314.804	70.871	−566.352	−564.948	22.700
1400	78.991	375.153	318.908	78.743	−567.958	−564.780	21.072
1500	79.468	380.620	322.842	86.666	−569.585	−564.497	19.658
1600	79.870	385.761	326.615	94.634	−571.236	−564.104	18.416
1700	80.211	390.614	330.239	102.638	−572.915	−563.606	17.318
1800	80.503	395.207	333.722	110.674	−574.624	−563.010	16.338
1900	80.754	399.567	337.073	118.737	−576.367	−562.317	15.459
2000	80.972	403.715	340.303	126.824	−578.146	−561.532	14.666
2100	81.162	407.670	343.417	134.931	−579.962	−560.657	13.946
2200	81.328	411.449	346.424	143.056	−581.818	−559.694	13.289
2300	81.475	415.068	349.331	151.196	−583.714	−558.646	12.687
2400	81.605	418.538	352.142	159.350	−635.911	−556.446	12.111
2500	81.721	421.872	354.865	167.517	−637.970	−553.093	11.556
2600	81.824	425.079	357.505	175.694	−640.039	−549.657	11.043
2700	81.916	428.169	360.065	183.881	−642.119	−546.141	10.566
2800	81.999	431.150	362.551	192.077	−938.112	−541.580	10.103
2900	82.074	434.028	364.966	200.280	−939.120	−527.401	9.500
3000	82.142	436.812	367.315	208.491	−940.141	−513.186	8.935
3100	82.204	439.506	369.600	216.709	−941.174	−498.937	8.407
3200	82.260	442.117	371.826	224.932	−942.220	−484.655	7.911
3300	82.312	444.649	373.995	233.161	−943.278	−470.340	7.445
3400	82.359	447.107	376.109	241.394	−944.348	−455.992	7.005
3500	82.402	449.495	378.172	249.632	−945.431	−441.614	6.591
3600	82.442	451.817	380.185	257.875	−946.525	−427.203	6.199
3700	82.479	454.077	382.152	266.121	−947.632	−412.763	5.827
3800	82.513	456.277	384.074	274.370	−948.752	−398.291	5.475
3900	82.544	458.420	385.953	282.623	−949.883	−383.790	5.140
4000	82.573	460.511	387.791	290.879	−951.027	−369.261	4.822
4100	82.600	462.550	389.589	299.138	−952.184	−354.702	4.519
4200	82.625	464.541	391.350	307.399	−1433.203	−333.091	4.143
4300	82.649	466.485	393.075	315.663	−1433.298	−306.897	3.728
4400	82.671	468.385	394.765	323.929	−1433.410	−280.701	3.332
4500	82.691	470.243	396.422	332.197	−1433.536	−254.502	2.954
4600	82.710	472.061	398.047	340.467	−1433.682	−228.300	2.592
4700	82.728	473.840	399.640	348.739	−1433.846	−202.094	2.246
4800	82.745	475.582	401.204	357.012	−1434.031	−175.884	1.914
4900	82.761	477.288	402.740	365.288	−1434.237	−149.670	1.596
5000	82.776	478.960	404.248	373.565	−1434.466	−123.452	1.290
5100	82.790	480.600	405.729	381.843	−1434.720	−97.229	0.996
5200	82.804	482.208	407.184	390.123	−1435.002	−71.002	0.713
5300	82.816	483.785	408.614	398.404	−1435.312	−44.768	0.441
5400	82.828	485.333	410.021	406.686	−1435.653	−18.529	0.179
5500	82.840	486.853	411.404	414.969	−1436.027	7.717	−0.073
5600	82.850	488.346	412.765	423.254	−1436.437	33.972	−0.317
5700	82.860	489.812	414.104	431.539	−1436.885	60.233	−0.552
5800	82.870	491.253	415.421	439.826	−1437.370	86.502	−0.779
5900	82.879	492.670	416.719	448.113	−1437.900	112.779	−0.998
6000	82.888	494.063	417.996	456.402	−1438.455	139.065	−1.211

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 239.62 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 23.13 \pm 12.55\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 15.90 \pm 12.55\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	23663.	2
$a^3\Pi$	23795.3	2
	[23920]	[2]
$A^1\Pi$	35837.8	2
$[b^3\Sigma^+]$	[43000]	[3]

$\omega_e = 377.61\ cm^{-1}$ $\omega_e x_e = 1.3239\ cm^{-1}$ $\sigma = 1$
$B_e = 0.15871\ cm^{-1}$ $\alpha_e = 0.0008583\ cm^{-1}$ $r_e = 2.294803$ Å

Enthalpy of Formation

Ram,[1] Gaydon,[2] Singh,[3] Rosen[4] and Barrow[5] reference possible spectroscopic values for the dissociation energy of AlBr(g). The $A^1\Pi$ state yielded three values for the dissociation energy: 106.9 kcal·mol^{-1} by a short extrapolation, a minimum of 104.4 kcal·mol^{-1} as indicated by the highest observed vibrational level, and a maximum of 105.7 kcal·mol^{-1} as determined by predissociation which sets in at $v' = 4$. Ram[1] has observed rotational predissociation in the AlBr band system and reports the dissociation energy at 105.85 ± 0.46 kcal·mol^{-1}. Gaydon[2] reports a value of 86.5 kcal·mol^{-1} based on a ground state linear Birge–Sponer extrapolation (v, 0–11). However, substituting the values tabulated above for ω_e and $x_e\omega_e$ into the equation $D° = \omega_e^2/4X_e\omega_e - 0.5\omega_e$, a value of 76.5 kcal·mol^{-1} is obtained for the dissociation energy. A value of 105 kcal·mol^{-1} is suggested by Barrow[5] based on wavelengths for maximum photoionization.

Semenkovich[6] measured the vapor pressure of the reaction Al(l) + NaBr(l) → Na(g) + AlBr(g) at 1175 K. By the 3rd law method $\Delta_f H°$(298.15 K) is equal to 108.134 kcal·mol^{-1}. Using JANAF auxiliary data,[7] $\Delta_f H°$(AlBr, g, 298.15 K) is equal to 3.829 kcal·mol^{-1} and the dissociation energy is 100.87 kcal·mol^{-1}.

Gross[8] studied the equilibrium involved in the reaction 2 Al(l) + $AlBr_3$(g) → 3 AlBr(g) in the range 550 − 1300°C. The reported $\Delta_f H°$(298.15 K) is 106.27 kcal·mol^{-1}. Using auxiliary JANAF data,[7] $\Delta_f H°$(298.15 K) is 4.43 kcal·mol^{-1} and $D_0°$ is 100.26 kcal·mol^{-1}.

It should be noted that the highest observed vibrational level in the $A^1\Pi$ state lies approximately 4 kcal·mol^{-1} above the thermochemical dissociation energy of Semenkovich[6] and Gross.[8] This suggests a potential maximum in the $A^1\Pi$ state as mentioned by Barrow.[5] A similar maximum is suggested for AlF(g) and AlCl(g).[7,9,5] In addition, Wyse and Gordy,[10] from nuclear quadrupole coupling, deduce that the ionic character of the AlBr bond is ≥8%. Thus the value of $D_0° = 76.5$ kcal·mol^{-1} as obtained by a linear Birge–Sponer extrapolation is undoubtedly too low.[2] This ground state extrapolation was adjusted to 99.5 kcal·mol^{-1} and 102.2 kcal·mol^{-1} using two ionic character correction factors as suggested by Hildenbrand.[9] The former value is more suitable for metal fluorides while the latter is for the more general case. A comparison of $D_0°$ values[7,2,4] for the group IIIA gaseous monohalides suggests a value of 96−103 kcal·mol^{-1}, which is consistent with the value obtained by Semenkovich[6] and Gross.[8]

Due to the high ionic character in the AlBr bond and the possible unreliability of extrapolations of excited states which contain a potential maximum, the spectroscopic data is suspect as to the determination of $\Delta_f H°$(298.15 K). The chosen value for $\Delta_f H°$(298.15 K), 15.90 kJ·mol^{-1}, is a rounded value from the vapor pressure work of Semenkovich.[6]

Heat Capacity and Entropy

The spectroscopic constants for $Al^{79}Br$ and $Al^{81}Br$ were taken from Wyse and Gordy[10] and averaged according to the natural isotopic abundance of bromine. The electronic states are taken from Rosen[4] with the exception of the upper $^3\Pi$ state and the $b^3\Sigma^+$ state. The upper $^3\Pi$ state is estimated to be approximately in a linear relationship with the two lower $^3\Pi$ state. The $b^3\Sigma^+$ state is assigned by analogy with AlF and AlCl.[7] Lakshminarayana and Haranath[11] also reported values for two of the $a^3\Pi$ states which are in excellent agreement with Rosen's values.[4]

References

[1]R. S. Ram, Spectroscopy Lett. **9**, 435 (1976); Opt. Pura. Y. Appli (Spain) **6**, 38 (1973).
[2]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules" 3rd ed.. Chapman and Hall, Ltd., London, 330 pp. (1968); refer to p. 260.
[3]J. Singh, K. P. R. Nair and D. K. Rai, J. Mol. Struct. **6**, 328 (1970).
[4]B. Rosen (ed.), "Donnes Spectroscopiques Relatives Aux Molecules Diatomiques," Pergamon Press, New York, 515 pp. (1970).
[5]R. F. Barrow, Trans. Faraday Soc. **56**, 952 (1960); Nature **189**, 480 (1961).
[6]S. A. Semenkovich, Zh. Prikl. Khim. **30**, 933 (1957).
[7]JANAF Thermochemical Tables: Al(l), Al(g), AlCl(g), AlF(g), and AlI(g), 9–30–79; NaBr(l), 9–30–64; Na(g), 6–30–62; Br(g), 6–30–74.
[8]P. Gross, Fulmer Research Institute, Ltd., personal communication to H. Prophet, (July, 1966).

Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.568	23.125	23.125	INFINITE
100	30.226	203.571	269.949	−6.638	24.175	7.209	−3.766
200	33.855	225.727	242.827	−3.420	23.141	−9.434	2.464
250	34.918	233.404	240.199	−1.699	22.340	−17.488	3.654
298.15	35.600	239.616	239.616	0.	15.899	−24.422	4.279
300	35.622	239.836	239.617	0.066	15.850	−24.672	4.296
350	36.102	245.366	240.052	1.860	0.084	−30.552	4.560
400	36.443	250.210	241.026	3.674	−0.290	−34.903	4.558
450	36.695	254.518	242.290	5.503	−0.685	−39.207	4.551
500	36.887	258.394	243.710	7.342	−1.100	−43.465	4.541
600	37.162	265.146	246.736	11.046	−1.992	−51.855	4.514
700	37.351	270.889	249.787	14.772	−2.982	−60.089	4.484
800	37.492	275.886	252.743	18.514	−4.097	−68.173	4.451
900	37.605	280.309	255.565	22.269	−5.365	−76.108	4.417
1000	37.700	284.276	258.241	26.035	−17.402	−83.132	4.342
1100	37.783	287.873	260.774	29.809	−18.695	−89.643	4.257
1200	37.858	291.164	263.172	33.591	−19.983	−96.036	4.180
1300	37.927	294.197	265.443	37.380	−21.269	−102.321	4.111
1400	37.992	297.010	267.599	41.176	−22.553	−108.508	4.048
1500	38.054	299.634	269.648	44.979	−23.835	−114.602	3.991
1600	38.114	302.091	271.600	48.787	−25.117	−120.612	3.938
1700	38.171	304.404	273.462	52.601	−26.398	−126.541	3.888
1800	38.228	306.587	275.242	56.421	−27.680	−132.395	3.842
1900	38.283	308.656	276.947	60.247	−28.964	−138.177	3.799
2000	38.337	310.621	278.582	64.078	−30.251	−143.892	3.758
2100	38.391	312.492	280.152	67.914	−31.541	−149.542	3.720
2200	38.445	314.280	281.663	71.756	−32.837	−155.131	3.683
2300	38.499	315.990	283.119	75.603	−34.137	−160.661	3.649
2400	38.553	317.629	284.523	79.456	−35.443	−166.134	3.616
2500	38.609	319.204	285.879	83.314	−36.755	−171.552	3.584
2600	38.666	320.720	287.190	87.178	−38.073	−176.918	3.554
2700	38.725	322.180	288.459	91.047	−39.397	−182.233	3.526
2800	38.788	323.590	289.689	94.923	−334.626	−186.532	3.480
2900	38.853	324.952	290.881	98.805	−334.862	−181.238	3.264
3000	38.924	326.270	292.039	102.694	−335.100	−175.937	3.063
3100	38.999	327.548	293.164	106.590	−335.340	−170.628	2.875
3200	39.081	328.787	294.258	110.494	−335.579	−165.311	2.698
3300	39.170	329.991	295.323	114.406	−335.815	−159.986	2.532
3400	39.267	331.162	296.359	118.328	−336.048	−154.654	2.376
3500	39.372	332.302	297.370	122.260	−336.274	−149.316	2.228
3600	39.487	333.412	298.356	126.203	−336.492	−143.971	2.089
3700	39.612	334.496	299.318	130.158	−336.699	−138.620	1.957
3800	39.749	335.554	300.258	134.126	−336.894	−133.265	1.832
3900	39.896	336.589	301.176	138.108	−337.074	−127.903	1.713
4000	40.056	337.601	302.074	142.105	−337.238	−122.538	1.600
4100	40.228	338.592	302.953	146.120	−337.384	−117.169	1.493
4200	40.413	339.563	303.813	150.152	−337.509	−111.796	1.390
4300	40.612	340.517	304.656	154.203	−337.612	−106.421	1.293
4400	40.823	341.453	305.481	158.274	−337.692	−101.043	1.200
4500	41.048	342.373	306.291	162.368	−337.744	−95.664	1.110
4600	41.286	343.277	307.085	166.484	−337.772	−90.284	1.025
4700	41.537	344.168	307.865	170.625	−337.772	−84.904	0.944
4800	41.801	345.045	308.630	174.792	−337.744	−79.524	0.865
4900	42.078	345.910	309.382	178.986	−337.685	−74.145	0.790
5000	42.368	346.763	310.121	183.208	−337.596	−68.768	0.718
5100	42.669	347.605	310.848	187.460	−337.477	−63.392	0.649
5200	42.982	348.436	311.563	191.743	−337.326	−58.019	0.583
5300	43.305	349.258	312.266	196.057	−337.144	−52.650	0.519
5400	43.639	350.071	312.959	200.404	−336.930	−47.284	0.457
5500	43.983	350.875	313.641	204.785	−336.684	−41.922	0.398
5600	44.336	351.670	314.313	209.201	−336.407	−36.566	0.341
5700	44.697	352.458	314.975	213.652	−336.099	−31.214	0.286
5800	45.066	353.239	315.628	218.141	−335.757	−25.868	0.233
5900	45.441	354.012	316.272	222.666	−335.388	−20.528	0.182
6000	45.822	354.779	316.908	227.229	−334.967	−15.197	0.132

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = 180.22 \pm 1.05\ J·K^{-1}·mol^{-1}$
$T_{fus} = 370.6 \pm 0.2\ K$

$\Delta_f H°(0\ K) = -491.90 \pm 0.84\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -511.28 \pm 0.84\ kJ·mol^{-1}$
$\Delta_{fus} H° = 11.25 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

The value chosen for the enthalpy of formation is the weighted average of the direct combination value reported by Gross *et al.*[1] and the solution calorimetry value given by Efimov, Kislova and Medvedev.[2]

Gross, Hayman, and Stuart[1] measured calorimetrically the standard enthalpy of formation of $AlBr_3$(cr) at 25°C by reacting Al with liquid bromine in a glass combustion vessel. They reported $\Delta_f H°(AlBr_3, cr, 298.15\ K) = -122.16 \pm 0.10\ kcal·mol^{-1}$.

Efimov *et. al.*[2] measured the heat of solution of $AlBr_3$(cr) in an aqueous HCl solution containing KCl(cr) and the heat of solution of $AlCl_3$(cr) in an aqueous HCl solution containing KBr(cr). From these heats of solution measurements and using the heats of formation of $AlCl_3$(cr),[3] KCl(cr)[4,5] and KBr(cr)[4,6] as auxiliary data, they obtained $\Delta_f H°(AlBr_3, cr, 298.15\ K) = -122.5 \pm 0.5\ kcal·mol^{-1}$.

Anthony *et al.*[10] measured the heat of solution of $AlBr_3$(cr) and $AlCl_3$(cr) in an aqueous alkaline solution containing dissolved sodium halides. They reported $\Delta_f H°(AlBr_3, cr, 298.15\ K) = -118.3 \pm 0.6\ kcal·mol^{-1}$. Eley and Watts,[11] in studying heats of solution of $AlBr_3$ and its complexes with pyridine, trimethylamine, and triethylamine in HCl, reported $\Delta_f H°(AlBr_3,cr,298.15K) -125.6\ kcal·mol^{-1}$. Klemm and Tanke[12] measured the heat of solution of $AlBr_3$(cr) at 0°C in aqueous HCl. Using auxiliary data, including estimated heat capacities, Klemm and Tanke[11] reported $\Delta_f H°(AlBr_3, cr, 298.15\ K) = -121\ kcal·mol^{-1}$. Gross, Hayman, and Stuart[1] have re-examined the data of Klemm and Tanke[12] and have calculated $\Delta_f H°(AlBr_3, cr, 298.15\ K) = -122.4\ kcal·mol^{-1}$. This latter value was based on the heat of solution measurements,[13] $\Delta_f H°(AlCl_3, cr, 298.15\ K) = -168.65\ kcal·mol^{-1}$, and on the enthalpies of formation difference of chloride and bromide ions at the proper concentration.

A number of other studies on the enthalpies of formation of $AlBr_3$(cr) are based on solution calorimetry. The earliest measurements in water[7,8,9] are probably not reliable because of hydrolysis of the aluminum halide, but estimates of the enthalpy of formation of $AlBr_3$(cr) based on measurements in aqueous acid or base are also in disagreement.

Heat Capacity and Entropy

The heat capacities, 11.6 – 308 K, have been measured by Webb, Justice, and Prophet.[13] Above 308 K they are derived[13] from the enthalpy data measured by Fischer.[14] The entropy of the crystal is based on a value of $S°(12\ K) = 4.021\ J·K^{-1}·mol^{-1}$, as discussed in Webb *et al.*[13]

Fusion Data

Fischer[14] determined the melting temperature (T_{fus}) for $AlBr_3$(cr). The heat of melting ($\Delta_{fus}H°$) is calculated from the enthalpies of $AlBr_3$(cr) and $AlBr_3$(l) at the melting temperature. The enthalpy of the crystal at T_{fus} was determined from the curve use[l]uccircld for the heat capacity calculations. The enthalpy of the liquid at T_{fus} was determined from a linear least squares fit to the enthalpy data for $AlBr_3$(l) reported by Fischer.[14] See Webb *et al.*[13] for details.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of the dimer and the crystal for the sublimation process, $2\ AlBr_3(cr) = Al_2Br_6(g)$, $\Delta_{sub}H°(298.15\ K) = +85.4 \pm 4.2\ kJ·mol^{-1}$. Also refer to the Al_2Br_6(g) table for additional comments.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.915	−491.896	−491.896	INFINITE
100	70.819	86.415	261.717	−17.530	−492.185	−492.051	257.021
200	89.947	142.206	189.044	−9.368	−493.176	−491.562	128.383
298.15	100.578	180.216	180.216	0.	−511.285	−488.515	85.586
300	100.816	180.839	180.218	0.186	−511.353	−488.374	85.033
370.600	113.078	203.294	182.510	7.703	--- CRYSTAL <--> LIQUID ---		
400	117.780	211.773	184.330	10.977	−554.791	−471.592	61.584
500	123.846	238.919	192.612	23.154	−550.784	−451.247	47.141
600	124.265	261.541	202.271	35.562	−546.690	−431.725	37.585
700	124.348	280.703	212.142	47.993	−542.715	−412.880	30.810
800	124.432	297.313	221.773	60.432	−538.885	−394.596	25.764
900	124.516	311.974	230.997	72.879	−535.225	−376.781	21.868
1000	124.600	325.097	239.762	85.335	−542.346	−358.604	18.732
1100	124.683	336.977	248.068	97.799	−538.731	−340.405	16.164
1200	124.767	347.829	255.936	110.272	−535.122	−322.535	14.040
1300	124.851	357.819	263.394	122.753	−531.517	−304.965	12.254
1400	124.934	367.075	270.473	135.242	−527.917	−287.674	10.733
1500	125.018	375.697	277.204	147.739	−524.323	−270.639	9.424

PREVIOUS: June 1972 CURRENT: September 1979

$S°(298.15\ K) = [206.481]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 370.6 \pm 0.2\ K$

$\Delta_f H°(298.15\ K) = [-501.381]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 11.25 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(AlBr_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(AlBr_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(370.6\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Fischer[1] has measured the enthalpy of $AlBr_3(l)$ from 374 K to 406 K. The heat capacity is derived from a linear least squares fit to his data. The resulting constant value for the heat capacity is adopted for temperatures above 400 K.

$S°(AlBr_3, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Refer to the $Al_2Br_6(g)$ table for details.

Reference

[1]W. Fischer, Z. anorg. allgem. Chem. **200**, 332 (1931).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	124.965	206.481	206.481	0.	−501.381	−486.442	85.223
300	124.965	207.254	206.483	0.231	−501.404	−486.350	84.681
370.600	124.965	233.664	209.234	9.054	--- CRYSTAL <~~> LIQUID ---		
400	124.965	243.204	211.385	12.728	−543.136	−472.510	61.703
500	124.965	271.089	220.641	25.224	−538.810	−455.357	47.571
600	124.965	293.873	231.005	37.721	−534.628	−439.062	38.224
700	124.965	313.136	241.397	50.217	−530.587	−423.455	31.599
800	124.965	329.823	251.431	62.714	−526.700	−408.418	26.667
900	124.965	344.542	260.975	75.210	−522.990	−393.858	22.859
1000	124.965	357.708	270.001	87.707	−530.070	−378.940	19.794
1100	124.965	369.618	278.525	100.203	−526.424	−364.003	17.285
1200	124.965	380.492	286.576	112.699	−522.790	−349.398	15.209
1300	124.965	390.494	294.190	125.196	−519.170	−335.096	13.464
1400	124.965	399.755	301.403	137.692	−515.562	−321.072	11.979
1500	124.965	408.377	308.251	150.189	−511.969	−307.305	10.701

PREVIOUS: June 1972 CURRENT: September 1979

0 to 370.6 K crystal
above 370.6 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−21.915	−491.896	−491.896	INFINITE
100	70.819	86.415	261.717	−17.530	−492.185	−492.051	257.021
200	89.947	142.206	189.044	−9.368	−493.176	−491.562	128.383
298.15	100.578	180.216	180.216	0.	−511.285	−488.515	85.586
300	100.816	180.839	180.218	0.186	−511.353	−488.374	85.033
370.600	113.078	203.294	182.510	7.703	____ CRYSTAL <--> LIQUID ____		
370.600	124.965	233.664	182.510	18.958	TRANSITION		
400	124.965	243.204	186.625	22.632	−543.136	−472.510	61.703
500	124.965	271.089	200.833	35.128	−538.810	−455.357	47.571
600	124.965	293.873	214.498	47.625	−534.628	−439.061	38.224
700	124.965	313.136	227.249	60.121	−530.587	−423.455	31.599
800	124.965	329.823	239.051	72.618	−526.700	−408.418	26.667
900	124.965	344.541	249.970	85.114	−522.990	−393.857	22.859
1000	124.965	357.708	260.097	97.610	−530.070	−378.939	19.794
1100	124.965	369.618	269.521	110.107	−526.424	−364.003	17.285
1200	124.965	380.492	278.322	122.603	−522.790	−349.398	15.209
1300	124.965	390.494	286.571	135.100	−519.170	−335.095	13.464
1400	124.965	399.755	294.329	147.596	−515.562	−321.071	11.979
1500	124.965	408.377	301.648	160.093	−511.969	−307.305	10.701

PREVIOUS: CURRENT: September 1979

$\Delta_{at}H°(0\ K) = 1068.2 \pm 2.1\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 349.44 \pm 1.26\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_fH°(0\ K) = -387.16 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = -410.45 \pm 1.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
228(1)	508.4(2)
155(1)	93.0(2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Al–Br = [2.27 ± 0.10] Å
Bond Angle: Br–Al–Br = 120°
Product of the Moments of Inertia: $I_AI_BI_C = [2.157410 \times 10^{-111}]\ g^3\ cm^6$

Enthalpy of Formation

Fischer, Rahlfs, and Benze[1] have determined the equilibrium constants for the reaction $Al_2Br_6(g) = 2\ AlBr_3(g)$ from vapor density measurements. The heats of reaction are calculated from these data using both 2nd law and 3rd law methods. The results of the calculations are as follows, where the $\Delta_fH°(298.15\ K)$ is based on the 3rd law value of $\Delta_rH°(298.15\ K)$, for the reaction as written above, and $\Delta_fH°(Al_2Br_6, g, 298.15\ K) = -224.0\ kcal \cdot mol^{-1}$.

T/K	Data Points	$\Delta_rH°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	Al_2Br_6 3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_fH°(298.15\ K)$ $kcal \cdot mol^{-1}$
613–846	4	29.6 ± 1.0	27.78 ± 0.6	−2.6 ± 1.3	−98.11
605–854	7	29.4 ± 0.5	27.73 ± 0.5	−2.2 ± 0.7	−98.14

The adopted value for the enthalpy of formation is $\Delta_fH°(AlBr_3, g, 298.15\ K) = -98.1 \pm 0.4\ kcal \cdot mol^{-1} (-410.45 \pm 1.7\ kJ \cdot mol^{-1})$.

Heat Capacity and Entropy

Beattie and Horder[2] studied the gas phase Raman spectra of monomeric $AlBr_3$. The results are consistent with a planar structure of D_{3h} symmetry with $\nu_1 = 228\ cm^{-1}$(polarized) and $\nu_4 = 93\ cm^{-1}$. The weak antisymmetric stretching mode was tentatively assigned as $\nu_3 = 360\ cm^{-1}$.

Pong *et al.*,[3] in examining the infrared spectrum of the monomeric $AlBr_3$ isolated in solid argon, reported $\nu_2 = 155.0\ cm^{-1}$, $\nu_3 = 510\ cm^{-1}$ and $\nu_4 = 92\ cm^{-1}$ for $AlBr_3$ isolated in xenon.

The adopted values for ν_1 and ν_4 are taken from Beattie and Horder[2] while ν_2 and ν_3 are taken from Pong *et al.*[3] The Al–Br bond distance was estimated by Heise and Weiland[5] and is consistent with the trend of experimentally known bond distances in the gaseous molecules AlF_3, $AlCl_3$, and AlI_3.[6] The principal moments of inertia are $I_A = I_B = 102.5575 \times 10^{-39}$, and $I_C = 205.1151 \times 10^{-39}\ g \cdot cm^2$.

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[6]JANAF Thermochemical Tables: $AlF_3(g)$, $AlCl_3(g)$, and $AlI_3(g)$, 9–30–79.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	$J \cdot K^{-1} mol^{-1}$		$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−18.015	−387.162	−387.162	INFINITE
100	57.421	276.467	412.068	−13.560	−387.381	−406.252	212.204
200	69.507	320.454	356.177	−7.144	−390.119	−424.154	110.778
250	73.019	336.366	350.669	−3.576	−391.887	−432.465	90.359
298.15	75.376	349.441	349.441	0.	−410.450	−438.135	76.759
300	75.451	349.907	349.442	0.140	−410.566	−438.307	76.316
350	77.155	361.673	350.367	3.957	−456.958	−440.380	65.723
400	78.376	372.060	352.443	7.847	−457.086	−438.002	57.197
450	79.271	381.346	355.147	11.789	−457.209	−435.609	50.564
500	79.943	389.734	358.193	15.770	−457.333	−433.203	45.256
600	80.861	404.398	364.707	23.814	−457.604	−428.352	37.291
700	81.439	416.909	371.293	31.931	−457.942	−423.451	31.598
800	81.825	427.810	377.691	40.096	−458.387	−418.495	27.325
900	82.094	437.464	383.806	48.293	−458.977	−413.475	23.997
1000	82.289	446.124	389.612	56.512	−470.334	−407.620	21.292
1100	82.434	453.975	395.112	64.749	−470.948	−401.319	19.057
1200	82.546	461.152	400.321	72.998	−471.561	−394.962	17.192
1300	82.633	467.763	405.258	81.257	−472.178	−388.554	15.612
1400	82.703	473.889	409.944	89.524	−472.800	−382.098	14.256
1500	82.759	479.597	414.399	97.797	−473.431	−375.597	13.079
1600	82.805	484.940	418.643	106.075	−474.071	−369.054	12.048
1700	82.844	489.961	422.692	114.358	−474.725	−362.470	11.137
1800	82.876	494.697	426.562	122.644	−475.395	−355.848	10.326
1900	82.903	499.179	430.267	130.933	−476.084	−349.188	9.600
2000	82.927	503.432	433.820	139.225	−476.796	−342.490	8.945
2100	82.947	507.479	437.232	147.518	−477.534	−335.757	8.352
2200	82.964	511.338	440.513	155.814	−478.299	−328.988	7.811
2300	82.979	515.026	443.673	164.111	−479.095	−322.184	7.317
2400	82.993	518.558	446.720	172.410	−479.923	−315.344	6.863
2500	83.005	521.946	449.662	180.709	−480.783	−308.469	6.445
2600	83.015	525.202	452.505	189.010	−481.677	−301.559	6.058
2700	83.024	528.335	455.256	197.312	−482.603	−294.613	5.700
2800	83.033	531.354	457.920	205.615	−777.462	−286.666	5.348
2900	83.040	534.268	460.503	213.919	−777.353	−269.139	4.848
3000	83.047	537.084	463.009	222.223	−777.272	−251.616	4.381
3100	83.053	539.807	465.443	230.528	−777.214	−234.095	3.944
3200	83.059	542.444	467.808	238.834	−777.177	−216.576	3.535
3300	83.064	545.000	470.109	247.140	−777.157	−199.057	3.151
3400	83.069	547.479	472.348	255.447	−777.150	−181.540	2.789
3500	83.073	549.887	474.529	263.754	−777.154	−164.022	2.448
3600	83.077	552.228	476.655	272.061	−777.163	−146.503	2.126
3700	83.080	554.504	478.728	280.369	−777.174	−128.985	1.821
3800	83.084	556.720	480.752	288.677	−777.184	−111.466	1.532
3900	83.087	558.878	482.728	296.986	−777.188	−93.947	1.258
4000	83.089	560.981	484.658	305.295	−777.185	−76.428	0.998
4100	83.092	563.033	486.544	313.604	−777.171	−58.910	0.751
4200	83.095	565.035	488.389	321.913	−777.144	−41.391	0.515
4300	83.097	566.991	490.195	330.223	−777.102	−23.874	0.290
4400	83.099	568.901	491.962	338.532	−777.042	−6.358	0.075
4500	83.101	570.769	493.693	346.842	−776.960	11.157	−0.130
4600	83.103	572.595	495.388	355.153	−776.860	28.670	−0.326
4700	83.105	574.382	497.050	363.463	−776.738	46.180	−0.513
4800	83.106	576.132	498.679	371.773	−776.595	63.687	−0.693
4900	83.108	577.846	500.277	380.084	−776.428	81.191	−0.866
5000	83.109	579.525	501.846	388.395	−776.239	98.692	−1.031
5100	83.110	581.170	503.385	396.706	−776.028	116.189	−1.190
5200	83.112	582.784	504.896	405.017	−775.795	133.681	−1.343
5300	83.113	584.367	506.381	413.328	−775.540	151.169	−1.490
5400	83.114	585.921	507.840	421.640	−775.265	168.651	−1.631
5500	83.115	587.446	509.273	429.951	−774.970	186.128	−1.768
5600	83.116	588.944	510.682	438.263	−774.656	203.600	−1.899
5700	83.117	590.415	512.068	446.574	−774.325	221.066	−2.026
5800	83.118	591.860	513.432	454.886	−773.975	238.525	−2.148
5900	83.119	593.281	514.773	463.198	−773.613	255.979	−2.266
6000	83.120	594.678	516.093	471.510	−773.215	273.424	−2.380

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = 227.957 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -51.66 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -51.46 \pm 6.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	24541.65	2
$a^3\Pi$	24615.31	2
	24680.00	2
$A^1\Pi$	38237.70	2
$b^3\Sigma^+$	43590.00	3

$\omega_e = 480.2903\ cm^{-1}$ $\omega_e x_e = 2.064\ cm^{-1}$ $\sigma = 1$
$B_e = 0.24255\ cm^{-1}$ $\alpha_e = 0.001598\ cm^{-1}$ $r_e = 2.130113$ Å

Enthalpy of Formation

Equilibrium constants as a function of temperature for the reaction 2 Al(l) + $AlCl_3$(g) → 3 AlCl(g) have been reported by many investigators. The heats of reaction are calculated from these data using second and third law methods. Unfortunately, most of the data are very discordant and of no help in defining $\Delta_f H°$(AlCl, g, 298.15 K). The results of Rao and Dadape[1] cover a temperature range of 300 K, show good compatibility with the thermodynamic functions, are near an average of all the data, and are judged most acceptable. The third-law heat of reaction derived from their data is adopted and combined with the heat of formation of $AlCl_3$(g)[12] to give $\Delta_f H°$(AlCl, g, 298.15 K) = −12.30 ± 1.5 kcal·mol^{-1} (−51.46 ± 6.3 kJ·mol^{-1}).

Source	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Rao and Dadape[1]	1125–1425	11	97.25 ± 1.6	97.71 ± 0.8	0.4 ± 1.3	−12.30
Frish *et al.*[2]	931–1034	9	94.58 ± 1.0	101.64 ± 0.5	7.2 ± 1.0	−10.99
Gross *et al.*[3]	1225–1278[a]	7	−−	104.60 ± 2.8	−−	−10.00
Ginsberg *et al.*[4]	1423–1500	8	86.34 ± 1.8	99.66 ± 0.8	9.1 ± 1.2	−11.65
Semenkovich[5]	1223–1473	6	84.19 ± 0.4	93.42 ± 1.3	6.9 ± 0.3	−13.73
Heimgartner[6]	978–1383	13	55.52 ± 2.6	94.90 ± 9.5	33.0 ± 2.2	−13.24
Weiss[7]	1273–1473	3	88.29 ± 3.7	81.26 ± 1.2	−5.1 ± 2.7	−17.78
Pinchuk *et al.*[8]	1173–1373	3	80.20 ± 7.4	89.92 ± 1.9	7.6 ± 5.8	−14.90
Mitani *et al.*[9]	1273–1473[b]	2	81.29 ± 0.0	94.18 ± 2.7	9.4 ± 0.0	−13.48
Tanabe *et al.*[10]	1173–1573[b]	2	88.23 ± 0.0	89.49 ± 0.5	0.9 ± 0.0	−15.04
Kikuch *et al.*[11]	1273–1523[b]	2	73.61 ± 0.0	93.60 ± 5.1	14.3 ± 0.0	−13.67

[a]Temperature range too small for significant second law calculation.
[b]Individual points not reported; calculation based on reported equation at extremes of temperature range cited.

Gross *et al.*[3] and Pinchuk *et al.*[8] have studied the reaction of sodium and potassium chloride with liquid aluminum to form aluminum monochloride. These studies lead to $\Delta_f H°$(298.15 K) values for AlCl(g) in the range of −12.69 ± 1.0 to −13.60 ± 1.5 kcal·mol^{-1}.

The adopted enthalpy of formation yields a dissociation energy of 498.57 kJ·mol^{-1} for AlCl(g). Barrow[13] and Ram[14] reference possible spectroscopic values for the dissociation energy. A short extrapolation of vibrational levels yields $D_0° = 519.2$ kJ·mol^{-1} but Barrow[13] speculates that a potential maximum in the A^1 state of AlF and AlCl causes extrapolation of levels to give erroneous heats of dissociation. Ram *et al.* has observed rotational predissociation in the AlCl bond system and reports the dissociation energy at 507.5 ± 0.97 kJ·mol^{-1}. This yields $\Delta_f H°$(AlCl, g, 298.15 K) = −60.42 kJ·mol^{-1} in reasonable agreement with the selected value.

Heat Capacity and Entropy

The spectrum of AlCl has been observed and analyzed by a number of investigators.[14,15,16,17] The spectroscopic constants for $Al^{35}Cl$ and $Al^{37}Cl$ are taken from the microwave study of Wyse and Gordy[17] and averaged according to the natural isotopic abundance of chlorine. The electronic levels are those reported by Sharma;[18] the value for the $b^3\Sigma^+$ state is somewhat uncertain. The assignment of electronic states is supported by theoretical calculations.[19]

References

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Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.323	−51.656	−51.656	INFINITE
100	29.527	193.170	257.245	−6.407	−50.681	−59.849	31.262
200	32.545	214.524	231.068	−3.309	−50.903	−68.982	18.016
250	33.787	221.927	228.523	−1.649	−51.166	−73.473	15.351
298.15	34.660	227.957	227.957	0.	−51.463	−77.743	13.620
300	34.689	228.171	227.957	0.064	−51.475	−77.906	13.565
350	35.338	233.570	228.382	1.816	−51.818	−82.284	12.280
400	35.814	238.321	229.334	3.595	−52.188	−86.611	11.39
450	36.170	242.561	230.572	5.395	−52.579	−90.891	10.550
500	36.445	246.387	231.965	7.211	−52.990	−95.126	9.938
600	36.835	253.068	234.942	10.876	−53.876	−103.472	9.008
700	37.099	258.768	237.948	14.574	−54.862	−111.661	8.332
800	37.291	263.735	240.868	18.294	−55.973	−119.701	7.816
900	37.439	268.136	243.658	22.030	−57.237	−127.593	7.405
1000	37.559	272.087	246.306	25.780	−69.271	−134.575	7.029
1100	37.660	275.671	248.815	29.541	−70.560	−141.042	6.698
1200	37.749	278.952	251.192	33.312	−71.846	−147.393	6.416
1300	37.829	281.977	253.445	37.091	−73.128	−153.637	6.173
1400	37.901	284.783	255.585	40.878	−74.407	−159.782	5.962
1500	37.969	287.400	257.619	44.671	−75.684	−165.835	5.775
1600	38.033	289.853	259.558	48.471	−76.959	−171.804	5.609
1700	38.095	292.160	261.409	52.278	−78.232	−177.693	5.460
1800	38.153	294.340	263.178	56.090	−79.503	−183.507	5.325
1900	38.211	296.404	264.873	59.908	−80.774	−189.250	5.203
2000	38.266	298.365	266.499	63.732	−82.044	−194.926	5.091
2100	38.321	300.234	268.061	67.562	−83.314	−200.539	4.988
2200	38.375	302.018	269.565	71.396	−84.584	−206.092	4.893
2300	38.428	303.725	271.013	75.236	−85.856	−211.586	4.805
2400	38.482	305.361	272.410	79.082	−87.130	−217.025	4.723
2500	38.536	306.933	273.760	82.933	−88.407	−222.411	4.647
2600	38.590	308.446	275.065	86.789	−89.687	−227.746	4.575
2700	38.647	309.903	276.329	90.651	−90.970	−233.032	4.508
2800	38.705	311.310	277.553	94.519	−386.158	−237.302	4.427
2900	38.766	312.669	278.741	98.392	−386.353	−231.983	4.178
3000	38.830	313.984	279.894	102.272	−386.552	−226.656	3.946
3100	38.898	315.258	281.014	106.158	−386.754	−221.323	3.729
3200	38.971	316.495	282.103	110.052	−386.959	−215.983	3.526
3300	39.050	317.695	283.164	113.953	−387.165	−210.637	3.334
3400	39.135	318.862	284.197	117.862	−387.372	−205.284	3.154
3500	39.228	319.998	285.203	121.780	−387.579	−199.926	2.984
3600	39.328	321.104	286.185	125.708	−387.783	−194.561	2.823
3700	39.437	322.183	287.144	129.646	−387.984	−189.191	2.671
3800	39.556	323.237	288.080	133.595	−388.179	−183.816	2.527
3900	39.684	324.266	288.995	137.557	−388.367	−178.436	2.390
4000	39.823	325.272	289.889	141.533	−388.546	−173.050	2.260
4100	39.973	326.257	290.764	145.522	−388.713	−167.661	2.136
4200	40.134	327.222	291.621	149.528	−388.868	−162.268	2.018
4300	40.308	328.169	292.460	153.550	−389.006	−156.871	1.906
4400	40.493	329.098	293.282	157.589	−389.128	−151.471	1.798
4500	40.690	330.010	294.088	161.649	−389.229	−146.068	1.696
4600	40.900	330.906	294.878	165.728	−389.311	−140.664	1.597
4700	41.122	331.788	295.654	169.829	−389.370	−135.258	1.503
4800	41.357	332.656	296.416	173.953	−389.405	−129.851	1.413
4900	41.603	333.512	297.165	178.101	−389.414	−124.443	1.327
5000	41.862	334.355	297.900	182.274	−389.397	−119.036	1.244
5100	42.132	335.186	298.623	186.473	−389.352	−113.629	1.164
5200	42.414	336.007	299.334	190.701	−389.278	−108.224	1.087
5300	42.706	336.818	300.034	194.957	−389.174	−102.820	1.013
5400	43.010	337.619	300.722	199.242	−389.040	−97.418	0.942
5500	43.323	338.411	301.400	203.559	−388.876	−92.019	0.874
5600	43.645	339.195	302.068	207.907	−388.680	−86.623	0.808
5700	43.977	339.970	302.726	212.288	−388.454	−81.231	0.744
5800	44.317	340.738	303.375	216.703	−388.193	−75.844	0.683
5900	44.665	341.498	304.015	221.152	−387.903	−70.461	0.624
6000	45.019	342.252	304.646	225.636	−387.560	−65.086	0.567

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = [232.19 \pm 1.7]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 855.7 \pm 40\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [861.904]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma]$	0	[2]
$[^2\Pi]$	[10000]	[4]

$\omega_e = [570]\ cm^{-1}$ $\omega_e x_e = [2]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.2618]\ cm^{-1}$ $\alpha_e = [0.0015]\ cm^{-1}$ $r_e = [2.05]$ Å

Enthalpy of Formation

We adopt $\Delta_f H°(0\ K) = 204.5 \pm 10\ kcal·mol^{-1}$ based on that of AlCl(g)[1] combined with the ionization potential IP(AlCl) = 9.4 ± 0.4 eV (216.8 ± 9 $kcal·mol^{-1}$). IP(AlCl) is assumed to be equal to the electron–impact appearance potential of $AlCl^+$ measured as 9.4 ± 0.4,[2] 9.5 ± 0.3[3] and 9.3 ± 0.6 eV.[4] Theoretical values include IP = 8.83 eV from an extended Huckel calcualtion[5] and from ab initio calculations[6,7] either 8.4 eV (direct value) or 9.8 eV derived from $D_0°(AlCl^+)$. Electron–impact formation of $AlCl^+$ from $AlCl_3$[8] apparently yields fragment ions with excess energy; i.e., we derive the upper limit IP<11.7 eV.

For the dissociation process $AlCl^+(X^2\Sigma) \rightarrow Al^+(^1S) + Cl(^2P)$, our adopted $\Delta_f H°$ yields $D_0°(AlCl^+) = 39 \pm 10\ kcal·mol^{-1}$. This compares with $-31\ kcal·mol^{-1}$ derived from the theoretical potential energy curve[6,7] which, however, has a maximum of $-8\ kcal·mol^{-1}$ arising from an avoided crossing with another $^2\Sigma$ state.

Heat Capacity and Entropy

Bonding in Group III monohalides and their ions was characterized by Berkowitz and Dehmer[7] from photoelectron spectra and theoretical calculations.[6,7] They concluded that ionization removes an electron from an antibonding orbital centered mainly on the metal. This shortens the bond length and enhances the ionic nature of the bond. A decrease in bond length is observed for BF^+,[9] predicted for AlF^+[1] from Rydberg states of AlF, and predicted for $AlCl^+$ from theoretical calculations.[6,7]

For $AlCl^+$, we adopt r_e = 2.05 Å based mainly on the theoretical prediction.[6,7] This may be compared with 2.13 Å for AlCl and 2.06 Å for $AlCl_3$.[1] Lacking data for Rydberg states of AlCl, we estimate ω_e from $k(AlCl^+)/k(MgCl) = 1.7$ transferred from the similar isoelectronic pair AlF^+ and MgF.[1] B_e is calculated from r_e, while α_e and $\omega_e x_e$ are estimated by comparison with AlF^+, AlF and AlCl.[1]

The electronic ground state and an approximate value for the $^2\Pi$ level are based on theoretical calculations.[6,7] These suggest that $^2\Pi$ has only a shallow minimum (r_e>3.6 Å) or possibly is repulsive. They also indicate the presence of a $^2\Sigma$ state having a double minimum above 30000 cm^{-1}. We include only the $^2\Pi$ state. If it is repulsive, our thermodynamic functions are upper–limit values. The bias would be quite small even at 3000 K.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.154	855.682		
100	29.269	198.245	260.674	−6.243			
200	31.566	219.136	235.214	−3.216			
250	32.825	226.319	232.738	−1.605			
298.15	33.794	232.187	232.187	0.	861.904	828.108	−145.081
300	33.826	232.396	232.188	0.063	861.929	827.899	−144.150
350	34.588	237.671	232.603	1.774	862.585	822.175	−122.703
400	35.165	242.329	233.533	3.518	863.220	816.358	−106.605
450	35.606	246.497	234.746	5.288	863.838	810.463	−94.076
500	35.948	250.267	236.112	7.077	864.439	804.500	−84.046
600	36.436	256.867	239.037	10.698	865.587	792.404	−68.985
700	36.762	262.510	241.997	14.359	866.643	780.121	−58.213
800	36.993	267.435	244.875	18.047	867.580	767.696	−50.125
900	37.166	271.802	247.629	21.756	868.365	755.161	−43.828
1000	37.302	275.725	250.246	25.479	858.384	743.309	−38.826
1100	37.415	279.286	252.727	29.215	859.148	731.764	−34.749
1200	37.516	282.546	255.078	32.962	859.917	720.150	−31.347
1300	37.612	285.553	257.308	36.718	860.691	708.471	−28.467
1400	37.711	288.344	259.426	40.485	861.470	696.733	−25.995
1500	37.818	290.949	261.442	44.261	862.254	684.939	−23.852
1600	37.939	293.394	263.363	48.049	863.046	673.092	−21.974
1700	38.077	295.698	265.198	51.849	863.846	661.195	−20.316
1800	38.235	297.878	266.954	55.665	864.656	649.251	−18.841
1900	38.414	299.950	268.636	59.497	865.478	637.262	−17.520
2000	38.615	301.926	270.252	63.348	866.314	625.229	−16.329
2100	38.837	303.815	271.805	67.221	867.166	613.154	−15.251
2200	39.079	305.627	273.302	71.116	868.034	601.038	−14.270
2300	39.338	307.370	274.745	75.037	868.922	588.882	−13.374
2400	39.613	309.050	276.140	78.984	869.828	576.687	−12.551
2500	39.901	310.673	277.489	82.960	870.755	564.454	−11.794
2600	40.199	312.244	278.796	86.965	871.702	552.183	−11.093
2700	40.503	313.766	280.063	91.000	872.671	539.875	−10.445
2800	40.811	315.245	281.293	95.066	579.760	528.499	−9.859
2900	41.120	316.682	282.489	99.162	581.866	526.631	−9.486
3000	41.428	318.082	283.652	103.290	583.994	524.691	−9.136
3100	41.732	319.445	284.785	107.448	586.142	522.679	−8.807
3200	42.029	320.775	285.889	111.636	588.310	520.597	−8.498
3300	42.319	322.072	286.965	115.853	590.499	518.447	−8.206
3400	42.600	323.340	288.017	120.099	592.707	516.230	−7.931
3500	42.870	324.579	289.044	124.373	594.935	513.949	−7.670
3600	43.127	325.790	290.048	128.673	597.181	511.603	−7.423
3700	43.373	326.975	291.030	132.998	599.446	509.195	−7.189
3800	43.604	328.135	291.991	137.347	601.729	506.725	−6.965
3900	43.823	329.270	292.932	141.718	604.029	504.195	−6.753
4000	44.027	330.383	293.855	146.111	606.346	501.606	−6.550
4100	44.217	331.472	294.759	150.523	608.680	498.958	−6.357
4200	44.393	332.540	295.646	154.954	611.030	496.254	−6.172
4300	44.555	333.586	296.516	159.401	613.395	493.493	−5.995
4400	44.703	334.612	297.370	163.864	615.775	490.677	−5.825
4500	44.838	335.618	298.209	168.341	618.171	487.807	−5.662
4600	44.961	336.605	299.033	172.831	620.578	484.884	−5.506
4700	45.071	337.573	299.843	177.333	622.999	481.907	−5.356
4800	45.169	338.523	300.639	181.845	625.430	478.880	−5.211
4900	45.256	339.456	301.422	186.367	627.874	475.801	−5.072
5000	45.333	340.371	302.191	190.896	630.326	472.673	−4.938
5100	45.399	341.269	302.949	195.433	632.786	469.496	−4.809
5200	45.456	342.151	303.694	199.976	635.255	466.270	−4.684
5300	45.504	343.017	304.428	204.524	637.729	462.996	−4.563
5400	45.543	343.868	305.151	209.076	640.208	459.676	−4.446
5500	45.575	344.704	305.862	213.632	642.690	456.310	−4.334
5600	45.600	345.526	306.563	218.191	645.175	452.899	−4.224
5700	45.618	346.333	307.254	222.752	647.660	449.444	−4.119
5800	45.630	347.127	307.934	227.314	650.148	445.944	−4.016
5900	45.636	347.907	308.605	231.878	652.630	442.402	−3.917
6000	45.637	348.674	309.267	236.441	655.131	438.816	−3.820

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [282.9 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-488.1 \pm 63]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-489.5 \pm 63]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
[20000]	2
[25000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[750](1)
[200](1)
[550](1)

Point Group: C_s $\sigma = 1$
Bond Distances: Al–F = [1.65] Å; Al–Cl = [2.10] Å
Bond Angle: Cl–Al–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.440958 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We tentatively adopt $\Delta_f H°(298.15\ K) = -117 \pm 15\ kcal \cdot mol^{-1}$ and $\Delta_{at} H°(0\ K) = 241 \pm 15\ kcal \cdot mol^{-1}$ based on our average bond energies for $AlF_2(g)$ and $AlCl_2(g)$.[1] Mass-spectrometric data[2,3] yield $\Delta_f H°(298.15\ K) = -142.6$ and $\Delta_{at} H°(0\ K) = 267\ kcal \cdot mol^{-1}$, corresponding to an enhancement of 26 $kcal \cdot mol^{-1}$ in the stability of AlClF(g). The same study[2,3] indicated stability enhancements of 22 (or 13) $kcal \cdot mol^{-1}$ for AlF_2, 19 $kcal \cdot mol^{-1}$ for $AlClF_2$, and 22 $kcal \cdot mol^{-1}$ for $AlCl_2F$. See the appropriate tables[1] for further details.

Farber *et al.*[2,3] used molecular flow effusion of vapors of AlF_3 and $AlCl_3$ over Al(l) in Al_2O_3(cr) to study the reaciton Al-Cl(g) + AlF(g) = AlClF(g) + Al(g). They calculated *Kp* (5 points, 1338–1537 K) directly from mass-spectrometric ion intensities. Using JANAF auxiliary data,[1] we derive $[\Delta_r S°(2nd\ law) - \Delta_r S°(3rd\ law)] = 0.8 \pm 18\ cal \cdot K^{-1} \cdot mol^{-1}$, $\Delta_f H°(298.15\ K) = 12 \pm 25$ (2nd law) or 11.2 ± 5 (3rd law) and $\Delta_f H°(298.15\ K) = -142.6 \pm 5\ kcal \cdot mol^{-1}$. These results are internally consistent but, as in the case of AlF_2,[2,3] we suspect that common problems may cause a negative bias in $\Delta_f H°$. The ionizing energy is ambiguous: 20 eV[3] or AP + 3 eV.[2] The appearance potential $AP(AlClF^+) = 11 \pm 1$ eV is biased by ~2 eV, raising several questions about interpretation of the data (see $AlCl_2^+$).[1] It is conceivable that $AlClF^+$ arises from a process other than direct ionization of AlClF.

We conclude from these speculations that the experimental data[2,3] are insufficient to establish the enhanced stability of AlClF. Mass-spectrometric data indicate very little enhanced stability in BClF,[4] in agreement with average bond energies summarized on the table for $AlCl_2$.[1]

Heat Capacity and Entropy

The electronic ground state, excited levels, bond distances and bond angle are assumed to be the same as in $AlCl_2$ and AlF_2.[1] Vibrational frequencies are estimated by comparison with $AlCl_2$ and AlF_2.[1] The principal moments of inertia are $I_A = 2.3419 \times 10^{-39}$, $I_B = 23.6618 \times 10^{-39}$ and I_C 26.0037×10^{-39} $g \cdot cm^2$.

References

[1]JANAF Thermochemical Tables: $AlCl_2$(g), $AlCl_{2+}$(g), AlF_2(g), $AlClF_2$(g), $AlCl_2F$(g) 6-30-76; AlF(g) 12-31-75; AlCl(g) 6-30-70; Al(g) 12-31-65; Cl(g) 6-30-72; F(g) 9-30-65.
[2]M. Farber and S. P. Harris, High Temp. Sci. **3**, 231 (1971).
[3]M. Farber, R. D. Srivastava and O. M. Uy, Space Sciences, Inc., AFRPL-TR-70-97, (July, 1970).
[4]R. D. Srivastava and M. Farber, Trans. Faraday Soc. **67**, 2298 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.133	−488.119	−488.119	INFINITE
100	37.818	236.245	322.865	−8.662	−488.041	−492.998	257.516
200	43.971	264.376	287.217	−4.568	−488.732	−497.717	129.990
250	46.668	274.486	283.688	−2.300	−489.139	−499.916	104.452
298.15	48.806	282.895	282.895	0.	−489.528	−501.957	87.941
300	48.879	283.198	282.896	0.090	−489.543	−502.034	87.412
350	50.619	290.869	283.498	2.580	−489.942	−504.084	75.230
400	51.969	297.720	284.855	5.146	−490.340	−506.077	66.087
450	53.019	303.904	286.634	7.772	−490.739	−508.020	58.969
500	53.842	309.534	288.647	10.444	−491.143	−509.919	53.271
600	55.016	319.463	292.977	15.891	−491.984	−513.596	44.712
700	55.785	328.005	297.386	21.434	−492.901	−517.126	38.588
800	56.312	335.491	301.690	27.040	−493.930	−520.518	33.986
900	56.686	342.146	305.823	32.691	−495.107	−523.773	30.399
1000	56.961	348.134	309.759	38.374	−507.053	−526.127	27.482
1100	57.168	353.573	313.499	44.081	−508.256	−527.976	25.072
1200	57.328	358.554	317.049	49.806	−509.460	−529.716	23.058
1300	57.454	363.148	320.421	55.546	−510.666	−531.355	21.350
1400	57.554	367.410	323.627	61.296	−511.877	−532.901	19.883
1500	57.636	371.383	326.679	67.056	−513.093	−534.361	18.608
1600	57.703	375.105	329.591	72.823	−514.316	−535.739	17.490
1700	57.759	378.605	332.372	78.596	−515.544	−537.040	16.501
1800	57.806	381.908	335.033	84.374	−516.780	−538.269	15.620
1900	57.846	385.034	337.583	90.157	−518.022	−539.429	14.830
2000	57.881	388.002	340.031	95.943	−519.270	−540.523	14.117
2100	57.911	390.827	342.383	101.733	−520.523	−541.555	13.470
2200	57.938	393.522	344.647	107.526	−521.781	−542.527	12.881
2300	57.963	396.098	346.828	113.321	−523.042	−543.442	12.342
2400	57.985	398.565	348.933	119.118	−524.306	−544.302	11.846
2500	58.007	400.933	350.966	124.918	−525.571	−545.109	11.389
2600	58.028	403.208	352.932	130.719	−526.836	−545.865	10.967
2700	58.049	405.399	354.834	136.523	−528.101	−546.573	10.574
2800	58.070	407.510	356.678	142.329	−823.264	−546.267	10.191
2900	58.093	409.548	358.466	148.137	−823.427	−536.371	9.661
3000	58.117	411.518	360.202	153.948	−823.586	−526.470	9.167
3100	58.143	413.424	361.888	159.761	−823.739	−516.563	8.704
3200	58.172	415.271	363.528	165.576	−823.884	−506.652	8.270
3300	58.204	417.061	365.123	171.395	−824.021	−496.736	7.863
3400	58.238	418.799	366.676	177.217	−824.147	−486.817	7.479
3500	58.276	420.488	368.190	183.043	−824.262	−476.894	7.117
3600	58.318	422.130	369.666	188.873	−824.364	−466.967	6.776
3700	58.364	423.729	371.105	194.707	−824.451	−457.038	6.452
3800	58.414	425.286	372.511	200.546	−824.522	−447.108	6.146
3900	58.468	426.804	373.883	206.390	−824.576	−437.175	5.855
4000	58.526	428.285	375.225	212.239	−824.612	−427.241	5.579
4100	58.589	429.731	376.537	218.095	−824.627	−417.306	5.317
4200	58.655	431.143	377.820	223.957	−824.622	−407.372	5.066
4300	58.727	432.524	379.076	229.826	−824.594	−397.437	4.828
4400	58.802	433.875	380.307	235.703	−824.544	−387.504	4.600
4500	58.881	435.198	381.512	241.587	−824.468	−377.572	4.383
4600	58.965	436.493	382.693	247.479	−824.369	−367.642	4.175
4700	59.052	437.762	383.851	253.380	−824.246	−357.715	3.976
4800	59.143	439.006	384.987	259.290	−824.097	−347.790	3.785
4900	59.237	440.226	386.102	265.209	−823.922	−337.869	3.602
5000	59.335	441.424	387.197	271.137	−823.723	−327.951	3.426
5100	59.436	442.600	388.272	277.076	−823.498	−318.038	3.257
5200	59.539	443.755	389.327	283.024	−823.248	−308.130	3.095
5300	59.645	444.890	390.365	288.984	−822.974	−298.226	2.939
5400	59.754	446.006	391.385	294.954	−822.675	−288.328	2.789
5500	59.865	447.104	392.388	300.935	−822.354	−278.435	2.644
5600	59.977	448.183	393.375	306.927	−822.010	−268.549	2.505
5700	60.091	449.246	394.346	312.930	−821.644	−258.669	2.370
5800	60.207	450.292	395.302	318.945	−821.255	−248.796	2.241
5900	60.323	451.322	396.242	324.971	−820.849	−238.929	2.115
6000	60.441	452.337	397.169	331.010	−820.403	−229.072	1.994

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [259.72 \pm 63]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 271 \pm 126\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [276.144]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[850](1)
[170](2)
[500](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: $[C_{\infty v}]$
Bond Distances: Al–F = [1.60] Å; Al–Cl = [2.05] Å
Bond Angle: F–Al–Cl = [180]°
Rotational Constant: $B_o = [0.095960]\ cm^{-1}$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = 66 \pm 30\ kcal \cdot mol^{-1}$ based on $\Delta_f H°$ of AlClF[1] combined with the ionization potential IP(AlClF) = 182 ± 23 $kcal \cdot mol^{-1}$ (7.9 ± 1 eV). IP is estimated by comparison with $IP(AlCl_2) = 7.8 \pm 0.9$ eV and $IP(AlF_2) = 8.1 \pm 0.9$ eV.[1] Farber and Harris[2] reported an appearance potential of $AP(AlClF^+) = 11 \pm 1$ eV which appears to be seriously biased. This is discussed on the tables for $AlCl_2^+(g)$ and AlClF(g).

Heat Capacity and Entropy

We assume the electronic ground state to be linear $^1\Sigma^+$ and neglect excited states.[1] Bond distances are estimated to be the same as in $AlCl_2^+$ and AlF_2^+.[1] Vibrational frequencies are estimated by comparison with AlClF, $AlCl_2^+$ and AlF_2^+.[1]

References

[1]JANAF Thermochemical Tables: AlClF(g), $AlCl_2^+(g)$, $AlF_2^+(g)$ 6–30–76.
[2]M. Farber and S. P. Harris, High Temp. Sci. **3**, 231 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.635	270.854		
100	39.763	209.503	302.848	−9.334			
200	47.610	239.743	264.378	−4.927			
250	50.330	250.669	260.574	−2.476			
298.15	52.450	259.722	259.722	0.	276.144	264.370	−46.316
300	52.522	260.047	259.723	0.097	276.174	264.297	−46.018
350	54.264	268.279	260.369	2.768	276.996	262.252	−39.139
400	55.638	275.618	261.825	5.517	277.820	260.090	−33.964
450	56.723	282.237	263.731	8.327	278.645	257.824	−29.927
500	57.585	288.259	265.887	11.186	279.466	255.466	−26.688
600	58.835	298.877	270.525	17.011	281.082	250.513	−21.809
700	59.668	308.013	275.243	22.939	282.629	245.295	−18.304
800	60.245	316.020	279.850	28.936	284.070	239.862	−15.661
900	60.658	323.141	284.272	34.983	285.366	234.256	−13.596
1000	60.963	329.549	288.484	41.064	275.898	229.276	−11.976
1100	61.194	335.370	292.486	47.173	277.175	224.551	−10.663
1200	61.372	340.703	296.285	53.301	278.453	219.711	−9.564
1300	61.513	345.621	299.893	59.446	279.730	214.764	−8.629
1400	61.626	350.184	303.325	65.603	281.005	209.719	−7.825
1500	61.718	354.439	306.592	71.770	282.275	204.583	−7.124
1600	61.794	358.425	309.708	77.946	283.540	199.362	−6.508
1700	61.857	362.173	312.685	84.129	284.799	194.062	−5.963
1800	61.910	365.710	315.534	90.317	286.052	188.689	−5.476
1900	61.955	369.059	318.264	96.511	287.300	183.245	−5.038
2000	61.994	372.237	320.883	102.708	288.542	177.737	−4.642
2100	62.027	375.263	323.401	108.909	289.778	172.166	−4.282
2200	62.056	378.149	325.825	115.113	291.011	166.537	−3.954
2300	62.082	380.908	328.160	121.320	292.240	160.851	−3.653
2400	62.104	383.551	330.414	127.530	293.467	155.112	−3.376
2500	62.124	386.087	332.590	133.741	294.692	149.322	−3.120
2600	62.141	388.523	334.695	139.954	295.917	143.483	−2.883
2700	62.157	390.869	336.732	146.169	297.142	137.597	−2.662
2800	62.171	393.130	338.706	152.386	4.468	132.633	−2.474
2900	62.184	395.312	340.621	158.603	6.793	137.170	−2.471
3000	62.195	397.420	342.479	164.822	9.121	141.626	−2.466
3100	62.205	399.459	344.284	171.042	11.454	146.004	−2.460
3200	62.215	401.435	346.040	177.263	13.793	150.307	−2.454
3300	62.223	403.349	347.748	183.485	16.138	154.537	−2.446
3400	62.231	405.207	349.410	189.708	18.491	158.696	−2.438
3500	62.238	407.011	351.030	195.931	20.852	162.785	−2.429
3600	62.245	408.764	352.610	202.156	23.223	166.807	−2.420
3700	62.251	410.470	354.151	208.380	25.605	170.762	−2.411
3800	62.256	412.130	355.655	214.606	27.999	174.653	−2.401
3900	62.261	413.747	357.124	220.832	30.406	178.481	−2.390
4000	62.266	415.323	358.559	227.058	32.826	182.248	−2.380
4100	62.270	416.861	359.962	233.285	35.260	185.953	−2.369
4200	62.275	418.362	361.335	239.512	37.709	189.599	−2.358
4300	62.278	419.827	362.678	245.740	40.173	193.186	−2.347
4400	62.282	421.259	363.993	251.968	42.654	196.716	−2.335
4500	62.285	422.659	365.282	258.196	45.153	200.189	−2.324
4600	62.288	424.028	366.544	264.425	47.667	203.607	−2.312
4700	62.291	425.367	367.781	270.654	50.197	206.969	−2.300
4800	62.294	426.679	368.995	276.883	52.744	210.278	−2.288
4900	62.297	427.963	370.185	283.113	55.308	213.534	−2.276
5000	62.299	429.222	371.353	289.342	57.887	216.736	−2.264
5100	62.301	430.455	372.500	295.572	60.482	219.888	−2.252
5200	62.304	431.665	373.626	301.803	63.092	222.988	−2.240
5300	62.306	432.852	374.733	308.033	65.716	226.038	−2.228
5400	62.307	434.017	375.820	314.264	68.354	229.038	−2.216
5500	62.309	435.160	376.888	320.495	71.004	231.989	−2.203
5600	62.311	436.283	377.939	326.726	73.666	234.892	−2.191
5700	62.313	437.386	378.972	332.957	76.338	237.747	−2.179
5800	62.314	438.469	379.989	339.188	79.022	240.556	−2.166
5900	62.316	439.535	380.989	345.420	81.711	243.318	−2.154
6000	62.317	440.582	381.973	351.651	84.429	246.032	−2.142

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [297.8 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -995.98 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -999.14 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[800](1)	[910](1)
[520](1)	[210](1)
[240](1)	[260](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $[C_{2v}]$
Bond Distances: Al–F = [1.63] Å; Al–Cl = [2.06] Å
Bond Angles: Cl–Al–F = [120]°; F–Al–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.281169] \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -238.8 \pm 1.5\ kcal \cdot mol^{-1}$ and $\Delta_{at} H° = 380.8 \pm 3\ kcal \cdot mol^{-1}$ based on $\Delta_f H°(298.15\ K) = 0.5 \pm 1\ kcal \cdot mol^{-1}$ for 1/3 $AlCl_3(g)$ + 2/3 $AlF_3(g)$ = $AlClF_2(g)$. Krause and Douglas[1] obtained this result by an entrainment method which measured enhanced volatility of AlF_3 in the presence of $AlCl_3$. Corrections were made for all the possible dimers which can form in this system. The entrainment data establish that aluminum fluoride–chloride exchange reactions are almost thermoneutral.

Our adopted $\Delta_f H°$ is compared below with an approximate mass–spectrometric K_p for reaciton of AlF_2 with $AlCl_2$.[2] The discrepancy in $\Delta_f H°(AlClF_2)$ is −19 $kcal \cdot mol^{-1}$ if we use $\Delta_f H° = -180$ (AlF_2) and −71 ($AlCl_2$) derived from the mass–spectrometric data.[2, 3] The discrepancy disappears if we use $\Delta_f H° = -166$ (AlF_2) and −67 ($AlCl_2$) derived from average bond energies in AlF_3 and $AlCl_3$.[4] This favors the latter values of $\Delta_f H°$ for AlF_2 and $AlCl_2$,[4] although the discrepancy might arise from the observed ion intensity of $AlClF_2^+$. The signal from $AlClF_2^+$ was very weak at 40 eV;[5] this high ionizing energy might bias K_p and cause considerable fragmentation. We can eliminate AlF_2 and $AlCl_2$ by taking the difference between the mass–spectrometric reactions for $AlClF_2$ and $AlCl_2F$.[4] *This yields* $[\Delta_f H°(AlClF_2) - \Delta_f H°(AlCl_2F)] = -47\ kcal \cdot mol^{-1}$ which agrees with $-49.8\ kcal \cdot mol^{-1}$ from entrainment data.[1] Thus, we tentatively ascribe the discrepancy to AlF_2[4] and $AlCl_2$.

Source	Method	Reaction	T/K	$\Delta_r H°(T)$	$\Delta_f H°(298.15\ K)$		$\Delta_f H°(298.15\ K)$
				kcal·mol^{-1}			
1	Entrainment	1/3 $AlCl_3(g)$ + 2/3 $AlF_3(g)$ = $AlClF_2(g)$	1196–1257	0.5 ± 1	0.5 ± 1		−238.8
2	Mass Spec.	$AlF_2(g) + AlCl_2(g) = AlCl(g) + AlClF_2(g)$	1491	—	−19.2		−240[a]
						or	−258[b]

[a]Assuming $\Delta_f H°(298.15\ K) = -166$ (AlF_2) and −67 ($AlCl_2$) $kcal \cdot mol^{-1}$
[b]Assuming $\Delta_f H°(298.15\ K) = -180$ (AlF_2) and −71 ($AlCl_2$) $kcal \cdot mol^{-1}$

Heat Capacity and Entropy

We adopt a C_{2v} structure with bond angles and bond distances assumed equal to those in AlF_3 and $AlCl_3$.[4] We assume a singlet electronic ground state and neglect excited states. Vibrational frequencies are estimated by comparison of AlF_3 and $AlCl_3$ with the series BF_3, $BClF_2$, BCl_2F and BCl_3.[6, 7] The principal moments of inertia are $I_A = 12.5730 \times 10^{-39}$, $I_B = 26.2481 \times 10^{-39}$, and $I_C = 38.8212 \times 10^{-39}\ g \cdot cm^2$.

References

[1]R. F. Krause and T. B. Douglas, J. Phys. Chem. **72**, 3444 (1968).
[2]M. Farber and S. P. Harris, High Temp. Sci. **3**, 231 (1971).
[3]O. M. Uy, R. D. Srivastava and M. Farber, High Temp. Sci. **4**, 227 (1972).
[4]JANAF Thermochemical Tables: $AlF_2(g)$, $AlCl_2(g)$, $AlCl_2F(g)$, 6–30–76; $AlF_3(g)$, $AlCl_3(g)$, 6–30–70.
[5]M. Farber, Space Sciences, Inc., Monrovia, Calif., personal communication, (August 30, 1976).
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[7]L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.795	−995.980	−995.980	INFINITE
100	43.865	238.385	350.065	−11.168	−997.199	−993.852	519.135
200	57.230	273.348	303.584	−6.047	−998.328	−990.042	258.572
250	61.827	286.629	298.897	−3.067	−998.774	−987.917	206.414
298.15	65.447	297.839	297.839	0.	−999.139	−985.793	172.707
300	65.572	298.245	297.841	0.121	−999.152	−985.710	171.627
350	68.588	308.588	298.651	3.478	−999.479	−983.443	146.771
400	70.996	317.910	300.485	6.970	−999.766	−981.132	128.123
450	72.917	326.387	302.899	10.569	−1000.025	−978.787	113.615
500	74.454	334.152	305.642	14.255	−1000.265	−976.414	102.005
600	76.700	347.939	311.571	21.821	−1000.724	−971.601	84.585
700	78.209	359.883	317.639	29.571	−1001.209	−966.709	72.137
800	79.259	370.399	323.590	37.447	−1001.773	−961.744	62.795
900	80.014	379.780	329.322	45.413	−1002.462	−956.700	55.525
1000	80.573	388.241	334.797	53.444	−1013.906	−950.811	49.665
1100	80.997	395.941	340.011	61.523	−1014.596	−944.469	44.849
1200	81.325	403.003	344.970	69.640	−1015.281	−938.063	40.833
1300	81.584	409.524	349.688	77.786	−1015.966	−931.600	37.432
1400	81.792	415.577	354.181	85.955	−1016.653	−925.085	34.515
1500	81.962	421.227	358.465	94.143	−1017.346	−918.520	31.986
1600	82.101	426.521	362.554	102.346	−1018.047	−911.909	29.771
1700	82.218	431.502	366.465	110.562	−1018.755	−905.254	27.815
1800	82.316	436.204	370.210	118.789	−1019.472	−898.556	26.075
1900	82.399	440.657	373.802	127.025	−1020.197	−891.819	24.518
2000	82.471	444.885	377.251	135.269	−1020.928	−885.044	23.115
2100	82.532	448.911	380.568	143.519	−1021.664	−878.231	21.845
2200	82.586	452.751	383.763	151.775	−1022.403	−871.384	20.689
2300	82.633	456.423	386.843	160.036	−1023.143	−864.503	19.633
2400	82.674	459.941	389.816	168.301	−1023.880	−857.590	18.665
2500	82.711	463.317	392.689	176.570	−1024.613	−850.646	17.773
2600	82.743	466.561	395.468	184.843	−1025.338	−843.673	16.950
2700	82.772	469.685	398.159	193.119	−1026.054	−836.672	16.186
2800	82.798	472.695	400.768	201.398	−1320.659	−828.677	15.459
2900	82.821	475.601	403.298	209.678	−1320.252	−811.113	14.610
3000	82.842	478.409	405.756	217.962	−1319.829	−793.564	13.817
3100	82.861	481.126	408.143	226.247	−1319.386	−776.029	13.076
3200	82.879	483.757	410.465	234.534	−1318.924	−758.509	12.381
3300	82.894	486.308	412.725	242.823	−1318.438	−741.003	11.729
3400	82.909	488.783	414.926	251.113	−1317.929	−723.513	11.115
3500	82.922	491.186	417.071	259.404	−1317.394	−706.038	10.537
3600	82.934	493.522	419.162	267.697	−1316.831	−688.578	9.991
3700	82.945	495.795	421.203	275.991	−1316.241	−671.135	9.475
3800	82.955	498.007	423.195	284.286	−1315.621	−653.708	8.986
3900	82.965	500.162	425.141	292.582	−1314.972	−636.298	8.522
4000	82.974	502.262	427.043	300.879	−1314.291	−618.904	8.082
4100	82.982	504.311	428.902	309.177	−1313.579	−601.528	7.664
4200	82.990	506.311	430.722	317.475	−1312.834	−584.170	7.265
4300	82.997	508.264	432.502	325.775	−1312.057	−566.830	6.886
4400	83.003	510.172	434.246	334.075	−1311.248	−549.509	6.523
4500	83.009	512.038	435.954	342.375	−1310.403	−532.206	6.178
4600	83.015	513.862	437.628	350.677	−1309.528	−514.922	5.847
4700	83.021	515.647	439.269	358.978	−1308.621	−497.658	5.531
4800	83.026	517.395	440.879	367.281	−1307.682	−480.413	5.228
4900	83.030	519.107	442.458	375.583	−1306.710	−463.188	4.938
5000	83.035	520.785	444.007	383.887	−1305.709	−445.984	4.659
5100	83.039	522.429	445.529	392.190	−1304.678	−428.800	4.392
5200	83.043	524.042	447.023	400.495	−1303.619	−411.636	4.135
5300	83.047	525.624	448.492	408.799	−1302.531	−394.493	3.888
5400	83.050	527.176	449.934	417.104	−1301.418	−377.370	3.650
5500	83.054	528.700	451.353	425.409	−1300.279	−360.269	3.422
5600	83.057	530.196	452.747	433.715	−1299.117	−343.188	3.201
5700	83.060	531.666	454.119	442.021	−1297.932	−326.129	2.989
5800	83.063	533.111	455.469	450.327	−1296.724	−309.090	2.784
5900	83.066	534.531	456.797	458.633	−1295.500	−292.072	2.586
6000	83.068	535.927	458.104	466.940	−1294.236	−275.078	2.395

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K)$ = [54.4 ± 4] $J·K^{-1}·mol^{-1}$
T_{fus} = Unknown
T_{dcm} = [500] K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -793.3 \pm 1.3\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°$(AlOCl, cr, 298.15 K) is calculated from $\Delta_r H°(298.15\ K) = 21.05\ kcal·mol^{-1}$ for the reaction $AlOCl(cr) + Cl_2(g) = AlCl_3(cr) + 1/2\ O_2(g)$ reported by Schafer *et al.*[1] This reaction is the overall reaction of the following four separate reactions:

Reaction	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$
$AlOCl(cr) + 2(HCl 299.5\ H_2O) = AlCl_3·600\ H_2O(l)$	−46.9
$AlCl_3·600\ H_2O(l) = AlCl_3(cr) + 600\ H_2O(l)$	+79.3
$H_2O(l) = H_2(g) + 1/2\ O_2(g)$	+68.32
$H_2(g) + Cl_2(g) + 599\ H_2O(l) = 2(HCl·299.5\ H_2O)$	−79.67
$AlOCl(cr) + Cl_2(g) = AlCl_3(cr) + 1/2\ O_2(g)$	+21.05

Heat Capacity and Entropy

The heat capacities for AlOCl(cr) are estimated based on the assumption that $\Delta C_p = 0$ for the reaction $AlCl_3(cr) + Al_2O_3(cr) = 3\ AlOCl(cr)$. $S°(298.15\ K) = 13\ cal·K^{-1}·mol^{-1}$ was estimated by Schafer *et al.*[1]

Decomposition Data

T_{dcm} is calculated as the temperature at which the Gibbs energy change of the reaction $6\ AlOCl(cr) \rightarrow 2\ Al_2O_3(cr) + Al_2Cl_6(g)$ is zero.

References

[1] H. Schafer, F. E. Wittig and W. Wilborn, Z. anorg. allgem. Chem. **297**, 48 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	56.902	54.392	54.392	0.	−793.286	−737.235	129.161
300	57.112	54.745	54.393	0.105	−793.284	−736.888	128.304
400	64.308	72.215	56.726	6.196	−792.923	−718.130	93.778
500	69.203	87.118	61.351	12.883	−792.183	−699.511	73.077
600	72.634	100.052	66.748	19.983	−791.215	−681.065	59.292
700	74.977	111.431	72.335	27.367	−790.141	−662.791	49.458
800	76.860	121.570	77.867	34.963	−789.045	−644.673	42.093
900	78.168	130.701	83.239	42.716	−787.995	−626.691	36.372
1000	79.245	138.995	88.406	50.589	−797.638	−608.060	31.762
1100	80.040	146.586	93.355	58.554	−796.477	−589.158	27.977
1200	80.709	153.580	98.086	66.592	−795.269	−570.363	24.827
1300	81.243	160.062	102.607	74.691	−794.023	−551.672	22.166
1400	81.672	166.099	106.929	82.837	−792.749	−533.077	19.889
1500	81.961	171.744	111.064	91.019	−791.459	−514.574	17.919
1600	82.216	177.041	115.024	99.228	−790.158	−496.157	16.198
1700	82.435	182.033	118.820	107.461	−788.850	−477.822	14.682
1800	82.620	186.750	122.464	115.714	−787.539	−459.564	13.336
1900	82.770	191.221	125.966	123.984	−786.228	−441.379	12.134
2000	82.885	195.470	129.336	132.267	−784.920	−423.263	11.055
2100	82.958	199.515	132.582	140.560	−783.619	−405.212	10.079
2200	83.011	203.376	135.713	148.858	−782.330	−387.223	9.194
2300	83.036	207.067	138.736	157.161	−781.055	−369.292	8.387
2400	83.052	210.601	141.657	165.465	−779.797	−351.417	7.648
2500	83.052	213.991	144.483	173.770	−778.557	−333.593	6.970
2600	83.052	217.249	147.220	182.075	−777.335	−315.819	6.345
2700	83.052	220.383	149.872	190.381	−776.134	−298.091	5.767
2800	83.052	223.403	152.444	198.686	−1068.853	−279.439	5.213
2900	83.052	226.318	154.942	206.991	−1066.595	−251.286	4.526
3000	83.052	229.133	157.368	215.296	−1064.357	−223.210	3.886

PREVIOUS: CURRENT: March 1964

$S°(298.15\ K) = [248.9 \pm 20]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-346.0 \pm 20]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-348.1 \pm 20]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[450](1)
[350](2)
[900](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distance: O–Al = [1.62] Å; Al–Cl = [2.14] Å
Bond Angle: O–Al–Cl = 180°
Rotational Constant: B_o = [0.097704] cm^{-1}

Enthalpy of Formation

The Gibbs energy change of the reaction 1/3 Al_2O_3(l) + 1/3 $AlCl_3$(g) = AlOCl(g), $\Delta_r G°(2400\ K) = 28 \pm 3\ kcal \cdot mol^{-1}$, has been determined by Greenbaum *et al.*[1] Incorporating appropriate auliliary data, the enthalpy of reaction is derived to be 82.9 $kcal \cdot mol^{-1}$, yielding $\Delta_f H°$(AlOCl, g, 298.15 K) = $-82.2 \pm 5\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Point group, ground state quantum weight and vibrational frequencies are obtained from Hilsenrath *et al.*[2] The bond distances of r(O–Al) and r(Al–Cl) are assumed to be the same as those in AlO(g) and AlCl(g) molecules, respectively. The three principal moments of inertia are: $I_A = 0$ and $I_B = I_C = 2.86467 \times 10^{-38} g \cdot cm^2$.

References

[1]M. A. Greenbaum *et al.*, Marimont Corporation, California, personal communication, (August 26, 1964).
[2]J. Hilsenrath, W. H. Evans and H. W. Wooley, U. S. Nat. Bur. Stand. Report 6484, 115 (July 1, 1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.407	−346.045	−346.045	INFINITE
100	32.420	204.221	288.567	−8.435	−346.464	−348.072	181.814
200	43.404	230.239	253.322	−4.617	−347.422	−349.296	91.227
250	47.248	240.357	249.740	−2.346	−347.803	−349.719	73.070
298.15	50.068	248.931	248.931	0.	−348.109	−350.059	61.329
300	50.162	249.241	248.932	0.093	−348.120	−350.071	60.953
350	52.394	257.148	249.551	2.659	−348.386	−350.375	52.291
400	54.118	264.262	250.953	5.324	−348.617	−350.643	45.789
450	55.464	270.717	252.796	8.065	−348.826	−350.884	40.730
500	56.527	276.618	254.887	10.865	−349.023	−351.102	36.679
600	58.059	287.069	259.403	16.600	−349.420	−351.481	30.599
700	59.076	296.101	264.015	22.460	−349.871	−351.789	26.251
800	59.780	304.038	268.532	28.405	−350.425	−352.027	22.985
900	60.284	311.110	272.877	34.410	−351.124	−352.187	20.440
1000	60.656	317.482	277.024	40.458	−362.591	−351.500	18.360
1100	60.938	323.276	280.969	46.538	−363.316	−350.356	16.637
1200	61.155	328.588	284.719	52.643	−364.041	−349.146	15.198
1300	61.327	333.491	288.285	58.767	−364.769	−347.875	13.978
1400	61.465	338.041	291.678	64.907	−365.502	−346.548	12.930
1500	61.577	342.285	294.912	71.060	−366.241	−345.169	12.020
1600	61.670	346.262	297.999	77.222	−366.987	−343.740	11.222
1700	61.747	350.003	300.949	83.393	−367.741	−342.263	10.516
1800	61.811	353.535	303.773	89.571	−368.505	−340.743	9.888
1900	61.867	356.878	306.481	95.755	−369.279	−339.180	9.325
2000	61.914	360.053	309.081	101.944	−370.065	−337.575	8.817
2100	61.955	363.075	311.581	108.137	−370.864	−335.931	8.356
2200	61.990	365.958	313.987	114.335	−371.676	−334.248	7.936
2300	62.021	368.714	316.307	120.535	−372.503	−332.529	7.552
2400	62.048	371.354	318.546	126.739	−373.346	−330.773	7.199
2500	62.072	373.887	320.709	132.945	−374.204	−328.981	6.874
2600	62.094	376.322	322.802	139.153	−375.080	−327.155	6.573
2700	62.113	378.666	324.828	145.363	−375.974	−325.295	6.293
2800	62.130	380.925	326.791	151.576	−670.786	−322.433	6.015
2900	62.145	383.106	328.696	157.789	−670.620	−309.995	5.584
3000	62.159	385.213	330.545	164.005	−670.471	−297.563	5.181
3100	62.172	387.251	332.341	170.221	−670.341	−285.134	4.804
3200	62.183	389.225	334.088	176.439	−670.229	−272.710	4.452
3300	62.193	391.139	335.788	182.658	−670.133	−260.289	4.120
3400	62.203	392.996	337.444	188.878	−670.053	−247.871	3.808
3500	62.212	394.799	339.057	195.098	−669.989	−235.455	3.514
3600	62.220	396.552	340.629	201.320	−669.939	−223.040	3.236
3700	62.227	398.256	342.164	207.542	−669.903	−210.627	2.974
3800	62.234	399.916	343.662	213.765	−669.879	−198.215	2.725
3900	62.240	401.533	345.125	219.989	−669.866	−185.802	2.489
4000	62.246	403.109	346.555	226.213	−669.863	−173.391	2.264
4100	62.251	404.646	347.953	232.438	−669.870	−160.979	2.051
4200	62.256	406.146	349.321	238.663	−669.885	−148.567	1.848
4300	62.261	407.611	350.660	244.889	−669.907	−136.154	1.654
4400	62.265	409.042	351.970	251.116	−669.935	−123.741	1.469
4500	62.269	410.441	353.254	257.342	−669.967	−111.328	1.292
4600	62.273	411.810	354.512	263.569	−670.006	−98.913	1.123
4700	62.277	413.149	355.746	269.797	−670.050	−86.497	0.961
4800	62.280	414.461	356.955	276.025	−670.099	−74.081	0.806
4900	62.283	415.745	358.142	282.253	−670.151	−61.663	0.657
5000	62.286	417.003	359.307	288.481	−670.209	−49.244	0.514
5100	62.289	418.237	360.450	294.710	−670.272	−36.824	0.377
5200	62.292	419.446	361.573	300.939	−670.341	−24.404	0.245
5300	62.294	420.633	362.676	307.168	−670.415	−11.981	0.118
5400	62.296	421.797	363.760	313.398	−670.497	0.443	−0.004
5500	62.299	422.940	364.826	319.628	−670.586	12.869	−0.122
5600	62.301	424.063	365.874	325.858	−670.685	25.296	−0.236
5700	62.303	425.165	366.904	332.088	−670.793	37.725	−0.346
5800	62.305	426.249	367.918	338.318	−670.910	50.157	−0.452
5900	62.306	427.314	368.916	344.549	−671.043	62.589	−0.554
6000	62.308	428.361	369.898	350.779	−671.167	75.023	−0.653

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

$S°1(298.15\ K) = [289.42 \pm 2.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -279.4 \pm 20\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -280.3 \pm 20\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			Vibrational Frequencies and Degeneracies
State	ϵ_i, cm^{-1}	g_i	ν, cm^{-1}
$^2A_1$	0	2	[430](1)
$^2B_1$	[20000]	2	[160](1)
$^2B_2$	[25000]	2	[570](1)

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distance: Al–Cl = [2.10] Å
Bond Angle: Cl–Al–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.925281 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -67 \pm 5$ kcal·mol^{-1} and $\Delta_{at}H° = 201.4 \pm 6$ kcal·mol^{-1}; i.e., the average bond energy $\Delta_{at}H°/2 = 101$ kcal·mol^{-1} is taken equal to that of $AlCl_3$.[1] $\Delta_f H°$ is consistent with experimental results of -66 ± 3[2] and $\geq -71 \pm 5$ kcal·mol^{-1} [3,4] but there may be significant bias in these values.

Chai *et al.*[2] derived $\Delta_f H°(298.15\ K) = -66 \pm 3$ kcal·mol^{-1} from study of reactions of Al(c,l) with the vapor of $AlCl_3$ in an argon carrier gas. Weight–loss data (800–1000 K) for Al and $AlCl_3$ were analyzed assuming five vapor species (AlCl, $AlCl_2$, $AlCl_3$, Al_2Cl_4, Al_2Cl_6) in four simultaneous equilibrium reactions. Experimental data were combined with auxiliary data, including $S°(AlCl_2)$ and K_p for two reactions, to derive $\Delta_f H°(AlCl_2)$ and K_p for another reaction involving Al_2Cl_4. Despite minor changes in $S°(AlCl_2)$, $\Delta_f H° = -66$ is till appropriate for the $AlCl_2$ equilibrium.[2] We suspect, however, that this equilibrium is strongly dependent on the other equilibria, particularly that involving Al_2Cl_4(g).

Farber and Harris[3,4] reported K_p (5 points, 1150–1430 K) for the reaction $AlCl(g) + AlCl_3(g) = 2\ AlCl_2(g)$. We obtain $[\Delta_r S°(2nd\ law) - \Delta_r S°(3rd\ law)] = -35 \pm 10$ cal·K^{-1}·mol^{-1}, $\Delta_f H°(298.15\ K) = -36 \pm 13$(2nd law) or 10.5 ± 9(3rd law) and $\Delta_f H°(298.15\ K) \geq -70.7 \pm 5$ kcal·mol^{-1}. We consider $\Delta_f H°$ to be a negative limit due to possible bias arising from the ionizing energy. Energy of the ionizing electrons was variously reported as 20 eV[4] or as 3 eV above the AP.[3] If 20 eV was used, we expect $AlCl_2^+$ to be enhanced due to fragmentation of $AlCl_3$. The alternative ionizing energy leads to another problem, since the authors[3,4] used literature values for the AP of $AlCl^+$ but their own value for $AlCl_2^+$. Their value has a bias of −3 eV which is discussed in detail on the table for $AlCl_2^+$(g).[1] We suspect that the mass spectrometer had a biased energy scale during the measurments.[3,4] This would induce negative bias in the ionizing energy used for $AlCl^+$ and $AlCl_3^+$, since the AP's were not based on the experimental energy scale. Again we expect $AlCl_2^+$ to be enhanced relative to $AlCl^+$ and $AlCl_3^+$. The large discrepancy in $\Delta_r S°$ is symptomatic of a temperature–dependent error; we expect that bias in K_p is greatest at low T. NO_2, and NO. Although $[BE(MX)–BE(MX_3)] = -20$ kcal·mol^{-1}, only the mass–spectrometric data of Farber *et al.*[3–6] yield $BE(MX_2) > BE(MX_3)$. Other data[1,2,7] and theoretical calculations[8] suggest that $BE(MX_2) \leq BE(MX_3)$.

Source	Method	Species	Average Bond Energy ($\Delta_{at}H°/n$), kcal·mol^{-1}				
			$AlCl_n$	BCl_n	AlF_n	BF_n	NO_n
JANAF[1]	Review	MX	118.4	127.1	159.3	179.4	150.0
JANAF[1]	Review	MX_3	100.8	104.5	140.2	152.5	90.3
JANAF[1]	Review	MX_2	101	—	140	—	111.0
Farber *et al.*[3,4]	Mass spec.	MX_2	102.6	—	146.5, 151	—	—
Srivastava *et al.*[5,6]	Mass spec.	MX_2	—	104.0	147.0	155.0	—
Dibeler *et al.*[7]	Photoionization	MX_2	—	102.6	—	145.6	—
Others[2, f]	Various	MX_2	100.2[2]	103.5[f]	132.4[f]	—	—

Heat Capacity and Entropy

The electronic ground state and excited levels are assumed to be the same as in AlF_2.[1] Vibrational frequencies are calculated from the estimated force constants $f_r = 2.2$ and $f_{rr}/r^2 = 0.13$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of $AlCl_2^+$, $AlCl_2$, $AlCl_2^-$ and the analogous boron species. We assume that frequency changes are qualitatively similar to those of NO_2^+, NO_2, and NO_2^-. Thus, in going from $AlCl_2^+$ to $AlCl_2$, we expect a large decrease in ν_3, an increase in ν_2 and a small increase in ν_1. By analogy with BF_2,[8] the odd electron of $AlCl_2$ should occupy an anti–bonding orbital which increases the bond length but decreases the bond angle and stretching force constant. We assume a bond length 0.05 Å longer than in $AlCl_2^+$ [1] and a bond angle equal to that in BF_2.[8] The principal moments of inertia are $I_A = 3.5781 \times 10^{-39}$, $I_B = 38.9438 \times 10^{-39}$ and $I_C = 42.5220 \times 10^{-39}$ g·cm^2.

Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.764	−279.371	−279.371	INFINITE
100	39.512	239.866	331.991	−9.212	−279.216	−283.603	148.139
200	47.065	269.680	294.017	−4.867	−279.710	−287.825	75.172
250	49.753	280.487	290.260	−2.443	−280.019	−289.818	60.554
298.15	51.635	289.420	289.420	0.	−280.328	−291.677	51.101
300	51.696	289.739	289.421	0.096	−280.340	−291.748	50.798
350	53.093	297.819	290.056	2.717	−280.672	−293.623	43.821
400	54.109	304.979	291.482	5.399	−281.015	−295.450	38.582
450	54.863	311.397	293.345	8.124	−281.369	−297.233	34.502
500	55.434	317.209	295.445	10.882	−281.736	−298.976	31.234
600	56.219	327.391	299.945	16.468	−282.518	−302.351	26.322
700	56.716	336.097	304.502	22.116	−283.389	−305.590	22.803
800	57.050	343.693	308.937	27.805	−284.380	−308.695	20.156
900	57.284	350.427	313.180	33.523	−285.524	−311.668	18.089
1000	57.453	356.472	317.212	39.260	−297.439	−313.743	16.388
1100	57.580	361.954	321.034	45.012	−298.612	−315.317	14.973
1200	57.677	366.968	324.656	50.775	−299.786	−316.784	13.789
1300	57.754	371.588	328.091	56.547	−300.961	−318.153	12.784
1400	57.814	375.870	331.352	62.325	−302.140	−319.431	11.918
1500	57.864	379.861	334.455	68.109	−303.322	−320.625	11.165
1600	57.904	383.597	337.411	73.898	−304.508	−321.740	10.504
1700	57.938	387.108	340.232	79.690	−305.700	−322.780	9.918
1800	57.966	390.421	342.929	85.485	−306.897	−323.751	9.395
1900	57.990	393.555	345.512	91.283	−308.102	−324.654	8.925
2000	58.011	396.530	347.989	97.083	−309.314	−325.494	8.501
2100	58.030	399.361	350.368	102.885	−310.535	−326.273	8.116
2200	58.046	402.061	352.657	108.689	−311.767	−326.993	7.764
2300	58.062	404.642	354.862	114.494	−313.011	−327.658	7.441
2400	58.076	407.113	356.988	120.301	−314.268	−328.268	7.145
2500	58.091	409.484	359.040	126.110	−315.540	−328.825	6.870
2600	58.105	411.763	361.025	131.919	−316.827	−329.331	6.616
2700	58.121	413.956	362.945	137.731	−318.131	−329.787	6.380
2800	58.137	416.070	364.805	143.544	−613.353	−329.227	6.142
2900	58.155	418.111	366.608	149.358	−613.596	−319.075	5.747
3000	58.175	420.082	368.358	155.175	−613.857	−308.915	5.379
3100	58.198	421.990	370.057	160.993	−614.135	−298.746	5.034
3200	58.223	423.838	371.709	166.814	−614.430	−288.567	4.710
3300	58.252	425.631	373.316	172.638	−614.741	−278.379	4.406
3400	58.284	427.370	374.880	178.465	−615.066	−268.182	4.120
3500	58.319	429.060	376.404	184.295	−615.403	−257.974	3.850
3600	58.359	430.703	377.890	190.129	−615.751	−247.757	3.595
3700	58.403	432.303	379.339	195.967	−616.107	−237.530	3.353
3800	58.450	433.861	380.753	201.810	−616.469	−227.294	3.124
3900	58.503	435.380	382.135	207.657	−616.833	−217.047	2.907
4000	58.559	436.862	383.484	213.510	−617.199	−206.792	2.700
4100	58.620	438.309	384.804	219.369	−617.563	−196.527	2.504
4200	58.685	439.722	386.095	225.234	−617.922	−186.254	2.316
4300	58.755	441.104	387.358	231.106	−618.273	−175.972	2.138
4400	58.829	442.455	388.595	236.986	−618.616	−165.682	1.967
4500	58.907	443.778	389.807	242.872	−618.944	−155.384	1.804
4600	58.990	445.074	390.994	248.767	−619.260	−145.079	1.647
4700	59.076	446.343	392.158	254.670	−619.559	−134.768	1.498
4800	59.166	447.588	393.300	260.582	−619.841	−124.450	1.354
4900	59.259	448.809	394.421	266.504	−620.103	−114.127	1.217
5000	59.356	450.007	395.520	272.434	−620.345	−103.798	1.084
5100	59.456	451.184	396.600	278.375	−620.564	−93.465	0.957
5200	59.559	452.339	397.661	284.326	−620.762	−83.128	0.835
5300	59.664	453.475	398.703	290.287	−620.935	−72.787	0.717
5400	59.772	454.591	399.728	296.259	−621.086	−62.443	0.604
5500	59.882	455.689	400.736	302.241	−621.212	−52.096	0.495
5600	59.994	456.769	401.727	308.235	−621.314	−41.748	0.389
5700	60.107	457.831	402.702	314.240	−621.393	−31.398	0.288
5800	60.222	458.878	403.661	320.257	−621.445	−21.047	0.190
5900	60.338	459.908	404.606	326.285	−621.477	−10.695	0.095
6000	60.455	460.923	405.536	332.324	−621.465	−0.345	0.003

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [268.26 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 475 \pm 75\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [481.160]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[390](1)
[120](2)
[690](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Al–Cl = [2.05] Å
Bond Angle: Cl–Al–Cl = [180]°
Rotational Constant: B_o = [0.056573] cm^{-1}

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = 115 \pm 18$ kcal·mol^{-1} and $IP(AlCl_2) = 7.8 \pm 0.9$ eV. Electron–impact studies gave 13.4 ± 0.5 eV[1] and 13.4 ± 0.7 eV[2] for the appearance potential (AP) of $AlCl_2^+$ from $AlCl_3$. The analogous process for onset of BCl_2^+ from BCl_3 has been studied by both photoionization[3] and electron impact.[2] Comparison indicates that BCl_2^+ from electron impact[2] carried an excess energy (E*) of ~0.9 eV. We estimate the excess energy for $AlCl_2^+$ as 1.2 ± 0.6 eV. Thus, we take $AP–E^* = \Delta_f H° = 12.2 \pm 0.8$ eV (281.3 ± 18 kcal·mol^{-1}) for the reaction $AlCl_3(g) + e^-(g) = AlCl_2^+(g) + Cl(g) + 2\ e^-(g)$. With JANAF auxiliary data[4] this yields $\Delta_f H°(AlCl_2^+) = 113.5 \pm 18$, $\Delta_f H°(298.15\ K) = 115 \pm 18$ and $IP(AlCl_2) = 180 \pm 20$ kcal·mol^{-1} (7.8 ± 0.9 eV).

Electron impact studies[5–7] of $AlCl_2$ and BCl_2 gave approximate appearance potentials $AP(MCl_2^+) = 12 \pm 1$ eV. This is −4 eV greater than our adiabatic IP values. Such a difference could arise from several factors including bias in the ionizing–energy scale, bias in threshold detection, excess energy in MCl_2^+ and misassignment of the ionization process. The studies[5–7] make no mention of a calibrant gas for the energy scale. Reactive radicals (e.g. $AlCl_2$ from a reducing environment) may induce a bias in the energy scale. Consistent with this hypothesis, the values reported[6,7] for $AP(BCl^+/BCl)$ and $AP(BCl_2^+/BCl_3)$ are ~2 and 3–4 eV higher than other electron–impact data.[2,8] $AP(MCl_2^+/MCl_2)$ was obtained[5–7] by a vanishing current (or initial break) method. We expect this to have a positive bias which increases as the pressure of MCl_2 decreases.[9] Electron impact on MCl_2 should yield a vertical AP corresponding to a nonlinear (excited) configuration of MCl_2^+. Excitation energies of >1 eV are expected if MCl_2^+ is similar to BF_2^+ and AlF_2^+.[4] Alternatively, $AP(MCl_2^+) = 12 \pm 1$ eV[5–7] is a magnitude which may not exclude processes such as fragmentation or ion–molecular reactions of MCl_3. $AP(MCl_2^+)$ almost overlaps with the onset of MCl_2^+ from MCl_3; i.e., 12.30 eV[3] (photoionization) or 13.0−13.2 eV[2,8] (electron impact) from BCl_3 and 13.4 ± 0.5 eV[1,2] (electron impact) from $AlCl_3$. On the other hand, the coincidence of $AP(BCl^+) = AP(BCl_2^+) = 12 \pm 1$ eV[6,7] suggests that the two ions might be related, possibly via $BCl^+ + BCl_3 = BCl_2^+$. The authors[5,6] did not measure $AP(AlCl^+)$, but the analogous ion–molecular reaction is also energetically feasible. In summary, there are three plausible factors which may contribute to positive bias in the observed $AP(AlCl_2^+)$ and some conceivable alternative interpretations of the data.[5–7] This precludes use of $AP(AlCl_2^+)$ in calculating $\Delta_f H°$ of $AlCl_2^+$.

Hastie and Margrave[10] used an extended Hucket method to calculate $IP(AlCl_2) = 6.65$ eV. This result should approximate the vertical IP which we expect at ~9 eV.

Heat Capacity and Entropy

We assume the electronic ground state to be linear $^1\Sigma^+$ and neglect excited states by analogy with $MgCl_2$[4,11] and other tratomic species having sixteen valence electrons.[12] We estimate the bond distance to be almost the same as in $AlCl_3$ and 0.05 Å shorter than in $AlCl_2$.[4] 0 Likewise, we transfer the stretching force constant from $AlCl_3$ and the ratio $f_r/f_\alpha = 19$ Å^{-2} from $MgCl_2$.[11] Thus, we calculate vibrational frequencies from the estimated force constants $f_r = 2.9$, $f_{rr} = 0.2$ and $f_\alpha/r^2 = 0.036$ mdyn/Å. The resulting values have been rounded upward.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.481	475.202		
100	43.152	214.688	314.010	−9.932			
200	50.669	247.132	273.173	−5.208			
250	53.206	258.723	269.158	−2.609			
298.15	55.063	268.261	268.261	0.	481.160	469.865	−82.318
300	55.124	268.602	268.262	0.102	481.193	469.794	−81.798
350	56.563	277.213	268.939	2.896	482.072	467.825	−69.819
400	57.646	284.840	270.459	5.752	482.944	465.730	−60.818
450	58.470	291.679	272.443	8.656	483.807	463.526	−53.805
500	59.106	297.874	274.681	11.596	484.662	461.227	−48.184
600	60.000	308.736	279.477	17.555	486.332	456.382	−39.732
700	60.579	318.031	284.337	23.586	487.922	451.264	−33.674
800	60.971	326.147	289.067	29.665	489.399	445.924	−29.116
900	61.249	333.346	293.594	35.776	490.728	440.408	−25.561
1000	61.452	339.810	297.898	41.912	481.290	435.514	−22.749
1100	61.604	345.674	301.979	48.065	482.596	430.873	−20.460
1200	61.721	351.040	305.847	54.232	483.905	426.113	−18.548
1300	61.813	355.984	309.516	60.408	485.213	421.244	−16.926
1400	61.887	360.568	313.001	66.594	486.520	416.275	−15.531
1500	61.946	364.840	316.316	72.785	487.824	411.211	−14.320
1600	61.996	368.839	319.475	78.983	489.125	406.062	−13.257
1700	62.036	372.599	322.490	85.184	490.422	400.830	−12.316
1800	62.071	376.146	325.374	91.390	491.713	395.523	−11.478
1900	62.100	379.503	328.135	97.598	492.998	390.144	−10.726
2000	62.125	382.688	330.784	103.809	494.275	384.698	−10.047
2100	62.146	385.720	333.328	110.023	495.544	379.187	−9.432
2200	62.165	388.612	335.776	116.239	496.802	373.617	−8.871
2300	62.181	391.375	338.134	122.456	498.049	367.990	−8.357
2400	62.196	394.022	340.408	128.675	499.282	362.309	−7.885
2500	62.208	396.561	342.603	134.895	500.501	356.576	−7.450
2600	62.219	399.001	344.726	141.116	501.704	350.795	−7.048
2700	62.230	401.350	346.780	147.339	502.890	344.969	−6.674
2800	62.238	403.613	348.769	153.562	210.157	340.066	−6.344
2900	62.247	405.797	350.698	159.786	212.402	344.666	−6.208
3000	62.254	407.908	352.570	166.012	214.629	349.189	−6.080
3100	62.260	409.949	354.389	172.237	216.836	353.638	−5.959
3200	62.266	411.926	356.156	178.464	219.025	358.016	−5.844
3300	62.272	413.842	357.875	184.690	221.196	362.326	−5.735
3400	62.277	415.701	359.549	190.918	223.350	366.570	−5.632
3500	62.281	417.506	361.179	197.146	225.489	370.751	−5.533
3600	62.286	419.261	362.768	203.374	227.615	374.871	−5.439
3700	62.289	420.967	364.318	209.603	229.728	378.933	−5.350
3800	62.293	422.629	365.831	215.832	231.832	382.937	−5.264
3900	62.296	424.247	367.308	222.062	233.927	386.886	−5.182
4000	62.299	425.824	368.751	228.291	236.017	390.782	−5.103
4100	62.302	427.362	370.162	234.521	238.103	394.625	−5.028
4200	62.305	428.864	371.542	240.752	240.188	398.417	−4.955
4300	62.307	430.330	372.892	246.982	242.273	402.160	−4.885
4400	62.309	431.762	374.214	253.213	244.361	405.854	−4.818
4500	62.312	433.163	375.508	259.444	246.456	409.501	−4.753
4600	62.314	434.532	376.777	265.676	248.555	413.101	−4.691
4700	62.315	435.872	378.020	271.907	250.662	416.655	−4.631
4800	62.317	437.184	379.239	278.139	252.778	420.165	−4.572
4900	62.319	438.469	380.434	284.370	254.906	423.630	−4.516
5000	62.320	439.728	381.608	290.602	257.044	427.051	−4.461
5100	62.322	440.962	382.759	296.834	259.194	430.430	−4.409
5200	62.323	442.173	383.890	303.067	261.357	433.767	−4.357
5300	62.325	443.360	385.001	309.299	263.533	437.061	−4.307
5400	62.326	444.525	386.093	315.532	265.723	440.315	−4.259
5500	62.327	445.668	387.166	321.764	267.925	443.528	−4.212
5600	62.328	446.791	388.220	327.997	270.140	446.701	−4.167
5700	62.329	447.895	389.258	334.230	272.368	449.834	−4.122
5800	62.330	448.979	390.278	340.463	274.611	452.928	−4.079
5900	62.331	450.044	391.282	346.696	276.862	455.983	−4.037
6000	62.332	451.092	392.270	352.929	279.147	458.997	−3.996

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [285.8 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-474 \pm 105]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-481.160]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[23000]	3
$^1B_1$	[30000]	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[430](1)
[160](1)
[460](1)

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distance: Al–Cl = [2.15] Å
Bond Angle: Cl–Al–Cl = [105]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.583526 \times 10^{-114}]\ g^3\ cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -115 \pm 25\ kcal \cdot mol^{-1}$ based on an estimated electron affinity of $EA(AlCl_2) = 46 \pm 23\ kcal \cdot mol^{-1}$ (2.0 ± 1 eV) and a fluoride-ion affinity of $IA(AlCl) = 46 \pm 25\ kcal \cdot mol^{-1}$. JANAF auxiliary data[1] are used in converting from one quantity to another. If AlX_2 radicals were analogous to X atoms,[2,3] then $EA(AlCl_2)$ should be approximately equal to $EA(AlF_2) = 0.2 \pm 0.4$ eV.[1] This analogy may not be justified, since the pertinent orbitals are quite different. An electron added to AlX_2 presumably occupies a molecular orbital centered mainly on the metal opposite the two halogens. We assume that the orbital energy is characteristic of the metal Al and is perturbed relatively little by substitution of Cl for F. This implies that $EA(AlCl_2) \approx EA(AlF_2)$.

The energy for the self-ionization process, $2\ AlF_2 = AlF_2^+ + AlF_2^-$, is $\Delta_f H° = [IP(AlF_2) - EA(AlF_2)] = 5.9 \pm 1$ eV.[1] Assuming $AlCl_2$ is similar, we estimate $EA(AlCl_2) = 1.9$ eV. The energy difference between the reactions $AlF_2^- = AlF + F^-$ and $AlF_2 = AlF + F$ is $\Delta_r H° = [IA(AlF) - D_0°(AlF_2)] = -29\ kcal \cdot mol^{-1}$. Assuming $AlCl_2^-$ is analogous, we estimate $EA(AlCl_2) = 2.3$ eV. We adopt the intermediate value $EA(AlCl_2) = 2.0 \pm 1$ eV but emphasize that all estimates depend on AlF_2.[1]

Heat Capacity and Entropy

Electronic levels and quantum weights are assumed equal to those of isoelectronic $SiCl_2$[1] calculated from the estimated force constants $f_r = 1.73$, $f_{r\pi} = 0.07$ and $f_{\alpha}/r^2 = 0.156$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of $AlCl_2$, $AlCl_2$, $AlCl_2^-$ and the analogous boron species. We assume that frequency changes are qualitatively similar in the two series $AlCl_2^+$, $AlCl_2$, $AlCl_2^-$ and NO_2^+, NO_2, NO_2^-[1] which have the same number of valence electrons. Furthermore, we expect isoelectronic $SiCl_2$[1] to provide upper-limit frequencies for $AlCl_2^-$. Thus, in going from $AlCl_2$ to $AlCl_2^-$, we assume little change in ν_1 and ν_2 but a significant decrease in ν_3.

By analogy with BF_2,[4,5] we expect that the odd electron in $AlCl_2$ occupies a molecular orbital centered mainly on the metal opposite the two chlorides. This orbital should be antibonding[4] in the sense that addition of an electron increases the bond length but decreases the bond angle and stretching force constant. We assume that the bond length is 0.05 Å longer and the bond angle is 15° smaller than in $AlCl_2$.[1] The principal moments of inertia are: $I_A = 5.5597 \times 10^{-39}$, $I_B = 34.2573 \times 10^{-39}$ and $I_C = 39.8170 \times 10^{-39}\ g \cdot cm^2$.

References

[1]JANAF Thermochemical Tables: $AlCl_2(g)$, $AlCl_2^+(g)$, $AlF_2(g)$, $AlF_2^+(g)$ and $AlF_2^-(g)$, 6–30–76; $NO_2^-(g)$, 6–30–72; $SiCl_2(g)$, 12–31–70; AlCl(g), 6–30–70; $Cl^-(g)$, 6–30–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.969	−474.211		
100	39.846	235.193	329.316	−9.412			
200	48.255	265.583	290.476	−4.979			
250	50.901	276.654	286.636	−2.496			
298.15	52.650	285.778	285.778	0.	−481.160	−485.169	85.000
300	52.706	286.104	285.779	0.097	−481.209	−485.193	84.480
350	53.953	294.328	286.426	2.766	−482.533	−485.753	72.495
400	54.836	301.593	287.877	5.487	−483.876	−486.122	63.481
450	55.478	308.091	289.768	8.245	−485.236	−486.321	56.451
500	55.957	313.962	291.899	11.032	−486.614	−486.368	50.810
600	56.606	324.227	296.456	16.663	−489.429	−486.055	42.315
700	57.013	332.985	301.064	22.345	−492.345	−485.264	36.211
800	57.283	340.617	305.541	28.061	−495.388	−484.047	31.605
900	57.471	347.376	309.821	33.799	−498.590	−482.439	28.000
1000	57.607	353.438	313.885	39.553	−512.566	−479.704	25.057
1100	57.708	358.934	317.734	45.319	−515.804	−476.261	22.616
1200	57.786	363.958	321.380	51.094	−519.045	−472.524	20.568
1300	57.847	368.586	324.836	56.876	−522.289	−468.515	18.825
1400	57.895	372.875	328.116	62.663	−525.537	−464.257	17.322
1500	57.934	376.871	331.234	68.455	−528.790	−459.767	16.010
1600	57.966	380.611	334.205	74.250	−532.049	−455.059	14.856
1700	57.993	384.126	337.039	80.048	−535.313	−450.147	13.831
1800	58.015	387.441	339.748	85.848	−538.584	−445.043	12.915
1900	58.034	390.578	342.341	91.651	−541.862	−439.757	12.090
2000	58.051	393.556	344.828	97.455	−545.149	−434.298	11.343
2100	58.065	396.388	347.217	103.261	−548.445	−428.674	10.663
2200	58.078	399.090	349.514	109.068	−551.752	−422.893	10.041
2300	58.090	401.672	351.726	114.876	−555.072	−416.962	9.469
2400	58.101	404.144	353.859	120.686	−558.405	−410.886	8.943
2500	58.112	406.516	355.918	126.496	−561.753	−404.670	8.455
2600	58.124	408.796	357.908	132.308	−565.116	−398.321	8.002
2700	58.136	410.990	359.834	138.121	−568.497	−391.841	7.581
2800	58.150	413.104	361.699	143.935	−865.796	−384.269	7.169
2900	58.166	415.145	363.507	149.751	−868.117	−367.030	6.611
3000	58.184	417.117	365.261	155.569	−870.456	−349.712	6.089
3100	58.205	419.025	366.965	161.388	−872.812	−332.315	5.599
3200	58.230	420.874	368.621	167.210	−875.185	−314.842	5.139
3300	58.259	422.666	370.231	173.034	−877.574	−297.294	4.706
3400	58.293	424.406	371.799	178.862	−879.976	−279.674	4.297
3500	58.332	426.096	373.326	184.693	−882.391	−261.982	3.910
3600	58.376	427.740	374.815	190.528	−884.816	−244.222	3.544
3700	58.427	429.340	376.267	196.368	−887.248	−226.394	3.196
3800	58.484	430.899	377.685	202.214	−889.686	−208.501	2.866
3900	58.547	432.419	379.069	208.065	−892.125	−190.543	2.552
4000	58.618	433.902	380.421	213.924	−894.564	−172.523	2.253
4100	58.696	435.350	381.743	219.789	−897.000	−154.441	1.968
4200	58.782	436.766	383.036	225.663	−899.429	−136.301	1.695
4300	58.875	438.150	384.302	231.546	−901.848	−118.103	1.435
4400	58.975	439.505	385.541	237.438	−904.256	−99.848	1.185
4500	59.083	440.831	386.755	243.341	−906.647	−81.539	0.946
4600	59.199	442.131	387.945	249.255	−909.022	−63.177	0.717
4700	59.322	443.405	389.112	255.181	−911.378	−44.764	0.497
4800	59.452	444.656	390.256	261.120	−913.712	−26.301	0.286
4900	59.589	445.883	391.378	267.072	−916.021	−7.789	0.083
5000	59.733	447.088	392.481	273.038	−918.306	10.769	−0.113
5100	59.884	448.273	393.563	279.018	−920.564	29.373	−0.301
5200	60.041	449.437	394.626	285.015	−922.795	48.021	−0.482
5300	60.204	450.582	395.671	291.027	−924.996	66.712	−0.657
5400	60.372	451.709	396.699	297.056	−927.168	85.444	−0.827
5500	60.545	452.818	397.709	303.101	−929.310	104.216	−0.990
5600	60.724	453.911	398.703	309.165	−931.421	123.026	−1.148
5700	60.906	454.987	399.681	315.246	−933.502	141.874	−1.300
5800	61.093	456.048	400.644	321.346	−935.549	160.758	−1.448
5900	61.283	457.094	401.592	327.465	−937.569	179.677	−1.591
6000	61.476	458.126	402.525	333.603	−939.537	198.628	−1.729

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [311.4 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -788.4 \pm 6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -790.8 \pm 6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[840](1)	[640](1)
[430](1)	[190](1)
[160](1)	[220](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: Al–F = [1.63] Å; Al–Cl = [2.06] Å
Bond Angles: Cl–Al–F = [120]°; Cl–Al–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.841449 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -189.0 \pm 1.5\ kcal \cdot mol^{-1}$ and $\Delta_a H° = 341.4 \pm 3\ kcal \cdot mol^{-1}$ based on $\Delta_f H°(298.15\ K) = 0.5 \pm 1\ kcal \cdot mol^{-1}$ for 2/3 $AlCl_3(g)$ + 1/3 $AlF_3(g)$ = $AlCl_2F(g)$. Krause and Douglas[1] obtained this result by an entrainment method which measured enhanced volatility of AlF_3 in the presence of $AlCl_3$. Corrections were made for all the possible dimers which can form in this system. The entrainment data establish that aluminum fluoride–chloride exchange reactions are almost thermoneutral.

Our adopted $\Delta_f H°$ is compared below with an approximate mass-spectrometric K_p for reaction of AlF_2 with $AlCl_2$.[2] The discrepancy in $\Delta_f H°(AlCl_2F)$ is −22 $kcal \cdot mol^{-1}$ if we use $\Delta_f H° = -180$ (AlF_2) and −71 ($AlCl_2$) derived from the mass-spectrometric data.[2, 3] The discrepancy almost disappears if we use $\Delta_f H° = -166$ (AlF_2) and −67 ($AlCl_2$) derived from average bond energies in AlF_3 and $AlCl_3$.[4] This favors the latter values of $\Delta_f H°$ for AlF_2 and $AlCl_2$,[4] although the discrepancy might arise from the observed ion intensity of $AlCl_2F^+$. The signal from $AlCl_2F^+$ was very weak at 40 eV;[5] this high ionizing energy might bias K_p and cause considerable fragmentation. We can eliminate AlF_2 and $AlCl_2$ by taking the difference between the mass–spectrometric reactions for $AlClF_2$[4] and $AlCl_2F$. This yields [$\Delta_f H°(AlClF_2)$–$\Delta_f H°(AlCl_2F)$] = −47 $kcal \cdot mol^{-1}$ which agrees with −49.8 $kcal \cdot mol^{-1}$ from entrainment data.[1] Thus, we tentatively ascribe the discrepancy to AlF_2[4] and $AlCl_2$.

Source	Method	Reaction	T/K	$\Delta_r H°(T)$	$\Delta_f H°(298.15\ K)$	$\Delta_f H°(298.15\ K)$
					kcal·mol^{-1}	
1	Entrainment	2/3 $AlCl_3(g)$ + 1/3 $AlF_3(g)$ = $AlCl_2F(g)$	1196–1257	0.5 ± 1	0.5 ± 1	−189.0
2	Mass Spec.	$AlF_2(g) + AlCl_2(g) = AlF(g) + AlCl_2F(g)$	1491	—	−23.4	−194[a]
					or	−211[b]

[a] Assuming $\Delta_f H°(298.15\ K) = -166$ (AlF_2) and −67 ($AlCl_2$) $kcal \cdot mol^{-1}$.
[b] Assuming $\Delta_f H°(298.15\ K) = -180$ (AlF_2) and −71 ($AlCl_2$) $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

We adopt a C_{2v} structure with bond angles and bond distances assumed equal to those in AlF_3 and $AlCl_3$.[4] We assume a singlet electronic ground state and neglect excited states. Vibrational frequencies are estimated by comparison of AlF_3 and $AlCl_3$with the series BF_3, $BClF_2$, BCl_2F and BCl_3.[6, 7] The principal moments of inertia are: $I_A = 18.3596 \times 10^{-39}$, $I_B = 37.4744 \times 10^{-39}$ and $I_C = 55.8339 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.747	−788.390	−788.390	INFINITE
100	47.886	247.731	366.958	−11.923	−789.415	−786.070	410.601
200	61.104	285.446	317.475	−6.406	−790.202	−782.405	204.343
250	65.494	299.572	312.518	−3.236	−790.517	−780.418	163.059
298.15	68.804	311.403	311.403	0.	−790.776	−778.449	136.381
300	68.916	311.829	311.404	0.127	−790.785	−778.372	135.527
350	71.562	322.660	312.253	3.642	−791.019	−776.284	115.854
400	73.607	332.355	314.171	7.274	−791.227	−774.165	101.096
450	75.197	341.120	316.686	10.995	−791.418	−772.021	89.614
500	76.446	349.110	319.535	14.788	−791.600	−769.856	80.426
600	78.234	363.218	325.671	22.528	−791.963	−765.473	66.640
700	79.411	375.372	331.923	30.414	−792.373	−761.026	56.788
800	80.220	386.032	338.034	38.398	−792.874	−756.516	49.395
900	80.797	395.515	343.904	46.451	−793.510	−751.934	43.641
1000	81.221	404.051	349.499	54.553	−804.905	−746.513	38.994
1100	81.541	411.808	354.816	62.691	−805.551	−740.643	35.170
1200	81.788	418.914	359.866	70.858	−806.194	−734.714	31.981
1300	81.983	425.469	364.663	79.047	−806.837	−728.731	29.281
1400	82.139	431.550	369.226	87.254	−807.483	−722.698	26.964
1500	82.265	437.222	373.572	95.474	−808.134	−716.620	24.955
1600	82.370	442.534	377.718	103.706	−808.791	−710.497	23.195
1700	82.457	447.531	381.679	111.947	−809.456	−704.334	21.642
1800	82.530	452.246	385.470	120.197	−810.129	−698.131	20.259
1900	82.592	456.710	389.103	128.453	−810.811	−691.890	19.021
2000	82.645	460.948	392.590	136.715	−811.502	−685.613	17.906
2100	82.691	464.981	395.942	144.982	−812.203	−679.302	16.897
2200	82.731	468.829	399.168	153.253	−812.912	−672.956	15.978
2300	82.765	472.507	402.278	161.528	−813.631	−666.579	15.138
2400	82.796	476.030	405.278	169.806	−814.358	−660.170	14.368
2500	82.823	479.411	408.176	178.087	−815.094	−653.730	13.659
2600	82.847	482.659	410.979	186.370	−815.839	−647.261	13.004
2700	82.869	485.787	413.692	194.656	−816.591	−640.762	12.396
2800	82.888	488.801	416.321	202.944	−1111.252	−633.269	11.814
2900	82.905	491.710	418.870	211.234	−1110.923	−616.204	11.099
3000	82.921	494.520	421.345	219.525	−1110.600	−599.150	10.432
3100	82.935	497.240	423.750	227.818	−1110.282	−582.107	9.808
3200	82.948	499.873	426.088	236.112	−1109.967	−565.074	9.224
3300	82.959	502.426	428.363	244.407	−1109.654	−548.051	8.675
3400	82.970	504.902	430.578	252.704	−1109.341	−531.037	8.158
3500	82.980	507.308	432.736	261.001	−1109.027	−514.033	7.672
3600	82.989	509.645	434.840	269.299	−1108.709	−497.037	7.212
3700	82.997	511.919	436.892	277.599	−1108.386	−480.051	6.777
3800	83.005	514.133	438.896	285.899	−1108.056	−463.074	6.365
3900	83.012	516.289	440.853	294.200	−1107.715	−446.105	5.975
4000	83.018	518.391	442.765	302.501	−1107.364	−429.145	5.604
4100	83.024	520.441	444.635	310.803	−1106.998	−412.194	5.251
4200	83.030	522.441	446.464	319.106	−1106.617	−395.252	4.916
4300	83.035	524.395	448.253	327.409	−1106.218	−378.319	4.596
4400	83.040	526.304	450.006	335.713	−1105.801	−361.396	4.290
4500	83.044	528.170	451.722	344.017	−1105.359	−344.483	3.999
4600	83.049	529.996	453.404	352.322	−1104.898	−327.580	3.720
4700	83.053	531.782	455.053	360.627	−1104.413	−310.687	3.453
4800	83.057	533.530	456.669	368.932	−1103.904	−293.804	3.197
4900	83.060	535.243	458.255	377.238	−1103.368	−276.933	2.952
5000	83.063	536.921	459.812	385.544	−1102.807	−260.073	2.717
5100	83.066	538.566	461.340	393.851	−1102.220	−243.223	2.491
5200	83.069	540.179	462.841	402.158	−1101.607	−226.386	2.274
5300	83.072	541.761	464.315	410.465	−1100.967	−209.561	2.065
5400	83.075	543.314	465.764	418.772	−1100.302	−192.748	1.864
5500	83.077	544.838	467.188	427.080	−1099.610	−175.948	1.671
5600	83.080	546.335	468.588	435.388	−1098.894	−159.161	1.485
5700	83.082	547.806	469.965	443.696	−1098.153	−142.387	1.305
5800	83.084	549.251	471.319	452.004	−1097.386	−125.626	1.131
5900	83.086	550.671	472.652	460.312	−1096.599	−108.878	0.964
6000	83.088	552.068	473.964	468.621	−1095.768	−92.146	0.802

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 109.29 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 465.7 \pm 0.2\ K$

$\Delta_f H°(0\ K) = -704.30 \pm 0.84\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -705.63 \pm 0.84\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 35.35 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°(AlCl_3, cr, 298.15\ K) = -168.65 \pm 0.20\ kcal \cdot mol^{-1}$ ($-705.632 \pm 0.84\ kJ \cdot mol^{-1}$) is a weighted average of the values of Gross and Hayman[1] and of Coughlin.[3] NBS[4] recommended a value of $-704.2\ kJ \cdot mol^{-1}$ based on data available prior to 1968.

Gross and Hayman[1] measured the enthalpy of direct combination of "spectrographically pure" aluminum and carefully purified chlorine and derived $\Delta_f H°(298.15\ K) = -168.80 \pm 0.16\ kcal \cdot mol^{-1}$. Siemonsen[2] also reported the enthalpy of direct combination and is in agreement at $-167.5\ kcal \cdot mol^{-1}$ within his relatively large uncertainty interval of $\pm 1.1\ kcal \cdot mol^{-1}$. Coughlin[3] determined the enthalpy of solution of 99.99+% pure Al in 4.360 m HCl and also the enthalpy of solution of anhydrous $AlCl_3$ in the same solvent. Enthalpies of mixing were measured to close a thermochemical cycle at 303.15 K (adjusted to 1981 relative atomic masses).

Source	Reaction	$\Delta_r H°(303.15\ K)$, $cal \cdot mol^{-1}$
1	$Al(cr) + 3H^+(sln) = Al^{+++}(sln) + 3/2\ H_2(g)$	-127057 ± 120
2	$3(HCl \cdot 12.731\ H_2O)(l) = 3H^+(sln) + 3\ Cl^-(sln) + 38.193\ H_2O(sln)$	0 ± 10
3	$AlCl_3(cr) = Al^{+++}(sln) + 3\ Cl^-(sln)$	-72504 ± 50
4	$38.193\ H_2O(l) = 38.193\ H_2O(sln)$	-3050 ± 20
5	$Al(cr) + 3\ (HCl \cdot 12.731\ H_2O)(l) = AlCl_3(cr) + 38.193\ H_2O(l) + 3/2\ H_2(g)$	-51503 ± 140

With auxiliary data from JANAF[12] and CODATA,[5] the enthalpy of reaction (5) at 298.15 K is $-51910 \pm 140\ cal \cdot mol^{-1}$ $AlCl_3$. Interpolation of data for $\Delta_f H°(HCl, aq, 298.15\ K)$[4] yields $\Delta_f H°(AlCl_3, cr, 298.15\ K) = -168.32\ kcal \cdot mol^{-1}$. The overall uncertainty is estimated as 300 $cal \cdot mol^{-1}$. Semenenko *et al.*[6] also determined the enthalpy of solution of Al in (HCl, 11.13 H_2O) and of $AlCl_3$in (HCl, 11.26 H_2O). Their results yield a more negative value, $\Delta_f H°(AlCl_3, cr, 298.15\ K) = -170.1 \pm 0.4\ kcal \cdot mol^{-1}$. This discrepancy is due both to differences in the solution enthalpies measured for Al and $AlCl_3$. When adjusted to the conditions of Coughlin's experiments, Semenenko's enthalpy of reaction (1) is calculated to be $-128.20\ kcal \cdot mol^{-1}$ which deviates more significantly than the values calculated for other authors.[7] Semenenko's enthalpy of solution of $AlCl_3$, recalculated to solution in pure water at 20°C is $-77.46\ kcal \cdot mol^{-1}$, a more positive value than those found for other investigators.[7] The enthalpy of solution of $AlCl_3$ measured by Krivtsov *et al.*[8] and recalculated to these same conditions is $-78.66\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Justice[9] reported low temperature heat capacity data (13 to 310 K) and presented smoothed thermodynamic functions, including $S°(298.15\ K) = 109.29\ J \cdot K^{-1} \cdot mol^{-1}$ of which $0.360\ J \cdot K^{-1} \cdot mol^{-1}$ is extrapolation below 13 K. Enthalpies relative to 273.15 K were measured by Fischer[10] from 298.15 K to 504 K and enthalpies relative to 298.15 K were measured by McDonald[11] from 310 K to 493 K. The enthalpy data for the crystal can be fit within about 2% by integration of $C_p°(cr) = 64.94 + 0.088\ T$ in $J \cdot K^{-1} \cdot mol^{-1}$, which is an extrapolation of $C_p°$ data reported by Justice.[9]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of the dimer and the crystal for the sublimation process, $2\ AlCl_3(cr) = Al_2Cl_6(g)$, $\Delta_{sub} H°(298.15\ K) = 115.52 \pm 2.3\ kJ \cdot mol^{-1}$. Also refer to the Al_2Cl_6(g) table for additional comments.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.979	−704.300	−704.300	INFINITE
100	47.112	30.798	180.962	−15.016	−707.189	−681.219	355.832
200	79.203	75.145	117.298	−8.431	−706.962	−655.173	171.114
298.15	91.128	109.286	109.286	0.	−705.632	−630.018	110.377
300	91.295	109.850	109.288	0.169	−705.602	−629.549	109.614
400	100.081	137.318	112.974	9.738	−703.746	−604.464	78.935
465.700	105.854	152.965	117.529	16.503	--- CRYSTAL <--> LIQUID ---		
500	108.868	160.594	120.224	20.185	−701.288	−579.914	60.583
600	117.654	181.219	128.701	31.511	−698.146	−555.922	48.397
700	126.440	200.016	137.565	43.716	−694.297	−532.513	39.737
800	135.227	217.473	146.474	56.799	−689.744	−509.703	33.280
900	144.013	233.908	155.284	70.761	−684.503	−487.506	28.294
1000	152.800	249.536	163.934	85.602	−689.183	−465.168	24.298
1100	161.586	264.511	172.401	101.321	−682.264	−443.094	21.041
1200	170.372	278.948	180.682	117.919	−674.484	−421.689	18.356
1300	179.159	292.932	188.781	135.396	−665.841	−400.967	16.111
1400	187.945	306.531	196.709	153.751	−656.333	−380.943	14.213
1500	196.732	319.797	204.474	172.985	−645.961	−361.629	12.593

PREVIOUS: June 1970 CURRENT: September 1979

$S°(298.15\ K) = [172.908]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-674.805]\ kJ·mol^{-1}$

$T_{fus} = 465.7 \pm 0.2\ K$ $\Delta_{fus}H° = 35.35 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(AlCl_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(AlCl_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(465.7\ K) - H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

Fischer[1] and McDonald[2] measured enthalpy data for the crystal and liquid. In each case, the liquid data extended over a short range of temperature, 473–504 K and 475–493 K, respectively. Their data can be represented within 2% by the heat capacity equation derived for the crystal [see $AlCl_3$(cr) table], a heat of fusion of 35.35 $kJ·mol^{-1}$, and a liquid heat capacity of 125.5 $J·K^{-1}·mol^{-1}$. Fischer's data are high, while McDonald's points lie below the selected values.

$S°(298.15\ K)$ is calculated in a manner similiar to that used for the enthalpy of formation.

Fusion Data

Kendall *et al.*[3] observed $AlCl_3$ to melt "sharply" at 463.4 K. Foster[4] noted that $AlCl_3$ began melting and melted completely in the range 465.7 ± 0.2 K. Johnson *et al.*[5], Nisel'son *et al.*,[6] and Ostrikova *et al.*[7] reported melting temperatures of 465.9 ± 0.3 K, 467.2 K, and 466 K, respectively. Smits and Meyering,[8] Treadwell and Terebesi[9] and Viola *et al.*[10] derived triple point temperatures of 465.8 K, 466.5 K, and 466.86 K, respectively, from intersection of vapor pressure curves for crystal and liquid. The value of Foster, T_{fus} = 465.7 ± 0.2 K, is adopted as most accurate. The vapor pressure (monomer and dimer contributions) at the triple point is 2.3 atm. $\Delta_{fus}H°$ is based on enthalpies measured by Fischer[1] and McDonald.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	125.520	172.908	172.908	0.	−674.805	−618.161	108.299
300	125.520	173.684	172.910	0.232	−674.712	−617.809	107.570
400	125.520	209.794	177.833	12.784	−669.873	−599.581	78.297
465.700	125.520	228.883	183.723	21.031	--- CRYSTAL <---> LIQUID ---		
500	125.520	237.803	187.130	25.336	−665.311	−582.541	60.858
600	125.520	260.688	197.541	37.888	−660.942	−566.400	49.309
700	125.520	280.037	207.979	50.440	−656.746	−550.977	41.114
800	125.520	296.798	218.057	62.992	−652.724	−536.143	35.007
900	125.520	311.582	227.644	75.544	−648.894	−521.803	30.285
1000	125.520	324.807	236.710	88.096	−655.862	−507.118	26.489
1100	125.520	336.770	245.272	100.648	−652.110	−492.425	23.383
1200	125.520	347.692	253.358	113.200	−648.376	−478.074	20.810
1300	125.520	357.739	261.006	125.752	−644.658	−464.032	18.645
1400	125.520	367.041	268.252	138.304	−640.953	−450.277	16.800
1500	125.520	375.701	275.130	150.856	−637.263	−436.786	15.210

PREVIOUS: June 1970 CURRENT: September 1979

0 to	465.7 K	crystal
above	465.7 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.979	−704.300	−704.300	INFINITE
100	47.112	30.798	180.962	−15.016	−707.189	−681.219	355.832
200	79.203	75.145	117.298	−8.431	−706.962	−655.173	171.114
298.15	91.128	109.286	109.286	0.	−705.632	−630.018	110.377
300	91.295	109.850	109.288	0.169	−705.602	−629.549	109.614
400	100.081	137.318	112.974	9.738	−703.746	−604.464	78.935
465.700	105.854	152.965	117.529	16.503	CRYSTAL <--> LIQUID		
465.700	125.520	228.883	117.529	51.857	TRANSITION		
500	125.520	237.803	125.478	56.163	−665.311	−582.541	60.858
600	125.520	260.688	146.164	68.715	−660.942	−566.400	49.309
700	125.520	280.037	163.942	81.267	−656.746	−550.977	41.114
800	125.520	296.798	179.525	93.819	−652.724	−536.144	35.007
900	125.520	311.582	193.393	106.371	−648.894	−521.803	30.285
1000	125.520	324.807	205.884	118.923	−655.862	−507.118	26.489
1100	125.520	336.770	217.248	131.475	−652.110	−492.426	23.383
1200	125.520	347.692	227.670	144.027	−648.376	−478.074	20.810
1300	125.520	357.739	237.294	156.579	−644.658	−464.033	18.645
1400	125.520	367.041	246.233	169.131	−640.953	−450.278	16.800
1500	125.520	375.701	254.579	181.683	−637.263	−436.787	15.210

PREVIOUS: CURRENT: September 1979

$\Delta_{at}H^\circ$ = 1269.0 ± 3.4 kJ·mol^{-1}
S°(298.15 K) = 314.49 ± 2.9 J·K^{-1}·mol^{-1}

Δ_fH°(0 K) = −582.85 ± 2.9 kJ·mol^{-1}
Δ_fH°(298.15 K) = −584.59 ± 2.9 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
371(1)	183(1)	610(2)	146(2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Al–Cl = 2.06 Å
Bond Angle: Cl–Al–Cl = 120°
Product of the Moments of Inertia: $I_AI_BI_C = 1.052528 \times 10^{-112}$ g^3·cm^6

Enthalpy of Formation

The enthalpy of formation is calculated from the value adopted for Al_2Cl_6(g) and the heat of dissociation of $Al_2Cl_6 \rightarrow 2AlCl_3$ derived from equilibrium *PVT* data on aluminum chloride vapor as listed below.

The four investigations are in reasonable agreement. Giving consideration also to equilibrium data on the reaction of $AlCl_3$(g) and Al(l) to form AlCl(g) [see AlCl(g) table], there is selected as a best value Δ_fH°(298.15 K) = 30.25 kcal·mol^{-1} Al_2Cl_6, which yields Δ_fH°($AlCl_3$, g, 298.15 K) = −139.72 kcal·mol^{-1} (−584.59 ± 2.9 kJ·mol^{-1}). NBS[15] recommended a value of −139.4 kcal·mol^{-1} (−583.250 kJ·mol^{-1}) for the enthalpy of formation of $AlCl_3$(g) based on data available prior to 1968.

Source	*T*/K	Data Points	Δ_fH°(298.15 K), kcal·mol^{-1} Al_2Cl_6 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Smits and Meijering[1]	669–816	6	29.45 ± 0.7	30.21 ± 0.2	1.0 ± 0.9
Fischer *et al.*[2]	647–869	17[a]	31.04 ± 0.3	30.42 ± 0.2	−0.8 ± 0.4
Vrieland and Stull[3]	669–825	19[b]	0.27 ± 0.3	30.50 ± 0.2	0.3 ± 0.4
Polyachenok *et al.*[4]	650–1100	2[c]	30.68 ± 0.0	30.03 ± 0.5	−0.7 ± 0.0

[a]Twenty–three points reported, points at 938, 881, 944, 734, 805 and 605 K rejected by statistical test.
[b]Twenty–six points reported, points at 627.9, 643.1, 671.3, 638.4, 671.6, 722.5 and 686.9 K rejected by statistical test.
[c]Individual points not reported, an equation for the equilibrium constant was used to calculate two points at the extremes of temperature.

Heat Capacity and Entropy

The structure of monomeric $AlCl_3$ has been the subject of considerable debate due to conflicting assignments made on the basis of the electron diffraction data of Zasorin and Rambidi[5] and the matrix–isolation IR study by Lesiecki and Shirk.[6] Electron diffraction of the vapor at 800 K yielded an Al–Cl bond length of 2.06 ± 0.01 Å and a Cl–Al–Cl angle of 118 ± 1.5°, which allowing for the possibility of "shrinkage" was taken to indicate a planar equilibrium D_{3h} geometry. The argon matrix spectra obtained by Lesiecki and Shirk[6] showed four infrared–active fundamentals including the symmetric stretch, implying a pyramidal C_{3v} structure; their normal coordinate analysis suggested a Cl–Al–Cl angle near 112°. Hargittai and Hargittai[7] argued, however, that the electron diffraction results for $AlCl_3$ are not compatible with a pyramidal model having an inversion frequency of 183 cm^{-1} and a barrier height equal to 2–3 vibrational quanta. Beattie *et al.*[8] were unable to reproduce the IR frequencies observed by Lesiecki and Shirk[6] in their own matrix isolation studies and it was later concluded that the earlier work by Lesiecki and Shirk was based on incorrect band assignments.[9] The D_{3h} structure is supported by the original electron diffraction work as well as theoretical calculations[10,11] and correlations[9] of the frequencies of $AlCl_3$, $AlCl_2Br$, $AlClBr_2$and $AlBr_3$.

For aluminum chloride vapor at high temperatures (monomer predominant), Klemperer[12] observed the band at 610 cm^{-1} in the IR spectrum and Beattie and Horder[13] reported Raman bands at 371 cm^{-1} and 146 cm^{-1}. The remaining fundamental is that reported by Lesiecki and Shirk;[6,9] a second experimental observation of ν_2 = 174 cm^{-1} was reported by Perov *et al.*[14] in a xenon matrix along with ν_1 = 350 cm^{-1}, ν_4 = 142 cm^{-1}. The principal moments of inertia are $I_A = I_B$ = 37.4744 × 10^{-39}, and I_C = 74.9488 × 10^{-39} g·cm^2.

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Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p° J·K^{-1}·mol^{-1}	S° J·K^{-1}·mol^{-1}	$-[G^\circ-H^\circ(T_r)]/T$ J·K^{-1}·mol^{-1}	$H^\circ-H^\circ(T_r)$ kJ·mol^{-1}	Δ_fH° kJ·mol^{-1}	Δ_fG° kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−16.575	−582.852	−582.852	INFINITE
100	51.072	247.272	372.957	−12.568	−583.698	−579.375	302.635
200	64.468	287.225	320.862	−6.728	−584.215	−574.842	150.133
250	68.798	302.100	315.662	−3.390	−584.420	−572.475	119.612
298.15	71.876	314.494	314.494	0.	−584.588	−570.158	99.889
300	71.976	314.939	314.496	0.133	−584.594	−570.069	99.258
350	74.300	326.218	315.381	3.793	−584.748	−567.635	84.715
400	76.014	336.257	317.375	7.553	−584.888	−565.181	73.805
450	77.300	345.288	319.983	11.387	−585.021	−562.710	65.318
500	78.281	353.485	322.930	15.278	−585.152	−560.223	58.526
600	79.643	367.888	329.255	23.179	−585.435	−555.212	48.335
700	80.514	380.235	335.677	31.190	−585.779	−550.149	41.053
800	81.100	391.027	341.936	39.273	−586.227	−545.029	35.587
900	81.513	400.604	347.932	47.405	−586.816	−539.846	31.332
1000	81.813	409.209	353.637	55.572	−598.170	−533.828	27.884
1100	82.038	417.017	359.049	63.765	−598.777	−527.364	25.042
1200	82.211	424.163	364.182	71.978	−599.382	−520.846	22.672
1300	82.346	430.749	369.053	80.206	−599.987	−514.276	20.664
1400	82.454	436.856	373.680	88.446	−600.595	−507.660	18.941
1500	82.542	442.548	378.084	96.696	−601.206	−501.001	17.446
1600	82.614	447.877	382.281	104.954	−601.823	−494.300	16.137
1700	82.674	452.888	386.289	113.218	−602.447	−487.561	14.981
1800	82.724	457.615	390.121	121.488	−603.078	−480.785	13.952
1900	82.767	462.088	393.792	129.763	−603.720	−473.974	13.030
2000	82.803	466.335	397.314	138.041	−604.372	−467.128	12.200
2100	82.835	470.376	400.698	146.323	−605.038	−460.249	11.448
2200	82.862	474.230	403.953	154.608	−605.719	−453.339	10.764
2300	82.886	477.914	407.089	162.896	−606.418	−446.397	10.138
2400	82.907	481.442	410.114	171.185	−607.137	−439.424	9.564
2500	82.925	484.826	413.036	179.477	−607.877	−432.421	9.035
2600	82.942	488.079	415.860	187.770	−608.642	−425.388	8.546
2700	82.956	491.210	418.593	196.065	−609.432	−418.324	8.093
2800	82.970	494.227	421.241	204.362	−904.150	−410.264	7.654
2900	82.981	497.139	423.808	212.659	−903.900	−392.629	7.072
3000	82.992	499.952	426.299	220.958	−903.677	−375.003	6.529
3100	83.002	502.673	428.719	229.258	−903.483	−357.384	6.022
3200	83.010	505.309	431.072	237.558	−903.317	−339.771	5.546
3300	83.018	507.863	433.360	245.860	−903.177	−322.162	5.099
3400	83.026	510.342	435.588	254.162	−903.061	−304.557	4.679
3500	83.032	512.748	437.759	262.465	−902.969	−286.956	4.283
3600	83.038	515.088	439.874	270.768	−902.896	−269.356	3.908
3700	83.044	517.363	441.938	279.072	−902.841	−251.759	3.554
3800	83.049	519.578	443.952	287.377	−902.800	−234.163	3.219
3900	83.054	521.735	445.919	295.682	−902.770	−216.567	2.901
4000	83.058	523.838	447.841	303.988	−902.748	−198.973	2.598
4100	83.063	525.889	449.719	312.294	−902.730	−181.378	2.311
4200	83.066	527.890	451.557	320.600	−902.712	−163.785	2.037
4300	83.070	529.845	453.355	328.907	−902.692	−146.191	1.776
4400	83.073	531.755	455.115	337.214	−902.666	−128.599	1.527
4500	83.076	533.622	456.839	345.522	−902.629	−111.007	1.289
4600	83.079	535.448	458.528	353.829	−902.581	−93.415	1.061
4700	83.082	537.234	460.184	362.138	−902.519	−75.826	0.843
4800	83.085	538.984	461.807	370.446	−902.439	−58.237	0.634
4900	83.087	540.697	463.400	378.754	−902.340	−40.651	0.433
5000	83.089	542.375	464.963	387.063	−902.220	−23.067	0.241
5100	83.091	544.021	466.497	395.372	−902.077	−5.485	0.056
5200	83.093	545.634	468.003	403.682	−901.910	12.093	−0.121
5300	83.095	547.217	469.483	411.991	−901.719	29.669	−0.292
5400	83.097	548.770	470.937	420.301	−901.501	47.240	−0.457
5500	83.099	550.295	472.366	428.610	−901.257	64.808	−0.615
5600	83.100	551.792	473.771	436.920	−900.987	82.370	−0.768
5700	83.102	553.263	475.153	445.230	−900.690	99.927	−0.916
5800	83.103	554.709	476.512	453.541	−900.363	117.479	−1.058
5900	83.105	556.129	477.849	461.851	−900.014	135.025	−1.195
6000	83.106	557.526	479.166	470.162	−899.616	152.562	−1.328

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = [196.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 529\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = -1196.6 \pm 10\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

The enthalpy of reaction of aluminum chloride and potassium chloride was measured by Baud.[1] From $\Delta_r H° = -26.38\ kcal \cdot mol^{-1}$ for the reaction: $Al_2Cl_6(cr) + 2\ KCl(cr) = 2\ KAlCl_4(cr)$, the value of $\Delta_f H°(KAlCl_4, cr, 298.15\ K)$ is calculated to be $-286\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Heat capacities are estimated by comparison with those for $KMgCl_3(cr)$ reported by Kelley.[5] $S°(298.15\ K) = 47 \pm 2\ cal \cdot K^{-1} \cdot mol^{-1}$ is estimated according to the methods suggested by Kubaschewski and Evans[2] and Kelley.[3]

References

[1]E. Baud, Ann. chim. phys. **1**, 8 (1904).
[2]O. Kubaschewski and E. Ll. Evans, Metallurgical Thermochemistry, Pergamon Press, 426 pp. (1958).
[3]K. K. Kelley, U. S. Bur. Mines, personal communication, (June, 1960).
[4]W. Fischer and A.-L. Simon, Z. anorg. allgem. Chem. **306**, 1 (1960).
[5]K. K. Kelley, U. S. Bur. Mines Bull. 584, 232 pp. (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	156.482	196.648	196.648	0.	−1196.624	−1094.521	191.755
300	156.649	197.616	196.651	0.290	−1196.559	−1093.887	190.463
400	165.477	243.891	202.901	16.396	−1195.380	−1059.743	138.388
500	174.305	281.763	214.994	33.385	−1191.274	−1026.295	107.216
600	183.176	314.346	228.897	51.269	−1186.429	−993.742	86.513
700	190.790	343.177	243.203	69.982	−1180.903	−962.056	71.789
800	196.648	369.064	257.345	89.375	−1174.867	−931.199	60.801
900	199.995	392.431	271.078	109.218	−1168.589	−901.117	52.299
1000	202.087	413.622	284.290	129.332	−1172.876	−870.976	45.495

PREVIOUS: June 1962 CURRENT: June 1963

$S°(298.15\ K) = [188.3 \pm 8]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 424\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1142.2 \pm 4\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(NaAlCl_4, cr, 298.15\ K)$ is calculated from $\Delta_r H° = -11.9\ kcal·mol^{-1}$ for the reaction $Al_2Cl_6(cr) + 2\ NaCl(cr) = 2\ NaAlCl_4(cr)$, as measured by Baud.[1]

Heat Capacity and Entropy

Heat capacities are estimated by comparison with those of $KAlCl_4(cr)$. $S°(298.15\ K) = 45 \pm 2\ cal·K^{-1}·mol^{-1}$ is estimated according to the methods suggested by Kubaschewski and Evans[2] and Kelley.[3]

Fusion Data

T_{fus} was reported by Fischer and Simon.[4]

References

[1] E. Baud, Ann. chim. phys. **1**, 8 (1904).
[2] O. Kubaschewski and E. Ll. Evans, 'Metallurgical Thermochemistry', Pergamon Press, 426 pp. (1958).
[3] K. K. Kelley, U. S Bur. Mines, personal communication, (June, 1960).
[4] W. Fischer and A.−L. Simon, Z. anorg. allgem. Chem. **306**, 1 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	154.975	188.280	188.280	.000	−1142.232	−1041.574	182.479
300	154.808	189.238	188.283	.287	−1142.168	−1040.950	181.245
400	164.808	235.161	194.477	16.274	−1141.251	−1007.533	131.570
500	174.054	272.947	206.498	33.224	−1137.177	−974.559	101.811
600	182.422	305.445	220.342	51.062	−1132.355	−942.476	82.050
700	189.117	334.098	234.587	69.658	−1126.902	−911.253	67.999
800	193.510	359.645	248.652	88.795	−1121.055	−880.842	57.513
900	197.276	382.673	262.285	108.350	−1114.969	−851.179	49.401
1000	199.158	403.572	275.385	128.187	−1119.408	−821.440	42.908

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = [376.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [800 \pm 20]\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -2092 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(K_3AlCl_6, cr, 298.15\ K)$ is recalculated from the same quantity given by Rossini *et al.*[1] The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(cr) + 6\ KCl(cr) = 2\ K_3AlCl_6(cr)$, as measured by Baud.[2]

Heat Capacity and Entropy

Heat capacities are estimated by comparison with the corresponding values of the sum of the constituent halides for K_3AlCl_6(cr). In a similar manner, $S°(298.15\ K)$ is estimated to be $90 \pm 2\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} is estimated by comparison with that for K_3AlF_6(cr).

References

[1]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2]E. Baud, Ann. chem. phys. **1**, 8 (1904).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
250							
298.15	248.906	376.560	376.560	0.	−2092.000	−1938.463	339.611
300	249.283	378.101	376.565	0.461	−2091.936	−1937.511	337.351
400	259.157	451.152	386.458	25.878	−2095.873	−1885.176	246.179
500	269.659	510.122	405.474	52.324	−2092.096	−1832.919	191.484
600	279.491	560.178	427.189	79.794	−2087.377	−1781.512	155.094
700	287.859	603.896	449.375	108.165	−2081.856	−1730.961	129.166
800	295.809	642.863	471.168	137.355	−2075.676	−1681.247	109.774
900	302.880	678.124	492.235	167.300	−2068.982	−1632.341	94.739
1000	308.779	710.343	512.458	197.885	−2072.560	−1583.440	82.710
1100	314.532	740.048	531.815	229.056	−2301.871	−1521.060	72.229
1200	319.658	767.640	550.331	260.771	−2290.853	−1450.560	63.141
1300	324.103	793.405	568.049	292.963	−2279.389	−1380.998	55.489
1400	328.026	817.571	585.018	325.574	−2267.536	−1312.333	48.964
1500	331.320	840.316	601.287	358.544	−2255.353	−1244.528	43.338
1600	334.302	861.796	616.904	391.827	−2242.885	−1177.544	38.443
1700	336.969	882.145	631.913	425.394	−2230.167	−1111.349	34.148
1800	339.322	901.473	646.356	459.211	−2217.233	−1045.908	30.351
1900	341.362	919.876	660.272	493.248	−2204.120	−981.191	26.975
2000	343.088	937.430	673.694	527.473	−2190.865	−917.169	23.954

PREVIOUS: June 1962 CURRENT: September 1963

$S°(298.15\ K) = [347.3 \pm 8]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [780 \pm 20]\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1979 \pm 4\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(Na_3AlCl_6, cr, 298.15\ K)$ is recalculated from the same quantity given by Rossini *et al.*[1] The latter value was derived from the enthalpy change for the reaction $Al_2Cl_6(cr) + 6\ NaCl(cr) = 2\ Na_3AlCl_6(cr)$, as measured by Baud.[2]

Heat Capacity and Entropy

Heat capacities are estimated by comparison with the corresponding values of the sum of the constituent halides for $Na_3AlF_6(cr)$. In a similar manner, $S°(298.15\ K)$ is estimated to be $83 \pm 2\ cal·K^{-1}·mol^{-1}$.

Fusion Data

T_{fus} is estimated by comparison with that for $Na_3AlF_6(cr)$.

References

[1] U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2] E. Baud, Ann. chim. phys. **1**, 8 (1904).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	244.136	347.272	347.272	0.	−1979.032	−1828.584	320.360
300	244.513	348.783	347.277	0.452	−1978.970	−1827.651	318.222
400	254.387	420.484	356.986	25.399	−1983.806	−1777.071	232.062
500	264.010	478.294	375.646	51.324	−1980.531	−1725.747	180.288
600	273.006	527.237	396.933	78.182	−1976.354	−1675.168	145.836
700	281.165	569.941	418.662	105.896	−1971.360	−1625.355	121.286
800	288.696	607.991	439.992	134.399	−1965.663	−1576.307	102.922
900	294.972	642.363	460.599	163.588	−1959.438	−1528.007	88.683
1000	300.620	673.738	480.367	193.372	−1963.442	−1479.661	77.290
1100	305.720	702.633	499.277	223.692	−1956.272	−1431.627	67.982
1200	310.453	729.439	517.353	254.503	−2239.053	−1376.941	59.937
1300	314.741	754.459	534.640	285.765	−2228.519	−1305.523	52.457
1400	318.821	777.935	551.189	317.445	−2217.595	−1234.930	46.076
1500	322.796	800.069	567.050	349.529	−2206.295	−1165.132	40.574
1600	326.352	821.018	582.274	381.990	−2194.644	−1096.100	35.784
1700	329.385	840.895	596.907	414.778	−2182.693	−1027.805	31.581
1800	332.210	859.803	610.992	447.860	−2170.477	−960.222	27.865
1900	334.825	877.835	624.565	481.213	−2158.018	−893.324	24.559
2000	337.230	895.072	637.663	514.818	−2145.341	−827.088	21.601

PREVIOUS: CURRENT: September 1963

$S°(298.15\ K) = 215.16 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -265.623 \pm 3.35\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -265.684 \pm 3.35\ kJ \cdot mol^{-1}$

State	Electronic Levels and Molecular Constants (σ = 1) ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0.0	1	802.26	4.77	0.5525	0.00495	1.6544
$a^3\Pi$	27254.	6	830.30	4.60	0.55718	0.00468	1.6474
$A^1\Pi$	43949.7	2	803.94	5.99	0.55640	0.00534	1.6485
$b^3\Sigma^+$	44804.5	3	786.37	7.64	0.56280	0.00651	1.6391
$B^1\Sigma^+$	54282.5	1	866.60	7.45	0.57968	0.00560	1.6151
$c^3\Sigma^+$	55023.4	3	938.22	4.81	0.58992	0.00458	1.6010
$C^1\Sigma^+$	57755.9	1	938.22	5.09	0.58992	0.00458	1.6010

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -63.5 \pm 0.8$ kcal·mol^{-1} (-265.684 ± 3.35 kJ·mol^{-1}) and $D_0° = 160.0 \pm 1.5$ kcal·mol^{-1} (669.440 ± 6.3 kJ·mol^{-1}) based on our analysis of numerous equilibrium data.[1-12] We only tabulate our analysis of three studies; the other analyses are essentially those which were reported earlier.[22] However, the previously calculated $D_0°$ values will differ due to a more current heat of formation for Al(g). Greatest weight is given to torsion effusion[2] and transport[5,12] data for the Al–AlF_3 system. Hildenbrand *et al.*[2] found that orifice area affected the torsion–effusion pressures of AlF from reaction A. They derived equilibrium pressures from a semi–empirical correlation of data for the four cells listed below. Mass–spectrometric studies[9] of the Al–AlF system near 950 K indicated that the vapor consists of AlF with a small amount of AlF. The adopted $D_0° = 669.440 \pm 6.3$ kJ·mol^{-1} is consistent with $D_0° > 665.6$ kJ·mol^{-1} derived from the highest observed level in $A^1\Pi$.[14] The potential energy curve of this excited state may have a maximum.[14,15]

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd Law	3rd Law	$\Delta_f H°_{(298.15\ K)}$	$D_0°$ kcal·mol^{-1}
Hildenbrand (1963)	torsion eff.[b]								
Cell 7	P=1.30P_t	A	882–931	8	−2.7 ± 2.1	54.1 ± 2.0	56.60 ± 0.2	−63.73 ± 0.8	160.3
Cell 9	P=1.72P_t	A	856–932	8	0.4 ± 1.5	57.3 ± 1.4	56.91 ± 0.2	−63.42 ± 0.8	160.0
Cell 15X	P=2.07P_t	A	866–931	8	1.0 ± 0.6	57.8 ± 0.5	56.85 ± 0.1	−63.48 ± 0.8	160.1
Cell 16X	P=3.13P_t	A	867–929	7[c]	0.5 ± 1.4	57.2 ± 1.3	56.79 ± 0.1	−63.54 ± 0.8	160.1
Semenkovitch (1960)	transport	B	1170–1373	5	−0.2 ± 0.2	55.3 ± 0.3	55.56 ± 0.1	−63.40 ± 0.8	160.0
Hildenbrand (1981)	torsion eff.[b]								
Cell G7S	P=1.12P_t	A	863–930	13	−1.0 ± 0.2	58.25 ± 0.21	57.37 ± 0.05	−62.96 ± 0.8	160.1
Cell G5Z	P=1.31P_t	A	839–928	6	−2.4 ± 0.2	57.61 ± 0.16	57.22 ± 0.04	−63.11 ± 0.8	159.7
Cell G6Z	P=1.65P_t	A	835–929	13	−0.4 ± 0.1	57.68 ± 0.07	57.25 ± 0.04	−63.08 ± 0.8	159.7
Cell G7L	P=2.10P_t	A	840–930	13	−1.0 ± 0.2	58.20 ± 0.19	57.31 ± 0.08	−63.02 ± 0.8	159.6

[a]Reactions: A: 1/3 AlF_3(cr) + 2/3 Al(cr) = AlF(g); B: 1/3 AlF_3(cr) + 2/3 Al(l) = AlF(g);
[b]P = equilibrium pressure and P_t = torsion pressure. [c]One point rejected.

Heat Capacity and Entropy

Electronic levels and molecular constants are based on the detailed analysis of electronic spectra published by Barrow, Kapp and Malmberg[16] and a follow-up to this investigation published by Kapp and coworkers.[20] Constants for the ground state are confirmed by microwave spectra.[11,17,18] The triplet–singlet separation, a^3–$X^1\Sigma^+$, calculated by Barrow *et al.*[16] is in excellent agreement with the results from the low resolution chemiluminiscence work of Rosenwaks *et al.*[21] We omit electronic states between 60000 and 68000 cm^{-1} including nine observed levels and one predicted level;[16] these would have negligible effects on the thermodynamic functions. The analysis of Barrow *et al.*[16] is supported by theoretical calculations.[20,21]

References

[1] P. E. Blackburn (A. D. Little, Inc., Cambridge, Mass.), AD–618523, 65 pp. (1965).
[2] D. L. Hildenbrand *et al.*, Ford Motor Co., Aeronutronic Div., Rept. No. U–2055, Contract No. 61–0905–c, (March 15, 1963).
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Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.891	−265.623	−265.623	INFINITE
100	29.121	182.450	242.280	−5.983	−264.653	−273.680	142.956
200	30.034	202.816	218.015	−3.040	−264.976	−282.645	73.819
298.15	31.932	215.157	215.157	0.	−265.684	−291.172	51.012
300	31.967	215.354	215.157	0.059	−265.699	−291.330	50.725
400	33.602	224.787	216.432	3.342	−266.534	−299.750	39.143
500	34.734	232.415	218.890	6.763	−267.429	−307.952	32.171
600	35.502	238.820	221.692	10.277	−268.387	−315.967	27.507
700	36.037	244.335	224.542	13.855	−269.431	−323.816	24.163
800	36.423	249.174	227.325	17.479	−270.593	−331.508	21.645
900	36.712	253.481	229.996	21.137	−271.904	−339.045	19.678
1000	36.937	257.362	232.542	24.819	−283.981	−345.667	18.056
1100	37.117	260.891	234.961	28.522	−285.313	−351.771	16.704
1200	37.265	264.127	237.259	32.242	−286.642	−357.754	15.573
1300	37.390	267.115	239.442	35.975	−287.969	−363.627	14.611
1400	37.499	269.890	241.519	39.719	−289.295	−369.397	13.782
1500	37.594	272.480	243.498	43.474	−290.620	−375.072	13.061
1600	37.679	274.909	245.386	47.238	−291.946	−380.659	12.427
1700	37.757	277.196	247.190	51.010	−293.272	−386.163	11.865
1800	37.828	279.356	248.918	54.789	−294.598	−391.589	11.364
1900	37.894	281.403	250.574	58.575	−295.922	−396.941	10.913
2000	37.957	283.348	252.165	62.368	−297.245	−402.224	10.505
2100	38.016	285.202	253.694	66.166	−298.565	−407.440	10.135
2200	38.073	286.972	255.167	69.971	−299.881	−412.594	9.796
2300	38.127	288.665	256.587	73.781	−301.190	−417.688	9.486
2400	38.180	290.289	257.957	77.596	−302.491	−422.725	9.200
2500	38.232	291.849	259.282	81.417	−303.783	−427.708	8.936
2600	38.282	293.349	260.564	85.242	−305.063	−432.640	8.692
2700	38.332	294.795	261.805	89.073	−306.331	−437.522	8.464
2800	38.382	296.190	263.008	92.909	−601.485	−441.391	8.234
2900	38.432	297.538	264.176	96.750	−601.627	−435.670	7.847
3000	38.483	298.841	265.310	100.595	−601.751	−429.945	7.486
3100	38.535	300.104	266.412	104.446	−601.858	−424.217	7.148
3200	38.589	301.328	267.484	108.303	−601.945	−418.485	6.831
3300	38.645	302.517	268.527	112.164	−602.011	−412.751	6.533
3400	38.704	303.671	269.544	116.032	−602.057	−407.015	6.253
3500	38.767	304.794	270.535	119.905	−602.081	−401.278	5.989
3600	38.833	305.887	271.502	123.785	−602.083	−395.541	5.739
3700	38.904	306.952	272.446	127.672	−602.063	−389.804	5.503
3800	38.979	307.990	273.368	131.566	−602.019	−384.067	5.279
3900	39.061	309.004	274.269	135.468	−601.953	−378.333	5.067
4000	39.148	309.994	275.149	139.378	−601.863	−372.600	4.866
4100	39.242	310.962	276.011	143.298	−601.749	−366.870	4.674
4200	39.344	311.909	276.855	147.227	−601.612	−361.142	4.491
4300	39.453	312.836	277.681	151.167	−601.451	−355.419	4.317
4400	39.570	313.744	278.490	155.118	−601.267	−349.699	4.151
4500	39.695	314.635	279.283	159.081	−601.056	−343.984	3.993
4600	39.829	315.509	280.061	163.057	−600.824	−338.274	3.841
4700	39.972	316.367	280.825	167.047	−600.569	−332.569	3.696
4800	40.125	317.210	281.574	171.052	−600.290	−326.870	3.557
4900	40.286	318.039	282.310	175.072	−599.987	−321.177	3.424
5000	40.458	318.854	283.032	179.110	−599.663	−315.490	3.296
5100	40.638	319.657	283.743	183.164	−599.316	−309.810	3.173
5200	40.829	320.448	284.441	187.238	−598.947	−304.137	3.055
5300	41.029	321.228	285.128	191.330	−598.556	−298.471	2.942
5400	41.239	321.997	285.803	195.444	−598.145	−292.813	2.832
5500	41.458	322.755	286.468	199.578	−597.712	−287.163	2.727
5600	41.687	323.504	287.123	203.736	−597.260	−281.521	2.626
5700	41.925	324.244	287.768	207.916	−596.788	−275.887	2.528
5800	42.171	324.976	288.403	212.121	−596.294	−270.262	2.434
5900	42.427	325.699	289.029	216.351	−595.784	−264.644	2.343
6000	42.691	326.414	289.646	220.607	−595.234	−259.039	2.255

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K)$ = [220.07 ± 0.9] $J·K^{-1}·mol^{-1}$

$\Delta_f H$ (0 K) = 686.0 ± 24 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [692.034] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma^+]$	0	[2]
$[^2\Pi]$	[5000]	[4]
$[^2\Sigma^+]$	[20000]	[2]
$[^2\Pi]$	[33000]	[4]

ω_e = [925] cm^{-1} $\omega_e x_e$ = [5.5] cm^{-1} σ = 1
B_e = [0.587] cm^{-1} α_e = [0.005] cm^{-1} r_e = [1.605] Å

Enthalpy of Formation

We adopt $\Delta_f H°$ = 164 ± 6 $kcal·mol^{-1}$ based on IP(AlF) = 9.86 ± 0.25 eV (227.5 ± 6 $kcal·mol^{-1}$). Barrow, Kopp and Malmberg[1] used the observed data for BF to predict that, to a good approximation, IP(AlF) = $T°$(AlF, 3d) + IP(Al, 3d). This gave IP(AlF) = 79335 cm^{-1} (9.84 eV) which the authors[1] rounded to 80000 cm^{-1} (9.92 eV). We adopt an intermediate value corresponding to $\Delta_f H°$ = 164 $kcal·mol^{-1}$. This yields $D_0°$ = 70 ± 6 $kcal·mol^{-1}$ for $AlF^+(g) \rightarrow Al^+(g) + F(g)$.

IP(AlF) = 9.86 ± 0.25 eV is consistent with electron impact data which gave the following values for the appearance potential of AlF + from AlF: 8.9 ± 0.6,[2] 9.0 ± 1,[3] 9.2,[4] 9.5 ± 0.5,[5] 9 to 10,[6] 9.7 ± 0.3,[7] 9.7 ± 0.5,[8] 9.9 ± 0.3,[8] and 10.1 ± 0.3 eV.[8]

Heat Capacity and Entropy

We assume the ground-state configuration to be the same as observed for BF^+ [9] and the isoelectronic molecules AlO and AlF.[10] Theoretical calculations for $AlCl^+$ [11] predict the same ground state; they also suggest that the $^2\Pi$ excited state is either repulsive or has a shallow potential minimum at a much longer bond length. We assume the $^2\Pi$ state in AlF^+ to be nonrepulsive and estimate excited state levels equal to those in AlO.[10] Comparison with $AlCl^+$ suggests that $^2\Pi$ should be in the range 5000–15000 cm^{-1}. Our thermodynamic functions would be upper-limit values if the $^2\Pi$ state were repulsive.

Bonding in Group III monohalides and their ions was characterized by Berkowitz and Dehmer[11] from photoelectron spectra and theoretical calculations. They concluded that ionization removes an electron from an antibonding orbital centered mainly on the metal. This shortens the bond length and enhances the ionic nature of the bond. A decrease in bond length is observed for BF^+ [9] and predicted by theroretical calculations for $AlCl^+$.[11,10] By analogy with BF^+ and BF,[9] we expect AlF^+ to have vibrational and rotational constants similar to those of the Rydberg excited states of AlF.[1,10] Our adopted constants are approximate avarages from the Rydberg states. The adopted bond length is 0.05 Å shorter than in ground state AlF; a similar difference is observed for BF^+.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.813	685.976		
100	29.110	187.705	246.750	−5.905			
200	29.620	207.970	222.861	−2.978			
250	30.336	214.653	220.573	−1.480			
298.15	31.155	220.065	220.065	0.	692.034	658.828	−115.424
300	31.187	220.258	220.066	0.058	692.056	658.621	−114.676
350	32.031	225.129	220.448	1.638	692.646	653.002	−97.455
400	32.797	229.458	221.309	3.259	693.219	647.299	−84.529
450	33.463	233.360	222.435	4.916	693.778	641.526	−74.466
500	34.030	236.916	223.708	6.604	694.326	635.690	−66.410
600	34.924	243.204	226.447	10.054	695.383	623.863	−54.312
700	35.599	248.640	229.238	13.582	696.365	611.864	−45.658
800	36.167	253.431	231.968	17.170	697.247	599.731	−39.158
900	36.705	257.722	234.595	20.814	698.001	587.495	−34.097
1000	37.260	261.618	237.106	24.512	688.017	575.942	−30.084
1100	37.850	265.196	239.499	28.267	688.816	564.696	−26.815
1200	38.476	268.516	241.780	32.083	689.663	553.376	−24.088
1300	39.127	271.622	243.958	35.963	690.562	541.982	−21.777
1400	39.785	274.545	246.039	39.909	691.516	530.518	−19.794
1500	40.434	277.313	248.033	43.920	692.525	518.983	−18.073
1600	41.055	279.942	249.945	47.995	693.589	507.379	−16.564
1700	41.637	282.449	251.784	52.130	694.705	495.707	−15.231
1800	42.169	284.844	253.555	56.320	695.869	483.968	−14.044
1900	42.644	287.137	255.262	60.561	697.078	472.163	−12.981
2000	43.060	289.335	256.912	64.847	698.326	460.293	−12.022
2100	43.417	291.445	258.506	69.171	699.611	448.360	−11.152
2200	43.715	293.472	260.050	73.529	700.927	436.365	−10.361
2300	43.958	295.420	261.545	77.913	702.270	424.310	−9.636
2400	44.150	297.296	262.996	82.318	703.638	412.195	−8.971
2500	44.297	299.101	264.405	86.741	705.027	400.023	−8.358
2600	44.402	300.840	265.773	91.176	706.434	387.795	−7.791
2700	44.471	302.518	267.103	95.620	707.859	375.513	−7.265
2800	44.509	304.136	268.397	100.070	415.397	364.146	−6.793
2900	44.521	305.698	269.656	104.521	417.945	362.270	−6.525
3000	44.511	307.207	270.883	108.973	420.505	360.307	−6.273
3100	44.483	308.666	272.078	113.423	423.076	358.258	−6.037
3200	44.441	310.078	273.244	117.869	425.658	356.126	−5.813
3300	44.387	311.445	274.381	122.311	428.249	353.913	−5.602
3400	44.324	312.769	275.490	126.746	430.850	351.621	−5.402
3500	44.255	314.053	276.574	131.175	433.460	349.253	−5.212
3600	44.181	315.298	277.632	135.597	436.078	346.810	−5.032
3700	44.105	316.508	278.667	140.011	438.705	344.294	−4.861
3800	44.028	317.683	279.678	144.418	441.340	341.707	−4.697
3900	43.951	318.826	280.667	148.817	443.982	339.051	−4.541
4000	43.875	319.937	281.635	153.208	446.632	336.327	−4.392
4100	43.801	321.020	282.583	157.592	449.288	333.536	−4.249
4200	43.729	322.074	283.511	161.969	451.951	330.681	−4.113
4300	43.661	323.103	284.419	166.338	454.620	327.762	−3.982
4400	43.596	324.106	285.310	170.701	457.295	324.781	−3.856
4500	43.535	325.085	286.183	175.057	459.978	321.739	−3.735
4600	43.478	326.041	287.039	179.408	462.663	318.637	−3.618
4700	43.425	326.975	287.879	183.753	465.352	315.477	−3.506
4800	43.376	327.889	288.703	188.093	468.044	312.260	−3.398
4900	43.332	328.783	289.512	192.429	470.741	308.986	−3.294
5000	43.292	329.658	290.306	196.760	473.438	305.658	−3.193
5100	43.256	330.515	291.086	201.087	476.136	302.276	−3.096
5200	43.225	331.355	291.852	205.411	478.834	298.840	−3.002
5300	43.197	332.178	292.606	209.732	481.532	295.353	−2.911
5400	43.174	332.985	293.346	214.051	484.227	291.815	−2.823
5500	43.155	333.777	294.074	218.367	486.920	288.227	−2.737
5600	43.139	334.554	294.790	222.682	489.609	284.590	−2.655
5700	43.128	335.318	295.494	226.995	492.292	280.905	−2.574
5800	43.119	336.068	296.187	231.307	494.972	277.173	−2.496
5900	43.115	336.805	296.869	235.619	497.642	273.395	−2.420
6000	43.113	337.529	297.541	239.930	500.326	269.570	−2.347

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K)$ = [237.3 ± 4 or 16] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = −579 ± 16 or 28 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = −582 ± 16 or 28 $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[675](1)	386 (2)	1022(1)

Ground State Quantum Weight: [1] σ = 1
Point Group: [$C_{\infty v}$]
Bond Distances: O–Al = [1.61] Å; Al–F = [1.63] Å
Bond Angle: O–Al–F = [180]°
Rotational Constant: B_o = [0.184214] cm^{-1}

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -139 \pm 4$ kcal·mol^{-1} and $\Delta_{at}H° = 293.2 \pm 4$ kcal·mol^{-1}, derived from effusion data for reaction A.[1] This reaction is analyzed along with limited equilibrium data for three other reactions. The latter are in satisfactory agreement with reaction A. Dissociation energies calculated from our adopted values[5] are 13.9 kcal·mol^{-1} larger than those of the corresponding diatomic molecules; i.e., $\Delta_{at}H°$ (FAl–O) = 133.9 ± 4, $\Delta_{at}H°$(OAl–F) = 173.2 ± 4, or $\Delta_r H° = 13.9 \pm 5$ kcal·mol^{-1} for the reaction OAlF(g) + Al(g) = AlF(g) + AlO(g). These values suggest that O=Al–F has enhanced stability, consistent with the observation of this reaction[4] by mass-spectrometric sampling of flames containing aluminum species. We assign $\Delta_f H°$ the alternative uncertainty of ±7 kcal·mol^{-1} in case OAlF is nonlinear. Farber and Srivastava[4] emphasized that $\Delta_f H°$ is much too negative to be compatible with the alternative arrangement Al–O–F.

Source	Method	Reaction[a]	T/K	Data Points	δS cal·$K^{-1}·mol^{-1}$	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	Reaction effus.	A	2203–2228[b]	8	−22 ± 26	43 ± 25	91.0 ± 1.6	−138.9 ± 3
2, 3	Mass spec.[c]	B	1540–1923	8	—	107.1 ± 3.2	—	−143.6 ± 7
4	Flame mass spec.	C	2250	1	—	—	−10.2	−135.3 ± 6
	Flame mass spec.	D	2250	1	—	—	−11.7	−133.0 ± 6

[a] Reactions:
A: 1/3 $AlF_3(g)$ + 1/3 $Al_2O_3(\alpha)$ = OAlF(g)
B: AlF(g) + $Al_2O(g)$ = OAlF(g) + 2 Al(g)
C: AlF(g) + AlO(g) = OAlF(g) + Al(g)
D: AlF(g) + $H_2O(g)$ = OAlF(g) + $H_2(g)$

[b] *T converted to IPTS–68 assuming published values to be IPTS–48.*

[c] Analysis based on relative ion intensities corrected [3] as follows: I(OAlF) = 66 at 1773 K and I(AlF) = 120 at 1923 K. Values of K_p were not measured, thus precluding third law analysis.

Heat Capacity and Entropy

Snelson[6] observed infrared spectra of OAlF, OBF, OBCl and OBBr isolated in inert gas matrices. He proposed linear structures for OBCl and OBBr based on agreement of observed and calculated shifts in isotopic frequencies. Isotopic shifts for OBF were consistent with linearity but were less conclusive. Lacking isotopic data, Snelson[6] assumed OAlF to be linear.

For triatomics having 16 valence electrons (either BAB or BAC types), a linear ground state is predicted by Walsh's correlation[7] and related semiempirical calculations.[8] These correlations derive mainly from covalent triatomics in which the central atom is carbon or some less electropositive element. Ionic triatomics can behave differently, e.g., the alkaine earth difluorides change from linear (BeF_2)[5] to bent configurations (CaF_2, SrF_2 and BaF_2).[9] OAlF is isoelectronic with and intermediate between MgF_2 and SiO_2. Electric deflection data indicated SiO_2 to be linear.[10] Data for MgF_2[5] are contradictory, indicating either a linear or slightly bent (~158°) structure. This comparison with SiO_2 *and MgF_2 favors linearity of OAlF but does not rule out a slightly bent structure.*

We adopt the linear structure O=Al–F with an O–Al distance slightly shorter than in AlO[5] and an Al–F distance equal to that in AlF_3.[5] We assume the ground-state configuration to be $^1\Sigma^+$ and neglect excited states which should be relatively unimportant.[8] Vibrational frequencies are those assigned by Snelson[6] from a comparison of derived force constants for OAlF and OBX molecules. Values of ν_2 and ν_3 from IR spectra in an argon matrix. Snelson[6] used a stretching force constant transferred from AlF_3 in order to estimate ν_1 = 675 cm^{-1}. Although a weak absorption was observed at 687 cm^{-1}, this band was not assigned[6] to ν_1 because it was not conclusively associated with ν_2 and ν_3.

We estimate the uncertainty to be ~1 cal·K^{-1}·mol in the entropy and Gibbs–energy function of linear OAlF. If OAlF were nonlinear with an angle of 160°, $S°$ would change by +3.8 (298 K) and +2.1 (2000 K) cal·K^{-1}·mol, while the Gibbs–energy function would change by +2.9 cal·K^{-1}·mol at 2000 K.

Enthalpy Reference Temperature = T_r = 298.15 K *Standard State Pressure = $p°$ = 0.1 MPa*

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.785	−579.067	−579.067	INFINITE
100	31.151	195.688	274.080	−7.839	−579.511	−581.198	303.586
200	40.013	219.989	241.397	−4.281	−580.675	−582.431	152.115
250	43.792	229.337	238.071	−2.183	−581.171	−582.810	121.772
298.15	46.806	237.316	237.316	0.	−581.576	−583.088	102.155
300	46.910	237.606	237.317	0.087	−581.590	−583.098	101.526
350	49.445	245.034	237.898	2.498	−581.947	−583.320	87.056
400	51.493	251.776	239.218	5.023	−582.257	−583.495	76.197
450	53.145	257.939	240.960	7.640	−582.535	−583.632	67.746
500	54.482	263.610	242.946	10.332	−582.793	−583.740	60.983
600	56.463	273.731	247.254	15.886	−583.291	−583.883	50.832
700	57.813	282.542	251.679	21.604	−583.824	−583.940	43.574
800	58.763	290.328	256.033	27.435	−584.446	−583.916	38.126
900	59.452	297.291	260.237	33.348	−585.205	−583.806	33.883
1000	59.964	303.582	264.262	39.320	−596.724	−582.842	30.445
1100	60.355	309.317	268.101	45.337	−597.497	−581.416	27.609
1200	60.658	314.582	271.758	51.388	−598.268	−579.920	25.243
1300	60.899	319.447	275.242	57.466	−599.041	−578.360	23.239
1400	61.092	323.967	278.563	63.566	−599.818	−576.740	21.518
1500	61.250	328.188	281.732	69.684	−600.602	−575.064	20.026
1600	61.380	332.145	284.760	75.815	−601.393	−573.336	18.718
1700	61.489	335.870	287.658	81.959	−602.193	−571.558	17.562
1800	61.581	339.387	290.435	88.113	−603.003	−569.733	16.533
1900	61.659	342.719	293.100	94.275	−603.821	−567.862	15.612
2000	61.726	345.883	295.661	100.444	−604.649	−565.948	14.781
2100	61.783	348.896	298.125	106.619	−605.485	−563.993	14.029
2200	61.834	351.771	300.498	112.800	−606.328	−561.997	13.344
2300	61.878	354.521	302.788	118.986	−607.177	−559.963	12.717
2400	61.916	357.155	304.999	125.176	−608.030	−557.892	12.142
2500	61.950	359.683	307.136	131.369	−608.886	−555.785	11.613
2600	61.981	362.114	309.204	137.566	−609.744	−553.644	11.123
2700	62.008	364.454	311.207	143.765	−610.602	−551.470	10.669
2800	62.032	366.709	313.149	149.967	−905.358	−548.297	10.229
2900	62.054	368.886	315.034	156.172	−905.115	−535.549	9.646
3000	62.074	370.990	316.864	162.378	−904.868	−522.810	9.103
3100	62.092	373.026	318.643	168.586	−904.614	−510.078	8.595
3200	62.108	374.998	320.374	174.796	−904.354	−497.356	8.118
3300	62.123	376.909	322.058	181.008	−904.087	−484.641	7.671
3400	62.136	378.764	323.699	187.221	−903.811	−471.935	7.250
3500	62.149	380.565	325.298	193.435	−903.526	−459.237	6.854
3600	62.160	382.316	326.858	199.651	−903.232	−446.547	6.479
3700	62.171	384.019	328.380	205.867	−902.929	−433.865	6.125
3800	62.180	385.677	329.866	212.085	−902.616	−421.192	5.790
3900	62.189	387.293	331.318	218.303	−902.294	−408.527	5.472
4000	62.198	388.867	332.737	224.523	−901.963	−395.870	5.170
4100	62.205	390.403	334.125	230.743	−901.623	−383.222	4.882
4200	62.213	391.902	335.482	236.964	−901.275	−370.583	4.609
4300	62.219	393.366	336.812	243.185	−900.919	−357.951	4.348
4400	62.225	394.797	338.113	249.407	−900.556	−345.328	4.100
4500	62.231	396.195	339.389	255.630	−900.185	−332.714	3.862
4600	62.237	397.563	340.638	261.854	−899.811	−320.108	3.635
4700	62.242	398.902	341.864	268.078	−899.433	−307.509	3.418
4800	62.247	400.212	343.066	274.302	−899.052	−294.919	3.209
4900	62.251	401.496	344.245	280.527	−898.669	−282.337	3.010
5000	62.255	402.753	345.403	286.752	−898.287	−269.763	2.818
5100	62.259	403.986	346.539	292.978	−897.906	−257.196	2.634
5200	62.263	405.195	347.656	299.204	−897.528	−244.637	2.457
5300	62.267	406.381	348.753	305.430	−897.155	−232.085	2.287
5400	62.270	407.545	349.831	311.657	−896.789	−219.540	2.124
5500	62.273	408.688	350.891	317.884	−896.432	−207.002	1.966
5600	62.276	409.810	351.933	324.112	−896.085	−194.469	1.814
5700	62.279	410.912	352.958	330.340	−895.750	−181.944	1.667
5800	62.282	411.995	353.966	336.568	−895.426	−169.424	1.526
5900	62.284	413.060	354.959	342.796	−895.122	−156.910	1.389
6000	62.287	414.107	355.936	349.024	−894.813	−144.402	1.257

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

Continued on page 171

$S°(298.15\ K) = [264.21 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -693 \pm 40\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -695 \pm 40\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[20000]	2
$^2B_2$	[25000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[730](1)
[280](1)
[880](1)

Point Group: $[C_{2v}]$ $\sigma = 2$

Bond Distance: Al–F = [1.65] Å

Bond Angle: F–Al–F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.369562 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We tentatively adopt $\Delta_f H°(298.15\ K) = -166 \pm 10\ kcal \cdot mol^{-1}$ which corresponds to an average bond energy, $\Delta_{at}H°/2 = 140\ kcal \cdot mol^{-1}$, similar to that in AlF_3(g).[1] $\Delta_f H°$ is a compromise between discrepant results (−0 and −151 $kcal \cdot mol^{-1}$) from two mass–spectrometric equilibria analyzed below. In our opinion there is possible cause to suspect K_p for either reaction. The large entropy discrepancy (δS) for reaction B suggests a temperature–dependent bias in the mass–spectrometric K_p.[5] If both AlF_2 and AlF_3 were determined from the intensity of AlF_2^+ at different ionizing energies, then we expect $\Delta_f H°$[5] to be a positive limit. Reaction A was studied twice by molecular flow effusion of AlF_3(g) over the system Al(l)–Al_2O_3(cr). The earlier study[3,4] yields $\Delta_f H°(298.15\ K) = -188$ or $-179\ kcal \cdot mol^{-1}$, depending on the ionizing energy. Unfortunately, the ionizing energy in the first case is ambiguous. We conclude that $\Delta_f H°$ is quite dependent on ionizing energy. In addition, K_p and $\Delta_f H°$ may be affected by bias in the ionizing energy scale or related problems. These are discussed in more detail on tables for AlF_2^+, $AlCl_2^+$ and $AlCl_2$.[1] We believe that $\Delta_f H°$ [3,4] may be a negative limit.

The later study[2] of reaction A yields $\Delta_f H° = -180\ kcal \cdot mol^{-1}$. Internal evidence[2] gives us no reason to suspect this value. The possibility of negative bias is suggested, however, by inference from average bond energies (see $AlCl_2$),[1] and by using $\Delta_f H° = -180$ to derive $\Delta_f H°$ of other species in related mass–spectrometric studies. Effects of alternative values of $\Delta_f H°(AlF_2)$ are discussed on the tables for Al_2^-, AlF_4^-, AlF_2O, AlClF, $AlClF_2$, and $AlCl_2F$.[1] Only for $AlClF_2$ and $AlCl_2F$ do we have reliable, independent values of $\Delta_f H°$. These are consistent with $\Delta_f H°(AlF_2) = -166$ instead of −180. Although an alternative explanation is conceivable (see $AlClF_2$),[1] we choose $\Delta_f H°(AlF_2) = -166\ kcal \cdot mol^{-1}$.

Source	Reaction[a]	Ionizing Energy, eV	Data Points	T/K	δS cal·K⁻¹·mol⁻¹	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol⁻¹	$\Delta_{at}H°/2$
2	A	AP+(2 or 3)	7	1453–1675	4.0 ± 1.7	31.0 ± 2.6	24.6 ± 0.9	−180.4	147.0
3,4	A	AP+−2	1	1538	—	—	25.8	−179.2	146.5
3,4	A	20(or AP+3)	5	1408–1633	3.6 ± 0.6	22.5 ± 0.9	17.0 ± 0.8	−188.0	150.9
5	B	?	4	1243–1301	−76 ± 10	−47 ± 13	50.2 ± 3.7	<−151.2	>132.4

[a] Reactions: A) 1 AlF(g) = Al(g) + AlF_2(g) B) AlF_3(g) + AlF(g) = 2 AlF_2(g)

Heat Capacity and Entropy

The electronic ground state is that predicted for BF_2 by theoretical calculations;[6] it is consistent with semiempirical calculations[7] for BF_2, AlF_2, BCl_2 and $AlCl_2$. We estimate excited states of BF_2 at −30000 ($^2B_1$) and −40000 ($^2B_2$) by assuming that approximate theoretical calculations[6] have a bias similar to analogous calculations[8] of NO_2.[9] Dissociative electron–attachment data[10] yield −43000 cm^{-1} for $BF_2(^2B_2)$ confirming the estimation method. We use $BF_2(^2B_1)$ to estimate a crude correlation–energy correction for $AlF_2(^2B_1)$.[7] Dissociative electron–attachment data[11] for $AlF_2(^2B_2)$ are approximate; they yield −20000 ± 10000 ($\Delta_f H° = -166$) or −25000 ± 10000 cm^{-1} ($\Delta_f H° = -180$).

Vibrational frequencies are calculated from the estimated force constants $f_r = 4.25$ and $f_\alpha/r^2 = 0.25$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of AlF_2^+, AlF_2, AlF_2^-[1] and the analogous boron species. We assume that frequency changes are qualitatively similar to those of NO_2^+, NO_2 and NO_2^-. In going from AlF_2^+ to AlF_2, we expect a large decrease in ν_3, an increase in ν_2 and some increase in ν_1. By analogy with BF_2,[6] the odd electron in AlF should occupy an antibonding orbital which increases the bond length but decreases the bond angle and stretching force constant. We assume a bond length 0.05 Å longer than AlF_2^+[1] and a bond angle equal to that in BF_2.[6] The principal moments of inertia are: $I_A = 1.7832 \times 10^{-39}$, $I_B = 12.8835 \times 10^{-39}$ and $I_C = 14.6667 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K⁻¹·mol⁻¹	$S°$ J·K⁻¹·mol⁻¹	$-[G°-H°(T_r)]/T$ J·K⁻¹·mol⁻¹	$H°-H°(T_r)$ kJ·mol⁻¹	$\Delta_f H°$ kJ·mol⁻¹	$\Delta_f G°$ kJ·mol⁻¹	log K_f
0	0.	0.	INFINITE	−11.505	−692.684	−692.684	INFINITE
100	35.777	220.448	301.626	−8.118	−692.688	−696.997	364.074
200	41.060	246.892	268.255	−4.273	−693.574	−700.993	183.081
250	43.614	256.331	264.952	−2.155	−694.073	−702.790	146.840
298.15	45.857	264.209	264.209	0.	−694.544	−704.426	123.413
300	45.937	264.493	264.210	0.085	−694.562	−704.487	122.662
350	47.921	271.728	264.777	2.433	−695.038	−706.104	105.380
400	49.558	278.237	266.059	4.871	−695.503	−707.653	92.410
450	50.888	284.154	267.746	7.384	−695.961	−709.144	82.315
500	51.967	289.573	269.662	9.956	−696.417	−710.584	74.234
600	53.559	299.199	273.803	15.237	−697.344	−713.331	62.101
700	54.637	307.541	278.040	20.651	−698.330	−715.919	53.423
800	55.391	314.889	282.196	26.154	−699.417	−718.359	46.904
900	55.935	321.446	286.199	31.722	−700.644	−720.655	41.826
1000	56.338	327.361	290.025	37.337	−712.635	−722.045	37.716
1100	56.644	332.746	293.667	42.986	−713.880	−722.925	34.329
1200	56.882	337.685	297.132	48.663	−715.124	−723.693	31.502
1300	57.070	342.246	300.429	54.361	−716.371	−724.356	29.105
1400	57.220	346.481	303.569	60.076	−717.622	−724.924	27.047
1500	57.343	350.433	306.563	65.804	−718.879	−725.401	25.261
1600	57.444	354.137	309.422	71.544	−720.143	−725.795	23.695
1700	57.529	357.622	312.156	77.292	−721.415	−726.109	22.311
1800	57.600	360.912	314.774	83.049	−722.693	−726.348	21.078
1900	57.661	364.028	317.285	88.812	−723.977	−726.517	19.973
2000	57.713	366.987	319.697	94.581	−725.264	−726.617	18.977
2100	57.759	369.804	322.016	100.355	−726.553	−726.653	18.075
2200	57.799	372.492	324.250	106.132	−727.840	−726.628	17.252
2300	57.835	375.062	326.404	111.914	−729.121	−726.544	16.500
2400	57.868	377.524	328.483	117.699	−730.394	−726.404	15.810
2500	57.898	379.887	330.492	123.488	−731.656	−726.212	15.173
2600	57.927	382.159	332.436	129.279	−732.902	−725.970	14.585
2700	57.955	384.345	334.318	135.073	−734.129	−725.680	14.039
2800	57.983	386.454	336.143	140.870	−1029.236	−724.377	13.513
2900	58.012	388.489	337.913	146.670	−1029.321	−713.487	12.851
3000	58.041	390.456	339.632	152.472	−1029.380	−702.596	12.233
3100	58.072	392.360	341.302	158.278	−1029.408	−691.702	11.655
3200	58.105	394.204	342.927	164.087	−1029.406	−680.808	11.113
3300	58.141	395.992	344.508	169.899	−1029.370	−669.915	10.604
3400	58.179	397.729	346.048	175.715	−1029.299	−659.024	10.125
3500	58.221	399.416	347.549	181.535	−1029.193	−648.135	9.673
3600	58.266	401.057	349.012	187.359	−1029.050	−637.249	9.246
3700	58.314	402.654	350.441	193.188	−1028.869	−626.368	8.843
3800	58.366	404.209	351.835	199.022	−1028.651	−615.493	8.461
3900	58.423	405.726	353.198	204.862	−1028.395	−604.623	8.098
4000	58.483	407.206	354.529	210.707	−1028.102	−593.761	7.754
4100	58.548	408.651	355.832	216.559	−1027.770	−582.907	7.426
4200	58.617	410.063	357.106	222.417	−1027.401	−572.060	7.115
4300	58.689	411.443	358.354	228.282	−1026.996	−561.224	6.818
4400	58.766	412.793	359.576	234.155	−1026.554	−550.397	6.534
4500	58.847	414.114	360.773	240.036	−1026.074	−539.581	6.263
4600	58.932	415.409	361.947	245.924	−1025.562	−528.775	6.004
4700	59.021	416.677	363.098	251.822	−1025.016	−517.981	5.757
4800	59.113	417.921	364.227	257.729	−1024.437	−507.199	5.519
4900	59.209	419.141	365.335	263.645	−1023.826	−496.430	5.292
5000	59.308	420.338	366.424	269.571	−1023.186	−485.673	5.074
5100	59.409	421.513	367.492	275.506	−1022.517	−474.930	4.864
5200	59.514	422.668	368.542	281.453	−1021.821	−464.199	4.663
5300	59.621	423.802	369.574	287.409	−1021.099	−453.482	4.469
5400	59.730	424.918	370.589	293.377	−1020.353	−442.780	4.283
5500	59.842	426.015	371.587	299.355	−1019.584	−432.091	4.104
5600	59.955	427.094	372.568	305.345	−1018.794	−421.416	3.931
5700	60.070	428.156	373.534	311.347	−1017.985	−410.757	3.764
5800	60.186	429.202	374.485	317.359	−1017.155	−400.111	3.603
5900	60.303	430.232	375.421	323.384	−1016.312	−389.479	3.448
6000	60.421	431.246	376.343	329.420	−1015.432	−378.864	3.298

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K)$ = [239.3 ± 4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) \approx 87 \pm 63$ $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) \approx$ [92.048] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[670](1)
[240](2)
[1000](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Al–F = [1.60] Å
Bond Angle: F–AL–F = [180]°
Rotational Constant: B_o = [0.173304] cm^{-1}

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = 22 \pm 15$ $kcal·mol^{-1}$ and $IP(AlF_2) = 8.1 \pm 0.9$ eV. Electron–impact studies[1,2] gave 15.2 ± 0.3 eV for the appearance potential (AP) of AlF_2^+ from AlF_3. The analogous process for onset of BF_2^+ from BF_3 has been studied by both photoionization[3] and electron impact.[4] Comparison indicates that BF_2^+ from electron impact[4] carried an excess energy (E*) of −0.4 to −0.9 eV. We estimate the excess energy for AlF_2^+ as 1.0 ± 0.5 eV. Thus, we take $AP–E^* = \Delta_f H° = 14.2 \pm 0.6$ eV (327.5 ± 14 $kcal·mol^{-1}$) for the reaction $AlF_3(g) + e^-(g) = AlF_2^+(g) + F(g) + 2\ e^-(g)$. With JANAF auxiliary data[5] this yields $\Delta_f H°(AlF_2^+) = 21 \pm 15$, $\Delta_f H°(298.15\ K) = 22 \pm 15$ and $IP(AlF_2) = 187 \pm 20$ $kcal·mol^{-1}$ (8.1 ± 0.9 eV).

Electron–impact studies of AlF_2 gave approximate appearance potentials $AP(AlF_2^+) = 9 \pm 1$,[1] 10 ± 1[6] and 11 ± 1 eV.[7] We dismiss the last value[7] due to possible bias analogous to that of $AlCl_2^+(g)$.[5] Electron impact on AlF_2 should yield a vertical AP corresponding to a nonlinear (excited) configuration of AlF_2^+. Theoretical calculations for the linear $^2B_1$ state of BF_2[8] suggest an excitation energy of −1.1 eV at a bond angle of 120°. Extended Huckel calculations for AlF_2[9] suggest −1.4 eV at 130°. Thus, we combine $E^* = 1.2 \pm 0.5$ eV with the observed AP values[1,6] to get $IP(AlF_2) = 7.8 \pm 1.2$ and 8.8 ± 1.2 eV. These are consistent with the adopted value.

The extended Huckel calculation[9] gave $IP(AlF_2) = 7.8$ eV at a bond angle of 130°. This result should approximate the vertical IP which we expect at −9.3 eV.

Heat Capacity and Entropy

We assume the electronic ground state to be $^1\Sigma^+$ and neglect excited states. We expect the ground state to be linear by analogy with other triatomic species having sixteen valence electrons.[10] Although conflicting data[5] suggest that isoelectronic MgF_2 is either linear or slightly nonlinear, recent Raman data[11] favor a linear structure. We estimate the bond distance to be slightly shorter than that in AlF_3 and 0.05 Å shorter than that estimated for AlF_2.[5] We transfer the stretching force constant from AlF_3 and the ratio $f_r/f_\alpha = \sim 13$ $Å^{-2}$ from MgF_2. This ratio is a compromise between very different values of ν_2 observed for MgF_2 in the gas[5] and matrix[11] phases. Thus, we calculate vibrational frequencies for AlF_2^+ from the force constants $f_r = 4.9$, $f_{rr} = 0.2$ and $f_\alpha/r^2 = 0.14$ mdyn/Å. The resulting values have been rounded downward.

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[5] JANAF Thermochemical Tables: AlF(g) and $AlCl_2^+(g)$, 6–30–76; AlFO(g), 12–31–75; $MgF_2(g)$, 6–30–75; $AlF_3(g)$, 6–30–70; F(g), 9–30–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−11.730	87.485		
100	35.844	193.010	279.338	−8.633			
200	44.056	220.679	243.650	−4.594			
250	46.927	230.826	240.097	−2.318			
298.15	49.281	239.299	239.299	0.	92.048	83.338	−14.601
300	49.364	239.604	239.300	0.091	92.075	83.284	−14.501
350	51.404	247.371	239.908	2.612	92.811	81.761	−12.202
400	53.086	254.349	241.285	5.226	93.561	80.131	−10.464
450	54.463	260.684	243.094	7.916	94.319	78.407	−9.101
500	55.589	266.482	245.147	10.668	95.083	76.598	−8.002
600	57.271	276.776	249.582	16.316	96.601	72.758	−6.334
700	58.428	285.697	254.119	22.105	98.069	68.668	−5.124
800	59.245	293.555	258.567	27.991	99.443	64.372	−4.203
900	59.839	300.569	262.851	33.946	100.682	59.912	−3.477
1000	60.282	306.898	266.944	39.953	91.162	56.083	−2.929
1100	60.619	312.660	270.842	45.999	92.392	52.516	−2.494
1200	60.882	317.946	274.550	52.075	93.625	48.836	−2.126
1300	61.091	322.828	278.079	58.174	94.858	45.054	−1.810
1400	61.258	327.361	281.439	64.292	96.089	41.176	−1.536
1500	61.395	331.593	284.643	70.424	97.315	37.211	−1.296
1600	61.508	335.559	287.703	76.570	98.535	33.165	−1.083
1700	61.603	339.291	290.629	82.725	99.749	29.042	−0.892
1800	61.682	342.814	293.431	88.890	100.957	24.848	−0.721
1900	61.750	346.151	296.118	95.062	102.160	20.586	−0.566
2000	61.808	349.320	298.700	101.240	103.361	16.262	−0.425
2100	61.858	352.337	301.183	107.423	104.561	11.878	−0.295
2200	61.902	355.215	303.574	113.611	105.763	7.436	−0.177
2300	61.940	357.968	305.879	119.803	106.970	2.940	−0.067
2400	61.974	360.605	308.105	125.999	108.186	−1.609	0.035
2500	62.004	363.135	310.256	132.198	109.414	−6.209	0.130
2600	62.030	365.568	312.337	138.400	110.657	−10.859	0.218
2700	62.054	367.909	314.352	144.604	111.918	−15.556	0.301
2800	62.075	370.166	316.305	150.810	−180.700	−19.333	0.361
2900	62.094	372.345	318.200	157.019	−178.298	−13.613	0.245
3000	62.111	374.450	320.041	163.229	−175.870	−7.975	0.139
3100	62.127	376.487	321.829	169.441	−173.414	−2.419	0.041
3200	62.141	378.460	323.568	175.654	−170.928	3.057	−0.050
3300	62.154	380.372	325.260	181.869	−168.412	8.456	−0.134
3400	62.165	382.228	326.909	188.085	−165.862	13.777	−0.212
3500	62.176	384.030	328.515	194.302	−163.280	19.023	−0.284
3600	62.186	385.782	330.082	200.520	−160.665	24.195	−0.351
3700	62.195	387.486	331.610	206.739	−158.016	29.293	−0.414
3800	62.204	389.144	333.102	212.959	−155.333	34.320	−0.472
3900	62.211	390.760	334.560	219.180	−152.617	39.276	−0.526
4000	62.219	392.335	335.985	225.401	−149.869	44.161	−0.577
4100	62.225	393.872	337.378	231.623	−147.088	48.977	−0.624
4200	62.231	395.371	338.741	237.846	−144.276	53.726	−0.668
4300	62.237	396.836	340.075	244.070	−141.433	58.406	−0.709
4400	62.243	398.267	341.382	250.294	−138.562	63.020	−0.748
4500	62.248	399.665	342.661	256.518	−135.660	67.569	−0.784
4600	62.252	401.034	343.915	262.743	−132.733	72.053	−0.818
4700	62.257	402.372	345.145	268.969	−129.780	76.473	−0.850
4800	62.261	403.683	346.351	275.195	−126.804	80.830	−0.880
4900	62.265	404.967	347.534	281.421	−123.804	85.125	−0.907
5000	62.269	406.225	348.695	287.648	−120.785	89.358	−0.934
5100	62.272	407.458	349.836	293.875	−117.746	93.531	−0.958
5200	62.275	408.667	350.955	300.102	−114.690	97.644	−0.981
5300	62.278	409.854	352.056	306.330	−111.618	101.698	−1.002
5400	62.281	411.018	353.137	312.558	−108.533	105.694	−1.022
5500	62.284	412.161	354.200	318.786	−105.436	109.632	−1.041
5600	62.287	413.283	355.245	325.015	−102.328	113.515	−1.059
5700	62.289	414.385	356.272	331.243	−99.213	117.341	−1.075
5800	62.292	415.469	357.284	337.472	−96.088	121.112	−1.091
5900	62.294	416.534	358.279	343.702	−92.962	124.831	−1.105
6000	62.296	417.581	359.259	349.931	−89.810	128.494	−1.119

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [260.05 \pm 3.3]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -900 \pm 84\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-907.928]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	[0]	1
$^3B_1$	[26000]	3
$^1B_1$	[44000]	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[730](1)
[280](1)
[780](1)

Point Group: $[C_{2v}]$ $\sigma = 2$

Bond Distance: Al–F = [1.70] Å

Bond Angle: F–Al–F = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.600099 \times 10^{-115}]\ g^3\cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -217 \pm 20\ kcal\cdot mol^{-1}$ which corresponds to an electron affinity of $EA(AlF_2) = 50 \pm 8\ kcal\cdot mol^{-1}$ (2.2 ± 0.4 eV) and a fluoride-ion affinity of $IA(AlF) = 92 \pm 20\ kcal\cdot mol^{-1}$. $\Delta_f H°$ is based on K_p data for the reaction $AlF_2(g) = F(g) + AlF_2^-(g)$ reported by Srivastava *et al.*[1] The authors measured K_p with a molecular-flow–effusion method using a mass spectrometer operating in both positive- and negative-ion modes. They give three points (1705–1900 K) obtained from study of the vapor species over the system AlF_3(cr)–KF(cr)–Al(l). Our analysis gives $[\Delta_r S°(2nd\ law) - \Delta_r S°(3rd\ law)] = -0.2 \pm 4.8\ cal\cdot K^{-1}\cdot mol^{-1}$ and $\Delta_f H°(298.15\ K) = 28.4 \pm 8.8$(2nd law) or 28.8 ± 1(3rd law) $kcal\cdot mol^{-1}$. Reducing the 3rd law $\Delta_f H°$ to absolute zero and combining with $EA(F) = 78.38\ kcal\cdot mol^{-1}$,[2] we derive $EA(AlF_2) = 49.7 \pm 8\ kcal\cdot mol^{-1}$. The uncertainty of ±8 $kcal\cdot mol^{-1}$ is our estimate of a reasonable bound for error in $\Delta_f H°$.

Depending on the value used for $\Delta_f H°(AlF_2)$, the above reaction yields $\Delta_f H°(AlF_2^-, g, 298.15\ K) = -231$,[3,2] -217[2] or -202[4,2] $kcal\cdot mol^{-1}$. In contrast, we derive $\Delta_f H°(AlF_2^-, g, 298.15\ K) = -181 \pm 25\ kcal\cdot mol^{-1}$, independent of $\Delta_f H°(AlF_2)$, from $\Delta_r H°(0\ K)$ AP–E* = 127 kcal[5] for the reaction $AlF_3(g) + e^-(g) = AlF_2^-(g) + F(g)$. Depending on $\Delta_f H°(AlF_2)$, this yields $EA(AlF_2) = 0 \pm 25$,[3,2] 14 ± 25[2] or 29 ± 25[4,2] $kcal\cdot mol^{-1}$. Petty *et al.*[5] measured the appearance potential (AP) and excess translational energy of AlF_2^- in the dissociative electron–attachment reaction. E*, the excess vibrational–translational energy of the products at threshold, was estimated[5] from the measured translational energy via an approximate empirical correlation. We estimate ±25 $kcal\cdot mol^{-1}$ as an approximate bound for error in E*.[6] The resulting $\Delta_f H°(AlF_2^-) = -181 \pm 25\ kcal^{-1}\cdot mol^{-1}$ is inconsistent with the two most likely values (−231 and −217) derived from AlF_2. Bias might exist in either experiment.[5,2] It is conceivable that AlF_2^- is formed[5] in an excited electronic state. Thus far, electronic excitation has been observed[7] in only one negative molecular ion, AsF_4^-. If it occurs for AlF_2^-, then $\Delta_f H° = -181 \pm 25$ refers to an excited electronic state. The electronic energy of this state would be $-13000 \pm 9000\ cm^{-1}$, based on the two most likely values of $\Delta_f H°(AlF_2^-)$. Such values are not unreasonable, so we cannot rule out electronic excitation.[5] We conclude that additional data are needed to confirm $\Delta_f H°(AlF_2^-)$.

Heat Capacity and Entropy

Electronic levels and quantum weights are assumed equal to those of isoelectronic SiF_2;[2,8] however, see the above comment on excited levels. Vibrational frequencies are calculated from the estimated force constants $f_r = 3.7$, $f_{rr} = 0.1$ and $f_\alpha/r^2 = 0.29$ mdyn/Å. Frequencies and force constants are estimated from simultaneous consideration of AlF_2^+, AlF_2, AlF_2^- and the analogous boron species. We assume that frequency changes are qualitatively similar in the two series AlF_2^+, AlF_2, AlF_2^- and NO_2^+, NO_2, NO_2^- [2] which have the same number of valence electrons. Furthermore, we expect isoelectronic SiF_2^{2-} to provide upper-limit frequencies for AlF_2^-. Thus, in going from AlF_2 to AlF_2^-, we assume little change in ν_1 and ν_2 but a significant decrease in ν_3.

By analogy with BF_2,[8,9] we expect that the odd electron in AlF_2 occupies a molecular orbital centered mainly on the metal opposite the two fluorines. This orbital should be antibonding[8] in the sense that addition of an electron increases the bond length but decreases the bond angle and stretching force constant. We assume that the bond length is 0.05 Å longer and the bond angle is 15° smaller than in AlF_2.[2] The principal moments of inertia are $I_A = 2.8061 \times 10^{-39}$, $I_B = 11.4773 \times 10^{-39}$and $I_C = 14.2834 \times 10^{-39}\ g\cdot cm^2$.

References

[1] R. D. Srivastava, O. M. Uy and M. Farber, J. Chem. Soc., Faraday Trans. I **70**, 1033 (1974); AD–731303, 50 pp. (1971).

[2] JANAF Thermochemical Tables: $AlF_2(g)$ and $SiF_2(g)$, 6–30–76; $NO_2^-(g)$, 6–30–72; $F^-(g)$, 12–31–71; F(g), 9–30–65.

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[7] J. L. Franklin, Rice University, Houston, Texas, personal communications, (September, 1976).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.573	−899.939		
100	35.786	215.980	297.844	−8.186			
200	41.429	242.516	264.145	−4.326			
250	44.174	252.060	260.799	−2.185			
298.15	46.511	260.046	260.046	0.	−907.928	−910.314	159.483
300	46.594	260.334	260.047	0.086	−907.983	−910.329	158.502
350	48.597	267.672	260.622	2.468	−909.465	−910.602	135.900
400	50.209	274.271	261.923	4.939	−910.936	−910.664	118.921
450	51.494	280.262	263.633	7.483	−912.402	−910.542	105.693
500	52.520	285.742	265.573	10.084	−913.868	−910.257	95.094
600	54.009	295.459	269.765	15.416	−916.824	−909.258	79.158
700	55.003	303.864	274.050	20.870	−919.848	−907.759	67.738
800	55.690	311.256	278.248	26.407	−922.980	−905.820	59.144
900	56.182	317.845	282.288	32.001	−926.259	−903.480	52.437
1000	56.545	323.785	286.146	37.639	−940.306	−900.006	47.011
1100	56.820	329.187	289.817	43.308	−943.610	−895.816	42.539
1200	57.032	334.141	293.307	49.001	−946.917	−891.325	38.798
1300	57.199	338.713	296.626	54.712	−950.228	−886.558	35.622
1400	57.333	342.957	299.786	60.439	−953.545	−881.536	32.891
1500	57.442	346.916	302.797	66.178	−956.871	−876.276	30.515
1600	57.532	350.626	305.672	71.927	−960.204	−870.794	28.429
1700	57.607	354.116	308.420	77.684	−963.546	−865.104	26.581
1800	57.670	357.411	311.051	83.448	−966.896	−859.217	24.934
1900	57.724	360.530	313.574	89.218	−970.251	−853.143	23.455
2000	57.770	363.493	315.996	94.993	−973.611	−846.893	22.119
2100	57.809	366.312	318.326	100.772	−976.973	−840.474	20.906
2200	57.844	369.002	320.568	106.554	−980.334	−833.895	19.799
2300	57.874	371.574	322.731	112.340	−983.690	−827.164	18.785
2400	57.901	374.038	324.817	118.129	−987.038	−820.287	17.853
2500	57.925	376.402	326.834	123.920	−990.375	−813.270	16.992
2600	57.947	378.674	328.784	129.714	−993.697	−806.120	16.195
2700	57.967	380.862	330.673	135.510	−997.001	−798.843	15.455
2800	57.986	382.970	332.503	141.307	−1294.186	−790.476	14.747
2900	58.005	385.005	334.279	147.107	−1296.350	−772.448	13.913
3000	58.023	386.972	336.003	152.908	−1298.488	−754.346	13.134
3100	58.041	388.875	337.678	158.711	−1300.598	−736.173	12.404
3200	58.060	390.718	339.306	164.517	−1302.678	−717.932	11.719
3300	58.079	392.505	340.892	170.323	−1304.726	−699.627	11.074
3400	58.101	394.239	342.435	176.132	−1306.741	−681.261	10.466
3500	58.124	395.923	343.939	181.944	−1308.722	−662.835	9.892
3600	58.149	397.561	345.406	187.757	−1310.668	−644.353	9.349
3700	58.177	399.155	346.838	193.574	−1312.579	−625.818	8.835
3800	58.209	400.707	348.235	199.393	−1314.455	−607.232	8.347
3900	58.243	402.219	349.600	205.215	−1316.294	−588.597	7.883
4000	58.281	403.694	350.934	211.042	−1318.098	−569.915	7.442
4100	58.324	405.134	352.238	216.872	−1319.866	−551.189	7.022
4200	58.370	406.540	353.514	222.706	−1321.600	−532.419	6.622
4300	58.422	407.914	354.764	228.546	−1323.298	−513.609	6.239
4400	58.477	409.258	355.987	234.391	−1324.963	−494.760	5.874
4500	58.538	410.572	357.185	240.242	−1326.592	−475.873	5.524
4600	58.604	411.860	358.360	246.099	−1328.190	−456.951	5.189
4700	58.675	413.121	359.512	251.963	−1329.756	−437.994	4.868
4800	58.751	414.357	360.641	257.834	−1331.292	−419.004	4.560
4900	58.832	415.569	361.750	263.713	−1332.796	−399.982	4.264
5000	58.919	416.759	362.838	269.601	−1334.273	−380.930	3.980
5100	59.011	417.926	363.907	275.497	−1335.722	−361.849	3.706
5200	59.108	419.073	364.957	281.403	−1337.145	−342.739	3.443
5300	59.210	420.200	365.989	287.319	−1338.542	−323.603	3.189
5400	59.317	421.308	367.003	293.245	−1339.916	−304.440	2.945
5500	59.429	422.397	368.000	299.182	−1341.267	−285.252	2.709
5600	59.545	423.469	368.981	305.131	−1342.597	−266.040	2.482
5700	59.666	424.524	369.946	311.092	−1343.907	−246.804	2.262
5800	59.792	425.563	370.896	317.064	−1345.195	−227.546	2.049
5900	59.921	426.586	371.832	323.050	−1346.470	−208.265	1.844
6000	60.055	427.594	372.753	329.049	−1347.706	−188.965	1.645

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [292.7 \pm 13]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) \approx -1105.4 \pm 30\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) \approx -1108.8 \pm 30\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2B_2]$	0	[2]
$[^2B_1]$	[1000]	[2]
$[^2B]$	[20000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[900](1)	[900](1)
[640](1)	[240](1)
[260](1)	[270](1)

Point Group: $[C_{2v}]$ σ = [2]
Bond Distances: Al–F = [1.63] Å; Al–O = [1.72] Å
Bond Angles: F–Al–F = [120]°; F–Al–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.719682 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -265 \pm 7$ kcal·mol^{-1} and $\Delta_{at} H° = 437 \pm 8$ kcal·mol^{-1} based on JANAF auxiliary data[1] combined with $\Delta_f H°(298.15\ K) = 15.5 \pm 5$ kcal·mol^{-1} for the reaction AlF(g) + AlFO(g) = Al(g) + AlF_2O(g). $\Delta_f H°$ is from our 3rd law analysis of K_p data reported by Uy *et al.*[2] They calculated K_p directly from ion intensities observed at 1453–1675 K in a mass-spectrometric study of vapor species over the system AlF_3(g)–Al(l)–Al_2O_3(cr). 2nd law analysis gives $\Delta_r H°(298.15\ K) = 20.8 \pm 0.8$ kcal·mol^{-1} and the difference $[\Delta_r S°(2nd\ law) - \Delta_r S°(3rd\ law)] = 3.4 \pm 0.5$ cal·K^{-1}·mol^{-1}. Uy *et al.*[2] assigned $\Delta_f H°$(2nd law) an overall uncertainty (including contributions from T) of ± 5 kcal·mol^{-1}.

The adopted $\Delta_{at} H° = 437$ kcal·mol^{-1} implies that AlF_2O is surprisingly stable. Average bond energies from AlF_3 (140 kcal·mol^{-1}) and AlO, AlO_2 and Al_2O (−120 kcal·mol^{-1}) yield an estimate of $\Delta_a H°(AlF_2O) = 400$ kcal·mol^{-1}. If we attribute all of the difference to the Al–O bond, then the AlF_2O data imply an Al–O bond energy of 157 kcal·mol^{-1}. This enhancement of 37 kcal·mol^{-1} contrasts with the near equality of Al–O bond energies in the oxides[1] and hydroxides.[8] An analogous treatment of AlFO(g)[1] yields an Al–O bond energy of 153 kcal·mol^{-1}, similar to that in AlF_2O. Existing data for BF_2O and BFO imply bond energies of −166 and −200 kcal·mol^{-1} compared with values of −130 (B–O) and −190 (B=O) from the oxides. There are obvious differences between the Al and B systems which we are unable to rationalize via existing knowledge of electronic structure. We feel that confirmation of the oxyfluoride data is desirable.

Heat Capacity and Entropy

Molecular parameters are all estimated by analogy with BF_2O and BF_2O^+. Two emission bands due to BF_2O or BF_2O^+ were analyzed by Mathews.[3] Vibrational analysis of the band with $\nu_\infty \approx 17171\ cm^{-1}$ gave the three symmetrical stretching modes of the lower state. Rotational analysis of the band with $\nu_o = 22391\ cm^{-1}$ gave structural parameters including the bond length B–O = 1.40 ± 0.05 Å. This value indicates a single bond which is longer than those of 1.36, 1.263 and 1.20 A observed for the various bond types in B_2O_3, BO_2 and BO. It is not known[3] whether the two emission bonds have a common lower state. Zahradnik and Carsky[4] used semiempirical CNDO calculations to predict the electronic transitions of BF_2O and BF_2O^+. They favored assignment of the 22391 cm^{-1} transition to BF_2O^+ and the other transition to either BF_2O^+ or BF_2O.

Due to the lengthened B–O bond and the theoretical results, we tentatively attribute both observed bands to BF_2O^+. We estimate the missing vibrational frequencies of BF_2O^+ and all those of BF_2O and BF_2O^- by comparison with HBF_2, BF_3 and $ClBF_2$. We assume that addition of an electron causes a large increase in ν_1 and ν_5 but a smaller increase in ν_2 and ν_6.

Vibrational frequencies of AlF_2O are estimated from those of BF_2O by comparison of AlF_3, AlFO, AlO and Al_2O[1] with the analogous boron species. Electronic levels are crude estimates based on calculations or data for the 24-valence-electron species BF_2O,[4] BF_3^+,[5,6] and NO_3.[5,7] Bond angles are assumed to be 120°. Bond distances are assumed equal to those of AlF_3 and Al_2O[1]. The principal moments of inertia are: $I_A = 12.0265 \times 10^{-39}$, $I_B = 12.5730 \times 10^{-39}$ and $I_C \approx 24.5995 \times 10^{-39}\ g \cdot cm^2$.

References

[1]JANAF Thermochemical Tables: AlFO(g) and AlO_2(g), 12–31–75; AlF(g), AlO(g) and Al_2O(g), 6–30–75; AlF_3(g), 6–30–70; Al(g), 12–31–65.
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Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.325	−1105.379	−1105.379	INFINITE
100	42.267	235.438	343.053	−10.761	−1106.659	−1103.801	576.567
200	55.050	269.080	298.254	−5.835	−1107.918	−1100.427	287.402
250	59.640	281.871	293.729	−2.964	−1108.393	−1098.497	229.518
298.15	63.390	292.705	292.705	0.	−1108.760	−1096.556	192.112
300	63.521	293.098	292.707	0.117	−1108.773	−1096.480	190.914
350	66.737	303.139	293.492	3.377	−1109.076	−1094.407	163.331
400	69.357	312.228	295.275	6.781	−1109.322	−1092.294	142.639
450	71.477	320.524	297.626	10.304	−1109.528	−1090.152	126.542
500	73.192	328.147	300.303	13.922	−1109.709	−1087.990	113.661
600	75.724	341.730	306.103	21.376	−1110.043	−1083.614	94.337
700	77.441	353.540	312.055	29.040	−1110.406	−1079.182	80.530
800	78.644	363.964	317.905	36.848	−1110.857	−1074.691	70.170
900	79.513	373.280	323.549	44.758	−1111.445	−1070.137	62.109
1000	80.158	381.693	328.950	52.743	−1122.796	−1064.748	55.617
1100	80.650	389.357	334.098	60.784	−1123.404	−1058.914	50.284
1200	81.035	396.391	339.000	68.869	−1124.015	−1053.024	45.837
1300	81.344	402.890	343.668	76.989	−1124.631	−1047.084	42.072
1400	81.600	408.928	348.116	85.136	−1125.256	−1041.095	38.844
1500	81.819	414.566	352.360	93.308	−1125.891	−1035.062	36.044
1600	82.013	419.852	356.415	101.499	−1126.537	−1028.985	33.593
1700	82.190	424.830	360.295	109.710	−1127.193	−1022.868	31.429
1800	82.358	429.532	364.012	117.937	−1127.858	−1016.712	29.504
1900	82.521	433.990	367.579	126.181	−1128.531	−1010.519	27.781
2000	82.683	438.226	371.006	134.441	−1129.208	−1004.291	26.229
2100	82.845	442.265	374.304	142.718	−1129.886	−998.028	24.825
2200	83.008	446.122	377.481	151.010	−1130.562	−991.733	23.547
2300	83.175	449.816	380.546	159.319	−1131.232	−985.408	22.379
2400	83.344	453.359	383.507	167.645	−1131.891	−979.054	21.309
2500	83.516	456.765	386.370	175.988	−1132.535	−972.672	20.323
2600	83.690	460.044	389.141	184.349	−1133.160	−966.265	19.413
2700	83.866	463.206	391.826	192.726	−1133.762	−959.834	18.569
2800	84.043	466.259	394.430	201.122	−1428.239	−952.414	17.768
2900	84.220	469.211	396.958	209.535	−1427.690	−935.430	16.849
3000	84.398	472.069	399.414	217.966	−1427.109	−918.466	15.992
3100	84.574	474.840	401.803	226.414	−1426.493	−901.521	15.191
3200	84.749	477.527	404.127	234.881	−1425.839	−884.597	14.440
3300	84.922	480.138	406.391	243.364	−1425.148	−867.694	13.734
3400	85.092	482.676	408.598	251.865	−1424.416	−850.812	13.071
3500	85.260	485.145	410.750	260.383	−1423.644	−833.952	12.446
3600	85.424	487.549	412.850	268.917	−1422.831	−817.115	11.856
3700	85.585	489.892	414.900	277.467	−1421.976	−800.302	11.298
3800	85.742	492.176	416.904	286.034	−1421.080	−783.511	10.770
3900	85.894	494.405	418.863	294.615	−1420.143	−766.745	10.269
4000	86.042	496.582	420.779	303.212	−1419.165	−750.004	9.794
4100	86.185	498.708	422.654	311.824	−1418.148	−733.287	9.342
4200	86.324	500.787	424.489	320.449	−1417.092	−716.596	8.912
4300	86.458	502.820	426.287	329.088	−1416.000	−699.931	8.502
4400	86.587	504.809	428.049	337.741	−1414.871	−683.291	8.112
4500	86.711	506.756	429.777	346.406	−1413.706	−666.677	7.739
4600	86.830	508.663	431.471	355.083	−1412.511	−650.090	7.382
4700	86.944	510.532	433.133	363.771	−1411.285	−633.529	7.041
4800	87.053	512.363	434.765	372.471	−1410.031	−616.994	6.714
4900	87.157	514.159	436.367	381.182	−1408.749	−600.485	6.401
5000	87.256	515.921	437.941	389.903	−1407.445	−584.003	6.101
5100	87.350	517.650	439.487	398.633	−1406.119	−567.547	5.813
5200	87.440	519.347	441.006	407.372	−1404.773	−551.118	5.536
5300	87.524	521.013	442.500	416.121	−1403.411	−534.714	5.270
5400	87.604	522.650	443.969	424.877	−1402.035	−518.337	5.014
5500	87.679	524.258	445.414	433.641	−1400.648	−501.985	4.767
5600	87.750	525.839	446.837	442.413	−1399.252	−485.658	4.530
5700	87.817	527.393	448.236	451.191	−1397.850	−469.357	4.301
5800	87.879	528.920	449.614	459.976	−1396.442	−453.080	4.080
5900	87.937	530.423	450.971	468.767	−1395.036	−436.827	3.867
6000	87.990	531.902	452.308	477.563	−1393.610	−420.600	3.662

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [284.9 \pm 13]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1300 \pm 105\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1309.592]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[950](1)	[900](1)
[650](1)	[270](1)
[260](1)	[300](1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Al–F = [1.63] Å; Al–O = [1.66] Å
Bond Angles: F–Al–F = [120]°; F–Al–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.468404 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -313 \pm 25$ kcal·mol^{-1} which corresponds to $EA(AlF_2O) = 46 \pm 25$ kcal·mol^{-1} (2.0 ± 1.1 eV) and the fluoride–ion affinity IA(AlFO) = 112 kcal·mol^{-1}. $\Delta_f H°$ is derived from Kp for reaction A (see below) observed by Faraber *et al.*[1] with a mass spectrometer operating in both positive– and negative–ion modes. Farber *et al.*[1] used a molecular–flow–effusion technique to study vapor species in the systems KF(g)–AlF_3(g)–Al_2O_3(cr), KF(g)–AlF_3(g)–Al_2O_3(cr), and KCl(g)–AlF_3(g)–Al_2O_3(cr). They considered the results to be limiting values; we presume this is due to very low intensities of AlF_2O^-.

The three reactions reported by Farber *et al.* are analyzed below using JANAF auxiliary data.[2] We give inequalities consistent with the authors' limiting values. Reactions B and C yield less stringent limits are are not used. Reaction A involves AlF_2^- which depends on our possibly biased value[2] of $\Delta_f H°(AlF_2)$. Use of the alternative $\Delta_f H°$ [2] based on mass spectrometry[1,3] reduces the discrepancy between reactions A and C form 35 to 21 kcal·mol^{-1}. This may mot be significant if B and C yield only limiting values. The alternative result from A would yield $EA(AlF_2O)$ = 61 and IA(AlFO) = 127 kcal·mol^{-1}.

Reaction	Data Points	T/K	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
A) $AlFO(g) + AlF_2^-(g) = AlF_2O^-(g) + AlF(g)$	1	1793	≥−21.1	≥−313.6[a] or ≥ − 327.8[a]
B) $AlF_2O(g) + F^-(g) = AlF_2O^-(g) + F(g)$	1	1753	>0.1	>−344.8
C) $AlF_2O(g) + Cl^-(g) = AlF_2O(g) + Cl(g)$	2	1653–1793	>0.8	>−349.1

[a]Assuming $\Delta_f H°(AlF_2^-, g, 298.15\ K)$ = −217 or −231.2 kcal·mol^{-1} depending on choice of $\Delta_f H°(AlF_2)$.[2]

Heat Capacity and Entropy

All molecular parameters are estimated via data for BF_2O^+ (or BF_2O) as discussed on the table for $AlF_2O(g)$.[2] We assume a C_{2v} structure with equal bond angles. Formation of the negative ion is assumed to decrease the Al–O bond distance by 0.06 Å but leave the Al–F distance unchanged. By analogy with AlF_3^2 we assume a singlet electronic ground state and neglect excited states. Formation of the negative ion is assumed to cause a significant increase in ν_1, ν_5, and ν_6. The principal moments of inertia are $I_A = 11.4723 \times 10^{-39}$, $I_B = 12.5732 \times 10^{-39}$, and $I_C = 24.0455 \times 10^{-39}$ g·cm^2.

References

[1]M. Farber, R. D. Srivastava and O. M. Uy, AD–731303, 50 pp. (1971).
[2]JANAF Thermochemical Tables: AlF_2^-(g), AlF_2(g) and AlF_2O(g), 6–30–76; AlFO(g), 12–31–75; AlF(g), 6–30–75; AlF_3(g), 6–30–70; Cl(g), 6–30–72; Cl (g), 6–30–65; F^-(g), 12–31–71; F(g), 9–30–65.
[3]O. M. Uy, T. D. Srivastava and M. Farber, High Temp. Sci. 4, 227 (1972).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.077	−1299.765		
100	41.036	228.775	334.358	−10.558			
200	54.051	261.603	290.340	−5.747			
250	58.755	274.184	285.880	−2.924			
298.15	62.592	284.870	284.870	0.	−1309.592	−1288.797	225.792
300	62.726	285.258	284.871	0.116	−1309.644	−1288.668	224.377
350	66.024	295.183	285.648	3.337	−1311.024	−1285.062	191.785
400	68.721	304.181	287.411	6.708	−1312.344	−1281.262	167.316
450	70.912	312.407	289.738	10.201	−1313.619	−1277.300	148.265
500	72.691	319.973	292.388	13.793	−1314.866	−1273.197	133.010
600	75.329	333.475	298.138	21.202	−1317.323	−1264.632	110.096
700	77.127	345.231	304.044	28.831	−1319.800	−1255.656	93.698
800	78.390	355.617	309.854	36.610	−1322.358	−1246.319	81.376
900	79.304	364.905	315.464	44.497	−1325.048	−1236.654	71.774
1000	79.983	373.298	320.835	52.463	−1338.497	−1225.921	64.036
1100	80.500	380.946	325.957	60.488	−1341.199	−1214.532	57.673
1200	80.902	387.969	330.836	68.559	−1343.903	−1202.898	52.361
1300	81.220	394.457	335.484	76.666	−1346.610	−1191.038	47.856
1400	81.475	400.486	339.914	84.801	−1349.326	−1178.969	43.988
1500	81.684	406.115	344.142	92.959	−1352.053	−1166.706	40.628
1600	81.856	411.392	348.182	101.137	−1354.791	−1154.260	37.683
1700	81.999	416.359	352.047	109.330	−1357.543	−1141.642	35.078
1800	82.120	421.049	355.752	117.536	−1360.309	−1128.863	32.759
1900	82.223	425.492	359.306	125.753	−1363.087	−1115.929	30.679
2000	82.311	429.712	362.722	133.980	−1365.876	−1102.848	28.803
2100	82.387	433.730	366.009	142.215	−1368.674	−1089.628	27.103
2200	82.454	437.564	369.175	150.457	−1371.479	−1076.274	25.554
2300	82.511	441.231	372.228	158.705	−1374.288	−1062.793	24.137
2400	82.562	444.743	375.177	166.959	−1377.098	−1049.190	22.835
2500	82.608	448.115	378.028	175.218	−1379.905	−1035.469	21.635
2600	82.648	451.355	380.786	183.480	−1382.707	−1021.637	20.525
2700	82.683	454.475	383.458	191.747	−1385.499	−1007.696	19.495
2800	82.715	457.483	386.048	200.017	−1682.180	−992.685	18.519
2900	82.744	460.386	388.562	208.290	−1683.849	−968.030	17.436
3000	82.770	463.192	391.003	216.566	−1685.502	−943.319	16.425
3100	82.794	465.906	393.376	224.844	−1687.134	−918.552	15.477
3200	82.815	468.535	395.684	233.124	−1688.746	−893.734	14.589
3300	82.835	471.084	397.930	241.407	−1690.334	−868.865	13.753
3400	82.852	473.557	400.118	249.691	−1691.897	−843.948	12.966
3500	82.869	475.959	402.251	257.977	−1693.435	−818.986	12.223
3600	82.884	478.293	404.331	266.265	−1694.947	−793.980	11.520
3700	82.898	480.564	406.361	274.554	−1696.432	−768.933	10.855
3800	82.910	482.775	408.343	282.844	−1697.891	−743.846	10.225
3900	82.922	484.929	410.279	291.136	−1699.322	−718.720	9.626
4000	82.933	487.029	412.171	299.429	−1700.727	−693.559	9.057
4100	82.943	489.077	414.022	307.723	−1702.106	−668.363	8.515
4200	82.953	491.075	415.833	316.017	−1703.460	−643.133	7.999
4300	82.961	493.027	417.606	324.313	−1704.789	−617.872	7.506
4400	82.970	494.935	419.342	332.610	−1706.096	−592.579	7.035
4500	82.977	496.799	421.042	340.907	−1707.377	−567.258	6.585
4600	82.984	498.623	422.709	349.205	−1708.639	−541.908	6.154
4700	82.991	500.408	424.343	357.504	−1709.882	−516.531	5.741
4800	82.997	502.155	425.946	365.803	−1711.107	−491.127	5.345
4900	83.003	503.867	427.519	374.103	−1712.314	−465.698	4.964
5000	83.009	505.544	429.063	382.404	−1713.508	−440.245	4.599
5100	83.014	507.188	430.579	390.705	−1714.690	−414.768	4.248
5200	83.019	508.800	432.068	399.007	−1715.861	−389.268	3.910
5300	83.024	510.381	433.530	407.309	−1717.023	−363.745	3.585
5400	83.028	511.933	434.968	415.611	−1718.180	−338.201	3.271
5500	83.032	513.456	436.381	423.914	−1719.332	−312.636	2.969
5600	83.036	514.953	437.771	432.218	−1720.483	−287.049	2.677
5700	83.040	516.422	439.138	440.522	−1721.634	−261.442	2.396
5800	83.043	517.867	440.483	448.826	−1722.785	−235.814	2.124
5900	83.047	519.286	441.806	457.130	−1723.945	−210.167	1.861
6000	83.050	520.682	443.109	465.435	−1725.089	−184.502	1.606

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 66.48 \pm 0.42\ J·K^{-1}·mol^{-1}$
$T_{trs} = 728 \pm 1\ K$
$T_{fus} = [2523 \pm 100]\ K$

$\Delta_f H°(0\ K) = -1504.3 \pm 1.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1510.4 \pm 1.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0.5632 \pm 0.042\ kJ·mol^{-1}$
$\Delta_{fus} H° = [98.3 \pm 12]\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted value is that recommended by CODATA.[1] It is based on separate calorimetric studies of the combustion in fluorine of aluminum[2] and aluminum–Teflon mixtures.[3] More extensive auxiliary data[3] for Teflon bring the aluminum–Teflon study into exact agreement with the aluminum study.[2] Calorimetric data relating AlF_3 to PbF_2[2,4] tend to confirm this value, but PbF_2 is probably less certain than is AlF_3.

Values for the $\Delta_f H°(298.15\ K)$ derived indirectly from equilibrium studies[5] and emf of solid galvanic cells[6,7,8,9] are tabulated below. The original data are reanalyzed with the use of the most recent auxiliary data.[4]

Source	Method	Reaction	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$* kcal·mol^{-1}
[5]	equilibria	A	849–1312	33.3 ± 0.20	33.11 ± 0.2	−0.2 ± 0.2	−358.6
[6]	emf	B	873	—	−43.01	—	−360.0
[7]	emf	B	873	—	−42.73	—	−360.3
[8]	emf	B	720–860	−40.26 ± 0.01	−41.47 ± 0.2	−1.5 ± 0.01	−361.6
[9]	emf	B	748–903	−42.1 ± 0.01	−40.58 ± 0.2	−1.8 ± 0.02	−362.5

*Derived from the third law enthalpy of reaction and is per mole of AlF_3(cr).
A. 2/3 AlF_3(cr) + H_2O(g) = 1/3 Al_2O_3(α,cr) + 2 HF(g) B. AlF_3(cr) + 1.5 Mg(cr) = Al(cr) + 1.5 MgF_2(cr)

With the exception of the equilibrium study of Mashovets and Yudin,[5] the results are in reasonable agreement with the directly measured calorimetric value. It has been suggested[2] that interaction of the condensed phases (activities1) caused the equilibria to deviate from the standard-state reaction assumed above. An alternative may be that the reaction with water vapor produced Al_2O_3 in a metastable form; such forms require ignition temperatures greater than 1400 K for complete conversion to α- Al_2O_3.[10]

Heat Capacity and Entropy

$C_p°$ and $S°(298.15\ K)$ are taken from Douglas and Ditmars,[11] whose tables are based on heat capacity measurements from 54 to 298 K[12] and relative enthalpy measurements from 323 to 1173 K.[11] The enthalpy data confirm earlier data (401–1401 K) of O'Brien and Kelley[13] rather than the adjusted values proposed by Frank.[14] Douglas and Ditmars[11] gave a detailed comparison with other data. The entropy is derived from $C_p°$ using the extrapolation $S°(50\ K) = 2.22 \pm 0.25\ J·K^{-1}·mol^{-1}$.

Transition Data

T_{trs} and $\Delta_{trs} H°$ for this crystalline first order transition are from Douglas and Ditmars.[11] The values were obtained from extensive enthalpy data for the transition region assuming the presence of a very small amount of impurity in solid solution.

Sublimation Data

$T_{sub} = 1549$ K is the temperature at which the calculated total pressure (monomer plus dimer) reaches one atm; the mole fraction of dimer is calculated as 0.109 at T_{sub}. Sublimation temperatures of 1533 and 1566 K were obtained in two sublimation- pressure studies[15,16] at the Techische Hochschule, Breslau. The selected enthalpies of sublimation to AlF_3(g) and Al_2F_6(g) reproduce closely the entrainment data of Krause and Douglas.[17] Selection of these values of $\Delta_{sub} H°$ and comparisons with other vapor-pressure data are discussed on the gas-phase tables.

Fusion Data

Refer to the liquid table for details.

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[4] JANAF Thermochemical Tables: PbF_2(cr), 12–31–73; H_2O(g), 3–31–79; Al_2O_3(α, cr), 12–31–79; HF(g), 6–30–77; Mg(cr), 9–30–62; and MgF_2(cr), 6–30–75.
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[6] R. J. Heus and J. J. Egan, Z. Phys. Chem. (Frankfurt) **49**, 38 (1966).
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Continued on page 171

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.625	−1504.272	−1504.272	INFINITE
100	24.932	12.058	119.836	−10.778	−1508.269	−1483.221	774.755
200	56.877	39.991	72.814	−6.565	−1510.252	−1457.225	380.588
298.15	75.132	66.484	66.484	0.	−1510.424	−1431.123	250.727
300	75.400	66.949	66.485	0.139	−1510.416	−1430.631	249.095
400	86.287	90.293	69.594	8.280	−1509.613	−1404.138	183.362
500	92.274	110.245	75.781	17.232	−1508.342	−1377.911	143.949
600	97.311	127.494	82.993	26.700	−1506.819	−1351.963	117.699
700	105.357	143.032	90.474	36.791	−1504.904	−1326.297	98.970
728.000	108.692	147.228	92.577	39.786	ALPHA <--> BETA		
728.000	97.579	148.001	92.577	40.349	TRANSITION		
800	98.516	157.248	97.987	47.409	−1502.681	−1300.966	84.944
900	99.717	168.922	105.231	57.322	−1501.390	−1275.830	74.047
1000	100.830	179.487	112.137	67.350	−1510.813	−1250.072	65.297
1100	101.893	189.147	118.705	77.486	−1509.431	−1224.064	58.126
1200	102.918	198.057	124.951	87.727	−1507.984	−1198.185	52.156
1300	103.918	206.334	130.897	98.069	−1506.471	−1172.429	47.109
1400	104.897	214.071	136.564	108.510	−1504.892	−1146.793	42.787
1500	105.864	221.341	141.976	119.048	−1503.244	−1121.271	39.046
1600	106.822	228.204	147.153	129.682	−1501.528	−1095.862	35.776
1700	107.771	234.709	152.114	140.412	−1499.741	−1070.562	32.894
1800	108.717	240.896	156.876	151.236	−1497.882	−1045.369	30.336
1900	109.663	246.799	161.454	162.155	−1495.946	−1020.283	28.050
2000	110.604	252.448	165.864	173.169	−1493.929	−995.299	25.995
2100	111.545	257.867	170.117	184.276	−1491.827	−970.419	24.138
2200	112.487	263.078	174.225	195.478	−1489.635	−945.641	22.452
2300	113.428	268.099	178.198	206.773	−1487.347	−920.965	20.916
2400	114.370	272.946	182.045	218.163	−1484.957	−896.391	19.509
2500	115.311	277.634	185.775	229.647	−1482.460	−871.918	18.218
2523.000	115.529	278.691	186.618	232.302	---- BETA <--> LIQUID ----		
2600	116.252	282.175	189.396	241.225	−1479.850	−847.547	17.027
2700	117.194	286.580	192.914	252.898	−1477.122	−823.279	15.927
2800	118.135	290.859	196.336	264.664	−1768.173	−798.147	14.890
2900	119.077	295.021	199.668	276.525	−1764.101	−763.575	13.753
3000	120.018	299.074	202.914	288.480	−1759.898	−729.145	12.696

PREVIOUS: June 1970 CURRENT: September 1979

$S°(298.15\ K) = [95.379]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [2523 \pm 100]\ K$

$\Delta_f H°(298.15\ K) = [-1422.760]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 98.3 \pm 12\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(AlF_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(AlF_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2523\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

There are no heat capacity or enthalpy measurements covering the liquid region of AlF_3. The pure solid does not melt at ordinary pressures. This AlF_3(l) table, therefore, is a non-standard state table for P = −4400 atm. By analogy[1] with $AlCl_3$(l), $AlBr_3$(l), and AlI_3(l), we estimate $C_p°(l) = 30\ cal·K^{-1}·mol^{-1}$; Holm[2,3] also assumed the same value. We assume a glass transition at 1850 K, below which we adopt the heat capacity data of AlF_3(cr); the transition at 728 K for AlF_3(cr) is not included.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The pure solid sublimes before melting at ordinary pressures. From studies on CaF_2–AlF_3 and NaCl–AlF_3 binary systems, Millet *et al.*[4] estimated a triple point temperature for AlF_3 of 2523 K at 30000 atm. Our adopted values lead to a pressure for $AlF_3(l) = AlF_3(g)$ of −2200 atm. The calculated dimer pressure at this temperature is also −2200 atm.

Holm,[3] attempted to relate his drop-calorimetric data on the melting of a Li_3AlF_6–AlF_3 system to the enthalpy of fusion of AlF_3. Based on the assumption that the enthalpy of mixing of Li_3AlF_6(l) with AlF_3(l) to form the eutectic mixture is small and positive, he obtained $\Delta_{fus}H° = 11.4\ kcal·mol^{-1}$ for AlF_3 at 1298 K. This result was challenged by Hong and Kleppa[4,5] who measured the enthalpy of mixing of AlF_3(cr) with a series of liquid alkali fluorides and derived $\Delta_{fus}H° = 26.5 \pm 2\ kcal·mol^{-1}$ at this temperature. These results suggest that Holm's assumed enthalpy of mixing is in error, both as to sign and magnitude. We adopt the $\Delta_{fus}H°$ value of Hong and Kleppa[5,6] but adjust the value to the adopted triple point of 2523 K (from 1298 K).

References

[1] JANAF Thermochemical Tables: $AlBr_3$(l), $AlCl_3$(l), AlI_3(l), and AlF_3(cr), 9–30–79.
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[3] J. L. Holm, High Temp. Sci. **6**, 16 (1974).
[4] J. P. Millet, H. Pham and M. Rolin, Rev. Int. Hautes Temp. Refract. **11**, 277 (1974).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$ (J·K⁻¹mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
298.15	97.475	95.379	95.379	0.	−1422.760	−1352.074	236.878
300	97.479	95.982	95.381	0.180	−1422.711	−1351.636	235.341
400	97.763	124.065	99.208	9.943	−1420.286	−1328.320	173.461
500	98.014	145.908	106.444	19.732	−1418.178	−1305.578	136.393
600	98.224	163.797	114.556	29.544	−1416.311	−1283.237	111.716
700	98.391	178.951	122.701	39.375	−1414.655	−1261.191	94.111
800	98.516	192.086	130.571	49.212	−1413.214	−1239.369	80.922
900	99.717	203.759	138.066	59.124	−1411.923	−1217.717	70.674
1000	100.830	214.324	145.172	69.152	−1421.346	−1195.442	62.444
1100	101.893	223.984	151.904	79.289	−1419.964	−1172.918	55.697
1200	102.918	232.894	158.286	89.529	−1418.518	−1150.523	50.081
1300	103.918	241.172	164.348	99.871	−1417.005	−1128.251	45.334
1400	104.897	248.909	170.114	110.312	−1415.425	−1106.098	41.269
1500	105.864	256.179	175.612	120.850	−1413.777	−1084.060	37.750
1600	106.822	263.042	180.864	131.485	−1412.061	−1062.135	34.675
1700	107.771	269.546	185.891	142.214	−1410.275	−1040.319	31.965
1800	108.717	275.733	190.712	153.039	−1408.415	−1018.610	29.559
1850.000	109.190	278.718	193.050	158.486	GLASS <---> LIQUID		
1850.000	125.520	278.718	193.050	158.486	TRANSITION		
1900	125.520	282.066	195.349	164.762	−1405.674	−997.017	27.410
2000	125.520	288.504	199.847	177.314	−1402.119	−975.601	25.480
2100	125.520	294.628	204.216	189.866	−1398.573	−954.363	23.738
2200	125.520	300.467	208.459	202.418	−1395.030	−933.293	22.159
2300	125.520	306.047	212.582	214.970	−1391.485	−912.384	20.721
2400	125.520	311.389	216.588	227.522	−1387.933	−891.629	19.406
2500	125.520	316.513	220.483	240.074	−1384.368	−871.023	18.199
2523.000	125.520	317.662	221.364	242.961	---- BETA <---> LIQUID ----		
2600	125.520	321.436	224.272	252.626	−1380.785	−850.560	17.088
2700	125.520	326.173	227.959	265.178	−1377.177	−830.235	16.062
2800	125.520	330.738	231.549	277.730	−1667.443	−809.077	15.094
2900	125.520	335.143	235.045	290.282	−1662.679	−778.505	14.022
3000	125.520	339.398	238.453	302.834	−1657.878	−748.098	13.026
3100	125.520	343.514	241.776	315.386	−1653.038	−717.852	12.096
3200	125.520	347.499	245.018	327.938	−1648.155	−687.762	11.227
3300	125.520	351.361	248.182	340.490	−1643.228	−657.826	10.413
3400	125.520	355.108	251.272	353.042	−1638.253	−628.040	9.649
3500	125.520	358.747	254.291	365.594	−1633.231	−598.401	8.931
3600	125.520	362.283	257.242	378.146	−1628.159	−568.905	8.255
3700	125.520	365.722	260.128	390.698	−1623.038	−539.552	7.617
3800	125.520	369.069	262.951	403.250	−1617.867	−510.338	7.015
3900	125.520	372.330	265.714	415.802	−1612.647	−481.260	6.446
4000	125.520	375.508	268.419	428.354	−1607.378	−452.317	5.907

PREVIOUS: CURRENT: September 1979

0 to 2523 K crystal
above 2523 K liquid*, p = ~4340 bars

*The liquid does not exist at 1 bar.

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−11.625	−1504.272	−1504.272	INFINITE
100	24.932	12.058	119.836	−10.778	−1508.269	−1483.221	774.755
200	56.877	39.991	72.814	−6.565	−1510.252	−1457.225	380.588
298.15	75.132	66.484	66.484	0.	−1510.424	−1431.123	250.727
300	75.400	66.949	66.485	0.139	−1510.416	−1430.631	249.095
400	86.287	90.293	69.594	8.280	−1509.613	−1404.138	183.362
500	92.274	110.245	75.781	17.232	−1508.342	−1377.911	143.949
600	97.311	127.494	82.993	26.700	−1506.819	−1351.963	117.699
700	105.357	143.032	90.474	36.791	−1504.904	−1326.297	98.970
728.000	108.692	147.228	92.577	39.786	ALPHA <--> BETA		
728.000	97.579	148.001	92.577	40.349	TRANSITION		
800	98.516	157.248	97.987	47.409	−1502.681	−1300.966	84.944
900	99.717	168.922	105.231	57.322	−1501.390	−1275.830	74.047
1000	100.830	179.487	112.137	67.350	−1510.813	−1250.072	65.297
1100	101.893	189.147	118.705	77.486	−1509.431	−1224.064	58.126
1200	102.918	198.057	124.951	87.727	−1507.984	−1198.185	52.156
1300	103.918	206.334	130.897	98.069	−1506.471	−1172.429	47.109
1400	104.897	214.071	136.564	108.510	−1504.892	−1146.793	42.787
1500	105.864	221.341	141.976	119.048	−1503.244	−1121.271	39.046
1600	106.822	228.204	147.153	129.682	−1501.528	−1095.862	35.776
1700	107.771	234.709	152.114	140.412	−1499.741	−1070.562	32.894
1800	108.717	240.896	156.876	151.236	−1497.882	−1045.369	30.336
1900	109.663	246.799	161.454	162.155	−1495.946	−1020.283	28.050
2000	110.604	252.448	165.864	173.169	−1493.929	−995.299	25.995
2100	111.545	257.867	170.117	184.276	−1491.827	−970.419	24.138
2200	112.487	263.078	174.225	195.478	−1489.635	−945.641	22.452
2300	113.428	268.099	178.198	206.773	−1487.347	−920.965	20.916
2400	114.368	272.946	182.045	218.163	−1484.957	−896.391	19.509
2500	115.311	277.634	185.775	229.647	−1482.460	−871.918	18.218
2523.000	115.529	278.691	186.618	232.302	BETA <--> LIQUID		
2523.000	125.520	317.662	186.618	330.626	TRANSITION		
2600	125.520	321.436	190.555	340.291	−1380.785	−850.560	17.088
2700	125.520	326.173	195.490	352.843	−1377.177	−830.235	16.062
2800	125.520	330.738	200.240	365.395	−1667.443	−809.076	15.094
2900	125.520	335.142	204.816	377.947	−1662.679	−778.504	14.022
3000	125.520	339.398	209.231	390.499	−1657.878	−748.097	13.026
3100	125.520	343.513	213.497	403.051	−1653.038	−717.851	12.096
3200	125.520	347.499	217.623	415.603	−1648.155	−687.761	11.227
3300	125.520	351.361	221.617	428.155	−1643.228	−657.825	10.413
3400	125.520	355.108	225.489	440.707	−1638.253	−628.039	9.649
3500	125.520	358.747	229.244	453.259	−1633.231	−598.400	8.931
3600	125.520	362.283	232.891	465.811	−1628.159	−568.904	8.255
3700	125.520	365.722	236.435	478.363	−1623.038	−539.551	7.617
3800	125.520	369.069	239.881	490.915	−1617.867	−510.337	7.015
3900	125.520	372.330	243.236	503.467	−1612.647	−481.259	6.446
4000	125.520	375.508	246.503	516.019	−1607.378	−452.316	5.907

PREVIOUS: CURRENT: September 1979

$S°(298.15\ K) = 276.69 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1205.60 \pm 2.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1209.32 \pm 2.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[650](1)	[935](2)
297 (1)	263 (2)

Ground State Quantum Weight: [1] $\sigma = 6$

Point Group: D_{3h}

Bond Distance: Al–F = 1.63 ± 0.01 Å

Bond Angle: F–Al–F = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 3.975102 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by use of $\Delta_{sub}H°(298.15\ K) = 71.965 \pm 0.5\ kcal \cdot mol^{-1}$. Sublimation studies by mass-spectrometric and entrainment techniques suggest the presence of a small amount of dimer in the saturated vapor. These studies are reviewed on the table for $Al_2F_6(g)$. The heats of sublimation for the monomer and dimer are selected by adopting the JANAF entropies for crystal, monomer and dimer, the mass spectrometric value of 2 $\Delta_{sub}H°$(monomer)–$\Delta_{sub}H°$(dimer) = −49 $kcal \cdot mol^{-1}$ at 1000 K, and the entrainment data of Krause and Douglas.[1] The resulting calculated pressures deviate by <0.5% from the entrainment data,[1] by <10% from the mass-spectrometric equation[3] and by <3% from the mass-effusion equation.[4]

Further comparisons with experimental data are given below. The adopted values favor the later[11] of two sublimation-point studies;[11, 12] both show considerable scatter and similar deviations from the calculated dP/dT. Torsion-effusion data suggest the possibility of more serious discrepancy. Although data of Witt and Barrow[9] are consistent with the JANAF pressures, Hildenbrand *et al.*[7, 8, 19] noted a trend toward increasing pressure with decreasing orifice area. The most recent study by Hildenbrand and Laughlin[19] yielded equilibrium pressures that are reasonably consistent with the adopted values, unlike the earlier study.[7] The 1981 communication[19] yielded a heat of sublimation value which is within 0.25 kcal·mol of our adopted value. In contrast, the JANAF predictions agree closely with mass-effusion data of Ko *et al.*,[4] who reported no significant effect from a twelvefold variation in orifice area.

Comparison of Calculated and Observed Total Pressures Over AlF_3(cr)

Source	Method	T/K	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range	Difference[a] in dP/dT
1	Entrainment	1194–1258	0.019–0.029	1.004–0.996	Very small (−)
2	Entrainment	1108–1273	0.010–0.032	0.73–2.22	Uncertain (?)
3	Mass Spec[b]	983–1165	0.003–0.016	1.09–0.91	Small (−)
4	Mass Effusion	1027–1184	0.005–0.018	0.994–0.972	Very small (−)
5	Mass Effusion	889–1006	0.001–0.004	1.42–1.66	Uncertain (+)
6	Mass Effusion	980–1123	0.003–0.012	1.64–0.88	Large (−)
19	Torsion Effusion	902–1098	0.001–0.010	0.88	Small
8	Torsion Effusion Cell Gr−7	992–1101	0.004–0.010	0.89–1.01	Small (+)
	Cell Gr−9	938–1080	0.002–0.008	0.94–1.34	Medium (+)
9	Torsion Effusion	955–1063	0.003–0.007	1.11–1.07	Small (−)
10	Dynamic B.P.	1335–1453	0.044–0.076	0.84–1.64	Large (+)
11	Dynamic B.P.	1367–1524	0.052–0.100	1.33–0.79	Large (−)
12	Dynamic B.P.	1371–1567	0.053–0.116	2.70–1.28	Large (−)

[a]Magnitude and sign of the difference, calculated minus observed, in dP/dT

[b]Absolute pressures of monomer were obtained by integration of the ion intensity during total sublimation.

Heat Capacity and Entropy

The molecular structure is that derived from electron-diffraction data by Akishin *et al.*[13] Observed vibrational frequencies are those reported by Buchler *et al.*[14] from infrared spectra of the vapor at 1000–1200 K. These frequencies are confirmed by infrared spectra of AlF_3 isolated in matricies of neon, argon and krypton.[15, 16] Drake and Rosenblatt[17] have estimated the Raman-active fundamentals based on a correlation of vibrational frequencies and internuclear distances for the Group IIIA trihalides. They estimated $\nu_1 = 685\ cm^{-1}$ which would decrease $S°(298.15\ K)$ by 0.05 $cal \cdot K^{-1} \cdot mol^{-1}$ from our adopted value. We adopt $\nu_1 = 650 \pm 50\ cm^{-1}$ as derived from three other methods: (a) calculation of the force constant k_1 from ν_3 and ν_4; (b) comparison of $k_1(XY_3)/k(XY)$ for X = B, Al and Y = F, Cl, and Br; and (c) extrapolation of $\nu_1(BY_3)/\nu_1(AY_3)$ to Y=F from Y=Cl, Br and *I*, using recent gas-phase Raman data[18] for AlY_3. The principal moments of inertia are: $I_A = I_B = 12.5730 \times 10^{-39}$ and $I_C = 25.1460 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 172

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−14.049	−1205.595	−1205.595	INFINITE
100	41.148	220.719	325.981	−10.526	−1206.916	−1202.734	628.244
200	53.850	253.541	282.132	−5.718	−1208.303	−1197.987	312.882
250	58.444	266.064	277.695	−2.908	−1208.861	−1195.342	249.753
298.15	62.239	276.691	276.691	0.	−1209.322	−1192.695	*208.955
300	62.373	277.076	276.692	0.115	−1209.339	−1192.592	207.649
350	65.670	286.947	277.464	3.319	−1209.754	−1189.767	177.563
400	68.387	295.899	279.218	6.673	−1210.119	−1186.887	154.991
450	70.606	304.086	281.533	10.149	−1210.446	−1183.963	137.431
500	72.415	311.622	284.170	13.726	−1210.746	−1181.004	123.379
600	75.107	325.079	289.894	21.111	−1211.307	−1175.002	102.293
700	76.949	336.804	295.776	28.720	−1211.873	−1168.907	87.225
800	78.245	347.169	301.565	36.483	−1212.505	−1162.727	75.918
900	79.185	356.442	307.156	44.357	−1213.254	−1156.461	67.119
1000	79.884	364.822	312.511	52.312	−1224.749	−1149.344	60.036
1100	80.416	372.462	317.619	60.328	−1225.488	−1141.768	54.218
1200	80.830	379.478	322.485	68.391	−1226.218	−1134.124	49.367
1300	81.158	385.961	327.122	76.491	−1226.947	−1126.420	45.260
1400	81.421	391.986	331.542	84.621	−1227.679	−1118.660	41.738
1500	81.636	397.611	335.761	92.774	−1228.416	−1110.847	38.683
1600	81.814	402.885	339.794	100.947	−1229.162	−1102.985	36.009
1700	81.962	407.850	343.652	109.136	−1229.916	−1095.076	33.648
1800	82.087	412.538	347.350	117.338	−1230.678	−1087.122	31.547
1900	82.193	416.979	350.899	125.552	−1231.447	−1079.126	29.667
2000	82.284	421.198	354.309	133.776	−1232.220	−1071.089	27.974
2100	82.362	425.214	357.591	142.009	−1232.993	−1063.014	26.441
2200	82.431	429.047	360.752	150.248	−1233.763	−1054.901	25.047
2300	82.491	432.713	363.802	158.495	−1234.524	−1046.754	23.773
2400	82.543	436.225	366.747	166.746	−1235.272	−1038.574	22.604
2500	82.590	439.595	369.594	175.003	−1236.002	−1030.363	21.528
2600	82.631	442.835	372.349	183.264	−1236.710	−1022.124	20.535
2700	82.668	445.955	375.018	191.529	−1237.389	−1013.857	19.614
2800	82.701	448.962	377.605	199.798	−1531.938	−1004.599	18.741
2900	82.731	451.864	380.116	208.069	−1531.455	−985.773	17.756
3000	82.758	454.669	382.555	216.344	−1530.932	−966.966	16.836
3100	82.782	457.383	384.925	224.621	−1530.367	−948.176	15.977
3200	82.804	460.012	387.231	232.900	−1529.756	−929.405	15.171
3300	82.824	462.560	389.475	241.182	−1529.099	−910.654	14.414
3400	82.843	465.033	391.661	249.465	−1528.393	−891.924	13.703
3500	82.860	467.435	393.792	257.750	−1527.638	−873.215	13.032
3600	82.875	469.769	395.870	266.037	−1526.832	−854.528	12.399
3700	82.889	472.040	397.898	274.325	−1525.974	−835.865	11.800
3800	82.903	474.251	399.879	282.615	−1525.066	−817.226	11.234
3900	82.915	476.404	401.813	290.906	−1524.107	−798.611	10.696
4000	82.926	478.504	403.704	299.198	−1523.097	−780.021	10.186
4100	82.936	480.552	405.554	307.491	−1522.038	−761.457	9.701
4200	82.946	482.550	407.363	315.785	−1520.931	−742.919	9.240
4300	82.955	484.502	409.135	324.080	−1519.776	−724.409	8.800
4400	82.964	486.409	410.869	332.376	−1518.576	−705.926	8.380
4500	82.972	488.274	412.569	340.673	−1517.328	−687.471	7.980
4600	82.979	490.098	414.234	348.970	−1516.040	−669.044	7.597
4700	82.986	491.882	415.868	357.268	−1514.710	−650.645	7.231
4800	82.992	493.629	417.470	365.567	−1513.341	−632.275	6.881
4900	82.999	495.341	419.041	373.867	−1511.935	−613.934	6.545
5000	83.004	497.018	420.584	382.167	−1510.493	−595.622	6.222
5100	83.010	498.661	422.099	390.468	−1509.018	−577.339	5.913
5200	83.015	500.273	423.587	398.769	−1507.513	−559.085	5.616
5300	83.020	501.855	425.049	407.071	−1505.978	−540.861	5.331
5400	83.024	503.406	426.486	415.373	−1504.417	−522.666	5.056
5500	83.028	504.930	427.898	423.676	−1502.831	−504.500	4.791
5600	83.033	506.426	429.287	431.979	−1501.223	−486.363	4.537
5700	83.036	507.896	430.653	440.282	−1499.595	−468.255	4.291
5800	83.040	509.340	431.997	448.586	−1497.947	−450.176	4.054
5900	83.044	510.759	433.320	456.890	−1496.285	−432.125	3.826
6000	83.047	512.155	434.623	465.195	−1494.588	−414.105	3.605

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = 294.75 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1980 \pm 105\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-1991.584]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
622(1)	760(3)
210(2)	322(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Al–F = 1.69 Å
Bond Angle: F–Al–F = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 1.387252 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -476 \pm 25\ kcal·mol^{-1}$ which corresponds to the fluoride-ion affinity $IA(AlF_3) = 125 \pm 25\ kcal·mol^{-1}$ for $AlF_4^-(g) = AlF_3(g) + F^-(g)$. $\Delta_f H°$ is a compromise based mainly on K_p data (7 points, 1130–1485 K) for the reaction $2\ AlF_2(g) + AlF_2^-(g) = 2\ AlF(g) + AlF_4^-(g)$. K_p data were measured by Srivastava *et al.*[1] with a mass spectrometer operating in both positive- and negative-ion modes. The authors used a molecular-flow-effusion technique to react vapors from AlF_3 and K_3AlF_6 or KF with Al(l). Analysis with JANAF auxiliary data[2] yields $\Delta_r H°(298.15\ K)$(3rd law) = −38.2 ± 2.7 and $\Delta_r H°(298.15\ K)$(2nd law) = −33.9 ± 6.3 $kcal·mol^{-1}$ with $[\Delta_r S°(2nd\ law) - \Delta_r S°(3rd\ law)] = -3.3 \pm 4.8\ cal·K^{-1}·mol^{-1}$. The 3rd law $\Delta_r H°$ yields $\Delta_f H°(AlF_4^-, g, 298.15\ K) = -460.4 \pm 14\ kcal·mol^{-1}$ or $-502.4 \pm 14\ kcal·mol^{-1}$, depending on the choice of $\Delta_f H°(AlF_2, g, 298.15\ K) = -166 \pm 10^2$ or $-180 \pm 5\ kcal·mol^{-1}$.[2,3]

The difference of 14 $kcal·mol^{-1}$ in $\Delta_f H°(AlF_2)$ causes a three-fold change (42 $kcal·mol^{-1}$) in $\Delta_f H°(AlF_4^-)$ and increases the fluoride-ion affinity $IA(AlF_3)$ from 109 ± 25 to 151 ± 15 $kcal·mol^{-1}$. The latter value seems rather large in comparison to related species:[2,1] ≤112 or ≤127(OAlF), 92 or 106 (AlF), ≤101 (BF_3), ≤92 (OBF) and 98 or 103 (BF).

By combining published data for $NaAlF_4$(g) with a coulomb-energy calculation, Holm[4] estimated $IA(AlF_3) = 131\ kcal·mol^{-1}$. This result has an unknown bias due to limitations of the calculational model and auxiliary data. Refined lattice energy calculations[5] yield halide-ion affinities IA = 87 ± 7 ($AlCl_3$) and ($AlBr_3$) $kcal·mol^{-1}$. $\Delta_f H°(BF_4^-) = -421\ kcal·mol^{-1}$ [6] derived from lattice energy yields $IA(BF_3) = 90$ compared to ≤101 $kcal·mol^{-1}$ from mass spectrometry. Comparison of stretching force constants[2,7,8] with average bond energies in AlX_3 and AlX_4^- suggests a slight, but not definitive, preference for $IA(AlF_3) = 109\ kcal·mol^{-1}$. As a compromise, we adopt $IA(AlF_3) = 125 \pm 25$ and $\Delta_f H°(AlF_4^-, g, 298.15\ K) = -476 \pm 25\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Vibrational frequencies are from Raman spectra of AlF_4^- observed in molten salt mixtures of AlF_3 with NaF or KF.[8] Similar spectra were observed in mixtures of AlF_3 with LiF.[9] The spectra[8] are consistent with T_d symmetry except for some asymmetry in ν_3 which was attributed to influence of the metal ion. By analogy with SiF_4,[2] we assume a singlet electronic ground state and neglect excited states. The bond distance *is that derived from high-temperature electron diffraction*[10] *of* $NaAlF_4$*(g). Within experimental uncertainty, the* AlF_4 *grouping was found to* be tetrahedral.[2,10] The principal moments of inertia are $I_A = I_B = I_C = 24.0280 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−16.981	−1980.178		
100	46.882	225.025	357.855	−13.283			
200	68.417	264.662	301.864	−7.440			
250	76.195	280.796	296.068	−3.818			
298.15	82.157	294.747	294.747	0.	−1991.584	−1943.855	340.555
300	82.359	295.256	294.749	0.152	−1991.631	−1943.558	338.404
350	87.157	308.328	295.770	4.395	−1992.840	−1935.449	288.850
400	90.872	320.219	298.094	8.850	−1993.959	−1927.173	251.663
450	93.760	331.096	301.166	13.469	−1995.016	−1918.761	222.724
500	96.025	341.097	304.666	18.216	−1996.036	−1910.233	199.561
600	99.261	358.912	312.259	27.992	−1998.020	−1892.886	164.790
700	101.387	374.383	320.053	38.031	−2000.010	−1875.206	139.930
800	102.844	388.022	327.714	48.247	−2002.073	−1857.238	121.265
900	103.881	400.199	335.103	58.586	−2004.262	−1839.003	106.733
1000	104.643	411.185	342.171	69.014	−2017.208	−1819.757	95.054
1100	105.218	421.187	348.907	79.508	−2019.407	−1799.905	85.470
1200	105.661	430.362	355.318	90.053	−2021.607	−1779.853	77.475
1300	106.010	438.834	361.420	100.637	−2023.815	−1759.618	70.702
1400	106.289	446.700	367.234	111.253	−2026.035	−1739.212	64.891
1500	106.516	454.042	372.779	121.893	−2028.269	−1718.646	59.849
1600	106.702	460.922	378.075	132.555	−2030.519	−1697.932	55.432
1700	106.858	467.396	383.141	143.233	−2032.785	−1677.075	51.530
1800	106.989	473.507	387.993	153.925	−2035.066	−1656.086	48.058
1900	107.100	479.295	392.648	164.630	−2037.359	−1634.969	44.948
2000	107.195	484.791	397.119	175.345	−2039.660	−1613.731	42.146
2100	107.277	490.023	401.419	186.069	−2041.964	−1592.378	39.608
2200	107.348	495.015	405.561	196.800	−2044.265	−1570.915	37.298
2300	107.411	499.789	409.555	207.538	−2046.557	−1549.347	35.187
2400	107.465	504.361	413.410	218.282	−2048.834	−1527.681	33.249
2500	107.514	508.749	417.137	229.031	−2051.088	−1505.920	31.464
2600	107.557	512.967	420.742	239.784	−2053.312	−1484.069	29.815
2700	107.595	517.027	424.233	250.542	−2055.501	−1462.133	28.287
2800	107.629	520.940	427.618	261.303	−2351.550	−1439.150	26.848
2900	107.660	524.718	430.901	272.068	−2352.555	−1406.546	25.335
3000	107.688	528.368	434.090	282.835	−2353.508	−1373.909	23.922
3100	107.713	531.899	437.188	293.605	−2354.406	−1341.241	22.600
3200	107.736	535.320	440.201	304.378	−2355.244	−1308.544	21.360
3300	107.757	538.635	443.134	315.152	−2356.020	−1275.823	20.195
3400	107.776	541.852	445.991	325.929	−2356.732	−1243.079	19.098
3500	107.794	544.977	448.774	336.708	−2357.377	−1210.314	18.063
3600	107.810	548.014	451.489	347.488	−2357.955	−1177.533	17.086
3700	107.824	550.968	454.138	358.269	−2358.465	−1144.736	16.161
3800	107.838	553.843	456.724	369.053	−2358.907	−1111.927	15.285
3900	107.851	556.645	459.250	379.837	−2359.282	−1079.106	14.453
4000	107.862	559.375	461.720	390.623	−2359.588	−1046.277	13.663
4100	107.873	562.039	464.134	401.409	−2359.828	−1013.441	12.911
4200	107.883	564.638	466.496	412.197	−2360.003	−980.600	12.196
4300	107.892	567.177	468.808	422.986	−2360.114	−947.756	11.513
4400	107.901	569.658	471.072	433.776	−2360.163	−914.910	10.861
4500	107.909	572.082	473.290	444.566	−2360.148	−882.063	10.239
4600	107.917	574.454	475.464	455.358	−2360.077	−849.218	9.643
4700	107.924	576.775	477.594	466.150	−2359.950	−816.374	9.073
4800	107.931	579.047	479.684	476.942	−2359.768	−783.534	8.527
4900	107.937	581.273	481.735	487.736	−2359.533	−750.698	8.003
5000	107.943	583.454	483.748	498.530	−2359.249	−717.868	7.500
5100	107.949	585.591	485.724	509.324	−2358.918	−685.043	7.016
5200	107.954	587.688	487.665	520.120	−2358.543	−652.225	6.552
5300	107.959	589.744	489.571	530.915	−2358.126	−619.415	6.105
5400	107.964	591.762	491.445	541.711	−2357.669	−586.614	5.674
5500	107.968	593.743	493.287	552.508	−2357.175	−553.822	5.260
5600	107.972	595.688	495.098	563.305	−2356.647	−521.037	4.860
5700	107.976	597.600	496.880	574.102	−2356.087	−488.265	4.474
5800	107.980	599.477	498.633	584.900	−2355.495	−455.501	4.102
5900	107.984	601.323	500.358	595.698	−2354.880	−422.747	3.743
6000	107.987	603.138	502.055	606.497	−2354.218	−390.007	3.395

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [326.5 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1846 \pm 12\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1854 \pm 12\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies					
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
817(1)	560 (1)	220 (1)	911 (1)	[157](1)	450(1)
608(1)	[361](1)	[269](1)	316 (1)	644(1)	270(1)

Ground State Quantum Weight: [1] σ = [2]

Point Group: [C_{2v}]

Bond Distances: Al–F_{br} = Al–F_{ter} = [1.69 ± 0.02] Å; Li–F_{br} = [1.68] Å

Bond Angles: F_{br}–Al–F_{br} = [110]°; F_{ter}–Al–F_{ter} = [109.47]°; F_{br}–Li–F_{br} = [110.98]°

Product of the Moments of Inertia: $I_A I_B I_C = 1.887733 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

Mass spectrometric studies[1,2,3] indicate that the vapor above the LiF–AlF_3 system is composed mainly of $LiAlF_4$, $(LiAlF_4)_2$, and Li_3AlF_5 with $LiAlF_4$ being the major component, 90% according to[1] or 77% according to.[3] For $(LiAlF_4)_2(g) = 2\ LiAlF_4(g)$, $\ln K_p = -48500/RT + 33.5/R$ at 946 K.[3] This is in agreement with the equilibrium constant for the dimer–monomer equilibrium of the sodium analog[4,5] which has been determined over a wider temperature range. As a first approximation, we ignore any gaseous species other than $LiAlF_4(g)$ and $(LiAlF_4)2$ (g) and adjust the total pressure measurements over the LiF–AlF_3 system to the partial pressure of $LiAlF_4(g)$ by assuming that $\ln K_p = -43900/RT + 28.50/R$ for the $(NaAlF_4)_2(g) = 2\ NaAlF_4(g)$ equilibrium[5] also represents the equilibrium of the lithium analog. Rao[6] has made a similar assumption.

$\Delta_f H°(298.15\ K)$ results from our 3rd law analysis of pressure measurements and equilibrium constants of the following:

[1] $Li_2F_2(g) + AlF_3(g) = LiF(g) + LiAlF_4(g)$

[2] $Li_3AlF_6(cr) = 2\ LiF(cr) + LiAlF_4(g)$

[3] $1/3\ Li_3AlF_6(cr) = 2/3\ AlF_3(cr) + LiAlF_4(g)$

[4] $LiAlF_4(g) = LiF(g) + AlF_3(g)$

[5] $LiF(l) + AlF_3(cr) = LiAlF_4(g)$

Source	Method	Reaction	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$[a] kcal·mol^{-1}
Porter and Zeller[7]	Mass Spec	1	1000–1100	−0.86	−6.036	−4.9	−438.95
Hildenbrand *et al.*[8]	Torsion–Effusion	2	987–1058	101.93	68.86	−32.3	−444.94
		3(cell 7)	899–980	71.10	66.97	−4.4	−443.27
		3(cell 9)	873–976	67.28	67.10	−0.2	−443.13
		3(cell 15x)	854–980	67.53	67.23	−0.3	−443.00
Rao[6]	Effusion	3	872–979	68.59	67.27	−1.4	−442.97
Shol'ts and Sidorov[3]	Mass Spec	3	946		68.28		−441.95
Sidorov *et al.*[9]	Mass Spec	4	946		72.02		−442.51
Dewing[10]	b	5	1293		59.155		−444.93

a. From third low heat of reaction plus auxiliary data.[11]

b. Dewing has determined activities of LiF and AlF_3 in LiF–AlF_3 melts and combined them with the vapor pressure measurement over the melts of Kuxmann and Tillessen[12] and Chin[13] to obtain an equilibrium constant for Reaction 5.

We give more weight to the results which lead to reasonable agreement in 2nd and 3rd law enthalpies of reaction and adopt $\Delta_f H°(LiAlF_4, g, 298.15\ K) = -443 \pm 3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

We adopt the structural and vibrational frequency assignments given by Huglen *et al.*[14] While the C_{2v} structure has not been conclusively established, it is strongly supported by the interpolation of the infra-red spectroscopic studies,[14] by an electron diffraction study of $NaAlF_4$,[15] and by ab initio molecular orbital calculations.[16] The C_{2v} structure consists of an irregular AlF_4 tetrahedron combined with Li to form a planar ring, AlF_2Li, through coordination with two fluorines. Thus luminum forms two types of bonds, Al–F_{bridge} and Al–$F_{terminal}$, considered by Huglen *et al.*[14] to be the same length. A C_s structure and two C_{3v} structures have also been considered.

The AlF_4 tetrahedral angles and the Al–F_{br} and Al–F_{ter} bond distances are those from an electron diffraction study of $NaAlF_4$.[15] These are assumed to be the same for $LiAlF_4$. The Li–F_{br} bond length is estimated.[17] The F_{br}–Al–F_{br} and the F_{ter}–Al–F_{ter} angles are from the sodium analog;[17] the F_{br}–Li–F_{br} angle results from the adopted dimensions. The slightly different dimensions for the $LiAlF_4$ C_{2v} structures used by Cyvin [17] lead to a $S°(298.15\ K)$ value 0.12 cal·K·mol^{-1} less than the adopted values. The dimensions derived by Curtiss[16] in his ab initio study are quite different, but $S°(298.15\ K)$ is only 0.20 cal·K·mol^{-1} greater.

Nine vibrational frequencies were assigned by Huglen *et al.*[14] from infra-red matrix-isolation studies; the remaining three were calculated by force field analysis.[14]

The principal moments of inertia are $I_A = 24.1060 \times 10^{-39}$, $I_B = 27.9447 \times 10^{-39}$ and $I_C = 28.0231 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 172

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−19.620	−1846.320	−1846.320	INFINITE
90	52.024	244.477	401.931	−15.745	−1849.239	−1838.179	960.167
200	81.507	290.240	335.102	−8.972	−1851.967	−1825.960	476.892
250	91.971	309.600	328.099	−4.625	−1852.866	−1819.349	380.132
298.15	99.790	326.497	326.497	0.	−1853.512	−1812.832	317.601
300	100.052	327.116	326.499	0.185	−1853.533	−1812.579	315.598
350	106.249	343.025	327.742	5.349	−1854.045	−1805.712	269.488
400	111.011	357.537	330.573	10.786	−1854.480	−1798.777	234.896
450	114.701	370.835	334.318	16.433	−1854.894	−1791.789	207.985
500	117.591	383.075	338.590	22.243	−1858.320	−1784.448	186.420
600	121.719	404.907	347.868	34.223	−1859.005	−1769.606	154.058
700	124.434	423.888	357.402	46.540	−1859.564	−1754.661	130.934
800	126.299	440.633	366.780	59.082	−1860.118	−1739.638	113.587
900	127.627	455.589	375.832	71.782	−1860.759	−1724.541	100.090
1000	128.603	469.089	384.493	84.596	−1872.126	−1708.605	89.248
1100	129.340	481.383	392.751	97.495	−1872.723	−1692.224	80.357
1200	129.909	492.662	400.614	110.458	−1873.303	−1675.789	72.945
1300	130.357	503.079	408.100	123.472	−1873.874	−1659.306	66.672
1400	130.716	512.753	415.234	136.527	−1874.442	−1642.780	61.293
1500	131.008	521.782	422.039	149.613	−1875.010	−1626.213	56.630
1600	131.248	530.244	428.540	162.726	−1875.578	−1609.608	52.548
1700	131.448	538.207	434.760	175.862	−2021.386	−1585.791	48.725
1800	131.616	545.726	440.717	189.015	−2021.208	−1560.173	45.275
1900	131.759	552.846	446.433	202.184	−2021.040	−1534.565	42.188
2000	131.881	559.607	451.924	215.366	−2020.878	−1508.965	39.410
2100	131.987	566.044	457.207	228.560	−2020.721	−1483.373	36.897
2200	132.079	572.187	462.294	241.763	−2020.561	−1457.789	34.612
2300	132.159	578.060	467.201	254.975	−2020.396	−1432.212	32.527
2400	132.229	583.686	471.938	268.194	−2020.220	−1406.642	30.615
2500	132.292	589.085	476.517	281.421	−2020.027	−1381.081	28.856
2600	132.347	594.275	480.947	294.653	−2019.812	−1355.527	27.233
2700	132.396	599.270	485.237	307.890	−2019.572	−1329.982	25.730
2800	132.441	604.086	489.396	321.132	−2313.202	−1303.479	24.317
2900	132.480	608.734	493.432	334.378	−2311.802	−1267.442	22.829
3000	132.516	613.226	497.350	347.628	−2310.365	−1231.454	21.442
3100	132.549	617.572	501.159	360.881	−2308.890	−1195.515	20.144
3200	132.578	621.781	504.863	374.137	−2307.373	−1159.623	18.929
3300	132.605	625.861	508.468	387.396	−2305.814	−1123.780	17.788
3400	132.630	629.820	511.979	400.658	−2304.212	−1087.985	16.715
3500	132.652	633.665	515.401	413.922	−2302.568	−1052.237	15.704
3600	132.673	637.402	518.738	427.188	−2300.881	−1016.537	14.750
3700	132.692	641.037	521.995	440.457	−2299.153	−980.884	13.848
3800	132.709	644.576	525.174	453.727	−2297.385	−945.280	12.994
3900	132.725	648.024	528.280	466.998	−2295.578	−909.721	12.184
4000	132.740	651.384	531.316	480.272	−2293.734	−874.209	11.416
4100	132.754	654.662	534.285	493.547	−2291.857	−838.745	10.686
4200	132.767	657.861	537.189	506.823	−2289.948	−803.326	9.991
4300	132.779	660.985	540.032	520.100	−2288.011	−767.953	9.329
4400	132.791	664.038	542.816	533.378	−2286.027	−732.627	8.697
4500	132.801	667.022	545.543	546.658	−2284.030	−697.345	8.095
4600	132.811	669.941	548.215	559.939	−2282.018	−662.108	7.518
4700	132.820	672.798	550.836	573.220	−2279.989	−626.914	6.967
4800	132.829	675.594	553.406	586.503	−2277.947	−591.764	6.440
4900	132.837	678.333	555.928	599.786	−2275.895	−556.656	5.934
5000	132.845	681.017	558.403	613.070	−2273.839	−521.591	5.449
5100	132.852	683.647	560.833	626.355	−2271.776	−486.567	4.983
5200	132.859	686.227	563.219	639.640	−2269.721	−451.582	4.536
5300	132.865	688.758	565.564	652.927	−2267.673	−416.638	4.106
5400	132.871	691.242	567.869	666.214	−2265.636	−381.732	3.693
5500	132.877	693.680	570.134	679.501	−2263.614	−346.864	3.294
5600	132.882	696.074	572.362	692.789	−2261.612	−312.031	2.911
5700	132.887	698.426	574.553	706.077	−2259.634	−277.236	2.541
5800	132.892	700.737	576.709	719.366	−2257.681	−242.474	2.184
5900	132.897	703.009	578.830	732.656	−2255.763	−207.745	1.839
6000	132.901	705.243	580.918	745.946	−2253.859	−173.051	1.507

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = 344.9 \pm 8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1834 \pm 12\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1841 \pm 12\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
808(1)	[291](1)	893(1)	669(1)
613(1)	[180](1)	304(1)	339(1)
378(1)	[269](1)	[102](1)	[200](1)

Ground State Quantum Weight: [1] σ = [2]

Point Group: $[C_{2v}]$

Bond Distances: Al–F_{br} = Al–F_{ter} = 1.69 ± 0.02 Å; Na–F_{br} = 2.11 ± 0.02 Å

Bond Angles: F_{br}–Al–F_{br} = 110°; F_{ter}–Al–F_{ter} 109.47°; F_{br}–Na–F_{br} = 82°

Product of the Moments of Inertia: $I_A I_B I_C = 4.775246 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is based on our 3rd law analysis of pressure measurements of the NaF–AlF_3 system for the equilibria:

[1] $Na_3AlF_6(cr, \beta) = 2\ NaF(cr) + NaAlF_4(g)$ [3] $0.2\ Na_5Al_3F_{14}(cr) + 0.4\ AlF_3(cr) = NaAlF_4(g)$

[2] $Na_3AlF_6(l) = 02\ NaF(l) + NaAlF_4(g)$ [4] $0.5\ Na_5Al_3F_{14}(cr) = 0.5\ Na_3AlF_6(cr, \beta) + NaAlF4(g)$

The mass-spectrometric measurements of Sidorov *et al.*[1] showed that the most important species over solid phases in the NaF–AlF_3 system are $NaAlF_4(g)$ and the dimer $[NaAlF_4]_2(g)$. We ignore any other gaseous species in our data treatment. The enthalpy and entropy for the $[NaAlF_4]_2(g) = 2\ NaAlF_4(g)$ dissociation have been determined.

Investigator	T/K	$\Delta_{dso}H°$, $cal \cdot mol^{-1}$	$\Delta_{dso}S°$, $cal \cdot K^{-1} \cdot mol^{-1}$
Sidorov and Kolosov[2]	910	42600	27.14
Shol'ts and Sidorov[3]	910	45000	33.6
Grjotheim, Kvande, and Motzfeldt[4]	1190–1420	43900	28.50

A plot of ln K_p vs 1/T shows Sidorov and Kolosov[2] and Grjotheim *et al.*[4] to be in excellent agreement. We use $\ln K_p = -43900/RT + 28.50/R$ to calculate the mole fraction $NaAlF_4$ monomer in the gas in order to correct the total pressure over the NaF–AlF_3 system to the partial pressure of monomer for the 3rd law analysis. The use of the total pressure rather than partial pressure leads to a heat of formation which is more negative by less than one $kcal \cdot mol^{-1}$.

Source	Method	Reaction	T/K	$\Delta_f H°$(298.15 K) 2nd law	$kcal \cdot mol^{-1}$ 3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal \cdot mol^{-1}$
Sidorov and Kolosov[2]*	Mass Spec	1	900–1050	63.27	62.27	−1.5	−449.16
Shol'ts and Sidorov[3]	Mass Spec	1	1100		67.76		−443.68
Kolosov *et al.*[5]	Mass Spec	1	910		65.78		−445.66
Grjotheim *et al.*[6]	Effusion	3	840–960	65.14	65.49	0.4	−440.03
Shol'ts and Sidorov[3]	Mass Spec	3	910		65.98		−439.54
Kolosov *et al.*[5]	Mass Spec	3	910		66.90		−439.43
Grjotheim *et al.*[6]	Effusion	4	840–960	66.41	70.21	4.3	−439.35
Kolosov *et al.*[5]	Mass Spec	4	910		71.62		−437.94

*Partial pressures by the investigator.

The total vapor pressure over molten cryolite, reaction [2], measured by effusion by Grjotheim *et al.*,[4] corrected to monomer partial pressure, leads to $\Delta_f H°(NaAlF_4, g, 298.15\ K) = -447.70\ kcal \cdot mol^{-1}$. Unit activity of NaF in molten cryolite was used in this calculation so that $-447.70\ kcal \cdot mol^{-1}$ is a lower limit. There is no evident explanation for the more negative grouping of heats of formation from reactions [1] and [2] compared with the grouping from reactions [3] and [4].

In view of the difficulties and uncertainties in working with the NaF–AlF_3 system, we adopt $\Delta_f H°(NaAlF_4, g, 298.15\ K) = -440 \pm 3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The adopted structure, C_{2v}, consists of an irregular AlF_4 tetrahedron combined with Na to form the planar ring, AlF_2Na, through coordination with two fluorines. The Al atom forms two types of bonds, Al–F_{bridge} and Al–$F_{terminal}$, which are of the same length.[8] Other structures have been considered, a C_s symmetry in which the ring is not planar and two C_{3v} structures where the Na is coordinated with one or three fluorines, but interpretation of the infra-red spectra supports the C_{2v} model.[9]

The bond distances and bond angles are from the electron diffraction study of Spiridonov and Erokin.[8] Seven vibrational frequencies were assigned from infrared matrx-isolation studies by Huglen *et al.*;[9] the remaining five were calculated by force field analysis.[9] The principal moments of inertia are $I_A = 24.1060 \times 10^{-39}$, $I_B = 44.4685 \times 10^{-39}$, and $I_C = 44.5470 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 172

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−21.223	−1833.547	−1833.547	INFINITE
100	59.284	255.634	425.562	−16.993	−1836.954	−1825.364	953.472
200	87.953	306.516	353.949	−9.487	−1839.564	−1812.638	473.412
250	97.151	327.177	346.571	−4.849	−1840.369	−1805.808	377.303
298.15	103.954	344.896	344.896	0.	−1840.960	−1799.096	315.194
300	104.182	345.539	344.898	0.193	−1840.980	−1798.836	313.205
350	109.570	362.022	346.187	5.542	−1841.496	−1791.771	267.407
400	113.718	376.936	349.113	11.129	−1844.612	−1784.428	233.022
450	116.938	390.523	352.971	16.899	−1845.043	−1776.878	206.255
500	119.464	402.980	357.358	22.811	−1845.395	−1769.285	184.836
600	123.080	425.105	366.852	34.952	−1845.954	−1754.008	152.700
700	125.464	444.269	376.573	47.387	−1846.421	−1738.646	129.739
800	127.102	461.135	386.111	60.020	−1846.897	−1723.218	112.515
900	128.270	476.177	395.298	72.791	−1847.462	−1707.725	99.114
1000	129.129	489.738	404.075	85.663	−1858.773	−1691.402	88.350
1100	129.778	502.077	412.432	98.610	−1859.349	−1674.637	79.522
1200	130.279	513.392	420.380	111.614	−1956.723	−1655.378	72.057
1300	130.674	523.836	427.942	124.663	−1956.466	−1630.277	65.505
1400	130.990	533.532	435.142	137.746	−1956.218	−1605.195	59.891
1500	131.247	542.578	442.006	150.859	−1955.980	−1580.130	55.025
1600	131.459	551.056	448.559	163.994	−1955.756	−1555.081	50.768
1700	131.635	559.031	454.826	177.149	−1955.545	−1530.045	47.013
1800	131.783	566.559	460.826	190.320	−1955.348	−1505.021	43.675
1900	131.909	573.688	466.580	203.505	−1955.161	−1480.009	40.688
2000	132.017	580.457	472.106	216.701	−1954.982	−1455.005	38.001
2100	132.110	586.900	477.420	229.908	−1954.806	−1430.011	35.570
2200	132.191	593.048	482.537	243.123	−1954.627	−1405.025	33.360
2300	132.262	598.926	487.471	256.346	−1954.440	−1380.047	31.342
2400	132.324	604.556	492.233	269.575	−1954.240	−1355.077	29.492
2500	132.379	609.959	496.835	282.810	−1954.019	−1330.117	27.791
2600	132.428	615.152	501.286	296.051	−1953.773	−1305.165	26.221
2700	132.471	620.150	505.596	309.296	−1953.496	−1280.224	24.767
2800	132.510	624.969	509.774	322.545	−2247.085	−1254.326	23.400
2900	132.545	629.619	513.827	335.798	−2245.638	−1218.895	21.955
3000	132.577	634.113	517.762	349.054	−2244.148	−1183.516	20.607
3100	132.605	638.461	521.586	362.313	−2242.612	−1148.187	19.347
3200	132.631	642.672	525.304	375.575	−2241.029	−1112.908	18.166
3300	132.655	646.753	528.923	388.839	−2239.397	−1077.679	17.058
3400	132.677	650.714	532.447	402.106	−2237.716	−1042.501	16.016
3500	132.697	654.560	535.882	415.374	−2235.986	−1007.372	15.034
3600	132.715	658.298	539.230	428.645	−2234.208	−972.294	14.108
3700	132.732	661.935	542.498	441.917	−2232.384	−937.266	13.232
3800	132.747	665.475	545.688	455.191	−2230.515	−902.288	12.403
3900	132.761	668.923	548.803	468.467	−2228.604	−867.359	11.617
4000	132.775	672.285	551.849	481.744	−2226.653	−832.480	10.871
4100	132.787	675.563	554.826	495.022	−2224.667	−797.651	10.162
4200	132.798	678.763	557.739	508.301	−2222.647	−762.869	9.488
4300	132.809	681.888	560.590	521.581	−2220.601	−728.138	8.845
4400	132.819	684.941	563.382	534.863	−2218.489	−693.456	8.232
4500	132.828	687.926	566.116	548.145	−2216.375	−658.821	7.647
4600	132.837	690.846	568.796	561.428	−2214.254	−624.232	7.088
4700	132.845	693.703	571.424	574.712	−2212.120	−589.689	6.554
4800	132.853	696.500	574.000	587.997	−2209.979	−555.192	6.042
4900	132.860	699.239	576.528	601.283	−2207.834	−520.740	5.551
5000	132.867	701.923	579.010	614.569	−2205.686	−486.332	5.081
5100	132.873	704.555	581.445	627.856	−2203.550	−451.966	4.629
5200	132.879	707.135	583.838	641.144	−2201.428	−417.641	4.195
5300	132.885	709.666	586.188	654.432	−2199.323	−383.358	3.778
5400	132.890	712.150	588.498	667.721	−2197.242	−349.114	3.377
5500	132.895	714.588	590.768	681.010	−2195.189	−314.909	2.991
5600	132.900	716.983	593.001	694.300	−2193.169	−280.740	2.619
5700	132.904	719.335	595.197	707.590	−2191.187	−246.608	2.260
5800	132.909	721.647	597.357	720.881	−2189.246	−212.510	1.914
5900	132.913	723.919	599.483	734.172	−2187.354	−178.443	1.580
6000	132.917	726.153	601.575	747.463	−2185.335	−144.431	1.257

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K)$ = [284.5 ± 4] $J·K^{-1}·mol^{-1}$
T_{fus} = 1293 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = [−3326 ± 21] $kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(K_3AlF_6, cr, 298.15\ K)$ is calculated from $\Delta_r H° = -30.2\ kcal·mol^{-1}$ for the reaction, $AlF_3(cr) + 3\ KF(cr) = K_3AlF_6(cr)$, which was estimated by comparison with the values of $\Delta_r H°$ of the similar reactions for $Na_3AlF_6(cr)$, $Na_3AlCl_6(cr)$ and $K_3AlCl_6(cr)$.

Heat Capacity and Entropy

Heat capacities are estimated by the addition of a correction term $3(M_{KF}-M_{NaF})$ to the corresponding values for $Na_3AlF_6(cr)$ where M denotes heat capacity. In a similar manner, $S°(298.15\ K)$ is calculated to be 68 ± 1 $cal·K^{-1}·mol^{-1}$.

Fusion Data

T_{fus} was determined from Hall and Insley.[1]

Reference

[1]F. P. Hall and H. Insley, J. Am. Ceram. Soc. **21**, 113 (1938).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	222.798	284.512	284.512	0.	−3326.280	−3163.447	554.223
300	223.384	285.892	284.516	0.413	−3326.250	−3162.437	550.629
400	241.082	352.662	293.500	23.665	−3331.598	−3106.741	405.699
500	255.308	408.026	311.022	48.502	−3328.814	−3050.825	318.718
600	267.399	455.652	331.248	74.642	−3324.948	−2995.574	260.788
700	278.905	497.740	352.082	101.960	−3320.120	−2941.047	219.464
800	290.077	535.740	372.702	130.431	−3314.390	−2887.274	188.520
900	298.738	570.425	392.772	159.888	−3307.984	−2834.264	164.496
1000	305.432	602.254	412.151	190.103	−3311.793	−2781.230	145.277
1100	311.290	631.646	430.786	220.946	−3541.341	−2714.695	128.910
1200	316.310	658.953	448.676	252.333	−3530.603	−2640.016	114.917
1300	320.390	684.437	465.842	284.173	−3519.481	−2566.249	103.113
1400	323.842	708.311	482.318	316.390	−3508.049	−2493.351	93.028
1500	326.509	730.746	498.139	348.910	−3496.374	−2421.279	84.316
1600	328.862	751.895	513.345	381.681	−3484.506	−2349.992	76.719
1700	330.954	771.898	527.971	414.676	−3472.470	−2279.452	70.039
1800	332.628	790.864	542.053	447.858	−3460.298	−2209.625	64.122
1900	333.883	808.883	555.627	481.187	−3448.026	−2140.478	58.846
2000	334.720	826.033	568.722	514.621	−3435.694	−2071.978	54.115

PREVIOUS: September 1963 CURRENT: December 1963

$S°(298.15\ K) = 187.89 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
T_{trs1} (β → γ) = 748 K
T_{trs2} (γ → δ) = 848 K
T_{trs3} (δ → ϵ) = 978 K
$T_{fus} = 1058 \pm 3$ K

$\Delta_f H°(0\ K) \approx -3370.9 \pm 4.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) \approx -3383.6 \pm 4.6\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = [2.092]\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = [1.255]\ kJ \cdot mol^{-1}$
$\Delta_{trs3} H° = [0.418]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 86.19 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is derived from $\Delta_f H°(298.15\ K) = -5.4 \pm 0.5$ kcal·mol^{-1} for the reaction 3 LiF(cr) + AlF_3(cr) → Li_3AlF_6(α, β mixture). Greene *et al.*[1] obtained this result by heating the fluorides under standardized conditions in a small electrical furnace contained in their calorimeter at 25°C. $\Delta_f H°$ includes a small endothermic effect observed during heating of the reaction product. The authors suggest that the enthalpy of conversion between the α– and β– forms is small and thus their result should apply to both forms.

Heat Capacity and Entropy

Furukawa *et al.*[2] measured $C_p°$ (15–370 K) using a sample prepared by stoichiometric proportions of LiF and AlF_3 in graphite. X–ray diffraction and petrographic examination of separate portions of the sample indicated a single phase identified as β–Li_3AlF_6. The authors tabulated values of $C_p°$ and $S°$ based on their data and the extrapolation $S°(15\ K) = 0.042$ cal·K^{-1}·mol^{-1}. These values are adopted.

Douglas and Neufer[3] reported relative enthalpy data (323–973 K) for part of the same sample used in measurement of $C_p°$.[2] Their study was made prior to discovery of the five crystalline phases, and their drop–calorimetric data reveal only the transition near 748 K. Reinterpretation of the data above 748 K is complicated by the proximity of the furnace temperatures to the transition temperatures and by the tendency of high– temperature forms to revert to both α– and β– forms under different conditions of cooling. Bjorge and and Jenssen[4] and Rolin *et al.*[5] also reported crystalline enthalpy data, but these are relatively imprecise and include similar uncertainties in the final state after the drop. These difficulties preclude the derivation of accurate heat capacities for the high–temperature forms.

$C_p°$ for the β– form is adopted from,[2,3] since the two methods are in good agreement. The curve is extrapolated linearly above 748 K to obtain $C_p°$ for the high–temperature forms. Obvious differences in $C_p°$ are not apparent in the observed data for the different forms, so this should be an adequate approximation.

Transition Data

Existence of five polymorphic forms was shown by high– temperature X–ray diffraction[1,6,7] and differential thermal analysis.[6,7] Both α– and β– forms persisted at room temperature, but the α– form appeared only on quenching of high–temperature forms.[1] The α– form transformed to β near 490 K,[1,6] but the reverse transformation was not observed. Single–crystal X–ray diffraction showed the α– form to be orthorhombic.[8]

The adopted values of T_{trs} are the lowest temperatures at which the high–temperature form was observed growing at the expense of the low–temperature form.[1] DTA data[6,7] were higher by roughly 30 K for T_{trs1} and 25 K for T_{trs2}. Combination of the observed enthalpies[3] with the adopted $C_p°$ yields $\Delta_{trs1} H° = 0.76$ and $\Delta_{trs2} H° = 0.03$ or 0.15 kcal·mol^{-1}; we prefer to adopt $\Delta_{trs} H°$ values (0.5 and 0.3 kcal·mol^{-1}) which are more consistent with the areas of peaks in the DTA curve.[7] Evidence suggests that $\Delta_{trs3} H°$ is small, so we estimate 0.1 kcal·mol^{-1}.

Fusion Data

Refer to the liquid table for details.

References

[1] P. D. Greene, P. Gross and C. Hayman, Trans. Faraday Soc. **64**, 633 (1968).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−32.146	−3370.866	−3370.866	INFINITE
100	70.982	38.225	333.657	−29.543	−3378.953	−3328.763	1738.767
200	156.222	115.960	205.121	−17.832	−3383.356	−3276.431	855.716
298.15	202.506	187.891	187.891	0.	−3383.601	−3223.790	564.795
300	203.133	189.145	187.895	0.375	−3383.581	−3222.799	561.139
400	229.869	251.549	196.222	22.131	−3381.793	−3169.443	413.887
500	248.111	304.904	212.753	46.075	−3388.377	−3115.708	325.496
600	262.295	351.440	232.072	71.621	−3384.937	−3061.477	266.525
700	274.052	392.779	252.131	98.453	−3380.383	−3007.913	224.453
748.000	279.073	411.132	261.751	111.737	BETA <--> GAMMA		
748.000	279.073	413.929	261.751	113.829	TRANSITION		
800	284.512	432.865	272.262	128.482	−3372.851	−2955.211	192.956
848.000	289.533	449.589	281.830	142.259	GAMMA <--> DELTA		
848.000	289.533	451.069	281.830	143.515	TRANSITION		
900	294.972	468.460	292.114	158.712	−3365.399	−2903.447	168.512
978.000	303.131	493.311	307.178	182.038	DELTA <--> EPSILON		
978.000	303.131	493.739	307.178	182.456	TRANSITION		
1000	305.432	500.508	311.357	189.150	−3368.604	−2851.735	148.959
1058.000	311.499	517.898	322.206	207.041	--- EPSILON <--> LIQUID ---		
1100	315.892	530.109	329.912	220.217	−3360.516	−2800.432	132.981
1200	326.352	558.044	347.770	252.329	−3351.444	−2749.908	119.700
1300	336.812	584.579	364.974	285.487	−3341.386	−2700.181	108.495
1400	347.272	609.922	381.571	319.691	−3330.327	−2651.266	98.920
1500	357.732	634.238	397.611	354.941	−3318.256	−2603.177	90.651
1600	368.192	657.660	413.136	391.238	−3305.169	−2555.926	83.442

PREVIOUS: December 1963 CURRENT: June 1970

$S°(298.15\ K) \approx [245.847]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1058 \pm 3\ K$

$\Delta_f H°(298.15\ K) = [-3317.640]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 86.190 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_3AlF_6, l, 298.15\ K)$ is calculated from $\Delta_f H°(Li_3AlF_6, l, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(1058\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Relative enthalpy data were measured by Bjorge and Jenssen[1] from 1065 to 1088 K and by Rolin *et al.*[2] from about 1075 to 1145 K. The data are consistent with liquid heat capacities in the range from roughly 82 to 92 $cal \cdot K^{-1} \cdot mol^{-1}$. We adopt the me[illegible]uccirclan value of 86 $cal \cdot K^{-1} \cdot mol^{-1}$ (359.824 $J \cdot K^{-1} \cdot mol^{-1}$) and extrapolate this to higher and lower temperatures. A glass transition is assumed at 750 K and $C_p°$ at lower temperatures is taken to be the same as that of β–Li_3AlF_6.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} was observed at 780°C,[3] 782°C,[2,4] 783°C[5,8] and 785°C.[1] The last and highest value is adopted for this table. Combination of the observed liquid enthalpies with the adopted crystal enthalpies yields values for $\Delta_{fus} H°$ of 19.7 $kcal \cdot mol^{-1}$ [1] (authors gave 20.2 ± 1.0) and 21.5 ± 0.3 $kcal \cdot mol^{-1}$ [2] (authors gave 21.5). We adopt the mean value of 20.6 $kcal \cdot mol^{-1}$ (86.190 $kJ \cdot mol^{-1}$) which is confirmed by values of 20.7,[8] 20.8,[4] 22.2,[4] 20.1,[4] and 22.0[2] derived from crystal–liquid phase data for binary systems. The agreement among values for $\Delta_{fus} H°$ seemingly excludes the possibility of large discrepancies in the enthalpies due to formation of the α–phase instead of β during drop–calorimetry from high temperatures.

Vaporization Data

Li_3AlF_6 vaporizes mainly to $LiAlF_4(g)$ with small contributions from species such as $Li_2AlF_5(g)$, $Li_2F_2(g)$ and LiF(g).[6,7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	202.506	245.847	245.847	0.	−3317.640	−3175.109	556.266
300	203.133	247.101	245.851	0.375	−3317.620	−3174.224	552.682
400	229.869	309.505	254.178	22.131	−3315.832	−3126.664	408.301
500	248.111	362.860	270.709	46.075	−3322.416	−3078.725	321.632
600	262.295	409.396	290.028	71.621	−3318.976	−3030.290	263.810
700	274.052	450.736	310.087	98.454	−3314.421	−2982.521	222.558
700.000	274.052	450.736	310.087	98.454	GLASS <--> LIQUID		
700.000	359.824	450.736	310.087	98.454	TRANSITION		
800	359.824	498.783	330.738	134.436	−3300.936	−2936.031	191.703
900	359.824	541.165	351.811	170.419	−3287.731	−2891.213	167.802
1000	359.824	579.076	372.675	206.401	−3285.392	−2847.092	148.717
1058.000	359.824	599.363	384.551	227.271	--- EPSILON <--> LIQUID ---		
1100	359.824	613.371	393.022	242.383	−3272.388	−2803.892	133.146
1200	359.824	644.680	412.708	278.366	−3259.446	−2761.873	120.221
1300	359.824	673.481	431.675	314.348	−3246.563	−2720.931	109.328
1400	359.824	700.147	449.911	350.331	−3233.726	−2680.980	100.029
1500	359.824	724.972	467.430	386.313	−3220.923	−2641.945	92.001
1600	359.824	748.194	484.260	422.295	−3208.150	−2603.763	85.004
1700	359.824	770.009	500.433	458.278	−3631.111	−2544.851	78.194
1800	359.824	790.576	515.987	494.260	−3616.124	−2481.386	72.008
1900	359.824	810.030	530.955	530.243	−3601.178	−2418.753	66.496
2000	359.824	828.487	545.374	566.225	−3586.265	−2356.906	61.556
2100	359.824	846.043	559.277	602.207	−3571.378	−2295.804	57.105
2200	359.824	862.782	572.696	638.190	−3556.510	−2235.411	53.075
2300	359.824	878.777	585.658	674.172	−3541.653	−2175.693	49.412
2400	359.824	894.091	598.193	710.155	−3526.799	−2116.622	46.067
2500	359.824	908.779	610.324	746.137	−3511.942	−2058.170	43.003
2600	359.824	922.892	622.077	782.119	−3497.076	−2000.313	40.187
2700	359.824	936.472	633.471	818.102	−3482.194	−1943.028	37.590
2800	359.824	949.558	644.528	854.084	−3761.194	−1885.326	35.171
2900	359.824	962.184	655.265	890.067	−3745.173	−1818.614	32.757
3000	359.824	974.383	665.700	926.049	−3729.127	−1752.454	30.513

PREVIOUS: CURRENT: June 1970

0	to	748 K	crystal, beta
748	to	848 K	crystal, gamma
848	to	978 K	crystal, delta
978	to	1058 K	crystal, epsilon
above		1058 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−32.146	−3370.866	−3370.866	INFINITE
100	70.982	38.225	333.657	−29.543	−3378.953	−3328.763	1738.767
200	156.222	115.960	205.121	−17.832	−3383.356	−3276.431	855.716
298.15	202.506	187.891	187.891	0.	−3383.601	−3223.790	564.795
300	203.133	189.145	187.895	0.375	−3383.581	−3222.799	561.139
400	229.869	251.549	196.222	22.131	−3381.793	−3169.443	413.887
500	248.111	304.904	212.753	46.075	−3388.377	−3115.708	325.496
600	262.295	351.440	232.072	71.621	−3384.937	−3061.477	266.525
700	274.052	392.779	252.131	98.453	−3380.383	−3007.913	224.453
748.000	279.073	411.132	261.751	111.737	BETA <--> GAMMA TRANSITION		
748.000	279.073	413.929	261.751	113.829			
800	284.512	432.865	272.262	128.482	−3372.851	−2955.211	192.956
848.000	289.533	449.589	281.830	142.259	GAMMA <--> DELTA TRANSITION		
848.000	289.533	451.069	281.830	143.515			
900	294.972	468.460	292.114	158.712	−3365.399	−2903.447	168.512
978.000	303.131	493.311	307.178	182.038	DELTA <--> EPSILON TRANSITION		
978.000	303.131	493.739	307.178	182.456			
1000	305.432	500.508	311.357	189.150	−3368.604	−2851.735	148.959
1058.000	311.499	517.898	322.206	207.041	EPSILON <--> LIQUID TRANSITION		
1058.000	359.824	599.363	322.206	293.232			
1100	359.824	613.371	333.058	308.344	−3272.388	−2803.892	133.146
1200	359.824	644.680	357.741	344.327	−3259.446	−2761.873	120.221
1300	359.824	673.481	380.935	380.309	−3246.563	−2720.931	109.328
1400	359.824	700.147	402.796	416.292	−3233.726	−2680.980	100.029
1500	359.824	724.972	423.456	452.274	−3220.923	−2641.945	92.001
1600	359.824	748.195	443.034	488.256	−3208.150	−2603.763	85.004
1700	359.824	770.009	461.633	524.239	−3631.111	−2544.851	78.194
1800	359.824	790.576	479.342	560.221	−3616.125	−2481.386	72.008
1900	359.824	810.030	496.239	596.204	−3601.178	−2418.753	66.496
2000	359.824	828.487	512.394	632.186	−3586.265	−2356.906	61.556
2100	359.824	846.043	527.867	668.168	−3571.378	−2295.805	57.105
2200	359.824	862.782	542.713	704.151	−3556.510	−2235.412	53.075
2300	359.824	878.777	556.980	740.133	−3541.653	−2175.694	49.412
2400	359.824	894.091	570.709	776.116	−3526.799	−2116.623	46.067
2500	359.824	908.779	583.940	812.098	−3511.942	−2058.171	43.003
2600	359.824	922.892	596.707	848.080	−3497.076	−2000.313	40.187
2700	359.824	936.472	609.041	884.063	−3482.194	−1943.028	37.590
2800	359.824	949.558	620.970	920.045	−3761.194	−1885.327	35.171
2900	359.824	962.184	632.520	956.028	−3745.173	−1818.614	32.757
3000	359.824	974.383	643.713	992.010	−3729.127	−1752.455	30.513

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = 238.47 \pm 1.7\ J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 836 \pm 2\ K$
$T_{fus} = 1285 \pm 3\ K$

$\Delta_f H°(0\ K) = -3304.65 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -3316.91 \pm 3.3\ kJ·mol^{-1}$
$\Delta_{trs} H°(\alpha \rightarrow \beta) = 9.456 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{fus} H° = 110.039 \pm 5.0\ kJ·mol^{-1}$

Enthalpy of Formation

The heats of solution of Al(cr), NaCl(cr), and Na_3AlF_6(cr) in 4.36 m HCl acid solution were determined at 303.15 K by Coughlin.[1] The enthalpy change for the reaction Al(cr) + 2.96 NaCl(cr) + 2.96(HF·5.716 H_2O) + 3.617 H_2O(l) = $Na_{2.96}AlF_{5.96}$(cr) + 2.96(HCl·12.731 H_2O) + 3/2 H_2(g) was derived as $\Delta_r H°(298.15\ K) = -153.22 \pm 0.14$ kcal·mol. Using auxiliary $\Delta_f H°(298.15\ K)$ data from,[2,3] we obtain $\Delta_f H°((Na_{2.96}AlF_{5.96}, cr, 298.15\ K) = -787.25 \pm 0.34\ kcal·mol^{-1}$. Assuming $\Delta_r H°(298.15\ K) = 0$ for the reaction $Na_{2.96}AlF_{5.96}$ + 0.04 NaF = Na_3AlF_6, we obtain $\Delta_f H°(Na_3AlF_6, cr, 298.15\ K) = -792.76 \pm 0.4\ kcal·mol^{-1}$).

Gross *et al.*[4] measured the heat of the reaction 3/2 PbF_2(cr) + Al(cr) + 3 NaF(cr) = 3/2 Pb(cr) + Na_3AlF_6(cr) directly in a bomb calorimeter. The average heat of the reaction was found to be $\Delta_r H°(298.15\ K) = -138.3\ kcal·mol^{-1}$. Using auxiliary data [2], we obtain $\Delta_f H°(Na_3AlF_6, cr, 298.15\ K) = -794.40 \pm 1.5\ kcal·mol^{-1}$. Gross *et al.*[4] also measured the heat of reaction for 3/2 PbF_2(cr) + Al(cr) = 3/2 Pb(cr) + AlF_3(cr) as $\Delta_r H°(AlF_3, cr, 298.15\ K) = -360.99 \pm 0.31\ kcal·mol^{-1}$), we obtain $\Delta_f H°(Na_3AlF_6, cr, 298.15\ K) = -794.19 \pm 1.0\ kcal·mol^{-1}$.

Baud[6] reported $\Delta_r H° = -40.7\ kcal·mol^{-1}$ for the reaction 2 AlF_3(cr) + 6 NaF(cr) = 2 Na_3AlF_6(cr). Using auxiliary data from 2, as above, we obtain $\Delta_f H°(Na_3AlF_6, cr, 298.15\ K) = -792.8 \pm 2.0\ kcal·mol^{-1}$.

Grjotheim *et al.*[7] measured the enthalpy of mixing of 3/4 NaF(cr) + 1/4 Na_3AlF_6(cr) as $\Delta_r H°(910\ K) = -3.8 \pm 0.8\ kcal·mol^{-1}$. When this result is combined with JANAF auxiliary data for the enthalpies and $\Delta_f H°(298.15\ K)$ values from[2] we obtain $\Delta_f H°(Na_3AlF_6, cr, 298.15\ K) = -792.8 \pm 2.0\ kcal·mol^{-1}$.

The amounts of sodium over mixtures of cryolite and aluminum have been measured by Ono *et al.*,[8] Dewing,[9] and by Stokes and Frank.[10] The data have been corrected for the formation of sodium dimer by using JANAF functions for Na_2(g) and Na(g) to determine the equilibrium constants for the reaction Na_2(g) = 2 Na(g). Our evaluation of this data is presented below. We were unable to evaluate the data of Stokes and Frank[10] due to lack of appropriate data on the activities of Na_3AlF_6(l). Also shown in the table are the emf work of Dewing,[11] and the equilibrium study of Mashovets and Yudin.[12]

Our adopted value for the heat of formation of cryolite, $\Delta_f H°(Na_3AlF_6, cr, 298.15\ K) = -792.76 \pm 0.8\ kcal·mol^{-1}(-3316.91\ kJ·mol^{-1})$ is based on the study by Coughlin[1] and discussions with Dewing.[23]

Source	Method	Reaction[a]	T/K	Data	δS cal·K^{-1}·mol^{-1}	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd Law	3rd Law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Mashovets[12] (1962)	transpiration	A	1101–1239	5	1.32 ± 1.3	48.11 ± 0.8	46.57 ± 0.2	−792.78 ± 1.0
Mashovets[12] (1962)	transpiration	B	1274	1	–	–	60.54	−792.81 ± 1.0
Ono[8] (1965)	DTA	C	1063–1153	eqn	4.98	115.86	110.38 ± 2.0	−793.22 ± 3.0
Dewing[8] (1969)	transpiration	C	949–1089	11	−3.71 ± 1.0	104.21 ± 1.0	108.03 ± 0.50	−795.57 ± 2.0
Dewing[9] (1969)	transpiration	D	908–913	2	−12.0	99.3	110.20 ± 0.1	−793.40 ± 1.5
Dewing[11] (1970)	emf	E	839–943	9	1.02 ± 0.2	−18.20 ± 0.2	−19.115 ± 0.09	−793.52 ± 0.6

[a]Reactions:
A) 2/3 Na_3AlF_6(cr) + H_2O(g) = 1/3 Al_2O_3(cr) + 2 HF(g) + 2 NaF(cr)
B) 2/3 Na_3AlF_6(cr) + H_2O(g) = 1/3 Al_2O_3(cr) + 2 HF(g) + 2 NaF(l)
C) 6 NaF(cr) + Al(l) = 3 Na(g) + Na_3AlF_6(cr)
D) 6 NaF(cr) + Al(cr) = 3 Na(g) + Na_3AlF_6(cr)
E) 3 NaF(cr) + AlF_3(cr) = Na_3AlF_6(cr)

Heat Capacity and Entropy

The low temperature heat capacities, 53.66–296.00 K, were measured by King.[13] The values of $C_p°$ below 53.66 K are extrapolated using the $C_p°$ equation (combination of Debye and Einstein functions) given by King. $S°(298.15\ K)$ is derived based on the low temperature heat capacities $S°(50\ K) = 3.953\ cal·K^{-1}·mol^{-1}$ and $H°(50\ K) = 0.140\ kcal·mol^{-1}$.

High temperature enthalpies have been determined by drop calorimetry by O'Brien and Kelley[14] (401.3–809.7 K), and by Albright[15] (349.99–812.70 K). The enthalpies reported by Albright are 7% higher than those reported by O'Brien and Kelley. Enthalpy data from these two calorimeters have been compared previously (see MoO_3(cr) table) indicating that the CRT calorimeter[15] results were 2% higher than the Bureau of Mines calorimeter.[14] Frank[16] commented that the enthalpies reported by O'Brien and Kelley were incorrect due to an apparent error in temperature measurement but Douglas and Ditmars[17] have questioned this correction (see NaF(cr) table for details). Our analysis indicates that the enthalpies of O'Brien and Kelley join smoothly with the low temperature $C_p°$s of King. This is not true of Albright's enthalpy data. We adopt heat capacities for the α–phase derived from the original enthalpy data reported by O'Brien and Kelley.[14]

The high temperature enthalpies have also been measured by the following investigators: Joly[18] (284.5–373.3 K), Baud[19] (289–328 K), Roth and Bertram[20] (369–802 K), Krestovnikov and Karetnikov[21] (288–1173 K), and by Lyshenko[22] (293–838 K). Their data are not used for evaluation due to inconsistencies among the reported values.

Transition Data and Fusion Data

Refer to the β–crystal table for details.

Continued on page 172

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−38.095	−3304.649	−3304.649	INFINITE
100	100.039	62.287	402.572	−34.028	−3313.806	−3261.080	1703.414
200	179.033	159.302	257.165	−19.573	−3317.306	−3206.528	837.459
298.15	215.727	238.467	238.467	0.	−3316.908	−3152.168	552.247
300	216.212	239.803	238.471	0.400	−3316.883	−3151.146	548.663
400	236.379	305.007	247.223	23.114	−3323.200	−3095.511	404.232
500	248.634	358.934	264.326	47.304	−3321.044	−3038.816	317.463
600	262.793	405.519	284.058	72.876	−3317.675	−2982.666	259.664
700	276.822	447.083	304.429	99.858	−3313.053	−2927.179	218.429
800	290.780	484.959	324.661	128.238	−3307.209	−2872.439	187.551
836.000	295.809	497.868	331.843	138.797	---- ALPHA <--> BETA ----		
900	304.691	520.012	344.443	158.013	−3300.200	−2818.502	163.582
1000	318.582	552.834	363.657	189.176	−3302.683	−2764.645	144.410
1100	332.461	583.849	382.277	221.729	−3293.191	−2711.290	128.748
1200	346.310	613.371	400.315	255.668	−3572.796	−2651.533	115.418

PREVIOUS: December 1968 CURRENT: December 1979

$S°$(298.15 K) = [284.881] J·K^{-1}·mol^{-1}
$T_{trs}(\alpha \rightarrow \beta)$ = 836 ± 2 K
$T_{fus}(\beta \rightarrow l)$ = 1285 ± 3 K

$\Delta_f H°$(298.15 K) = [−3288.781] kJ·mol^{-1}
$\Delta_{trs}H°(\alpha \rightarrow \beta)$ = 9.456 ± 1.7 kJ·mol^{-1}
$\Delta_{fus}H°(\beta \rightarrow l)$ = 110.039 ± 5.0 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(Na_3AlF_6, cr, \beta, 298.15\ K)$ is calculated from $\Delta_f H°(Na_3AlF_6, cr, \alpha, 298.15\ K)$ by adding the enthalpy of transition, $\Delta_{trs}H°$, and the difference in enthalpy, $H°(836\ K)–H°(298.15\ K)$, between the α– and β–phases.

Heat Capacity and Entropy

High–temperature enthalpies of the β–phase have been determined by drop calorimetry by O'Brien and Kelley[1] (846.7–1263.5 K), Albright[2] (824.21–1267.17 K), and by Holm and Gronvold[3] (1070–1175 K). The data of Holm and Gronvold is in very good agreement with the data of Albright but the data of O'Brien and Kelley are systematically lower by 2%. We have already discussed the discrepancy between the data of O'Brien and Kelley and that of Albright (see the discussion on the Na_3AlF_6(cr, α) table). Our experience with the enthalpies reported by Holm, which are primarily aimed at determining heats of fusion, is that the enthalpies show a positive bias (see the $Na_5Al_3F_{14}$(cr) table) of 2–4%. For these reasons, we adopt the enthalpies from the work of O'Brien and Kelley.[1] Heat capacities derived from these enthalpies have been extended smoothly below 836 K and above 1285 K.

$S°$(298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

The α–phase is the low temperature monoclinic modification of cryolite (sodium hexafluoroaluminate), space group $P2_1/n$.[4, 10] The transition to the cubic high–temperature β–phase (space group Fm3m) occurs at 836 ± 2 K. Reported values for $T_{trs}(\alpha \rightarrow \beta)$ are 823 K,[2] 832 K,[6] 833 K,[7] 833.5 K,[6] 834 K,[8] 834.5 K,[9] 837 K,[9] 838 K,[10, 11, 12] and 845 K.[1] The value of $\Delta H_{trs}H°(\alpha \rightarrow \beta)$ is calculated as the difference between the adopted enthalpies for the α– and β–phases at 836 K. Reported values of $\Delta H_{trs}H°(\alpha \rightarrow \beta)$ are (in kJ·mol^{-1}) = 5.19,[12] 9.04,[1] 9.37 ± 1.7,[9] 9.87,[9] and 9.96.[2] The cause of the discrepancies among the reported values for T_{trs}, $\Delta_{trs}H°$ and the high temperature enthalpies may be due to differences in the sample composition. The samples used have normally been hand–picked naturally occurring crystals.

Fusion Data

Our adopted value for the melting point of cryolite is 1285 ± 3 K. Reported values include (all in K): 1273,[12] 1279,[2] 1281,[7] 1282,[13, 14] 1284,[3,15] 1285,[10] 1293,[8] and 1300.[1] The value of $\Delta_{fus}H°$ is calculated as the difference between the adopted enthalpies of the β–crystal and liquid at 1285 K. Other reported values of $\Delta_{fus}H°$ are (in kJ·mol^{-1}): 69.62,[12] 106.7 ± 10.5,[15] 111.3 ± 0.8,[16] 111.75,[6] 113.4 ± 2.1,[3] 115.65,[1] and 116.77.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	194.723	284.881	284.881	0.	−3288.781	−3137.880	549.744
300	194.744	286.086	284.885	0.360	−3288.796	−3136.943	546.190
400	200.916	342.763	292.572	20.077	−3298.111	−3085.524	402.928
500	212.464	388.778	307.340	40.719	−3299.502	−3032.196	316.771
600	226.103	428.705	324.306	62.639	−3299.786	−2978.688	259.318
700	240.747	464.652	341.827	85.977	−3298.807	−2925.231	218.283
800	255.977	497.791	359.276	110.812	−3296.509	−2872.005	187.523
836.000	261.500	509.179	363.999	121.370	---- ALPHA <--> BETA ----		
900	271.458	528.831	376.408	137.181	−3292.905	−2819.145	163.619
1000	287.148	558.243	393.133	165.109	−3298.624	−2765.994	144.481
1100	302.963	586.352	409.430	194.615	−3292.178	−2713.032	128.831
1200	318.863	613.395	425.307	225.706	−3574.631	−2653.397	115.499
1285.000	332.461	635.677	438.489	253.387	---- BETA <--> LIQUID ----		
1300	334.846	639.549	440.786	258.392	−3562.664	−2577.103	103.549
1400	350.870	664.950	455.895	292.678	−3549.161	−2501.787	93.343
1500	366.895	689.704	470.661	328.566	−3534.115	−2427.490	84.533

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K)$ = [286.058] $J·K^{-1}·mol^{-1}$
$T_{fus}(\beta \rightarrow l)$ = 1285 ± 3 K

$\Delta_f H°(298.15\ K)$ = [−3246.472] $kJ·mol^{-1}$
$\Delta_{fus}H°(\beta \rightarrow l)$ = 110.039 ± 5.0 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_3AlF_6, 1298.15\ K)$ is calculated from $\Delta_f H°(Na_3AlF_6, cr, \beta, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1285\ K) - H°(298.15\ K)$, between the β–crystal and liquid.[1]

Hong and Kleppa,[2] using a twin micro calorimeter, have determined the enthalpy of mixing for the reaction 3 NaF(l) + AlF_3(cr) = $NaAlF_6$(l) as $\Delta_r H°(1298\ K) = -10.595 \pm 0.05$ $kcal·mol^{-1}$. When this result is combined with JANAF auxiliary data and heats of formation from 3, we obtain $\Delta_f H°(Na_3AlF_6, l, 298.15\ K) = -775.1 \pm 1.0$ $kcal·mol^{-1}$.

Yudin and Mashovets[5] studied the equilibrium reaction between water vapor and cryolite (reaction B below). Results of our analysis of these studies are given below. The average of the three experimental values, $\Delta_f H°(Na_3AlF_6, l, 298.15\ K) = -776.2 \pm 1.5$ $kcal·mol^{-1}$, is in good agreement with our adopted value.

Source	Reaction[a]	T/K	Data Points	δS $cal·K^{-1}·mol^{-1}$	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(Na_3AlF_6, l, 298.15\ K)$ $kcal·mol^{-1}$
Yudin[3] (1963)	A	1300	1	–	–	24.30 ± 2.0	−777.76 ± 2.0
Mashovets[2] (1962)	B	1286–1315	3	−6.15 ± 0.1	41.10 ± 0.1	49.12 ± 0.2	−775.67 ± 2.0

[a]Reactions:
A $Na_3AlF_6(l) = 3\ NaF(l) + AlF_3(cr)$
B $2/3\ Na_3AlF_6(l) + H_2O(g) = 1/3\ Al_2O_3(cr) + 2\ HF(g) + 2\ NaF(l)$

Heat Capacity and Entropy

The high temperature enthalpies, 1285.5–1370.5 K, were measured by O'Brien and Kelley.[6] Using their data and smoothing, we derive a constant $C_p° = 94.53\ cal·K^{-1}·mol^{-1}$ (395.514 $J·K^{-1}·mol^{-1}$) for Na_3AlF_6(l). A hypothetical glass transition is assumed at 790 K. The $C_p°$ values above 1370.5 K are obtained by linear extrapolation. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Albright[7] meaured the high temperature enthalpies of Na_3AlF_6(l) in the temperature range 1298.1–1311.8 K. His data are systematically higher (5%) than the values determined by O'Brien and Kelley. Holm and Gronvold[8] also measured enthalpies of Na_3AlF_6(l) by drop calorimetry (1290.3–1333.1 K). Their data are intermediate between that of Albright and that of O'Brien and Kelley. For reasons discussed previously (see the Na_3AlF_6(cr, β) table), we believe both sets[7,8] are biased and have not used the data in this evaluation.

Fusion Data

Refer to the β–crystal table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}mol^{-1}$		$kJ·mol^{-1}$			
0							
100							
200							
298.15	215.727	286.058	286.058	0.	−3246.472	−3095.921	542.393
300	216.212	287.394	286.062	0.400	−3246.447	−3094.987	538.885
400	236.379	352.597	294.813	23.114	−3252.764	−3044.111	397.520
500	248.634	406.524	311.917	47.304	−3250.608	−2992.175	312.590
600	262.793	453.110	331.649	72.876	−3247.240	−2940.784	256.018
700	276.822	494.674	352.020	99.858	−3246.799	−2894.239	215.971
790.000	289.366	528.901	370.246	125.337	GLASS <--> LIQUID		
790.000	395.514	528.901	370.246	125.337	TRANSITION		
800	395.514	533.876	372.260	129.292	−3235.719	−2840.082	185.438
836.000	395.514	551.285	379.597	143.531	---- ALPHA <--> BETA ----		
900	395.514	580.461	392.856	168.844	−3218.933	−2791.638	162.022
1000	395.514	622.132	413.737	208.395	−3213.029	−2744.289	143.347
1100	395.514	659.829	434.423	247.946	−3196.537	−2698.214	128.128
1200	395.514	694.243	454.661	287.498	−3470.530	−2646.313	115.191
1285.000	395.514	721.311	471.415	321.116	---- BETA <--> LIQUID ----		
1300	395.514	725.901	474.324	327.049	−3451.697	−2578.393	103.601
1400	395.514	755.211	493.354	366.600	−3432.929	−2511.920	93.721
1500	395.514	782.499	511.731	406.152	−3414.220	−2446.787	85.205
1600	395.514	808.025	529.460	445.703	−3395.566	−2382.900	77.794
1700	395.514	832.003	546.559	485.254	−3376.962	−2320.178	71.290
1800	395.514	854.610	563.051	524.806	−3358.402	−2258.550	65.541
1900	395.514	875.994	578.964	564.357	−3339.880	−2197.953	60.426
2000	395.514	896.281	594.327	603.909	−3321.387	−2138.329	55.847
2100	395.514	915.578	609.169	643.460	−3302.915	−2079.631	51.728
2200	395.514	933.978	623.518	683.011	−3284.455	−2021.812	48.004
2300	395.514	951.559	637.401	722.563	−3265.996	−1964.832	44.623
2400	395.514	968.392	650.844	762.114	−3247.531	−1908.656	41.541
2500	395.514	984.537	663.871	801.665	−3229.049	−1853.249	38.722
2600	395.514	1000.050	676.505	841.217	−3210.544	−1798.582	36.134
2700	395.514	1014.977	688.766	880.768	−3192.008	−1744.628	33.752
2800	395.514	1029.360	700.675	920.319	−3467.335	−1690.393	31.535
2900	395.514	1043.240	712.250	959.871	−3447.624	−1627.279	29.310
3000	395.514	1056.648	723.507	999.422	−3427.867	−1564.845	27.246

PREVIOUS: December 1968 CURRENT: December 1979

CRYSTAL(α-β)–LIQUID

0 to 836 K	crystal, alpha
836 to 1285 K	crystal, beta
above 100285 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−38.095	−3304.649	−3304.649	INFINITE
100	100.039	62.287	402.572	−34.028	−3313.806	−3261.080	1703.414
200	179.033	159.302	257.165	−19.573	−3317.306	−3206.528	837.459
298.15	215.727	238.467	238.467	0.	−3316.908	−3152.168	552.247
300	216.212	239.803	238.471	0.400	−3316.883	−3151.146	548.663
400	236.379	305.007	247.223	23.114	−3323.200	−3095.511	404.232
500	248.634	358.934	264.326	47.304	−3321.044	−3038.816	317.463
600	262.793	405.519	284.058	72.876	−3317.675	−2982.666	259.664
700	276.822	447.083	304.429	99.858	−3313.053	−2927.179	218.429
800	290.780	484.959	324.661	128.238	−3307.209	−2872.439	187.551
836.000	295.809	497.868	331.843	138.797	ALPHA <--> BETA		
836.000	261.500	509.179	331.843	148.253	TRANSITION		
900	271.458	528.831	345.157	165.307	−3292.905	−2819.145	163.619
1000	287.148	558.243	365.007	193.236	−3298.624	−2765.994	144.481
1100	302.963	586.352	383.860	222.741	−3292.178	−2713.032	128.831
1200	318.863	613.395	401.868	253.832	−3574.631	−2653.397	115.499
1285.000	332.461	635.677	416.601	281.513	BETA <--> LIQUID		
1285.000	395.514	721.311	416.601	391.552	TRANSITION		
1300	395.514	725.901	420.143	397.485	−3451.697	−2578.392	103.601
1400	395.514	755.211	443.043	437.036	−3432.929	−2511.920	93.721
1500	395.514	782.499	464.774	476.588	−3414.220	−2446.787	85.205
1600	395.514	808.025	485.438	516.139	−3395.566	−2382.900	77.794
1700	395.514	832.003	505.126	555.690	−3376.962	−2320.178	71.290
1800	395.514	854.610	523.920	595.242	−3358.402	−2258.550	65.541
1900	395.514	875.994	541.892	634.793	−3339.880	−2197.953	60.426
2000	395.514	896.281	559.109	674.345	−3321.387	−2138.329	55.847
2100	395.514	915.578	575.628	713.896	−3302.915	−2079.631	51.728
2200	395.514	933.978	591.502	753.447	−3284.454	−2021.812	48.004
2300	395.514	951.559	606.777	792.999	−3265.996	−1964.832	44.623
2400	395.514	968.392	621.496	832.550	−3247.531	−1908.656	41.541
2500	395.514	984.537	635.697	872.101	−3229.049	−1853.249	38.722
2600	395.514	1000.050	649.414	911.653	−3210.544	−1798.582	36.134
2700	395.514	1014.977	662.679	951.204	−3192.008	−1744.628	33.752
2800	395.514	1029.360	675.519	990.755	−3467.335	−1690.393	31.535
2900	395.514	1043.240	687.961	1030.307	−3447.624	−1627.278	29.310
3000	395.514	1056.648	700.029	1069.858	−3427.867	−1564.845	27.246

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = 187.86 \pm 0.5\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 259.5 \pm 20\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 259.4 \pm 20\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 1682.56\ cm^{-1}$ $\omega_e x_e = 29.09\ cm^{-1}$ $\sigma = 1$
$B_e = 6.3907\ cm^{-1}$ $\alpha_e = 0.1858\ cm^{-1}$ $r_e = 1.6477$ Å

Enthalpy of Formation

Gaydon[1] extrapolated the available $X^1\Sigma$ vibrational levels, also considered predissociation in the A^1 state and concluded that the best value of $D_0°$ was 2.9 ± 0.2 ev. The linear Birge–Sponer extrapolation gave a value of 3.05 ev while the predissociation limit was 3.07 ev. The value recommended by Gaydon[1] is adopted here and leads to a value of $\Delta_f H°$(AlH, g, 298.15 K) = 62.16 ± 0 5.0 kcal·mol^{-1}, using JANAF auxiliary data.

Heat Capacity and Entropy

Zeeman and Ritter[2] examined the UV band system of AlH under high resolution and reported the molecular constants adopted above.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.669	259.512	259.512	INFINITE
100	29.124	156.000	213.828	−5.783	260.415	250.550	−130.874
200	29.154	176.194	190.540	−2.869	260.180	240.711	−62.867
250	29.220	182.705	188.346	−1.410	259.827	235.882	−49.285
298.15	29.373	187.864	187.864	0.	259.408	231.308	−40.524
300	29.381	188.045	187.864	0.054	259.391	231.133	−40.244
350	29.658	192.594	188.223	1.530	258.907	226.462	−33.798
400	30.041	196.578	189.023	3.022	258.397	221.861	−28.972
450	30.498	200.142	190.064	4.535	257.877	217.325	−25.226
500	30.996	203.381	191.236	6.072	257.354	212.848	−22.236
600	32.008	209.122	193.751	9.223	256.304	204.045	−17.764
700	32.942	214.128	196.312	12.471	255.236	195.419	−14.582
800	33.754	218.581	198.822	15.807	254.115	186.949	−12.207
900	34.441	222.597	201.244	19.218	252.897	178.626	−10.367
1000	35.018	226.257	203.565	22.692	240.954	171.204	−8.943
1100	35.505	229.618	205.783	26.218	239.786	164.286	−7.801
1200	35.917	232.725	207.900	29.790	238.643	157.473	−6.855
1300	36.271	235.615	209.922	33.400	237.518	150.755	−6.057
1400	36.577	238.314	211.855	37.043	236.403	144.123	−5.377
1500	36.844	240.847	213.704	40.714	235.296	137.570	−4.791
1600	37.081	243.232	215.476	44.410	234.191	131.091	−4.280
1700	37.293	245.487	217.176	48.129	233.089	124.681	−3.831
1800	37.484	247.624	218.808	51.868	231.985	118.336	−3.434
1900	37.658	249.655	220.379	55.626	230.881	112.052	−3.081
2000	37.818	251.591	221.891	59.399	229.775	105.826	−2.764
2100	37.966	253.440	223.350	63.189	228.667	99.656	−2.479
2200	38.104	255.209	224.758	66.992	227.556	93.539	−2.221
2300	38.234	256.906	226.119	70.809	226.442	87.472	−1.987
2400	38.356	258.536	227.436	74.639	225.326	81.454	−1.773
2500	38.473	260.104	228.712	78.480	224.207	75.482	−1.577
2600	38.584	261.615	229.948	82.333	223.086	69.555	−1.397
2700	38.691	263.073	231.148	86.197	221.963	63.671	−1.232
2800	38.793	264.482	232.314	90.071	−73.064	58.797	−1.097
2900	38.893	265.845	233.447	93.955	−73.096	63.507	−1.144
3000	38.989	267.165	234.549	97.850	−73.130	68.218	−1.188
3100	39.082	268.445	235.622	101.753	−73.166	72.930	−1.229
3200	39.174	269.688	236.667	105.666	−73.205	77.644	−1.267
3300	39.263	270.894	237.686	109.588	−73.245	82.358	−1.304
3400	39.350	272.068	238.680	113.518	−73.288	87.074	−1.338
3500	39.435	273.210	239.650	117.458	−73.333	91.791	−1.370
3600	39.520	274.322	240.598	121.406	−73.380	96.510	−1.400
3700	39.602	275.406	241.524	125.362	−73.430	101.230	−1.429
3800	39.684	276.463	242.430	129.326	−73.483	105.951	−1.456
3900	39.764	277.495	243.316	133.298	−73.540	110.674	−1.482
4000	39.844	278.503	244.183	137.279	−73.600	115.398	−1.507
4100	39.922	279.487	245.032	141.267	−73.664	120.124	−1.530
4200	40.000	280.450	245.864	145.263	−73.732	124.851	−1.553
4300	40.077	281.393	246.679	149.267	−73.805	129.580	−1.574
4400	40.154	282.315	247.479	153.279	−73.883	134.311	−1.594
4500	40.229	283.218	248.263	157.298	−73.965	139.043	−1.614
4600	40.305	284.103	249.032	161.324	−74.055	143.778	−1.633
4700	40.379	284.971	249.788	165.359	−74.152	148.514	−1.651
4800	40.454	285.821	250.530	169.400	−74.256	153.253	−1.668
4900	40.527	286.656	251.259	173.449	−74.367	157.994	−1.684
5000	40.601	287.476	251.975	177.506	−74.488	162.737	−1.700
5100	40.674	288.281	252.679	181.570	−74.618	167.483	−1.715
5200	40.746	289.071	253.371	185.641	−74.758	172.231	−1.730
5300	40.819	289.848	254.052	189.719	−74.909	176.982	−1.744
5400	40.891	290.612	254.722	193.804	−75.071	181.737	−1.758
5500	40.963	291.363	255.381	197.897	−75.246	186.494	−1.771
5600	41.034	292.101	256.030	201.997	−75.433	191.254	−1.784
5700	41.106	292.828	256.670	206.104	−75.634	196.018	−1.796
5800	41.177	293.544	257.299	210.218	−75.846	200.786	−1.808
5900	41.247	294.248	257.920	214.339	−76.076	205.557	−1.820
6000	41.318	294.942	258.531	218.467	−76.300	210.331	−1.831

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 215.3 \pm 2.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [37.6 \pm 84]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [33.5 \pm 84]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[900] (1)
[1000] (2)
[1600] (1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Al–O = [1.62] Å; A–H = [1.64] Å
Bond Angle: H–Al–O = [180]°
B_0 = [0.538347] cm^{-1}

Enthalpy of Formation

The enthalpy of formation is estimated by summing the constituent bond energies. The Al=O was taken as that in AlO(g) and the Al–H bond was taken as that in AlH(g); this gave a heat of atomization of 182 kcal·mol^{-1}.

Heat Capacity and Entropy

Vibrational frequencies, bond lengths and angles and point group are taken from NBS.[1]

References

[1]U. S. Nat. Bur. Stand. Report 6297, 148 pp. (January 1, 1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.018	37.569	37.569	INFINITE
100	29.106	182.067	243.166	−6.110	37.041	33.235	−17.360
200	30.298	202.437	218.263	−3.165	35.382	30.013	−7.839
250	32.196	209.387	215.811	−1.606	34.400	28.784	−6.014
298.15	34.569	215.256	215.256	0.	33.472	27.787	−4.868
300	34.666	215.470	215.257	0.064	33.437	27.752	−4.832
350	37.323	221.013	215.688	1.864	32.539	26.876	−4.011
400	39.919	226.168	216.680	3.795	31.722	26.124	−3.411
450	42.325	231.011	218.006	5.852	30.987	25.469	−2.956
500	44.491	235.584	219.537	8.024	30.327	24.892	−2.600
600	48.094	244.029	222.927	12.661	29.184	23.916	−2.082
700	50.851	251.659	226.496	17.614	28.194	23.118	−1.725
800	52.953	258.593	230.081	22.809	27.263	22.457	−1.466
900	54.567	264.927	233.606	28.189	26.312	21.912	−1.272
1000	55.822	270.744	237.033	33.711	14.685	22.238	−1.162
1100	56.810	276.112	240.345	39.344	13.870	23.033	−1.094
1200	57.598	281.091	243.536	45.066	13.103	23.901	−1.040
1300	58.235	285.727	246.605	50.859	12.369	24.830	−0.998
1400	58.755	290.062	249.556	56.709	11.655	25.816	−0.963
1500	59.186	294.131	252.393	62.607	10.953	26.852	−0.935
1600	59.545	297.963	255.123	68.544	10.256	27.934	−0.912
1700	59.847	301.582	257.750	74.514	9.558	29.061	−0.893
1800	60.105	305.010	260.281	80.512	8.856	30.228	−0.877
1900	60.325	308.266	262.722	86.534	8.147	31.434	−0.864
2000	60.514	311.365	265.077	92.576	7.428	32.679	−0.853
2100	60.679	314.322	267.352	98.636	6.697	33.959	−0.845
2200	60.823	317.148	269.552	104.711	5.954	35.275	−0.838
2300	60.949	319.854	271.681	110.800	5.197	36.625	−0.832
2400	61.061	322.451	273.742	116.900	4.425	38.007	−0.827
2500	61.160	324.945	275.741	123.011	3.639	39.423	−0.824
2600	61.248	327.346	277.680	129.132	2.837	40.870	−0.821
2700	61.327	329.659	279.562	135.261	2.020	42.348	−0.819
2800	61.397	331.891	281.392	141.397	−292.713	44.825	−0.836
2900	61.461	334.046	283.170	147.540	−292.466	56.875	−1.024
3000	61.519	336.131	284.901	153.689	−292.233	68.918	−1.200
3100	61.571	338.149	286.586	159.844	−292.017	80.953	−1.364
3200	61.619	340.104	288.229	166.003	−291.815	92.980	−1.518
3300	61.662	342.001	289.829	172.167	−291.629	105.002	−1.662
3400	61.702	343.843	291.391	178.335	−291.458	117.019	−1.798
3500	61.738	345.632	292.915	184.507	−291.302	129.030	−1.926
3600	61.772	347.371	294.404	190.683	−291.161	141.038	−2.046
3700	61.803	349.064	295.859	196.862	−291.036	153.041	−2.161
3800	61.831	350.713	297.280	203.043	−290.926	165.042	−2.269
3900	61.858	352.319	298.671	209.228	−290.831	177.041	−2.371
4000	61.882	353.886	300.032	215.415	−290.752	189.036	−2.469
4100	61.905	355.414	301.364	221.604	−290.689	201.030	−2.561
4200	61.926	356.906	302.669	227.796	−290.643	213.022	−2.649
4300	61.945	358.363	303.947	233.989	−290.613	225.014	−2.733
4400	61.964	359.788	305.200	240.185	−290.600	237.005	−2.814
4500	61.981	361.181	306.429	246.382	−290.603	248.996	−2.890
4600	61.997	362.543	307.634	252.581	−290.626	260.987	−2.964
4700	62.012	363.876	308.817	258.781	−290.668	272.979	−3.034
4800	62.026	365.182	309.977	264.983	−290.729	284.972	−3.101
4900	62.040	366.461	311.117	271.187	−290.810	296.967	−3.166
5000	62.052	367.715	312.236	277.391	−290.913	308.964	−3.228
5100	62.064	368.944	313.336	283.597	−291.038	320.962	−3.287
5200	62.075	370.149	314.417	289.804	−291.186	332.963	−3.345
5300	62.086	371.331	315.480	296.012	−291.359	344.968	−3.400
5400	62.096	372.492	316.525	302.221	−291.557	356.976	−3.453
5500	62.105	373.632	317.553	308.431	−291.781	368.987	−3.504
5600	62.114	374.751	318.565	314.642	−292.033	381.004	−3.554
5700	62.122	375.850	319.560	320.854	−292.314	393.025	−3.602
5800	62.130	376.931	320.540	327.067	−292.621	405.051	−3.648
5900	62.138	377.993	321.505	333.280	−292.962	417.082	−3.693
6000	62.145	379.037	322.455	339.494	−293.314	429.118	−3.736

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

Aluminum Hydroxide (AlOH) IDEAL GAS M_r = 43.98888

$S°(298.15\ K) = [216.4 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-175.6 \pm 13]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-179.9 \pm 13]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1000](1)
[1300](2)
[3600](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Al–O = [1.87] Å; O–H = [0.96] Å
Bond Angle: Al–O–H = [180]°
Rotational Constant: B_0 = [0.425629] cm^{-1}

Enthalpy of Formation

From a mass–spectrometric investigation of the equilibrium 1/3 Al_2O_3(cr) + 1/3 Al(g) + 1/2 D_2(g) = AlOD(g), Farber *et al.*[1] report second law heats of reaction of 56.7 + 0.6 kcal·mol^{-1} at 1980 K, 57.1 ± 2.8 kcal·mol^{-1} at 2060 K and 62.7 ± 1.4 kcal·mol^{-1} at 2000 K. Using JANAF auxiliary data, assuming AlOD to be AlOH, we obtain $\Delta_f H°$(AlOD, g, 298.15 K) = −44.6 ± 1, −44.0 ± 3.2 and −38.6 ± 1.8 kcal·mol^{-1}. A second equilibrium in the same investigation was Al_2O(g) + D_2O(g) = 2 AlOD(g). for which second law heats of reaction of 6.3 ± 2.1 kcal·mol^{-1} at 2060 K and 5.7 ± 0.8 kcal·mol^{-1} at 2000 K were reported. Farber *et al.*[1] also measured the heat of reaction 1/3 Al_2O_3(cr) + 4/3 Al(g) = Al_2O(g) at the same temperatures as −10.7 ± 2.8 kcal·mol^{-1} at 2060° and −10.3 ± 10.2 kcal·mol^{-1} at 2000 K. Combining these reactions and eliminating Al_2O(g) yields $\Delta_f H°$(2060 K) = −4.4 ± 5.0 kcal·mol^{-1} and $\Delta H°$(2000 K) = −5 ± 11 kcal·mol^{-1} for the reaction 1/3 Al_2O_3(cr) + 4/3 Al(g) + 2 AlOD(g).

Using auxiliary JANAF values for Al_2O_3(cr) and Al(g), $\Delta_f H°$(D_2O, g, 298.15 K) = −59.56 kcal·mol^{-1} [2] and functions for D_2O(g) from Friedman and Haar,[3] we obtain $\Delta_f H°$(AlOD, g, 298.15 K) = −43.9 ± 6 kcal·mol^{-1} and −43.4 ± 3 kcal·mol^{-1}. From all the above results we adopt a value of $\Delta_f H°$(AlOD, g, 298.15 K) = −44 ± 3 kcal·mol^{-1}, assuming that AlOH is less stable than AlOD by 1 kcal·mol^{-1} as is the case for H_2O, HDO and D_2O, we obtain $\Delta_f H°$(AlOH, g, 298.15 K) = −43 ± 3 kcal·mol^{-1}.

Farber *et al.*[1] also performed weight loss experiments under molecular flow conditions by allowing hydrogen to flow over Al_2O_3(cr). The products assumed were AlOH(g), Al(g), Al_2O(g), H(g) and H_2O(g) and the equilibrium amounts of H(g), Al(g) and Al_2O(g) were assumed to be those predicted by the free energies from the JANAF tables. A 3rd law analysis of the equilibrium constants given by Farber for the reaction 2 H_2(g) + Al_2O_3(cr) = 2 AlOH(g) + H_2O(g) yields $\Delta_f H°$(298.15 K) = 238 ± 12 kcal·mol^{-1} and $\Delta_f H°$(AlOH, g, 298.15 K) = −52 ± 6 kcal·mol^{-1}. However, the assumed equilibria involving Al_2O(g) and Al(g) may be significantly in error and thus the $\Delta_f H°$(298.15 K) should be considered as simply confirming the magnitude determined mass–spectrometrically.

Heat Capacity and Entropy

The vibrational frequencies are estimated by using the AlO(g) fundamental as approximately the Al–O stretch; the O–H stretch is that in H_2O(g); and the bending frequency is approximately the OH bend in CD_3OH(g) reported by Shimanouchi.[4]

The AlO bond length was taken from NBS,[5] and the OH bond length is assumed to be that in H_2O(g). The bond angle is assumed to be 180° using the prediction of Walsh[6] for "HAB" molecules with less than 11 valence electrons. Confirmation of this prediction is scanty for molecules having A more electronegative than B; however, Kuczkowski *et al.*[7] confirmed the linearity of KOH and CsOH which have B valence electrons.

References

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[2] U. S. Nat. Bur. Stand. Tech. Note 270–1, 124 pp. (1965).
[3] A. S. Friedman and L. Haar, J. Chem. Phys. **22**, 2051 (1954).
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[6] A. D. Walsh, J. Chem. Soc. **1953**, 2288.
[7] R. L. Kuczkowski, D. R. Lide, Jr., and L. C. Krishner, J. Chem. Phys. **44**, 3131 (1966).

Aluminum Hydroxide (AlOH) $Al_1H_1O_1$(g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.830	−175.627	−175.627	INFINITE
100	29.101	184.020	243.238	−5.922	−176.155	−180.156	94.104
200	29.550	204.257	219.257	−3.000	−177.837	−183.570	47.944
250	30.503	210.942	216.947	−1.501	−178.879	−184.884	38.629
298.15	31.918	216.430	216.430	0.	−179.912	−185.947	32.577
300	31.979	216.628	216.431	0.059	−179.952	−185.984	32.383
350	33.772	221.689	216.826	1.702	−181.006	−186.906	27.894
400	35.672	226.323	217.728	3.438	−182.019	−187.679	24.508
450	37.532	230.633	218.925	5.269	−182.981	−188.328	21.861
500	39.273	234.678	220.300	7.189	−183.892	−188.873	19.731
600	42.302	242.116	223.327	11.273	−185.588	−189.708	16.516
700	44.763	248.828	226.499	15.631	−187.174	−190.268	14.198
800	46.782	254.941	229.678	20.211	−188.719	−190.604	12.445
900	48.471	260.552	232.801	24.976	−190.285	−190.747	11.071
1000	49.912	265.735	235.838	29.897	−202.512	−189.951	9.922
1100	51.158	270.552	238.778	34.952	−203.907	−188.626	8.957
1200	52.245	275.051	241.615	40.123	−205.224	−187.179	8.148
1300	53.200	279.271	244.351	45.397	−206.477	−185.624	7.458
1400	54.041	283.245	246.989	50.759	−207.679	−183.974	6.864
1500	54.784	287.000	249.532	56.201	−208.836	−182.241	6.346
1600	55.442	290.557	251.986	61.713	−209.959	−180.431	5.890
1700	56.026	293.936	254.355	67.287	−211.052	−178.552	5.486
1800	56.546	297.153	256.644	72.916	−212.123	−176.609	5.125
1900	57.010	300.223	258.857	78.595	−213.176	−174.607	4.800
2000	57.424	303.158	261.000	84.317	−214.215	−172.550	4.507
2100	57.796	305.969	263.075	90.078	−215.245	−170.441	4.239
2200	58.130	308.665	265.086	95.875	−216.267	−168.284	3.996
2300	58.430	311.256	267.037	101.703	−217.284	−166.080	3.772
2400	58.702	313.749	268.932	107.560	−218.300	−163.832	3.566
2500	58.948	316.150	270.773	113.442	−219.314	−161.542	3.375
2600	59.171	318.466	272.563	119.348	−220.330	−159.211	3.199
2700	59.373	320.703	274.305	125.276	−221.349	−156.841	3.034
2800	59.558	322.866	276.001	131.223	−516.272	−153.465	2.863
2900	59.727	324.959	277.653	137.187	−516.203	−140.509	2.531
3000	59.882	326.987	279.264	143.167	−516.139	−127.555	2.221
3100	60.023	328.952	280.835	149.163	−516.081	−114.603	1.931
3200	60.154	330.860	282.369	155.172	−516.030	−101.653	1.659
3300	60.274	332.713	283.867	161.193	−515.987	−88.705	1.404
3400	60.385	334.514	285.330	167.226	−515.951	−75.757	1.164
3500	60.487	336.266	286.760	173.270	−515.923	−62.811	0.937
3600	60.582	337.971	288.159	179.323	−515.905	−49.865	0.724
3700	60.670	339.632	289.528	185.386	−515.895	−36.920	0.521
3800	60.752	341.251	290.868	191.457	−515.896	−23.974	0.330
3900	60.828	342.831	292.180	197.536	−515.907	−11.029	0.148
4000	60.899	344.371	293.466	203.623	−515.928	1.917	−0.025
4100	60.965	345.876	294.726	209.716	−515.962	14.863	−0.189
4200	61.027	347.346	295.961	215.815	−516.007	27.811	−0.346
4300	61.085	348.783	297.173	221.921	−516.065	40.760	−0.495
4400	61.139	350.188	298.362	228.032	−516.137	53.710	−0.638
4500	61.190	351.562	299.529	234.149	−516.220	66.661	−0.774
4600	61.238	352.908	300.675	240.270	−516.320	79.615	−0.904
4700	61.283	354.225	301.800	246.396	−516.437	92.572	−1.029
4800	61.325	355.516	302.906	252.527	−516.570	105.531	−1.148
4900	61.365	356.781	303.993	258.661	−516.719	118.493	−1.263
5000	61.403	358.021	305.061	264.800	−516.888	131.458	−1.373
5100	61.439	359.237	306.111	270.942	−517.077	144.427	−1.479
5200	61.472	360.430	307.144	277.087	−517.287	157.399	−1.581
5300	61.504	361.602	308.161	283.236	−517.519	170.377	−1.679
5400	61.535	362.752	309.161	289.388	−517.774	183.358	−1.774
5500	61.563	363.881	310.146	295.543	−518.053	196.344	−1.865
5600	61.591	364.990	311.115	301.701	−518.358	209.336	−1.953
5700	61.616	366.081	312.070	307.861	−518.690	222.334	−2.037
5800	61.641	367.153	313.011	314.024	−519.048	235.337	−2.119
5900	61.664	368.207	313.937	320.189	−519.437	248.346	−2.199
6000	61.687	369.243	314.850	326.357	−519.835	261.361	−2.275

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = [228.7 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [541.9 \pm 109]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [543.920]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[900](1)
[1100](2)
[3600](1)

Ground State Quantum Weight: [4] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Al–O = [1.90] Å; O–H = [0.96] Å
Bond Angle: Al–O–H = [180]°
Rotational Constant: B_0 = [0.412959] cm^{-1}

Enthalpy of Formation

The enthalpy of formation is obtained from $\Delta_f H°$(AlOH, g, 298.15 K) and its ionization potential, which is estimated to be 7.5 ± 1 eV (173 ± 23 kcal·mol^{-1}). The ionization potential is estimated from a reported value of 7.5 eV for the appearance potential of AlOD$^+$, presumably from the parent AlOD, by Farber *et al.*[1]

Heat Capacity and Entropy

According to the correlation diagram given by Walsh[2] for "HAB" molecules, a compound with 9 valence electrons would have the three outermost electrons is an unfilled Π orbital. Thus, it would be a $^2\Pi$ state since the molecule ought to be linear if it has less than 11 valence electrons. The outermost orbital is a bonding orbital and thus the loss of an electron from it would weaken the bonding. The vibrational frequencies are estimated from those for AlOH(g) with somewhat lower frequencies due to the weaker bonding. Similarly, the Al–O bond length is slightly increased over that in AlOH(g).

References

[1] M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, Space Sciences, Inc., Final Report, USAF contract F04611–67–C–0010, AFRPL–TR–67–144, (November 1967).
[2] A. D. Walsh, J. Chem. Soc. **1953**, 2288.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.947	541.890		
100	29.104	195.798	256.187	−6.039			
200	30.021	216.119	231.632	−3.103			
250	31.562	222.970	229.234	−1.566			
298.15	33.535	228.693	228.693	0.	543.920	527.974	−92.499
300	33.616	228.901	228.694	0.062	543.922	527.875	−91.911
350	35.837	234.250	229.111	1.798	544.000	525.195	−78.381
400	37.986	239.177	230.066	3.645	544.136	522.500	−68.232
450	39.947	243.766	231.336	5.594	544.333	519.784	−60.335
500	41.684	248.067	232.796	7.636	544.582	517.044	−54.015
600	44.529	255.930	236.009	11.953	545.198	511.480	−44.528
700	46.724	262.966	239.367	16.520	545.900	505.806	−37.744
800	48.476	269.324	242.720	21.283	546.616	500.029	−32.649
900	49.928	275.119	246.003	26.205	547.286	494.165	−28.681
1000	51.167	280.446	249.184	31.261	537.272	488.990	−25.542
1100	52.245	285.374	252.253	36.433	538.074	484.124	−22.989
1200	53.191	289.961	255.207	41.706	538.936	479.182	−20.858
1300	54.029	294.253	258.047	47.068	539.850	474.166	−19.052
1400	54.771	298.284	260.778	52.508	540.805	469.077	−17.501
1500	55.432	302.086	263.407	58.019	541.795	463.920	−16.155
1600	56.020	305.683	265.938	63.592	542.813	458.695	−14.975
1700	56.544	309.095	268.377	69.221	543.852	453.406	−13.931
1800	57.013	312.341	270.730	74.899	544.909	448.055	−13.002
1900	57.432	315.434	273.002	80.622	545.979	442.645	−12.169
2000	57.809	318.390	275.198	86.384	547.059	437.178	−11.418
2100	58.147	321.219	277.323	92.182	548.145	431.658	−10.737
2200	58.451	323.931	279.380	98.013	549.235	426.085	−10.117
2300	58.726	326.536	281.374	103.872	550.327	420.463	−9.549
2400	58.975	329.040	283.308	109.757	551.419	414.793	−9.028
2500	59.200	331.452	285.186	115.666	552.509	409.078	−8.547
2600	59.405	333.778	287.010	121.596	553.596	403.319	−8.103
2700	59.591	336.024	288.784	127.546	554.678	397.519	−7.690
2800	59.761	338.194	290.511	133.514	261.855	392.647	−7.325
2900	59.917	340.294	292.191	139.498	264.022	397.279	−7.156
3000	60.059	342.328	293.829	145.497	266.183	401.838	−6.997
3100	60.190	344.299	295.425	151.509	268.337	406.324	−6.847
3200	60.311	346.212	296.982	157.534	270.482	410.741	−6.705
3300	60.422	348.070	298.503	163.571	272.620	415.091	−6.570
3400	60.524	349.875	299.987	169.618	274.749	419.376	−6.443
3500	60.619	351.631	301.438	175.676	276.868	423.599	−6.322
3600	60.707	353.340	302.856	181.742	278.978	427.761	−6.207
3700	60.788	355.004	304.243	187.817	281.078	431.865	−6.097
3800	60.864	356.626	305.600	193.899	283.168	435.913	−5.992
3900	60.934	358.208	306.929	199.989	285.247	439.905	−5.892
4000	61.000	359.752	308.230	206.086	287.314	443.844	−5.796
4100	61.061	361.259	309.505	212.189	289.369	447.732	−5.704
4200	61.119	362.731	310.755	218.298	291.412	451.570	−5.616
4300	61.173	364.170	311.981	224.413	293.441	455.359	−5.532
4400	61.223	365.576	313.183	230.533	295.457	459.101	−5.450
4500	61.270	366.953	314.362	236.657	297.460	462.798	−5.372
4600	61.315	368.300	315.520	242.787	299.446	466.450	−5.297
4700	61.357	369.619	316.657	248.920	301.416	470.059	−5.224
4800	61.396	370.911	317.774	255.058	303.369	473.627	−5.154
4900	61.433	372.178	318.872	261.199	305.305	477.154	−5.087
5000	61.468	373.419	319.950	267.345	307.221	480.642	−5.021
5100	61.501	374.637	321.011	273.493	309.117	484.091	−4.958
5200	61.533	375.831	322.053	279.645	310.992	487.503	−4.897
5300	61.563	377.004	323.079	285.800	312.845	490.880	−4.838
5400	61.591	378.155	324.088	291.957	314.674	494.222	−4.781
5500	61.617	379.285	325.082	298.118	316.479	497.530	−4.725
5600	61.643	380.395	326.060	304.281	318.258	500.806	−4.671
5700	61.667	381.487	327.023	310.446	320.010	504.050	−4.619
5800	61.690	382.559	327.971	316.614	321.736	507.264	−4.568
5900	61.711	383.614	328.905	322.784	323.430	510.447	−4.519
6000	61.732	384.652	329.825	328.956	325.115	513.601	−4.471

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = [239.8 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-221 \pm 95]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-230.120]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[900](1)
[1100](1)
[3600](1)

Ground State Quantum Weight: [2] $\sigma = 1$
Point Group: [C_s]
Bond Distances: Al–O = [1.90] Å; O–H = [0.96] Å
Bond Angle: Al–O–H = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.487473 \times 10^{-117}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation is obtained from $\Delta_f H°$(AlOH, g, 298.15 K) and its electron affinity, which is estimated to be 0.5 ± 0.9 eV (12 ± 20 kcal·mol^{-1}). The electron affinity is estimated to be small, or even negative, since the additional electron must go into an antibonding orbital, according to the correlation diagram of Walsh.[1]

Heat Capacity and Entropy

Since the molecule now has 11 valence electrons, the Walsh correlation diagram predicts a bent molecule. The extra electron is antibonding thus making the bonds weaker than in AlOH(g). The vibrational frequencies and bond lengths are taken to be the same as in $AlOH^+$(g), which is also less strongly bound than AlOH(g). The bond angle is arbitrarily chosen as 120°. The principal moments of inertia are $I_A = 0.1049 \times 10^{-39}$, $I_B = 6.4867 \times 10^{-39}$, and $I_C = 6.5917 \times 10^{-39}$ g·cm^2.

Reference

[1] A. D. Walsh, J. Chem. Soc. **1953**, 2288.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	*0.*	*0.*	*INFINITE*	*−10.123*	*−220.931*		
100	33.261	202.633	270.605	−6.797			
200	33.987	225.808	243.059	−3.450			
250	35.123	233.506	240.403	−1.724			
298.15	36.521	239.810	239.810	0.	−230.120	−236.871	41.499
300	36.578	240.036	239.810	0.068	−230.190	−236.912	41.250
350	38.106	245.789	240.261	1.935	−232.059	−237.885	35.502
400	39.556	250.973	241.281	3.877	−233.906	−238.591	*31.157*
450	40.861	255.709	242.625	5.888	−235.726	−239.067	27.750
500	42.009	260.075	244.155	7.960	−237.524	−239.341	25.004
600	43.887	267.908	247.476	12.259	−241.084	−239.370	20.839
700	45.359	274.788	250.896	16.724	−244.641	−238.804	17.820
800	46.572	280.926	254.273	21.322	−248.247	−237.725	15.522
900	47.619	286.473	257.548	26.033	−251.946	−236.188	13.708
1000	48.548	291.539	260.697	30.842	−266.364	−233.474	12.195
1100	49.385	296.206	263.716	35.740	−269.994	−230.008	10.922
1200	50.141	300.536	266.606	40.717	−273.584	−226.214	9.847
1300	50.826	304.577	269.373	45.766	−277.141	−222.123	8.925
1400	51.446	308.367	272.025	50.880	−280.669	−217.758	8.125
1500	52.005	311.936	274.567	56.053	−284.175	−213.142	7.422
1600	52.508	315.309	277.009	61.279	−287.661	−208.292	6.800
1700	52.962	318.506	279.357	66.553	−291.134	−203.225	6.244
1800	53.371	321.545	281.617	71.870	−294.595	−197.955	5.744
1900	53.740	324.440	283.795	77.226	−298.049	−192.491	5.292
2000	54.072	327.206	285.897	82.616	−301.498	−186.846	4.880
2100	54.372	329.851	287.928	88.039	−304.945	−181.029	4.503
2200	54.644	332.387	289.891	93.490	−308.391	−175.047	4.156
2300	54.889	334.821	291.792	98.967	−311.839	−168.909	3.836
2400	55.112	337.162	293.634	104.467	−315.289	−162.621	3.539
2500	55.315	339.416	295.421	109.989	−318.744	−156.189	3.263
2600	55.500	341.589	297.155	115.529	−322.204	−149.618	3.006
2700	55.668	343.687	298.840	121.088	−325.670	−142.915	2.765
2800	55.822	345.714	300.478	126.663	−623.043	−135.115	2.521
2900	55.963	347.676	302.072	132.252	−625.428	−117.647	2.119
3000	56.092	349.575	303.624	137.855	−627.820	−100.096	1.743
3100	56.211	351.416	305.136	143.470	−630.221	−82.466	1.390
3200	56.321	353.203	306.610	149.097	−632.631	−64.758	1.057
3300	56.422	354.938	308.048	154.734	−635.050	−46.975	0.744
3400	56.515	356.623	309.452	160.381	−637.479	−29.118	0.447
3500	56.602	358.263	310.824	166.037	−639.918	−11.189	0.167
3600	56.682	359.858	312.164	171.701	−642.367	6.809	−0.099
3700	56.756	361.413	313.474	177.373	−644.827	24.875	−0.351
3800	56.826	362.927	314.755	183.052	−647.298	43.009	−0.591
3900	*56.890*	*364.404*	*316.010*	188.738	−649.781	*61.208*	−0.820
4000	56.950	365.845	317.238	194.430	−652.276	79.469	−1.038
4100	57.007	367.252	318.440	200.128	−654.783	97.794	−1.246
4200	57.059	368.626	319.619	205.831	−657.303	116.180	−1.445
4300	57.109	369.970	320.774	211.540	−659.837	134.627	−1.635
4400	57.155	371.283	321.907	217.253	−662.385	153.131	−1.818
4500	57.198	372.568	323.019	222.971	−664.946	171.694	−1.993
4600	57.239	373.826	324.110	228.692	−667.525	190.315	−2.161
4700	57.278	375.057	325.181	234.418	−670.120	208.992	−2.323
4800	57.314	376.263	326.232	240.148	−672.732	227.724	−2.478
4900	57.348	377.445	327.266	245.881	−675.362	246.510	−2.628
5000	57.380	378.604	328.281	251.617	−678.011	265.351	−2.772
5100	57.411	379.741	329.279	257.357	−680.682	284.245	−2.911
5200	57.440	380.856	330.260	263.100	−683.373	303.191	−3.046
5300	57.467	381.950	331.225	268.845	−686.087	322.190	−3.175
5400	57.493	383.025	332.174	274.593	−688.824	341.239	−3.301
5500	57.517	384.080	333.108	280.343	−691.587	360.339	−3.422
5600	57.541	385.117	334.028	286.096	−694.375	379.491	−3.540
5700	57.563	386.135	334.933	291.851	−697.191	398.692	−3.654
5800	57.584	387.136	335.825	297.609	−700.032	417.943	−3.764
5900	57.604	388.121	336.703	303.368	−702.906	437.242	−3.871
6000	57.623	389.089	337.568	309.129	−705.789	456.589	−3.975

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = 254.4 \pm 6\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-455 \pm 63]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-460 \pm 63]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[3400](1)	[700](1)
[1200](1)	[500](1)
[1100](1)	[400](1)

Ground State Quantum Weight: 1 $\alpha = 1$
Point Group: $[C_s]$
Bond Distances: Al=O = [1.62] Å; Al–O = [1.87] Å; O–H = [0.94] Å
Bond Angles: O–Al–O = [180]°; Al–O–H = [105]°
Product of the Moments of Inertia: $I_A I_B I_C = [37.497324 \times 10^{-117}]\ gm^3 \cdot cm^6$

Enthalpy of Formation

The hydroxyl group can often be considered as intermediate between F and Cl as is illustrated by the following examples of bond energies from these tables. $D_0°$(F–H) = 136 kcal·mol^{-1}, $D_0°$(Cl–H) = 103 kcal·mol^{-1} and $D_0°$(HO–H) = 119 kcal·mol^{-1}; also, $D_0°$(F–BO) = 163 kcal·mol^{-1}, $D_0°$(Cl–BO) = 105 kcal·mol^{-1} and $D_0°$(HO–BO) = 143 kcal·mol^{-1}. Thus from $D_0°$(F–AlO) = 181 kcal·mol^{-1} and $D_0°$(Cl–AlO) = 134 kcal·mol^{-1}, we estimate $D_0°$(HO–AlO) = 158 ± 20 kcal·mol^{-1}. This yields $\Delta_f H°$(HOAlO, g, 298.15 K) = −127 ± 20 kcal·mol^{-1}.

Consider also $D_0°$(FB–O) = 175 kcal·mol^{-1} and $D_0°$(ClB–O) = 169 kcal·mol^{-1}; and $D_0°$(FAl–O) = 138 kcal·mol^{-1} and $D_0°$(ClAl–O) = 132 kcal·mol^{-1}; it is evident that the substituent F or Cl has little effect on the B–O and Al–O bonds. Thus, we assume that $D_0°$(HOAl–O) = 135 ± 10 kcal·mol^{-1} which leads to $\Delta_f H°$(HOAlO, g, 298.15 K) = −119 ± 10 kcal·mol^{-1}.

Farber *et al.*[1] found no evidence for the ion $DOAlO^+$ when reacting $D_2O(g) + Al_2O_3(cr)$. Form estimates of the pressure needed to ensure detection of DOAlO and a knowledge of the D_2O pressure, they calculated the most negative value of $\Delta_f H°$(HOAlO, g, 298.15 K) = −104 ± 10 kcal·mol^{-1}. The absence of $DOAlO^+$ may be caused by fragmentation by the ionizing electrons and thus the value quoted may not be a real limit.

We adopt $\Delta_f H°$(HOAlO, g, 298.15 K) = −110 ± 15 kcal·mol^{-1} which encompasses all the values.

Heat Capacity and Entropy

Vibrational frequencies, bond distances, bond angles, and the product of the moments of inertia are taken from NBS.[2] The principal moments of inertia are: $I_A = 0.1301 \times 10^{-39}$, $I_B = 16.9121 \times 10^{-39}$, and $I_C = 17.0422 \times 10^{-39}$ g·cm^2.

References

[1]M. Farber, M. A. Frisch, G. Grenier, and H. C. Ko, "Investigation of the Thermodynamic Properties of Rocket Combustion Products", AFRPL–TR–67–244, (November, 1967).
[2]U. S. Nat. Bur. Stand. Report 6297, 148 pp. (January 1, 1959).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.722	−454.505	−454.505	INFINITE
100	34.495	209.798	293.555	−8.376	−456.047	−453.961	237.125
200	42.414	235.968	258.738	−4.554	−458.285	−451.012	117.792
250	46.534	245.881	255.197	−2.329	−459.330	−449.071	93.828
298.15	50.137	254.391	254.391	0.	−460.240	−447.011	78.314
300	50.267	254.702	254.392	0.093	−460.273	−446.929	77.817
350	53.561	262.704	255.017	2.690	−461.111	−444.637	66.358
400	56.415	270.047	256.443	5.442	−461.856	−442.231	57.750
450	58.859	276.837	258.336	8.325	−462.524	−439.738	51.043
500	60.945	283.149	260.506	11.322	−463.130	−437.173	45.671
600	64.267	294.569	265.252	17.590	−464.220	−431.877	37.598
700	66.781	304.673	270.176	24.148	−465.234	−426.406	31.819
800	68.767	313.725	275.063	30.929	−466.247	−420.790	27.475
900	70.398	321.921	279.821	37.890	−467.320	−415.045	24.089
1000	71.774	329.412	284.411	45.000	−479.089	−408.414	21.333
1100	72.954	336.309	288.820	52.238	−480.054	−401.300	19.056
1200	73.978	342.702	293.047	59.586	−480.970	−394.099	17.155
1300	74.871	348.659	297.098	67.029	−481.845	−386.825	15.543
1400	75.653	354.237	300.983	74.556	−482.688	−379.483	14.159
1500	76.341	359.481	304.709	82.157	−483.508	−372.083	12.957
1600	76.948	364.427	308.289	89.822	−484.311	−364.629	11.904
1700	77.484	369.109	311.730	97.544	−485.102	−357.124	10.973
1800	77.959	373.551	315.042	105.317	−485.888	−349.574	10.144
1900	78.382	377.778	318.234	113.134	−486.671	−341.979	9.402
2000	78.758	381.808	321.312	120.991	−487.456	−334.343	8.732
2100	79.094	385.659	324.285	128.884	−488.247	−326.668	8.125
2200	79.396	389.345	327.160	136.809	−489.045	−318.955	7.573
2300	79.667	392.881	329.941	144.762	−489.853	−311.206	7.068
2400	79.911	396.277	332.634	152.742	−490.672	−303.421	6.604
2500	80.131	399.543	335.246	160.744	−491.505	−295.602	6.176
2600	80.330	402.690	337.780	168.767	−492.352	−287.749	5.781
2700	80.512	405.725	340.240	176.809	−493.214	−279.863	5.414
2800	80.676	408.656	342.632	184.869	−787.993	−270.977	5.055
2900	80.827	411.490	344.957	192.944	−787.792	−252.517	4.548
3000	80.964	414.232	347.221	201.034	−787.607	−234.062	4.075
3100	81.090	416.889	349.426	209.137	−787.440	−215.613	3.633
3200	81.206	419.466	351.575	217.251	−787.290	−197.170	3.218
3300	81.313	421.966	353.670	225.377	−787.157	−178.731	2.829
3400	81.411	424.395	355.715	233.514	−787.042	−160.295	2.463
3500	81.501	426.756	357.711	241.659	−786.945	−141.863	2.117
3600	81.585	429.053	359.661	249.814	−786.865	−123.433	1.791
3700	81.663	431.290	361.567	257.976	−786.803	−105.006	1.482
3800	81.735	433.469	363.430	266.146	−786.759	−86.579	1.190
3900	81.802	435.593	365.253	274.323	−786.732	−68.153	0.913
4000	81.865	437.665	367.038	282.506	−786.725	−49.729	0.649
4100	81.923	439.687	368.785	290.696	−786.736	−31.304	0.399
4200	81.978	441.662	370.497	298.891	−786.767	−12.878	0.160
4300	82.029	443.591	372.175	307.091	−786.817	5.549	−0.067
4400	82.077	445.477	373.819	315.297	−786.888	23.976	−0.285
4500	82.121	447.322	375.432	323.507	−786.976	42.405	−0.492
4600	82.164	449.128	377.015	331.721	−787.089	60.837	−0.691
4700	82.203	450.895	378.568	339.939	−787.224	79.272	−0.881
4800	82.240	452.626	380.093	348.161	−787.383	97.710	−1.063
4900	82.276	454.322	381.590	356.387	−787.565	116.151	−1.238
5000	82.309	455.985	383.062	364.616	−787.774	134.597	−1.406
5100	82.340	457.615	384.508	372.849	−788.010	153.047	−1.568
5200	82.370	459.214	385.929	381.084	−788.274	171.500	−1.723
5300	82.398	460.784	387.327	389.323	−788.567	189.961	−1.872
5400	82.424	462.324	388.701	397.564	−788.893	208.426	−2.016
5500	82.449	463.837	390.054	405.808	−789.250	226.898	−2.155
5600	82.473	465.323	391.384	414.054	−789.642	245.378	−2.289
5700	82.496	466.783	392.694	422.302	−790.071	263.864	−2.418
5800	82.517	468.217	393.984	430.553	−790.534	282.358	−2.543
5900	82.538	469.628	395.254	438.806	−791.040	300.859	−2.664
6000	82.557	471.016	396.506	447.060	−791.565	319.369	−2.780

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [87.86 \pm 0.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) =$ Unknown

$\Delta_f H°(298.15\ K) = -117.15 \pm 8.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heats of solution of $LiAlH_4$(cr) in HCl(aq) were measured calorimetrically by Davis *et al.*,[1] Fasolino *et al.*,[2] and Smith and Bass.[3] The results are given in the following table.

Source	Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}
Davis *et al.*[1]	(1) $LiAlH_4$(cr) + 10 HCl(aq, 50 H_2O) → [LiCl + $AlCl_3$ + 6 HCl](aq, 500 H_2O) + 4 H_2(g)	−165.87
	(2) [$AlCl_3$ + LiCl + 6 HCl](aq, 500 H_2O) + 41020 H_2O(l) → [$AlCl_3$ + LiCl + 6 HCl](aq, 41520 H_2O)	−4.43
	(3) [$AlCl_3$ + LiCl + 6 HCl](aq, 41520 H_2O) → [$AlCl_3$ + LiCl + 6 HCl](aq, 5190 H_2O)	0.00(assumed)
	(1) + (2) + (3)	−170.30
Fasolino *et al.*[2]	(4) Al + 60 HCl(aq, 14 H_2O) → [$AlCl_3$ + 57 HCl](aq, 840 H_2O) + 3/2 H_2(g)	−128.14
	(5) Li + 60 HCl(aq, 14 H_2O) → [LiCl + 59 HCl](aq, 840 H_2O) + 1/2 H_2(g)	−67.05
	(6) $LiAlH_4$(cr) + 60 HCl(aq, 14 H_2O) → [LiCl + $AlCl_3$ + 56 HCl](aq, 840 H_2O) + 4 H_2(g)	−170.52
	(4) + (5) − (6)	−24.67
Smith and Bass[3]	(7) $LiAlH_4$(cr) + 39.715 HCl(aq, 11.624 H_2O) → [LiCl + $AlCl_3$ + 35.715 HCl](aq, 12.926 H_2O) + 4 H_2(g)	−164.6
	(8) LiCl(cr) + [$AlCl_3$ + 35.715 HCl](aq, 12.926 H_2O) → [LiCl + $AlCl_3$ + 35.715 HCl](aq, 12.926 H_2O)	−6.75
	(7) − (8)	−157.85

Incorporating appropriate thermal data, the values for $\Delta_f H°(LiAlH_4, cr, 298.15\ K)$ were derived as −28.51 (recalculated value, by Smith and Bass),[3] −24.67 ± 1.31 and −28.4 ± 1.5 kcal·mol^{-1}, respectively. The adopted value, −28.0 ± 2.0 kcal·mol^{-1} (−117.152 ± 8.4 kJ·mol^{-1}), is the weighted average of the above three values.

Heat Capacity and Entropy

Bonnetot *et al.*[4] measured $C_p°$ in the region 15 to 308 K. Our adopted thermal functions at 300 K and below are based on the smoothed values and integration by those authors using $S°(15\ K) = 0.10\ J \cdot K^{-1} \cdot mol^{-1}$. Above 300 K we have used $C_p°$ values estimated by comparison with those for $LiBH_4$(cr), $LiBO_2$(cr) and $LiAlO_2$(cr).[5]

Decomposition Data

T_{dcm}(410 ± 10 K) was reported by Finholt *et al.*[6] The decomposition products are aluminum, hydrogen, and lithium hydride. This reaction is apparently kinetically controlled since the Gibbs free energy for the decomposition is negative even at room temperature.

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[5]JANAF Thermochemical Tables: $LiBH_4$(cr) 12-31-64; $LiBO_2$(cr) 6-30-71; $LiAlO_2$(cr) 12-31-79.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	86.400	87.864	87.864	0.	−117.152	−48.323	8.466
300	86.944	88.400	87.866	0.160	−117.189	−47.895	8.339
400	93.722	114.323	91.354	9.187	−119.082	−24.508	3.200
500	101.253	136.080	98.176	18.952	−123.729	−0.360	0.038
600	106.901	155.059	106.109	29.370	−124.888	24.431	−2.127
700	111.294	171.886	114.327	40.292	−125.614	49.379	−3.685
800	114.223	186.947	122.480	51.574	−126.114	74.414	−4.859
900	116.200	200.519	130.409	63.099	−126.571	99.507	−5.775
1000	117.780	212.847	138.046	74.801	−137.678	125.414	−6.551
1100	118.847	224.124	145.366	86.634	−137.979	151.738	−7.205
1200	119.746	234.505	152.368	98.565	−138.256	178.088	−7.752
1300	120.416	244.116	159.060	110.573	−138.536	204.461	−8.215
1400	121.043	253.063	165.459	122.646	−138.832	230.857	−8.613
1500	121.615	261.434	171.581	134.779	−139.148	257.274	−8.959
1600	122.173	269.301	177.445	146.969	−139.485	283.713	−9.262
1700	122.717	276.724	183.069	159.213	−285.080	317.350	−9.751
1800	123.247	283.753	188.469	171.512	−284.705	352.776	−10.237
1900	123.763	290.431	193.661	183.862	−284.357	388.182	−10.672
2000	124.265	296.792	198.660	196.264	−284.034	423.570	−11.063

PREVIOUS: June 1963 CURRENT: March 1964

$S°(298.15\ K) = 247.830 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 69.34 \pm 4.18\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 67.95 \pm 4.18\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
	21899.6	2
$a^3\Pi$	[22290.]	[2]
$A^1\Pi$	31487.	2
$[b^3\Sigma^+]$	[43000.]	3

$\omega_e = 316.16\ cm^{-1}$ $\omega_e x_e = 0.960\ cm^{-1}$ $\sigma = 1$

$B_e = 0.11770\ cm^{-1}$ $\alpha_e = 0.0005586\ cm^{-1}$ $r_e = 2.5371$

Enthalpy of Formation

Gaydon,[1] Rosen[2] and Huber and Herzberg[3] reference the analysis by Barrow[4] for values of the dissociation energy of AlI(g). Barrow[4] reports $D_0^o = 364.0\ kJ \cdot mol^{-1}$ from an analysis of fluctuation bonds in the AlI spectrum. Martin and Barrow[5] report a value of $365.97 \pm 1.92\ kJ \cdot mol^{-1}$ for the dissociation energy of AlI based on previous observations of the $A^1 - X^1\Sigma^+$continuum and calculated potentials for these states. Our adopted dissociation energy is the average of these values, $365.01 \pm 0.21\ kJ \cdot mol^{-1}$, and yields $\Delta_f H°$(AlI, g, 298.15 K) = $67.95 \pm 4.18\ kJ \cdot mol^{-1}$.

Heat Capacity and Entropy

Molecular and spectroscopic constants are based on the analysis of electronic spectra published by Martin and Barrow.[5] The constants are in excellent agreement with those from earlier studies.[6,7] The electronic states are taken from Rosen[2] with the exception of the upper $^3\Pi$ state and the $b^3\Sigma^+$ state. The upper $^3\Pi$ state is estimated to be approximately in a linear relationship with the two lower $^3\Pi$ states. The $b^3\Sigma^+$ state is assigned by analogy with AlF, AlCl and AlBr, JANAF Thermochemical Tables, 3rd ed.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.749	69.337	69.337	INFINITE
100	31.012	210.863	278.841	−6.798	70.280	52.942	−27.654
200	34.703	233.666	251.098	−3.486	69.323	35.915	−9.380
250	35.586	241.513	248.422	−1.727	68.655	27.638	−5.775
298.15	36.127	247.830	247.830	0.	67.948	19.802	−3.469
300	36.144	248.054	247.831	0.067	67.920	19.503	−3.396
350	36.516	253.655	248.273	1.884	67.096	11.497	−1.716
400	36.778	258.549	249.258	3.717	58.242	3.887	−0.508
450	36.971	262.893	250.536	5.561	56.766	−2.819	0.327
500	37.119	266.796	251.970	7.413	35.208	−7.460	0.779
600	37.333	273.584	255.023	11.136	34.318	−15.912	1.385
700	37.484	279.351	258.097	14.877	33.328	−24.207	1.806
800	37.601	284.364	261.074	18.632	32.212	−32.351	2.112
900	37.697	288.798	263.913	22.397	30.941	−40.347	2.342
1000	37.780	292.774	266.604	26.171	18.899	−47.432	2.478
1100	37.856	296.379	269.149	29.953	17.598	−54.002	2.564
1200	37.925	299.676	271.558	33.742	16.296	−60.454	2.632
1300	37.990	302.714	273.839	37.538	14.988	−66.797	2.684
1400	38.053	305.532	276.003	41.340	13.672	−73.039	2.725
1500	38.113	308.159	278.060	45.148	12.342	−79.186	2.758
1600	38.171	310.621	280.019	48.962	10.992	−85.244	2.783
1700	38.228	312.937	281.888	52.782	9.619	−91.217	2.803
1800	38.284	315.123	283.674	56.608	8.219	−97.108	2.818
1900	38.340	317.195	285.385	60.439	6.790	−102.921	2.829
2000	38.396	319.163	287.025	64.276	5.332	−108.658	2.838
2100	38.451	321.037	288.600	68.118	3.845	−114.321	2.844
2200	38.507	322.827	290.115	71.966	2.333	−119.912	2.847
2300	38.564	324.540	291.575	75.820	0.799	−125.435	2.849
2400	38.623	326.183	292.983	79.679	−0.752	−130.890	2.849
2500	38.685	327.761	294.343	83.544	−2.314	−136.280	2.847
2600	38.750	329.279	295.658	87.416	−3.880	−141.608	2.845
2700	38.819	330.743	296.930	91.295	−5.445	−146.875	2.841
2800	38.893	332.156	298.163	95.180	−300.904	−151.117	2.819
2900	38.974	333.522	299.359	99.073	−301.352	−145.760	2.625
3000	39.063	334.845	300.520	102.975	−301.782	−140.387	2.444
3100	39.159	336.127	301.648	106.886	−302.188	−135.000	2.275
3200	39.266	337.372	302.745	110.807	−302.565	−129.601	2.116
3300	39.383	338.582	303.813	114.740	−302.910	−124.191	1.966
3400	39.512	339.760	304.853	118.684	−303.218	−118.770	1.825
3500	39.653	340.907	305.867	122.643	−303.488	−113.341	1.692
3600	39.808	342.027	306.856	126.616	−303.717	−107.905	1.566
3700	39.977	343.120	307.821	130.605	−303.902	−102.463	1.447
3800	40.160	344.188	308.764	134.611	−304.041	−97.017	1.334
3900	40.359	345.234	309.686	138.637	−304.134	−91.568	1.226
4000	40.572	346.258	310.587	142.684	−304.178	−86.117	1.125
4100	40.802	347.263	311.470	146.752	−304.173	−80.665	1.028
4200	41.047	348.249	312.334	150.844	−304.118	−75.214	0.935
4300	41.307	349.218	313.180	154.962	−304.012	−69.765	0.847
4400	41.583	350.171	314.010	159.106	−303.856	−64.319	0.764
4500	41.875	351.108	314.824	163.279	−303.646	−58.878	0.683
4600	42.180	352.032	315.623	167.482	−303.387	−53.441	0.607
4700	42.500	352.943	316.407	171.716	−303.076	−48.011	0.534
4800	42.834	353.841	317.178	175.982	−302.714	−42.588	0.463
4900	43.181	354.728	317.935	180.283	−302.301	−37.173	0.396
5000	43.540	355.604	318.680	184.619	−301.838	−31.767	0.332
5100	43.910	356.469	319.412	188.991	−301.325	−26.370	0.270
5200	44.291	357.326	320.133	193.401	−300.764	−20.984	0.211
5300	44.681	358.173	320.843	197.850	−300.154	−15.610	0.154
5400	45.080	359.012	321.542	202.338	−299.497	−10.247	0.099
5500	45.486	359.843	322.231	206.866	−298.794	−4.897	0.047
5600	45.899	360.666	322.910	211.435	−298.045	0.440	−0.004
5700	46.318	361.482	323.579	216.046	−297.253	5.763	−0.053
5800	46.740	362.291	324.240	220.699	−296.416	11.072	−0.100
5900	47.167	363.094	324.892	225.394	−295.540	16.366	−0.145
6000	47.595	363.890	325.535	230.132	−294.602	21.642	−0.188

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = [196.10]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 464.15 \pm 0.2\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -302.9 \pm 2.0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 15.9 \pm 1.3\ kJ·mol^{-1}$

Enthalpy of Formation

Literature values for the enthalpy of formation of AlI_3(cr) are based on solution calorimetry measurements and differ considerably in magnitude. The heat of solution of the crystal in H_2O at 298.15 K was measured by Dear and Eley[1] and reported as $-91.4 \pm 1.5\ kcal·mol^{-1}$. Adopting CODATA's[2] values for the enthalpies of formation of the aqueous ions, this yields $\Delta_f H°(AlI_3, cr, 298.15\ K) = -78.0 \pm 2.0\ kcal·mol^{-1}$. This estimate is undoubtedly high because of hydrolysis of the salt.

More reliable measurements have been attempted in aqueous acid and base. Klemm and Tanke[3] measured the heat of solution of AlI_3(cr) at 273 K in aqueous HCl. Using auxiliary data including estimated heat capacities, they reported $\Delta_f H°(AlI_3, cr, 298.15\ K) = -70.6 \pm 0.7\ kcal·mol^{-1}$. Efimov, Kislova and Medvedev[4] measured the heat of solution of AlI_3(cr) in an aqueous HCl solution containing KCl(cr) and the heat of solution of $AlCl_3$(cr) in an aqueous HCl solution containing KI(cr). From these heats of solution measurements and using the heats of formation of $AlCl_3$,[5] KCl[6,7] and KI[6,8] as auxiliary data, they obtained $\Delta_f H°(AlI_3, cr, 298.15\ K) = -72.4 \pm 0.5\ kcal·mol^{-1}$. In a similar study, Anthoney *et al.*[9] measured the heat of solution of AlI_3(cr) and $AlCl_3$(cr) in an aqueous alkaline solution containing dissolved sodium halides. They reported $\Delta_f H°(AlI_3, cr, 298.15\ K = -67.0 \pm 0.6\ kcal·mol^{-1}$.

Corbett and Gregory[10] investigated the equilibrium $AlI_3(cr) + 3\ HCl(g) \rightarrow AlCl_3(cr) + 3\ HI(g)$ and reported $\Delta_r G°(298.15\ K) = -8.7 \pm 0.2\ kcal·mol^{-1}$. Using auxiliary data, the derived heat of reaction is $-10.7 \pm 0.2\ kcal·mol^{-1}$ and the heat of formation of AlI_3, $\Delta_f H°(AlI_3, cr, 298.15\ K)$ is evaluated to be $-73.6 \pm 0.8\ kcal·mol^{-1}$. The value reported by Efimov *et al.*[4] is chosen as most reliable and is adopted for the heat of formation.

Heat Capacity and Entropy

The heat capacities, 298.15–464 K, were taken from Kelley,[11] whose values were derived from the enthalpy data measured by Fischer.[12] Above 464 K the $C_p°$ values are obtained by graphical extrapolation. The entropy, $S°(AlI_3, cr, 298.15\ K)$, is calculated from $S°(AlI_3, l, 298.15\ K)$ by subtracting $\Delta_{fus}S°$ and the difference between $S°(464.15\ K) - S°(298.15\ K)$ for crystal and liquid.

Fusion Data

The temperature and enthalpy of melting were measured by Fischer.[12]

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 116.3\ kJ·mol^{-1}$ for the process $2\ AlI_3(cr) = 2\ Al_2I_6(g)$, is calculated from vapor pressure data reported by Fischer, Rahlfs and Benze[13] by both the 2nd and 3rd law methods. Refer to the Al_2I_6(g) table for details.

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[10]K. K. Kelley, U.S. Bur. Mines Bull. 584, 232 pp. (1960); refer to p. 13.
[11]W. Fischer, Z. anorg. allgem. Chem. **200**, 332 (1931).
[12]W. Fischer, O. Rahlfs and B. Benze, Z. anorg. allgem. Chem., **205**, 1 (1932).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	98.910	196.104	196.104	0.	−302.922	−301.018	52.737
300	99.077	196.716	196.106	0.183	−302.934	−301.006	52.410
400	108.533	226.513	200.105	10.563	−327.520	−299.436	39.102
464.150	114.614	243.098	204.919	17.721	--- CRYSTAL <--> LIQUID ---		
500	116.901	251.742	207.972	21.885	−391.126	−286.306	29.910
600	121.986	273.543	217.126	33.850	−387.527	−265.674	23.129
700	125.063	292.599	226.576	46.216	−383.660	−245.669	18.332
800	126.918	309.430	235.902	58.823	−379.703	−226.226	14.771
900	127.901	324.444	244.921	71.571	−375.781	−207.277	12.030
1000	128.449	337.949	253.560	84.390	−382.581	−187.999	9.820
1100	128.875	350.213	261.798	97.257	−378.611	−168.733	8.012
1200	129.160	361.440	269.640	110.160	−374.632	−149.829	6.522
1300	129.319	371.784	277.105	123.084	−370.667	−131.256	5.274
1400	129.501	381.374	284.214	136.024	−366.732	−112.988	4.216
1500	129.704	390.316	290.993	148.984	−362.838	−95.000	3.308

PREVIOUS: June 1964 CURRENT: September 1979

$S°(298.15\ K) = [223.648]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 464.15 \pm 0.2\ K$

$\Delta_f H°(298.15\ K) = [-289.444]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 15.9 \pm 1.3\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(AlI_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(AlI_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(464.15\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities, 464–500 K, were taken from Kelley,[1] whose values were derived from the enthalpy data measured by Fischer.[2] The $C_p°$ values above 500 K were assumed to be the same as that at 500 K. $S°(298.15\ K)$ is estimated so that the values of $\Delta_{vap} H°$ calculated from vapor pressure data by the 2nd and 3rd law methods are in reasonable agreement. Refer to the Al_2I_6(g) table for details.

Fusion Data

The temperature and enthalpy of melting were reported by Fischer.[2]

References

[1]K. K. Kelley, U. S. Bur. Mines Bull. 584, 232 pp. (1960); refer to p. 13.
[2]W. Fischer, Z. anorg. allgem. Chem. **200**, 332 (1931).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	121.336	223.648	223.648	0.	−289.444	−295.752	51.815
300	121.336	224.398	223.650	0.224	−289.415	−295.792	51.502
400	121.336	259.305	228.409	12.358	−312.247	−297.280	38.821
464.150	121.336	277.352	233.957	20.142	--- CRYSTAL <--> LIQUID ---		
500	121.336	286.380	237.397	24.492	−375.041	−287.541	30.039
600	121.336	308.502	247.460	36.625	−371.274	−270.397	23.540
700	121.336	327.206	257.551	48.759	−367.639	−253.873	18.944
800	121.336	343.408	267.293	60.892	−364.155	−237.860	15.531
900	121.336	357.700	276.559	73.026	−360.848	−222.274	12.900
1000	121.336	370.484	285.324	85.160	−368.333	−206.286	10.775
1100	121.336	382.048	293.600	97.293	−365.097	−190.238	9.034
1200	121.336	392.606	301.417	109.427	−361.887	−174.483	7.595
1300	121.336	402.318	308.810	121.560	−358.713	−158.995	6.389
1400	121.336	411.310	315.814	133.694	−355.585	−143.750	5.363
1500	121.336	419.681	322.463	145.828	−352.517	−128.726	4.483
1600	121.336	427.512	328.786	157.961	−349.524	−113.905	3.719
1700	121.336	434.868	334.812	170.095	−346.619	−99.268	3.050
1800	121.336	441.803	340.565	182.228	−343.812	−84.800	2.461
1900	121.336	448.364	346.068	194.362	−341.109	−70.485	1.938
2000	121.336	454.587	351.339	206.496	−338.511	−56.309	1.471

PREVIOUS: June 1964 CURRENT: September 1979

0	to	464.15 K	crystal
above		464.15 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
90							
200							
250							
298.15	98.910	196.104	196.104	0.	−302.922	−301.018	52.737
300	99.077	196.716	196.106	0.183	−302.934	−301.006	52.410
400	108.533	226.513	200.105	10.563	−327.520	−299.436	39.102
464.150	114.614	243.098	204.919	17.721	CRYSTAL <--> LIQUID TRANSITION		
464.150	121.336	277.352	204.919	33.620			
500	121.336	286.380	210.440	37.970	−375.041	−287.540	30.039
600	121.336	308.502	224.996	50.103	−371.274	−270.396	23.540
700	121.336	327.206	238.296	62.237	−367.639	−253.873	18.944
800	121.336	343.408	250.445	74.371	−364.155	−237.860	15.531
900	121.336	357.699	261.584	86.504	−360.848	−222.274	12.900
1000	121.336	370.483	271.846	98.638	−368.332	−206.285	10.775
1100	121.336	382.048	281.347	110.771	−365.097	−190.237	9.034
1200	121.336	392.606	290.185	122.905	−361.887	−174.483	7.595
1300	121.336	402.318	298.442	135.039	−358.712	−158.995	6.388
1400	121.336	411.310	306.187	147.172	−355.584	−143.750	5.363
1500	121.336	419.681	313.477	159.306	−352.517	−128.726	4.483

PREVIOUS: CURRENT: September 1979

$S°(298.15\ K) = 373.62 \pm 08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -187.9 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -193.3 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
156 (1)	[450](2)
[140](1)	64 (2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: Al–I = 2.449 ± 0.013 Å
Bond Angle: I–Al–I = 120 ± 4°
Product of the Moments of Inertia: $I_A I_B I_C = 1.362810 \times 10^{-110}\ g^3 \cdot cm^6$

Enthalpy of Formation

Fischer, Rahlfs and Benze[1] have determined the equilibrium constants for the reaction $Al_2I_6(g) = 2\ AlI_3(g)$ from vapor density measurements. The heats of reaction are calculated from these data using both 2nd and 3rd Law methods. The results are summarized below:

	Data	$\Delta_f H°$(298.15 K), $kcal \cdot mol^{-1}$ Al_2I_6		Drift	$\Delta_f H°$(298.15 K)
T/K	Points	2nd law	3rd law	$cal \cdot K^{-1} \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
656–819	11[a]	24.39 ± 0.5	24.56 ± 0.2	0.2 ± 0.6	−46.2

[a]Points at 614.15, 644.15, 843.15 rejected due to statistical test.

The adopted value, $\Delta_f H°(AlI_3, g, 298.15\ K) = -46.2 \pm 2.0\ kcal \cdot mol^{-1}$ ($-193.3 \pm 8.4\ kJ \cdot mol^{-1}$), is based on the 3rd law enthalpy of reaction and $\Delta_f H°(Al_2I_6, g, 298.15\ K) = -489.5 \pm 8.4\ kJ \cdot mol^{-1}$.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were taken from the electron diffraction work reported by Shen.[2] These values are in good agreement with those determined by Akishin, Rambidi and Zasorin.[3] Beattie and Horder[4] studied the gas phase Raman spectra of monomeric AlI_3 and reported $\nu_1 = 156\ cm^{-1}$ and $\nu_4 = 64\ cm^{-1}$. The other vibrational frequencies were adjusted not only for consistency with the frequencies chosen for AlF_3(g), $AlCl_3$(g) and $AlBr_3$(g)[5] but also for agreement between the 2nd and 3rd Law $\Delta_f H°(298.15\ K)$ in the data set tabulated above. The principal moments of inertia are $I_A = 189.5840 \times 10^{-39}$, $I_B = 189.5841 \times 10^{-39}$, and $I_C = 379.1681 \times 10^{-39}\ g \cdot cm^2$.

References

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[4]I. R. Beattie and J. R. Horder, J. Chem. Soc. (London)*A* **1969**, 2655.
[5]JANAF Thermochemical Tables: AlF_3(g), $AlCl_3$(g) and $AlBr_3$(g), 9–30–79.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.930	−187.894	−187.894	INFINITE
100	61.385	297.474	438.424	−14.095	−188.118	−208.018	108.658
200	72.150	343.761	380.536	−7.355	−190.578	−227.014	59.290
250	75.138	360.205	374.875	−3.668	−191.946	−235.966	49.302
298.15	77.081	373.616	373.616	0.	−193.301	−244.323	42.804
300	77.142	374.093	373.617	0.143	−193.354	−244.639	42.595
350	78.515	386.094	374.562	4.036	−194.914	−253.067	37.768
400	79.482	396.645	376.676	7.987	−220.475	−260.444	34.010
450	80.184	406.049	379.427	11.980	−223.836	−265.238	30.788
500	80.706	414.526	382.520	16.003	−287.387	−263.960	27.576
600	81.414	429.308	389.122	24.112	−287.645	−259.251	22.570
700	81.856	441.894	395.784	32.277	−287.978	−254.494	18.991
800	82.149	452.844	402.247	40.478	−288.427	−249.681	16.302
900	82.353	462.533	408.417	48.704	−289.027	−244.803	14.208
1000	82.501	471.217	414.271	56.947	−300.403	−239.089	12.489
1100	82.611	479.086	419.811	65.203	−301.045	−232.927	11.061
1200	82.695	486.278	425.054	73.468	−301.703	−226.706	9.868
1300	82.760	492.900	430.022	81.741	−302.389	−220.428	8.857
1400	82.813	499.035	434.735	90.020	−303.116	−214.097	7.988
1500	82.855	504.750	439.214	98.303	−303.899	−207.711	7.233
1600	82.890	510.098	443.479	106.590	−304.752	−201.271	6.571
1700	82.919	515.124	447.547	114.881	−305.690	−194.775	5.985
1800	82.943	519.865	451.435	123.174	−306.724	−188.222	5.462
1900	82.963	524.350	455.155	131.469	−307.859	−181.608	4.993
2000	82.981	528.606	458.722	139.767	−309.097	−174.931	4.569
2100	82.996	532.655	462.147	148.065	−310.435	−168.191	4.184
2200	83.009	536.516	465.441	156.366	−311.866	−161.384	3.832
2300	83.021	540.206	468.612	164.667	−313.377	−154.510	3.509
2400	83.031	543.740	471.669	172.970	−314.955	−147.570	3.212
2500	83.040	547.129	474.620	181.273	−316.583	−140.562	2.937
2600	83.047	550.386	477.472	189.578	−318.243	−133.488	2.682
2700	83.054	553.521	480.231	197.883	−319.918	−126.350	2.444
2800	83.061	556.541	482.902	206.189	−615.492	−118.183	2.205
2900	83.066	559.456	485.492	214.495	−616.052	−100.412	1.809
3000	83.071	562.272	488.005	222.802	−616.580	−82.622	1.439
3100	83.076	564.996	490.445	231.109	−617.063	−64.815	1.092
3200	83.080	567.634	492.816	239.417	−617.490	−46.994	0.767
3300	83.084	570.190	495.122	247.725	−617.852	−29.160	0.462
3400	83.087	572.671	497.367	256.034	−618.142	−11.317	0.174
3500	83.091	575.079	499.553	264.343	−618.353	6.535	−0.098
3600	83.094	577.420	501.683	272.652	−618.483	24.390	−0.354
3700	83.096	579.697	503.761	280.961	−618.528	42.249	−0.596
3800	83.099	581.913	505.789	289.271	−618.486	60.108	−0.826
3900	83.101	584.071	507.769	297.581	−618.356	77.964	−1.044
4000	83.103	586.175	509.703	305.891	−618.139	95.815	−1.251
4100	83.105	588.227	511.593	314.202	−617.836	113.661	−1.448
4200	83.107	590.230	513.441	322.512	−617.448	131.498	−1.635
4300	83.109	592.186	515.250	330.823	−616.977	149.324	−1.814
4400	83.110	594.096	517.020	339.134	−616.426	167.139	−1.984
4500	83.112	595.964	518.754	347.445	−615.794	184.940	−2.147
4600	83.113	597.791	520.452	355.756	−615.090	202.726	−2.302
4700	83.114	599.578	522.117	364.068	−614.314	220.497	−2.451
4800	83.116	601.328	523.749	372.379	−613.469	238.250	−2.593
4900	83.117	603.042	525.350	380.691	−612.558	255.985	−2.729
5000	83.118	604.721	526.921	389.003	−611.587	273.700	−2.859
5100	83.119	606.367	528.462	397.315	−610.557	291.396	−2.985
5200	83.120	607.981	529.976	405.626	−609.473	309.071	−3.105
5300	83.121	609.564	531.463	413.939	−608.337	326.724	−3.220
5400	83.122	611.118	532.924	422.251	−607.154	344.356	−3.331
5500	83.122	612.643	534.359	430.563	−605.926	361.965	−3.438
5600	83.123	614.141	535.770	438.875	−604.658	379.552	−3.540
5700	83.124	615.612	537.158	447.187	−603.352	397.116	−3.639
5800	83.125	617.058	538.524	455.500	−602.009	414.656	−3.734
5900	83.125	618.479	539.867	463.812	−600.637	432.173	−3.826
6000	83.126	619.876	541.189	472.125	−599.215	449.664	−3.915

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = 53.31 \pm 1.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1973 \pm 15\ K$

$\Delta_f H°(0\ K) = -1180.52 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1188.67 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [87.864 \pm 21]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is based on the solution calorimetric studies of Coughlin.[1] From measurements of the heat of solution of $LiAlO_2$(cr) in aqueous HCl and of four auxiliary reactions, Coughlin reported $\Delta_r H°(303.15\ K) = -89.12 \pm 0.14\ kcal \cdot mol^{-1}$ for Al(cr) + LiCl(cr) + 14.731 H_2O(l) → $LiAlO_2$(cr) + HCl·12.731 H_2O(aq) + 3/2 H_2(g). This value is corrected to $\Delta_r H°(298.15\ K) = -88.9 \pm 0.14$ $kcal \cdot mol^{-1}$ using heat capacities of the materials. This value, when combined with auxiliary heats of formation[2,3] yields our adopted value of $\Delta_f H°(LiAlO_2, cr, 298.15\ K) = -284.1 \pm 0.5\ kcal \cdot mol^{-1}$ ($-1188.674\ kJ \cdot mol^{-1}$).

Gross *et al.*[4] measured the heats of solution of $LiAlO_2$(cr) and of $Al_2O_3 3\ H_2O$(cr, gibbsite) + Li_2O(cr) in aqueous HF. From these and the heat of solution of three moles of H_2O in HF(aq) they report $\Delta_r H°(298.15\ K) = -11.3\ kcal \cdot mol^{-1}$ for Li_2O(cr) + $Al_2O_3 3\ H_2O$(cr, gibbsite) → 2 $LiAlO_2$(cr) + 3 H_2O(l). Combining this $\Delta_r H°$ with auxiliary heats of formation[2,5] yields $\Delta_f H°(LiAlO_2, cr, 298.15\ K) = -283.8 \pm 0.7$ $kcal \cdot mol^{-1}$, in excellent agreement with the adopted value.

Equilibrium studies of vapor pressure over $LiAlO_2$(cr) by the torsion effusion technique support the adopted value of $\Delta_f H°(298.15\ K)$. Potter *et al.*[6] and Popkov and Semenov[7] both studied the equilibrium $LiAlO_2$(cr) → Li(g) + $x/4\ O_2$(g) + $(1-x)/2$ O(g) + 1/2 Al_2O_3(cr, α) in the temperature range from 1500 to 1820 K where $1-x \cong 0.13$. Neither author reports the raw data but they do report 2nd and 3rd law values for $\Delta_r H°(298.15\ K)$. Based on these reported values and auxiliary $\Delta_f H°(298.15\ K)$ data[2] we calculate 2nd and 3rd law values for $\Delta_f H°(LiAlO_2$, cr, 298.15 K) of −283.9 and −282.8 $kcal \cdot mol^{-1}$, respectively, from the data of Potter *et al.*[6] 2nd and 3rd law values for $\Delta_f H°(298.15\ K)$ calculated from the results of Popkov and Semenov[7] are −283.8 and −277.9 $kcal \cdot mol^{-1}$, respectively. The expected uncertainty in these determinations is of the order of 2 to 5 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The adopted values of $C_p°$ below 300 K are taken from Douglas and Beckett[8] based on the low temperature $C_p°$ measurements of King (53–296 K).[9] At higher temperatures the adopted $C_p°$ data are based on the drop calorimetric enthalpy data of Christensen *et al.* (399–1795 K).[10] No transitions were detected in either study.

Phase Data

The data in this table are for the γ or tetragonal phase of $LiAlO_2$. The crystal structure is $P4_12_12$.[11,12] A hexagonal (α) phase may be prepared but converts to the γ phase on heating. Byker *et al.*[13] recently reviewed the phase data and constructed a phase diagram for the Al_2OLi_2O system. The reader is referred to their paper for details but the following comments may be informative. The α to γ phase transformation occurs above 1173 K but may occur at lower temperature. The transition has frequently been reported as irreversible although Lejus and Collongues[14] report that the γ to α transformation does occur if aided by prolonged grinding. Measurements of the heat of the α–γ transition are hampered by its slow nature but apparently imply that it is slightly exothermic near 1200 K. Based on the above data and the known density change between α and γ phases, Byker *et al.* constructed a phase diagram which indicates that the α phase is the thermodynamically stable phase below −550 K at 1 atm pressure. This seems to support the observation of Lejus and Collongues. The uncertainties are such that this temperature may be off by several hundred Kelvin. Thus, while it is clear that the γ phase is the thermodynamically stable phase above 1200 K, its stability at low temperature may be controlled by kinetic factors.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.693	−1180.523	−1180.523	INFINITE
100	17.966	8.046	99.257	−9.121	−1183.834	−1165.875	608.991
200	47.999	30.154	58.942	−5.758	−1187.025	−1146.565	299.452
298.15	67.777	53.313	53.313	0.	−1188.674	−1126.303	197.324
300	68.128	53.733	53.314	0.126	−1188.693	−1125.916	196.039
400	81.546	75.421	56.180	7.697	−1189.202	−1104.891	144.284
500	88.408	94.425	61.974	16.226	−1192.298	−1083.492	113.192
600	92.688	110.947	68.790	25.294	−1192.108	−1061.744	92.433
700	95.751	125.475	75.871	34.723	−1191.706	−1040.047	77.609
800	98.165	138.424	82.896	44.423	−1191.220	−1018.414	66.496
900	100.203	150.107	89.725	54.343	−1190.737	−996.843	57.855
1000	102.006	160.759	96.303	64.455	−1200.889	−974.563	50.906
1100	103.654	170.559	102.614	74.740	−1200.170	−951.964	45.205
1200	105.198	179.645	108.660	85.183	−1199.326	−929.436	40.457
1300	106.671	188.124	114.450	95.777	−1198.363	−906.983	36.443
1400	108.089	196.082	119.999	106.515	−1197.279	−884.609	33.005
1500	109.466	203.586	125.324	117.393	−1196.075	−862.317	30.029
1600	110.813	210.694	130.439	128.408	−1194.752	−840.109	27.427
1700	112.140	217.452	135.361	139.556	−1338.549	−810.812	24.913
1800	113.449	223.899	140.102	150.835	−1336.240	−779.835	22.630
1900	114.746	230.068	144.676	162.245	−1333.827	−748.988	20.591
1973.000	115.679	234.411	147.916	170.656	--- CRYSTAL <--> LIQUID ---		
2000	116.022	235.986	149.094	173.784	−1331.309	−718.272	18.759
2100	117.294	241.678	153.368	185.449	−1328.691	−687.684	17.105
2200	118.558	247.163	157.508	197.242	−1325.971	−657.223	15.604

PREVIOUS: June 1972 CURRENT: December 1979

$S°(298.15\ K) = [93.711]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1973 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-1107.739]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [87.864 \pm 21]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(LiAlO_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(LiAlO_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1973\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of $LiAlO_2$(l) is estimated to be 30 $cal·K^{-1}·mol^{-1}$ (125.52 $J·K^{-1}·mol^{-1}$) above a hypothetical glass transition temperature of 1450 K. Below this temperature the heat capacity is taken to be the same as the crystal. The adopted $C_p° = 30\ cal·K^{-1}·mol^{-1}$ is based on an estimated value of $C_p° = 7.5\ cal·K^{-1}·g·atom^{-1}$ recommended by Kubaschewski and Alcock.[2] $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy formation.

Fusion Data

The adopted melting point, $T_{fus} = 1973 \pm 15$ K, is based on the phase study of Strickler and Roy[3] and is suppported by the value 1975 K reported by Prophet.[4] The older study of Ballo and Dittler[5] reported T_{fus} to lie between 2173 and 2273 K and Hummel *et al.*[6] reported $T_{fus} = 1883 \pm 15$ K. Hummel *et al.* also stated that their samples were only partially fused after considerable time at 1973 K. Prophet also reported that his samples slowly decomposed on fusion and that successive melting points approached that of aluminum oxide at 2308 K. After fusing seven times X-ray analysis indicated the sample was 95% α-aluminum oxide and 5% $LiAl_5O_8$ with Li_2O being lost by vaporization. The adopted $\Delta_{fus}H°$ is estimated by assuming the entropy of melting to be approximately the same on a gram-atom basis as that of $BeAl_2O_4$.[1]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	67.777	93.711	93.711	0.	-1107.739	-1057.412	185.254
300	68.128	94.131	93.712	0.126	-1107.758	-1057.100	184.057
400	81.546	115.820	96.578	7.697	-1108.267	-1040.115	135.825
500	88.408	134.823	102.372	16.226	-1111.362	-1022.756	106.847
600	92.688	151.345	109.189	25.294	-1111.172	-1005.048	87.497
700	95.751	165.874	116.270	34.723	-1110.771	-987.390	73.680
800	98.165	178.822	123.294	44.423	-1110.285	-969.797	63.321
900	100.203	190.505	130.124	54.343	-1109.801	-952.266	55.268
1000	102.006	201.158	136.702	64.455	-1119.953	-934.026	48.789
1100	103.654	210.958	143.013	74.740	-1119.234	-915.467	43.472
1200	105.198	220.044	149.058	85.183	-1118.391	-896.979	39.044
1300	106.671	228.523	154.848	95.777	-1117.427	-878.566	35.301
1400	108.089	236.480	160.398	106.515	-1116.343	-860.232	32.096
1450.000	108.784	240.285	163.087	111.937	GLASS <--> LIQUID		
1450.000	125.520	240.285	163.087	111.937	TRANSITION		
1500	125.520	244.541	165.732	118.213	-1114.319	-841.994	29.321
1600	125.520	252.642	170.913	130.765	-1111.459	-823.932	26.899
1700	125.520	260.251	175.947	143.317	-1253.851	-798.873	24.546
1800	125.520	267.426	180.832	155.869	-1250.271	-772.213	22.409
1900	125.520	274.212	185.570	168.421	-1246.715	-745.751	20.502
1973.000	125.520	278.945	188.937	177.584	--- CRYSTAL <--> LIQUID ---		
2000	125.520	280.651	190.164	180.973	-1243.184	-719.476	18.791
2100	125.520	286.775	194.620	193.525	-1239.679	-693.377	17.247
2200	125.520	292.614	198.943	206.077	-1236.201	-667.443	15.847
2300	125.520	298.194	203.137	218.629	-1232.750	-641.669	14.573
2400	125.520	303.536	207.210	231.181	-1229.327	-616.043	13.408
2500	125.520	308.660	211.166	243.733	-1225.934	-590.560	12.339
2600	125.520	313.583	215.011	256.285	-1222.571	-565.211	11.355
2700	125.520	318.320	218.750	268.837	-1219.240	-539.991	10.447
2800	125.520	322.885	222.388	281.389	-1509.843	-513.926	9.587
2900	125.520	327.289	225.930	293.941	-1505.483	-478.435	8.618
3000	125.520	331.545	229.380	306.493	-1501.159	-443.093	7.715
3100	125.520	335.660	232.743	319.045	-1496.871	-407.895	6.873
3200	125.520	339.645	236.021	331.597	-1492.620	-372.835	6.086
3300	125.520	343.508	239.220	344.149	-1488.408	-337.907	5.349
3400	125.520	347.255	242.343	356.701	-1484.235	-303.106	4.657
3500	125.520	350.894	245.393	369.253	-1480.103	-268.428	4.006
3600	125.520	354.430	248.373	381.805	-1476.013	-233.866	3.393
3700	125.520	357.869	251.286	394.357	-1471.966	-199.418	2.815
3800	125.520	361.216	254.135	406.909	-1467.963	-165.078	2.269
3900	125.520	364.477	256.922	419.461	-1464.005	-130.843	1.752
4000	125.520	367.654	259.651	432.013	-1460.094	-96.710	1.263

PREVIOUS: June 1972 CURRENT: December 1979

0	to 1973 K	crystal
above	1973 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.693	−1180.523	−1180.523	INFINITE
90	17.966	8.046	99.257	−9.121	−1183.834	−1165.875	608.991
200	47.999	30.154	58.942	−5.758	−1187.025	−1146.565	299.452
298.15	67.777	53.313	53.313	0.	−1188.674	−1126.303	197.324
300	68.128	53.733	53.314	0.126	−1188.693	−1125.916	196.039
400	81.546	75.421	56.180	7.697	−1189.202	−1104.891	144.284
500	88.408	94.425	61.974	16.226	−1192.298	−1083.492	113.192
600	92.688	110.947	68.790	25.294	−1192.108	−1061.744	92.433
700	95.751	125.475	75.871	34.723	−1191.706	−1040.047	77.609
800	98.165	138.424	82.896	44.423	−1191.220	−1018.414	66.496
900	100.203	150.107	89.725	54.343	−1190.737	−996.843	57.855
1000	102.006	160.759	96.303	64.455	−1200.889	−974.563	50.906
1100	103.654	170.559	102.614	74.740	−1200.170	−951.964	45.205
1200	105.198	179.645	108.660	85.183	−1199.326	−929.436	40.457
1300	106.671	188.124	114.450	95.777	−1198.363	−906.983	36.443
1400	108.089	196.082	119.999	106.515	−1197.279	−884.609	33.005
1500	109.466	203.586	125.324	117.393	−1196.075	−862.317	30.029
1600	110.813	210.694	130.439	128.408	−1194.752	−840.109	27.427
1700	112.140	217.452	135.361	139.556	−1338.549	−810.812	24.913
1800	113.449	223.899	140.102	150.835	−1336.240	−779.835	22.630
1900	114.746	230.068	144.676	162.245	−1333.827	−748.988	20.591
1973.000	115.679	234.411	147.916	170.656	CRYSTAL <--> LIQUID		
1973.000	125.520	278.945	147.916	258.520	TRANSITION		
2000	125.520	280.651	149.696	261.909	−1243.184	−719.476	18.791
2100	125.520	286.775	156.079	274.461	−1239.679	−693.377	17.247
2200	125.520	292.614	162.154	287.013	−1236.201	−667.444	15.847
2300	125.520	298.194	167.948	299.565	−1232.750	−641.669	14.573
2400	125.520	303.536	173.487	312.117	−1229.327	−616.044	13.408
2500	125.520	308.660	178.792	324.669	−1225.934	−590.560	12.339
2600	125.520	313.583	183.882	337.221	−1222.571	−565.211	11.355
2700	125.520	318.320	188.774	349.773	−1219.240	−539.991	10.447
2800	125.520	322.885	193.483	362.325	−1509.843	−513.926	9.587
2900	125.520	327.289	198.021	374.877	−1505.483	−478.436	8.618
3000	125.520	331.545	202.402	387.429	−1501.159	−443.094	7.715
3100	125.520	335.660	206.634	399.981	−1496.871	−407.895	6.873
3200	125.520	339.646	210.729	412.533	−1492.621	−372.836	6.086
3300	125.520	343.508	214.694	425.085	−1488.408	−337.908	5.349
3400	125.520	347.255	218.538	437.637	−1484.235	−303.106	4.657
3500	125.520	350.894	222.268	450.189	−1480.104	−268.428	4.006
3600	125.520	354.430	225.891	462.741	−1476.013	−233.866	3.393
3700	125.520	357.869	229.411	475.293	−1471.966	−199.419	2.815
3800	125.520	361.216	232.836	487.845	−1467.963	−165.078	2.269
3900	125.520	364.477	236.170	500.397	−1464.005	−130.843	1.752
4000	125.520	367.654	239.417	512.949	−1460.094	−96.710	1.263

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = 20.14 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -312.98 \pm 2.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -317.98 \pm 2.5\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalps of formation is the average value of the calorimetric determinations of Neugebauer and Margrave[1] and Mah *et al.*[2] Neugebauer and Margrave obtained $\Delta_f H°(298.15\ K) = -76.47 \pm 0.2$ kcal·mol^{-1} by direct nitridation. Mah *et al.* obtained $\Delta_f H°(298.15\ K) = -75.6 \pm 0.4$ kcal·mol^{-1} via oxygen combustion calorimetry. The older direct nitridation study of Neumann *et al.*[3] yields $\Delta_f H°(298.15\ K) = -57.4 \pm 0.8$ kcal·mol^{-1}; the source of bias in this study is not apparent. Fichter and Jenny[4] also made measurements using oxygen combustion calorimetry; our recalculation of their data using the modern accepted value for the heat of formation of Al_2O_3(cr, α)[5] yields $\Delta_f H°(298.15\ K) = -71.5 \pm 1.0$ kcal·mol^{-1}.

Equilibrium data supports the calorimetric determinations but is less certain due largely to corrections for a condensation coefficient significantly different from unity. We have adopted a condensation coefficient (fraction of incident molecules which condense on the vaporizing surface) of $\alpha = 2 \times 10^{-3}$ from Hildenbrand and Hall[6] and used that value to convert measured pressures to equilibrium pressures, $P_e = P_m/\alpha$. This is a large correction, equivalent in some cases to 50 kcal·mol^{-1} in the $\Delta_f H°(298.15\ K)$ values. The data below corresponds to the dissociation of 2 AlN(cr) = 2 Al(g) + N_2(g).

Source	Method	Data Point	T/K	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Hildenbrand and Hall[a 6]	torsion–effusion	29[b]	1776–1972	309.3 ± 6.0	307.2 ± 1.5	−1.1 ± 3.2	−74.8 ± 1.2
Hoch and White[a 7]	Langmuir	13[b]	1660–1948	342.6 ± 18.5	307.6 ± 7.6	−19.3 ± 10.2	−75.0 ± 3.9
Dreger *et al.*[a 8]	Knudsen–effusion	11[c]	1450–1870	391.5 ± 17.6	308.9 ± 12.0	−48.2 ± 10.2	−75.6 ± 6.1
Bolgar *et al.*[a 9]	Langmuir	10	1718–1829	388.5 ± 9.7	315.3 ± 4.2	−41.5 ± 5.5	−78.8 ± 2.3
Linevsky [10]	atomic resonance	7	1641–1707	290.1 ± 18.8	299.7 ± 1.8	5.8 ± 11.2	−71.0 ± 1.4

[a] Raw pressure data corrected using $\alpha = 2 \times 10^{-3}$
[b] Two points rejected by a statistical test.
[c] One point rejected by a statistical test.

Studies not re-evaluated above include those of Blank[11] and Wu.[12] Blank's[11] Knudsen and Langmuir effusion studies yield a third law value of $\Delta_f H°(298.15\ K) = -306.4$ kcal·mol^{-1} ($\Delta_f H°$(AlN, cr, 298.15 K) = −74.4 kcal·mol^{-1}) when corrected for condensation coefficient according to the author. We have not reanalyzed this data since not all of the measured points from the graph are given in tabular form. Wu's Knudsen effusion study[12] leads to a value of $\Delta_f H°(AlN, cr, 298.15\ K) = -62.2 \pm 1.1$ kcal·mol^{-1} as reported by the author based on a second-law analysis. The data are presented graphically only. Wu also suggests that AlN decomposes incongruently with loss of N_2 until a composition of Al_2N is reached.

Heat Capacity and Entropy

The adopted heat capacity data is derived by using orthogonal polynomials to smoothly merge the heat capacity–enthalpy data of Mah *et al.*[2] These authors reported heat capacity data in the 53–296 K range and enthalpy data (via drop calorimetry) in the 399–1799 K range. The entropy is based on $S°(50\ K) = 0.0692$ cal·K^{-1}·mol^{-1}. The $C_p°$ data above 1799 K are a smooth extrapolation of the merged data and will approach a constant $C_p° = 12.521$ cal·K^{-1}·mol^{-1} at very high temperature. Demidenko *et al.*[13] measured heat capacity over the range 55 to 330 K and their values for $S°(298.15\ K) = 4.804$ cal·K^{-1}·mol^{-1} and $H°(298.15\ K) - H°(0\ K) = 925$ cal·K^{-1}·mol^{-1} are in excellent agreement with the adopted values; their complete data are not available. Mezaki *et al.*[14] measured enthalpies via drop calorimetry over the range 478 to 1113 K; their values are −1.5% lower than the adopted values.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S° - [G° - H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H° - H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−3.871	−312.980	−312.980	INFINITE
100	5.678	2.164	39.274	−3.711	−314.756	−306.283	159.986
200	19.332	10.267	22.581	−2.463	−316.764	−296.990	77.566
298.15	30.097	20.142	20.142	0.	−317.984	−286.995	50.280
300	30.254	20.329	20.143	0.056	−318.000	−286.803	49.937
400	36.692	29.987	21.416	3.428	−318.594	−276.301	36.081
500	40.799	38.647	24.013	7.317	−318.808	−265.697	27.757
600	43.538	46.341	27.106	11.541	−318.811	−255.072	22.206
700	45.434	53.201	30.353	15.994	−318.727	−244.455	18.241
800	46.791	59.361	33.601	20.608	−318.648	−233.850	15.269
900	47.792	64.932	36.777	25.339	−318.647	−223.252	12.957
1000	48.550	70.008	39.850	30.158	−329.363	−211.887	11.068
1100	49.136	74.664	42.807	35.043	−329.302	−200.142	9.504
1200	49.598	78.960	45.643	39.981	−329.214	−188.404	8.201
1300	49.970	82.945	48.361	44.960	−329.107	−176.674	7.099
1400	50.272	86.660	50.965	49.972	−328.986	−164.953	6.154
1500	50.521	90.137	53.462	55.012	−328.856	−153.240	5.336
1600	50.728	93.404	55.857	60.075	−328.717	−141.537	4.621
1700	50.903	96.485	58.157	65.157	−328.573	−129.843	3.990
1800	51.052	99.399	60.368	70.255	−328.425	−118.157	3.429
1900	51.180	102.162	62.496	75.366	−328.273	−106.480	2.927
2000	51.290	104.790	64.545	80.490	−328.119	−94.810	2.476
2100	51.385	107.295	66.522	85.624	−327.963	−83.149	2.068
2200	51.469	109.688	68.430	90.767	−327.805	−71.495	1.697
2300	51.543	111.977	70.274	95.917	−327.646	−59.848	1.359
2400	51.609	114.172	72.058	101.075	−327.486	−48.208	1.049
2500	51.666	116.280	73.785	106.239	−327.325	−36.574	0.764
2600	51.718	118.308	75.458	111.408	−327.165	−24.948	0.501
2700	51.765	120.260	77.082	116.582	−327.003	−13.327	0.258
2800	51.807	122.144	78.658	121.761	−620.743	−0.744	0.014
2900	51.845	123.962	80.189	126.943	−619.486	21.376	−0.385
3000	51.878	125.721	81.677	132.130	−618.229	43.454	−0.757

PREVIOUS: December 1962 CURRENT: December 1979

$S°(298.15\ K) = 228.6 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 523 \pm 3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 523 \pm 38\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3\Pi$	0	6
$^3\Pi$	19727.4	6

$\omega_e = 746.9\ cm^{-1}$ $\omega_e x_e = [5.59]\ cm^{-1}$ $\sigma = 1$

$B_e = 0.5730\ cm^{-1}$ $\alpha_e = 0.0056\ cm^{-1}$ $r_e = 1.65$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from the adopted dissociation energy using auxiliary JANAF data.[1] Simmons and McDonald[2] observed an apparent predissociation from the J=47 rotational level during their emission spectroscopic study of AlN. They have shown that it is possible to assign this predissociation as being from the excited $^3\Pi$ state of AlN(g) to ground state Al(g) + N(g). If this assignment is correct, we calculate $D_0° = 21{,}000\ cm^{-1}$ using their value of $B_o = 0.5811\ cm^{-1}$ for the excited $^3\Pi$ state rotational constant. A linear Birge–Sponer extrapolation using the adopted molecular constant data yields $D_0° = 25{,}000\ cm^{-1}$. Considering the nature of the uncertainties in these calculations, we adopt an average value of $D_0° = 23{,}000 \pm 3{,}000\ cm^{-1}$ or $D_0° = 66 \pm 9\ kcal \cdot mol^{-1}$. With auxiliary JANAF data[1] this yields an adopted value of $\Delta_f H°(298.15\ K) = 125 \pm 9\ kcal \cdot mol^{-1}$ ($523.000 \pm 38\ kJ \cdot mol^{-1}$).

Heat Capacity and Entropy

The adopted molecular constant data are taken from the emission spectroscopy work of Simmons and McDonald[2] except for $\omega_e x_e$ which we estimate from the Pekeris relationship $\omega_e x_e = B_e(1 + \omega_e \alpha_e / 6B_e^2)$.[2,3] Although the energy difference between the two $^3\Pi$ states is well established, it is not certain that the lowest $^3\Pi$ state is the ground state since it has only been studied in emission. We assume it to be the ground state by analogy with the BN molecule where the $^3\Pi$ state has been shown theoretically and experimentally (via absorption spectroscopy) to be the ground state.[4] For BN, SCF calculations[5] indicate $^3\Sigma$, $^1\Sigma$ and $^1\Pi$ states lying between 3400 and 4800 cm^{-1}. If these states lie at the same energy for AlN, they would have no effect on the thermochemical properties below 500 K but would increase the entropy at 6000 K by 5.0 $J \cdot K^{-1} \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−8.942	522.933	522.933	INFINITE
100	29.134	195.617	255.951	−6.033	523.906	513.034	−267.981
200	30.316	216.062	231.448	−3.077	523.605	502.220	−131.166
250	31.378	222.940	229.080	−1.535	523.306	496.908	−103.823
298.15	32.367	228.553	228.553	0.	523.000	491.851	−86.170
300	32.403	228.753	228.553	0.060	522.988	491.658	−85.605
350	33.288	233.817	228.951	1.703	522.668	486.462	−72.600
400	34.019	238.311	229.846	3.386	522.348	481.311	−62.853
450	34.612	242.353	231.015	5.102	522.028	476.201	−55.276
500	35.093	246.026	232.335	6.845	521.704	471.126	−49.218
600	35.808	252.491	235.170	10.393	521.025	461.074	−40.140
700	36.304	258.051	238.051	14.000	520.263	451.141	−33.665
800	36.663	262.923	240.862	17.649	519.377	441.325	−28.816
900	36.934	267.258	243.558	21.330	518.328	431.630	−25.051
1000	37.147	271.160	246.127	25.034	506.497	422.821	−22.086
1100	37.320	274.709	248.566	28.758	505.396	414.507	−19.683
1200	37.465	277.963	250.882	32.497	504.286	406.293	−17.685
1300	37.589	280.967	253.082	36.250	503.167	398.172	−15.999
1400	37.699	283.756	255.175	40.014	502.040	390.138	−14.556
1500	37.797	286.361	257.168	43.789	500.905	382.184	−13.309
1600	37.886	288.803	259.070	47.573	499.765	374.307	−12.220
1700	37.969	291.102	260.887	51.366	498.620	366.501	−11.261
1800	38.046	293.275	262.627	55.167	497.471	358.762	−10.411
1900	38.119	295.334	264.294	58.975	496.320	351.087	−9.652
2000	38.189	297.291	265.896	62.791	495.166	343.473	−8.971
2100	38.257	299.156	267.435	66.613	494.011	335.917	−8.355
2200	38.322	300.937	268.918	70.442	492.855	328.416	−7.798
2300	38.387	302.642	270.347	74.278	491.698	320.967	−7.289
2400	38.450	304.277	271.727	78.119	490.542	313.569	−6.825
2500	38.514	305.848	273.061	81.968	489.387	306.219	−6.398
2600	38.577	307.360	274.351	85.822	488.234	298.915	−6.005
2700	38.641	308.817	275.601	89.683	487.082	291.655	−5.642
2800	38.706	310.223	276.812	93.550	192.031	285.406	−5.324
2900	38.772	311.583	277.988	97.424	191.979	288.742	−5.201
3000	38.840	312.898	279.130	101.305	191.930	292.079	−5.086
3100	38.910	314.173	280.240	105.192	191.884	295.418	−4.978
3200	38.981	315.409	281.320	109.087	191.842	298.759	−4.877
3300	39.056	316.610	282.371	112.989	191.804	302.101	−4.782
3400	39.133	317.777	283.395	116.898	191.770	305.444	−4.693
3500	39.212	318.913	284.394	120.815	191.741	308.787	−4.608
3600	39.294	320.018	285.368	124.741	191.716	312.132	−4.529
3700	39.379	321.096	286.319	128.674	191.696	315.477	−4.454
3800	39.467	322.148	287.248	132.616	191.681	318.823	−4.383
3900	39.558	323.174	288.157	136.568	191.671	322.169	−4.315
4000	39.652	324.177	289.045	140.528	191.665	325.515	−4.251
4100	39.748	325.157	289.913	144.498	191.665	328.861	−4.190
4200	39.847	326.116	290.764	148.478	191.670	332.207	−4.132
4300	39.949	327.055	291.597	152.468	191.679	335.553	−4.076
4400	40.053	327.974	292.413	156.468	191.693	338.899	−4.023
4500	40.159	328.876	293.214	160.478	191.713	342.244	−3.973
4600	40.268	329.759	293.999	164.500	191.735	345.589	−3.924
4700	40.378	330.627	294.769	168.532	191.760	348.934	−3.878
4800	40.490	331.478	295.525	172.575	191.788	352.277	−3.834
4900	40.604	332.314	296.267	176.630	191.819	355.621	−3.791
5000	40.720	333.135	296.996	180.696	191.851	358.963	−3.750
5100	40.836	333.943	297.713	184.774	191.884	362.305	−3.711
5200	40.954	334.737	298.417	188.864	191.917	365.646	−3.673
5300	41.073	335.518	299.110	192.965	191.948	368.987	−3.637
5400	41.192	336.287	299.791	197.078	191.978	372.327	−3.602
5500	41.313	337.044	300.462	201.203	192.005	375.667	−3.568
5600	41.433	337.790	301.122	205.341	192.028	379.006	−3.535
5700	41.554	338.524	301.771	209.490	192.046	382.344	−3.504
5800	41.675	339.248	302.411	213.651	192.060	385.682	−3.473
5900	41.795	339.961	303.042	217.825	192.064	389.021	−3.444
6000	41.916	340.665	303.663	222.010	192.082	392.357	−3.416

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = 70.40 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 740\ K$
$T_{fus} = > 1923\ K$

$\Delta_f H°(0\ K) = -1137.32 \pm 0.71\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1133.19 \pm 0.71\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.297\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was reported by Coughlin.[1] The value was calculated from the measured heat of solution of $NaAlO_2$(cr) at 303.15 K in 4.360m hydrochloric acid solution.

Heat Capacity and Entropy

The low temperature heat capacities, below 350 K, were measured by Westrum.[2] Heat capacities above 350 K, 399.4–1698.6 K, were measured by Christensen *et al.*[3] These two sets of $C_p°$ data were plotted graphically and joined smoothly at 350 K. Low temperature heat capacities 51 K–298.15 K, were also determined by King[4] and agree very well with those reported by Westrum.[2] $S°(298.15\ K)$ was reported by Westrum[2] based on $S°(10\ K) = 0.01\ J \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

T_{trs} and $\Delta_{trs} H°$ were obtained from Christensen *et al.*[3]

Fusion Data

T_{trs} is taken from Kammermeyer *et al.*[5]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−23.794	−1137.319	−1137.319	INFINITE
100	28.259	15.004	123.662	−10.866	−1129.119	−1110.209	579.914
200	56.907	44.279	76.663	−6.477	−1131.899	−1090.089	284.702
298.15	73.638	70.400	70.400	0.	−1133.195	−1069.248	187.328
300	73.889	70.856	70.401	0.136	−1133.209	−1068.851	186.104
400	83.412	93.498	73.424	8.030	−1136.417	−1047.095	136.737
500	89.563	112.798	79.417	16.690	−1136.549	−1024.739	107.054
600	94.270	129.554	86.408	25.888	−1136.263	−1002.398	87.267
700	98.291	144.393	93.651	35.519	−1135.686	−980.130	73.138
740.000	99.788	149.896	96.544	39.481	ALPHA <- -> BETA		
740.000	97.696	151.649	96.544	40.778	TRANSITION		
800	98.751	159.306	100.967	46.671	−1133.761	−958.058	62.555
900	100.525	171.040	108.112	56.635	−1133.231	−936.128	54.331
1000	102.299	181.723	114.946	66.776	−1143.354	−913.493	47.716
1100	104.073	191.556	121.470	77.095	−1142.628	−890.541	42.288
1200	105.847	200.688	127.695	87.591	−1238.567	−865.220	37.662
1300	107.621	209.230	133.642	98.264	−1236.730	−834.182	33.518
1400	109.395	217.270	139.331	109.115	−1234.746	−803.290	29.971
1500	111.169	224.878	144.783	120.143	−1232.613	−772.545	26.902
1600	112.943	232.110	150.017	131.349	−1230.328	−741.948	24.222
1700	114.751	239.011	155.050	142.734	−1227.889	−711.498	21.862
1800	116.491	245.620	159.900	154.297	−1225.296	−681.196	19.768
1900	118.233	251.965	164.579	166.034	−1222.553	−651.042	17.898
2000	119.858	258.072	169.102	177.939	−1219.665	−621.037	16.220
2100	121.366	263.957	173.480	190.002	−1216.644	−591.179	14.705
2200	122.759	269.635	177.722	202.209	−1213.503	−561.468	13.331
2300	124.034	275.121	181.838	214.549	−1210.252	−531.903	12.080
2400	125.194	280.424	185.836	227.012	−1206.905	−502.481	10.936
2500	126.237	285.557	189.723	239.584	−1203.473	−473.200	9.887
2600	127.163	290.526	193.505	252.255	−1199.968	−444.058	8.921
2700	127.973	295.341	197.188	265.013	−1196.403	−415.052	8.030
2800	128.666	300.008	200.777	277.846	−1486.690	−385.211	7.186
2900	129.243	304.533	204.277	290.742	−1481.946	−345.957	6.231
3000	129.704	308.923	207.693	303.691	−1477.178	−306.866	5.343

PREVIOUS: December 1960 CURRENT: March 1963

Aluminum Oxide (AlO) IDEAL GAS $M_r = 42.98094$ Aluminum Oxide (AlO) $Al_1O_1(g)$

$S°(298.15\ K) = 218.38 \pm 0.08\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 67.0 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 66.9 \pm 8\ kJ·mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)								
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X^2\Sigma^+$	0.0	2	979.23	6.97	0.64136	0.0058	1.6178	1
$A^2\Pi_i$	5282	4	728.5	4.15	0.5365	0.0050	1.769	2, 1
$B^2\Sigma^+$	20635.2	2	870.05	3.52	0.60408	0.00447	1.6670	1
$C^2\Pi_r$	33055.	4	856.	6.	[0.60]	[0.004]	[1.67]	1, 3–4
$^4\Sigma^+$	[30200]	4	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^4\Delta$	[31600]	8	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^4\Sigma^-$	[33000]	4	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^2\Delta$	[34700]	4	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$^2\Sigma^-$	[34900]	2	[820]	[5.0]	[0.565]	[0.004]	[1.724]	3–4
$D^2\Sigma^+$	40187	2	817.5	4.8	0.5652	0.0046	1.7234	1–2

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = 16.0 \pm 2$ kcal·mol^{-1} ($D_0° = 121.193 \pm 2$ kcal·mol^{-1}) based mainly on $D_0° \geq 121.0 \pm 0.6$ kcal·mol^{-1} [5] from laser-induced fluorescence of AlO and on $D_0° = 122.0 \pm 2.5$ and 121.6 kcal·mol^{-1} [6] from recent mass spectrometry of the evaporation of Al_2O_3. The mass-spectrometric values of $D_0°$[6] become 121.5 ± 3 and -120.8 ± 3 kcal·mol^{-1} when we convert to $\Delta_f H°(298.15\ K) = 78.8 \pm 1.0$ kcal·mol^{-1} for Al(g) and to a temperature scale based on $T_{fus} = 2327$ K for $\alpha-Al_2O_3$ instead of 2318 K.

The adopted $\Delta_f H°$ was selected by Pedley and Marshall[7] from a network analysis of thermochemical data on $D_0°$ of AlO, BO, BaO, SiO and TiO. They considered over two dozen studies on AlO plus many studies on related oxides. We concur in their selection.

Our previous JANAF Thermochemical Table[8] summarized older mass-spectrometric values of $D_0°$ ranging from 113.5 to 119.9 kcal·mol^{-1}. We now give less weight to the lower values for two reasons: they are less consistent with the network of data for other oxides and they all may have a negative bias arising from ionization cross sections. These lower values converge toward the adopted value if they are recalculated using alternative approximations for ionization cross sections[9–11] of reactants and calibrants. Ho and Burns[6] and Drowart[11] gave some examples of similar recalculations. We conclude that errors in cross sections provide a plausible, though unproved, explanation of much of the discrepancy between the mass-spectrometric and fluorescence values of $D_0°$. Errors in the interpretation of fluorescence data[5] appear to be less likely, though not impossible. Plausibility of the fluorescence interpretation rests in part on the spectroscopic limit $D_0° \leq 122.1 \pm 0.6$ kcal·mol^{-1} derived by Drowart[11] from reinterpretation of absorption edges observed by Tyte and previously interpreted to give $D_0° \leq 119.9$ kcal·mol^{-1}.[12] Additional results on $D_0°$ have been summarized elsewhere.[5] Gurvich *et al.*[13] selected $D_0° = 121.176 \pm 1.2$ kcal·mol^{-1}.

Heat Capacity and Entropy

Electronic levels (ν_{oo}) and vibration–rotation constants of the observed states are from Huber and Herzberg[1] and recent studies.[2] Schamps[3] made extensive predictions of the unobserved levels of AlO and MgO. We adopt these estimates since additional data for MgO[4] and the F state of AlO confirm that they are reasonably accurate. Estimated molecular constants are derived from isoconfigurational levels whenever possible. We omit levels above 40187 cm^{-1} since they will have a negligible effect. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_r^i in the partition function $Q = Q_t \Sigma\, Q_v^i Q_r^i g_i \exp(-c_2\epsilon_i/T)$. Functions calculated by Gurvich *et al.*[13] are in close agreement; their values of the Gibbs energy function differ by ≤ 0.01 at $T \leq 5000$ K and by only 0.026 cal·K^{-1}·mol^{-1} at 6000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.788	67.037	67.037	INFINITE
100	29.108	186.129	244.933	−5.880	68.009	58.760	−30.693
200	29.504	206.370	221.161	−2.958	67.673	49.577	−12.948
298.15	30.883	218.386	218.386	0.	66.944	40.845	−7.156
300	30.913	218.577	218.387	0.057	66.929	40.683	−7.084
400	32.489	227.691	219.619	3.229	66.107	32.057	−4.186
500	33.750	235.083	221.995	6.544	65.260	23.642	−2.470
600	34.685	241.323	224.710	9.968	64.369	15.401	−1.341
700	35.399	246.726	227.478	13.474	63.400	7.315	−0.546
800	36.001	251.492	230.187	17.044	62.321	−0.625	0.041
900	36.583	255.766	232.796	20.673	61.106	−8.422	0.489
1000	37.205	259.652	235.290	24.362	49.149	−15.315	0.800
1100	37.898	263.230	237.670	28.116	47.973	−21.704	1.031
1200	38.669	266.560	239.940	31.944	46.852	−27.988	1.218
1300	39.506	269.688	242.109	35.852	45.793	−34.182	1.373
1400	40.386	272.648	244.186	39.847	44.806	−40.296	1.503
1500	41.283	275.465	246.178	43.930	43.893	−46.343	1.614
1600	42.167	278.157	248.093	48.103	43.057	−52.331	1.708
1700	43.015	280.739	249.938	52.362	42.296	−58.269	1.790
1800	43.805	283.221	251.719	56.704	41.605	−64.164	1.862
1900	44.523	285.609	253.440	61.121	40.977	−70.023	1.925
2000	45.158	287.909	255.106	65.606	40.405	−75.850	1.981
2100	45.706	290.126	256.721	70.150	39.881	−81.649	2.031
2200	46.165	292.263	258.288	74.744	39.396	−87.425	2.076
2300	46.538	294.324	259.811	79.380	38.942	−93.179	2.116
2400	46.830	296.311	261.290	84.049	38.509	−98.914	2.153
2500	47.047	298.227	262.730	88.743	38.091	−104.632	2.186
2600	47.196	300.075	264.131	93.456	37.681	−110.333	2.217
2700	47.286	301.858	265.495	98.180	37.272	−116.018	2.244
2800	47.325	303.579	266.825	102.911	−257.042	−120.719	2.252
2900	47.321	305.240	268.121	107.644	−256.368	−115.863	2.087
3000	47.279	306.843	269.385	112.374	−255.706	−111.029	1.933
3100	47.209	308.393	270.619	117.099	−255.059	−106.217	1.790
3200	47.115	309.890	271.823	121.815	−254.430	−101.426	1.656
3300	47.003	311.338	272.998	126.521	−253.820	−96.654	1.530
3400	46.878	312.739	274.147	131.215	−253.231	−91.901	1.412
3500	46.744	314.096	275.269	135.896	−252.663	−87.164	1.301
3600	46.605	315.411	276.366	140.564	−252.118	−82.443	1.196
3700	46.464	316.686	277.438	145.217	−251.596	−77.737	1.097
3800	46.324	317.923	278.487	149.857	−251.096	−73.045	1.004
3900	46.187	319.125	279.514	154.482	−250.619	−68.365	0.916
4000	46.055	320.293	280.519	159.094	−250.163	−63.698	0.832
4100	45.930	321.428	281.503	163.694	−249.730	−59.042	0.752
4200	45.813	322.534	282.467	168.281	−249.318	−54.396	0.677
4300	45.704	323.610	283.411	172.857	−248.928	−49.760	0.604
4400	45.606	324.660	284.337	177.422	−248.557	−45.133	0.536
4500	45.518	325.684	285.244	181.978	−248.205	−40.514	0.470
4600	45.441	326.683	286.134	186.526	−247.874	−35.902	0.408
4700	45.376	327.660	287.008	191.067	−247.561	−31.297	0.348
4800	45.322	328.615	287.864	195.601	−247.268	−26.699	0.291
4900	45.280	329.549	288.706	200.131	−246.993	−22.106	0.236
5000	45.250	330.463	289.532	204.658	−246.736	−17.520	0.183
5100	45.232	331.359	290.343	209.182	−246.498	−12.937	0.133
5200	45.226	332.237	291.140	213.705	−246.278	−8.360	0.084
5300	45.231	333.099	291.924	218.227	−246.077	−3.787	0.037
5400	45.248	333.944	292.694	222.751	−245.894	0.783	−0.008
5500	45.276	334.775	293.452	227.277	−245.730	5.349	−0.051
5600	45.315	335.591	294.197	231.807	−245.585	9.913	−0.092
5700	45.365	336.394	294.930	236.341	−245.461	14.474	−0.133
5800	45.425	337.183	295.652	240.880	−245.354	19.034	−0.171
5900	45.494	337.960	296.363	245.426	−245.270	23.591	−0.209
6000	45.574	338.725	297.062	249.980	−245.186	28.145	−0.245

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = [231.0 \pm 13]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 986.6 \pm 20\ kJ \cdot mol^{-1}$

$\Delta_H H°(298.15\ K) = [992.993]\ kJ \cdot mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$^3\Pi$	[0]	6	[710]	[4]	[0.5066]	[0.004]	[1.82]
$^1\Pi$	[2000]	2	[710]	[4]	[0.5066]	[0.004]	[1.82]
$^1\Sigma$	[300]	1	[820]	[5]	[0.5806]	[0.005]	[1.70]
$^3\Sigma$	[12000]	3	[870]	[5]	[0.5806]	[0.005]	[1.70]
$^1\Sigma$	[20000]	1	[870]	[5]	[0.5806]	[0.005]	[1.70]

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of AlO[1] using Hildenbrand's appearance potential[2] of 9.53 ± 0.15 eV (219.8 ± 3.5 $kcal \cdot mol^{-1}$), assuming that it is identical with the ionization potential for $AlO(g) \rightarrow AlO^+(g) + e\ (g)$. Other reported values for the appearance potential range from 9 to 10.3 ± 1 eV, including several values of 9.5.[3-5] These values are consistent with, but less precise than, the adopted value. $\Delta_f H°(0\ K)$ yields $D_0° = 39.5 \pm 5$ kcal·mol for $AlO^+ \rightarrow Al^+ + O$; this is larger than the value of −26 $kcal \cdot mol^{-1}$ predicted by Schamps[6] from his SCF calculation of IP(AlO) = 10.08 eV. MNDO calculations[7] differ by only 3.5 $kcal \cdot mol^{-1}$ from our $[\Delta_f H°(AlO^+, 298.15\ K) - \Delta_f H°(AlO, 298.15\ K)]$ even though the MNDO values of $\Delta_f H°(298.15\ K)$ deviate by −14 and −18 $kcal \cdot mol^{-1}$, respectively.

$\Delta_f H°(AlO^+, g, 298.15\ K)$ is obtained from $\Delta_f H°(AlO)$ by using IP(AlO) with JANAF [1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for AlO(g), $AlO^+(g)$ and $e^-(g)$. $\Delta_r H°(Al0 \rightarrow A10^+ + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by −1.481 $kcal \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

No spectroscopic data have been observed for AlO^+ but Schamps[6] recently predicted electronic levels and molecular constants from variational calculations with semiempirical estimates of correlation energy differences. Similar calculations were reasonably accurate for MgO.[6] The predictions for AlO^+ yield almost equal energies for $^3\Pi$ and $^1\Sigma^+$; thus they do not distinquish which is the ground state. AlO^+ is isoelectronic with MgO and AlN. MgO has a $^1\Sigma^+$ ground state with the low-lying $^3\Pi$ level at 2600 cm^{-1}.[8] Triplet-triplet bands are observed for AlN[9, 10] and it is quite likely that the lower $^3\Pi$ level is the ground state.[10] We conclude for AlO^+ that $^3\Pi$ is very low lying and probably the ground state; it will dominate the electronic partition function.

The adopted electronic levels are minor modifications of the predictions of Schamps.[6] Molecular constants of the $^3\Pi$ state are estimated to be intermediate between those of MgO[1] and AlN.[9] The r_e adopted for $^3\Pi$ is −0.1 Å longer than that of Al_2O.[1] Values of r_e adopted for AlO^+ are also longer than those of their Π and Σ counterparts in AlO.[1] Values of ω_e are based on force-constant comparisons. Other constants are based on comparisons with the observed and calculated values for MgO.[1, 6]

The low-lying electronic levels cause an entropy uncertainty of perhaps 3 $cal/(mol \cdot K)^{-1}$ at 298 K but <1 $cal/(mol \cdot K)^{-1}$ at T>2000 K. Uncertainty in the enthalpy is large (perhaps 4 $kcal \cdot mol^{-1}$) at high temperature. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_t^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_t^i Q_v^i g_i \exp(-c_2 \epsilon_i / T)$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.090	986.587		
100	29.445	197.312	259.050	−6.174			
200	31.118	218.161	233.943	−3.156			
298.15	33.135	230.975	230.975	0.	992.993	956.886	−167.642
300	33.168	231.180	230.975	0.061	993.021	956.661	−166.570
400	34.685	240.942	232.296	3.458	994.503	944.317	−123.315
500	35.770	248.805	234.837	6.984	995.945	931.603	−97.324
600	36.583	255.401	237.729	10.603	997.327	918.604	−79.972
700	37.206	261.090	240.669	14.294	998.622	905.379	−67.560
800	37.686	266.091	243.541	18.040	999.797	891.977	−58.240
900	38.052	270.551	246.298	21.828	1000.820	878.437	−50.983
1000	38.330	274.576	248.928	25.647	991.071	865.552	−45.212
1100	38.539	278.239	251.429	29.491	992.064	852.952	−40.503
1200	38.696	281.600	253.805	33.354	993.056	840.261	−36.576
1300	38.813	284.702	256.064	37.229	994.043	827.488	−33.249
1400	38.900	287.581	258.214	41.115	995.026	814.639	−30.395
1500	38.966	290.268	260.262	45.009	996.003	801.720	−27.918
1600	39.017	292.784	262.217	48.908	996.972	788.737	−25.750
1700	39.057	295.151	264.085	52.812	997.933	775.692	−23.834
1800	39.091	297.384	265.874	56.719	998.886	762.592	−22.130
1900	39.120	299.499	267.588	60.630	999.831	749.439	−20.604
2000	39.147	301.506	269.234	64.543	1000.766	736.236	−19.229
2100	39.174	303.417	270.817	68.459	1001.693	722.986	−17.983
2200	39.202	305.240	272.341	72.378	1002.611	709.693	−16.850
2300	39.231	306.983	273.809	76.300	1003.521	696.358	−15.815
2400	39.262	308.653	275.226	80.224	1004.423	682.984	−14.865
2500	39.295	310.256	276.596	84.152	1005.317	669.572	−13.990
2600	39.331	311.798	277.920	88.083	1006.203	656.125	−13.182
2700	39.369	313.283	279.203	92.018	1007.083	642.644	−12.433
2800	39.410	314.716	280.446	95.957	714.056	630.098	−11.755
2900	39.453	316.100	281.651	99.900	716.019	627.064	−11.295
3000	39.499	317.438	282.822	103.848	717.977	623.964	−10.864
3100	39.546	318.734	283.960	107.800	719.930	620.798	−10.460
3200	39.595	319.990	285.066	111.757	721.879	617.569	−10.081
3300	39.647	321.209	286.143	115.719	723.824	614.279	−9.723
3400	39.699	322.394	287.192	119.686	725.764	610.930	−9.386
3500	39.753	323.545	288.214	123.659	727.702	607.525	−9.067
3600	39.808	324.666	289.211	127.637	729.636	604.064	−8.765
3700	39.863	325.757	290.184	131.621	731.567	600.549	−8.478
3800	39.919	326.821	291.134	135.610	733.495	596.982	−8.206
3900	39.976	327.859	292.063	139.604	735.421	593.365	−7.947
4000	40.034	328.872	292.970	143.605	737.343	589.698	−7.701
4100	40.091	329.861	293.858	147.611	739.262	585.983	−7.466
4200	40.149	330.828	294.727	151.623	741.177	582.221	−7.241
4300	40.206	331.773	295.577	155.641	743.088	578.414	−7.026
4400	40.264	332.698	296.411	159.664	744.995	574.562	−6.821
4500	40.321	333.604	297.227	163.694	746.900	570.667	−6.624
4600	40.378	334.490	298.028	167.729	748.796	566.730	−6.435
4700	40.435	335.359	298.813	171.769	750.687	562.751	−6.254
4800	40.491	336.211	299.583	175.816	752.570	558.733	−6.080
4900	40.547	337.047	300.339	179.868	754.447	554.675	−5.913
5000	40.602	337.866	301.081	183.925	756.313	550.579	−5.752
5100	40.657	338.671	301.811	187.988	758.168	546.447	−5.597
5200	40.711	339.461	302.527	192.056	760.013	542.277	−5.447
5300	40.765	340.237	303.231	196.130	761.844	538.072	−5.303
5400	40.818	340.999	303.924	200.209	763.660	533.833	−5.164
5500	40.871	341.749	304.605	204.294	765.461	529.560	−5.029
5600	40.922	342.486	305.274	208.384	767.244	525.255	−4.899
5700	40.974	343.211	305.934	212.478	769.008	520.918	−4.774
5800	41.024	343.924	306.583	216.578	770.755	516.550	−4.652
5900	41.074	344.625	307.221	220.683	772.476	512.152	−4.534
6000	41.123	345.316	307.851	224.793	774.195	507.724	−4.420

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = [212.81 \pm 1.7]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -263.2 \pm 17\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-269.425]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma^+]$	0	[1]
$[^3\Pi]$	[27000]	[6]

$\omega_e = [900]\ cm^{-1}$ $\omega_e x_e = [5.4]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.640]\ cm^{-1}$ $\alpha_e = [0.006]\ cm^{-1}$ $r_e = [1.62]$ Å

Enthalpy of Formation

We adopt $\Delta_f H°(0\ K) = -62.9 \pm 4\ kcal·mol^{-1}$ based on equilibrium data for $AlO(g) + Cl^-(g) = Cl(g) + AlO^-(g)$ obtained using effusion mass spectrometry by Srivastava *et al.*[1, 2] Our analysis of the data is summarized below. For the process $AlO^-(g) \rightarrow Al(g) + O^-(g)$ we calculate a dissociation energy $D_0° = 166.4 \pm 4\ kcal·mol^{-1}$; this is comparable to $D_0°(AlF) = 159.3 \pm 1.5\ kcal·mol^{-1}$ [3] and much larger than $D_0°(AlO) = 121.2 \pm 2\ kcal·mol^{-1}$.[3] The corresponding electron affinity, EA(AlO) = 78.9 ± 4 kcal·mol^{-1} (3.42 eV), is 4.4 kcal·mol^{-1} less than EA(Cl) = 83.3 kcal·mol^{-1}.[3] Gaines and Page[4] used a semi-empirical method to predict EA(AlO) = 60 and EA(BO) = 49 kcal·mol^{-1}, corresponding to a difference of 11 kcal·mol^{-1}. Although this difference is comparable with the experimental difference of 9 kcal·mol^{-1}, the values predicted for EA(AlO) and EA(BO) are −20 kcal·mol^{-1} lower than the experimental results.[1, 2] MNDO calculations[5] predicted $\Delta_f H°(298.15\ K) = -55.9$ and $[\Delta_f H°(AlO^-, 298.15\ K) - \Delta_f H°(AlO, 298.15\ K)] = 54\ kcal·mol^{-1}$, but these values have a large uncertainty. Gurvich *et al.*[6] selected EA(AlO) = 79.8 ± 2.4 kcal·mol^{-1} based on the equilibrium data.[1]

The value of $\Delta_r H°(AlO^- \rightarrow AlO + e^-, 298.15\ K)$ calculated from our tables will differ from a room temperature threshold energy due to inclusion of the enthalpies, $H°(0\ K) - H°(298.15\ K)$, of $AlO^-(g)$, AlO(g) and $e^-(g)$ and to the threshold effects discussed by Rosenstock *et al.*[7]

Source	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Srivastava (1972)[1, 2]	2082–2222	5	−5.8 ± 3.8	−8.1 ± 8.3	4.48 ± 1.1	−64.39

Heat Capacity and Entropy

All of the molecular constants are estimated by comparison with AlF and AlO.[3] We estimate the electronic states and levels from the low-lying states of isoelectronic AlF. The bond distance is taken equal to that in AlO and slightly shorter than that in AlF. B_e is calculated from r_e. We derive $\omega_e = 900 \pm 100\ cm^{-1}$ from k = 4.8 mdyn/Å estimated from k(AlF) = 4.23 and k(AlO) = 5.68. Similar comparisons of $\omega_e x_e/\omega_e$ and α_e/B_e are used to estimated $\omega_e x_e$ and α_e.

Gurvich *et al.*[6] calculated $C_p°$, $S°$ and $H°$ using somewhat larger estimates for ω_e and B_e. Their values of $S°$ differ from ours by −0.21 (298.15 K), −0.56 (2000 K) and −0.63 (4000 K) cal·K^{-1}·mol^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.826	−263.172		
100	29.112	180.387	239.570	−5.918			
200	29.690	200.668	215.615	−2.989			
250	30.453	207.371	213.318	−1.487			
298.15	31.303	212.807	212.807	0.	−269.424	−287.606	50.387
300	31.335	213.001	212.808	0.058	−269.477	−287.718	50.096
350	32.194	217.897	213.193	1.646	−270.901	−290.646	43.377
400	32.961	222.247	214.057	3.276	−272.332	−293.369	38.310
450	33.622	226.168	215.189	4.941	−273.768	−295.913	34.349
500	34.179	229.740	216.468	6.636	−275.212	−298.296	31.163
600	35.041	236.053	219.220	10.100	−278.142	−302.639	26.347
700	35.654	241.503	222.023	13.636	−281.159	−306.484	22.870
800	36.102	246.295	224.763	17.225	−284.298	−309.890	20.234
900	36.439	250.567	227.397	20.853	−287.593	−312.893	18.160
1000	36.699	254.420	229.910	24.510	−301.660	−314.759	16.441
1100	36.907	257.928	232.300	28.191	−304.988	−315.908	15.001
1200	37.077	261.147	234.572	31.890	−308.317	−316.754	13.788
1300	37.219	264.121	236.732	35.605	−311.647	−317.322	12.750
1400	37.341	266.883	238.788	39.334	−314.979	−317.633	11.851
1500	37.446	269.463	240.748	43.073	−318.314	−317.706	11.064
1600	37.539	271.883	242.619	46.822	−321.652	−317.557	10.367
1700	37.623	274.161	244.408	50.581	−324.993	−317.199	9.746
1800	37.699	276.314	246.122	54.347	−328.339	−316.644	9.189
1900	37.769	278.354	247.765	58.120	−331.688	−315.903	8.685
2000	37.835	280.293	249.343	61.900	−335.043	−314.985	8.227
2100	37.896	282.141	250.861	65.687	−338.403	−313.900	7.808
2200	37.954	283.905	252.323	69.479	−341.768	−312.654	7.423
2300	38.009	285.593	253.734	73.278	−345.139	−311.255	7.069
2400	38.062	287.212	255.095	77.081	−348.516	−309.710	6.741
2500	38.113	288.767	256.411	80.890	−351.898	−308.023	6.436
2600	38.164	290.263	257.684	84.704	−355.286	−306.202	6.152
2700	38.213	291.704	258.918	88.523	−358.679	−304.249	5.886
2800	38.262	293.095	260.114	92.346	−655.979	−301.203	5.619
2900	38.312	294.438	261.274	96.175	−658.287	−288.492	5.196
3000	38.362	295.738	262.402	100.009	−660.601	−275.701	4.800
3100	38.414	296.997	263.497	103.848	−662.918	−262.833	4.429
3200	38.467	298.217	264.563	107.692	−665.240	−249.890	4.079
3300	38.523	299.402	265.601	111.541	−667.565	−236.874	3.749
3400	38.582	300.552	266.612	115.396	−669.893	−223.788	3.438
3500	38.645	301.672	267.598	119.258	−672.224	−210.634	3.144
3600	38.712	302.761	268.560	123.126	−674.557	−197.412	2.864
3700	38.784	303.823	269.499	127.000	−676.892	−184.126	2.599
3800	38.861	304.858	270.416	130.882	−679.228	−170.777	2.347
3900	38.944	305.869	271.312	134.773	−681.565	−157.366	2.108
4000	39.035	306.856	272.188	138.672	−683.902	−143.895	1.879
4100	39.132	307.821	273.045	142.580	−686.238	−130.366	1.661
4200	39.237	308.765	273.885	146.498	−688.573	−116.780	1.452
4300	39.350	309.690	274.707	150.427	−690.908	−103.138	1.253
4400	39.471	310.596	275.512	154.368	−693.241	−89.442	1.062
4500	39.602	311.484	276.302	158.322	−695.569	−75.694	0.879
4600	39.741	312.356	277.076	162.289	−697.897	−61.893	0.703
4700	39.890	313.212	277.836	166.271	−700.223	−48.042	0.534
4800	40.048	314.054	278.581	170.267	−702.546	−34.141	0.372
4900	40.216	314.881	279.314	174.281	−704.866	−20.192	0.215
5000	40.393	315.696	280.033	178.311	−707.184	−6.195	0.065
5100	40.580	316.497	280.741	182.359	−709.500	7.848	−0.080
5200	40.776	317.287	281.436	186.427	−711.814	21.935	−0.220
5300	40.982	318.066	282.120	190.515	−714.126	36.069	−0.355
5400	41.197	318.834	282.792	194.624	−716.437	50.245	−0.486
5500	41.420	319.592	283.455	198.755	−718.747	64.463	−0.612
5600	41.652	320.340	284.107	202.908	−721.057	78.725	−0.734
5700	41.893	321.080	284.749	207.085	−723.368	93.027	−0.852
5800	42.141	321.810	285.381	211.287	−725.677	107.370	−0.967
5900	42.397	322.533	286.005	215.514	−727.991	121.752	−1.078
6000	42.660	323.248	286.620	219.767	−730.286	136.172	−1.185

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$\Delta_{at}H°(0\ K) = 216.52 \pm 8$ kJ·mol^{-1}
$S°(298.15\ K) = [251.83 \pm 8]$ J·K^{-1}·mol^{-1}

$\Delta_fH°(0\ K) -85.01 \pm 32$ kJ·mol^{-1}
$\Delta_fH°(298.15\ K) = -86.19 \pm 32$ kJ·mol^{-1}

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[4]
[15000]	[4]
[20000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[700](1)
[200](2)
[930](1)

Point Group: [$D_{\infty h}$] $\sigma = 2$
Bond Distance: Al–O = [1.69] Å
Bond Angle: O–Al–O = [180]°
Rotational Constant: B_0 = [0.184455] cm^{-1}

Enthalpy of Formation

We adopt $\Delta_fH°(298.15\ K) = -20.6 \pm 8$ kcal·mol^{-1} and $\Delta_{at}H°(0\ K) = 216.52$ kcal·mol^{-1} derived from mass–spectrometric data measured by Ho and Burns[1] during laser evaporation of single crystals of Al_2O_3. $\Delta_fH°$ and $\Delta_{at}H°$ are consistent with limiting values from studies in two other laboratories that were unable to detect AlO_2^+.[2-3] AlO_2 appears to be much less stable than predicted by earlier data;[4-5] those differ from the adopted $\Delta_fH°$ by −19 to −23 kcal·mol^{-1}. Our analyses of the data are given below.

AlO_2 is the least abundant of the five Al–containing species identified in the vapor over Al_2O_3. Ho and Burns,[1] unlike Farber *et al.*,[4-5] identified AlO_2 as the source of the mass = 59 ion by accurate mass data combined with intensities and appearance potentials of AlO_2^+ and conceivable impurity ions. Their partial pressure[1] should be free of large error from mass = 59 ions other than AlO_2^+. Error does arise from *uncertainties in the evaporation coefficients, ionization cross sections and total flux of species.*[1] *An extreme example of this error is the* formation of α–Al_2O_3, which is biased by −9 kcal·mol^{-1} if calculated from the reported[1] pressures of Al and O. Our assigned uncertainty includes contributions from this error and that of the Gibbs–energy function.

Semiempirical calculations predicted $\Delta_fH°(298.15\ K) = -14.6$ and −24.3 kcal·mol^{-1} by the MNDO half–electron[6] and unrestricted Hartree–Fock[7] methods. These values agree with our adopted $\Delta_fH°$ but may be too uncertain to exclude the more negative value. Recent summaries[1,8] cite many other AlO_2 papers, including emission spectra and kinetic data that may not involve AlO_2. New studies[9] reassign much of the emission to an aluminum hydrate. We discount the bond–dissociation energies estimated from kinetics since formation of AlO_2 was inferred only from disappearance of AlO. Gurvich *et al.*[10] selected $\Delta_{at}H° = 215.1 \pm 7.2$ kcal·mol^{-1} based on different Gibbs–energy functions.

Source	Method	Reaction[a]	T/K	δS[b] cal·K^{-1}·mol^{-1}	$\Delta_rH°(298.15)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_fH°(298.15\ K)$ kcal·mol^{-1}	$\Delta_{at}H°(0\ K)$
1	Mass spec.	A	2221–2327[c]	−26 ± 5	−279 ± 12	−218.5 ± 2.7	−20.6 ± 8	216.5
2	Eff. mass spec.	B	2600	—	—	>25.1[d]	>−21.7 ± 8	<216.6
3	Mass spec.	B	2450	—	—	>24.9[d]	>−18.9 ± 8	<214.8
4	Eff. mass spec.	B	1943–2093	−1 ± 1	2.5 ± 1.4	3.6 ± 0.2	−43.2 ± 8	239.1
4	Flow eff. mass spec	B	1663–1983	−9 ± 6	−14 ± 12	3.2 ± 3.8	−43.6 ± 8	239.5
5	Flame mass spec.	C	2250	—	—	2.5	−39.3 ± 12	235.2

[a]Reactions: A) Al(g) + 2 O(g) = AlO_2(g); B) AlO(g) = AlO_2(g) + Al(g); C) AlO(g) + H_2O(g) = AlO_2(g) + H_2(g).
[b]$\delta S = \Delta_rS°$(2nd law) − $\Delta_rS°$(3rd law). [c]Temperature scale adjusted.
[d]AlO_2 not detected; detection limits estimated as $P(AlO_2) < P(Al_2O_2)/10$ in[3] and $P(AlO_2) < P(Al_2O_2, 2300\ K)$ in.[2]

Heat Capacity and Entropy

We adopt a linear OAlO structure and estimate the bond length by correcting the predicted value[6] for OAlO using the bias[6,11] in predicted values for AlO and Al_2O. Electronic states are estimated from BO_2 and vibrational frequencies from several related molecules. The adopted frequencies correspond to $k_1 \approx 14.2$, $k_{12} \approx 0.5$ and $(k_8/l) \approx 0.086$ mdyn/Å. The Al–O stretching constant k_1 may be compared to 3.6 for Al_2O,[11] 4.0 for AlOH,[12] 5.5 for AlO[11] and 6.6 for FAlO.[12] We assume that $k_1/(k_8/l^2)49$ compared to 31 in BO_2 and 39 in FBO.

Linear OAlO is the most stable structure according to MNDO[6] and unrestricted Hartree–Fock[7] calculations. The latter predicts that linear A100 and cyclic AlO_2 are less stable by 22 and 38 kcal·mol^{-1}.[7] These predictions are not decisive but they are the best available. Spectral assignments are conflicting. IR bands in gas–plus–O_2 matrices have been assigned to each of three structures. A band at 523 cm^{-1} in neon was tentatively assigned[13] to OAlO, but comparison with GaO_2[14] suggests that it is more likely to be ν_2 of cyclic AlO_2. Assignments for ν_2 in argon include 496[15] and 717[16] cm^{-1}. Other assignments for cyclic AlO_2 include ν_1 = 1096[15] (Ar), 1177[16] (Ar), 1116[17] (Ar) and 1096[17] (N_2). and ν_3 = 525 cm^{-1},[16] (Ar). Assignments to A100 include 1336 and 1091 cm^{-1},[18] (N_2). Gurvich *et al.*[10] calculated functions for cyclic AlO_2 using 1096, 496 and 550 cm^{-1}; their values of the Gibbs energy function differ from ours by 1.4 and 0.2 J·K^{-1}·mol^{-1} at 298 and 2000 K.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.042	−85.010	−85.010	INFINITE
100	37.838	204.213	292.685	−8.847	−85.203	−87.595	45.755
200	44.987	232.915	256.245	−4.666	−85.735	−89.792	23.451
250	47.638	243.244	252.641	−2.349	−85.990	−90.776	18.967
298.15	49.892	251.832	251.832	0.	−86.190	−91.679	16.062
300	49.972	252.140	251.833	0.092	−86.197	−91.713	15.969
350	51.950	259.997	252.448	2.642	−86.359	−92.619	13.823
400	53.583	267.044	253.840	5.282	−86.487	−93.504	12.210
450	54.914	273.435	255.668	7.995	−86.594	−94.375	10.955
500	55.998	279.279	257.741	10.769	−86.692	−95.234	9.949
600	57.605	289.640	262.216	16.454	−86.901	−96.924	8.438
700	58.700	298.607	266.789	22.273	−87.185	−98.573	7.356
800	59.469	306.499	271.269	28.184	−87.592	−100.174	6.541
900	60.025	313.537	275.582	34.160	−88.162	−101.714	5.903
1000	60.438	319.883	279.700	40.184	−99.515	−102.421	5.350
1100	60.753	325.659	283.619	46.244	−100.139	−102.681	4.876
1200	60.997	330.956	287.346	52.332	−100.775	−102.885	4.478
1300	61.190	335.847	290.891	58.442	−101.424	−103.034	4.140
1400	61.346	340.387	294.267	64.569	−102.085	−103.133	3.848
1500	61.473	344.624	297.484	70.710	−102.760	−103.185	3.593
1600	61.578	348.595	300.556	76.863	−103.450	−103.191	3.369
1700	61.667	352.331	303.493	83.025	−104.154	−103.153	3.170
1800	61.744	355.858	306.305	89.196	−104.875	−103.074	2.991
1900	61.812	359.198	309.001	95.374	−105.611	−102.953	2.830
2000	61.873	362.370	311.591	101.558	−106.365	−102.794	2.685
2100	61.930	365.390	314.082	107.748	−107.135	−102.597	2.552
2200	61.984	368.273	316.480	113.944	−107.923	−102.362	2.430
2300	62.038	371.029	318.792	120.145	−108.727	−102.091	2.319
2400	62.092	373.670	321.024	126.351	−109.549	−101.786	2.215
2500	62.148	376.206	323.181	132.563	−110.387	−101.445	2.120
2600	62.207	378.645	325.268	138.781	−111.240	−101.070	2.031
2700	62.269	380.994	327.288	145.005	−112.109	−100.663	1.947
2800	62.335	383.260	329.247	151.235	−406.892	−99.255	1.852
2900	62.405	385.448	331.148	157.472	−406.693	−88.272	1.590
3000	62.480	387.565	332.993	163.716	−406.505	−77.295	1.346
3100	62.560	389.615	334.787	169.968	−406.329	−66.323	1.118
3200	62.644	391.603	336.531	176.228	−406.162	−55.359	0.904
3300	62.734	393.532	338.229	182.497	−406.005	−44.399	0.703
3400	62.828	395.406	339.884	188.775	−405.856	−33.443	0.514
3500	62.927	397.228	341.496	195.063	−405.714	−22.492	0.336
3600	63.030	399.003	343.069	201.361	−405.578	−11.545	0.168
3700	63.137	400.731	344.604	207.669	−405.448	−0.601	0.008
3800	63.247	402.416	346.104	213.988	−405.322	10.340	−0.142
3900	63.361	404.061	347.569	220.319	−405.201	21.277	−0.285
4000	63.478	405.666	349.001	226.661	−405.084	32.210	−0.421
4100	63.596	407.235	350.402	233.014	−404.971	43.141	−0.550
4200	63.717	408.769	351.774	239.380	−404.861	54.069	−0.672
4300	63.840	410.270	353.117	245.758	−404.755	64.995	−0.790
4400	63.963	411.739	354.432	252.148	−404.653	75.918	−0.901
4500	64.088	413.178	355.722	258.551	−404.553	86.838	−1.008
4600	64.212	414.588	356.986	264.966	−404.460	97.757	−1.110
4700	64.337	415.970	358.227	271.393	−404.372	108.674	−1.208
4800	64.461	417.326	359.444	277.833	−404.291	119.589	−1.301
4900	64.585	418.656	360.639	284.285	−404.217	130.503	−1.391
5000	64.707	419.962	361.812	290.750	−404.153	141.415	−1.477
5100	64.828	421.245	362.965	297.227	−404.099	152.326	−1.560
5200	64.947	422.505	364.098	303.715	−404.058	163.235	−1.640
5300	65.065	423.743	365.212	310.216	−404.030	174.145	−1.716
5400	65.180	424.960	366.307	316.728	−404.018	185.053	−1.790
5500	65.293	426.157	367.384	323.252	−404.024	195.961	−1.861
5600	65.403	427.335	368.444	329.787	−404.049	206.871	−1.930
5700	65.511	428.493	369.488	336.332	−404.098	217.781	−1.996
5800	65.615	429.634	370.515	342.889	−404.167	228.692	−2.060
5900	65.717	430.756	371.526	349.455	−404.267	239.602	−2.121
6000	65.816	431.861	372.523	356.032	−404.373	250.515	−2.181

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

Continued on page 172

$\Delta_a H°(AlO_2^- \rightarrow Al + 2O + e^-) = 311.2 \pm 12$ kJ·mol^{-1}
$S°(298.15\ K) = [235.09 \pm 6.3]$ J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = -481 \pm 50$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = [-489.210]$ kJ·mol^{-1}

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[780](1)
[270](2)
[1120](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Al–O = [1.68] Å
Bond Angle: O–Al–O = [180]°
Rotational Constant: B_0 = [0.186657] cm^{-1}

Enthalpy of Formation

We adopt the rounded value $\Delta_f H°(0\ K) = -115 \pm 12$ kcal·mol^{-1}, which corresponds to the electron affinity EA = 94.68 kcal·mol^{-1} for AlO_2.[1] This is based on equilibrium data[2-3] that yield [EA(AlO_2)–EA(Cl)] = 11.6 kcal·mol^{-1} and EA(AlO_2) = 94.9 kcal·mol^{-1}. Data for the reaction $AlO_2(g) + Cl^-(g) = AlO_2^-(g) + Cl(g)$ at 2080–2222 K were obtained by Srivastava, Uy and Farber[2-3] using effusion mass spectrometry. From their data we derive the values $\Delta_r H°(298.15\ K) = -11.7 \pm 0.9$ (3rd law) and -8.7 ± 8.6 (2nd law) kcal·mol^{-1} plus [$\Delta_r S°$(2nd law)–$\Delta_r S°$(3rd law)] = 1.4 ± 4.0 cal·K^{-1}·mol^{-1}). The third-law $\Delta_f H°$ yields $\Delta_f H°(AlO_2^-, g, 0\ K) = -115.2$ and EA(AlO_2) = 94.9 kcal·mol^{-1}. Gurvich *et al.*[9] selected $\Delta_f H°(0\ K) = -115.7 \pm 14.3$ and EA = 96.8 ± 12 kcal·mol^{-1} based on Srivastava *et al.*[2]

It is conceivable that this electron affinity is biased. New data show that similar studies of Farber *et al.* on $\Delta_a H°(AlO_2, g, 0\ K)$ may be biased by >20 kcal·mol^{-1}.[1] Two calculations[4-5] provide a test for bias in EA = $\Delta_r H°(AlO_2^- \rightarrow AlO_2 + e^-) = 94.9$ kcal·mol^{-1}. Vertical ionization potentials of 85.3 and 78.4 kcal·mol^{-1} were calculated for AlO_2^- by Gutsev and Boldyrev[4] using two different bases in the non–empirical discrete–variation Xα method. MNDO calculations of Davis *et al.*[5] gave 76.0 kcal·mol^{-1} instead of our adopted difference [$\Delta_f H°(AlO_2)$–$\Delta_f H°(AlO_2^-)$] = 96.3 kcal·mol^{-1} at 298.15 K. Although both calculations favor smaller values of EA, they may be too uncertain to yield a definite conclusion. New data are desirable for both AlO_2^- and AlO^-.[1]

The value of $\Delta_r H°(AlO_2^- \rightarrow AlO_2 + e^-, 298.15\ K)$ calculated from our tables will differ from a room temperature threshold energy due to inclusion of JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$ of $AlO_2^-(g)$, $AlO_2(g)$ and $e^-(g)$ and to threshold effects discussed by Rosenstock *et al.*[6]

Heat Capacity and Entropy

We adopt a linear, symmetric structure and estimate the bond length to be 0.01 Å shorter than in AlO_2.[1] MNDO calculations[5] support this linear structure and also predict that the bond length of AlO_2^- is 0.007 Å shorter than in AlO_2. AlO_2^- is isoelectronic with SiO_2 and MgF_2, which are also believed to be linear.

We estimate the vibrational frequencies of AlO_2^-, together with those of AlO_2, from comparisons with SiO_2, OAlF, MgF_2, CO_2, OBF, BeF_2, BO_2^-, and BO_2. Our adopted values correspond to $k_1 \approx 5.6$, $k_{12} \approx 0.2$ and $(k_\delta/l^2) \approx 0.16$ mdyn/Å. The Al–O stretching constant k_1 may be compared to 5.5 in AlO,[1] 6.6 in OAlF and OAlCl[7] and 4.2 assumed in AlO_2.[1] We assume that $k_1/(k_\delta/l^2) \approx 35$. We take the ground state to be $^1\Sigma^+$ by analogy to other triatomics with 16 valence electrons.[8]

Gurvich *et al.*[9] calculated functions that differ by -1.3 cal·K^{-1}·mol^{-1} in entropy and Gibbs energy function.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.368	−481.158		
100	34.491	190.471	273.699	−8.323			
200	42.492	217.143	239.288	−4.429			
250	45.226	226.927	235.864	−2.234			
298.15	47.528	235.094	235.094	0.	−489.210	−483.454	84.699
300	47.611	235.388	235.095	0.088	−489.260	−483.418	84.171
350	49.683	242.887	235.682	2.522	−490.577	−482.339	71.985
400	51.455	249.640	237.012	5.051	−491.854	−481.075	62.822
450	52.950	255.789	238.761	7.662	−493.103	−479.652	55.677
500	54.203	261.435	240.750	10.342	−494.334	−478.092	49.946
600	56.131	271.498	245.057	15.865	−496.785	−474.613	41.319
700	57.493	280.259	249.474	21.550	−499.280	−470.722	35.126
800	58.475	288.004	253.815	27.351	−501.876	−466.466	30.457
900	59.198	294.935	258.006	33.236	−504.615	−461.877	26.807
1000	59.743	301.201	262.017	39.184	−518.123	−456.214	23.830
1100	60.161	306.916	265.843	45.180	−520.890	−449.889	21.363
1200	60.489	312.165	269.487	51.214	−523.659	−443.312	19.297
1300	60.750	317.018	272.959	57.276	−526.434	−436.504	17.539
1400	60.960	321.528	276.269	63.362	−529.215	−429.482	16.024
1500	61.133	325.739	279.428	69.467	−532.005	−422.261	14.704
1600	61.275	329.690	282.447	75.587	−534.805	−414.853	13.544
1700	61.395	333.408	285.337	81.721	−537.617	−407.270	12.514
1800	61.496	336.920	288.106	87.866	−540.442	−399.522	11.594
1900	61.582	340.248	290.763	94.020	−543.281	−391.615	10.766
2000	61.656	343.408	293.317	100.182	−546.135	−383.559	10.018
2100	61.719	346.418	295.775	106.350	−549.005	−375.360	9.337
2200	61.775	349.290	298.143	112.525	−551.893	−367.023	8.714
2300	61.824	352.038	300.427	118.705	−554.797	−358.555	8.143
2400	61.867	354.670	302.632	124.890	−557.719	−349.961	7.617
2500	61.904	357.196	304.765	131.078	−560.659	−341.244	7.130
2600	61.938	359.625	306.828	137.271	−563.617	−332.409	6.678
2700	61.968	361.963	308.827	143.466	−566.592	−323.459	6.258
2800	61.995	364.217	310.765	149.664	−863.486	−313.432	5.847
2900	62.020	366.393	312.646	155.865	−865.401	−293.754	5.291
3000	62.042	368.496	314.473	162.068	−867.334	−274.009	4.771
3100	62.061	370.530	316.249	168.273	−869.283	−254.199	4.283
3200	62.079	372.501	317.976	174.480	−871.248	−234.327	3.825
3300	62.096	374.412	319.657	180.689	−873.230	−214.392	3.394
3400	62.111	376.266	321.295	186.899	−875.227	−194.397	2.987
3500	62.125	378.066	322.892	193.111	−877.239	−174.344	2.602
3600	62.137	379.816	324.449	199.324	−879.267	−154.232	2.238
3700	62.149	381.519	325.968	205.539	−881.309	−134.065	1.893
3800	62.160	383.177	327.452	211.754	−883.366	−113.841	1.565
3900	62.170	384.791	328.902	217.971	−885.437	−93.563	1.253
4000	62.179	386.366	330.319	224.188	−887.523	−73.232	0.956
4100	62.188	387.901	331.704	230.406	−889.624	−52.849	0.673
4200	62.196	389.400	333.060	236.626	−891.739	−32.414	0.403
4300	62.203	390.863	334.388	242.845	−893.869	−11.929	0.145
4400	62.210	392.293	335.687	249.066	−896.016	8.606	−0.102
4500	62.217	393.692	336.961	255.287	−898.175	29.189	−0.339
4600	62.223	395.059	338.209	261.509	−900.354	49.821	−0.566
4700	62.228	396.397	339.433	267.732	−902.550	70.501	−0.784
4800	62.234	397.707	340.633	273.955	−904.764	91.227	−0.993
4900	62.239	398.991	341.811	280.179	−906.998	112.001	−1.194
5000	62.243	400.248	342.968	286.403	−909.252	132.820	−1.388
5100	62.248	401.481	344.103	292.627	−911.529	153.684	−1.574
5200	62.252	402.690	345.218	298.852	−913.830	174.592	−1.754
5300	62.256	403.875	346.314	305.078	−916.156	195.546	−1.927
5400	62.260	405.039	347.390	311.303	−918.509	216.543	−2.095
5500	62.263	406.182	348.449	317.530	−920.891	237.584	−2.256
5600	62.266	407.303	349.490	323.756	−923.304	258.670	−2.413
5700	62.270	408.406	350.514	329.983	−925.750	279.798	−2.564
5800	62.273	409.489	351.521	336.210	−928.227	300.970	−2.711
5900	62.276	410.553	352.513	342.437	−930.744	322.183	−2.852
6000	62.278	411.600	353.489	348.665	−933.279	343.439	−2.990

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = 230.601 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 238.4 \pm 8.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 238.5 \pm 8.5\ kJ \cdot mol^{-1}$

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
	Electronic States Molecular Constants (σ = 1)						
$X^2\Sigma^+$	0	2	617.1	3.33	0.2799	0.0018	2.029
$A^2\Pi_i$	[4500]	4	[459]	[2]	[0.234]	[0.001]	
$B^2\Sigma^+$	23381.1	2	510.9	1.45	0.2461	0.0012	2.164
$C\ ^2\Pi_{r1/2}$	29942.5	2	545	6	[0.2600]	[0.0028]	3.090
$C^2\Pi_{r3/2}$	30059.7	2	559	14	[0.2539]	[0.0044]	3.127
$D^2\Sigma^+$	35714.9	2	430	14	0.2402	0.0036	2.190

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ is an average of 3rd law values from the equilibrium studies of Ficalora *et al.*[1] and Uy and Drowart.[2] Ficalora *et al.*[1] used mass spectrometric ion intensity data to study the equilibrium Al(g) + 1/2 S_2(g) AlS(g) and they reported 2nd and 3rd law values for $\Delta_f H°(298.15\ K)$ of -37.3 ± 3.0 kcal·mol^{-1} and -35.4 ± 2.0 kcal·mol^{-1}, respectively. Uy and Drowart[2] used mass spectrometric ion intensity data to study two different equilibria and report an average value of $D_0° = 88.4 \pm 1.9$ kcal·mol^{-1} via 3rd law techniques. Using auxiliary JANAF data[3] we calculate 3rd law values of $\Delta_f H°(298.15\ K) = 58.8 \pm 2.0$ kcal·mol^{-1} and $\Delta_f H°(298.15\ K) = 55.2 \pm 1.9$ kcal·mol^{-1} from the data of Ficalora *et al.*[1] and Uy Drowart[2] respectively. A complete reanalysis is impossible since neither set of authors report their raw data. Reanalysis is desirable since the free energy functions in this table differ from those in the older table[4] used by both sets of authors, due to inclusion of excited electronic states. A crude calculation shows that these differences are large enough to affect third-law results by as much as ±0.2 kcal·mol^{-1} which is within the uncertainty of the reported values. The adopted value of $\Delta_f H°(298.15\ K)$, coupled with auxiliary JANAF data,[3] yields an adopted $D_0° = 86.9 \pm 2.0$ kcal·mol^{-1}.

Heat Capacity and Entropy

With the exception of the two $^2\Pi$ states the adopted molecular constant data are from Huber and Herzberg[5] based on earlier absorption and emission spectroscopic studies by several authors. We have adopted a modified nomenclature system consistent with states for AlO,[3] but different from that of Huber and Herzberg for AlS.[5] This is desirable to accommodate the predicted low lying $^2\Pi_i$ state which is unobserved for AlS but has been observed for AlO. The energy of this $A^2\Pi$ state for AlS is predicted from relative energies of the two $^2\Pi$ states for AlO[3] and is consistent with INDO/S calculations[6] if the bias in these calculations for AlO is directly transferable to AlS. Molecular constant data for the $A^2\Pi$ state is predicted assuming the same relative differences between this state and the ground state as in AlO.

We adopt Lavendy's[7] molecular constant data for the $C^2\Pi$ state, except we use his experimental values of $B_0 = 0.2572$ cm^{-1} and $B_0 = 0.2495$ cm^{-1} for the 1/2 and 3/2 components in conjunction with the Pekeris relationship[8] to estimate values of B_e and α_e. Lavendy's emission spectroscopy measurements indicate that this state is highly perturbed and this is reflected in the unusually large differences between molecular constant data for the 1/2 and 3/2 components. The nature of the perturbing state was not identified. We treat the $C^2\Pi$ state as two separate electronic states separated by the spin–orbit coupling constant of 117.2 cm^{-1}. This approximation introduces little uncertainty since the entire $C^2\Pi$ state makes an entropy contribution of less than 0.1 cal·mol^{-1}·K^{-1} at 6000 K.

The largest uncertainty in the table is due to uncertainty in the estimated $A^2\Pi$ state. This state makes no contribution to the thermochemical functions below 500 K so its uncertainty is not reflected in that given for the $S°(298.15\ K)$ value. This state makes the following entropy contributions in cal·K^{-1}·mol^{-1}; 0.05 at 1000 K, 0.9 at 2000 K, 1.8 at 3000 K, 2.2 at 4000 K, 2.4 at 5000 K and 2.5 at 6000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.087	238.352	238.352	INFINITE
100	29.206	196.985	258.754	−6.177	240.089	222.341	−116.139
200	31.167	217.716	233.589	−3.175	239.647	204.661	−53.452
298.15	33.398	230.601	230.601	0.	238.488	187.722	−32.888
300	33.432	230.807	230.601	0.062	238.463	187.407	−32.630
400	34.871	240.640	231.932	3.483	234.779	170.692	−22.290
500	35.749	248.523	234.488	7.017	231.752	155.008	−16.194
600	36.348	255.096	237.390	10.624	229.039	139.919	−12.181
700	36.861	260.738	240.332	14.284	226.505	125.267	−9.348
800	37.417	265.695	243.199	17.997	224.026	110.974	−7.246
900	38.085	270.140	245.949	21.771	168.402	98.073	−5.692
1000	38.884	274.193	248.574	25.619	156.478	91.088	−4.758
1100	39.797	277.941	251.075	29.552	155.365	84.604	−4.018
1200	40.783	281.445	253.462	33.581	154.331	78.218	−3.405
1300	41.794	284.750	255.742	37.709	153.382	71.914	−2.890
1400	42.782	287.883	257.927	41.939	152.519	65.680	−2.451
1500	43.708	290.867	260.025	46.264	151.735	59.505	−2.072
1600	44.543	293.715	262.042	50.677	151.025	53.380	−1.743
1700	45.266	296.438	263.986	55.169	150.379	47.297	−1.453
1800	45.870	299.043	265.862	59.726	149.785	41.251	−1.197
1900	46.353	301.536	267.674	64.339	149.233	35.236	−0.969
2000	46.720	303.924	269.427	68.993	148.711	29.250	−0.764
2100	46.979	306.210	271.125	73.679	148.209	23.289	−0.579
2200	47.144	308.400	272.770	78.386	147.719	17.352	−0.412
2300	47.225	310.497	274.365	83.105	147.231	11.437	−0.260
2400	47.235	312.508	275.912	87.828	146.738	5.544	−0.121
2500	47.188	314.435	277.415	92.550	146.236	−0.329	0.007
2600	47.094	316.284	278.875	97.264	145.720	−6.181	0.124
2700	46.963	318.059	280.293	101.968	145.186	−12.014	0.232
2800	46.804	319.764	281.673	106.656	−149.270	−16.858	0.314
2900	46.624	321.404	283.015	111.328	−148.751	−12.138	0.219
3000	46.431	322.981	284.321	115.980	−148.257	−7.436	0.129
3100	46.229	324.500	285.593	120.614	−147.787	−2.750	0.046
3200	46.024	325.965	286.831	125.226	−147.342	1.922	−0.031
3300	45.818	327.378	288.039	129.818	−146.922	6.580	−0.104
3400	45.614	328.742	289.216	134.390	−146.528	11.225	−0.172
3500	45.415	330.062	290.364	138.941	−146.159	15.860	−0.237
3600	45.223	331.338	291.485	143.473	−145.814	20.484	−0.297
3700	45.039	332.575	292.579	147.986	−145.494	25.099	−0.354
3800	44.864	333.774	293.647	152.481	−145.197	29.705	−0.408
3900	44.698	334.937	294.691	156.959	−144.923	34.304	−0.459
4000	44.543	336.067	295.711	161.421	−144.672	38.897	−0.508
4100	44.399	337.165	296.709	165.868	−144.443	43.483	−0.554
4200	44.265	338.233	297.685	170.301	−144.236	48.064	−0.598
4300	44.142	339.273	298.640	174.721	−144.050	52.640	−0.639
4400	44.031	340.287	299.575	179.130	−143.885	57.213	−0.679
4500	43.930	341.275	300.491	183.528	−143.739	61.781	−0.717
4600	43.840	342.239	301.388	187.916	−143.615	66.347	−0.753
4700	43.761	343.181	302.267	192.296	−143.511	70.910	−0.788
4800	43.692	344.102	303.129	196.669	−143.427	75.471	−0.821
4900	43.633	345.002	303.975	201.035	−143.363	80.031	−0.853
5000	43.584	345.883	304.804	205.396	−143.319	84.590	−0.884
5100	43.545	346.746	305.618	209.752	−143.296	89.148	−0.913
5200	43.515	347.591	306.417	214.105	−143.293	93.705	−0.941
5300	43.495	348.420	307.202	218.456	−143.311	98.263	−0.968
5400	43.484	349.233	307.973	222.804	−143.350	102.821	−0.995
5500	43.481	350.031	308.730	227.153	−143.409	107.381	−1.020
5600	43.487	350.814	309.475	231.501	−143.490	111.941	−1.044
5700	43.501	351.584	310.207	235.850	−143.593	116.503	−1.068
5800	43.524	352.341	310.927	240.201	−143.715	121.067	−1.090
5900	43.554	353.085	311.635	244.555	−143.862	125.634	−1.112
6000	43.592	353.817	312.332	248.912	−144.010	130.201	−1.133

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = 233.5 \pm 0.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 486.3 \pm 3.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 487.0 \pm 3.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3\Sigma_g^-$	0	3
$^5\Sigma_u^-$	[1000.]	[5]
$1^3\Sigma_u^-$	[10000]	[3]
$2^3\Sigma_u^-$	17269.36	3

$\omega_e = 350.01\ cm^{-1}$ $\omega_e x_e = 2.022\ cm^{-1}$ $\omega_e y_e = -0.0105\ cm^{-1}$ $\sigma = 2$

$B_e = 0.2054\ cm^{-1}$ $\alpha_e = 0.0012\ cm^{-1}$ $D_e = 3.07 \times 10^{-7}\ cm^{-1}$ $r_e = 2.4668$ Å

Enthalpy of Formation

From a mass–spectrometric investigation of the equilibria

$$AlAu(g) + Al(g) = Al_2(g) + Au(g)$$
$$2\ AlAu(g) = Al_2(g) + Au_2(g)$$

at 1921–2032 K and a 2nd law and 3rd law treatment of the data, Sterns and Kohl[1] derived the dissociation energy, $D_0° = 1.55 \pm 0.15$ eV for Al_2. Using current auxiliary data for $Al_2(g)$ and Al(g),[7] this value is corrected to 1.56 eV. As discussed by Stearns and Kohl,[1] it is likely that all of the previous mass spectrometic determinations[2, 3, 4] resulted in slightly high values for $D_0°$ (<1.96 ± 0.4 eV, 1.78 ± 0.19 eV and 1.80 eV, respectively) because of interferences due to the measurement of Al^+ ion intensities from extraneous sources. The dissociation energy of Al_2 has also been evaluated by a linear Birge–Sponer extrapolation[5] as 1.87 ± 0.2 eV and a graphical Birge–Sponer extrapolation[6] as 1.6 ± 0.2 eV. An ab initio calculation (LCAO–STO–MO–SCF–CI) by Leleyter and Joyes[9] yielded a dissociation energy of 1.03 eV. Based on the Stearns and Kohl result and auxiliary JANAF data,[7] we adopt $\Delta_f H°(298.15\ K) = 116.4 \pm 3.5$ kcal·mol for $Al_2(g)$.

Heat Capacity and Entropy

The bond spectrum of Al_2 was first reported by Zeeman[6] who wrongly attributed the emission to the AlC molecule. The vibrational constants are those reported by him. Values for the rotational constants are taken from Ginter *et al.*[5] who also assigned the upper and lower $^3\Sigma$ state configurations and energies. The electronic energies for the $^5\Sigma$ state and 1 $^3\Sigma$ state have been estimated by analogy with B_2. An ab initio SCF calculation of the ground state potential curve for Al_2^8 is reported but without inclusion of configuration interaction the calculated separations between states are not reliable.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.816	486.280	486.280	INFINITE
100	30.569	196.386	265.163	−6.878	488.251	470.010	−245.508
200	34.832	218.934	236.936	−3.600	487.925	451.796	−117.997
298.15	38.448	233.531	233.531	0.	487.018	434.251	−76.079
300	38.511	233.769	233.532	0.071	486.999	433.923	−75.553
400	41.208	245.250	235.079	4.068	485.980	416.384	−54.374
500	42.539	254.607	238.079	8.264	484.910	399.107	−41.694
600	42.884	262.401	241.502	12.539	483.715	382.056	−33.261
700	42.718	269.002	244.971	16.821	482.301	365.221	−27.253
800	42.350	274.682	248.339	21.075	480.594	348.608	−22.762
900	41.941	279.646	251.547	25.289	478.526	332.230	−19.282
1000	41.559	284.045	254.581	29.464	454.869	317.624	−16.591
1100	41.230	287.990	257.442	33.603	452.658	304.006	−14.436
1200	40.961	291.566	260.139	37.712	450.417	290.591	−12.649
1300	40.749	294.836	262.684	41.797	448.152	277.363	−11.145
1400	40.587	297.849	265.090	45.863	445.868	264.311	−9.862
1500	40.470	300.645	267.368	49.916	443.571	251.423	−8.755
1600	40.392	303.255	269.530	53.959	441.263	238.688	−7.792
1700	40.348	305.702	271.587	57.995	438.950	226.098	−6.947
1800	40.334	308.008	273.547	62.029	436.634	213.645	−6.200
1900	40.345	310.188	275.418	66.063	434.317	201.319	−5.535
2000	40.380	312.259	277.209	70.099	432.003	189.116	−4.939
2100	40.435	314.230	278.925	74.140	429.694	177.029	−4.403
2200	40.507	316.113	280.573	78.187	427.391	165.051	−3.919
2300	40.595	317.915	282.158	82.242	425.096	153.178	−3.479
2400	40.697	319.645	283.684	86.306	422.810	141.404	−3.078
2500	40.810	321.309	285.156	90.382	420.535	129.726	−2.710
2600	40.934	322.912	286.578	94.469	418.272	118.138	−2.373
2700	41.066	324.459	287.952	98.569	416.022	106.638	−2.063
2800	41.207	325.955	289.283	102.682	−174.017	97.155	−1.812
2900	41.355	327.404	290.572	106.810	−174.048	106.841	−1.924
3000	41.509	328.808	291.824	110.953	−174.064	116.527	−2.029
3100	41.668	330.172	293.039	115.112	−174.065	126.213	−2.127
3200	41.831	331.497	294.220	119.287	−174.050	135.899	−2.218
3300	41.999	332.787	295.369	123.479	−174.020	145.585	−2.304
3400	42.169	334.043	296.488	127.687	−173.974	155.269	−2.385
3500	42.343	335.268	297.579	131.913	−173.912	164.952	−2.462
3600	42.519	336.464	298.643	136.156	−173.834	174.633	−2.534
3700	42.696	337.631	299.681	140.416	−173.741	184.311	−2.602
3800	42.876	338.772	300.694	144.695	−173.634	193.987	−2.667
3900	43.056	339.888	301.685	148.992	−173.511	203.659	−2.728
4000	43.238	340.980	302.654	153.306	−173.375	213.329	−2.786
4100	43.420	342.050	303.602	157.639	−173.225	222.995	−2.841
4200	43.604	343.099	304.530	161.990	−173.064	232.657	−2.894
4300	43.787	344.127	305.439	166.360	−172.890	242.314	−2.944
4400	43.970	345.136	306.329	170.748	−172.707	251.968	−2.991
4500	44.155	346.126	307.203	175.154	−172.510	261.617	−3.037
4600	44.338	347.098	308.060	179.579	−172.308	271.263	−3.080
4700	44.522	348.054	308.900	184.022	−172.100	280.903	−3.122
4800	44.706	348.993	309.726	188.483	−171.886	290.539	−3.162
4900	44.889	349.917	310.537	192.963	−171.668	300.171	−3.200
5000	45.073	350.826	311.333	197.461	−171.449	309.798	−3.236
5100	45.255	351.720	312.117	201.977	−171.229	319.421	−3.272
5200	45.438	352.600	312.887	206.512	−171.012	329.039	−3.305
5300	45.620	353.468	313.644	211.065	−170.799	338.653	−3.338
5400	45.802	354.322	314.390	215.636	−170.592	348.264	−3.369
5500	45.984	355.164	315.123	220.225	−170.393	357.870	−3.399
5600	46.165	355.994	315.846	224.833	−170.204	367.473	−3.428
5700	46.346	356.813	316.557	229.458	−170.028	377.073	−3.455
5800	46.526	357.621	317.258	234.102	−169.862	386.669	−3.482
5900	46.707	358.418	317.949	238.764	−169.717	396.264	−3.508
6000	46.887	359.204	318.630	243.443	−169.548	405.851	−3.533

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

$S°(298.15\ K) = 66.29 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2146 \pm 10\ K$

$\Delta_f H°(0\ K) = -2285.5 \pm 3.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2300.78 \pm 3.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 170.008 \pm 3.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ is calculated from $\Delta_r H°(968\ K) = -4.0 \pm 0.3$ kcal·mol^{-1} for BeO(cr, α) + Al_2O_3(cr, α) → $BeAl_2O_4$(cr) using current values of $\Delta_f H°$ for the reactants.[1] The value of $\Delta_r H°(968\ K)$ was determined by Holm and Kleppa[2] from the difference in heats of solution of the three components in an oxide melt.

For comparison, a second-law treatment of the equilibrium data of Young[3] yields $\Delta_r H°(298.15\ K) = -2.3$ kcal·mol^{-1} for the same reaction. This is obtained from a suitable linear combination of the three equilibria studied by Young and leads to $\Delta_f H°(298.15\ K) = -548.2$ kcal·mol^{-1} in good agreement with the adopted value.

Heat Capacity and Entropy

Heat capacity and derived properties at and below 298.15 K are taken from the calorimetric data (16–380 K) of Furukawa and Saba.[4] The entropy is based on $S°(16\ K) = 0.004$ cal·K^{-1}·mol^{-1}. Above 298.15 K the adopted $C_p°$ are based on Ishihara and West's[5] merging of enthalpy data of Ditmar and Douglas[6] (323–1173 K) and Ishihara and West[5] (1182–2137) with the $C_p°$ data of Furukawa and Saba.[4] Values above 2137 K are our extrapolation. Ishihara and West report a sharp rise in enthalpy data above 2030 K, apparently associated with premelting phenomena. Data in this region was ignored by Ishihara and West during their treatment.

Fusion Data

Refer to the liquid table for details.

References

[1]JANAF Thermochemical Tables: BeO(cr, α), 6–30–75; Al_2O_3(cr, α), 12–31–79.
[2]J. L. Holm and O. J. Kleppa, Acta Chem. Scand. **20**, 2568 (1966).
[3]W. A. Young, J. Phys. Chem. **64**, 1003 (1960).
[4]G. T. Furukawa and W. G. Saba, J. Res. Nat. Bur. Stand. **69A**, 13 (1965).
[5]S. Ishihara and E. D. West, J. Res. Nat. Bur. Stand. **80A**, 65 (1976).
[6]D. A. Ditmars and T. B. Douglas, J. Res. Nat. Bur. Stand. **71A**, 89 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.088	−2285.491	−2285.491	INFINITE
100	16.365	5.523	132.214	−12.669	−2291.889	−2256.332	1178.587
200	66.430	31.982	74.785	−8.560	−2297.784	−2218.294	579.359
298.15	105.380	66.291	66.291	0.	−2300.782	−2178.542	381.672
300	105.940	66.945	66.293	0.195	−2300.815	−2177.784	379.186
400	130.280	101.047	70.777	12.108	−2301.703	−2136.594	279.011
500	145.250	131.854	79.971	25.942	−2301.355	−2095.338	218.899
600	154.970	159.252	90.946	40.983	−2300.371	−2054.220	178.836
700	161.750	183.668	102.480	56.832	−2299.118	−2013.292	150.234
800	166.830	205.612	114.024	73.271	−2297.811	−1972.550	128.794
900	170.870	225.503	125.322	90.163	−2296.605	−1931.966	112.128
1000	174.200	243.683	136.263	107.421	−2316.784	−1889.987	98.723
1100	177.030	260.423	146.799	124.986	−2315.359	−1847.375	87.725
1200	179.480	275.934	156.922	142.814	−2313.836	−1804.898	78.565
1300	181.670	290.388	166.639	160.873	−2312.239	−1762.550	70.820
1400	183.750	303.927	175.967	179.144	−2310.577	−1720.329	64.186
1500	185.910	316.677	184.926	197.625	−2308.849	−1678.228	58.441
1600	188.410	328.752	193.541	216.337	−2321.567	−1635.720	53.401
1700	191.560	340.263	201.836	235.326	−2319.211	−1592.925	48.945
1800	195.790	351.326	209.835	254.683	−2316.556	−1550.278	44.988
1900	201.570	362.058	217.566	274.535	−2313.473	−1507.788	41.452
2000	209.490	372.588	225.054	295.068	−2309.778	−1465.476	38.274
2100	220.190	383.055	232.329	316.525	−2305.227	−1423.369	35.404
2146.000	226.250	387.890	235.612	326.790	− − − CRYSTAL <− −> LIQUID − − −		
2200	233.098	393.597	239.419	339.191	−2299.533	−1381.503	32.801
2300	248.548	404.290	246.354	363.252	−2292.510	−1339.927	30.431
2400	266.455	415.238	253.162	388.982	−2283.885	−1298.690	28.265

PREVIOUS: June 1972 CURRENT: December 1979

$S°(298.15\ K) = [126.406]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-2163.842]\ kJ·mol^{-1}$

$T_{fus} = 2146 \pm 10\ K$ $\Delta_{fus}H° = 170.008 \pm 3.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(BeAl_2O_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(BeAl_2O_4, cr, 298.5\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2146\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Ishihara and West[2] reported enthalpy data from 2177 to 2355 K and reported a quadratic enthalpy equation for the liquid. This equation yields a temperature dependence for $C_p°$ which is unreasonably large. Therefore we have fit their enthalpy data to a linear equation which fits their measured points with an average deviation of 0.15 kcal·mol^{-1} and a maximum deviation of 0.35 kcal·mol^{-1}. Based on the scatter in the data we believe higher fits are unjustified and adopt the resulting constant value of $C_p° = 58.893\ cal·K^{-1}·mol^{-1}$ (246.408 J·K^{-1}·mol^{-1}) above the assumed glass transition at 1450 K. Below T_{gls}, $C_p°$ is taken to be the same as the crystal.

$S°(298.15\ K)$ is calculated in a manner analagous to that used for enthalpy of formation.

Fusion Data

The adopted melting point is taken from the phase study of Lang *et al.*[3] after adjustment to IPTS–68. We calculate $\Delta_{fus}H°$ from the difference between $H°(2146; 298.15)$ for the crystal[1] and liquid using our adopted linear enthalpy equation for the liquid.

References

[1]JANAF Thermochemical Tables: $BeAl_2O_4$(cr), 12–31–79.

[2]S. Ishihara and E. D. West, J. Res. Nat. Bur. Stand. **80A**, 65 (1976).

[3]S. M. Lang, C. L. Fillmore and L. H. Maxwell, J. Res. Nat. Bur. Stand. **48**, 298 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	105.380	126.406	126.406	0.	−2163.842	−2059.526	360.820
300	105.940	127.060	126.408	0.195	−2163.876	−2058.879	358.483
400	130.280	161.162	130.892	12.108	−2164.764	−2023.701	264.268
500	145.250	191.969	140.086	25.942	−2164.416	−1988.456	207.733
600	154.970	219.367	151.061	40.983	−2163.431	−1953.350	170.054
700	161.750	243.783	162.595	56.832	−2162.179	−1918.434	143.155
800	166.830	265.727	174.139	73.271	−2160.872	−1883.703	122.993
900	170.870	285.618	185.438	90.163	−2159.665	−1849.131	107.321
1000	174.200	303.799	196.378	107.421	−2179.845	−1813.163	94.710
1100	*177.030*	*320.538*	*206.914*	*124.986*	−2178.419	−1776.562	84.362
1200	179.480	336.049	217.037	142.814	−2176.897	−1740.096	75.744
1300	181.670	350.503	226.754	160.873	−2175.299	−1703.761	68.458
1400	183.750	364.042	236.082	179.144	−2173.638	−1667.550	62.217
1450.000	184.800	370.508	240.606	188.358	____ GLASS <--> LIQUID ____		
1450.000	246.409	370.508	240.606	188.358	TRANSITION		
1500	246.409	378.862	245.076	200.679	−2168.857	−1631.514	56.814
1600	246.409	394.765	253.940	225.320	−2175.646	−1595.419	52.085
1700	246.409	409.703	262.668	249.960	−2167.637	−1559.400	47.915
1800	246.409	423.788	271.231	274.601	−2159.697	−1523.851	44.221
1900	246.409	437.110	279.615	299.242	−2151.827	−1488.741	40.928
2000	246.409	449.750	287.808	323.883	−2144.023	−1454.044	37.976
2100	246.409	461.772	295.808	348.524	−2136.288	−1419.736	35.314
2146.000	246.409	467.111	299.423	359.859	--- CRYSTAL <--> LIQUID ---		
2200	246.409	473.235	303.614	373.165	−2128.619	−1385.793	32.903
2300	246.409	484.188	311.229	397.806	−2121.017	−1352.200	30.709
2400	246.409	494.675	318.656	422.447	−2113.480	−1318.935	28.706
2500	246.409	504.734	325.899	447.088	−2106.009	−1285.983	26.869
2600	246.409	514.399	332.964	471.729	−2098.603	−1253.328	25.180
2700	246.409	523.698	339.858	496.370	−2091.260	−1220.956	23.621
2800	246.409	532.660	346.584	521.011	−2962.738	−1180.698	22.026
2900	246.409	541.306	353.151	545.652	−2952.264	−1117.240	20.124
3000	246.409	549.660	359.562	570.293	−2941.834	−1054.141	18.354
3100	246.409	557.740	365.826	594.934	−2931.448	−991.388	16.705
3200	246.409	565.563	371.946	619.575	−2921.107	−928.972	15.164
3300	246.409	573.145	377.929	644.216	−2910.809	−866.877	13.722
3400	246.409	580.501	383.779	668.857	−2900.558	−805.093	12.369
3500	246.409	587.644	389.502	693.498	−2890.353	−743.611	11.098
3600	246.409	594.586	395.103	718.139	−2880.194	−682.419	9.902
3700	246.409	601.337	400.586	742.779	−2870.085	−621.510	8.774
3800	246.409	607.909	405.956	767.420	−2860.026	−560.871	7.710
3900	246.409	614.309	411.216	792.061	−2850.018	−500.497	6.703
4000	246.409	620.548	416.372	816.702	−2840.064	−440.380	5.751

PREVIOUS: June 1972 CURRENT: December 1979

0 to 2146 K crystal
above 2146 K liquid

Refer to individual tables for details

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.088	−2285.491	−2285.491	INFINITE
100	16.365	5.523	132.214	−12.669	−2291.889	−2256.332	1178.587
200	66.430	31.982	74.785	−8.560	−2297.784	−2218.294	579.359
298.15	105.380	66.291	66.291	0.	−2300.782	−2178.542	381.672
300	105.940	66.945	66.293	0.195	−2300.815	−2177.784	379.186
400	130.280	101.047	70.777	12.108	−2301.703	−2136.594	279.011
500	145.250	131.854	79.971	25.942	−2301.355	−2095.338	218.899
600	154.970	159.252	90.946	40.983	−2300.371	−2054.220	178.836
700	161.750	183.668	102.480	56.832	−2299.118	−2013.292	150.234
800	166.830	205.612	114.024	73.271	−2297.811	−1972.550	128.794
900	170.870	225.503	125.322	90.163	−2296.605	−1931.966	112.128
1000	174.200	243.683	136.263	107.421	−2316.784	−1889.987	98.723
1100	177.030	260.423	146.799	124.986	−2315.359	−1847.375	87.725
1200	179.480	275.934	156.922	142.814	−2313.836	−1804.898	78.565
1300	181.670	290.388	166.639	160.873	−2312.239	−1762.550	70.820
1400	183.750	303.927	175.967	179.144	−2310.577	−1720.329	64.186
1500	185.910	316.677	184.926	197.625	−2308.849	−1678.228	58.441
1600	188.410	328.752	193.541	216.337	−2321.567	−1635.720	53.401
1700	191.560	340.263	201.836	235.326	−2319.211	−1592.925	48.945
1800	195.790	351.326	209.835	254.683	−2316.556	−1550.278	44.988
1900	201.570	362.058	217.566	274.535	−2313.473	−1507.788	41.452
2000	209.490	372.588	225.054	295.068	−2309.778	−1465.476	38.274
2100	220.190	383.055	232.329	316.525	−2305.227	−1423.369	35.404
2146.000	226.250	387.890	235.612	326.790	CRYSTAL <--> LIQUID TRANSITION		
2146.000	246.409	467.111	235.612	496.798			
2200	246.409	473.235	241.369	510.105	−2128.619	−1385.793	32.903
2300	246.409	484.188	251.690	534.745	−2121.017	−1352.200	30.709
2400	246.409	494.675	261.598	559.386	−2113.480	−1318.935	28.706
2500	246.409	504.734	271.123	584.027	−2106.009	−1285.983	26.869
2600	246.409	514.399	280.295	608.668	−2098.603	−1253.328	25.180
2700	246.409	523.698	289.139	633.309	−2091.260	−1220.957	23.621
2800	246.409	532.660	297.677	657.950	−2962.738	−1180.698	22.026
2900	246.409	541.306	305.930	682.591	−2952.264	−1117.240	20.124
3000	246.409	549.660	313.916	707.232	−2941.834	−1054.141	18.354
3100	246.409	557.740	321.652	731.873	−2931.448	−991.388	16.705
3200	246.409	565.563	329.152	756.514	−2921.107	−928.972	15.164
3300	246.409	573.145	336.432	781.155	−2910.810	−866.878	13.722
3400	246.409	580.501	343.503	805.796	−2900.558	−805.093	12.369
3500	246.409	587.644	350.377	830.437	−2890.353	−743.611	11.098
3600	246.409	594.586	357.064	855.078	−2880.194	−682.419	9.902
3700	246.409	601.337	363.575	879.719	−2870.085	−621.510	8.774
3800	246.409	607.909	369.919	904.360	−2860.026	−560.871	7.710
3900	246.409	614.309	376.104	929.001	−2850.018	−500.497	6.703
4000	246.409	620.548	382.137	953.642	−2840.064	−440.380	5.751

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = 547.2 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -892.9 \pm 3.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -937.2 \pm 3.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies					
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
409 (1)	59 (1)	76 (1)	[8] (1)	346 (1)	376 (1)
203 (1)	[30](1)	500 (1)	489 (1)	90 (1)	199 (1)
139 (1)	[250](1)	{110](1)	114 (1)	[67](1)	112 (1)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: D_{2h}

Bond Distances: Al–Br = 2.222 ± 0.005 Å; Al–Br(bridge) = 2.414 ± 0.007 Å

Bond Angles: Br–Al–Br = 122.8 ± 3.3°; Br(bridge)–Al–Br(bridge) = 92.3 ± 0.9°

Product of the Moments of Inertia: $I_A I_B I_C = 8.865729 \times 10^{-110}\ g^3 \cdot cm^6$

Enthalpy of Formation

Vapor pressures over $AlBr_3$(cr) and $AlBr_3$(l) have been measured by Dunne and Gregory,[1] Fischer *et. al.*[2] and Sulzmann.[3] The vapor pressures were corrected for vapor non–ideality by means of the equation $\Delta G°/T = -R\ln P - BP/T$. The Bertholot equation of state and critical constants T_c=763 K and P_c=28.5 atm reported by Johnson, Silva and Cubicciotti[4] were used to calculate B. The corrected vapor pressures were used to calculate $\Delta_r H°(298.15\ K)$ by both 2nd and 3rd law methods. The results of the calculations are as follows with reaction (A) corresponding to 2 $AlBr_3$(cr)=Al_2Br_6(g) and reaction (B) corresponding to 2 $AlBr_3$(l)=Al_2Br_6(g).

Source	Reaction	Method	Data Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[3]	A	Manometric	13	302–334	21.2 ± 0.2	20.54 ± 0.1	−2.2 ± 0.5	−223.86
[1]	A	Effusion	3	273–310	19.6 ± 0.7	20.26 ± 0.1	2.2 ± 2.4	−224.14
[2]	B	Mass Loss	18[a]	413–522	15.6 ± 0.0	15.62 ± 0.0	0.1 ± 0.1	−223.98
[2]	B	Transport	4	396–470	16.0 ± 0.1	15.61 ± 0.1	−0.9 ± 0.3	−223.99

[a]Point at 436.2 K rejected due to statistical test.

Heat Capacity and Entropy

Structural assignments for the dimer of aluminum tribromide are based on the electron diffraction data reported by Shen.[5] These values are in good agreement with earlier diffraction studies by Palmer and Elliott[6] and Akishin *et al.*[7] The principal moments of inertia are $I_A = 282.4212 \times 10^{-39}$, $I_B = 502.7859 \times 10^{-39}$ and $I_C = 624.3585 \times 10^{-39}\ g \cdot cm^2$. Beattie *et.al.*[8] measured the condensed phase IR and Raman bands for aluminum tribromide while Beattie and Horder[9] measured the gas phase Raman spectra. Perov *et al.*[10] investigated the IR spectra of monomeric and dimeric aluminum tribromide in a xenon matrix at 20–30 K. It has been established that the condensed phases of $AlBr_3$ are dimeric,[11,12] thus spectroscopic studies of the crystal and liquid pertain to the structure of Al_2Br_6(g). However, gas phase values are adopted in preference to condensed phase frequencies whenever possible. Five frequencies (ν_5, ν_6, ν_9, ν_{10}, ν_{15}) adjusted not only for consistency with the frequencies chosen for Al_2F_6(g) and Al_2Cl_6(g) but also for agreement between 2nd and 3rd law $\Delta_r H°(298.15\ K)$ values in the second data set tabulated above.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−38.309	−892.918	−892.918	INFINITE
100	122.051	386.605	686.066	−29.946	−893.902	−915.011	477.953
200	154.379	482.768	562.199	−15.886	−898.150	−934.593	244.091
250	162.423	518.147	549.952	−7.951	−900.889	−943.399	197.112
298.15	167.514	547.220	547.220	0.	−937.216	−947.368	165.975
300	167.672	548.257	547.223	0.310	−937.415	−947.430	164.962
350	171.215	574.387	549.279	8.788	−1029.359	−944.065	140.894
400	173.690	597.420	553.885	17.414	−1028.768	−931.920	121.696
450	175.474	617.986	559.886	26.145	−1028.167	−919.850	106.773
500	176.796	636.546	566.639	34.954	−1027.568	−907.847	94.842
600	178.581	668.951	581.068	52.730	−1026.422	−884.012	76.960
700	179.692	696.569	595.644	70.648	−1025.414	−860.359	64.201
800	180.428	720.615	609.795	88.656	−1024.625	−836.837	54.640
900	180.939	741.898	623.313	106.726	−1024.129	−813.397	47.208
1000	181.309	760.982	636.142	124.839	−1045.169	−788.473	41.186
1100	181.584	778.276	648.290	142.985	−1044.723	−762.825	36.224
1200	181.794	794.085	659.790	161.154	−1044.280	−737.217	32.090
1300	181.959	808.643	670.688	179.342	−1043.844	−711.647	28.594
1400	182.090	822.133	681.029	197.545	−1043.419	−686.109	25.599
1500	182.195	834.699	690.860	215.759	−1043.012	−660.601	23.004
1600	182.282	846.461	700.221	233.983	−1042.625	−635.120	20.735
1700	182.354	857.514	709.152	252.215	−1042.266	−609.662	18.733
1800	182.415	867.939	717.687	270.453	−1041.940	−584.225	16.954
1900	182.466	877.803	725.857	288.698	−1041.652	−558.804	15.363
2000	182.510	887.163	733.690	306.946	−1041.410	−533.397	13.931
2100	182.548	896.069	741.212	325.199	−1041.219	−508.001	12.636
2200	182.580	904.562	748.445	343.456	−1041.085	−482.613	11.459
2300	182.609	912.678	755.411	361.715	−1041.012	−457.230	10.384
2400	182.634	920.451	762.127	379.977	−1041.002	−431.848	9.399
2500	182.656	927.906	768.610	398.242	−1041.059	−406.466	8.493
2600	182.676	935.071	774.875	416.509	−1041.182	−381.081	7.656
2700	182.693	941.965	780.937	434.777	−1041.370	−355.688	6.881
2800	182.709	948.610	786.807	453.047	−1629.423	−328.353	6.126
2900	182.723	955.022	792.498	471.319	−1627.541	−281.919	5.078
3000	182.736	961.216	798.019	489.592	−1625.713	−235.551	4.101
3100	182.747	967.208	803.381	507.866	−1623.934	−189.241	3.189
3200	182.758	973.011	808.591	526.141	−1622.196	−142.989	2.334
3300	182.767	978.634	813.659	544.417	−1620.492	−96.789	1.532
3400	182.776	984.091	818.592	562.694	−1618.815	−50.642	0.778
3500	182.784	989.389	823.397	580.972	−1617.158	−4.544	0.068
3600	182.791	994.538	828.080	599.251	−1615.512	41.508	−0.602
3700	182.798	999.547	832.647	617.531	−1613.871	87.514	−1.235
3800	182.804	1004.422	837.103	635.811	−1612.226	133.475	−1.835
3900	182.810	1009.170	841.454	654.091	−1610.572	179.393	−2.403
4000	182.815	1013.799	845.705	672.373	−1608.903	225.268	−2.942
4100	182.820	1018.313	849.861	690.654	−1607.211	271.101	−3.454
4200	182.824	1022.718	853.924	708.936	−1605.494	316.893	−3.941
4300	182.829	1027.020	857.900	727.219	−1603.744	362.644	−4.405
4400	182.833	1031.224	861.791	745.502	−1601.961	408.353	−4.848
4500	182.836	1035.332	865.602	763.786	−1600.134	454.021	−5.270
4600	182.840	1039.351	869.336	782.069	−1598.271	499.649	−5.674
4700	182.843	1043.283	872.995	800.354	−1596.364	545.235	−6.060
4800	182.846	1047.133	876.583	818.638	−1594.414	590.781	−6.429
4900	182.849	1050.903	880.102	836.923	−1592.417	636.285	−6.783
5000	182.852	1054.597	883.555	855.208	−1590.376	681.748	−7.122
5100	182.854	1058.218	886.945	873.493	−1588.290	727.171	−7.448
5200	182.857	1061.769	890.273	891.779	−1586.161	772.550	−7.760
5300	182.859	1065.252	893.541	910.064	−1583.988	817.890	−8.061
5400	182.861	1068.670	896.753	928.350	−1581.774	863.188	−8.350
5500	182.863	1072.025	899.909	946.637	−1579.520	908.444	−8.628
5600	182.865	1075.320	903.012	964.923	−1577.229	953.659	−8.895
5700	182.867	1078.557	906.064	983.210	−1574.904	998.833	−9.153
5800	182.868	1081.737	909.065	1001.496	−1572.541	1043.964	−9.402
5900	182.870	1084.863	912.018	1019.783	−1570.153	1089.056	−9.642
6000	182.872	1087.937	914.925	1038.070	−1567.695	1134.103	−9.873

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = 475.0 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1293.02 \pm 3.35\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1295.74 \pm 3.35\ kJ \cdot mol^{-1}$

Vibrational Frequencies (all singly degenerate), cm^{-1}										
A_g	A_g	A_u	B_{1g}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	B_{3u}
501	217	[60]	289	[10]	625	610	420	[161]	484	144
336	99		166		175		116	135		320

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Al–Cl = 2.065 ± 0.002 Å; Al–Cl(bridge) = 2.252 ± 0.004 Å
Bond Angles: Cl–Al–Cl=123.4 ± 1.6°; Cl(bridge)–Al–Cl(bridge) = 91.0 ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 5.687094 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from the value for $AlCl_3$(cr) and the heat of sublimation as derived from vapor pressure data. Vapor pressures were corrected for vapor non-ideality by means of the equation $\Delta G°/T = -R \ln P - BP/T$. The Berthelot equation of state and critical constants T_c = 620 K[1] and P_c = 24.3 atm were used to calculate B. P_c is an extrapolation of the data given by Denisova and Baskova.[2] The corrected vapor pressures were used to derive $\Delta_{sub}H°(298.15\ K)$ by both 2nd law and 3rd law methods. The first nine data sets show good agreement between 2nd and 3rd law values and an average of $\Delta_{sub}H°(298.15\ K) = 27.61 \pm 0.55\ kcal \cdot mol^{-1}$ Al_2Cl_6 is adopted. The remaining data sets show serious discrepancies between 2nd and 3rd law values, indicating temperature dependent errors in measurement, and are given no weight.

Source	T/K	Data Points*	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Viola *et al.*[3]	389.9–466.3	44(4)	27.48 ± 0.0	27.62 ± 0.0	0.3 ± 0.1
Viola *et al.*[3]	467.7–510.0	67(4)	26.82 ± 0.0	27.65 ± 0.1	1.7 ± 0.1
Smits and Meijering [4] liq.	444.7–464.6	7(2)	27.44 ± 0.1	27.59 ± 0.0	0.3 ± 0.3
Smits and Meijering [4]	462.4–481.8	10	27.07 ± 0.1	27.61 ± 0.0	1.1 ± 0.2
Treadwell and Terebesi [5] liq.	388.7–461.7	11	28.31 ± 0.2	27.55 ± 0.1	−1.8 ± 0.3
Treadwell and Terebesi [5]	466.5–476.2	3	27.39 ± 0.1	27.60 ± 0.0	0.5 ± 0.2
Fischer *et al.* [6] liq.	392.8–428.3	9	27.65 ± 0.4	27.61 ± 0.1	−0.1 ± 1.1
Fischer *et al.* [6]	403.8–450.4	12(2)	27.70 ± 0.1	27.60 ± 0.0	−0.2 ± 0.3
Nisel'son *et al.* [7] liq.	471.2–506.5	18(1)	27.28 ± 0.1	27.64 ± 0.0	0.7 ± 0.1
Friedel and Crafts [8]	441.0–455.9	5	29.80 ± 1.6	27.80 ± 0.1	−4.5 ± 3.5
Friedel and Crafts [8] liq.	477.4–486.2	3	29.92 ± 1.4	27.76 ± 0.0	−4.5 ± 3.0
Maier [9]	392.8–454.4	v 8(1)	25.87 ± 0.7	27.38 ± 0.2	3.5 ± 1.7
Dunne and Gregory [10]	294.2–322.2	2	29.97 ± 0.0	27.79 ± 0.3	−7.1 ± 0.0
Denisova and Baskova [2] liq.	467.8–511.6	8	26.31 ± 0.2	27.56 ± 0.1	2.5 ± 0.3

*First number indicates number of data points used in calculation; number in parentheses indicates number of data points rejected.

Heat Capacity and Entropy

Structural assignments for the dimer of aluminum trichloride are based on the electron diffraction data reported by Shen.[11] These values are in good agreement with earlier electron diffraction studies by Palmer and Elliott[12] and Akishin *et al.*[13] and a theoretical investigation by Curtiss.[14] The principal moments of inertia are: $I_A = 108.2257 \times 10^{-39}$, $I_B = 206.7252 \times 10^{-39}$ and $I_C = 254.1948 \times 10^{-39}$ g cm^2. Klemperer[15] observed three frequencies in the infrared spectrum of Al_2Cl_6 vapor, Beattie and Horder[16] and Maroni *et al.*[17] reported gas phase Raman spectra, and Gerding and Smit[18] and Pershina and Raskin[19] measured liquid phase Raman frequencies. These earlier vibrational assignments were supplemented by matrix isolated/IR and Raman studies reported by Beattie et al[20] and Perov *et al.*[21] and the detailed vibrational analysis given by Tranquille and Fouassier.[22] Normal coordinate calculations have been reported by several investigators[23,24,17,25] but their basis on incomplete data makes many assignments doubtful. The new vibrational assignment incorporates the additional frequencies observed by Tranquille and Fouassier and differs with earlier calculations primarily in reassignment of the frequencies at 289 cm^{-1} and 161 cm^{-1}. The estimated fundamentals are based on comparisons with Al_2F_6, Al_2Br_6, and Al_2I_6 and are adjusted such that the entropy is consistent for the 2nd and 3rd law calculations above.

Continued on page 173

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−33.898	−1293.019	−1293.019	INFINITE
100	101.982	330.759	602.707	−27.195	−1296.020	−1270.996	663.900
200	140.807	415.028	489.094	−14.813	−1296.355	−1245.724	325.350
250	151.631	447.687	477.628	−7.485	−1296.111	−1233.091	257.640
298.15	158.858	475.050	475.050	0.	−1295.743	−1220.985	213.912
300	159.089	476.033	475.053	0.294	−1295.727	−1220.522	212.512
350	164.322	500.973	477.011	8.387	−1295.260	−1208.023	180.288
400	168.079	523.174	481.419	16.702	−1294.746	−1195.596	156.129
450	170.844	543.138	487.186	25.178	−1294.204	−1183.234	137.346
500	172.925	561.251	493.701	33.775	−1293.652	−1170.934	122.327
600	175.775	593.052	507.683	51.221	−1292.573	−1146.493	99.811
700	177.576	620.293	521.871	68.895	−1291.609	−1122.224	83.741
800	178.779	644.089	535.692	86.717	−1290.848	−1098.082	71.697
900	179.621	665.197	548.931	104.639	−1290.369	−1074.018	62.334
1000	180.232	684.155	561.522	122.633	−1311.416	−1048.469	54.766
1100	180.688	701.356	573.464	140.680	−1310.969	−1022.196	48.540
1200	181.038	717.093	584.787	158.768	−1310.518	−995.964	43.353
1300	181.312	731.595	595.529	176.886	−1310.067	−969.770	38.966
1400	181.530	745.040	605.734	195.028	−1309.620	−943.610	35.207
1500	181.707	757.571	615.444	213.190	−1309.181	−917.482	31.950
1600	181.852	769.302	624.697	231.368	−1308.752	−891.382	29.101
1700	181.972	780.331	633.531	249.560	−1308.336	−865.310	26.588
1800	182.074	790.735	641.978	267.762	−1307.937	−839.261	24.355
1900	182.159	800.582	650.069	285.974	−1307.557	−813.234	22.357
2000	182.233	809.927	657.830	304.194	−1307.200	−787.226	20.560
2100	182.296	818.820	665.286	322.420	−1306.869	−761.236	18.935
2200	182.351	827.302	672.459	340.653	−1306.569	−735.260	17.457
2300	182.399	835.408	679.369	358.890	−1306.304	−709.298	16.109
2400	182.441	843.172	686.034	377.132	−1306.078	−683.346	14.873
2500	182.478	850.621	692.469	395.378	−1305.897	−657.403	13.736
2600	182.511	857.778	698.691	413.628	−1305.763	−631.466	12.686
2700	182.541	864.667	704.711	431.880	−1305.681	−605.533	11.715
2800	182.567	871.306	710.543	450.136	−1893.454	−577.667	10.777
2900	182.591	877.713	716.198	468.393	−1891.290	−530.713	9.559
3000	182.612	883.903	721.685	486.654	−1889.183	−483.832	8.424
3100	182.631	889.891	727.015	504.916	−1887.132	−437.021	7.364
3200	182.649	895.690	732.196	523.180	−1885.136	−390.276	6.371
3300	182.665	901.311	737.236	541.445	−1883.193	−343.591	5.439
3400	182.679	906.764	742.142	559.713	−1881.300	−296.965	4.562
3500	182.693	912.059	746.922	577.981	−1879.451	−250.394	3.737
3600	182.705	917.206	751.581	596.251	−1877.644	−203.875	2.958
3700	182.716	922.212	756.125	614.522	−1875.870	−157.406	2.222
3800	182.727	927.085	760.560	632.794	−1874.126	−110.985	1.526
3900	182.736	931.832	764.891	651.068	−1872.403	−64.609	0.865
4000	182.745	936.458	769.123	669.342	−1870.696	−18.277	0.239
4100	182.753	940.971	773.260	687.617	−1868.996	28.013	−0.357
4200	182.761	945.375	777.305	705.892	−1867.299	74.261	−0.924
4300	182.768	949.675	781.264	724.169	−1865.595	120.468	−1.463
4400	182.775	953.877	785.140	742.446	−1863.880	166.636	−1.978
4500	182.781	957.985	788.935	760.724	−1862.143	212.764	−2.470
4600	182.787	962.002	792.654	779.002	−1860.385	258.854	−2.939
4700	182.792	965.933	796.299	797.281	−1858.597	304.905	−3.389
4800	182.798	969.782	799.873	815.561	−1856.776	350.918	−3.819
4900	182.802	973.551	803.379	833.841	−1854.914	396.893	−4.231
5000	182.807	977.244	806.820	852.121	−1853.011	442.828	−4.626
5100	182.811	980.864	810.197	870.402	−1851.063	488.726	−5.006
5200	182.815	984.414	813.513	888.683	−1849.067	534.584	−5.370
5300	182.819	987.896	816.771	906.965	−1847.020	580.404	−5.720
5400	182.823	991.314	819.972	925.247	−1844.922	626.185	−6.057
5500	182.826	994.668	823.118	943.530	−1842.771	671.927	−6.381
5600	182.829	997.963	826.211	961.812	−1840.567	717.629	−6.694
5700	182.832	1001.199	829.252	980.095	−1838.311	763.291	−6.995
5800	182.835	1004.379	832.244	998.379	−1835.995	808.913	−7.285
5900	182.838	1007.504	835.188	1016.662	−1833.633	854.494	−7.565
6000	182.841	1010.577	838.086	1034.946	−1831.175	900.030	−7.835

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

Potassium Aluminum Chloride ($K_3Al_2Cl_9$) CRYSTAL M_r = 490.33498

$\Delta_f H°$(0 K) = Unknown

$S°$(298.15 K) = [468.608] J·K^{-1}·mol^{-1} $\Delta_f H°$(298.15 K) = −2860 ± 12 kJ·mol^{-1}

T_{fus} = Unknown

Enthalpy of Formation

$\Delta_f H°(K_3Al_2Cl_9, cr, 298.15\ K)$ is calculated from the heat of solution, $\Delta_r H° = -112.07$ kcal·mol^{-1}, of $K_3Al_2Cl_9$(cr) in water (one mole of solute in 36 l. of water), as determined by Baud.[1]

Heat Capacity and Entropy

Heat capacities are estimated based on the assumption that the property of the mixed chloride ($2AlCl_3 + 3KCl$) is the sum of the corresponding values for its component chlorides, i.e. AlCl(cr) and KCl(cr). In a similar manner, $S°$(298.15 K) is estimated to be 112 cal·K^{-1}·mol^{-1}.

Reference

[1]E. Baud, Ann. chim. Phys. **1**, 8 (1904).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	337.230	468.608	468.608	0.	−2860.182	−2625.893	460.046
300	337.858	470.696	468.614	0.624	−2860.094	−2624.440	456.956
400	353.130	570.010	482.052	35.183	−2862.602	−2545.238	332.374
500	367.272	650.359	507.925	71.217	−2857.227	−2466.497	257.673
600	379.740	718.443	537.478	108.579	−2850.799	−2388.938	207.976
700	390.807	777.827	567.660	147.116	−2843.468	−2312.529	172.563
800	400.660	830.668	597.294	186.700	−2835.425	−2237.222	146.076
900	407.940	878.265	625.912	227.117	−2826.979	−2162.952	125.534
1000	416.726	921.687	653.349	268.338	−2839.443	−2088.115	109.072
1100	427.019	961.876	679.592	310.513	−3066.550	−1999.618	94.954
1200	438.818	999.527	704.700	353.792	−3052.785	−1903.224	82.845
1300	452.123	1035.166	728.761	398.327	−3037.812	−1808.025	72.647
1400	466.934	1069.205	751.871	444.267	−3021.478	−1714.029	63.951
1500	483.252	1101.968	774.125	491.764	−3003.629	−1621.254	56.457

PREVIOUS: June 1962 CURRENT: September 1964

$S°(298.15\ K) = 387.3 \pm 12\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2624.08 \pm 16\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2633.62 \pm 16\ kJ \cdot mol^{-1}$

Vibrational Frequencies, ν, cm^{-1}(all single degenerate)					
[830]	[200]	[210]	[30]	600	805
[600]	[90]	980	[970]	[230]	575
[370]	[630]	340	[260]	[310]	300

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: [D_{2h}]
Bond Distances: Al–F = [1.63] Å; Al–F(bridge) = [1.80] Å
Bond Angles: F–Al–F = [120°]; F(bridge)–Al–F(bridge) = [90]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.669982 × 10^{-112}] $g^3 \cdot cm^6$

Enthalpy of Formation

The existence of small amounts of dimer in the saturated vapor was inferred from the intensities of AlF_2^+, AlF_3^+ and $Al_2F_5^+$ observed by mass spectrometry.[1,2,3] Buchler *et al.*[1] concluded that the precursor of the first two ions was mainly AlF_3, while the dimer was the precursor of $Al_2F_5^+$. Intensities of $Al_2F_5^+$ relative to those of AlF_2^+ were observed as 0.0057,[1] 0.007[2] and 0.025[3] at ionizing energies of 60, 90 and 100 V for vapor at 1025, 1100 and 1025 K, respectively.

The temperature dependence of ion intensities was used to derive 2nd law values of $\Delta_{sub}H°$ for monomer and dimer[1,2] and a value of $\Delta_{dim}H°$ based on an estimate for the $\Delta_{dim}S°$.[3] The absolute pressure of the monomer was obtained[2] from the relative ion intensity assuming a relative ionization cross section equal to two and neglecting other effects. Krause and Douglas[4] reported values for $\Delta_{sub}H°$(monomer), $\Delta_{dim}H°$, and $\Delta_{dim}S°$; these were derived by combination of $\Delta_{sub}H°$(dimer)[1] with precise sublimation pressures from entrainment data near 1200 K, where the dimer is more abundant. After reduction to 1000 K with JANAF functions, these results may be summarized as follows:

Source	Method	$\Delta_r H°$, kcal·mol^{-1}*			$\Delta_r S°$, cal·K^{-1}·mol^{-1}*		
		c → m	2c → d	2m → d	c → m	2c → d	2m → d
[4]	Entrainment	68.1 ± 0.4	[86]	−50 ± 3	[44.04]	—	−35 ± 3
[1]	Ion Intensities	67.3 ± 3	85.8 ± 3	−4.8 ± 3	—	—	—
[2]	Ion Intensities	70.5	92.1	−49.0	46.4	55.1	−37.7
[3]	Ion Intensities	—	—	−48.0 ± 4	—	—	[−32 ± 3]
JANAF	Adopted	68.4	87.8	[−49]	[44.37]	[52.83]	[−35.9]

*Reactions are abbreviated by c = crystal, d = dimer gas and m = monomer gas. Brackets enclose those values assumed in deriving the other values.

JANAF values are given in the last line. These are based on JANAF entropies, on $\Delta_{dim}H° = -49$ kcal·mol^{-1} for which there is close agreement, and on the entrainment pressures of Krause and Douglas.[4] Reduction of the dimer value to 298.15 K gives $\Delta_{sub}H° = 92.55 \pm 4$ and $\Delta_f H° = -629.45 \pm 4$ kcal·mol^{-1}. The table for AlF_3(g) gives a detailed comparison of observed and predicted total pressure along with predictions of the mole fraction of dimer in the saturated vapor. The latter are reasonably consistent with the relative ion intensities.

Heat Capacity and Entropy

The molecular structure is assumed to be similar to that of Al_2Cl_6. Bond distances and bond angles are estimated by comparison with AlF_3,[5] $AlCl_3$[5] and Al_2Cl_6.[5] The principal moments of inertia are $I_A = 35.3676 \times 10^{-39}$, $I_B = 79.7440 \times 10^{-39}$, $I_C = 94.6684 \times 10^{-39}$ g·cm^2.

Six observed vibrational frequencies are from infrared spectra of the dimer isolated in rare-gas matrices.[6] Unobserved fundamentals (2 in infrared, 9 in Raman and 1 inactive) are estimated such that the entropy is consistent with the result of Krause and Douglas[4] as given above. The estimated fundamentals are based on comparisons with Al_2Cl_6, Al_2Br_6 and Al_2I_6. Assignments used in the comparisons are minor modifications of those given by Beattie *et al.*[7]

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[5] JANAF Thermochemical Tables: AlF_3(g), $AlCl_3$(g), Al_2Cl_6(g), Al_2Br_6(g), and Al_2I_6(g), 9–30–79.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−26.015	−2624.080	−2624.080	INFINITE
100	70.831	277.577	487.750	−21.017	−2628.771	−2604.020	1360.201
200	108.448	339.120	398.728	−11.922	−2632.066	−2577.841	673.263
250	122.124	364.842	389.423	−6.145	−2633.025	−2564.166	535.753
298.15	132.744	387.294	387.294	0.	−2633.619	−2550.845	446.897
300	133.107	388.117	387.297	0.246	−2633.636	−2550.331	444.052
350	141.826	409.316	388.951	7.128	−2633.991	−2536.416	378.539
400	148.717	428.722	392.727	14.398	−2634.158	−2522.464	329.400
450	154.175	446.566	397.731	21.976	−2634.188	−2508.499	291.179
500	158.525	463.044	403.449	29.797	−2634.122	−2494.536	260.602
600	164.854	492.546	415.899	45.988	−2633.822	−2466.645	214.741
700	169.093	518.297	428.727	62.699	−2633.461	−2438.810	181.986
800	172.039	541.080	441.375	79.764	−2633.186	−2411.024	157.424
900	174.155	561.472	453.606	97.079	−2633.115	−2383.260	138.321
1000	175.720	579.906	465.329	114.577	−2654.519	−2353.970	122.959
1100	176.906	596.712	476.521	132.211	−2654.394	−2323.921	110.354
1200	177.826	612.146	487.188	149.949	−2654.244	−2293.884	99.850
1300	178.551	626.410	497.356	167.770	−2654.082	−2263.861	90.963
1400	179.134	639.664	507.053	185.655	−2653.918	−2233.850	83.346
1500	179.608	652.039	516.311	203.593	−2653.762	−2203.851	76.745
1600	179.999	663.644	525.160	221.574	−2653.618	−2173.861	70.969
1700	180.325	674.566	533.631	239.590	−2653.487	−2143.880	65.873
1800	180.600	684.881	541.750	257.637	−2653.370	−2113.907	61.344
1900	180.833	694.652	549.542	275.709	−2653.264	−2083.940	57.292
2000	181.033	703.933	557.032	293.802	−2653.164	−2053.978	53.644
2100	181.206	712.770	564.239	311.915	−2653.063	−2024.022	50.345
2200	181.356	721.203	571.184	330.043	−2652.953	−1994.070	47.345
2300	181.487	729.268	577.883	348.185	−2652.826	−1964.123	44.607
2400	181.602	736.994	584.353	366.340	−2652.671	−1934.183	42.096
2500	181.704	744.410	590.608	384.505	−2652.480	−1904.249	39.787
2600	181.795	751.538	596.661	402.680	−2652.242	−1874.325	37.656
2700	181.876	758.401	602.525	420.864	−2651.947	−1844.410	35.682
2800	181.948	765.016	608.211	439.055	−3239.391	−1812.572	33.814
2900	182.013	771.402	613.729	457.253	−3236.769	−1761.660	31.731
3000	182.072	777.574	619.088	475.458	−3234.068	−1710.841	29.788
3100	182.126	783.545	624.297	493.668	−3231.281	−1660.112	27.973
3200	182.174	789.328	629.365	511.883	−3228.404	−1609.475	26.272
3300	182.218	794.934	634.297	530.102	−3225.433	−1558.929	24.676
3400	182.258	800.375	639.102	548.326	−3222.365	−1508.475	23.175
3500	182.295	805.659	643.786	566.554	−3219.196	−1458.112	21.761
3600	182.329	810.794	648.354	584.785	−3215.926	−1407.841	20.427
3700	182.360	815.791	652.812	603.019	−3212.553	−1357.663	19.167
3800	182.389	820.654	657.165	621.257	−3209.078	−1307.578	17.974
3900	182.416	825.392	661.418	639.497	−3205.501	−1257.584	16.843
4000	182.440	830.011	665.576	657.740	−3201.824	−1207.683	15.771
4100	182.463	834.516	669.642	675.985	−3198.047	−1157.877	14.752
4200	182.485	838.913	673.620	694.233	−3194.173	−1108.163	13.782
4300	182.504	843.207	677.514	712.482	−3190.204	−1058.544	12.859
4400	182.523	847.403	681.327	730.733	−3186.143	−1009.017	11.979
4500	182.540	851.505	685.064	748.987	−3181.989	−959.583	11.139
4600	182.556	855.518	688.726	767.241	−3177.752	−910.243	10.336
4700	182.571	859.444	692.317	785.498	−3173.433	−860.996	9.569
4800	182.586	863.288	695.839	803.756	−3169.036	−811.841	8.835
4900	182.599	867.053	699.294	822.015	−3164.562	−762.779	8.131
5000	182.612	870.742	702.687	840.275	−3160.019	−713.809	7.457
5100	182.623	874.358	706.017	858.537	−3155.409	−664.931	6.810
5200	182.635	877.904	709.289	876.800	−3150.737	−616.143	6.189
5300	182.645	881.383	712.503	895.064	−3146.007	−567.446	5.593
5400	182.655	884.797	715.662	913.329	−3141.224	−518.839	5.019
5500	182.664	888.149	718.768	931.595	−3136.392	−470.321	4.467
5600	182.673	891.440	721.822	949.862	−3131.515	−421.890	3.935
5700	182.682	894.674	724.826	968.130	−3126.599	−373.549	3.423
5800	182.690	897.851	727.782	986.398	−3121.640	−325.294	2.930
5900	182.697	900.974	730.691	1004.668	−3116.657	−277.122	2.453
6000	182.705	904.045	733.555	1022.938	−3111.601	−229.042	1.994

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K)$ = [597.38 ± 1] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = −481.80 ± 8.4 $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = −489.53 ± 8.4 $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies					
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
339 (1)	42 (1)	54 (1)	[7](1)	296 (1)	316 (1)
145 (1)	[20](1)	416 (1)	408 (1)	65 (1)	141 (1)
93 (1)	[220](1)	[100](1)	82 (1)	[50] (1)	75 (1)

Ground State Quantum Weight: [1] σ = 4

Point Group: D_{2h}

Bond Distances: Al–I = 2.449 ± 0.013 Å; Al–I (bridge) = 2.634 ± 0.03 Å

Bond Angles: I–Al–I = 115.0 ± 7.4°; I (bridge)–Al–I (bridge) = 99.6 ± 4.5°

Product of the Moments of Inertia: $I_A I_B I_C = 5.884591 \times 10^{-109}\ g^3\ cm^6$.

Enthalpy of Formation

The vapor pressure over $AlBr_3$(l) has been measured by Fischer, Rahlfs and Benze.[1] The vapor consists of both Al_2I_6(g) and AlI_3(g). Equilibrium constants for the reaction $Al_2I_6(g) = 2\ AlI_3(g)$ have also been determined by Fischer *et al.*[1] in the temperature range 614–843 K. From this data equilibrium constants at other temperatures were estimated and the partial pressures of Al_2I_6(g) over AlI_3(l) were calculated from the total pressure using these estimated values. The heats of reaction are calculated from the vaporization data using 2nd and 3rd law methods. The results of the calculations are as follows, where the $\Delta_f H°(298.15\ K)$ value is based on the 3rd law value of $\Delta_f H°(298.15\ K)$ and $\Delta_f H°(AlI_3, I, 298.15\ K) = -69.2\ kcal·mol^{-1}$.

Method	T/K	Data Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Mass Loss	513.15–645.35	19[a]	21.50 ± 0.1	21.34 ± 0.0	−0.3 ± 0.1	−117.06
Transport	513.95–578.15	7[b]	20.80 ± 0.1	21.51 ± 0.1	1.3 ± 0.3	−116.89

[a]One point at 493.95 rejected due to statistical test.
[b]One point at 482.95 rejected due to statistical test.

The adopted enthalpy of formation is $\Delta_f H°(Al_2I_6, g, 298.15\ K) = -117.0 \pm 2.0\ kcal·mol^{-1}$ (−489.528 ± 8.4 $kJ·mol^{-1}$)

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from the electron diffraction work of Shen.[2] These values are in good agreement with the earlier electron diffraction work by Akishin, Rambidi and Zasorin[3] and Palmer and Elliot.[4] The principal moments of inertia are $I_A = 530.1962 \times 10^{-39}$, $I_B = 963.2338 \times 10^{-39}$, and $I_C = 1152.2532 \times 10^{-39}\ g·cm^2$. Beattie, Gilson and Ozin[5] measured the condensed phase IR and Raman bonds for Al_2I_6 and Beattie and Horder[6] measured the gas phase Raman spectra. Five frequencies (ν_5, ν_6, ν_9, ν_{10}, ν_{15}) were adjusted not only for consistency with the frequencies chosen for Al_2F_6(g), Al_2Cl_6(g) and Al_2Br_6(g),[7] but also for agreement between 2nd and 3rd law $\Delta_f H°(298.15\ K)$ values in the data sets tabulated above.

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[6]I. R. Beattie and J. R. Horder, J. Chem. Soc. (London)*A* **1969**, 2655.
[7]JANAF Thermochemical Tables: Al_2F_6(g), Al_2Cl_6(g) and Al_2Br_6(g), 9–30–79.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−40.941	−481.796	−481.796	INFINITE
100	133.463	427.756	742.263	−31.451	−482.424	−505.504	264.048
200	161.741	530.588	612.847	−16.452	−485.826	−527.310	137.719
250	168.093	567.419	600.192	−8.193	−487.677	−537.470	112.298
298.15	171.953	597.380	597.380	0.	−489.528	−546.893	95.813
300	172.071	598.444	597.384	0.318	−489.602	−547.249	95.285
350	174.684	625.179	599.489	8.991	−491.834	−556.688	83.081
400	176.475	648.629	604.196	17.773	−542.078	−564.151	73.671
450	177.749	669.492	610.313	26.630	−547.927	−566.559	65.764
500	178.685	688.270	617.186	35.542	−674.164	−556.918	58.181
600	179.935	720.969	631.838	53.479	−672.960	−533.585	46.453
700	180.707	748.768	646.606	71.514	−671.923	−510.440	38.090
800	181.215	772.934	660.920	89.611	−671.124	−487.429	31.826
900	181.567	794.299	674.575	107.751	−670.637	−464.500	26.959
1000	181.820	813.443	687.522	125.921	−691.704	−440.085	22.988
1100	182.009	830.782	699.769	144.113	−691.308	−414.943	19.704
1200	182.153	846.625	711.357	162.322	−690.948	−389.835	16.969
1300	182.265	861.210	722.330	180.543	−690.644	−364.755	14.656
1400	182.354	874.720	732.739	198.774	−690.424	−339.696	12.674
1500	182.426	887.304	742.628	217.013	−690.317	−314.648	10.957
1600	182.485	899.079	752.043	235.259	−690.353	−289.603	9.455
1700	182.534	910.144	761.021	253.510	−690.559	−264.551	8.129
1800	182.576	920.579	769.598	271.765	−690.957	−239.481	6.950
1900	182.611	930.451	777.806	290.025	−691.558	−214.384	5.894
2000	182.640	939.818	785.675	308.287	−692.367	−189.249	4.943
2100	182.666	948.730	793.229	326.553	−693.376	−164.069	4.081
2200	182.688	957.228	800.492	344.820	−694.570	−138.838	3.296
2300	182.708	965.349	807.484	363.090	−695.926	−113.547	2.579
2400	182.725	973.126	814.225	381.362	−697.414	−88.195	1.920
2500	182.740	980.585	820.731	399.635	−699.003	−62.778	1.312
2600	182.753	987.753	827.018	417.910	−700.658	−37.296	0.749
2700	182.765	994.650	833.100	436.186	−702.342	−11.750	0.227
2800	182.776	1001.297	838.989	454.463	−1291.825	15.793	−0.295
2900	182.785	1007.711	844.697	472.741	−1291.280	62.484	−1.125
3000	182.794	1013.908	850.235	491.020	−1290.670	109.156	−1.901
3100	182.802	1019.902	855.612	509.299	−1289.971	155.805	−2.625
3200	182.809	1025.706	860.837	527.580	−1289.160	202.430	−3.304
3300	182.815	1031.331	865.919	545.861	−1288.219	249.028	−3.942
3400	182.821	1036.789	870.864	564.143	−1287.134	295.596	−4.541
3500	182.826	1042.088	875.681	582.425	−1285.893	342.129	−5.106
3600	182.831	1047.239	880.375	600.708	−1284.488	388.624	−5.639
3700	182.836	1052.248	884.953	618.992	−1282.913	435.079	−6.142
3800	182.840	1057.124	889.420	637.276	−1281.164	481.488	−6.619
3900	182.844	1061.874	893.781	655.560	−1279.241	527.849	−7.070
4000	182.848	1066.503	898.042	673.844	−1277.143	574.158	−7.498
4100	182.851	1071.018	902.206	692.129	−1274.873	620.412	−7.904
4200	182.854	1075.424	906.278	710.415	−1272.432	666.610	−8.291
4300	182.857	1079.727	910.262	728.700	−1269.826	712.747	−8.658
4400	182.860	1083.931	914.161	746.986	−1267.060	758.822	−9.008
4500	182.862	1088.040	917.980	765.272	−1264.133	804.831	−9.342
4600	182.865	1092.059	921.720	783.558	−1261.060	850.774	−9.661
4700	182.867	1095.992	925.387	801.845	−1257.844	896.650	−9.965
4800	182.869	1099.842	928.981	820.132	−1254.491	942.456	−10.256
4900	182.871	1103.613	932.507	838.419	−1251.006	988.189	−10.534
5000	182.873	1107.307	935.966	856.706	−1247.399	1033.850	−10.801
5100	182.874	1110.928	939.361	874.993	−1243.676	1079.439	−11.056
5200	182.876	1114.480	942.695	893.281	−1239.844	1124.953	−11.300
5300	182.878	1117.963	945.969	911.568	−1235.909	1170.391	−11.535
5400	182.879	1121.381	949.186	929.856	−1231.879	1215.756	−11.760
5500	182.880	1124.737	952.347	948.144	−1227.760	1261.045	−11.976
5600	182.882	1128.032	955.455	966.432	−1223.560	1306.259	−12.184
5700	182.883	1131.269	958.511	984.721	−1219.284	1351.396	−12.384
5800	182.884	1134.450	961.517	1003.009	−1214.935	1396.457	−12.576
5900	182.885	1137.576	964.475	1021.297	−1210.528	1441.443	−12.762
6000	182.886	1140.650	967.386	1039.586	−1206.021	1486.350	−12.940

PREVIOUS: September 1979 (1 atm) CURRENT: September 1979 (1 bar)

$S°(298.15\ K) = 88.7 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2048 \pm 20\ K$

$\Delta_f H°(0\ K) = -2283.07 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2299.11 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [192.464 \pm 21]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

From differences in heats of solution of MgO(cr), Al_2O_3(cr, α) and $MgAl_2O_4$(cr) in a melt of $2PbOB_2O_3$ at 970 K, Charlu *et al.*,[1] derived $\Delta_f H°(970\ K) = -5.38 \pm 0.18\ kcal \cdot mol^{-1}$ for Al_2O_3(cr, α) + MgO(cr) → $MgAl_2O_4$(cr). When combined with auxiliary JANAF data,[2] this yields our adopted heat of formation. This value is within 3 $kcal \cdot mol^{-1}$ of earlier values determined via a similar method.[3,4] The direct measurement for formation from the elements, $\Delta_f H°(298.15\ K) = -567.1 \pm 0.3\ kcal \cdot mol^{-1}$, by Zaionchkovskii and Rubalskaya[5] appears to be widely discordant with other values.

Our 2nd and 3rd law analysis of all the equilibrium data is given below. Heats of formation based on the 3rd law analysis support the adopted heat of formation even though agreement between 2nd and 3rd law values is only fair. The two studies by Grojtheim *et al.* involving reaction 1 require significant activity corrections since the Al(l) is not pure as indicated but is alloyed with Mg[6] or Si.[8] Activities were obtained assuming the AlMg(l) solution is ideal as stated by the authors[6] and supported independently.[13] Activities used to correct the other study[8] are given by the authors in their paper.

Source	Reaction	T/K	Data Points	$\Delta_f H°$(298.15 $kcal \cdot mol^{-1}$) 2nd law	3rd law	Drift $J \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal \cdot mol^{-1}$
Grjotheim *et al.*[6]	1	1143–1414	9	140.2 ± 1.7	126.0 ± 2.3	−10.8 ± 1.3	−549.5 ± 2.4
Grjotheim *et al.*[7]	2	1324–1452	7	307.8 ± 6.6	306.6 ± 1.0	−0.8 ± 4.8	−553.1 ± 1.1
Grjotheim *et al.*[8]	1	1216–1423	7	133.5 ± 0.7	127.0 ± 0.8	−5.0 ± 0.5	−548.5 ± 1.0
Rao and Dadape[9]	3	1025–1192	7	25.9 ± 3.4	25.3 ± 0.7	−0.5 ± 2.5	−552.6 ± 4.6
Taylor and Schmalzreid[10]	4	803	1	—	−0.4	—	−544.6
Rein and Chipman[11]	4	1873	1	—	−2.2	—	−546.4
Rosen and Muan[12]	4	1673	1	—	−4.0	—	−548.2

Reactions:
(1) 4 MgO(cr) + 2 Al(l) → $MgAl_2O_4$(cr) + 3 Mg(g)
(2) 8 MgO(cr) + Al_4C_3(cr) → 2 $MgAl_2O_4$(cr) + 3 C(ref) + 6 Mg(g)
(3) 4 MgO(cr) + 3 AlCl(g) → $MgAl_2O_4$(cr) + $AlCl_3$(g) + 3 Mg(g)
(4) MgO(cr) + Al_2O_3(cr, α) → $MgAl_2O_4$(cr)

Heat Capacity and Entropy

The adopted low temperature $C_p°$ to 300 K is taken from the analysis of Douglas and Beckett[14] and based on the measurements of King[15] (54–296 K). The high temperature heat capacities are calculated from the equation given by Landa and Naumova[16] based on their enthalpy measurements (1500–2200 K) as well as those of Bonnickson[17] (421–1805 K). Enthalpies in the overlapping regions of these two studies agree within ±1%.

Integration of the low temperature heat capacity data leads to $S°(50\ K) = 0.299\ cal \cdot K^{-1} \cdot mol^{-1}$ and $S°(298.15\ K) = 19.268\ cal \cdot K^{-1} \cdot mol^{-1}$.[14] We assume that $S°(0\ K) = 1.93\ cal \cdot K^{-1} \cdot mol^{-1}$ to correct for the ~0.15 mole fraction of inverted cations present in synthetic samples of $MgAl_2O_4$; the method of calculation is given by Navrostsky and Kleppa.[18] This configurational entropy term cannot be determined from integration of the $C_p°$ data since the disorder remains at zero Kelvin.

Fusion Data

Refer to the liquid table for details.

Phase Data

This table refers to $MgAl_2O_4$ (spinel) with 15% inversion. Navrotsky and Kleppa[18] have discussed the thermodynamics of spinels in detail and the 15% inversion is typical of most synthetic spinels or of natural spinel after heating above ~1300 K. Natural spinel which has been annealed through geologic time may have the completely normal (ordered) structure. If so its entropy will be 1.93 $cal \cdot K^{-1} \cdot mol^{-1}$ less than in this table and its heat of formation will be ~0.9 $kcal \cdot mol^{-1}$ more exothermic than given here based on annealing–heat of solution experiments on natural spinel.[18] These measurements found the order–disorder transition to occur in the range 973–1300 K. There have been recent reports of second–order phase transitions in the 723–873 K range detected by X-ray[19] and thermal expansion studies[20] but these are not obvious in the enthalpy data given above.

References

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[2] JANAF Thermochemical Tables: Al_2O_3(cr, α), 12–31–79; MgO(cr), 12–31–74; Al(l), 6–30–79; Mg(g), 9–30–72; Al_4C_3(cr), 9–30–65; C(ref. st.), 3–31–78; AlCl(g), 9–30–79; $AlCl_3$(g), 9–30–79.
[3] A. Navrotsky and O. J. Kleppa, J. Inorg. Nucl. Chem. **30**, 479 (1968); A. Navrotsky and O. J. Kleppa, Inorg. Chem. **5**, 192 (1966).
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[6] K. Grjotheim, O. Herstad and J. M. Toguri, Can. J. Chem. **39**, 443 (1961).

Continued on page 173

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	8.075	INFINITE	−15.411	−2283.075	−2283.075	INFINITE
100	22.669	16.757	164.497	−14.774	−2289.857	−2254.524	1177.642
200	78.069	49.819	98.221	−9.681	−2296.197	−2216.480	578.885
298.15	116.198	88.692	88.692	0.	−2299.108	−2176.621	381.335
300	116.533	89.412	88.695	0.215	−2299.137	−2175.861	378.851
400	137.988	126.244	93.571	13.069	−2299.797	−2134.626	278.754
500	149.829	158.409	103.398	27.506	−2299.410	−2093.365	218.692
600	157.887	186.474	114.956	42.911	−2298.562	−2052.230	178.663
700	164.155	211.299	126.980	59.023	−2297.527	−2011.255	150.082
800	169.473	233.573	138.935	75.710	−2296.463	−1970.433	128.656
900	174.238	253.814	150.592	92.899	−2295.485	−1929.739	111.999
1000	178.657	272.403	161.856	110.546	−2324.450	−1886.914	98.562
1100	182.853	289.629	172.698	128.623	−2323.172	−1843.219	87.527
1200	186.895	305.713	183.120	147.112	−2321.562	−1799.655	78.337
1300	190.828	320.829	193.137	165.999	−2319.622	−1756.239	70.567
1400	194.686	335.112	202.773	185.275	−2444.763	−1709.818	63.794
1500	198.485	348.674	212.051	204.934	−2440.816	−1657.458	57.718
1600	202.238	361.604	220.997	224.970	−2436.542	−1605.372	52.410
1700	205.962	373.976	229.635	245.381	−2431.944	−1553.563	47.735
1800	209.652	385.853	237.986	266.162	−2427.024	−1502.034	43.588
1900	213.325	397.287	246.071	287.311	−2421.783	−1450.787	39.885
2000	216.982	408.322	253.909	308.826	−2416.221	−1399.824	36.560
2100	220.622	418.997	261.518	330.706	−2410.341	−1349.148	33.558
2200	224.254	429.344	268.912	352.950	−2404.143	−1298.758	30.836
2300	227.877	439.393	276.107	375.557	−2397.627	−1248.658	28.358
2400	231.488	449.167	283.115	398.525	−2390.796	−1198.849	26.092
2408.000	231.777	449.938	283.668	400.378	--- CRYSTAL <--> LIQUID ---		
2500	235.095	458.690	289.949	421.854	−2383.648	−1149.330	24.014
2600	238.697	467.981	296.618	445.544	−2376.185	−1100.104	22.101
2700	242.291	477.057	303.133	469.594	−2368.406	−1051.170	20.336
2800	245.885	485.934	309.504	494.002	−2948.114	−1000.595	18.666

PREVIOUS: June 1972 CURRENT: December 1979

Magnesium Aluminum Oxide ($MgAl_2O_4$) LIQUID M_r = 142.26568

$S°(298.15\ K)$ = [168.473] $J·K^{-1}·mol^{-1}$
T_{fus} = 2408 ± 20 K

$\Delta_f H°(298.15\ K)$ = [−2106.527] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [192.464 ± 21] $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the liquid is calculated from that of the crystal by adding the enthalpy of $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2408\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The adopted $C_p°$ for the liquid is estimated to be 52.5 $cal·K^{-1}·mol^{-1}$ (219.66 $J·K^{-1}·mol^{-1}$) above an assumed glass transition at 1750 K. Below T_{gls}, the heat capacity is taken to be that of the crystal.[1] The heat capacity is estimated by assuming $C_p°$ = 7.5 $cal·K^{-1}·g·atom^{-1}$ as suggested by Kubaschewski and Alcock.[2]

$S°(298.15\ K)$ is calculated in manner similar to that used for the enthalpy of formation.

Fusion Data

Rankin and Merwin[3] studied the binary system alumina + magnesia and reported T_{fus} = 2408 ± 20 K for $MgAl_2O_4$(cr). Wilde and Rees[4] confirm this value in a later paper. The adopted heat of melting is 46 ± 5 $kcal·mol^{-1}$. This is estimated assuming that the entropy of melting per $g–atom^{-1}$ (2.7 $cal·K^{-1}$) is the same as that of Be_2O_4(cr).[1]

References

[1]JANAF Thermochemical Tables: $MgAl_2O_4$(cr), 12–31–79; Be_2O_4(l), 12–31–79.
[2]O. Kubaschewski and C. B. Alcock, "Metallurgical Thermochemistry", 5th ed., Pergamon, Oxford, 449 pp. (1979).
[3]G. A. Rankin and H. E. Merwin, J. Amer. Chem. Soc. **38**, 568 (1916).
[4]W. T. Wilde and W. J. Rees, Trans. Brit. Ceramic Soc. **42**, 123 (1943).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	116.198	168.473	168.473	0.	−2106.527	−2007.826	351.763
300	116.533	169.193	168.475	0.215	−2106.556	−2007.214	349.487
400	137.988	206.024	173.351	13.069	−2107.216	−1973.957	257.772
500	149.829	238.190	183.178	27.506	−2106.829	−1940.674	202.741
600	157.887	266.255	194.736	42.911	−2105.981	−1907.517	166.064
700	164.155	291.079	206.760	59.023	−2104.945	−1874.521	139.878
800	169.473	313.354	218.716	75.710	−2103.882	−1841.676	120.249
900	174.238	333.594	230.373	92.899	−2102.904	−1808.961	104.989
1000	178.657	352.183	241.637	110.546	−2131.868	−1774.113	92.670
1100	182.853	369.409	252.479	128.623	−2130.591	−1738.396	82.550
1200	186.895	385.494	262.900	147.112	−2128.981	−1702.811	74.121
1300	190.828	400.609	272.918	165.999	−2127.041	−1667.373	66.996
1400	194.686	414.893	282.553	185.275	−2252.182	−1628.930	60.776
1500	198.485	428.454	291.832	204.934	−2248.234	−1584.548	55.179
1600	202.238	441.384	300.778	224.970	−2243.961	−1540.439	50.290
1700	205.962	453.757	309.415	245.381	−2239.363	−1496.608	45.985
1750.000	207.811	459.754	313.625	255.725	____ GLASS <--> LIQUID ____		
1750.000	219.660	459.754	313.625	255.725	TRANSITION		
1800	219.660	465.942	317.771	266.708	−2233.896	−1453.066	42.167
1900	219.660	477.818	325.885	288.674	−2227.838	−1409.852	38.760
2000	219.660	489.085	333.765	310.640	−2221.826	−1366.955	35.701
2100	219.660	499.803	341.419	332.606	−2215.860	−1324.359	32.942
2200	219.660	510.021	348.852	354.572	−2209.940	−1282.044	30.440
2300	219.660	519.785	356.073	376.538	−2204.065	−1239.999	28.161
2400	219.660	529.134	363.091	398.504	−2198.236	−1198.209	26.078
2408.000	219.660	529.865	363.644	400.261	--- CRYSTAL <--> LIQUID ---		
2500	219.660	538.101	369.913	420.470	−2192.452	−1156.661	24.167
2600	219.660	546.716	376.549	442.436	−2186.712	−1115.342	22.408
2700	219.660	555.006	383.006	464.402	−2181.016	−1074.243	20.782
2800	219.660	562.995	389.292	486.368	−2763.167	−1031.419	19.241
2900	219.660	570.703	395.415	508.334	−2755.368	−969.710	17.466
3000	219.660	578.150	401.383	530.300	−2747.614	−908.268	15.814
3100	219.660	585.352	407.202	552.266	−2739.904	−847.082	14.273
3200	219.660	592.326	412.879	574.232	−2732.239	−786.147	12.833
3300	219.660	599.086	418.420	596.198	−2724.618	−725.450	11.483
3400	219.660	605.643	423.830	618.164	−2717.043	−664.982	10.216
3500	219.660	612.010	429.116	640.130	−2709.515	−604.738	9.025
3600	219.660	618.199	434.283	662.096	−2702.035	−544.707	7.903
3700	219.660	624.217	439.335	684.062	−2694.603	−484.885	6.845
3800	219.660	630.075	444.278	706.028	−2687.223	−425.260	5.846
3900	219.660	635.781	449.116	727.994	−2679.895	−365.830	4.900
4000	219.660	641.342	453.852	749.960	−2672.622	−306.588	4.004

PREVIOUS: June 1972 CURRENT: December 1979

0 to 2408 K crystal
above 2408 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	8.075	INFINITE	−15.411	−2283.075	−2283.075	INFINITE
100	22.669	16.757	164.497	−14.774	−2289.857	−2254.524	1177.642
200	78.069	49.819	98.221	−9.681	−2296.197	−2216.480	578.885
298.15	116.198	88.692	88.692	0.	−2299.108	−2176.621	381.335
300	116.533	89.412	88.695	0.215	−2299.137	−2175.861	378.851
400	137.988	126.244	93.571	13.069	−2299.797	−2134.626	278.754
500	149.829	158.409	103.398	27.506	−2299.410	−2093.365	218.692
600	157.887	186.474	114.956	42.911	−2298.562	−2052.230	178.663
700	164.155	211.299	126.980	59.023	−2297.527	−2011.255	150.082
800	169.473	233.573	138.935	75.710	−2296.463	−1970.433	128.656
900	174.238	253.814	150.592	92.899	−2295.485	−1929.739	111.999
1000	178.657	272.403	161.856	110.546	−2324.450	−1886.914	98.562
1100	182.853	289.629	172.698	128.623	−2323.172	−1843.219	87.527
1200	186.895	305.713	183.120	147.112	−2321.562	−1799.655	78.337
1300	190.828	320.829	193.137	165.999	−2319.622	−1756.239	70.567
1400	194.686	335.112	202.773	185.275	−2444.763	−1709.818	63.794
1500	198.485	348.674	212.051	204.934	−2440.816	−1657.458	57.718
1600	202.238	361.604	220.997	224.970	−2436.542	−1605.372	52.410
1700	205.962	373.976	229.635	245.381	−2431.944	−1553.563	47.735
1800	209.652	385.853	237.986	266.162	−2427.024	−1502.034	43.588
1900	213.325	397.287	246.071	287.311	−2421.783	−1450.787	39.885
2000	216.982	408.322	253.909	308.826	−2416.221	−1399.824	36.560
2100	220.622	418.997	261.518	330.706	−2410.341	−1349.148	33.558
2200	224.254	429.344	268.912	352.950	−2404.143	−1298.758	30.836
2300	227.877	439.393	276.107	375.557	−2397.627	−1248.658	28.358
2400	231.488	449.167	283.115	398.525	−2390.796	−1198.849	26.092
2408.000	231.777	449.938	283.668	400.378	CRYSTAL <--> LIQUID TRANSITION		
2408.000	219.660	529.865	283.668	592.842			
2500	219.660	538.101	292.881	613.051	−2192.452	−1156.661	24.167
2600	219.660	546.716	302.479	635.017	−2186.712	−1115.343	22.408
2700	219.660	555.006	311.679	656.983	−2181.016	−1074.244	20.782
2800	219.660	562.995	320.513	678.949	−2763.167	−1031.420	19.241
2900	219.660	570.703	329.008	700.915	−2755.369	−969.711	17.466
3000	219.660	578.150	337.189	722.881	−2747.614	−908.268	15.814
3100	219.660	585.352	345.079	744.847	−2739.904	−847.083	14.273
3200	219.660	592.326	352.697	766.813	−2732.239	−786.148	12.833
3300	219.660	599.086	360.062	788.779	−2724.618	−725.451	11.483
3400	219.660	605.643	367.189	810.745	−2717.043	−664.983	10.216
3500	219.660	612.011	374.093	832.711	−2709.515	−604.739	9.025
3600	219.660	618.199	380.788	854.677	−2702.035	−544.708	7.904
3700	219.660	624.217	387.286	876.643	−2694.603	−484.885	6.845
3800	219.660	630.075	393.599	898.609	−2687.223	−425.260	5.846
3900	219.660	635.781	399.736	920.575	−2679.895	−365.830	4.900
4000	219.660	641.342	405.707	942.541	−2672.622	−306.589	4.004

PREVIOUS: CURRENT: December 1979

$\Delta_{at}H°$ = 250 ± 4 kJ·mol^{-1}
$S°$(298.15 K) = 252.33 ± 3.3 J·K^{-1}·mol^{-1}

$\Delta_fH°$(0 K) = −144.5 ± 17 kJ·mol^{-1}
$\Delta_fH°$(298.15 K) = −145.2 ± 17 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
471(1)	[160](2)	994(1)

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X	0	1	B	34331	[3]
A	23286	[1]	C	36233	[1]

Point Group: $D_{\infty h}$ σ = 2
Bond Distance: Al–O = 1.73 Å
Bond Angle: Al–O–Al = 180° ± 10°
Rotational Constant: B_o = 0.104378 cm^{-1}

Enthalpy of Formation

We adopt the heat of atomization $\Delta_{at}H°$ = 250 ± 4 kcal·mol^{-1} and $\Delta_fH°$(298.15 K) = −34.7 ± 4 kcal·mol^{-1}. Six reactions analyzed below yield $D°$ values ranging from 247.4 to 252.7 kcal·mol^{-1}.[1–10] These values show no obvious dependence on the reaction and eight of the eleven fall in the range 250 ± 2 kcal·mol^{-1}. The overall uncertainty is about twice this range due to possible error in the data and the thermodynamic functions. The mass–spectrometric methods are uncertain due to use of several different approximations for ionization cross sections; some of these must be significantly in error. Other methods have their own uncertainties. We omit below two studies that were recently revised by Ho and Burns[1] and others, such as,[11] that we believe to be seriously biased.

Source	Method	Reaction[a]	T/K	δS cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_fH°$(298.15 K) kcal·mol^{-1}	$\Delta_{at}H°$(0 K)
[1]Ho (1980)	Mass spec.	A	2221–2327[b]	4.6 ± 3.2	−240.6 ± 7.3	−251.0 ± 0.6	−33.9 ± 4	249.2
[1]Fu (1976)	Mass spec.	A	2056–2327[b]	0.4 ± 1.3	−251.4 ± 3.0	−252.4 ± 0.8	−35.2 ± 4	250.5
[2]Smoes (1976)	Mass spec.v	B	1198–1461	−0.2 ± 0.3	18.8 ± 0.4	19.1 ± 0.2	−34.8 ± 3	250.1
[3]Hildenbrand (1973)	Mass spec.	C	2104–2256	−0.5 ± 1.4	−10.0 ± 3.1	−9.0 ± 0.4	−36.6 ± 5	251.9
[4]Farber (1972)	Mass spec.	D	1943–2093	0.0 ± 5.5	−129 ± 11	−128.8 ± 1.3	−34.0 ± 5	249.3
[5]Thompson (1973)	Mass spec.	E	1438–1580	−0.2 ± 1.9	92.3 ± 2.8	92.7 ± 0.6	−37.4 ± 4	252.7
[6]Rao (1970)	Knudsen eff.	E	1556	–	–	97.4	−32.7 ± 5	248.0
[7]Kulifeev (1969)	Knudsen eff.	E	1443–1576	19 ± 5	123 ± 7	93.6 ± 2.0	−36.5 ± 5	251.8
[8]Herstad (1966)	K.E. + P.C.[c]	E	1585–2129	0.0 ± 1.0	96.5 ± 2.0	96.4 ± 1.1	−33.7 ± 4	249.0
[9]DeMaria (1968)	Mass spec.	F	1313–1511	−1.0 ± 0.5	−5.1 ± 0.7	−3.7 ± 0.3	−32.1 ± 5	247.4
[10]Brewer (1951)	Volatilization	F	1466–1725	5.1 ± 2.7	−0.5 ± 4.3	−8.6 ± 1.4	−37.0 ± 5	252.3

[a]Reactions: A) 2 Al(g) + O(g) → Al_2O(g); B) 1/3 Al_2O_3(cr) + 1/3 Al(l) + Al(g) = Al_2O(g); C) 2AlO(g) = Al_2O(g) + O(g)
D) Al(g) + AlO(g) = Al_2O(g); E) 1/3 Al_2O_3(cr) + 4/3 Al(l) = Al_2O(g); F) 1/3 Al_2O_3(cr) + 4/3 Al(g) = Al_2O(g).
[b]Temperature scale adjusted. [c]Knudsen effusion plus pressure compensation.

Heat Capacity and Entropy

We adopt a linear Al–O–Al structure with a low bending frequency. The long–standing controversy over these properties has been greatly resolved by Douglas[12] who studied electronic absorption and emission spectra of Al_2O in Kr and Ar matrices. Vibrational progressions in the spectra[12] gave 471 ± 15, ~482 and ~452 cm^{-1} for ν_1 of the X, A and C states, respectively, plus ~133 and ~170 cm^{-1} for ν_2 of the A and C states. This supplements previous evidence of linearity, i.e. absence of υ_1 in IR spectra[13–18] absence of deflection by an inhomogenous electric field[19] and theoretical predictions.[20] IR spectra[13–18] also failed to show ν_2, which has been estimated as 102 or 120 ± 30 cm^{-1} from SCF calculations[20] or force constants.[17] The evidence suggests that the X state has $\nu_2 \leq$ 170 cm^{-1} implying that the equilibrium bond angle[21] is much closer to 180° than the uncorrected angle of 141° derived from electron diffraction. Likewise, the angle of 140°–150°[15] derived from the isotopic shift of ν_3 becomes nearly 180°[12] if corrected for anharmonicity.

We conclude that the bond angle is 180° ± 10° and adopt the bond distance from electron diffraction.[21] Frequencies ν_1 and ν_3 are from[12] and,[13–18] while ν_2 = 160 cm^{-1} is chosen to reproduce the entropy derived from equilibria (see δS in the table above). Electronic levels are from;[12] states A and C probably are bent. The band found[18] at ~24400 cm^{-1} is from Al_2.[12] Values of Gibbs energy function from Gurvich *et al.*[22] are 1.0 cal·K^{-1}·mol^{-1} larger than ours at T>1400 K.

References

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Continued on page 173

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_fH°$ kJ·mol^{-1}	$\Delta_fG°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−12.710	−144.474	−144.474	INFINITE
100	40.424	201.813	295.494	−9.368	−143.552	−153.671	80.269
200	47.795	232.403	256.967	−4.913	−144.156	−163.630	42.736
250	50.162	243.332	253.179	−2.462	−144.662	−168.442	35.194
298.15	52.032	252.332	252.332	0.	−145.185	−172.975	30.304
300	52.098	252.654	252.333	0.096	−145.205	−173.147	30.148
350	53.696	260.809	252.973	2.742	−145.767	−177.760	26.529
400	55.010	268.068	254.415	5.461	−146.342	−182.291	23.805
450	56.087	274.611	256.301	8.239	−146.929	−186.750	21.677
500	56.971	280.568	258.435	11.067	−147.532	−191.142	19.968
600	58.297	291.080	263.023	16.834	−148.815	−199.746	17.389
700	59.213	300.139	267.693	22.713	−150.259	−208.123	15.530
800	59.863	308.091	272.256	28.668	−151.933	−216.278	14.121
900	60.337	315.171	276.638	34.679	−153.907	−224.206	13.013
1000	60.691	321.547	280.815	40.732	−177.417	−230.375	12.034
1100	60.961	327.345	284.786	46.815	−179.438	−235.573	11.186
1200	61.172	332.658	288.557	52.922	−181.456	−240.587	10.472
1300	61.339	337.562	292.140	59.048	−183.472	−245.433	9.862
1400	61.473	342.112	295.549	65.188	−185.488	−250.124	9.332
1500	61.583	346.357	298.796	71.341	−187.505	−254.670	8.868
1600	61.674	350.335	301.895	77.504	−189.526	−259.082	8.458
1700	61.750	354.076	304.855	83.676	−191.551	−263.368	8.092
1800	61.814	357.608	307.689	89.854	−193.581	−267.534	7.764
1900	61.869	360.951	310.405	96.038	−195.616	−271.587	7.466
2000	61.915	364.126	313.012	102.227	−197.658	−275.532	7.196
2100	61.956	367.148	315.519	108.421	−199.708	−279.376	6.949
2200	61.991	370.031	317.931	114.618	−201.764	−283.121	6.722
2300	62.022	372.787	320.257	120.819	−203.829	−286.773	6.513
2400	62.050	375.427	322.501	127.023	−205.902	−290.335	6.319
2500	62.075	377.961	324.669	133.229	−207.984	−293.810	6.139
2600	62.097	380.396	326.766	139.438	−210.073	−297.202	5.971
2700	62.118	382.740	328.796	145.649	−212.171	−300.513	5.814
2800	62.138	384.999	330.763	151.861	−802.079	−301.811	5.630
2900	62.156	387.180	332.671	158.076	−802.003	−283.946	5.114
3000	62.174	389.288	334.523	164.293	−801.934	−266.083	4.633
3100	62.192	391.327	336.323	170.511	−801.873	−248.222	4.183
3200	62.210	393.301	338.073	176.731	−801.820	−230.363	3.760
3300	62.229	395.216	339.776	182.953	−801.775	−212.506	3.364
3400	62.248	397.074	341.434	189.177	−801.737	−194.650	2.990
3500	62.269	398.879	343.049	195.403	−801.707	−176.795	2.639
3600	62.291	400.633	344.625	201.631	−801.684	−158.941	2.306
3700	62.315	402.340	346.162	207.861	−801.669	−141.087	1.992
3800	62.341	404.002	347.662	214.094	−801.661	−123.233	1.694
3900	62.369	405.622	349.127	220.329	−801.661	−105.380	1.411
4000	62.399	407.202	350.560	226.567	−801.669	−87.526	1.143
4100	62.433	408.743	351.960	232.809	−801.685	−69.673	0.888
4200	62.470	410.248	353.330	239.054	−801.710	−51.818	0.644
4300	62.509	411.718	354.671	245.303	−801.744	−33.963	0.413
4400	62.553	413.156	355.984	251.556	−801.788	−16.108	0.191
4500	62.600	414.562	357.270	257.814	−801.839	1.749	−0.020
4600	62.651	415.938	358.530	264.076	−801.904	19.607	−0.223
4700	62.705	417.286	359.766	270.344	−801.983	37.467	−0.416
4800	62.764	418.607	360.978	276.617	−802.075	55.328	−0.602
4900	62.827	419.902	362.168	282.897	−802.180	73.192	−0.780
5000	62.895	421.172	363.335	289.183	−802.303	91.058	−0.951
5100	62.967	422.418	364.481	295.476	−802.445	108.927	−1.116
5200	63.044	423.641	365.607	301.777	−802.606	126.798	−1.274
5300	63.125	424.843	366.714	308.085	−802.789	144.673	−1.426
5400	63.211	426.024	367.801	314.402	−802.995	162.551	−1.572
5500	63.301	427.184	368.870	320.727	−803.227	180.434	−1.714
5600	63.396	428.326	369.922	327.062	−803.487	198.321	−1.850
5700	63.496	429.449	370.956	333.407	−803.776	216.213	−1.981
5800	63.601	430.554	371.974	339.761	−804.092	234.110	−2.108
5900	63.710	431.642	372.977	346.127	−804.448	252.012	−2.231
6000	63.823	432.714	373.963	352.503	−804.796	269.918	−2.350

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K)$ = [260.6 ± 8] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) \approx 646.7 \pm 25\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [652.436] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[450] (1)
[140] (2)
[900] (1)

Ground State Quantum Weight: [2] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Al–O = [1.73] Å
Bond Angle: Al–O–Al = [180]°
Rotational Constant: B_0 = [0.104379] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(Al_2O^+, g, 0\ K)$ is calculated from that of Al_2O[1] using Hildenbrand's appearance potential[2] of 8.20 ± 0.15 eV (189.1 ± 3.5 $kcal·mol^{-1}$. We assume that the appearance potential is identical with the ionization potential for $Al_2O(g) \rightarrow Al_2O^+(g) + e^-(g)$. Other values reported for the appearance potential include 7.7 ± 0.5,[3,4] 7.9 ± 0.3,[5] 8.0 ± 0.5,[6] 8.5 ± 0.5[7] and 8.5 ± 0.2 eV.[8] These values are consistent with, but less precise than, the adopted value.

$\Delta_f H°(298.15\ K)$ is obtained from $\Delta_f H°(Al_2O)$ by using IP(Al_2O) with JANAF[1] enthalpies, $H°(0\ K)–H°(298.15\ K)$, for $Al_2O(g)$, $Al_2O^+(g)$ and e^- (g). $\Delta_f H°(Al_2O \rightarrow Al_2O^+ + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°(298.15\ K)$ should be changed by −1.481 $kcal·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron. MNDO calculations[10] differ by only −9.9 $kcal·mol^{-1}$ from our value of [$\Delta_f H°(Al_2O^+, 298.15\ K) - \Delta_f H°(Al_2O, 298.15\ K)$] even though the MNDO values of $\Delta_f H°(298.15\ K)$ differ by −47 and −37 $kcal·mol^{-1}$.

Heat Capacity and Entropy

Al_2O^+ is assumed to be linear as predicted by MNDO calculations[10] and by the correlation of Walsh.[11] We assume that the bond distance is the same as that in Al_2O[1] since the change in bond length on ionization was predicted to be only 0.004 Å.[10] Vibrational frequencies are estimated to be somewhat lower than those of Al_2O since the ion has one less bonding electron. The electronic ground state is doublet due to the odd number of electrons.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.981	646.679		
100	41.629	209.128	304.597	−9.547			
200	48.639	240.389	265.373	−4.997			
250	51.019	251.507	261.521	−2.503			
298.15	52.897	260.660	260.660	0.	652.436	615.909	−107.905
300	52.962	260.987	260.661	0.098	652.456	615.682	−107.200
350	54.537	269.274	261.312	2.787	652.976	609.512	−90.965
400	55.804	276.642	262.776	5.546	653.481	603.268	−78.779
450	56.821	283.276	264.691	8.363	653.972	596.961	−69.293
500	57.641	289.306	266.856	11.225	654.444	590.602	−61.700
600	58.846	299.930	271.507	17.054	655.300	577.750	−50.298
700	59.661	309.066	276.235	22.982	655.984	564.769	−42.144
800	60.231	317.072	280.850	28.978	656.429	551.704	−36.023
900	60.642	324.191	285.277	35.023	656.567	538.602	−31.260
1000	60.947	330.597	289.494	41.103	635.164	527.023	−27.529
1100	61.179	336.417	293.499	47.210	635.245	516.205	−24.513
1200	61.358	341.748	297.301	53.337	635.326	505.379	−21.999
1300	61.500	346.665	300.912	59.480	635.406	494.547	−19.871
1400	61.615	351.227	304.345	65.636	635.484	483.709	−18.047
1500	61.708	355.482	307.614	71.802	635.558	472.865	−16.467
1600	61.784	359.467	310.731	77.977	635.628	462.017	−15.083
1700	61.848	363.214	313.709	84.159	635.692	451.164	−13.863
1800	61.902	366.751	316.559	90.346	635.750	440.308	−12.777
1900	61.948	370.099	319.289	96.539	635.801	429.448	−11.806
2000	61.987	373.278	321.910	102.736	635.845	418.586	−10.932
2100	62.021	376.303	324.429	108.936	635.882	407.723	−10.142
2200	62.051	379.189	326.853	115.140	635.910	396.857	−9.423
2300	62.077	381.948	329.189	121.346	635.929	385.991	−8.766
2400	62.099	384.590	331.442	127.555	635.940	375.123	−8.164
2500	62.119	387.126	333.619	133.766	635.942	364.256	−7.611
2600	62.137	389.562	335.724	139.979	635.935	353.389	−7.100
2700	62.153	391.908	337.762	146.193	635.919	342.522	−6.626
2800	62.167	394.168	339.736	152.409	48.093	333.592	−6.223
2900	62.180	396.350	341.651	158.627	50.251	343.749	−6.192
3000	62.192	398.458	343.510	164.845	52.401	353.834	−6.161
3100	62.202	400.498	345.315	171.065	54.541	363.846	−6.131
3200	62.212	402.473	347.071	177.286	56.673	373.789	−6.101
3300	62.220	404.387	348.779	183.507	58.797	383.666	−6.073
3400	62.228	406.245	350.442	189.730	60.912	393.479	−6.045
3500	62.236	408.049	352.062	195.953	63.018	403.230	−6.018
3600	62.242	409.802	353.642	202.177	65.115	412.921	−5.991
3700	62.248	411.508	355.183	208.401	67.204	422.553	−5.965
3800	62.254	413.168	356.687	214.626	69.282	432.129	−5.940
3900	62.259	414.785	358.156	220.852	71.351	441.651	−5.915
4000	62.264	416.361	359.592	227.078	73.410	451.120	−5.891
4100	62.269	417.899	360.995	233.305	75.458	460.537	−5.867
4200	62.273	419.399	362.368	239.532	77.493	469.905	−5.844
4300	62.277	420.865	363.711	245.760	79.516	479.224	−5.821
4400	62.280	422.296	365.026	251.987	81.525	488.496	−5.799
4500	62.284	423.696	366.315	258.216	83.524	497.722	−5.777
4600	62.287	425.065	367.577	264.444	85.503	506.905	−5.756
4700	62.290	426.405	368.815	270.673	87.465	516.045	−5.735
4800	62.293	427.716	370.028	276.902	89.407	525.143	−5.715
4900	62.295	429.000	371.218	283.132	91.330	534.201	−5.695
5000	62.298	430.259	372.387	289.361	93.229	543.220	−5.675
5100	62.300	431.493	373.534	295.591	95.103	552.201	−5.656
5200	62.302	432.702	374.660	301.821	96.950	561.145	−5.637
5300	62.304	433.889	375.766	308.052	98.768	570.055	−5.618
5400	62.306	435.054	376.853	314.282	100.554	578.930	−5.600
5500	62.308	436.197	377.922	320.513	102.306	587.772	−5.582
5600	62.310	437.320	378.973	326.744	104.021	596.584	−5.565
5700	62.312	438.423	380.006	332.975	105.696	605.365	−5.548
5800	62.313	439.506	381.023	339.206	107.335	614.116	−5.531
5900	62.315	440.572	382.023	345.438	108.924	622.839	−5.514
6000	62.316	441.619	383.008	351.669	110.510	631.533	−5.498

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$\Delta_{at}H°$ = 1540 ± 32 kJ·mol^{-1} $\Delta_fH°$(0 K) = −391.3 ± 32 kJ·mol^{-1}

$S°$(298.15 K) = [280.98 ± 12] J·K·mol^{-1} $\Delta_fH°$(298.15 K) = −394.6 ± 32 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[600](1)	[350](1)	496 (1)
[400](1)	[200](1)	[650](1)

Ground State Quantum Weight: [1] σ = [4]

Bond Distance: Al–O = [1.80] Å; Point Group: [D_{2h}]

Bond Angles: O–Al–O = [90]°; Al–O–Al = [90]°

Product of the Moments of Inertia: $I_AI_BI_C$ = [2.889675 × 10^{-114}] g^3 cm^6

Enthalpy of Formation

We adopt $\Delta_fH°$(298.15 K) = −94.3 ± 8 and $\Delta_{at}H°$ = 368 ± 8 kcal·mol^{-1} based on the mass-spectrometric studies summarized below. Data of Chervonnyi[2] and Drowart[4] are analyzed using the isomolecular reaction B instead of the atomization reaction A, which is much affected by probable bias in calibrations and relative ionization cross sections. Reaction A would give discrepancies of −16 to +5 kcal·mol^{-1} in $\Delta_{at}H°$. Use of reaction B emphasizes the consistency among the studies. Only the result of Farber *et al.*[3] appears to be discrepant. JANAF auxiliary data[5] have been used to calculate the $\Delta_fH°$ values; their uncertainties include a large contribution from possible bias in the Gibbs-energy function. Gurvich *et al.*[6] selected $\Delta_fH°$(298.15 K) = −96.96 and $\Delta_{at}H°$ = 370.5 ± 12 kcal·mol^{-1} based on somewhat different functions and without benefit of the data of Ho.[1]

Source	Method	Reaction[a]	δS T/K	$\Delta H°$(298.15 K), kcal·mol cal·K^{-1}·mol^{-1}	2nd law	$\Delta_fH°$(298.15 K) 3rd law	kcal·mol^{-1}	$\Delta_{at}H°$
[1]Ho (1980)	Mass spec.	A	2221–2327[c]	−31 ± 1	−442 ± 3	−371.3 ± 2.8	−94.6 ± 8	368.2
[1]Fu (1976)	Mass spec.	A	2327	—	—	−368.4	−91.7 ± 8	365.4[d]
[2]Chervonnyi (1977)	Eff. mass spec.[c]	B[b]	2300–2600	−0.3 ± 3	1 ± 6	2.1 ± 1.0	−95.4 ± 10	369.0
[3]Farber (1972)	Eff. mass spec.	B	1943–2093	−7.1 ± 1	−22 ± 2	−7.3 ± 0.8	104.8 ± 10	378.5
[4]Drowart (1960)	Eff. mass spec.[c]	B[b]	2464–2594	31 ± 23	79 ± 57	1.3 ± 5.4	−96.2 ± 13	369.9[d]
[4]Drowart (1960)	Eff. mass spec.[f]	B[b]	2281–2466	−32 ± 17	−72 ± 39	4.1 ± 6.9	−93.4 ± 13	367.1[d]

[a]Reactions: A) 2 Al(g) + 2 O(g) = Al_2O_2(g); B) Al_2O(g) + AlO(g) = Al(g) + Al_2O_2(g).

[b]Reaction B used instead of A to minimize bias from calibrations and ionization cross sections.

[c]Temperature scale adjusted to T = 2327 K instead of 2318 K for α–Al_2O_3.

[d]Ho and Burn's recalculations[1] ofthe results of Fu[1] and Drowart[4] yield $\Delta_{at}H°$ = 367.0[1] and −364.6[4] kcal·mol^{-1} when converted to our new Al_2O_2 functions.

[e]Tungsten cell.

[f]Molybdenum cell.

Heat Capacity and Entropy

We adopt a square–planar structure of D_{2h} symmetry. The Al–O bond distance is taken as 1.8 Å, i.e., 0.1 Å longer than the predictions of ab initio[7] and MNDO[8] calculations and 0.07 Å longer than observed in Al_2O.[5] Similar predictions for Al_2O are I_A = 8.6080 × 10^{-39}, I_B = 14.5167 × 10^{-39} and I_C = 23.1247 × 10^{-39} g·cm^2.

Vibrational frequencies are estimated to be lower than values from MNDO calculations[8] but higher than Al_2F_2 values from ionic model calculations.[10] Matrix IR spectra gave a band near 496 cm^{-1} that was assigned to D_{2h} Al_2O_2 in three studies[11] but to cyclic AlO_2 in another.[12] A band at 686 cm^{-1}, once assigned to Al_2O_2,[13] was reassigned to $Al(O_2)_2$ by Finn[11] who also attributed bands at 490 and −1215 cm^{-1} to a C_{2v} form of Al_2O_2.

Evidence is contradictory on the most stable geometry. The square–planar form is 15 kcal·mol^{-1} more stable than linear AlOAlO according to ab initio calculations[7] but 27 kcal·mol^{-1} less stable according to MNDO calculations.[8-9] Also possible is rhombic D_{2h} AlO_2Al with an O–O bond similar to that predicted by ab initio methods for LiO_2Li.[14] This geometry was not considered in the ab initio study[7] and showed no minimum in the MNDO study.[8] Better calculations are needed to resolve the question. Thermochemical and spectral evidence is inconclusive.[15] Uncertainties in the structure and vibrational frequencies cause an uncertainty of ≤3 cal·K^{-1}·mol^{-1} in $S°$ and $-(G°-H°)/T$ at 2000 K. Estimated values for the rhombic peroxide[6] are ~1 cal·K^{-1}·mol^{-1} lower at 2000 K but this difference could be plausibly reversed by use of lower frequencies.

Continued on page 173

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.518	−391.307	−391.307	INFINITE
100	40.385	223.077	333.078	−11.000	−391.661	−395.241	206.453
200	56.664	256.193	286.829	−6.127	−393.303	−398.187	103.996
250	62.784	269.527	282.062	−3.134	−393.995	−399.325	83.434
298.15	67.164	280.980	280.980	0.	−394.551	−400.300	70.131
300	67.307	281.395	280.981	0.124	−394.571	−400.336	69.705
350	70.614	292.032	281.813	3.577	−395.065	−401.257	59.884
400	73.052	301.629	283.700	7.171	−395.511	−402.110	52.510
450	74.877	310.343	286.184	10.872	−395.935	−402.910	46.769
500	76.268	318.308	289.004	14.652	−396.355	−403.662	42.170
600	78.197	332.397	295.093	22.383	−397.255	−405.041	35.262
700	79.429	344.551	301.310	30.268	−398.319	−406.257	30.315
800	80.259	355.215	307.395	38.255	−399.630	−407.305	26.594
900	80.842	364.703	313.246	46.312	−401.261	−408.170	23.690
1000	81.266	373.244	318.825	54.418	−424.448	−407.314	21.276
1100	81.583	381.005	324.131	62.562	−426.164	−405.518	19.256
1200	81.827	388.114	329.171	70.733	−427.892	−403.565	17.567
1300	82.018	394.672	333.960	78.925	−429.632	−401.467	16.131
1400	82.171	400.756	338.517	87.135	−431.386	−399.235	14.896
1500	82.295	406.430	342.857	95.359	−433.154	−396.877	13.820
1600	82.396	411.744	346.998	103.593	−434.937	−394.400	12.876
1700	82.481	416.742	350.955	111.837	−436.735	−391.811	12.039
1800	82.552	421.459	354.742	120.089	−438.549	−389.117	11.292
1900	82.612	425.924	358.372	128.347	−440.380	−386.321	10.621
2000	82.663	430.162	361.857	136.611	−442.229	−383.428	10.014
2100	82.708	434.197	365.206	144.880	−444.096	−380.442	9.463
2200	82.746	438.045	368.430	153.152	−445.982	−377.366	8.960
2300	82.780	441.724	371.538	161.429	−447.886	−374.205	8.498
2400	82.810	445.248	374.536	169.708	−449.810	−370.961	8.074
2500	82.836	448.629	377.432	177.991	−451.752	−367.635	7.681
2600	82.859	451.878	380.234	186.275	−453.714	−364.232	7.318
2700	82.879	455.006	382.945	194.562	−455.694	−360.752	6.979
2800	82.898	458.020	385.573	202.851	−1045.495	−355.264	6.628
2900	82.915	460.929	388.122	211.142	−1045.321	−330.617	5.955
3000	82.930	463.741	390.596	219.434	−1045.166	−305.974	5.327
3100	82.943	466.460	392.999	227.728	−1045.027	−281.336	4.740
3200	82.955	469.094	395.336	236.023	−1044.907	−256.703	4.190
3300	82.967	471.646	397.610	244.319	−1044.803	−232.074	3.673
3400	82.977	474.123	399.825	252.616	−1044.715	−207.447	3.187
3500	82.986	476.529	401.982	260.914	−1044.645	−182.823	2.728
3600	82.995	478.867	404.085	269.213	−1044.590	−158.200	2.295
3700	83.003	481.141	406.137	277.513	−1044.552	−133.579	1.886
3800	83.010	483.354	408.140	285.814	−1044.531	−108.957	1.498
3900	83.017	485.511	410.097	294.115	−1044.526	−84.337	1.130
4000	83.023	487.613	412.008	302.417	−1044.538	−59.717	0.780
4100	83.029	489.663	413.877	310.720	−1044.567	−35.096	0.447
4200	83.034	491.664	415.706	319.023	−1044.615	−10.474	0.130
4300	83.039	493.618	417.495	327.327	−1044.681	14.149	−0.172
4400	83.044	495.527	419.247	335.631	−1044.767	38.774	−0.460
4500	83.049	497.393	420.963	343.935	−1044.869	63.400	−0.736
4600	83.053	499.218	422.644	352.240	−1044.998	88.029	−1.000
4700	83.056	501.004	424.293	360.546	−1045.150	112.662	−1.252
4800	83.060	502.753	425.909	368.852	−1045.327	137.298	−1.494
4900	83.063	504.466	427.495	377.158	−1045.529	161.939	−1.726
5000	83.067	506.144	429.051	385.464	−1045.763	186.583	−1.949
5100	83.070	507.789	430.579	393.771	−1046.028	211.233	−2.163
5200	83.073	509.402	432.079	402.078	−1046.326	235.887	−2.370
5300	83.075	510.984	433.553	410.386	−1046.661	260.549	−2.568
5400	83.078	512.537	435.001	418.693	−1047.036	285.217	−2.759
5500	83.080	514.062	436.425	427.001	−1047.453	309.891	−2.943
5600	83.082	515.559	437.825	435.309	−1047.915	334.575	−3.121
5700	83.085	517.029	439.202	443.618	−1048.425	359.266	−3.292
5800	83.087	518.474	440.556	451.926	−1048.981	383.968	−3.458
5900	83.088	519.895	441.889	460.235	−1049.597	408.677	−3.618
6000	83.090	521.291	443.200	468.544	−1050.227	433.396	−3.773

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K)$ = [289.7 ± 16] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 564.0 ± 60 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [567.414] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[560](1)	[320](1)	[460](1)
[370](1)	[180](1)	[600](1)

Ground State Quantum Weight: [2] σ = [4]
Point Group: [D_{2h}]
Bond Distance: Al–O = [1.80] Å
Bond Angles: O–Al–O = [90]°; Al–O–Al = [90]°
Product of the Moments of Inertia: $I_A I_B I_C$=[2.889607 × 10^{-114}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°$(0 K) is calculated from that of Al_2O_2[1] using the appearance potential 9.9 ± 0.5 eV.[2-3] We assume that the appearance potential is equal to the ionization potential for $Al_2O_2(g) \rightarrow Al_2O_2(g) + e^-(g)$. Other reported appearance potentials include 10 ± 1[4-5] and 10 eV.[6]

$\Delta_f H°$(298.15 K) is obtained from $\Delta_f H°(Al_2O_2, 0\ K)$ by using IP(Al_2O_2) with JANAF[1] enthalpies $H°(0\ K)-H°(298.15\ K)$ for Al_2O_2(g), Al_2O_2 (g) and e (g). $\Delta_r H°(Al_2O_2 \rightarrow Al_2O_2^+ + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[7] $\Delta_f H°$(298.15 K) should be changed by −1.481 $kcal·mol^{-1}$ if it is to be used in the convention that excludes the enthalpy of the electron. MNDO calculations[8] predicted $\Delta_f H°(Al_2O_2^+, 298.15\ K)$ = 78.7 and $[\Delta_f H°(Al_2O_2^+, 298.15\ K) - \Delta_f H°(Al_2O_2, 298.15\ K)]$ = 186.7 $kcal·mol^{-1}$ for the linear Al–O–Al–O ion and neutral molecule; our adopted values are larger by 43 and 57 $kcal·mol^{-1}$, respectively.

Heat Capacity and Entropy

The structure of $Al_2O_2^+$ is probably even more uncertain than that of Al_2O_2.[1] MNDO calculations[8] predict an Al–O–Al–O ion that is essentially linear, but a similar prediction for the neutral molecule is contradicted by ab initio calculations.[1] Pending resolution of this discrepancy, we arbitrarily adopt a square-planar structure like that adopted for Al_2O_2.[1] We assume the same bond distance as in Al_2O_2 since the changes on ionization are predicted to be small.[8] Vibrational frequencies are estimated to be slightly lower than those of Al_2O_2.[1] We assume the ground electronic state to be doublet, due to the odd number of electrons, and neglect excited states. The principal moments of inertia are: I_A = 8.6079 × 10^{-39}, I_B = 14.5167 × 10^{-39} and I_C = 23.1246 × 10^{-39} $g·cm^2$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.975	564.004		
100	41.878	229.595	343.628	−11.403			
200	58.897	264.099	295.729	−6.326			
250	64.816	277.913	290.814	−3.225			
298.15	68.923	289.700	289.700	0.	567.414	552.810	−96.850
300	69.056	290.127	289.701	0.128	567.436	552.719	−96.237
350	72.091	301.013	290.554	3.660	568.061	550.218	−82.115
400	74.295	310.790	292.483	7.323	568.722	547.624	−71.512
450	75.927	319.640	295.017	11.080	569.395	544.946	−63.256
500	77.162	327.706	297.888	14.909	570.062	542.194	−56.643
600	78.860	341.937	304.076	22.717	571.318	536.500	−46.706
700	79.936	354.180	310.379	30.661	572.391	530.609	−39.594
800	80.657	364.904	316.539	38.692	573.203	524.581	−34.252
900	81.162	374.435	322.452	46.785	573.687	518.470	−30.091
1000	81.529	383.006	328.086	54.920	552.608	513.846	−26.841
1100	81.803	390.790	333.438	63.087	552.994	509.951	−24.216
1200	82.013	397.918	338.519	71.279	553.365	506.021	−22.027
1300	82.178	404.489	343.344	79.489	553.720	502.061	−20.173
1400	82.309	410.584	347.932	87.713	554.060	498.075	−18.583
1500	82.415	416.266	352.300	95.950	554.384	494.064	−17.205
1600	82.503	421.588	356.466	104.196	554.691	490.033	−15.998
1700	82.575	426.592	360.445	112.450	554.982	485.983	−14.932
1800	82.636	431.314	364.253	120.710	555.255	481.916	−13.985
1900	82.688	435.783	367.901	128.977	555.510	477.834	−13.137
2000	82.732	440.026	371.402	137.248	555.747	473.740	−12.373
2100	82.770	444.063	374.766	145.523	555.965	469.634	−11.682
2200	82.803	447.914	378.005	153.801	556.164	465.519	−11.053
2300	82.832	451.596	381.125	162.083	556.344	461.394	−10.479
2400	82.857	455.122	384.135	170.368	556.504	457.262	−9.952
2500	82.880	458.504	387.043	178.655	556.644	453.124	−9.468
2600	82.900	461.755	389.854	186.944	556.766	448.981	−9.020
2700	82.917	464.884	392.575	195.234	556.868	444.834	−8.606
2800	82.933	467.900	395.212	203.527	−30.851	442.619	−8.257
2900	82.947	470.811	397.769	211.821	−28.595	459.488	−8.276
3000	82.960	473.623	400.251	220.116	−26.358	476.280	−8.293
3100	82.972	476.343	402.662	228.413	−24.138	492.999	−8.307
3200	82.982	478.978	405.006	236.711	−21.936	509.645	−8.319
3300	82.992	481.531	407.286	245.010	−19.750	526.223	−8.329
3400	83.001	484.009	409.506	253.309	−17.582	542.735	−8.338
3500	83.009	486.415	411.670	261.610	−15.431	559.183	−8.345
3600	83.016	488.754	413.779	269.911	−13.295	575.571	−8.351
3700	83.023	491.028	415.836	278.213	−11.177	591.899	−8.356
3800	83.029	493.243	417.844	286.516	−9.075	608.171	−8.360
3900	83.035	495.399	419.805	294.819	−6.989	624.387	−8.363
4000	83.041	497.502	421.721	303.123	−4.921	640.549	−8.365
4100	83.046	499.552	423.595	311.427	−2.870	656.661	−8.366
4200	83.050	501.554	425.427	319.732	−0.837	672.722	−8.367
4300	83.054	503.508	427.220	328.037	1.177	688.736	−8.366
4400	83.059	505.417	428.976	336.343	3.170	704.702	−8.366
4500	83.062	507.284	430.695	344.649	5.148	720.623	−8.365
4600	83.066	509.110	432.380	352.955	7.100	736.500	−8.363
4700	83.069	510.896	434.032	361.262	9.028	752.336	−8.361
4800	83.072	512.645	435.651	369.569	10.931	768.131	−8.359
4900	83.075	514.358	437.240	377.876	12.808	783.887	−8.356
5000	83.078	516.036	438.799	386.184	14.654	799.605	−8.353
5100	83.080	517.681	440.330	394.492	16.469	815.286	−8.350
5200	83.083	519.295	441.833	402.800	18.250	830.931	−8.347
5300	83.085	520.877	443.310	411.108	19.994	846.543	−8.343
5400	83.087	522.430	444.761	419.417	21.699	862.122	−8.339
5500	83.089	523.955	446.187	427.726	23.362	877.670	−8.335
5600	83.091	525.452	447.589	436.035	24.980	893.189	−8.331
5700	83.093	526.923	448.968	444.344	26.549	908.678	−8.327
5800	83.095	528.368	450.324	452.653	28.072	924.141	−8.323
5900	83.096	529.788	451.659	460.963	29.536	939.576	−8.318
6000	83.098	531.185	452.973	469.273	30.986	954.985	−8.314

PREVIOUS: December 1979 (1 atm) CURRENT: December 1979 (1 bar)

$S°(298.15\ K) = 50.950 \pm 0.08\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 2327 \pm 6\ K$

$\Delta_f H°(0\ K) = -1663.6 \pm 1.2\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1675.7 \pm 1.2\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 111.1 \pm 4\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°$ is from calorimetric heats of combustion measured by Mah[1] and Holley and Huber.[2] Early measurements of the heat of combustion of Al were seriously biased,[3] but the sources of bias were minimized in later studies. After conversion to the present atomic weight of Al these studies yield $\Delta_f H°$ values of -400.5 ± 0.25,[1] -400.5 ± 0.3,[2] -399.2 ± 0.3,[3] and -402 ± 2 or -400.6 ± 1.4[4] $kcal\cdot mol^{-1}$.

$\Delta_f H°$ is the value adopted by CODATA.[5] This direct calorimetric result has been criticized by various authors who proposed less negative $\Delta_f H°$ values, for example -393[6] and -397.1[7] $kcal\cdot mol^{-1}$ based on emf and mineralogical data, respectively. Plausible explanations have been suggested[8,9] for these different values. Moreover, the adopted $\Delta_f H°$ is confirmed by several direct and indirect measurements.

New direct confirmation includes $\Delta_f H° = -400.2 \pm 0.4$ *and* $\Delta_f H° < -399.9\ kcal\cdot mol^{-1}$ *obtained, respectively, from emf measurements*[10] of $\Delta_f G°(1030–1250\ K)$ and from heat of combustion.[11] Indirect confirmation comes from data on reactions that link $\alpha-Al_2O_3$ to other aluminum compounds. K_p data[12,13] at high temperature yield $\Delta_f H° = -401.9 \pm 1.5\ kcal\cdot mol^{-1}$ from $AlCl_3(g)$ and -405.2 ± 1.5 from $AlF_3(cr)$, although the latter value may be biased if aluminum oxyfluorides[14] were formed. $\Delta_f H°$ is confirmed to within 1.0 $kcal\cdot mol^{-1}$ by equilibria and calorimetry for independent reaction cycles involving each of the minerals mullite,[11] kaolinite[9] and gibbsite.[15] Data on many related minerals have been carefully evaluated by Haas *et al.*,[16] they found no inconsistency large enough to require a change in $\Delta_f H°$ of Al_2O_3.

Heat Capacity and Entropy

$C_p°$ is from the equations of Ditmars *et al.*[17,19] for NBS Standard Reference Material 720 ($\alpha-Al_2O_3$). These equations are based on NBS data: $C_p°$ of Chang[18] (8.6 to 371 K) and enthalpy data of Ditmars and Douglas[19] (323 to 1173 K) and Ditmars *et al.*[17] (1173 to 2257 K). We increase $C_p°$ slightly (by <0.2%) above 1700 K to avoid a rapidly rising extrapolation above T_{fus}. $C_p°$ from the equation[17,19] has an upward inflection point near 2050 K that is not necessarily justified by the data.[17]

$S°(298.15\ K) = 12.177 \pm 0.02\ cal\cdot K^{-1}\cdot mol^{-1}$ is obtained from $C_p°$ based on $S°(9\ K) = 0.00053\ cal\cdot K^{-1}\cdot mol^{-1}$. CODATA[5] and Gurvich *et al.*[20] selected the slightly smaller values $S° = 12.17 \pm 0.02\ cal\cdot K^{-1}\cdot mol^{-1}$ and $H°(298.15\ K)–H°(0\ K) = 2.394 \pm 0.005\ kcal\cdot mol^{-1}$. We choose instead to be consistent with newly certified values for SRM 720.

Fusion Data and Sublimation Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.020	−1663.608	−1663.608	INFINITE
100	12.855	4.295	101.230	−9.693	−1668.606	−1641.642	857.506
200	51.120	24.880	57.381	−6.500	−1673.383	−1612.656	421.183
298.15	79.015	50.950	50.950	0.	−1675.692	−1582.275	277.208
300	79.416	51.440	50.951	0.147	−1675.717	−1581.696	275.398
400	96.086	76.779	54.293	8.995	−1676.342	−1550.226	202.439
500	106.131	99.388	61.098	19.145	−1676.045	−1518.718	158.659
600	112.545	119.345	69.177	30.101	−1675.300	−1487.319	129.483
700	116.926	137.041	77.632	41.586	−1674.391	−1456.059	108.652
800	120.135	152.873	86.065	53.447	−1673.498	−1424.931	93.038
900	122.662	167.174	94.296	65.591	−1672.744	−1393.908	80.900
1000	124.771	180.210	102.245	77.965	−1693.394	−1361.437	71.114
1100	126.608	192.189	109.884	90.535	−1692.437	−1328.286	63.075
1200	128.252	203.277	117.211	103.280	−1691.366	−1295.228	56.380
1300	129.737	213.602	124.233	116.180	−1690.190	−1262.264	50.718
1400	131.081	223.267	130.965	129.222	−1688.918	−1229.393	45.869
1500	132.290	232.353	137.425	142.392	−1687.561	−1196.617	41.670
1600	133.361	240.925	143.628	155.675	−1686.128	−1163.934	37.999
1700	134.306	249.039	149.592	169.060	−1684.632	−1131.342	34.762
1800	135.143	256.740	155.333	182.533	−1683.082	−1098.841	31.888
1900	135.896	264.067	160.864	196.085	−1681.489	−1066.426	29.318
2000	136.608	271.056	166.201	209.710	−1679.858	−1034.096	27.008
2100	137.319	277.738	171.354	223.407	−1678.190	−1001.849	24.920
2200	138.030	284.143	176.336	237.174	−1676.485	−969.681	23.023
2300	138.741	290.294	181.158	251.013	−1674.743	−937.593	21.293
2327.000	138.934	291.914	182.434	254.761	−−− ALPHA <−−> LIQUID −−−		
2400	139.453	296.214	185.829	264.922	−1672.963	−905.582	19.709
2500	140.206	301.922	190.360	278.905	−1671.142	−873.645	18.254
2600	140.959	307.435	194.757	292.963	−1669.279	−841.781	16.912
2700	141.754	312.770	199.030	307.098	−1667.369	−809.990	15.670
2800	142.591	317.940	203.185	321.315	−2253.212	−776.335	14.483
2900	143.511	322.960	207.229	335.620	−2249.002	−723.665	13.035
3000	144.474	327.841	211.168	350.019	−2244.729	−671.139	11.686

PREVIOUS: June 1975 CURRENT: December 1979

$S°(298.15\ K)$ = [50.6 ± 4] $J·K^{-1}·mol^{-1}$
T_{fus} = [2308] K

$\Delta_f H°(0\ K)$ = [−1653.9 ± 4] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = −1666.5 ± 4 $kJ·mol^{-1}$
$\Delta_{fus} H°$ = [93.3] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–Al_2O_3[1] using $\Delta_f H°(978\ K)$ = −2.7 ± 0.4 $kcal·mol^{-1}$ for the irreversible process $\delta \rightarrow \alpha$. This yields $\Delta_f H°(298.15\ K)$ = −2.2 $kcal·mol^{-1}$ based on our adopted functions. Yokokawa and Kleppa[2] determined $\Delta_f H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. DTA studies by Gani and McPherson[3] gave $\Delta_f H°$ = −2.8 ± 0.5 $kcal·mol^{-1}$. Assuming T = −1400 K, we derive $\Delta_f H°(298.15\ K)$ = −1.9 $kcal·mol^{-1}$. This confirms the calometric result. Both samples of δ–Al_2O_3 had been obtained by rapid quenching from high temperature, one[2] from combustion of Al_4C_3 and the other[3] by a plasma method.

Heat Capacity and Entropy

$C_p°$ is assumed to be 3% larger than that of α–Al_2O_3[1] by comparison with the observed values for κ–Al_2O_3[1] and the adopted values for γ–Al_2O_3.[1] $S°$ is selected such that $\Delta_r G°(\kappa \rightarrow \delta) < 0$ below T_{fus} and $\Delta_r G°(\delta \rightarrow \alpha) < 0$ at $T \leq 2400$ K.

Marchidan *et al.*[4] measured enthalpy data (573–1177 K) for a sample designated only as TA–600 alumina. They attributed a transition at ~993 K (720°C) to the irreversible process $\eta \rightarrow \delta$. This temperature corresponds roughly to processes designated as either (γ or η) $\rightarrow \theta$ or $\gamma \rightarrow \delta$ by Lippens and Steggerda.[5] DTA data of Alevra *et al.*[6] showed an endotherm near 750 °C subsequent to the dehydration of hydroxide samples; however, TGA data indicated that the resulting alumina still retained considerable water at this temperature. The enthalpy data,[4] (1003–1177 K) are 4.7 ± 0.3% larger than those of α–Al_2O_3[1] and presumably correspond to an alumina containing a significant amount of water. The δ–Al_2O_3 used in $\Delta_f H°$ studies was presumably essentially anhydrous. Thus, we omit the enthalpy data[4] on the presumption that they are larger than those of our standard state which is anhydrous δ–Al_2O_3.

Phase Data

The stable crystalline form is corundum (α–alumina). Δ–alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied[5] due to their importance in adsorbents and catalysts. Lippens and Steggerda[5] summarized the classifications of metastable forms, their crystal stuctures and conditions of formaiton by dehydration. Mixtures of the closely related δ– and θ–aluminas are also formed by rapid cooling of droplets of molten alumina following their passage through a flame.[7] There is some controversy[5] over the X–ray data and unit–cell dimensions of δ–Al_2O_3 formed by the two methods. Recent data[8] for θ–Al_2O_3[5] suggest a similar controversy. Δ–alumina belongs to the "nearly anhydrous", high–temperature classification[5] based on the temperature of 600° to 900°C at which it forms during dehydration. The irreversible transitions $\delta \rightarrow \theta(+\alpha) \rightarrow \alpha$ are thermally activated at tempertures of 800°–1050 °C for the first step[5,6] and −1200 °C for the final step.[5]

Fusion Data

The hypothetical melting point of metastable δ–phase is calculated as the temperature at which $\Delta_r G°(\delta \rightarrow l) = 0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

References

[1]JANAF Thermochemical Tables: Al_2O_3(cr, α), Al_2O_3(cr, κ), and Al_2O_3(cr, γ), 12–31–79.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	81.385	50.626	50.626	0.	−1666.487	−1572.974	275.579
300	81.799	51.131	50.628	0.151	−1666.507	−1572.394	273.778
400	98.968	77.231	54.070	9.264	−1666.867	−1540.932	201.225
500	109.315	100.518	61.079	19.719	−1666.266	−1509.504	157.697
600	115.922	121.073	69.400	31.004	−1665.192	−1478.248	128.693
700	120.434	139.300	78.109	42.834	−1663.938	−1447.188	107.991
800	123.739	155.608	86.795	55.050	−1662.689	−1416.311	92.476
900	126.342	170.338	95.273	67.558	−1661.571	−1385.582	80.417
1000	128.514	183.764	103.460	80.304	−1681.850	−1353.447	70.697
1100	130.406	196.103	111.329	93.251	−1680.516	−1320.670	62.713
1200	132.100	207.524	118.875	106.378	−1679.063	−1288.021	56.066
1300	133.630	218.159	126.108	119.666	−1677.500	−1255.496	50.446
1400	135.013	228.113	133.042	133.099	−1675.837	−1223.096	45.634
1500	136.258	237.471	139.696	146.664	−1674.084	−1190.819	41.468
1600	137.362	246.301	146.085	160.346	−1672.253	−1158.660	37.826
1700	138.336	254.658	152.228	174.132	−1670.355	−1126.618	34.617
1800	139.197	262.590	158.141	188.009	−1668.402	−1094.690	31.767
1900	139.973	270.137	163.838	201.968	−1666.402	−1062.872	29.220
2000	140.706	277.336	169.335	216.002	−1664.362	−1031.160	26.931
2100	141.438	284.218	174.643	230.109	−1662.283	−999.550	24.862
2200	142.171	290.815	179.774	244.289	−1660.165	−968.040	22.984
2300	142.904	297.151	184.741	258.543	−1658.008	−936.629	21.272
2400	143.636	303.248	189.552	272.870	−1655.810	−905.312	19.704
2500	144.412	309.128	194.219	287.272	−1653.570	−874.087	18.263
2600	145.188	314.806	198.748	301.752	−1651.285	−842.953	16.935
2700	146.007	320.301	203.149	316.311	−1648.952	−811.907	15.707
2800	146.868	325.626	207.428	330.954	−2234.367	−779.013	14.533
2900	147.817	330.797	211.594	345.688	−2229.729	−727.118	13.097
3000	148.808	335.824	215.651	360.519	−2225.023	−675.384	11.759

PREVIOUS: June 1975 CURRENT: December 1979

$S°(298.15\ K) = [52.3 \pm 8]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = [2289]\ K$

$\Delta_f H°(0\ K) = [-1644.3 \pm 6.3]\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1656.9 \pm 6.3\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = [78.49]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of $\alpha-Al_2O_3$[1] using $\Delta_f H°(978\ K) = -5.3\ kcal\cdot mol^{-1}$ for the irreversible process $\gamma \rightarrow \alpha$. Yokokawa and Kleppa[2] determined $\Delta_f H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. This yields $\Delta_f H°(298.15\ K) = -4.5\ kcal\cdot mol^{-1}$ based on our adopted functions. DTA studies by Gani and McPherson[3] gave $\Delta_f H°(\gamma \rightarrow \alpha) = -5.8 \pm 1.6\ kcal\cdot mol^{-1}$. Assuming $T = -1400$ K, we derive $\Delta_f H°(298.15\ K) = -4.4\ kcal\cdot mol^{-1}$ which confirms the calorimetric result.[2] Yamada *et al.*[4] used dynamic, adiabatic calorimetry to measure $\Delta_f H°(773\ K) = 12.6 \pm 1.1\ kcal\cdot mol^{-1}$ for $Al_2O_3H_2O$(cr, boehmite) $\rightarrow Al_2O_3(\gamma) + H_2O(g)$. Enthalpies from[4,1] convert this to $\Delta_f H°(298.15\ K) = 17.54 \pm 1.3\ kcal\cdot mol^{-1}$, yielding $\Delta_f H°(\gamma-Al_2O_3, 298.15\ K) = -398.1 \pm 1.5$ or $-396.7 \pm 2\ kcal\cdot mol^{-1}$ based on new or old values for $\Delta_f H°$(boehmite, 298.15 K)) $= -473.4 \pm 0.4$[5] or -472.0[6] $kcal\cdot mol^{-1}$.

We adopt $\Delta_f H°(\gamma, 298.15\ K) = -396.0 \pm 1.5\ kcal\cdot mol^{-1}$ and $\Delta_f H°(\gamma \rightarrow \alpha, 298.15\ K) = -4.5\ kcal\cdot mol^{-1}$. These values derive[2] from the highest ignition temperature prior to the appearance of a more stable phase ($\kappa-$ or $\alpha-Al_2O_3$) in the sample. This standard state should involve maximum attainable crystal development and minimum residual water. γ-alumina shows much variability depending on its thermal history. Lower ignition temperatures gave values of $\Delta_f H°(\gamma \rightarrow \alpha)$ more negative by as much as 2.5 $kcal\cdot mol^{-1}$.[1,2] Other reported values of $\Delta_f H°(\gamma \rightarrow \alpha)$, including -4.5 to -7.5,[3] -7.7,[7] -9.1,[8] -11.0[9] and -7.8[10] $kcal\cdot mol^{-1}$, tend to be skewed toward more negative values. These values correspond to less stable samples, presumably with more residual water and less well developed crystal structure. This is consistent with $\Delta_f H°(298.15\ K) = -388 \pm 2\ kcal\cdot mol^{-1}$ observed[4] for $\rho'-Al_2O_3$ which is nearly amorphous.

Heat Capacity and Entropy

$C_p°$ is assumed to be 4.7% larger than that of $\alpha-Al_2O_3$.[1] Structural and related characteristics[11] suggest that $C_p°(\gamma) > C_p°(\kappa)$ which in turn is ~2.2% larger[1,4] than $C_p°(\alpha)$. Our estimate is derived from Marchidan *et al.*[12] who measured enthalpies (1003–1177 K) which are $4.7 \pm 0.3\%$ larger than those of $\alpha-Al_2O_3$. $S°$ is estimated such that $\Delta_f G°(\gamma \rightarrow \alpha) < 0$ at $T \leq 2400$ K. This is consistent with observed stability relationships.[11,2]

Marchidan *et al.*[12] measured enthalpy data (573–1177 K) for a sample designated only as TA–600 alumina. They attributed a transition at -993 K to the irreversible process $\eta \rightarrow \delta$. Comtemporary studies[13] from the same institution lead us to presume that the TA–600 sample retained a significant amount of water even above the transition. The "low–temperature" forms γ and η are difficult to distinquish;[11] they retain more water[11,13] than the "high–temperature" forms. This may explain the unusual enthalpy data attributed[12] to $\eta-Al_2O_3$; these deviate from $\alpha-Al_2O_3$ by + 12.4% at 573 to 620 K and then decrease linearly to +3.8% at 991 K. These data do not seem suitable for standard–state $\gamma-Al_2O_3$ having minimum water content and maximum crystal development. We adopt instead the constant deviation of +4.7% found at higher temperature. Differential enthalpy analysis[8] gave an enthalpy 2% larger than $\alpha-Al_2O_3$ at 1290 K, but the error is large (±4% in enthalpy) and no information is given on the sample history. The observed $\Delta_f H(\gamma \rightarrow \alpha) = -9.1\ kcal\cdot mol^{-1}$ [8] suggests the sample differed from our desired standard state.

The adopted entropy may be compared with the value $\Delta S°(\alpha \rightarrow \gamma) = 1.56\ cal\cdot K^{-1}\cdot mol^{-1}$ estimated by Borer and Gunthard[14] for the "defect" spinel structure of $\gamma-Al_2O_3$. This yields $S°(\gamma, 298.15\ K)) = 13.7$ or 14.3 $cal\cdot K^{-1}\cdot mol^{-1}$ assuming $C_p°(\gamma)/C_p°(\alpha) = 1.00$ or 1.047, respectively. The authors' assumption[14] concerning the structure of $\gamma-Al_2O_3$[11] is overly simplified.

Phase Data

The stable crystalline form is corundum (α–alumina). γ–alumina is one of several structurally related, metastable forms. These occur in "*active alumina*" *and are much studied*[11] *due to their importance in adsorbents and catalysts. Lippens and Steggerda*[11] *summarized the* classifications of metastable forms, their crystal structures and conditions of formation by dehydration. "Low–temperature" forms γ and η have similar X–ray diffraction patterns. Their nomenclature is confused in the literature. The term $\gamma-Al_2O_3$ has been applied to either form and as a generic term for all low temperature forms. γ and η are often poorly crystallized and difficult to distinquish.[11] They retain various amounts of water[11,13] depending on their thermal history. The low–temperature forms are obtained by dehydrating temperatures not exceeding 600 °C and change irreversibly to "high–temperature" forms (δ, θ or κ) at 600° to 900 °C.[11,13,2]

Fusion Data

The hypothetical melting point of metastable γ–phase is calculated as the temperature at which $\Delta_f G°(\gamma \rightarrow l) = 0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

References

[1]JANAF Thermochemical Tables: Al_2O_3(cr, α), Al_2O_3(cr, δ) and Al_2O_3(cr, κ); 12–31–79; H_2O(g), 3–31–79.
[2]T. Yokokawa and O. J. Kleppa, J. Phys. Chem. **68**, 3246 (1964).
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Continued on page 173

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
0							
100							
200							
298.15	82.729	52.300	52.300	0.	−1656.864	−1563.850	273.980
300	83.149	52.813	52.302	0.153	−1656.882	−1563.273	272.190
400	100.602	79.343	55.800	9.417	−1657.091	−1532.001	200.059
500	111.120	103.015	62.925	20.045	−1656.317	−1500.804	156.788
600	117.835	123.909	71.384	31.515	−1655.057	−1469.815	127.959
700	122.422	142.438	80.236	43.541	−1653.608	−1439.054	107.384
800	125.782	159.014	89.066	55.959	−1652.158	−1408.504	91.966
900	128.427	173.987	97.683	68.674	−1650.833	−1378.128	79.985
1000	130.635	187.635	106.006	81.629	−1670.901	−1346.370	70.327
1100	132.558	200.178	114.005	94.790	−1669.354	−1313.990	62.396
1200	134.280	211.787	121.675	108.134	−1667.684	−1281.757	55.793
1300	135.835	222.597	129.028	121.641	−1665.902	−1249.668	50.212
1400	137.241	232.716	136.076	135.296	−1664.017	−1217.720	45.434
1500	138.507	242.229	142.839	149.084	−1662.040	−1185.911	41.297
1600	139.629	251.204	149.334	162.992	−1659.983	−1154.236	37.682
1700	140.619	259.700	155.579	177.006	−1657.858	−1122.691	34.496
1800	141.495	267.762	161.589	191.112	−1655.675	−1091.274	31.668
1900	142.283	275.434	167.381	205.301	−1653.445	−1059.979	29.141
2000	143.028	282.751	172.968	219.567	−1651.174	−1028.802	26.870
2100	143.773	289.747	178.363	233.907	−1648.862	−997.740	24.817
2200	144.518	296.453	183.580	248.321	−1646.510	−966.788	22.954
2300	145.262	302.893	188.628	262.810	−1644.117	−935.946	21.256
2400	146.007	309.091	193.519	277.374	−1641.683	−905.209	19.701
2500	146.796	315.068	198.262	292.014	−1639.206	−874.573	18.273
2600	147.584	320.840	202.866	306.732	−1636.681	−844.037	16.957
2700	148.416	326.426	207.340	321.532	−1634.108	−813.599	15.740
2800	149.292	331.839	211.690	336.417	−2219.282	−781.322	14.576
2900	150.256	337.094	215.924	351.394	−2214.400	−730.053	13.150
3000	151.264	342.205	220.049	366.469	−2209.450	−678.952	11.822

PREVIOUS: June 1975 CURRENT: December 1979

$S°(298.15\ K) = [53.6 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [2312]\ K$

$\Delta_f H°(0\ K) = [-1650.0 \pm 4]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1662.3 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [91.2]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–Al_2O_3[1] using $\Delta_f H°(978\ K) = -3.6\ kcal \cdot mol^{-1}$ for the irreversible process κ → α. This yields $\Delta_f H°(298.15\ K) = -3.2\ kcal \cdot mol^{-1}$ based on our adopted functions. Yokokawa and Kleppa[2] determined $\Delta_f H°$ for the two crystalline forms from the difference in their heats of solution in an oxide melt at 978 K. Yamada *et al.*[3] derived $\Delta_f H°(298.15\ K) = -397 \pm 1\ kcal \cdot mol^{-1}$ from the same data.

Heat Capacity and Entropy

$C_p°$ (380 to 1110 K) was measured by Takahashi *et al.*[4] using a dynamic, adiabatic calorimeter with an open–type container for the sample. Reproducibility of the data was reported to be within ±1.5% up to 1100 K. We represent the observed data by a $C_p°$ curve which is 2.2% larger than that of α–Al_2O_3.[1] Deviations from the adopted curve exceed 1.0% for only 3 of the 39 points:[4] i.e., −1.6% (400 K), +1.4% (993.8 K) and +1.3% (1070.8 K). Takahashi *et al.*[4] prepared their κ–Al_2O_3 by dehydration of tohdite ($Al_2O_3$1/5 H_2O) at 840 °C under a vacuum of 10^{-5} torr.

$S°$ is selected arbitrarily so that $\Delta_r G°(\kappa \rightarrow \alpha) = 0$ near 2400 K. This is consistent with the view that κ–phase is unstable with respect to α–phase at all temperatures below T_{fus}.

Phase Data

The stable crystalline form is corundum (α–alumina). Kappa–alumina is one of several structurally related, metastable forms. These occur in "active alumina" and are much studied[5] due to their importance in adsorbents and catalysts. Lippens and Steggerda[5] summarized the classifications of metastable forms, their crystal structures and conditions of formation by dehydration. Okumiya *et al.*[6] recently published an extensive study on the formation and structural relations of κ–Al_2O_3 and its precursors κ'–Al_2O_3 and tohdite. κ–alumina belongs to the "nearly anhydrous", high–temperature classification[5] based on its formation temperture of 900° to 1000 °C (somewhat lower in vacuo). The irreversible transition κ → α is thermally activated at −1200 °C.[2,5] Thermochemical studies cited in this table presume that the samples of κ–Al_2O_3 were essentially anhydrous.

Fusion Data

The hypothetical melting point of metastable κ–phase is calculated as the temperature at which $\Delta_r G°(\kappa \rightarrow l) = 0$. $\Delta_{fus} H°$ is the corresponding difference in $\Delta_f H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	80.753	53.555	53.555	0.	−1662.303	−1569.663	274.998
300	81.164	54.056	53.557	0.150	−1662.325	−1569.088	273.203
400	98.199	79.953	56.972	9.192	−1662.755	−1537.909	200.830
500	108.466	103.059	63.926	19.566	−1662.235	−1506.744	157.408
600	115.021	123.455	72.183	30.763	−1661.249	−1475.734	128.474
700	119.498	141.540	80.824	42.501	−1660.087	−1444.905	107.820
800	122.778	157.721	89.443	54.622	−1658.933	−1414.245	92.341
900	125.361	172.337	97.855	67.034	−1657.912	−1383.722	80.309
1000	127.516	185.659	105.979	79.680	−1678.290	−1351.782	70.610
1100	129.393	197.902	113.786	92.527	−1677.056	−1319.189	62.643
1200	131.074	209.234	121.274	105.552	−1675.705	−1286.715	56.009
1300	132.592	219.786	128.451	118.736	−1674.245	−1254.358	50.401
1400	133.964	229.663	135.331	132.065	−1672.687	−1222.116	45.598
1500	135.200	238.949	141.933	145.525	−1671.039	−1189.990	41.439
1600	136.295	247.710	148.272	159.100	−1669.314	−1157.976	37.804
1700	137.261	256.003	154.368	172.779	−1667.524	−1126.072	34.600
1800	138.116	263.873	160.235	186.549	−1665.678	−1094.275	31.755
1900	138.886	271.361	165.888	200.399	−1663.787	−1062.582	29.212
2000	139.613	278.504	171.342	214.324	−1661.856	−1030.989	26.927
2100	140.340	285.333	176.608	228.322	−1659.886	−999.494	24.861
2200	141.067	291.878	181.700	242.392	−1657.878	−968.093	22.985
2300	141.794	298.165	186.628	256.535	−1655.832	−936.785	21.275
2400	142.521	304.215	191.402	270.751	−1653.746	−905.567	19.709
2500	143.290	310.049	196.032	285.041	−1651.617	−874.437	18.270
2600	144.060	315.683	200.526	299.408	−1649.445	−843.392	16.944
2700	144.873	321.135	204.893	313.855	−1647.225	−812.432	15.717
2800	145.728	326.419	209.139	328.384	−2232.754	−779.619	14.544
2900	146.668	331.549	213.272	343.003	−2228.230	−727.802	13.109
3000	147.652	336.538	217.298	357.719	−2223.639	−676.141	11.773

PREVIOUS: June 1975 CURRENT: December 1979

$S°(298.15\ K) = [67.298]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2327 \pm 6\ K$

$\Delta_f H°(298.15\ K) = [-1620.567]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 111.1 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°(2327\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Enthalpy data for the liquid include those of Shpil'rain *et al.*,[1,2] (2326 to 3104 K), Sheindlin *et al.*,[3] (2350 to 2800 K), Kantor *et al.*[4,5] (2337 to 2480 K), and approximate values of West and Ishihara[6] (2345 to 2495 K). The latest study[1,2] is the most extensive. It satisfactorily resolves the discrepancy in $C_p°$ which was reported earlier to be 47.7[3] or 34.6[4] $cal·K^{-1}·mol^{-1}$. The new data[1,2] yield 46.0 $cal·K^{-1}·mol^{-1}$, assuming $C_p°$ is independent of temperature. Although Shpil'rain *et al.*[1,2] derived a $C_p°$ which decreases linearly with increasing temperature, this does not significantly improve the fit of the enthalpy data. The apparent value of the temperature coefficient of $C_p°$ is very data dependent; it changes sign on omission of the point at 2326 K (2323 K, IPTS-48).

We adopt $C_p° = 46.0\ cal·K^{-1}·mol^{-1}$. Compared to our adopted functions, the enthalpy data deviate by $< \pm 1.0\%$,[1,2] −0.9 to −0.1%.[3] (equation), +2.4 to +0.2%[4,5] and +2 to +5%.[6] We assume a glass transition at 1350 K, below which $C_p°$ is taken to be the same as for Al_2O_3(cr, α). The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

$T_{fus} = 2054 \pm 6°C$ was recommended by Schneider[7] as the result of a cooperative measurement of the melting point by nine groups in seven countries. We adopt this value. It is confirmed by several recent studies (e.g.8–10); however, Nelson *et al.*[11] suggested the possibility that T_{fus} may be somewhat different in an oxygen atmosphere than in inert gases or vacuum.

$\Delta_{fus} H°$ is the difference at T_{fus} between the adopted enthalpy fits of Al_2O_3(l) and Al_2O_3(α). Reported calorimetric values of $\Delta_{fus} H°$ include 25.7 ± 1.3,[1,2] 25.9,[3] and 28.3 ± 0.6[4,5] $kcal·mol^{-1}$.

Sublimation and Vaporization Data

Vaporization of Al_2O_3(α) and Al_2O_3(l) has been studied by several methods.[12-22] Additional references are cited by Farber *et al.*[14] and Burns.[16] Vaporization is sometimes considered to be congruent but the vapor composition is complex.[14,16] Atomic species predominate below T_{fus}, but molecular species (e.g., AlO and Al_2O) become increasingly important at higher temperatures. For the crystal the average vaporization coefficient is $\alpha < 0.3$.[12,14-16] The rate of evaporation increases discontinuously during melting by radiative heating; this has been attributed to a change in α[16] or to a change in absorbance and emittance.[19] Other work[11] suggests that the radiative properties change on melting. Container materials such as Mo or W cause changes in the partial pressures of O, Al and the molecular species observed in effusion studies;[14,16,21] these effects can be predicted with a model developed by Banon *et al.*[20] Partial pressures reported[14,22] for all observed vapor species yield an overall O/Al ratio of −1.1 instead of the value 1.5 required for congruent vaporization; however, these data do not yield a definite conclusion about congruency due to their relatively large uncertainties.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0						
100						
200						
298.15	79.015	67.298	0.	−1620.567	−1532.025	268.404
300	79.416	67.788	67.299	0.147	−1620.592	−1531.475	266.654
400	96.086	93.127	70.641	8.995	−1621.217	−1501.641	196.094
500	106.131	115.736	77.446	19.145	−1620.920	−1471.768	153.755
600	112.545	135.693	85.525	30.101	−1620.175	−1442.003	125.538
700	116.926	153.389	93.980	41.586	−1619.266	−1412.378	105.393
800	120.135	169.222	102.413	53.447	−1618.373	−1382.885	90.293
900	122.662	183.522	110.644	65.591	−1617.619	−1353.496	78.555
1000	124.771	196.558	118.593	77.965	−1638.269	−1322.660	69.089
1100	126.608	208.537	126.233	90.535	−1637.312	−1291.144	61.311
1200	128.252	219.625	133.559	103.280	−1636.241	−1259.721	54.834
1300	129.737	229.951	140.581	116.180	−1635.065	−1228.392	49.357
1350.000	130.424	234.860	143.983	122.684	GLASS <- -> LIQUID		
1350.000	192.464	234.860	143.983	122.684	TRANSITION		
1400	192.464	241.859	147.354	132.308	−1630.708	−1197.213	44.669
1500	192.464	255.138	154.102	151.554	−1623.274	−1166.509	40.621
1600	192.464	267.559	160.809	170.800	−1615.878	−1136.299	37.096
1700	192.464	279.227	167.435	190.047	−1608.520	−1106.551	34.000
1800	192.464	290.228	173.954	209.293	−1601.197	−1077.235	31.261
1900	192.464	300.634	180.350	228.540	−1593.910	−1048.325	28.820
2000	192.464	310.507	186.613	247.786	−1586.658	−1019.797	26.634
2100	192.464	319.897	192.739	267.032	−1579.440	−991.632	24.665
2200	192.464	328.850	198.724	286.279	−1572.256	−963.809	22.884
2300	192.464	337.406	204.569	305.525	−1565.106	−936.313	21.264
2327.000	192.464	339.652	206.123	310.722	- - - ALPHA <- - > LIQUID - - -		
2400	192.464	345.597	210.275	324.772	−1557.989	−909.127	19.787
2500	192.464	353.454	215.846	344.018	−1550.905	−882.237	18.433
2600	192.464	361.002	221.285	363.264	−1543.853	−855.629	17.190
2700	192.464	368.266	226.595	382.511	−1536.832	−829.292	16.044
2800	192.464	375.265	231.781	401.757	−2117.645	−801.279	14.948
2900	192.464	382.019	236.845	421.004	−2108.494	−754.429	13.589
3000	192.464	388.544	241.794	440.250	−2099.372	−707.892	12.325
3100	192.464	394.855	246.630	459.496	−2090.279	−661.658	11.149
3200	192.464	400.965	251.358	478.743	−2081.214	−615.720	10.051
3300	192.464	406.888	255.982	497.989	−2072.175	−570.063	9.023
3400	192.464	412.633	260.505	517.236	−2063.163	−524.679	8.061
3500	192.464	418.212	264.932	536.482	−2054.176	−479.561	7.157
3600	192.464	423.634	269.265	555.728	−2045.214	−434.699	6.307
3700	192.464	428.908	273.509	574.975	−2036.276	−390.086	5.507
3800	192.464	434.040	277.666	594.221	−2027.363	−345.712	4.752
3900	192.464	439.040	281.740	613.468	−2018.474	−301.574	4.039
4000	192.464	443.912	285.734	632.714	−2009.610	−257.664	3.365

PREVIOUS: June 1975 CURRENT: December 1979

0	to 2327 K	crystal, alpha (corundum)
above	2327 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.020	−1663.608	−1663.608	INFINITE
100	12.855	4.295	101.230	−9.693	−1668.606	−1641.642	857.506
200	51.120	24.880	57.381	−6.500	−1673.383	−1612.656	421.183
298.15	79.015	50.950	50.950	0.	−1675.692	−1582.275	277.208
300	79.416	51.440	50.951	0.147	−1675.717	−1581.696	275.398
400	96.086	76.779	54.293	8.995	−1676.342	−1550.226	202.439
500	106.131	99.388	61.098	19.145	−1676.045	−1518.718	158.659
600	112.545	119.345	69.177	30.101	−1675.300	−1487.319	129.483
700	116.926	137.041	77.632	41.586	−1674.391	−1456.059	108.652
800	120.135	152.873	86.065	53.447	−1673.498	−1424.931	93.038
900	122.662	167.174	94.296	65.591	−1672.744	−1393.908	80.900
1000	124.771	180.210	102.245	77.965	−1693.394	−1361.437	71.114
1100	126.608	192.189	109.884	90.535	−1692.437	−1328.286	63.075
1200	128.252	203.277	117.211	103.280	−1691.366	−1295.228	56.380
1300	129.737	213.602	124.233	116.180	−1690.190	−1262.264	50.718
1400	131.081	223.267	130.965	129.222	−1688.918	−1229.393	45.869
1500	132.290	232.353	137.425	142.392	−1687.561	−1196.617	41.670
1600	133.361	240.925	143.628	155.675	−1686.128	−1163.934	37.999
1700	134.306	249.039	149.592	169.060	−1684.632	−1131.342	34.762
1800	135.143	256.740	155.333	182.533	−1683.082	−1098.841	31.888
1900	135.896	264.067	160.864	196.085	−1681.489	−1066.426	29.318
2000	136.608	271.056	166.201	209.710	−1679.858	−1034.096	27.008
2100	137.319	277.738	171.354	223.407	−1678.190	−1001.849	24.920
2200	138.030	284.143	176.336	237.174	−1676.485	−969.681	23.023
2300	138.741	290.294	181.158	251.013	−1674.743	−937.593	21.293
2327.000	138.934	291.914	182.434	254.761	ALPHA <--> LIQUID		
2327.000	192.464	339.652	182.434	365.847	TRANSITION		
2400	192.464	345.597	187.307	379.896	−1557.989	−909.127	19.787
2500	192.464	353.454	193.796	399.143	−1550.905	−882.237	18.433
2600	192.464	361.002	200.083	418.389	−1543.853	−855.629	17.190
2700	192.464	368.266	206.179	437.636	−1536.832	−829.292	16.044
2800	192.464	375.265	212.093	456.882	−2117.645	−801.279	14.948
2900	192.464	382.019	217.837	476.128	−2108.494	−754.429	13.589
3000	192.464	388.544	223.419	495.375	−2099.372	−707.892	12.325
3100	192.464	394.855	228.848	514.621	−2090.279	−661.658	11.149
3200	192.464	400.965	234.132	533.868	−2081.214	−615.719	10.051
3300	192.464	406.888	239.277	553.114	−2072.175	−570.063	9.023
3400	192.464	412.633	244.292	572.360	−2063.162	−524.679	8.061
3500	192.464	418.212	249.182	591.607	−2054.176	−479.561	7.157
3600	192.464	423.634	253.953	610.853	−2045.213	−434.699	6.307
3700	192.464	428.908	258.610	630.100	−2036.276	−390.086	5.507
3800	192.464	434.040	263.160	649.346	−2027.363	−345.712	4.752
3900	192.464	439.040	267.606	668.592	−2018.474	−301.574	4.039
4000	192.464	443.912	271.953	687.839	−2009.609	−257.664	3.365

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = 93.22 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2575.16 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -2592.07 \pm kJ \cdot mol^{-1}$

Enthalpy of Formation

The heat of the reaction Al_2O_3(cr, α) + SiO_2(quartz) → Al_2SiO_5 (andalusite) has been determined at 968 K by Holm and Kleppa[1,2] to be -1.99 ± 0.17 kcal·mol^{-1}. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_f H°(298.15\ K) = -1.42$ kcal·mol^{-1} which is used to calculate the adopted value for the enthalpy of formation.

The above value is in serious disagreement with the solution data of Neumann;[3] this work, however, has recently been questioned by several workers. Flood *et al.*[4] suggested that $\Delta_f H°$ was between 0 and -10 kcal·mol^{-1}. Pankratz *et al.*[5] conclude that $\Delta_f H°$ should lie between 0 and -6 kcal·mol^{-1}. Waldbaum[6] calculated $\Delta_f H° = -1.108$ kcal·mol^{-1} from high temperature–high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.9 to 296.2 K by Todd.[7] The entropy is based on $S°(51\ K) = 0.62$ cal·K^{-1}·mol^{-1}. The high temperature enthalpy has been measured to 1600 K by Pankratz *et al.*[5] The low and high temperature data were joined smoothly together by means of a Shomate function plot.[8] Since all the aluminum and silicon atoms occupy differently coordinated sites, there is no possibility of any residual entropy of mixing in this polymorph.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.093	−2575.159	−2575.159	INFINITE
100	30.323	13.563	174.899	−16.134	−2582.696	−2538.944	1326.209
200	84.605	51.844	103.323	−10.296	−2588.917	−2492.553	650.988
298.15	122.755	93.221	93.221	0.	−2592.072	−2444.482	428.263
300	123.320	93.982	93.223	0.228	−2592.107	−2443.567	425.463
400	149.565	133.277	98.402	13.950	−2592.950	−2393.872	312.608
500	165.368	168.473	108.968	29.752	−2592.338	−2344.152	244.892
600	174.515	199.471	121.524	46.768	−2591.068	−2294.628	199.765
700	181.067	226.884	134.656	64.560	−2589.556	−2245.340	167.549
800	186.121	251.401	147.744	82.926	−2588.003	−2196.273	143.402
900	190.351	273.572	160.512	101.754	−2586.532	−2147.396	124.632
1000	194.041	293.822	172.845	120.977	−2606.407	−2097.155	109.544
1100	197.380	312.475	184.702	140.550	−2604.612	−2046.314	97.171
1200	200.481	329.783	196.080	160.444	−2602.639	−1995.646	86.868
1300	203.414	345.947	206.993	180.640	−2600.491	−1945.149	78.157
1400	206.225	361.125	217.466	201.122	−2598.175	−1894.824	70.697
1500	208.949	375.446	227.525	221.882	−2595.693	−1844.671	64.237
1600	211.602	389.016	237.198	242.910	−2593.049	−1794.688	58.591
1700	214.200	401.923	246.511	264.200	−2640.423	−1744.428	53.600
1800	216.756	414.238	255.489	285.748	−2637.235	−1691.815	49.095
1900	219.283	426.026	264.157	307.550	−2633.851	−1639.382	45.070
2000	221.781	437.337	272.535	329.604	−2630.273	−1587.133	41.452
2100	224.258	448.218	280.644	351.906	−2626.505	−1535.068	38.183
2200	226.714	458.707	288.500	374.455	−2622.546	−1483.186	35.215
2300	229.149	468.839	296.122	397.248	−2618.399	−1431.490	32.510
2400	231.563	478.642	303.524	420.284	−2614.066	−1379.978	30.034
2500	233.957	488.144	310.720	443.560	−2609.546	−1328.650	27.761
2600	236.329	497.366	317.722	467.075	−2604.842	−1277.506	25.665
2700	238.680	506.329	324.542	490.825	−2599.954	−1226.546	23.729
2800	241.011	515.052	331.191	514.810	−3182.686	−1173.836	21.898
2900	243.321	523.550	337.678	539.027	−3175.242	−1102.224	19.853
3000	245.609	531.837	344.013	563.473	−3167.617	−1030.869	17.949

PREVIOUS: September 1966 CURRENT: September 1967

$S°(298.15\ K) = 83.815 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2576.37 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -2594.33 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heat of the reaction Al_2O_3(cr, α) + SiO_2(quartz) → Al_2SiO_5(cr, kyanite) has been determined at 968 K by Holm and Kleppa[1, 2] to be -2.37 ± 0.15 kcal·mol^{-1}. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_f H°(298.15\ K) = -1.96$ kcal·mol^{-1}, which is used to calculate the adopted value for the heat of formation of kyanite.

The above value is in serious disagreement with the solution data of Neumann.[3] This work, however, has recently been questioned by several workers. Flood and Knapp[4] suggested that $\Delta_f H°$ was between 0 and -10 kcal·mol^{-1}. Pankratz Kelley[5] conclude that $\Delta_f H°$ should lie between 0 and -6 kcal·mol^{-1}. From phase equilibria, Haskell and DeVries[6] obtained $\Delta_f H° = -2 \pm 7$ kcal·mol^{-1}. Waldbaum[7] calculated $\Delta_f H° = -0.622$ kcal·mol^{-1} from high temperature–high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.8 to 296.3 K by Todd.[8] The entropy is based on $S°(51\ K) = 0.33$ cal·K^{-1}·mol^{-1}. The high temperature enthalpy has been measured to 1500K by Pankratz and Kelley.[5] The low and high temperature data were joined smoothly together by means of a Shomate function plot.[9] The high temperature heat capacity has been measured between 100° and 1200°C by Leonidov, Barskii and Khitarov.[10] The values reported are in excellent agreement with the adopted functions. Since the aluminum atoms and the silicon atoms occupy different types of sites there is no possibility of any residual entropy of mixing in this polymorph.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.045	−2576.370	−2576.370	INFINITE
100	23.695	8.935	162.808	−15.387	−2584.209	−2539.995	1326.757
200	80.977	43.273	93.769	−10.099	−2590.980	−2492.902	651.079
298.15	121.751	83.815	83.815	0.	−2594.331	−2443.937	428.168
300	122.306	84.570	83.817	0.226	−2594.368	−2443.004	425.365
400	148.277	123.509	88.949	13.824	−2595.336	−2392.351	312.409
500	165.498	158.566	99.433	29.567	−2594.783	−2341.644	244.630
600	176.230	189.745	111.939	46.684	−2593.412	−2291.137	199.461
700	183.238	217.463	125.072	64.674	−2591.701	−2240.890	167.217
800	188.280	242.271	138.199	83.258	−2589.930	−2190.896	143.051
900	192.359	264.685	151.027	102.292	−2588.254	−2141.119	124.267
1000	196.213	285.154	163.431	121.723	−2607.920	−2090.000	109.170
1100	199.761	304.023	175.366	141.523	−2605.899	−2038.304	96.791
1200	203.167	321.554	186.826	161.673	−2603.669	−1986.801	86.483
1300	206.100	337.933	197.827	182.138	−2601.253	−1935.492	77.769
1400	208.861	353.308	208.389	202.887	−2598.670	−1884.376	70.307
1500	211.451	367.806	218.538	223.902	−2595.932	−1833.450	63.846
1600	214.129	381.538	228.300	245.181	−2593.037	−1782.711	58.200
1700	216.727	394.598	237.701	266.724	−2640.158	−1731.712	53.209
1800	219.302	407.059	246.766	288.526	−2636.716	−1678.373	48.705
1900	221.853	418.984	255.519	310.584	−2633.077	−1625.229	44.681
2000	224.380	430.428	263.980	332.896	−2629.241	−1572.283	41.064
2100	226.855	441.436	272.170	355.458	−2625.212	−1519.533	37.796
2200	229.321	452.046	280.107	378.267	−2620.994	−1466.979	34.831
2300	231.776	462.294	287.806	401.322	−2616.585	−1414.623	32.127
2400	234.221	472.210	295.284	424.622	−2611.987	−1362.462	29.653
2500	236.655	481.821	302.554	448.165	−2607.200	−1310.496	27.381
2600	239.079	491.150	309.630	471.952	−2602.224	−1258.725	25.288
2700	241.493	500.218	316.521	495.981	−2597.058	−1207.149	23.354
2800	243.896	509.044	323.240	520.251	−3179.505	−1153.832	21.525
2900	246.289	517.644	329.796	544.760	−3171.768	−1081.625	19.482
3000	248.672	526.034	336.198	569.508	−3163.841	−1009.684	17.580

PREVIOUS: September 1966 CURRENT: September 1967

$S°(298.15\ K) = 96.179 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2572.52 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -2589.10 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heat of the reaction Al_2O_3(cr, α) + SiO_2(quartz) → Al_2SiO_5(sillimanite) has been determined at 968 K by Holm and Kleppa[1,2] to be -1.51 ± 0.15 kcal·mol^{-1}. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_f H°(298.15\ K) = -0.71$ kcal·mol^{-1} which is used to calculate the adopted value for the enthalpy of formation.

The above value is in serious disagreement with the solution data of Neumann;[3] this work, however, has recently been questioned by several workers. Flood and Knapp[4] suggested that $\Delta_f H°$ was between 0 and -10 kcal·mol^{-1}. Pankratz and Kelley[5] conclude that $\Delta_f H°$ should lie between 0 and -6 kcal·mol^{-1}. Waldbaum[6] calculated $\Delta_f H° = -0.356$ kcal·mol^{-1} from high temperature–high pressure equilibria. These latter values are all in good agreement with the adopted calorimetric value.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 54.4 to 296.5 K by Todd.[7] The entropy is based on $S°(51\ K) = 0.73$ cal·K^{-1}·mol^{-1}. The high temperature enthalpy has been measured to 1500 K by Pankratz and Kelley.[5] The low and high temperature data were joined smoothly together by means of a Shomate function plot.[8] The crystal structure of sillimanite indicates that there is no mixing of the tetra-coordinated aluminum and silicon atoms.[9] Thus there should be no residual entropy at 0 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.424	−2572.519	−2572.519	INFINITE
100	32.277	15.099	178.603	−16.350	−2579.942	−2536.344	1324.850
200	85.773	54.593	106.303	−10.342	−2585.993	−2490.179	650.368
298.15	122.215	96.179	96.179	0.	−2589.101	−2442.394	427.897
300	122.769	96.937	96.182	0.227	−2589.137	−2441.483	425.100
400	147.478	135.871	101.322	13.820	−2590.110	−2392.070	312.372
500	163.197	170.578	111.773	29.402	−2589.718	−2342.584	244.728
600	173.025	201.248	124.183	46.239	−2588.627	−2293.253	199.645
700	179.757	228.445	137.172	63.891	−2587.254	−2244.131	167.459
800	184.996	252.798	150.130	82.135	−2585.824	−2195.211	143.333
900	189.510	274.853	162.782	100.864	−2584.452	−2146.468	124.578
1000	193.535	295.031	175.012	120.019	−2604.393	−2096.351	109.502
1100	197.158	313.647	186.780	139.554	−2602.637	−2045.629	97.139
1200	200.765	330.958	198.082	159.451	−2600.661	−1995.078	86.843
1300	204.292	347.168	208.933	179.706	−2598.455	−1944.701	78.139
1400	207.577	362.429	219.357	200.300	−2596.027	−1894.501	70.685
1500	210.777	376.860	229.381	221.218	−2593.386	−1844.484	64.231
1600	213.911	390.563	239.030	242.453	−2590.535	−1794.649	58.589
1700	216.999	403.624	248.331	263.999	−2637.654	−1744.552	53.604
1800	220.045	416.114	257.308	285.852	−2634.161	−1692.117	49.104
1900	223.062	428.092	265.983	308.007	−2630.424	−1639.881	45.083
2000	226.053	439.610	274.378	330.463	−2626.444	−1587.849	41.470
2100	229.013	450.711	282.512	353.216	−2622.224	−1536.022	38.206
2200	231.964	461.432	290.403	376.265	−2617.765	−1484.400	35.244
2300	234.906	471.809	298.066	399.609	−2613.068	−1432.989	32.544
2400	237.840	481.868	305.516	423.246	−2608.133	−1381.787	30.074
2500	240.764	491.637	312.766	447.176	−2602.959	−1330.795	27.805
2600	243.680	501.136	319.829	471.399	−2597.547	−1280.014	25.716
2700	246.586	510.387	326.716	495.912	−2591.897	−1229.446	23.785
2800	249.484	519.408	333.438	520.716	−3173.809	−1177.155	21.960
2900	252.373	528.213	340.003	545.809	−3165.489	−1105.994	19.921
3000	255.253	536.817	346.420	571.190	−3156.929	−1035.121	18.023

PREVIOUS: September 1966 CURRENT: September 1967

$S°(298.15\ K) = 116.85 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -647.35 \pm 3.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -651.03 \pm 3.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted value for $\Delta_f H°(298.15\ K)$ is taken from the recent solution calorimetric studies of Ko *et al.*[1] The discrepancy between this value and other measured values is quite large. Korshunov[2] and Kapustinskii and Golutvin[3] determined values of $\Delta_f H°(298.15\ K) = -121.5 \pm 0.4\ kcal \cdot mol^{-1}$ and $-172.9 \pm 4.3\ kcal \cdot mol^{-1}$, respectively, by direct combination of the elements. Sabatier[4] measured a value of $-75.0\ kcal \cdot mol^{-1}$ for the reaction $Al_2S_3(cr) + 3H_2O(l) \rightarrow Al_2O_3 3H_2O(cr) + H_2S(g)$. The heat of formation of Al_2S_3 based on this heat has been widely quoted[1, 5] as $-140.5\ kcal \cdot mol^{-1}$ which is an apparent misinterpretation. Sabatier gives a value of $\Delta_f H°(298.15\ K) = -124.4\ kcal \cdot mol^{-1}$ based on heats of formation for the other materials as accepted at that time. Our reanalysis of Sabatier's data using currently accepted heats of formation[6, 7] yields $\Delta_f H°(298.15\ K) = -148.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The adopted $C_p°$ data are based on the low temperature $C_p°$ measurements (12–312 K) of Ho *et al.*[1] and the high temperature enthalpy measurements (403–852 K) of Ferrante and McCune.[8] We have not reanalyzed these results except to extrapolate them to higher temperature. The entropy is based on $S°(15\ K) = 0.046\ cal \cdot K^{-1} \cdot mol^{-1}$.

Phase Data

This table is for the hexagonal phase of Al_2S_3 usually designated as the α phase.[8] Other phases known to exist at higher temperatures are the rhombohedral (γ) and face centered cubic phases. Ferrante and McCune[8] observed an extra enthalpy effect at 878.5 K which they confirmed to be partial conversion to the metastable γ phase via X-ray diffraction. They further showed via X-ray techniques that conversion to the γ phase is essentially complete after heating in the 1320–1500 K range. They were unable to measure the enthalpy of the γ phase since conversion to the γ phase appears to be slow and rapid quenching in the drop calorimeter leads to mixed phases. The α–γ transition temperature was reported as 1273 K[9] and melting points of 1403 K[10] and 1373 K[9] were reported.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−18.634	−647.350	−647.350	INFINITE
100	48.677	30.970	197.042	−16.607	−648.360	−646.303	337.594
200	87.571	78.115	126.026	−9.582	−649.864	−643.647	168.103
298.15	105.064	116.847	116.847	0.	−651.030	−640.335	112.184
300	105.282	117.497	116.849	0.195	−651.052	−640.269	111.481
400	114.947	149.264	121.114	11.260	−658.794	−636.244	83.085
500	120.365	175.538	129.449	23.045	−664.059	−630.029	65.819
600	124.135	197.832	139.035	35.278	−668.050	−622.827	54.222
700	127.127	217.199	148.848	47.846	−671.218	−615.032	45.894
800	129.700	234.346	158.484	60.690	−673.970	−606.814	39.621
900	132.039	249.760	167.784	73.778	−835.933	−595.021	34.534
1000	134.051	263.777	176.693	87.084	−856.026	−566.794	29.606
1100	135.825	276.639	185.202	100.580	−854.495	−537.943	25.545
1200	137.327	288.523	193.323	114.240	−852.846	−509.238	22.167
1300	138.566	299.566	201.076	128.037	−851.107	−480.674	19.314
1400	139.536	309.872	208.483	141.944	−849.304	−452.247	16.874
1500	140.235	319.524	215.568	155.935	−847.463	−423.949	14.763

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = 483.54 \pm 0.8\ J·K^{-1}·mol^{-1}$
$T_{tus} = 1010 \pm 2\ K$

$\Delta_f H°(0\ K) = -7554.7 \pm 16\ kJ·mol^{-1}$
$\Delta_f H°(298.15) = -7581.4 \pm 16\ kJ·mol^{-1}$
$\Delta_{fus} H° = 228.9 \pm 8\ kJ·mol^{-1}$

Enthalpy of Formation

Our adopted value of the heat of formation, $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K) = -1812.0 \pm 4\ kcal·mol^{-1}$ is based on the emf work of Dewing.[1] Dewing used solid–electrolyte emf cells of the type Al/Na_3AlF_6, $Na_5Al_3F_{14}/Na$ /$Na_5Al_3F_{14}$, AlF_3/Al to determine the free energies for the reaction 5 NaF(cr) + 3 AlF_3(cr) = $Na_5Al_3F_{14}$(cr) over the range 844–996 K. Based on Dewing's[1] reported $\Delta_r G°$ values (20 points), we evaluate $\Delta_r H°(298.15\ K) = -36.58 \pm 0.36\ kcal·mol^{-1}$ and $-39.97 \pm 0.42\ kcal·mol^{-1}$ by the 2nd and 3rd law methods, respectively. From the 3rd law value, we calculate $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K) = -1811.95 \pm 2.1\ kcal·mol^{-1}$. There has been some confusion over the exact reaction to which Dewing's $\Delta_r G°$ values apply. Both Dewing[1] and Stuve and Ferrante[2] applied the reported $\Delta_r G°$ values to the erroneous reaction 3 Na_3AlF_6(cr) = $Na_5Al_3F_{14}$(cr) + 4 NaF(cr). Our adopted heat of formation is 58 $kcal·mol^{-1}$ less stable than their reported values.[1,2]

Holm[3] estimated $\Delta_r H°(910\ K) = -2.7 \pm 1.2\ kcal·mol^{-1}$ for the reaction 5/8 NaF(cr) + 3/8 AlF_3(cr) = 1/8 $Na_5Al_3F_{14}$(cr). Converting to a molar basis, we obtain $\Delta_f H°(910\ K) = -21.6 \pm 10\ kcal·mol^{-1}$ for the reaction 5 NaF(cr) + 3 AlF_3(cr) = $Na_5Al_3F_{14}$(cr). Using JANAF enthalpies[4] and auxiliary data from,[4,5] we obtain $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K) = -1791.7 \pm 12\ kcal·mol^{-1}$.

Grjotheim *et al.*[6] studied the vapor pressures over the solid systems $Na_5Al_3F_{14}/AlF_3$ and $Na_5Al_3F_{14}/Na_3AlF_6$ by the weight–loss effusion method. Their results are in good agreement with the mass–spectrometric observations of Sidorov *et al.*[7] on similar systems. Results have been sumamrized by Grjotheim *et al.*[6] who obtained $\Delta_r H°(910\ K) = 60.65 \pm 1.5\ kcal·mol^{-1}$ for the reaction 1/5 $Na_5Al_3F_{14}$(cr) + 2/5 AlF_3(cr) = $NaAlF_4$(g). Using JANAF enthalpies[4] and $\Delta_f H°(298.15\ K)$ values from,[4,5] we obtain $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K) = -1831.0 \pm 20\ kcal·mol^{-1}$. Similarly, Grjotheim *et al.*[6] obtained $\Delta_r H°(910\ K) = 59.74 \pm 2.0\ kcal·mol^{-1}$ and recalculated $\Delta_r H°(910\ K) = 60.4 \pm 2\ kcal·mol^{-1}$ from the data of Sidorov *et al.*[7] for the reaction 1/2 $Na_5Al_3F_{14}$(cr) = 1/2 Na_3AlF_6(cr) + $NaAlF_4$(g). Using the same auxiliary data as above, we obtain $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K) = -1808.3 \pm 10\ kcal·mol^{-1}$ from[6] and $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K) = -1809.6 \pm 10\ kcal·mol^{-1}$ from.[7] These results are in very good agreement with the recalculated value from Dewing.[1]

Heat Capacity and Entropy

Low–temperature heat capacities of chiolite were determined by Stuve and Ferrante[2] by adiabatic calorimetry over the range 5.83–315.75 K. A slight bump was noted in the heat capacity curve between 140 and 175 K. $S°(298.15\ K) = 115.57 \pm 0.2\ cal·K^{-1}·mol^{-1}$ is based on $S°(5\ K) = 0.022\ cal·K^{-1}·mol^{-1}$ obtained by extrapolating the function C_p/T versus T^{2}.[2] $H°(298.15\ K)–H°(0\ K) = 19.338\ kcal·mol^{-1}$.

High temperature enthalpies were measured by Stuve and Ferrante[2] (402.8–991.5 K) and by Holm[3] (677.0–931.7 K). The data of Holm are consistently higher (2.3 ± 0.3 kcal, corresponding to 3–4%) than the data of Stuve and Ferrante and show more scatter. This positive bias ascribed to the calorimeter of Holm was also evident in a study on cryolite (see the Na_3AlF_6, cr, β table). We adopt heat capacities for chiolite based on the drop calorimetry work of Stuve and ferante.[2]

Fusion Data

Chiolite is the mineral name for $Na_5Al_3F_{14}$ (corresponds to 5 NaF + 3 AlF_3). The crystals are tetragonal, space group P_4/mnc.[8] Chiolite melts incongruently at 1010 K[1,3,6] to a combination of cryolite and AlF_3. The value of $\Delta_{fus} H°$ for this process is calculated as the difference between the enthalpies of the crystal and liquid at 1010 K.

References

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[4]JANAF Thermochemical tables: NaF(cr), 12–31–68; AlF_3(cr), 9–30–79.
[5]U.S. Nat. Bur. Stand. IR 75–968, (1976).
[6]K. Grjotheim, K. Motzfeldt, and D. B. Rao, paper No. A71–22 presented at the Metallurgical Society of AIME conference, TMS Session, New York, (1971).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−80.910	−7554.692	−7554.692	INFINITE
100	214.723	142.800	861.276	−71.848	−7574.128	−7455.146	3894.169
200	370.912	317.691	522.895	−41.041	−7581.508	−7325.950	1913.342
298.15	454.006	483.545	483.545	0.	−7581.408	−7200.348	1261.471
300	455.094	486.357	483.554	0.841	−7581.368	−7197.984	1253.280
400	499.570	623.823	501.993	48.732	−7591.644	−7069.564	923.190
500	525.092	738.188	538.126	100.031	−7587.309	−6939.508	724.965
600	542.665	835.534	579.783	153.451	−7581.492	−6810.474	592.904
700	556.472	920.245	622.500	208.421	−7574.685	−6682.498	498.654
800	568.606	995.357	664.500	264.686	−7567.175	−6555.548	428.033
900	579.484	1062.962	705.080	322.094	−7559.205	−6429.570	373.163
1000	589.944	1124.591	743.994	380.597	−7582.715	−6302.216	329.194
1010.000	590.781	1130.465	747.792	386.500	--- CRYSTAL <--> LIQUID ---		
1100	600.319	1181.296	781.205	440.100	−7573.318	−6174.615	293.208
1200	610.864	1233.983	816.767	500.660	−8047.057	−6035.700	262.727
1300	621.324	1283.291	850.776	562.269	−8031.751	−5868.701	235.807
1400	631.784	1329.719	883.344	624.925	−8015.548	−5702.916	212.778
1500	642.244	1373.664	914.580	688.626	−7998.439	−5538.319	192.861

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = [532.124]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1010 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-7497.408]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 228.9 \pm 8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_5Al_3F_{14}, l, 298.15\ K)$ is calculated from $\Delta_f H°(Na_5Al_3F_{14}, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(1010\ K) - H°(298.15\ K)$, between the crystal and liquid.

Hong and Kleppa[2] measured the enthalpies of mixing for the reaction 5/8 NaF(l) + 3/8 AlF (cr) = 1/8 $Na_5Al_3F_{14}$(l) as $\Delta_r H°(298.15\ K) = -0.591\ kcal·mol^{-1}$. Converting to a molar basis, we obtain $\Delta_r H°(1298\ K) = -4.725\ kcal·mol^{-1}$ for the reaction 5 NaF(l) + 3 AlF_3(cr) = $Na_5Al_3F_{14}$(l), using JANAF data[1] for the enthalpies of formation from JANAF[1] and NBS,[3] we obtain $\Delta_f H°(Na_5Al_3F_{14}, l, 298.15\ K) = -1793.5 \pm 10\ kcal·mol^{-1}$.

Hong and Kleppa[4] also measured the enthalpy of mixing for the reaction 5/9 Na_3AlF_6(l) + 4/9 AlF_3(cr) = 1/3 $Na_5Al_3F_{14}$(l) as $\Delta_r H°(1298\ K) = 4.49\ kcal·mol^{-1}$. Converting to a molar basis, we obtain $\Delta_r H°(1298\ K) = 40.40\ kcal·mol^{-1}$ for the reaction 5 Na_3AlF_6(l) + 4 AlF_3(cr) = 3 $Na_5Al_3F_{14}$(l). Using enthalpies from JANAF[1] and enthalpies of formation from JANAF[1] and NBS,[3] we obtain $\Delta_f H°(Na_5Al_3F_{14}, l, 298.15\ K) = -1794.1 \pm 10\ kcal·mol^{-1}$. These results are in good agreement with adopted enthalpy of formation.

Heat Capacity and Entropy

High temperature enthalpies were measured by drop calorimetry by Holm,[5] (1046.6–1172.9 K). Our analysis of his experimental data leads to a constant heat capacity of 232.76 $cal·K^{-1}·mol^{-1}$. We have corrected his experimental enthalpies for what we believe to be a positive bias by subtracting 2.3 $kcal·mol^{-1}$ from his measured data. Our adopted enthalpies can be represented by the equation $H°(T) - H°(298.15\ K) = -88{,}000 + 232.76\ T\ cal·mol^{-1}$ (1010–1200 K). A hypothetical glass transition is assumed at 650 K. The $C_p°$ values above 1172.9 K are obtained by linear extrapolation. The entropy, $S°(298.15\ K)$, is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

References

[1]JANAF Thermochemical Tables: $Na_5Al_3F_{14}$(cr) and Na_3AlF_6(l), 12–30–79; AlF_3(cr), 9–30–79.
[2]K. C. Hong and U. J. Kleppa, J. Phys. Chem. **82**, 176 (1978).
[3]U. S. Nat. Bur. Stand. IR 75–968, (1976).
[4]K. C. Hong and U. J. Kleppa, High Temp. Sci. **8**, 299 (1976).
[5]J. L. Holm, High Temp. Sci. **6**, 16 (1974).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$	$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0						
100						
200						
298.15	454.006	532.124	0.	−7497.408	−7130.832	1249.292
300	455.094	534.935	0.841	−7497.367	−7128.557	1241.192
400	499.570	672.402	48.732	−7507.644	−7004.995	914.759
500	525.092	786.767	100.031	−7503.309	−6879.797	718.727
600	542.665	884.124	153.456	−7497.486	−6755.621	588.129
650.000	549.778	927.848	180.772	GLASS <--> LIQUID		
650.000	973.868	927.848	649.737	180.772	TRANSITION	
700	973.868	1000.020	672.212	229.465	−7469.641	−6633.296	494.983
800	973.868	1130.062	721.496	326.852	−7421.008	−6517.144	425.526
900	973.868	1244.767	773.390	424.239	−7373.059	−6407.048	371.855
1000	973.868	1347.374	825.748	521.626	−7357.686	−6299.969	329.077
1010.000	973.868	1357.064	830.961	531.365	--- CRYSTAL <--> LIQUID ---		
1100	973.868	1440.193	877.455	619.013	−7310.405	−6196.490	294.247
1200	973.868	1524.931	927.932	716.399	−7747.317	−6085.098	264.877
1300	973.868	1602.882	976.893	813.786	−7696.233	−5948.652	239.020
1400	973.868	1675.053	1024.216	911.173	−7645.300	−5816.135	217.003
1500	973.868	1742.243	1069.870	1008.560	−7594.505	−5687.253	198.048
1600	973.868	1805.095	1113.879	1105.947	−7543.838	−5561.756	181.573
1700	973.868	1864.136	1156.293	1203.333	−7493.288	−5439.424	167.133
1800	973.868	1919.800	1197.178	1300.720	−7442.840	−5320.064	154.384
1900	973.868	1972.455	1236.609	1398.107	−7392.479	−5203.508	143.054
2000	973.868	2022.408	1274.661	1495.494	−7342.185	−5089.599	132.927
2100	973.868	2069.923	1311.408	1592.880	−7291.938	−4978.207	123.826
2200	973.868	2115.227	1346.924	1690.267	−7241.715	−4869.206	115.610
2300	973.868	2158.517	1381.276	1787.654	−7191.493	−4762.488	108.160
2400	973.868	2199.965	1414.531	1885.041	−7141.249	−4657.956	101.378
2500	973.868	2239.720	1446.749	1982.428	−7090.962	−4555.519	95.182
2600	973.868	2277.916	1477.987	2079.814	−7040.610	−4455.095	89.504
2700	973.868	2314.670	1508.299	2177.201	−6990.174	−4356.609	84.284
2800	973.868	2350.087	1537.734	2274.588	−7821.342	−4257.091	79.417
2900	973.868	2384.261	1566.339	2371.975	−7767.406	−4130.747	74.403
3000	973.868	2417.277	1594.157	2469.362	−7713.346	−4006.267	69.755

PREVIOUS: CURRENT: December 1979

0 to	1010 K	crystal
above	1010 K	liquid

Refer to the individual tables for details.

Adopted enthalpy equations used to prepare this tabulation:

$Na_5Al_3F_{14}$(cr)

$H_T - H_{298} = 17.894 \times 10^5/T - -43{,}416 + 122.461\ T + 10.158 \times 10^{-3}\ T^2$ cal·mol^{-1} (298.15–1010 K)

$Na_5Al_3F_{14}$(l)

$H_T - H_{298} = -88{,}000 + 232.76\ T$ cal·mol^{-1} (1010–1200 K)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−80.910	−7554.692	−7554.692	INFINITE
100	214.723	142.800	861.276	−71.848	−7574.128	−7455.146	3894.169
200	370.912	317.691	522.895	−41.041	−7581.508	−7325.950	1913.342
298.15	454.006	483.545	483.545	0.	−7581.408	−7200.348	1261.471
300	455.094	486.357	483.554	0.841	−7581.368	−7197.984	1253.280
400	499.570	623.823	501.993	48.732	−7591.644	−7069.564	923.190
500	525.092	738.188	538.126	100.031	−7587.309	−6939.508	724.965
600	542.665	835.534	579.783	153.451	−7581.492	−6810.474	592.904
700	556.472	920.245	622.500	208.421	−7574.685	−6682.498	498.654
800	568.606	995.357	664.500	264.686	−7567.175	−6555.548	428.033
900	579.484	1062.962	705.080	322.094	−7559.205	−6429.570	373.163
1000	589.944	1124.591	743.994	380.597	−7582.715	−6302.216	329.194
1010.000	590.781	1130.465	747.792	386.500	CRYSTAL <--> LIQUID		
1010.000	973.868	1357.064	747.792	615.365	TRANSITION		
1100	973.868	1440.193	801.090	703.013	−7310.405	−6196.490	294.247
1200	973.868	1524.931	857.931	800.400	−7747.317	−6085.097	264.877
1300	973.868	1602.882	912.277	897.787	−7696.233	−5948.652	239.020
1400	973.868	1675.053	964.215	995.174	−7645.299	−5816.135	217.003
1500	973.868	1742.243	1013.870	1092.560	−7594.504	−5687.253	198.048
1600	973.868	1805.095	1061.378	1189.947	−7543.838	−5561.756	181.573
1700	973.868	1864.136	1106.880	1287.334	−7493.287	−5439.424	167.133
1800	973.868	1919.800	1150.511	1384.721	−7442.840	−5320.064	154.384
1900	973.868	1972.455	1192.398	1482.108	−7392.479	−5203.507	143.054
2000	973.868	2022.408	1232.660	1579.494	−7342.185	−5089.598	132.927
2100	973.868	2069.923	1271.408	1676.881	−7291.937	−4978.206	123.826
2200	973.868	2115.227	1308.742	1774.268	−7241.714	−4869.206	115.610
2300	973.868	2158.517	1344.754	1871.655	−7191.493	−4762.488	108.159
2400	973.868	2199.965	1379.531	1969.042	−7141.249	−4657.956	101.378
2500	973.868	2239.720	1413.149	2066.428	−7090.962	−4555.518	95.182
2600	973.868	2277.916	1445.679	2163.815	−7040.610	−4455.094	89.504
2700	973.868	2314.670	1477.188	2261.202	−6990.174	−4356.609	84.284
2800	973.868	2350.087	1507.734	2358.589	−7821.342	−4257.090	79.417
2900	973.868	2384.261	1537.373	2455.975	−7767.406	−4130.747	74.403
3000	973.868	2417.277	1566.156	2553.362	−7713.346	−4006.267	69.755

PREVIOUS: CURRENT: December 1979

$S°(298.15\ K) = 175.55 \pm 0.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2186 \pm 10\ K$

$\Delta_f H°(0\ K) = -5585.7 \pm 5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -5624.1 \pm 5\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [402]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Al_6BeO_{10}, cr, 298.15\ K)$ is calculated from $\Delta_f H°(298.15\ K) = 2.71 \pm 0.45$ kcal·mol^{-1} for $BeO(cr, \alpha) + 3\ Al_2O_3(cr, \alpha) \rightarrow Al_6BeO_{10}(cr)$ using current value of $\Delta_f H°$ for the reactants.[1] $\Delta_r H°$ is based on the value 2.9 ± 0.45 kcal·mol^{-1} at 968 K determined by Holm and Kleppa[2] from the difference in heats of solution of the three components in an oxide melt.

For comparison with the above reaction, we derive $\Delta_f H°(298.15\ K) = 0.6$ kcal·mol^{-1} from $\Delta_f G°(1800\ K) = -3.95$ kcal·mol^{-1} based on equilibrium data. Young[3] used water vapor as a carrier gas to determine the transport of BeO, presumably as $Be(OH)_2$, in equilibrium with BeO(cr) and Al_6BeO_{10}(cr). The difference between the two equilibria gives the above reaction. We compare at 1800 K, near the upper limit of the data, where the experimental method is most sensitive. The resulting difference in $\Delta_f H°(298.15\ K)$ is -2.1 kcal·mol^{-1}, roughly twice the uncertainty claimed for $\Delta_f G°$.[3]

Heat Capacity and Entropy

$C_p°$ and the derived properties below 298.15 K are taken from calorimetric data (15–380 K) of Furukawa and Saba.[4] The entropy is based on $S°(15\ K) = 0.011$ cal·K^{-1}·mol^{-1}. The heat capacity is extrapolated above 1200 K by comparison with current values[1] for $BeAl_2O_4$(cr), Al_2O_3(cr, α), and BeO(cr, α).

Holm and Kleppa[2] combined their $\Delta_f H°$ for formation from the oxides with the corresponding $\Delta_f G°$ from Young[3] in order to calculate $\Delta_f S°$. Based on the present functions and Young's result at 1800 K, we calculate an entropy which is 1.2 cal·K^{-1}·mol^{-1}larger than the adopted calorimetric value. To explain the difference, Holm and Kleppa[2] proposed Be–Al disorder in the crystal, which might provide extra entropy up to 2.76 cal·K^{-1}·mol^{-1}. Crystal structure data were recently published [6], but they do not appear to be sufficient to test the hypothesis of disorder. Although we believe that the discrepancy is within the uncertainty of the equilibrium data, further information is desirable.

Fusion Data

Refer to the liquid table for details.

References

[1]JANAF Thermochemical Tables: BeO(cr, α), 6–30–71; Al_2O_3(cr, α) and $BeAl_2O_4$(cr), 6–30–77.
[2]J. L. Holm and O. J. Kleppa, Acta Chem. Scand. **20**, 2568 (1966).
[3]W. A. Young, J. Phys. Chem. **64**, 1003 (1960).
[4]G. T. Furukawa and bW. G. Saba, J. Res. Nat. Bur. Stand. **71A**, 3 (1967).
[5]D. A. Ditmars and T. B. Douglas, J. Res. Nat. Bur. Stand. **71A**, 97 (1967).
[6]L. A. Harris and H. L. Yakel, J. Amer. Ceram. Soc. **53**, 359 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−34.112	−5585.659	−5585.659	INFINITE
100	47.049	16.606	345.259	−32.865	−5601.878	−5512.643	2879.509
200	172.929	87.939	197.142	−21.840	−5616.797	−5417.092	1414.799
298.15	265.186	175.552	175.552	0.	−5624.133	−5317.254	931.561
300	266.546	177.197	175.557	0.492	−5624.212	−5315.350	925.485
400	324.268	262.481	186.792	30.275	−5626.175	−5211.985	680.616
500	358.527	338.838	209.722	64.558	−5625.087	−5108.521	533.684
600	380.560	406.278	236.976	101.581	−5622.541	−5005.431	435.762
700	396.083	466.167	265.522	140.452	−5619.419	−4902.822	365.853
800	407.827	519.854	294.016	180.671	−5616.267	−4800.669	313.452
900	417.249	568.451	321.852	221.939	−5613.464	−4698.893	272.717
1000	425.178	612.834	348.763	264.071	−5674.818	−4592.838	239.905
1100	431.998	653.685	374.651	306.937	−5671.319	−4484.805	212.966
1200	437.939	691.532	399.500	350.439	−5667.470	−4377.108	190.531
1300	443.295	726.800	423.336	394.503	−5663.316	−4269.745	171.560
1400	448.316	759.835	446.204	439.084	−5658.886	−4162.711	155.313
1500	453.336	790.936	468.159	484.165	−5654.182	−4056.005	141.243
1600	458.566	820.358	489.260	529.756	−5663.723	−3949.095	128.925
1700	464.215	848.326	509.566	575.892	−5657.995	−3842.104	118.053
1800	470.282	875.028	529.133	622.612	−5651.825	−3735.464	108.400
1900	476.976	900.632	548.016	669.969	−5645.155	−3629.179	99.773
2000	484.298	925.281	566.267	718.028	−5637.922	−3523.259	92.018
2100	492.248	949.100	583.933	766.850	−5630.062	−3417.716	85.011
2186.000	499.586	969.001	598.692	809.495	− − − CRYSTAL <− −> LIQUID − − −		
2200	500.825	972.195	601.059	816.498	−5621.511	−3312.561	78.650
2300	510.030	994.658	617.686	867.036	−5612.205	−3207.816	72.852
2400	519.862	1016.570	633.851	918.525	−5602.079	−3103.493	67.546
2500	530.322	1038.002	649.590	971.029	−5591.070	−2999.608	62.673
2600	541.410	1059.015	664.934	1024.610	−5579.112	−2896.182	58.185
2700	553.125	1079.666	679.914	1079.332	−5566.140	−2793.234	54.038
2800	565.468	1100.003	694.554	1135.256	−7606.453	−2678.757	49.973
2900	578.438	1120.071	708.882	1192.446	−7583.620	−2503.171	45.087
3000	592.036	1139.908	722.920	1250.965	−7559.563	−2328.388	40.541

PREVIOUS: CURRENT: June 1972

$S°(298.15\ K)$ = [314.903] $J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K)$ = [−5299.312] $kJ·mol^{-1}$

T_{fus} = 2186 ± 10 K $\Delta_{fus}H°$ = [402] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Al_6BeO_{10}, l, 298.15\ K)$ is calculated from $\Delta_f H°(Al_6BeO_{10}, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2186\ K)$–$H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is assumed to be 136 $cal·K^{-1}·mol^{-1}$, corresponding to 8 $cal·K^{-1}$ g–atom^{-1}, by analogy with current tables[1] for $BeAl_2O_4$(l) and Al_2O_3(l). Below the assumed glass transition at 1400 K, $C_p°$ is taken to be the same as that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus}, adjusted to IPTS–68, is from the phase study of Lang *et al.*[2] $\Delta_{fus}H°$ is estimated as being slightly smaller than the sum of $\Delta_{fus}H°$ for the component oxides.[1] Data for $BeAl_2O_4$ are consistent with this approach.

References

[1]JANAF Thermochemical Tables: BeO(l), 6–30–71; Al_2O_3(l) and $BeAl_2O_4$(l), 6–30–72.
[2]S. M. Lang, C. L. Fillmore, and L. H. Maxwell, J. Res. Nat. Bur. Stand. **48**, 298 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	265.186	314.903	314.903	0.	−5299.312	−5033.981	881.933
300	266.546	316.548	314.908	0.492	−5299.391	−5032.335	876.207
400	324.268	401.832	326.143	30.275	−5301.355	−4942.905	645.477
500	358.527	478.189	349.073	64.558	−5300.266	−4853.375	507.029
600	380.560	545.629	376.328	101.581	−5297.720	−4764.221	414.762
700	396.083	605.518	404.873	140.452	−5294.599	−4675.547	348.894
800	407.827	659.205	433.367	180.671	−5291.446	−4587.329	299.522
900	417.249	707.802	461.203	221.939	−5288.643	−4499.488	261.143
1000	425.178	752.185	488.114	264.071	−5349.998	−4407.369	230.217
1100	431.998	793.036	514.002	306.937	−5346.498	−4313.271	204.820
1200	437.939	830.883	538.851	350.439	−5342.649	−4219.509	183.670
1300	443.295	866.151	562.687	394.503	−5338.496	−4126.080	165.788
1400	448.316	899.188	585.555	439.087	−5334.063	−4032.982	150.472
1400.010	448.316	899.191	585.557	439.091	GLASS <– –> LIQUID		
1400.010	569.024	899.191	585.557	439.091	TRANSITION		
1500	569.024	938.446	607.787	495.988	−5317.538	−3940.627	137.225
1600	569.024	975.170	629.614	552.890	−5315.768	−3848.840	125.652
1700	569.024	1009.667	650.965	609.793	−5299.273	−3757.662	115.459
1800	569.024	1042.191	671.805	666.695	−5282.920	−3667.453	106.427
1900	569.024	1072.957	692.116	723.598	−5266.706	−3578.147	98.370
2000	569.024	1102.144	711.894	780.500	−5250.630	−3489.692	91.141
2100	569.024	1129.907	731.144	837.402	−5234.689	−3402.038	84.621
2186.000	569.024	1152.745	747.284	886.338	– – – CRYSTAL <– – –> LIQUID – – –		
2200	569.024	1156.378	749.876	894.305	−5218.884	−3315.136	78.711
2300	569.024	1181.672	768.104	951.207	−5203.212	−3228.956	73.332
2400	569.024	1205.889	785.844	1008.110	−5187.674	−3143.454	68.415
2500	569.024	1229.118	803.113	1065.012	−5172.266	−3058.595	63.906
2600	569.024	1251.436	819.930	1121.914	−5156.987	−2974.350	59.755
2700	569.024	1272.911	836.312	1178.817	−5141.834	−2890.689	55.924
2800	569.024	1293.605	852.277	1235.719	−7181.169	−2795.558	52.152
2900	569.024	1313.573	867.841	1292.622	−7158.624	−2639.331	47.539
3000	569.024	1332.863	883.022	1349.524	−7136.183	−2483.875	43.248
3100	569.024	1351.522	897.836	1406.426	−7113.842	−2329.164	39.246
3200	569.024	1369.587	912.297	1463.329	−7091.601	−2175.178	35.506
3300	569.024	1387.097	926.421	1520.231	−7069.458	−2021.884	32.004
3400	569.024	1404.084	940.221	1577.134	−7047.412	−1869.255	28.718
3500	569.024	1420.579	953.711	1634.036	−7025.465	−1717.278	25.629
3600	569.024	1436.609	966.904	1690.938	−7003.614	−1565.924	22.721
3700	569.024	1452.199	979.810	1747.841	−6981.861	−1415.179	19.979
3800	569.024	1467.374	992.442	1804.743	−6960.207	−1265.014	17.389
3900	569.024	1482.155	1004.810	1861.646	−6938.652	−1115.420	14.939
4000	569.024	1496.561	1016.924	1918.548	−6917.201	−966.382	12.620

PREVIOUS: CURRENT: June 1972

0 *to* 2186 K	*crystal*
above 2186 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	*0.*	*0.*	INFINITE	−34.112	−5585.659	−5585.659	INFINITE
100	47.049	16.606	345.259	−32.865	−5601.878	−5512.643	2879.509
200	172.929	87.939	197.142	−21.840	−5616.797	−5417.092	1414.799
298.15	265.186	175.552	175.552	0.	−5624.133	−5317.254	931.561
300	266.546	177.197	175.557	0.492	−5624.212	−5315.350	925.485
400	324.268	262.481	186.792	30.275	−5626.175	−5211.985	680.616
500	358.527	338.838	209.722	64.558	−5625.087	−5108.521	533.684
600	380.560	406.278	236.976	101.581	−5622.541	−5005.431	435.762
700	396.083	466.167	265.522	140.452	−5619.419	−4902.822	365.853
800	407.827	519.854	294.016	180.671	−5616.267	−4800.669	313.452
900	417.249	568.451	321.852	221.939	−5613.464	−4698.893	272.717
1000	425.178	612.834	348.763	264.071	−5674.818	−4592.838	239.905
1100	431.998	653.685	374.651	306.937	−5671.319	−4484.805	212.966
1200	437.939	691.532	399.500	350.439	−5667.470	−4377.108	190.531
1300	443.295	726.800	423.336	394.503	−5663.316	−4269.745	171.560
1400	448.316	759.835	446.204	439.084	−5658.886	−4162.711	155.313
1500	453.336	790.936	468.159	484.165	−5654.182	−4056.005	141.243
1600	458.566	820.358	489.260	529.756	−5663.723	−3949.095	128.925
1700	464.215	848.326	509.566	575.892	−5657.995	−3842.104	118.053
1800	470.282	875.028	529.133	622.612	−5651.825	−3735.464	108.400
1900	476.976	900.632	548.016	669.969	−5645.155	−3629.179	99.773
2000	484.298	925.281	566.267	718.028	−5637.922	−3523.259	92.018
2100	492.248	949.100	583.933	766.850	−5630.062	−3417.716	85.011
2186.000	499.586	969.001	598.692	809.495	CRYSTAL <--> LIQUID TRANSITION		
2186.000	569.024	1152.745	598.692	1211.159			
2200	569.024	1156.378	602.230	1219.126	−5218.884	−3315.136	78.711
2300	569.024	1181.672	626.877	1276.028	−5203.212	−3228.956	73.332
2400	569.024	1205.889	650.502	1332.930	−5187.673	−3143.454	68.415
2500	569.024	1229.118	673.185	1389.833	−5172.266	−3058.595	63.906
2600	569.024	1251.436	694.999	1446.735	−5156.987	−2974.350	59.755
2700	569.024	1272.911	716.008	1503.638	−5141.834	−2890.689	55.924
2800	569.024	1293.605	736.269	1560.540	−7181.169	−2795.558	52.152
2900	569.024	1313.573	755.834	1617.442	−7158.624	−2639.331	47.539
3000	569.024	1332.863	774.748	1674.345	−7136.183	−2483.874	43.248
3100	569.024	1351.522	793.055	1731.247	−7113.842	−2329.163	39.246
3200	569.024	1369.587	810.791	1788.150	−7091.601	−2175.178	35.506
3300	569.024	1387.097	827.991	1845.052	−7069.458	−2021.884	32.004
3400	569.024	1404.084	844.686	1901.954	−7047.412	−1869.255	28.718
3500	569.024	1420.579	860.905	1958.857	−7025.465	−1717.278	25.629
3600	569.024	1436.609	876.676	2015.759	−7003.614	−1565.924	22.721
3700	569.024	1452.199	892.021	2072.662	−6981.861	−1415.179	19.979
3800	569.024	1467.374	906.963	2129.564	−6960.207	−1265.014	17.389
3900	569.024	1482.155	921.523	2186.466	−6938.652	−1115.420	14.939
4000	569.024	1496.561	935.719	2243.369	−6917.201	−966.382	12.620

PREVIOUS: CURRENT: June 1972

$S°(298.15\ K) = 274.9 \pm 12\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2123 \pm 15\ K$

$\Delta_f H°(0\ K) = -6775.17 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -6819.21 \pm 6.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heat of the reaction 3 Al_2O_3(cr, α) + 2 SiO_2(quartz) → $Al_6Si_2O_{13}$(cr) has been determined at 968 K by Holm and Kleppa[1, 2] to be +5.44 ± 0.35 kcal·mol^{-1}. This value was obtained from heat of solution measurements in a high temperature oxide melt calorimeter. Using the JANAF functions, this reduces to $\Delta_f H°(298.15\ K) = 6.77$ kcal·mol^{-1}, which is used to calculate the adopted value for the enthalpy of formation.

Heat Capacity and Entropy

The low temperature heat capacity and high temperature enthalpy of mullite have been measured by Pankratz *et al.*[3] The low temperature investigations extended from 53.5 K to 296.4 K; the Debye–Einstein equation 3D(182/T) + 15E(350/T) + 10E(502/T) + 15E(897/T) represented the data from 53.5 to 114.6 K within 1.4 percent and gave a smooth extrapolation to zero. From this equation, the entropy at 51 K was found to be 2.17 cal·K^{-1}·mol^{-1} as opposed to the value 1.96 cal·K^{-1}·mol^{-1} found by Pankratz *et al.*[5] However, since it is known that mullite has some of its Al atoms on Si sites, there will be configurational entropy remaining at 0 K. This is borne out by the free energy determinations of Rein and Chipman[4] and Kay and Taylor,[5] who obtain $\Delta_f G°(1823\ K) = -5.7 \pm 0.1$ kcal·mol^{-1} for the formation from oxide. If the entropies and enthalpies reported by Pankratz *et al.* are used with the heat of formation, they yield $\Delta_f G°(1823\ K) = +2.9$ kcal·mol^{-1}. Holm and Kleppa[1,2] calcualte that random mixing of tetra-coordinated aluminum and silicon atoms could produce 7 cal·K^{-1}·mol^{-1} residual entropy. We have added 4.7 cal·K^{-1}·mol^{-1} in order to match the measured $\Delta_f G°(1823\ K)$.

A review of the enthalpy determination indicated that the values might easily be 2 percent low if as little as 4 percent of kyanite remained unchanged in the sample used for measurement. Since X-ray could not detect this amount, it is not an unreasonable assumption. Accordingly, we have checked the effect of increasing the heat capacity above 298.15 K by 2 percent; this then gives $\Delta_f G°(1823\ K) = -2.10$ kcal·mol^{-1}. In order to bring this within reasonable agreement with the observations, a residual configurational entropy of 2 cal·K^{-1}·mol^{-1} would be needed. Thus the uncertainty in the residual entropy is of the order of 2 cal·K^{-1}·mol^{-1} due to possible uncertainty in the high temperature heat capacity.

Fusion Data

The congruent melting point of mullite was reported by Aramaki and Roy.[6]

References

[1] J. L. Holm and O. J. Kleppa, J. Phys. Chem. **70**, 1690 (1966).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−46.072	−6775.166	−6775.166	INFINITE
100	85.264	60.703	493.090	−43.239	−6794.649	−6683.111	3490.899
200	225.957	164.662	301.776	−27.423	−6810.923	−6564.686	1714.520
298.15	325.641	274.889	274.889	0.	−6819.209	−6441.793	1128.575
300	327.031	276.907	274.895	0.604	−6819.302	−6439.451	1121.208
400	390.744	380.251	288.552	36.680	−6821.830	−6312.326	824.305
500	431.998	472.124	316.267	77.929	−6820.816	−6185.013	646.144
600	459.822	553.470	349.157	122.588	−6817.859	−6058.108	527.405
700	479.486	625.893	383.614	169.595	−6813.987	−5931.782	442.635
800	494.130	690.919	418.033	218.309	−6809.866	−5806.035	379.095
900	504.800	749.756	451.675	268.273	−6806.008	−5680.793	329.705
1000	513.377	803.395	484.205	319.190	−6866.308	−5551.389	289.975
1100	519.705	852.625	515.491	370.848	−6861.822	−5420.111	257.380
1200	525.618	898.102	545.504	423.117	−6857.067	−5289.254	230.235
1300	531.115	940.394	574.273	475.957	−6852.049	−5158.805	207.283
1400	536.198	979.942	601.852	529.326	−6846.783	−5028.752	187.625
1500	540.866	1017.097	628.309	583.183	−6841.293	−4899.084	170.601
1600	544.325	1052.115	653.713	637.443	−6835.652	−4769.787	155.718
1700	547.766	1085.217	678.131	692.047	−6930.264	−4639.951	142.568
1800	551.188	1116.624	701.626	746.995	−6923.960	−4505.410	130.744
1900	554.593	1146.516	724.261	802.285	−6917.466	−4371.222	120.173
2000	557.978	1175.049	746.093	857.913	−6910.783	−4237.380	110.669
2100	561.098	1202.348	767.174	913.866	−6903.926	−4103.878	102.078
2200	564.323	1228.525	787.554	970.136	−6896.898	−3970.703	94.276
2300	567.653	1253.683	807.277	1026.734	−6889.690	−3837.857	87.160
2400	571.089	1277.914	826.385	1083.670	−6882.287	−3705.329	80.644
2500	574.631	1301.299	844.916	1140.956	−6874.678	−3573.111	74.656
2600	578.277	1323.907	862.907	1198.600	−6866.849	−3441.202	69.135
2700	582.030	1345.801	880.388	1256.615	−6858.786	−3309.596	64.028
2800	585.887	1367.038	897.391	1315.010	−8613.882	−3172.488	59.183
2900	589.850	1387.666	913.943	1373.796	−8598.737	−2978.424	53.647
3000	593.919	1407.731	930.070	1432.983	−8583.318	−2784.880	48.489

PREVIOUS: September 1966 CURRENT: September 1967

Continued from page 67

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0 to 6000 K Ideal Monatomic Gas

IP(Ar, g) = 12710 ± 0.1 cm^{-1}
$S°(298.15\ K) = 154.845 \pm 0.003\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[1,9] All predicted levels have been observed for n=3 and 4 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[2] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 93000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.[2]

The thermodynamic functions at 298.15 K agree exactly with recent CODATA recommendations[3] except for two minor differences. First, the entropy differs by 0.1094 $J \cdot K^{-1} \cdot mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J \cdot K^{-1} \cdot mol^{-1}$ for the rare gases arise due to the use of slightly different values for R; this table uses R = 8.31441 $J \cdot K^{-1} \cdot mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[4] McBride *et al.*,[5] Gurvich *et al.*,[8] and Wagman *et al.*[12] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[6] and the 1973 values,[7] respectively.

Phase Data

The triple point, 83.798 K, and boiling point, 87.294 K, are a defining fixed point and a secondary reference point, respectively of IPTS–68.[10,11] Hultgren *et al.*[4] had recommended a triple point of 83.81 K (0.6801 atm) and a boiling point of 87.30 K (1 atm). These values are provided for the convenience of the reader and have not been evaluated by the present authors. As a result of these low values, the reference state for argon is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$S°$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$H°-H°(T_r)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H°$ ($kJ \cdot mol^{-1}$)	$\Delta_f G°$ ($kJ \cdot mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−6.197	0.	0.	0.
100	20.786	132.137	173.325	−4.119	0.	0.	0.
200	20.786	146.545	156.746	−2.040	0.	0.	0.
250	20.786	151.183	155.187	−1.001	0.	0.	0.
298.15	20.786	154.845	154.845	0.	0.	0.	0.
300	20.786	154.973	154.845	0.038	0.	0.	0.
350	20.786	158.177	155.098	1.078	0.	0.	0.
400	20.786	160.953	155.660	2.117	0.	0.	0.
450	20.786	163.401	156.387	3.156	0.	0.	0.
500	20.786	165.591	157.200	4.196	0.	0.	0.
600	20.786	169.381	158.924	6.274	0.	0.	0.
700	20.786	172.585	160.653	8.353	0.	0.	0.
800	20.786	175.361	162.321	10.431	0.	0.	0.
900	20.786	177.809	163.909	12.510	0.	0.	0.
1000	20.786	179.999	165.410	14.589	0.	0.	0.
1100	20.786	181.980	166.828	16.667	0.	0.	0.
1200	20.786	183.789	168.167	18.746	0.	0.	0.
1300	20.786	185.453	169.434	20.824	0.	0.	0.
1400	20.786	186.993	170.634	22.903	0.	0.	0.
1500	20.786	188.427	171.773	24.982	0.	0.	0.
1600	20.786	189.769	172.856	27.060	0.	0.	0.
1700	20.786	191.029	173.888	29.139	0.	0.	0.
1800	20.786	192.217	174.874	31.217	0.	0.	0.
1900	20.786	193.341	175.816	33.296	0.	0.	0.
2000	20.786	194.407	176.719	35.375	0.	0.	0.
2100	20.786	195.421	177.586	37.453	0.	0.	0.
2200	20.786	196.388	178.419	39.532	0.	0.	0.
2300	20.786	197.312	179.220	41.610	0.	0.	0.
2400	20.786	198.197	179.993	43.689	0.	0.	0.
2500	20.786	199.045	180.738	45.768	0.	0.	0.
2600	20.786	199.860	181.458	47.846	0.	0.	0.
2700	20.786	200.645	182.154	49.925	0.	0.	0.
2800	20.786	201.401	182.828	52.004	0.	0.	0.
2900	20.786	202.130	183.481	54.082	0.	0.	0.
3000	20.786	202.835	184.115	56.161	0.	0.	0.
3100	20.786	203.516	184.730	58.239	0.	0.	0.
3200	20.786	204.176	185.327	60.318	0.	0.	0.
3300	20.786	204.816	185.908	62.397	0.	0.	0.
3400	20.786	205.436	186.473	64.475	0.	0.	0.
3500	20.786	206.039	187.024	66.554	0.	0.	0.
3600	20.786	206.625	187.560	68.632	0.	0.	0.
3700	20.786	207.194	188.083	70.711	0.	0.	0.
3800	20.786	207.748	188.593	72.790	0.	0.	0.
3900	20.786	208.288	189.091	74.868	0.	0.	0.
4000	20.786	208.815	189.578	76.947	0.	0.	0.
4100	20.786	209.328	190.053	79.025	0.	0.	0.
4200	20.786	209.829	190.518	81.104	0.	0.	0.
4300	20.786	210.318	190.973	83.183	0.	0.	0.
4400	20.786	210.796	191.418	85.261	0.	0.	0.
4500	20.786	211.263	191.854	87.340	0.	0.	0.
4600	20.786	211.720	192.281	89.418	0.	0.	0.
4700	20.786	212.167	192.699	91.497	0.	0.	0.
4800	20.786	212.604	193.109	93.576	0.	0.	0.
4900	20.786	213.033	193.512	95.654	0.	0.	0.
5000	20.786	213.453	193.906	97.733	0.	0.	0.
5100	20.786	213.864	194.294	99.811	0.	0.	0.
5200	20.786	214.268	194.674	101.890	0.	0.	0.
5300	20.786	214.664	195.047	103.969	0.	0.	0.
5400	20.786	215.053	195.414	106.047	0.	0.	0.
5500	20.786	215.434	195.775	108.126	0.	0.	0.
5600	20.786	215.808	196.129	110.204	0.	0.	0.
5700	20.786	216.176	196.478	112.283	0.	0.	0.
5800	20.786	216.538	196.820	114.362	0.	0.	0.
5900	20.786	216.893	197.158	116.440	0.	0.	0.
6000	20.786	217.243	197.489	118.519	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

IP(Ar^+, g) = 222848.2 ± 0.1 cm^{-1}
8.15 K) = 166.404 ± 0.003 $J \cdot K^{-1} \cdot mol^{-1}$

$H°(0\ K) = 1520.573 \pm 0.001\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1526.778]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	1431.41	2

Enthalpy of Formation

The ionization limit of neutral argon (127109.9 ± 0.1 cm^{-1}) reported by Moore[1] is adopted as $\Delta_f H°(0\ K)$ for $Ar^+(g)$. The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the latest CODATA fundamental constants.[2] The uncertainty in the ionization limit corresponds to an uncertainty of ±0.001 $kJ \cdot mol^{-1}$ in the heat of formation. Rosenstock *et al.*[9] and Levin and Lias[11] have summarized additional ionization potential and appearance potential data. A recent atomic spectroscopic study by Minnhagen[12] yielded an ionization potential within 0.13 cm^{-1} of our adopted value. Gurvich *et al.*[8] and Wagman *et al.*[10] adopted the same ionization potential, but the use of slightly different fundamental constants by Wagman *et al.*[10] resulted in a heat of formation difference of 0.015 $kJ \cdot mol^{-1}$.

$\Delta_f H°(Ar^+, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ar, g, 0\ K)$ by using IP(Ar) with JANAF[3] enthalpies $H°(0\ K) - H°(298.15\ K)$ for $Ar^+(r)$, Ar(g), and $e^-(r)$. $\Delta_r H°(Ar \rightarrow Ar^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights given by Moore[4] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[5] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 108000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore.[1] The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[5]

The thermodynamic functions reported here agree with those of Green *et al.*,[6] Hilsenrath *et al.*,[7] and Gurvich *et al.*[8] except for one or two minor changes. First, the entropy differs by 0.1094 $J \cdot K^{-1} \cdot mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the cited references used a pressure of 1 atm. Second, smaller differences arise from the use of slightly different values for the fundamental constants, the relative ionic mass, and the position of the $^2P_{1/2}$ electronic level.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.206	1520.573		
100	20.786	143.663	184.937	−4.127			
200	20.801	158.073	168.315	−2.048			
250	20.861	162.720	166.748	−1.007			
298.15	20.984	166.404	166.404	0.	1526.778	1517.077	−265.786
300	20.990	166.533	166.404	0.039	1526.817	1517.017	−264.136
350	21.185	169.783	166.660	1.093	1527.871	1515.300	−226.146
400	21.422	172.627	167.232	2.158	1528.936	1513.432	−197.634
450	21.673	175.165	167.975	3.235	1530.014	1511.429	−175.442
500	21.915	177.461	168.810	4.325	1531.104	1509.306	−157.676
600	22.318	181.494	170.597	6.538	1533.316	1504.740	−130.999
700	22.588	184.956	172.407	8.784	1535.563	1499.800	−111.916
800	22.734	187.983	174.169	11.051	1537.830	1494.536	−97.583
900	22.786	190.665	175.856	13.328	1540.106	1488.988	−86.419
1000	22.773	193.065	177.459	15.606	1542.385	1483.186	−77.474
1100	22.718	195.234	178.978	17.881	1544.660	1477.156	−70.144
1200	22.639	197.207	180.416	20.149	1546.928	1470.919	−64.027
1300	22.546	199.015	181.778	22.409	1549.187	1464.493	−58.844
1400	22.449	200.683	183.070	24.658	1551.437	1457.893	−54.395
1500	22.350	202.228	184.296	26.898	1553.677	1451.134	−50.533
1600	22.254	203.668	185.462	29.129	1555.907	1444.225	−47.149
1700	22.162	205.014	186.573	31.349	1558.128	1437.176	−44.159
1800	22.076	206.278	187.633	33.561	1560.340	1429.998	−41.497
1900	21.995	207.470	188.646	35.765	1562.543	1422.696	−39.113
2000	21.919	208.596	189.616	37.960	1564.739	1415.279	−36.963
2100	21.849	209.664	190.545	40.149	1566.927	1407.752	−35.016
2200	21.785	210.679	191.437	42.330	1569.109	1400.121	−33.243
2300	21.725	211.646	192.295	44.506	1571.284	1392.391	−31.622
2400	21.670	212.569	193.121	46.675	1573.454	1384.567	−30.134
2500	21.619	213.453	193.917	48.840	1575.618	1376.652	−28.764
2600	21.571	214.299	194.684	50.999	1577.778	1368.651	−27.497
2700	21.528	215.113	195.426	53.154	1579.933	1360.567	−26.322
2800	21.487	215.895	196.143	55.305	1582.083	1352.403	−25.229
2900	21.450	216.648	196.837	57.452	1584.230	1344.162	−24.211
3000	21.415	217.375	197.510	59.595	1586.374	1335.847	−23.259
3100	21.383	218.077	198.162	61.735	1588.513	1327.461	−22.368
3200	21.353	218.755	198.795	63.872	1590.650	1319.006	−21.531
3300	21.326	219.412	199.410	66.006	1592.784	1310.484	−20.743
3400	21.300	220.048	200.008	68.137	1594.915	1301.897	−20.001
3500	21.276	220.665	200.589	70.266	1597.044	1293.248	−19.301
3600	21.253	221.264	201.155	72.392	1599.171	1284.538	−18.638
3700	21.232	221.846	201.706	74.516	1601.295	1275.769	−18.011
3800	21.212	222.412	202.244	76.639	1603.417	1266.943	−17.415
3900	21.194	222.963	202.768	78.759	1605.537	1258.060	−16.850
4000	21.176	223.499	203.280	80.877	1607.656	1249.124	−16.312
4100	21.160	224.022	203.779	82.994	1609.773	1240.134	−15.800
4200	21.145	224.532	204.267	85.110	1611.888	1231.093	−15.311
4300	21.130	225.029	204.744	87.223	1614.002	1222.002	−14.844
4400	21.117	225.515	205.211	89.336	1616.114	1212.861	−14.398
4500	21.104	225.989	205.667	91.447	1618.225	1203.672	−13.972
4600	21.092	226.453	206.114	93.556	1620.335	1194.437	−13.563
4700	21.080	226.906	206.552	95.665	1622.443	1185.155	−13.172
4800	21.070	227.350	206.981	97.773	1624.551	1175.829	−12.796
4900	21.059	227.784	207.401	99.879	1626.657	1166.459	−12.435
5000	21.050	228.210	207.813	101.984	1628.763	1157.046	−12.088
5100	21.040	228.626	208.217	104.089	1630.867	1147.590	−11.754
5200	21.032	229.035	208.613	106.193	1632.971	1138.094	−11.432
5300	21.023	229.435	209.002	108.295	1635.074	1128.557	−11.123
5400	21.015	229.828	209.384	110.397	1637.176	1118.980	−10.824
5500	21.008	230.214	209.759	112.498	1639.277	1109.365	−10.536
5600	21.001	230.592	210.128	114.599	1641.377	1099.711	−10.258
5700	20.994	230.964	210.490	116.699	1643.477	1090.020	−9.989
5800	20.987	231.329	210.847	118.798	1645.576	1080.292	−9.729
5900	20.981	231.688	211.197	120.896	1647.675	1070.527	−9.478
6000	20.975	232.040	211.541	122.994	1649.772	1060.728	−9.234

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

REFERENCE STATE

0	to	2350 K	crystal
2350	to	4137.895 K	liquid
above		137.895 K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−1.214	0.	0.	0.
100	1.076	0.308	12.207	−1.190	0.	0.	0.
200	5.998	2.419	6.704	−0.857	0.	0.	0.
298.15	11.315	5.834	5.834	0.	0.	0.	0.
300	11.405	5.904	5.834	0.021	0.	0.	0.
400	15.693	9.794	6.335	1.384	0.	0.	0.
500	18.722	13.644	7.415	3.115	0.	0.	0.
600	20.778	17.251	8.758	5.096	0.	0.	0.
700	22.249	20.570	10.212	7.251	0.	0.	0.
800	23.361	23.617	11.699	9.534	0.	0.	0.
900	24.245	26.421	13.181	11.915	0.	0.	0.
1000	24.978	29.014	14.637	14.378	0.	0.	0.
1100	25.606	31.425	16.055	16.908	0.	0.	0.
1200	26.161	33.677	17.430	19.496	0.	0.	0.
1300	26.663	35.792	18.762	22.138	0.	0.	0.
1400	27.125	37.785	20.051	24.828	0.	0.	0.
1500	27.557	39.671	21.296	27.562	0.	0.	0.
1600	27.966	41.463	22.501	30.338	0.	0.	0.
1700	28.356	43.170	23.667	33.155	0.	0.	0.
1800	28.732	44.801	24.796	36.009	0.	0.	0.
1900	29.097	46.365	25.891	38.901	0.	0.	0.
2000	29.452	47.866	26.952	41.828	0.	0.	0.
2100	29.799	49.312	27.983	44.791	0.	0.	0.
2200	30.140	50.706	28.984	47.788	0.	0.	0.
2300	30.475	52.053	29.958	50.819	0.	0.	0.
2350.000	30.641	52.710	30.435	52.346	BETA <--> LIQUID TRANSITION		
2350.000	31.750	74.075	30.435	102.554			
2400	31.750	74.744	31.351	104.142	0.	0.	0.
2500	31.750	76.040	33.113	107.317	0.	0.	0.
2600	31.750	77.285	34.788	110.492	0.	0.	0.
2700	31.750	78.483	36.384	113.667	0.	0.	0.
2800	31.750	79.638	37.909	116.842	0.	0.	0.
2900	31.750	80.752	39.367	120.017	0.	0.	0.
3000	31.750	81.828	40.764	123.192	0.	0.	0.
3100	31.750	82.869	42.106	126.367	0.	0.	0.
3200	31.750	83.877	43.396	129.542	0.	0.	0.
3300	31.750	84.854	44.637	132.717	0.	0.	0.
3400	31.750	85.802	45.834	135.892	0.	0.	0.
3500	31.750	86.723	46.989	139.067	0.	0.	0.
3600	31.750	87.617	48.105	142.242	0.	0.	0.
3700	31.750	88.487	49.185	145.417	0.	0.	0.
3800	31.750	89.334	50.231	148.592	0.	0.	0.
3900	31.750	90.158	51.244	151.767	0.	0.	0.
4000	31.750	90.962	52.227	154.942	0.	0.	0.
4100	31.750	91.746	53.181	158.117	0.	0.	0.
4139.449	31.750	92.050	53.550	159.369	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
4139.449	20.860	208.131	53.550	639.878			
4200	20.870	208.434	55.781	641.141	0.	0.	0.
4300	20.887	208.925	59.337	643.229	0.	0.	0.
4400	20.906	209.405	62.742	645.319	0.	0.	0.
4500	20.928	209.875	66.006	647.410	0.	0.	0.
4600	20.952	210.336	69.139	649.504	0.	0.	0.
4700	20.979	210.786	72.148	651.601	0.	0.	0.
4800	21.009	211.228	75.041	653.700	0.	0.	0.
4900	21.042	211.662	77.825	655.803	0.	0.	0.
5000	21.078	212.087	80.506	657.909	0.	0.	0.
5100	21.117	212.505	83.090	660.018	0.	0.	0.
5200	21.160	212.916	85.583	662.132	0.	0.	0.
5300	21.206	213.319	87.989	664.251	0.	0.	0.
5400	21.255	213.716	90.313	666.374	0.	0.	0.
5500	21.308	214.107	92.561	668.502	0.	0.	0.
5600	21.365	214.491	94.735	670.635	0.	0.	0.
5700	21.425	214.870	96.839	672.775	0.	0.	0.
5800	21.489	215.243	98.877	674.921	0.	0.	0.
5900	21.557	215.611	100.853	677.073	0.	0.	0.
6000	21.628	215.974	102.768	679.232	0.	0.	0.

PREVIOUS: March 1979 (1 atm) CURRENT: June 1983 (1 bar)

$S°(298.15\ K) = 5.83 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2350 \pm 50\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 50.2 \pm 1.7\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted low temperature heat capacity values ($T < 298.15$ K) are based on the heat capacity studies of Biler,[1,2] Johnston *et al.*,[3] and Bogdanov *et al.*[4] The adopted high temperature heat capacities ($T > 298.15$ K) are derived from the enthalpy studies of McDonald and Stull[5] and Stout *et al.*[6] The mathematical and graphical treatment of these five studies, providing experimental measurements in the 2–2218 K range, yield a continuous and smooth heat capacity curve. The resulting entropy, $S°(298.15\ K) = 5.83 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$, is 0.07 $J \cdot K^{-1} \cdot mol^{-1}$ less than the CODATA recommended entropy[7] due to the differing interpretation of the C_p results for T<50 K. In this analysis, the scatter in the experimental data obscures any differences that may arise in the thermal functions due to crystallographic differences in the various crystalline samples.

Biler[1,2] measured the heat capacity of B(cr, β) in the region 2–15 K. He reported $\theta_D = 1480$ K derived from his extrapolation to $T/K = 0$ of a graph of $(C_p - \gamma T)/T^3$ vs T^2. For boron, there is no electronic contribution, i.e. $\gamma = 0$. Only graphical data was presented. The sample, stated to be the β-rhombohedral modification based on X-ray data, contained 50 ppm Cu whereas the other impurities were reported as <1ppm (via electron micro-probe analysis).

Johnston *et al.*[3] measured 46 heat capacity values in the range 16.90–303.71 K. This study indicated a shallow maximum near 25 K at which temperature $C_p° = 0.038\ J \cdot K^{-1} \cdot mol^{-1}$. A graph of the results by Biler[1,2] tends to agree with the observations of Johnston *et al.*[3] and to support the presence of a C_p anomaly. The purity of Johnston's sample was not reported. Hultgren *et al.*[8] stated that the sample was of the tetragonal (α) modification. This inference is presumably based on Johnston's reported method of preparation and X-ray data.

Bogdanov *et al.*[4] measured the heat capacity from 16 to 280 K. Metallic impurity content was stated to be <0.01 %. X-ray analysis was used to infer that the sample was the β-polymorph. Bogdanov *et al.* also inferred that the sample of Johnston *et al.* was not of a specific crystalline modification. They surmised that impurities caused the shallow maximum seen by Johnston *et al.*[3] near 25 K. Bogdanov *et al.* found no maximum, but their smooth values level out below 40 K in contradiction to theory. Their last five values (20–40 K) vary linearly with T and extrapolate to $C_p = 0.0126\ J \cdot K^{-1} \cdot mol^{-1}$ at $T/K = 0$. The authors did not publish their experimental data, so it is difficult to interpret this behavior. It may arise from bias of their calorimeter near its limit of sensitivity or from anomalous behavior of their sample.

McDonald and Stull[5] measured enthalpies in a copper block drop calorimeter, 20 points in the range 282.8 to 1667.8 K. The sample was reported to be the β-rhombohedral form (based on X-ray data) with a metallic impurity of 0.59%. Stout *et al.*,[6] also using a copper block drop calorimeter, measured enthalpies, five data points in the range 1820–2218 K. The sample was reported to have 0.04% metallic impurities and to contain 300 ppm O and 6300 ppm C. No information as to crystalline form was given. Wise *et al.*[9] measured the enthalpy of two crystalline boron samples (each reportedly containing some of the β-modification) in the temperature range 515–1103 K.

The adopted heat capacity values below 25 K are derived from the θ_D value of Biler.[1,2] From 25 K to 300 K, the derived values are a compromise of the data of Johnston *et al.*[3] and Bogdanov *et al.*,[4] but excluding in each the effect of the possible anomalous behavior. In the region 25 to 95 K, there is large scatter in each data set, so that large deviations occur, up to 23%. In the region 95–300 K, Johnston's data shows deviations of −2.1 to +1.8% while Bogdanov's data shows derviations of −2.9 to +1.7% from the adopted values. The two sets of data are intertwined, one is not always above the other.

In the enthalpy data, 26 of the 30 points of McDonald and Stull[5] are within +0.6% to −0.5%. Stout's[6] data deviates from −0.7% at 1819.5 K to +0.7% at 2217.7 K. The data of McDonald and Stull and Stout *et al.* are slightly skewed to each other. The observed enthalpies of McDonald and Stull[5] fall between the enthalpies of the two samples measured by Wise *et al.*[9]

Other heat capacity and enthalpy studies are available but were excluded from this analysis. A detailed discussion of the Group IIIA metals (B, Al, and Ga) is in preparation by the JANAF staff.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The adopted value of $\Delta_{sub} H°(298.15\ K)$ is the value recommended by CODATA.[7] See the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−1.214	0.	0.	0.
100	1.076	0.308	12.207	−1.190	0.	0.	0.
200	5.998	2.419	6.704	−0.857	0.	0.	0.
250	8.821	4.063	6.007	−0.486	0.	0.	0.
298.15	11.315	5.834	5.834	0.	0.	0.	0.
300	11.405	5.904	5.834	0.021	0.	0.	0.
350	13.654	7.834	5.981	0.648	0.	0.	0.
400	15.693	9.794	6.335	1.384	0.	0.	0.
450	17.361	11.742	6.828	2.211	0.	0.	0.
500	18.722	13.644	7.415	3.115	0.	0.	0.
600	20.778	17.251	8.758	5.096	0.	0.	0.
700	22.249	20.570	10.212	7.251	0.	0.	0.
800	23.361	23.617	11.699	9.534	0.	0.	0.
900	24.245	26.421	13.181	11.915	0.	0.	0.
1000	24.978	29.014	14.637	14.378	0.	0.	0.
1100	25.606	31.425	16.055	16.908	0.	0.	0.
1200	26.161	33.677	17.430	19.496	0.	0.	0.
1300	26.663	35.792	18.762	22.138	0.	0.	0.
1400	27.125	37.785	20.051	24.828	0.	0.	0.
1500	27.557	39.671	21.296	27.562	0.	0.	0.
1600	27.966	41.463	22.501	30.338	0.	0.	0.
1700	28.356	43.170	23.667	33.155	0.	0.	0.
1800	28.732	44.801	24.796	36.009	0.	0.	0.
1900	29.097	46.365	25.891	38.901	0.	0.	0.
2000	29.452	47.866	26.952	41.828	0.	0.	0.
2100	29.799	49.312	27.983	44.791	0.	0.	0.
2200	30.140	50.706	28.984	47.788	0.	0.	0.
2300	30.475	52.053	29.958	50.819	0.	0.	0.
2350.000	30.641	52.710	30.435	52.346	---- BETA <--> LIQUID ----		
2400	30.806	53.357	30.906	53.883	−50.259	1.069	−0.023
2500	31.133	54.621	31.829	56.980	−50.337	3.209	−0.067
2600	31.457	55.848	32.730	60.109	−50.383	5.352	−0.108
2700	31.778	57.042	33.608	63.271	−50.396	7.496	−0.145
2800	32.096	58.203	34.466	66.465	−50.377	9.640	−0.180

PREVIOUS: March 1979 CURRENT: June 1983

$S°(298.15\ K) = [26.555]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2350 \pm 50\ K$

$\Delta_f H°(298.15\ K) = [48.927]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 50.2 \pm 1.7\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of liquid boron is calculated from that of the crystal (β–rhomohedral) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2350\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

There are no heat capacity or enthalpy studies which adequately define the liquid phase heat capacity values. Tsagareishvili and Tsagareishvili[1] estimated $C_p°(l) = 39.04\ J·K^{-1}·mol^{-1}$ at T_{fus} by means of quasi–thermodynamic correlations. Using our adopted $C_p°$ value for the crystal at T_{fus}, we recalculate this to be $C_p°(l) = 35.98\ J·K^{-1}·mol^{-1}$ at T_{fus}. This value appears to be too large. Even though B(cr) and Al(cr) have different crystal structures, the heat capacity values of the crystals at their respective T_{fus} are very similar, $30.64\ J·K^{-1}·mol^{-1}$ for B(β–cr) and $32.96\ J·K^{-1}·mol^{-1}$ for Al(cr). We estimate that the B(l) heat capacity is $31.75\ J·K^{-1}·mol^{-1}$, as is the value for Al(l).

A glass transition is assumed at 1760 K. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted value for the melting point of β–rhombohedral boron is $T_{fus} = 2350 \pm 50$ K. This value is within 2 K of the value recommended by Charlesworth.[2] The value is based primarily on the work of Kimpel and Moss.[3] These authors[3] used a disappearing hole technique to measure $T_{fus} = 2352 \pm 20$ K for a 99.5% pure sample. Other studies are by Wisnyi and Pijanowski[4] (2313 ± 30 K), Cueilleron[5] (2273–2348 K), and Mar[6] (2315 ± 20 K).

The enthalpy of melting was measured by Stout et al.[7] using drop calorimetry. The enthalpy of melting, $\Delta_{fus}H° = 50.2 \pm 1.7\ kJ·mol^{-1}$, was the result of three calorimetric determinations involving different samples and containers. It leads to an entropy of fusion, $\Delta_{fus}S° = 21.4\ J·K^{-1}·mol^{-1}$, which is more than twice as large as previous estimates.

Vaporization Data

There are no vaporization studies involving liquid boron. The boiling point, T_{vap}(1 bar) = 4137.895 K, is calculated as the temperature for which $\Delta_f G°=0$ for B(l)=B(g). The difference in the enthalpy of formation of B(l) and B(g) at T_{vap} is the enthalpy of vaporization, $\Delta_{vap}H° = 480.344\ kJ·mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	11.315	26.555	26.555	0.	48.927	42.749	−7.490
300	11.405	26.625	26.555	0.021	48.927	42.711	−7.437
350	13.654	28.554	26.702	0.648	48.927	41.675	−6.220
400	15.693	30.515	27.056	1.384	48.927	40.639	−5.307
450	17.361	32.463	27.549	2.211	48.927	39.603	−4.597
500	18.722	34.365	28.136	3.115	48.927	38.567	−4.029
600	20.778	37.971	29.479	5.096	48.927	36.495	−3.177
700	22.249	41.291	30.932	7.251	48.927	34.423	−2.569
800	23.361	44.337	32.420	9.534	48.927	32.351	−2.112
900	24.245	47.142	33.902	11.915	48.927	30.279	−1.757
1000	24.978	49.735	35.357	14.378	48.927	28.207	−1.473
1100	25.606	52.146	36.775	16.908	48.927	26.135	−1.241
1200	26.161	54.398	38.151	19.496	48.927	24.062	−1.047
1300	26.663	56.512	39.483	22.138	48.927	21.990	−0.884
1400	27.125	58.505	40.771	24.828	48.927	19.918	−0.743
1500	27.557	60.392	42.017	27.562	48.927	17.846	−0.621
1600	27.966	62.183	43.222	30.338	48.927	15.774	−0.515
1700	28.356	63.891	44.388	33.155	48.927	13.702	−0.421
1750.000	28.546	64.715	44.957	34.577	GLASS <--> LIQUID TRANSITION		
1750.000	31.750	64.715	44.957	34.577			
1800	31.750	65.610	45.518	36.165	49.083	11.628	−0.337
1900	31.750	67.326	46.621	39.340	49.366	9.539	−0.262
2000	31.750	68.955	47.698	42.515	49.614	7.436	−0.194
2100	31.750	70.504	48.747	45.690	49.826	5.322	−0.132
2200	31.750	71.981	49.770	48.865	50.004	3.199	−0.076
2300	31.750	73.392	50.766	52.040	50.148	1.068	−0.024
2350.000	31.750	74.075	51.255	53.627	BETA <--> LIQUID		
2400	31.750	74.744	51.737	55.215	0.	0.	0.
2500	31.750	76.040	52.684	58.390	0.	0.	0.
2600	31.750	77.285	53.606	61.565	0.	0.	0.
2700	31.750	78.483	54.506	64.740	0.	0.	0.
2800	31.750	79.638	55.383	67.915	0.	0.	0.
2900	31.750	80.752	56.238	71.090	0.	0.	0.
3000	31.750	81.828	57.074	74.265	0.	0.	0.
3100	31.750	82.869	57.889	77.440	0.	0.	0.
3200	31.750	83.877	58.685	80.615	0.	0.	0.
3300	31.750	84.854	59.464	83.790	0.	0.	0.
3400	31.750	85.802	60.224	86.965	0.	0.	0.
3500	31.750	86.723	60.968	90.140	0.	0.	0.
3600	31.750	87.617	61.696	93.315	0.	0.	0.
3700	31.750	88.487	62.409	96.490	0.	0.	0.
3800	31.750	89.334	63.106	99.665	0.	0.	0.
3900	31.750	90.158	63.789	102.840	0.	0.	0.
4000	31.750	90.962	64.459	106.015	0.	0.	0.
4100	31.750	91.746	65.115	109.190	0.	0.	0.
4139.449	31.750	92.050	65.370	110.442	FUGACITY = 1 bar		
4200	31.750	92.511	65.758	112.365	−479.849	7.024	−0.087
4300	31.750	93.258	66.389	115.540	−478.762	18.603	−0.226
4400	31.750	93.988	67.008	118.715	−477.677	30.158	−0.358
4500	31.750	94.702	67.615	121.890	−476.593	41.687	−0.484

PREVIOUS: March 1979 CURRENT: June 1983

0 to 2350 K crystal
above 2350 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−1.214	0.	0.	0.
100	1.076	0.308	12.207	−1.190	0.	0.	0.
200	5.998	2.419	6.704	−0.857	0.	0.	0.
250	8.821	4.063	6.007	−0.486	0.	0.	0.
298.15	11.315	5.834	5.834	0.	0.	0.	0.
300	11.405	5.904	5.834	0.021	0.	0.	0.
350	13.654	7.834	5.981	0.648	0.	0.	0.
400	15.693	9.794	6.335	1.384	0.	0.	0.
450	17.361	11.742	6.828	2.211	0.	0.	0.
500	18.722	13.644	7.415	3.115	0.	0.	0.
600	20.778	17.251	8.758	5.096	0.	0.	0.
700	22.249	20.570	10.212	7.251	0.	0.	0.
800	23.361	23.617	11.699	9.534	0.	0.	0.
900	24.245	26.421	13.181	11.915	0.	0.	0.
1000	24.978	29.014	14.637	14.378	0.	0.	0.
1100	25.606	31.425	16.055	16.908	0.	0.	0.
1200	26.161	33.677	17.430	19.496	0.	0.	0.
1300	26.663	35.792	18.762	22.138	0.	0.	0.
1400	27.125	37.785	20.051	24.828	0.	0.	0.
1500	27.557	39.671	21.296	27.562	0.	0.	0.
1600	27.966	41.463	22.501	30.338	0.	0.	0.
1700	28.356	43.170	23.667	33.155	0.	0.	0.
1800	28.732	44.801	24.796	36.009	0.	0.	0.
1900	29.097	46.365	25.891	38.901	0.	0.	0.
2000	29.452	47.866	26.952	41.828	0.	0.	0.
2100	29.799	49.312	27.983	44.791	0.	0.	0.
2200	30.140	50.706	28.984	47.788	0.	0.	0.
2300	30.475	52.053	29.958	50.819	0.	0.	0.
2350.000	30.641	52.710	30.435	52.346	BETA <--> LIQUID TRANSITION		
2350.000	31.750	74.075	30.435	102.554			
2400	31.750	74.744	31.351	104.142	0.	0.	0.
2500	31.750	76.040	33.113	107.317	0.	0.	0.
2600	31.750	77.285	34.788	110.492	0.	0.	0.
2700	31.750	78.483	36.384	113.667	0.	0.	0.
2800	31.750	79.638	37.909	116.842	0.	0.	0.
2900	31.750	80.752	39.367	120.017	0.	0.	0.
3000	31.750	81.828	40.764	123.192	0.	0.	0.
3100	31.750	82.869	42.106	126.367	0.	0.	0.
3200	31.750	83.877	43.396	129.542	0.	0.	0.
3300	31.750	84.854	44.637	132.717	0.	0.	0.
3400	31.750	85.802	45.834	135.892	0.	0.	0.
3500	31.750	86.723	46.989	139.067	0.	0.	0.
3600	31.750	87.617	48.105	142.242	0.	0.	0.
3700	31.750	88.487	49.185	145.417	0.	0.	0.
3800	31.750	89.334	50.231	148.592	0.	0.	0.
3900	31.750	90.158	51.244	151.767	0.	0.	0.
4000	31.750	90.962	52.227	154.942	0.	0.	0.
4100	31.750	91.746	53.181	158.117	0.	0.	0.
4139.449	31.750	92.050	53.550	159.369	FUGACITY = 1 bar		
4200	31.750	92.511	54.109	161.292	−479.849	7.024	−0.087
4300	31.750	93.258	55.010	164.467	−478.762	18.604	−0.226
4400	31.750	93.988	55.888	167.642	−477.677	30.158	−0.358
4500	31.750	94.702	56.743	170.817	−476.593	41.687	−0.484

PREVIOUS: March 1979 CURRENT: June 1983

IP(B, g) = 66928.10 ± 1 cm^{-1}
$S°$(298.15 K) = 153.435 ± 0.035 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 555 ± 12 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 560 ± 12 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P°_{1/2}$	0.00	2
$^2P°_{3/2}$	15.254	4
$^4P_{1/2}$	28870.0	2
.	.	.
.	.	.
.	.	.
$^2D_{5/2}$	66855.78	6
IP	66928.10	

Enthalpy of Formation

The enthalpy of formation is derived from the measurements of Paule and Margrave,[1] Robson and Gilles,[2] Hildenbrand and Hall,[3] Akishin *et al.*,[4] and Schissel and Trulson.[5] $\Delta_f H°$(B, g, 298.15 K) = 560 ± 12 $kJ·mol^{-1}$ is the value recommended by CODATA.[6] CODATA stated that these measurements were selected from the many sets of data available as being the most self-consistent. The difference in $S°$(B, cr, 298.15 K) between our adopted value and that of CODATA,[6] will create a change of less than 0.2 $kJ·mol^{-1}$ in $\Delta_f H°$(B, g, 298.15 K). Not included in this analysis are other vaporization studies by Trulson *et al.* (1923–2249 K),[7] Burns *et al.* (2403 K),[8] Mar and Bedford (1823–2253 K),[9] and Storms and Mueller (1750–2050 K).[10] The two latter studies were published after the time of the CODATA analysis. Inclusion of these studies would suggest a somewhat larger value for $\Delta_f H$. The $\Delta_f H°$(B, g, 298.15 K) values reported by Mar and Bedford[9] are 563.6 ± 33.4 $kJ·mol^{-1}$ (2nd law) and 561.1 ± 3.3 $kJ·mol^{-1}$ (3rd law) from torsion data and 566.1 ± 13.3 $kJ·mol^{-1}$ from mass spectrometric data; Storms and Mueller[10] reported 574.9 ± 0.8 $kJ·mol^{-1}$ as the 2nd law value derived from a mass spectrometric study.

Heat Capacity and Entropy

The electronic levels are from the recent analysis by Odintzova and Striganov.[11] Although only the ground state, first two excited states, and the highest observed state (below the ionization limit) are listed, all reported states below the ionization limit are used in the calculations. The 164 observed levels are too numerous to list completely, but do include contributions from observed levels to n=39.

The level at 15.254 cm^{-1} has a large effect on the heat capacity and entropy below 100 K. The heat capacity effect decreases to zero above 600 K where the 15.254 cm^{-1} level is fully populated. The higher excited states affect the heat capacity values above 3000 K. The Gibbs energy function values up to 6000 K are essentially independent of the cut–off procedure, the inclusion of levels for n>2, and the estimated missing levels (for n<39).

The thermal functions at 298.15 K agree with recent CODATA recommendations[1] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, an entropy difference of 0.001 $J·K^{-1}·mol^{-1}$ arises due to the use of slightly different values for the fundamental constants.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.316	554.898	554.898	INFINITE
100	20.881	130.687	171.936	−4.125	557.065	544.027	−284.171
200	20.809	145.130	155.338	−2.042	558.815	530.273	−138.493
250	20.801	149.772	153.778	−1.001	559.485	523.057	−109.287
298.15	20.796	153.435	153.435	0.	560.000	515.993	−90.400
300	20.796	153.564	153.436	0.038	560.017	515.720	−89.795
350	20.793	156.769	153.689	1.078	560.430	508.302	−75.860
400	20.792	159.546	154.251	2.118	560.734	500.834	−65.402
450	20.790	161.995	154.978	3.157	560.946	493.332	−57.265
500	20.790	164.185	155.791	4.197	561.082	485.812	−50.752
600	20.789	167.975	157.516	6.276	561.180	470.745	−40.982
700	20.788	171.180	159.245	8.355	561.104	455.677	−34.003
800	20.787	173.956	160.914	10.433	560.900	440.628	−28.770
900	20.787	176.404	162.502	12.512	560.597	425.612	−24.702
1000	20.787	178.594	164.003	14.591	560.213	410.633	−21.449
1100	20.787	180.575	165.421	16.669	559.762	395.697	−18.790
1200	20.787	182.384	166.761	18.748	559.252	380.804	−16.576
1300	20.787	184.048	168.027	20.827	558.689	365.955	−14.704
1400	20.786	185.588	169.227	22.905	558.078	351.152	−13.102
1500	20.786	187.023	170.366	24.984	557.422	336.395	−11.714
1600	20.786	188.364	171.450	27.063	556.724	321.682	−10.502
1700	20.786	189.624	172.482	29.141	555.987	307.014	−9.433
1800	20.786	190.812	173.468	31.220	555.211	292.391	−8.485
1900	20.786	191.936	174.411	33.299	554.398	277.812	−7.638
2000	20.786	193.002	175.314	35.377	553.549	263.277	−6.876
2100	20.786	194.017	176.180	37.456	552.665	248.785	−6.188
2200	20.786	194.984	177.013	39.535	551.747	234.335	−5.564
2300	20.786	195.908	177.815	41.613	550.795	219.929	−4.995
2400	20.786	196.792	178.587	43.692	499.550	206.633	−4.497
2500	20.786	197.641	179.333	45.770	498.453	194.451	−4.063
2600	20.787	198.456	180.052	47.849	497.357	182.312	−3.663
2700	20.787	199.240	180.749	49.928	496.261	170.216	−3.293
2800	20.787	199.996	181.423	52.006	495.165	158.160	−2.951
2900	20.788	200.726	182.076	54.085	494.068	146.144	−2.632
3000	20.789	201.431	182.709	56.164	492.972	134.165	−2.336
3100	20.791	202.112	183.324	58.243	491.876	122.223	−2.059
3200	20.793	202.772	183.922	60.322	490.780	110.316	−1.801
3300	20.795	203.412	184.503	62.402	489.685	98.444	−1.558
3400	20.798	204.033	185.068	64.481	488.589	86.604	−1.331
3500	20.803	204.636	185.619	66.561	487.494	74.797	−1.116
3600	20.808	205.222	186.155	68.642	486.400	63.021	−0.914
3700	20.814	205.792	186.678	70.723	485.306	51.276	−0.724
3800	20.822	206.348	187.188	72.805	484.213	39.560	−0.544
3900	20.831	206.889	187.687	74.887	483.120	27.873	−0.373
4000	20.842	207.416	188.173	76.971	482.029	16.214	−0.212
4100	20.855	207.931	188.649	79.056	480.939	4.582	−0.058
4139.449	20.860	208.131	188.834	79.879	----- FUGACITY = 1 bar -----		
4200	20.870	208.434	189.114	81.142	0.	0.	0.
4300	20.887	208.925	189.569	83.230	0.	0.	0.
4400	20.906	209.405	190.015	85.319	0.	0.	0.
4500	20.928	209.875	190.451	87.411	0.	0.	0.
4600	20.952	210.336	190.878	89.505	0.	0.	0.
4700	20.979	210.786	191.297	91.602	0.	0.	0.
4800	21.009	211.228	191.707	93.701	0.	0.	0.
4900	21.042	211.662	192.110	95.803	0.	0.	0.
5000	21.078	212.087	192.506	97.909	0.	0.	0.
5100	21.117	212.505	192.894	100.019	0.	0.	0.
5200	21.160	212.916	193.275	102.133	0.	0.	0.
5300	21.206	213.319	193.649	104.251	0.	0.	0.
5400	21.255	213.716	194.017	106.374	0.	0.	0.
5500	21.308	214.107	194.379	108.502	0.	0.	0.
5600	21.365	214.491	194.735	110.636	0.	0.	0.
5700	21.425	214.870	195.084	112.776	0.	0.	0.
5800	21.489	215.243	195.429	114.921	0.	0.	0.
5900	21.557	215.611	195.768	117.073	0.	0.	0.
6000	21.628	215.974	196.101	119.233	0.	0.	0.

PREVIOUS: March 1979 (1 atm) CURRENT: June 1983 (1 bar)

$IP(B^+, g) = 202887.4 \pm 0.8$ cm^{-1}
$S°(298.15\ K) = 138.542 \pm 0.04$ J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = 1356 \pm 12$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = [1366.717]$ kJ·mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_0$	0.0	1
$^3P_0$	37333.6	1
$^3P_1$	37340.0	3
$^3P_2$	37356.4	5

Enthalpy of Formation

$\Delta_f H°(B^+, g, 0\ K)$ is calculated from $\Delta_f H°(B, g, 0\ K)$[1] using the spectroscopic value of IP(B) = 66928.10 ± 0.1 cm^{-1} (800.638 ± 0.001 kJ·mol^{-1}) from Odintzova and Striganov.[2] The ionization limit is converted from cm^{-1} to kJ·mol^{-1} using the factor, 1 cm^{-1} = 0.01196266 kJ·mol^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(B^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(B, g, 0\ K)$ by using IP(B) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for B(g), B^+(g), and e^-(ref). $\Delta_f H°(B \rightarrow B^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6,7] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[8] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first three excited states; the next excited state is 73396.7 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first three excited states. The energies of the ^3P levels are uncertain by 249 cm^{-1}. No intersystem combinations have been observed. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[8]

Refereces

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	1355.536		
100	20.786	115.835	157.023	−4.119			
200	20.786	130.243	140.444	−2.040			
250	20.786	134.881	138.885	−1.001			
298.15	20.786	138.542	138.542	0.	1366.717	1320.895	−231.415
300	20.786	138.671	138.543	0.038	1366.773	1320.611	−229.939
350	20.786	141.875	138.796	1.078	1368.224	1312.801	−195.925
400	20.786	144.651	139.358	2.117	1369.567	1304.790	−170.388
450	20.786	147.099	140.085	3.156	1370.818	1296.617	−150.507
500	20.786	149.289	140.898	4.196	1371.994	1288.309	−134.589
600	20.786	153.079	142.622	6.274	1374.170	1271.364	−110.682
700	20.786	156.283	144.350	8.353	1376.172	1254.069	−93.580
800	20.786	159.058	146.019	10.431	1378.046	1236.497	−80.735
900	20.786	161.507	147.607	12.510	1379.822	1218.696	−70.731
1000	20.786	163.697	149.108	14.589	1381.517	1200.701	−62.718
1100	20.786	165.678	150.526	16.667	1383.144	1182.540	−56.154
1200	20.786	167.486	151.865	18.746	1384.712	1164.234	−50.678
1300	20.786	169.150	153.131	20.824	1386.228	1145.799	−46.039
1400	20.786	170.691	154.331	22.903	1387.695	1127.249	−42.058
1500	20.786	172.125	155.470	24.982	1389.118	1108.596	−38.605
1600	20.786	173.466	156.553	27.060	1390.499	1089.849	−35.580
1700	20.786	174.726	157.586	29.139	1391.840	1071.017	−32.908
1800	20.786	175.914	158.571	31.217	1393.143	1052.108	−30.531
1900	20.786	177.038	159.514	33.296	1394.408	1033.127	−28.403
2000	20.786	178.104	160.417	35.375	1395.638	1014.080	−26.485
2100	20.786	179.119	161.284	37.453	1396.833	994.972	−24.749
2200	20.786	180.086	162.117	39.532	1397.993	975.809	−23.169
2300	20.786	181.010	162.918	41.610	1399.119	956.593	−21.725
2400	20.786	181.894	163.690	43.689	1349.953	938.398	−20.424
2500	20.786	182.743	164.436	45.768	1350.935	921.230	−19.248
2600	20.786	183.558	165.156	47.846	1351.917	904.023	−18.162
2700	20.786	184.342	165.852	49.925	1352.900	886.777	−17.156
2800	20.786	185.098	166.526	52.004	1353.882	869.495	−16.221
2900	20.786	185.828	167.179	54.082	1354.864	852.179	−15.349
3000	20.786	186.532	167.812	56.161	1355.846	834.828	−14.536
3100	20.787	187.214	168.427	58.239	1356.829	817.444	−13.774
3200	20.787	187.874	169.025	60.318	1357.811	800.029	−13.059
3300	20.788	188.514	169.606	62.397	1358.793	782.583	−12.387
3400	20.789	189.134	170.171	64.476	1359.776	765.108	−11.754
3500	20.790	189.737	170.721	66.555	1360.758	747.603	−11.157
3600	20.792	190.323	171.258	68.634	1361.741	730.070	−10.593
3700	20.794	190.892	171.781	70.713	1362.724	712.511	−10.059
3800	20.797	191.447	172.291	72.792	1363.707	694.924	−9.552
3900	20.801	191.987	172.789	74.872	1364.690	677.312	−9.072
4000	20.806	192.514	173.276	76.953	1365.674	659.674	−8.614
4100	20.812	193.028	173.751	79.034	1366.659	642.012	−8.179
4200	20.820	193.529	174.216	81.115	887.795	631.350	−7.852
4300	20.830	194.019	174.671	83.198	889.868	625.219	−7.595
4400	20.841	194.498	175.116	85.281	891.940	619.041	−7.349
4500	20.856	194.967	175.552	87.366	894.012	612.815	−7.113
4600	20.872	195.425	175.979	89.452	896.083	606.544	−6.888
4700	20.892	195.874	176.398	91.540	898.153	600.227	−6.671
4800	20.915	196.314	176.808	93.631	900.223	593.866	−6.463
4900	20.941	196.746	177.211	95.724	902.292	587.462	−6.262
5000	20.972	197.169	177.606	97.819	904.360	581.016	−6.070
5100	21.006	197.585	177.993	99.918	906.428	574.529	−5.884
5200	21.046	197.993	178.374	102.021	908.495	568.001	−5.706
5300	21.090	198.395	178.748	104.127	910.562	561.433	−5.533
5400	21.139	198.789	179.115	106.239	912.629	554.827	−5.367
5500	21.194	199.178	179.477	108.355	914.696	548.182	−5.206
5600	21.254	199.560	179.832	110.478	916.764	541.499	−5.051
5700	21.321	199.937	180.181	112.606	918.831	534.779	−4.901
5800	21.393	200.308	180.525	114.742	920.900	528.024	−4.755
5900	21.473	200.675	180.864	116.885	922.970	521.232	−4.615
6000	21.558	201.036	181.197	119.037	925.040	514.406	−4.478

PREVIOUS: March 1979 (1 atm) CURRENT: June 1983 (1 bar)

EA(B, g) = 0.277 ± 0.010 eV
$S°(298.15\ K) = 156.811 \pm 0.005\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 528 \pm 12\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [527.033]\ kJ \cdot mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0.0	1
$^3P_1$	4.0	3
$^3P_2$	9.0	5

Enthalpy of Formation

$\Delta_f H°(B^-, g, 0\ K)$ is calculated from $\Delta_f H°(B, g, 0\ K)$[1] using the adopted election affinity of EA(B) = 0.277 ± 0.010 eV (26.726 ± 0.965 $kJ \cdot mol^{-1}$). This value, recommended by Hotop and Lineberger[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on B^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(B^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(B, g, 0\ K)$ by using EA(B) with JANAF [1]enthalpies, $H°(0\ K) - H°(298.15\ K)$, for B^-(g), B(g), and e^-(ref). $\Delta_r H°(B^- \rightarrow B + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for B^-(g) is given by Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6] The fine-structure separation has been calculated via an isoelectronic extrapolation of ratios of fine structure separations[4] and is that recommended by Hotop and Lineberger.[2]

A comparison of the isoelectronic sequence B^-(g), C(g), N^+(g), O^{++}(g) would suggest that a state, $^1D_2$, may exist at low energy, 5000 cm^{-1}. However, this is most likely a metastable state lying at an energy greater than the electron affinity. As discussed by Hotop and Lineberger,[2,4] no stable excited states have been observed. Thus we assume no stable excited states exist.

References

[1]JANAF Thermochemical Tables: B(g), 6-30-83; e^-(ref), 3-31-82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731, (1985).
[3]C. S. Feigerle, R. R. Corderman and W. C. Lineberger, J. Chem. Phys. **74**, 1513 (1981).
[4]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[5]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[6]H. S. W. Massey, "Negative Ions", 3rd ed., Cambridge University Press, Cambridge, 741 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.273	528.172		
100	20.804	134.096	175.295	−4.120			
200	20.790	148.511	158.713	−2.040			
250	20.789	153.150	157.153	−1.001			
298.15	20.788	156.811	156.811	0.	527.033	488.274	−85.544
300	20.788	156.940	156.812	0.038	527.012	488.034	−84.974
350	20.787	160.144	157.065	1.078	526.385	481.585	−71.873
400	20.787	162.920	157.627	2.117	525.650	475.234	−62.059
450	20.787	165.368	158.354	3.157	524.822	468.981	−54.438
500	20.787	167.558	159.167	4.196	523.919	462.824	−48.351
600	20.787	171.348	160.891	6.275	521.938	450.788	−39.245
700	20.786	174.553	162.619	8.353	519.783	439.098	−32.766
800	20.786	177.328	164.288	10.432	517.500	427.726	−27.928
900	20.786	179.776	165.876	12.510	515.118	416.647	−24.182
1000	20.786	181.966	167.377	14.589	512.656	405.837	−21.199
1100	20.786	183.948	168.795	16.668	510.126	395.277	−18.770
1200	20.786	185.756	170.134	18.746	507.537	384.950	−16.756
1300	20.786	187.420	171.401	20.825	504.896	374.841	−15.061
1400	20.786	188.960	172.601	22.904	502.206	364.938	−13.616
1500	20.786	190.395	173.740	24.982	499.472	355.228	−12.370
1600	20.786	191.736	174.823	27.061	496.695	345.702	−11.286
1700	20.786	192.996	175.855	29.139	493.879	336.351	−10.335
1800	20.786	194.184	176.841	31.218	491.025	327.167	−9.494
1900	20.786	195.308	177.784	33.297	488.133	318.142	−8.746
2000	20.786	196.374	178.687	35.375	485.206	309.271	−8.077
2100	20.786	197.388	179.553	37.454	482.243	300.547	−7.476
2200	20.786	198.355	180.386	39.532	479.246	291.965	−6.932
2300	20.786	199.279	181.188	41.611	476.215	283.520	−6.439
2400	20.786	200.164	181.960	43.690	422.892	276.276	−6.013
2500	20.786	201.013	182.705	45.768	419.717	270.232	−5.646
2600	20.786	201.828	183.425	47.847	416.542	264.315	−5.310
2700	20.786	202.612	184.121	49.925	413.367	258.521	−5.001
2800	20.786	203.368	184.795	52.004	410.192	252.844	−4.717
2900	20.786	204.098	185.448	54.083	407.017	247.280	−4.454
3000	20.786	204.802	186.082	56.161	403.842	241.826	−4.211
3100	20.786	205.484	186.697	58.240	400.667	236.478	−3.985
3200	20.786	206.144	187.294	60.318	397.492	231.232	−3.774
3300	20.786	206.783	187.875	62.397	394.317	226.086	−3.579
3400	20.786	207.404	188.441	64.476	391.142	221.036	−3.396
3500	20.786	208.007	188.991	66.554	387.967	216.079	−3.225
3600	20.786	208.592	189.527	68.633	384.792	211.213	−3.065
3700	20.786	209.162	190.050	70.711	381.617	206.435	−2.914
3800	20.786	209.716	190.561	72.790	378.442	201.743	−2.773
3900	20.786	210.256	191.059	74.869	375.267	197.134	−2.640
4000	20.786	210.782	191.545	76.947	372.092	192.607	−2.515
4100	20.786	211.295	192.021	79.026	368.917	188.159	−2.397
4200	20.786	211.796	192.486	81.104	−114.108	190.813	−2.373
4300	20.786	212.285	192.940	83.183	−116.195	198.097	−2.406
4400	20.786	212.763	193.386	85.262	−118.285	205.431	−2.439
4500	20.786	213.230	193.821	87.340	−120.377	212.811	−2.470
4600	20.786	213.687	194.248	89.419	−122.471	220.239	−2.501
4700	20.786	214.134	194.667	91.498	−124.567	227.712	−2.531
4800	20.786	214.572	195.077	93.576	−126.666	235.229	−2.560
4900	20.786	215.000	195.479	95.655	−128.769	242.790	−2.588
5000	20.786	215.420	195.874	97.733	−130.875	250.395	−2.616
5100	20.786	215.832	196.261	99.812	−132.985	258.041	−2.643
5200	20.786	216.236	196.641	101.891	−135.099	265.729	−2.669
5300	20.786	216.632	197.015	103.969	−137.217	273.457	−2.695
5400	20.786	217.020	197.382	106.048	−139.340	281.225	−2.720
5500	20.786	217.401	197.742	108.126	−141.468	289.033	−2.745
5600	20.786	217.776	198.097	110.205	−143.602	296.880	−2.769
5700	20.786	218.144	198.445	112.284	−145.741	304.765	−2.793
5800	20.786	218.505	198.788	114.362	−147.887	312.687	−2.816
5900	20.786	218.861	199.125	116.441	−150.039	320.646	−2.839
6000	20.786	219.210	199.457	118.519	−152.198	328.642	−2.861

PREVIOUS: March 1979 (1 atm) CURRENT: June 1983 (1 bar)

$S°(298.15\ K)$ = [265.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -481.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -482.0\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[2000](1)	[600](1)
[1000](1)	[400](1)
[900](1)	[800](1)

Ground State Quantum Weight: [2] σ = [1]
Point Group: [C_s]
Bond Distances: Be–O = [1.40] Å; O–B = [1.36] Å; B=O = [1.20] Å
Bond Angles: Be–O–B = [120]°; O–B = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.451196 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

Since Blackburn and Buchler[1] have postulated that the BO_2^- group has the pseudochloride character in bond strength, the enthalpy of formation of $BeBO_2(g)$ is estimated by adding the difference of the enthalpies of formation of BeCl(g) and AlCl(g) to the enthalpies of formation of $AlBO_2(g)$, using all JANAF values: $\Delta_f H°$(BeCl, g, 298.15 K) = 3.0, $\Delta_f H°$(AlCl, g, 298.15 K) = −11.2 and $\Delta_f H°$($AlBO_2$, g, 298.15 K) = −129.4 $kcal·mol^{-1}$.

Heat Capacity and Entropy

All molecular constants are estimated by comparison with those in $LiBO_2(g)$, $AlBO_2(g)$, $B_2O_3(g)$ and BeCl(g). The principal moments of inertia are $I_A = 1.1016 \times 10^{-39}$, $I_B = 14.3762 \times 10^{-39}$ and $I_C = 15.4778 \times 10^{-39}$ $g·cm^2$.

Reference

[1]P. E. Blackburn and A. Buchler, J. Phys. Chem. **69**, 4250 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.594	−481.761	−481.761	INFINITE
100	34.261	221.501	304.015	−8.251	−481.387	−486.125	253.926
200	41.473	247.191	269.710	−4.504	−481.461	−490.883	128.206
250	46.006	256.932	266.199	−2.317	−481.694	−493.214	103.051
298.15	50.168	265.396	265.396	0.	−481.997	−495.406	86.793
300	50.320	265.707	265.397	0.093	−482.010	−495.489	86.272
350	54.165	273.759	266.024	2.707	−482.377	−497.707	74.279
400	57.492	281.215	267.463	5.501	−482.778	−499.870	65.276
450	60.347	288.155	269.381	8.449	−483.201	−501.982	58.269
500	62.797	294.644	271.586	11.529	−483.642	−504.045	52.657
600	66.738	306.459	276.434	18.015	−484.564	−508.040	44.229
700	69.721	316.981	281.488	24.845	−485.535	−511.876	38.197
800	72.017	326.447	286.527	31.936	−486.560	−515.570	33.663
900	73.810	335.037	291.447	39.231	−487.645	−519.132	30.130
1000	75.228	342.890	296.204	46.686	−488.797	−522.569	27.296
1100	76.363	350.115	300.781	54.267	−490.026	−525.888	24.972
1200	77.282	356.800	305.174	61.951	−491.338	−529.091	23.031
1300	78.033	363.017	309.387	69.718	−492.741	−532.180	21.383
1400	78.655	368.823	313.428	77.554	−494.241	−535.159	19.967
1500	79.173	374.268	317.304	85.446	−495.845	−538.026	18.736
1600	79.609	379.392	321.026	93.385	−512.094	−540.257	17.638
1700	79.978	384.230	324.603	101.365	−513.520	−541.974	16.653
1800	80.295	388.810	328.044	109.379	−514.997	−543.606	15.775
1900	80.567	393.159	331.358	117.423	−516.525	−545.154	14.987
2000	80.802	397.298	334.552	125.491	−518.109	−546.620	14.276
2100	81.007	401.245	337.635	133.582	−519.751	−548.005	13.631
2200	81.187	405.018	340.612	141.692	−521.452	−549.310	13.042
2300	81.346	408.630	343.492	149.819	−523.213	−550.538	12.503
2400	81.486	412.095	346.278	157.961	−575.297	−550.618	11.984
2500	81.611	415.424	348.978	166.116	−577.262	−549.550	11.482
2600	81.722	418.627	351.596	174.282	−579.258	−548.402	11.018
2700	81.822	421.714	354.136	182.460	−581.286	−547.177	10.586
2800	81.911	424.691	356.603	190.646	−874.304	−539.653	10.067
2900	81.992	427.567	359.001	198.842	−875.334	−527.684	9.505
3000	82.066	430.348	361.333	207.045	−876.380	−515.678	8.979
3100	82.132	433.040	363.603	215.255	−877.445	−503.636	8.486
3200	82.193	435.648	365.814	223.471	−878.529	−491.561	8.024
3300	82.248	438.178	367.968	231.693	−879.634	−479.452	7.589
3400	82.299	440.634	370.070	239.920	−880.761	−467.308	7.179
3500	82.346	443.021	372.120	248.153	−881.911	−455.131	6.792
3600	82.388	445.341	374.122	256.389	−883.088	−442.921	6.427
3700	82.428	447.599	376.077	264.630	−884.291	−430.678	6.080
3800	82.464	449.798	377.988	272.875	−885.524	−418.400	5.751
3900	82.498	451.940	379.857	281.123	−886.788	−406.091	5.439
4000	82.530	454.029	381.686	289.374	−888.085	−393.750	5.142
4100	82.559	456.067	383.475	297.629	−889.417	−381.375	4.859
4200	82.586	458.057	385.227	305.886	−1370.635	−361.943	4.501
4300	82.611	460.001	386.944	314.146	−1370.957	−337.922	4.105
4400	82.635	461.900	388.626	322.408	−1371.321	−313.895	3.726
4500	82.657	463.758	390.275	330.673	−1371.730	−289.858	3.365
4600	82.678	465.575	391.892	338.940	−1372.188	−265.812	3.018
4700	82.697	467.353	393.479	347.208	−1372.695	−241.754	2.687
4800	82.715	469.094	395.036	355.479	−1373.255	−217.686	2.369
4900	82.732	470.800	396.565	363.751	−1373.870	−193.605	2.064
5000	82.748	472.471	398.066	372.025	−1374.542	−169.511	1.771
5100	82.764	474.110	399.541	380.301	−1375.272	−145.403	1.489
5200	82.778	475.717	400.991	388.578	−1376.064	−121.281	1.218
5300	82.792	477.294	402.416	396.857	−1376.919	−97.142	0.957
5400	82.804	478.842	403.817	405.136	−1377.840	−72.987	0.706
5500	82.817	480.361	405.195	413.417	−1378.827	−48.815	0.464
5600	82.828	481.854	406.550	421.700	−1379.883	−24.622	0.230
5700	82.839	483.320	407.884	429.983	−1381.010	−0.412	0.004
5800	82.849	484.761	409.197	438.267	−1382.209	23.820	−0.215
5900	82.859	486.177	410.490	446.553	−1383.481	48.071	−0.426
6000	82.868	487.570	411.763	454.839	−1384.829	72.347	−0.630

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 225.00\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 239 \pm 42\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 234 \pm 42\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 689.04\ cm^{-1}$ $\omega_e x_e = 3.57\ cm^{-1}$ $\sigma = 1$
$B_e = 0.497\ cm^{-1}$ $\alpha_e = 0.0036\ cm^{-1}$ $r_e = 1.887$ Å

Enthalpy of Formation

Herzberg[1] reported $D_0^\circ = 4.1$ eV which corresponds to a enthalpy of formation of 64 kcal·mol^{-1}. Gaydon[2] gives essentially the same value, with a provisor that the value is unreliable due to the ionic nature of the bonding. Barrow[3] made a critical evaluation of the bond dissociation energies of the group III halides and concluded $D_0^\circ(BBr) = 103.5$ which gives $\Delta_f H°(298.15\ K) = 56$ kcal·mol^{-1}. An estimate of the dissociation energy by taking the ratio $D_0^\circ(BF)/[\Delta_{at}H°(BF_3, g, 0\ K)/3] = 1.177$ and applying this to BBr_3 yields $D_0^\circ(BBr) = 103$ kcal·mol^{-1}; this was the value adopted.

Heat Capacity and Entropy

The vibrational and rotational constants are all taken from NBS.[4]

References

[1]G. Herzberg, "Molecular Spectra and Molecular Structure of Diatomic Molecules," 2nd ed., D. van Nostrand Co., New York, 658 pp. (1950) refer to p. 506.
[2]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall, London, 261 pp. (1953).
[3]R. F. Barrow, Trans. Faraday Soc. **56**, 952 (1960).
[4]U. S. Nat. Bur. Stand. Report 7093, 255 pp. (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.997	238.775	238.775	INFINITE
100	29.154	191.806	252.688	−6.088	240.264	223.806	−116.904
200	30.637	212.350	227.930	−3.116	240.453	207.208	−54.117
250	31.784	219.311	225.531	−1.555	240.234	198.918	−41.562
298.15	32.788	224.997	224.997	0.	234.304	191.651	−33.576
300	32.824	225.200	224.998	0.061	234.274	191.386	−33.323
350	33.684	230.327	225.400	1.724	218.985	185.073	−27.621
400	34.373	234.871	226.306	3.426	219.037	180.225	−23.535
450	34.921	238.953	227.488	5.159	219.021	175.373	−20.357
500	35.359	242.656	228.822	6.917	218.950	170.527	−17.815
600	35.999	249.163	231.685	10.487	218.679	160.865	−14.005
700	36.435	254.747	234.590	14.110	218.278	151.260	−11.287
800	36.747	259.633	237.422	17.770	217.779	141.719	−9.253
900	36.981	263.976	240.135	21.456	217.202	132.245	−7.675
1000	37.164	267.882	242.718	25.164	216.560	122.839	−6.416
1100	37.311	271.431	245.169	28.888	215.863	113.500	−5.390
1200	37.434	274.683	247.495	32.626	215.116	104.227	−4.537
1300	37.539	277.684	249.703	36.374	214.322	95.019	−3.818
1400	37.631	280.469	251.803	40.133	213.487	85.872	−3.204
1500	37.714	283.068	253.801	43.900	212.610	76.787	−2.674
1600	37.788	285.505	255.707	47.675	211.694	67.762	−2.212
1700	37.857	287.798	257.528	51.458	210.740	58.796	−1.807
1800	37.921	289.963	259.271	55.247	209.747	49.886	−1.448
1900	37.982	292.015	260.941	59.042	208.717	41.033	−1.128
2000	38.039	293.965	262.543	62.843	207.647	32.235	−0.842
2100	38.094	295.822	264.084	66.650	206.540	23.491	−0.584
2200	38.147	297.596	265.568	70.462	205.393	14.801	−0.351
2300	38.199	299.292	266.997	74.279	204.207	6.165	−0.140
2400	38.249	300.919	268.377	78.101	152.722	−1.351	0.029
2500	38.297	302.482	269.710	81.929	151.379	−7.743	0.162
2600	38.345	303.985	271.000	85.761	150.029	−14.081	0.283
2700	38.392	305.433	272.248	89.598	148.674	−20.368	0.394
2800	38.438	306.830	273.459	93.439	147.312	−26.604	0.496
2900	38.483	308.179	274.633	97.285	145.944	−32.791	0.591
3000	38.528	309.485	275.773	101.136	144.572	−38.931	0.678
3100	38.573	310.749	276.881	104.991	143.196	−45.025	0.759
3200	38.617	311.974	277.958	108.850	141.818	−51.074	0.834
3300	38.660	313.163	279.007	112.714	140.438	−57.081	0.904
3400	38.703	314.318	280.029	116.582	139.059	−63.046	0.969
3500	38.746	315.440	281.025	120.455	137.680	−68.970	1.029
3600	38.789	316.532	281.996	124.332	136.304	−74.854	1.086
3700	38.831	317.596	282.944	128.213	134.931	−80.701	1.139
3800	38.873	318.632	283.869	132.098	133.564	−86.511	1.189
3900	38.915	319.642	284.774	135.987	132.203	−92.284	1.236
4000	38.957	320.628	285.658	139.881	130.850	−98.023	1.280
4100	38.999	321.590	286.522	143.779	129.505	−103.728	1.322
4200	39.040	322.531	287.369	147.681	−351.680	−102.377	1.273
4300	39.082	323.450	288.197	151.587	−351.918	−96.438	1.171
4400	39.123	324.349	289.009	155.497	−352.147	−90.494	1.074
4500	39.164	325.228	289.804	159.411	−352.365	−84.545	0.981
4600	39.205	326.090	290.583	163.330	−352.574	−78.591	0.892
4700	39.246	326.933	291.348	167.252	−352.771	−72.633	0.807
4800	39.287	327.760	292.098	171.179	−352.959	−66.670	0.726
4900	39.328	328.571	292.834	175.110	−353.135	−60.704	0.647
5000	39.369	329.365	293.557	179.045	−353.300	−54.734	0.572
5100	39.409	330.145	294.266	182.984	−353.455	−48.761	0.499
5200	39.450	330.911	294.964	186.927	−353.599	−42.786	0.430
5300	39.491	331.663	295.649	190.874	−353.732	−36.807	0.363
5400	39.531	332.401	296.323	194.825	−353.855	−30.826	0.298
5500	39.571	333.127	296.985	198.780	−353.969	−24.843	0.236
5600	39.612	333.841	297.637	202.739	−354.073	−18.858	0.176
5700	39.652	334.542	298.279	206.702	−354.168	−12.871	0.118
5800	39.693	335.232	298.910	210.669	−354.254	−6.883	0.062
5900	39.733	335.911	299.531	214.641	−354.332	−0.893	0.008
6000	39.773	336.579	300.143	218.616	−354.402	5.098	−0.044

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 289.03\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -4.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -10.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[660](1)
[195](1)
[905](1)

Ground State Quantum Weight: [2] $\sigma = 1$
Point Group: C_s
Bond Distances: B–Cl = [1.73] Å; B–Br = [1.87] Å
Bond Angle: Cl–B–Br = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.193041 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming $\Delta_f H° = 0$ for the reaction $BCl_2(g) + BBr_2(g) = 2\ BBrCl(g)$.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those for BBr_2 and BCl_2. The bond distances, angles, and quantum weight are assumed the same as in the dihalides. The principal moments of inertia are $I_A = 1.2989 \times 10^{-39}$, $I_B = 40.4453 \times 10^{-39}$, and $I_C = 41.7442 \times 10^{-39}\ g·cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.889	−4.290	−4.290	INFINITE
100	37.800	243.541	327.661	−8.412	−3.690	−15.870	8.290
200	42.512	271.227	293.183	−4.391	−3.971	−27.994	7.311
250	44.812	280.962	289.793	−2.208	−4.376	−33.957	7.095
298.15	46.846	289.033	289.033	0.	−10.460	−38.950	6.824
300	46.919	289.323	289.034	0.087	−10.496	−39.127	6.813
350	48.726	296.695	289.612	2.479	−25.915	−43.053	6.425
400	50.221	303.303	290.917	4.954	−25.966	−45.498	5.941
450	51.439	309.291	292.631	7.497	−26.060	−47.934	5.564
500	52.429	314.763	294.575	10.094	−26.188	−50.358	5.261
600	53.895	324.461	298.769	15.415	−26.524	−55.162	4.802
700	54.891	332.848	303.052	20.858	−26.942	−59.903	4.470
800	55.589	340.226	307.247	26.384	−27.425	−64.580	4.217
900	56.093	346.804	311.283	31.969	−27.963	−69.192	4.016
1000	56.467	352.735	315.137	37.598	−28.552	−73.742	3.852
1100	56.752	358.130	318.803	43.260	−29.187	−78.231	3.715
1200	56.973	363.078	322.290	48.946	−29.866	−82.660	3.598
1300	57.147	367.646	325.605	54.653	−30.588	−87.030	3.497
1400	57.287	371.886	328.761	60.375	−31.351	−91.343	3.408
1500	57.401	375.843	331.770	66.109	−32.156	−95.601	3.329
1600	57.496	379.550	334.641	71.854	−33.001	−99.803	3.258
1700	57.574	383.038	337.387	77.608	−33.889	−103.951	3.194
1800	57.641	386.331	340.015	83.369	−34.818	−108.046	3.135
1900	57.697	389.449	342.536	89.136	−35.791	−112.088	3.082
2000	57.745	392.410	344.956	94.908	−36.808	−116.077	3.032
2100	57.787	395.228	347.283	100.684	−37.870	−120.015	2.985
2200	57.823	397.917	349.524	106.465	−38.979	−123.901	2.942
2300	57.855	400.488	351.685	112.249	−40.135	−127.735	2.901
2400	57.883	402.951	353.770	118.036	−91.600	−130.449	2.839
2500	57.907	405.315	355.785	123.825	−92.933	−132.041	2.759
2600	57.929	407.586	357.734	129.617	−94.284	−133.579	2.684
2700	57.949	409.773	359.621	135.411	−95.652	−135.064	2.613
2800	57.966	411.881	361.450	141.207	−97.040	−136.498	2.546
2900	57.982	413.915	363.224	147.004	−98.445	−137.883	2.484
3000	57.996	415.881	364.947	152.803	−99.867	−139.219	2.424
3100	58.009	417.783	366.621	158.604	−101.306	−140.507	2.368
3200	58.021	419.625	368.248	164.405	−102.761	−141.748	2.314
3300	58.032	421.410	369.832	170.208	−104.229	−142.943	2.263
3400	58.041	423.143	371.375	176.012	−105.708	−144.095	2.214
3500	58.050	424.826	372.878	181.816	−107.197	−145.202	2.167
3600	58.059	426.461	374.344	187.622	−108.694	−146.267	2.122
3700	58.066	428.052	375.774	193.428	−110.196	−147.290	2.079
3800	58.073	429.601	377.170	199.235	−111.701	−148.272	2.038
3900	58.080	431.109	378.534	205.042	−113.207	−149.215	1.999
4000	58.085	432.580	379.867	210.851	−114.711	−150.119	1.960
4100	58.091	434.014	381.170	216.659	−116.210	−150.985	1.924
4200	58.096	435.414	382.445	222.469	−597.552	−144.792	1.801
4300	58.101	436.781	383.693	228.279	−597.949	−134.007	1.628
4400	58.105	438.117	384.915	234.089	−598.337	−123.213	1.463
4500	58.110	439.423	386.112	239.900	−598.715	−112.410	1.305
4600	58.114	440.700	387.284	245.711	−599.080	−101.599	1.154
4700	58.117	441.950	388.434	251.522	−599.432	−90.781	1.009
4800	58.121	443.173	389.562	257.334	−599.768	−79.955	0.870
4900	58.124	444.372	390.668	263.147	−600.089	−69.122	0.737
5000	58.127	445.546	391.754	268.959	−600.393	−58.283	0.609
5100	58.130	446.697	392.820	274.772	−600.680	−47.438	0.486
5200	58.132	447.826	393.867	280.585	−600.948	−36.587	0.368
5300	58.135	448.933	394.896	286.398	−601.198	−25.732	0.254
5400	58.137	450.020	395.907	292.212	−601.429	−14.872	0.144
5500	58.140	451.087	396.900	298.026	−601.640	−4.007	0.038
5600	58.142	452.134	397.877	303.840	−601.833	6.860	−0.064
5700	58.144	453.163	398.838	309.654	−602.006	17.731	−0.162
5800	58.146	454.175	399.784	315.469	−602.160	28.605	−0.258
5900	58.148	455.169	400.714	321.283	−602.295	39.482	−0.350
6000	58.149	456.146	401.630	327.098	−602.412	50.360	−0.438

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 310.40\ J·K^{-1}·mol^{-1}$

$\Delta H_f°(0\ K) = -328.7 \pm 10\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -336.8 \pm 10\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
885(1)	959 (1)
406(1)	[208](1)
218(1)	433 (1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distances: B–Cl = 1.73 Å; B–Br = 1.87 Å

Bond Angles: Cl–B–Cl = [120]°; Br–B–Cl = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = 9.196849 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming $\Delta_r H° = 0$ for the reaction $BBr_3(g) + 2\ BCl_3(g) = 3\ BBrCl_2(g)$.

Heat Capacity and Entropy

Vibrational frequencies are obtained from Lindeman and Wilson.[1] The b_1 mode was the only unobserved frequency and was calculated from a normal coordinate treatment. Bond distances were reported by Wentink and Tiensuu.[2] Bond angles were estimated by analogy with the other trihalides of boron. The principal moments of inertia are $I_A = 26.4297 \times 10^{-39}$, $I_B = 47.2365 \times 10^{-39}$, and $I_C = 73.6662 \times 10^{-39}\ g·cm^{-1}$.

References

[1]L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).

[2]T. Wentink and V. H. Tiensuu, J. Chem. Phys. **28**, 826 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	-14.547	-328.709	-328.709	INFINITE
100	42.752	252.188	361.654	-10.947	-329.442	-333.037	173.960
200	56.153	286.331	316.048	-5.943	-330.260	-336.307	87.834
250	60.770	299.375	311.440	-3.016	-330.730	-337.767	70.573
298.15	64.398	310.400	310.400	0.	-336.812	-338.417	59.289
300	64.523	310.798	310.401	0.119	-336.847	-338.427	58.925
350	67.577	320.982	311.198	3.424	-352.212	-337.848	50.421
400	70.050	330.173	313.005	6.867	-352.171	-335.799	43.851
450	72.048	338.543	315.384	10.422	-352.141	-333.754	38.741
500	73.665	346.221	318.090	14.066	-352.121	-331.712	34.654
600	76.059	359.878	323.945	21.560	-352.100	-327.633	28.523
700	77.689	371.733	329.943	29.252	-352.103	-323.555	24.144
800	78.834	382.185	335.833	37.082	-352.133	-319.475	20.860
900	79.662	391.521	341.512	45.009	-352.190	-315.390	18.305
1000	80.278	399.948	346.941	53.007	-352.277	-311.297	16.260
1100	80.747	407.622	352.114	61.059	-352.397	-307.193	14.587
1200	81.111	414.664	357.037	69.153	-352.550	-303.078	13.193
1300	81.399	421.168	361.723	77.279	-352.738	-298.947	12.012
1400	81.631	427.209	366.187	85.431	-352.962	-294.802	10.999
1500	81.819	432.848	370.446	93.604	-353.224	-290.638	10.121
1600	81.975	438.134	374.513	101.794	-353.525	-286.456	9.352
1700	82.106	443.107	378.403	109.998	-353.866	-282.254	8.673
1800	82.215	447.804	382.129	118.214	-354.249	-278.031	8.068
1900	82.309	452.251	385.704	126.440	-354.676	-273.785	7.527
2000	82.388	456.475	389.138	134.675	-355.148	-269.516	7.039
2100	82.458	460.497	392.441	142.918	-355.669	-265.222	6.597
2200	82.518	464.334	395.622	151.167	-356.240	-260.901	6.195
2300	82.570	468.003	398.690	159.421	-356.863	-256.554	5.827
2400	82.616	471.518	401.652	167.680	-407.800	-251.110	5.465
2500	82.657	474.892	404.514	175.944	-408.611	-244.564	5.110
2600	82.694	478.134	407.284	184.212	-409.447	-237.986	4.781
2700	82.726	481.256	409.966	192.483	-410.309	-231.375	4.476
2800	82.755	484.265	412.566	200.757	-411.197	-224.732	4.192
2900	82.781	487.170	415.089	209.034	-412.112	-218.056	3.928
3000	82.805	489.976	417.539	217.313	-413.053	-211.349	3.680
3100	82.826	492.692	419.919	225.595	-414.019	-204.609	3.448
3200	82.846	495.322	422.235	233.878	-415.009	-197.839	3.229
3300	82.863	497.871	424.488	242.164	-416.021	-191.036	3.024
3400	82.880	500.345	426.683	250.451	-417.053	-184.203	2.830
3500	82.894	502.748	428.822	258.739	-418.101	-177.340	2.647
3600	82.908	505.083	430.909	267.030	-419.162	-170.446	2.473
3700	82.920	507.355	432.944	275.321	-420.234	-163.522	2.309
3800	82.932	509.567	434.931	283.614	-421.313	-156.570	2.152
3900	82.943	511.721	436.873	291.907	-422.395	-149.589	2.004
4000	82.953	513.821	438.771	300.202	-423.477	-142.580	1.862
4100	82.962	515.869	440.626	308.498	-424.555	-135.544	1.727
4200	82.970	517.869	442.442	316.795	-905.475	-121.458	1.511
4300	82.978	519.821	444.218	325.092	-905.447	-102.791	1.249
4400	82.986	521.729	445.958	333.390	-905.407	-84.125	0.999
4500	82.993	523.594	447.663	341.689	-905.351	-65.460	0.760
4600	82.999	525.418	449.334	349.989	-905.277	-46.796	0.531
4700	83.005	527.203	450.971	358.289	-905.183	-28.135	0.313
4800	83.011	528.951	452.578	366.590	-905.066	-9.476	0.103
4900	83.016	530.662	454.154	374.891	-904.924	9.181	-0.098
5000	83.021	532.340	455.701	383.193	-904.755	27.835	-0.291
5100	83.026	533.984	457.220	391.495	-904.558	46.485	-0.476
5200	83.031	535.596	458.712	399.798	-904.331	65.130	-0.654
5300	83.035	537.178	460.177	408.101	-904.074	83.771	-0.826
5400	83.039	538.730	461.618	416.405	-903.785	102.407	-0.991
5500	83.043	540.253	463.034	424.709	-903.463	121.038	-1.150
5600	83.046	541.750	464.426	433.014	-903.108	139.662	-1.303
5700	83.050	543.220	465.795	441.318	-902.720	158.279	-1.450
5800	83.053	544.664	467.143	449.624	-902.299	176.890	-1.593
5900	83.056	546.084	468.469	457.929	-901.844	195.493	-1.731
6000	83.059	547.480	469.774	466.235	-901.356	214.087	-1.864

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [275.77]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -233.9 \pm 10\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -240.6 \pm 10\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[860](1)
[310](1)
[1140](1)

Ground State Quantum Weight: [2] $\sigma = 1$

Point Group: C_s

Bond Distances: B–F = [1.3] Å; B–Br = [1.87] Å

Bond Angle: Br–B–F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.131563 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming $\Delta_f H° = 0$ for the reaction $BBr_2(g) + BF_2(g) \rightarrow 2\ BBrF(g)$.

Heat Capacity and Entropy

The vibrational frequencies, bond lengths, angles and quantum weight are estimated by comparison with the respective dihalides. The principal moments of inertia are $I_A = 0.8401 \times 10^{-39}$, $I_B = 21.7603 \times 10^{-39}$, and $I_C = 22.6004 \times 10^{-39}$ g·cm².

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.207	−233.906	−233.906	INFINITE
100	35.220	233.363	311.742	−7.838	−233.411	−245.506	128.239
200	39.650	259.208	279.627	−4.084	−233.905	−257.455	67.240
250	41.650	268.270	276.476	−2.051	−234.402	−263.290	55.011
298.15	43.546	275.770	275.770	0.	−240.580	−268.140	46.977
300	43.617	276.039	275.770	0.081	−240.619	−268.311	46.717
350	45.462	282.903	276.308	2.308	−256.138	−272.073	40.605
400	47.115	289.084	277.525	4.624	−256.289	−274.339	35.825
450	48.554	294.719	279.127	7.016	−256.478	−276.585	32.105
500	49.787	299.900	280.949	9.476	−256.696	−278.807	29.127
600	51.720	309.158	284.897	14.556	−257.193	−283.184	24.653
700	53.110	317.241	288.953	19.801	−257.748	−287.473	21.451
800	54.123	324.402	292.945	25.166	−258.348	−291.678	19.045
900	54.874	330.822	296.803	30.617	−258.987	−295.807	17.168
1000	55.442	336.635	300.500	36.134	−259.664	−299.862	15.663
1100	55.881	341.940	304.030	41.702	−260.378	−303.848	14.429
1200	56.225	346.818	307.395	47.307	−261.130	−307.766	13.397
1300	56.499	351.330	310.603	52.944	−261.920	−311.621	12.521
1400	56.721	355.525	313.664	58.606	−262.748	−315.413	11.768
1500	56.903	359.445	316.587	64.287	−263.616	−319.145	11.114
1600	57.054	363.122	319.381	69.985	−264.523	−322.818	10.539
1700	57.180	366.585	322.057	75.697	−265.471	−326.432	10.030
1800	57.286	369.856	324.623	81.420	−266.459	−329.990	9.576
1900	57.377	372.956	327.086	87.154	−267.487	−333.492	9.168
2000	57.456	375.901	329.453	92.895	−268.556	−336.938	8.800
2100	57.523	378.706	331.733	98.644	−269.665	−340.330	8.465
2200	57.582	381.384	333.929	104.400	−270.814	−343.668	8.160
2300	57.634	383.944	336.048	110.161	−272.001	−346.953	7.880
2400	57.679	386.398	338.096	115.926	−323.484	−349.117	7.598
2500	57.719	388.754	340.075	121.696	−324.821	−350.158	7.316
2600	57.755	391.018	341.991	127.470	−326.160	−351.145	7.055
2700	57.787	393.198	343.848	133.247	−327.499	−352.080	6.811
2800	57.816	395.300	345.648	139.027	−328.836	−352.966	6.585
2900	57.841	397.330	347.395	144.810	−330.169	−353.804	6.373
3000	57.865	399.291	349.093	150.595	−331.497	−354.597	6.174
3100	57.886	401.189	350.743	156.383	−332.818	−355.345	5.988
3200	57.905	403.027	352.348	162.173	−334.129	−356.051	5.812
3300	57.922	404.809	353.911	167.964	−335.429	−356.716	5.646
3400	57.938	406.538	355.433	173.757	−336.716	−357.341	5.490
3500	57.953	408.218	356.918	179.552	−337.989	−357.930	5.342
3600	57.967	409.851	358.365	185.348	−339.245	−358.481	5.201
3700	57.979	411.439	359.778	191.145	−340.483	−358.999	5.068
3800	57.990	412.986	361.158	196.943	−341.703	−359.483	4.941
3900	58.001	414.492	362.507	202.743	−342.902	−359.935	4.821
4000	58.011	415.961	363.825	208.543	−344.080	−360.357	4.706
4100	58.020	417.393	365.114	214.345	−345.235	−360.749	4.596
4200	58.028	418.791	366.375	220.147	−826.217	−354.090	4.404
4300	58.036	420.157	367.610	225.951	−826.238	−342.848	4.165
4400	58.044	421.491	368.820	231.755	−826.237	−331.607	3.937
4500	58.050	422.796	370.005	237.559	−826.214	−320.365	3.719
4600	58.057	424.072	371.166	243.365	−826.168	−309.125	3.510
4700	58.063	425.320	372.305	249.171	−826.099	−297.885	3.311
4800	58.069	426.543	373.423	254.977	−826.009	−286.648	3.119
4900	58.074	427.740	374.519	260.784	−825.896	−275.412	2.936
5000	58.079	428.914	375.595	266.592	−825.761	−264.179	2.760
5100	58.084	430.064	376.652	272.400	−825.606	−252.949	2.591
5200	58.088	431.192	377.690	278.209	−825.430	−241.722	2.428
5300	58.092	432.298	378.710	284.018	−825.234	−230.498	2.272
5400	58.096	433.384	379.712	289.827	−825.018	−219.279	2.121
5500	58.100	434.450	380.698	295.637	−824.784	−208.064	1.976
5600	58.104	435.497	381.667	301.447	−824.532	−196.853	1.836
5700	58.107	436.525	382.621	307.258	−824.264	−185.647	1.701
5800	58.110	437.536	383.559	313.069	−823.978	−174.446	1.571
5900	58.113	438.529	384.482	318.880	−823.678	−163.249	1.445
6000	58.116	439.506	385.391	324.691	−823.363	−152.058	1.324

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 286.39\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-811 \pm 10]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-820 \pm 10]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
1215 (1)	1427 (1)
633 (1)	[346](1)
[330](1)	573 (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–F = 1.295 Å; B–Br = 1.87 Å
Bond Angles: F–B–F = [120]°; Br–B–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = 8.471599 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming $\Delta_f H° = 0$ for the reaction $2\ BF_3(g) + BBr_3(g) \rightarrow 3\ BBrF_2(g)$.

Heat Capacity and Entropy

All but two of the vibrational frequencies have been observed and assigned by Lindeman and Wilson.[1] The two remaining frequencies were calculated by a normal coordinate treatment. The bond distances were reported by Wentink and Tiensuu.[2] The bond angles were estimated by analogy with the other boron trihalides. The principal moments of inertia are $I_A = 7.9360 \times 10^{-39}$, $I_B = 28.9444 \times 10^{-39}$, and $I_C = 36.8805 \times 10^{-39}\ g·cm^2$.

References

[1]L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).
[2]T. Wentink and V. H. Tiensuu, J. Chem. Phys. **28**, 826 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.778	−810.549	−810.549	INFINITE
100	36.575	236.647	330.512	−9.387	−811.485	−815.389	425.916
200	47.998	265.547	291.299	−5.150	−812.961	−818.714	213.826
250	52.679	276.777	287.296	−2.630	−813.722	−820.066	171.343
298.15	56.450	286.387	286.387	0.	−820.064	−820.559	143.759
300	56.583	286.737	286.388	0.105	−820.108	−820.562	142.873
350	59.897	295.715	287.090	3.019	−835.735	−819.775	122.345
400	62.745	303.903	288.687	6.087	−835.948	−817.480	106.752
450	65.198	311.439	290.802	9.287	−836.164	−815.159	94.621
500	67.311	318.420	293.219	12.601	−836.376	−812.813	84.914
600	70.693	331.007	298.491	19.509	−836.782	−808.062	70.348
700	73.200	342.102	303.945	26.710	−837.157	−803.245	59.939
800	75.075	352.005	309.344	34.128	−837.508	−798.376	52.129
900	76.495	360.933	314.589	41.710	−837.844	−793.465	46.051
1000	77.589	369.052	319.635	49.417	−838.177	−788.516	41.188
1100	78.444	376.489	324.470	57.220	−838.515	−783.534	37.207
1200	79.122	383.344	329.095	65.099	−838.866	−778.520	33.888
1300	79.667	389.700	333.515	73.040	−839.237	−773.476	31.079
1400	80.111	395.620	337.742	81.029	−839.632	−768.403	28.669
1500	80.477	401.160	341.787	89.059	−840.056	−763.301	26.580
1600	80.781	406.364	345.662	97.123	−840.513	−758.169	24.752
1700	81.038	411.269	349.379	105.214	−841.003	−753.007	23.137
1800	81.255	415.908	352.947	113.329	−841.530	−747.816	21.701
1900	81.440	420.306	356.378	121.464	−842.093	−742.595	20.415
2000	81.600	424.488	359.679	129.616	−842.692	−737.343	19.257
2100	81.739	428.472	362.861	137.783	−843.326	−732.060	18.209
2200	81.860	432.278	365.931	145.963	−843.995	−726.746	17.255
2300	81.966	435.919	368.895	154.155	−844.695	−721.401	16.384
2400	82.060	439.409	371.761	162.356	−895.684	−714.956	15.561
2500	82.143	442.761	374.534	170.566	−896.519	−707.408	14.780
2600	82.217	445.984	377.221	178.785	−897.344	−699.827	14.060
2700	82.283	449.088	379.825	187.010	−898.159	−692.215	13.392
2800	82.342	452.082	382.353	195.241	−898.958	−684.573	12.771
2900	82.395	454.972	384.807	203.478	−899.740	−676.902	12.192
3000	82.444	457.766	387.193	211.720	−900.502	−669.205	11.652
3100	82.487	460.470	389.513	219.966	−901.241	−661.483	11.146
3200	82.527	463.090	391.772	228.217	−901.954	−653.738	10.671
3300	82.564	465.630	393.972	236.472	−902.639	−645.970	10.225
3400	82.597	468.095	396.116	244.730	−903.293	−638.183	9.804
3500	82.627	470.490	398.207	252.991	−903.915	−630.376	9.408
3600	82.655	472.818	400.247	261.255	−904.502	−622.552	9.033
3700	82.681	475.083	402.239	269.522	−905.053	−614.712	8.678
3800	82.705	477.288	404.185	277.791	−905.567	−606.859	8.342
3900	82.727	479.437	406.087	286.063	−906.043	−598.991	8.023
4000	82.747	481.532	407.947	294.336	−906.478	−591.113	7.719
4100	82.766	483.575	409.767	302.612	−906.874	−583.224	7.430
4200	82.784	485.570	411.548	310.890	−1387.078	−568.301	7.068
4300	82.800	487.518	413.293	319.169	−1386.304	−548.816	6.667
4400	82.816	489.422	415.001	327.450	−1385.491	−529.349	6.284
4500	82.830	491.283	416.676	335.732	−1384.638	−509.900	5.919
4600	82.843	493.104	418.318	344.016	−1383.746	−490.471	5.569
4700	82.856	494.885	419.928	352.301	−1382.816	−471.062	5.235
4800	82.868	496.630	421.508	360.587	−1381.847	−451.673	4.915
4900	82.879	498.339	423.058	368.874	−1380.842	−432.305	4.608
5000	82.889	500.013	424.581	377.162	−1379.800	−412.958	4.314
5100	82.899	501.655	426.076	385.452	−1378.722	−393.631	4.032
5200	82.908	503.264	427.545	393.742	−1377.610	−374.327	3.760
5300	82.917	504.844	428.988	402.034	−1376.464	−355.044	3.499
5400	82.925	506.394	430.408	410.326	−1375.285	−335.783	3.248
5500	82.933	507.915	431.803	418.619	−1374.075	−316.544	3.006
5600	82.941	509.410	433.175	426.912	−1372.835	−297.327	2.773
5700	82.948	510.878	434.526	435.207	−1371.566	−278.133	2.549
5800	82.954	512.321	435.855	443.502	−1370.269	−258.961	2.332
5900	82.961	513.739	437.163	451.798	−1368.945	−239.812	2.123
6000	82.967	515.133	438.451	460.094	−1367.596	−220.686	1.921

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [248.89]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-244 \pm 7]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-251 \pm 7]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[550](1)
[370](2)
[1800](1)

Ground State Quantum Weight: [1] α = 1
Point Group: $[C_v]$
Bond Distances: O–B = [1.20] Å; B–Br = [1.87] Å
Bond Angle: O–B–Br = [180]°
Rotation Constant: B_0 = [0.117436] cm^{-1}

Enthalpy of Formation

The value of $\Delta_f H°$(BOBr, g, 298.15 K) is calculated based on an assumption that $D_0°$(BO–Br) = 92.5 kcal·mol^{-1} which is estimated by comparison with the following related bond energy values: $D_0°(BF_2–F)$ = 159, $D_0°$(BO–F) = 169, $D_0°(BCl_2–Cl)$ = 105, $D_0°$(BO–Cl) = 110 and $D_0°(BBr_2–Br)$ = 90.5 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular structure is assumed to be linear. The vibrational frequencies (ν) are estimated from the ν values calculated by the valence force method by Herzberg[1] using estimated force constants, $k_1 = 4.2 \times 105$, $k_2 = 16.9 \times 105$ dynes cm^{-1} and $k_g = 0.37 \times 10^{-11}$ dynes·cm·rad^{-1}. The B=O and B–F[1] bond distances are assumed to be the same as those in BO(g) and BBr_3(g), respectively.

Reference

[1]G. Herzberg, Infrared and Raman Spectra, D. Van Nostrand Company, Inc., (1945).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.961	−244.191	−244.191	INFINITE
100	31.611	206.321	286.380	−8.006	−244.108	−253.352	132.338
200	41.199	231.278	253.022	−4.349	−244.690	−262.372	68.524
250	44.510	240.848	249.654	−2.201	−245.051	−266.753	55.735
298.15	46.810	248.895	248.895	0.	−251.040	−270.236	47.344
300	46.885	249.185	248.896	0.087	−251.072	−270.355	47.073
350	48.664	256.552	249.474	2.477	−266.371	−272.732	40.703
400	50.078	263.145	250.778	4.947	−266.299	−273.647	35.735
450	51.262	269.114	252.489	7.481	−266.272	−274.567	31.871
500	52.290	274.569	254.428	10.071	−266.282	−275.489	28.780
600	54.011	284.261	258.612	15.389	−266.384	−277.322	24.143
700	55.392	292.694	262.892	20.862	−266.563	−279.132	20.829
800	56.505	300.166	267.093	26.459	−266.794	−280.912	18.342
900	57.401	306.875	271.147	32.155	−267.063	−282.661	16.405
1000	58.127	312.962	275.029	37.933	−267.366	−284.378	14.854
1100	58.716	318.530	278.734	43.776	−267.699	−286.063	13.584
1200	59.198	323.661	282.267	49.673	−268.062	−287.717	12.524
1300	59.596	328.415	285.636	55.613	−268.455	−289.339	11.626
1400	59.927	332.844	288.852	61.590	−268.879	−290.930	10.855
1500	60.204	336.989	291.924	67.597	−269.337	−292.489	10.185
1600	60.438	340.882	294.864	73.629	−269.829	−294.017	9.599
1700	60.637	344.552	297.680	79.683	−270.357	−295.513	9.080
1800	60.808	348.023	300.381	85.756	−270.924	−296.976	8.618
1900	60.955	351.314	302.976	91.844	−271.532	−298.407	8.204
2000	61.082	354.444	305.471	97.946	−272.181	−299.805	7.830
2100	61.193	357.427	307.875	104.060	−272.875	−301.169	7.491
2200	61.291	360.276	310.193	110.184	−273.613	−302.499	7.182
2300	61.377	363.003	312.430	116.317	−274.399	−303.795	6.899
2400	61.453	365.617	314.592	122.459	−325.491	−303.987	6.616
2500	61.521	368.127	316.684	128.608	−326.450	−303.071	6.332
2600	61.582	370.541	318.709	134.763	−327.424	−302.117	6.070
2700	61.636	372.866	320.672	140.924	−328.415	−301.125	5.826
2800	61.685	375.108	322.576	147.090	−329.421	−300.096	5.598
2900	61.729	377.274	324.425	153.261	−330.442	−299.031	5.386
3000	61.769	379.367	326.222	159.436	−331.479	−297.930	5.187
3100	61.805	381.393	327.969	165.614	−332.529	−296.794	5.001
3200	61.838	383.356	329.669	171.797	−333.591	−295.624	4.826
3300	61.868	385.259	331.325	177.982	−334.665	−294.422	4.660
3400	61.896	387.107	332.939	184.170	−335.748	−293.186	4.504
3500	61.922	388.901	334.512	190.361	−336.841	−291.918	4.357
3600	61.945	390.646	336.047	196.554	−337.940	−290.619	4.217
3700	61.966	392.343	337.546	202.750	−339.045	−289.289	4.084
3800	61.986	393.996	339.010	208.948	−340.154	−287.929	3.958
3900	62.005	395.607	340.441	215.147	−341.266	−286.541	3.838
4000	62.022	397.177	341.839	221.349	−342.379	−285.123	3.723
4100	62.038	398.708	343.208	227.552	−343.493	−283.678	3.614
4200	62.053	400.203	344.547	233.756	−824.456	−275.182	3.422
4300	62.067	401.664	345.859	239.962	−824.481	−262.103	3.184
4400	62.079	403.091	347.143	246.169	−824.506	−249.025	2.956
4500	62.092	404.486	348.402	252.378	−824.529	−235.945	2.739
4600	62.103	405.851	349.636	258.588	−824.551	−222.866	2.531
4700	62.113	407.187	350.846	264.799	−824.572	−209.785	2.332
4800	62.123	408.494	352.034	271.010	−824.591	−196.704	2.141
4900	62.133	409.775	353.199	277.223	−824.609	−183.623	1.957
5000	62.142	411.031	354.343	283.437	−824.626	−170.541	1.782
5100	62.150	412.261	355.467	289.652	−824.642	−157.459	1.613
5200	62.158	413.468	356.571	295.867	−824.658	−144.378	1.450
5300	62.165	414.652	357.656	302.083	−824.674	−131.295	1.294
5400	62.172	415.814	358.722	308.300	−824.691	−118.212	1.143
5500	62.179	416.955	359.770	314.517	−824.709	−105.129	0.998
5600	62.185	418.076	360.802	320.736	−824.729	−92.046	0.859
5700	62.191	419.176	361.816	326.955	−824.753	−78.962	0.724
5800	62.197	420.258	362.814	333.174	−824.781	−65.877	0.593
5900	62.202	421.321	363.797	339.394	−824.814	−52.793	0.467
6000	62.207	422.367	364.764	345.614	−824.853	−39.707	0.346

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K) = [294.66]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [76.3 \pm 15]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [62.8 \pm 15]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[600](1)
[150](1)
[830](1)

Ground State Quantum Weight: [2] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distance: B–Br = [1.87] Å
Bond Angle: Br–B–Br = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.270321 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by analogy with BF_3, specifically the ratio $\Delta_f H°(BX_3 \rightarrow BX_2 + X)/\Delta_f H°(BX_3 \rightarrow B + 3X)$ is taken as 0.347.

Heat Capacity and Entropy

The vibrational frequencies were obtained from force constants transferred from the trihalide given by Herzberg.[1] The bond length is taken between those of the mono and trihalide and the angle is estimated to be the same as that in the trihalides. The ground state quantum weight is taken as two due to the one unpaired electron.

The principal moments of inertia are $I_A = 1.4699 \times 10^{-39}$, $I_B = 69.5984 \times 10^{-39}$, and $I_C = 71.0683 \times 10^{-39}\ g·cm^2$.

Reference

[1] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Inc., (1945).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.209	76.274	76.274	INFINITE
100	39.095	247.877	334.353	−8.648	77.019	57.646	−30.111
200	43.694	276.369	298.924	−4.511	75.921	38.615	−10.085
250	46.046	286.375	295.442	−2.267	74.979	29.392	−6.141
298.15	48.056	294.662	294.662	0.	62.760	22.026	−3.859
300	48.127	294.959	294.663	0.089	62.688	21.774	−3.791
350	49.854	302.512	295.255	2.540	31.862	16.646	−2.484
400	51.245	309.264	296.592	5.069	31.825	14.475	−1.890
450	52.357	315.366	298.344	7.660	31.747	12.310	−1.429
500	53.245	320.930	300.329	10.301	31.635	10.156	−1.061
600	54.539	330.760	304.603	15.694	31.328	5.888	−0.513
700	55.403	339.237	308.959	21.194	30.934	1.678	−0.125
800	56.003	346.676	313.218	26.766	30.471	−2.471	0.161
900	56.432	353.299	317.311	32.389	29.948	−6.557	0.381
1000	56.750	359.262	321.213	38.049	29.371	−10.583	0.553
1100	56.990	364.682	324.922	43.737	28.746	−14.549	0.691
1200	57.176	369.649	328.445	49.445	28.074	−18.455	0.803
1300	57.322	374.232	331.793	55.170	27.357	−22.304	0.896
1400	57.440	378.484	334.978	60.909	26.596	−26.096	0.974
1500	57.535	382.451	338.012	66.658	25.792	−29.832	1.039
1600	57.614	386.166	340.907	72.415	24.944	−33.512	1.094
1700	57.680	389.661	343.673	78.180	24.051	−37.139	1.141
1800	57.735	392.960	346.320	83.951	23.114	−40.711	1.181
1900	57.782	396.083	348.858	89.727	22.129	−44.230	1.216
2000	57.822	399.047	351.294	95.507	21.096	−47.697	1.246
2100	57.857	401.869	353.636	101.291	20.014	−51.110	1.271
2200	57.887	404.562	355.890	107.078	18.880	−54.470	1.293
2300	57.914	407.135	358.062	112.868	17.694	−57.778	1.312
2400	57.937	409.601	360.159	118.661	−33.805	−59.964	1.305
2500	57.957	411.966	362.184	124.455	−35.175	−61.026	1.275
2600	57.975	414.240	364.143	130.252	−36.567	−62.033	1.246
2700	57.992	416.428	366.039	136.050	−37.979	−62.985	1.219
2800	58.006	418.537	367.877	141.850	−39.411	−63.886	1.192
2900	58.019	420.573	369.659	147.652	−40.861	−64.734	1.166
3000	58.031	422.540	371.389	153.454	−42.329	−65.532	1.141
3100	58.042	424.443	373.070	159.258	−43.812	−66.281	1.117
3200	58.052	426.286	374.704	165.063	−45.308	−66.982	1.093
3300	58.061	428.073	376.294	170.868	−46.814	−67.636	1.071
3400	58.069	429.806	377.843	176.675	−48.329	−68.245	1.048
3500	58.076	431.489	379.352	182.482	−49.849	−68.808	1.027
3600	58.083	433.126	380.823	188.290	−51.372	−69.328	1.006
3700	58.089	434.717	382.258	194.098	−52.895	−69.806	0.985
3800	58.095	436.266	383.659	199.908	−54.416	−70.243	0.966
3900	58.100	437.775	385.027	205.717	−55.932	−70.640	0.946
4000	58.105	439.246	386.365	211.528	−57.441	−70.998	0.927
4100	58.110	440.681	387.672	217.338	−58.941	−71.318	0.909
4200	58.114	442.082	388.951	223.150	−540.279	−64.578	0.803
4300	58.118	443.449	390.202	228.961	−540.668	−53.247	0.647
4400	58.122	444.785	391.428	234.773	−541.044	−41.907	0.498
4500	58.125	446.091	392.628	240.586	−541.406	−30.559	0.355
4600	58.128	447.369	393.804	246.398	−541.753	−19.203	0.218
4700	58.131	448.619	394.957	252.211	−542.084	−7.840	0.087
4800	58.134	449.843	396.088	258.025	−542.399	3.531	−0.038
4900	58.137	451.042	397.197	263.838	−542.696	14.907	−0.159
5000	58.140	452.216	398.286	269.652	−542.977	26.290	−0.275
5100	58.142	453.368	399.355	275.466	−543.240	37.678	−0.386
5200	58.144	454.497	400.404	281.280	−543.486	49.071	−0.493
5300	58.146	455.604	401.435	287.095	−543.714	60.469	−0.596
5400	58.148	456.691	402.449	292.910	−543.925	71.870	−0.695
5500	58.150	457.758	403.445	298.724	−544.119	83.276	−0.791
5600	58.152	458.806	404.424	304.540	−544.296	94.684	−0.883
5700	58.154	459.835	405.387	310.355	−544.458	106.096	−0.972
5800	58.155	460.847	406.335	316.170	−544.603	117.510	−1.058
5900	58.157	461.841	407.267	321.986	−544.734	128.927	−1.141
6000	58.158	462.818	408.185	327.802	−544.850	140.346	−1.222

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 321.89\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-257 \pm 10]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-272 \pm 10]\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
925(1)	834(1)
344(1)	195(1)
166(1)	409(1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–Br = 1.87 Å; B–Cl = 1.75 Å
Bond Angles: Br–B–Br = [120]°; Cl–B–Br = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = 2.555411 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming $\Delta_r H° = 0$ for the reaction $2\ BBr_3(g) + BCl_3(g) \rightarrow 3\ BBr_2Cl(g)$.

Heat Capacity and Entropy

The vibrational frequencies have all been observed and assigned by Lindeman and Wilson.[1] The bond lengths were reported by Wentink and Tiensuu.[2] Bond angles are estimated by analogy with the other trihalides of boron. The principal moments of inertia are $I_A = 35.0767 \times 10^{-39}$, $I_B = 69.5984 \times 10^{-39}$, and $I_C = 104.6751 \times 10^{-39}\ g·cm^2$.

References

[1]L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).
[2]T. Wentink and V. H. Tiensuu, J. Chem. Phys. **28**, 826 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.092	−256.738	−256.738	INFINITE
100	45.297	261.227	374.950	−11.372	−257.292	−268.549	140.275
200	58.289	297.067	327.702	−6.127	−258.799	−279.248	72.932
250	62.626	310.557	322.958	−3.100	−259.769	−284.253	59.391
298.15	66.028	321.889	321.889	0.	−271.960	−287.556	50.379
300	66.145	322.298	321.890	0.122	−272.030	−287.652	50.085
350	68.994	332.716	322.707	3.503	−302.786	−288.570	43.067
400	71.286	342.084	324.553	7.012	−302.717	−286.544	37.419
450	73.127	350.591	326.981	10.624	−302.663	−284.525	33.027
500	74.609	358.375	329.736	14.319	−302.619	−282.512	29.514
600	76.790	372.184	335.690	21.896	−302.558	−278.497	24.245
700	78.265	384.139	341.776	29.654	−302.531	−274.490	20.483
800	79.296	394.661	347.742	37.535	−302.535	−270.484	17.661
900	80.040	404.046	353.486	45.503	−302.572	−266.476	15.466
1000	80.591	412.509	358.972	53.536	−302.644	−262.462	13.710
1100	81.010	420.211	364.195	61.617	−302.751	−258.439	12.272
1200	81.336	427.274	369.161	69.735	−302.895	−254.404	11.074
1300	81.593	433.795	373.885	77.882	−303.076	−250.356	10.059
1400	81.799	439.849	378.383	86.052	−303.296	−246.293	9.189
1500	81.967	445.499	382.672	94.241	−303.556	−242.212	8.435
1600	82.106	450.793	386.765	102.445	−303.858	−238.113	7.774
1700	82.222	455.775	390.680	110.661	−304.202	−233.994	7.190
1800	82.319	460.477	394.428	118.888	−304.593	−229.853	6.670
1900	82.402	464.930	398.022	127.125	−305.030	−225.689	6.205
2000	82.473	469.159	401.474	135.369	−305.518	−221.501	5.785
2100	82.535	473.184	404.794	143.619	−306.059	−217.287	5.405
2200	82.588	477.025	407.991	151.875	−306.654	−213.046	5.058
2300	82.635	480.697	411.073	160.136	−307.306	−208.777	4.741
2400	82.676	484.215	414.047	168.402	−358.275	−203.409	4.427
2500	82.712	487.591	416.922	176.671	−359.124	−196.939	4.115
2600	82.745	490.835	419.703	184.944	−360.000	−190.434	3.826
2700	82.773	493.959	422.396	193.220	−360.904	−183.895	3.558
2800	82.799	496.969	425.006	201.499	−361.837	−177.322	3.308
2900	82.822	499.875	427.537	209.780	−362.797	−170.716	3.075
3000	82.843	502.684	429.996	218.063	−363.783	−164.076	2.857
3100	82.862	505.400	432.385	226.349	−364.793	−157.402	2.652
3200	82.879	508.031	434.708	234.636	−365.824	−150.696	2.460
3300	82.895	510.582	436.968	242.924	−366.875	−143.956	2.279
3400	82.909	513.057	439.170	251.215	−367.941	−137.186	2.108
3500	82.923	515.460	441.316	259.506	−369.019	−130.383	1.946
3600	82.935	517.797	443.408	267.799	−370.107	−123.549	1.793
3700	82.946	520.069	445.449	276.093	−371.199	−116.685	1.647
3800	82.956	522.281	447.442	284.388	−372.294	−109.792	1.509
3900	82.966	524.436	449.389	292.684	−373.386	−102.870	1.378
4000	82.974	526.537	451.291	300.981	−374.473	−95.920	1.253
4100	82.982	528.586	453.152	309.279	−375.552	−88.943	1.133
4200	82.990	530.585	454.972	317.578	−856.467	−74.915	0.932
4300	82.997	532.538	456.753	325.877	−856.431	−56.307	0.684
4400	83.004	534.446	458.497	334.177	−856.378	−37.700	0.448
4500	83.010	536.312	460.206	342.478	−856.307	−19.095	0.222
4600	83.016	538.136	461.880	350.779	−856.215	−0.491	0.006
4700	83.021	539.922	463.522	359.081	−856.100	18.111	−0.201
4800	83.026	541.670	465.132	367.383	−855.961	36.710	−0.399
4900	83.031	543.382	466.711	375.686	−855.796	55.305	−0.590
5000	83.035	545.059	468.261	383.989	−855.603	73.897	−0.772
5100	83.039	546.704	469.783	392.293	−855.382	92.485	−0.947
5200	83.043	548.316	471.278	400.597	−855.133	111.068	−1.116
5300	83.047	549.898	472.747	408.902	−854.854	129.647	−1.278
5400	83.051	551.450	474.190	417.207	−854.544	148.219	−1.434
5500	83.054	552.974	475.608	425.512	−854.205	166.786	−1.584
5600	83.057	554.471	477.003	433.818	−853.835	185.346	−1.729
5700	83.060	555.941	478.375	442.123	−853.436	203.899	−1.869
5800	83.063	557.385	479.725	450.430	−853.006	222.445	−2.003
5900	83.066	558.805	481.054	458.736	−852.546	240.983	−2.134
6000	83.068	560.202	482.361	467.043	−852.058	259.514	−2.259

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [309.99] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−499 ± 10] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−515 ± 10] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1310(1)	869 (1)
[418](1)	[283](1)
[183](1)	[496](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–Br = 1.87 Å; B–Cl = 1.295 Å
Bond Angles: Br–B–Br = [120]°; Br–B–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = 8.725604 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming $\Delta_f H° = 0$ for the reaction 2 $BBr_3(g)$ + $BF_3(g)$ → 3 $BBr_2F(g)$.

Heat Capacity and Entropy

Two of the vibrational frequencies were observed and assigned by Lindeman and Wilson.[1] The remaining frequencies were calculated by a normal coordinate treatment using force constants obtained by comparison with the other mixed trihalides. The bond distances were reported by Wentink and Tiensuu.[2] The bond angles are estimated by analogy with the other trihalides. The principal moments of inertia are $I_A = 14.8465 \times 10^{-39}$, $I_B = 69.5984 \times 10^{-39}$, and $I_C = 84.4449 \times 10^{-39}\ g·cm^2$.

References

[1]L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).
[2]T. Wentink and V. H. Tiensuu, J. Chem. Phys. **28**, 826 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−14.170	−498.666	−498.666	INFINITE
100	41.579	253.624	359.617	−10.599	−499.366	−510.795	266.812
200	54.385	286.688	315.462	−5.755	−501.220	−521.525	136.208
250	58.848	299.322	311.001	−2.920	−502.323	−526.478	110.001
298.15	62.316	309.994	309.994	0.	−514.632	−529.706	92.802
300	62.436	310.380	309.995	0.115	−514.707	−529.799	92.246
350	65.384	320.233	310.766	3.313	−545.581	−530.619	79.191
400	67.832	329.128	312.515	6.645	−545.629	−528.478	69.012
450	69.875	337.239	314.818	10.090	−545.687	−526.331	61.095
500	71.585	344.692	317.438	13.627	−545.752	−524.177	54.760
600	74.230	357.991	323.115	20.926	−545.891	−519.849	45.257
700	76.122	369.584	328.943	28.448	−546.038	−515.497	38.467
800	77.502	379.843	334.677	36.133	−546.193	−511.124	33.373
900	78.530	389.034	340.215	43.937	−546.362	−506.730	29.410
1000	79.310	397.350	345.519	51.831	−546.550	−502.317	26.238
1100	79.913	404.939	350.581	59.793	−546.760	−497.884	23.643
1200	80.388	411.913	355.406	67.809	−546.998	−493.430	21.478
1300	80.768	418.363	360.003	75.868	−547.266	−488.955	19.646
1400	81.076	424.360	364.389	83.960	−547.568	−484.459	18.075
1500	81.329	429.963	368.576	92.081	−547.906	−479.939	16.713
1600	81.538	435.219	372.578	100.225	−548.282	−475.396	15.520
1700	81.714	440.167	376.410	108.388	−548.699	−470.828	14.467
1800	81.863	444.842	380.083	116.567	−549.158	−466.235	13.530
1900	81.990	449.272	383.609	124.759	−549.662	−461.614	12.691
2000	82.099	453.480	386.998	132.964	−550.211	−456.966	11.935
2100	82.193	457.488	390.260	141.179	−550.806	−452.289	11.250
2200	82.276	461.314	393.404	149.402	−551.448	−447.583	10.627
2300	82.348	464.973	396.436	157.633	−552.137	−442.847	10.057
2400	82.411	468.479	399.366	165.872	−603.132	−437.010	9.511
2500	82.468	471.844	402.198	174.116	−603.991	−430.071	8.986
2600	82.518	475.080	404.939	182.365	−604.861	−423.097	8.500
2700	82.563	478.195	407.595	190.619	−605.740	−416.090	8.050
2800	82.603	481.198	410.171	198.877	−606.628	−409.050	7.631
2900	82.639	484.097	412.670	207.139	−607.520	−401.977	7.240
3000	82.672	486.900	415.098	215.405	−608.416	−394.874	6.875
3100	82.701	489.611	417.458	223.674	−609.311	−387.742	6.533
3200	82.728	492.237	419.754	231.945	−610.203	−380.580	6.212
3300	82.753	494.783	421.989	240.219	−611.089	−373.391	5.910
3400	82.775	497.254	424.167	248.496	−611.966	−366.174	5.626
3500	82.796	499.653	426.289	256.774	−612.830	−358.933	5.357
3600	82.815	501.986	428.360	265.055	−613.680	−351.666	5.103
3700	82.832	504.255	430.381	273.337	−614.512	−344.377	4.862
3800	82.848	506.465	432.354	281.621	−615.323	−337.065	4.633
3900	82.863	508.617	434.282	289.907	−616.111	−329.732	4.416
4000	82.877	510.715	436.167	298.194	−616.875	−322.379	4.210
4100	82.890	512.762	438.010	306.482	−617.611	−315.008	4.013
4200	82.901	514.759	439.814	314.771	−1098.169	−300.594	3.738
4300	82.913	516.710	441.579	323.062	−1097.759	−281.609	3.421
4400	82.923	518.616	443.308	331.354	−1097.319	−262.634	3.118
4500	82.933	520.480	445.003	339.647	−1096.849	−243.669	2.828
4600	82.942	522.303	446.663	347.940	−1096.348	−224.715	2.552
4700	82.950	524.087	448.292	356.235	−1095.814	−205.772	2.287
4800	82.958	525.833	449.889	364.530	−1095.249	−186.841	2.033
4900	82.965	527.544	451.457	372.827	−1094.652	−167.922	1.790
5000	82.973	529.220	452.995	381.123	−1094.022	−149.015	1.557
5100	82.979	530.863	454.506	389.421	−1093.361	−130.122	1.333
5200	82.985	532.474	455.990	397.719	−1092.668	−111.241	1.117
5300	82.991	534.055	457.448	406.018	−1091.944	−92.374	0.910
5400	82.997	535.606	458.881	414.318	−1091.190	−73.522	0.711
5500	83.002	537.129	460.290	422.618	−1090.407	−54.683	0.519
5600	83.007	538.625	461.675	430.918	−1089.594	−35.859	0.334
5700	83.012	540.094	463.038	439.219	−1088.753	−17.050	0.156
5800	83.016	541.538	464.379	447.520	−1087.885	1.744	−0.016
5900	83.021	542.957	465.699	455.822	−1086.991	20.523	−0.182
6000	83.025	544.353	466.998	464.124	−1086.071	39.287	−0.342

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [292.27]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-87 \pm 5]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-105 \pm 5]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
2600 (1)	1044(1)
[532](1)	775(1)
[158](1)	783(1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: B–H = 1.20 Å; B–Br = [1.87] Å

Bond Angles: Br–B–Br = 119.3 ± 2°; Br–B–H = 120.3 ± 1°

Product of the Moments of Inertia: $I_A I_B I_C = 1.096494 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The value of $\Delta_f H°(BBr_2H, g, 298.15\ K)$ is derived by assuming the B–H bond strength to be 92 $kcal·mol^{-1}$, the same as that in $BCl_2H(g)$.

Heat Capacity and Entropy

The molecular structure, B–H bond distance and bond angle were obtained from Lynds and Bass.[1] The B–Br bond distance is taken from that in $BBr_3(g)$ molecule. The vibrational frequencies adopted and corrected to the average isotopic species were assigned to Brieux de Mandirola and Westerkamp[2] from infrared spectrum. The values in brackets are calculated by the Wilson's FG method. Infrared spectrum of $BBr_2H(g)$ was also reported by Wason and Porter[3] and three frequencies, υ_1, υ_4, and υ_5, were assigned. The principal moments of inertia are: $I_A = 2.2244 \times 10^{-39}$, $I_B = 69.1057 \times 10^{-39}$, and $I_C = 71.3302 \times 10^{-39}\ g·cm^2$.

References

[1]L. Lynds and C. D. Bass, J. Phys. Chem. **41**, 3165 (1964).

[2]O. Brieux de Mandirola and J. F. Westerkamp, Spectrochim. Acta **21**, 1101 (1965).

[3]S. K. Wason and R. F. Porter, J. Phys. Chem. **69**, 2461 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.624	−87.267	−87.267	INFINITE
100	39.016	243.626	334.406	−9.078	−88.038	−101.949	53.252
200	45.697	272.588	296.897	−4.862	−90.403	−115.011	30.038
250	49.642	283.208	293.122	−2.478	−91.904	−120.994	25.280
298.15	53.246	292.265	292.265	0.	−104.600	−125.138	21.924
300	53.377	292.595	292.266	0.099	−104.689	−125.265	21.811
350	56.661	301.076	292.929	2.852	−135.938	−126.969	18.949
400	59.453	308.830	294.439	5.756	−136.327	−125.661	16.410
450	61.805	315.972	296.440	8.790	−136.693	−124.305	14.429
500	63.795	322.590	298.728	11.931	−137.036	−122.910	12.840
600	66.971	334.516	303.721	18.477	−137.655	−120.025	10.449
700	69.410	345.030	308.886	25.301	−138.194	−117.043	8.734
800	71.355	354.430	314.002	32.342	−138.664	−113.989	7.443
900	72.944	362.929	318.974	39.560	−139.080	−110.879	6.435
1000	74.259	370.685	323.763	46.922	−139.456	−107.725	5.627
1100	75.357	377.815	328.357	54.405	−139.806	−104.535	4.964
1200	76.281	384.413	332.757	61.988	−140.142	−101.313	4.410
1300	77.063	390.550	336.969	69.656	−140.477	−98.064	3.940
1400	77.728	396.286	341.003	77.396	−140.817	−94.789	3.537
1500	78.296	401.669	344.870	85.198	−141.173	−91.489	3.186
1600	78.785	406.738	348.580	93.053	−141.549	−88.165	2.878
1700	79.207	411.527	352.143	100.953	−141.953	−84.816	2.606
1800	79.573	416.065	355.569	108.893	−142.389	−81.443	2.363
1900	79.893	420.376	358.868	116.866	−142.862	−78.044	2.146
2000	80.174	424.482	362.047	124.870	−143.376	−74.619	1.949
2100	80.420	428.399	365.114	132.900	−143.936	−71.168	1.770
2200	80.639	432.146	368.076	140.953	−144.543	−67.689	1.607
2300	80.833	435.735	370.940	149.027	−145.201	−64.181	1.458
2400	81.006	439.179	373.712	157.119	−196.170	−59.574	1.297
2500	81.160	442.489	376.398	165.227	−197.012	−53.865	1.125
2600	81.299	445.674	379.001	173.350	−197.876	−48.123	0.967
2700	81.424	448.745	381.528	181.487	−198.762	−42.346	0.819
2800	81.537	451.708	383.982	189.635	−199.671	−36.537	0.682
2900	81.640	454.571	386.367	197.794	−200.601	−30.694	0.553
3000	81.733	457.341	388.687	205.963	−201.551	−24.819	0.432
3100	81.818	460.022	390.945	214.140	−202.520	−18.912	0.319
3200	81.896	462.621	393.144	222.326	−203.506	−12.974	0.212
3300	81.967	465.142	395.288	230.519	−204.506	−7.004	0.111
3400	82.032	467.590	397.379	238.719	−205.520	−1.004	0.015
3500	82.092	469.969	399.419	246.925	−206.543	5.026	−0.075
3600	82.147	472.282	401.411	255.137	−207.574	11.086	−0.161
3700	82.199	474.534	403.357	263.355	−208.611	17.174	−0.242
3800	82.246	476.727	405.259	271.577	−209.651	23.290	−0.320
3900	82.290	478.864	407.119	279.804	−210.692	29.434	−0.394
4000	82.331	480.947	408.939	288.035	−211.731	35.604	−0.465
4100	82.369	482.981	410.720	296.270	−212.767	41.800	−0.533
4200	82.404	484.966	412.464	304.508	−693.648	55.046	−0.685
4300	82.437	486.906	414.173	312.751	−693.584	72.871	−0.885
4400	82.468	488.801	415.848	320.996	−693.515	90.695	−1.077
4500	82.497	490.655	417.489	329.244	−693.437	108.517	−1.260
4600	82.524	492.468	419.100	337.495	−693.351	126.337	−1.435
4700	82.550	494.243	420.680	345.749	−693.255	144.155	−1.602
4800	82.574	495.982	422.230	354.005	−693.149	161.972	−1.763
4900	82.596	497.684	423.753	362.264	−693.032	179.785	−1.917
5000	82.618	499.353	425.248	370.524	−692.903	197.597	−2.064
5100	82.638	500.989	426.718	378.787	−692.762	215.405	−2.206
5200	82.656	502.594	428.161	387.052	−692.610	233.211	−2.343
5300	82.674	504.169	429.581	395.318	−692.445	251.014	−2.474
5400	82.691	505.714	430.976	403.587	−692.269	268.813	−2.600
5500	82.707	507.232	432.349	411.857	−692.080	286.609	−2.722
5600	82.723	508.722	433.699	420.128	−691.878	304.402	−2.839
5700	82.737	510.187	435.029	428.401	−691.665	322.191	−2.953
5800	82.751	511.626	436.337	436.675	−691.440	339.976	−3.062
5900	82.764	513.040	437.625	444.951	−691.203	357.757	−3.167
6000	82.776	514.432	438.893	453.228	−690.954	375.533	−3.269

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K)$ = [228.9] $J·K^{-1}·mol^{-1}$
T_{fus} = 228.9 K

$\Delta_f H°(298.15\ K)$ = [−238.49 ± 0.2] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = Unknown

Enthalpy of Formation

The enthalpy of formation of boron tribromide liquid has been determined by Skinner and Smith[1] by hydrolysis to H_3BO_3 and HBr. The adopted enthalpy of formation is calculated from the hydrolysis data[1] using $\Delta_f H°(H_3BO_3, cr, 298.15\ K)$ from these tables, $\Delta_{sol}H°(H_3BO_3, cr)$, from Fasilino[2] with the dilution data of Smisko and Mason.[3] The $\Delta_f H°$(HBr, aq) was taken from Evans.[4]

Heat Capacity and Entropy

The heat capacity was estimated from that of the gas by Kelley.[5] The entropy is back calculated from that of the gas by adjusting the free energy functions to give the best fit of the vapor pressure data.

Fusion Data

The temperature of melting was reported by Boubeau and Keller,[6] and Stock and Kuss.[7] This value was recently confirmed by the triple point measurement of 227.31 K by Barber, Boynton, and Gallagher.[8]

Vaporization Data

The boiling point is from the data of Stock and Kuss.[7] A 2nd and 3rd law analysis of the vapor pressure data of Stock and Kuss[7] and Barber *et al.*[8] indicated that the data of Stock and Kuss[7] gave the best agreement as indicated below.

Sources	$\Delta_{vap}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	
		$S°(298.15\ K)$ = 54.7	$S°(298.15\ K)$ = 54.26
[7]	8.175 ± 0.03	8.222 (−0.02)	8.361 (0.42)
[8]	8.229 ± 0.03	8.203 (−0.44)	8.347 (0.00)

Stock and Kuss[7] had the first eight data points rejected due to a statistical test on the 3rd law values. The values in parentheses are values of the 3rd law drift measured as $\Delta(\Delta H)/\Delta T$. The 2nd law entropy also confirmed the choice of the data of Stock and Kuss[7] and an entropy of 54.7 $cal·K^{-1}·mol^{-1}$.

References

[1] H. A. Skinner and N. B. Smith, Trans. Faraday Soc. **51**, 19 (1955).
[2] L. G. Fasilino, National Research Corporation, Special Report NONR 3608(00), (June 2, 1964).
[3] J. Smisko and L. S. Mason, J. Am. Chem. Soc. **72**, 3679 (1950).
[4] W. H. Evans, U. S. Nat. Bur. Stand. Report 8504, Appendix III, (1964).
[5] K. K. Kelley, U. S. Bur. Mines Bull. 383, 166 pp. (1935).
[6] J. Goubeau and H. Keller, Z. anorg. allgem. Chem. **267**, 1 (1951).
[7] A. Stock and E. Kuss, Ber. **47**, 3113 (1914).
[8] W. F. Barber, C. F. Boynton and P. E. Gallagher, J. Chem. Eng. Data **9**, 137 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200	128.030	177.745	240.576	−12.566	−224.975	−233.814	61.066
298.15	128.030	228.865	228.865	*0.*	−238.488	−236.914	41.506
300	128.030	229.657	228.867	0.237	−238.482	−236.904	41.249
400	128.030	266.489	233.889	13.040	−278.762	−227.783	29.745
500	128.030	295.058	243.372	25.843	−273.227	−215.687	22.533
600	128.030	318.400	253.990	38.646	−267.984	−204.675	17.819
700	128.030	338.136	264.638	51.449	−262.944	−194.524	14.516
800	128.030	355.233	274.917	64.252	−258.053	−185.085	12.085
900	128.030	370.312	284.696	77.055	−253.277	−176.252	10.229
1000	128.030	383.802	293.944	89.858	−248.598	−167.946	8.773

PREVIOUS: September 1962 CURRENT: December 1964

$S°(298.15\ K) = 324.31\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -181.9 \pm 0.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -204.2 \pm 0.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
278(1)
379(1)
827(2)
150(2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: B–Br = 1.87 ± 0.02 Å
Bond Angle: Br–B = 120° ± 6°
Product of the Moments of Inertia: $I_A I_B I_C = 6.742600 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is obtained from the enthalpy of formation of the liquid plus the heat of vaporization at 298.15 K, taken as 8.20 $kcal·mol^{-1}$ as the average 2nd and 3rd law value derived from the vapor pressures of Stock and Kuss.[1] Refer to $BBr_3(l)$ table for details.

Heat Capacity and Entropy

Vibrational frequencies were obtained from Wentink and Tiensuu[2] and modified for the natural isotopic abundance (^{10}B 18.83%, ^{11}B 81.1%). B–Br bond distance was reported by Wentink and Tiensuu.[2] Br–B–Br angle was taken from Sutton.[3] The principal moments of inertia are $I_A = I_B = 69.5984 \times 10^{-39}$, $I_C = 139.1968 \times 10^{-39}\ g·cm^2$.

References

[1]A. Stock and E. Kuss, Ber. **47**, 3113 (1914).
[2]T. Wentink, Jr., and V. H. Tiensuu, J. Chem. Phys. **28**, 825 (1958).
[3]L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions", Special Publication No. 11, The Chemical Society, London, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.711	−181.912	−181.912	INFINITE
100	48.309	260.958	379.306	−11.835	−182.250	−200.238	104.593
200	60.557	298.686	330.295	−6.322	−184.421	−217.449	56.792
250	64.597	312.649	325.406	−3.189	−185.884	−225.543	47.125
298.15	67.771	324.307	324.307	0.	−204.179	−231.062	40.481
300	67.880	324.727	324.309	0.125	−204.285	−231.228	40.260
350	70.521	335.397	325.145	3.588	−250.425	−233.188	34.801
400	72.626	344.956	327.034	7.169	−250.324	−230.733	30.131
450	74.301	353.611	329.514	10.843	−250.239	−228.289	26.499
500	75.640	361.511	332.325	14.593	−250.168	−225.854	23.595
600	77.590	375.487	338.384	22.261	−250.060	−221.002	19.240
700	78.897	387.552	344.566	30.090	−249.994	−216.165	16.130
800	79.804	398.150	350.615	38.028	−249.968	−211.335	13.799
900	80.455	407.589	356.431	46.042	−249.981	−206.505	11.985
1000	80.936	416.092	361.979	54.113	−250.034	−201.672	10.534
1100	81.301	423.824	367.255	62.226	−250.126	−196.832	9.347
1200	81.583	430.910	372.268	70.370	−250.258	−191.981	8.357
1300	81.806	437.450	377.034	78.540	−250.430	−187.118	7.518
1400	81.985	443.519	381.569	86.730	−250.644	−182.240	6.799
1500	82.130	449.180	385.889	94.936	−250.901	−177.346	6.176
1600	82.250	454.485	390.013	103.155	−251.202	−172.432	5.629
1700	82.350	459.474	393.953	111.386	−251.549	−167.499	5.147
1800	82.434	464.184	397.725	119.625	−251.946	−162.544	4.717
1900	82.506	468.643	401.342	127.872	−252.393	−157.565	4.332
2000	82.567	472.876	404.813	136.126	−252.895	−152.561	3.984
2100	82.620	476.906	408.151	144.385	−253.454	−147.531	3.670
2200	82.666	480.751	411.364	152.649	−254.073	−142.472	3.383
2300	82.706	484.426	414.462	160.918	−254.753	−137.385	3.120
2400	82.742	487.947	417.451	169.191	−305.756	−131.197	2.855
2500	82.773	491.325	420.339	177.466	−306.640	−123.906	2.589
2600	82.801	494.572	423.132	185.745	−307.556	−116.579	2.342
2700	82.825	497.697	425.836	194.026	−308.503	−109.215	2.113
2800	82.848	500.710	428.457	202.310	−309.480	−101.817	1.899
2900	82.867	503.618	430.998	210.596	−310.484	−94.382	1.700
3000	82.885	506.427	433.466	218.883	−311.515	−86.913	1.513
3100	82.902	509.145	435.864	227.173	−312.568	−79.409	1.338
3200	82.917	511.778	438.195	235.464	−313.640	−71.871	1.173
3300	82.930	514.329	440.464	243.756	−314.729	−64.298	1.018
3400	82.942	516.805	442.673	252.050	−315.829	−56.693	0.871
3500	82.954	519.210	444.826	260.344	−316.938	−49.056	0.732
3600	82.964	521.547	446.924	268.640	−318.051	−41.386	0.600
3700	82.974	523.820	448.972	276.937	−319.164	−33.685	0.476
3800	82.982	526.033	450.971	285.235	−320.273	−25.955	0.357
3900	82.991	528.188	452.923	293.534	−321.376	−18.196	0.244
4000	82.998	530.290	454.831	301.833	−322.468	−10.408	0.136
4100	83.005	532.339	456.697	310.133	−323.546	−2.593	0.033
4200	83.012	534.340	458.522	318.434	−804.457	12.272	−0.153
4300	83.018	536.293	460.308	326.736	−804.412	31.718	−0.385
4400	83.023	538.202	462.057	335.038	−804.347	51.162	−0.607
4500	83.029	540.067	463.769	343.340	−804.260	70.604	−0.820
4600	83.034	541.892	465.448	351.644	−804.150	90.045	−1.022
4700	83.038	543.678	467.094	359.947	−804.014	109.482	−1.217
4800	83.043	545.426	468.707	368.251	−803.853	128.917	−1.403
4900	83.047	547.139	470.291	376.556	−803.664	148.347	−1.581
5000	83.051	548.816	471.844	384.860	−803.448	167.774	−1.753
5100	83.054	550.461	473.370	393.166	−803.203	187.197	−1.917
5200	83.058	552.074	474.868	401.471	−802.931	206.613	−2.075
5300	83.061	553.656	476.340	409.777	−802.630	226.025	−2.228
5400	83.064	555.209	477.786	418.083	−802.301	245.431	−2.374
5500	83.067	556.733	479.207	426.390	−801.943	264.830	−2.515
5600	83.070	558.230	480.605	434.697	−801.559	284.222	−2.651
5700	83.072	559.700	481.980	443.004	−801.147	303.608	−2.782
5800	83.075	561.145	483.332	451.311	−800.708	322.985	−2.909
5900	83.077	562.565	484.663	459.619	−800.244	342.355	−3.031
6000	83.079	563.961	485.973	467.927	−799.755	361.717	−3.149

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 213.24\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 138.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 141.4\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 843.65\ cm^{-1}$ $\omega_e x_e = 5.167\ cm^{-1}$ $\sigma = 1$
$B_e = 0.6914\ cm^{-1}$ $\alpha_e = 0.00657\ cm^{-1}$ $r_e = 1.7157$ Å

Enthalpy of Formation

Dissociation energies of BCl(g) has been reported by Herzberg,[1] Gaydon,[2] and Barrow.[3] The corresponding values of $\Delta_f H°$(BCl, g, 298.15 K) are derived. The results are given as follows:

Source	Dissociation Energy, $D_0°$ eV	$D_0°$ kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[1]	4.2	96.9	62.6
[2]	5.1 ± 0.4	117.6 ± 9.2	41.8 ± 9.2
[3]	—	127	33.8 ± 4

The last value of $\Delta_f H°$(298.15 K) listed in the above table is adopted. Using the bond energy, $D_0°$(B–Cl), obtained from BCl_3(g) molecule, $\Delta_f H°$(298.15 K) for BCl(g) is calculated as 37.8 kcal·mol^{-1} employing the same ratio of $D_0°$(B–X)/ average bond energy of BX_3 as found in BF(g) and BF_3(g), which is within the uncertainty of the value evaluated from dissociation energy.

Heat Capacity and Entropy

The spectroscopic constants are obtained from Herzberg[1] and corrected to the average isotopic species.

References

[1]G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand Company, Inc., New York, (1950).
[2]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall Ltd., London, 261 pp. (1953).
[3]R. F. Barrow, Trans. Faraday Soc. **56**, 952 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−8.862	138.362	138.362	INFINITE
100	29.117	180.668	240.206	−5.954	139.790	131.204	−68.534
200	29.874	200.994	216.081	−3.017	140.875	122.156	−31.904
250	30.748	207.751	213.761	−1.502	141.209	117.435	−24.537
298.15	31.659	213.245	213.245	0.	141.419	112.835	−19.768
300	31.693	213.441	213.245	0.059	141.425	112.658	−19.615
350	32.572	218.394	213.635	1.666	141.546	107.852	−16.096
400	33.335	222.794	214.510	3.314	141.583	103.036	−13.455
450	33.976	226.759	215.654	4.997	141.551	98.219	−11.401
500	34.510	230.367	216.948	6.710	141.462	93.408	−9.758
600	35.322	236.735	219.729	10.204	141.159	83.823	−7.297
700	35.892	242.225	222.560	13.766	140.730	74.300	−5.544
800	36.307	247.046	225.325	17.377	140.209	64.844	−4.234
900	36.619	251.342	227.982	21.024	139.614	55.459	−3.219
1000	36.861	255.213	230.514	24.698	138.958	46.143	−2.410
1100	37.054	258.735	232.922	28.394	138.249	36.895	−1.752
1200	37.214	261.967	235.210	32.108	137.493	27.714	−1.206
1300	37.348	264.951	237.384	35.836	136.693	18.598	−0.747
1400	37.464	267.723	239.453	39.577	135.853	9.545	−0.356
1500	37.566	270.311	241.425	43.329	134.975	0.554	−0.019
1600	37.656	272.738	243.307	47.090	134.060	−8.378	0.274
1700	37.739	275.024	245.106	50.860	133.109	−17.251	0.530
1800	37.814	277.183	246.829	54.637	132.124	−26.068	0.756
1900	37.884	279.230	248.481	58.422	131.103	−34.829	0.958
2000	37.950	281.174	250.067	62.214	130.049	−43.535	1.137
2100	38.012	283.028	251.593	66.012	128.960	−52.187	1.298
2200	38.071	284.797	253.063	69.816	127.837	−60.787	1.443
2300	38.128	286.491	254.479	73.626	126.679	−69.335	1.575
2400	38.182	288.115	255.847	77.442	75.227	−76.763	1.671
2500	38.235	289.674	257.169	81.263	73.920	−83.069	1.736
2600	38.286	291.175	258.449	85.089	72.611	−89.323	1.795
2700	38.336	292.621	259.688	88.920	71.297	−95.526	1.848
2800	38.385	294.016	260.889	92.756	69.978	−101.681	1.897
2900	38.433	295.364	262.055	96.597	68.655	−107.788	1.941
3000	38.480	296.668	263.187	100.443	67.327	−113.850	1.982
3100	38.527	297.930	264.287	104.293	65.994	−119.867	2.020
3200	38.572	299.154	265.358	108.148	64.656	−125.841	2.054
3300	38.617	300.342	266.400	112.008	63.313	−131.774	2.086
3400	38.662	301.495	267.415	115.872	61.967	−137.665	2.115
3500	38.706	302.617	268.405	119.740	60.618	−143.517	2.142
3600	38.750	303.708	269.371	123.613	59.266	−149.330	2.167
3700	38.793	304.770	270.313	127.490	57.913	−155.106	2.190
3800	38.837	305.805	271.234	131.372	56.560	−160.845	2.211
3900	38.879	306.814	272.133	135.257	55.208	−166.549	2.231
4000	38.922	307.799	273.012	139.147	53.859	−172.218	2.249
4100	38.964	308.761	273.873	143.042	52.513	−177.853	2.266
4200	39.006	309.700	274.714	146.940	−428.678	−176.431	2.194
4300	39.048	310.619	275.539	150.843	−428.926	−170.422	2.070
4400	39.090	311.517	276.346	154.750	−429.168	−164.408	1.952
4500	39.131	312.396	277.138	158.661	−429.404	−158.388	1.839
4600	39.173	313.256	277.914	162.576	−429.632	−152.363	1.730
4700	39.214	314.099	278.675	166.495	−429.852	−146.333	1.626
4800	39.255	314.925	279.421	170.419	−430.063	−140.298	1.527
4900	39.296	315.735	280.154	174.346	−430.264	−134.259	1.431
5000	39.337	316.529	280.874	178.278	−430.455	−128.217	1.339
5100	39.378	317.309	281.580	182.214	−430.635	−122.170	1.251
5200	39.419	318.074	282.275	186.154	−430.803	−116.120	1.166
5300	39.459	318.825	282.957	190.098	−430.960	−110.067	1.085
5400	39.500	319.563	283.629	194.046	−431.106	−104.011	1.006
5500	39.541	320.288	284.288	197.998	−431.239	−97.952	0.930
5600	39.581	321.001	284.938	201.954	−431.359	−91.892	0.857
5700	39.621	321.702	285.577	205.914	−431.468	−85.829	0.787
5800	39.662	322.391	286.205	209.878	−431.565	−79.764	0.718
5900	39.702	323.070	286.824	213.846	−431.650	−73.698	0.652
6000	39.742	323.737	287.434	217.818	−431.723	−67.630	0.589

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [219.1 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [1225 \pm 42]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1234 \pm 42]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma]$	0	[2]
	[2800]	[4]

$\omega_e = [845]\ cm^{-1}$ $\omega_e x_e = [5]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.68]\ cm^{-1}$ $\alpha_e = [0.0056]\ cm^{-1}$ $r_e = [1.73]$ Å

Enthalpy of Formation

Several values of the appearance potential of BCl^+ from BCl_3 have been reported. Osberghaus[1] gave 19.2 eV, Marriott and Craggs[2] reported 18.54 ± 0.07 eV, and Koski *et al.*[3] obtained two values of 17.2 ± 0.2 Ev and 20 ± 0.2 eV. We make the presumption that the higher values, 19.2 and 20, refer to the reaction $BCl_3(g) + e^-$, $2\ Cl(g) + 2e^-$ and the other values to $BCl_3(g) + e^- \rightarrow BCl^+ + Cl_2(g) + 2\ e^-$. Using the lower value in each case to help eliminate any excess kinetic energy, we obtain $\Delta_f H°(BCl^+, g, 298.15\ K) = 289$ and 300 $kcal \cdot mol^{-1}$, respectively. We adopt an average value of $\Delta_f H°(BCl^+, g, 298.15\ K) = 295 \pm 10\ kcal \cdot mol^{-1}$, which corresponds to an ionization potential for BCl(g) of 11.3 ± 0.3 eV.

Heat Capacity and Entropy

BCl^+ is isoelectronic with BeCl, and the ground state configuration and electronic levels are estimated by comparison with BeCl. The bond length, frequency and anharmonicity constant are estimated between the value for BCl and BeCl; the rotational constant is calculated from the bond length and atomic masses, and α_e is obtained from the above constants assuming a Morse potential function.

References

[1]O. Osberghaus, Z. Phys. **128**, 366 (1950).
[2]J. Marriott and J. D. Craggs, J. Electron. Contr. **3**, 194 (1957).
[3]W. S. Koski, J. J. Kaufman and C. F. Pachuki, J. Am. Chem. Soc. **81**, 1326 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.860	1225.027		
100	29.117	186.560	246.084	−5.952			
200	29.867	206.884	221.965	−3.016			
250	30.736	213.639	219.647	−1.502			
298.15	31.643	219.131	219.131	0.	1234.280	1197.686	−209.830
300	31.678	219.326	219.131	0.059	1234.325	1197.459	−208.496
350	32.555	224.277	219.520	1.665	1235.484	1191.222	−177.780
400	33.316	228.675	220.395	3.312	1236.559	1184.825	−154.722
450	33.957	232.637	221.538	4.994	1237.565	1178.297	−136.773
500	34.490	236.243	222.831	6.706	1238.515	1171.660	−122.402
600	35.300	242.608	225.611	10.198	1240.288	1158.120	−100.823
700	35.869	248.094	228.440	13.758	1241.936	1144.294	−85.388
800	36.282	252.912	231.204	17.367	1243.491	1130.238	−73.797
900	36.592	257.205	233.859	21.011	1244.972	1115.991	−64.770
1000	36.832	261.073	236.390	24.683	1246.391	1101.584	−57.541
1100	37.024	264.593	238.796	28.376	1247.758	1087.036	−51.619
1200	37.181	267.821	241.082	32.086	1249.077	1072.367	−46.679
1300	37.313	270.803	243.255	35.811	1250.353	1057.589	−42.494
1400	37.426	273.572	245.323	39.548	1251.588	1042.714	−38.904
1500	37.526	276.158	247.294	43.296	1252.785	1027.752	−35.790
1600	37.614	278.582	249.174	47.053	1253.944	1012.712	−33.062
1700	37.694	280.865	250.972	50.819	1255.068	997.601	−30.653
1800	37.767	283.022	252.693	54.592	1256.156	982.424	−28.509
1900	37.835	285.065	254.343	58.372	1257.210	967.188	−26.590
2000	37.898	287.008	255.929	62.158	1258.229	951.897	−24.861
2100	37.957	288.858	257.453	65.951	1259.213	936.556	−23.296
2200	38.014	290.625	258.921	69.750	1260.163	921.169	−21.871
2300	38.068	292.316	260.336	73.554	1261.078	905.739	−20.570
2400	38.120	293.938	261.703	77.363	1211.698	891.340	−19.400
2500	38.171	295.495	263.024	81.178	1212.464	877.976	−18.344
2600	38.220	296.993	264.302	84.997	1213.226	864.581	−17.370
2700	38.268	298.436	265.539	88.822	1213.984	851.157	−16.467
2800	38.315	299.829	266.739	92.651	1214.738	837.706	−15.628
2900	38.361	301.174	267.903	96.485	1215.486	824.227	−14.846
3000	38.407	302.475	269.034	100.323	1216.229	810.723	−14.116
3100	38.453	303.735	270.133	104.166	1216.967	797.193	−13.433
3200	38.499	304.957	271.203	108.014	1217.700	783.641	−12.792
3300	38.545	306.142	272.244	111.866	1218.429	770.065	−12.189
3400	38.591	307.294	273.258	115.723	1219.154	756.467	−11.622
3500	38.638	308.413	274.246	119.584	1219.876	742.848	−11.086
3600	38.686	309.502	275.210	123.450	1220.597	729.209	−10.581
3700	38.735	310.563	276.152	127.321	1221.316	715.549	−10.102
3800	38.785	311.597	277.071	131.197	1222.037	701.870	−9.648
3900	38.837	312.605	277.969	135.079	1222.759	688.172	−9.217
4000	38.890	313.589	278.847	138.965	1223.484	674.456	−8.807
4100	38.945	314.550	279.706	142.857	1224.214	660.721	−8.418
4200	39.002	315.489	280.547	146.754	745.101	653.993	−8.134
4300	39.062	316.407	281.371	150.657	746.932	651.802	−7.918
4400	39.124	317.306	282.177	154.566	748.770	649.568	−7.711
4500	39.188	318.186	282.968	158.482	750.618	647.293	−7.514
4600	39.255	319.048	283.743	162.404	752.475	644.976	−7.324
4700	39.324	319.893	284.503	166.333	754.343	642.619	−7.142
4800	39.397	320.721	285.249	170.269	756.223	640.222	−6.967
4900	39.472	321.535	285.981	174.213	758.117	637.786	−6.799
5000	39.550	322.333	286.700	178.164	760.024	635.311	−6.637
5100	39.631	323.117	287.406	182.123	761.946	632.798	−6.481
5200	39.715	323.887	288.101	186.090	763.883	630.246	−6.331
5300	39.802	324.644	288.783	190.066	765.837	627.658	−6.186
5400	39.892	325.389	289.454	194.051	767.807	625.032	−6.046
5500	39.985	326.122	290.114	198.044	769.795	622.370	−5.911
5600	40.081	326.843	290.764	202.048	771.800	619.671	−5.780
5700	40.180	327.554	291.403	206.061	773.822	616.937	−5.654
5800	40.282	328.253	292.032	210.084	775.863	614.167	−5.531
5900	40.386	328.943	292.652	214.117	777.922	611.361	−5.413
6000	40.493	329.623	293.262	218.161	780.000	608.520	−5.298

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [264.65]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-315 \pm 29]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-314 \pm 29]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[920](1)
[360](1)
[1220](1)

Ground State Quantum Weight: [2] $\sigma = 1$
Point Group: C_s
Bond Distances: B–Cl = [1.73] Å; B–F = [1.295] Å
Bond Angle: F–B–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.811033 \times 10^{-115}]\ g^3\ cm^6$

Enthalpy of Formation

The value of $\Delta_f H°(298.15\ K)$ for BClF(g) is estimated based on an assumption that $\Delta_f H° = 0$ for the reaction $BCl_2(g) + BF_2(g) = 2\ BClF(g)$. The values of $\Delta_f H°(298.15\ K)$ of $BCl_2(g)$ and $BF_2(g)$, used for calculation, are −20 and −130 $kcal·mol^{-1}$, respectively.

Heat Capacity and Entropy

The ground state quantum weight and bond angle are assumed to be the same as those for $BF_2(g)$. The bond distances of B–Cl and B–F are estimated by comparison with those in $BCl_3(g)$ and $BF_3(g)$ molecules, respectively. The vibrational frequencies were estimated from the corresponding values for $BCl_2(g)$ and $BF_2(g)$. The principal moments of inertia are: $I_A = 0.7794 \times 10^{-39}$, $I_B = 14.8586 \times 10^{-39}$, and $I_C = 15.6380 \times 10^{-39}$ g cm^2.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.008	−314.591	−314.591	INFINITE
100	34.530	223.216	299.791	−7.657	−314.174	−318.496	166.365
200	38.735	248.470	268.419	−3.990	−313.823	−322.971	84.351
250	40.690	257.324	265.340	−2.004	−313.769	−325.267	67.961
298.15	42.547	264.650	264.650	0.	−313.800	−327.480	57.373
300	42.617	264.913	264.651	0.079	−313.803	−327.564	57.034
350	44.450	271.622	265.176	2.256	−313.906	−329.851	49.228
400	46.125	277.669	266.366	4.521	−314.067	−332.118	43.370
450	47.610	283.189	267.933	6.865	−314.273	−334.363	38.812
500	48.901	288.274	269.716	9.279	−314.509	−336.582	35.163
600	50.964	297.382	273.586	14.277	−315.045	−340.948	29.682
700	52.475	305.357	277.567	19.453	−315.636	−345.219	25.761
800	53.590	312.441	281.492	24.759	−316.267	−349.402	22.814
900	54.425	318.803	285.290	30.162	−316.933	−353.505	20.517
1000	55.061	324.572	288.934	35.638	−317.633	−357.531	18.676
1100	55.554	329.844	292.417	41.169	−318.366	−361.486	17.166
1200	55.942	334.695	295.741	46.745	−319.134	−365.372	15.904
1300	56.253	339.185	298.912	52.355	−319.936	−369.193	14.834
1400	56.505	343.364	301.940	57.994	−320.773	−372.951	13.915
1500	56.712	347.270	304.833	63.655	−321.647	−376.648	13.116
1600	56.884	350.935	307.601	69.335	−322.557	−380.285	12.415
1700	57.028	354.388	310.253	75.031	−323.505	−383.864	11.795
1800	57.150	357.652	312.796	80.740	−324.489	−387.386	11.242
1900	57.254	360.744	315.239	86.460	−325.510	−390.853	10.745
2000	57.344	363.683	317.588	92.190	−326.566	−394.265	10.297
2100	57.421	366.483	319.851	97.929	−327.658	−397.623	9.890
2200	57.489	369.156	322.031	103.674	−328.785	−400.928	9.519
2300	57.548	371.713	324.136	109.426	−329.945	−404.182	9.179
2400	57.600	374.163	326.170	115.183	−381.397	−406.315	8.843
2500	57.646	376.516	328.137	120.946	−382.699	−407.327	8.511
2600	57.687	378.777	330.042	126.713	−384.000	−408.286	8.203
2700	57.724	380.955	331.887	132.483	−385.297	−409.195	7.916
2800	57.757	383.055	333.677	138.257	−386.592	−410.057	7.650
2900	57.787	385.082	335.415	144.034	−387.881	−410.872	7.401
3000	57.813	387.042	337.104	149.815	−389.166	−411.643	7.167
3100	57.838	388.938	338.745	155.597	−390.444	−412.371	6.948
3200	57.860	390.775	340.343	161.382	−391.715	−413.058	6.742
3300	57.880	392.555	341.898	167.169	−392.978	−413.705	6.548
3400	57.898	394.283	343.413	172.958	−394.231	−414.315	6.365
3500	57.915	395.962	344.891	178.749	−395.474	−414.887	6.192
3600	57.931	397.594	346.332	184.541	−396.706	−415.424	6.028
3700	57.945	399.181	347.739	190.335	−397.924	−415.928	5.872
3800	57.958	400.727	349.114	196.130	−399.129	−416.398	5.724
3900	57.970	402.232	350.456	201.926	−400.318	−416.837	5.583
4000	57.982	403.700	351.769	207.724	−401.492	−417.246	5.449
4100	57.992	405.132	353.053	213.523	−402.647	−417.625	5.321
4200	58.002	406.530	354.310	219.322	−883.634	−410.952	5.111
4300	58.011	407.895	355.540	225.123	−883.665	−399.698	4.855
4400	58.019	409.228	356.745	230.924	−883.677	−388.443	4.611
4500	58.027	410.532	357.926	236.727	−883.670	−377.187	4.378
4600	58.035	411.808	359.084	242.530	−883.643	−365.932	4.155
4700	58.042	413.056	360.219	248.334	−883.595	−354.678	3.942
4800	58.048	414.278	361.332	254.138	−883.527	−343.425	3.737
4900	58.054	415.475	362.425	259.943	−883.438	−332.174	3.541
5000	58.060	416.648	363.498	265.749	−883.328	−320.925	3.353
5100	58.066	417.798	364.551	271.555	−883.196	−309.678	3.172
5200	58.071	418.925	365.586	277.362	−883.044	−298.434	2.998
5300	58.076	420.031	366.603	283.170	−882.870	−287.193	2.830
5400	58.080	421.117	367.603	288.977	−882.674	−275.956	2.669
5500	58.084	422.183	368.585	294.786	−882.459	−264.722	2.514
5600	58.089	423.229	369.552	300.594	−882.222	−253.493	2.364
5700	58.092	424.258	370.503	306.403	−881.966	−242.268	2.220
5800	58.096	425.268	371.438	312.213	−881.689	−231.048	2.081
5900	58.100	426.261	372.359	318.023	−881.394	−219.832	1.946
6000	58.103	427.238	373.265	323.833	−881.079	−208.622	1.816

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 274.83\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -883.0 \pm 20\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -885.3 \pm 20\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
1250(1)	1430(1)
697(1)	366(1)
429(1)	608(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–Cl = [1.73] Å; B–F = [1.295] Å
Bond Angles: F–B–Cl = [120]°; F–B–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.568886 \times 10^{-114}]\ g^3\cdot cm^6$

Enthalpy of Formation

The values for BCl_2F and $BClF_2$ of $\Delta_f H°(298.15\ K) = -154$ and $\Delta_f H°(298.15\ K) = -211.6\ kcal\cdot mol^{-1}$, respectively, are obtained from the average bond energies of BF_3 and BCl_3. The calculated values are each made less negative by about 0.8 $kcal\cdot mol^{-1}$ in order to make them consistent with the equilibrium measurements of Higgins, Leisegang, Raw and Rossow[2] and Gunn and Sanborn[2] for the reaction $BF_3(g) + BCl_3(g) \rightarrow BClF_2(g) + BCl_2F(g)$. Values for the heat of reaction are $\Delta_r H°(298.15\ K) = +1.68\ kcal\cdot mol^{-1}$ and $\Delta_r H°(298.15\ K) = 1.1$ (uncertainty of 0.5 to + 0.8) $kcal\cdot mol^{-1}$, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of $\Delta_r H°(298.15\ K) = 1.6\ kcal\cdot mol^{-1}$ fixes the sum of the enthalpy of formation of $BClF_2$ and BCl_2F as $-365.6\ kcal\cdot mol^{-1}$, but it does not determine the individual values. Thus, the selected enthalpies of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be ± 5 $kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The observed frequencies of Lindeman and Wilson[3] were adjusted to the normal isotopic composition of 81.2% ^{10}B and 18.8% ^{11}B. The bond angles are assumed to be 120° and the bond lengths are taken to be the same as in the respective trihalides. The principal moments of inertia are: $I_A = 7.9360 \times 10^{-39}$, $I_B = 17.6063 \times 10^{-39}$, and $I_C = 25.5423 \times 10^{-39}\ g\cdot cm^2$.

References

[1]T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw, and A. J. Rossouw, J. Chem. Phys. **23**, 1544 (1955).
[2]S. R. Gunn and R. H. Sanborn, J. Chem. Phys. **33**, 955 (1960).
[3]L. P. Lindeman and M. K. Wilson, J. Chem. Phys. **24**, 242 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.320	−883.026	−883.026	INFINITE
100	35.262	227.389	316.986	−8.960	−884.052	−880.272	459.807
200	45.615	254.879	279.545	−4.933	−884.806	−876.171	228.832
250	50.457	265.591	275.705	−2.528	−885.084	−873.980	182.608
298.15	54.466	274.830	274.830	0.	−885.334	−871.818	152.739
300	54.609	275.167	274.831	0.101	−885.344	−871.734	151.782
350	58.172	283.860	275.509	2.923	−885.597	−869.446	129.758
400	61.242	291.833	277.058	5.910	−885.852	−867.121	113.234
450	63.887	299.203	279.115	9.040	−886.105	−864.765	100.379
500	66.163	306.055	281.470	12.292	−886.351	−862.381	90.092
600	69.800	318.456	286.623	19.100	−886.815	−857.542	74.656
700	72.492	329.428	291.970	26.221	−887.236	−852.630	63.624
800	74.504	339.246	297.276	33.576	−887.624	−847.659	55.346
900	76.027	348.113	302.440	41.106	−887.990	−842.641	48.906
1000	77.199	356.187	307.417	48.769	−888.347	−837.583	43.751
1100	78.114	363.589	312.192	56.537	−888.704	−832.490	39.532
1200	78.840	370.418	316.763	64.386	−889.071	−827.363	36.014
1300	79.424	376.753	321.137	72.300	−889.453	−822.206	33.037
1400	79.899	382.657	325.323	80.267	−889.858	−817.018	30.483
1500	80.290	388.183	329.331	88.277	−890.288	−811.800	28.269
1600	80.616	393.375	333.174	96.323	−890.747	−806.553	26.331
1700	80.891	398.271	336.860	104.399	−891.237	−801.276	24.620
1800	81.123	402.902	340.402	112.500	−891.759	−795.969	23.098
1900	81.322	407.293	343.808	120.622	−892.314	−790.632	21.736
2000	81.493	411.469	347.087	128.763	−892.900	−785.266	20.509
2100	81.641	415.449	350.249	136.920	−893.517	−779.869	19.398
2200	81.771	419.250	353.299	145.091	−894.163	−774.442	18.388
2300	81.884	422.887	356.246	153.274	−894.837	−768.985	17.464
2400	81.984	426.374	359.096	161.467	−945.794	−762.430	16.594
2500	82.073	429.723	361.855	169.670	−946.593	−754.773	15.770
2600	82.152	432.943	364.527	177.881	−947.380	−747.084	15.009
2700	82.223	436.045	367.119	186.100	−948.153	−739.366	14.304
2800	82.286	439.036	369.634	194.326	−948.909	−731.619	13.649
2900	82.343	441.925	372.078	202.557	−949.648	−723.846	13.038
3000	82.395	444.717	374.453	210.794	−950.366	−716.047	12.467
3100	82.442	447.420	376.763	219.036	−951.062	−708.225	11.934
3200	82.484	450.038	379.012	227.282	−951.735	−700.381	11.433
3300	82.523	452.577	381.203	235.533	−952.382	−692.516	10.962
3400	82.559	455.041	383.339	243.787	−953.002	−684.632	10.518
3500	82.591	457.434	385.422	252.044	−953.594	−676.730	10.100
3600	82.621	459.762	387.455	260.305	−954.157	−668.811	9.704
3700	82.649	462.026	389.440	268.569	−954.688	−660.878	9.330
3800	82.674	464.230	391.379	276.835	−955.187	−652.931	8.975
3900	82.698	466.378	393.275	285.103	−955.652	−644.970	8.638
4000	82.720	468.472	395.128	293.374	−956.083	−636.998	8.318
4100	82.740	470.515	396.942	301.647	−956.479	−629.016	8.014
4200	82.759	472.509	398.718	309.922	−1436.688	−614.001	7.636
4300	82.776	474.456	400.457	318.199	−1435.923	−594.422	7.221
4400	82.793	476.360	402.160	326.477	−1435.123	−574.861	6.824
4500	82.808	478.220	403.830	334.757	−1434.286	−555.319	6.446
4600	82.822	480.041	405.467	343.039	−1433.413	−535.796	6.084
4700	82.836	481.822	407.073	351.322	−1432.504	−516.292	5.738
4800	82.848	483.566	408.648	359.606	−1431.558	−496.808	5.406
4900	82.860	485.274	410.194	367.891	−1430.576	−477.345	5.089
5000	82.871	486.948	411.713	376.178	−1429.558	−457.901	4.784
5100	82.882	488.590	413.204	384.466	−1428.504	−438.479	4.491
5200	82.892	490.199	414.669	392.754	−1427.415	−419.077	4.210
5300	82.901	491.778	416.109	401.044	−1426.291	−399.696	3.939
5400	82.910	493.328	417.525	409.335	−1425.133	−380.337	3.679
5500	82.919	494.849	418.917	417.626	−1423.941	−361.000	3.428
5600	82.926	496.343	420.287	425.918	−1422.716	−341.685	3.187
5700	82.934	497.811	421.634	434.211	−1421.459	−322.392	2.954
5800	82.941	499.254	422.960	442.505	−1420.171	−303.122	2.730
5900	82.948	500.672	424.265	450.800	−1418.852	−283.873	2.513
6000	82.954	502.066	425.550	459.095	−1417.504	−264.648	2.304

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [237.42] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−316.8 ± 29] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = −316.3 ± 29 $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[690](1)
[400](2)
[1850](1)

Ground State Quantum Weight: [1] σ = 1
Point Group: [$C_{\infty v}$]
Bond Distances: Cl–B = [1.75] Å; B–O = [1.20] Å
Bond Angle: Cl–B–O = [180]°
Rotational Constant: B_0 = [0.165056] cm^{-1}

Enthalpy of Formation

The vapor–phase equilibria existing in the $B_2O_3 + BCl_3$ system were determined by an effusion method in the temperature range 1234–1389 K by Blauer and Farber.[1] Based on the equilbrium constants reported for the reaction 1/3 B_2O_3(l) + 1/3 BCl_3(g) = BOCl(g), the 2nd and 3rd law values of $\Delta_f H°(298.15\ K)$ were evaluated as 57.7 and 56.3 $kcal·mol^{-1}$, respectively. The 3rd law value for $\Delta_f H°(298.15\ K)$ was adopted for the calculation of the enthalpy of formation, $\Delta_f H°$(BOCl, g, 298.15 K).

Heat Capacity and Entropy

The molecular structure is assumed to be linear. The vibrational frequencies are estimated from the values calculated by the valence force method described by Herzberg[2] using estimated force constants, $k_1 = 5.2 \times 10^5$, $k_2 = 16.7 \times 10^5$ dynes·cm^{-1} and $k_3 = 0.40 \times 10^{-11}$ dynes·cm·rad^{-1}. The B=O and B–Cl bond distances were assumed to be the same as those in BO(g) and BCl_3(g), respectively.

References

[1] J. Blauer and M. Farber, Trans. Faraday Soc. **60**, 301 (1964).
[2] G. Herzberg, Infrared and Raman Spectra, D. van Nostrand Company, Inc., (1945).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.609	−316.774	−316.774	INFINITE
100	30.896	196.590	273.283	−7.669	−316.766	−318.278	166.252
200	39.254	220.565	241.372	−4.161	−316.565	−319.850	83.536
250	42.577	229.698	238.145	−2.112	−316.425	−320.687	67.004
298.15	45.040	237.417	237.417	0.	−316.310	−321.519	56.329
300	45.123	237.696	237.418	0.083	−316.307	−321.551	55.987
350	47.105	244.806	237.975	2.391	−316.224	−322.432	48.120
400	48.708	251.204	239.235	4.788	−316.185	−323.323	42.222
450	50.054	257.021	240.893	7.258	−316.190	−324.215	37.634
500	51.216	262.356	242.776	9.790	−316.229	−325.105	33.963
600	53.146	271.871	246.852	15.012	−316.384	−326.867	28.456
700	54.680	280.184	251.032	20.406	−316.608	−328.597	24.520
800	55.909	287.568	255.146	25.938	−316.878	−330.291	21.566
900	56.898	294.213	259.124	31.580	−317.180	−331.950	19.266
1000	57.696	300.250	262.939	37.311	−317.511	−333.574	17.424
1100	58.344	305.781	266.586	43.114	−317.867	−335.163	15.916
1200	58.875	310.881	270.068	48.976	−318.250	−336.719	14.657
1300	59.313	315.611	273.391	54.886	−318.659	−338.242	13.591
1400	59.677	320.020	276.566	60.836	−319.096	−339.732	12.676
1500	59.982	324.148	279.602	66.819	−319.563	−341.190	11.881
1600	60.239	328.028	282.509	72.831	−320.062	−342.615	11.185
1700	60.459	331.687	285.295	78.866	−320.593	−344.009	10.570
1800	60.647	335.148	287.969	84.921	−321.159	−345.370	10.022
1900	60.809	338.431	290.540	90.994	−321.760	−346.699	9.531
2000	60.949	341.554	293.013	97.083	−322.400	−347.995	9.089
2100	61.072	344.531	295.396	103.184	−323.078	−349.258	8.687
2200	61.180	347.374	297.694	109.296	−323.797	−350.488	8.322
2300	61.275	350.096	299.914	115.419	−324.557	−351.685	7.987
2400	61.359	352.706	302.060	121.551	−375.620	−351.778	7.656
2500	61.434	355.212	304.136	127.691	−376.545	−350.766	7.329
2600	61.500	357.623	306.147	133.837	−377.482	−349.716	7.026
2700	61.560	359.945	308.097	139.991	−378.433	−348.630	6.745
2800	61.614	362.185	309.989	146.149	−379.397	−347.509	6.483
2900	61.663	364.348	311.826	152.313	−380.376	−346.353	6.238
3000	61.707	366.439	313.612	158.482	−381.370	−345.163	6.010
3100	61.747	368.463	315.349	164.655	−382.379	−343.939	5.795
3200	61.784	370.424	317.039	170.831	−383.402	−342.683	5.594
3300	61.817	372.326	318.686	177.011	−384.440	−341.395	5.404
3400	61.848	374.172	320.291	183.194	−385.491	−340.074	5.225
3500	61.876	375.965	321.856	189.381	−386.554	−338.723	5.055
3600	61.902	377.708	323.384	195.570	−387.629	−337.341	4.895
3700	61.925	379.405	324.875	201.761	−388.715	−335.930	4.742
3800	61.947	381.057	326.332	207.955	−389.810	−334.488	4.598
3900	61.968	382.666	327.756	214.150	−390.913	−333.018	4.460
4000	61.987	384.235	329.148	220.348	−392.023	−331.519	4.329
4100	62.004	385.766	330.510	226.548	−393.138	−329.993	4.204
4200	62.021	387.260	331.844	232.749	−874.106	−321.415	3.997
4300	62.036	388.720	333.150	238.952	−874.141	−308.255	3.745
4400	62.050	390.146	334.429	245.156	−874.179	−295.095	3.503
4500	62.064	391.541	335.683	251.362	−874.219	−281.934	3.273
4600	62.076	392.905	336.912	257.569	−874.261	−268.771	3.052
4700	62.088	394.240	338.117	263.777	−874.303	−255.608	2.841
4800	62.099	395.547	339.300	269.986	−874.346	−242.444	2.638
4900	62.109	396.828	340.461	276.197	−874.388	−229.278	2.444
5000	62.119	398.083	341.601	282.408	−874.429	−216.113	2.258
5100	62.128	399.313	342.721	288.620	−874.470	−202.946	2.079
5200	62.137	400.519	343.821	294.834	−874.509	−189.779	1.906
5300	62.145	401.703	344.902	301.048	−874.547	−176.610	1.741
5400	62.153	402.865	345.964	307.263	−874.585	−163.441	1.581
5500	62.160	404.005	347.009	313.478	−874.621	−150.272	1.427
5600	62.167	405.125	348.037	319.695	−874.657	−137.101	1.279
5700	62.174	406.226	349.048	325.912	−874.694	−123.930	1.136
5800	62.180	407.307	350.044	332.129	−874.731	−110.758	0.997
5900	62.186	408.370	351.023	338.348	−874.769	−97.587	0.864
6000	62.191	409.415	351.988	344.566	−874.809	−84.414	0.735

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [272.7 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -80.9 \pm 17.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -79.5 \pm 12.6\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
[11000]	[2]
28003	1
28153	1
29455	1
29542	1

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[700] (1)
250 (1)
[725] (1)

Point Group: [C_{2v}] $\sigma = 2$

Bond Distance: B–Cl = [1.73] Å

Bond Angle: Cl–B–Cl = [112]°

Product of the Moments of Inertia: $I_A I_B I_C = 9.065976 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

Srivastava and Farber[1] have investigated the equilibrium vapors over the boron trichloride–boron system by mass spectrometry. Gaseous BCl_3 was allowed to flow into a boron nitride effusion cell which contained metallic boron. A flow variation study indicated that thermal equilibrium had been achieved during their experiments. Ion intensities for the species $BCl_3(g)$, $Bcl_2(g)$, and $BCl(g)$ were measured at electron energies slightly above appearance potentials in the temperature range 1513 to 1813 K. JANAF analysis of equiibrium constants for the reaction $BCl_3(g) + BCl(g) = 2BCl_2(g)$ which are obtained from their ion intenesity data yields a 3rd law $\Delta_r H$(298.15 K) value of 24.56 ± 1.00 kcal·mol^{-1} with a drift of −2.1 ± 2.0 cal·K^{-1}mol^{-1}. The 2nd law $\Delta_r H$ value at 298.15 K is 28.1 kcal·mol^{-1}. Using the 3rd law $\Delta_r H$ value in conjunction with JANAF enthalpies of formation [2] for $BCl_3(g)$ and BCl(g) and BCl(g), we calculate $\Delta_f H°(BCl_2, g, 298.15\ K) = -19.0 \pm 3.0$ kcal·mol^{-1}.

The only other reported data on the enthalpy of formation of BCl_2 comes from explosion studies carried out at elevated temperatures by Rusin and Tatevskii.[3] The BCl_2 radical was found to be stable at 2250 K in H_2–Cl_2–BCl_3 mixtures. These workers reported $\Delta_f H°(BCl_2, g, 298.15\ K) = -18.4 \pm 1.5$ kcal·mol^{-1} which confirms the results of Srivastava and Farber.[1]

We adopt $\Delta_f H°(BCl_2, g, 298.15\ K) = -19.0 \pm 3.0$ kcal·mol^{-1}. This value also leads to a realistic progression in the stepwise bond dissociation energies for BCl(g), BCl_2(g), and BCl_3(g). Using all JANAF data,[2] we calculate D_1(B–Cl) = 127.9, D_2(BCl–Cl) = 81.7, and D_3(BCl_2–Cl) = 106.2 kcal·mol^{-1}. This bond energy scheme, $D_1 > D_2 < D_3$, is consistent with that predicted for the Group III A fluorides by Hildenbrand.[4]

Heat Capacity and Entropy

The point group and the Cl–B–Cl bond angle are assumed to be the same as those for BF_2.[2] The B–Cl bond length is estimated to lie between those for BCl and BCl_3.[2] The principal moments of inertia are: $I_A = 1.4577 \times 10^{-39}$, $I_B = 24.2203 \times 10^{-39}$, and $I_C = 25.6780 \times 10^{-39}$ g·cm^2.

Dessaux *et al.*[5,6] observed a diffuse system of bands in the near ultraviolet which they attributed to the BCl_2 radical. The emission spectrum was obtained as chemiluminescence in the reaction between BCl_3 and atomic hydrogen. They indicated that the frequencies $\upsilon_1 = 470$, $\upsilon_2 = 240$, and $\upsilon_3 = 990\ cm^{-1}$ were consistent with their spectral data; however, alternate assignments are possible. We prefer the frequencies $\upsilon_1 = 700$, υ_2 250, and $\upsilon_3 = 725\ cm^{-1}$, since these values are more consistent with those for CCl_2, $SiCl_2$, and $AlCl_2$.[2]

By analogy with the isoelectronic molecule NO_2,[7] the ground state for BCl_2 is assumed to be $^2A_1$. Huckel–molecular–orbital calculations by Hastie and Margrave[8] suggest a doublet excited state ($^2B_1$) near 11,000 cm^{-1} which is included. The upper electronic levels are those observed by Dessaux *et al.*[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.759	−80.860	−80.860	INFINITE
100	36.437	227.742	311.228	−8.349	−80.386	−84.228	43.996
200	42.282	254.796	276.857	−4.412	−79.820	−88.303	23.062
250	45.066	264.535	273.444	−2.227	−79.625	−90.447	18.898
298.15	47.375	272.677	272.677	0.	−79.496	−92.544	16.213
300	47.455	272.970	272.678	0.088	−79.492	−92.625	16.127
350	49.389	280.436	273.263	2.511	−79.415	−94.821	14.151
400	50.918	287.135	274.585	5.020	−79.392	−97.024	12.670
450	52.122	293.205	276.322	7.597	−79.419	−99.226	11.518
500	53.073	298.747	278.292	10.228	−79.487	−101.424	10.596
600	54.439	308.553	282.540	15.608	−79.720	−105.792	9.210
700	55.341	317.018	286.874	21.100	−80.055	−110.112	8.217
800	55.962	324.450	291.116	26.667	−80.470	−114.378	7.468
900	56.404	331.069	295.194	32.287	−80.953	−118.588	6.883
1000	56.729	337.029	299.085	37.944	−81.494	−122.741	6.411
1100	56.975	342.448	302.784	43.630	−82.088	−126.838	6.023
1200	57.166	347.414	306.299	49.337	−82.732	−130.878	5.697
1300	57.319	351.996	309.641	55.062	−83.421	−134.862	5.419
1400	57.445	356.248	312.820	60.800	−84.154	−138.792	5.178
1500	57.553	360.215	315.849	66.550	−84.930	−142.668	4.968
1600	57.650	363.933	318.739	72.310	−85.745	−146.491	4.782
1700	57.740	367.431	321.501	78.080	−86.601	−150.262	4.617
1800	57.828	370.733	324.146	83.858	−87.494	−153.981	4.468
1900	57.917	373.862	326.681	89.646	−88.426	−157.649	4.334
2000	58.009	376.836	329.115	95.442	−89.395	−161.268	4.212
2100	58.106	379.668	331.455	101.248	−90.400	−164.837	4.100
2200	58.207	382.374	333.708	107.063	−91.442	−168.357	3.997
2300	58.315	384.963	335.881	112.889	−92.521	−171.829	3.902
2400	58.428	387.448	337.978	118.726	−143.896	−174.185	3.791
2500	58.547	389.835	340.005	124.575	−145.127	−175.422	3.665
2600	58.671	392.134	341.966	130.436	−146.363	−176.609	3.548
2700	58.800	394.350	343.865	136.309	−147.605	−177.748	3.439
2800	58.932	396.491	345.707	142.196	−148.852	−178.842	3.336
2900	59.067	398.562	347.494	148.096	−150.105	−179.891	3.240
3000	59.205	400.566	349.230	154.010	−151.365	−180.897	3.150
3100	59.344	402.510	350.917	159.937	−152.629	−181.860	3.064
3200	59.484	404.396	352.559	165.878	−153.899	−182.783	2.984
3300	59.623	406.229	354.158	171.834	−155.172	−183.666	2.907
3400	59.762	408.011	355.716	177.803	−156.448	−184.510	2.835
3500	59.900	409.745	357.235	183.786	−157.726	−185.317	2.766
3600	60.037	411.435	358.717	189.783	−159.003	−186.087	2.700
3700	60.171	413.081	360.164	195.793	−160.278	−186.822	2.637
3800	60.302	414.688	361.578	201.817	−161.548	−187.523	2.578
3900	60.431	416.256	362.960	207.854	−162.812	−188.190	2.521
4000	60.557	417.787	364.312	213.903	−164.066	−188.824	2.466
4100	60.680	419.284	365.634	219.965	−165.310	−189.428	2.413
4200	60.800	420.748	366.929	226.039	−646.390	−182.977	2.276
4300	60.917	422.180	368.197	232.125	−646.518	−171.942	2.089
4400	61.030	423.582	369.440	238.223	−646.629	−160.904	1.910
4500	61.140	424.954	370.659	244.331	−646.723	−149.864	1.740
4600	61.247	426.299	371.854	250.451	−646.796	−138.821	1.576
4700	61.351	427.618	373.026	256.581	−646.848	−127.778	1.420
4800	61.452	428.910	374.177	262.721	−646.878	−116.733	1.270
4900	61.550	430.179	375.307	268.871	−646.882	−105.689	1.127
5000	61.645	431.423	376.417	275.031	−646.862	−94.644	0.989
5100	61.737	432.645	377.507	281.200	−646.814	−83.600	0.856
5200	61.827	433.844	378.579	287.378	−646.739	−72.558	0.729
5300	61.914	435.023	379.633	293.565	−646.635	−61.517	0.606
5400	61.999	436.181	380.670	299.761	−646.503	−50.478	0.488
5500	62.081	437.319	381.689	305.965	−646.341	−39.441	0.375
5600	62.161	438.439	382.693	312.177	−646.149	−28.409	0.265
5700	62.239	439.540	383.680	318.397	−645.927	−17.380	0.159
5800	62.316	440.623	384.653	324.625	−645.675	−6.354	0.057
5900	62.390	441.689	385.611	330.860	−645.393	4.666	−0.041
6000	62.462	442.738	386.554	337.102	−645.082	15.681	−0.137

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = [257.8 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 665.4 \pm 25\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 674.0 \pm 25\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[16000]	1
$^1A_1$	[35000]	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[500] (1)
[150] (2)
[800] (1)

Point Group: [$D_{\infty h}$] $\sigma = 2$
Bond Distances: B–Cl = [1.74] Å
Bond Angle: Cl–B–Cl = [180]°
Product of the Moments of Inertia: B_0 = [0.078526] cm^{-1}

Enthalpy of Formation

The appearance potential of the positive ion fragment $BCl_2^+(g)$ from $BCl_3(g)$ was determined mass spectrometrically by Osberghaus,[1] Marriott,[2] and Koski[3] as 13.2 ± 0.5, 13.01 ± 0.02, and 11.8 ± 0.2 eV, respectively. From the reaction $BCl_3 + e^- = BCl_2^+ + Cl + 2e^-$, the corresponding values of $\Delta_f H°(298.15\ K)$ for $BCl_2^+(g)$ are derived to be 181.9 ± 11.5, 177.5 ± 0.5, and 149.6 ± 4.6 $kcal \cdot mol^{-1}$, using $\Delta_f H°(0\ K) = -96.078$ and 28.520 $kcal \cdot mol^{-1}$ for $BCl_3(g)$ and Cl(g). These electron impact values are superseded by the photoionization results of Dibeler and Walker[7] who report the onset of BCl_2^+ from BCl_3 as 12.30 ± 0.02 eV (283.65 ± 0.05 $kcal \cdot mol^{-1}$). This yields $\Delta_f H°(0\ K) = 159.05 \pm 0.6\ kcal \cdot mol^{-1}$ or $\Delta_f H°(298.15\ K) = 161.1 \pm 0.6\ kcal \cdot mol^{-1}$, which are adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh[4] predictions for 16 valence electron XY_2 molecules. The electronic states, levels and vibrational frequencies are estimated by comparison with those for CO_2.[5] The B–Cl bond distance is estimated using the method of Krasnov.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.848	665.391		
100	40.874	206.815	301.467	−9.465			
200	48.200	237.603	262.511	−4.982			
250	50.884	248.657	258.666	−2.502			
298.15	52.974	257.805	257.805	0.	674.042	659.173	−115.484
300	53.046	258.133	257.806	0.098	674.095	659.081	−114.756
350	54.747	266.443	258.459	2.795	675.485	656.468	−97.972
400	56.076	273.844	259.928	5.567	676.810	653.660	−85.359
450	57.115	280.511	261.851	8.397	678.076	650.690	−75.530
500	57.934	286.573	264.024	11.274	679.294	647.581	−67.652
600	59.110	297.247	268.696	17.131	681.616	641.018	−55.806
700	59.887	306.422	273.445	23.083	683.820	634.076	−47.315
800	60.422	314.455	278.080	29.100	685.933	626.825	−40.927
900	60.803	321.595	282.526	35.163	687.972	619.313	−35.944
1000	61.084	328.017	286.759	41.258	689.946	611.578	−31.946
1100	61.296	333.849	290.779	47.377	691.864	603.648	−28.665
1200	61.460	339.190	294.594	53.515	693.730	595.546	−25.923
1300	61.588	344.115	298.216	59.668	695.548	587.290	−23.598
1400	61.692	348.683	301.660	65.832	697.319	578.895	−21.599
1500	61.776	352.942	304.938	72.006	699.046	570.376	−19.862
1600	61.846	356.931	308.064	78.187	700.730	561.743	−18.339
1700	61.904	360.682	311.050	84.374	702.371	553.006	−16.992
1800	61.955	364.222	313.907	90.567	703.970	544.173	−15.791
1900	61.999	367.573	316.644	96.765	705.528	535.253	−14.715
2000	62.038	370.754	319.271	102.967	707.044	526.252	−13.744
2100	62.075	373.782	321.795	109.173	708.517	517.176	−12.864
2200	62.110	376.671	324.224	115.382	709.947	508.030	−12.062
2300	62.145	379.432	326.565	121.595	711.333	498.821	−11.329
2400	62.180	382.078	328.823	127.811	662.416	490.621	−10.678
2500	62.216	384.617	331.005	134.031	663.634	483.438	−10.101
2600	62.254	387.058	333.114	140.254	664.840	476.207	−9.567
2700	62.295	389.408	335.156	146.482	666.031	468.929	−9.072
2800	62.339	391.674	337.134	152.713	667.207	461.607	−8.611
2900	62.387	393.863	339.053	158.949	668.369	454.244	−8.182
3000	62.437	395.979	340.915	165.191	669.516	446.841	−7.780
3100	62.492	398.027	342.724	171.437	670.649	439.399	−7.404
3200	62.551	400.012	344.484	177.689	671.768	431.922	−7.050
3300	62.613	401.937	346.196	183.947	672.876	424.410	−6.718
3400	62.679	403.808	347.863	190.212	673.974	416.864	−6.404
3500	62.749	405.625	349.487	196.483	675.063	409.286	−6.108
3600	62.822	407.394	351.071	202.762	676.147	401.677	−5.828
3700	62.899	409.117	352.617	209.048	677.226	394.038	−5.563
3800	62.978	410.795	354.126	215.342	678.305	386.369	−5.311
3900	63.061	412.432	355.600	221.644	679.385	378.673	−5.072
4000	63.145	414.030	357.041	227.954	680.469	370.949	−4.844
4100	63.232	415.590	358.450	234.273	681.561	363.197	−4.627
4200	63.321	417.115	359.829	240.601	202.814	362.443	−4.508
4300	63.412	418.606	361.178	246.937	205.015	366.218	−4.449
4400	63.504	420.065	362.500	253.283	207.231	369.941	−4.392
4500	63.597	421.493	363.795	259.638	209.462	373.614	−4.337
4600	63.690	422.891	365.065	266.002	211.712	377.237	−4.284
4700	63.785	424.262	366.310	272.376	213.982	380.811	−4.232
4800	63.879	425.606	367.531	278.759	216.275	384.336	−4.182
4900	63.974	426.924	368.730	285.152	218.591	387.814	−4.134
5000	64.069	428.218	369.907	291.554	220.933	391.243	−4.087
5100	64.163	429.487	371.063	297.966	223.302	394.626	−4.042
5200	64.257	430.734	372.198	304.387	225.699	397.962	−3.998
5300	64.351	431.959	373.314	310.817	228.124	401.251	−3.955
5400	64.443	433.163	374.411	317.257	230.579	404.495	−3.913
5500	64.535	434.346	375.490	323.706	233.065	407.693	−3.872
5600	64.626	435.510	376.552	330.164	235.581	410.845	−3.832
5700	64.715	436.654	377.596	336.631	238.129	413.953	−3.793
5800	64.804	437.781	378.624	343.107	240.707	417.015	−3.756
5900	64.891	438.889	379.636	349.592	243.317	420.032	−3.719
6000	64.977	439.981	380.633	356.085	245.958	423.005	−3.683

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [266.3 \pm 4.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-142 \pm 105]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-146 \pm 105]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[12000]	3
$^1B_1$	[17000]	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[750] (1)
[250] (1)
[775] (1)

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distances: B–Cl = [1.716] Å
Bond Angle: Cl–B–Cl = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [8.575781 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation $\Delta_f H°(BCl_2^-, g, 0\ K) = -33.8 \pm 25\ kcal·mol^{-1}$, is obtained from an estimated electron affinity for BCl_2 and $\Delta_f H°(BCl_2, g, 0\ K) = -19.3 \pm 3.0\ kcal·mol^{-1}$.[1] Comparison of the ionization potentials and electron affinities for the isoelectronic molecules NO_2,[1,2] BF_2,[1] and AlF_2[1] indicates that in each case the difference between these two quantities (*IP–EA*) is roughly 7.1 eV. From this relationship, we estimate EA (BCl_2) = 0.63 ± 1.0 eV with IP (BCl_2) = 7.73 eV.[1]

Heat Capacity and Entropy

The correlation diagram of Walsh[3] predicts a bent configuration for BCl_2^- (18 valence electrons) with a bond angle considerably reduced from that for BCl_2. Based on the adopted angle for BCl_2 (112°),[1] we estimate the angle in BCl_2^- at 100°. Comparison with angles for CF_2 and SiF_2^+ indicates that the estimated angle is reasonable. The B–Cl bond length is taken equal to that for BCl.[1] The principal moments of inertia are: $I_A = 1.8951 \times 10^{-39}$, $I_B = 20.3463 \times 10^{-39}$, and $I_C = 22.2413 \times 10^{-39}\ g·cm^2$.

The ground state electronic configuration ($^1A_1$) and first excited singlet state ($^1B_1$) for BCl_2^- are estimated by analogy with those for CCl_2 and $SiCl_2$.[1] Also included is a triplet level at 12000 cm^{-1}. The energy separation (5000 cm^{-1}) of the $^3B_1$ and $^1B_1$ levels is estimated by comparison with the corresponding values for SO_2,[4] $SiCl_2$,[1] $GeCl_2$, and $SnCl_2$.[5] The vibrational frequencies are estimated from those for BCl_2, CCl_2, and $SiCl_2$.[1]

References

[1]JANAF Thermochemical Tables: $BCl_2(g)$, $NO_2^-(g)$, $BF_2^-(g)$, $AlF_2^-(g)$, 6–30–72; $BF_2^+(g)$, $BCl_2^+(g)$, and $SiCl_2(g)$, 12–31–70; $CF_2(g)$, 6–30–70; $SiF_2(g)$ and $CCl_2(g)$, 12–31–68; BCl(g), 12–31–64.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.666	−141.514		
100	36.409	221.745	304.298	−8.255			
200	41.747	248.642	270.365	−4.345			
250	44.356	258.240	267.006	−2.191			
298.15	46.614	266.251	266.251	0.	−146.440	−151.317	26.510
300	46.694	266.539	266.252	0.086	−146.476	−151.348	26.352
350	48.651	273.889	266.828	2.472	−147.476	−152.081	22.697
400	50.236	280.493	268.130	4.945	−148.528	−152.668	19.936
450	51.507	286.486	269.842	7.490	−149.627	−153.120	17.774
500	52.524	291.968	271.784	10.092	−150.763	−153.447	16.031
600	54.006	301.684	275.979	15.423	−153.123	−153.764	13.386
700	54.997	310.089	280.265	20.877	−155.575	−153.679	11.468
800	55.684	317.480	284.464	26.413	−158.100	−153.236	10.005
900	56.176	324.068	288.505	32.007	−160.687	−152.473	8.849
1000	56.540	330.007	292.363	37.643	−163.328	−151.420	7.909
1100	56.815	335.409	296.035	43.312	−166.018	−150.099	7.128
1200	57.030	340.362	299.525	49.005	−168.754	−148.531	6.465
1300	57.203	344.934	302.845	54.716	−171.535	−146.734	5.896
1400	57.346	349.179	306.004	60.444	−174.357	−144.720	5.400
1500	57.472	353.140	309.016	66.185	−177.220	−142.504	4.962
1600	57.590	356.853	311.891	71.938	−180.122	−140.095	4.574
1700	57.705	360.347	314.640	77.703	−183.060	−137.503	4.225
1800	57.826	363.649	317.272	83.480	−186.035	−134.738	3.910
1900	57.958	366.779	319.796	89.269	−189.043	−131.806	3.624
2000	58.105	369.756	322.220	95.072	−192.083	−128.715	3.362
2100	58.270	372.594	324.552	100.890	−195.155	−125.471	3.121
2200	58.456	375.309	326.797	106.726	−198.255	−122.080	2.899
2300	58.664	377.912	328.964	112.582	−201.383	−118.548	2.692
2400	58.896	380.414	331.056	118.460	−254.796	−113.810	2.477
2500	59.151	382.823	333.078	124.362	−258.052	−107.869	2.254
2600	59.428	385.149	335.037	130.291	−261.299	−101.797	2.045
2700	59.727	387.397	336.935	136.248	−264.535	−95.601	1.850
2800	60.044	389.575	338.776	142.237	−267.759	−89.285	1.666
2900	60.379	391.688	340.564	148.258	−270.970	−82.855	1.492
3000	60.728	393.740	342.303	154.313	−274.166	−76.313	1.329
3100	61.090	395.737	343.994	160.404	−277.346	−69.666	1.174
3200	61.460	397.683	345.642	166.531	−280.508	−62.916	1.027
3300	61.837	399.580	347.248	172.696	−283.650	−56.068	0.887
3400	62.218	401.432	348.814	178.899	−286.772	−49.124	0.755
3500	62.600	403.241	350.343	185.140	−289.870	−42.090	0.628
3600	62.980	405.009	351.837	191.419	−292.943	−34.967	0.507
3700	63.355	406.740	353.298	197.736	−295.990	−27.759	0.392
3800	63.725	408.435	354.727	204.090	−299.009	−20.469	0.281
3900	64.086	410.095	356.125	210.480	−301.997	−13.100	0.175
4000	64.436	411.722	357.495	216.907	−304.954	−5.654	0.074
4100	64.775	413.317	358.837	223.367	−307.878	1.865	−0.024
4200	65.100	414.882	360.153	229.861	−790.616	16.478	−0.205
4300	65.411	416.417	361.443	236.387	−792.383	35.716	−0.434
4400	65.706	417.924	362.710	242.943	−794.114	54.994	−0.653
4500	65.984	419.404	363.954	249.527	−795.810	74.311	−0.863
4600	66.246	420.857	365.175	256.139	−797.470	93.666	−1.064
4700	66.490	422.285	366.375	262.776	−799.094	113.055	−1.256
4800	66.716	423.687	367.554	269.437	−800.681	132.480	−1.442
4900	66.924	425.065	368.714	276.119	−802.233	151.937	−1.620
5000	67.114	426.419	369.855	282.821	−803.748	171.425	−1.791
5100	67.287	427.749	370.977	289.541	−805.228	190.943	−1.956
5200	67.442	429.058	372.081	296.277	−806.673	210.490	−2.114
5300	67.580	430.344	373.168	303.029	−808.084	230.064	−2.267
5400	67.701	431.608	374.239	309.793	−809.461	249.665	−2.415
5500	67.806	432.851	375.293	316.568	−810.806	269.291	−2.558
5600	67.896	434.074	376.332	323.354	−812.120	288.941	−2.695
5700	67.970	435.276	377.356	330.147	−813.404	308.614	−2.828
5800	68.030	436.459	378.364	336.947	−814.658	328.310	−2.957
5900	68.076	437.622	379.359	343.753	−815.885	348.027	−3.081
6000	68.109	438.767	380.340	350.562	−817.085	367.764	−3.202

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = 287.7\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -643 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -644 \pm 21\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
1320 (1)	1000 (1)
[554] (1)	[339] (1)
[266] (1)	528 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–Cl = [1.73] Å; B–F = [1.295] Å
Bond Angles: Cl–B–Cl = [120]°; F–B–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = 1.202356 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The values for BCl_2F and $BClF_2$ of $\Delta_f H°(298.15\ K) = -154$ and $\Delta_f H°(298.15\ K) = -211.6\ kcal·mol^{-1}$, respectively, are obtained from the average bond energies of BF_3 and BCl_3. The calculated values were each made less negative by about 0.8 $kcal·mol^{-1}$ in order to make them consistent with the equilibrium measurements of Higgins, Leisegang, Raw, and Rossouw,[1] and Gunn and Sanborn[2] for the reaction.

$$BF_3(g) + BCl_3(g) \rightarrow BClF_2(g) + BCl_2F(g).$$

Values for the enthalpy of reaction are $\Delta_r H(298.15\ K) = +1.68\ kcal·mol^{-1}$ and $\Delta_r H(298.15\ K) = 1.1$ (uncertainty of -0.5 to $+0.8$) $kcal·mol^{-1}$, the former calculated from the measured equilibrium constant and the statistical entropy change and the latter obtained from the variation of the equilibrium constant with temperature. Selection of $\Delta_r H(298.15\ K) = 1.6\ kcal·mol^{-1}$ fixes the sum of the enthalpies of formation of $BClF_2$ and BCl_2F as $-365.6\ kcal·mol^{-1}$, but it does not determine the individual values. Thus, the selected enthalpies of formation are only as accurate as the average bond energy calculations on which they are based. A reasonable estimate of the uncertainty would be $\pm 5\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The spectroscopic constants are based on the work of Lindeman and Wilson,[3] who observed υ_1, υ_4, and υ_6 and calculated υ_2, υ_3, and υ_5. The frequencies were adjusted to the normal isotopic composition of 81.2% ^{11}B and 18.8% ^{10}B. The bond angles were taken to be 120° while the bond lengths were assumed to be the same as in the respective trihalides. The principal moments of inertia are $I_A = 11.8761 \times 10^{-39}$, $I_B = 26.4297 \times 10^{-39}$, and $I_C = 38.3059 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.267	−642.796	−642.796	INFINITE
100	37.983	235.579	333.920	−9.834	−643.752	−639.860	334.229
200	50.361	265.837	292.820	−5.397	−644.150	−635.776	166.048
250	55.201	277.612	288.627	−2.754	−644.248	−633.670	132.398
298.15	59.063	287.675	287.675	0.	−644.336	−631.625	110.658
300	59.198	288.041	287.677	0.109	−644.339	−631.546	109.962
350	62.535	297.425	288.410	3.155	−644.434	−629.407	93.934
400	65.335	305.963	290.078	6.354	−644.537	−627.253	81.911
450	67.688	313.799	292.285	9.681	−644.647	−625.086	72.558
500	69.666	321.036	294.803	13.117	−644.759	−622.906	65.075
600	72.738	334.024	300.282	20.245	−644.981	−618.515	53.847
700	74.942	345.412	305.933	27.635	−645.194	−614.087	45.824
800	76.552	355.529	311.512	35.214	−645.402	−609.629	39.805
900	77.751	364.618	316.916	42.932	−645.613	−605.145	35.122
1000	78.662	372.860	322.105	50.755	−645.834	−600.636	31.374
1100	79.368	380.391	327.066	58.658	−646.071	−596.105	28.307
1200	79.923	387.322	331.803	66.623	−646.330	−591.552	25.750
1300	80.367	393.737	336.323	74.638	−646.613	−586.975	23.585
1400	80.726	399.707	340.640	82.694	−646.924	−582.377	21.729
1500	81.022	405.287	344.766	90.782	−647.267	−577.754	20.119
1600	81.267	410.524	348.714	98.896	−647.643	−573.108	18.710
1700	81.472	415.457	352.496	107.034	−648.053	−568.437	17.466
1800	81.646	420.119	356.125	115.190	−648.499	−563.741	16.359
1900	81.795	424.537	359.610	123.362	−648.981	−559.020	15.369
2000	81.922	428.736	362.962	131.548	−649.501	−554.271	14.476
2100	82.033	432.736	366.190	139.746	−650.057	−549.496	13.668
2200	82.129	436.554	369.302	147.954	−650.652	−544.694	12.933
2300	82.213	440.207	372.306	156.171	−651.284	−539.864	12.261
2400	82.288	443.708	375.209	164.396	−702.212	−533.936	11.621
2500	82.353	447.068	378.017	172.629	−702.997	−526.909	11.009
2600	82.412	450.299	380.735	180.867	−703.787	−519.850	10.444
2700	82.464	453.410	383.369	189.111	−704.581	−512.760	9.920
2800	82.511	456.410	385.925	197.360	−705.380	−505.641	9.433
2900	82.554	459.307	388.406	205.613	−706.183	−498.493	8.979
3000	82.592	462.106	390.816	213.870	−706.989	−491.318	8.555
3100	82.626	464.815	393.159	222.131	−707.798	−484.115	8.157
3200	82.658	467.438	395.440	230.395	−708.607	−476.887	7.784
3300	82.687	469.982	397.660	238.663	−709.417	−469.633	7.434
3400	82.713	472.451	399.824	246.933	−710.225	−462.355	7.103
3500	82.737	474.849	401.933	255.205	−711.029	−455.053	6.791
3600	82.759	477.180	403.991	263.480	−711.827	−447.728	6.496
3700	82.779	479.448	406.000	271.757	−712.617	−440.381	6.217
3800	82.798	481.656	407.962	280.036	−713.398	−433.013	5.952
3900	82.815	483.807	409.880	288.316	−714.166	−425.624	5.701
4000	82.832	485.904	411.754	296.599	−714.919	−418.216	5.461
4100	82.846	487.949	413.588	304.883	−715.655	−410.789	5.234
4200	82.860	489.946	415.382	313.168	−1196.221	−396.321	4.929
4300	82.873	491.896	417.139	321.455	−1195.828	−377.280	4.583
4400	82.885	493.801	418.860	329.743	−1195.413	−358.249	4.253
4500	82.897	495.664	420.546	338.032	−1194.975	−339.227	3.938
4600	82.907	497.486	422.199	346.322	−1194.510	−320.216	3.636
4700	82.917	499.269	423.820	354.613	−1194.018	−301.215	3.348
4800	82.927	501.015	425.410	362.905	−1193.497	−282.224	3.071
4900	82.935	502.725	426.970	371.198	−1192.946	−263.245	2.806
5000	82.944	504.401	428.502	379.492	−1192.364	−244.278	2.552
5100	82.951	506.043	430.006	387.787	−1191.750	−225.322	2.308
5200	82.959	507.654	431.484	396.083	−1191.103	−206.378	2.073
5300	82.965	509.234	432.936	404.379	−1190.423	−187.448	1.847
5400	82.972	510.785	434.364	412.676	−1189.709	−168.530	1.630
5500	82.978	512.308	435.767	420.973	−1188.961	−149.626	1.421
5600	82.984	513.803	437.147	429.271	−1188.178	−130.736	1.219
5700	82.990	515.272	438.505	437.570	−1187.361	−111.861	1.025
5800	82.995	516.715	439.841	445.869	−1186.510	−93.000	0.838
5900	83.000	518.134	441.156	454.169	−1185.625	−74.153	0.657
6000	83.005	519.529	442.451	462.469	−1184.707	−55.323	0.482

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [268.3]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -245 \pm 4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -248 \pm 4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[2610] (1)	1091 (1)
744 (1)	[894] (1)
[287] (1)	786 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–H = 1.13 ± 0.2 Å; B–Cl = [1.75] Å
Bond Angles: Cl–B–Cl = 119.7 ± 3°; Cl–B–H = 120.15 ± 1.5°
Product of the Moments of Inertia: $I_A I_B I_C = 1.392331 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The chemical equilibria for the following two reactions: (A) $BCl_3(g) + H_2(g) = BHCl_2(g) + HCl(g)$, and (B) $6BHCl_2(g) = B_2H_6(g) + 4BCl_3(l, g)$ were investigated by Murib, Horvitz, and Bonecutter,[1] Mook, Seiler, and Watson[2] and Lynds and Bass.[3] Using the reported equilibrium constants, the corresponding enthalpy changes and the respective $\Delta_f H°(298.15\ K)$ values were evaluated. The results obtained are presented as follows.

Source	Reaction	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[1]	A	873 – 973	15.57 ± 0.8	16.19	−58.06 ± 0.5
[2]	A	1073 – 1273	13.50 ± 3.0	13.91	−60.3 ± 0.7
[1]	B	273	—	−17.85	−59.6
[3]	B	298	—	−19.09	−59.4

The value of $\Delta_f H°(298.15\ K)$ for $BHCl_2(g)$ is selected as − 59.3 ± 1 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular structure, B–H bond distance and Cl–B–Cl bond angle were obtained from Lynds and Bass.[4] The B–Cl bond distance was assumed to be the same as that in $BCl_3(g)$. The vibrational frequencies adopted were reported by Bass, Lynds, Wolfram, DeWames[5] and corrected to the average isotopic species. It has been pointed out that the complete assignment of the infrared spectra of $HBCl_2(g)$ is quite difficult due to the unavoidable presence of $BCl_3(g)$. The adopted frequencies were obtained using the Green's function and partitioning techniques, taking $HBCl_2$ as an "isotopic" species of BCl_3. An excellent agreement between the calculated and observed spectra reported Lynds and Bass[5] was claimed. Spectra of the mixture of BCl_3, $HBCl_2$ and $DBCl_2$ are quite complex and have been observed by Lynds and Stern,[6] Nadean and Oaks,[7] Mayers and Putnam[8] and only three bands were correlated with $HBCl_2$. Analysis of infrared data from previous works, according to the conventional Wilson's method of symmetry coordinates, has been undertaken by de Mandirola and Westerkamp.[9] Based on four observed frequencies, a set of six frequencies was derived and assigned. The principal moments of inertia are: $I_A = 1.7957 \times 10^{-39}$, $I_B = 26.9625 \times 10^{-39}$, and $I_C = 28.7581 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.744	−245.227	−245.227	INFINITE
100	35.653	223.535	307.156	−8.362	−246.280	−244.666	127.800
200	41.988	250.084	272.565	−4.496	−247.132	−242.731	63.395
250	45.882	259.867	269.069	−2.301	−247.624	−241.574	50.474
298.15	49.644	268.272	268.272	0.	−248.111	−240.365	42.111
300	49.784	268.580	268.273	0.092	−248.130	−240.317	41.843
350	53.357	276.528	268.893	2.672	−248.620	−238.976	35.665
400	56.480	283.862	270.311	5.420	−249.087	−237.566	31.023
450	59.157	290.673	272.200	8.313	−249.528	−236.099	27.406
500	61.447	297.027	274.369	11.329	−249.941	−234.584	24.507
600	65.120	308.571	279.127	17.666	−250.682	−231.442	20.149
700	67.933	318.829	284.080	24.325	−251.320	−228.183	17.027
800	70.157	328.051	289.009	31.233	−251.870	−224.839	14.680
900	71.956	336.422	293.820	38.342	−252.351	−221.431	12.852
1000	73.433	344.082	298.468	45.614	−252.780	−217.972	11.386
1100	74.657	351.140	302.940	53.020	−253.173	−214.472	10.184
1200	75.681	357.682	307.233	60.539	−253.544	−210.937	9.182
1300	76.543	363.774	311.350	68.151	−253.906	−207.372	8.332
1400	77.274	369.474	315.301	75.843	−254.268	−203.779	7.603
1500	77.896	374.827	319.092	83.602	−254.638	−200.160	6.970
1600	78.430	379.872	322.735	91.419	−255.022	−196.515	6.416
1700	78.890	384.641	326.238	99.286	−255.427	−192.846	5.925
1800	79.289	389.162	329.609	107.195	−255.857	−189.153	5.489
1900	79.636	393.458	332.857	115.142	−256.316	−185.435	5.098
2000	79.941	397.551	335.990	123.121	−256.806	−181.692	4.745
2100	80.208	401.458	339.016	131.129	−257.332	−177.923	4.426
2200	80.445	405.195	341.939	139.162	−257.897	−174.129	4.134
2300	80.654	408.775	344.768	147.217	−258.502	−170.308	3.868
2400	80.841	412.212	347.507	155.292	−309.410	−165.391	3.600
2500	81.009	415.516	350.162	163.384	−310.182	−159.374	3.330
2600	81.159	418.696	352.737	171.493	−310.969	−153.326	3.080
2700	81.294	421.761	355.237	179.616	−311.774	−147.248	2.849
2800	81.416	424.720	357.666	187.751	−312.597	−141.139	2.633
2900	81.526	427.579	360.028	195.898	−313.440	−135.001	2.432
3000	81.627	430.345	362.326	204.056	−314.303	−128.833	2.243
3100	81.718	433.023	364.563	212.223	−315.188	−122.636	2.066
3200	81.802	435.618	366.744	220.399	−316.094	−116.411	1.900
3300	81.878	438.137	368.869	228.584	−317.021	−110.156	1.744
3400	81.949	440.582	370.942	236.775	−317.967	−103.874	1.596
3500	82.013	442.959	372.966	244.973	−318.932	−97.563	1.456
3600	82.073	445.270	374.943	253.177	−319.914	−91.224	1.324
3700	82.128	447.519	376.874	261.388	−320.911	−84.858	1.198
3800	82.179	449.710	378.762	269.603	−321.921	−78.464	1.079
3900	82.226	451.845	380.609	277.823	−322.943	−72.044	0.965
4000	82.270	453.928	382.416	286.048	−323.974	−65.598	0.857
4100	82.311	455.960	384.185	294.277	−325.011	−59.126	0.753
4200	82.349	457.944	385.917	302.510	−805.902	−45.604	0.567
4300	82.385	459.882	387.615	310.747	−805.857	−27.502	0.334
4400	82.418	461.776	389.279	318.987	−805.813	−9.401	0.112
4500	82.449	463.629	390.911	327.231	−805.769	8.698	−0.101
4600	82.478	465.441	392.511	335.477	−805.720	26.797	−0.304
4700	82.506	467.215	394.082	343.726	−805.667	44.895	−0.499
4800	82.532	468.953	395.624	351.978	−805.606	62.991	−0.685
4900	82.556	470.655	397.138	360.232	−805.537	81.086	−0.864
5000	82.579	472.323	398.625	368.489	−805.456	99.180	−1.036
5100	82.600	473.958	400.086	376.748	−805.364	117.272	−1.201
5200	82.621	475.562	401.522	385.009	−805.258	135.361	−1.360
5300	82.640	477.136	402.934	393.272	−805.138	153.449	−1.512
5400	82.658	478.681	404.322	401.537	−805.002	171.535	−1.659
5500	82.675	480.198	405.688	409.804	−804.849	189.617	−1.801
5600	82.691	481.688	407.032	418.072	−804.679	207.697	−1.937
5700	82.707	483.152	408.355	426.342	−804.491	225.773	−2.069
5800	82.722	484.590	409.657	434.613	−804.283	243.847	−2.196
5900	82.736	486.004	410.939	442.886	−804.056	261.916	−2.319
6000	82.749	487.395	412.202	451.161	−803.809	279.981	−2.437

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 290.17\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -402.0 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -403.0 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
471.0 (1)	986.3 (2)
470.6 (1)	243.0 (1)

Ground State Quantum Weight: 1 $\sigma = 6$
Point Group: D_{3h}
Bond Distance: B−Cl = 1.75 Å
Bond Angle: Cl−B−Cl = 120°
Product of the Moments of Inertia: $I_A I_B I_C = 3.956022 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy change of the reaction B(am) + 3/2 Cl_2(g) = BCl_3(g) has been determined in a calorimeter by Johnson, Miller and Prosen.[1] From the reported value $\Delta_r H°(298.15\ K) = -97.51 + 0.32\ kcal·mol^{-1}$, the enthalpy of formation for BCl_3(g) was derived as $-96.31 \pm 0.50\ kcal·mol^{-1}$, using $\Delta_f H°(298.15\ K) = 1.20 \pm 0.40\ kcal·mol^{-1}$ for the reaction B(cr) = B(am). Some other related enthalpies of reaction reported by previous investigators are presented as follows.

Source	Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[2]	B(am) + 3/2 Cl_2(g) = BCl_3(g)	−97.4 ± 0.7	−96.2 ± 0.8
	B(am) + 3/2 Cl_2(g) = BCl_3(l)	−103.3 ± 0.6	−96.5 ± 0.7
[3]	B_2H_6(g) + 6 Cl_2(g) = 2 BCl_3(g) + 6 HCl(g)	−342.9	−100.4 ± 5.0
[4]	BCl_3(l) + (n+3)H_2O(l) = (H_3BO_3+3HCl)n H_2O (Sln)	−69.2 ± 1.0	−97.2 ± 1.0
[5]	BCl_3(l) + 2403 H_2O(l) = (H_3BO_3+3HCl)2400 H_2O (Sln)	−68.68 ± 0.06	−96.3 ± 0.2
[6]	BCl_3(l) + 593 H_2O(l) = (H_3BO_3+3HCl)590 H_2O (Sln)	−69.12 ± 0.11	−95.44 ± 0.39

The enthalpies of formation for BCl_3(l) derived from the enthalpies of hydrolysis reported by other investigatoars were reviewed by Johnson, Miller and Prosen.[1]

Heat Capacity and Entropy

The bond distance of B and Cl atoms has been reported to be 1.73 ± 0.02 and 1.76 ± 0.02, 1.75 Å by Levy and Brockway,[7] Gregg, Hampson and Jenkins, Jones, and Sutton,[8] and Spencer and Lipscomb,[9] respectively. The last value is adopted. The values of vibrational frequencies used were reported by Lindeman and Wilson.[10] The vibrational frequencies were also determined by Cassie,[11] Lassettre and Yost,[12] Scruby, Lacher and Park.[13] The molecular structure was given by Levy amd Brockway.[7] The principal moments of inertia are: $I_A = I_B = 27.0443 \times 10^{-39}$, and $I_C = 54.0887 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.021	−401.997	−401.997	INFINITE
100	40.687	234.433	339.441	−10.501	−402.868	−397.930	207.857
200	53.832	266.971	295.623	−5.730	−402.987	−392.909	102.617
250	58.598	279.513	291.176	−2.916	−402.972	−390.391	81.568
298.15	62.392	290.169	290.169	0.	−402.961	−387.969	67.971
300	62.524	290.555	290.170	0.116	−402.961	−387.876	67.535
350	65.763	300.445	290.944	3.325	−402.956	−385.362	57.512
400	68.421	309.406	292.700	6.682	−402.962	−382.849	49.995
450	70.595	317.594	295.018	10.159	−402.976	−380.334	44.148
500	72.374	325.127	297.657	13.735	−402.997	−377.817	39.470
600	75.037	338.574	303.383	21.114	−403.047	−372.776	32.453
700	76.872	350.287	309.265	28.715	−403.109	−367.726	27.440
800	78.172	360.641	315.053	36.471	−403.185	−362.667	23.680
900	79.118	369.906	320.642	44.338	−403.281	−357.596	20.754
1000	79.824	378.280	325.994	52.286	−403.399	−352.514	18.413
1100	80.363	385.915	331.099	60.297	−403.544	−347.419	16.498
1200	80.783	392.926	335.963	68.355	−403.717	−342.309	14.900
1300	81.116	399.406	340.597	76.451	−403.922	−337.184	13.548
1400	81.384	405.427	345.016	84.576	−404.159	−332.041	12.389
1500	81.603	411.050	349.233	92.726	−404.430	−326.881	11.383
1600	81.783	416.322	353.263	100.895	−404.736	−321.701	10.502
1700	81.934	421.285	357.119	109.081	−405.079	−316.501	9.725
1800	82.062	425.972	360.816	117.281	−405.460	−311.280	9.033
1900	82.170	430.412	364.363	125.493	−405.881	−306.036	8.414
2000	82.263	434.629	367.771	133.715	−406.343	−300.770	7.855
2100	82.344	438.645	371.052	141.945	−406.848	−295.479	7.350
2200	82.414	442.477	374.212	150.183	−407.398	−290.163	6.889
2300	82.475	446.142	377.260	158.428	−407.995	−284.821	6.468
2400	82.529	449.653	380.204	166.678	−458.902	−278.383	6.059
2500	82.576	453.023	383.050	174.933	−459.679	−270.845	5.659
2600	82.619	456.262	385.804	183.193	−460.477	−263.276	5.289
2700	82.656	459.381	388.471	191.457	−461.298	−255.676	4.946
2800	82.690	462.388	391.058	199.724	−462.144	−248.045	4.627
2900	82.721	465.290	393.568	207.995	−463.016	−240.383	4.330
3000	82.748	468.095	396.005	216.268	−463.914	−232.691	4.052
3100	82.773	470.809	398.375	224.544	−464.839	−224.968	3.791
3200	82.796	473.437	400.680	232.823	−465.789	−217.216	3.546
3300	82.816	475.985	402.923	241.104	−466.764	−209.432	3.315
3400	82.835	478.458	405.109	249.386	−467.762	−201.620	3.098
3500	82.853	480.859	407.239	257.671	−468.781	−193.777	2.892
3600	82.868	483.193	409.317	265.957	−469.818	−185.905	2.697
3700	82.883	485.464	411.344	274.244	−470.871	−178.004	2.513
3800	82.896	487.675	413.324	282.533	−471.935	−170.075	2.338
3900	82.909	489.828	415.258	290.823	−473.008	−162.117	2.171
4000	82.921	491.927	417.149	299.115	−474.086	−154.132	2.013
4100	82.931	493.975	418.997	307.408	−475.164	−146.120	1.862
4200	82.941	495.973	420.807	315.701	−956.089	−131.057	1.630
4300	82.950	497.925	422.577	323.996	−956.071	−111.414	1.353
4400	82.959	499.832	424.312	332.291	−956.044	−91.771	1.089
4500	82.967	501.697	426.011	340.588	−956.005	−72.129	0.837
4600	82.975	503.520	427.676	348.885	−955.950	−52.487	0.596
4700	82.982	505.305	429.309	357.182	−955.878	−32.848	0.365
4800	82.989	507.052	430.910	365.481	−955.783	−13.210	0.144
4900	82.995	508.763	432.482	373.780	−955.665	6.426	−0.069
5000	83.001	510.440	434.024	382.080	−955.521	26.059	−0.272
5100	83.006	512.084	435.539	390.380	−955.348	45.689	−0.468
5200	83.012	513.696	437.026	398.681	−955.145	65.315	−0.656
5300	83.016	515.277	438.488	406.983	−954.909	84.937	−0.837
5400	83.021	516.829	439.924	415.284	−954.641	104.554	−1.011
5500	83.026	518.352	441.336	423.587	−954.337	124.167	−1.179
5600	83.030	519.848	442.725	431.890	−953.998	143.773	−1.341
5700	83.034	521.318	444.091	440.193	−953.623	163.372	−1.497
5800	83.037	522.762	445.435	448.496	−953.210	182.966	−1.648
5900	83.041	524.181	446.758	456.800	−952.760	202.551	−1.793
6000	83.044	525.577	448.060	465.105	−952.273	222.128	−1.934

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 200.479\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -119.0 \pm 13.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -115.9 \pm 13.8\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 1410.3\ cm^{-1}$ $\omega_e x_e = 11.98\ cm^{-1}$ $\sigma = 1$
$B_e = 1.5286\ cm^{-1}$ $\alpha_e = 0.0168\ cm^{-1}$ $r_e = 1.265$ Å

Enthalpy of Formation

The equilibria of the reaction 2/3 B(cr) + 1/3 BF_3(g) = BF(g) were studied by Blauer, Greenbaum and Farber[1] by means of transpiratio at pressures below 300 μ. The values of log $K_p°$ at 1375 and 1476 K were reported as -3.99 ± 0.02 and -3.30 ± 0.05, respectively. By the 3rd law method the value of $\Delta_f H°$(298.15 K) for the reaction was derived to be 61.38 kcal·mol^{-1}, yielding $\Delta_f H°$(BF, g, 298.15 K) = -28.7 ± 2.6 kcal·mol^{-1}. The system B + CaF_2 was studied mass spectrometrically in a graphite Knudsen cell by Hildenbrand.[6] The equilibria involving BF(g) were observed. Intensity measurements were made at temperatures, 1583 1734 K. From the 3rd law value, $\Delta_f H°(298.15\ K) = 12.2 + 0.3$ kcal·mol^{-1}, for the reaction BF_3(g) + Ca(g) = BF(g) + CaF_2(g), the value of $\Delta_f H$d(298.15 K) for BF(g) was derived as -26.7 ± 2 kcal·mol^{-1}. The dissociation energy of BF(g) molecule has been reported by Herzberg,[2] Gaydon[3] and Barrow.[4] The corresponding values of $\Delta_f H°$(298.15 K) for BF(g) were derived. The results are compared with those obtained from equilibrium data as follows:

Source	Reaction	$\Delta_r H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	2/3 B(cr) + 1/3 BF_3(g) = BF(g)	61.38	-28.7 ± 2.6
2	BF(g) = B(g) + F(g)	100.2	+51.5
3	BF(g) = B(g) + F(g)	197.0	-45.3 ± 11.5
4	BF(g) = B(g) + F(g)	186.0	−34.3
5	2/3 B(cr) + 1/3 BF_3 = BF(g)	—	-28 ± 3
6	BF_3(g) + Ca(g) = BF(g) + CaF_2(g)	12.2	-26.7 ± 2

The value of $\Delta_f H°$(298.15 K) adopted is the average of the first and last $\Delta_f H°$(298.15 K) values listed in the above table.

Heat Capacity and Entropy

The spectroscopic constants used were obtained from Onaka[7] and to the average isotopic species. Spectroscopic constants for BF(g) were also reported by Herzberg.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.694	−118.965	−118.965	INFINITE
100	29.108	168.594	226.494	−5.790	−117.538	−125.848	65.736
200	29.154	188.777	203.167	−2.878	−116.423	−134.630	35.162
250	29.302	195.296	200.965	−1.417	−116.085	−139.224	29.089
298.15	29.591	200.479	200.479	0.	−115.897	−143.699	25.176
300	29.605	200.662	200.480	0.055	−115.892	−143.872	25.050
350	30.047	205.258	200.842	1.546	−115.823	−148.542	22.169
400	30.579	209.304	201.652	3.061	−115.858	−153.215	20.008
450	31.149	212.939	202.707	4.604	−115.976	−157.879	18.326
500	31.719	216.250	203.898	6.176	−116.157	−162.525	16.979
600	32.768	222.128	206.459	9.401	−116.649	−171.755	14.953
700	33.646	227.247	209.071	12.724	−117.258	−180.893	13.498
800	34.356	231.788	211.632	16.125	−117.944	−189.937	12.402
900	34.926	235.869	214.102	19.590	−118.688	−198.892	11.543
1000	35.385	239.573	216.467	23.107	−119.479	−207.762	10.852
1100	35.757	242.964	218.724	26.664	−120.311	−216.550	10.283
1200	36.064	246.089	220.876	30.256	−121.181	−225.261	9.805
1300	36.319	248.986	222.928	33.875	−122.088	−233.898	9.398
1400	36.535	251.686	224.887	37.518	−123.030	−242.464	9.046
1500	36.719	254.213	226.759	41.181	−124.006	−250.961	8.739
1600	36.879	256.588	228.549	44.861	−125.017	−259.392	8.468
1700	37.018	258.828	230.265	48.556	−126.061	−267.758	8.227
1800	37.141	260.947	231.911	52.264	−127.137	−276.062	8.011
1900	37.252	262.958	233.493	55.984	−128.245	−284.306	7.816
2000	37.351	264.872	235.014	59.714	−129.383	−292.490	7.639
2100	37.441	266.696	236.480	63.454	−130.549	−300.617	7.477
2200	37.524	268.440	237.893	67.202	−131.743	−308.688	7.329
2300	37.601	270.110	239.258	70.959	−132.961	−316.704	7.193
2400	37.672	271.712	240.577	74.722	−184.463	−323.597	7.043
2500	37.739	273.251	241.854	78.493	−185.804	−329.367	6.882
2600	37.801	274.732	243.090	82.270	−187.134	−335.083	6.732
2700	37.861	276.160	244.288	86.053	−188.449	−340.748	6.592
2800	37.917	277.538	245.451	89.842	−189.749	−346.365	6.462
2900	37.971	278.869	246.581	93.636	−191.032	−351.936	6.339
3000	38.023	280.157	247.679	97.436	−192.298	−357.463	6.224
3100	38.072	281.405	248.747	101.241	−193.545	−362.948	6.116
3200	38.120	282.615	249.786	105.051	−194.774	−368.393	6.013
3300	38.167	283.788	250.799	108.865	−195.982	−373.799	5.917
3400	38.212	284.928	251.786	112.684	−197.170	−379.170	5.825
3500	38.256	286.037	252.749	116.507	−198.338	−384.506	5.738
3600	38.299	287.115	253.689	120.335	−199.484	−389.808	5.656
3700	38.341	288.165	254.606	124.167	−200.610	−395.080	5.578
3800	38.382	289.188	255.503	128.003	−201.714	−400.321	5.503
3900	38.422	290.185	256.379	131.843	−202.797	−405.533	5.432
4000	38.461	291.159	257.237	135.687	−203.859	−410.718	5.363
4100	38.500	292.109	258.076	139.536	−204.900	−415.877	5.298
4200	38.539	293.037	258.897	143.388	−685.770	−413.986	5.149
4300	38.576	293.944	259.702	147.243	−685.683	−407.516	4.950
4400	38.614	294.832	260.490	151.103	−685.577	−401.048	4.761
4500	38.651	295.700	261.263	154.966	−685.454	−394.583	4.580
4600	38.687	296.550	262.021	158.833	−685.313	−388.120	4.407
4700	38.723	297.382	262.764	162.703	−685.156	−381.661	4.242
4800	38.759	298.198	263.494	166.578	−684.984	−375.206	4.083
4900	38.794	298.997	264.210	170.455	−684.796	−368.754	3.931
5000	38.830	299.781	264.914	174.336	−684.594	−362.306	3.785
5100	38.865	300.551	265.605	178.221	−684.378	−355.863	3.645
5200	38.899	301.306	266.285	182.109	−684.149	−349.423	3.510
5300	38.934	302.047	266.952	186.001	−683.908	−342.989	3.380
5400	38.968	302.775	267.609	189.896	−683.656	−336.558	3.256
5500	39.002	303.490	268.255	193.795	−683.393	−330.133	3.135
5600	39.036	304.193	268.890	197.696	−683.120	−323.713	3.019
5700	39.069	304.885	269.516	201.602	−682.837	−317.297	2.908
5800	39.103	305.564	270.132	205.510	−682.547	−310.887	2.800
5900	39.136	306.233	270.738	209.422	−682.248	−304.481	2.696
6000	39.169	306.891	271.335	213.338	−681.943	−298.081	2.595

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [224.8] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -602 \pm 13\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -602 \pm 13\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[1050](1)
[500](2)
[1900](1)

Ground State Quantum Weight: [1] σ = 1
Point Group: [$C_{\infty v}$]
Bond Distances: B–F = [1.30] Å; B–O = [1.20] Å
Bond Angle: O–B–F = [180]°
Rotational Constant: B_0 = [0.309392] cm^{-1}

Enthalpy of Formation

The equilbrium constants for the reaction $B_2O_3(l) + BF_3(g) = 3\ BOF(g)$ in the temperature range 1054–1253 K were determined by Farber and Blauer[1] using the so-called Molecular Flow Reaction Method. The value of $\Delta_f H°$ for this reaction was evaluated by both the 2nd and 3rd law methods, using the equilibrium constants corrected for the trimer and correcting $K_p°$ at 1200 K from 9.6×10^{-11} to 9.6×10^{-10}. Hildebrand, Theard and Saul[2] analyzed the vapor above mixture of MgF_2 and B_2O_3 contained in a Knudsen cell with a mass spectrometer and found that in the temperature range 980–1230 K the vapor is composed of $BF_3(g)$, $(BOF)_3(g)$ and BOF(g) species. From the reported temperature dependence of appropriate ion intensities the enthalpy change of the reaction $(BOF)_3(g) = 3\ BOF(g)$ was derived by the 2nd law method as 127.9 $kcal·mol^{-1}$ at 1115 K or 129.75 $kcal·mol^{-1}$ at 298.15 K. The results obtained are presented as follows, using JANAF free energy functions and auxiliary data.

Source	Reaction	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$		$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Farber and Blauer	$B_2O_3(l) + BF_3(g) = 3\ BOF(g)$	150.2 ± 16.6	149.0	−140.1 ± 6*
Hildenbrand *et al.*	$(BOF)_3(g) = 3\ BOF(g)$	129.8 ± 3	–	−145.2 ± 1.5

*Calculation based on the 3rd law value and one point rejected due to statistical test.

The adopted value of $\Delta_f H°(298.15\ K)$ for BOF(g) is the weighted average of the two values listed above.

Heat Capacity and Entropy

The molecular structure is assumed to be linear. The vibrational frequencies (υ) are estimated from the values calculated by the valence force method described by Herzberg[3] using estimated force constants, $k_1 = 10 \times 10^5$ dynes cm^{-1} and $k_2 = 0.47 \times 10^{-11}$ dynes cm rad^{-1}. The B=O and B–F bond distances are assumed to be the same as those in BO(g) and $BF_3(g)$ molecules.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.934	−602.462	−602.462	INFINITE
100	29.748	187.280	257.440	−7.016	−602.474	−603.987	315.491
200	35.585	209.533	228.390	−3.771	−602.482	−605.491	158.138
250	38.542	217.799	225.465	−1.916	−602.478	−606.244	126.668
298.15	40.996	224.803	224.803	0.	−602.496	−606.969	106.338
300	41.083	225.057	224.804	0.076	−602.497	−606.996	105.687
350	43.261	231.558	225.312	2.186	−602.547	−607.743	90.701
400	45.151	237.461	226.468	4.397	−602.634	−608.479	79.459
450	46.811	242.877	227.994	6.697	−602.754	−609.203	70.714
500	48.281	247.886	229.736	9.075	−602.899	−609.912	63.717
600	50.752	256.916	233.530	14.032	−603.240	−611.284	53.217
700	52.719	264.893	237.452	19.209	−603.621	−612.594	45.712
800	54.286	272.039	241.336	24.562	−604.024	−613.849	40.080
900	55.539	278.508	245.113	30.056	−604.442	−615.052	35.697
1000	56.547	284.413	248.752	35.662	−604.874	−616.208	32.187
1100	57.362	289.842	252.244	41.359	−605.322	−617.320	29.314
1200	58.028	294.863	255.589	47.129	−605.787	−618.390	26.918
1300	58.575	299.530	258.792	52.960	−606.274	−619.421	24.889
1400	59.030	303.888	261.859	58.841	−606.785	−620.413	23.148
1500	59.410	307.974	264.798	64.764	−607.323	−621.368	21.638
1600	59.731	311.819	267.618	70.721	−607.889	−622.286	20.316
1700	60.004	315.449	270.326	76.708	−608.487	−623.168	19.148
1800	60.238	318.885	272.929	82.721	−609.117	−624.014	18.108
1900	60.439	322.147	275.434	88.755	−609.780	−624.823	17.178
2000	60.614	325.252	277.848	94.808	−610.477	−625.597	16.339
2100	60.766	328.213	280.177	100.877	−611.206	−626.335	15.579
2200	60.900	331.043	282.425	106.960	−611.969	−627.038	14.888
2300	61.017	333.753	284.598	113.056	−612.763	−627.705	14.256
2400	61.121	336.352	286.701	119.163	−663.847	−627.269	13.652
2500	61.214	338.849	288.737	125.280	−664.780	−625.725	13.074
2600	61.297	341.252	290.711	131.406	−665.709	−624.145	12.539
2700	61.371	343.566	292.626	137.539	−666.632	−622.528	12.044
2800	61.438	345.800	294.485	143.680	−667.549	−620.878	11.583
2900	61.498	347.957	296.292	149.827	−668.459	−619.196	11.153
3000	61.553	350.042	298.049	155.979	−669.361	−617.481	10.751
3100	61.603	352.061	299.759	162.137	−670.253	−615.737	10.375
3200	61.648	354.018	301.424	168.300	−671.135	−613.965	10.022
3300	61.689	355.916	303.047	174.466	−672.007	−612.165	9.690
3400	61.727	357.758	304.629	180.637	−672.867	−610.338	9.377
3500	61.762	359.548	306.173	186.812	−673.715	−608.487	9.081
3600	61.794	361.288	307.680	192.989	−674.552	−606.611	8.802
3700	61.823	362.981	309.152	199.170	−675.375	−604.713	8.537
3800	61.850	364.631	310.590	205.354	−676.186	−602.792	8.286
3900	61.876	366.237	311.996	211.540	−676.984	−600.850	8.047
4000	61.899	367.804	313.372	217.729	−677.769	−598.888	7.821
4100	61.921	369.333	314.718	223.920	−678.542	−596.906	7.605
4200	61.941	370.825	316.037	230.113	−1159.151	−587.882	7.311
4300	61.960	372.283	317.328	236.308	−1158.811	−574.284	6.976
4400	61.978	373.708	318.593	242.505	−1158.461	−560.694	6.656
4500	61.994	375.101	319.833	248.704	−1158.101	−547.113	6.351
4600	62.009	376.464	321.050	254.904	−1157.733	−533.540	6.059
4700	62.024	377.797	322.243	261.106	−1157.356	−519.974	5.779
4800	62.038	379.103	323.414	267.309	−1156.972	−506.417	5.511
4900	62.050	380.383	324.564	273.513	−1156.581	−492.867	5.254
5000	62.062	381.636	325.693	279.719	−1156.185	−479.326	5.007
5100	62.074	382.865	326.802	285.925	−1155.784	−465.793	4.771
5200	62.084	384.071	327.891	292.133	−1155.380	−452.268	4.543
5300	62.095	385.254	328.963	298.342	−1154.973	−438.750	4.324
5400	62.104	386.414	330.016	304.552	−1154.565	−425.241	4.113
5500	62.113	387.554	331.052	310.763	−1154.157	−411.739	3.910
5600	62.122	388.673	332.071	316.975	−1153.750	−398.243	3.715
5700	62.130	389.773	333.073	323.188	−1153.345	−384.756	3.526
5800	62.138	390.853	334.060	329.401	−1152.943	−371.275	3.344
5900	62.145	391.916	335.032	335.615	−1152.546	−357.802	3.168
6000	62.152	392.960	335.989	341.830	−1152.155	−344.335	2.998

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [247.16 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -590.5 \pm 13\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -589.9 \pm 13\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[16000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1080](1)
[500](1)
[1213](1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: B–F = [1.30] Å
Bond Angle: F–B–F = 112°
Product of Moments of Inertia: $I_A I_B I_C = [4.36647 \times 10^{-116}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Srivastava and Farber,[1] using a gas inlet boron nitride effusion cell, performed a mass spectrometric study of the equilibrium vapor species over the system $BF_3(g) + B(cr)$. Ion intensities for $BF_3(g)$, BF(g) and $BF_2(g)$ were measured at ionizing electron energies slightly above appearance potentials (≈3 eV) in the temperature range 1477 to 1850 K and were used to obtain equilibrium data for the reaction $BF_3(g) + BF(g) = 2\ BF_2(g)$. We have analyzed their results and obtain $\Delta_r H°(298.15\ K) = 17.1 \pm 1.0\ kcal \cdot mol^{-1}$ from the 3rd law method with a drift of $-7.4 \pm 2.0\ cal \cdot K^{-1} \cdot mol^{-1}$ with JANAF heats of formation[2] for $BF_3(g)$ and BF(g).

Although no other experimental determinations of enthalpy of formation of BF_2 have been reported, Margrave[3] combined the appearance potential of BF_2^+ from BF_3 of 16.5 eV with an estimated ionization potential for BF_2 (IP = 9.4 ± 0.1 eV)[4] and calculated $\Delta_f H°(BF_2, g) \leq -124 \pm 9\ kcal \cdot mol^{-1}$. Based on the JANAF value for $AP(BF_2^+)$ of 15.81 eV.[2] we calculate $\Delta_f H°(BF_2, g, 0\ K) = -141.3\ kcal \cdot mol^{-1}$ by the same method. Margrave[3] also derived $\Delta_f H° = -135\ kcal \cdot mol^{-1}$ for BF_2 from average bond energy calculations and selected $\Delta_f H°(BF_2, g) = -130 \pm 6\ kcal \cdot mol^{-1}$ as the 'best' value. It is now apparent that this value is several kilocalories too positive.

We note that the adopted enthalpy of formation leads to a progression in the stepwise bond dissociation energies for BF(g), $BF_2(g)$ and $BF_3(g)$ which is consistent with the bond energy scheme predicted by Hildenbrand[5] for the Group III A fluorides, namely $D_1 > D_2 < D_3$. Using all JANAF data[2] we calculate bond dissociation energies of $D_1(B–F) = 179.4$, $D_2(BF–F) = 132.2$, and $D_3(BF_2–F) = 149.3\ kcal \cdot mol^{-1}$. The adopted value also corresponds to an ionization potential for BF_2 of $9.4 \pm 0.2\ eV^2$ which appears reasonable in comparison with IP's for other Group III A dihalides[6] and is the value estimated for BF_2 by Steele *et al.*[4]

Heat Capacity and Entropy

Nelson and Gordy[7] were successful in producing trapped BF_2 radicals by gamma irradiation of solid xenon which contained small concentrations of BF_3. From observations on the electron spin resonance spectra of these radicals, a bond angle of 112° for BF_2 was derived by these workers to account for the hybridization of the α bonding orbitals of the boron atom. We adopt their result and assume the B–F bond length to be the same as that for BHF_2.[2] The three principal moments of inertia are: $I_A = 0.7385 \times 10^{-39}$, $I_B = 7.3289 \times 10^{-39}$, and $I_C = 8.0674 \times 10^{-39}\ g \cdot cm^2$.

The ground state electronic configuration ($^2A_1$) and doublet excited state ($^2B_1$) are estimated by analogy with those for NO_2.[8] The vibrational frequencies are calculated from the stretching and bending force constants of $k = 4.82 \times 10^5$ and $k\delta/l^2 = 0.84 \times 10^5$ dynes/cm by the valence force method. These force constants are estimated from those for CF_2 and SiF_2.[2]

References

[1]R. D. Srivastava and M. Farber, Trans. Faraday Soc. **67**, 2298 (1971).
[2]JANAF Thermochemical Tables: $BF_3(g)$, 6–30–69; BF(g), 12–31–64; BF_2,(g), 12–31–70; $BNF_2(g)$, 12–31–65; $CF_2(g)$, 6–30–70; $SiF_2(g)$, 12–31–68.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.617	−590.522	−590.522	INFINITE
100	33.582	207.676	280.540	−7.286	−590.123	−593.822	310.181
200	36.689	231.795	250.739	−3.789	−589.887	−597.632	156.085
250	38.629	240.188	247.813	−1.906	−589.878	−599.571	125.273
298.15	40.555	247.157	247.157	0.	−589.944	−601.433	105.369
300	40.629	247.408	247.157	0.075	−589.948	−601.504	104.731
350	42.585	253.819	247.659	2.156	−590.083	−603.420	90.056
400	44.409	259.626	248.798	4.331	−590.273	−605.313	79.046
450	46.050	264.953	250.301	6.594	−590.506	−607.179	70.480
500	47.494	269.882	252.015	8.933	−590.768	−609.018	63.624
600	49.827	278.757	255.749	13.805	−591.351	−612.614	53.333
700	51.554	286.575	259.606	18.878	−591.985	−616.109	45.975
800	52.837	293.547	263.421	24.101	−592.654	−619.510	40.450
900	53.801	299.828	267.123	29.435	−593.356	−622.825	36.148
1000	54.538	305.537	270.683	34.854	−594.090	−626.060	32.702
1100	55.111	310.763	274.092	40.337	−594.856	−629.220	29.879
1200	55.563	315.578	277.352	45.872	−595.656	−632.309	27.524
1300	55.925	320.040	280.466	51.447	−596.492	−635.330	25.528
1400	56.219	324.196	283.443	57.055	−597.364	−638.285	23.815
1500	56.461	328.083	286.291	62.689	−598.275	−641.176	22.328
1600	56.662	331.734	289.018	68.345	−599.223	−644.006	21.025
1700	56.831	335.174	291.633	74.020	−600.210	−646.775	19.873
1800	56.975	338.427	294.143	79.711	−601.234	−649.484	18.848
1900	57.100	341.510	296.555	85.415	−602.294	−652.136	17.928
2000	57.209	344.442	298.877	91.130	−603.387	−654.731	17.100
2100	57.306	347.236	301.114	96.856	−604.510	−657.271	16.349
2200	57.393	349.904	303.271	102.591	−605.662	−659.757	15.665
2300	57.474	352.457	305.355	108.334	−606.838	−662.189	15.039
2400	57.550	354.904	307.369	114.086	−658.293	−663.501	14.441
2500	57.622	357.255	309.317	119.844	−659.584	−663.692	13.867
2600	57.693	359.517	311.205	125.610	−660.855	−663.831	13.337
2700	57.762	361.695	313.035	131.383	−662.104	−663.922	12.844
2800	57.832	363.797	314.810	137.163	−663.327	−663.967	12.386
2900	57.903	365.828	316.535	142.949	−664.521	−663.968	11.959
3000	57.975	367.792	318.211	148.743	−665.683	−663.929	11.560
3100	58.048	369.694	319.841	154.544	−666.812	−663.852	11.186
3200	58.124	371.538	321.428	160.353	−667.904	−663.739	10.834
3300	58.202	373.328	322.974	166.169	−668.959	−663.593	10.504
3400	58.283	375.067	324.480	171.993	−669.974	−663.415	10.192
3500	58.365	376.757	325.950	177.826	−670.948	−663.207	9.898
3600	58.450	378.403	327.384	183.667	−671.881	−662.973	9.619
3700	58.538	380.005	328.785	189.516	−672.771	−662.713	9.356
3800	58.627	381.568	330.153	195.374	−673.619	−662.430	9.106
3900	58.718	383.092	331.491	201.241	−674.423	−662.125	8.868
4000	58.811	384.580	332.800	207.118	−675.184	−661.800	8.642
4100	58.904	386.033	334.081	213.004	−675.901	−661.456	8.427
4200	58.999	387.453	335.335	218.899	−1156.425	−654.071	8.135
4300	59.095	388.843	336.563	224.803	−1155.970	−642.116	7.800
4400	59.191	390.203	337.767	230.718	−1155.473	−630.172	7.481
4500	59.288	391.534	338.947	236.642	−1154.938	−618.239	7.176
4600	59.385	392.838	340.104	242.575	−1154.363	−606.319	6.885
4700	59.481	394.116	341.240	248.519	−1153.751	−594.411	6.606
4800	59.577	395.369	342.354	254.472	−1153.101	−582.517	6.339
4900	59.672	396.599	343.449	260.434	−1152.416	−570.637	6.083
5000	59.766	397.805	344.524	266.406	−1151.696	−558.771	5.837
5100	59.858	398.990	345.580	272.387	−1150.943	−546.920	5.602
5200	59.950	400.153	346.619	278.377	−1150.158	−535.084	5.375
5300	60.040	401.296	347.640	284.377	−1149.341	−523.263	5.157
5400	60.128	402.419	348.644	290.385	−1148.495	−511.458	4.947
5500	60.215	403.523	349.632	296.403	−1147.621	−499.670	4.745
5600	60.299	404.609	350.604	302.428	−1146.719	−487.896	4.551
5700	60.381	405.677	351.560	308.462	−1145.792	−476.140	4.363
5800	60.462	406.728	352.503	314.504	−1144.840	−464.401	4.182
5900	60.540	407.762	353.430	320.555	−1143.864	−452.677	4.008
6000	60.615	408.780	354.344	326.612	−1142.867	−440.970	3.839

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = [225.1 \pm 1]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 315.8 \pm 2.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 322.6 \pm 2.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[25000]	1

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[900](1)
[370](2)
[1550](1)

Point Group: [$D_{\infty h}$] $\sigma = 2$
Bond Distance: B–F = [1.31] Å
Bond Angle: F–B–F = [180]°
Rotational Constant: B_0 = [0.258528] cm^{-1}

Enthalpy of Formation

The electron impact reaction at low pressure in BF_3(g) has been studied with a mass spectrometer by Osberghaus,[1] Law[2] and Marriott.[3] From the reported appearance potentials 17.0 ± 0.5, 16.2 ± 0.2, and 16.7 ± 0.05 eV and assumed process $BF_3 + e = BF_2^+ + F + 2\ e^-$, we calculate the corresponding values of $\Delta_f H°(BF_2^+, g, 298.15\ K)$ as 104.5 ± 11.5, 86.1 ± 4.6, and 85.4 ± 1.2 $kcal·mol^{-1}$, using $\Delta_f H°(0\ K) = -170.747$ and 18.357 $kcal·mol^{-1}$ for BF_3(g) and F(g). These electron impact values are superseded by the photoionization results of Dibeler and Liston[7] who report the onset of BF_2^+ from BF_3 as 15.81 eV (364.6 $kcal·mol^{-1}$). This yields $\Delta_f H°(0\ K) = 75.5 \pm 0.6\ kcal·mol^{-1}$ or $\Delta_f H°(298.15\ K) = 77.1 \pm 0.6\ kcal·mol^{-1}$, which are adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh[4] prediction for 16 valence electron XY_2 molecules. The electronic states, levels, and vibrational frequencies are estimated by comparison with those for CO_2.[5] The B–F bond distances is calculated by the method recommended by Krasnov.[5]

References

[1]O. Osberghaus, Z. Phys. **128**, 366 (1950).
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[6]K. S. Krasnov, Zhur. Strukt. Khim. **1**, 209 (1960).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.611	315.817		
100	31.424	184.214	260.803	−7.659			
200	39.162	208.493	229.047	−4.111			
250	42.008	217.548	225.865	−2.079			
298.15	44.291	225.148	225.148	0.	322.586	311.405	−54.557
300	44.371	225.422	225.149	0.082	322.628	311.335	−54.208
350	46.401	232.418	225.697	2.353	323.722	309.366	−46.170
400	48.172	238.732	226.938	4.718	324.761	307.244	−40.122
450	49.727	244.498	228.573	7.166	325.753	304.994	−35.403
500	51.091	249.809	230.435	9.687	326.712	302.636	−31.616
600	53.333	259.332	234.476	14.914	328.562	297.645	−25.912
700	55.047	267.688	238.636	20.336	330.357	292.350	−21.815
800	56.360	275.128	242.741	25.910	332.116	286.800	−18.726
900	57.375	281.827	246.718	31.598	333.848	281.032	−16.311
1000	58.168	287.915	250.538	37.377	335.553	275.071	−14.368
1100	58.794	293.489	254.193	43.226	337.231	268.942	−12.771
1200	59.296	298.627	257.684	49.132	338.880	262.661	−11.433
1300	59.702	303.390	261.019	55.082	340.499	256.243	−10.296
1400	60.035	307.827	264.206	61.070	342.084	249.702	−9.317
1500	60.311	311.979	267.254	67.088	343.636	243.049	−8.464
1600	60.541	315.879	270.172	73.131	345.152	236.294	−7.714
1700	60.736	319.555	272.970	79.195	346.634	229.445	−7.050
1800	60.901	323.031	275.656	85.277	348.080	222.509	−6.457
1900	61.043	326.328	278.236	91.374	349.492	215.494	−5.924
2000	61.165	329.462	280.720	97.485	350.873	208.406	−5.443
2100	61.272	332.449	283.113	103.607	352.224	201.249	−5.006
2200	61.365	335.302	285.421	109.739	353.548	194.029	−4.607
2300	61.446	338.031	287.649	115.879	354.848	186.749	−4.241
2400	61.519	340.648	289.803	122.028	305.868	180.482	−3.928
2500	61.583	343.161	291.888	128.183	307.052	175.233	−3.661
2600	61.640	345.577	293.907	134.344	308.255	169.936	−3.414
2700	61.692	347.905	295.864	140.511	309.479	164.593	−3.184
2800	61.739	350.149	297.763	146.682	310.727	159.204	−2.970
2900	61.782	352.316	299.607	152.858	312.001	153.770	−2.770
3000	61.821	354.411	301.399	159.038	313.303	148.292	−2.582
3100	61.858	356.439	303.142	165.222	314.636	142.770	−2.406
3200	61.893	358.404	304.838	171.410	316.001	137.204	−2.240
3300	61.925	360.309	306.490	177.601	317.400	131.595	−2.083
3400	61.956	362.158	308.100	183.795	318.833	125.943	−1.935
3500	61.986	363.954	309.671	189.992	320.302	120.249	−1.795
3600	62.016	365.701	311.203	196.192	321.808	114.512	−1.662
3700	62.045	367.400	312.699	202.395	323.350	108.732	−1.535
3800	62.074	369.055	314.160	208.601	324.928	102.911	−1.415
3900	62.103	370.668	315.589	214.810	326.544	97.047	−1.300
4000	62.133	372.241	316.985	221.022	328.198	91.142	−1.190
4100	62.163	373.775	318.352	227.237	329.888	85.194	−1.085
4200	62.194	375.274	319.689	233.454	−148.235	86.230	−1.072
4300	62.226	376.738	320.999	239.675	−145.385	91.778	−1.115
4400	62.259	378.169	322.282	245.900	−142.500	97.261	−1.155
4500	62.293	379.568	323.540	252.127	−139.582	102.677	−1.192
4600	62.328	380.938	324.773	258.358	−136.631	108.028	−1.227
4700	62.365	382.278	325.982	264.593	−133.649	113.315	−1.259
4800	62.402	383.592	327.169	270.831	−130.636	118.538	−1.290
4900	62.442	384.879	328.333	277.073	−127.592	123.697	−1.319
5000	62.482	386.141	329.477	283.320	−124.519	128.794	−1.346
5100	62.524	387.379	330.600	289.570	−121.418	133.830	−1.371
5200	62.568	388.593	331.704	295.825	−118.290	138.804	−1.394
5300	62.613	389.785	332.788	302.084	−115.136	143.718	−1.416
5400	62.659	390.956	333.855	308.347	−111.956	148.573	−1.437
5500	62.706	392.106	334.903	314.615	−108.752	153.368	−1.457
5600	62.755	393.237	335.935	320.888	−105.524	158.105	−1.475
5700	62.805	394.348	336.950	327.166	−102.274	162.783	−1.492
5800	62.856	395.440	337.949	333.449	−99.003	167.405	−1.508
5900	62.908	396.515	338.933	339.737	−95.711	171.970	−1.523
6000	62.961	397.573	339.901	346.031	−92.400	176.479	−1.536

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [240.7 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -796.4 \pm 32\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -802.1 \pm 32\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[15000]	3
$^1B_1$	[35000]	1

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[1175](1)
[495](1)
[1188](1)

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distance: B–F = [1.265] Å
Bond Angle: F–B–F = [100]°
Product of Moments of Inertia: $I_A I_B I_C = [3.74972 \times 10^{-116}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The BF_2 ion has been detected mass spectrometrically by MacNeil and Thynne[1] and Farber *et al.*[2] MacNeil and Thynne[1] reported the formation of the negative ion at electron energies of approximately 7.6 eV as a result of electron bombardment of BF_3(g). Assuming the ionization process to be $BF_3(g) + e = BF_2\ (g) + F(g)$, we calculate $\Delta_f H°(BF_2\ ,\ g,\ 0\ K) = -113.8\ kcal \cdot mol^{-1}$ from their results with JANAF enthalpies of formation[3] for BF_3(g) and F(g). This value leads to an unrealistic electron affinity (EA) for BF_2 of −1.1 eV. It seems most likely that the BF_2^- ion was formed in the dissociative ionization of BF_3(g) with considerable excess energy.

Farber, *et al.*[2] observed the formation of the BF_2^- ion in a molecular flow effusion mass spectrometric study of the $BF_3(g) + KF(g) + B(cr)$ system. Equilibrium data for the electron transfer reaction $BF_2\ (g) + F(g) = BF_2(g) + F\ (g)$ were reported for the temperature range 1253 to 1640 K. We have analyzed their results with JANAF functions and obtain $\Delta_f H°(298.15\ K) = -26.3 \pm 1.8\ kcal \cdot mol^{-1}$ by the 3rd law method with a drift of $-1.5 \pm 3.1\ cal \cdot K^{-1} \cdot mol^{-1}$, the 2nd law $\Delta_r H°(298.15\ K)$ value is $-24.2\ kcal \cdot mol^{-1}$. We adopt the 3rd law value and calculate $\Delta_f H°(BF_2\ ,\ g,\ 298.15\ K) = -191.7 \pm 8.0\ kcal \cdot mol^{-1}$ with JANAF auxiliary data. The adopted enthalpy of formation leads to EA $(BF_2) = 2.14 \pm 0.5$ eV.

Heat Capacity and Entropy

The correlation diagram of Walsh[4] predicts a bent configuration for BF_2^- (18 valence electrons) with a bond angle considerably reduced from that for BF_2(112°).[3] These predictions are supported by the experimentally determined bond angles for the isoelectronic molecules CF_2(104.9°),[3] SiF_2(101°)[3] and GeF_2(94°).[5] Thus we adopt a bond angle for BF_2^- of 100° and assume the B–F bond length to be the same as that for BF.[3] The principal moments of inertia are: $I_A = 0.9240 \times 10^{-39}$, $I_B = 5.9251 \times 10^{-39}$, and $I_C = 6.8491 \times 10^{-39}\ g \cdot cm^2$.

The electronic states, levels, and quantum weights are estimated by analogy with those for CF_2.[3] The vibrational frequencies are calculated form the stretching and bending force constants of $k = 5.16 \times 10^5$ and $k\delta/l^2 = 0.91 \times 10^5$ dynes/cn by the valence force method. These force constants are estimated by comparison with those for CF_2, SiF_2, and BF_2.[3]

References

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[3]JANAF Thermochemical Tables: BF_3(g), 6–30–69; F(g), 9–30–65; CF_2(g), 6–30–70; SiF_2(g), 12–31–68; BF(g), 12–31–64; BF_2(g), 6–30–72.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.609	−796.445		
100	33.599	201.283	274.065	−7.278			
200	36.676	225.419	244.310	−3.778			
250	38.519	233.799	241.394	−1.899			
298.15	40.352	240.740	240.740	0.	−802.073	−805.394	141.102
300	40.423	240.990	240.741	0.075	−802.115	−805.414	140.235
350	42.310	247.364	241.240	2.143	−803.302	−805.871	120.270
400	44.094	253.131	242.371	4.304	−804.547	−806.153	105.273
450	45.720	258.420	243.865	6.550	−805.835	−806.277	93.590
500	47.165	263.314	245.568	8.873	−807.153	−806.256	84.229
600	49.525	272.132	249.277	13.713	−809.846	−805.825	70.153
700	51.290	279.905	253.108	18.758	−812.586	−804.938	60.065
800	52.610	286.845	256.899	23.956	−815.359	−803.657	52.473
900	53.607	293.101	260.580	29.269	−818.160	−802.026	46.548
1000	54.372	298.791	264.121	34.670	−820.991	−800.082	41.792
1100	54.968	304.002	267.513	40.138	−823.851	−797.853	37.887
1200	55.439	308.806	270.756	45.659	−826.743	−795.362	34.621
1300	55.817	313.259	273.857	51.223	−829.669	−792.629	31.848
1400	56.124	317.407	276.821	56.820	−832.630	−789.669	29.463
1500	56.378	321.288	279.657	62.446	−835.628	−786.496	27.388
1600	56.591	324.934	282.374	68.095	−838.663	−783.121	25.566
1700	56.774	328.370	284.980	73.763	−841.735	−779.556	23.953
1800	56.933	331.620	287.482	79.449	−844.842	−775.809	22.513
1900	57.075	334.702	289.886	85.149	−847.984	−771.889	21.221
2000	57.207	337.633	292.201	90.863	−851.157	−767.801	20.053
2100	57.333	340.427	294.432	96.590	−854.358	−763.555	18.992
2200	57.457	343.097	296.583	102.330	−857.584	−759.156	18.025
2300	57.583	345.654	298.662	108.082	−860.829	−754.609	17.138
2400	57.713	348.107	300.671	113.847	−914.350	−748.852	16.298
2500	57.850	350.466	302.616	119.625	−917.700	−741.887	15.501
2600	57.995	352.738	304.500	125.417	−921.024	−734.789	14.762
2700	58.151	354.929	306.328	131.224	−924.317	−727.564	14.076
2800	58.319	357.047	308.102	137.048	−927.574	−720.217	13.436
2900	58.498	359.097	309.825	142.888	−930.793	−712.754	12.838
3000	58.689	361.083	311.501	148.748	−933.968	−705.182	12.278
3100	58.893	363.011	313.131	154.627	−937.098	−697.504	11.753
3200	59.108	364.884	314.719	160.526	−940.177	−689.726	11.259
3300	59.334	366.706	316.267	166.448	−943.205	−681.852	10.793
3400	59.570	368.481	317.777	172.394	−946.177	−673.887	10.353
3500	59.816	370.211	319.250	178.363	−949.093	−665.836	9.937
3600	60.070	371.900	320.690	184.357	−951.951	−657.702	9.543
3700	60.331	373.549	322.096	190.377	−954.750	−649.490	9.169
3800	60.597	375.162	323.471	196.423	−957.488	−641.203	8.814
3900	60.868	376.739	324.817	202.497	−960.164	−632.845	8.476
4000	61.142	378.284	326.134	208.597	−962.780	−624.419	8.154
4100	61.418	379.797	327.425	214.725	−965.334	−615.928	7.847
4200	61.694	381.280	328.690	220.881	−1447.676	−600.351	7.466
4300	61.970	382.735	329.930	227.064	−1449.020	−580.161	7.048
4400	62.244	384.163	331.146	233.275	−1450.307	−559.940	6.647
4500	62.515	385.565	332.340	239.513	−1451.535	−539.690	6.265
4600	62.782	386.942	333.512	245.778	−1452.708	−519.414	5.898
4700	63.045	388.295	334.663	252.069	−1453.826	−499.113	5.547
4800	63.302	389.625	335.794	258.386	−1454.891	−478.789	5.210
4900	63.552	390.933	336.906	264.729	−1455.904	−458.443	4.887
5000	63.795	392.219	338.000	271.096	−1456.867	−438.076	4.577
5100	64.031	393.485	339.075	277.488	−1457.782	−417.692	4.278
5200	64.258	394.730	340.134	283.902	−1458.652	−397.289	3.991
5300	64.477	395.956	341.175	290.339	−1459.476	−376.870	3.714
5400	64.687	397.163	342.201	296.797	−1460.259	−356.436	3.448
5500	64.887	398.352	343.211	303.276	−1461.002	−335.988	3.191
5600	65.078	399.523	344.206	309.775	−1461.706	−315.527	2.943
5700	65.260	400.677	345.187	316.292	−1462.374	−295.054	2.704
5800	65.431	401.813	346.153	322.826	−1463.008	−274.569	2.473
5900	65.593	402.933	347.106	329.377	−1463.611	−254.073	2.249
6000	65.745	404.037	348.046	335.944	−1464.183	−233.568	2.033

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = 244.0\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -730.3 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -733.9 \pm 3.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
2640(1)	1411 (1)
1174(1)	[1158](1)
544(1)	928 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: B–H = 1.15 Å; B–F = 1.30 ± 0.15 Å
Bond Angles: F–B–F = 120 ± 5°; F–B–H = 120 ± 2.5°
Product of the Moments of Inertia: $I_A I_B I_C = 7.51811 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

The equilibrium pressures at 296 and 360 K for the reaction 1/6 B_2H_6(g) + 2/3 BF_3(g) = HBF_2(g) were determined by Porter and Wason.[1] By the 3rd law method, the enthalpy change was evaluated to be 3.06 ± 0.33 kcal·mol^{-1}. Based on the values of $\Delta_f H°(298.15\ K)$ for B_2H_6(g) and BF_3(g) as 9.8 and −270.1 kcal·mol^{-1}, respectively, the enthalpy of formation for BHF_2(g) was derived to be −175.4 ± 0.8 kcal·mol^{-1}. The drift in the 3rd law enthalpy of reaction is 3.6 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The infrared spectrum of BHF_2(g) has been observed by Coyle *et al.*,[2] Ritter, and Farrar,[2] Perec and Becks,[3] Lynds,[4] and Porter and Wason.[1]

The vibrational frequencies, except υ_5, were obtained form Porter and Wason[1] and corrected to the average isotopic species. The value of υ_5 was estimated by comparison with the same value reported by other investigators. The molecular structure, bond distances and angles were obtained from Perec and Becks.[3] The principal moments of inertia are: $I_A = 1.0402 \times 10^{-39}$, $I_B = 7.9974 \times 10^{-39}$, and $I_C = 9.0376 \times 10^{-39}$ g·cm^2.

The vibrational rotational spectrum of BHF_2(g) has been studied by Lynds and Bass.[5] The values of υ_1, υ_2, υ_3, and υ_6 were assigned as 1164.2, 2620.8, 541.5 and 923.5 cm^{-1}, respectively, which are in fair agreement with the adopted values reported by Porter and Wason.[1]

References

[1]R. F. Porter and S. K. Wason, J. Phys. Chem. **69**, 2208 (1965).
[2]T. D. Coyle, J. J. Ritter and T. C. Farrar, Proc. Chem. Soc. 25 (1964).
[3]M. Perec and L. N. Becks, J. Chem. Phys. **43**, 721 (1965).
[4]L. Lynds, J. Chem. Phys. **42**, 1124 (1965).
[5]L. Lynds and C. D. Bass, J. Chem Phys. **43**, 4357 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.671	−730.272	−730.272	INFINITE
100	33.464	204.405	277.831	−7.343	−731.374	−729.711	381.162
200	36.674	228.378	247.707	−3.866	−732.506	−727.627	190.037
250	39.376	236.842	244.709	−1.967	−733.179	−726.330	151.758
298.15	42.358	244.029	244.029	0.	−733.874	−724.949	127.008
300	42.476	244.291	244.030	0.078	−733.901	−724.893	126.215
350	45.706	251.082	244.559	2.283	−734.637	−723.334	107.952
400	48.856	257.392	245.773	4.648	−735.366	−721.669	94.240
450	51.806	263.319	247.396	7.165	−736.074	−719.914	83.565
500	54.504	268.919	249.271	9.824	−736.748	−718.082	75.018
600	59.136	279.281	253.424	15.514	−737.977	−714.231	62.179
700	62.868	288.688	257.800	21.621	−739.046	−710.187	52.995
800	65.882	297.286	262.206	28.064	−739.971	−705.999	46.097
900	68.332	305.192	266.549	34.779	−740.780	−701.703	40.726
1000	70.340	312.499	270.783	41.716	−741.497	−697.322	36.424
1100	71.997	319.283	274.888	48.835	−742.147	−692.873	32.902
1200	73.374	325.609	278.854	56.106	−742.750	−688.366	29.964
1300	74.528	331.529	282.681	63.503	−743.325	−683.811	27.476
1400	75.500	337.089	286.370	71.005	−743.884	−679.212	25.342
1500	76.325	342.326	289.928	78.598	−744.441	−674.573	23.491
1600	77.030	347.275	293.359	86.266	−745.003	−669.897	21.870
1700	77.636	351.964	296.670	94.000	−745.577	−665.185	20.439
1800	78.159	356.417	299.866	101.791	−746.168	−660.439	19.165
1900	78.614	360.655	302.955	109.630	−746.779	−655.660	18.025
2000	79.011	364.698	305.942	117.512	−747.411	−650.848	16.998
2100	79.360	368.561	308.832	125.431	−748.064	−646.004	16.068
2200	79.667	372.260	311.632	133.382	−748.738	−641.128	15.222
2300	79.940	375.808	314.346	141.363	−749.432	−636.221	14.449
2400	80.182	379.215	316.978	149.369	−800.403	−630.215	13.716
2500	80.399	382.493	319.534	157.398	−801.209	−623.107	13.019
2600	80.593	385.650	322.016	165.448	−801.995	−615.968	12.375
2700	80.767	388.695	324.430	173.516	−802.760	−608.798	11.778
2800	80.925	391.635	326.778	181.601	−803.503	−601.601	11.223
2900	81.068	394.477	329.063	189.701	−804.221	−594.377	10.706
3000	81.197	397.228	331.290	197.814	−804.912	−587.129	10.223
3100	81.315	399.892	333.460	205.940	−805.576	−579.859	9.771
3200	81.423	402.476	335.577	214.077	−806.211	−572.568	9.346
3300	81.522	404.983	337.642	222.224	−806.816	−565.257	8.947
3400	81.612	407.418	339.659	230.381	−807.391	−557.928	8.572
3500	81.695	409.785	341.629	238.546	−807.935	−550.583	8.217
3600	81.772	412.087	343.554	246.720	−808.447	−543.223	7.882
3700	81.843	414.329	345.437	254.901	−808.928	−535.848	7.565
3800	81.908	416.512	347.279	263.088	−809.378	−528.462	7.264
3900	81.969	418.641	349.081	271.282	−809.798	−521.064	6.979
4000	82.025	420.717	350.846	279.482	−810.186	−513.655	6.708
4100	82.078	422.743	352.575	287.687	−810.545	−506.238	6.450
4200	82.127	424.721	354.269	295.897	−1290.723	−491.787	6.116
4300	82.172	426.654	355.930	304.112	−1289.936	−472.775	5.743
4400	82.215	428.544	357.559	312.332	−1289.123	−453.780	5.387
4500	82.255	430.392	359.157	320.555	−1288.284	−434.804	5.047
4600	82.292	432.200	360.726	328.783	−1287.421	−415.848	4.722
4700	82.328	433.970	362.265	337.014	−1286.534	−396.910	4.411
4800	82.361	435.704	363.777	345.248	−1285.625	−377.991	4.113
4900	82.392	437.403	365.263	353.486	−1284.695	−359.092	3.828
5000	82.421	439.067	366.722	361.726	−1283.744	−340.211	3.554
5100	82.448	440.700	368.157	369.970	−1282.773	−321.351	3.291
5200	82.475	442.301	369.567	378.216	−1281.785	−302.508	3.039
5300	82.499	443.872	370.954	386.465	−1280.778	−283.686	2.796
5400	82.522	445.415	372.319	394.716	−1279.755	−264.882	2.562
5500	82.545	446.929	373.662	402.969	−1278.716	−246.098	2.337
5600	82.565	448.416	374.984	411.225	−1277.663	−227.332	2.120
5700	82.585	449.878	376.285	419.482	−1276.595	−208.586	1.911
5800	82.604	451.314	377.566	427.742	−1275.514	−189.859	1.710
5900	82.622	452.727	378.828	436.003	−1274.420	−171.150	1.515
6000	82.639	454.116	380.071	444.266	−1273.314	−152.460	1.327

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [269.17]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-1077 \pm 20]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1084 \pm 20]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[3680](1)	[888](1)
[1463](1)	[696](1)
[1420](1)	[480](1)
[1250](1)	[480](1)
[1250](1)	

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_s

Bond Distances: B–F = *[1.30]* Å; B–O = *[1.36]* Å; O–H = *[0.96]* Å

Bond Angles: F–B–F = [120]°; F–B–O = [120]°; B–O–H = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.051510 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

The value of enthalpy of formation, $\Delta_f H°(298.15\ K)$, was calculated based on an assumption that $\Delta_f H°(298.15\ K) = 0$ for the reaction 2/3 $BF_3(g)$ + 1/3 $B(OH)_3(g)$ = $BOHF_2(g)$.

Heat Capacity and Entropy

The vibrational frequencies were obtained from Gordon.[1] The B–F and O–H bond distances were assumed to be the same as those in $BF_3(g)$ and $H_2O(g)$ molecules, respectively. The B–O bond distance and the bond angles were estimated from related molecules. The principal moments of inertia are: $I_A = 7.8128 \times 10^{-39}$, $I_B = 8.3349 \times 10^{-39}$, and $I_C = 16.1476 \times 10^{-39}\ g·cm^2$.

Reference

[1] J. S. Gordon, Astrosystems International, Inc. (1962).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.726	−1076.768	−1076.768	INFINITE
100	34.095	224.715	308.596	−8.388	−1079.313	−1071.015	559.441
200	42.159	250.509	273.610	−4.620	−1081.609	−1061.807	277.316
250	47.167	260.453	270.002	−2.387	−1082.677	−1056.732	220.792
298.15	51.982	269.174	269.174	0.	−1083.656	−1051.646	184.244
300	52.164	269.496	269.175	0.096	−1083.692	−1051.447	183.073
350	56.990	277.902	269.828	2.826	−1084.641	−1045.997	156.106
400	61.514	285.812	271.336	5.790	−1085.519	−1040.415	135.864
450	65.653	293.300	273.364	8.971	−1086.322	−1034.728	120.108
500	69.373	300.413	275.716	12.349	−1087.048	−1028.956	107.494
600	75.605	313.636	280.952	19.610	−1088.285	−1017.217	88.557
700	80.471	325.671	286.494	27.424	−1089.275	−1005.291	75.016
800	84.305	336.676	292.089	35.670	−1090.065	−993.237	64.852
900	87.380	346.790	297.613	44.260	−1090.702	−981.094	56.941
1000	*89.894*	*356.131*	*303.003*	*53.127*	*−1091.219*	−968.887	50.609
1100	91.983	364.799	308.232	62.224	−1091.646	−956.632	45.427
1200	93.744	372.881	313.286	71.513	−1092.006	−944.342	41.106
1300	95.244	380.445	318.165	80.964	−1092.317	−932.023	37.449
1400	96.532	387.552	322.870	90.555	−1092.596	−919.683	34.314
1500	97.647	394.251	327.407	100.265	−1092.855	−907.323	31.596
1600	98.617	400.584	331.785	110.079	−1093.105	−894.946	29.217
1700	*99.465*	*406.589*	*336.010*	*119.984*	*−1093.354*	−882.553	27.118
1800	100.210	412.296	340.091	129.969	−1093.609	−870.146	25.251
1900	100.868	417.732	344.035	140.024	−1093.874	−857.724	23.580
2000	101.451	422.921	347.851	150.140	−1094.152	−845.288	22.077
2100	101.969	427.883	351.544	160.312	−1094.446	−832.838	20.716
2200	102.432	432.638	355.123	170.532	−1094.755	−820.373	19.478
2300	102.847	437.200	358.593	180.796	−1095.081	−807.893	18.348
2400	103.219	441.585	361.960	191.100	−1145.681	−794.331	17.288
2500	103.554	445.806	365.230	201.439	−1146.114	−779.683	16.291
2600	103.857	449.873	368.408	211.810	−1146.527	−765.017	15.369
2700	104.132	453.798	371.499	222.210	−1146.920	−750.336	14.516
2800	104.382	457.590	374.506	232.635	−1147.290	−735.641	13.724
2900	104.609	461.257	377.434	243.085	−1147.637	−720.933	12.985
3000	104.817	464.807	380.288	253.557	−1147.959	−706.213	12.296
3100	105.007	468.247	383.070	264.048	−1148.255	−691.484	11.651
3200	105.182	471.584	385.784	274.558	−1148.524	−676.745	11.047
3300	105.342	474.823	388.434	285.084	−1148.766	−661.998	10.479
3400	105.490	477.970	391.021	295.626	−1148.979	−647.244	9.944
3500	105.626	481.030	393.549	306.182	−1149.164	−632.485	9.439
3600	105.753	484.007	396.021	316.751	−1149.321	−617.720	8.963
3700	105.870	486.906	398.438	327.332	−1149.449	−602.951	8.512
3800	105.978	489.731	400.803	337.924	−1149.548	−588.180	8.085
3900	106.079	492.485	403.119	348.527	−1149.620	−573.405	7.680
4000	106.173	495.172	405.387	359.140	−1149.663	−558.630	7.295
4100	106.260	497.795	407.609	369.761	−1149.679	−543.854	6.929
4200	106.342	500.356	409.787	380.392	−1629.519	−522.054	6.493
4300	106.419	502.860	411.922	391.030	−1628.395	−495.699	6.022
4400	106.490	505.307	414.017	401.675	−1627.249	−469.371	5.572
4500	106.558	507.701	416.072	412.328	−1626.080	−443.068	5.143
4600	106.621	510.043	418.090	422.987	−1624.890	−416.793	4.733
4700	106.680	512.337	420.071	433.652	−1623.681	−390.542	4.340
4800	106.736	514.584	422.017	444.323	−1622.453	−364.318	3.965
4900	106.789	516.785	423.928	454.999	−1621.208	−338.120	3.604
5000	106.838	518.943	425.807	465.680	−1619.947	−311.947	3.259
5100	106.885	521.059	427.654	476.366	−1618.671	−285.800	2.927
5200	106.929	523.135	429.470	487.057	−1617.381	−259.678	2.608
5300	*106.971*	525.172	431.257	497.752	*−1616.080*	−233.580	2.302
5400	107.011	527.172	433.015	508.451	−1614.768	−207.508	2.007
5500	107.049	529.136	434.744	519.154	−1613.447	−181.460	1.723
5600	107.085	531.065	436.447	529.861	−1612.118	−155.435	1.450
5700	107.118	532.961	438.124	540.571	−1610.782	−129.435	1.186
5800	107.151	534.824	439.775	551.285	−1609.440	−103.458	0.932
5900	107.181	536.656	441.402	562.001	−1608.095	−77.505	0.686
6000	107.211	538.458	443.004	572.721	−1606.746	−51.574	0.449

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K)$ = [267.8] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−834 ± 15] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−837 ± 15] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
17171	[2]
22390	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	v_i, cm^{-1}
1377(1)	[850](1)
856(1)	[1100](1)
491(1)	[500](1)

Point Group: C_{2v} $\sigma = 2$
Bond Distances: B–F = 1.30 ± 0.05 Å; B–O = 1.40 ± 0.05 Å
Bond Angles: F–B–O = 117 ± 5°; F–B–F = 126 ± 5°
Product of the Moments of Inertia: $I_A I_B I_C = 9.948921 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

The molecule BF_2O(g) is similar to BO_2(g) in that both have an extra electron. Based on an assumption that $D_0°(F_2B–O) = D_0°(OB–O) – 10 = 134.3$ kcal·mol^{-1} where the quantity −10 kcal·mol^{-1} is estimated as the resonance stabilization energy in BO_2(g), $\Delta_f H°(F_2BO, g, 298.15\ K)$ is calculated to be −206 kcal·mol^{-1}.

Assuming $D_0°(F_2BO–H) = D_0°(HO–H) = 118$ kcal·mol^{-1}, the value of $\Delta_f H°(F_2BO, g, 298.15\ K)$ is evaluated as −191.6 kcal·mol^{-1}, using $\Delta_f H°(0\ K) = 51.63$ and −257.35 kcal·mol^{-1} for H(g) and F_2BOH(g), respectively.

The value of $\Delta_f H°(F_2BO, g, 298.15\ K)$ is tentatively adopted as −200 ± 15 kcal·mol^{-1}

Heat Capacity and Entropy

The 4465–A emission spectrum was observed in a discharge through BF_3 and O_2 by Mathews.[1] The emitter of the discharge was shown to be either the planar BOF_2 molecule or molecule–ion BOF_2^+. No experimental evidence has been found to distinguish between them. The molecular structure, bond distances and angles were reported by Mathews,[1] based on a rotational analysis of the emission spectrum. These values are adopted here.

Three vibrational frequencies for both $^{11}B^{16}OF_2$ and $^{10}B^{16}OF_2$ molecules (or ions) were deermined by vibrational analysis of the 5800–Å bands of the emission spectrum by Mathews and Innes.[2] These values are corrected to the average isotopic species and adopted. The last three frequencies are estimated from values calculated by the valence–force method, using force constants transferred from COF_2(g).

The ground state quantum weight is taken as 2 because of the extra electron. The other two electronic levels are estimated from the band systems at 5800 and 4465 Å, assuming that two systems have a common lower state, i.e. the ground state.

The principal moments of inertia are: $I_A = 7.4051 \times 10^{-39}$, $I_B = 8.4655 \times 10^{-39}$, and $I_C = 15.8706 \times 10^{-39}\ g·cm^2$.

References

[1] C. W. Mathews, J. Mol. Spectry. **19**, 203 (1966).
[2] C. W. Mathews and K. K. Innes, J. Mol. Spectry. **15**, 199 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.535	−833.955	−833.955	INFINITE
100	33.949	224.266	306.266	−8.200	−835.003	−831.696	434.434
200	41.185	249.703	272.146	−4.489	−836.009	−827.987	216.248
250	45.839	259.392	268.645	−2.313	−836.436	−825.931	172.569
298.15	50.199	267.842	267.842	0.	−836.800	−823.874	144.339
300	50.360	268.153	267.843	0.093	−836.813	−823.794	143.435
350	54.500	276.233	268.472	2.716	−837.144	−821.597	122.617
400	58.160	283.755	269.918	5.535	−837.438	−819.355	106.997
450	61.331	290.793	271.850	8.524	−837.703	−817.079	94.844
500	64.045	297.399	274.078	11.660	−837.939	−814.774	85.119
600	68.325	309.475	278.991	18.290	−838.344	−810.102	70.526
700	71.432	320.254	284.130	25.287	−838.682	−805.368	60.097
800	73.715	329.949	289.262	32.550	−838.979	−800.588	52.273
900	75.422	338.734	294.278	40.010	−839.257	−795.772	46.185
1000	76.721	346.751	299.131	47.620	−839.530	−790.926	41.314
1100	77.729	354.113	303.799	55.345	−839.810	−786.052	37.327
1200	78.523	360.911	308.279	63.159	−840.105	−781.152	34.003
1300	79.158	367.222	312.573	71.044	−840.422	−776.227	31.189
1400	79.674	373.108	316.689	78.987	−840.767	−771.276	28.777
1500	80.097	378.620	320.636	86.976	−841.143	−766.299	26.685
1600	80.449	383.801	324.424	95.004	−841.554	−761.297	24.854
1700	80.744	388.687	328.061	103.064	−842.001	−756.267	23.237
1800	80.994	393.310	331.559	111.151	−842.487	−751.210	21.800
1900	81.209	397.695	334.926	119.261	−843.009	−746.125	20.512
2000	81.394	401.865	338.169	127.392	−843.569	−741.011	19.353
2100	81.557	405.840	341.298	135.540	−844.163	−735.869	18.304
2200	81.700	409.638	344.318	143.702	−844.791	−730.698	17.349
2300	81.829	413.272	347.238	151.879	−845.449	−725.497	16.477
2400	81.945	416.757	350.062	160.068	−896.393	−719.198	15.653
2500	82.053	420.105	352.798	168.268	−897.180	−711.799	14.872
2600	82.153	423.325	355.449	176.478	−897.955	−704.369	14.151
2700	82.249	426.427	358.020	184.698	−898.715	−696.908	13.483
2800	82.341	429.420	360.517	192.928	−899.457	−689.420	12.861
2900	82.431	432.311	362.943	201.166	−900.178	−681.906	12.282
3000	82.520	435.107	365.302	209.414	−900.875	−674.368	11.742
3100	82.610	437.814	367.598	217.671	−901.546	−666.806	11.236
3200	82.701	440.439	369.834	225.936	−902.188	−659.224	10.761
3300	82.793	442.985	372.012	234.211	−902.800	−651.622	10.314
3400	82.888	445.458	374.136	242.495	−903.379	−644.001	9.894
3500	82.985	447.862	376.208	250.788	−903.924	−636.365	9.497
3600	83.085	450.201	378.231	259.092	−904.434	−628.713	9.122
3700	83.189	452.479	380.207	267.405	−904.907	−621.047	8.768
3800	83.296	454.699	382.138	275.730	−905.343	−613.369	8.431
3900	83.407	456.864	384.027	284.065	−905.740	−605.680	8.112
4000	83.521	458.977	385.874	292.411	−906.099	−597.982	7.809
4100	83.639	461.041	387.683	300.769	−906.418	−590.275	7.520
4200	83.760	463.058	389.453	309.139	−1386.548	−575.536	7.158
4300	83.884	465.030	391.188	317.521	−1385.702	−556.237	6.757
4400	84.011	466.960	392.888	325.916	−1384.818	−536.957	6.374
4500	84.141	468.850	394.555	334.324	−1383.898	−517.698	6.009
4600	84.273	470.700	396.191	342.744	−1382.941	−498.460	5.660
4700	84.408	472.514	397.795	351.178	−1381.949	−479.242	5.326
4800	84.544	474.293	399.371	359.626	−1380.923	−460.046	5.006
4900	84.682	476.037	400.917	368.087	−1379.863	−440.872	4.700
5000	84.822	477.750	402.437	376.563	−1378.770	−421.720	4.406
5100	84.962	479.431	403.930	385.052	−1377.646	−402.590	4.123
5200	85.103	481.082	405.398	393.555	−1376.492	−383.483	3.852
5300	85.244	482.704	406.841	402.072	−1375.309	−364.397	3.591
5400	85.385	484.299	408.261	410.604	−1374.099	−345.335	3.340
5500	85.526	485.867	409.658	419.149	−1372.863	−326.296	3.099
5600	85.667	487.409	411.033	427.709	−1371.604	−307.278	2.866
5700	85.806	488.927	412.386	436.283	−1370.321	−288.284	2.642
5800	85.945	490.420	413.718	444.870	−1369.017	−269.312	2.425
5900	86.082	491.891	415.031	453.472	−1367.694	−250.363	2.217
6000	86.218	493.339	416.324	462.087	−1366.354	−231.437	2.015

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 254.36 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1132.8 \pm 1.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1135.6 \pm 1.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
888 (1)
696.7 (1)
1463.3 (2)
480.7 (2)

Ground State Quantum Weight: 1 $\sigma = 6$

Point Group: D_{3h}

Bond Distance: B–F = 1.307 ± 0.002 Å

Bond Angle: F–B–F = 120°

Products of the Moments of Inertia: $I_A I_B I_C = 1.056517 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted enthalpy of formation was selected by a simultaneous adjustment of several interrelated pieces of data relating to the heat of formation of HF (see HF, g table 12–31–68). The data which were considered relating directly to BF_3 were as follows:

A. $NF_3(g) + B(cr, \beta) \rightarrow BF_3(g) + 0.5\ N_2$ and $\Delta_f H°(298.15\ K) = 239.46 \pm 1.2\ kcal \cdot mol^{-1}$.

Ludwig and Cooper[1] report the above value after corretion for 0.44 percent impurities in the boron. As much as 5 percent unburned boron was determined by analysis.

B. $1.5\ F_2(g) + B(cr, \beta) \rightarrow BF_3(g)$

Wise *et al.*[2] originally reported $\Delta_f H°(298.15\ K) = -270.1 \pm 0.24\ kcal \cdot mol^{-1}$ but later reanalysis [3] of the impurities and due allowance for their effect changed this to $-271.6 \pm 0.9\ kcal \cdot mol^{-1}$. Johnson *et al.*[3] using zone refined boron obtained $\Delta_f H°(298.15\ K) = -271.65 \pm 0.22\ kcal \cdot mol^{-1}$ after correction for 0.12 percent impurities. Domalski and Armstrong[4] obtained $\Delta_f H°(298.15\ K) = -271.03 \pm 0.51\ kcal \cdot mol^{-1}$ from a combustion in the presence of Teflon, the boron contained 0.32 percent impurities and corrections were included. The above reaction constituted about 0.35 of the total energy measured. The measurements of Gross *et al.*,[5] although on a zone refined sample, did not include a complete purity analysis and their data were not included since probable impurities could introduce serious errors.

C. $3\ HF(50\ H_2O) + B(cr, \beta) + 0.75\ O_2(g) \rightarrow BF_3(g) + 1.5\ H_2O(l)$

From the measurements of Gunn[6] on the reaction of $BF_3(g) + 15.67\ HF(3.747\ H_2O) \rightarrow$ [solution] and Good and Mansson[7] for the reaction $B(cr, \beta) + 0.75\ O_2(g) + 18.57\ HF(3.065\ H_2O) \rightarrow$ [solution] $+ 1.5\ H_2O(l)$, where the resulting solutions have the same composition, we obtain $\Delta_f H°(298.15\ K) = -142.77 \pm 0.5\ kcal \cdot mol^{-1}$. Further details of the simultaneous solution are given by Syverud.[8]

Heat Capacity and Entropy

The fundamental frequencies were selected from the measurements of Lindeman and Wilson,[9] McKean,[10] Nielsen,[11] Anderson *et al.*[12] and Yost *et al.*[13] The bond length and structure of those reported by Gin *et al.*[14] which are in agreement with those of Kuchitsu and Konaka[15] from gas phase electron diffraction. These measurements disagree with the earlier determinations of Nielsen[11] and Levy and Brockway[16] but are considerably more precise and are adopted.

The principal moments of inertia are $I_A = I_B = 8.0838 \times 10^{-39}$, and $I_C = 16.1676 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.647	−1132.817	−1132.817	INFINITE
100	34.089	210.208	293.304	−8.310	−1133.864	−1129.299	589.885
200	41.964	235.971	258.706	−4.547	−1134.828	−1124.343	293.648
250	46.471	245.824	255.164	−2.335	−1135.240	−1121.673	234.361
298.15	50.446	254.355	254.355	0.	−1135.621	−1119.025	196.049
300	50.590	254.668	254.356	0.093	−1135.636	−1118.922	194.822
350	54.273	262.749	254.986	2.717	−1136.023	−1116.106	166.570
400	57.539	270.213	256.429	5.514	−1136.407	−1113.235	145.374
450	60.420	277.160	258.351	8.464	−1136.785	−1110.315	128.882
500	62.945	283.660	260.560	11.550	−1137.150	−1107.355	115.685
600	67.071	295.518	265.418	18.060	−1137.831	−1101.330	95.879
700	70.195	306.103	270.488	24.931	−1138.443	−1095.198	81.725
800	72.569	315.638	275.546	32.074	−1138.997	−1088.981	71.103
900	74.389	324.295	280.489	39.426	−1139.508	−1082.698	62.838
1000	75.802	332.209	285.271	46.938	−1139.993	−1076.360	56.223
1100	76.914	339.488	289.873	54.576	−1140.465	−1069.974	50.809
1200	77.800	346.220	294.292	62.314	−1140.935	−1063.545	46.295
1300	78.516	352.476	298.530	70.131	−1141.413	−1057.076	42.474
1400	79.101	358.317	302.594	78.013	−1141.907	−1050.570	39.197
1500	79.584	363.792	306.493	85.948	−1142.422	−1044.028	36.356
1600	79.988	368.941	310.237	93.927	−1142.963	−1037.451	33.869
1700	80.327	373.801	313.834	101.943	−1143.531	−1030.840	31.674
1800	80.616	378.401	317.295	109.991	−1144.127	−1024.194	29.721
1900	80.863	382.766	320.627	118.065	−1144.752	−1017.514	27.973
2000	81.076	386.919	323.838	126.162	−1145.404	−1010.800	26.399
2100	81.261	390.880	326.937	134.279	−1146.080	−1004.054	24.974
2200	81.423	394.664	329.930	142.413	−1146.777	−997.274	23.678
2300	81.564	398.286	332.824	150.563	−1147.491	−990.462	22.494
2400	81.689	401.760	335.625	158.726	−1198.477	−982.551	21.385
2500	81.800	405.097	338.337	166.900	−1199.289	−973.537	20.341
2600	81.899	408.308	340.967	175.085	−1200.072	−964.492	19.377
2700	81.988	411.400	343.519	183.280	−1200.822	−955.416	18.484
2800	82.067	414.383	345.997	191.483	−1201.536	−946.314	17.654
2900	82.139	417.265	348.405	199.693	−1202.209	−937.187	16.881
3000	82.203	420.050	350.747	207.910	−1202.839	−928.038	16.159
3100	82.262	422.747	353.026	216.133	−1203.422	−918.868	15.483
3200	82.315	425.359	355.246	224.362	−1203.957	−909.680	14.849
3300	82.364	427.893	357.409	232.596	−1204.442	−900.476	14.253
3400	82.408	430.352	359.519	240.835	−1204.875	−891.259	13.693
3500	82.449	432.742	361.577	249.078	−1205.255	−882.029	13.164
3600	82.487	435.065	363.586	257.325	−1205.581	−872.789	12.664
3700	82.521	437.326	365.549	265.575	−1205.852	−863.541	12.191
3800	82.553	439.527	367.466	273.829	−1206.069	−854.286	11.743
3900	82.583	441.671	369.342	282.086	−1206.232	−845.026	11.318
4000	82.610	443.763	371.176	290.346	−1206.341	−835.763	10.914
4100	82.636	445.803	372.972	298.608	−1206.396	−826.498	10.530
4200	82.660	447.794	374.730	306.873	−1686.248	−810.208	10.076
4300	82.682	449.740	376.451	315.140	−1685.110	−789.364	9.589
4400	82.702	451.641	378.139	323.409	−1683.924	−768.546	9.124
4500	82.721	453.500	379.793	331.680	−1682.689	−747.755	8.680
4600	82.739	455.318	381.415	339.953	−1681.408	−726.993	8.255
4700	82.756	457.097	383.006	348.228	−1680.081	−706.259	7.849
4800	82.772	458.840	384.568	356.504	−1678.710	−685.554	7.460
4900	82.787	460.547	386.101	364.782	−1677.297	−664.878	7.088
5000	82.801	462.219	387.607	373.062	−1675.842	−644.231	6.730
5100	82.814	463.859	389.086	381.343	−1674.349	−623.613	6.387
5200	82.827	465.468	390.540	389.625	−1672.817	−603.025	6.057
5300	82.839	467.045	391.968	397.908	−1671.249	−582.467	5.741
5400	82.850	468.594	393.373	406.192	−1669.647	−561.939	5.436
5500	82.860	470.114	394.755	414.478	−1668.011	−541.442	5.142
5600	82.870	471.607	396.114	422.764	−1666.344	−520.973	4.859
5700	82.880	473.074	397.451	431.052	−1664.647	−500.536	4.587
5800	82.889	474.516	398.767	439.340	−1662.921	−480.128	4.324
5900	82.897	475.933	400.063	447.630	−1661.168	−459.749	4.070
6000	82.905	477.326	401.339	455.920	−1659.389	−439.401	3.825

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 133.89 \pm 4.0\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 556\ K$
$T_{fus} = 843\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1887 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 14.06 \pm 0.16\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 17.66 \pm 0.16\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Bills and Cotton[1] measured the enthalpies of several reactions at 25°C which led to the following result:

$H_3BO_3(cr) + 4(HF23\ H_2O) + KNO_3(cr) \rightarrow KBF_4(cr) + HNO_3 92\ H_2O + 3\ H_2O$.

Combining this result with the following enthalpy of formation data,

$\Delta_f H°(H_3BO_3, cr) = -261.47 \pm 0.2$ kcal·mol^{-1} [2]
$\Delta_f H°(HF23\ H_2O) = -76.75 \pm 0.1$ kcal·mol^{-1} [3]
$\Delta_f H°(KNO_3, cr) = -118.22$ kcal·mol^{-1} [4]
$\Delta_f H°(HNO_3 92\ H_2O) = -49.44$ kcal·mol^{-1} [5]
$\Delta_f H°(H_2O, l) = -68.315$ kcal·mol^{-1}

We derive, $\Delta_f H°(KBF_4, cr) = -451.6 \pm 1.2$ kcal·mol^{-1}.

Gross, Hayman and Joel[6] recently measured the following enthalpies of reaction:

$NaF(cr) + BF_3(g) \rightarrow NaBF_4(cr)$ $\Delta_r H° = -32.04 \pm 0.12$ kcal·mol^{-1}
$[KBF_4 + NaF](cr) + HF(aq) \rightarrow$ Soln A $\Delta_{sol} H° = +8.14 \pm 0.18$ kcal·mol^{-1}
$[NaBF_4 + KF](cr) + HF(aq) \rightarrow$ Soln A $\Delta_{sol} H° = -2.94 \pm 0.13$ kcal·mol^{-1}

These data combine to give $\Delta H_r = -43.13 \pm 0.22$ kcal·mol^{-1} for the reaction $KF(cr) + BF_3(g) \rightarrow KBF_4(cr)$. Combining this result with the following enthalpies of formation: $\Delta_f H°(KF, cr) = -135.9 \pm 0.1$ kcal·mol^{-1};[7] $\Delta_f H°(BF_3, g) = -271.42 \pm 0.4$ kcal·mol^{-1},[7] we derive $\Delta_f H°(KBF_4, cr) = -450.5 \pm 0.7$ kcal·mol^{-1}. An average value, $\Delta_f H°(KBF_4, cr) = -451.0 \pm 1$ kcal·mol^{-1}, of these two results is adopted here.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig.[8] $S°(298.15\ K)$ is chosen such that a 3rd law analysis of the equilibrium data for the reaction $KBF_4(cr, l) = KF(cr, l) + BF_3(g)$ reported by de Boer and van Liempt[9] gives the experimentally determined heat of reaction at 25°C.[6]

Transition Data

T_{trs} is from the high temperature studies of Dworkin and Bredig.[8] $\Delta_{trs} H°$ is calcualted from their high temperature enthalpy data.

Fusion Data

T_{fus} has been reported as 803 K by de Boer and van Liempt[9] and 843 K by Dworkin and Bredig.[8] Dworkin and Bredig's value is adopted here. $\Delta_{fus} H°$ is calculated from their high temperature enthalpy data.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is estimated by comparison with data for $LiALF_4(cr)$ reported by Hildenbrand and Theard.[10]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	114.483	133.888	133.888	0.	−1886.984	−1784.958	312.717
300	114.780	134.597	133.890	0.212	−1886.963	−1784.325	310.679
400	130.817	169.809	138.583	12.490	−1887.964	−1749.854	228.507
500	146.963	200.734	147.976	26.379	−1885.646	−1715.571	179.224
556.000	156.027	216.808	154.105	34.863		I <--> II	
556.000	140.146	242.093	154.105	48.921		TRANSITION	
600	142.097	252.840	160.956	55.130	−1868.862	−1682.950	146.514
700	146.519	275.076	175.703	69.561	−1866.685	−1652.134	123.284
800	150.938	294.930	189.387	84.434	−1864.291	−1621.644	105.882
843.000	152.838	302.881	194.975	90.965	----- II <--> LIQUID -----		
900	155.356	312.963	202.131	99.749	−1861.649	−1591.469	92.366
1000	159.779	329.560	214.054	115.505	−1858.748	−1561.602	81.570
1100	164.197	344.996	225.264	131.704	−1934.537	−1527.429	72.532
1200	168.619	359.472	235.851	148.345	−1930.056	−1490.614	64.885
1300	173.038	373.143	245.891	165.428	−1925.232	−1454.187	58.430
1400	177.456	386.129	255.448	182.953	−1920.057	−1418.145	52.912
1500	181.878	398.523	264.576	200.919	−1914.526	−1382.485	48.142

PREVIOUS: March 1965 CURRENT: December 1969

Potassium Tetraflouroborate (KBF_4) LIQUID M_r = 125.901912

$S°(298.15\ K) = [150.129]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 843\ K$

$\Delta_f H°(0\ K) = Unknown$
$\Delta_f H°(298.15\ K) = [-1869.415]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.66 \pm 0.16\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(843\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity data are calculated from the high temperature enthalpy data of Dworkin and Bredig.[1] $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} has been reported as 803 K by de Boer and van Liempt[2] and 843 K by Dworkin and Bredig.[1] Dworkin and Bredig's value is adopted here. $\Delta_{fus} H°$ is calculated from their high temperature enthalpy data.

References

[1]A. S. Dworkin and M. A. Bredig, Oak Ridge Natl. Lab., personal communication, (September 23, 1969).
[2]J. H. de Boer and J. A. M. van Liempt, Rec. Trav. Chim. **46**, 124 (1927).

Potassium Tetrafluoroborate (KBF_4) $B_1F_4K_1$(l)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	167.117	150.129	150.129	0.	−1869.415	−1772.232	310.488
300	167.117	151.163	150.133	0.309	−1869.298	−1771.630	308.468
400	167.117	199.240	156.688	17.021	−1865.865	−1739.527	227.159
500	167.117	236.531	169.066	33.733	−1860.724	−1708.547	178.491
600	167.117	267.000	182.926	50.444	−1855.979	−1678.563	146.132
700	167.117	292.761	196.824	67.156	−1851.522	−1649.350	123.076
800	167.117	315.077	210.242	83.868	−1847.289	−1620.759	105.825
843.000	167.117	323.826	215.814	91.054	----- II <--> LIQUID -----		
900	167.117	334.760	223.005	100.580	−1843.250	−1592.688	92.437
1000	167.117	352.368	235.077	117.291	−1839.393	−1565.056	81.750
1100	167.117	368.296	246.475	134.003	−1914.670	−1533.192	72.805
1200	167.117	382.837	257.241	150.715	−1910.118	−1498.713	65.237
1300	167.117	396.213	267.424	167.426	−1905.665	−1464.611	58.849
1400	167.117	408.598	277.071	184.138	−1901.303	−1430.848	53.386
1500	167.117	420.128	286.228	200.850	−1897.026	−1397.394	48.662

PREVIOUS: CURRENT: December 1969

Potassium Tetrafluoroborate (KBF_4) $B_1F_4K_1$(l)

0	to	556 K	crystal, I
556	to	843 K	crystal, II
above		843 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	114.483	133.888	133.888	0.	−1886.984	−1784.958	312.717
300	114.780	134.597	133.890	0.212	−1886.963	−1784.325	310.679
400	130.817	169.809	138.583	12.490	−1887.964	−1749.854	228.507
500	146.963	200.734	147.976	26.379	−1885.646	−1715.571	179.224
556.000	156.027	216.808	154.105	34.863	I <--> II		
556.000	140.146	242.093	154.105	48.921	TRANSITION		
600	142.097	252.840	160.956	55.130	−1868.862	−1682.950	146.514
700	146.519	275.076	175.703	69.561	−1866.685	−1652.134	123.284
800	150.938	294.930	189.387	84.434	−1864.291	−1621.644	105.882
843.000	152.838	302.881	194.975	90.965	II <--> LIQUID		
843.000	167.117	323.826	194.975	108.622	TRANSITION		
900	167.117	334.760	203.485	118.147	−1843.251	−1592.688	92.437
1000	167.117	352.368	217.509	134.859	−1839.394	−1565.057	81.750
1100	167.117	368.296	230.504	151.571	−1914.671	−1533.192	72.805
1200	167.117	382.837	242.601	168.283	−1910.118	−1498.714	65.237
1300	167.117	396.213	253.910	184.994	−1905.665	−1464.612	58.849
1400	167.117	408.598	264.522	201.706	−1901.304	−1430.849	53.386
1500	167.117	420.128	274.516	218.418	−1897.027	−1397.394	48.662

PREVIOUS: CURRENT: December 1969

$S(298.15\ K) = [315.4 \pm 3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [1543.9 \pm 5]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1552.3 \pm 5]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[900](1)	[1000](1)	[300](2)
[450](1)	[300](1)	[500](2)
[350](1)	[250](1)	[1400](2)

Ground State Quantum Weight: [1] α = [3]
Point Group: $[C_{3v}]$
Bond Distances: B-F = 1.380 Å; K-F = 2.752 Å; B-K = [2.863] Å
Bond Angles: F-B-F = 109°28'; F_{ax}-B-K = [180]°
Product of Moments of Inertia: $I_A I_B I_C = [4.547923 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H$(g) is calculated from Δ_fH(cr) and the estimated enthalpy of sublimation.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with data for BF_4^-, BF_3, KF, and K_2F_2. The infrared and Raman spectra of BF_4^- in various phases have been reported by.[1-4] The molecular structure is assumed to be the same as for $LiAlF_4$ as discussed by Porter and Zeller.[5] The B–F and K–F bond lengths and F–B–F bond angle are average values of the crystallographic data recently reported by Clark and Lynton.[6] The B–K bond length is calcualted from the above structural data according to the assumed molecular model. The principal moments of inertia are $I_A = I_B = 16.0214 \times 10^{-39}$, and $I_B = I_C = 53.2791 \times 10^{-39}\ g \cdot cm^2$.

References

[1]G. L. Cote and H. W. Thompson, Proc. Royal Soc. (London), **210A**, 217 (1951).
[2]J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, J. Amer. Chem. Soc. **77**, 266 (1955).
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[4]J. A. A. Ketelaar and R. L. Fulton, Z. Elektrochem. **64**, 641 (1960).
[5]R. F. Porter and E. E. Zeller, J. Chem. Phys. **33**, 858 (1960).
[6]M. J. R. Clark and H. Lynton, Can. J. Chem. **47**, 2579 (1969).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.598	−1543.916	−1543.916	INFINITE
100	45.326	242.588	382.561	−13.997	−1547.886	−1534.479	801.530
200	72.713	283.084	323.060	−7.995	−1550.669	−1519.843	396.942
250	81.920	300.343	316.820	−4.119	−1551.543	−1512.031	315.922
298.15	88.941	315.394	315.394	0.	−1552.264	−1504.354	263.557
300	89.184	315.944	315.395	0.165	−1552.291	−1504.057	261.880
350	95.129	330.153	316.504	4.777	−1555.374	−1495.865	223.246
400	100.093	343.189	319.036	9.661	−1556.073	−1487.315	194.223
450	104.277	355.227	322.397	14.774	−1556.687	−1478.683	171.641
500	107.817	366.402	326.245	20.078	−1557.226	−1469.986	153.568
600	113.376	386.578	334.657	31.153	−1558.120	−1452.450	126.447
700	117.425	404.375	343.370	42.703	−1558.823	−1434.781	107.065
800	120.418	420.260	352.007	54.603	−1559.403	−1417.020	92.522
900	122.668	434.579	360.399	66.762	−1559.916	−1399.191	81.207
1000	124.391	447.597	368.478	79.119	−1560.414	−1381.306	72.152
1100	125.731	459.518	376.220	91.628	−1639.894	−1358.760	64.522
1200	126.792	470.505	383.625	104.256	−1639.425	−1333.223	58.034
1300	127.643	480.689	390.705	116.979	−1638.961	−1307.725	52.545
1400	128.334	490.174	397.475	129.779	−1638.511	−1282.262	47.842
1500	128.903	499.049	403.954	142.642	−1638.083	−1256.831	43.767
1600	129.376	507.383	410.160	155.557	−1637.683	−1231.427	40.202
1700	129.774	515.239	416.113	168.515	−1637.314	−1206.048	37.057
1800	130.111	522.666	421.828	181.509	−1636.979	−1180.689	34.263
1900	130.399	529.709	427.322	194.535	−1636.677	−1155.348	31.763
2000	130.646	536.404	432.610	207.588	−1636.408	−1130.022	29.513
2100	130.861	542.784	437.706	220.663	−1636.171	−1104.709	27.478
2200	131.048	548.876	442.622	233.759	−1635.962	−1079.406	25.628
2300	131.212	554.705	447.369	246.872	−1635.777	−1054.112	23.940
2400	131.357	560.292	451.959	260.001	−1685.874	−1027.757	22.369
2500	131.485	565.657	456.400	273.143	−1685.808	−1000.337	20.901
2600	131.600	570.816	460.702	286.298	−1685.723	−972.920	19.546
2700	131.702	575.785	464.873	299.463	−1685.618	−945.506	18.292
2800	131.793	580.576	468.920	312.638	−1685.491	−918.097	17.127
2900	131.876	585.203	472.850	325.821	−1685.339	−890.692	16.043
3000	131.950	589.675	476.671	339.012	−1685.162	−863.294	15.031
3100	132.018	594.002	480.386	352.211	−1684.959	−835.902	14.085
3200	132.079	598.195	484.002	365.416	−1684.732	−808.516	13.198
3300	132.135	602.260	487.525	378.626	−1684.472	−781.139	12.364
3400	132.186	606.205	490.958	391.843	−1684.195	−753.769	11.580
3500	132.233	610.038	494.305	405.064	−1683.895	−726.408	10.841
3600	132.277	613.764	497.572	418.289	−1683.580	−699.056	10.143
3700	132.316	617.388	500.762	431.519	−1683.251	−671.712	9.483
3800	132.353	620.917	503.877	444.752	−1682.913	−644.379	8.858
3900	132.387	624.356	506.923	457.989	−1682.570	−617.053	8.264
4000	132.419	627.708	509.901	471.230	−1682.221	−589.737	7.701
4100	132.448	630.978	512.814	484.473	−1681.879	−562.430	7.165
4200	132.475	634.170	515.666	497.719	−2161.400	−528.105	6.568
4300	132.500	637.288	518.458	510.968	−2160.002	−489.235	5.943
4400	132.524	640.334	521.193	524.219	−2158.351	−450.422	5.347
4500	132.546	643.312	523.874	537.473	−2156.940	−411.621	4.778
4600	132.567	646.226	526.502	550.728	−2155.552	−372.852	4.234
4700	132.586	649.077	529.080	563.986	−2154.174	−334.114	3.713
4800	132.604	651.869	531.609	577.246	−2152.719	−295.418	3.215
4900	132.622	654.603	534.091	590.507	−2151.402	−256.738	2.737
5000	132.638	657.283	536.529	603.770	−2150.122	−218.084	2.278
5100	132.653	659.909	538.922	617.034	−2148.883	−179.456	1.838
5200	132.667	662.485	541.274	630.300	−2147.687	−140.851	1.415
5300	132.681	665.013	543.585	643.568	−2146.536	−102.269	1.008
5400	132.693	667.493	545.856	656.837	−2145.433	−63.709	0.616
5500	132.706	669.928	548.090	670.106	−2144.378	−25.168	0.239
5600	132.717	672.319	550.287	683.378	−2143.373	13.354	−0.125
5700	132.728	674.668	552.449	696.650	−2142.074	51.810	−0.475
5800	132.738	676.976	554.576	709.923	−2141.126	90.291	−0.813
5900	132.748	679.246	556.670	723.197	−2140.225	128.757	−1.140
6000	132.757	681.477	558.731	736.473	−2139.370	167.206	−1.456

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K)$ = [171.85] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 439.5 ± 8.4 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 442.7 ± 8.4 $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

ω_e = [2368] cm^{-1} $\omega_e x_e$ = [49] cm^{-1} σ = 1
B_e = 12.036 cm^{-1} α_e = 0.413 cm^{-1} r_e = 1.2325 Å

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from $D_0°(BH) \approx 3.39 \pm 0.04$ e.v. reported by Hurley.[1] Hurley stated "by combining an analysis of the spectroscopic data with theoretical calculations, we obtain a greatly improved estimate of $D_0°(BH)$". This value and the other $D_0°(BH)$ values which are tabulated below are based on the same spectroscopic data but differ due to different methods of analysis.

$D_0°(BH)$, eV	Method	Source
3.0 ± 0.4	Birge Sponer extrapolations	(2)
3.6	Observed predissociation by rotation in BH, A'Π and deduced $D_0°(BH)$	(3)
<3.51	Pre dissociation limit. This is only an upper limit due to a maximum in the potential curve of the A'Π state	(4)
3.38 ± 0.04	The potential energy curve of the A'Π state was determined and was found to have a maximum and a minimum in agreement with Herzberg and Mundie	The selected $D_0°(BH)$ value as reported by Hurley (1).

Heat Capacity and Entropy

The molecular constants from Herzberg[4] were adjusted for the natural abundance of ^{10}B and ^{11}B. Because the constants ω_e and $\omega_e x_e$ could not be determined directly from the spectrum, Almy and Horsfall[3] obtained estimates for the ground state $X\ ^1\Sigma^+$ from the rotational constants for this state and the relations $D_e = 4B_e^3/\omega_e^2$ and $\omega_e x_e/\omega_e = 0.6\ \alpha_e/B_e$.

References

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[4]G. Herzberg and L. G. Mundle, J. Chem. Phys. **8**, 263 (1940) and G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Co., Inc., York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.639	439.476	439.476	INFINITE
90	29.126	140.014	197.766	−5.775	440.816	431.882	−225.592
200	29.143	160.207	174.516	−2.862	442.050	422.433	−110.328
250	29.156	166.712	172.329	−1.404	442.438	417.481	−87.228
298.15	29.181	171.849	171.849	0.	442.667	412.651	−72.295
300	29.182	172.029	171.849	0.054	442.673	412.465	−71.816
350	29.240	176.532	172.205	1.514	442.782	407.420	−60.804
400	29.347	180.442	172.995	2.979	442.783	402.367	−52.544
450	29.514	183.908	174.019	4.450	442.696	397.319	−46.120
500	29.741	187.029	175.166	5.931	442.543	392.285	−40.982
600	30.340	192.502	177.612	8.934	442.100	382.272	−33.280
700	31.052	197.231	180.084	12.003	441.545	372.344	−27.785
800	31.792	201.426	182.495	15.145	440.928	362.500	−23.669
900	32.503	205.212	184.812	18.360	440.274	352.735	−20.472
1000	33.160	208.671	187.027	21.644	439.594	343.045	−17.919
1100	33.752	211.860	189.142	24.990	438.890	333.424	−15.833
1200	34.280	214.820	191.160	28.392	438.164	323.868	−14.098
1300	34.748	217.583	193.087	31.844	437.414	314.373	−12.632
1400	35.162	220.173	194.930	35.340	436.639	304.938	−11.377
1500	35.530	222.612	196.695	38.875	435.835	295.558	−10.292
1600	35.859	224.916	198.388	42.445	435.003	286.233	−9.345
1700	36.152	227.099	200.013	46.046	434.141	276.961	−8.510
1800	36.417	229.173	201.576	49.674	433.248	267.741	−7.770
1900	36.657	231.148	203.081	53.328	432.324	258.571	−7.109
2000	36.875	233.034	204.531	57.005	431.368	249.451	−6.515
2100	37.075	234.838	205.932	60.703	430.381	240.379	−5.979
2200	37.259	236.567	207.285	64.419	429.361	231.356	−5.493
2300	37.429	238.227	208.595	68.154	428.309	222.379	−5.050
2400	37.587	239.823	209.863	71.905	376.966	214.517	−4.669
2500	37.736	241.361	211.092	75.671	375.772	207.773	−4.341
2600	37.875	242.844	212.285	79.452	374.579	201.077	−4.040
2700	38.007	244.275	213.444	83.246	373.386	194.426	−3.761
2800	38.132	245.660	214.570	87.053	372.193	187.820	−3.504
2900	38.250	247.000	215.665	90.872	371.001	181.256	−3.265
3000	38.364	248.299	216.731	94.703	369.808	174.733	−3.042
3100	38.472	249.559	217.770	98.544	368.615	168.251	−2.835
3200	38.577	250.782	218.783	102.397	367.421	161.806	−2.641
3300	38.677	251.970	219.770	106.260	366.227	155.399	−2.460
3400	38.775	253.126	220.734	110.132	365.033	149.028	−2.290
3500	38.869	254.252	221.676	114.015	363.837	142.693	−2.130
3600	38.961	255.348	222.596	117.906	362.641	136.391	−1.979
3700	39.050	256.417	223.496	121.807	361.445	130.123	−1.837
3800	39.137	257.459	224.376	125.716	360.247	123.887	−1.703
3900	39.222	258.477	225.237	129.634	359.048	117.683	−1.576
4000	39.305	259.471	226.081	133.560	357.848	111.509	−1.456
4100	39.386	260.443	226.907	137.495	356.648	105.366	−1.342
4200	39.467	261.393	227.717	141.437	−124.404	106.276	−1.322
4300	39.545	262.322	228.511	145.388	−124.520	111.769	−1.358
4400	39.623	263.232	229.290	149.346	−124.639	117.266	−1.392
4500	39.699	264.123	230.054	153.313	−124.761	122.765	−1.425
4600	39.774	264.997	230.804	157.286	−124.886	128.267	−1.457
4700	39.848	265.853	231.541	161.267	−125.015	133.771	−1.487
4800	39.922	266.693	232.264	165.256	−125.148	139.279	−1.516
4900	39.994	267.517	232.975	169.252	−125.285	144.789	−1.543
5000	40.066	268.325	233.674	173.255	−125.425	150.303	−1.570
5100	40.137	269.119	234.362	177.265	−125.570	155.818	−1.596
5200	40.207	269.900	235.038	181.282	−125.719	161.337	−1.621
5300	40.277	270.666	235.703	185.306	−125.872	166.859	−1.644
5400	40.346	271.420	236.357	189.337	−126.030	172.384	−1.667
5500	40.415	272.161	237.001	193.375	−126.192	177.911	−1.690
5600	40.483	272.889	237.636	197.420	−126.358	183.442	−1.711
5700	40.551	273.606	238.261	201.472	−126.529	188.976	−1.732
5800	40.618	274.312	238.876	205.530	−126.704	194.513	−1.752
5900	40.685	275.007	239.483	209.596	−126.884	200.052	−1.771
6000	40.752	275.692	240.080	213.667	−127.068	205.595	−1.790

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [202.6 \pm 0.5]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -197.7 \pm 3.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -198.3 \pm 3.0 \cdot kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	[35000]	[6]
[30000]	[3]	[40000]	[3]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[2802](1)
757 (2)
1822 (1)

Ground State Configuration: $[^1\Sigma^+]$ $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: H–B = [1.17] Å; H–O = [1.19] Å
Bond Angle: H–B–O = [180°]
Rotational Constant: B_O = [1.341144] cm^{-1}

Enthalpy of Formation

We calculate $\Delta_f H°$ from a selected value, $\Delta_f H°$(DBO, g) = −47.95 kcal·mol^{-1}, by combining this value with zero-point energies and relative enthalpies, $H°(298.15\ K)-E_0°$, for HBO, D_2, DBO and H_2. All ancillary data are from JANAF[1] unless otherwise indicated. The zero-point energies are estimated as one-half the sum of the vibrational frequencies. The vibrational frequencies for DBO are taken from the matrix-isolation results of Lory and Porter.[2] We assume that DBO and HBO have similar structures, and we calculate the relative enthalpy for DBO as $H°(298.15\ K)-E_0° = -2.27$ kcal·mol^{-1}. Data for D_2 are taken from NBS.[3]

The selected value of $\Delta_f H°$ for DBO is obtained from the results of a mass-spectrometric study[4,5] of the reaction of D (g) with B_2O_3(l). The thermal results which were initially reported[4] for a study of the reactions (A) $D_2(g) + B_2O_3(l) = DBO(g) + DOBO(g)$ and (B) $D_2O(g) + B_2O_3(l) = 2DOBO(g)$ are unreliable due to erroneous equilibrium constants. 2nd-law enthalpies for these two reactions have been reported in revised form in a later publication.[5] Apparently, no attempt was made in this study to perform calibration experiments which would have allowed the ion intensity data to be converted to absolute partial pressures; thus, precluding a 3rd law analysis. We combine their 2nd law values[5] for $\Delta_r H$ (1296 K) for reactions (A) and (B) to give $\Delta_r H(1296\ K) = 135 \pm 4$ kcal·mol^{-1} for the process $2D_2(g) + B_2O_3(l) = 2DBO(g) + D_2O(g)$. Corrected to 298.15 K this value is 144.1 kcal·mol^{-1} which leads to $\Delta_f H°$(DBO,g, 298.15 K) = −47.95 ± 2.3 kcal·mol^{-1} with $\Delta_f H°(D_2O, g, 298.15\ K) = -59.561 \pm 0.02$ kcal·mol^{-1}[13] and $\Delta_f H°(B_2O_3, l, 298.15\ K) = 299.56 \pm 0.6$ kcal·mol^{-1}.[1]

Comparison of values for the stretching force constants in HBO, BH_3,[6] BO, and B_2O_2[1] suggests a similarity in the bonds of these molecules. Using $D_0°(298.15\ K)$ (H–B) = $D°(298.15\ K)$ (BH_3) = 87.9 kcal·mol^{-1} and $D_0°(298.15\ K)$ (B=O) = $D_0°(298.15\ K)$ (BO) + $D_0°(298.15\ K)$ (B_2O_2) /2 = 202 kcal·mol^{-1},[1] we calculate an enthalpy of atomization for HBO of 298.9 kcal·mol. This corresponds to $\Delta_f H°$(HBO, g, 298.15 K) = −45.4 kcal·mol^{-1} which lends support to the experimental measurements at Farber *et al.*[4,5] Pervious JANAF estimates[7] of $\Delta_f H°$ via bond energy calculations led to results which were too positive due to the use of an inaccurate value (168 kcal·mol^{-1}) for $D_0°$ (B=O). A recent ab-initio LCAO-MO-SCF investigation[8] of HBO yields $\Delta_{at}H$ = 232.2 kcal·mol^{-1}; however, this value does not include a contribution from correlation effects[9,16] and therefore is too low.

Heat Capacity and Entropy

The B=O stretching $(\upsilon)_3$ and bending $(\upsilon)_2$ frequencies for the isotopes $H^{11}BO$ and $H^{10}BO$ have been measured in a low-temperature argon matrix.[2] These values are corrected for the natural isotopic abundances of boron. The H–B stretching frequency $(\upsilon)_1$ is calculated from an estimated force constant by the valence force method.[10] The stretching force constant K_1 is estimated from the ratio $K_1/K_D/l_1l_2$ = 17.47 which is the value we calculate for DBO from the measured frequencies of Lory and Porter.[2] These workers[2] used a slightly different value for K_1 and obtained a value for υ_1 which is roughly 50 cm^{-1} higher than our result. We believe our estimate is probably more nearly correct, since it agrees much better with the H–B stretching frequency (2808 cm^{-1}) observed for BH_3.[6] MO calculations show that the pattern of valence orbitals for HBO is similar to that in HCN[8] and HCP.[11,16] The ordering is substantiated by the photoelectron spectra[12] which have been observed for HCN and HCP. This suggests that the ground and excited electronic states for these isoelectronic molecules are quite similar. We assume that the ground state configuration is $^1\Sigma^+$ by analogy with those for HCN and HCP.[1] We also include three triplet levels which are estimated from those observed for HCP[1] and predicted for HCN.[13]

Continued on page 317

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.156	−197.688	−197.688	INFINITE
100	29.137	168.766	231.276	−6.251	−197.759	−200.903	104.941
200	31.249	189.398	205.712	−3.263	−197.906	−204.013	53.283
250	33.279	196.585	203.187	−1.650	−198.092	−205.519	42.941
298.15	35.260	202.617	202.617	0.	−198.322	−206.929	36.253
300	35.334	202.836	202.618	0.065	−198.331	−206.983	36.039
350	37.224	208.427	203.055	1.880	−198.606	−208.403	31.102
400	38.923	213.510	204.049	3.785	−198.913	−209.782	27.395
450	40.455	218.185	205.363	5.770	−199.244	−211.121	24.506
500	41.853	222.521	206.865	7.828	−199.591	−212.422	22.192
600	44.343	230.377	210.142	12.141	−200.304	−214.921	18.711
700	46.511	237.379	213.542	16.686	−201.010	−217.302	16.215
800	48.408	243.716	216.924	21.434	−201.690	−219.582	14.337
900	50.061	249.516	220.228	26.359	−202.336	−221.779	12.872
1000	51.495	254.866	223.427	31.439	−202.952	−223.907	11.696
1100	52.734	259.834	226.514	36.652	−203.543	−225.973	10.731
1200	53.802	264.469	229.486	41.980	−204.117	−227.987	9.924
1300	54.724	268.813	232.346	47.407	−204.683	−229.953	9.240
1400	55.520	272.898	235.098	52.920	−205.249	−231.876	8.651
1500	56.208	276.753	237.748	58.508	−205.820	−233.758	8.140
1600	56.806	280.400	240.300	64.159	−206.404	−235.601	7.692
1700	57.327	283.860	242.762	69.866	−207.006	−237.408	7.295
1800	57.783	287.150	245.137	75.622	−207.629	−239.178	6.941
1900	58.182	290.285	247.431	81.421	−208.278	−240.914	6.623
2000	58.534	293.278	249.650	87.257	−208.956	−242.614	6.336
2100	58.846	296.142	251.796	93.126	−209.665	−244.279	6.076
2200	59.122	298.886	253.874	99.025	−210.407	−245.910	5.839
2300	59.369	301.519	255.889	104.950	−211.183	−247.507	5.621
2400	59.589	304.051	257.843	110.898	−262.256	−248.000	5.398
2500	59.786	306.487	259.741	116.867	−263.184	−247.387	5.169
2600	59.964	308.836	261.584	122.855	−264.119	−246.737	4.957
2700	60.125	311.102	263.376	128.859	−265.060	−246.050	4.760
2800	60.271	313.291	265.120	134.879	−266.008	−245.329	4.577
2900	60.404	315.409	266.818	140.913	−266.965	−244.574	4.405
3000	60.525	317.458	268.472	146.960	−267.931	−243.785	4.245
3100	60.636	319.445	270.084	153.018	−268.906	−242.964	4.094
3200	60.739	321.372	271.657	159.087	−269.890	−242.112	3.952
3300	60.835	323.242	273.192	165.165	−270.883	−241.228	3.818
3400	60.924	325.060	274.691	171.253	−271.886	−240.314	3.692
3500	61.008	326.827	276.155	177.350	−272.899	−239.371	3.572
3600	61.088	328.547	277.587	183.455	−273.921	−238.399	3.459
3700	61.165	330.221	278.987	189.567	−274.953	−237.398	3.351
3800	61.239	331.854	280.357	195.688	−275.994	−236.369	3.249
3900	61.312	333.445	281.698	201.815	−277.044	−235.312	3.152
4000	61.385	334.998	283.011	207.950	−278.103	−234.229	3.059
4100	61.457	336.515	284.297	214.092	−279.171	−233.119	2.970
4200	61.531	337.997	285.558	220.242	−760.096	−224.959	2.798
4300	61.606	339.446	286.795	226.398	−760.092	−212.217	2.578
4400	61.684	340.863	288.008	232.563	−760.098	−199.476	2.368
4500	61.766	342.250	289.198	238.735	−760.113	−186.735	2.168
4600	61.851	343.608	290.366	244.916	−760.136	−173.993	1.976
4700	61.941	344.940	291.513	251.106	−760.168	−161.250	1.792
4800	62.036	346.245	292.640	257.305	−760.208	−148.507	1.616
4900	62.138	347.525	293.747	263.513	−760.256	−135.762	1.447
5000	62.246	348.781	294.835	269.732	−760.311	−123.017	1.285
5100	62.361	350.015	295.905	275.963	−760.372	−110.270	1.129
5200	62.483	351.227	296.957	282.205	−760.441	−97.523	0.980
5300	62.614	352.419	297.992	288.460	−760.515	−84.773	0.835
5400	62.753	353.590	299.011	294.728	−760.595	−72.023	0.697
5500	62.901	354.743	300.014	301.010	−760.679	−59.271	0.563
5600	63.058	355.878	301.001	307.308	−760.768	−46.517	0.434
5700	63.225	356.995	301.974	313.622	−760.861	−33.762	0.309
5800	63.401	358.096	302.932	319.954	−760.957	−21.005	0.189
5900	63.587	359.182	303.876	326.303	−761.056	−8.247	0.073
6000	63.783	360.252	304.807	332.671	−761.158	4.514	−0.039

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [214.57 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [1182.0 \pm 12]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [1187.5 \pm 12]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ, cm^{-1}	g_i
$X^2\Pi$	0	[4]
$A^2\Sigma^+$	[6000]	[2]
$B^2\Sigma^+$	[40000]	[2]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[2559](1)
[801](2)
[1617](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$

Bond Distances: H–B = [1.19] Å; B–O = [1.25] Å

Bond Angle: H–B–O = [180]°

Rotational Constant: B_0 = [1.228629] cm^{-1}

Enthalpy of Formation

The HBO⁺ ion has been detected mass spectrometrically by Sholette and Porter[1] *and Farber and Frisch.*[2] However, no appearance potential data have been reported for the ion. Kroto *et al.*[3] recently attempted to measure the photelectron spectrum of HBO by passing water vapor over heated boron. The spectrum showed no bands which could be definitely assigned to HBO monomer. Unfortunately, the region of their spectrum (~14–15 eV) where the first photoelectron band of HBO would be expected to lie shows a broad band which also appeared in the spectrum of HBS above 1150°C. Kroto *et al.*[4] have assigned this band to diborane. We believe the HBO band may well be hidden under this broad band.

We employ Koopmans' theorem[4] to obtain the ionization potential of HBO as 14.3 eV from the one electron orbital energies reported by Thomson and Wishart.[5] A comparison of Koopmans' theorem IP's for the related species HBS,[6] HCN,[5] and HCP[7] with experimental values[8,9] shows that the theoretical calculations correctly predict these ionization potentials to within about ± 0.4 eV. We adopt $\Delta_f H° = 329.7_6 \pm 9$ $kcal \cdot mol^{-1}$ for the ionization process $HBO(g) + e^- = HBO^+(g) + 2e^-$ at 0 K, and we obtain $\Delta_f H°(HBO^+, g, 0\ K) = 282.6 \pm 12.0\ kcal \cdot mol^{-1}$ when the former value is combined with $\Delta_f H°(HBO, g, 0\ K) = -47.2 \pm 3.0\ kcal \cdot mol^{-1}$[18]. $\Delta_f H°(298.15\ K)$ is 283.8 ± 12.0 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Extensive ab initio MO calculations[5] reported for HBO show that the highest occupied orbital is of Π–symmetry and is localized mainly on the oxygen atom. The Walsh diagram[10] for HAB molecules predicts that this orbital is bonding. We would expect therefore that the ion is less strongly bound than the parent molecule. For HCN which has the same orbital ordering as HBO,[5] ionization[11] occurs with a 2.2% increase in the H–C bond length and a 4.7% increase in the C≡N bond length. We assume a similar increase in the bond lengths of HBO[8] upon loss of the bonding electron. A linear configuration is assumed by analogy with that for HBS^+.[8] This assumption is supported by predictions from the Walsh diagram.[10]

All vibrational frequencies are calculated from estimated force constants by a valence force method.[12] The force constants are estimated from those for HBO[8] by comparison with the changes in the changes in the force constants for HCN[8] produced on ionization.[9] The electronic states and levels are estimated from those observed for isoelectronic ions HBS^+, and HCP^+.[9] We estimate the uncertainties in our calculated frequencies as ±50 cm^{-1} which introduces an error of only about ±0.1 $cal \cdot K^{-1} \cdot mol^{-1}$ in the value of $S°(298.15\ K)$. The uncertainty in the *electronic levels contribute the majority of the error in the entropy.* We predict that the energy separation of the $^2\Pi$–$^2\Sigma$ states is small. Thus, it is possible that the ground state is $^2\Sigma$ as is the case for the isoelectronic ions CO^+ and N_2^+.[13] If the ground state is $^2\Sigma$, then our entropies should be decreased by roughly 1.5 gibbs/mol at all temperatures above 298.15 K. The enthalpy is much more certain than the entropy. Below 2000 K the uncertainty in our relative enthalpies probably does not exceed a few calories. The uncertainty increases at higher temperatures and is about 1.0 $kcal \cdot mol^{-1}$ at 4000 K. All excited states are expected to be linear as observed for HBS^+.[3]

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Continued on page 317

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.090	1182.047		
90	29.122	181.019	242.861	−6.184			
200	30.857	201.543	217.612	−3.214			
250	32.755	208.626	215.126	−1.625			
298.15	34.744	214.565	214.565	0.	1187.545	1169.120	−204.825
300	34.821	214.780	214.566	0.064	1187.573	1169.006	−203.542
350	36.828	220.300	214.997	1.856	1188.314	1165.852	−173.994
400	38.701	225.342	215.979	3.745	1189.031	1162.594	−151.819
450	40.425	230.001	217.282	5.724	1189.732	1159.248	−134.562
500	42.011	234.343	218.773	7.785	1190.428	1155.823	−120.748
600	44.817	242.258	222.041	12.130	1191.826	1148.771	−90.009
700	47.203	249.351	225.444	16.734	1193.258	1141.483	−85.178
800	49.235	255.790	228.841	21.559	1194.733	1133.986	−74.042
900	50.965	261.692	232.168	26.571	1196.252	1126.302	−65.369
1000	52.442	267.140	235.396	31.744	1197.808	1118.447	−58.422
1100	53.711	272.199	238.515	37.053	1199.392	1110.434	−52.730
1200	54.808	276.921	241.520	42.480	1200.995	1102.276	−47.981
1300	55.765	281.346	244.416	48.010	1202.610	1093.984	−43.957
1400	56.606	285.510	247.204	53.629	1204.230	1085.568	−40.503
1500	57.350	289.442	249.890	59.328	1205.848	1077.035	−37.506
1600	58.012	293.164	252.479	65.096	1207.460	1068.395	−34.880
1700	58.605	296.699	254.977	70.928	1209.061	1059.655	−32.559
1800	59.138	300.065	257.389	76.816	1210.648	1050.820	−30.494
1900	59.618	303.275	259.720	82.754	1212.217	1041.898	−28.644
2000	60.050	306.344	261.975	88.738	1213.765	1032.894	−26.976
2100	60.441	309.284	264.159	94.762	1215.291	1023.813	−25.466
2200	60.794	312.104	266.274	100.824	1216.791	1014.660	−24.091
2300	61.112	314.813	268.326	106.920	1218.263	1005.439	−22.834
2400	61.400	317.420	270.318	113.046	1169.447	997.223	−21.704
2500	61.659	319.932	272.253	119.199	1170.782	990.020	−20.685
2600	61.893	322.355	274.133	125.377	1172.116	982.763	−19.744
2700	62.103	324.695	275.963	131.577	1173.449	975.455	−18.871
2800	62.292	326.957	277.744	137.797	1174.779	968.097	−18.060
2900	62.462	329.146	279.479	144.035	1176.105	960.692	−17.304
3000	62.614	331.266	281.170	150.289	1177.425	953.242	−16.597
3100	62.749	333.321	282.819	156.557	1178.739	945.747	−15.936
3200	62.870	335.316	284.429	162.838	1180.046	938.210	−15.315
3300	62.978	337.252	286.000	169.130	1181.345	930.633	−14.731
3400	63.074	339.133	287.535	175.433	1182.635	923.016	−14.180
3500	63.159	340.963	289.036	181.745	1183.916	915.362	−13.661
3600	63.233	342.743	290.503	188.065	1185.187	907.671	−13.170
3700	63.299	344.477	291.939	194.391	1186.448	899.944	−12.705
3800	63.356	346.166	293.344	200.724	1187.698	892.185	−12.264
3900	63.407	347.812	294.719	207.062	1188.938	884.392	−11.845
4000	63.450	349.418	296.067	213.405	1190.165	876.567	−11.447
4100	63.487	350.985	297.387	219.752	1191.381	868.712	−11.068
4200	63.519	352.515	298.681	226.102	712.735	867.852	−10.793
4300	63.546	354.010	299.951	232.456	715.014	871.518	−10.587
4400	63.569	355.472	301.196	238.812	717.278	875.131	−10.389
4500	63.588	356.900	302.418	245.169	719.527	878.693	−10.200
4600	63.603	358.298	303.618	251.529	721.761	882.206	−10.018
4700	63.615	359.666	304.796	257.890	723.979	885.670	−9.843
4800	63.624	361.005	305.953	264.252	726.181	889.087	−9.675
4900	63.630	362.317	307.090	270.614	728.366	892.458	−9.514
5000	63.635	363.603	308.207	276.978	730.534	895.785	−9.358
5100	63.637	364.863	309.306	283.341	732.684	899.069	−9.208
5200	63.638	366.099	310.386	289.705	734.816	902.310	−9.064
5300	63.637	367.311	311.449	296.069	736.929	905.511	−8.924
5400	63.634	368.500	312.495	302.432	739.023	908.672	−8.790
5500	63.631	369.668	313.523	308.796	741.098	911.794	−8.659
5600	63.627	370.815	314.536	315.158	743.153	914.880	−8.534
5700	63.621	371.941	315.534	321.521	745.187	917.928	−8.412
5800	63.615	373.047	316.516	327.883	747.200	920.942	−8.294
5900	63.609	374.135	317.483	334.244	749.191	923.919	−8.180
6000	63.602	375.204	318.436	340.604	751.160	926.864	−8.069

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [227.1 \pm 2.0]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°\ (0\ K) = [-238.5 \pm 24]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-244.5 \pm 24]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ, cm^{-1}	g_i
0	[2]
[10000]	[2]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[2000] (1)
[1000] (1)
[1500] (1)

Ground State Quantum Weight: [2] $\sigma = 1$

Point Group: C_s

Bond Distances: H–B = [1.25] Å; B–O = [1.37] Å

Bond Angle: H–B–O = 123°

Product of Moments of Inertia: $I_A I_B I_C = [9.09027 \times 10^{-118}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The identification of the HBO^- radical has been made from observations of its electron spin resonance spectra which was measured[1,2] in γ–irradiated polycrystalline potassium borohydride. This assignment is confirmed by the fact that hyperfine coupling constants calculated by INDO[3] and UHF[4,5] methods are in reasonable agreement with the spectral data.[2] No experimental measurement of the electron affinity (EA) has been reported: however, recent MO calculations[6] predict that the value is small. We note that these calculations predict incorrectly the relative stabilities of HBO and HBO^- and therefore are of no use in the establishment of the absolute value of EA. This inversion in the predicted stabilities of the radical and parent molecule most likely arises from the neglect of correlation effects.

We estimate $\Delta_f H°$ from a consideration of bond–energy schemes. For the dissociative process $HBO^-(g) = H(g) + B(g) + O^-(g)$, we assume $\Delta_{at}H°(HBO,g,\ 0\ K) = 289.4\ kcal \cdot mol^{-1}$.[7] This atomization energy gives $\Delta_f H°(HBO^-,\ g,\ 0\ K) \approx -81.0\ kcal \cdot mol^{-1}$ which we believe is an upper limit since the unpaired electron in HBO^- is antibonding[8] and consequently, one would expect $\Delta_{at}H°(HBO^-) < \Delta_{at}H°(HBO)$. A lower limit of $\Delta_f H°$ can be obtained from a consideration of the H–B bond dissociation energy. It is very unlikely that $D_0°(H–BO^-) < D_0°(H–CO)$ which is equal to 14.1 $kcal \cdot mol^{-1}$. Using this value for $D_0°(H–BO^-)$, we obtain $\Delta_f H°(HBO^-,\ g,\ 0\ K) = -33\ kcal \cdot mol^{-1}$ with $\Delta_f H°(H,g,\ 0\ K) = 52.103\ kcal \cdot mol^{-1}$ [7] and $\Delta_f H°(BO^-,\ g,\ 0\ K) = -71.0\ kcal \cdot mol^{-1}$.[9] We adopt an average ($-57 \pm 24\ kcal \cdot mol^{-1}$) of the upper and lower limit values. Our adopted $\Delta_f H°$ value corresponds to an EA(HBO^-) of 0.42 ± 1.0 eV.

Heat Capacity and Entropy

The bond lengths are those reported by Thomson[3] who performed an INDO calculation in which the bond lengths were determined by minimization of the total energy. The esr spectrum[1,2] of HBO^- is consistent with a bent structure. Catton *et al.*[2] obtained bond angles of 121° and 125° from the p:s ratios deduced from estimated and observed anisotropic components of the hyperfine tensors. A similar calculation[2] for HCO and HCN^- led to bond angles which agreed with independent values to within ±5°. We adopt a bond angle of 123 ± 5°. MO calculations[3] give an angle of 129°. However, the energy minimization procedure with the INDO method generally over–estimates the angle as evidenced by the results for HCO[10] and HCN.[2,3] The principal moments of inertia are: $I_A = 0.1484 \times 10^{-39}$, $I_B = 2.4017 \times 10^{-39}$, and $I_C = 2.5501 \times 10^{-39}\ g \cdot cm^2$.

The electronic levels and quantum weights are taken from those for HCO,[7] which is isoelectronic with HBO^-. The vibrational frequencies arae estimated by comparison with the corresponding values for HBO, HBO^+, HCO and HCO^+.[7]

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[7]JANAF Thermochemical Tables: HBO(g) and HBO ($^+$g), 12–31–75; H(g), 6–30–74; B(g), 12–31–64; O ($^-$g), 6–30–65; HCO(g) and HCO (g),$^+$12–31–70.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.027	−238.827		
100	33.259	190.280	257.292	−6.701			
200	33.602	213.386	230.216	−3.366			
250	34.257	220.947	227.632	−1.671			
298.15	35.199	227.058	227.058	0.	−244.471	−254.111	44.519
300	35.240	227.276	227.058	0.065	−244.519	−254.171	44.255
350	36.456	232.797	227.492	1.857	−245.857	−255.674	38.157
400	37.806	237.752	228.470	3.713	−247.251	−256.982	33.558
450	39.211	242.286	229.756	5.638	−248.682	−258.113	29.961
500	40.609	246.490	231.222	7.634	−250.131	−259.083	27.066
600	43.240	254.131	234.416	11.829	−253.040	−260.600	22.687
700	45.531	260.973	237.729	16.270	−255.928	−261.632	19.523
800	47.454	267.182	241.029	20.923	−258.782	−262.251	17.123
900	49.042	272.866	244.255	25.750	−261.605	−262.515	15.236
1000	50.345	278.103	247.381	30.722	−264.407	−262.466	13.710
1100	51.417	282.953	250.397	35.811	−267.200	−262.136	12.448
1200	52.304	287.466	253.301	40.999	−269.994	−261.553	11.385
1300	53.044	291.683	256.093	46.267	−272.797	−260.736	10.476
1400	53.669	295.637	258.778	51.604	−275.618	−259.702	9.690
1500	54.205	299.359	261.360	56.998	−278.461	−258.467	9.001
1600	54.672	302.873	263.846	62.443	−281.331	−257.040	8.391
1700	55.085	306.200	266.240	67.931	−284.230	−255.433	7.849
1800	55.457	309.359	268.549	73.458	−287.161	−253.655	7.361
1900	55.798	312.367	270.777	79.021	−290.124	−251.713	6.920
2000	56.115	315.237	272.928	84.617	−293.120	−249.614	6.519
2100	56.413	317.982	275.009	90.244	−296.150	−247.364	6.153
2200	56.697	320.613	277.022	95.899	−299.214	−244.969	5.816
2300	56.968	323.139	278.973	101.583	−302.311	−242.435	5.506
2400	57.230	325.569	280.864	107.293	−355.700	−238.696	5.195
2500	57.484	327.911	282.699	113.028	−358.940	−233.754	4.884
2600	57.729	330.170	284.482	118.789	−362.180	−228.682	4.594
2700	57.968	332.353	286.215	124.574	−365.419	−223.486	4.324
2800	58.199	334.466	287.901	130.382	−368.658	−218.170	4.070
2900	58.423	336.512	289.542	136.213	−371.896	−212.739	3.832
3000	58.639	338.496	291.141	142.067	−375.134	−207.195	3.608
3100	58.848	340.422	292.699	147.941	−378.371	−201.544	3.396
3200	59.049	342.294	294.220	153.836	−381.608	−195.788	3.196
3300	59.242	344.114	295.705	159.751	−384.844	−189.931	3.006
3400	59.427	345.885	297.155	165.684	−388.080	−183.976	2.826
3500	59.603	347.610	298.572	171.636	−391.316	−177.926	2.655
3600	59.771	349.292	299.957	177.604	−394.553	−171.783	2.493
3700	59.930	350.932	301.313	183.590	−397.791	−165.551	2.337
3800	60.081	352.532	302.640	189.590	−401.030	−159.230	2.189
3900	60.223	354.095	303.939	195.605	−404.271	−152.825	2.047
4000	60.357	355.621	305.212	201.634	−407.515	−146.337	1.911
4100	60.482	357.113	306.460	207.676	−410.761	−139.767	1.781
4200	60.599	358.572	307.683	213.731	−893.860	−126.094	1.568
4300	60.707	359.999	308.884	219.796	−896.027	−107.788	1.309
4400	60.808	361.396	310.061	225.872	−898.200	−89.432	1.062
4500	60.902	362.763	311.217	231.957	−900.380	−71.026	0.824
4600	60.988	364.103	312.352	238.052	−902.568	−52.572	0.597
4700	61.066	365.415	313.468	244.155	−904.766	−34.070	0.379
4800	61.138	366.702	314.563	250.265	−906.973	−15.521	0.169
4900	61.203	367.963	315.640	256.382	−909.190	3.073	−0.033
5000	61.262	369.200	316.699	262.505	−911.420	21.714	−0.227
5100	61.315	370.414	317.740	268.634	−913.662	40.399	−0.414
5200	61.362	371.605	318.765	274.768	−915.917	59.127	−0.594
5300	61.404	372.774	319.773	280.907	−918.186	77.900	−0.768
5400	61.441	373.922	320.765	287.049	−920.470	96.716	−0.936
5500	61.472	375.050	321.742	293.195	−922.770	115.573	−1.098
5600	61.499	376.158	322.704	299.343	−925.087	134.474	−1.254
5700	61.522	377.247	323.651	305.494	−927.422	153.415	−1.406
5800	61.541	378.317	324.584	311.648	−929.775	172.398	−1.553
5900	61.555	379.369	325.504	317.802	−932.147	191.420	−1.695
6000	61.566	380.404	326.410	323.959	−934.539	210.484	−1.832

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [48.95 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 509 \pm 1\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -802.8 \pm 0.84\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy change ($\Delta_r H°$) of the reaction HBO_2(cr, I) + H_2O(l) = H_3BO_3(cr) has been determined Kilday.[1] From the value, $\Delta_r H°(298.15\ K) = -1.28\ kcal·mol^{-1}$, the enthalpy of formation $\Delta_f H°(298.15\ K)$ for HBO_2 (cr, I) is derived to be $-191.87 \pm 0.20\ kcal·mol^{-1}$ which is adopted. The enthalpies of solution of HBO_2 (cr, I) in H_2O(l) were measured by Sokolova, *et al.*[2] Based on the reported value, $\Delta_r H°(298.15\ K) = 1.76 \pm 0.01\ kcal·mol^{-1}$ for the reaction HBO_2(cr, I) + 501 H_2O(l) = H_3BO_3·500 H_2O(Sol), the enthalpy of formation for HBO_2(cr, I) was derived as $-189.46 \pm 0.20\ kcal·mol^{-1}$, using $\Delta_f H°$(H_2O, l, 298.15 K) = −68.317 and $\Delta_f H°$(H_3BO_3·500 H_2O, Sol, 298.15 K), ≈ $-256.02 \pm 0.20\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The values of heat capacity for HBO_2(cr, I) were estimated by comparison with those of its constituent oxides. $S°(298.15\ K)$ was calculated as the sum of the entropy contributions from H^+ and BO_2^- in HBO_2(c) suggested by Kelley and Kubaschewski and Evans.

Fusion Data

Kracek, Morey and Merwin reported the existence of three crystal forms of HBO_2(c), namely HBO_2(cr, I), $T_{fus} = 509 \pm 1K$; HBO_2(cr, II), $T_{fus} = 474.1 \pm 0.5\ K$; and HBO_2(cr, III), $T_{fus} = 449.2 \pm 0.2\ K$. However, there was no solid phase equilibrium found among these crystals. Sokolova, Skuratov, Shemonaeva and Yuldasheva measured the enthalpies of solution in water of HBO_2(cr, I) and HBO_2(cr, II) and derived the enthalpy of transition as $\Delta_{trs} H°(II \rightarrow I, 298.15\ K) = 1.29\ kcal·mol^{-1}$.

Sublimation Data

The value of $\Delta_{sub} H°(298.15\ K)$ is calculated as the difference between the $\Delta_f H°(298.15\ K)$ values for HBO_2(g) and HBO_2(c).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	54.392	48.953	48.953	.000	−802.784	−734.994	128.768
300	54.810	49.291	48.954	.101	−802.785	−734.574	127.901
400	61.505	66.015	51.189	5.931	−802.742	−711.839	92.957
500	66.526	80.279	55.615	12.332	−802.592	−689.128	71.993
600	71.546	92.835	60.791	19.227	−802.303	−666.460	58.020
700	78.921	104.435	66.205	26.761	−801.647	−643.864	48.046
800	84.935	115.381	71.675	34.965	−800.539	−621.395	40.573
900	89.642	125.671	77.109	43.706	−799.072	−599.086	34.770
1000	92.885	135.297	82.452	52.845	−797.360	−576.956	30.137
1100	94.056	144.207	87.667	62.194	−795.569	−555.002	26.355
1200	94.977	152.432	92.725	71.648	−793.792	−533.211	23.210
1300	95.646	160.062	97.615	81.181	−792.044	−511.567	20.555
1400	96.065	167.167	102.332	90.769	−790.341	−490.056	18.284
1500	96.232	173.802	106.878	100.386	−788.704	−468.665	16.320

PREVIOUS: September 1962 CURRENT: December 1964

$S°(298.15\ K) = [239.73]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -557.2 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -560.7 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
3680(1)	[1250](1)
2030(1)	[600](1)
1420(1)	[700](1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: [C_s]
Bond Distances: H–O = [1.0] Å; O–B = [1.34] Å; B–O = [1.20] Å
Bond Angles: H–O–B = [120]°; O–B–O = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [9.70076 \times 10^{-117}]\ g^3·cm^6$

Enthalpy of Formation

The equilibrium pressures of the reaction 1/2 B_2O_3(l) + 1/2 H_2O(g) = HBO_2(g) have been measured by several investigators. Using the equilibrium data reported, the enthalpies of reaction, $\Delta_r H°(298.15\ K)$, were evaluated by both the 2nd and 3rd law methods. The corresponding enthalpies of formation for HBO_2(g) were derived based on the $\Delta_r H°(298.15\ K)$ values obtained by the 3rd law method. The results are presented as follows:

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[1]	1061 – 1451	45.4 ± 0.6	45.16	−133.38 ± 0.50
	1323 – 1451	0.25 ± 6.0	−5.15	−133.62 ± 0.50
[2]	1250 – 1450	39.7 ± 2.5	—	−138.87 ± 2.50*
[3]	1273	—	44.12	−134.42 ± 1.0
[4]	1070 – 1323	31.0 ± 10.0	44.07	−134.47 ± 3.20
	1143	—	40.9	−137.64 ± 0.70*
	1071 – 1325	44.2 ± 1.8	39.3	−139.3 ± 1.0*
	1148	—	43.2	−135.3 ± 0.4

*The value not used for the calculation of the weighted average of $\Delta_f H°(298.15\ K)$ for HBO_2(g)

Heat Capacity and Entropy

All molecular and spectroscopic constants were taken from White and Mann *et al.*[2] The principal moments of inertia are: $I_A = 0.1155 \times 10^{-39}$, $I_B = 9.1066 \times 10^{-39}$ and $I_C = 9.2221 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.687	−557.212	−557.212	INFINITE
100	33.404	200.044	273.638	−7.359	−558.313	−555.919	290.382
200	36.887	224.017	243.422	−3.881	−559.425	−553.107	144.457
250	39.583	232.535	240.414	−1.970	−560.041	−551.456	115.221
298.15	42.232	239.734	239.734	0.	−560.656	−549.748	96.313
300	42.332	239.995	239.735	0.078	−560.680	−549.680	95.708
350	45.007	246.723	240.260	2.262	−561.324	−547.796	81.754
400	47.553	252.901	241.459	4.577	−561.968	−545.819	71.277
450	49.941	258.641	243.053	7.015	−562.605	−543.762	63.118
500	52.157	264.019	244.883	9.568	−563.228	−541.635	56.584
600	56.073	273.885	248.910	14.985	−564.416	−537.203	46.768
700	59.364	282.783	253.124	20.762	−565.518	−532.579	39.742
800	62.136	290.896	257.345	26.841	−566.535	−527.803	34.462
900	64.489	298.354	261.493	33.175	−567.476	−522.904	30.349
1000	66.505	305.256	265.529	39.727	−568.349	−517.905	27.053
1100	68.244	311.678	269.436	46.467	−569.168	−512.820	24.352
1200	69.752	317.682	273.209	53.368	−569.944	−507.663	22.098
1300	71.066	323.318	276.849	60.411	−570.686	−502.443	20.188
1400	72.215	328.628	280.359	67.576	−571.406	−497.166	18.549
1500	73.223	333.645	283.746	74.849	−572.113	−491.839	17.127
1600	74.111	338.400	287.015	82.216	−572.814	−486.464	15.881
1700	74.894	342.917	290.171	89.668	−573.518	−481.046	14.781
1800	75.588	347.218	293.222	97.192	−574.231	−475.586	13.801
1900	76.203	351.321	296.173	104.782	−574.958	−470.086	12.924
2000	76.752	355.244	299.029	112.431	−575.705	−464.547	12.133
2100	77.242	359.001	301.796	120.131	−576.475	−458.970	11.416
2200	77.681	362.605	304.479	127.877	−577.273	−453.356	10.764
2300	78.075	366.067	307.082	135.666	−578.102	−447.705	10.168
2400	78.430	369.397	309.609	143.491	−629.224	−440.949	9.597
2500	78.751	372.605	312.065	151.350	−630.199	−433.084	9.049
2600	79.041	375.700	314.454	159.240	−631.179	−425.180	8.542
2700	79.305	378.688	316.778	167.158	−632.166	−417.238	8.072
2800	79.545	381.576	319.041	175.100	−633.161	−409.259	7.635
2900	79.764	384.372	321.245	183.066	−634.165	−401.246	7.227
3000	79.964	387.079	323.395	191.053	−635.179	−393.196	6.846
3100	80.148	389.704	325.492	199.058	−636.204	−385.113	6.489
3200	80.316	392.252	327.539	207.082	−637.240	−376.997	6.154
3300	80.472	394.725	329.537	215.121	−638.288	−368.849	5.838
3400	80.615	397.130	331.490	223.176	−639.349	−360.668	5.541
3500	80.747	399.469	333.399	231.244	−640.422	−352.456	5.260
3600	80.869	401.745	335.266	239.325	−641.508	−344.213	4.994
3700	80.982	403.962	337.093	247.417	−642.607	−335.940	4.743
3800	81.088	406.123	338.881	255.521	−643.719	−327.636	4.504
3900	81.185	408.231	340.632	263.635	−644.844	−319.303	4.277
4000	81.277	410.288	342.348	271.758	−645.982	−310.942	4.060
4100	81.362	412.296	344.030	279.890	−647.134	−302.551	3.855
4200	81.441	414.257	345.679	288.030	−1128.149	−287.109	3.571
4300	81.516	416.174	347.296	296.178	−1128.242	−267.082	3.244
4400	81.585	418.049	348.883	304.333	−1128.350	−247.055	2.933
4500	81.651	419.883	350.440	312.495	−1128.474	−227.025	2.635
4600	81.712	421.679	351.969	320.663	−1128.615	−206.991	2.350
4700	81.770	423.437	353.471	328.837	−1128.774	−186.954	2.078
4800	81.824	425.159	354.947	337.017	−1128.950	−166.913	1.816
4900	81.876	426.846	356.397	345.202	−1129.146	−146.868	1.566
5000	81.924	428.501	357.823	353.392	−1129.360	−126.819	1.325
5100	81.970	430.124	359.225	361.586	−1129.595	−106.766	1.094
5200	82.013	431.716	360.603	369.786	−1129.850	−86.709	0.871
5300	82.054	433.279	361.960	377.989	−1130.127	−66.645	0.657
5400	82.092	434.813	363.295	386.196	−1130.427	−46.577	0.451
5500	82.129	436.319	364.609	394.407	−1130.750	−26.504	0.252
5600	82.164	437.799	365.903	402.622	−1131.098	−6.422	0.060
5700	82.197	439.254	367.177	410.840	−1131.472	13.664	−0.125
5800	82.229	440.684	368.432	419.061	−1131.872	33.758	−0.304
5900	82.258	442.090	369.668	427.286	−1132.299	53.857	−0.477
6000	82.287	443.473	370.887	435.513	−1132.756	73.966	−0.644

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [214.96 ± 0.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [50.8 ± 10.0] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [50.2 ± 10.0] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	[35000]	[1]
[25000]	[3]	[37000]	[2]
[30000]	[6]	[40000]	[6]
[31000]	[3]		

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
2742(1)
[715](2)
[1156](1)

Point Group: $C_{\infty v}$ σ = 1
Bond Distances: H–B = 1.1692 Å; B–S = 1.5994 Å
Bond Angle: H–B–S = 180°
Rotational constant: B_0 = 0.643679 cm^{-1}

Enthalpy of Formation

The transient thioborine molecule, HBS, has been identified by Kirk and Timms[1] in the mass spectra of the products fromed by the high temperature (1150–1300°C) reaction of hydrogen sulfide on crystalline boron. The best yields of HBS were found at low pressures (<1 torr) but even under thses conditions the half-life is relatively short (<3 min).[1,2] No experimental measurement of its enthalpy of formation has been reported.

We estimate $\Delta_f H°$ from a consideration of bond-energy schemes. A comparison of the values for the H–B stretching force constants in HBS (K = 4.021 × 10^5 dynes/cm) and HBO (K = 4.080 × 10^5 dynes/cm)[3] suggests that the H–B bonds in these two molecules are quite similar. Assuming $\Delta_{at}H°$(H–BO, 298.15 K) = 99.5 $kcal·mol^{-1}$,[3] we calculate $\Delta_f H°(298.15\ K)$ = 10.7 $kcal·mol^{-1}$with $\Delta_f H°$(H, g, 298.15 K) = 52.103 $kcal·mol^{-1}$ and $\Delta_f H°$(BS, g 298.15 K) = 58.1 ± 4.0 $kcal·mol^{-1}$.[3]

A comparison of force constants also suggests that the H–B bonds in BH_3[4] and the B=S bond in BS[3] are similar to those in HBS. Using $\Delta_{at}H°$(H–B, 298.15 K) = $\Delta_{at}H°(BH_3, g, 298.15\ K)/3$ = 87.9 $kcal·mol^{-1}$ and $\Delta_{at}H°$(B=S, 298.15 K) = $\Delta_{at}H°$(BS, 298.15 K) = 141.0 $kcal·mol^{-1}$, we calculate $\Delta_{at}H°(298.15\ K)$ = 228.9 $kcal·mol^{-1}$ which leads to $\Delta_f H°(298.15\ K)$ = 22.3 $kcal·mol^{-1}$. All bond dissociation energies are derived from JANAF data.[3]

A value for $\Delta_{at}H°(298.15\ K)$ can also be obtained from the results of MO calculations on HBS. Thomson[5] has shown that dissociation energies obtained from MO calculations when combined with estimates of the molecular extra correlation energy (MECE) give reliable atomization energies. The change in the relativistic energy between the isolated atoms and molecule is assumed small. It is reasonable to assume that the contribution to the atomization energy from correlation effects would be similar for the isoelectronic molecules HBS and HBO. We estimate the MECE for HBO as 56.5 $kcal·mol^{-1}$ from the difference in the experimental $\Delta_{at}H°$ [3] and the reported Hartree–Fock dissociation energy.[6] This value of MECE when added to the computed dissociation energy[7] of 191.7 $kcal·mol^{-1}$ gives $\Delta_{at}H°(298.15\ K)$ = 248.2 $kcal·mol^{-1}$ which corresponds to $\Delta_f H°$(HBS, g, 298.15 K) = 3.0 $kcal·mol^{-1}$. We believe these three estimates of $\Delta_f H°$(10.7, 22.3, 3.0 $kcal·mol^{-1}$) to be equally probable; therefore, we adopt the mean value of 12.0 $kcal·mol^{-1}$. An uncertainty of ±10.0 $kcal·mol^{-1}$ is assigned which covers the range of possible values.

Heat Capacity and Entropy

The microwave measurements on HBS by Pearson and McCormick[8] have shown that the molecule is linear in its ground state. They observed the millimeter-wave spectra for eight isotopic species and evaluated structural parameters by the substitution method. We adopt their mean values for the H–B and B=S bond lengths.

Sams and Maki[2] have observed the υ_1 vibrational fundamental (2742 cm^{-1}) in the high-resolution infrared spectra of HBS(g). Frequencies (υ_1) were recorded for four isotopic species. The value of υ_1(2742 cm^{-1}) is corrected for the natural isotopic abundances of boron: the correction for the sulfur isotopes is negligible. Values of υ_2 and υ_3 are calculated from force constants by a valence force method.[9] The B=S stretching force constant (K = 6.9 × 10^5 dynes/cm) is estimated from the value for BS (K = 6.7 × 10^5 dynes/cm) by comparison with the B=O stretching force constants for BO and HBO.[3] The bending force constant (K_D = 3.2 × 10^{12} dynes/cm) is taken equal to the value for HBO.[3] Sams and Maki[2] also performed a detailed force field calculation on HBS which gave υ_2 = 635 cm^{-1} for $H^{11}B^{32}S$. Results of a similar

Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.287	50.781	50.781	INFINITE
100	29.161	180.556	244.344	−6.379	51.475	39.739	−20.758
200	31.839	201.339	218.167	−3.366	51.167	28.051	−7.326
250	34.328	208.706	215.556	−1.713	50.731	22.320	−4.664
298.15	36.789	214.964	214.964	0.	50.208	16.894	−2.960
300	36.881	215.192	214.965	0.068	50.186	16.688	−2.906
350	39.237	221.057	215.422	1.972	49.573	11.152	−1.664
400	41.313	226.435	216.468	3.987	46.693	5.797	−0.757
450	43.113	231.408	217.855	6.099	45.321	0.758	−0.088
500	44.673	236.033	219.444	8.294	43.880	−4.114	0.430
600	47.240	244.414	222.922	12.895	41.450	−13.478	1.173
700	49.284	251.855	226.534	17.725	39.309	−22.460	1.676
800	50.966	258.549	230.124	22.740	37.354	−31.149	2.034
900	52.379	264.636	233.626	27.909	−17.603	−38.520	2.236
1000	53.577	270.219	237.010	33.209	−18.124	−40.816	2.132
1100	54.598	275.374	240.266	38.619	−18.634	−43.061	2.045
1200	55.470	280.163	243.394	44.123	−19.145	−45.259	1.970
1300	56.219	284.633	246.396	49.709	−19.664	−47.414	1.905
1400	56.863	288.824	249.278	55.364	−20.199	−49.529	1.848
1500	57.419	292.766	252.047	61.078	−20.756	−51.605	1.797
1600	57.901	296.488	254.710	66.845	−21.339	−53.642	1.751
1700	58.320	300.011	257.272	72.657	−21.953	−55.643	1.710
1800	58.686	303.355	259.740	78.507	−22.601	−57.606	1.672
1900	59.008	306.537	262.120	84.392	−23.283	−59.532	1.637
2000	59.291	309.571	264.417	90.308	−24.002	−61.421	1.604
2100	59.541	312.470	266.637	96.249	−24.758	−63.274	1.574
2200	59.763	315.245	268.784	102.215	−25.551	−65.090	1.545
2300	59.961	317.906	270.862	108.201	−26.383	−66.868	1.519
2400	60.139	320.462	272.876	114.206	−77.513	−67.541	1.470
2500	60.299	322.920	274.829	120.228	−78.499	−67.106	1.402
2600	60.444	325.288	276.724	126.266	−79.492	−66.630	1.339
2700	60.576	327.572	278.565	132.317	−80.490	−66.117	1.279
2800	60.697	329.777	280.355	138.380	−81.494	−65.566	1.223
2900	60.810	331.909	282.096	144.456	−82.504	−64.979	1.170
3000	60.915	333.972	283.791	150.542	−83.520	−64.358	1.121
3100	61.016	335.971	285.443	156.639	−84.541	−63.702	1.073
3200	61.112	337.910	287.052	162.745	−85.569	−63.014	1.029
3300	61.207	339.792	288.622	168.861	−86.601	−62.293	0.986
3400	61.301	341.620	290.154	174.987	−87.639	−61.541	0.945
3500	61.396	343.399	291.650	181.121	−88.682	−60.758	0.907
3600	61.493	345.130	293.111	187.266	−89.730	−59.945	0.870
3700	61.594	346.816	294.540	193.420	−90.781	−59.103	0.834
3800	61.701	348.460	295.938	199.585	−91.836	−58.233	0.800
3900	61.814	350.064	297.305	205.761	−92.894	−57.335	0.768
4000	61.935	351.631	298.644	211.948	−93.955	−56.410	0.737
4100	62.066	353.162	299.955	218.148	−95.017	−55.458	0.707
4200	62.206	354.659	301.239	224.361	−575.929	−47.456	0.590
4300	62.359	356.124	302.499	230.590	−575.903	−34.874	0.424
4400	62.524	357.560	303.734	236.834	−575.878	−22.292	0.265
4500	62.703	358.967	304.946	243.095	−575.852	−9.711	0.113
4600	62.897	360.347	306.135	249.375	−575.824	2.870	−0.033
4700	63.106	361.702	307.303	255.675	−575.793	15.450	−0.172
4800	63.331	363.033	308.450	261.996	−575.757	28.029	−0.305
4900	63.574	364.341	309.578	268.342	−575.716	40.607	−0.433
5000	63.833	365.628	310.686	274.712	−575.667	53.185	−0.556
5100	64.111	366.895	311.776	281.109	−575.609	65.762	−0.674
5200	64.407	368.143	312.848	287.535	−575.541	78.337	−0.787
5300	64.721	369.372	313.903	293.991	−575.461	90.911	−0.896
5400	65.054	370.585	314.941	300.479	−575.366	103.483	−1.001
5500	65.405	371.782	315.964	307.002	−575.256	116.053	−1.102
5600	65.774	372.964	316.971	313.561	−575.129	128.621	−1.200
5700	66.162	374.132	317.964	320.158	−574.982	141.187	−1.294
5800	66.567	375.286	318.942	326.794	−574.814	153.750	−1.385
5900	66.989	376.427	319.907	333.471	−574.623	166.310	−1.472
6000	67.428	377.557	320.858	340.192	−574.408	178.866	−1.557

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

Continued on page 317

$S°(298.15\ K)$ = [225.4 ± 0.4] J·K⁻¹·mol⁻¹

$\Delta_f H°(0\ K)$=[1123.2 ± 11] kJ·mol⁻¹
$\Delta_f H°(298.15\ K)$ = [1129.5 ± 11 kJ·mol⁻¹

Electronic Levels and Quantum Weights		
State	ϵ_i, cm⁻¹	g_i
$X^2\Pi_{1/2}$	0	2
$X^2\Pi_{3/2}$	[300]	2
$A^2\Sigma^+$	19599	2
$B^2\Sigma^+$	38069	2

Vibrational Frequencies and Degeneracies
υ, cm⁻¹
[2550](1)
[764](2)
973 (1)

Point Group: $C_{\infty v}$ σ = 1
Bond Distances: H–B = [1.192] Å; B–S = [1.680] Å
Bond Angle: H–B–S = 180°
Rotational Constant: B_o = [0.586979] cm⁻¹

Enthalpy of Formation

Kroto *et al.*[1] and Fehler and Turner[2] have independently measured the 584 Å photoelectron spectra of HBS(g). The reported value of 11.11 ± 0.03 eV[1] and 11.12 eV[2] for the first adiabatic ionization potential are in excellent agreement. We adopt an average (11.115 ± 0.03 eV) of these two IP values, and we assume $\Delta_f H°$ = 256.32 ± 0.7 kcal·mol⁻¹ refers to the ionization process HBS(g) + e⁻ + HBS⁺(g) + 2 e⁻ at 0 K. The latter value yields $\Delta_f H°$(HBS⁺, g, 0 K) = 268.4 ± 11.0 kcal·mol⁻¹ when combined with $\Delta_f H°$(HBS, g, 0 K) = 12.1 ± 10.0 kcal·mol⁻¹.[3] The adopted $\Delta_f H°$ value is placed in brackets to emphasize the uncertainty in the estimated $\Delta_f H°$ value[3] for HBS. $\Delta_f H°(298.15\ K)$ corresponds to 270.0 ± 11.0 kcal·mol⁻¹.

Heat Capacity and Entropy

Extensive ab initio MO calculations[4] recently reported for HBS show that the highest occupied orbital is of Π–symmetry and is localized mainly on the sulfur atom. The shape of the first photoelectron band in the HBS spectra[1,2] suggests that this orbital is bonding. The bonding nature of this Π orbital is also predicted from the Walsh diagram[5] for HAB molecules. As a consequence, we would expect the ion to be less strongly bound than the parent molecule. In the related species HCN[6] which has the same orbital ordering as HBS,[4] ionization[7] occurs with a 2.2% increase in the H–C bond length and a 4.7% increase in the C=N bond length. We assume a similar increase in the bond lengths of HBS[3] upon ionization. If the ion was nonlinear, one would expect to find a vibrational spacing in the photoelectron spectra of HBS which could be associated with the bending frequency of the ion. No frequency as low as 764 cm⁻¹ has been observed;[1,2] thus, it is likely that HBS⁺ is linear in its ground state. This prediction is supported by the Walsh diagram.[5] We assume that the ion is linear.

The progression in the first photoelectron band of the HBS spectra has been reported as 955 ± 40 cm⁻¹ [1] and 990 cm⁻¹.[2] By comparison with changes observed in vibrational frequencies on ionization of HCN and HCP,[3,8] the vibrational mode excited is most certainly the B=S stretching frequency, υ_3. We adopt the average (973 cm⁻¹) of these two values. The values of υ_1 and are calculated from estimated force constants by a valence force method.[9] The two force constants are estimated form those for HCN⁺,[8] NCH and NBS.[3] We estimate the uncertainties in our frequencies are no greater than ±50 cm⁻¹ which corresponds to an error in the value of $S°$(298.15 K) of only ±0.12 kcal·mol⁻¹.

The electronic states and upper levels are taken from the photoelectron spectrometric study of Kroto *et al.*[1] Relative term values for the $A^2\Sigma^+$ and $B^2\Sigma^+$ states are calculated as differences in the reported adiabatic ionization potentials.[1] Fehler and Turner[2] have estimated the ground state splitting to be ~300 cm⁻¹ from the observed peak widths in the first band of the HBS photoelectron spectra. We adopt this result since it compares favorably with the splitting (~278 cm⁻¹) observed for the $^2\Pi$ state of the isoelectronic molecules CS^+.[10] Relative term values for the two $^2\Sigma$ states calculated from the adiabatic ionization potentials of Fehler and Turner[2] agree within about 160 cm⁻¹ with the values adopted here. Fehler and Turner[2] have also reported a photoelectron band at 17.9 eV which was not observed by Kroto *et al.*[1] This band could not be definitely assigned to HBS⁺. If this state does exist, it lies above 50000 cm⁻¹ and has a negligible effect on the thermodynamic functions of the ion. We prefer not to include it. Kroto *et al.*[1] have interpreted their photoelectron results in terms of a linear configuration for the three observed states of HBS⁺. Thus, we feel our functions are not significantly influenced by the use of the ground state vibrational frequencies and rotational constant for the excited states.

Continued on page 317

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.934	1123.199		
100	31.149	187.666	257.455	−6.979			
200	35.146	210.523	228.818	−3.659			
250	37.309	218.594	225.988	−1.848			
298.15	39.455	225.350	225.350	0.	1129.471	1086.806	−190.404
300	39.535	225.594	225.351	0.073	1129.493	1086.541	−189.184
350	41.615	231.848	225.840	2.103	1130.044	1079.338	−161.082
400	43.459	237.528	226.951	4.231	1128.316	1072.148	−140.008
450	45.064	242.741	228.420	6.445	1128.086	1065.132	−123.637
500	46.464	247.563	230.096	8.734	1127.777	1058.156	−110.545
600	48.787	256.248	233.747	13.501	1127.593	1044.255	−90.910
700	50.657	263.914	237.520	18.476	1127.676	1030.362	−76.887
800	52.207	270.783	241.256	23.621	1127.929	1016.444	−66.367
900	53.508	277.009	244.888	28.909	1075.170	1003.568	−58.246
1000	54.607	282.705	248.389	34.316	1076.835	995.523	−52.001
1100	55.538	287.955	251.750	39.825	1078.502	987.311	−46.883
1200	56.329	292.822	254.973	45.419	1080.160	978.948	−42.612
1300	57.004	297.358	258.061	51.087	1081.801	970.447	−38.993
1400	57.581	301.604	261.021	56.817	1083.420	961.820	−35.886
1500	58.076	305.594	263.861	62.600	1085.011	953.079	−33.189
1600	58.503	309.356	266.588	68.430	1086.568	944.232	−30.826
1700	58.873	312.914	269.209	74.299	1088.091	935.289	−28.738
1800	59.195	316.289	271.732	80.203	1089.575	926.258	−26.879
1900	59.477	319.497	274.162	86.137	1091.020	917.145	−25.214
2000	59.725	322.554	276.506	92.097	1092.425	907.957	−23.713
2100	59.943	325.474	278.769	98.081	1093.790	898.700	−22.354
2200	60.137	328.267	280.955	104.085	1095.114	889.379	−21.117
2300	60.309	330.944	283.071	110.107	1096.396	879.999	−19.985
2400	60.464	333.514	285.120	116.146	1047.379	871.632	−18.971
2500	60.603	335.985	287.105	122.200	1048.502	864.286	−18.058
2600	60.729	338.364	289.031	128.266	1049.618	856.895	−17.215
2700	60.844	340.659	290.901	134.345	1050.726	849.462	−16.434
2800	60.949	342.873	292.718	140.435	1051.827	841.988	−15.707
2900	61.046	345.014	294.485	146.535	1052.920	834.474	−15.031
3000	61.136	347.085	296.204	152.644	1054.005	826.923	−14.398
3100	61.220	349.091	297.877	158.762	1055.083	819.336	−13.806
3200	61.299	351.036	299.508	164.887	1056.154	811.714	−13.250
3300	61.373	352.923	301.099	171.021	1057.218	804.059	−12.727
3400	61.444	354.756	302.650	177.162	1058.274	796.371	−12.235
3500	61.512	356.538	304.164	183.310	1059.323	788.653	−11.770
3600	61.577	358.272	305.643	189.464	1060.364	780.905	−11.331
3700	61.641	359.960	307.089	195.625	1061.398	773.128	−10.915
3800	61.702	361.605	308.502	201.792	1062.423	765.323	−10.520
3900	61.762	363.208	309.884	207.966	1063.442	757.491	−10.145
4000	61.821	364.773	311.237	214.145	1064.452	749.633	−9.789
4100	61.879	366.300	312.561	220.330	1065.453	741.750	−9.450
4200	61.937	367.792	313.858	226.521	586.597	740.867	−9.214
4300	61.993	369.250	315.130	232.717	588.670	744.516	−9.044
4400	62.049	370.676	316.376	238.919	590.732	748.116	−8.881
4500	62.105	372.071	317.598	245.127	592.783	751.670	−8.725
4600	62.160	373.437	318.797	251.340	594.823	755.178	−8.575
4700	62.216	374.774	319.974	257.559	596.851	758.643	−8.431
4800	62.270	376.084	321.129	263.783	598.868	762.064	−8.293
4900	62.325	377.369	322.264	270.013	600.873	765.443	−8.160
5000	62.380	378.629	323.379	276.248	602.865	768.781	−8.031
5100	62.434	379.864	324.474	282.489	604.845	772.080	−7.908
5200	62.488	381.077	325.551	288.735	606.813	775.340	−7.788
5300	62.542	382.268	326.610	294.987	608.767	778.562	−7.673
5400	62.596	383.438	327.652	301.244	610.708	781.747	−7.562
5500	62.649	384.587	328.677	307.506	612.636	784.897	−7.454
5600	62.703	385.716	329.685	313.773	614.551	788.012	−7.350
5700	62.756	386.826	330.678	320.046	616.453	791.092	−7.250
5800	62.808	387.918	331.655	326.325	618.341	794.140	−7.152
5900	62.861	388.992	332.618	332.608	620.216	797.155	−7.057
6000	62.913	390.049	333.566	338.897	622.078	800.138	−6.966

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K)$ = [180.19] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 202 ± 63 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 201 ± 63 $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[2430]	[840](2)	[2650](1)

Ground State Quantum Weight: [2] σ = 2
Point Group: [$D_{\infty h}$]
Bond Distance: B–H = [1.20] Å
Bond Angle: H–B–H = [180]°
Rotational Constant: B_o = [5.807235] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from appearance potentials reported by Fehlner and Koski[1] and the JANAF Thermochemical Table.[2] For example:

	$\Delta_r H°(0\ K)$
$B_2H_6(g) \rightarrow BH_2^+(ion) + BH_2(g) + H_2(g)$	13.4 eV
$BH_2(g) \rightarrow BH_2^+(ion)$	9.8 eV
$B_2H_6(g) \rightarrow 2\ BH_2(g) + H_2(g)$	3.6 eV

The $\Delta_f H°$ data is summarized below.

Source	Method	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$
[2]	Appearance Potentials	48
[3]	Estimate	66
[4]	Estimate	93

Heat Capacity and Entropy

The bond distance B–H = 1.20 Å was estimated from a consideration of BH(g), BH_3(g) and other molecules. The bond angle H–B–H = 180° and the electronic configuration of the ground state [$^2A_2$] were estimated by Jordan and Longuet Higgins.[4] The frequencies were estimated assuming valence forces, Herzberg,[5] and using force constants, $k_1 = 3.5 \times 10^5$ dynes cm^{-1} and $k\delta 1' = 0.35 \times 10^5$ dynes cm^{-1}, estimated from BH_3, Shepp and Bauer.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.008	201.505	201.505	INFINITE
100	29.115	146.922	208.138	−6.122	201.368	196.780	−102.787
200	30.550	167.371	183.190	−3.164	201.300	192.192	−50.195
250	32.243	174.363	180.745	−1.595	201.101	189.935	−39.685
298.15	34.026	180.195	180.195	0.	200.832	187.809	−32.903
300	34.094	180.405	180.195	0.063	200.821	187.728	−32.686
350	35.849	185.795	180.617	1.812	200.494	185.571	−27.695
400	37.432	190.687	181.574	3.645	200.134	183.463	−23.958
450	38.855	195.179	182.840	5.553	199.754	181.402	−21.057
500	40.154	199.341	184.284	7.528	199.364	179.384	−18.740
600	42.509	206.874	187.435	11.664	198.589	175.461	−15.275
700	44.645	213.590	190.700	16.023	197.855	171.665	−12.810
800	46.593	219.681	193.948	20.587	197.183	167.970	−10.967
900	48.350	225.272	197.122	25.335	196.576	164.356	−9.539
1000	49.913	230.449	200.199	30.250	196.025	160.806	−8.400
1100	51.287	235.272	203.170	35.312	195.517	157.309	−7.470
1200	52.487	239.787	206.036	40.502	195.040	153.857	−6.697
1300	53.531	244.030	208.797	45.804	194.580	150.444	−6.045
1400	54.439	248.032	211.458	51.203	194.126	147.066	−5.487
1500	55.228	251.815	214.023	56.688	193.668	143.720	−5.005
1600	55.916	255.402	216.498	62.246	193.198	140.406	−4.584
1700	56.517	258.810	218.888	67.868	192.711	137.121	−4.213
1800	57.043	262.056	221.197	73.546	192.201	133.865	−3.885
1900	57.505	265.153	223.429	79.274	191.664	130.639	−3.592
2000	57.913	268.113	225.590	85.046	191.098	127.442	−3.328
2100	58.274	270.947	227.683	90.855	190.500	124.274	−3.091
2200	58.595	273.666	229.712	96.699	189.868	121.135	−2.876
2300	58.880	276.277	231.680	102.573	189.200	118.025	−2.680
2400	59.136	278.788	233.591	108.474	138.236	116.014	−2.525
2500	59.366	281.207	235.447	114.399	137.417	115.105	−2.405
2600	59.572	283.539	237.252	120.347	136.591	114.229	−2.295
2700	59.759	285.791	239.009	126.313	135.758	113.385	−2.194
2800	59.927	287.968	240.718	132.298	134.918	112.571	−2.100
2900	60.081	290.073	242.384	138.298	134.070	111.788	−2.014
3000	60.220	292.112	244.008	144.313	133.213	111.035	−1.933
3100	60.348	294.089	245.592	150.342	132.347	110.309	−1.859
3200	60.464	296.007	247.137	156.383	131.470	109.613	−1.789
3300	60.571	297.869	248.647	162.434	130.584	108.943	−1.724
3400	60.669	299.679	250.121	168.496	129.687	108.301	−1.664
3500	60.760	301.439	251.562	174.568	128.778	107.685	−1.607
3600	60.843	303.152	252.972	180.648	127.859	107.095	−1.554
3700	60.921	304.820	254.351	186.737	126.927	106.531	−1.504
3800	60.992	306.446	255.700	192.832	125.984	105.993	−1.457
3900	61.059	308.031	257.022	198.935	125.028	105.479	−1.413
4000	61.120	309.577	258.316	205.044	124.060	104.990	−1.371
4100	61.178	311.087	259.585	211.159	123.079	104.526	−1.332
4200	61.232	312.562	260.829	217.279	−357.764	111.109	−1.382
4300	61.282	314.004	262.049	223.405	−357.684	122.272	−1.485
4400	61.329	315.413	263.246	229.536	−357.618	133.433	−1.584
4500	61.373	316.792	264.420	235.671	−357.568	144.593	−1.678
4600	61.414	318.141	265.574	241.810	−357.533	155.751	−1.769
4700	61.452	319.462	266.706	247.953	−357.513	166.909	−1.855
4800	61.489	320.756	267.819	254.100	−357.509	178.068	−1.938
4900	61.523	322.025	268.912	260.251	−357.521	189.225	−2.017
5000	61.555	323.268	269.987	266.405	−357.548	200.384	−2.093
5100	61.586	324.487	271.044	272.562	−357.591	211.542	−2.167
5200	61.614	325.683	272.083	278.722	−357.650	222.703	−2.237
5300	61.642	326.857	273.105	284.885	−357.724	233.864	−2.305
5400	61.667	328.010	274.112	291.050	−357.813	245.027	−2.370
5500	61.692	329.141	275.102	297.218	−357.917	256.191	−2.433
5600	61.715	330.253	276.077	303.389	−358.036	267.358	−2.494
5700	61.737	331.346	277.037	309.561	−358.169	278.527	−2.552
5800	61.758	332.420	277.982	315.736	−358.316	289.699	−2.609
5900	61.778	333.476	278.914	321.913	−358.476	300.872	−2.664
6000	61.796	334.514	279.832	328.091	−358.649	312.049	−2.717

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [249.02]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-470 \pm 15]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-477 \pm 15]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[2500](1)	[750](1)	[1300](1)
[1150](1)	[460](1)	[1000](1)
[1100](1)	[3000](1)	[450](1)

Ground State Quantum Weight: [2] $\sigma = 2$

Point Group: [C_{2h}]

Bond Distances: B–O = [1.27] Å; O–H = [0.97] Å

Bond Angles: H–O–B = [105]°; O–B–O = [180]°

Product of the Moments of Inertia: $I_A I_B I_C = [24.2754 \times 10^{-117}]\ g^3·cm^6$

Enthalpy of Formation

The value of $\Delta_f H°(B(OH)_2, g, 298.15\ K)$ was calculated by using the bond energy, $D°_0(B–OH) = 132.7\ kcal·mol^{-1}$, and the enthalpies of formation for B(g) and OH(g) as 132.80 and 9.33 $kcal·mol^{-1}$, respectively.

Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with those for $BO_2(g)$, $B(OH)_3(g)$ and other related molecules. The bond distances and angles were estimated by comparison with those for $BO_2(g)$ and $H_2O_2(g)$ molecules. The molecular configuration is assumed to be trans which is considered as more stable than the cis–form. The principal moments of inertia are: $I_A = 0.2688 \times 10^{-39}$, $I_B = 9.3699 \times 10^{-39}$, and $I_C = 9.6387 \times 10^{-39}\ g·cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.772	−470.383	−470.383	INFINITE
100	34.306	204.305	288.605	−8.430	−472.969	−465.966	243.395
200	42.381	230.309	253.468	−4.632	−475.109	−458.108	119.645
250	47.278	240.289	249.853	−2.391	−476.093	−453.742	94.804
298.15	52.015	249.023	249.023	.000	−476.976	−449.356	78.725
300	52.195	249.345	249.024	.096	−477.008	−449.185	78.210
350	56.883	257.747	249.677	2.825	−477.833	−444.481	66.335
400	61.190	265.629	251.183	5.778	−478.566	−439.665	57.414
450	65.065	273.064	253.205	8.936	−479.213	−434.763	50.466
500	68.519	280.102	255.546	12.278	−479.779	−429.793	44.900
600	74.344	293.129	260.743	19.432	−480.695	−419.705	36.539
700	79.038	304.954	266.227	27.109	−481.365	−409.484	30.556
800	82.894	315.768	271.753	35.212	−481.835	−399.181	26.064
900	86.106	325.723	277.204	43.666	−482.142	−388.829	22.567
1000	88.805	334.938	282.523	52.416	−482.321	−378.451	19.768
1100	91.088	343.513	287.682	61.414	−482.401	−368.059	17.478
1200	93.028	351.524	292.672	70.622	−482.408	−357.663	15.569
1300	94.683	359.037	297.491	80.010	−482.366	−347.269	13.953
1400	96.102	366.107	302.142	89.551	−482.292	−336.880	12.569
1500	97.324	372.780	306.631	99.224	−482.203	−326.497	11.370
1600	98.380	379.096	310.965	109.010	−482.111	−316.119	10.320
1700	99.298	385.088	315.150	118.895	−482.028	−305.747	9.394
1800	100.098	390.787	319.195	128.866	−481.961	−295.380	8.572
1900	100.800	396.218	323.107	138.911	−481.920	−285.016	7.836
2000	101.417	401.405	326.893	149.023	−481.908	−274.653	7.173
2100	101.962	406.366	330.560	159.192	−481.932	−264.290	6.574
2200	102.445	411.121	334.115	169.413	−481.995	−253.924	6.029
2300	102.876	415.685	337.563	179.680	−482.101	−243.555	5.531
2400	103.260	420.071	340.910	189.987	−532.512	−232.112	5.052
2500	103.605	424.294	344.161	200.330	−532.788	−219.590	4.588
2600	103.915	428.363	347.322	210.707	−533.081	−207.056	4.160
2700	104.195	432.290	350.397	221.112	−533.392	−194.510	3.763
2800	104.448	436.084	353.390	231.545	−533.721	−181.953	3.394
2900	104.678	439.754	356.305	242.001	−534.071	−169.384	3.051
3000	104.887	443.306	359.146	252.480	−534.442	−156.802	2.730
3100	105.078	446.748	361.917	262.978	−534.834	−144.208	2.430
3200	105.253	450.087	364.620	273.495	−535.248	−131.601	2.148
3300	105.413	453.328	367.259	284.028	−535.684	−118.980	1.883
3400	105.560	456.478	369.837	294.577	−536.143	−106.346	1.634
3500	105.696	459.540	372.357	305.140	−536.623	−93.698	1.398
3600	105.821	462.519	374.820	315.716	−537.127	−81.036	1.176
3700	105.937	465.420	377.230	326.304	−537.652	−68.360	.965
3800	106.044	468.246	379.588	336.903	−538.201	−55.668	.765
3900	106.143	471.002	381.897	347.512	−538.772	−42.962	.575
4000	106.236	473.691	384.158	358.131	−539.366	−30.242	.395
4100	106.322	476.315	386.374	368.759	−539.982	−17.506	.223
4200	106.402	478.878	388.546	379.395	−1020.471	2.269	−.028
4300	106.477	481.383	390.676	390.039	−1020.046	26.615	−.323
4400	106.547	483.831	392.765	400.691	−1019.646	50.951	−.605
4500	106.613	486.227	394.816	411.349	−1019.270	75.278	−.874
4600	106.674	488.570	396.828	422.013	−1018.920	99.597	−1.131
4700	106.732	490.865	398.805	432.683	−1018.596	123.909	−1.377
4800	106.787	493.113	400.746	443.359	−1018.298	148.215	−1.613
4900	106.838	495.315	402.654	454.041	−1018.027	172.515	−1.839
5000	106.886	497.474	404.529	464.727	−1017.783	196.809	−2.056
5100	106.932	499.591	406.372	475.418	−1017.567	221.099	−2.265
5200	106.975	501.668	408.185	486.113	−1017.378	245.384	−2.465
5300	107.016	503.706	409.968	496.813	−1017.218	269.667	−2.658
5400	107.054	505.707	411.722	507.516	−1017.088	293.946	−2.843
5500	107.091	507.672	413.449	518.223	−1016.987	318.223	−3.022
5600	107.125	509.601	415.149	528.934	−1016.916	342.500	−3.195
5700	107.158	511.498	416.823	539.648	−1016.877	366.774	−3.361
5800	107.189	513.362	418.471	550.366	−1016.869	391.050	−3.522
5900	107.219	515.194	420.095	561.086	−1016.893	415.322	−3.677
6000	107.247	516.997	421.695	571.810	−1016.949	439.598	−3.827

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [187.88] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 110.5 \pm 10\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 106.7 \pm 10\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[2384](1)	[802](1)
[1765](2)	[2976](2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: [D_{3h}]
Bond Distance: B–H = [1.16] Å
Bond Angle: H–B–H = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = 7.71122 \times 10^{-119}$] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from appearance potentials by Fehlner and Koski.[1] For example:

$B_2H_6(g) \rightarrow BH_3^+(ion) + BH_3(g)$	13.1 eV
$BH_3^+(ion) \rightarrow BH_3(g)$	−11.4 eV
$B_2H_6(g) \rightarrow 2\ BH_3(g)$	1.7 eV

The enthalpy of formation data is summarized below.

Reaction: $B_2H_6(g) \rightarrow 2\ BH_3(g)$*

*The auxiliary $\Delta_f H°(B_2H_6, g, 298.15\ K)$ was from the JANAF table dated December 31, 1964.

Source	Method	$\Delta_f H°(0\ K)$, $kcal·mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$*
[2]	Bond energy parameters obtained by linear extrapolation from NH and CH bonds	69.9	41.7
[3]	Apparent equilibrium constants	55 ± 8	33
[3]	A recalculation by JANAF using α values and $P = 10^{-7}$ atm [α = degree of dissociation)	49 ± 8	30
[4]	Correlations of ionization and dissociation energies of hydrides and fluorides in relation to electronic structure	41.5	26.6
[1]	Appearance potentials	39.2	25.5
[5]	From kinetic data for the decomposition of BH_3CO	32–38	22–25
[6]	From calorimetric measurements of analogous compounds	28.4 ± 2	20.1
[7]	From electronegativities	23.9	18

Heat Capacity and Entropy

The molecular configuration, [planar, H–B–H angle 120°], was estimated by Shepp and Bauer[8] as well as by Jordan and Longuet Higgins.[2] In addition, Shepp and Bauer estimated the bond distance and the vibrational frequencies. Jordan and Longuet Higgins estimated the electronic configuration [$^1A_1$]. The principal moments of inertia are: $I_A = I_B = 0.3378 \times 10^{-39}$ and $I_C = 0.6757 \times 10^{-39}$ $g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.129	110.478	110.478	INFINITE
100	33.268	150.652	218.682	−6.803	109.281	109.356	−57.122
200	34.135	173.880	191.116	−3.447	108.263	109.795	−28.675
250	35.114	181.598	188.466	−1.717	107.528	110.259	−23.037
298.15	36.221	187.876	187.876	0.	106.692	110.859	−19.422
300	36.266	188.100	187.876	0.067	106.658	110.885	−19.307
350	37.539	193.784	188.323	1.912	105.702	111.665	−16.665
400	38.929	198.886	189.329	3.823	104.692	112.585	−14.702
450	40.434	203.557	190.654	5.806	103.658	113.633	−13.190
500	42.038	207.900	192.164	7.868	102.622	114.797	−11.993
600	45.449	215.863	195.462	12.241	100.620	117.423	−10.223
700	48.945	223.132	198.902	16.961	98.778	120.371	−8.982
800	52.339	229.891	202.358	22.026	97.132	123.571	−8.068
900	55.510	236.241	205.774	27.421	95.683	126.964	−7.369
1000	58.397	242.242	209.123	33.119	94.413	130.510	−6.817
1100	60.980	247.931	212.395	39.090	93.296	134.175	−6.371
1200	63.268	253.337	215.583	45.305	92.305	137.935	−6.004
1300	65.282	258.483	218.687	51.735	91.412	141.775	−5.697
1400	67.049	263.387	221.706	58.353	90.594	145.680	−5.435
1500	68.599	268.067	224.642	65.137	89.832	149.642	−5.211
1600	69.959	272.538	227.497	72.066	89.108	153.653	−5.016
1700	71.153	276.816	230.273	79.123	88.409	157.708	−4.846
1800	72.206	280.914	232.973	86.292	87.722	161.804	−4.695
1900	73.135	284.843	235.601	93.560	87.040	165.939	−4.562
2000	73.959	288.616	238.158	100.916	86.353	170.109	−4.443
2100	74.690	292.242	240.647	108.349	85.655	174.314	−4.336
2200	75.342	295.732	243.072	115.851	84.942	178.552	−4.239
2300	75.925	299.094	245.435	123.415	84.209	182.824	−4.152
2400	76.447	302.337	247.739	131.034	33.193	188.196	−4.096
2500	76.917	305.467	249.986	138.703	32.331	194.673	−4.067
2600	77.341	308.492	252.178	146.416	31.473	201.183	−4.042
2700	77.725	311.419	254.319	154.170	30.615	207.727	−4.019
2800	78.073	314.252	256.409	161.960	29.756	214.302	−3.998
2900	78.389	316.997	258.451	169.783	28.894	220.908	−3.979
3000	78.677	319.659	260.447	177.637	28.026	227.544	−3.962
3100	78.941	322.244	262.399	185.518	27.153	234.209	−3.946
3200	79.183	324.754	264.309	193.424	26.271	240.902	−3.932
3300	79.404	327.194	266.177	201.354	25.380	247.624	−3.920
3400	79.608	329.567	268.007	209.305	24.480	254.372	−3.908
3500	79.796	331.878	269.799	217.275	23.568	261.146	−3.897
3600	79.970	334.128	271.555	225.263	22.644	267.947	−3.888
3700	80.131	336.321	273.276	233.269	21.707	274.774	−3.879
3800	80.280	338.460	274.963	241.289	20.756	281.627	−3.871
3900	80.418	340.547	276.618	249.324	19.791	288.504	−3.864
4000	80.547	342.585	278.242	257.372	18.811	295.407	−3.858
4100	80.667	344.575	279.836	265.433	17.816	302.334	−3.852
4200	80.779	346.521	281.400	273.506	−463.045	316.310	−3.934
4300	80.884	348.423	282.937	281.589	−462.986	334.865	−4.068
4400	80.982	350.283	284.446	289.682	−462.945	353.419	−4.196
4500	81.073	352.104	285.930	297.785	−462.924	371.973	−4.318
4600	81.160	353.887	287.388	305.897	−462.921	390.526	−4.435
4700	81.240	355.633	288.821	314.017	−462.939	409.079	−4.546
4800	81.317	357.345	290.231	322.145	−462.976	427.634	−4.654
4900	81.388	359.022	291.618	330.280	−463.033	446.188	−4.756
5000	81.456	360.667	292.983	338.422	−463.109	464.745	−4.855
5100	81.520	362.281	294.326	346.571	−463.206	483.302	−4.950
5200	81.580	363.864	295.648	354.726	−463.322	501.863	−5.041
5300	81.637	365.419	296.950	362.887	−463.457	520.425	−5.129
5400	81.691	366.945	298.232	371.053	−463.611	538.990	−5.214
5500	81.742	368.445	299.495	379.225	−463.783	557.558	−5.295
5600	81.791	369.918	300.739	387.401	−463.973	576.130	−5.374
5700	81.837	371.366	301.965	395.583	−464.181	594.705	−5.450
5800	81.880	372.790	303.174	403.769	−464.404	613.284	−5.523
5900	81.922	374.190	304.366	411.959	−464.644	631.866	−5.594
6000	81.962	375.567	305.541	420.153	−464.898	650.453	−5.663

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 88.74 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 444.1 \pm 0.2\ K$
$T_{dcm} = [330\ K]$

$\Delta_f H°(0\ K) = -1080 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1094 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

The enthalpy of formation of $\Delta_f H°(H_3BO_3, cr, 298.15\ K)$ was taken from Good and Mansson *et al.*[1] The value was derived based on the following measurements.

	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}
$B(cr) + 0.75\ O_2(g) + 18.674\ HF \cdot 57.219\ H_2O(l) = HBF_4 \cdot 14.674\ HF \cdot 58.719\ H_2O(l)$	-173.4 ± 0.2
$H_3BO_3(cr) + 18.674\ HF \cdot 55.719\ H_2O(l) = HBF_4 \cdot 14.674\ HF \cdot 58.719\ H_2O(l)$	$+14.6 \pm 0.1$

The enthalpy of solution of H_3BO_3(cr) in water have been measured by many investigators. Fasolino[2] obtained the value, $\Delta_r H°(298.15\ K) = 5.45 \pm 0.01$ kcal·mol^{-1} for the reaction $H_3BO_3(cr) + 504\ H_2O(l) = H_3BO_3 504\ H_2O(sol)$ which leads to $\Delta_f H°(H_3BO_3 504\ H_2O, sol, 298.15\ K) = -256.02$ kcal·mol^{-1}. The $\Delta_r H°(298.15\ K)$ value is in reasonable agreement with the value reported by Smisko and Mason[3] in which the enthalpies of solution and dilution of H_3BO_3(cr) were given. The enthalpies of solution of H_3BO_3(cr) in water measured y other previous investigators were reviewed by Fasolino.[2]

Heat Capacity and Entropy

The low temperature (16–298.15 K) heat capacities were reported by Johnston and Kerr.[5] The heat capacities above 300 K were estimated with those of its constituent oxides. $S°(298.15\ K)$ was obtained from Johnston and Kerr using $S°(17\ K) = 0.18$ kcal·mol^{-1}.

Fusion Data

The value of T_{fus} was taken from Kracek and Morey *et al.*[6] However, H_3BO_3(cr) is in a metastable state at T_{fus}. Measurements of the decomposition pressure of H_3BO_3(cr) to form HBO_2(cr, II or III) and H_2O(g) have been made by Menzel, Schulz and Deckert,[7] Thiel and Stiebeneck,[8] Stackelberg, Quatran and Dressel,[9] and Bezzi and Hazaki.[10] The decomposition pressures of the system $H_3BO_3(cr) = H_2O(g) + HBO_2$(cr, I), at the temperatures of 312 to 352 K, have been reported by West.[11]

Decomposition Data

The decomposition temperature (T_{dcm}) is calculated as the temperature at which the Gibbs energy change of the reaction $H_3BO_3(cr) \rightarrow HBO_2(cr) + H_2O(g)$ is zero.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K)$, is derived as the difference between the $\Delta_f H°(298.15\ K)$ values for H_3BO_3(g) and H_3BO_3(cr).

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[9] Z. Bezzi, Gass. chim. ital. **65**, 766 (1935).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−13.393	−1080.444	−1080.444	INFINITE
100	35.920	28.983	145.340	−11.636	−1087.566	−1049.328	548.113
200	58.743	61.128	95.458	−6.866	−1091.537	−1009.409	263.631
298.15	81.337	88.743	88.743	0.	−1093.990	−968.520	169.681
300	81.755	89.247	88.744	0.151	−1094.022	−967.741	168.499
400	100.207	115.390	92.184	9.282	−1095.069	−925.455	120.852
500	114.642	139.336	99.255	20.041	−1095.014	−883.037	92.250
600	127.194	161.372	107.795	32.146	−1094.023	−840.720	73.191
700	137.915	181.802	116.926	45.413	−1092.200	−798.636	59.595
800	147.277	200.844	126.239	59.684	−1089.646	−756.865	49.418
900	155.017	218.646	135.529	74.806	−1086.476	−715.452	41.524
1000	161.921	235.343	144.684	90.659	−1082.783	−674.421	35.228
1100	167.974	251.066	153.647	107.161	−1078.633	−633.781	30.096
1200	173.218	265.913	162.390	124.227	−1074.097	−593.538	25.836
1300	177.653	279.958	170.898	141.778	−1069.244	−553.686	22.247
1400	181.279	293.261	179.168	159.731	−1064.147	−514.218	19.186
1500	184.096	305.869	187.198	178.006	−1058.879	−475.121	16.545

PREVIOUS: September 1962 CURRENT: December 1964

$S°$(298.15 K) = [295.237] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = Unknown
$\Delta_f H°$(298.15 K) = −992.28 ± 2.5 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3250(1)	Rotation	1185(2)
1060(1)	3150(2)	Rotation
861(1)	1440(2)	Rotation
652(1)	544(2)	

Ground State Quantum Weight: 1 σ = 3
Point Group: C_{3h}
Bond Distances: B-O = [1.36] Å; O-H = [0.96] Å
Bond Angles: H-O-B = [114]°; O-B-O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.157449 × 10^{-114}] g^3·cm^6

Enthalpy of Formation

The vapor pressures of H_3BO_3(cr), 109–140°C, were measured by Stackelberg, Quatram and Dressel.[1] Using the vapor pressures reported, the enthalpies of sublimation of H_3BO_3(cr) were evaluated to be 24.4 ± 0.6 and 24.22 kcal·mol^{-1} by the 2nd and 3rd law methods, respectively. $\Delta_f H°(H_3BO_3, g, 298.15\ K)$ was calculated from the $\Delta_f H°(H_3BO_3, cr, 298.15\ K)$ and $\Delta_{sub} H°(H_3BO_3, cr, 298.15\ K)$. The $\Delta_{sub} H°$(298.15 K) value adopted is the average of the 2nd and 3rd law values mentioned previously.

Heat Capacity and Entropy

The molecular structure and constants were taken from Pistorius[2] based on an x-ray diffraction study on H_3BO_3(cr) by Zachariasen.[2] The O-H bond distance was reestimated as 0.96 Å instead of 0.88 Å reported. From the existing infrared and Raman spectra data on H_3BO_3(cr) and its aqueous solution, Pistorius carried out a normal coordinate treatment by means of Wilson's F-G matrix method and calculated the fifteen fundamental frequencies for H_3BO_3(cr). For H_3BO_3(g), twelve reported frequencies were used and corrected to the average isotopic species. The three torsional frequencies, 824(1) and 209(2) cm^{-1}, were not used based on an assumption that there are three internal rotations, i.e. three OH groups, each rotates about its own B-O bond. Employing the model of having three free rotating OH tops, the value of $S°$(400 K) was evaluated statistically as 75.522 kcal mol^{-1}. The corresponding value obtained by using the 2nd law value of $\Delta_{sub} H°$(400 K), 48.39 ± 1.42 kcal·mol^{-1}, for the reaction H_3BO_3(g), is 75.97 ± 1.43 kcal·mol^{-1} which is in good agreement with the $S°$(400 K) value based on a model having three free rotating groups. Thus the assumed model is adopted to evaluate the thermodynamic functions. The reduced moment of inertia for the OH top is I_r = 1.15321 × 10^{-40} g cm^2 . The principal moments of inertia are: $I_A = I_B$ = 8.3334 × 10^{-39} and I_C = 16.6669 × 10^{-39} g·cm^2. The infrared absorption spectrum of H_3BO_3(g) was observed under conditions where one atmosphere of water vapor with a path length of approximately one meter as background, by Greene, Leroi, Randall *et al.*[4] The following fundamentals were obtained: 3220 cm^{-1} S, 1490 cm^{-1} S, 1199 cm^{-1} S, 881 cm^{-1} W, and 669 cm^{-1} W.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	12.472	0.	INFINITE	−15.356	−980.694	−980.694	INFINITE
100	46.202	237.715	345.491	−10.778	−984.995	−967.630	505.438
200	53.861	271.626	300.833	−5.841	−988.799	−948.771	247.794
250	59.585	284.250	296.280	−3.007	−990.617	−938.553	196.100
298.15	65.338	295.237	295.237	0.	−992.277	−928.373	162.647
300	65.558	295.642	295.238	0.121	−992.339	−927.976	161.575
350	71.395	306.189	296.058	3.546	−993.930	−917.121	136.873
400	76.864	316.085	297.949	7.254	−995.384	−906.048	118.318
450	81.857	325.431	300.488	11.224	−996.708	−894.800	103.866
500	86.355	334.293	303.429	15.432	−997.910	−883.411	92.289
600	94.017	350.739	309.966	24.464	−999.992	−860.309	74.897
700	100.271	365.717	316.876	34.188	−1001.711	−836.888	62.449
800	105.498	379.457	323.852	44.484	−1003.133	−813.242	53.099
900	109.953	392.147	330.744	55.262	−1004.306	−789.433	45.818
1000	113.798	403.935	337.481	66.454	−1005.275	−765.505	39.986
1100	117.137	414.942	344.028	78.005	−1006.076	−741.487	35.210
1200	120.047	425.262	350.372	89.868	−1006.743	−717.404	31.228
1300	122.589	434.973	356.510	102.002	−1007.306	−693.269	27.856
1400	124.814	444.141	362.445	114.375	−1007.789	−669.093	24.964
1500	126.764	452.821	368.183	126.956	−1008.217	−644.886	22.457
1600	128.478	461.058	373.733	139.720	−1008.607	−620.651	20.262
1700	129.988	468.893	379.102	152.645	−1008.976	−596.392	18.325
1800	131.321	476.361	384.299	165.711	−1009.338	−572.113	16.602
1900	132.501	483.494	389.334	178.904	−1009.706	−547.812	15.060
2000	133.550	490.317	394.214	192.207	−1010.089	−523.492	13.672
2100	134.484	496.856	398.947	205.610	−1010.495	−499.152	12.416
2200	135.319	503.132	403.541	219.101	−1010.932	−474.792	11.273
2300	136.067	509.164	408.003	232.671	−1011.405	−450.412	10.229
2400	136.740	514.969	412.340	246.312	−1062.178	−424.942	9.249
2500	137.346	520.564	416.557	260.017	−1062.816	−398.377	8.324
2600	137.893	525.962	420.662	273.779	−1063.470	−371.787	7.469
2700	138.390	531.175	424.659	287.594	−1064.142	−345.170	6.678
2800	138.841	536.216	428.554	301.456	−1064.836	−318.529	5.942
2900	139.251	541.096	432.351	315.360	−1065.553	−291.863	5.257
3000	139.626	545.823	436.055	329.305	−1066.296	−265.171	4.617
3100	139.970	550.407	439.670	343.285	−1067.064	−238.454	4.018
3200	140.284	554.856	443.200	357.298	−1067.860	−211.713	3.456
3300	140.574	559.177	446.650	371.341	−1068.683	−184.946	2.927
3400	140.840	563.378	450.021	385.412	−1069.535	−158.153	2.430
3500	141.086	567.464	453.319	399.508	−1070.417	−131.335	1.960
3600	141.313	571.442	456.545	413.628	−1071.328	−104.491	1.516
3700	141.524	575.316	459.703	427.770	−1072.269	−77.622	1.096
3800	141.719	579.093	462.795	441.932	−1073.241	−50.726	0.697
3900	141.901	582.777	465.825	456.114	−1074.243	−23.804	0.319
4000	142.070	586.372	468.794	470.312	−1075.276	3.142	−0.041
4100	142.227	589.882	471.704	484.527	−1076.340	30.116	−0.384
4200	142.374	593.311	474.559	498.757	−1557.285	64.140	−0.798
4300	142.512	596.663	477.360	513.002	−1557.325	102.747	−1.248
4400	142.641	599.940	480.109	527.259	−1557.399	141.353	−1.678
4500	142.762	603.147	482.807	541.530	−1557.507	179.961	−2.089
4600	142.875	606.286	485.458	555.812	−1557.650	218.573	−2.482
4700	142.982	609.360	488.061	570.104	−1557.828	257.189	−2.858
4800	143.082	612.371	490.620	584.408	−1558.042	295.809	−3.219
4900	143.176	615.323	493.135	598.721	−1558.293	334.434	−3.565
5000	143.266	618.216	495.608	613.043	−1558.581	373.064	−3.897
5100	143.350	621.054	498.040	627.374	−1558.907	411.700	−4.217
5200	143.429	623.838	500.432	641.713	−1559.272	450.342	−4.524
5300	143.505	626.571	502.786	656.059	−1559.675	488.993	−4.819
5400	143.576	629.254	505.104	670.413	−1560.119	527.651	−5.104
5500	143.643	631.889	507.385	684.774	−1560.604	566.317	−5.378
5600	143.707	634.478	509.631	699.142	−1561.130	604.994	−5.643
5700	143.768	637.022	511.844	713.516	−1561.698	643.679	−5.899
5800	143.826	639.523	514.024	727.895	−1562.309	682.377	−6.145
5900	143.881	641.982	516.172	742.281	−1562.964	721.081	−6.384
6000	143.934	644.401	518.289	756.672	−1563.664	759.801	−6.615

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 106.61\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -218.19 \pm 2.30\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -226.90 \pm 2.30\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction of KBH_4(cr) with hydrochloric acid has been measured by solution calorimetry and reported by Johnson, Schumm, Wilson, and Prosen.[4]

$$KBH_4(cr) + HCl(g) + 3H_2O(l) \rightarrow KCl(cr) + H_3BO_3(cr) + 4H_2(g)\ \Delta_r H° = -84.62 \pm 0.44\ kcal·mol^{-1}$$

The $\Delta_f H$(298.15 K) values for HCl(g) and H_3BO_3(cr) were obtained from the JANAF Tables. The $\Delta_f H°$(298.15 K) value for KCl(cr) was calculated from $\Delta_f H°(K^+, aq, \infty, 298.15\ K) = -60.32\ kcal·mol^{-1}$, $\Delta_f H°(Cl^-, aq, \infty, 298.15\ K) = -39.952\ kcal·mol^{-1}$ and $\Delta_{dil} H° = 4.12\ kcal·mol^{-1}$ obtained by Evans.[4] $\Delta_f H°$(298.15 K) for H_2O(l) was obtained from Evans.[4] Unpublished data of The Dow Chemical Company Thermal laboratory give a value of $\Delta_f H°(298.15\ K) = -55.0 \pm 1.0\ kcal·mol^{-1}$ by solution calorimetry.

Heat Capacity and Entropy

C_p and $S°$ at temperatures below 298.15 K were reported by Furukawa, Reilly, and Henning.[2] The values of C_p in the range from 298.15 to 700 K were obtained from Douglas and Harman.[3] These two sets of C_p data were plotted and joined smoothly at 298.15 K. The values of C_p above 700 K are estimated by graphical extrapolation.

Decomposition Data

The temperature of decomposition (into constituent elements) was estimated to be 770 K, according to a report by Douglas and Harman.[3]

References

[1]W. H. Johnson, R. H. Schumm, I. H. Wilson, and E. J. Prosen, J. Res. Nat. Bur. Stand. **65A**, 97 (1961).
[2]G. T. Furukawa, M. L. Reilly, and J. M. Henning, J. Res. Nat. Bur. Stand. **68A**, 651 (1964).
[3]T. B. Douglas and A. W. Harman, J. Res. Nat. Bur. Stand. **60**, 117 (1958).
[4]W. H. Evans, U. S. Nat. Bur. Stand. Report 8504, Appendix III, 164 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.523	−218.190	−218.190	INFINITE
100	43.388	32.560	176.531	−14.397	−223.820	−203.339	106.213
200	73.580	72.530	114.809	−8.456	−226.193	−181.752	47.469
298.15	96.571	106.608	106.608	0.	−226.898	−159.738	27.986
300	96.734	107.206	106.610	0.179	−226.902	−159.322	27.740
400	100.918	135.797	110.480	10.127	−229.606	−136.305	17.800
500	102.131	158.434	117.887	20.273	−230.144	−112.920	11.797
600	106.033	177.333	126.258	30.645	−230.651	−89.424	7.785
700	115.227	194.306	134.780	41.668	−230.655	−65.874	4.916
800	118.407	209.909	143.213	53.356	−230.132	−42.368	2.766
900	120.625	223.988	151.419	65.312	−229.490	−18.935	1.099
1000	122.340	236.790	159.326	77.464	−228.820	4.424	−0.231
1100	123.386	248.501	166.908	89.752	−307.159	32.327	−1.535
1200	124.265	259.276	174.162	102.136	−305.599	63.120	−2.748
1300	124.919	269.248	181.098	114.596	−304.101	93.786	−3.768
1400	125.520	278.528	187.730	127.118	−302.676	124.339	−4.639
1500	126.060	287.207	194.075	139.697	−301.326	154.792	−5.390
1600	126.566	295.359	200.153	152.329	−300.054	185.158	−6.045
1700	127.037	303.046	205.982	165.009	−298.859	215.447	−6.620
1800	127.473	310.320	211.578	177.735	−297.741	245.667	−7.129
1900	127.873	317.223	216.958	190.503	−296.700	275.828	−7.583
2000	128.240	323.791	222.137	203.309	−295.735	305.936	−7.990

PREVIOUS: March 1963 CURRENT: December 1964

$S°(298.15\ K) = 75.82\ J·K^{-1}·mol^{-1}$
T_{fus} = [750] K

$\Delta_f H°(0\ K) = -180.391 \pm 0.21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -190.464 \pm 0.21\ kJ·mol^{-1}$
$\Delta_{fus}H°$ = Unknown

Enthalpy of Formation

The enthalpy of formation of LiBH4(cr) was calculated from the solution calorimetry of Davis, Mason and Stegeman.[1] The enthalpies of reaction were measured for the following reactions:

$LiBH_4(cr) + 1.25(HCl·200\ H_2O) + 3\ H_2O(l) \rightarrow (NaCl + H_3BO_3 + 0.25\ HCl)247\ H_2O + 4\ H_2(g)$ $\Delta H_1(298.15\ K) = -72.14\ kcal\ mol^{-1}$

$LiCl·60\ H_2O + H_3BO_3·60\ H_2O + 0.25(HCl·506\ H_2O) \rightarrow (LiCl + H_3BO_3 + 0.25\ HCl)·247\ H_2O$ $\Delta H_2(298.15\ K) = 0.00\ kcal\ mol^{-1}$ (assumed)

$H_3BO_3·60\ H_2O + \infty\ H_2O \rightarrow H_3BO_3·\infty\ H_2O$ $*\Delta H_3(298.15\ K) = 0.200\ kcal\ mol^{-1}$

The summation of the above reactions yields:

$LiBH_4(cr) + 1.25(HCl·200\ H_2O) + 3\ H_2O(l) + \infty\ H_2O \rightarrow LiCl·60\ H_2O + H_3BO_3·\infty\ H_2O + 0.25(HCl·508\ H_2O) + 4\ H_2(g)$ $\Delta H(298.15\ K) = -71.94$

*This $\Delta_f H°(298.15\ K)$ value was obtained from J. Smisko and L. S. Mason loc. cit.

The enthalpy of formation of lithium borohydride crystal was calculated to be −45.522 kcal mol^{-1} with the following auxiliary data:

Compound	$\Delta_f H°(298.15\ K)$	Source
HCl (508 H_2O)	−39.815	HCl(g) JANAF; dilution data from NBS Rept. 8504, 1 July 1964 Appendix III by W. H. Evans
HCl (200 H_2O)	−39.696	HCl(g) JANAF; dilution data fromW. H. Evans, loc. cit.
LiCl (60 H_2O)	−106.023	Li^+ see NaBH4 table; Cl^- and dilution data, W. H. Evans, loc. cit.
H_3BO_3(∞H_2O)	−256.05	JANAF H_3BO_3(cr) and dilution data from J. Smisko and L. S. Mason, J. Am. Chem. Soc. **72**, 3679 (1950).

Heat Capacity and Entropy

The low temperature heat capacities, 15.72–302.88 K, were obtained from the measurements by Hallett and Johnston.[2] The C_p values above 298.15 K were estimated by comparison with the C_p's for $NaBH_4$.

The entropy was based on $S°(15\ K, extrap) = 0.0874\ cal·K^{-1}·mol^{-1}$ reported by Hallett and Johnston.[2]

Fusion Data

T_{fus} was estimated by comparison with the T_{fus} for $NaBH_4$.

References

[1]W. D. Davis, L. S. Mason and G. Stegeman, J. Am. Chem. Soc. **71**, 2775 (1949).
[2]N. C. Hallett and H. L. Johnston, J. Am. Chem. Soc. **75**, 1496 (1953).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.697	−180.391	−180.391	INFINITE
90	30.019	17.086	132.466	−11.538	−185.749	−166.547	86.995
200	59.575	47.990	82.538	−6.910	−188.682	−146.067	38.149
298.15	82.539	75.815	75.815	0.	−190.464	−124.733	21.853
300	82.989	76.326	75.817	0.153	−190.484	−124.325	21.647
400	91.002	101.384	79.181	8.881	−191.531	−102.115	13.335
500	98.282	122.480	85.783	18.349	−195.573	−79.333	8.288
600	105.144	141.037	93.475	28.537	−196.207	−56.016	4.877
700	109.914	157.625	101.476	39.304	−196.396	−32.631	2.435
800	113.052	172.527	109.442	50.468	−196.317	−9.239	0.603
900	114.349	185.920	117.209	61.840	−196.167	14.136	−0.820
1000	115.353	198.020	124.695	73.325	−196.037	37.496	−1.959
1100	116.392	209.064	131.870	84.913	−195.938	60.844	−2.889
1200	117.319	219.232	138.732	96.600	−195.873	84.185	−3.664
1300	118.019	228.650	145.291	108.367	−195.861	107.522	−4.320
1400	118.684	237.421	151.562	120.203	−195.910	130.861	−4.882
1500	119.316	245.631	157.563	132.103	−196.017	154.205	−5.370
1600	119.913	253.351	163.311	144.065	−196.184	177.558	−5.797
1700	120.477	260.638	168.823	156.084	−341.644	208.100	−6.394
1800	121.007	267.539	174.118	168.159	−341.173	240.424	−6.977
1900	121.502	274.095	179.209	180.285	−340.766	272.723	−7.498
2000	121.964	280.339	184.110	192.458	−340.424	305.003	−7.966

PREVIOUS: March 1963 CURRENT: December 1964

$S°(298.15\ K) = 101.39\ J·K^{-1}·mol^{-1}$
$T_{trs} = 189.9\ K$
$T_{fus} = 770\ K$

$\Delta_f H°(0\ K) = -183.3 \pm 0.39\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -191.84 \pm 0.39\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0.999\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy of formation is calculated from the solution calorimetry of Davis, Mason and Stegeman.[1] The enthalpies of reaction and mixing were measured for the following reactions:

$NaBH_4 + 1.25(HCl·200H_2O) \rightarrow (NaCl + H_3BO_3 + 0.25HCl)·247H_2O + 4H_2$ $\Delta_r H = -63.880\ kcal·mol^{-1}$
$NaCl·60H_2O + H_3BO_3·60H_2O \rightarrow (NaCl + H_3BO_3)·120H_2O$ $\Delta_r H = -0.026\ kcal·mol^{-1}$
$NaCl + (H_3BO_3)·120H_2O + 0.25(HCl·508H_2O) \rightarrow (NaCl + H_3BO_3 + 0.25HCl)·247H_2O$ $\Delta_r H = +0.083\ kcal·mol^{-1}$
$H_3BO_3·60H_2O + \infty H_2O \rightarrow H_3BO_3\infty H_2O$ $\Delta_r H = +0.068\ kcal·mol^{-1}$

The summation of the above equations yields:

$NaBH_4(cr) + 1.25(HCl·200H_2O) + 3H_2O(l) + \infty H_2O \rightarrow NaCl·60H_2O + H_3BO_3\infty H_2O + 0.25(HCl·508H_2O) + 4H_2(g)$
$\Delta_r H = -63.869\ kcal·mol^{-1}$

The $\Delta_f H(298.15\ K)$ values for HCl were obtained from JANAF value[5] for HCl(g) and enthalpy of dilution data of Evans.[6] The $\Delta_f H(298.15\ K)$ for $H_2O(l)$ value was obtained from Evans.[6] The $\Delta_f H(298.15\ K)$ value for NaCl was obtained from JANAF value[5] of NaCl(cr) together with dilution data from Evans.[6] The $\Delta_f H(298.15\ K)$ value for H_3BO_3 was obtained from JANAF value[5] for H_3BO_3(cr) together with dilution data of Smisko and Mason.[2]

Heat Capacity And Entropy

The low temperature heat capacity (15.76–301.26 K) was obtained from Johnston and Hallett.[3] In the area of transition (169–193.5 K) the average $\Delta_{trs} H = 635.3\ cal·mol^{-1}$ and the average $\Delta_{trs} S = 3.35\ cal·K^{-1}·mol^{-1}$ were adopted from Johnston and Hallett.[3] Using the present base line these ΔH and ΔS values yield a enthalpy of transition of $0.2388\ kcal·mol^{-1}$. The low temperature heat capacity was fitted with the smoothed enthalpy capacity data (298.15–700 K) of Douglas and Harman.[4] The heat capacity above 700 K was extrapolated from the plot of both sets of data.

Transition Data

The temperature and heat of transition were obtained from Johnston and Hallett.[3]

Fusion Data

The fusion data was obtained from Douglas and Harman.[4]

References

[1]W. D. Davis, L. S. Mason, and G. Stegeman, J. Amer. Chem. Soc. **71**, 2775 (1949).
[2]J. Smisko and L. S. Mason, J. Am. Chem. Soc. **72**, 3679 (1950).
[3]H. L. Johnston and N. C. Hallett, J. Amer. Chem. Soc. **75**, 1467 (1953).
[4]T. B. douglas and A. W. Harman, J. Res. Nat. Bur. Stand. **60**, 117 (1958).
[5]JANAF Thermochemical Tables: HCl(g), 9–30–64; NaCl(cr), 9–30–64; H_3BO_3(cr), 12–31–64.
[6]W. H. Evans, U.S. Nat. Bur. Stand., Report 8504, Appendix III, (1964).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.288	−183.530	−183.530	INFINITE
100	40.158	26.309	172.080	−14.577	−189.180	−169.254	88.409
200	71.446	69.772	108.872	−7.820	−190.599	−148.166	38.697
298.15	86.483	101.387	101.387	0.	−191.836	−127.060	22.260
300	86.642	101.922	101.388	0.160	−191.856	−126.658	22.053
400	94.558	127.958	104.885	9.229	−195.583	−104.556	13.654
500	101.797	149.845	111.743	19.051	−196.439	−81.690	8.534
600	108.617	169.013	119.722	29.575	−196.771	−58.700	5.110
700	115.269	186.259	128.014	40.771	−196.558	−35.697	2.664
800	120.248	201.987	136.293	52.555	−195.870	−12.759	0.833
900	124.265	216.397	144.404	64.793	−194.851	10.071	−0.585
1000	127.445	229.654	152.275	77.379	−193.622	32.776	−1.712
1100	130.039	241.923	159.874	90.253	−192.264	55.351	−2.628
1200	131.754	253.314	167.192	103.346	−287.627	80.239	−3.493
1300	132.675	263.902	174.229	116.575	−285.360	110.802	−4.452
1400	133.135	273.754	180.990	129.869	−283.162	141.193	−5.268
1500	133.302	282.945	187.485	143.191	−281.069	171.431	−5.970
1600	133.428	291.553	193.723	156.528	−279.090	201.532	−6.579
1700	133.511	299.644	199.718	169.875	−277.224	231.513	−7.114
1800	133.553	307.276	205.483	183.228	−275.473	261.388	−7.585
1900	133.679	314.500	211.033	196.589	−273.829	291.168	−8.005
2000	133.888	321.362	216.379	209.966	−272.279	320.864	−8.380

PREVIOUS: December 1960 CURRENT: December 1964

$S°(298.15\ K) = [232.75]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [304 \pm 42]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [305 \pm 42]\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma^+]$	0	[1]

$\omega_e = [600]\ cm^{-1}$ $\omega_e x_e = [3.04]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.3912]\ cm^{-1}$ $\alpha_e = [0.0027]\ cm^{-1}$ $r_e = [2.08]$ Å

Enthalpy of Formation

The ratio, $D_0°(BF)$ / $(\Delta_{at}H°(BF_3, g, 0\ K)/3) = 1.177$, was applied to BI_3 giving $D_0°(BI) = 84.4\ kcal·mol^{-1}$ and $\Delta_f H°(298.15\ K) = 73 \pm 10\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The bond length was first estimated by comparison with the ratio of the bond lengths in the other boron trihalides and monohalides. The vibrational frequency was then calculated using Guggenheimer's Relation[1] which was checked using BBr_3 and shown to give an excellent fit. The quantity $x_e\mu^{1/2}$, where μ is the reduced mass, has been shown to be for similar molecules and its value was transferred from BBr to give x_e and $\omega_e x_e$ for BI. α_e was then calculated using the Morse potential function and B_e was determined from the bond length. The ground state configuration was assumed to be the same as that in BBr.

Reference

[1]E. A. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.113	304.132	304.132	INFINITE
100	29.230	199.010	261.032	−6.202	305.494	288.673	−150.787
200	31.317	219.800	235.754	−3.191	305.706	271.726	−70.967
250	32.566	226.926	233.297	−1.593	305.619	263.238	−55.001
298.15	33.558	232.750	232.750	0.	305.432	255.091	−44.691
300	33.592	232.958	232.751	0.062	305.423	254.779	−44.361
350	34.389	238.198	233.163	1.763	305.090	246.362	−36.767
400	35.002	242.832	234.087	3.498	296.677	238.274	−31.115
450	35.475	246.983	235.294	5.260	295.595	231.038	−26.818
500	35.846	250.741	236.654	7.044	274.394	225.825	−23.592
600	36.381	257.327	239.566	10.657	274.149	216.132	−18.816
700	36.742	262.964	242.515	14.314	273.767	206.491	−15.409
800	37.001	267.888	245.386	18.002	273.282	196.912	−12.857
900	37.197	272.258	248.133	21.712	272.716	187.399	−10.876
1000	37.351	276.186	250.746	25.440	272.080	177.953	−9.295
1100	37.478	279.752	253.223	29.182	271.384	168.573	−8.005
1200	37.586	283.017	255.572	32.935	270.633	159.259	−6.932
1300	37.679	286.030	257.800	36.698	269.826	150.011	−6.028
1400	37.763	288.825	259.918	40.471	268.965	140.826	−5.254
1500	37.839	291.433	261.933	44.251	268.048	131.705	−4.586
1600	37.909	293.877	263.854	48.038	267.070	122.647	−4.004
1700	37.975	296.178	265.688	51.832	266.030	113.652	−3.492
1800	38.037	298.350	267.443	55.633	264.926	104.720	−3.039
1900	38.096	300.408	269.124	59.440	263.756	95.851	−2.635
2000	38.153	302.364	270.738	63.252	262.521	87.046	−2.273
2100	38.208	304.227	272.288	67.070	261.222	78.304	−1.948
2200	38.262	306.005	273.781	70.894	259.863	69.625	−1.653
2300	38.314	307.707	275.219	74.723	258.449	61.009	−1.386
2400	38.365	309.339	276.607	78.557	206.724	53.525	−1.165
2500	38.415	310.906	277.948	82.396	205.136	47.174	−0.986
2600	38.465	312.414	279.245	86.240	203.542	40.888	−0.821
2700	38.514	313.866	280.500	90.089	201.948	34.662	−0.671
2800	38.562	315.268	281.717	93.942	200.358	28.495	−0.532
2900	38.609	316.622	282.897	97.801	198.780	22.385	−0.403
3000	38.657	317.932	284.044	101.664	197.216	16.329	−0.284
3100	38.704	319.200	285.157	105.532	195.673	10.325	−0.174
3200	38.750	320.429	286.240	109.405	194.152	4.370	−0.071
3300	38.797	321.623	287.295	113.282	192.658	−1.537	0.024
3400	38.843	322.781	288.321	117.164	191.192	−7.400	0.114
3500	38.888	323.908	289.322	121.051	189.758	−13.220	0.197
3600	38.934	325.004	290.298	124.942	188.355	−18.999	0.276
3700	38.979	326.072	291.251	128.838	186.986	−24.740	0.349
3800	39.025	327.112	292.181	132.738	185.650	−30.444	0.418
3900	39.070	328.126	293.089	136.642	184.349	−36.114	0.484
4000	39.115	329.116	293.978	140.552	183.082	−41.751	0.545
4100	39.160	330.082	294.847	144.465	181.849	−47.356	0.603
4200	39.204	331.026	295.697	148.384	−299.200	−45.908	0.571
4300	39.249	331.949	296.529	152.306	−299.279	−39.876	0.484
4400	39.293	332.852	297.345	156.233	−299.328	−33.843	0.402
4500	39.338	333.736	298.143	160.165	−299.346	−27.809	0.323
4600	39.382	334.601	298.927	164.101	−299.336	−21.775	0.247
4700	39.427	335.448	299.695	168.041	−299.298	−15.741	0.175
4800	39.471	336.279	300.448	171.986	−299.233	−9.708	0.106
4900	39.515	337.093	301.188	175.936	−299.143	−3.678	0.039
5000	39.559	337.892	301.914	179.889	−299.029	2.351	−0.025
5100	39.603	338.676	302.627	183.847	−298.892	8.377	−0.086
5200	39.647	339.445	303.328	187.810	−298.733	14.401	−0.145
5300	39.691	340.201	304.016	191.777	−298.553	20.421	−0.201
5400	39.735	340.943	304.693	195.748	−298.354	26.437	−0.256
5500	39.779	341.672	305.359	199.724	−298.136	32.450	−0.308
5600	39.823	342.390	306.014	203.704	−297.901	38.459	−0.359
5700	39.867	343.095	306.658	207.689	−297.650	44.463	−0.407
5800	39.911	343.789	307.293	211.677	−297.383	50.463	−0.454
5900	39.955	344.471	307.917	215.671	−297.103	56.457	−0.500
6000	39.999	345.143	308.532	219.668	−296.810	62.448	−0.544

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [309.56]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [245 \pm 63]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [243 \pm 63]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[550](1)
[110](1)
[770](1)

Ground State Quantum Weight: [2] $\sigma = 2$

Point Group: [C_{2v}]

Bond Distance: B–I = [2.06] Å

Bond Angle: I–B–I = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.331449 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation was estimated by analogy with BF_3, specifically the ratio $\Delta_f H°(BX_3 \rightarrow BX_2 + X) / \Delta_f H°(BX_3 \rightarrow B + 3X)$ was taken as 0.347.

Heat Capacity and Entropy

The vibrational frequencies were obtained from force constants transferred from the trihalide given by Herzberg.[1] The bond length was taken between those of the mono and trihalide and the angle was estimated to be the same as that in the trihalides. The ground state quantum weight was taken as two on account of the one unpaired electron.

The principal moments of inertia are: $I_A = 1.8266 \times 10^{-39}$, $I_B = 134.1401 \times 10^{-39}$, and $I_C = 135.9667 \times 10^{-39}\ g·cm^2$.

Reference

[1]G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand, Inc., (1945).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.522	244.562	244.562	INFINITE
100	40.240	261.642	350.181	−8.854	245.156	225.122	−117.592
200	44.749	290.842	313.919	−4.615	244.129	205.436	−53.654
250	47.122	301.087	310.357	−2.318	243.428	195.842	−40.919
298.15	49.083	309.560	309.560	0.	242.672	186.744	−32.717
300	49.151	309.864	309.561	0.091	242.641	186.397	−32.455
350	50.786	317.568	310.165	2.591	241.702	177.094	−26.430
400	52.076	324.437	311.528	5.164	224.713	168.481	−22.001
450	53.089	330.632	313.312	7.794	222.482	161.585	−18.756
500	53.889	336.268	315.330	10.469	180.091	158.739	−16.583
600	55.037	346.202	319.670	15.920	179.806	154.494	−13.450
700	55.796	354.747	324.085	21.464	179.428	150.304	−11.216
800	56.317	362.234	328.395	27.071	178.973	146.173	−9.544
900	56.689	368.890	332.532	32.722	178.452	142.104	−8.247
1000	56.962	374.877	336.472	38.405	177.871	138.096	−7.213
1100	57.168	380.316	340.214	44.112	177.233	134.149	−6.370
1200	57.328	385.298	343.767	49.838	176.537	130.262	−5.670
1300	57.453	389.892	347.140	55.577	175.779	126.436	−5.080
1400	57.554	394.153	350.348	61.327	174.952	122.671	−4.577
1500	57.635	398.127	353.402	67.087	174.050	118.968	−4.143
1600	57.702	401.849	356.315	72.854	173.064	115.327	−3.765
1700	57.758	405.349	359.098	78.627	171.985	111.751	−3.434
1800	57.805	408.651	361.760	84.405	170.808	108.242	−3.141
1900	57.845	411.778	364.311	90.188	169.529	104.800	−2.881
2000	57.880	414.746	366.759	95.974	168.147	101.429	−2.649
2100	57.909	417.571	369.112	101.764	166.666	98.129	−2.441
2200	57.935	420.265	371.376	107.556	165.091	94.902	−2.253
2300	57.957	422.841	373.558	113.350	163.429	91.748	−2.084
2400	57.977	425.308	375.663	119.147	111.432	89.737	−1.953
2500	57.994	427.675	377.697	124.946	109.552	88.872	−1.857
2600	58.010	429.950	379.663	130.746	107.651	88.082	−1.770
2700	58.024	432.140	381.566	136.548	105.741	87.366	−1.690
2800	58.036	434.250	383.410	142.351	103.833	86.720	−1.618
2900	58.047	436.287	385.199	148.155	101.937	86.143	−1.552
3000	58.057	438.255	386.935	153.960	100.064	85.630	−1.491
3100	58.066	440.159	388.621	159.766	98.222	85.179	−1.435
3200	58.074	442.002	390.261	165.573	96.418	84.787	−1.384
3300	58.082	443.789	391.856	171.381	94.657	84.451	−1.337
3400	58.089	445.523	393.409	177.190	92.946	84.168	−1.293
3500	58.095	447.207	394.922	182.999	91.288	83.934	−1.253
3600	58.101	448.844	396.397	188.809	89.685	83.747	−1.215
3700	58.106	450.436	397.836	194.619	88.140	83.603	−1.180
3800	58.111	451.986	399.241	200.430	86.655	83.501	−1.148
3900	58.116	453.495	400.613	206.241	85.229	83.437	−1.118
4000	58.120	454.967	401.953	212.053	83.863	83.408	−1.089
4100	58.124	456.402	403.264	217.865	82.556	83.413	−1.063
4200	58.127	457.802	404.546	223.678	−398.541	90.473	−1.125
4300	58.131	459.170	405.800	229.490	−398.644	102.117	−1.240
4400	58.134	460.507	407.029	235.304	−398.692	113.764	−1.351
4500	58.137	461.813	408.232	241.117	−398.686	125.411	−1.456
4600	58.139	463.091	409.410	246.931	−398.630	137.057	−1.556
4700	58.142	464.341	410.566	252.745	−398.524	148.701	−1.653
4800	58.144	465.565	411.699	258.559	−398.371	160.343	−1.745
4900	58.147	466.764	412.811	264.374	−398.173	171.981	−1.833
5000	58.149	467.939	413.901	270.189	−397.931	183.614	−1.918
5100	58.151	469.091	414.972	276.004	−397.648	195.242	−2.000
5200	58.153	470.220	416.024	281.819	−397.326	206.864	−2.078
5300	58.155	471.328	417.057	287.634	−396.967	218.480	−2.153
5400	58.156	472.415	418.072	293.450	−396.572	230.088	−2.226
5500	58.158	473.482	419.070	299.266	−396.144	241.689	−2.295
5600	58.159	474.530	420.051	305.081	−395.685	253.282	−2.363
5700	58.161	475.559	421.016	310.897	−395.196	264.867	−2.427
5800	58.162	476.571	421.965	316.714	−394.680	276.442	−2.490
5900	58.164	477.565	422.899	322.530	−394.137	288.009	−2.550
6000	58.165	478.542	423.818	328.346	−393.570	299.566	−2.608

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [348.72]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 75 \pm 50\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 71 \pm 50\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
190(1)
339(1)
710(2)
100(2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: B–I = [2.03 ± 0.03] Å
Bond Angle: I–B–I = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.420581 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

Koski *et al.*[2] measured the appearance potential of the B^+ ion from BI_3. Assuming the reaction $BI_3 + e^- \rightarrow B^+ + 3I + 2e^-$, one can calculate the enthalpy of atomization of BI_3 as 8.31 ± 0.5 eV. The analogous reaction for BBr_3 can be checked independently and shows the process to be valid. This value leads to $\Delta_f H°(298.15\ K) = 17.0 \pm 12\ kcal·mol^{-1}$ if the process is assumed to occur at 298.15 K.

Heat Capacity and Entropy

Vibrational frequencies were taken from Wentink and Tiensuu,[1] modified according to the natural abundance of boron. The B–I distance was estimated by Koski *et al.*[2] and the angle was estimated by analogy with the other boron trihalides. The three principal moments of inertia are: $I_A = I_B = 130.2616 \times 10^{-39}$, and $I_C = 260.5232 \times 10^{-39}\ g·cm^2$.

References

[1]T. Wentink and V. H. Tiensuu, J. Chem. Phys. **28**, 826 (1958).
[2]W. S. Koski, J. J. Kaufman, and C. F. Pochuki, J. Am. Chem. Soc. **81**, 1326 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.839	75.300	75.300	INFINITE
100	53.503	281.071	406.863	−12.579	74.961	56.033	−29.269
200	64.157	321.770	355.004	−6.647	73.162	37.779	−9.867
250	67.907	336.504	349.871	−3.342	72.154	29.048	−6.069
298.15	70.787	348.721	348.721	0.	71.128	20.838	−3.651
300	70.884	349.159	348.723	0.131	71.087	20.526	−3.574
350	73.197	360.268	349.595	3.736	69.846	12.193	−1.820
400	74.982	370.163	351.559	7.442	44.578	4.867	−0.636
450	76.365	379.078	354.129	11.227	41.485	0.089	−0.010
500	77.445	387.182	357.035	15.073	−21.816	1.355	−0.142
600	78.984	401.449	363.281	22.901	−21.602	5.967	−0.519
700	79.991	413.705	369.630	30.853	−21.456	10.550	−0.787
800	80.680	424.434	375.824	38.888	−21.372	15.115	−0.987
900	81.169	433.966	381.764	46.982	−21.345	19.674	−1.142
1000	81.527	442.538	387.420	55.118	−21.375	24.233	−1.266
1100	81.798	450.321	392.790	63.284	−21.461	28.797	−1.367
1200	82.006	457.448	397.885	71.475	−21.608	33.372	−1.453
1300	82.170	464.019	402.723	79.684	−21.824	37.962	−1.525
1400	82.301	470.113	407.322	87.908	−22.120	42.572	−1.588
1500	82.407	475.795	411.699	96.144	−22.510	47.206	−1.644
1600	82.495	481.116	415.873	104.389	−23.007	51.869	−1.693
1700	82.568	486.120	419.860	112.642	−23.624	56.567	−1.738
1800	82.629	490.841	423.673	120.902	−24.370	61.305	−1.779
1900	82.681	495.310	427.327	129.168	−25.251	66.088	−1.817
2000	82.726	499.552	430.833	137.438	−26.268	70.921	−1.852
2100	82.765	503.589	434.202	145.713	−27.418	75.808	−1.886
2200	82.798	507.440	437.445	153.991	−28.693	80.753	−1.917
2300	82.827	511.122	440.569	162.272	−30.080	85.759	−1.948
2400	82.853	514.647	443.582	170.556	−81.825	91.895	−2.000
2500	82.875	518.030	446.493	178.843	−83.470	99.167	−2.072
2600	82.896	521.281	449.307	187.131	−85.145	106.506	−2.140
2700	82.914	524.410	452.031	195.422	−86.835	113.909	−2.204
2800	82.930	527.425	454.670	203.714	−88.522	121.375	−2.264
2900	82.944	530.336	457.230	212.007	−90.190	128.901	−2.322
3000	82.957	533.148	459.714	220.303	−91.825	136.484	−2.376
3100	82.969	535.868	462.127	228.599	−93.414	144.121	−2.428
3200	82.980	538.503	464.472	236.896	−94.946	151.807	−2.478
3300	82.989	541.056	466.755	245.195	−96.412	159.541	−2.525
3400	82.998	543.534	468.977	253.494	−97.805	167.319	−2.571
3500	83.007	545.940	471.141	261.794	−99.119	175.136	−2.614
3600	83.014	548.278	473.252	270.095	−100.349	182.989	−2.655
3700	83.021	550.553	475.310	278.397	−101.492	190.876	−2.695
3800	83.027	552.767	477.320	286.700	−102.547	198.792	−2.733
3900	83.033	554.924	479.282	295.003	−103.512	206.735	−2.769
4000	83.039	557.026	481.199	303.306	−104.388	214.701	−2.804
4100	83.044	559.076	483.074	311.610	−105.174	222.688	−2.837
4200	83.048	561.078	484.907	319.915	−585.722	237.718	−2.956
4300	83.053	563.032	486.702	328.220	−585.246	257.318	−3.126
4400	83.057	564.941	488.458	336.526	−584.688	276.906	−3.287
4500	83.061	566.808	490.179	344.831	−584.049	296.481	−3.441
4600	83.064	568.633	491.864	353.138	−583.332	316.040	−3.589
4700	83.068	570.420	493.517	361.444	−582.540	335.583	−3.730
4800	83.071	572.169	495.137	369.751	−581.675	355.109	−3.864
4900	83.074	573.882	496.727	378.058	−580.741	374.616	−3.993
5000	83.077	575.560	498.287	386.366	−579.740	394.102	−4.117
5100	83.079	577.205	499.818	394.674	−578.675	413.569	−4.236
5200	83.082	578.818	501.322	402.982	−577.550	433.014	−4.350
5300	83.084	580.401	502.799	411.290	−576.366	452.436	−4.459
5400	83.086	581.954	504.251	419.599	−575.128	471.836	−4.564
5500	83.088	583.479	505.677	427.907	−573.837	491.213	−4.665
5600	83.090	584.976	507.080	436.216	−572.496	510.566	−4.762
5700	83.092	586.446	508.460	444.525	−571.108	529.894	−4.856
5800	83.094	587.892	509.817	452.835	−569.675	549.197	−4.946
5900	83.096	589.312	511.152	461.144	−568.200	568.475	−5.033
6000	83.097	590.709	512.466	469.454	−566.685	587.728	−5.117

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 79.98 \pm 0.12\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 1220 \pm 3\ K$

$\Delta_f H°(0\ K) = -990.1 \pm 8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -995.0 \pm 8\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = 31.38 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Shartsis and Capps[1] measured the enthalpies of solution in 2N nitric acid of various K_2O–B_2O glass and crystalline mixtures containing 1.1–41.0 mole % of K_2O. When these results are extrapolated to 50 mole %, we obtain $\Delta_{sol}H°$ (25°C) = −11.9 ± 2 kcal·mol^{-1} for KBO_2(cr) + HNO_3(27.75 H_2O, aq) + H_2O(l) → KNO_3(27.75 H_2O, aq) + H_3BO_3(27.75 H_2O, aq) which leads to $\Delta_f H°(KBO_2$, cr, 298.15 K) = −237.8 ± 2 kcal·mol^{-1}, using the following auxiliary data: $\Delta_f H°(HNO_3 \cdot 27.75\ H_2O$, aq) = −256.37 kcal·mol^{-1}.[4] The value, $\Delta_f H°(KBO_2$, cr, 298.15 K) = −237.8 ± 2 kcal·mol^{-1}, is adopted in the tabulation. Since the enthalpies of formation of $LiBO_2$(cr) and $NaBO_2$(cr) derived from the enthalpy of solution data are in good agreement with those values[5] adopted, their enthalpy of solution data should be reasonably reliable, although the calorimetric treatment was loose.

Heat Capacity and Entropy

Paukov *et al.*[6] have measured low temperature heat capacities from 12.11 to 312.22 K in an adiabatic calorimeter. The adopted C_p are derived from their experimental heat capacites by a polynomial curve fitting technique. The derived entropy $S°(298.15\ K)$ is 19.116 ± 0.03 cal·K^{-1}·mol^{-1} based on $S°(12.11\ K) = 0.0353$ cal·K^{-1}·mol^{-1}. Heat capacities above 310 K are estimated by comparison with those of $NaBO_2$(cr)[5] since both $NaBO_2$ and KBO_2 have same type of crystal structure.[7]

Thermal analysis data[8] have been interpreted in terms of a crystal transition at 785°C. Details of these studies are not available and it is not clear how reliable this interpretation is. We note, however, that the reported temperature (785°C) is essentially the same as the eutectic temperature of KBO_2 with $K_2B_4O_7$.[9, 10] We tentatively adopt a single C_p curve without a transition.

Fusion Data

Our analysis of several sets of binary phase data[8, 9, 11–14] yields the enthalpy of fusion, $\Delta_{fus}H° = 7.5 \pm 1$ kcal·mol^{-1}. The adopted melting point (947°C) is a weighted average of the observed data[8–15] which vary from 940 to 950°C.

References

[1] L. Shartsis and W. Capps, J. Amer. Ceram. Soc. **37**, 27 (1954).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, 264 pp. (1968).
[3] The heat of formation of KNO_3(aq) is calculated from JANAF $\Delta_f H°(KNO_3, \infty H_2O$, aq, 298.15 K) = −109.86 kcal·mol^{-1} with the enthalpy of dilution ϕ_L given by V. B. Parker, U. S. Nat. Bur. Stand. NSRDS–NBS 2, 66 pp. (1965).
[4] This value, −256.37 kcal·mol^{-1}, is extrapolated from the enthalpies of formation of $H_3BO_3 \cdot 60\ H_2O$ and $H_3BO_3 \cdot 100\ H_2O$ listed in reference 2.
[5] JANAF Thermochemical Tables: $LiBO_2$(cr) and $NaBO_2$(cr), 6–30–71.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.108	−990.083	−990.083	INFINITE
100	35.012	25.125	130.260	−10.513	−993.150	−974.741	509.152
200	54.095	55.873	85.716	−5.968	−994.444	−955.739	249.613
298.15	67.028	79.981	79.981	0.	−994.955	−936.616	164.091
300	67.237	80.397	79.983	0.124	−994.961	−936.254	163.016
400	76.651	101.079	82.739	7.336	−997.561	−916.196	119.643
500	83.973	118.997	88.238	15.379	−997.415	−895.863	93.590
600	89.830	134.842	94.710	24.079	−996.896	−875.596	76.227
700	94.558	149.054	101.476	33.305	−996.076	−855.441	63.834
800	98.491	161.945	108.241	42.963	−995.014	−835.420	54.547
900	101.755	173.739	114.873	52.980	−993.767	−815.544	47.333
1000	104.474	184.607	121.310	63.297	−992.387	−795.814	41.569
1100	106.525	194.666	127.527	73.853	−1069.889	−771.617	36.641
1200	107.864	204.001	133.516	84.582	−1067.376	−744.612	32.412
1220.0200	107.989	205.785	134.686	86.741	− − − CRYSTAL <− −> LIQUID − − −		
1300	108.575	212.662	139.275	95.403	−1064.859	−717.817	28.842
1400	109.383	220.738	144.809	106.301	−1062.343	−691.216	25.790
1500	110.190	228.312	150.126	117.280	−1059.820	−664.795	23.150
1600	110.997	235.449	155.237	128.339	−1057.284	−638.542	20.846
1700	111.804	242.203	160.156	139.479	−1054.735	−612.449	18.818
1800	112.611	248.616	164.894	150.700	−1052.169	−586.506	17.020
1900	113.417	254.726	169.462	162.001	−1049.588	−560.706	15.415
2000	114.223	260.564	173.873	173.383	−1046.990	−535.043	13.974

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K)$ = [88.455] $J·K^{-1}·mol^{-1}$
T_{fus} = 1220 ± 3 K

$\Delta_f H°(298.15\ K)$ = [−980.730] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 31.38 ± 4.2 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(KBO_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1220\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The constant heat capacity of the liquid is estimated to be 36 $J·K^{-1}·mol^{-1}$ based on that of $LiBO_2$(l)[1] which was derived from high temperature enthalpy measurements. A glass transition is assumed at 812 K below which the heat capacities are assumed to be the same as the crystal.

$S°(KBO_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which the fugacity is 1 atm for $KOB_2(l) \rightarrow KBO_2(g)$. The enthalpy of vaporization is the difference in $\Delta_f H°$ at the boiling point between liquid and gas.

Reference

[1]JANAF Thermochemical Table: $LiBO_2$(l), 6–30–71.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0							
100							
200							
298.15	67.028	88.455	88.455	0.	−980.730	−924.917	162.042
300	67.237	88.871	88.457	0.124	−980.735	−924.571	160.982
400	76.651	109.553	91.213	7.336	−983.335	−905.360	118.228
500	83.973	127.471	96.712	15.379	−983.190	−885.875	92.547
600	89.830	143.316	103.184	24.079	−982.670	−866.455	75.432
700	94.558	157.528	109.950	33.305	−981.850	−847.147	63.215
800	98.491	170.420	116.715	42.964	−980.788	−827.974	54.061
812.000	98.910	171.890	117.520	44.149	GLASS <--> LIQUID		
812.000	146.440	171.890	117.520	44.149	TRANSITION		
900	146.440	186.958	123.585	57.035	−975.486	−809.159	46.962
1000	146.440	202.387	130.707	71.679	−969.779	−790.986	41.317
1100	146.440	216.344	137.868	86.323	−1043.193	−768.766	36.506
1200	146.440	229.086	144.946	100.967	−1036.765	−744.103	32.390
1220.000	146.440	231.506	145.346	103.896	--- CRYSTAL <--> LIQUID ---		
1300	146.440	240.807	151.876	115.611	−1030.425	−719.972	28.929
1400	146.440	251.660	158.620	130.255	−1024.163	−696.326	25.980
1500	146.440	261.763	165.163	144.899	−1017.974	−673.126	23.440
1600	146.440	271.214	171.499	159.543	−1011.854	−650.336	21.231
1700	146.440	280.092	177.629	174.187	−1005.801	−627.927	19.294
1800	146.440	288.462	183.556	188.831	−999.812	−605.872	17.582
1900	146.440	296.380	189.287	203.475	−993.888	−584.148	16.059
2000	146.440	303.891	194.832	218.119	−988.029	−562.735	14.697

PREVIOUS: CURRENT: June 1971

0	to	1220 K	crystal
above		220 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.98	−990.083	−990.083	INFINITE
100	35.012	25.125	130.260	−10.513	−993.150	−974.741	509.152
200	54.095	55.873	85.716	−5.968	−994.444	−955.739	249.613
298.15	67.028	79.981	79.981	0.	−994.955	−936.616	164.091
300	67.237	80.397	79.983	0.124	−994.961	−936.254	163.016
400	76.651	101.079	82.739	7.336	−997.561	−916.196	119.643
500	83.973	118.997	88.238	15.379	−997.415	−895.863	93.590
600	89.830	134.842	94.710	24.079	−996.896	−875.596	76.227
700	94.558	149.054	101.476	33.305	−996.076	−855.441	63.834
800	98.491	161.945	108.241	42.963	−995.014	−835.420	54.547
900	101.755	173.739	114.873	52.980	−993.767	−815.544	47.333
1000	104.474	184.607	121.310	63.297	−992.387	−795.814	41.569
1100	106.525	194.666	127.527	73.853	−1069.889	−771.617	36.641
1200	107.864	204.001	133.516	84.582	−1067.376	−744.612	32.412
1220.000	107.989	205.785	134.686	86.741	CRYSTAL <--> LIQUID TRANSITION		
1220.000	146.440	231.506	134.686	118.121			
1300	146.440	240.807	140.933	129.836	−1030.426	−719.973	28.929
1400	146.440	251.660	148.460	144.480	−1024.164	−696.327	25.980
1500	146.440	261.763	155.680	159.124	−1017.975	−673.127	23.440
1600	146.440	271.214	162.609	173.768	−1011.855	−650.337	21.231
1700	146.440	280.092	169.261	188.412	−1005.802	−627.928	19.294
1800	146.440	288.462	175.653	203.056	−999.813	−605.873	17.582
1900	146.440	296.380	181.801	217.700	−993.889	−584.149	16.059
2000	146.440	303.891	187.719	232.344	−988.030	−562.736	14.697

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = [297.4 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -671 \pm 25\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -674 \pm 25\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1952(1)	577(1)
1081(1)	265(1)
581(1)	88(1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_s

Bond Distances: K–O = [2.4] Å; O–B = [1.36] Å; B–O = [1.20] Å

Bond Angles: K–O–B = [90]°; O–B–O = [180]°

Product of the Moments of Inertia: $I_A I_B I_C = [5.790543 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Jensen[1] determined the equilbrium constants for the reaction: $K(g) + HBO_2(g) \rightarrow KBO_2(g) + H(g)$ by flame studies. This technique involved several assumptions, the most basic of which is that boron added to $H_2/N_2/O_2$ flames was converted completely to HBO_2. The hydrogen atom concentration was taken from previous studies on such flames. Potassium metaborate was assumed to be formed in the flame. The concentration of K atom was determined by atomic absorption spectrophotometry. JANAF 3rd law analysis of his equilibrium constant equation in the temperature range from 2000 to 2600 K yields $\Delta_f H°(298.15\ K) = 3.66 \pm 0.54\ kcal \cdot mol^{-1}$and the drift is $1.26\ cal \cdot K^{-1} \cdot mol^{-1}$. (2nd law enthalpy of reaction is $\Delta_r H°(298.15\ K) = 0.78\ kcal \cdot mol^{-1}$.) Using the 3rd law $\Delta_r H°(298.15\ K)$ and JANAF auxiliary data, we obtain $\Delta_f H°(KBO_2, g, 298.15\ K) = -161.1\ kcal \cdot mol^{-1}$. The uncertainty in this measurement was about $\pm 6\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Seshadri, Nimon and White[2] observed the infrared spectra of KBO_2 in an argon matrix and made a complete assignment of all six fundamentals which are adopted in the tabulation. The uncertainty of the calculated statistical entropy at 298.15 K is estimated to be ± 1 eu which is due to the magnitude of the matrix shifts from the free molecule spectrum, particularly for the lower frequency modes.

The molecular structure, bond distance and bond angle of KBO_2(g) are assumed to be the same as those of $LiBO_2$(g) and $NaBO_2$(g),[1] except the bond distance K–O which was estimated to be intermediate between those of potassium fluoride and chloride. The principal moments of inertia are: $I_A = 6.1073 \times 10^{-39}$, $I_B = 27.8891 \times 10^{-39}$, and $I_C = 33.9965 \times 10^{-39}\ g \cdot cm.^2$

References

[1]D. E. Jensen, Trans. Faraday Soc. **65**, 2123 (1969).
[2]K. S. Seshadri, L. A. Nimon and D. White, J. Mol. Specry. **30**, 128 (1969).
[3]JANAF Thermochemical Tables: $LiBO_2$(g) and $NaBO_2$(g), 6–30–71.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.103	−671.166	−671.166	INFINITE
100	43.615	242.225	345.119	−10.289	−672.013	−675.314	352.748
200	52.329	275.193	302.607	−5.483	−673.045	−678.205	177.129
250	56.018	287.277	298.364	−2.772	−673.537	−679.438	141.961
298.15	59.027	297.408	297.408	0.	−674.042	−680.529	119.226
300	59.133	297.774	297.410	0.109	−674.063	−680.569	118.498
350	61.757	307.092	298.139	3.133	−677.034	−681.511	101.710
400	63.992	315.488	299.792	6.279	−677.706	−682.105	89.074
450	65.921	323.139	301.967	9.528	−678.366	−682.615	79.236
500	67.602	330.174	304.441	12.867	−679.015	−683.052	71.358
600	70.385	342.756	309.803	19.772	−680.291	−683.739	59.525
700	72.568	353.776	315.314	26.924	−681.544	−684.215	51.057
800	74.296	363.584	320.746	34.270	−682.794	−684.511	44.694
900	75.672	372.417	326.004	41.771	−684.063	−684.650	39.736
1000	76.776	380.449	331.053	49.395	−685.376	−684.645	35.762
1100	77.669	387.810	335.883	57.119	−765.710	−679.895	32.286
1200	78.397	394.600	340.497	64.924	−766.122	−672.076	29.255
1300	78.997	400.900	344.904	72.794	−766.554	−664.222	26.689
1400	79.495	406.773	349.116	80.720	−767.011	−656.333	24.488
1500	79.911	412.272	353.145	88.691	−767.496	−648.411	22.580
1600	80.263	417.441	357.003	96.700	−768.011	−640.455	20.909
1700	80.562	422.316	360.703	104.741	−768.559	−632.466	19.433
1800	80.818	426.928	364.256	112.811	−769.146	−624.444	18.121
1900	81.038	431.304	367.670	120.904	−769.773	−616.388	16.946
2000	81.230	435.466	370.957	129.017	−770.443	−608.298	15.887
2100	81.397	439.433	374.124	137.149	−771.161	−600.174	14.929
2200	81.543	443.223	377.179	145.296	−771.930	−592.013	14.056
2300	81.672	446.851	380.130	153.457	−772.752	−583.817	13.259
2400	81.787	450.329	382.983	161.630	−823.891	−574.516	12.504
2500	81.888	453.670	385.744	169.814	−824.908	−564.104	11.786
2600	81.979	456.883	388.419	178.007	−825.956	−553.651	11.123
2700	82.061	459.979	391.012	186.209	−827.039	−543.157	10.508
2800	82.134	462.964	393.529	194.419	−828.159	−532.622	9.936
2900	82.200	465.848	395.973	202.636	−829.320	−522.048	9.403
3000	82.260	468.636	398.349	210.859	−830.526	−511.432	8.905
3100	82.314	471.334	400.660	219.088	−831.780	−500.774	8.438
3200	82.364	473.948	402.910	227.322	−833.085	−490.076	8.000
3300	82.409	476.483	405.101	235.560	−834.436	−479.338	7.587
3400	82.451	478.944	407.237	243.803	−835.852	−468.555	7.198
3500	82.489	481.334	409.320	252.051	−837.326	−457.732	6.831
3600	82.524	483.659	411.353	260.301	−838.868	−446.864	6.484
3700	82.557	485.920	413.338	268.555	−840.479	−435.954	6.155
3800	82.586	488.122	415.277	276.812	−842.165	−424.997	5.842
3900	82.614	490.268	417.172	285.072	−843.928	−413.996	5.545
4000	82.640	492.360	419.026	293.335	−845.768	−402.950	5.262
4100	82.664	494.401	420.840	301.600	−847.696	−391.856	4.992
4200	82.686	496.393	422.615	309.868	−1329.568	−373.690	4.648
4300	82.707	498.339	424.353	318.138	−1330.600	−350.919	4.263
4400	82.726	500.240	426.057	326.409	−1331.457	−328.150	3.896
4500	82.744	502.100	427.726	334.683	−1332.630	−305.335	3.544
4600	82.761	503.919	429.363	342.958	−1333.904	−282.493	3.208
4700	82.777	505.699	430.968	351.235	−1335.260	−259.623	2.885
4800	82.792	507.442	432.543	359.513	−1336.612	−236.736	2.576
4900	82.806	509.149	434.089	367.793	−1338.175	−213.805	2.279
5000	82.819	510.822	435.607	376.075	−1339.846	−190.842	1.994
5100	82.832	512.462	437.098	384.357	−1341.626	−167.844	1.719
5200	82.844	514.071	438.563	392.641	−1343.518	−144.811	1.455
5300	82.855	515.649	440.002	400.926	−1345.523	−121.739	1.200
5400	82.865	517.198	441.418	409.212	−1347.643	−98.630	0.954
5500	82.875	518.718	442.809	417.499	−1349.876	−75.480	0.717
5600	82.885	520.211	444.178	425.787	−1352.225	−52.287	0.488
5700	82.894	521.679	445.525	434.076	−1354.344	−29.101	0.267
5800	82.902	523.120	446.850	442.365	−1356.878	−5.828	0.052
5900	82.910	524.538	448.155	450.656	−1359.522	17.487	−0.155
6000	82.918	525.931	449.440	458.947	−1362.276	40.850	−0.356

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = 51.73 \pm 0.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1117 \pm 1\ K$

$\Delta_f H°(0\ K) = -1013.7 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1019.2 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 33.81 \pm 0.5\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Sinke[1] measured calorimetrically the enthalpy of solution of $LiBO_2$(cr) in 0.5 N HNO_3, $\Delta_{sol}H°(25°C) = -10.93 \pm 0.05$ kcal·mol^{-1} for $LiBO_2$(cr) + HNO_3(aq, 111 H_2O) → H_3BO_3(aq, 111 H_2O) + $LiNO_3$(aq, 111 H_2O), which leads to the adopted enthalpy of formation, $\Delta_f H°(LiBO_2$, cr, 298.15 K) = -243.6 ± 0.2 kcal·mol^{-1} using the following auxiliary data: $\Delta_f H°(HNO_3 \cdot 111\ H_2O$, aq, 298.15 K) = −49.411 kcal·mol^{-1},[2] $\Delta_f H°(H_2O$, l, 298.15 K) = −68.315 kcal·mol^{-1},[2] $\Delta_f H°(H_3BO_3 \cdot 111\ H_2O$, aq, 298.15 K) = −256.336 kcal·mol^{-1} [2] and $\Delta_f H°(LiNO_3 \cdot 111\ H_2O$, aq, 298.15 K) = −115.944 kcal·mol^{-1}.[3]

Shartsis and Capps[4] measured enthalpies of solution in 2N nitric acid of various Li_2O–B_2O_3 glass and crystalline mixtures containing 2.5–48.4 mole % of Li_2O. When their results are extrapolated to 50 mole %, we obtain $\Delta_{sol}H°(25°C) = -10.8 \pm 0.5$ kcal·mol^{-1} for $LiBO_2$(cr) + HNO_3(27.75 H_2O, aq) + H_2O(l) → $LiNO_3$(27.75 H_2O, aq) + H_3BO_3(27.75 H_2O, aq). The calculated enthalpy of formation is based on the following data: $\Delta_f H°(HNO_3 \cdot 27.75\ H_2O$, aq, 298.15 K) = −49.433 kcal·mol^{-1},[2] $\Delta_f H°(LiNO_3 \cdot 27.75\ H_2O$, aq, 298.15 K) = −115.854 kcal·mol^{-1} [5] and $\Delta_f H°(H_3BO_3 \cdot 27.75\ H_2O$, aq, 298.15 K) = −256.37 kcal·mol^{-1}.[6] The value is $\Delta_f H°(LiBO_2$, cr, 298.15 K) = -243.9 ± 0.5 kcal·mol^{-1}, which is in very good agreement with the adopted value.

Heat Capacity and Entropy

Stull *et al.*[7] measured low temperature C_p data from 15 to 320 K. We use their smoothed C_p values to derive $S°(298.15\ K) = 12.36 \pm 0.05$ cal·K^{-1}·mol^{-1} based on $S°(15\ K) = 0.017$ cal·K^{-1}·mol^{-1}. McDonald[8] determined high temperature enthalpy data from 288 to 1116 K by drop calorimetry. The low temperature C_p and high temperature enthalpy data are smoothly joined at 298.15 K by a polynomial curve fitting technique. The average deviation of the observed enthalpy data from the adopted values is about 0.3% in the temperature range from 428–1062 K, and the maximum is 0.56% at 922 K. The C_p values above T_{fus} are extrapolated from the adopted polynomial function.

Turdakin and Tarasov[9] also measured low temperature heat capacities (55–300 K) in an adiabatic calorimeter. Their values deviate from the adopted C_p by approximately 2%.

Melting curves from binary phase studies[10–12] have been interpreted in terms of a crystal transition near 800°C, although the most recent paper[13] indicated no transition. Two high-pressure polymorphs have been observed[14] but there is no evidence of their stability at atmospheric pressure. Enthalpy data[8] showed no obvious transition near 800°C; points at 829 and 815°C showed reasonable premelting contributions of about 200 and 300 kcal·mol^{-1}, respectively. Although this evidence does not preclude the existence of a transition, definite evidence would be needed to establish such a transition.

Fusion Data

Refer to the liquid table for details.

References

[1]G. C. Sinke, Thermal Research Lab., The Dow Chemical Company, Midland, Michigan, personal communication, (April, 1961).
[2]U. S. Nat. Bur. Stand. Tech. Note 270–3, 264 pp. (1968).
[3]This value, ($LiNO_3 \cdot 111\ H_2O$, aq $\Delta_f H°298.15\ K) = -115.944$ kcal·mol^{-1}, is calculated based on the follwoing auxiliary data:
a. $\phi_L = 0.171$ kcal mol^{-1} for $LiNO_3(\infty\ H_2O) \rightarrow LiNO_3 \cdot (111\ H_2O)$ ϕ_L was obtained fromV.B. Parker, U. S. Nat. Bur. Stand., NSRDS–NBS 2, 66 pp. (1965).
b. $\Delta_f H°(LiNO_3$ [aq, ∞], 298.15 K) = −116.115 kcal·mol^{-1}.
This value is the sum of $\Delta_f H°(Li^+$ [aq, ∞] 298.15 K) = −66.555 kcal·mol^{-1} and $\Delta_f H°(NO_3^-$ [aq, ∞], 298.15 K) = 49.56 kcal·mol^{-1}.[2]
The former is derived from $\Delta_f H°(LiOH$ [aq, ∞], 298.15 K = −121.525 kcal·mol^{-1} and $\Delta_f H°(OH^-$ [aq, ∞] = −54.97 kcal·mol^{-1}.[2]
[4]L. Shartsis and W. Capps. J. Am. Chem. Soc. **37**, 27 (1954).
[5]This value, −115.854 kcal·mol^{-1}, is calculated from $\Delta_f H°(LiNO_3$ [aq. ∞], 298.15 K = −116.115 kcal·mol^{-1} and $\phi_L = 0.261$ kcal·mol^{-1} for $LiNO_3(\infty\ H_2O) \rightarrow LiNO_3 \cdot (27.75\ H_2O)$ reported by V. B. Parker, U. S. Nat. Bur. Stand. NSRDS–NBS 2, 66 pp. (1965).
[6]This value, −256.37 kcal·mol^{-1}, is extrapolated from the enthalpies of formation of $H_3BO_3 \cdot 60H_2O$ and $H_3BO_3 \cdot 100\ H_2O$ listed by NBS.[2]
[7]D. R. Stull, D. L. Hildenbrand, F. L. Oetting and G. C. Sinke, J. Chem. Eng. Data **15**, 52 (1970).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.975	−1013.678	−1013.678	INFINITE
100	18.795	10.192	93.035	−8.284	−1016.411	−999.334	521.999
200	43.133	31.104	56.731	−5.125	−1018.338	−981.412	256.319
298.15	60.371	51.731	51.731	0.	−1019.222	−963.070	168.726
300	60.618	52.105	51.732	0.112	−1019.231	−962.722	167.625
400	71.145	71.112	54.252	6.744	−1019.534	−943.833	123.252
500	78.605	87.818	59.329	14.244	−1022.756	−924.575	96.590
600	85.057	102.728	65.341	22.432	−1022.692	−904.938	78.782
700	91.098	116.297	71.665	31.242	−1022.217	−885.344	66.065
800	96.939	128.844	78.038	40.645	−1021.330	−865.847	56.534
900	102.675	140.594	84.342	50.627	−1020.027	−846.485	49.129
1000	108.353	151.706	90.528	61.178	−1018.286	−827.292	43.213
1100	113.989	162.298	96.574	72.296	−1016.088	−808.295	38.383
1117.000	114.943	164.053	97.588	74.241	--- CRYSTAL <--> LIQUID ---		
1200	119.604	172.457	102.477	83.975	−1013.422	−789.519	34.367
1300	125.202	182.251	108.239	96.216	−1010.279	−770.984	30.979
1400	130.788	191.734	113.866	109.015	−1006.649	−752.710	28.084
1500	136.369	200.948	119.366	122.373	−1002.524	−734.713	25.585
1600	141.938	209.927	124.747	136.288	−997.901	−717.007	23.408
1700	147.507	218.699	130.016	150.761	−1138.015	−692.429	21.276
1800	153.072	227.288	135.182	165.790	−1131.636	−666.400	19.338
1900	158.636	235.713	140.252	181.375	−1124.764	−640.739	17.615
2000	164.193	243.991	145.233	197.517	−1117.396	−615.452	16.074

PREVIOUS: December 1964 CURRENT: June 1971

$S°(298.15\ K) = [65.547]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1117 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1000.259]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 33.81 \pm 0.5\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(LiBO_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1117\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

McDonald[1] *measured high temperature enthalpy data of the liquid from 1118 to 1707 K by drop calorimetry. The adopted heat capacities* are derived from his observed data. The average deviation of the observed enthalpy data from the adopted values is about 0.1%. A glass transition is assumed at 745 K below which the C_p is assumed to be the same as that of the crystal.

$S°(LiBO_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted enthalpy of fusion, $\Delta_{fus}H°(1117\ K) = 8.08 \pm 0.12\ kcal·mol^{-1}$, is calculated from the observed enthalpies[1] by use of the adopted C_p functions of both crystal and liquid.

Petit and Jaeger[2] derived $\Delta_{fus}H°(1109\ K) = 7.4\ kcal·mol^{-1}$ from phase data for the $LiBO_2$–LiF system. Darmois and Zarzycki[3] determined $\Delta_{fus}H°(1113\ K) = 8.3 \pm 0.6\ kcal·mol^{-1}$ from cryoscopic studies involving several secondary components.

Vaporization Data

The boiling point is calculated as the temperature at which the fugacity is 1 atm for $LiBO_2(l) \rightarrow LiBO_2(g)$. The enthalpy of vaporization is the difference in $\Delta_f H°$ at the boiling point between liquid and gas.

Prophet[4] determined the boiling point under argon atmosphere as 2050 ± 100 K which is in good agreement with the value calculated.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	60.371	65.547	65.547	0.	−1000.259	−948.226	166.125
300	60.618	65.921	65.548	0.112	−1000.268	−947.903	165.045
400	71.145	84.928	68.069	6.744	−1000.570	−930.396	121.497
500	78.605	101.634	73.146	14.244	−1003.793	−912.520	95.330
600	85.057	116.544	79.158	22.432	−1003.729	−894.264	77.853
700	91.098	130.113	85.482	31.242	−1003.254	−876.052	65.372
745.000	93.741	135.871	88.352	35.401	GLASS <--> LIQUID TRANSITION		
745.000	144.310	135.871	88.352	35.401			
800	144.310	146.149	91.977	43.338	−999.673	−858.034	56.024
900	144.310	163.147	98.959	57.769	−993.921	−840.677	48.792
1000	144.310	178.351	106.151	72.200	−988.300	−823.952	43.039
1100	144.310	192.106	113.350	86.631	−982.789	−807.784	38.358
1117.000	144.310	194.319	114.565	89.085	--- CRYSTAL <--> LIQUID ---		
1200	144.310	204.662	120.444	101.062	−977.372	−792.115	34.480
1300	144.310	216.213	127.372	115.493	−972.038	−776.894	31.216
1400	144.310	226.908	134.105	129.924	−966.776	−762.080	28.434
1500	144.310	236.864	140.627	144.355	−961.578	−747.641	26.035
1600	144.310	246.178	146.936	158.786	−956.440	−733.546	23.948
1700	144.310	254.927	153.034	173.218	−1096.594	−712.595	21.895
1800	144.310	263.175	158.926	187.649	−1090.814	−690.175	20.028
1900	144.310	270.978	164.620	202.080	−1085.096	−668.073	18.367
2000	144.310	278.380	170.124	216.511	−1079.438	−646.271	16.879
2100	144.310	285.421	175.448	230.942	−1073.842	−624.751	15.540
2200	144.310	292.134	180.601	245.373	−1068.306	−603.495	14.329
2300	144.310	298.549	185.591	259.804	−1062.832	−582.490	13.229
2400	144.310	304.691	190.426	274.235	−1107.678	−560.653	12.202
2500	144.310	310.582	195.115	288.666	−1102.406	−537.969	11.240
2600	144.310	316.242	199.666	303.097	−1097.164	−515.495	10.356
2700	144.310	321.688	204.085	317.528	−1091.954	−493.222	9.542
2800	144.310	326.936	208.379	331.959	−1086.777	−471.141	8.789
2900	144.310	332.000	212.555	346.390	−1081.634	−449.246	8.092
3000	144.310	336.893	216.619	360.821	−1076.526	−427.526	7.444

PREVIOUS: December 1964 CURRENT: June 1971

0	to 1117 K	crystal
above	1117 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.975	−1013.678	−1013.678	INFINITE
100	18.795	10.192	93.035	−8.284	−1016.411	−999.334	521.999
200	43.133	31.104	56.731	−5.125	−1018.338	−981.412	256.319
298.15	60.371	51.731	51.731	0.	−1019.222	−963.070	168.726
300	60.618	52.105	51.732	0.112	−1019.231	−962.722	167.625
400	71.145	71.112	54.252	6.744	−1019.534	−943.833	123.252
500	78.605	87.818	59.329	14.244	−1022.756	−924.575	96.590
600	85.057	102.728	65.341	22.432	−1022.692	−904.938	78.782
700	91.098	116.297	71.665	31.242	−1022.217	−885.344	66.065
800	96.939	128.844	78.038	40.645	−1021.330	−865.847	56.534
900	102.675	140.594	84.342	50.627	−1020.027	−846.485	49.129
1000	108.353	151.706	90.528	61.178	−1018.286	−827.292	43.213
1100	113.989	162.298	96.574	72.296	−1016.088	−808.295	38.383
1117.000	114.943	164.053	97.588	74.241	CRYSTAL <--> LIQUID TRANSITION		
1117.000	144.310	194.319	97.588	108.048			
1200	144.310	204.662	104.641	120.026	−977.372	−792.115	34.480
1300	144.310	216.213	112.785	134.457	−972.038	−776.894	31.216
1400	144.310	226.908	120.559	148.888	−966.776	−762.080	28.434
1500	144.310	236.864	127.985	163.319	−961.578	−747.641	26.035
1600	144.310	246.178	135.084	177.750	−956.440	−733.546	23.948
1700	144.310	254.927	141.879	192.181	−1096.594	−712.595	21.895
1800	144.310	263.175	148.391	206.612	−1090.814	−690.175	20.028
1900	144.310	270.978	154.639	221.043	−1085.096	−668.073	18.367
2000	144.310	278.380	160.643	235.474	−1079.438	−646.271	16.879
2100	144.310	285.421	166.418	249.905	−1073.842	−624.751	15.540
2200	144.310	292.134	171.981	264.336	−1068.306	−603.495	14.329
2300	144.310	298.549	177.346	278.767	−1062.832	−582.490	13.229
2400	144.310	304.691	182.525	293.198	−1107.678	−560.653	12.202
2500	144.310	310.582	187.530	307.629	−1102.406	−537.969	11.240
2600	144.310	316.242	192.372	322.060	−1097.164	−515.495	10.356
2700	144.310	321.688	197.061	336.491	−1091.954	−493.222	9.542
2800	144.310	326.936	201.607	350.923	−1086.777	−471.141	8.789
2900	144.310	332.000	206.016	365.354	−1081.634	−449.246	8.092
3000	144.310	336.893	210.298	379.785	−1076.526	−427.526	7.444

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = 274.7 \pm 42\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -645.8 \pm 12.6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -646.8 \pm 12.6\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1976(1)	569(1)
1094(1)	471(1)
578(1)	107(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: Li-O = 1.82 Å; O-B = 1.36 Å; B-O = 1.20 Å
Bond Angles: Li-O-B = 90°; O-B-O = 180°
Product of the Moments of Inertia: $I_A I_B I_C = 3.915323 \times 10^{-115}\ g^3\cdot cm^6$

Enthalpy of Formation

Jensen[1] determined the equilibrium constants for reaction (A) Li(g) + HBO_2(g) $LiBO_2$(g) + H(g) by flame studies. This technique involves several assumptions, the most basic of which is that boron added to $H_2/N_2/O_2$ flames is converted completely to HBO_2. The hydrogen atom concentration was taken from previous studies on such flames. Lithium metaborate was assumed to be formed in the flame. The concentration of Li atoms was determined by atomic absorption spectrophotometry. JANAF 3rd law analysis of his equilibrium constant equation in the temperature range from 2000 to 2600 K yields $\Delta_f H°(298.15\ K) = -2.95 \pm 1.07\ kcal\cdot mol^{-1}$ and the drift 2.47 $cal\cdot K^{-1}\cdot mol^{-1}$ (the 2nd law enthalpy of reaction being $-8.62\ kcal\cdot mol^{-1}$). Using the 3rd law $\Delta_f H°(298.15\ K)$ and JANAF auxiliary data, we obtain $\Delta_f H°(LiBO_2, g, 298.15\ K) = -150.6\ kcal\cdot mol^{-1}$. The uncertainty in this measurement is about 6 $kcal\cdot mol^{-1}$.

Buchler and Berkowitz-Mattuck[2] studied mass spectrometrically the vaporization of lithium metaborate and reported $\Delta_{vap}H°(1160\ K) = 70 \pm 3\ kcal\cdot mol^{-1}$ for $LiBO_2$(l) → $LiBO_2$(g) and $\Delta_{sub}H°(1060\ K) = 79 \pm 3\ kcal\cdot mol^{-1}$ for $LiBO_2$(cr) → $LiBO_2$(g) by a 2nd law method. JANAF reduction to 298.15 K gives vap H(298.15 K) = 78.1 → 3 $kcal\cdot mol^{-1}$ and $\Delta_{sub}H°(298.15\ K) = 82.4 \pm 3\ kcal\cdot mol^{-1}$. They also determined the vapor pressure of $LiBO_2$ at 1160 K as 2.0×10^{-6} atm by comparison with the vapor pressure of silver. JANAF 3rd law analysis of this single vapor pressure point gives $\Delta_{vap}H°(298.15\ K) = 85.0\ kcal\cdot mol^{-1}$ which leads to $\Delta_f H°(LiBO_2, g, 298.15\ K) = -154.0 \pm 3\ kcal\cdot mol^{-1}$. The latter is in good agreement with the value adopted in the tabulation. The 2nd law enthalpies of vaporization and sublimation are probably in error by about 6 $kcal\cdot mol^{-1}$.

Hildenbrand *et al.*[3] measured the total vapor pressure over liquid $LiBO_2$ in the temperature range from 1120 to 1280 K by a torsion-effusion method. Assuming 100% monomeric vapor species, JANAF 3rd law analysis of their vapor pressure data yields the enthalpy of vaporization, $\Delta_{vap}H°(298.15\ K) = 84.47\ kcal\cdot mol^{-1}$, and a drift of $0.93 \pm 1.0\ cal\cdot K^{-1}\cdot mol^{-1}$, this corresponds to $\Delta_{sub}H°(298.15\ K) = 89.0\ kcal\cdot mol^{-1}$. (2nd law heat of vaporization is $\Delta_{vap}H°(298.15\ K) = 83.25 \pm 1.20\ kcal\cdot mol^{-1}$. Using the 3rd law $\Delta_{vap}H°(298.15\ K)$, we obtain $\Delta_f H°(LiBO_2, g, 298.15\ K) = -154.6\ kcal\cdot mol^{-1}$. If there are 10% of $LiBO_2$ dimer molecules present in the vapor phase as suggested by Buchler,[2] the correction in the 3rd law $\Delta_{vap}H°(298.15\ K)$ is about 0.3 $kcal\cdot mol^{-1}$ is about 0.3 $kcal\cdot mol^{-1}$which is much less than the uncertainty assigned to derive $\Delta_{vap}H°(298.15\ K)$. The value, $\Delta_f H°(LiBO, g, 298.15\ K) = -154.6 \pm 3\ kcal\cdot mol^{-1}$, is adopted in the tabulation.

Heat Capacity and Entropy

The adopted vibrational frequencies are obtained from Seshadri, Nimon and White[4] who observed the infrared spectra of $LiBO_2$ in an argon matrix and made a complete assignement of all six fundamentals. The uncertainty of the calculated statistical entropy at 298.15 K is estimated to be 1 $cal\cdot K^{-1}\cdot mol^{-1}$ which is due to the magnitude of the matrix shifts from the free molecule spectrum, particularly for the lower frequency modes.

Buchler and Marram[5] observed only two vibrational frequencies, 1935 and 600 cm^{-1}, in their infrared spectra. These two frequencies are in reasonable agreement with those reported by Seshadri.[4]

By electron diffraction studies, Akishin and Spiridonov[6] determined the molecular structure of gaseous lithium metaborate and found the bond lengths and angles which are adopted in the tabulation. We tentatively select the bond angles Li-O-B as 90 from their reported data, i.e, 90-105 because Seshadri *et al.*[4] treated this bond angle as a parameter in the force constant calculations and found that the best fit to the infrared spectrometric data occurs at approximately 90. A recent electron diffraction study[7] on lithium metaborate confirms the results given by Akishin.[6]

The principal moments of inertia are $I_A = 2.5800 \times 10^{-39}$, $I_B = 11.0962 \times 10^{-39}$ and $I_C = 13.6763 \times 10^{-39}\ g\cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.445	−645.772	−645.772	INFINITE
100	40.840	222.599	320.197	−9.760	−645.510	−649.674	339.355
200	49.547	253.423	279.734	−5.262	−646.098	−653.637	170.712
250	53.797	264.948	275.651	−2.676	−646.469	−655.479	136.955
298.15	57.246	274.727	274.727	0.	−646.846	−657.181	115.135
300	57.366	275.082	274.728	0.106	−646.861	−657.245	114.436
350	60.331	284.154	275.438	3.051	−647.283	−658.943	98.342
400	62.816	292.377	277.050	6.131	−647.770	−660.576	86.262
450	64.932	299.901	279.176	9.326	−648.343	−662.143	76.860
500	66.756	306.839	281.600	12.619	−652.005	−663.335	69.298
600	69.739	319.286	286.868	19.451	−653.298	−665.478	57.935
700	72.055	330.217	292.296	26.545	−654.538	−667.410	49.803
800	73.876	339.963	297.656	33.845	−655.754	−669.166	43.692
900	75.323	348.751	302.853	41.308	−656.970	−670.769	38.930
1000	76.481	356.749	307.849	48.900	−658.188	−672.237	35.114
1100	77.416	364.084	312.632	56.597	−659.411	−673.582	31.986
1200	78.179	370.853	317.205	64.378	−660.644	−674.816	29.374
1300	78.806	377.137	321.577	72.228	−661.891	−675.947	27.160
1400	79.327	382.996	325.757	80.135	−663.153	−676.981	25.258
1500	79.762	388.485	329.758	88.090	−664.431	−677.925	23.607
1600	80.130	393.645	333.591	96.085	−665.728	−678.782	22.160
1700	80.443	398.512	337.268	104.115	−812.285	−672.381	20.660
1800	80.711	403.118	340.800	112.173	−812.878	−664.135	19.273
1900	80.941	407.488	344.196	120.255	−813.507	−655.855	18.031
2000	81.142	411.645	347.465	128.360	−814.177	−647.540	16.912
2100	81.316	415.608	350.616	136.483	−814.888	−639.191	15.899
2200	81.469	419.395	353.657	144.622	−815.644	−630.806	14.977
2300	81.604	423.019	356.595	152.776	−816.447	−622.387	14.135
2400	81.724	426.495	359.435	160.943	−867.558	−612.863	13.339
2500	81.830	429.833	362.185	169.121	−868.539	−602.231	12.583
2600	81.925	433.044	364.849	177.308	−869.540	−591.559	11.885
2700	82.011	436.138	367.432	185.505	−870.564	−580.847	11.237
2800	82.087	439.122	369.940	193.710	−871.613	−570.098	10.635
2900	82.156	442.004	372.375	201.922	−872.689	−559.311	10.074
3000	82.219	444.790	374.743	210.141	−873.793	−548.486	9.550
3100	82.276	447.487	377.046	218.366	−874.927	−537.623	9.059
3200	82.328	450.100	379.288	226.596	−876.093	−526.724	8.598
3300	82.375	452.634	381.473	234.832	−877.292	−515.789	8.164
3400	82.419	455.094	383.602	243.071	−878.526	−504.815	7.756
3500	82.459	457.483	385.679	251.315	−879.795	−493.805	7.370
3600	82.496	459.807	387.706	259.563	−881.101	−482.759	7.005
3700	82.529	462.068	389.685	267.814	−882.446	−471.676	6.659
3800	82.561	464.269	391.619	276.069	−883.830	−460.554	6.331
3900	82.590	466.414	393.510	284.326	−885.254	−449.397	6.019
4000	82.617	468.505	395.359	292.587	−886.720	−438.203	5.722
4100	82.642	470.546	397.168	300.850	−888.230	−426.971	5.440
4200	82.665	472.537	398.939	309.115	−1369.633	−408.678	5.083
4300	82.686	474.483	400.673	317.382	−1370.146	−385.792	4.686
4400	82.707	476.384	402.372	325.652	−1370.688	−362.896	4.308
4500	82.726	478.243	404.037	333.924	−1371.291	−339.985	3.946
4600	82.743	480.061	405.670	342.197	−1371.948	−317.061	3.600
4700	82.760	481.841	407.272	350.472	−1372.659	−294.120	3.269
4800	82.776	483.583	408.844	358.749	−1373.425	−271.165	2.951
4900	82.790	485.290	410.387	367.028	−1374.248	−248.192	2.646
5000	82.804	486.963	411.902	375.307	−1375.132	−225.202	2.353
5100	82.817	488.603	413.390	383.588	−1376.072	−202.195	2.071
5200	82.830	490.211	414.851	391.871	−1377.080	−179.169	1.800
5300	82.841	491.789	416.288	400.154	−1378.156	−156.121	1.539
5400	82.852	493.338	417.701	408.439	−1379.302	−133.054	1.287
5500	82.863	494.858	419.090	416.725	−1380.521	−109.964	1.044
5600	82.873	496.351	420.456	425.011	−1381.815	−86.851	0.810
5700	82.882	497.818	421.801	433.299	−1383.187	−63.715	0.584
5800	82.891	499.260	423.124	441.588	−1384.640	−40.553	0.365
5900	82.899	500.677	424.426	449.877	−1386.177	−17.368	0.154
6000	82.907	502.070	425.709	458.168	−1387.802	5.847	−0.051

PREVIOUS: June 1971 (1 atm) *CURRENT: June 1971 (1 bar)*

$\Delta_f H°(0\ K) = -247.99 \pm 1.55$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = -250.91 \pm 1.55$ kJ·mol^{-1}

$S°(298.15\ K) = 14.795$ J·K^{-1}·mol^{-1}
$T_{dcm} = 2600 \pm 100$ K

Enthalpy of Formation

The adopted enthalpy of formation was determined by Wise *et al.*[5] using combustion in fluorine. Other recent calorimetric values are in good agreement as summarized below. Torsion effusion studies of the decomposition BN(cr) → B(am) + 0.5 N_2(g) by Hildebrand and Hall[7] yield essentially the same $\Delta_f H°$ and indicate that the condensation coefficient $\alpha < 6 \times 10^{-3}$ for N_2(g) on the surface of the sample. Use of $\alpha = 6 \times 10^{-3}$ brings the following decomposition studies into reasonable agreement: Langmuir studies by Dreger *et al.*;[8] mass spectrometric studies by Schissel and Williams;[9] and Knudsen effusion studies by Hoch and White.[10]

Source	Reaction	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{1}
[1]	BN(cr) + 3/4 O_2(g) 0.5 B_2O_3(am) + 0.5 N_2	−90.1 ± 0.5	−59.7 ± 0.7
[2]	B(am) + 0.5 N_2(g) → BN(cr)	−60.8 ± 0.3	−59.6 ± 0.8
[3]	BN(cr) + 1.5 F_2(g) → BF_3(g) + 0.5 N_2	−211.2 ± 0.1	
		−271.4	−60.2
[4]	BN(cr) + NF_3(g) → BF_3(g) + N_2	−177.63 ± 0.3	
	B(cr) + NF_3(g) → BF_3(g) + 0.5 N_2	−237.77 ± 0.5	−60.1 ± 2
[5]	Combustion in O_2–H_2O	—	−59.9 ± 1.5
[6]	BN(cr) + 1.5 F_2(g) → BF_3(g) + 0.5 N_2	−211.68 ± 0.3	−59.97 ± 0.37

Heat Capacity and Entropy

The low temperature heat capacity was taken from Westrum.[11] The intermediate heat capacity (300–1650°C) was obtained from McDonald and Stull.[12] The high temperature C_p was taken from Prophet and Stull.[13] The heat capacities in the three temperature ranges were plotted and then graphically smoothed. Dworkin *et al.*[1] also reported that heat capacity (50–300 K) not employed in this table.

The entropy was obtained by integration of the heat capacity data from Westrum[11] based upon $S°(10\ K) = 0.0028$ cal·K^{-1}mol^{-1}.

Decomposition Data

Observations by the Dow Chemical Company under contract No. AF 33(616) 6194 show decomposition to elements at 1 atm total pressure at 2600 ± 100 K. The decomposition temperature calculated from these tables is 2832 K; presumably this discrepancy is associated with uncertainties in the high temperature enthalpies of BN(cr), B(cr), and B(l) and the enthalpy of melting of B(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−2.628	−247.993	−247.993	INFINITE
100	4.950	2.791	27.183	−2.439	−249.280	−241.538	126.166
200	12.414	8.473	16.359	−1.577	−250.206	−233.418	60.963
298.15	19.719	14.795	14.795	0.	−250.914	−225.022	39.423
300	19.849	14.917	14.795	0.037	−250.926	−224.861	39.152
400	26.276	21.539	15.654	2.354	−251.430	−216.091	28.219
500	31.380	27.974	17.480	5.247	−251.737	−207.217	21.648
600	35.229	34.051	19.741	8.586	−251.871	−198.298	17.263
700	38.074	39.701	22.194	12.255	−251.879	−189.367	14.131
800	40.459	44.943	24.714	16.184	−251.787	−180.442	11.782
900	42.593	49.836	27.236	20.339	−251.602	−171.534	9.956
1000	44.350	54.417	29.728	24.689	−251.334	−162.652	8.496
1100	45.815	58.716	32.170	29.201	−251.001	−153.799	7.303
1200	46.861	62.749	34.552	33.836	−250.629	−144.979	6.311
1300	47.698	66.534	36.868	38.566	−250.237	−136.190	5.472
1400	48.283	70.091	39.115	43.367	−249.844	−127.432	4.755
1500	48.702	73.438	41.293	48.218	−249.461	−118.702	4.134
1600	48.911	76.589	43.401	53.099	−249.105	−109.996	3.591
1700	48.939	79.555	45.442	57.992	−248.791	−101.312	3.113
1800	48.953	82.352	47.415	62.887	−248.526	−92.645	2.688
1900	48.953	84.999	49.324	67.782	−248.307	−83.991	2.309
2000	48.953	87.510	51.171	72.677	−248.134	−75.347	1.968
2100	48.953	89.899	52.959	77.573	−248.003	−66.711	1.659
2200	48.953	92.176	54.690	82.468	−247.915	−58.080	1.379
2300	48.953	94.352	56.368	87.363	−247.867	−49.453	1.123
2400	48.953	96.435	57.994	92.258	−298.118	−39.758	0.865
2500	48.953	98.434	59.572	97.154	−298.226	−28.990	0.606
2600	48.953	100.354	61.104	102.049	−298.339	−18.219	0.366
2700	48.953	102.201	62.592	106.944	−298.456	−7.443	0.144
2800	48.953	103.981	64.039	111.840	−298.578	3.338	−0.062
2900	48.953	105.699	65.446	116.735	−298.704	14.123	−0.254
3000	48.953	107.359	66.815	121.630	−298.834	24.912	−0.434
3100	48.953	108.964	68.149	126.525	−298.966	35.706	−0.602
3200	48.953	110.518	69.449	131.421	−299.103	46.504	−0.759
3300	48.953	112.024	70.717	136.316	−299.242	57.306	−0.907
3400	48.953	113.486	71.953	141.211	−299.384	68.113	−1.046
3500	48.953	114.905	73.160	146.107	−299.528	78.923	−1.178

PREVIOUS: March 1964 CURRENT: June 1966

$S°(298.15\ K) = 212.36\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 474 \pm 125\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 477 \pm 125\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3\Pi$	0	6
	[8500]	1
	[8900]	2
	27877	6

$\omega_e = 1514.6\ cm^{-1}$ $\omega_e x_e = 12.3\ cm^{-1}$ $\sigma = 1$
$B_e = 1.666\ cm^{-1}$ $\alpha_e = 0.025\ cm^{-1}$ $r_e = 1.281$ Å

Enthalpy of Formation

The enthalpy of formation is based on $D_0^\circ = 5.7$ eV which was calculated from ω_e and $\omega_e x_e$ observed by Douglas and Herzberg.[1] An uncertainty of ±1.3 eV was assigned from consideration of other information which places the dissociation energy between 4 and 7 eV. The value $D_0^\circ = 4.0 \pm 0.5$ eV was selected by Gaydon[2] from his own extrapolation of the spectroscopic data. An upper limit of $D_0^\circ < 7.0$ eV results from the upper limit for the pressure of BN(cr) → BN(g) obtained from the B^+ ion intensity at 1600°C observed by Akishin and Klodeev.[3] It is likely that the BN(g) pressure is even smaller since it is known that BN(cr) → B(s) + 0.5 N_2(g) and Akishin's pressure limit is the same magnitude as that of B(cr) → B(g). Fesenko[4] reports a standard enthalpy of sublimation of 160 kcal·mol^{-1} for BN(cr) → BN(g) and also gives pressures for BN(g) at 2500 and 3000 K which are stated to be two orders less than the equilibrium pressure of nitrogen. Fesenko's original article is not yet available to us and it is not clear from the abstract whether the values are based on new data or are merely calculations. The *reported pressures yield* $D_0^\circ = 6.2$ eV *but here again the* BN(g) *pressures are of the same magnitude as the* JANAF *values for* B(s) → B(g).

Some estimated values for D_0° (ranging from 5.4 to 6.4 eV) are summarized below along with the experimental evidence.

Source	D_0°(ev)	$\Delta_{sub}H°$(298.15 K), kcal·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1}
Gaydon's extrapolation of spectroscopic data	4.0 ± 0.5	213	153
Linear Birge Sponer extrapolation	5.7	174	114
Fesenko's BN(g) pressures	6.2	161	101
Akishin's upper limit for BN(g) pressure	7.0	145	85
Estimate from geometric mean of $D°$ for B_2 and N_2	5.4	180	120
Estimate from $D°$ for series N_2, CN, BN, BeN	5.6	177	117
Estimate $M_2 + N_2 = 2$ MN for M=B from M=C	6.0	166	106
Estimate from arithmetic mean of $D°$ *for* B_2 *and* N_2	6.4	158	98

Heat Capacity and Entropy

The molecular constants are based on emission spectra of the $^3\Pi$–$^3\Pi$ transition otained by Douglas and Herzberg.[1] Observations of the same triplet in absorption by Thrush[5] strongly suggests that the ground state of BN is $^3\Pi$ in contrast to $^1\Sigma$ as observed for the isoelectronic molecules BeO and C_2. Electronic levels for the $^3\Pi$ states are taken from Douglas and Herzberg[1] while values for $^1\Sigma^+$ and $^1\Pi$ have been estimated from the SCF calculations of Masse and Barlochter.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
T/K	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.686	473.839	473.839	INFINITE
100	29.107	180.503	238.329	−5.783	475.267	465.238	−243.016
200	29.136	200.682	215.038	−2.871	476.391	454.736	−118.765
250	29.235	207.192	212.842	−1.412	476.751	449.278	−93.872
298.15	29.450	212.358	212.358	0.	476.976	443.965	−77.781
300	29.461	212.541	212.359	0.054	476.983	443.760	−77.265
350	29.820	217.107	212.719	1.536	477.108	438.212	−65.400
400	30.280	221.119	213.523	3.038	477.145	432.652	−56.499
450	30.797	224.715	214.570	4.565	477.111	427.091	−49.575
500	31.333	227.987	215.751	6.118	477.024	421.538	−44.038
600	32.362	233.792	218.286	9.304	476.737	410.465	−35.734
700	33.257	238.850	220.870	12.586	476.343	399.450	−29.807
800	34.001	243.341	223.403	15.950	475.870	388.497	−25.366
900	34.609	247.382	225.847	19.382	475.331	377.607	−21.916
1000	35.105	251.055	228.187	22.868	474.735	366.780	−19.159
1100	35.514	254.421	230.421	26.400	474.088	356.015	−16.906
1200	35.857	257.526	232.552	29.969	473.394	345.312	−15.031
1300	36.150	260.408	234.585	33.570	472.656	334.668	−13.447
1400	36.405	263.096	236.527	37.198	471.878	324.082	−12.092
1500	36.633	265.616	238.383	40.850	471.061	313.554	−10.919
1600	36.841	267.987	240.160	44.523	470.209	303.081	−9.895
1700	37.034	270.226	241.863	48.217	469.324	292.662	−8.992
1800	37.218	272.348	243.498	51.930	468.408	282.296	−8.192
1900	37.394	274.365	245.070	55.661	467.462	271.983	−7.477
2000	37.565	276.288	246.584	59.409	466.488	261.719	−6.835
2100	37.732	278.125	248.042	63.174	465.488	251.505	−6.256
2200	37.895	279.884	249.450	66.955	464.463	241.340	−5.730
2300	38.055	281.572	250.810	70.752	463.413	231.221	−5.251
2400	38.211	283.195	252.126	74.566	412.080	222.217	−4.836
2500	38.364	284.758	253.400	78.395	410.905	214.331	−4.478
2600	38.514	286.265	254.635	82.239	409.741	206.491	−4.148
2700	38.661	287.722	255.834	86.097	408.587	198.695	−3.844
2800	38.803	289.130	256.998	89.971	407.443	190.942	−3.562
2900	38.941	290.494	258.130	93.858	406.309	183.230	−3.300
3000	39.076	291.817	259.230	97.759	405.185	175.557	−3.057
3100	39.205	293.100	260.302	101.673	404.071	167.921	−2.829
3200	39.331	294.347	261.347	105.600	402.967	160.321	−2.617
3300	39.452	295.559	262.365	109.539	401.872	152.755	−2.418
3400	39.569	296.738	263.359	113.490	400.786	145.223	−2.231
3500	39.681	297.887	264.329	117.452	399.708	137.722	−2.055
3600	39.789	299.006	265.277	121.426	398.639	130.252	−1.890
3700	39.893	300.098	266.203	125.410	397.579	122.811	−1.734
3800	39.994	301.163	267.110	129.404	396.526	115.399	−1.586
3900	40.090	302.203	267.996	133.409	395.481	108.015	−1.447
4000	40.183	303.220	268.864	137.422	394.443	100.657	−1.314
4100	40.272	304.213	269.714	141.445	393.412	93.325	−1.189
4200	40.359	305.184	270.547	145.477	−87.461	93.043	−1.157
4300	40.442	306.135	271.364	149.517	−87.391	97.339	−1.182
4400	40.523	307.066	272.165	153.565	−87.317	101.635	−1.207
4500	40.602	307.977	272.950	157.621	−87.238	105.928	−1.230
4600	40.678	308.871	273.722	161.685	−87.156	110.220	−1.252
4700	40.752	309.746	274.479	165.757	−87.070	114.510	−1.273
4800	40.824	310.605	275.222	169.836	−86.982	118.798	−1.293
4900	40.894	311.447	275.953	173.922	−86.892	123.084	−1.312
5000	40.963	312.274	276.671	178.014	−86.800	127.368	−1.331
5100	41.031	313.086	277.377	182.114	−86.706	131.650	−1.348
5200	41.097	313.883	278.072	186.221	−86.612	135.931	−1.365
5300	41.163	314.667	278.755	190.334	−86.517	140.210	−1.382
5400	41.227	315.437	279.427	194.453	−86.422	144.487	−1.398
5500	41.291	316.194	280.089	198.579	−86.327	148.762	−1.413
5600	41.353	316.939	280.740	202.711	−86.233	153.035	−1.427
5700	41.416	317.671	281.382	206.850	−86.141	157.307	−1.442
5800	41.477	318.392	282.014	210.994	−86.051	161.578	−1.455
5900	41.538	319.101	282.636	215.145	−85.963	165.846	−1.468
6000	41.599	319.800	283.250	219.302	−85.878	170.113	−1.481

PREVIOUS: June1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 73.538 \pm 0.08\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1240 \pm 2\ K$

$\Delta_f H°(0\ K) = -971.0 \pm 2.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -975.7 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus} H° = 33.47 \pm 2.0\ kJ·mol^{-1}$

Enthalpy of Formation

Adami and Joe[1] measured enthalpies of solution of B_2O_3(cr), NaCl(cr) and $NaBO_2$(cr) in aqueous HCl solution and derived $\Delta_f H°(298.15\ K) = -12.43 \pm 0.1$ kcal·mol^{-1} for $NaBO_2$(cr) + HCl(12.732 H_2O, aq) → NaCl(cr) + 1/2 B_2O_3(cr) + 1/2 H_2O(l) which leads to $\Delta_f H°(NaBO_2$, cr, 298.15 K) = -233.2 ± 0.6 kcal·mol^{-1} using JANAF auxiliary data.[2] This value is adopted.

Grenier and White[3] measured the enthalpy of solution of crystal $Na_2OB_2O_3$ in 2N nitric acid solution at 0°C as -20.43 ± 0.36 kcal·mol^{-1}. Since the correction term for $\Delta_{sol}H°$ from 0° to 25°C is generally small, we may assume the enthalpy of solution is the same at 0°C as at 25°C within the uncertainty of ±1 kcal·mol^{-1}. Thus we obtain $\Delta_{sol}H°(25°C) = -10.22 \pm 1$ kcal·mol^{-1} for $NaBO_2$(cr) + HNO_3(27.75 H_2O, aq) + H_2O(l) → $NaNO_3$(27.75 H_2O, aq) + H_3BO_3(27.75 H_2O, aq) from which we derived $\Delta_f H°(NaBO_2$, cr, 298.15 K) = -234.7 ± 1.5 kcal·mol^{-1} based on JANAF auxiliary data.[4]

Shartsis and Capps[5] measured the heats of solution in 2N nitric acid of various Na_2O–B_2O_3 glass and crystalline mixtures containing 1.0–38.7 mole % of Na_2O. When their data are extrapolated to 50 mole %, we obtain $\Delta_{sol}H°(25°C) = -11.5 \pm 1.5$ kcal·mol^{-1} for the same reaction as given before. The derived enthalpy of formation is -233.4 ± 1.5 kcal·mol^{-1} which is in good agreement with the value adopted.

Heat Capacity and Entropy

Grenier and Westrum[6] measured low temperature heat capacities from 5 to 346 K. The adopted C_p are derived from their experimental heat capacities by a polynomial curve fitting technique. The derived entropy, $S°(298.15\ K)$, is 17.576 ± 0.02 cal·K^{-1}·mol^{-1} based on $S° = 0.001$ cal·K^{-1}·mol^{-1} at 5.48 K. Pankratz[7] measured high temperature enthalpy data by drop calorimetry in the temperature range 404–1200.3 K. We adopt the smooth C_p derived by Pankratz. The average deviation of the observed enthalpy data from the adopted values is about 0.1%.

Fusion Data

Our analysis of several sets of binary phase data[8–10] yields the enthalpy of fusion, $\Delta_{fus}H° = 8.0 \pm 0.5$ kcal·mol^{-1}. Petit and Jaeger[11] derived $\Delta_{fus}H°(1239\ K) = 8.0$ kcal·mol^{-1} from their phase data for the $NaBO_2$–NaF system. The adopted melting point (1240 K) is obtained from Pankratz.[7] Literature value include 1239 K,[8–12] 1238 K[13] and 1237 K.[14]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.634	−970.998	−970.998	INFINITE
100	32.430	20.000	123.003	−10.300	−973.933	−956.190	499.463
200	53.371	49.752	79.193	−5.888	−975.221	−937.851	244.942
298.15	65.940	73.538	73.538	0.	−975.709	−919.389	161.073
300	66.149	73.947	73.539	0.122	−975.714	−919.039	160.019
400	75.396	94.289	76.250	7.215	−978.576	−899.905	117.516
500	82.718	111.927	81.660	15.133	−978.549	−880.232	91.957
600	88.575	127.543	88.030	23.707	−978.132	−860.601	74.922
700	93.303	141.562	94.693	32.808	−977.394	−841.067	62.761
800	97.236	154.285	101.359	42.340	−976.390	−821.658	53.649
900	100.500	165.932	107.896	52.232	−975.173	−802.387	46.569
1000	103.219	176.667	114.244	62.423	−973.793	−783.262	40.913
1100	105.269	186.607	120.376	72.854	−972.310	−764.280	36.293
1200	106.608	195.831	126.284	83.456	−1067.556	−742.995	32.342
1240.000	106.859	199.331	128.584	87.726	--- CRYSTAL <- -> LIQUID ---		
1300	107.320	204.391	131.967	94.151	−1065.165	−716.045	28.771
1400	108.127	212.374	137.429	104.923	−1062.774	−689.279	25.717
1500	108.935	219.861	142.677	115.776	−1060.375	−662.685	23.077
1600	109.742	226.917	147.724	126.710	−1057.963	−636.251	20.771
1700	110.549	233.595	152.580	137.724	−1055.536	−609.968	18.742
1800	111.356	239.936	157.259	148.820	−1053.090	−583.829	16.942
1900	112.162	245.979	161.770	159.996	−1050.624	−557.826	15.336
2000	112.968	251.752	166.126	171.252	−1048.138	−531.953	13.893

PREVIOUS: March 1965 CURRENT: June 1971

$S°(298.15\ K) = [82.958]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1240 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-960.019]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 33.47 \pm 2.0\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NaBO_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1240\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The constant heat capacity of the liquid is estimated to be 35 $cal·K^{-1}·mol^{-1}$ based on that of $LiBO_2$(l), 34.491 $cal·K^{-1}·mol^{-1}$,[1] which was derived from high temperature enthalpy measurements. A glass transition is assumed at 826 K below which the heat capacities are assumed to be the same as the crystal.

$S°(NaBO_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

See the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which the fugacity is 1 bar for the reaction $NaBO_2(l) \rightarrow NaBO_2(g)$. The enthalpy of vaporization is the difference in $\Delta_f H°$ at the boiling point between liquid and gas.

Reference

[1]JANAF Thermochemical Table: $LiBO_2$(l), 6–30–71.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	65.940	82.958	82.958	0.	−960.019	−906.507	158.816
300	66.149	83.366	82.959	0.122	−960.024	−906.175	157.779
400	75.396	103.708	85.670	7.215	−962.886	−887.983	115.959
500	82.718	121.346	91.080	15.133	−962.859	−869.251	90.810
600	88.575	136.962	97.450	23.707	−962.442	−850.563	74.048
700	93.303	150.981	104.113	32.808	−961.704	−831.971	62.082
800	97.236	163.706	110.779	42.342	−960.699	−813.504	53.116
826.000	98.129	166.830	112.494	44.881	GLASS <- -> LIQUID		
826.000	146.440	166.830	112.494	44.881	TRANSITION		
900	146.440	179.395	117.486	55.718	−955.997	−795.328	46.160
1000	146.440	194.824	124.462	70.362	−950.164	−777.790	40.628
1100	146.440	208.781	131.503	85.006	−944.468	−760.829	36.129
1200	146.440	221.523	138.481	99.650	−1035.672	−741.941	32.296
1240.000	146.440	226.325	141.238	105.508	--- CRYSTAL <- -> LIQUID ---		
1300	146.440	233.244	145.326	114.294	−1029.331	−717.722	28.838
1400	146.440	244.097	151.998	128.938	−1023.069	−693.987	25.893
1500	146.440	254.200	158.479	143.582	−1016.879	−670.698	23.356
1600	146.440	263.651	164.760	158.226	−1010.757	−647.819	21.149
1700	146.440	272.529	170.841	172.870	−1004.700	−625.321	19.214
1800	146.440	280.899	176.725	187.514	−998.706	−603.178	17.504
1900	146.440	288.817	182.418	202.158	−992.772	−581.366	15.983
2000	146.440	296.328	187.927	216.802	−986.898	−559.866	14.622
2100	146.440	303.473	193.261	231.446	−981.083	−538.657	13.398
2200	146.440	310.285	198.426	246.090	−975.327	−517.724	12.292
2300	146.440	316.795	203.432	260.734	−969.629	−497.052	11.288
2400	146.440	323.027	208.287	275.378	−1014.248	−475.558	10.350
2500	146.440	329.005	212.997	290.022	−1008.744	−453.225	9.470

PREVIOUS: March 1965 CURRENT: June 1971

0	to	1240 K	crystal
above		1240 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.634	−970.998	−970.998	INFINITE
100	32.430	20.000	123.003	−10.300	−973.933	−956.190	499.463
200	53.371	49.752	79.193	−5.888	−975.221	−937.851	244.942
298.15	65.940	73.538	73.538	0.	−975.709	−919.389	161.073
300	66.149	73.947	73.539	0.122	−975.714	−919.039	160.019
400	75.396	94.289	76.250	7.215	−978.576	−899.905	117.516
500	82.718	111.927	81.660	15.133	−978.549	−880.232	91.957
600	88.575	127.543	88.030	23.707	−978.132	−860.601	74.922
700	93.303	141.562	94.693	32.808	−977.394	−841.067	62.761
800	97.236	154.285	101.359	42.340	−976.390	−821.658	53.649
900	100.500	165.932	107.896	52.232	−975.173	−802.387	46.569
1000	103.219	176.667	114.244	62.423	−973.793	−783.262	40.913
1100	105.269	186.607	120.376	72.854	−972.310	−764.280	36.293
1200	106.608	195.831	126.284	83.456	−1067.556	−742.995	32.342
1240.000	106.859	199.331	128.584	87.726	CRYSTAL <--> LIQUID		
1240.000	146.440	226.325	128.584	121.198	TRANSITION		
1300	146.440	233.244	133.256	129.984	−1029.331	−717.721	28.838
1400	146.440	244.097	140.791	144.628	−1023.069	−693.986	25.893
1500	146.440	254.200	148.019	159.272	−1016.879	−670.697	23.356
1600	146.440	263.651	154.953	173.916	−1010.757	−647.818	21.149
1700	146.440	272.529	161.611	188.560	−1004.700	−625.321	19.214
1800	146.440	280.899	168.008	203.204	−998.705	−603.178	17.504
1900	146.440	288.817	174.160	217.848	−992.772	−581.366	15.983
2000	146.440	296.328	180.082	232.492	−986.898	−559.865	14.622
2100	146.440	303.473	185.789	247.136	−981.083	−538.657	13.398
2200	146.440	310.285	191.294	261.780	−975.326	−517.723	12.292
2300	146.440	316.795	196.610	276.424	−969.628	−497.052	11.288
2400	146.440	323.027	201.749	291.068	−1014.248	−475.557	10.350
2500	146.440	329.005	206.720	305.712	−1008.744	−453.225	9.470

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = 287.2 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -645.9 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -648.5 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
1960(1)	573(1)
1087(1)	363(1)
576(1)	108(1)

Ground State Quantum Weight: *1* $\sigma = 1$
Point Group: C_s
Bond Distances: Na–O = 2.14 Å; O–B = 1.36 Å; B=O = 1.20 Å
Bond Angles: Na–O–B = 90°; O–B–O = 180°
Product of the Moments of Inertia: $I_A I_B I_C = 2.407470 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Jensen[1] determined equilibrium constants for the reaction: $Na(g) + HBO_2(g) \rightarrow NaBO_2(g) + H(g)$ by flame studies. This technique involved several assumptions, the most basic of which was that boron added to $H_2/N_2/O_2$ flames was converted completely to HBO_2. The hydrogen atom concentration was taken from previous studies on such flames. Sodium metaborate was assumed to be formed in the flame. The concentration of Na atom was determined by atomic absorption spectrophotometry. JANAF 3rd law analysis of his equilibrium constant equation in the temperature range from 2000 to 2600 K yields $\Delta_f H(298.15\ K) = 7.55 \pm 1.08\ kcal \cdot mol^{-1}$ and the drift $2.50\ cal \cdot K^{-1} \cdot mol^{-1}$. (The 2nd law enthalpy of reaction is $\Delta_r H°(298.15\ K) = 1.81\ kcal \cdot mol^{-1}$.) Using the 3rd law $\Delta_r H°(298.15\ K)$ and JANAF auxiliary data, we obtain $\Delta_f H°(NaBO_2, g, 298.15\ K) = -152.8\ kcal \cdot mol^{-1}$. The uncertainty in this result is about $\pm 6\ kcal \cdot mol^{-1}$.

Buchler and Berkowitz–Mattuck[2] studied mass spectrometrically the sublimation of sodium metaborate and obtained $\Delta_{sub} H°(1070\ K) = 73 \pm 3\ kcal \cdot mol^{-1}$ for $NaBO_2(cr) \rightarrow NaBO_2(g)$ by a 2nd law method. JANAF reduction to 298.15 K gives $\Delta_{sub} H°(298.15\ K) = 76.6 \pm 3\ kcal \cdot mol^{-1}$ which leads to $\Delta_f H°(298.15\ K)(NaBO_2, g) = -156.6 \pm 3\ kcal \cdot mol^{-1}$. They also determined the vapor pressure of $NaBO_2$ at 1070 K as 5×10^{-7} atm by comparison with the vapor pressure of silver. JANAF 3rd law analysis of this single vapor pressure point gives $\Delta_{sub} H°(298.15\ K) = 83.37\ kcal \cdot mol^{-1}$ which leads to $\Delta_f H°(NaBO_2, g, 298.15\ K) = -149.8\ kcal \cdot mol^{-1}$.

Cole and Taylor[3] determined the vapor pressures of $NaBO_2(g)$ by a dynamic method with dry N_2 as carrier gas. Their vapor pressure data were taken over a flow–rate range where the apparent vapor pressure increased with decreasing flow rate, and the data were then extrapolated to zero flow rate. The vapor species of the sample was also assumed to be monomeric $NaBO_2(g)$. JANAF 3rd law analyses of their reported vapor pressure data over the liquid $NaBO_2$ in the temperature range 1150°C–1350°C yield $\Delta_{vap} H°(298.15\ K) = 75.37 \pm 3.32\ kcal \cdot mol^{-1}$ and the drift $-20.6\ cal \cdot K^{-1} \cdot mol^{-1}$. (The 2nd law enthalpy of vaporization is $\Delta_{vap} H°(298.15\ K) = 107\ kcal \cdot mol^{-1}$). Using the 3rd law $\Delta_{vap} H°(298.15\ K)$, we obtain $\Delta_f H°(298.15\ K) = -154.1 \pm 4\ kcal \cdot mol^{-1}$.

A weighted average, $\Delta_f H°(NaBO_2, g, 298.15\ K) = -155 \pm 3\ kcal \cdot mol^{-1}$, is adopted in the tabulation.

Heat Capacity and Entropy

The adopted vibrational frequencies are obtained from Seshadri *et al.*,[4] who observed the infrared spectra of $NaBO_2$ in an argon matrix and made a complete assignment of all six fundamentals. The uncertainty of the calculated statistical entropy at 298.15 K is estimated to be $\pm 1\ cal \cdot mol^{-1}\ K^{-1}$ which is due to the magnitude of the matrix shifts from the free molecule spectrum, particularly for the lower frequency modes.

Buchler and Marran[5] observed only two vibrational frequencies, 1935 and 600 cm^{-1}, in their gas–phase infrared spectra. These two frequencies are in reasonable agreement with those reported by Seshadri.[4]

By electron diffraction studies, Akishin and Spiridonov[6] determined the molecular structure of gaseous sodium metaborate and found the bond length and angles which are adopted in the tabulation. The angle Na–O–B is taken as 90° based on that of $LiBO_2(g)$.[7]

The three principal moments of inertia are $I_A = 5.1904 \times 10^{-39}$, $I_B = 19.0974 \times 10^{-39}$, and $I_C = 24.2878 \times 10^{-39}\ g \cdot cm^2$.

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[7]JANAF Thermochemical Tables: $LiBO_2(g)$, 6-30-71.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.703	−645.879	−645.879	INFINITE
100	41.612	233.779	333.819	−10.004	−646.448	−650.083	339.569
200	50.926	265.464	292.357	−5.379	−647.523	−653.295	170.623
250	54.980	277.277	288.189	−2.728	−648.025	−654.680	136.788
298.15	58.233	287.248	287.248	0.	−648.520	−655.918	114.914
300	58.346	287.608	287.249	0.108	−648.540	−655.964	114.213
350	61.142	296.819	287.970	3.097	−649.107	−657.157	98.075
400	63.496	305.141	289.604	6.215	−652.388	−658.058	85.934
450	65.510	312.739	291.759	9.441	−653.069	−658.726	76.463
500	67.255	319.734	294.211	12.761	−653.733	−659.318	68.879
600	70.125	332.261	299.533	19.636	−655.015	−660.314	57.485
700	72.365	343.246	305.009	26.765	−656.247	−661.100	49.332
800	74.131	353.029	310.412	34.094	−657.448	−661.711	43.205
900	75.536	361.844	315.645	41.580	−658.636	−662.172	38.431
1000	76.662	369.863	320.672	49.192	−659.836	−662.501	34.605
1100	77.572	377.214	325.482	56.905	−661.070	−662.708	31.469
1200	78.314	383.996	330.079	64.700	−759.123	−660.360	28.745
1300	78.924	390.290	334.472	72.563	−759.563	−652.112	26.202
1400	79.431	396.158	338.671	80.482	−760.027	−643.830	24.022
1500	79.855	401.653	342.688	88.446	−760.516	−635.513	22.131
1600	80.212	406.818	346.537	96.450	−761.034	−627.163	20.475
1700	80.517	411.690	350.227	104.487	−761.584	−618.779	19.013
1800	80.777	416.300	353.771	112.552	−762.169	−610.363	17.712
1900	81.002	420.674	357.178	120.641	−762.790	−601.912	16.548
2000	81.196	424.834	360.458	128.752	−763.450	−593.428	15.499
2100	81.366	428.799	363.619	136.880	−764.150	−584.910	14.549
2200	81.515	432.588	366.668	145.024	−764.894	−576.357	13.684
2300	81.647	436.215	369.614	153.182	−765.681	−567.770	12.894
2400	81.763	439.692	372.462	161.353	−816.774	−558.079	12.146
2500	81.866	443.032	375.218	169.535	−817.733	−547.280	11.435
2600	81.959	446.244	377.888	177.726	−818.708	−536.443	10.777
2700	82.042	449.339	380.478	185.926	−819.700	−525.567	10.168
2800	82.116	452.324	382.991	194.134	−820.711	−514.655	9.601
2900	82.184	455.207	385.431	202.349	−821.743	−503.707	9.073
3000	82.245	457.994	387.804	210.570	−822.798	−492.722	8.579
3100	82.300	460.692	390.112	218.798	−823.876	−481.701	8.117
3200	82.351	463.306	392.359	227.030	−824.979	−470.646	7.683
3300	82.397	465.840	394.547	235.268	−826.107	−459.556	7.274
3400	82.439	468.301	396.680	243.509	−827.264	−448.431	6.889
3500	82.478	470.691	398.761	251.755	−828.451	−437.272	6.526
3600	82.513	473.015	400.791	260.005	−829.668	−426.078	6.182
3700	82.546	475.276	402.774	268.258	−830.919	−414.851	5.857
3800	82.577	477.478	404.711	276.514	−832.205	−403.588	5.548
3900	82.605	479.623	406.605	284.773	−833.527	−392.291	5.254
4000	82.631	481.715	408.456	293.035	−834.889	−380.960	4.975
4100	82.655	483.756	410.268	301.299	−836.292	−369.595	4.709
4200	82.678	485.748	412.042	309.566	−1317.585	−351.171	4.367
4300	82.699	487.694	413.779	317.835	−1317.991	−328.156	3.986
4400	82.719	489.595	415.480	326.106	−1318.406	−305.135	3.622
4500	82.737	491.454	417.148	334.379	−1318.893	−282.102	3.275
4600	82.754	493.273	418.783	342.653	−1319.443	−259.056	2.942
4700	82.771	495.053	420.387	350.930	−1320.051	−235.998	2.623
4800	82.786	496.796	421.961	359.207	−1320.719	−212.926	2.317
4900	82.800	498.503	423.505	367.487	−1321.451	−189.839	2.024
5000	82.814	500.176	425.022	375.767	−1322.243	−166.737	1.742
5100	82.826	501.816	426.512	384.049	−1323.111	−143.618	1.471
5200	82.838	503.424	427.976	392.333	−1324.054	−120.483	1.210
5300	82.850	505.002	429.414	400.617	−1325.075	−97.327	0.959
5400	82.860	506.551	430.828	408.903	−1326.178	−74.152	0.717
5500	82.870	508.071	432.219	417.189	−1327.366	−50.956	0.484
5600	82.880	509.565	433.587	425.477	−1328.643	−27.736	0.259
5700	82.889	511.032	434.933	433.765	−1330.012	−4.494	0.041
5800	82.898	512.473	436.257	442.054	−1331.478	18.774	−0.169
5900	82.906	513.890	437.561	450.345	−1333.043	42.066	−0.372
6000	82.914	515.284	438.845	458.636	−1334.552	65.369	−0.569

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = 203.47 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -3.1 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0 \pm 8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	23836	2
$A'^2\Pi$	23959	2
$B'^2\Sigma$	39957	2
$B^2\Sigma^+$	43175	2

$\omega_e = 1895.66\ cm^{-1}$ $\omega_e x_e = 11.90\ cm^{-1}$ $\sigma = 1$
$B_e = 1.800\ cm^{-1}$ $\alpha_e = 0.01676\ cm^{-1}$ $r_e = 1.2049$ Å

Enthalpy of Formation

The enthalpy of formation has recently been determined by several workers whose values are in close agreement. Blackburn, *et al.*[1] measured the ion currents corresponding to BO^+ and $B_2O_2^+$ as a function of temperature in a mass spectrometer. From a least squares fit of the data they report $\Delta H = 56.6 \pm 1.8\ kcal \cdot mol^{-1}$ for the reaction $1/2B_2O_2(g) \rightarrow BO(g)$; this yields $\Delta_f H°(BO, g, 298.15\ K) = 2.1 \pm 2.8\ kcal \cdot mol^{-1}$ using $\Delta_f H°(B_2O_2, g, 298.15\ K) = -109 \pm 2\ kcal \cdot mol^{-1}$.

De Galan, *et al.*[2] from flame photometric measurements reports $D_0°(BO) = 8.3eV(191.4\ kcal \cdot mol^{-1})$, which corresponds to $\Delta_f H°(BO, g, 298.15\ K) = -0.1\ kcal \cdot mol^{-1}$.

Coppens, *et al.*[3] from a mass spectometric study of several isomolecular exchange reactions, conclude that $D_0°(BO) = 8.29 \pm 0.1$ eV$(191.2 \pm 2.3\ kcal \cdot mol^{-1})$ or $\Delta_f H°(BO, g, 298.15\ K) = 0.1 \pm 2.3\ kcal \cdot mol^{-1}$.

Farber, *et al.*[4] investigated the same reaction as Blackburn *et al.* and reported $\Delta_f H°(1800\ K) = 53.8 \pm 1.9\ kcal \cdot mol^{-1}$, which yields $\Delta_f H°(BO, g, 298.15\ K) = 0.9 \pm 2.9\ kcal \cdot mol^{-1}$.

We adopt a median value of $0 \pm 2\ kcal \cdot mol^{-1}$ which includes all the determinations

Heat Capacity and Entropy

The molecular and vibrational constants for the ground state are from Herzberg.[5] The electronic levels are also given by Herzberg with the exception of the level at 39957, the $A^2\Sigma$ level designated B' by Mal'tsev and Kataev.[6] The molecular constants were all adjusted to reflect normal isotopic abundancies.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.674	−3.118	−3.118	INFINITE
100	29.105	171.662	229.370	−5.771	−1.692	−10.162	5.308
200	29.112	191.838	206.138	−2.860	−0.569	−19.105	4.990
250	29.133	198.336	203.952	−1.404	−0.213	−23.783	4.969
298.15	29.196	203.472	203.472	0.	0.	−28.343	4.966
300	29.200	203.652	203.472	0.054	0.006	−28.519	4.966
350	29.343	208.163	203.828	1.517	0.104	−33.283	4.967
400	29.574	212.096	204.621	2.990	0.094	−38.053	4.969
450	29.882	215.596	205.649	4.476	−0.007	−42.816	4.970
500	30.250	218.763	206.805	5.979	−0.178	−47.564	4.969
600	31.076	224.350	209.276	9.045	−0.673	−56.997	4.962
700	31.910	229.204	211.783	12.194	−1.306	−66.336	4.950
800	32.677	233.516	214.235	15.425	−2.027	−75.578	4.935
900	33.350	237.404	216.597	18.727	−2.809	−84.725	4.917
1000	33.926	240.949	218.858	22.091	−3.638	−93.783	4.899
1100	34.415	244.206	221.016	25.509	−4.505	−102.756	4.879
1200	34.829	247.219	223.075	28.972	−5.405	−111.648	4.860
1300	35.181	250.021	225.042	32.473	−6.337	−120.464	4.840
1400	35.481	252.639	226.920	36.006	−7.300	−129.208	4.821
1500	35.739	255.096	228.718	39.568	−8.294	−137.881	4.801
1600	35.961	257.410	230.439	43.153	−9.318	−146.487	4.782
1700	36.155	259.596	232.091	46.759	−10.375	−155.028	4.763
1800	36.324	261.667	233.677	50.383	−11.463	−163.505	4.745
1900	36.473	263.635	235.202	54.023	−12.584	−171.922	4.726
2000	36.606	265.510	236.671	57.677	−13.739	−180.278	4.708
2100	36.724	267.299	238.087	61.344	−14.928	−188.576	4.691
2200	36.831	269.010	239.454	65.022	−16.151	−196.816	4.673
2300	36.928	270.649	240.775	68.710	−17.409	−205.000	4.656
2400	37.016	272.222	242.053	72.407	−68.961	−212.060	4.615
2500	37.098	273.735	243.290	76.113	−70.368	−217.994	4.555
2600	37.173	275.192	244.489	79.826	−71.778	−223.871	4.498
2700	37.244	276.596	245.653	83.547	−73.190	−229.694	4.444
2800	37.310	277.952	246.782	87.275	−74.607	−235.464	4.393
2900	37.374	279.262	247.880	91.009	−76.026	−241.185	4.344
3000	37.435	280.530	248.947	94.749	−77.449	−246.855	4.298
3100	37.495	281.759	249.986	98.496	−78.876	−252.478	4.254
3200	37.554	282.950	250.997	102.248	−80.305	−258.056	4.212
3300	37.613	284.106	251.983	106.007	−81.737	−263.589	4.172
3400	37.672	285.230	252.945	109.771	−83.172	−269.078	4.134
3500	37.731	286.323	253.883	113.541	−84.609	−274.525	4.097
3600	37.792	287.387	254.799	117.317	−86.047	−279.930	4.062
3700	37.855	288.423	255.693	121.100	−87.487	−285.296	4.028
3800	37.920	289.433	256.568	124.888	−88.927	−290.623	3.995
3900	37.987	290.419	257.424	128.684	−90.368	−295.912	3.963
4000	38.057	291.382	258.261	132.486	−91.809	−301.164	3.933
4100	38.130	292.323	259.080	136.295	−93.249	−306.380	3.903
4200	38.206	293.242	259.882	140.112	−574.537	−304.537	3.787
4300	38.285	294.142	260.669	143.936	−574.887	−298.104	3.621
4400	38.368	295.023	261.439	147.769	−575.237	−291.663	3.462
4500	38.455	295.887	262.195	151.610	−575.586	−285.215	3.311
4600	38.546	296.733	262.937	155.460	−575.935	−278.758	3.165
4700	38.640	297.563	263.665	159.319	−576.284	−272.294	3.026
4800	38.738	298.377	264.380	163.188	−576.632	−265.823	2.893
4900	38.840	299.177	265.082	167.067	−576.980	−259.343	2.765
5000	38.946	299.963	265.771	170.956	−577.327	−252.858	2.642
5100	39.055	300.735	266.449	174.856	−577.674	−246.365	2.523
5200	39.169	301.495	267.116	178.768	−578.020	−239.865	2.409
5300	39.285	302.242	267.772	182.690	−578.368	−233.359	2.300
5400	39.406	302.977	268.417	186.625	−578.715	−226.846	2.194
5500	39.529	303.701	269.052	190.571	−579.064	−220.327	2.092
5600	39.656	304.415	269.677	194.531	−579.414	−213.801	1.994
5700	39.787	305.118	270.293	198.503	−579.766	−207.269	1.899
5800	39.920	305.811	270.899	202.488	−580.120	−200.731	1.808
5900	40.055	306.494	271.497	206.487	−580.477	−194.187	1.719
6000	40.194	307.169	272.086	210.499	−580.838	−187.637	1.634

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 229.81 \pm 0.20\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -285 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -285 \pm 8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_g$	0	2
$^2\Pi_g$	1.49	2
$^2\Pi_u$	18291.6	4
$^2\Sigma_u^+$	24508.0	2

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
1056 (1)
454 (2)
1321.7 (1)

Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distance: B–O = 1.263 Å
Bond Angle: O–B–O = 180°
Rotational Constant : $B_O = 0.33026\ cm^{-1}$

Enthalpy of Formation

Greene[1] measured the vapor pressure of B_2O_3 and examined the infrared absorption spectra of B_2O_3, B_2O_2 and BO_2. The isotope shift and oxygen and temperature dependencies of the boric acid fluctuation bands were studied. The enthalpy change, $\Delta_r H°(2100\ K) = 76 \pm 2$ kcal·mol^{-1}, for the reaction 1/2 B_2O_3(l) + 1/4 O_2(g) = BO_2(g), was obtained spectroscopically. Based on this data and $\Delta_f H°(B_2O_3, l, 2100\ K) = -291.05$ kcal·mol^{-1}, we derive $\Delta_f H°(BO_2, g, 298.15\ K) = -68.4 \pm 2$ kcal·mol^{-1}.

Rusin[2] determined the equilibrium constant of the reaction $HBO_2(g) + OH(g) = BO_2(g) + H_2O(g)$ by simultaneously recording the pressure and spectra at 3000–3200 K of HBO_2 and BO_2, which were produced from the combustion in a bomb of mixtures of H, O, CO and a small amount of B_2H_6. Using the experimental value $K_p(3100\ K) = 0.9$, and JANAF Gibbs energy functions for the reactants and products, we obtain $\Delta_r H°(298.15\ K) = 0.53$ kcal·mol^{-1} for that reaction. Employing $\Delta_f H°(298.15\ K) = -134.00$, 9.43 and −57.80 kcal·mol^{-1} for HBO_2(g), OH(g) and H_2O(g), respectively, we derive the value $\Delta_f H°(BO_2, g, 298.15\ K) = -66.24$ kcal·mol^{-1}.

In a study of gases from flames containing trimethylborate stabilized on flat porous metal burners, Kaskan[3] obtained data consistent with the bands being due to the molecule BO_2(g). The temperature dependence of the equilibrium constants for the reaction $OH(g) + HBO_2(g) = H_2O(g) + BO_2(g)$ was investigated and the data were reported to be consistent with a value $\Delta_r H°(1800\ K) = -16$ kcal·mol^{-1}. Based on this $\Delta_r H°(1800\ K)$ value, we calculate $\Delta_f H°(BO_2, g, 298.15\ K) = -83.62$ kcal·mol^{-1}. Kaskan[4] has studied the effect of oxygen on the intensity of absorption (5470 Å) in the green or "fluctuation" bands of the gas phase in equilibrium with B_2O_3(l). At constant temperature the absorptivity was found to depend on the 1/4 power of the oxygen pressure. This is interpreted as evidence that the absorbing species is BO_2(g). The reaction 1/2 B_2O_3(l) + 1/4 O_2(g) = BO_2(g) was found to be 70 kcal·mol^{-1} endothermic in the temperature range 1660–1950 K, yielding $\Delta_f H°(BO_2, g, 298.15\ K) = -75.28$ kcal·mol^{-1}. Rusin *et al.*[2] discussed the discrepancy between their results and those of the above two investigations and commented that the results of Kaskan[3,4] were derived based on the assumption that Beer's law was obeyed over the temperature range 1400–2200 K. Actually, the relative population α of the principal electronic state $X^2\Pi$ of the BO_2 molecule changes greatly over this temperature range. Therefore the expression for the dependence of the optical density on the concentration of BO_2 must be corrected to allow for the variation of α with temperature.

The enthalpy of formation of BO_2(g) at 298.15 K is selected as -68 ± 2 kcal·mol^{-1}.

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Johns.[5] Vibrational frequencies, bond distance and rotational constant were reported by Johns,[5] Sommer,[6] and Snowden.[7] The values adopted are those determined by Snowden.[7] Snowden used a (1:1) mixture of KBF_4 and B_2O_3 placed in a 13 mm Vycor tube. The mixture was heated to produce a vapor which passed through an external electrodeless discharge. The intense emission spectrum of the BO_2 molecule was observed. The fluorescence spectrum obtained by Johns was too weak for a full characterization of the electronic ground state.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.731	−285.346	−285.346	INFINITE
100	33.725	188.764	264.960	−7.620	−285.163	−286.678	149.745
200	38.528	213.526	233.623	−4.019	−284.807	−288.331	75.304
250	41.020	222.394	230.514	−2.030	−284.646	−289.231	60.432
298.15	43.276	229.814	229.814	0.	−284.512	−290.127	50.829
300	43.359	230.082	229.815	0.080	−284.507	−290.162	50.522
350	45.527	236.931	230.351	2.303	−284.388	−291.114	43.446
400	47.495	243.141	231.567	4.630	−284.292	−292.082	38.142
450	49.246	248.838	233.174	7.049	−284.217	−293.060	34.018
500	50.780	254.108	235.007	9.550	−284.160	−294.046	30.719
600	53.263	263.597	238.999	14.759	−284.093	−296.030	25.772
700	55.110	271.953	243.122	20.182	−284.080	−298.021	22.239
800	56.490	279.406	247.200	25.765	−284.116	−300.011	19.589
900	57.533	286.123	251.158	31.469	−284.200	−301.994	17.527
1000	58.333	292.228	254.964	37.264	−284.329	−303.964	15.877
1100	58.957	297.818	258.610	43.129	−284.502	−305.920	14.527
1200	59.451	302.970	262.094	49.051	−284.719	−307.857	13.401
1300	59.847	307.745	265.425	55.016	−284.978	−309.776	12.447
1400	60.169	312.192	268.608	61.018	−285.280	−311.672	11.629
1500	60.435	316.353	271.654	67.048	−285.624	−313.546	10.919
1600	60.655	320.260	274.571	73.103	−286.013	−315.395	10.297
1700	60.841	323.943	277.368	79.178	−286.446	−317.218	9.747
1800	60.998	327.425	280.053	85.270	−286.924	−319.015	9.258
1900	61.133	330.727	282.634	91.377	−287.449	−320.783	8.819
2000	61.250	333.866	285.118	97.496	−288.019	−322.523	8.423
2100	61.352	336.857	287.511	103.627	−288.637	−324.233	8.065
2200	61.443	339.713	289.819	109.766	−289.302	−325.912	7.738
2300	61.523	342.446	292.048	115.915	−290.016	−327.561	7.439
2400	61.597	345.066	294.203	122.071	−341.036	−328.109	7.141
2500	61.664	347.582	296.288	128.234	−341.923	−327.552	6.844
2600	61.728	350.002	298.308	134.404	−342.824	−326.959	6.569
2700	61.788	352.332	300.266	140.579	−343.741	−326.332	6.313
2800	61.847	354.581	302.166	146.761	−344.672	−325.670	6.075
2900	61.904	356.752	304.011	152.949	−345.617	−324.975	5.853
3000	61.961	358.852	305.804	159.142	−346.575	−324.247	5.646
3100	62.019	360.884	307.548	165.341	−347.547	−323.486	5.451
3200	62.078	362.854	309.246	171.546	−348.531	−322.695	5.267
3300	62.138	364.765	310.900	177.757	−349.526	−321.872	5.095
3400	62.201	366.621	312.511	183.974	−350.532	−321.019	4.932
3500	62.265	368.425	314.083	190.197	−351.548	−320.136	4.778
3600	62.333	370.180	315.617	196.427	−352.572	−319.224	4.632
3700	62.403	371.889	317.115	202.663	−353.604	−318.284	4.493
3800	62.475	373.554	318.579	208.907	−354.644	−317.315	4.362
3900	62.551	375.178	320.009	215.159	−355.690	−316.318	4.237
4000	62.629	376.763	321.408	221.418	−356.741	−315.296	4.117
4100	62.711	378.310	322.777	227.685	−357.798	−314.247	4.004
4200	62.795	379.822	324.117	233.960	−838.708	−306.148	3.808
4300	62.882	381.301	325.430	240.244	−838.686	−293.467	3.565
4400	62.971	382.747	326.716	246.536	−838.669	−280.789	3.333
4500	63.062	384.164	327.977	252.838	−838.657	−268.110	3.112
4600	63.156	385.551	329.214	259.149	−838.650	−255.432	2.901
4700	63.252	386.910	330.427	265.469	−838.649	−242.753	2.698
4800	63.350	388.243	331.618	271.799	−838.653	−230.074	2.504
4900	63.449	389.550	332.787	278.139	−838.664	−217.395	2.317
5000	63.549	390.833	333.935	284.489	−838.680	−204.715	2.139
5100	63.651	392.092	335.063	290.849	−838.705	−192.036	1.967
5200	63.754	393.329	336.172	297.219	−838.736	−179.357	1.802
5300	63.857	394.545	337.262	303.600	−838.777	−166.675	1.643
5400	63.961	395.739	338.333	309.991	−838.828	−153.994	1.490
5500	64.065	396.914	339.388	316.392	−838.889	−141.312	1.342
5600	64.169	398.069	340.425	322.804	−838.962	−128.627	1.200
5700	64.273	399.206	341.447	329.226	−839.048	−115.942	1.062
5800	64.377	400.324	342.452	335.658	−839.149	−103.254	0.930
5900	64.480	401.426	343.443	342.101	−839.266	−90.567	0.802
6000	64.582	402.510	344.418	348.554	−839.400	−77.875	0.678

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K)$ = [215.9 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -688 \pm 25\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -695 \pm 25\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^1B_2$	[35000]	1

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[1150] (1)
[580] (2)
[2200] (1)

Point Group: $[D_{\infty h}]$ $\sigma = 2$
Bond Distance: B–O = [1.25] Å
Bond Angle: O–B–O = [180]°
Rotational Constant: B_O = [0.337159] cm^{-1}

Enthalpy of Formation

Jensen[4] has obtained equilibrium constants for the reaction $HBO_2 + e^- \rightarrow H + BO_2^-$. This involves several assumptions the most basic of which is that boron added to $H_2/N_2/O_2$ flames is converted completely to HBO_2. The free electrons are produced by addition of potassium to the flame, and their concentration is measured directly by a microwave cavity resonance method. The hydrogen atom concentration is taken from previous studies on such flames. The BO_2^- concentration is obtained from the difference between the K^+ concentration and the free electron measurement. The K^+ concentration is measured by an electrostatic probe.

By 2nd and 3rd analysis of the data, 11 points read back from a plot, we obtain $\Delta_f H°$(II, 298.15 K) = 27.5 ± 4 $kcal·mol^{-1}$ and $\Delta_f H°$ (III, 298.15 K) = 20 ± 2 $kcal·mol^{-1}$ with a drift of -3.7 ± 1.5 $cal·K^{-1}·mol^{-1}$. The 3rd law value yields $\Delta_f H°(BO_2^-, 298.15\ K) = -166 \pm 6$ $kcal·mol^{-1}$ where the uncertainty includes possible errors in the functions. This corresponds to an electron affinity of BO_2 equal to 98 ± 6 $kcal·mol^{-1}$ (4.25 eV).

Heat Capacity and Entropy

The molecular structure is assumed to be linear using the Walsh[1] prediction for 16 valence electron XY_2 molecules. The electronic states are taken from those for CO_2(g) (2), which is isoelectronic with BO_2^- (g). The electronic level 35000 cm^{-1} and vibrational frequencies are estimated by comparison with the corresponding values for CO_2, CO_2^+, and BO_2, and, the data of Vasco and Srb[3] on the BO_2^- ion in alkali halide lattices. The B–O bond distance in BO_2^-(g) is assumed to be smaller than the B–O bond in BO_2(g), because the BO_2^-(g) molecule has one more bonding electron than the BO_2(g) molecule.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.629	−688.078		
100	29.376	179.892	247.061	−6.717			
200	33.849	201.391	219.337	−3.589			
250	36.665	209.250	216.552	−1.826			
298.15	39.119	215.922	215.922	0.	−694.544	−689.762	120.843
300	39.207	216.164	215.923	0.072	−694.585	−689.733	120.093
350	41.425	222.378	216.408	2.090	−695.711	−688.835	102.803
400	43.352	228.039	217.514	4.210	−696.860	−687.774	89.814
450	45.040	233.244	218.976	6.421	−698.033	−686.569	79.695
500	46.533	238.069	220.647	8.711	−699.228	−685.231	71.586
600	49.058	246.784	224.293	13.495	−701.663	−682.204	59.391
700	51.105	254.506	228.068	18.507	−704.140	−678.765	50.650
800	52.779	261.443	231.813	23.704	−706.641	−674.970	44.071
900	54.151	267.741	235.461	29.052	−709.158	−670.860	38.936
1000	55.280	273.507	238.981	34.526	−711.687	−666.469	34.813
1100	56.213	278.821	242.365	40.102	−714.229	−661.824	31.427
1200	56.988	283.746	245.610	45.763	−716.784	−656.947	28.596
1300	57.635	288.334	248.722	51.495	−719.355	−651.857	26.192
1400	58.179	292.626	251.707	57.287	−721.945	−646.567	24.124
1500	58.638	296.656	254.570	63.128	−724.558	−641.092	22.325
1600	59.030	300.453	257.320	69.012	−727.196	−635.442	20.745
1700	59.365	304.042	259.964	74.932	−729.863	−629.626	19.346
1800	59.654	307.444	262.508	80.884	−732.561	−623.652	18.098
1900	59.904	310.676	264.959	86.862	−735.292	−617.527	16.977
2000	60.122	313.754	267.322	92.863	−738.059	−611.258	15.964
2100	60.314	316.692	269.604	98.885	−740.864	−604.849	15.045
2200	60.482	319.502	271.809	104.925	−743.707	−598.305	14.206
2300	60.631	322.194	273.941	110.981	−746.592	−591.632	13.436
2400	60.763	324.777	276.006	117.051	−799.777	−583.763	12.705
2500	60.881	327.260	278.007	123.133	−802.823	−574.700	12.008
2600	60.986	329.650	279.947	129.227	−805.879	−565.515	11.361
2700	61.081	331.953	281.831	135.330	−808.947	−556.211	10.761
2800	61.166	334.176	283.661	141.442	−812.026	−546.794	10.201
2900	61.243	336.324	285.440	147.563	−815.117	−537.268	9.677
3000	61.314	338.401	287.171	153.691	−818.219	−527.634	9.187
3100	61.377	340.413	288.856	159.825	−821.334	−517.896	8.726
3200	61.436	342.363	290.498	165.966	−824.461	−508.058	8.293
3300	61.489	344.254	292.099	172.112	−827.599	−498.123	7.885
3400	61.538	346.090	293.660	178.264	−830.749	−488.091	7.499
3500	61.583	347.875	295.183	184.420	−833.910	−477.967	7.133
3600	61.625	349.610	296.671	190.580	−837.083	−467.752	6.787
3700	61.663	351.299	298.125	196.745	−840.266	−457.450	6.458
3800	61.699	352.944	299.546	202.913	−843.460	−447.059	6.145
3900	61.733	354.547	300.936	209.085	−846.664	−436.586	5.847
4000	61.764	356.111	302.296	215.259	−849.878	−426.031	5.563
4100	61.794	357.636	303.627	221.437	−853.103	−415.395	5.292
4200	61.822	359.125	304.931	227.618	−1336.186	−397.656	4.946
4300	61.848	360.580	306.208	233.802	−1338.343	−375.284	4.559
4400	61.873	362.003	307.460	239.988	−1340.511	−352.863	4.189
4500	61.897	363.393	308.688	246.176	−1342.690	−330.392	3.835
4600	61.921	364.754	309.892	252.367	−1344.882	−307.873	3.496
4700	61.943	366.086	311.073	258.560	−1347.087	−285.305	3.171
4800	61.965	367.390	312.233	264.756	−1349.304	−262.690	2.859
4900	61.986	368.668	313.372	270.953	−1351.536	−240.029	2.559
5000	62.008	369.921	314.490	277.153	−1353.781	−217.322	2.270
5100	62.028	371.149	315.589	283.355	−1356.042	−194.570	1.993
5200	62.049	372.353	316.669	289.559	−1358.319	−171.775	1.726
5300	62.070	373.536	317.731	295.765	−1360.613	−148.934	1.468
5400	62.091	374.696	318.775	301.973	−1362.925	−126.051	1.219
5500	62.112	375.836	319.802	308.183	−1365.256	−103.125	0.979
5600	62.133	376.955	320.813	314.395	−1367.607	−80.155	0.748
5700	62.154	378.055	321.808	320.609	−1369.980	−57.144	0.524
5800	62.176	379.136	322.787	326.826	−1372.375	−34.091	0.307
5900	62.198	380.199	323.751	333.045	−1374.795	−10.998	0.097
6000	62.221	381.245	324.700	339.265	−1377.239	12.139	−0.106

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 216.19 \pm 0.42\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 240.0 \pm 17\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 243.1 \pm 17.0\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	{15663 / 15996}	2
$B^2\Sigma^+$	35849	2
$C^2\Pi$	{38782 / 38897}	2

$\omega_e = 1188.14\ cm^{-1}$ $\omega_e x_e = 6.397\ cm^{-1}$ $\sigma = 1$
$B_e = 0.80586\ cm^{-1}$ $\alpha_e = 0.00617\ cm^{-1}$ $r_e = 1.609$ Å

Enthalpy of Formation

Gingerich,[1] empolying mass spectrometric investigations of the Au–Ce–CeS–BN–C system from a tungsten Knudsen effusion cell, reports two values of the BS(g) dissociation energy. The reaction enthalplies were evaluated by the 3rd law method. The two values reported are 140.4 ± 6.0 kcal·mol^{-1}, based on the dissociation energy of CS(g), and 145.4 ± 6.0 kcal·mol^{-1}, based on the dissociation energy of CeS(g).

Uy and Drowart[2] also studied the dissociation energy of BS(g) by two different exchange reactions using mass spectrometric Knudsen cell techniques. Molybdenum cells were used. Based on an exchange between B(g) and YS(g), they reported D_0° = 138.8 ± 3.2 kcal·mol^{-1} for BS(g). A second determination based on an exchange between BO(g) and YS(g) was reported as D_0° = 137.0 ± 3.2 kcal·mol^{-1}

Gaydon[3] suggests a value of 118 kcal·mol^{-1} for the dissociation energy based on two linear Birge–Sponer extrapolations from the data of Zeeman.[4] This data gave values of 154.5 kcal·mol^{-1} and 131.4 kcal·mol^{-1} for extrapolations from the ground state and $A^2\Pi$ state, respectively. McDonald and Innes[5] extended Zeeman's analysis,[4] examined perturbative effects, and calculated $\omega_e y_e = -0.004\ cm^{-1}$ for the ground state. This perturbative interpretation was supported by Singh, Tewari, and Mohan.[7] Accounting for $\omega_e y_e$ value, the Birge–Sponer extrapolation yields a value D_0° = 142.3 kcal·mol^{-1} for BS(g). This value was adjusted to 140.0 kcal·mol^{-1} using an ionic character correction factor as suggested by Hildenbrand and Murad.[6]

The value of 140.0 ± 4.0 kcal·mol^{-1} for the dissociation energy of BS(g) is chosen as the best value. It is an average of the four reported thermochemical values and is the adjusted Birge–Sponer value, the adjustment arising from a correction technique which has been shown to be quite dependable. This value leads to a enthalpy of formation $\Delta_f H°(298.15\ K)$ = 58.1 ± 4.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The spectroscopic constants for the $X^2\Sigma^+$ state are from Zeeman[4] and are corrected to account for the natural abundances of the elements. The electronic states X, A, and C are reported by Zeeman.[4] The $B^2\Sigma^+$ state is reported by McDonald and Innes.[5]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.724	239.992	239.992	INFINITE
100	29.106	184.196	242.369	−5.817	242.185	225.049	−117.553
200	29.239	204.389	218.907	−2.903	243.124	207.457	−54.182
250	29.557	210.944	216.682	−1.434	243.203	198.527	−41.480
298.15	*30.051*	*216.190*	*216.190*	0.	243.090	189.930	−33.275
300	30.073	216.376	216.191	0.056	243.083	189.600	−33.012
350	30.706	221.058	216.559	1.575	242.809	180.706	−26.969
400	31.376	225.202	217.385	3.127	240.195	171.948	−22.454
450	32.028	228.936	218.465	4.712	239.027	163.478	−18.976
500	32.631	232.342	219.685	6.329	237.738	155.155	−16.209
600	33.656	238.386	222.310	9.645	235.488	138.854	−12.088
700	34.449	243.636	224.990	13.052	233.393	122.915	−9.172
800	35.057	248.278	227.617	16.529	231.376	107.271	−7.004
900	35.527	252.435	230.147	20.059	176.267	92.958	−5.395
1000	35.895	256.198	232.567	23.631	175.521	83.741	−4.374
1100	36.188	259.634	234.874	27.236	174.724	74.601	−3.542
1200	36.426	262.793	237.071	30.867	173.879	65.536	−2.853
1300	36.622	265.716	239.163	34.519	172.988	56.543	−2.272
1400	36.786	268.437	241.158	38.190	172.051	47.620	−1.777
1500	36.926	270.979	243.062	41.876	171.069	38.766	−1.350
1600	37.046	273.367	244.882	45.575	170.043	29.979	−0.979
1700	37.153	275.616	246.625	49.285	168.974	21.258	−0.653
1800	37.249	277.742	248.295	53.005	167.864	12.601	−0.366
1900	37.338	279.758	249.898	56.734	166.712	4.006	−0.110
2000	37.421	281.676	251.440	60.472	165.521	−4.527	0.118
2100	37.502	283.504	252.923	64.218	164.292	−12.999	0.323
2200	37.583	285.250	254.353	67.973	163.027	−21.412	0.508
2300	37.664	286.922	255.733	71.735	161.727	−29.767	0.676
2400	37.749	288.527	257.066	75.506	110.133	−36.995	0.805
2500	37.838	290.070	258.356	79.285	108.689	−43.096	0.900
2600	37.933	291.556	259.604	83.073	107.246	−49.139	0.987
2700	38.033	292.989	260.815	86.872	105.808	−55.126	1.066
2800	38.142	294.374	261.989	90.680	104.373	−61.060	1.139
2900	38.257	295.715	263.129	94.500	102.945	−66.944	1.206
3000	38.381	297.014	264.236	98.332	101.523	−72.777	1.267
3100	38.513	298.274	265.314	102.177	100.109	−78.564	1.324
3200	38.653	299.499	266.363	106.035	98.705	−84.305	1.376
3300	38.801	300.691	267.386	109.908	97.310	−90.003	1.425
3400	38.957	301.852	268.382	113.795	95.927	−95.658	1.470
3500	39.120	302.983	269.355	117.699	94.555	−101.273	1.511
3600	39.289	304.088	270.304	121.620	93.196	−106.849	1.550
3700	39.466	305.167	271.232	125.557	91.850	−112.387	1.587
3800	39.647	306.221	272.139	129.513	90.518	−117.889	1.621
3900	39.834	307.254	273.026	133.487	89.200	−123.356	1.652
4000	40.026	308.265	273.895	137.480	87.897	−128.790	1.682
4100	40.221	309.255	274.745	141.492	86.607	−134.191	1.710
4200	40.419	310.227	275.578	145.524	−394.516	−132.537	1.648
4300	40.620	311.180	276.395	149.576	−394.688	−126.297	1.534
4400	40.822	312.117	277.197	153.648	−394.847	−120.054	1.425
4500	41.026	313.036	277.983	157.741	−394.994	−113.807	1.321
4600	41.230	313.940	278.755	161.853	−395.128	−107.557	1.221
4700	41.435	314.829	279.513	165.987	−395.250	−101.304	1.126
4800	41.639	315.704	280.258	170.140	−395.360	−95.048	1.034
4900	41.842	316.564	280.990	174.314	−395.460	−88.791	0.947
5000	42.043	317.412	281.710	178.509	−395.549	−82.531	0.862
5100	42.243	318.246	282.418	182.723	−395.629	−76.270	0.781
5200	42.441	319.068	283.115	186.957	−395.700	−70.008	0.703
5300	42.637	319.879	283.801	191.211	−395.763	−63.744	0.628
5400	42.830	320.677	284.477	195.484	−395.818	−57.479	0.556
5500	43.019	321.465	285.142	199.777	−395.866	−51.213	0.486
5600	43.206	322.242	285.797	204.088	−395.908	−44.946	0.419
5700	43.390	323.008	286.444	208.418	−395.945	−38.678	0.354
5800	43.569	323.764	287.081	212.766	−395.978	−32.410	0.292
5900	43.746	324.511	287.709	217.132	−396.007	−26.142	0.231
6000	43.918	325.247	288.328	221.515	−396.032	−19.872	0.173

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = [34.7 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{dcm} = [2500]\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = -160.2 \pm 38\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Schissel and Trulson[1] used a mass spectrometer with Knudsen cells to study the vaporization of the titanium–boron system and obtained $\Delta_r G°(2340\ K) = -118.54\ kcal \cdot mol^{-1}$ for the reaction TiB(c) = Ti(g) + B(g). This corresponds to $\Delta_f G°(TiB, cr, 2340\ K) = -33.266 \pm 9\ kcal \cdot mol^{-1}$, where $4\ kcal \cdot mol^{-1}$ of the uncertainty is due to the enthalpy of sublimation of boron. When this is reduced to 298.15 K one obtains $\Delta_f H°(TiB, cr, 298.15\ K) = -38.3 \pm 9\ kcal \cdot mol^{-1}$. This value implies a high stability for TiB. This is also indicated by the phase studies of Nowotny *et al.*[2]

Heat Capacity and Entropy

The heat capacities fron 298 to 1200 K were estimated from that of TiB_2 by assuming the difference to be the same as that between CrB and CrB_2 as determined by R. Mezaki, E. W. Tilleux, D. W. Barnes and J. L. Margrave (Paper presented at the International Symposium on Nuclear Materials, Vienna, May 1962). A linear extrapolation was assumed above 1200 K.

The heat capacities above 298 K were also estimated from the relationship $C_p(Ti) + C_p(2B) - C_p(TiB_2) = 2/3\ [C_p(Ti) + C_p(B) - C_p(TiB)]$. This estimation agreed with the above to 4% over the temperature range 400 to 1000 K.

$S°(TiB, cr, 298.15\ K) = 8.3\ cal \cdot K^{-1} \cdot mol^{-1}$ was calculated by the method of Latimer.[3] Using JANAF $S°(TiB_2, cr, 298.15\ K) = 6.8\ cal^{-1}\ K^{-1} \cdot mol^{-1}$ and Latimer's value of $9.8\ cal \cdot K^{-1} \cdot mol^{-1}$ for the entropy contribution of Ti, an entropy contribution of $-1.5\ cal \cdot K^{-1} \cdot mol^{-1}$ per boron atom was calculated.

Decomposition Data

The phase diagram given by McQuillan and McQuillan[4] was used to estimate the decomposition temperature. This diagram shows the decomposition products are TiB_2 and Ti_2B. However, Nowotny *et al.*[2] have shown Ti_2B to be nonexistent and so the decomposition products are not defined; probably an eutectic of TiB and TiB_2 is involved.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	29.673	34.727	34.727	0.	−160.247	−159.691	27.977
300	29.916	34.911	34.728	0.055	−160.260	−159.687	27.804
400	40.334	45.065	36.041	3.610	−160.681	−159.420	20.818
500	45.714	54.690	38.824	7.933	−160.829	−159.085	16.620
600	48.568	63.297	42.200	12.658	−160.911	−158.729	13.819
700	50.124	70.910	45.769	17.599	−161.013	−158.358	11.817
800	50.911	77.657	49.341	22.652	−161.167	−157.968	10.314
900	51.488	83.688	52.829	27.774	−161.419	−157.555	9.144
1000	51.915	89.137	56.191	32.945	−161.831	−157.105	8.206
1100	52.191	94.099	59.415	38.152	−162.469	−156.604	7.436
1200	52.325	98.646	62.498	43.377	−167.327	−155.914	6.787
1300	52.459	102.839	65.442	48.617	−167.710	−154.948	6.226
1400	52.593	106.732	68.254	53.869	−168.206	−153.948	5.744
1500	52.727	110.365	70.941	59.135	−168.824	−152.909	5.325
1600	52.861	113.772	73.513	64.415	−169.576	−151.824	4.957
1700	52.995	116.981	75.976	69.707	−170.472	−150.688	4.630
1800	53.128	120.014	78.339	75.013	−171.524	−149.495	4.338
1900	53.262	122.890	80.609	80.333	−172.744	−148.239	4.075
2000	53.396	125.625	82.792	85.666	−188.831	−146.460	3.825
2100	53.530	128.233	84.894	91.012	−191.171	−144.284	3.589
2200	53.664	130.727	86.921	96.372	−193.532	−141.996	3.371
2300	53.798	133.115	88.878	101.745	−195.913	−139.600	3.170
2400	53.932	135.408	90.770	107.132	−248.574	−136.032	2.961
2500	54.066	137.612	92.599	112.531	−251.073	−131.291	2.743
2600	54.200	139.735	94.372	117.945	−253.558	−126.451	2.540
2700	54.333	141.783	96.090	123.371	−256.030	−121.515	2.351
2800	54.467	143.762	97.757	128.811	−258.489	−116.488	2.173
2900	54.601	145.675	99.377	134.265	−260.934	−111.373	2.006
3000	54.735	147.528	100.951	139.732	−263.366	−106.174	1.849
3100	54.869	149.325	102.483	145.212	−265.785	−100.895	1.700
3200	55.003	151.070	103.974	150.705	−268.190	−95.537	1.559
3300	55.137	152.764	105.427	156.212	−270.582	−90.105	1.426
3400	55.271	154.412	106.844	161.733	−272.960	−84.600	1.300
3500	55.405	156.016	108.226	167.267	−275.325	−79.026	1.179
3600	55.538	157.579	109.575	172.814	−277.677	−73.384	1.065
3700	55.672	159.102	110.893	178.374	−689.113	−59.888	0.845
3800	55.806	160.589	112.181	183.948	−690.204	−42.868	0.589
3900	55.940	162.040	113.441	189.535	−691.336	−25.818	0.346
4000	56.074	163.458	114.674	195.136	−692.509	−8.739	0.114

PREVIOUS: March 1963 CURRENT: June 1965

$S°(298.15\ K) = 202.07 \pm 0.17\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 823.3 \pm 33.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 829.7 \pm 33.5\ kJ·mol^{-1}$

Electronic and Molecular Constants ($\sigma = 2$)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$^3\Sigma_g^-$	0.0	3	1061.61	9.536	1.236121	0.01442411	1.589	1,2,3
$^5\Sigma_u^-$	[1271.]	[5]	[1215.81]	[9.995]	[1.305]	[0.0113]	[1.546]	4
$1^3\Sigma_u^-$	[14829.]	[3]	[1114.83]	[16.318]	[1.275]	[0.0175]	[1.565]	4
$2^3\Sigma_u^-$	30573.4	3	946.59	2.652	1.183086	0.01133323	1.625	1,2,3

Enthalpy of Formation

The equilbrium vapor pressure of the reaction $B_2(g) \rightarrow B(g) + B(cr)$ was determined by Verhaegen and Drowart.[5] Using the value, $p(B_2,g)/p(B,g) = 9 \times 10^{-5}$ at 2330 K where p is partial pressure, the enthalpy of reaction, $\Delta_r H°(298.15\ K)$, was evaluated by the 3rd law method to be -64.5 ± 5.0 kcal·mol^{-1}. Using auxiliary data,[6] this leads to $\Delta_f H°(298.15\ K) = 198.3 \pm 8.0$ kcal·mol^{-1} for $B_2(g)$ or $D_0° = 2.97 \pm 0.61$ eV.

Heat Capacity and Entropy

The thermodynamic functions are calculated using first order anharmonic corrections to Q_t^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_t^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$. Molecular and spectroscopic constants for the $^3\Sigma_g^-$ ground state and the $2^3\Sigma_u^-$ state are taken from a study[3] which revises the values of Douglas and Herzberg.[1,2] The molecular constants and electronic levels for the lowest $^5\Sigma_u^-$ state and $1^3\Sigma_u^-$ state are based on the ab initio configuration interaction calculations of Dupuis and Liu.[4] These calculations, along with the optical absorption and ESR spectra of B_2 at 4 K reported by Graham and Weltner,[7] support a $^3\Sigma_g^-$ ground state rather than $^5\Sigma_u^-$ favored by previous ab initio work.[8,9] All molecular and spectroscopic constants have been corrected to the average isotopic species.

Differences between our calculated thermodynamic functions and those given by Feber and Herrick[10] using direct summation techniques can be attributed to inclusion of the low lying $^5\Sigma_u^-$ state and $1^3\Sigma_u^-$ state in our calculations. The JANAF adopted entropy is 0.35–1.6 cal·K^{-1}·mol^{-1} higher than their values in the 500–600 K temperature range. The JANAF adopted heat capacities are also higher in the low temperature range, 0.2–0.9 cal·K^{-1}·mol^{-1} larger between 298–1000 K. A comparison of the thermodynamic functions calculated using only the ground and upper $2^3\Sigma_u^-$ state shows no major numerical difference with this earlier tabulation,[10] however.

References

[1] A. E. Douglas and G. Herzberg, Phys. Rev. **57**, 752 (1940).
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[3] R. W. Nicholls, P. A. Fraser and W. R. Jarmain, Combus. and Flame **3**, 13 (1959).
[4] M. DuPuis and B. Liu, J. Chem. Phys. **68**, 2902 (1978).
[5] G. Verhaegen and J. Drowart, J. Chem. Phys. **37**, 1367 (1962).
[6] JANAF Thermochemical Tables: B(cr) and B(g), 3–31–79.
[7] W. R. M. Graham and W. Weltner, Jr., J. Chem. Phys. **65**, 1516 (1976).
[8] A. A. Padgett and V. Griffing, J. Chem. Phys. **30**, 1286 (1959).
[9] C. F. Bender and E. R. Davidson, J. Chem. Phys. **46**, 3313 (1967).
[10] R. C. Feber and C. C. Herrick, LASL Report LA–3597 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.810	823.305	823.305	INFINITE
100	29.111	169.727	228.775	−5.905	826.162	809.251	−422.709
200	29.500	189.962	204.880	−2.984	828.418	791.393	−206.691
250	30.345	196.626	202.585	−1.490	829.169	782.044	−163.399
298.15	31.594	202.072	202.072	0.	829.687	772.918	−135.412
300	31.648	202.268	202.073	0.058	829.704	772.566	−134.516
350	33.187	207.260	202.464	1.679	830.070	763.012	−113.873
400	34.737	211.794	203.351	3.377	830.297	753.415	−98.386
450	36.146	215.969	204.524	5.150	830.415	743.797	−86.338
500	37.335	219.841	205.864	6.988	830.446	734.170	−76.698
600	39.012	226.809	208.788	10.813	830.309	714.924	−62.240
700	39.916	232.899	211.807	14.765	829.950	695.719	−51.915
800	40.310	238.259	214.785	18.779	829.399	676.578	−44.176
900	40.410	243.015	217.663	22.817	828.673	657.517	−38.161
1000	40.355	247.271	220.415	26.856	827.788	638.546	−33.354
1100	40.226	251.111	223.033	30.886	826.758	619.671	−29.426
1200	40.071	254.605	225.521	34.901	825.595	600.895	−26.156
1300	39.914	257.806	227.883	38.900	824.311	582.221	−23.394
1400	39.766	260.758	230.127	42.884	822.915	563.651	−21.030
1500	39.632	263.497	232.262	46.853	821.417	545.183	−18.985
1600	39.516	266.051	234.295	50.811	819.821	526.819	−17.199
1700	39.416	268.444	236.234	54.757	818.135	508.558	−15.626
1800	39.332	270.694	238.086	58.694	816.363	490.398	−14.231
1900	39.263	272.819	239.859	62.624	814.510	472.339	−12.986
2000	39.207	274.832	241.558	66.547	812.578	454.380	−11.867
2100	39.164	276.743	243.188	70.466	810.572	436.519	−10.858
2200	39.132	278.564	244.755	74.381	808.492	418.755	−9.943
2300	39.110	280.303	246.263	78.293	806.343	401.088	−9.109
2400	39.098	281.968	247.716	82.203	703.606	385.653	−8.394
2500	39.095	283.564	249.119	86.112	701.166	372.455	−7.782
2600	39.099	285.097	250.473	90.022	698.725	359.355	−7.220
2700	39.112	286.573	251.783	93.933	696.286	346.349	−6.701
2800	39.131	287.996	253.051	97.845	693.848	333.432	−6.220
2900	39.156	289.369	254.280	101.759	691.412	320.603	−5.775
3000	39.188	290.697	255.472	105.676	688.979	307.858	−5.360
3100	39.224	291.983	256.629	109.597	686.550	295.195	−4.974
3200	39.266	293.229	257.753	113.521	684.124	282.609	−4.613
3300	39.312	294.438	258.847	117.450	681.703	270.099	−4.275
3400	39.362	295.612	259.911	121.384	679.287	257.662	−3.958
3500	39.416	296.754	260.947	125.323	676.876	245.297	−3.661
3600	39.474	297.865	261.957	129.267	674.470	233.000	−3.381
3700	39.534	298.947	262.943	133.217	672.071	220.770	−3.117
3800	39.597	300.002	263.904	137.174	669.677	208.605	−2.867
3900	39.663	301.032	264.843	141.137	667.290	196.502	−2.632
4000	39.731	302.037	265.760	145.107	664.910	184.461	−2.409
4100	39.801	303.019	266.657	149.083	662.536	172.479	−2.197
4200	39.872	303.979	267.534	153.067	−299.529	174.604	−2.172
4300	39.945	304.918	268.393	157.058	−299.713	185.895	−2.258
4400	40.020	305.837	269.233	161.056	−299.894	197.190	−2.341
4500	40.095	306.737	270.057	165.062	−300.072	208.489	−2.420
4600	40.172	307.619	270.864	169.075	−300.247	219.793	−2.496
4700	40.249	308.484	271.655	173.096	−300.418	231.100	−2.568
4800	40.328	309.332	272.431	177.125	−300.588	242.411	−2.638
4900	40.406	310.164	273.193	181.162	−300.757	253.725	−2.705
5000	40.486	310.982	273.940	185.206	−300.924	265.042	−2.769
5100	40.565	311.784	274.675	189.259	−301.091	276.363	−2.831
5200	40.645	312.573	275.396	193.319	−301.258	287.688	−2.890
5300	40.725	313.348	276.105	197.388	−301.426	299.015	−2.947
5400	40.805	314.110	276.801	201.464	−301.596	310.346	−3.002
5500	40.885	314.859	277.487	205.549	−301.768	321.680	−3.055
5600	40.966	315.596	278.160	209.641	−301.942	333.017	−3.106
5700	41.046	316.322	278.824	213.742	−302.121	344.357	−3.156
5800	41.126	317.037	279.476	217.850	−302.303	355.700	−3.203
5900	41.206	317.740	280.119	221.967	−302.491	367.046	−3.250
6000	41.285	318.434	280.752	226.092	−302.685	378.396	−3.294

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$S°(298.15\ K)$ = [326.79] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1348 \pm 42\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1351 \pm 42\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[2000](1)	[1050](1)	[400](1)
[1600](1)	[650](1)	[350](1)
[1200](1)	[650](1)	[200](1)
[1200](1)	[600](1)	[150](1)
[1050](1)	[500](1)	[120](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Point: [C_{2h}]

Bond Distances: Be–O = [1.63] Å; O–B = [1.34] Å; B=O = [1.20] Å

Bond Angles: O=B–O = [180]°; O–Be–O = [180]°; B–O–Be = [95]°

Product of the Moments of Inertia: $I_A I_B I_C = [5.382534 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation was obtained from mass spectrometric studies; the following reactions at 1500 K were reported by Blackburn and Buchler.[1]

Reaction	$\Delta_r H°$, $kcal·mol^{-1}$
1. $B_2O_3(l) \rightarrow B_2O_3(g)$	$\Delta H_1 = 92.226$
2. $1/3\ Be_3B_2O_6(cr) + 2/3\ B_2O_3(l) \rightarrow Be(BO_2)_2(g)$	$\Delta H_2 = 118 \pm 2$
3. $Be_3B_2O_6(cr) \rightarrow 3\ BeO(cr) + B_2O_3(g)$	$\Delta H_3 = 112 \pm 1$
4. $Be_3B_2O_6(cr) \rightarrow 2\ BeO(cr) + Be(BO_2)_2(g)$	$\Delta H_4 = 137 \pm 3$
5. $3\ BeO(cr) + B_2O_3(l) \rightarrow Be_3B_2O_6(cr)$	$\Delta H_5 = 23$
6. $BeO(cr) + B_2O_3(g) \rightarrow Be(BO_2)_2(g)$	$\Delta H_6 = 22$

ΔH_1 was obtained from JANAF values[2] for $B_2O_3(l)$ and $B_2O_3(g)$. The values for ΔH_2, ΔH_3, and ΔH_4 were obtained from Blackburn and Buchler.[1] ΔH_5 was obtained by taking the average of $\Delta H_5 = -20$ $kcal·mol^{-1}$ in a weight loss experiment, $\Delta H_5 = \Delta H_1 - \Delta H_3 = -19.774$ $kcal·mol^{-1}$, and $\Delta H_5 = 3/2\ (\Delta H_2 - \Delta H_4) = 28.5$ $kcal·mol^{-1}$. The ΔH_6 value was obtained by taking the average of $\Delta H_6 = \Delta H_4 - \Delta H_3 = 25$ $kcal·mol^{-1}$ and $\Delta H_6 = \Delta H_2 - \Delta H_1 + 1/3\ \Delta H_5 = 18.107$ $kcal·mol^{-1}$. The $\Delta_f H°(298.15\ K)$ of BeB_2O_4 was calculated from reaction 6 with auxiliary JANAF values.

Heat Capacity and Entropy

The vibrational frequencies estimated by comparison with B_2O_3 were adjusted to obtain an $S°(1500\ K) = 127$ obtained in a manner analogous with $\Delta_f H°$ from the report of Blackburn and Buchler.[1] The frequencies listed are not in point group order. All other molecular constants were estimated by comparison with related boron oxide molecules. The principal moments of inertia are $I_A = 8.5573 \times 10^{-39}$, $I_B = 75.1462 \times 10^{-39}$, and $I_C = 83.7035 \times 10^{-39}$ $g·cm^2$.

References

[1]P. E. Blackburn and A. Buchler, Tech. Report No. 1 (1965).

[2]JANAF Thermochemical Tables: $B_2O_3(l)$ and $B_2O_3(g)$, 6–30–71.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.639	−1348.345	−1348.345	INFINITE
100	52.679	250.301	396.063	−14.576	−1350.178	−1340.435	700.171
200	74.445	293.699	334.648	−8.190	−1350.857	−1330.401	347.465
250	83.774	311.333	328.252	−4.230	−1351.147	−1325.253	276.897
298.15	91.764	326.785	326.785	0.	−1351.432	−1320.240	231.301
300	92.053	327.354	326.787	0.170	−1351.443	−1320.047	229.841
350	99.380	342.106	327.935	4.960	−1351.739	−1314.791	196.222
400	105.839	355.807	330.573	10.094	−1352.029	−1309.492	171.002
450	111.510	368.608	334.096	15.530	−1352.309	−1304.158	151.383
500	116.475	380.619	338.154	21.233	−1352.572	−1298.794	135.684
600	124.603	402.607	347.099	33.305	−1353.048	−1287.993	112.130
700	130.814	422.303	356.460	46.090	−1353.475	−1277.116	95.300
800	135.589	440.096	365.821	59.420	−1353.880	−1266.180	82.673
900	139.296	456.289	374.987	73.172	−1354.296	−1255.193	72.849
1000	142.208	471.122	383.869	87.253	−1354.746	−1244.158	64.988
1100	144.522	484.788	392.430	101.594	−1355.254	−1233.074	58.554
1200	146.384	497.446	400.661	116.142	−1355.839	−1221.942	53.190
1300	147.899	509.225	408.564	130.859	−1356.517	−1210.757	48.649
1400	149.144	520.233	416.152	145.713	−1357.302	−1199.516	44.754
1500	150.179	530.559	423.438	160.681	−1358.206	−1188.215	41.377
1600	151.047	540.280	430.440	175.743	−1373.776	−1176.324	38.403
1700	151.781	549.459	437.174	190.886	−1374.547	−1163.960	35.764
1800	152.406	558.153	443.655	206.096	−1375.398	−1151.549	33.417
1900	152.943	566.408	449.901	221.364	−1376.333	−1139.087	31.316
2000	153.407	574.265	455.924	236.682	−1377.357	−1126.575	29.423
2100	153.811	581.760	461.739	252.043	−1378.476	−1114.008	27.709
2200	154.164	588.923	467.359	267.443	−1379.693	−1101.385	26.150
2300	154.475	595.783	472.794	282.875	−1381.011	−1088.707	24.725
2400	154.750	602.364	478.057	298.336	−1482.951	−1073.831	23.371
2500	154.994	608.686	483.156	313.824	−1484.633	−1056.750	22.080
2600	155.211	614.769	488.102	329.334	−1486.357	−1039.600	20.886
2700	155.406	620.631	492.903	344.865	−1488.124	−1022.383	19.779
2800	155.581	626.286	497.566	360.415	−1780.891	−998.878	18.634
2900	155.739	631.748	502.099	375.981	−1781.683	−970.936	17.488
3000	155.882	637.030	506.509	391.562	−1782.504	−942.965	16.418
3100	156.012	642.144	510.803	407.157	−1783.354	−914.965	15.417
3200	156.130	647.099	514.985	422.764	−1784.236	−886.940	14.478
3300	156.237	651.905	519.062	438.382	−1785.150	−858.886	13.595
3400	156.336	656.570	523.038	454.011	−1786.098	−830.802	12.764
3500	156.427	661.103	526.918	469.649	−1787.082	−802.692	11.980
3600	156.510	665.511	530.707	485.296	−1788.103	−774.552	11.238
3700	156.587	669.801	534.408	500.951	−1789.161	−746.384	10.537
3800	156.658	673.977	538.027	516.613	−1790.260	−718.184	9.872
3900	156.723	678.048	541.565	532.283	−1791.400	−689.957	9.241
4000	156.784	682.016	545.027	547.958	−1792.584	−661.701	8.641
4100	156.841	685.888	548.415	563.639	−1793.812	−633.413	8.070
4200	156.893	689.668	551.734	579.326	−2754.787	−591.047	7.351
4300	156.942	693.361	554.985	595.018	−2753.937	−539.539	6.554
4400	156.988	696.969	558.171	610.714	−2753.143	−488.052	5.794
4500	157.031	700.498	561.294	626.415	−2752.406	−436.582	5.068
4600	157.071	703.950	564.358	642.121	−2751.729	−385.127	4.373
4700	157.109	707.328	567.364	657.830	−2751.115	−333.685	3.708
4800	157.144	710.636	570.315	673.542	−2750.568	−282.256	3.072
4900	157.177	713.877	573.212	689.258	−2750.089	−230.837	2.461
5000	157.209	717.052	576.057	704.978	−2749.682	−179.428	1.874
5100	157.238	720.166	578.852	720.700	−2749.350	−128.026	1.311
5200	157.266	723.219	581.599	736.425	−2749.096	−76.632	0.770
5300	157.292	726.215	584.300	752.153	−2748.923	−25.238	0.249
5400	157.317	729.156	586.955	767.884	−2748.834	26.150	−0.253
5500	157.340	732.042	589.567	783.616	−2748.832	77.537	−0.736
5600	157.363	734.878	592.136	799.352	−2748.920	128.928	−1.203
5700	157.384	737.663	594.665	815.089	−2749.101	180.319	−1.652
5800	157.404	740.401	597.154	830.828	−2749.378	231.716	−2.087
5900	157.423	743.091	599.605	846.570	−2749.754	283.114	−2.507
6000	157.441	745.737	602.019	862.313	−2750.233	334.525	−2.912

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K) = [100 \pm 13]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1768 \pm 5\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -3104 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -741.96 \pm 2\ kcal \cdot mol^{-1}$ was calculated from $\Delta_r H°(298.15\ K) = -13.38 \pm 0.5\ kcal \cdot mol^{-1}$ for $3BeO(cr) + B_2O_3(g, l) = Be_3B_2O_6(cr)$ measured calorimetrically by Gross.[1] From equilibrium data relating to the same reaction at 1500 K, Blackburn and Buchler[2] report enthalpies of reaction of -21 ± 2 and $-28.5 \pm 5\ kcal \cdot mol^{-1}$ which correspond to -21.7 and $-29.2\ kcal \cdot mol^{-1}$ at 298.15 K. The discrepancy of 8 to 16 $kcal \cdot mol^{-1}$ is attributed primarily to the equilibrium values. These values result from differences between 2nd law enthalpies of reaction derived from the variation with temperature of ion intensities for $B_2O_3^+$ and $Be(BO_2)_2^+$, respectively, over the systems $B_2O_3(l)$–$Be_3B_2O_6(cr)$ and $Be_3B_2O_6(cr)$–BeO(cr). The reported reactions and their heats are:

Reaction	$\Delta_r H°(1500\ K)$ $kcal \cdot mol^{-1}$
(a) $B_2O_3(l) \rightarrow B_2O_3(g)$	91 ± 0.5
(b) $Be_3B_2O_6(cr) \rightarrow 3\ BeO(cr) + B_2O_3(g)$	112 ± 1
(c) $1/3\ Be_3B_2O_6(cr) + 2/3\ B_2O_3(l) \rightarrow Be(BO_2)(g)$	118 ± 2
(d) $Be_3B_2O_6(cr) \rightarrow 2\ BeO(cr) + Be(BO_2)_2(g)$	137 ± 3

Heat Capacity and Entropy

The heat capacity was estimated from that for BeO(cr) and B_2O_3(cr). The adopted $S°(298.15\ K) = 24 \pm 3$ eu is an average value from the following three estimates. Blackburn and Buchler[2] report $K_p = 2.7 \times 10^{-5}$ atm and 9.3×10^{-6} atm at 1500 K for reactions a and b (see enthalpy of formation), based on vacuum balance data and ion intensities, respectively. Three K_p's yield $\Delta_r G°(1500\ K) = -3.17\ kcal \cdot mol^{-1}$ for $3\ BeO(cr) + B_2O_3(l) \rightarrow Be_3B_2O_6(cr)$. Combining this with the JANAF value for $\Delta_r H°(1500\ K) = -12.64\ kcal \cdot mol^{-1}$, we get $\Delta_r S°(1500\ K) = -6.3$ and $S°(Be_3B_2O_6, cr, 298.15\ K) = 22.9\ cal \cdot K^{-1} \cdot mol^{-1}$. This entropy agrees with 23 $cal \cdot K^{-1} \cdot mol^{-1}$ estimated from the sum of entropies for the component oxides; however, the entropy for $Ca_3B_2O_6(cr)$ observed by Kelley *et al.*[3] is larger than that of the component oxides by 2.5 $cal \cdot K^{-1} \cdot mol^{-1}$. Use of this increment leads to 25.5 $cal \cdot K^{-1} \cdot mol^{-1}$ for $Be_3B_2O_6(cr)$.

Fusion Data

T_{fus} was obtained from Blackburn and Buchler.[2]

References

[1] P. Gross, Fulmer Research Institute, Report No. 5 (1966).
[2] P. E. Blackburn and A. Buchler, J. Phys. Chem. 69, 4250 (1965).
[3] K. K. Kelley, S. S. Todd and C. H. Shomate, J. Am. Chem. Soc. 70, 1350 (1948).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	139.746	100.416	100.416	0.	−3104.361	−2938.883	514.880
300	140.415	101.282	100.419	0.259	−3104.398	−2937.857	511.526
400	175.017	146.578	106.360	16.087	−3105.734	−2882.104	376.364
500	202.840	188.696	118.669	35.014	−3105.754	−2826.167	295.248
600	226.605	227.822	133.639	56.510	−3104.501	−2770.347	241.180
700	247.567	264.375	149.733	80.249	−3102.009	−2714.835	202.583
800	264.805	298.608	166.227	105.905	−3098.420	−2659.758	173.664
900	277.567	330.574	182.733	133.058	−3094.025	−2605.183	151.201
1000	286.269	360.294	199.021	161.272	−3089.170	−2551.124	133.257
1100	292.211	387.871	214.951	190.211	−3084.132	−2497.562	118.599
1200	296.395	413.483	230.442	219.650	−3079.092	−2444.461	106.405
1300	299.574	437.336	245.450	249.453	−3074.156	−2391.776	96.103
1400	302.210	459.635	259.961	279.544	−3069.382	−2339.466	87.287
1500	304.553	480.567	273.977	309.884	−3064.796	−2287.491	79.658
1600	306.729	500.292	287.512	340.448	−3104.023	−2234.237	72.940
1700	308.905	518.951	300.582	371.229	−3098.644	−2180.040	66.984
1800	311.206	536.674	313.210	402.235	−3093.254	−2126.161	61.700
1900	313.382	553.558	325.419	433.465	−3087.848	−2072.581	56.979
2000	315.474	569.686	337.232	464.907	−3082.437	−2019.285	52.738
2100	317.649	585.131	348.672	496.565	−3077.013	−1966.261	48.908
2200	319.658	599.955	359.759	528.431	−3071.583	−1913.494	45.432
2300	321.582	614.207	370.514	560.494	−3066.155	−1860.976	42.264
2400	323.423	627.932	380.956	592.745	−3161.256	−1806.557	39.319
2500	325.180	641.170	391.101	625.173	−3156.012	−1750.218	36.569
2600	327.105	653.962	400.966	657.789	−3150.710	−1694.091	34.035
2700	328.904	666.340	410.567	690.588	−3145.352	−1638.168	31.692
2800	330.829	678.337	419.917	723.575	−4012.804	−1563.777	29.173
2900	332.754	689.979	429.030	756.754	−4004.125	−1476.466	26.594
3000	334.720	701.293	437.918	790.127	−3995.326	−1389.454	24.193

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = 358.96\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -489.1 \pm 5.0\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
1131(1)	Rotation	917(2)
401(1)	730(1)	617(2)
225(1)	291(1)	180(2)

Ground State Quantum Weight: 1 $\sigma = 4$

Point Group: D_{2d}

Bond Distances: B–Cl = 1.73 ± 0.02 Å; B–B = 1.75 ± 0.01 Å

Bond Angles: Cl–B–Cl = 120 ± 2°

Dihedral angle between two BCl_2 planes = 90°

Product of the Moments of Inertia: $I_A I_B I_C = 5.336257 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

Gunn *et al.*[1] determined the enthalpy change ($\Delta_r H°$) of the reaction $B_2Cl_4(l) + Cl_2(g) = 2\ BCl_3(g)$. From the value, $\Delta_r H°(298.15\ K) = 67.3 \pm 0.6\ kcal·mol^{-1}$, the enthalpy of formation for $B_2Cl_4(l)$ was calculated as $125.32 \pm 1.20\ kcal·mol^{-1}$. Based on $\Delta_{vap} H°(338.7\ K) = 8.029\ kcal·mol^{-1}$ reported by Urry *et al.*,[2] the enthalpy of formation for $B_2Cl_4(g)$ was derived to be $116.9 \pm 1.2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies, molecular structure and constants were taken from Mann and Fano.[3] The barrier restricting internal rotation about the B–B single bond is fixed at 1.53 ± 0.60 $kcal·mol^{-1}$ obtained from Mason and Kreevoy.[4] The reduced moment of inertia for BCl_2 top is $I_r = 13.2149 \times 10^{-39}\ g·cm^2$. The principal moments of inertia are: $I_A = 52.8594 \times 10^{-39}$, $I_B = I_C = 100.4748 \times 10^{-39}\ g·cm^2$.

References

[1]S. R. Gunn, L. G. Green, and A. I. Von Egidy, J. Phys. Chem. **63**, 1787 (1959).

[2]G. Urry, L. Wartik, R. E. Moore and H. I. Schlesinger, J. Am. Chem. Soc. **76**, 5293 (1954).

[3]D. E. Mann and L. Fano, J. Chem. Phys. **26**, 1665 (1957).

[4]E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc. **77**, 5808 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100	59.208	275.789	433.035	−15.725	−489.916	−479.632	250.534
200	80.655	323.936	367.210	−8.655	−489.588	−469.422	122.600
298.15	94.839	358.956	358.956	0.	−489.110	−459.631	80.526
300	95.056	359.543	358.958	0.176	−489.102	−459.448	79.997
400	104.801	388.301	362.812	10.195	−488.747	−449.622	58.715
500	111.307	412.425	370.388	21.019	−488.528	−439.868	45.953
600	115.683	433.124	379.160	32.378	−488.395	−430.149	37.448
700	118.541	451.179	388.187	44.095	−488.333	−420.448	31.374
800	120.792	467.162	397.079	56.066	−488.326	−410.751	26.819
900	122.242	481.475	405.675	68.220	−488.377	−401.052	23.276
1000	123.474	494.420	413.913	80.507	−488.487	−391.343	20.442
1100	124.199	506.223	421.776	92.892	−488.663	−381.621	18.122
1200	124.851	517.058	429.271	105.345	−488.911	−371.880	16.188
1300	125.430	527.075	436.414	117.859	−489.224	−362.115	14.550
1400	125.936	536.389	443.226	130.428	−489.598	−352.323	13.145
1500	126.369	545.093	449.730	143.044	−490.033	−342.503	11.927
1600	126.621	553.257	455.948	155.694	−490.535	−332.652	10.860
1700	126.854	560.940	461.900	168.368	−491.111	−322.767	9.917
1800	127.069	568.197	467.606	181.064	−491.759	−312.846	9.079
1900	127.266	575.073	473.083	193.781	−492.480	−302.887	8.327
2000	127.445	581.605	478.347	206.516	−493.274	−292.889	7.649
2100	127.548	587.826	483.413	219.266	−494.147	−282.848	7.035
2200	127.645	593.762	488.295	232.026	−495.102	−272.764	6.476
2300	127.738	599.438	493.005	244.795	−496.143	−262.635	5.965
2400	127.825	604.876	497.554	257.573	−597.789	−250.321	5.448
2500	127.907	610.096	501.952	270.360	−599.162	−235.815	4.927
2600	127.984	615.114	506.208	283.155	−600.561	−221.254	4.445
2700	128.056	619.946	510.332	295.957	−601.989	−206.637	3.998
2800	128.122	624.604	514.330	308.766	−603.448	−191.968	3.581
2900	128.184	629.101	518.211	321.581	−604.939	−177.246	3.193
3000	128.240	633.448	521.980	334.402	−606.464	−162.473	2.829
3100	128.273	637.653	525.644	347.228	−608.022	−147.647	2.488
3200	128.305	641.726	529.208	360.057	−609.615	−132.771	2.167
3300	128.336	645.675	532.678	372.889	−611.241	−117.844	1.865
3400	128.365	649.506	536.058	385.724	−612.897	−102.869	1.580
3500	128.393	653.228	539.353	398.562	−614.580	−87.843	1.311
3600	128.419	656.845	542.567	411.402	−616.287	−72.769	1.056
3700	128.444	660.364	545.703	424.245	−618.014	−57.648	0.814
3800	128.468	663.790	548.766	437.091	−619.756	−42.480	0.584
3900	128.491	667.127	551.758	449.939	−621.509	−27.266	0.365
4000	128.512	670.380	554.683	462.789	−623.268	−12.006	0.157
4100	128.527	673.554	557.544	475.641	−625.027	3.298	−0.042
4200	128.543	676.651	560.343	488.495	−1586.482	32.692	−0.407
4300	128.557	679.676	563.083	501.350	−1586.054	71.239	−0.865
4400	128.572	682.632	565.767	514.206	−1585.615	109.775	−1.303
4500	128.585	685.521	568.396	527.064	−1585.161	148.302	−1.721
4600	128.598	688.347	570.973	539.923	−1584.688	186.818	−2.121
4700	128.611	691.113	573.500	552.784	−1584.192	225.323	−2.504
4800	128.623	693.821	575.978	565.645	−1583.669	263.819	−2.871
4900	128.635	696.473	578.410	578.508	−1583.116	302.302	−3.223
5000	128.645	699.072	580.798	591.372	−1582.530	340.774	−3.560
5100	128.656	701.620	583.142	604.237	−1581.908	379.234	−3.884
5200	128.666	704.118	585.444	617.103	−1581.248	417.681	−4.196
5300	128.675	706.569	587.707	629.970	−1580.547	456.116	−4.495
5400	128.684	708.974	589.930	642.838	−1579.806	494.537	−4.784
5500	128.692	711.336	592.116	655.707	−1579.021	532.944	−5.061
5600	128.700	713.655	594.266	668.577	−1578.192	571.335	−5.329
5700	128.707	715.933	596.381	681.447	−1577.318	609.712	−5.587
5800	128.713	718.171	598.461	694.318	−1576.399	648.073	−5.837
5900	128.719	720.371	600.509	707.190	−1575.435	686.418	−6.077
6000	128.725	722.535	602.525	720.062	−1574.424	724.745	−6.309

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [318.47] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1431.8 \pm 4.2$ $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
1380 (1)	1155(1)	325(1)
[630](1)	542(1)	1378(1)
[304](1)	1386(1)	662(1)
Rotation	657(1)	325(1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2d}
Bond Distances: B–B = 1.67 Å; B–F = 1.32 Å
Bond Angles: F–B–F = 120°; F–B–B = 120°
Dihedral angle between two BF_2 planes = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 2.502146 \times 10^{-113}$ $g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation was calculated based on the value, $\Delta_f H° = -82.0 \pm 1.0$ $kcal·mol^{-1}$ for the reaction $B_2F_4(g) + Cl_2(g) = 0.92\ BF_3(g) + 0.46\ BF_2Cl(g) + 0.32\ BFCl_2(g) + 0.30\ BCl_3(g)$ reported by Gunn and Green.[1]

Heat Capacity and Entropy

The molecular and spectroscopic constants were obtained from Gayles and Self.[2] The vibrational frequencies were corrected to the average isotropic species. The molecular configuration was reported to be staggered, analogous to that observed for B_2Cl_4(g). The angle between two $B–BF_2$ planes is approximately 90°. The thermodynamic functions were evaluated based on an assumption that there is free rotation at the B–B bond. The reduced moment of inertia for the BF_2 top is $I_r = 4.1231 \times 10^{-39}$ $g·cm^2$. The principal moments of inertia are: $I_A = 16.4908 \times 10^{-39}$. $I_B = I_C = 38.9529 \times 10^{-39}$ $g·cm^2$.

References

[1] S. R. Gunn and L. G. Green, J. Phys. Chem. **65**, 178 (1961).
[2] J. N. Gayles and J. Self, J. Chem. Phys. **40**, 3530 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100	43.322	255.051	376.204	−12.115	−1429.664	−1421.034	742.272
200	61.947	290.817	325.053	−6.847	−1430.920	−1411.855	368.739
250	70.075	305.535	319.702	−3.542	−1431.362	−1407.037	293.984
298.15	76.891	318.473	318.473	0.	−1431.765	−1402.315	245.680
300	77.135	318.950	318.475	0.142	−1431.780	−1402.133	244.133
350	83.308	331.314	319.437	4.157	−1432.198	−1397.158	208.514
400	88.716	342.799	321.648	8.461	−1432.626	−1392.124	181.793
450	93.438	353.528	324.601	13.017	−1433.059	−1387.035	161.003
500	97.541	363.590	328.002	17.794	−1433.485	−1381.898	144.366
600	104.163	381.988	335.496	27.895	−1434.294	−1371.504	119.400
700	109.105	398.435	343.334	38.571	−1435.032	−1360.979	101.558
800	112.815	413.257	351.163	49.675	−1435.712	−1350.354	88.169
900	115.634	426.715	358.822	61.104	−1436.355	−1339.645	77.751
1000	117.806	439.016	366.235	72.781	−1436.982	−1328.866	69.413
1100	119.505	450.327	373.372	84.650	−1437.613	−1318.024	62.588
1200	120.855	460.785	380.227	96.670	−1438.262	−1307.123	56.898
1300	121.940	470.503	386.802	108.812	−1438.942	−1296.168	52.081
1400	122.824	479.573	393.108	121.051	−1439.663	−1285.159	47.950
1500	123.553	488.073	399.158	133.371	−1440.433	−1274.096	44.368
1600	124.161	496.067	404.968	145.758	−1441.256	−1262.980	41.232
1700	124.671	503.610	410.551	158.200	−1442.137	−1251.811	38.463
1800	125.104	510.748	415.921	170.690	−1443.077	−1240.589	36.001
1900	125.475	517.522	421.091	183.219	−1444.074	−1229.313	33.796
2000	125.794	523.967	426.075	195.783	−1445.127	−1217.982	31.810
2100	126.070	530.111	430.884	208.376	−1446.233	−1206.598	30.012
2200	126.311	535.982	435.529	220.996	−1447.387	−1195.160	28.377
2300	126.523	541.601	440.019	233.638	−1448.583	−1183.668	26.882
2400	126.710	546.990	444.365	246.300	−1550.335	−1169.986	25.464
2500	126.875	552.166	448.574	258.979	−1551.754	−1154.109	24.114
2600	127.023	557.145	452.655	271.674	−1553.134	−1138.176	22.866
2700	127.154	561.941	456.614	284.383	−1554.468	−1122.191	21.710
2800	127.273	566.568	460.459	297.104	−1555.751	−1106.157	20.636
2900	127.379	571.036	464.195	309.837	−1556.980	−1090.078	19.634
3000	127.475	575.356	467.829	322.580	−1558.150	−1073.958	18.699
3100	127.563	579.537	471.366	335.332	−1559.257	−1057.800	17.824
3200	127.642	583.588	474.810	348.092	−1560.299	−1041.607	17.002
3300	127.715	587.517	478.166	360.860	−1561.272	−1025.383	16.230
3400	127.781	591.331	481.438	373.635	−1562.176	−1009.130	15.503
3500	127.842	595.036	484.631	386.416	−1563.008	−992.851	14.817
3600	127.898	598.638	487.748	399.203	−1563.768	−976.550	14.169
3700	127.949	602.143	490.793	411.996	−1564.455	−960.229	13.556
3800	127.997	605.556	493.768	424.793	−1565.069	−943.890	12.975
3900	128.040	608.881	496.678	437.595	−1565.610	−927.536	12.423
4000	128.081	612.124	499.523	450.401	−1566.079	−911.169	11.899
4100	128.119	615.287	502.308	463.211	−1566.475	−894.791	11.400
4200	128.154	618.374	505.035	476.025	−2526.500	−864.356	10.750
4300	128.187	621.390	507.706	488.842	−2524.581	−824.804	10.019
4400	128.218	624.338	510.324	501.662	−2522.597	−785.297	9.323
4500	128.246	627.219	512.889	514.485	−2520.551	−745.836	8.657
4600	128.273	630.038	515.406	527.311	−2518.443	−706.421	8.022
4700	128.298	632.797	517.874	540.140	−2516.276	−667.052	7.413
4800	128.322	635.499	520.296	552.971	−2514.052	−627.730	6.831
4900	128.344	638.145	522.675	565.804	−2511.773	−588.456	6.273
5000	128.365	640.738	525.010	578.639	−2509.442	−549.228	5.738
5100	128.384	643.280	527.304	591.477	−2507.060	−510.047	5.224
5200	128.403	645.773	529.559	604.316	−2504.631	−470.913	4.730
5300	128.420	648.219	531.774	617.157	−2502.156	−431.827	4.256
5400	128.437	650.620	533.953	630.000	−2499.638	−392.788	3.799
5500	128.452	652.977	536.096	642.845	−2497.079	−353.796	3.360
5600	128.467	655.291	538.204	655.691	−2494.481	−314.850	2.937
5700	128.481	657.565	540.278	668.538	−2491.847	−275.952	2.529
5800	128.495	659.800	542.319	681.387	−2489.178	−237.100	2.135
5900	128.507	661.997	544.329	694.237	−2486.478	−198.294	1.756
6000	128.519	664.157	546.308	707.088	−2483.748	−159.535	1.389

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [337.52 + 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -1898.07 + 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[1400](1)	[145](1)	[1370](1)
[670](1)	[800](1)	[145](1)
[320](1)	[660](1)	[1800](1)
rotation	[660](1)	[1155](1)
[1370](1)	[1600](1)	[540](1)

Ground State Quantum Weight: 1 $\sigma = 4$

Point Group: D_{2h}

Bond Distances: B–O = [1.4] Å; B–F = [1.32] Å

Bond Angles: B–O–B = [180]°; F–B–F = [120]°

Dihedral angle between the two BF_2 planes = 90°

Product of the Moments of Inertia: $I_A I_B I_C = [7.701231 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

Bidinosti and Coatsworth[1] have reported $\Delta_f H°(1100\ K) = 18.5 \pm 3$ kcal·mol^{-1} for the reaction 4 $BF_3(g) + B_2O_3(l) = 3\ B_2OF_4(g)$. This value was obtained from a mass spectrometric study of the variation of the ion intensities with temperature of the BF_3^+ and $B_2OF_4^+$ species. Employing JANAF auxiliary values[2] we obtain $\Delta_f H°(B_2F_4O, g, 1100\ K) = -455.75 \pm 2$ kcal·mol^{-1} which reduces to $\Delta_f H°(298.15\ K) = -453.65 \pm 2$ kcal·mol^{-1}.

Heat Capacity and Entropy

By analogy with $B_2F_4(g)$[3] free rotation of the BF_2 groups is assumed. Because of the large separation of the two BF_2 groups the molecule is considered to be planar. The B–O distance is assumed to be that in $BF_2O(g)$[2] and the B–F distance that in $B_2F_4(g)$.[2] The vibrational frequencies are estimated by comparison with those for B_2F_4;[3] the values are given above in the order $3A_g$, A_u, $2B_{1g}$, $2B_{1u}$, B_{2g}, $3B_{2u}$, $3B_{3u}$. The thermodynamic functions were evaluated based on an assumption that there is free rotation at the two B–O bonds. The reduced moment of inertia for the BF_2 top is $I_r = 4.1227 \times 10^{-39}$ g·cm^2. The principal moments of inertia are: $I_A = 16.4908 \times 10^{-39}$, $I_B = 60.5877 \times 10^{-39}$, and $I_C = 77.0785 \times 10^{-39}$ g·cm^2.

References

[1]D. R. Bidinosti and L. L. Coatsworth, Can. J. Chem. **48**, 2484 (1970).

[2]JANAF Thermochemical Tables: $BF_3(g)$, 6–30–69; $B_2O_3(l)$, 6–30–71; $BF_2O(g)$, 12–31–66; $B_2F_4(g)$, 12–31–64.

[3]L. A. Nimon, K. S. Seshadri, D. White and R. C. Taylor, AD–693614, (1969).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100	51.315	267.752	399.768	−13.202	−1894.168	−1878.142	981.041
200	66.790	307.999	344.533	−7.307	−1896.253	−1861.276	486.115
250	74.652	323.753	338.831	−3.770	−1897.191	−1852.422	387.042
298.15	81.853	337.523	337.523	0.	−1898.072	−1843.720	323.012
300	82.121	338.031	337.525	0.152	−1898.105	−1843.382	320.961
350	89.101	351.220	338.551	4.434	−1898.993	−1834.191	273.738
400	95.547	363.545	340.913	9.053	−1899.853	−1824.875	238.304
450	101.427	375.144	344.078	13.980	−1900.674	−1815.453	210.732
500	106.733	386.110	347.738	19.186	−1901.443	−1805.942	188.665
600	115.686	406.393	355.852	30.325	−1902.793	−1786.711	155.547
700	122.698	424.775	364.406	42.258	−1903.900	−1767.273	131.876
800	128.153	441.531	373.015	54.812	−1904.799	−1747.692	114.113
900	132.412	456.881	381.493	67.849	−1905.537	−1728.007	100.291
1000	135.763	471.012	389.748	81.265	−1906.157	−1708.248	89.230
1100	138.428	484.082	397.737	94.979	−1906.696	−1688.430	80.177
1200	140.570	496.222	405.444	108.933	−1907.187	−1668.566	72.631
1300	142.311	507.544	412.868	123.080	−1907.653	−1648.662	66.244
1400	143.742	518.145	420.013	137.385	−1908.116	−1628.722	60.768
1500	144.929	528.104	426.890	151.820	−1908.591	−1608.749	56.022
1600	145.923	537.490	433.512	166.364	−1909.090	−1588.743	51.867
1700	146.763	546.362	439.892	180.999	−1909.624	−1568.706	48.200
1800	147.479	554.772	446.043	195.712	−1910.197	−1548.635	44.940
1900	148.093	562.762	451.977	210.492	−1910.815	−1528.532	42.022
2000	148.623	570.372	457.708	225.328	−1911.477	−1508.395	39.395
2100	149.084	577.635	463.247	240.214	−1912.183	−1488.224	37.018
2200	149.487	584.580	468.606	255.143	−1912.931	−1468.018	34.855
2300	149.841	591.233	473.794	270.110	−1913.718	−1447.777	32.880
2400	150.154	597.617	478.821	285.110	−2015.058	−1425.363	31.022
2500	150.432	603.752	483.696	300.139	−2016.065	−1400.772	29.268
2600	150.679	609.657	488.428	315.195	−2017.031	−1376.141	27.647
2700	150.901	615.348	493.024	330.274	−2017.954	−1351.474	26.146
2800	151.100	620.840	497.492	345.375	−2018.827	−1326.773	24.751
2900	151.280	626.145	501.837	360.494	−2019.648	−1302.042	23.452
3000	151.442	631.277	506.067	375.630	−2020.413	−1277.284	22.239
3100	151.590	636.245	510.186	390.782	−2021.118	−1252.501	21.105
3200	151.724	641.060	514.201	405.948	−2021.762	−1227.697	20.040
3300	151.847	645.730	518.116	421.126	−2022.340	−1202.873	19.040
3400	151.959	650.265	521.937	436.317	−2022.852	−1178.033	18.098
3500	152.062	654.672	525.667	451.518	−2023.296	−1153.179	17.210
3600	152.156	658.957	529.310	466.729	−2023.672	−1128.313	16.371
3700	152.244	663.127	532.870	481.949	−2023.978	−1103.437	15.578
3800	152.324	667.188	536.352	497.177	−2024.215	−1078.555	14.826
3900	152.399	671.146	539.758	512.413	−2024.383	−1053.666	14.112
4000	152.468	675.005	543.091	527.657	−2024.482	−1028.774	13.434
4100	152.532	678.770	546.354	542.907	−2024.513	−1003.882	12.790
4200	152.592	682.447	549.551	558.163	−2984.176	−964.940	12.001
4300	152.647	686.038	552.683	573.425	−2981.899	−916.890	11.138
4400	152.699	689.548	555.754	588.692	−2979.561	−868.893	10.315
4500	152.748	692.980	558.766	603.965	−2977.164	−820.950	9.529
4600	152.793	696.338	561.720	619.242	−2974.710	−773.062	8.778
4700	152.836	699.624	564.619	634.523	−2972.202	−725.227	8.060
4800	152.876	702.842	567.466	649.809	−2969.640	−677.445	7.372
4900	152.914	705.995	570.261	665.098	−2967.029	−629.718	6.713
5000	152.949	709.085	573.006	680.392	−2964.371	−582.045	6.081
5100	152.983	712.114	575.704	695.688	−2961.667	−534.425	5.474
5200	153.014	715.085	578.356	710.988	−2958.922	−486.859	4.891
5300	153.044	718.000	580.964	726.291	−2956.136	−439.345	4.330
5400	153.072	720.861	583.528	741.597	−2953.314	−391.886	3.791
5500	153.099	723.670	586.050	756.905	−2950.458	−344.479	3.272
5600	153.124	726.428	588.533	772.216	−2947.571	−297.122	2.771
5700	153.148	729.139	590.976	787.530	−2944.655	−249.820	2.289
5800	153.171	731.803	593.381	802.846	−2941.713	−202.567	1.824
5900	153.192	734.421	595.749	818.164	−2938.749	−155.366	1.376
6000	153.213	736.996	598.082	833.484	−2935.764	−108.215	0.942

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = [126 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = Unknown

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1410 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy change, $\Delta_f H°(298.15\ K) = -91.3 \pm 1$ kcal·mol^{-1}, for the reaction $B_2(OH)_4$(cr) + (m + 2)$AgNO_3$(aq) + (n + 2) H_2O(l) = 2 Ag(cr) + [2 H_3BO_3 + 2 HNO_3 + m$AgNO_3$]nH_2O(aq) was determined electrically by Finch *et al.*[1] The enthalpy of formation of $B_2(OH)_4$(cr) was reported to be −335.1 kcal·mol^{-1}. This value was corrected to be 337.1 ± 2 kcal·mol^{-1} by use of more recent data on the $\Delta_f H°(298.15\ K)$ values used for calculation.

Heat Capacity and Entropy

The heat capacity for $B_2(OH)_4$(cr) was estimated by comparison with those for $B(OH)_3$(cr). $S°(298.15\ K)$ was calculated based on 3 cal·K^{-1}·mol^{-1} per atom for $B_2(OH)_4$(cr), which was obtained from the corresponding values for HBO_2(cr) and $B(OH)_3$(cr).

Sublimation Data

The value, $\Delta_{sub} H°(298.15\ K)$, was as the difference between $\Delta_f H°(298.15\ K)$ for $B_2(OH)_4$(g) and $B_2(OH)_4$(cr).

Reference

[1] A. Finch, P. J. Gardner, and I. J. Hyams, Trans. Faraday Soc. **61**, 649 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	116.190	125.520	125.520	0.	−1410.426	−1244.118	217.964
300	116.775	126.241	125.522	0.215	−1410.468	−1243.086	216.441
400	143.135	163.582	130.435	13.259	−1411.904	−1187.032	155.010
500	163.762	197.787	140.535	28.626	−1411.962	−1130.781	118.132
600	181.711	229.271	152.735	45.922	−1410.806	−1074.634	93.555
700	197.025	258.456	165.779	64.874	−1408.549	−1018.770	76.022
800	210.413	285.665	179.083	85.266	−1405.302	−963.298	62.897
900	221.459	311.098	192.354	106.869	−1401.222	−908.284	52.715
1000	231.333	334.953	205.434	129.519	−1396.428	−853.764	44.596
1100	239.994	357.417	218.239	153.095	−1391.008	−799.755	37.977
1200	247.442	378.626	230.729	177.476	−1385.059	−746.264	32.484
1300	253.801	398.691	242.885	202.548	−1378.678	−693.287	27.857
1400	258.990	417.697	254.699	228.197	−1371.963	−640.814	23.909
1500	263.006	435.709	266.171	254.307	−1365.021	−588.831	20.505

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K)$ = [348.93] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K)$ = [−1284 ± 20] $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[1380](1)	[1386](1)	[824](2)
[630](1)	[657](1)	[209](2)
[304](1)	[325](1)	[3200](4)
Rotation	[1378](1)	[1200](2)
[1155](1)	[662](1)	[880](2)
[542](1)	[325](1)	

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: $[C_2]$

Bond Distances: B–B = [1.67] Å; B–O = [1.36] Å; O–H = [0.96] Å

Bond Angles: H–O–B = [114]°; O–B–O = [120]°; O–B–B = [120]°

Dihedral angle between two $B(OH)_2$ planes = 90°

Product of the Moments of Inertia: $I_A I_B I_C$ = [2.299983 × 10^{-113}] $g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(B_2(OH)_4, g, 298.15\ K)$, is calculated using bond energies, $D°_0$(B–OH) = 132 and $D°_0$(B–B) = 78 $kcal \cdot mol^{-1}$. The bond energy $D°_0$(B–OH) was taken from that in $B(OH)_3$(g) and $D°_0$(B–B) was estimated by comparison with that in B_2F_4(g).

Heat Capacity and Entropy

The molecular structure was assumed to be the same as that for B_2F_4(g), i.e. the two $B(OH)_2$ units have staggered configuration, and free rotation about B–B bond. The B–B bond distance was taken as that in B_2F_4 molecule. Those for B–O and B–H bond and bond angles were adopted from H_3BO_3 molecule. Eleven vibratonal frequencies were assumed to be the same as those for B_2F_4(g). In addition to these were added four OH torsion frequencies, 824(2) and 209(2), four OH stretching, 3200(4), and four B–O–H bending frequencies, 1200(2) and 880(2). The thermodynamic functions were evaluated based on an assumption that there is free rotation at the B–B bond. The reduced moment of inertia for the $B(OH)_2$ top is I_r = 4.1012 × 10^{-39} $g \cdot cm^{-2}$. The principal moments of inertia are: I_A = 16.4048 × 10^{-39}, I_B = 37.4430 × 10^{-39}, and I_C = 37.4441 × 10^{-39} $g \cdot cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100	51.574	268.590	423.555	−15.496	−1275.111	−1247.102	651.419
200	78.745	312.793	357.611	−8.964	−1280.454	−1216.886	317.818
250	91.679	331.764	350.567	−4.701	−1282.641	−1200.736	250.880
298.15	103.433	348.929	348.929	0.	−1284.488	−1184.789	207.570
300	103.867	349.571	348.931	0.192	−1284.554	−1184.170	206.182
350	114.997	366.432	350.238	5.668	−1286.183	−1167.307	174.211
400	124.923	382.450	353.272	11.671	−1287.553	−1150.228	150.204
450	133.648	397.679	357.367	18.140	−1288.695	−1132.992	131.514
500	141.275	412.164	362.128	25.018	−1289.632	−1115.639	116.550
600	153.812	439.078	372.747	39.799	−1290.991	−1080.703	94.084
700	163.658	463.556	383.998	55.691	−1291.794	−1045.585	78.022
800	171.644	485.948	395.362	72.469	−1292.160	−1010.383	65.971
900	178.299	506.561	406.588	89.976	−1292.177	−975.156	56.597
1000	183.944	525.646	417.551	108.095	−1291.914	−939.943	49.098
1100	188.786	543.411	428.195	126.738	−1291.427	−904.768	42.964
1200	192.966	560.021	438.496	145.830	−1290.767	−869.645	37.855
1300	196.593	575.613	448.450	165.312	−1289.975	−834.583	33.534
1400	199.750	590.300	458.062	185.133	−1289.089	−799.585	29.833
1500	202.506	604.178	467.345	205.249	−1288.140	−764.654	26.628
1600	204.921	617.326	476.312	225.623	−1287.156	−729.787	23.825
1700	207.043	629.814	484.977	246.224	−1286.158	−694.982	21.354
1800	208.912	641.703	493.356	267.023	−1285.167	−660.236	19.160
1900	210.566	653.043	501.465	287.999	−1284.199	−625.544	17.197
2000	212.032	663.882	509.317	309.130	−1283.268	−590.902	15.433
2100	213.337	674.259	516.926	330.400	−1282.385	−556.305	13.837
2200	214.502	684.211	524.305	351.793	−1281.560	−521.749	12.388
2300	215.545	693.769	531.467	373.296	−1280.802	−487.230	11.065
2400	216.482	702.963	538.422	394.899	−1380.634	−450.605	9.807
2500	217.326	711.818	545.182	416.590	−1380.183	−411.863	8.605
2600	218.089	720.356	551.756	438.361	−1379.750	−373.139	7.496
2700	218.779	728.600	558.154	460.205	−1379.339	−334.430	6.470
2800	219.406	736.568	564.384	482.115	−1378.953	−295.736	5.517
2900	219.977	744.278	570.455	504.084	−1378.597	−257.058	4.630
3000	220.498	751.744	576.375	526.109	−1378.271	−218.389	3.802
3100	220.975	758.982	582.149	548.183	−1377.978	−179.730	3.028
3200	221.412	766.005	587.785	570.302	−1377.720	−141.083	2.303
3300	221.814	772.824	593.290	592.464	−1377.497	−102.442	1.622
3400	222.184	779.452	598.668	614.664	−1377.311	−63.806	0.980
3500	222.525	785.897	603.926	636.900	−1377.163	−25.176	0.376
3600	222.841	792.170	609.068	659.168	−1377.053	13.451	−0.195
3700	223.133	798.280	614.100	681.467	−1376.981	52.074	−0.735
3800	223.404	804.234	619.025	703.794	−1376.950	90.699	−1.247
3900	223.656	810.041	623.849	726.147	−1376.957	129.321	−1.732
4000	223.890	815.706	628.575	748.525	−1377.005	167.943	−2.193
4100	224.109	821.237	633.207	770.925	−1377.094	206.568	−2.632
4200	224.313	826.640	637.748	793.346	−2336.923	259.244	−3.224
4300	224.504	831.921	642.203	815.787	−2334.920	321.035	−3.900
4400	224.682	837.084	646.573	838.246	−2332.962	382.777	−4.544
4500	224.850	842.135	650.863	860.723	−2331.051	444.476	−5.159
4600	225.007	847.079	655.075	883.216	−2329.187	506.133	−5.747
4700	225.155	851.919	659.212	905.724	−2327.371	567.751	−6.310
4800	225.294	856.661	663.276	928.247	−2325.605	629.331	−6.849
4900	225.425	861.308	667.271	950.783	−2323.889	690.875	−7.365
5000	225.548	865.863	671.197	973.331	−2322.225	752.385	−7.860
5100	225.665	870.331	675.058	995.892	−2320.613	813.861	−8.336
5200	225.775	874.714	678.856	1018.464	−2319.054	875.304	−8.793
5300	225.880	879.016	682.592	1041.047	−2317.551	936.722	−9.232
5400	225.978	883.239	686.268	1063.640	−2316.104	998.108	−9.655
5500	226.072	887.386	689.888	1086.242	−2314.714	1059.468	−10.062
5600	226.161	891.460	693.451	1108.854	−2313.383	1120.807	−10.454
5700	226.245	895.464	696.960	1131.474	−2312.112	1182.120	−10.833
5800	226.325	899.400	700.416	1154.103	−2310.902	1243.413	−11.198
5900	226.401	903.269	703.822	1176.739	−2309.754	1304.680	−11.551
6000	226.474	907.075	707.178	1199.383	−2308.671	1365.935	−11.892

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 233.17\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 56.7 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 41.0 \pm 16.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies			
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
2532(1)	2600(1)	1026(1)	2615(1)
2109(1)	919(1)	584(1)	1601(1)
1184(1)	1755(1)	1905(1)	1174(1)
788(1)	942(1)	973(1)	
2612(1)	950(1)	368(1)	

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distances: B–B = 1.775 ± 0.004 Å; B–H_t = 1.196 ± 0.016 Å; B–H_b = 1.339 ± 0.013 Å
H_t = terminal hydrogen, H_b = bridge hydrogens.
Bond Angles: H_t–B–H_t = 120.2 ± 1.6°
Product of the Moments of Inertia: $I_A I_B I_C = 2.459830 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is a weighted average of the following data. The older data of Roth *et al.*[8] deviates from the rest of the investigations and is not included.

Source	Reaction	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	$B_2H_6(g) \rightarrow 2\ B(am) + 3\ H_2(g)$	−5.0	7.4
2	$B_2H_6(g) \rightarrow 2\ B(am) + 3\ H_2(g)$	−6.73	9.13
3	$B_2H_6(g) + 6\ Cl_2 \rightarrow 2\ BCl_3(g) + 6\ HCl(g)$	−342.3	17.3
4	$B_2H_6(g) + 6\ H_2O(l) + [2000\ H_2O](l) \rightarrow 2[H_3BO_3 + 1000\ H_2O](soln) + 6\ H_2(g)$	−111.46 ± 0.54	9.32
7a	$B_2H_6(g) + 2006\ H_2O \rightarrow 2(H_3BO_3 + 1000\ H_2O) + 6\ H_2(g)$	−112.22 ± 0.10	10.08
7b	$BCl_3(l) + 130.3\ H_2O \rightarrow (H_3BO_3 + 1000\ H_2O) + 3(HCl + 100\ H_2O)$	−68.14	—
(a) − 2(b) + (c)	$B_2H_6(g) + 6(HCl100\ H_2O) \rightarrow 2\ BCl(l) + 6\ H_2(g)$	+24.06	10.06
9	$(CH_3)_3\ N(g) + 1/2\ B_2H_6(g) \rightarrow (CH_3)_3N{:}BH_3(cr)$	−32.33 ± 0.06	8.3
13	$(CH_3)_3N(g) + 1/2\ B_2H_6(g) \rightarrow CH_3)_3N{:}BH_3(cr)$	−31.40	6.5

Sources of Auxiliary Data: From the JANAF tables, $\Delta_f H°(298.15\ K) = 1.2, -96.31, -22.063\ kcal·mol^{-1}$ of B(am), $BCl_3(g)$ and HCl(g), respectively. From Rossini,[11] the $\Delta_{vap}H°(298.15\ K) = 5.6\ kcal·mol^{-1}$ of BCl_3. From Wagman,[12] the $\Delta_f H°(298.15\ K)$ of (HCl + 1000 H_2O) = −39.657 $kcal·mol^{-1}$. From Good *et al.*,[5] the $\Delta_f H°(H_3BO_3, cr, 298.15\ K) = -261.47 \pm 0.20\ kcal·mol^{-1}$ and the H_3BO_3 solution data of Fasolino.[6] $\Delta_f H°((CH_3)_3N, g, 298.15\ K) = -5.9 \pm 0.4\ kcal·mol^{-1}$ from Jaffe.[10]

Heat Capacity and Entropy

The molecular constants reported by Carroll,[14] were selected. They agree well with those reported by Hedberg and Schomaker.[15] The principal moments of inertia are $I_A = 1.0562 \times 10^{-39}$, $I_B = 4.6381 \times 10^{-39}$, and $I_C = 5.0213 \times 10^{-39}\ g·cm^2$.

The vibrational frequencies for $B_2{}^{11}H_6$ were those listed by Wu[16] except for υ_8, υ_{10} and υ_{14} which were taken from the calculated frequency column of Table VIII–1 (page 55) of the Thesis.

References

[1] S. R. Gunn and L. G. Green, J. Phys. Chem. **65**, 779 83 (1961); J. Chem. Phys. **36**, 1118 (1962). Explosive decomposition while mixed with stibine.

[2] E. J. Prosen, W. H. Johnson and F. Y. Pergiel, J. Res. Nat. Bur. Stand. **61**, 247 250 (1958). Decomposition by heating in a flow type calorimeter.

[3] J. R. Lacher, R. E. Scruby, and J. D. Park, J. Am. Chem. Soc. **74**, 5292 4 (1952). A vapor phase chlorination in a flow type calorimeter.

[4] E. J. Prosen, W. H. Johnson, and F. Y. Pergiel, J. Res. Nat. Bur. Stand. **62**, 43 47 (1959). Heat of reaction of diborane with water in a flow type calorimeter.

[5] W. D. Good, M. Mansson, and J. P. McCullough, Thermochemistry of Boron and Some of its Compoudns. The heats of Formation of Trimethylamineborane and Orthaboric Acid, Symp. on Thermodynamics and Thermochemistry, Lund, Sweden, (July 1963).

Continued on page 317

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.149	56.684	56.684	INFINITE
100	34.592	186.917	274.911	−8.799	50.988	62.576	−32.686
200	43.499	213.191	237.985	−4.959	46.081	76.058	−19.864
250	50.526	223.629	234.083	−2.613	43.496	83.850	−17.519
298.15	58.100	233.170	233.170	0.	41.003	91.849	−16.092
300	58.397	233.530	233.171	0.108	40.909	92.165	−16.047
350	66.435	243.137	233.911	3.229	38.429	100.905	−15.059
400	74.255	252.522	235.653	6.748	36.106	109.991	−14.363
450	81.690	261.701	238.039	10.648	33.970	119.357	−13.855
500	88.683	270.674	240.856	14.909	32.037	128.950	−13.471
600	101.331	287.988	247.280	24.425	28.803	148.650	−12.941
700	112.275	304.451	254.282	35.119	26.373	168.828	−12.598
800	121.655	320.072	261.538	46.827	24.659	189.303	−12.360
900	129.635	334.875	268.871	59.403	23.547	209.956	−12.186
1000	136.394	348.893	276.179	72.714	22.922	230.706	−12.051
1100	142.112	362.168	283.398	86.647	22.678	251.499	−11.943
1200	146.952	374.747	290.491	101.107	22.725	272.300	−11.853
1300	151.059	386.676	297.435	116.013	22.986	293.089	−11.776
1400	154.558	398.002	304.217	131.298	23.400	313.851	−11.710
1500	157.550	408.770	310.832	146.908	23.917	334.580	−11.651
1600	160.122	419.022	317.276	162.794	24.497	355.272	−11.598
1700	162.342	428.798	323.551	178.920	25.110	375.927	−11.551
1800	164.269	438.133	329.659	195.253	25.732	396.546	−11.507
1900	165.949	447.060	335.605	211.766	26.343	417.130	−11.468
2000	167.421	455.611	341.393	228.436	26.928	437.682	−11.431
2100	168.716	463.811	347.028	245.244	27.475	458.206	−11.397
2200	169.860	471.687	352.517	262.174	27.975	478.705	−11.366
2300	170.876	479.260	357.864	279.212	28.418	499.183	−11.337
2400	171.780	486.552	363.075	296.345	−71.719	521.780	−11.356
2500	172.589	493.581	368.155	313.565	−71.560	546.506	−11.419
2600	173.315	500.365	373.111	330.861	−71.407	571.225	−11.476
2700	173.969	506.918	377.946	348.225	−71.265	595.939	−11.529
2800	174.559	513.256	382.666	365.652	−71.137	620.648	−11.578
2900	175.094	519.391	387.275	383.135	−71.025	645.353	−11.624
3000	175.581	525.335	391.779	400.669	−70.932	670.054	−11.667
3100	176.023	531.100	396.180	418.250	−70.862	694.752	−11.706
3200	176.428	536.695	400.485	435.873	−70.815	719.448	−11.744
3300	176.798	542.130	404.695	453.534	−70.793	744.144	−11.779
3400	177.139	547.413	408.815	471.232	−70.799	768.839	−11.812
3500	177.451	552.552	412.849	488.961	−70.834	793.535	−11.843
3600	177.740	557.555	416.799	506.721	−70.899	818.232	−11.872
3700	178.006	562.429	420.670	524.509	−70.996	842.931	−11.900
3800	178.253	567.179	424.463	542.322	−71.125	867.634	−11.926
3900	178.482	571.812	428.182	560.159	−71.288	892.340	−11.952
4000	178.694	576.334	431.829	578.017	−71.486	917.050	−11.975
4100	178.892	580.749	435.408	595.897	−71.719	941.767	−11.998
4200	179.076	585.062	438.920	613.795	−1031.687	980.538	−12.195
4300	179.248	589.278	442.368	631.712	−1029.819	1028.426	−12.493
4400	179.409	593.400	445.754	649.645	−1027.991	1076.270	−12.777
4500	179.559	597.434	449.080	667.593	−1026.205	1124.074	−13.048
4600	179.700	601.382	452.348	685.556	−1024.461	1171.838	−13.307
4700	179.833	605.248	455.560	703.533	−1022.759	1219.566	−13.554
4800	179.957	609.035	458.718	721.522	−1021.099	1267.258	−13.791
4900	180.075	612.747	461.824	739.524	−1019.481	1314.914	−14.017
5000	180.185	616.386	464.879	757.537	−1017.906	1362.540	−14.234
5100	180.289	619.955	467.885	775.561	−1016.373	1410.133	−14.443
5200	180.387	623.457	470.843	793.595	−1014.881	1457.697	−14.643
5300	180.480	626.894	473.755	811.638	−1013.430	1505.233	−14.835
5400	180.568	630.269	476.622	829.691	−1012.018	1552.742	−15.020
5500	180.651	633.583	479.446	847.752	−1010.645	1600.224	−15.198
5600	180.730	636.838	482.228	865.821	−1009.310	1647.683	−15.369
5700	180.805	640.038	484.968	883.898	−1008.010	1695.118	−15.534
5800	180.876	643.183	487.669	901.982	−1006.745	1742.530	−15.693
5900	180.944	646.276	490.331	920.073	−1005.513	1789.920	−15.847
6000	181.008	649.317	492.956	938.170	−1004.313	1837.290	−15.995

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$\Delta_f H°(0\ K) = -91.3 \pm 8.4\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 35.98 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -92.0 \pm 8.4\ kJ \cdot mol^{-1}$

T_{dcm} = [1320] K

Enthalpy of Formation

The equilibrium constants (993–1108 K) for the reaction 2 MgB_2(cr) = Mg(g) + MgB_4(cr) were determined by Wright and Walsh.[1] The corresponding 2nd and 3rd law values of $\Delta_f H°(298.15\ K)$ for this reaction were derived as 53.1 ± 4.7 and 54.1 kcal·mol^{-1}, respectively. Using the 3rd law value obtained, i.e., $\Delta_r H°(298.15\ K) = 54.1$ kcal·mol^{-1}, for the reaction, $\Delta_f H°(MgB_2, cr, 298.15\ K)$ was evaluated as −22.0 ± 2.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The low temperature (21.12–304.22 K) heat capacities were measured by Swift and White.[2] Above 298.15 K, the values of C_p were estimated with those of other related borides. $S°(298.15\ K)$ was reported by Swift and White[2] using $S°(extrap, 20\ K) = 0.005$ cal·K^{-1}·mol^{-1}.

Decomposition Data

T_{dcm} was taken from Markovsky *et al.*[3] On heating to high temperatures, MgB_2(cr) decomposes into boride phases, A, B, and C with the separation of Mg. The composition of phase A is close to MgB_6 and that of C is close to MgB_{12}.

References

[1]M. Wright and P. N. Walsh, The Vaporization of MgB_4(cr), Ohio State University Research Foundation, Tech. Research Report OMCC–HEF–55 (1958).
[2]R. M. Swift and D. White, J. Am. Chem. Soc. **79**, 3641 (1957).
[3]L. Y. Markovsky, Y. D. Kondrashev, and G. V. Kaputovskaya, Zhur. Obshchei Khim. **25**, 409 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.799	−91.337	−91.337	INFINITE
100	11.171	4.025	68.961	−6.494	−91.722	−91.112	47.592
200	34.392	19.205	40.125	−4.184	−92.085	−90.330	23.592
298.15	47.823	35.982	35.982	0.	−91.964	−89.473	15.675
300	47.865	36.278	35.983	0.089	−91.964	−89.457	15.576
400	54.392	51.002	37.946	5.222	−92.110	−88.609	11.571
500	58.409	63.590	41.848	10.871	−92.590	−87.684	9.160
600	61.379	74.507	46.402	16.863	−93.328	−86.638	7.542
700	64.015	84.168	51.120	23.134	−94.239	−85.452	6.377
800	66.526	92.879	55.804	29.660	−95.267	−84.128	5.493
900	69.162	100.867	60.373	36.445	−96.364	−82.670	4.798
1000	71.714	108.288	64.798	43.490	−106.100	−80.376	4.198
1100	74.078	115.233	69.070	50.779	−107.301	−77.744	3.692
1200	76.442	121.780	73.193	58.305	−108.384	−75.008	3.265
1300	78.795	127.992	77.171	66.067	−109.336	−72.188	2.901
1400	81.170	133.918	81.014	74.065	−237.558	−66.131	2.467
1500	83.643	139.603	84.732	82.307	−236.863	−53.910	1.877
1600	85.981	145.077	88.333	90.789	−236.012	−41.740	1.363
1700	88.162	150.355	91.827	99.497	−235.015	−29.628	0.910
1800	90.249	155.454	95.221	108.419	−233.881	−17.578	0.510
1900	92.242	160.387	98.522	117.544	−232.618	−5.595	0.154
2000	94.140	165.167	101.735	126.864	−231.232	6.318	−0.165

PREVIOUS: March 1963 CURRENT: March 1965

$S°(298.15\ K)$ = [227.7] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 93 \pm 105\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 96 \pm 105\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[1250](1)
[600](1)
[1800](1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distance: B–O = [1.26] Å
Bond Angle: B–O–B = [150]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [4.732389 × 10^{-117}] $g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation was calculated from the estimated enthalpy of reaction $\Delta_f H°(0\ K) = 300 \pm 25$ kcal·mol^{-1} for $B_2O(g) \rightarrow 2B(g) + O(g)$, using the JANAF auxiliary data[2] for B(g) and O(g). The value of $\Delta_f H°(0\ K)$ was assumed to be the sum of the enthalpies of dissociation, 120 kcal·mol^{-1} for $B_2O(g) \rightarrow BO(g) + B(g)$ and 180 kcal·mol^{-1} for $BO(g) \rightarrow B(g) + O(g)$. The former was estimated and the latter was derived from the JANAF values.[2]

The possible existence of $B_2O(g)$ in the burning of boron under reducing conditions was discussed by Bahn.[1] He estimated the enthalpy of formation to lie between −27 and +23 kcal·mol^{-1} but favored the value of +23 kcal·mol^{-1} in the theoretical calculations of boron burning *in air*.

Heat Capacity and Entropy

The bent molecular structure and the molecular constants were estimated by comparison with those in BO(g), AlO(g) and $Al_2O(g)$. The principal moments of inertia are $I_A = 0.1624 \times 10^{-39}$, $I_B = 5.3179 \times 10^{-39}$, and $I_C = 5.4803 \times 10^{-39}$ $g·cm^2$.

References

[1]G. S. Bahn, Combustion Institute, University of Denver (1966).
[2]JANAF Thermochemical Tables: B(g), 12–31–64; and O(g), 6–30–62.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−10.375	92.626	92.626	INFINITE
100	33.368	189.391	259.874	−7.048	94.453	84.241	−44.003
200	35.469	213.037	231.161	−3.625	95.755	73.464	−19.187
250	36.956	221.110	228.368	−1.814	96.094	67.847	−14.176
298.15	38.410	227.744	227.744	0.	96.232	62.391	−10.931
300	38.466	227.982	227.745	0.071	96.234	62.181	−10.827
350	39.966	234.024	228.218	2.032	96.202	56.506	−8.433
400	41.433	239.457	229.289	4.067	96.019	50.846	−6.640
450	42.841	244.419	230.698	6.174	95.712	45.217	−5.249
500	44.168	249.002	232.303	8.350	95.311	39.627	−4.140
600	46.530	257.270	235.790	12.888	94.307	28.581	−2.488
700	48.483	264.595	239.391	17.642	93.123	17.718	−1.322
800	50.064	271.176	242.960	22.572	91.819	7.034	−0.459
900	51.336	277.149	246.432	27.645	90.425	−3.482	0.202
1000	52.359	282.612	249.781	32.831	88.957	−13.838	0.723
1100	53.186	287.643	252.997	38.110	87.421	−24.043	1.142
1200	53.861	292.300	256.081	43.464	85.822	−34.106	1.485
1300	54.414	296.634	259.036	48.878	84.162	−44.033	1.769
1400	54.873	300.684	261.867	54.343	82.441	−53.831	2.008
1500	55.256	304.483	264.583	59.850	80.659	−63.503	2.211
1600	55.579	308.060	267.190	65.392	78.815	−73.053	2.385
1700	55.853	311.438	269.694	70.964	76.909	−82.487	2.535
1800	56.088	314.637	272.103	76.562	74.939	−91.807	2.664
1900	56.289	317.675	274.422	82.181	72.905	−101.015	2.777
2000	56.464	320.567	276.658	87.819	70.807	−110.115	2.876
2100	56.616	323.326	278.815	93.473	68.643	−119.108	2.963
2200	56.750	325.963	280.898	99.141	66.413	−127.997	3.039
2300	56.867	328.488	282.913	104.822	64.117	−136.782	3.106
2400	56.971	330.911	284.863	110.514	−38.764	−143.329	3.119
2500	57.064	333.238	286.752	116.216	−41.349	−147.633	3.085
2600	57.147	335.478	288.583	121.927	−43.937	−151.833	3.050
2700	57.220	337.636	290.360	127.645	−46.527	−155.934	3.017
2800	57.287	339.718	292.086	133.371	−49.120	−159.938	2.984
2900	57.347	341.730	293.763	139.103	−51.718	−163.851	2.951
3000	57.401	343.675	295.395	144.840	−54.319	−167.673	2.919
3100	57.451	345.558	296.983	150.583	−56.924	−171.408	2.888
3200	57.496	347.382	298.529	156.330	−59.533	−175.060	2.858
3300	57.537	349.152	300.037	162.082	−62.147	−178.630	2.827
3400	57.575	350.870	301.506	167.837	−64.765	−182.120	2.798
3500	57.609	352.540	302.941	173.597	−67.388	−185.534	2.769
3600	57.641	354.163	304.341	179.359	−70.015	−188.872	2.740
3700	57.670	355.743	305.709	185.125	−72.647	−192.138	2.712
3800	57.697	357.281	307.046	190.893	−75.283	−195.331	2.685
3900	57.722	358.780	308.354	196.664	−77.923	−198.456	2.658
4000	57.746	360.242	309.633	202.437	−80.567	−201.513	2.631
4100	57.767	361.668	310.884	208.213	−83.216	−204.504	2.605
4200	57.787	363.060	312.110	213.991	−1045.567	−193.382	2.405
4300	57.806	364.420	313.311	219.770	−1046.050	−173.086	2.103
4400	57.824	365.750	314.488	225.552	−1046.541	−152.779	1.814
4500	57.840	367.049	315.641	231.335	−1047.040	−132.461	1.538
4600	57.855	368.321	316.773	237.120	−1047.548	−112.132	1.273
4700	57.870	369.565	317.883	242.906	−1048.066	−91.791	1.020
4800	57.883	370.784	318.972	248.694	−1048.595	−71.439	0.777
4900	57.896	371.977	320.042	254.483	−1049.135	−51.076	0.544
5000	57.908	373.147	321.092	260.273	−1049.687	−30.701	0.321
5100	57.919	374.294	322.124	266.064	−1050.252	−10.316	0.106
5200	57.930	375.419	323.138	271.857	−1050.832	10.080	−0.101
5300	57.940	376.522	324.135	277.650	−1051.426	30.488	−0.300
5400	57.949	377.605	325.115	283.445	−1052.037	50.907	−0.492
5500	57.958	378.669	326.080	289.240	−1052.665	71.338	−0.678
5600	57.967	379.713	327.028	295.036	−1053.312	91.780	−0.856
5700	57.975	380.739	327.961	300.833	−1053.978	112.234	−1.029
5800	57.982	381.747	328.880	306.631	−1054.665	132.700	−1.195
5900	57.990	382.739	329.784	312.430	−1055.375	153.177	−1.356
6000	57.997	383.713	330.675	318.229	−1056.108	173.668	−1.512

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 242.60\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -457.3 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -456.1 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2065(1)	565(2)
570(1)	285(2)
1910(1)	

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distances: O–B = 1.20 Å; B–B = 1.70 Å
Bond Angle: O–B–B = 180°
Rotational Constant: $B_0 = 0.112313\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(B_2O_2, g, 298.15\ K)$ adopted is the weighted average of three $\Delta_f H°(298.15\ K)$ values derived from two different chemical reactions. The chemical reactions related to the production of $B_2O_2(g)$ have been studied by several investigators. Using the equilibrium vapor pressure data, the respective values of $\Delta_r H°(298.15\ K)$ were evaluated by both the 2nd and 3rd law methods. The results obtained are based on the latter and presented as follows:

Source	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[1]	2/3 B(cr) + 2/3 B_2O_3(l) = B_2O_2(g)	94.0	91.8 ± 2.2	−105.5 ± 0.7*
	2/3 B(cr) + 2/3 B_2O_3(g) = B_2O_2(g)	24.8	25.4 ± 0.2	−108.0 ± 0.5
[2]	2 MgO(cr) + 2 B(cr) = 2 Mg(g) + B_2O_2(g)	255.4	—	−102.6 ± 10*
[3]	2/3 B(cr) + 2/3 B_2O_3(l) = B_2O_2(g)	89.3	77.9 ± 0.2	−110.2 ± 0.9
[4]	B_2O_3(l) + 3 C(cr) = 3 CO(g) + 2 B(cr)	—	—	−108.5 ± 1.5
	B_2O_3(l) + C(cr) = B_2O_2(g) + CO(g)	—	—	

*The value not used for the calculation of the weighted average of $\Delta_f H°(B_2O_2, g, 298.15\ K)$.

Heat Capacity and Entropy

The molecular structure and constants, and vibrational frequencies, corrected to the average isotopic species, were taken from Sommer *et al.*[5]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.398	−457.343	−457.343	INFINITE
100	34.367	193.295	286.969	−9.367	−457.265	−459.202	239.863
200	48.231	221.483	247.582	−5.220	−456.694	−461.326	120.486
250	53.477	232.836	243.520	−2.671	−456.345	−462.525	96.639
298.15	57.297	242.597	242.597	0.	−456.056	−463.743	81.246
300	57.424	242.952	242.598	0.106	−456.046	−463.791	80.753
350	60.445	252.040	243.309	3.056	−455.827	−465.100	69.412
400	62.871	260.275	244.923	6.141	−455.708	−466.434	60.910
450	64.921	267.802	247.053	9.337	−455.684	−467.777	54.298
500	66.722	274.737	249.479	12.629	−455.741	−469.118	49.008
600	69.820	287.184	254.750	19.461	−456.031	−471.770	41.071
700	72.409	298.147	260.182	26.576	−456.480	−474.359	35.397
800	74.575	307.962	265.551	33.928	−457.030	−476.877	31.137
900	76.378	316.853	270.765	41.479	−457.649	−479.321	27.819
1000	77.874	324.980	275.786	49.194	−458.320	−481.694	25.161
1100	79.116	332.462	280.603	57.045	−459.038	−483.996	22.983
1200	80.149	339.392	285.217	65.010	−459.800	−486.232	21.165
1300	81.013	345.842	289.635	73.069	−460.607	−488.402	19.624
1400	81.739	351.873	293.868	81.208	−461.461	−490.509	18.301
1500	82.353	357.534	297.925	89.413	−462.365	−492.552	17.152
1600	82.876	362.866	301.819	97.675	−463.323	−494.534	16.145
1700	83.323	367.904	305.560	105.986	−464.337	−496.454	15.254
1800	83.709	372.678	309.157	114.338	−465.410	−498.313	14.461
1900	84.042	377.213	312.621	122.726	−466.544	−500.110	13.749
2000	84.333	381.532	315.959	131.145	−467.743	−501.846	13.107
2100	84.588	385.653	319.180	139.591	−469.007	−503.520	12.524
2200	84.812	389.593	322.292	148.062	−470.339	−505.132	11.993
2300	85.010	393.367	325.301	156.553	−471.740	−506.683	11.507
2400	85.185	396.989	328.213	165.063	−573.730	−506.034	11.014
2500	85.342	400.470	331.034	173.589	−575.428	−503.178	10.513
2600	85.482	403.820	333.770	182.131	−577.133	−500.254	10.050
2700	85.608	407.048	336.424	190.685	−578.846	−497.265	9.620
2800	85.722	410.164	339.002	199.252	−580.567	−494.211	9.220
2900	85.824	413.174	341.508	207.829	−582.297	−491.098	8.846
3000	85.917	416.085	343.946	216.416	−584.037	−487.923	8.495
3100	86.002	418.903	346.319	225.012	−585.787	−484.690	8.167
3200	86.079	421.635	348.630	233.617	−587.546	−481.401	7.858
3300	86.150	424.285	350.883	242.228	−589.316	−478.057	7.567
3400	86.214	426.858	353.079	250.846	−591.095	−474.658	7.292
3500	86.274	429.358	355.223	259.471	−592.885	−471.208	7.032
3600	86.328	431.789	357.317	268.101	−594.684	−467.706	6.786
3700	86.379	434.155	359.361	276.736	−596.492	−464.154	6.553
3800	86.426	436.459	361.360	285.377	−598.311	−460.552	6.331
3900	86.469	438.705	363.315	294.021	−600.138	−456.903	6.120
4000	86.509	440.894	365.227	302.670	−601.975	−453.208	5.918
4100	86.547	443.031	367.099	311.323	−603.820	−449.466	5.726
4200	86.581	445.117	368.931	319.979	−1565.374	−431.630	5.368
4300	86.614	447.155	370.727	328.639	−1565.063	−404.640	4.915
4400	86.644	449.146	372.487	337.302	−1564.766	−377.657	4.483
4500	86.672	451.094	374.212	345.968	−1564.481	−350.681	4.071
4600	86.699	452.999	375.904	354.637	−1564.211	−323.711	3.676
4700	86.724	454.864	377.564	363.308	−1563.955	−296.746	3.298
4800	86.747	456.690	379.194	371.981	−1563.715	−269.787	2.936
4900	86.769	458.479	380.794	380.657	−1563.492	−242.831	2.589
5000	86.790	460.232	382.365	389.335	−1563.287	−215.881	2.255
5100	86.810	461.951	383.909	398.015	−1563.101	−188.935	1.935
5200	86.828	463.637	385.426	406.697	−1562.935	−161.993	1.627
5300	86.846	465.291	386.917	415.381	−1562.791	−135.052	1.331
5400	86.862	466.914	388.384	424.066	−1562.670	−108.116	1.046
5500	86.878	468.508	389.826	432.753	−1562.573	−81.181	0.771
5600	86.893	470.074	391.245	441.442	−1562.503	−54.246	0.506
5700	86.907	471.612	392.641	450.132	−1562.461	−27.314	0.250
5800	86.920	473.124	394.016	458.823	−1562.449	−0.381	0.003
5900	86.933	474.609	395.370	467.516	−1562.468	26.550	−0.235
6000	86.945	476.071	396.702	476.210	−1562.521	53.484	−0.466

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 53.95 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 723 \pm 0.5\ K$

$\Delta_f H°(0\ K) = -1265.8 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1271.9 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 24.071 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(B_2O_3, cr, 298.15\ K) = 304.0 \pm 0.5\ kcal \cdot mol^{-1}$ is calculated from JANAF $\Delta_f H°(BF_3, g, 298.15\ K) = -271.42 \pm 0.4\ kcal \cdot mol^{-1}$ [1] and $\Delta_c H°(298.15\ K) = -238.82 \pm 0.39\ kcal \cdot mol^{-1}$ for $B_2O_c(cr) + 3\ F_2(g) \rightarrow 2\ BF_3(g) + 1.5\ O_2(g)$. The enthalpy of combustion of B_2O_3(cr) in fluorine was determined by Johnson and Hubbard.[2] The direct combusion of boron in oxygen has led to $\Delta_f H°$(glass, 298.15 K) values which range from −280 to −368 $kcal \cdot mol^{-1}$ [3-9] due to incomplete combustions or ill-defined states of combustion products. These values are not reliable.

A reliable enthalpy of formation of boric oxide can be derived from enthalpies of solution of H_3BO_3(cr) and B_2O_3(cr) which are listed below. Since the enthalpies of dilution of aqueous H_3BO_3[10] are relatively small, no correction has been applied to the reported enthalpy of solution data. The derived $\Delta_f H°$ values are in very good agreement with the values adopted.

Source	Enthalpy of Solution, $kcal \cdot mol^{-1}$ $\Delta_{sol} H°(B_2O_3, cr)$[a]	$\Delta_{sol} H°(H_3BO_3, cr)$[b]	$\Delta_f H°(cr)$[c] $kcal \cdot mol^{-1}$	$\Delta_f H°(B_2O_3, cr, 298.15\ K)$[d] $kcal \cdot mol^{-1}$
[11]	−3.56*	+5.3	−14.16	−303.83
[12]	−3.41*	+5.10	−13.61	−304.38
[13]	−3.49*	+5.3	−14.09	−303.90
[14]	−3.48	+5.27	−14.02	−303.97
[15]	−3.49	+5.17	−13.83	−304.16
[16]	−3.45	+5.45	−14.35	−303.64

*The enthalpy of solution of B_2O_3(am) was combined with $\Delta_f H°(25°C) = 4.44\ kcal \cdot mol^{-1}$ [2] to obtain the $\Delta_{sol} H°(B_2O_3, cr)$
[a] $B_2O_3(cr) + 3\ H_2O(l) \rightarrow 2\ H_3BO_3(aq)$ [b] $H_3BO_3(cr) \rightarrow H_3BO_3(aq)$ [c] $B_2O_3(cr) + 3\ H_2O(l) \rightarrow 2\ H_3BO_3(cr)$
[d] the auxiliary data $\Delta_f H°(H_3BO_3, cr, 298.15\ K)$[1] $= -261.47 \pm 0.2\ kcal/mol^{-1}$ and $\Delta_f H°(H_2O, l, 298.15\ K)$[10] $= -68.315\ kcal\ mol^{-1}$ are used in the calculation.

Other solution calorimetric measurements[17-19] which involve the hydrolysis of B_2H_6(g) and BCl_3(l) lead to enthalpies of formation of boric oxide (cr) with a relatively large uncertainty since the techniques were indirect, and many questionable auxiliary data were employed in the derivation.

Heat Capacity and Entropy

The adopted heat capacities are derived from C_p data of Kerr, Hersh and Johnston[20] and Shmidt[21] in the temperature regions 18–296.6 K and 303–703 K, respectively. These two sets of C_p data were measured adiabatically and are smoothly joined at 298.15 K by a polynomial curve fitting technique. The derived entropy, $S°(298.15\ K)$, is based on $S°(18.08\ K) = 0.025\ cal \cdot K^{-1} \cdot mol^{-1}$.

Kelley[22] also measured low temperature C_p from 53 to 295 K which are in very good agreement with the values adopted. Southard[23] determined high temperature enthalpy data from 350 to 721.5 K by drop calorimetry. The deviations of the observed enthalpy data from the adopted values are about 5% at 360 K, 1% at 570 K and 0.5% at 720 K.

Fusion Data

The melting point, 723 ± 0.5 K, was determined by Schmidt[21] in excellent agreement with the value 723 ± 2 K reported by Kracek *et al.*[24] The adopted enthalpy of fusion, $\Delta_{fus} H° = 5.75 \pm 0.1\ kcal \cdot mol^{-1}$, is derived from $\Delta_f H°(298.15\ K) = 4.44\ kcal \cdot mol^{-1}$ for B_2O_3(crystal) → B_2O_3(am)[2] and the adopted relative enthalpies of the two forms at 723 K. This value is reasonable agreement with $\Delta_{fus} H°(723\ K) = 5.87 \pm 0.1\ kcal \cdot mol^{-1}$ determined calorimetrically by Schmidt.[21]

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Continued on page 318

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.293	−1265.776	−1265.776	INFINITE
100	20.740	10.983	96.353	−8.537	−1269.425	−1244.466	650.042
200	43.844	32.869	59.093	−5.245	−1271.165	−1218.726	318.299
298.15	62.588	53.953	53.953	0.	−1271.936	−1192.796	208.973
300	62.927	54.341	53.954	0.116	−1271.944	−1192.305	207.599
400	77.948	74.600	56.614	7.194	−1272.047	−1165.729	152.229
500	89.287	93.269	62.105	15.582	−1271.710	−1139.180	119.009
600	98.115	110.360	68.744	24.969	−1271.024	−1112.733	96.872
700	105.228	126.039	75.825	35.149	−1270.036	−1086.426	81.070
723.000	106.692	129.464	77.477	37.587	--- CRYSTAL <~~> LIQUID ---		
800	111.169	140.489	83.017	45.978	−1268.779	−1060.279	69.229
900	116.190	153.879	90.156	57.351	−1267.277	−1034.304	60.029
1000	120.625	166.356	97.159	69.197	−1265.548	−1008.509	52.679
1100	124.516	178.039	103.986	81.458	−1263.611	−982.897	46.674
1200	128.072	189.029	110.620	94.092	−1261.478	−957.470	41.678
1300	131.294	199.409	117.054	107.061	−1259.167	−932.228	37.457
1400	134.306	209.251	123.291	120.344	−1256.684	−907.171	33.847
1500	137.110	218.614	129.336	133.916	−1254.042	−882.298	30.724

PREVIOUS: December 1964 CURRENT: June 1971

$S°(298.15\ K) = [78.443 \pm 0.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 723 \pm 0.5\ K$

$\Delta_f H°(298.15\ K) = [-1253.359 \pm 2.5]\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = 24.071 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K), is calculated from $\Delta_f H°(25°C) = 4.44 \pm 0.06$ kcal·mol^{-1}[1] for B_2O_3(cr) → B_2O_3(glass), using the JANAF value $\Delta_f H°(B_2O_3, cr, 298.15\ K) = -304.0 \pm 0.5$ kcal·mol^{-1}. The value of $\Delta_t H°$ is the difference between the enthalpies of crystalline and glassy B_2O_3 determined by Johnson and Hubbard.[1]

Heat Capacity and Entropy

Heat capacities of B_2O_3(glass) have been measured adiabatically in the temperature regions 59.6–295 K by Turdakin and Tarasov,[2] and 306.7–910.8 K by Schmidt.[3] Thomas and Parks[4] also measured isothermally the heat capacities from 308 to 594 K in a radiation calorimeter. Both Schmidt[3] and Thomas and Parks[4] observed a rapid rise in heat capacity in the region 500–580 K. This rise indicates a glass transition in liquid B_2O_3.

Southard[5] and Krasovitskaya *et al.*[6] determined enthalpy changes by drop calorimetry in the temperature regions 381.7–1776.8 K and 1015–2154 K, respectively.

We have adopted the C_p data of Turdakin (60–295 K) and Shmidt (307–600 K) which are smoothly joined at 298.15 K by a polynomial curve fitting technique. The drop calorimetric data of Southard in this region 381 to 600 K are less reliable since the final state of the sample was dependent upon previous thermal history through the glass transition region. Above the melting point, we have chosen a constant C_p, 31.0 cal·K^{-1}·mol^{-1}, which is a compromise between the adiabatic C_p and drop calorimetric data. The uncertainty of this choice, ±0.6 cal·K^{-1}·mol^{-1}, is within the experimental errors of both techniques.

$S°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°/T_{fus}$ and the difference in entropy, $S°(723\ K) - S°(298.15\ K)$, between the crystal and liquid.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point is calculated as the temperature at which the fugacity is 1 bar for $B_2O_3(l) \rightarrow B_2O_3(g)$. The enthalpy of vaporization is the difference in $\Delta_f H°$ at the boiling point between liquid and gas.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$		$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	16.617	INFINITE	−10.060	−1247.966	−1247.966	INFINITE
100	25.786	32.674	122.342	−8.967	−1251.278	−1228.488	641.696
200	45.915	56.849	83.667	−5.363	−1252.707	−1205.064	314.730
298.15	62.802	78.443	78.443	0.	−1253.359	−1181.521	206.998
300	63.095	78.832	78.444	0.116	−1253.366	−1181.075	205.644
400	77.404	98.998	81.097	7.160	−1253.504	−1156.945	151.082
500	89.203	117.606	86.563	15.522	−1253.193	−1132.832	118.346
600	132.842	138.348	93.368	26.988	−1250.428	−1108.930	96.541
700	129.788	158.562	101.280	40.097	−1246.511	−1085.668	81.014
723.000	129.704	162.757	103.170	43.081	--- CRYSTAL <--> LIQUID ---		
800	129.704	175.883	109.547	53.069	−1243.111	−1062.926	69.402
900	129.704	191.160	117.783	66.039	−1240.012	−1040.592	60.394
1000	129.704	204.826	125.816	79.009	−1237.159	−1018.589	53.206
1100	129.704	217.188	133.570	91.980	−1234.512	−996.861	47.337
1200	129.704	228.474	141.015	104.950	−1232.043	−975.367	42.457
1300	129.704	238.855	148.147	117.921	−1229.730	−954.072	38.335
1400	129.704	248.468	154.974	130.891	−1227.560	−932.950	34.809
1500	129.704	257.416	161.509	143.861	−1225.520	−911.979	31.758
1600	129.704	265.787	167.767	156.832	−1223.603	−891.139	29.093
1700	129.704	273.650	173.767	169.802	−1221.802	−870.416	26.745
1800	129.704	281.064	179.524	182.773	−1220.115	−849.796	24.660
1900	129.704	288.077	185.054	195.743	−1218.537	−829.266	22.798
2000	129.704	294.730	190.373	208.713	−1217.065	−808.817	21.124
2100	129.704	301.058	195.494	221.684	−1215.698	−788.438	19.611
2200	129.704	307.092	200.431	234.654	−1214.434	−768.122	18.238
2300	129.704	312.857	205.195	247.625	−1213.271	−747.862	16.984
2400	129.704	318.378	209.796	260.595	−1312.727	−725.513	15.790
2500	129.704	323.672	214.246	273.565	−1311.919	−701.062	14.648
2600	129.704	328.759	218.553	286.536	−1311.143	−676.643	13.594
2700	129.704	333.654	222.726	299.506	−1310.398	−652.253	12.619
2800	129.704	338.371	226.773	312.477	−1309.685	−627.890	11.713
2900	129.704	342.923	230.700	325.447	−1309.001	−603.554	10.871
3000	129.704	347.320	234.514	338.417	−1308.346	−579.238	10.085

PREVIOUS: December 1964 CURRENT: June 1971

0	to	723 K	crystal
above		723 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−9.293	−1265.776	−1265.776	INFINITE
100	20.740	10.983	96.353	−8.537	−1269.425	−1244.466	650.042
200	43.844	32.869	59.093	−5.245	−1271.165	−1218.726	318.299
298.15	62.588	53.953	53.953	0.	−1271.936	−1192.796	208.973
300	62.927	54.341	53.954	0.116	−1271.944	−1192.305	207.599
400	77.948	74.600	56.614	7.194	−1272.047	−1165.729	152.229
500	89.287	93.269	62.105	15.582	−1271.710	−1139.180	119.009
600	98.115	110.360	68.744	24.969	−1271.024	−1112.733	96.872
700	105.228	126.039	75.825	35.149	−1270.036	−1086.426	81.070
723.000	106.692	129.464	77.477	37.587	CRYSTAL <--> LIQUID TRANSITION		
723.000	129.704	162.757	77.477	61.657			
800	129.704	175.883	86.328	71.644	−1243.112	−1062.927	69.402
900	129.704	191.160	97.144	84.615	−1240.014	−1040.593	60.394
1000	129.704	204.826	107.241	97.585	−1237.160	−1018.590	53.206
1100	129.704	217.188	116.683	110.556	−1234.514	−996.863	47.337
1200	129.704	228.474	125.535	123.526	−1232.044	−975.368	42.457
1300	129.704	238.855	133.858	136.496	−1229.732	−954.074	38.335
1400	129.704	248.468	141.706	149.467	−1227.561	−932.951	34.809
1500	129.704	257.416	149.125	162.437	−1225.521	−911.980	31.758
1600	129.704	265.787	156.157	175.408	−1223.604	−891.141	29.093
1700	129.704	273.650	162.840	188.378	−1221.804	−870.417	26.745
1800	129.704	281.064	169.204	201.348	−1220.116	−849.797	24.660
1900	129.704	288.077	175.277	214.319	−1218.538	−829.267	22.798
2000	129.704	294.730	181.085	227.289	−1217.066	−808.818	21.124
2100	129.704	301.058	186.649	240.260	−1215.699	−788.439	19.611
2200	129.704	307.092	191.987	253.230	−1214.435	−768.123	18.238
2300	129.704	312.857	197.118	266.200	−1213.272	−747.863	16.985
2400	129.704	318.378	202.056	279.171	−1312.728	−725.514	15.790
2500	129.704	323.672	206.816	292.141	−1311.920	−701.063	14.648
2600	129.704	328.759	211.409	305.112	−1311.144	−676.644	13.594
2700	129.704	333.654	215.846	318.082	−1310.400	−652.254	12.619
2800	129.704	338.372	220.139	331.052	−1309.686	−627.891	11.713
2900	129.704	342.923	224.294	344.023	−1309.002	−603.555	10.871
3000	129.704	347.320	228.322	356.993	−1308.347	−579.240	10.085

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = [283.8 \pm 4.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -834.8 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -836.0 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies (all single degenerate)								
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ,cm^{-1}	ν, cm^{-1}
2073	730	521	[172]	[460]	2073	1240	457	480

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: O–B = 1.36 ± 0.02 Å; B–O = 1.20 ± 0.03 Å

Bond Angles: O–B–O = 180°; B–O–B = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = 3.153764 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The vapor pressure of B_2O_3(l) was measured by many investigators using various methods. 2nd and 3rd law analyses of these data[1-11] are given below. We have adopted the 3rd law enthalpy of vaporization, $\Delta_{vap}H°(298.15\ K) = 99.75$ kcal·mol^{-1}, to derive $\Delta_f H°(B_2O_3, g, 298.15\ K) = -199.8 \pm 1$ kcal·mol^{-1}, using $\Delta_f H°(B_2O_3, l, 298.15\ K) = -299.56$ kcal·mol^{-1}. The adopted $\Delta_{vap}H°(298.15\ K)$ is calculated from Hildenbrand's data[1] and this value also serves as an average of all derived enthalpies of vaporization except that of Cole.[11] The uncertainty is assigned to be at least ±1 kcal·mol^{-1} since the bending frequency was estimated to be either 172 or 260 cm^{-1} [12] which could lead to a difference ±1 kcal·mol^{-1} in the $\Delta_{vap}H°$ calculation through the Gibbs energy functions of B_2O_3(g).

Source	T/K	Method	Data Points	$\Delta_{vap}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	1436–1584	Torsion–effusion	24	100.97 ± 1.34	99.75 ± 0.35	−0.8 ± 0.7	−199.81
2	1946–2419	Transpiration and direct boiling point	16	92.55 ± 2.52	102.80 ± 1.8	4.6 ± 1.2	−196.76
3	1300	Mass spectrometric	—	100.5 ± 3	—	—	−199.06
4	1325–1547	Knudsen–effusion	9	93.08 ± 1.37	99.08 ± 0.74	4.2 ± 1.0	−200.48
5	1228l–1641	Mass spectrometric	16	92.32 ± 0.94	99.17 ± 1.40	4.6 ± 0.6	−200.39
6	1229–1515	Knudsen–effusion	12	82.65 ± 2.85	98.52 ± 1.70	11.1 ± 2.0	−201.04
7	1414–1621	Torsion–effusion	19	95.55 ± 0.91	101.50 ± 0.56	3.80 ± 0.62	−198.06
8	1501–1566	Effusion	6	101.67 ± 12.46	98.31 ± 0.79	−2.2 ± 8.1	−201.25
9	1567–1808	Carrier gas	6	66.17 ± 7.8	98.00 ± 5.06	18.8 ± 4.9	−201.56
10	1331–1642	Knudsen effusion	22[a]	89.64 ± 1.62	99.06 ± 1.44	6.4 ± 1.1	−200.50
11	1473–1673	Carrier gas	6	73.27 ± 2.28	87.36 ± 1.48	9.0 ± 1.4	−212.20

[a] Four points were rejected due to failure of a statistical test.

Heat Capacity and Entropy

The V shaped molecular structure for B_2O_3 was proposed by many investigators on the basis of infrared spectrometry[12, 13] and electron diffraction.[14] This structure has been reconfirmed by recent electric deflection[15] and electron diffraction[16] studies which definitely rule out any non polar structure such as the bipyramidal model as suggested by Hanst *et al.*[17] Thus the assignment of vibrational frequencies, based on the V shaped structure, should be valid. The adopted vibrational frequencies (including two estimated values) were obtained from Sommer *et al.*[12] in their infrared spectrometric studies. Their values have been adjusted to the average isotopic species. Other spectrometric data[13, 18] are in reasonable agreement with those adopted in the tabulation.

Akishin and Spiridonov[14] determined the bond distances and bond angle (B–O–B = 95°) by electron diffraction. We have adopted their bond distances in the tabulation, but tentatively select an apex angle B–O–B = 120° based on force constant calculations of Weltner and Warn[13] and Sommer *et al.*[12] The principal moments of inertia are $I_A = 2.9763 \times 10^{-39}$, $I_B = 31.0977 \times 10^{-39}$ and $I_C = 34.0740 \times 10^{-39}$ g·cm^2.

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Continued on page 318

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.337	−834.847	−834.847	INFINITE
100	40.042	226.986	334.961	−10.797	−835.713	−832.354	434.777
200	55.330	259.361	289.548	−6.037	−835.985	−828.844	216.472
250	61.832	272.432	284.842	−3.102	−835.979	−827.059	172.805
298.15	66.855	283.768	283.768	0.	−835.963	−825.343	144.597
300	67.028	284.182	283.769	0.124	−835.963	−825.277	143.694
350	71.228	294.841	284.601	3.584	−835.972	−823.496	122.900
400	74.727	304.587	286.499	7.235	−836.033	−821.710	107.304
450	77.728	313.566	289.014	11.048	−836.152	−819.913	95.173
500	80.362	321.894	291.891	15.002	−836.317	−818.100	85.466
600	84.817	336.954	298.173	23.269	−836.752	−814.418	70.901
700	88.439	350.310	304.685	31.938	−837.275	−810.655	60.492
800	91.403	362.320	311.151	40.935	−837.849	−806.814	52.680
900	93.830	373.230	317.452	50.200	−838.455	−802.898	46.599
1000	95.822	383.223	323.537	59.686	−839.087	−798.914	41.731
1100	97.462	392.435	329.387	69.353	−839.743	−794.864	37.745
1200	98.819	400.975	335.001	79.169	−840.428	−790.755	34.421
1300	99.950	408.931	340.386	89.109	−841.146	−786.586	31.605
1400	100.897	416.374	345.550	99.153	−841.902	−782.361	29.190
1500	101.696	423.363	350.507	109.284	−842.701	−778.081	27.095
1600	102.375	429.949	355.269	119.488	−843.550	−773.746	25.260
1700	102.955	436.173	359.846	129.755	−844.453	−769.355	23.639
1800	103.454	442.072	364.252	140.076	−845.415	−764.911	22.197
1900	103.886	447.677	368.496	150.444	−846.440	−760.411	20.905
2000	104.262	453.016	372.590	160.852	−847.531	−755.855	19.741
2100	104.591	458.111	376.542	171.295	−848.691	−751.243	18.686
2200	104.880	462.983	380.361	181.769	−849.924	−746.573	17.726
2300	105.136	467.651	384.056	192.270	−851.230	−741.847	16.848
2400	105.363	472.131	387.633	202.795	−953.131	−734.924	15.995
2500	105.565	476.436	391.099	213.342	−954.747	−725.799	15.165
2600	105.746	480.580	394.462	223.907	−956.376	−716.609	14.397
2700	105.908	484.574	397.726	234.490	−958.019	−707.356	13.685
2800	106.054	488.428	400.897	245.088	−959.677	−698.041	13.022
2900	106.186	492.152	403.980	255.700	−961.351	−688.669	12.404
3000	106.306	495.754	406.979	266.325	−963.042	−679.237	11.827
3100	106.415	499.242	409.899	276.961	−964.749	−669.748	11.285
3200	106.515	502.622	412.744	287.608	−966.474	−660.205	10.777
3300	106.606	505.901	415.518	298.264	−968.214	−650.608	10.298
3400	106.689	509.085	418.223	308.929	−969.971	−640.956	9.847
3500	106.765	512.178	420.864	319.602	−971.744	−631.254	9.421
3600	106.836	515.187	423.442	330.282	−973.532	−621.500	9.018
3700	106.901	518.115	425.961	340.969	−975.337	−611.697	8.636
3800	106.961	520.967	428.424	351.662	−977.156	−601.843	8.273
3900	107.017	523.746	430.833	362.361	−978.991	−591.943	7.928
4000	107.069	526.456	433.190	373.065	−980.840	−581.996	7.600
4100	107.117	529.100	435.497	383.774	−982.703	−572.001	7.287
4200	107.161	531.682	437.756	394.488	−1944.280	−547.913	6.814
4300	107.203	534.204	439.970	405.206	−1943.998	−514.669	6.252
4400	107.242	536.669	442.140	415.929	−1943.734	−481.433	5.715
4500	107.279	539.080	444.267	426.655	−1943.488	−448.202	5.203
4600	107.313	541.438	446.354	437.384	−1943.261	−414.977	4.712
4700	107.345	543.746	448.402	448.117	−1943.055	−381.755	4.243
4800	107.375	546.006	450.412	458.853	−1942.871	−348.538	3.793
4900	107.403	548.221	452.386	469.592	−1942.709	−315.323	3.361
5000	107.430	550.391	454.324	480.334	−1942.570	−282.113	2.947
5100	107.455	552.518	456.229	491.078	−1942.457	−248.904	2.549
5200	107.479	554.605	458.101	501.825	−1942.370	−215.700	2.167
5300	107.502	556.653	459.941	512.574	−1942.312	−182.494	1.799
5400	107.523	558.662	461.750	523.325	−1942.285	−149.291	1.444
5500	107.543	560.636	463.530	534.078	−1942.289	−116.088	1.103
5600	107.562	562.574	465.282	544.834	−1942.328	−82.883	0.773
5700	107.580	564.477	467.005	555.591	−1942.403	−49.678	0.455
5800	107.597	566.349	468.702	566.350	−1942.517	−16.470	0.148
5900	107.613	568.188	470.373	577.110	−1942.672	16.736	−0.148
6000	107.629	569.997	472.018	587.872	−1942.870	49.949	−0.435

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = [130.5 \pm 12]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -1556 \pm 6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Evans[1] analyzed the enthalpies of formation of the lead borate system. Shartsis and Newman measured enthalpies of solution of the lead borate glasses in 2 N HNO_3. In their phase studies, Mazzetti and De Carli[3] established that the compounds formed were $PbO \cdot B_2O_3$, $PbO \cdot 2B_2O_3$ and $2PbO \cdot 5B_2O_3$. From the Shartsis and Newman[2] paper, Evans[1] obtained the following:

$$PbO(cr) + B_2O_3(cr) \rightarrow PbOB_2O_3(gls) \qquad \Delta_r H° = -16.2\ kcal \cdot mol^{-1}$$

and estimated a $\Delta_f H°(298.15\ K)$ of 7.0 $kcal \cdot mol^{-1}$ for the conversion to the $PbOB_2O_3$(cr). With auxiliary JANAF values, the $\Delta_f H°(298.15\ K)$ was calculated to be −372 $kcal \cdot mol^{-1}$. The results of Lepinskikh and Esin[4] studying the lead borate system at 1000 K with cells of the type $Pb(l)/PbO,B_2O_3/Pt/O_2(g)$ were in fair agreement with the results of Shartsis and Newman.[2]

Heat Capacity and Entropy

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities for $B_2O_3$and PbO.

The entropy at 298.15 was obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by Kelley and King.[5] These indicate for the reaction $MO + B_2O_3 \rightarrow MoB_2O_3$ that the simple addition of entropies will give values at least 2.7 $cal \cdot K^{-1} \cdot mol^{-1}$ too low for the reaction. The reason for this is probably structural, the $B_2O_4^{--}$ ion is a flexible chain. Therefore, $S°(PbB_2O_4$, cr, 298.15 K) was obtained from the summation of $S°(298.15\ K)$ for constituent oxides and the addition of 2.7 $cal \cdot K^{-1} \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	107.110	130.541	130.541	0.	−1556.448	−1450.245	254.077
300	107.529	131.205	130.543	0.199	−1556.450	−1449.586	252.395
400	129.704	165.276	135.038	12.095	−1555.950	−1414.009	184.651
500	147.695	196.213	144.227	25.993	−1554.445	−1378.679	144.030
600	162.339	224.474	155.281	41.516	−1552.093	−1343.734	116.982
700	174.473	250.436	167.046	58.374	−1553.877	−1308.443	97.637
800	184.514	274.413	178.987	76.340	−1550.166	−1273.627	83.159
900	192.464	296.613	190.839	95.196	−1545.870	−1239.312	71.928
1000	199.577	317.281	202.462	114.819	−1541.050	−1205.503	62.969
1100	204.179	336.522	213.785	135.011	−1535.862	−1172.197	55.663
1200	208.363	354.479	224.770	155.652	−1530.390	−1139.376	49.596
1300	210.874	371.262	235.400	176.620	−1524.741	−1107.020	44.481
1400	212.547	386.945	245.671	197.784	−1519.046	−1075.101	40.113
1500	215.058	401.700	255.586	219.172	−1513.274	−1043.592	36.341
1600	216.731	415.631	265.157	240.758	−1507.448	−1012.470	33.054
1700	218.823	428.833	274.400	262.535	−1501.572	−981.713	30.164
1800	220.915	441.402	283.332	284.526	−1495.624	−951.305	27.606
1900	222.589	453.391	291.969	306.701	−1489.630	−921.228	25.326
2000	224.262	464.851	300.329	329.044	−1483.608	−891.468	23.283

PREVIOUS: December 1962 CURRENT: March 1965

$S°(298.15\ K) = 28.48 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 3193\ K$

$\Delta_f H°(0\ K) = -277.8 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -279.5 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [100.4]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Kibler *et al.*[1] studied the vapor pressure of the reaction $TiB_2(cr) + 1/2\ C(cr) = Ti(g) + 1/2\ B_4C(cr)$ by comparing the absorption intensity of the 3371.45 Å Ti resonance line of the above reaction at temperature T_1 to Ti(g) over pure titanium metal at temperature T_2. Using JANAF auxiliary data, $\Delta G°(2475\ K) = 81.612\ kcal \cdot mol^{-1}$ for the above reaction and $\Delta_f H°(TiB_2, cr, 298.15\ K) = -66.9\ kcal \cdot mol^{-1}$ were calculated.

Williams[2] found 2150 ± 25 K to be the temperature at which $TiB_2(cr)$ was formed from a mixture of TiN(cr) and BN(cr). If $\Delta G°(2150\ K) = 0$ is assumed for the reaction $TiN(cr) + 2\ BN(cr) = TiB_2(cr) + 3/2\ N_2(g)$, then $\Delta_f H°(TiB_2, cr, 298.15\ K) = -70.7\ kcal \cdot mol^{-1}$. If, however, $N_2(g)$ is 1/2 atm, then $\Delta G°(2150\ K) = 4.4\ kcal \cdot mol^{-1}$ and $\Delta_f H°(TiB_2, cr, 298.15\ K) = -66.3\ kcal \cdot mol^{-1}$. He has also shown by stability comparisons that ΔG and $\Delta H > 0$ for the reaction $TiB_2 + 3/2\ C = TiC + 1/2\ B_4C$. Thus $\Delta_f H°(TiB_2, 298.15\ K) < -51\ kcal \cdot mol^{-1}$.

Schissel and Trulson[3] used a mass spectrometer with Knudsen cells to study the vaporization of the titanium–boron system. Only the set of measurements without excess boron or titanium was used. The value $\Delta G°(2261\ K) = 194.9\ kcal \cdot mol^{-1}$ for the reaction $TiB_2(cr) = Ti(g) + 2\ B(g)$ was obtained. This corresponds to $\Delta_f H°(TiB_2, cr, 298.15\ K) = -62.9\ kcal \cdot mol^{-1}$ using JANAF auxiliary data.

Epel'baum and M. I. Starostina[4] report $\Delta_f H°(TiB_2, cr, 298.15\ K) = -66.85 \pm 2.7\ kcal \cdot mol^{-1}$ from combustion calorimetry.

Lowell and Williams[5] used high temperature calorimetry to obtain the enthalpy of formation of $TiB_2(cr)$. From their data and JANAF auxiliary data, $\Delta_f H°(TiB_2, cr, 298.15\ K) = -48.2 \pm 5\ kcal \cdot mol^{-1}$ was calculated. We question the authenticity of the experiment and believe their value is an upper limit.

$\Delta_f H°(TiB_2, cr, 298.15\ K) = -66.8 \pm 4\ kcal \cdot mol^{-1}$ was chosen as representative of the first four investigations.

Heat Capacity and Entropy

The heat capacity of $TiB_2(cr)$ has been determined by the following investigators.

Source	Method	T/K
[6]	Adiabatic Calorimetry	5–350
[7]	Drop calorimeter	373–977
[8]	Drop type ice calorimeter	586–2689
[9]	Copper–block drop calorimeter	420–1180
[10]	Arc–imaging furnace	1300–2150
[11]	Pulse–method	1733–2417

The low temperature data of Westrum[1] and the medium range data of Walker *et al.*[7] were used to obtain the C_p's of this tabulation. Their data were fitted to a Shomate plot and extrapolated to 4000 K.

$S°(298.15\ K) = 6.808\ cal \cdot K^{-1} \cdot mol^{-1}$ was determined by Westrum.[1]

Fusion Data

The melting point has been reported as 3063 K, 3193 K, and 3203 K by Glaser,[12] Post *et al.*,[13] and Samsonov and Petrash,[14] respectively. The enthalpy of fusion is derived from an estimated $\Delta_{fus} S = 2.5\ cal \cdot K^{-1}\ g\ atom^{-1}$ at 3193 K. It should be pointed out that an error of 0.5 $cal \cdot K^{-1} \cdot mol^{-1}\ g\ atom^{-1}$ in the estimation of $\Delta_{fus} S°$ is 5 $kcal \cdot mol^{-1}$ in $\Delta_{fus} H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−5.577	−277.811	−277.811	INFINITE
100	7.523	2.518	56.366	−5.385	−278.227	−277.591	144.999
200	28.125	14.046	32.058	−3.602	−279.027	−276.623	72.247
298.15	44.279	28.485	28.485	0.	−279.491	−275.334	48.237
300	44.522	28.759	28.486	0.082	−279.498	−275.308	47.935
400	54.890	43.136	30.375	5.104	−279.814	−273.864	35.763
500	61.668	56.156	34.253	10.952	−280.169	−272.336	28.451
600	66.166	67.815	38.893	17.353	−280.556	−270.734	23.569
700	69.496	78.274	43.785	24.142	−280.964	−269.064	20.078
800	72.069	87.723	48.696	31.222	−281.376	−267.336	17.455
900	74.534	96.355	53.519	38.553	−281.799	−265.556	15.412
1000	76.889	104.331	58.206	46.125	−282.273	−263.727	13.776
1100	79.136	111.765	62.741	53.927	−282.845	−261.846	12.434
1200	81.283	118.744	67.120	61.949	−287.496	−259.788	11.308
1300	83.320	125.331	71.347	70.180	−287.529	−257.477	10.346
1400	85.249	131.577	75.428	78.609	−287.537	−255.165	9.520
1500	87.069	137.521	79.371	87.226	−287.539	−252.853	8.805
1600	88.780	143.196	83.184	96.019	−287.553	−250.540	8.179
1700	90.383	148.627	86.875	104.978	−287.599	−248.225	7.627
1800	91.876	153.836	90.451	114.092	−287.698	−245.907	7.136
1900	93.261	158.841	93.920	123.350	−287.872	−243.581	6.696
2000	94.537	163.657	97.287	132.741	−302.828	−240.789	6.289
2100	95.705	168.298	100.558	142.254	−303.964	−237.659	5.911
2200	96.763	172.775	103.740	151.878	−305.057	−234.476	5.567
2300	97.713	177.098	106.836	161.603	−306.118	−231.244	5.252
2400	98.554	181.275	109.851	171.416	−407.675	−225.829	4.915
2500	99.391	185.315	112.789	181.314	−408.851	−218.227	4.560
2600	100.228	189.229	115.654	191.295	−409.944	−210.581	4.231
2700	101.065	193.028	118.450	201.359	−410.953	−202.893	3.925
2800	101.901	196.718	121.180	211.507	−411.879	−195.170	3.641
2900	102.738	200.309	123.847	221.739	−412.721	−187.415	3.376
3000	103.575	203.806	126.454	232.055	−413.479	−179.633	3.128
3100	104.412	207.215	129.004	242.454	−414.153	−171.827	2.895
3193.000	105.190	210.313	131.328	252.201	--- CRYSTAL <--> LIQUID ---		
3200	105.249	210.544	131.501	252.937	−414.744	−164.000	2.677
3300	106.085	213.795	133.945	263.504	−415.251	−156.157	2.472
3400	106.922	216.975	136.341	274.154	−415.674	−148.299	2.278
3500	107.759	220.086	138.689	284.889	−416.014	−140.429	2.096
3600	108.596	223.133	140.993	295.706	−416.270	−132.552	1.923
3700	109.433	226.120	143.253	306.608	−825.541	−116.880	1.650
3800	110.269	229.050	145.473	317.593	−824.395	−97.742	1.344
3900	111.106	231.925	147.653	328.662	−823.221	−78.635	1.053
4000	111.943	234.748	149.795	339.814	−822.017	−59.558	0.778

PREVIOUS: December 1962 CURRENT: June 1965

$S°(298.15\ K)$ = [56.365] $J·K^{-1}·mol^{-1}$
T_{fus} = 3193 K
T_{dcm} = [4250] K

$\Delta_f H°(298.15\ K)$ = [−188.029] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [100.4] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TiB_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(TiB_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(3193\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2100 K. Heat capacities at and below 2100 K are assumed to be equal to those of TiB_2(cr). Above 2100 K the heat capacities are estimated to be constant.

$S°(TiB_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

T_{dcm} is estimated as the temperature for which $\Delta_r G° = 0$ for the reaction $TiB_2(l) \rightarrow Ti(g) + 2\ B(g)$.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	44.279	56.365	56.365	0.	−188.029	−192.185	33.670
300	44.522	56.640	56.366	0.082	−188.036	−192.211	33.467
400	54.890	71.016	58.256	5.104	−188.352	−193.554	25.276
500	61.668	84.036	62.133	10.952	−188.707	−194.814	20.352
600	66.166	95.695	66.773	17.353	−189.094	−196.000	17.063
700	69.496	106.154	71.665	24.142	−189.502	−197.119	14.709
800	72.069	115.603	76.576	31.222	−189.914	−198.179	12.940
900	74.534	124.235	81.399	38.553	−190.337	−199.187	11.560
1000	76.889	132.211	86.086	46.125	−190.811	−200.145	10.455
1100	79.136	139.646	90.621	53.927	−191.383	−201.052	9.547
1200	81.283	146.624	95.000	61.949	−196.034	−201.782	8.783
1300	83.320	153.211	99.227	70.180	−196.067	−202.260	8.127
1400	85.249	159.457	103.308	78.609	−196.075	−202.736	7.564
1500	87.069	165.402	107.251	87.226	−196.077	−203.211	7.076
1600	88.780	171.076	111.064	96.019	−196.091	−203.687	6.650
1700	90.383	176.507	114.755	104.978	−196.137	−204.160	6.273
1800	91.876	181.716	118.331	114.092	−196.236	−204.629	5.938
1900	93.261	186.721	121.800	123.350	−196.409	−205.091	5.638
2000	94.537	191.538	125.167	132.741	−211.366	−205.088	5.356
2100	95.705	196.179	128.439	142.254	−212.502	−204.746	5.093
2100.000	95.705	196.179	128.439	142.254	GLASS <--> LIQUID		
2100.000	108.784	196.179	128.439	142.254	TRANSITION		
2200	108.784	201.240	131.634	153.132	−212.341	−204.381	4.853
2300	108.784	206.075	134.766	164.011	−212.248	−204.022	4.633
2400	108.784	210.705	137.835	174.889	−312.740	−201.527	4.386
2500	108.784	215.146	140.839	185.768	−312.935	−196.889	4.114
2600	108.784	219.412	143.779	196.646	−313.131	−192.243	3.862
2700	108.784	223.518	146.657	207.524	−313.326	−187.590	3.629
2800	108.784	227.474	149.473	218.403	−313.521	−182.930	3.413
2900	108.784	231.292	152.229	229.281	−313.717	−178.262	3.211
3000	108.784	234.979	154.926	240.160	−313.912	−173.588	3.022
3100	108.784	238.546	157.567	251.038	−314.107	−168.907	2.846
3193.000	108.784	241.762	159.972	261.155	--- CRYSTAL <--> LIQUID ---		
3200	108.784	242.000	160.151	261.916	−314.303	−164.220	2.681
3300	108.784	245.348	162.683	272.795	−314.498	−159.527	2.525
3400	108.784	248.595	165.162	283.673	−314.693	−154.828	2.379
3500	108.784	251.749	167.591	294.552	−314.889	−150.124	2.240
3600	108.784	254.813	169.971	305.430	−315.084	−145.413	2.110
3700	108.784	257.794	172.305	316.308	−724.378	−132.909	1.876
3800	108.784	260.695	174.593	327.187	−723.339	−116.937	1.607
3900	108.784	263.521	176.837	338.065	−722.355	−100.992	1.353
4000	108.784	266.275	179.039	348.944	−721.426	−85.072	1.111
4100	108.784	268.961	181.199	359.822	−720.549	−69.174	0.881
4200	108.784	271.582	183.320	370.700	−1679.422	−39.249	0.488
4300	108.784	274.142	185.403	381.579	−1676.470	−0.232	0.003
4400	108.784	276.643	187.448	392.457	−1673.570	38.717	−0.460
4500	108.784	279.088	189.457	403.336	−1670.720	77.600	−0.901
4600	108.784	281.479	191.432	414.214	−1667.918	116.421	−1.322
4700	108.784	283.818	193.373	425.092	−1665.163	155.181	−1.725
4800	108.784	286.108	195.281	435.971	−1662.453	193.883	−2.110
4900	108.784	288.351	197.158	446.849	−1659.788	232.529	−2.479
5000	108.784	290.549	199.004	457.728	−1657.165	271.121	−2.832
5100	108.784	292.703	200.820	468.606	−1654.583	309.661	−3.172
5200	108.784	294.816	202.607	479.484	−1652.041	348.151	−3.497
5300	108.784	296.888	204.367	490.363	−1649.538	386.592	−3.810
5400	108.784	298.921	206.099	501.241	−1647.072	424.986	−4.111
5500	108.784	300.917	207.805	512.120	−1644.642	463.335	−4.400
5600	108.784	302.877	209.485	522.998	−1642.247	501.640	−4.679
5700	108.784	304.803	211.140	533.876	−1639.886	539.903	−4.948
5800	108.784	306.695	212.772	544.755	−1637.558	578.125	−5.207
5900	108.784	308.554	214.379	555.633	−1635.262	616.306	−5.456
6000	108.784	310.383	215.964	566.512	−1632.997	654.449	−5.697

PREVIOUS: December 1962 CURRENT: June 1965

0	to 3193 K	crystal
above	3193 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−5.577	−277.811	−277.811	INFINITE
100	7.523	2.518	56.366	−5.385	−278.227	−277.591	144.999
200	28.125	14.046	32.058	−3.602	−279.027	−276.623	72.247
298.15	44.279	28.485	28.485	0.	−279.491	−275.334	48.237
300	44.522	28.759	28.486	0.082	−279.498	−275.308	47.935
400	54.890	43.136	30.375	5.104	−279.814	−273.864	35.763
500	61.668	56.156	34.253	10.952	−280.169	−272.336	28.451
600	66.166	67.815	38.893	17.353	−280.556	−270.734	23.569
700	69.496	78.274	43.785	24.142	−280.964	−269.064	20.078
800	72.069	87.723	48.696	31.222	−281.376	−267.336	17.455
900	74.534	96.355	53.519	38.553	−281.799	−265.556	15.412
1000	76.889	104.331	58.206	46.125	−282.273	−263.727	13.776
1100	79.136	111.765	62.741	53.927	−282.845	−261.846	12.434
1200	81.283	118.744	67.120	61.949	−287.496	−259.788	11.308
1300	83.320	125.331	71.347	70.180	−287.529	−257.477	10.346
1400	85.249	131.577	75.428	78.609	−287.537	−255.165	9.520
1500	87.069	137.521	79.371	87.226	−287.539	−252.853	8.805
1600	88.780	143.196	83.184	96.019	−287.553	−250.540	8.179
1700	90.383	148.627	86.875	104.978	−287.599	−248.225	7.627
1800	91.876	153.836	90.451	114.092	−287.698	−245.907	7.136
1900	93.261	158.841	93.920	123.350	−287.872	−243.581	6.696
2000	94.537	163.657	97.287	132.741	−302.828	−240.789	6.289
2100	95.705	168.298	100.558	142.254	−303.964	−237.659	5.911
2200	96.763	172.775	103.740	151.878	−305.057	−234.476	5.567
2300	97.713	177.098	106.836	161.603	−306.118	−231.244	5.252
2400	98.554	181.275	109.851	171.416	−407.675	−225.829	4.915
2500	99.391	185.315	112.789	181.314	−408.851	−218.227	4.560
2600	100.228	189.229	115.654	191.295	−409.944	−210.581	4.231
2700	101.065	193.028	118.450	201.359	−410.953	−202.893	3.925
2800	101.901	196.718	121.180	211.507	−411.879	−195.170	3.641
2900	102.738	200.309	123.847	221.739	−412.721	−187.415	3.376
3000	103.575	203.806	126.454	232.055	−413.479	−179.633	3.128
3100	104.412	207.215	129.004	242.454	−414.153	−171.827	2.895
3193.000	105.190	210.313	131.328	252.201	CRYSTAL <---> LIQUID		
3193.000	108.784	241.762	131.328	352.617	TRANSITION		
3200	108.784	242.000	131.569	353.378	−314.303	−164.220	2.681
3300	108.784	245.348	134.967	364.257	−314.498	−159.527	2.525
3400	108.784	248.595	138.261	375.135	−314.693	−154.828	2.379
3500	108.784	251.749	141.459	386.014	−314.889	−150.124	2.240
3600	108.784	254.813	144.565	396.892	−315.084	−145.413	2.110
3700	108.784	257.794	147.586	407.770	−724.378	−132.909	1.876
3800	108.784	260.695	150.524	418.649	−723.339	−116.937	1.607
3900	108.784	263.521	153.385	429.527	−722.355	−100.993	1.353
4000	108.784	266.275	156.173	440.406	−721.426	−85.072	1.111
4100	108.784	268.961	158.892	451.284	−720.549	−69.174	0.881
4200	108.784	271.582	161.544	462.162	−1679.422	−39.249	0.488
4300	108.784	274.142	164.133	473.041	−1676.470	−0.232	0.003
4400	108.784	276.643	166.661	483.919	−1673.570	38.717	−0.460
4500	108.784	279.088	169.133	494.798	−1670.720	77.600	−0.901
4600	108.784	281.479	171.549	505.676	−1667.918	116.421	−1.322
4700	108.784	283.818	173.913	516.554	−1665.163	155.181	−1.725
4800	108.784	286.108	176.227	527.433	−1662.453	193.883	−2.110
4900	108.784	288.351	178.492	538.311	−1659.788	232.529	−2.479
5000	108.784	290.549	180.711	549.190	−1657.165	271.121	−2.832
5100	108.784	292.703	182.886	560.068	−1654.583	309.661	−3.172
5200	108.784	294.816	185.018	570.946	−1652.041	348.150	−3.497
5300	108.784	296.888	187.110	581.825	−1649.538	386.592	−3.810
5400	108.784	298.921	189.161	592.703	−1647.072	424.986	−4.111
5500	108.784	300.917	191.175	603.582	−1644.642	463.335	−4.400
5600	108.784	302.877	193.152	614.460	−1642.247	501.640	−4.679
5700	108.784	304.803	195.094	625.338	−1639.886	539.903	−4.948
5800	108.784	306.695	197.002	636.217	−1637.558	578.125	−5.207
5900	108.784	308.554	198.877	647.095	−1635.262	616.306	−5.456
6000	108.784	310.383	200.721	657.974	−1632.997	654.449	−5.697

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 35.94 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 3323\ K$

$\Delta_f H°(0\ K) = -321.3 \pm 6.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -322.6 \pm 6.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [104.6]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Johnson[1] reported $\Delta_f H°(ZrB_{1.999 \pm 0.006}, cr, 298.15\ K) = -78.7 \pm 1.5\ kcal \cdot mol^{-1}$. Their value was obtained by fluorine bomb calorimetry and was based on their recently redetermined value of $\Delta_f H°(BF_3, g, 298.15\ K) = -271.80 \pm 0.20\ kcal \cdot mol^{-1}$.

Kibler *et al.*[2] studied the vaporization of $ZrB_{1.931}$ by the Knudsen effusion method. Over the range 2260 to 2500 K, $\log K_p = 22.038 - 0.164 \times 10^4/T$ for the reaction $ZrB_{1.931}(cr) = Zr(g) + 1.931\ B(g)$. JANAF auxiliary data were used to calcuate $\Delta_r H°(298.15\ K) = 478.5 \pm 1.5\ kcal \cdot mol^{-1}$ by the 3rd law method and $\Delta_f H°(ZrB_{1.932}, cr, 298.15\ K) = -76.7 \pm 3.2\ kcal \cdot mol^{-1}$.

Trulson and Goldstein[3] investigated the decomposition vapor pressure of the reaction $ZrB_2(cr) = Zr(g) + 2\ B(g)$ and reported $\Delta_f H°(ZrB_2, cr, 298.15\ K) = -72.1 \pm 5.3\ kcal \cdot mol^{-1}$. They also reported $\Delta_r H°(298.15\ K) = 289.7\ kcal \cdot mol^{-1}$ for the reaction $ZrB_2(cr) + C(cr) = ZrC(cr) + 2\ B(g)$. Using the JANAF $\Delta_f H°(ZrC, cr, 298.15\ K) = -47.0 \pm 3\ kcal \cdot mol^{-1}$, $\Delta_f H°(ZrB_2, cr, 298.15\ K) = -76.1 \pm 3\ kcal \cdot mol^{-1}$ was calculated. JANAF values for $\Delta_{vap} H°(B, g, 298.15\ K)$ and Zr(g) were not used since their independent determinations serve to cancel instrumental constants.

From oxygen bomb calorimetry, Huber *et al.*[4] reported $\Delta_f H°(ZrB_2, cr, 298.15\ K) = -77.2 \pm 1.2\ kcal \cdot mol^{-1}$.

$\Delta_f H°(ZrB_2, cr, 298.15\ K) = -77.1 \pm 1.6\ kcal \cdot mol^{-1}$ was chosen as a value representative of the above.

Heat Capacity and Entropy

The heat capacity of ZrB_2(cr) has been determined by the following investigators.

	Source	Method	T/K
5		Adiabatic calorimetry	5–350
6		Copper–block drop calorimeter	410–1125
7		Copper–block drop calorimeter	430–1170
8		Arc–imaging furnace	1300–2150
9		Pulse–method	1740–2520
10		Drop type ice calorimeter	500–2500

Westrum and Feick's[5] values were adopted to 350 K. The disparities in heat capacities above room temperatures seem too great to be errors in measurement and are probably due to sample differences. Since the samples used by Westrum and Feick[5] and by Valentine *et al.*[6] were from the same batch, Valentine's data were used above 350 K. The two sets of data were fitted to a Shomate plot which was extrapolated to 4000 K. However, in consideration of the results of Mezsaki,[7] Prophet[8] and Neel *et al.*,[10] the C_p extrapolation ran somewhat higher than a direct extrapolation of Valentine's data would yield.

$S°(ZrB_2, 298.15\ K) = 8.59\ cal \cdot K^{-1} \cdot mol^{-1}$ was determined by Westrum.[5]

Fusion Data

The melting point has been reported as 3313, 3323 and 3265 K by Glaser and Post,[11] Post *et al.*[12] and Greenwood,[13] respectively. The enthalpy of fusion is derived from an estimated $\Delta_{fus} S° = 2.5\ cal \cdot K^{-1}$ g-atom^{-1} at 3323 K. It should be pointed out that an error of 0.5 $cal \cdot K^{-1}$ g-atom^{-1} in the estimation of $\Delta_{fus} S°$ is 5 $kcal \cdot mol^{-1}$ in $\Delta_{fus} H°$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.653	−321.314	−321.314	INFINITE
100	12.008	4.926	67.811	−6.289	−321.884	−320.909	167.626
200	32.803	19.732	39.899	−4.033	−322.488	−319.657	83.486
298.15	48.242	35.941	35.941	0.	−322.586	−318.234	55.753
300	48.488	36.240	35.941	0.089	−322.586	−318.207	55.405
400	57.505	51.582	37.972	5.444	−322.516	−316.760	41.365
500	62.634	65.010	42.068	11.471	−322.575	−315.317	32.941
600	65.810	76.725	46.889	17.902	−322.798	−313.847	27.323
700	68.028	87.043	51.903	24.598	−323.179	−312.327	23.306
800	69.710	96.240	56.881	31.487	−323.705	−310.743	20.289
900	71.090	104.534	61.723	38.530	−324.373	−309.084	17.939
1000	72.153	112.079	66.387	45.693	−325.191	−307.343	16.054
1100	73.174	119.004	70.860	52.959	−326.156	−305.512	14.508
1200	74.195	125.415	75.142	60.327	−330.967	−303.366	13.205
1300	75.216	131.394	79.242	67.798	−331.648	−301.039	12.096
1400	76.237	137.005	83.169	75.370	−332.366	−298.658	11.143
1500	77.258	142.300	86.937	83.045	−333.123	−296.224	10.315
1600	78.278	147.319	90.555	90.822	−333.926	−293.738	9.590
1700	79.299	152.095	94.036	98.701	−334.780	−291.200	8.947
1800	80.320	156.656	97.389	106.682	−335.694	−288.611	8.375
1900	81.341	161.026	100.624	114.765	−336.675	−285.969	7.862
2000	82.362	165.225	103.750	122.950	−337.731	−283.273	7.398
2100	83.383	169.268	106.774	131.237	−338.872	−280.522	6.978
2200	84.404	173.170	109.704	139.627	−361.430	−276.970	6.576
2300	85.425	176.945	112.546	148.118	−363.185	−273.091	6.202
2400	86.446	180.602	115.306	156.712	−465.422	−266.999	5.811
2500	87.467	184.152	117.989	165.407	−467.260	−258.694	5.405
2600	88.487	187.602	120.600	174.205	−468.997	−250.316	5.029
2700	89.508	190.961	123.144	183.105	−470.631	−241.874	4.679
2800	90.529	194.234	125.625	192.107	−472.163	−233.373	4.354
2900	91.550	197.429	128.046	201.211	−473.593	−224.820	4.049
3000	92.571	200.550	130.411	210.417	−474.921	−216.218	3.765
3100	93.592	203.602	132.723	219.725	−476.147	−207.575	3.498
3200	94.613	206.589	134.985	229.135	−477.271	−198.893	3.247
3300	95.634	209.516	137.199	238.647	−478.292	−190.177	3.010
3323.000	95.868	210.181	137.702	240.850	--- CRYSTAL <--> LIQUID ---		
3400	96.655	212.387	139.368	248.262	−479.212	−181.433	2.787
3500	97.675	215.203	141.495	257.978	−480.029	−172.662	2.577
3600	98.696	217.969	143.581	267.797	−480.745	−163.870	2.378
3700	99.717	220.687	145.628	277.717	−481.358	−155.059	2.189
3800	100.738	223.360	147.639	287.740	−481.869	−146.233	2.010
3900	101.759	225.990	149.614	297.865	−482.278	−137.395	1.840
4000	102.780	228.579	151.556	308.092	−482.585	−128.548	1.679

PREVIOUS: March 1963 CURRENT: June 1965

$S°(298.15\ K) = [64.742]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3323\ K$
$T_{dcm} = [4466]\ K$

$\Delta_f H°(298.15\ K) = [-224.832]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [104.6]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrB_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(ZrB_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(3323\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200 K. The heat capacities at and below 2200 K are assumed to be equal to those of ZrB_2(cr). Above 2200 K the heat capacities were estimated to be constant.

$S°(ZrB_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

T_{dcm} is estimated as the temperature for which $\Delta_r G° = 0$ for the reaction $ZrB_2(l) = Zr(g) + 2\ B(g)$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	48.242	64.742	64.742	0.	−224.832	−229.067	40.132
300	48.488	65.041	64.743	0.089	−224.831	−229.094	39.889
400	57.505	80.383	66.774	5.444	−224.761	−230.526	30.104
500	62.634	93.812	70.869	11.471	−224.821	−231.963	24.233
600	65.810	105.527	75.691	17.902	−225.044	−233.374	20.317
700	68.028	115.845	80.705	24.598	−225.424	−234.734	17.516
800	69.710	125.042	85.683	31.487	−225.950	−236.030	15.411
900	71.090	133.335	90.524	38.530	−226.619	−237.251	13.770
1000	72.153	140.881	95.188	45.693	−227.437	−238.390	12.452
1100	73.174	147.806	99.661	52.959	−228.401	−239.440	11.370
1200	74.195	154.216	103.944	60.327	−233.213	−240.174	10.454
1300	75.216	160.196	108.043	67.798	−233.894	−240.727	9.673
1400	76.237	165.807	111.971	75.370	−234.611	−241.226	9.000
1500	77.258	171.102	115.738	83.045	−235.369	−241.672	8.416
1600	78.278	176.120	119.357	90.822	−236.171	−242.066	7.903
1700	79.299	180.896	122.837	98.701	−237.026	−242.409	7.448
1800	80.320	185.458	126.190	106.682	−237.939	−242.699	7.043
1900	81.341	189.828	129.425	114.765	−238.920	−242.937	6.679
2000	82.362	194.026	132.551	122.950	−239.977	−243.122	6.350
2100	83.383	198.069	135.575	131.237	−241.118	−243.251	6.051
2200	84.404	201.972	138.505	139.627	−263.676	−242.579	5.760
2200.000	84.404	201.972	138.505	139.627	GLASS <-- --> LIQUID		
2200.000	96.232	201.972	138.505	139.627	TRANSITION		
2300	96.232	206.250	141.358	149.250	−264.298	−241.606	5.487
2400	96.232	210.345	144.148	158.873	−365.506	−238.467	5.190
2500	96.232	214.274	146.875	168.496	−366.417	−233.155	4.872
2600	96.232	218.048	149.540	178.119	−367.328	−227.807	4.577
2700	96.232	221.680	152.145	187.743	−368.238	−222.423	4.303
2800	96.232	225.179	154.692	197.366	−369.149	−217.006	4.048
2900	96.232	228.556	157.181	206.989	−370.060	−211.556	3.811
3000	96.232	231.819	159.615	216.612	−370.971	−206.075	3.588
3100	96.232	234.974	161.995	226.235	−371.882	−200.564	3.379
3200	96.232	238.029	164.324	235.859	−372.792	−195.023	3.183
3300	96.232	240.991	166.602	245.482	−373.703	−189.453	2.999
3323.000	96.232	241.659	167.119	247.695	--- CRYSTAL <--> LIQUID ---		
3400	96.232	243.863	168.833	255.105	−374.614	−183.856	2.825
3500	96.232	246.653	171.016	264.728	−375.525	−178.233	2.660
3600	96.232	249.364	173.155	274.351	−376.436	−172.583	2.504
3700	96.232	252.001	175.251	283.975	−377.346	−166.908	2.356
3800	96.232	254.567	177.304	293.598	−378.257	−161.208	2.216
3900	96.232	257.067	179.318	303.221	−379.168	−155.484	2.082
4000	96.232	259.503	181.292	312.844	−380.079	−149.737	1.955
4100	96.232	261.879	183.229	322.467	−380.990	−143.967	1.834
4200	96.232	264.198	185.129	332.091	−1341.599	−124.127	1.544
4300	96.232	266.463	186.994	341.714	−1340.336	−95.155	1.156
4400	96.232	268.675	188.826	351.337	−1339.076	−66.211	0.786
4500	96.232	270.838	190.624	360.960	−1337.820	−37.297	0.433
4600	96.232	272.953	192.391	370.583	−1336.568	−8.410	0.095
4700	96.232	275.022	194.127	380.207	−1335.322	20.449	−0.227
4800	96.232	277.048	195.834	389.830	−1895.018	60.900	−0.663
4900	96.232	279.032	197.511	399.453	−1893.436	101.632	−1.083
5000	96.232	280.977	199.161	409.076	−1891.877	142.331	−1.487

PREVIOUS: December 1962 CURRENT: June 1965

0	to 3323 K	crystal
above	3323 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.653	−321.314	−321.314	INFINITE
100	12.008	4.926	67.811	−6.289	−321.884	−320.909	167.626
200	32.803	19.732	39.899	−4.033	−322.488	−319.657	83.486
298.15	48.242	35.941	35.941	0.	−322.586	−318.234	55.753
300	48.488	36.240	35.941	0.089	−322.586	−318.207	55.405
400	57.505	51.582	37.972	5.444	−322.516	−316.760	41.365
500	62.634	65.010	42.068	11.471	−322.575	−315.317	32.941
600	65.810	76.725	46.889	17.902	−322.798	−313.847	27.323
700	68.028	87.043	51.903	24.598	−323.179	−312.327	23.306
800	69.710	96.240	56.881	31.487	−323.705	−310.743	20.289
900	71.090	104.534	61.723	38.530	−324.373	−309.084	17.939
1000	72.153	112.079	66.387	45.693	−325.191	−307.343	16.054
1100	73.174	119.004	70.860	52.959	−326.156	−305.512	14.508
1200	74.195	125.415	75.142	60.327	−330.967	−303.366	13.205
1300	75.216	131.394	79.242	67.798	−331.648	−301.039	12.096
1400	76.237	137.005	83.169	75.370	−332.366	−298.658	11.143
1500	77.258	142.300	86.937	83.045	−333.123	−296.224	10.315
1600	78.278	147.319	90.555	90.822	−333.926	−293.738	9.590
1700	79.299	152.095	94.036	98.701	−334.780	−291.200	8.947
1800	80.320	156.656	97.389	106.682	−335.694	−288.611	8.375
1900	81.341	161.026	100.624	114.765	−336.675	−285.969	7.862
2000	82.362	165.225	103.750	122.950	−337.731	−283.273	7.398
2100	83.383	169.268	106.774	131.237	−338.872	−280.522	6.978
2200	84.404	173.170	109.704	139.627	−361.430	−276.970	6.576
2300	85.425	176.945	112.546	148.118	−363.185	−273.091	6.202
2400	86.446	180.602	115.306	156.712	−465.422	−266.999	5.811
2500	87.467	184.152	117.989	165.407	−467.260	−258.694	5.405
2600	88.487	187.602	120.600	174.205	−468.997	−250.316	5.029
2700	89.508	190.961	123.144	183.105	−470.631	−241.874	4.679
2800	90.529	194.234	125.625	192.107	−472.163	−233.373	4.354
2900	91.550	197.429	128.046	201.211	−473.593	−224.820	4.049
3000	92.571	200.550	130.411	210.417	−474.921	−216.218	3.765
3100	93.592	203.602	132.723	219.725	−476.147	−207.575	3.498
3200	94.613	206.589	134.985	229.135	−477.271	−198.893	3.247
3300	95.634	209.516	137.199	238.647	−478.292	−190.177	3.010
3323.000	95.868	210.181	137.702	240.850	CRYSTAL <--> LIQUID TRANSITION		
3323.000	96.232	241.659	137.702	345.450			
3400	96.232	243.863	140.081	352.859	−374.614	−183.856	2.825
3500	96.232	246.653	143.087	362.483	−375.525	−178.233	2.660
3600	96.232	249.364	146.001	372.106	−376.436	−172.583	2.504
3700	96.232	252.001	148.831	381.729	−377.346	−166.908	2.356
3800	96.232	254.567	151.580	391.352	−378.257	−161.208	2.216
3900	96.232	257.067	154.252	400.975	−379.168	−155.484	2.082
4000	96.232	259.503	156.853	410.599	−380.079	−149.737	1.955
4100	96.232	261.879	159.386	420.222	−380.990	−143.967	1.834
4200	96.232	264.198	161.854	429.845	−1341.599	−124.127	1.544
4300	96.232	266.463	164.261	439.468	−1340.336	−95.154	1.156
4400	96.232	268.675	166.609	449.091	−1339.076	−66.211	0.786
4500	96.232	270.837	168.901	458.715	−1337.820	−37.297	0.433
4600	96.232	272.953	171.140	468.338	−1336.568	−8.410	0.095
4700	96.232	275.022	173.328	477.961	−1335.322	20.449	−0.227
4800	96.232	277.048	175.468	487.584	−1895.018	60.900	−0.663
4900	96.232	279.032	177.561	497.207	−1893.436	101.632	−1.083
5000	96.232	280.977	179.610	506.831	−1891.877	142.331	−1.487

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K)$ = [382.38] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1627 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1632 \pm 8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[807] (1)	[980] (2)	[600] (1)
[690] (1)	[1300] (2)	[140] (1)
[333] (1)	[920] (2)	[400] (2)
[1037] (1)	[390] (2)	[120] (2)
[400] (1)	[150] (2)	

Ground State Quantum Weight: [1] $\sigma = 6$

Point Group: [D_{3h}]

Bond Distances: B–Cl = [1.75] Å; B–O = [1.36] Å

Bond Angles: Cl–B–O = [120]°; B–O–B = [120]°

Product of the Moments of Inertia: $I_A I_B I_C$ = [1.868800 × 10^{-111}] $g^3·cm^6$

Enthalpy of Formation

The equilibrium constants for the reaction $B_2O_3(l) + BCl_3(g) = (BOCl)_3(g)$ were determined by Blauer and Farber in the temperature range 536–825 K by a transpiration method,[1] and in the temperature range 1234–1309 K by an effusion method.[2] Using the reported equilibrium constants, the enthalpy changes for this reaction were evaluated by both the 2nd and 3rd law methods.

Method Used	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 3rd law	2nd law	$\Delta_f H°(293.15\ K)$ $kcal·mol^{-1}$
Transpiration	5.31	5.07 ± 0.4	−390 ± 2
Effusion	12.57	5.85 ± 3.3	−386 ± 3

By a mass spectroscopic method the enthalpy change $\Delta_f H°(1000\ F) = 16.6 \pm 2.5$ kcal mol^{-1}, for the reaction $BCl_3(g) + B_2O_3(l) = (BOCl)_3(g)$ was determined by Porter and Gupta.[3] The $\Delta_f H°(298.15\ K)$ value for $(BOCl)_3(g)$ was derived as -377 ± 3 $kcal·mol^{-1}$. However, it is possible that the intensity of $B_3O_3Cl_3^+$, employed to plot the ion ratios $I(B_3O_3Cl_3^+)/I(BCl_2^+)$ versus $1/T$, does not fully reflect the concentration of $B_3O_3Cl_3$ especially at the highest temperatures, due to changes in the fragmentation pattern with temperature.

The value of $\Delta_f H°(298.15\ K)$ adopted for $(BOCl)_3(g)$ is 390 ± 2 $kcal·mol^{-1}$ derived from transpiration data. The effusion data were measured in the temperature range where Porter and Gupta[3] found the presence of $(BOCl)_4(g)$. However, this point was not taken into consideration in the report. Hence, the corresponding $\Delta_f H°(298.15\ K)$ value was not adopted.

Heat Capacity and Entropy

The vibration frequencies are estimated by comparison with related molecules such as $B_3O_3F_3(g)$ and $(BH_2O)_3(g)$. The B–Cl bond distance is assumed to be the same as that in $BCl_3(g)$. The B–O bond distance and all bond angles are estimated. The principal moments of inertia are: $I_A = I_B = 97.7637 \times 10^{-39}$, and $I_C = 195.5274 \times 10^{-39}$ $g·cm^2$.

References

[1] J. Blauer and M. Farber, J. Chem. Phys. **39**, 158 (1963).

[2] J. Blauer and M. Farber, Trans. Faraday Soc. **60**, 301 (1964).

[3] R. F. Porter and S. K. Gupta, J. Phys. Chem. **68**, 280 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−25.342	−1626.664	−1626.664	INFINITE
100	70.079	275.129	480.665	−20.554	−1630.672	−1603.746	837.711
200	105.432	335.190	393.615	−11.685	−1631.726	−1576.278	411.682
250	119.582	360.271	384.479	−6.052	−1631.820	−1562.401	326.446
298.15	131.525	382.378	382.378	0.	−1631.760	−1549.034	271.384
300	131.953	383.193	382.381	0.244	−1631.755	−1548.521	269.622
350	142.628	404.357	384.028	7.115	−1631.558	−1534.663	229.036
400	151.707	424.012	387.812	14.480	−1631.268	−1520.839	198.601
450	159.351	442.335	392.864	22.262	−1630.909	−1507.057	174.935
500	165.756	459.466	398.677	30.394	−1630.492	−1493.317	156.006
600	175.618	490.611	411.458	47.492	−1629.526	−1465.970	127.624
700	182.610	518.238	424.777	65.423	−1628.450	−1438.795	107.364
800	187.665	542.970	438.032	83.950	−1627.326	−1411.778	92.180
900	191.400	565.300	450.953	102.912	−1626.198	−1384.903	80.378
1000	194.220	585.618	463.419	122.199	−1625.095	−1358.152	70.943
1100	196.392	604.236	475.386	141.735	−1624.038	−1331.509	63.228
1200	198.095	621.400	486.848	161.462	−1623.043	−1304.960	56.803
1300	199.452	637.311	497.818	181.342	−1622.121	−1278.491	51.370
1400	200.549	652.134	508.317	201.344	−1621.281	−1252.090	46.716
1500	201.448	666.002	518.372	221.445	−1620.531	−1225.746	42.684
1600	202.193	679.028	528.010	241.628	−1619.878	−1199.449	39.158
1700	202.817	691.305	537.258	261.880	−1619.325	−1173.189	36.048
1800	203.344	702.913	546.141	282.188	−1618.881	−1146.960	33.284
1900	203.793	713.919	554.685	302.546	−1618.548	−1120.751	30.812
2000	204.179	724.383	562.910	322.945	−1618.331	−1094.558	28.587
2100	204.513	734.353	570.839	343.380	−1618.235	−1068.372	26.574
2200	204.804	743.874	578.489	363.846	−1618.263	−1042.187	24.745
2300	205.059	752.983	585.879	384.340	−1618.419	−1015.999	23.074
2400	205.283	761.715	593.025	404.857	−1769.485	−986.595	21.473
2500	205.482	770.100	599.941	425.395	−1770.141	−953.961	19.932
2600	205.658	778.162	606.642	445.953	−1770.836	−921.301	18.509
2700	205.816	785.927	613.139	466.526	−1771.573	−888.612	17.191
2800	205.957	793.415	619.445	487.115	−1772.354	−855.895	15.967
2900	206.085	800.644	625.569	507.717	−1773.181	−823.151	14.827
3000	206.200	807.633	631.522	528.332	−1774.054	−790.376	13.762
3100	206.304	814.396	637.313	548.957	−1774.973	−757.571	12.765
3200	206.399	820.947	642.949	569.592	−1775.937	−724.738	11.830
3300	206.485	827.300	648.440	590.236	−1776.945	−691.872	10.951
3400	206.564	833.465	653.792	610.889	−1777.995	−658.975	10.124
3500	206.636	839.454	659.011	631.549	−1779.084	−626.048	9.343
3600	206.703	845.276	664.105	652.216	−1780.209	−593.087	8.605
3700	206.764	850.940	669.078	672.889	−1781.367	−560.097	7.907
3800	206.821	856.455	673.937	693.569	−1782.554	−527.072	7.245
3900	206.873	861.828	678.686	714.253	−1783.765	−494.017	6.617
4000	206.921	867.066	683.330	734.943	−1784.998	−460.932	6.019
4100	206.966	872.176	687.874	755.638	−1786.247	−427.814	5.450
4200	207.008	877.164	692.322	776.336	−3227.058	−373.594	4.646
4300	207.047	882.035	696.678	797.039	−3225.067	−305.678	3.713
4400	207.083	886.796	700.945	817.746	−3223.088	−237.809	2.823
4500	207.117	891.450	705.126	838.456	−3221.115	−169.984	1.973
4600	207.149	896.003	709.227	859.169	−3219.148	−102.203	1.161
4700	207.179	900.458	713.248	879.885	−3217.183	−34.465	0.383
4800	207.207	904.820	717.194	900.605	−3215.219	33.232	−0.362
4900	207.233	909.093	721.067	921.327	−3213.255	100.889	−1.075
5000	207.258	913.280	724.869	942.051	−3211.289	168.504	−1.760
5100	207.281	917.384	728.604	962.778	−3209.321	236.082	−2.418
5200	207.303	921.409	732.273	983.508	−3207.349	303.617	−3.050
5300	207.324	925.358	735.879	1004.239	−3205.375	371.118	−3.658
5400	207.343	929.234	739.424	1024.972	−3203.398	438.580	−4.242
5500	207.362	933.039	742.910	1045.708	−3201.419	506.006	−4.806
5600	207.380	936.775	746.338	1066.445	−3199.440	573.397	−5.348
5700	207.396	940.446	749.712	1087.183	−3197.462	640.750	−5.872
5800	207.412	944.053	753.031	1107.924	−3195.485	708.072	−6.377
5900	207.427	947.599	756.299	1128.666	−3193.512	775.355	−6.864
6000	207.441	951.085	759.517	1149.409	−3191.547	842.608	−7.336

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K)$ = [314.84] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1587 \pm 25\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1598 \pm 25\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[2100] (1)	[880] (1)	[350] (1)
[870] (1)	[1460] (1)	[225] (1)
[670] (1)	[520] (1)	[800] (1)
[2200] (1)	[2230] (1)	[225] (1)
[1390] (1)	[1390] (1)	[840] (1)
[1200] (1)	[1200] (1)	[800] (1)
[880] (1)	[350] (1)	[260] (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: B–O = [1.36] Å; B–H = [1.18] Å; B–F = [1.41] Å
Bond Angles: B–O–B = [120]°; O–B–H = [120]°; O–B–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.164977 × 10^{-113}] $g^3·cm^6$

Enthalpy of Formation

The equilibrium constants (K), 1246–1326 K, for the two reactions $2B_3O_3F_2H(g) = B_3O_3FH_2(g) + B_3O_3F_3(g)$ and $2B_3O_3FH_2(g) = B_3O_3H_3(g) + B_3O_3F_2H(g)$ were reported by Porter and Sholette.[1] The $\Delta_f H°(298.15\ K)$ for $B_3O_3H_2F(g)$ adopted was evaluated by use of K values slightly outside the ranges given by Porter and Sholette. See the table for $B_3O_3F_2H(g)$ for details.

Heat Capacity and Entropy

The structure is assumed to be a planar six membered ring structure of C_{2v} symmetry, which has 21 vibrations of the type $8A_1$, $7B_1$, $2A_2$, and $4B_2$. These frequencies are estimated from the values for boroxin and trifluoroboroxin, the symmetry being reduced from D_{3h} as follows: $3A'_1 \rightarrow 3A_1$, $2A'_2 \rightarrow 2B_1$, $5E' \rightarrow 5A_1 + 5B_1$, $2A_2 \rightarrow 2B_2$ and $2E'' \rightarrow 2A_2 + 2B_2$.

The B–F distance is taken as approximately equal to that in $(CH_3)_2O\ BF_3$ reported by Bauer, Findlay and Laubengayer.[2] The other bond lengths and angles are taken equal to those in boroxin. The principal moments of inertia are: $I_A = 13.9711 \times 10^{-39}$, $I_B = 32.9946 \times 10^{-39}$, and $I_C = 46.9657 \times 10^{-39}$ $g·cm^2$.

References

[1] R. F. Porter and W. P. Sholette, J. Chem. Phys. **37**, 198 (1962).
[2] S. H. Bauer, G. R. Findlay, and A. W. Laubengayer, J. Am. Chem. Soc. **67**, 339 (1945).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.877	−1586.619	−1586.619	INFINITE
100	46.702	241.315	383.279	−14.196	−1591.820	−1571.271	820.748
200	72.105	281.675	322.817	−8.228	−1595.375	−1549.266	404.627
250	84.135	299.063	316.347	−4.321	−1596.915	−1537.558	321.255
298.15	95.245	314.841	314.841	0.	−1598.288	−1526.000	267.349
300	95.659	315.432	314.843	0.177	−1598.338	−1525.551	265.622
350	106.362	330.993	316.047	5.231	−1599.624	−1513.316	225.850
400	116.099	345.842	318.851	10.797	−1600.778	−1500.906	195.998
450	124.856	360.032	322.644	16.825	−1601.803	−1488.359	172.764
500	132.685	373.600	327.066	23.267	−1602.695	−1475.705	154.166
600	145.879	399.004	336.970	37.220	−1604.090	−1450.168	126.248
700	156.339	422.308	347.520	52.351	−1605.020	−1424.435	106.293
800	164.653	443.748	358.227	68.417	−1605.565	−1398.596	91.319
900	171.295	463.539	368.843	85.226	−1605.811	−1372.708	79.670
1000	176.637	481.873	379.241	102.633	−1605.833	−1346.804	70.350
1100	180.969	498.919	389.355	120.520	−1605.698	−1320.907	62.725
1200	184.511	514.822	399.155	138.800	−1605.459	−1295.026	56.371
1300	187.433	529.710	408.631	157.402	−1605.162	−1269.169	50.996
1400	189.864	543.692	417.784	176.270	−1604.842	−1243.335	46.389
1500	191.902	556.862	426.621	195.362	−1604.529	−1217.525	42.398
1600	193.625	569.304	435.154	214.640	−1604.246	−1191.734	38.906
1700	195.093	581.088	443.395	234.078	−1604.010	−1165.959	35.826
1800	196.351	592.275	451.358	253.652	−1603.838	−1140.197	33.088
1900	197.436	602.921	459.057	273.343	−1603.740	−1114.442	30.638
2000	198.379	613.073	466.506	293.134	−1603.725	−1088.690	28.434
2100	199.202	622.772	473.718	313.014	−1603.800	−1062.937	26.439
2200	199.924	632.056	480.706	332.971	−1603.970	−1037.177	24.626
2300	200.562	640.958	487.481	352.996	−1604.238	−1011.409	22.970
2400	201.126	649.506	494.055	373.081	−1755.386	−982.420	21.382
2500	201.629	657.726	500.439	393.220	−1756.092	−950.199	19.853
2600	202.078	665.643	506.641	413.405	−1756.805	−917.949	18.442
2700	202.481	673.277	512.672	433.634	−1757.525	−885.671	17.134
2800	202.844	680.648	518.541	453.900	−1758.253	−853.367	15.920
2900	203.172	687.772	524.254	474.201	−1758.990	−821.037	14.788
3000	203.469	694.665	529.820	494.534	−1759.736	−788.681	13.732
3100	203.739	701.341	535.246	514.894	−1760.491	−756.300	12.744
3200	203.985	707.813	540.538	535.280	−1761.256	−723.895	11.816
3300	204.209	714.094	545.703	555.690	−1762.029	−691.466	10.945
3400	204.415	720.193	550.745	576.122	−1762.810	−659.012	10.124
3500	204.605	726.121	555.672	596.573	−1763.601	−626.537	9.351
3600	204.779	731.888	560.487	617.042	−1764.399	−594.038	8.619
3700	204.939	737.501	565.196	637.528	−1765.206	−561.517	7.927
3800	205.088	742.968	569.802	658.030	−1766.022	−528.973	7.271
3900	205.225	748.297	574.311	678.545	−1766.846	−496.408	6.649
4000	205.353	753.495	578.726	699.074	−1767.679	−463.823	6.057
4100	205.471	758.567	583.051	719.616	−1768.521	−431.216	5.494
4200	205.582	763.519	587.289	740.168	−3208.919	−377.516	4.695
4300	205.685	768.358	591.444	760.732	−3206.518	−310.129	3.767
4400	205.781	773.088	595.518	781.305	−3204.132	−242.800	2.882
4500	205.871	777.713	599.516	801.888	−3201.763	−175.524	2.037
4600	205.955	782.239	603.439	822.479	−3199.411	−108.301	1.230
4700	206.034	786.669	607.291	843.079	−3197.080	−41.127	0.457
4800	206.109	791.008	611.073	863.686	−3194.769	25.996	−0.283
4900	206.178	795.258	614.789	884.300	−3192.481	93.073	−0.992
5000	206.244	799.424	618.440	904.921	−3190.217	160.102	−1.673
5100	206.306	803.509	622.029	925.549	−3187.980	227.086	−2.326
5200	206.365	807.516	625.558	946.182	−3185.771	294.025	−2.954
5300	206.420	811.447	629.028	966.822	−3183.591	360.925	−3.557
5400	206.472	815.306	632.442	987.466	−3181.445	427.782	−4.138
5500	206.522	819.095	635.801	1008.116	−3179.332	494.599	−4.697
5600	206.569	822.817	639.108	1028.771	−3177.256	561.380	−5.236
5700	206.613	826.473	642.363	1049.430	−3175.219	628.123	−5.756
5800	206.655	830.067	645.568	1070.093	−3173.222	694.832	−6.258
5900	206.696	833.600	648.725	1090.761	−3171.268	761.503	−6.742
6000	206.734	837.074	651.836	1111.432	−3169.360	828.145	−7.210

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [328.99]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1977 \pm 21\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1987 \pm 21\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[1650] (1)	[660] (1)	[300] (1)
[830] (1)	[1370] (1)	[220] (1)
[610] (1)	[490] (1)	[710] (1)
[1800] (1)	[1840] (1)	[220] (1)
[1385] (1)	[1385] (1)	[780] (1)
[1080] (1)	[1080] (1)	[700] (1)
[660] (1)	[310] (1)	[230] (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: B–O = [1.36] Å; B–H = [1.18] Å; B–F = [1.41] Å
Bond Angles: B–O–B = [120]°; O–B–H = [120]°; O–B–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.586853 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The stabilities of gaseous boroxin ($B_3O_3H_3$) and its fluoro derivatives have been studied by Porter and Sholette.[1] From the mass spectra of the gaseous reaction products generated by reaction of an H_2–BF_3 mixture on B_2O_3 at 1250 K, the equilibrium constants (K) for the following proposed reactions were reported.

Reaction	T/K	K	$\Delta_f H°$(298.15 K), $kcal·mol^{-1}$
(1) $H_2(g) + B_3O_3F_3(g) = HF(g) + B_3O_3F_2H(g)$	1246–1326	4.2×10^{-3}–2.3×10^{-2}	20.45–17.17
(2) $2B_3O_3F_2H(g) = B_3O_3FH_2(g) + B_3O_3F_3(g)$	1246–1326	0.62–0.46	1.28–2.15
(3) $2B_3O_3FH_2(g) = B_3O_3H_3(g) + B_3O_3F_2H(g)$	1246–1326	1.0–0.63	−2.56–−1.51

Using these reported K values the corresponding enthalpy changes are evaluated by the 3rd law method. The results obtained are listed in the above table. Based on $\Delta_f H°(298.15\ K) = -565.3$ and $-64.8\ kcal·mol^{-1}$ for $B_3O_3F_3(g)$ and HF(g), respectively, the value of $\Delta_f H°(298.15\ K)$ for $B_3O_3F_2H(g)$ is calculated from Reaction (1) as $-482\ kcal·mol^{-1}$. From Reaction (2), the $\Delta_f H°(298.15\ K)$ value for $B_3O_3FH_2(g)$ is calculated as $-397\ kcal·mol^{-1}$. However, employing $\Delta_f H°(B_3O_3H_3, g, 298.15\ K) = -291\ kcal·mol^{-1}$, the values of $\Delta_f H°(298.15\ K)$ for $B_3O_3FH_2(g)$ and $B_3O_3F_2H(g)$ thus obtained do not fit properly for Reaction (3). Therefore, the $\Delta_f H°(298.15\ K)$ for $B_3O_3FH_2(g)$ and $B_3O_3F_2H(g)$ adopted are evaluated by use of K values slightly outside the ranges given by Porter and Sholette.[1]

Heat Capacity and Entropy

The vibrational frequencies are obtained by comparison with $B_3O_3F_3(g)$ and $B_3H_3O_3(g)$. The types of vibration and symmetry are identical to those given for $B_3O_3H_2F(g)$. The bond angles and lengths are taken equal to those for $B_3O_3H_2F(g)$. The principal moments of inertia are: $I_A = 22.0494 \times 10^{-39}$, $I_B = 48.6611 \times 10^{-39}$, and $I_C = 70.7105 \times 10^{-39}\ g·cm^2$.

Reference

[1]R. F. Porter and W. P. Sholette, J. Chem. Phys. **37**, 198 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.127	−1976.801	−1976.801	INFINITE
100	49.248	249.646	403.289	−15.364	−1981.875	−1958.677	1023.108
200	78.340	292.875	337.680	−8.961	−1985.112	−1934.119	505.140
250	91.721	311.813	330.633	−4.705	−1986.357	−1921.223	401.418
298.15	103.528	328.994	328.994	0.	−1987.400	−1908.582	334.376
300	103.959	329.636	328.996	0.192	−1987.437	−1908.093	332.228
350	114.983	346.504	330.303	5.670	−1988.368	−1894.793	282.782
400	124.838	362.514	333.337	11.671	−1989.175	−1881.368	245.682
450	133.599	377.734	337.432	18.136	−1989.866	−1867.850	216.814
500	141.353	392.220	342.192	25.014	−1990.440	−1854.261	193.713
600	154.206	419.177	352.812	39.819	−1991.256	−1826.941	159.049
700	164.136	443.727	364.073	55.758	−1991.685	−1799.516	134.282
800	171.816	466.168	375.453	72.572	−1991.811	−1772.052	115.703
900	177.795	486.764	386.693	90.064	−1991.713	−1744.586	101.253
1000	182.495	505.750	397.662	108.088	−1991.461	−1717.140	89.694
1100	186.231	523.325	408.297	126.531	−1991.110	−1689.724	80.238
1200	189.236	539.663	418.571	145.310	−1990.706	−1662.343	72.360
1300	191.679	554.909	428.479	164.360	−1990.286	−1634.997	65.695
1400	193.686	569.190	438.025	183.631	−1989.876	−1607.682	59.983
1500	195.353	582.612	447.221	203.086	−1989.501	−1580.396	55.034
1600	196.750	595.265	456.082	222.693	−1989.178	−1553.133	50.705
1700	197.930	607.230	464.625	242.428	−1988.921	−1525.889	46.885
1800	198.936	618.572	472.865	262.273	−1988.740	−1498.658	43.490
1900	199.799	629.352	480.820	282.211	−1988.645	−1471.434	40.453
2000	200.544	639.620	488.505	302.229	−1988.639	−1444.212	37.719
2100	201.193	649.420	495.936	322.317	−1988.727	−1416.990	35.246
2200	201.760	658.793	503.127	342.465	−1988.911	−1389.759	32.997
2300	202.258	667.773	510.092	362.666	−1989.192	−1362.520	30.944
2400	202.699	676.391	516.843	382.915	−2140.347	−1332.059	28.992
2500	203.090	684.673	523.391	403.204	−2141.054	−1298.366	27.128
2600	203.439	692.645	529.749	423.531	−2141.758	−1264.645	25.407
2700	203.751	700.329	535.925	443.891	−2142.458	−1230.896	23.813
2800	204.032	707.744	541.930	464.280	−2143.152	−1197.121	22.333
2900	204.285	714.909	547.772	484.696	−2143.840	−1163.323	20.954
3000	204.513	721.838	553.459	505.136	−2144.520	−1129.500	19.666
3100	204.721	728.548	559.000	525.598	−2145.191	−1095.654	18.462
3200	204.910	735.050	564.400	546.080	−2145.852	−1061.789	17.332
3300	205.083	741.358	569.667	566.580	−2146.502	−1027.902	16.270
3400	205.241	747.483	574.808	587.096	−2147.138	−993.995	15.271
3500	205.386	753.435	579.827	607.628	−2147.762	−960.070	14.328
3600	205.519	759.222	584.730	628.173	−2148.371	−926.127	13.438
3700	205.642	764.855	589.522	648.731	−2148.966	−892.168	12.595
3800	205.756	770.341	594.209	669.301	−2149.547	−858.192	11.797
3900	205.861	775.687	598.794	689.882	−2150.112	−824.201	11.039
4000	205.958	780.900	603.282	710.473	−2150.663	−790.197	10.319
4100	206.049	785.987	607.676	731.073	−2151.199	−756.179	9.634
4200	206.133	790.953	611.981	751.683	−3591.269	−701.075	8.719
4300	206.211	795.804	616.200	772.300	−3588.516	−632.293	7.681
4400	206.285	800.546	620.336	792.925	−3585.755	−563.576	6.691
4500	206.353	805.182	624.392	813.557	−3582.988	−494.922	5.745
4600	206.417	809.719	628.372	834.195	−3580.217	−426.329	4.841
4700	206.477	814.158	632.278	854.840	−3577.444	−357.796	3.976
4800	206.534	818.506	636.112	875.490	−3574.670	−289.322	3.148
4900	206.587	822.765	639.878	896.147	−3571.898	−220.905	2.355
5000	206.637	826.939	643.578	916.808	−3569.129	−152.545	1.594
5100	206.684	831.032	647.213	937.474	−3566.367	−84.241	0.863
5200	206.729	835.046	650.787	958.145	−3563.614	−15.992	0.161
5300	206.771	838.984	654.301	978.819	−3560.872	52.207	−0.515
5400	206.810	842.849	657.757	999.499	−3558.145	120.352	−1.164
5500	206.848	846.644	661.157	1020.181	−3555.435	188.446	−1.790
5600	206.883	850.372	664.502	1040.868	−3552.744	256.494	−2.392
5700	206.917	854.034	667.796	1061.558	−3550.076	324.491	−2.974
5800	206.949	857.633	671.038	1082.251	−3547.434	392.444	−3.534
5900	206.980	861.171	674.230	1102.948	−3544.820	460.348	−4.076
6000	207.009	864.650	677.375	1123.647	−3542.238	528.212	−4.598

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°$(298.15 K) = [217.6] J·K^{-1}·mol^{-1}
T_{fus} = 353 K

$\Delta_f H°$(0 K) = Unknown
$\Delta_f H°$(298.15 K) = −2454 ± 12 kJ·mol^{-1}
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpies of solution of the compounds: B_2O_3(gl), BF_3(g) and $(BOF)_3$(cr) in water and methanol, respectively, were reported by Magee.[1] The corresponding enthalpy changes for the reaction B_2O_3(gl) + BF_3(g) = $(BOF)_3$(cr) were derived as −19.8 and −14.4 kcal·mol^{-1}, yielding $\Delta_f H°$(298.15 K) values for $(BOF)_3$(cr) as −589.18 and −583.78 kcal·mol^{-1}, respectively. The adopted value of $\Delta_f H°$(298.15 K) for $(BOF)_3$(cr) is the average of these two values obtained.

Heat Capacity and Entropy

The heat capacities for $(BOF)_3$(cr) are estimated from the C_p values for B_2O_3(cr) and BF_3(g), according to the method suggested by Kubaschewski and Evans.[2]

$S°$(298.15 K) for $(BOF)_3$(cr) was estimated by Magee.[1]

Fusion Data

The value of T_{fus} was reported by Magee.[1]

Sublimation Data

The enthalpy of sublimation for $(BOF)_3$(cr) is calculated as the difference in $\Delta_f H°$(298.15 K) between the crystal and gas.

References

[1]E. M. Magee, J. Inorg. Nucl. Chem. **22**, 156 (1961).
[2]O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," 3rd ed., Pergamon Press, New York, 426 pp. (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	125.520	217.568	217.568	0.	−2453.916	−2331.126	408.404
300	125.874	218.346	217.570	0.233	−2453.915	−2330.364	405.753
400	144.766	257.156	222.735	13.769	−2453.752	−2289.199	298.939
500	163.176	291.484	233.111	29.187	−2453.164	−2248.116	234.859
600	178.761	322.641	245.476	46.299	−2451.944	−2207.210	192.155
700	192.464	351.250	258.570	64.876	−2450.042	−2166.562	161.671
800	204.284	377.743	271.831	84.729	−2447.457	−2126.234	138.829
900	214.221	402.396	284.985	105.670	−2444.251	−2086.267	121.084
1000	222.170	425.393	297.889	127.504	−2440.532	−2046.687	106.908
1100	228.446	446.875	310.468	150.048	−2436.420	−2007.498	95.328
1200	232.840	466.950	322.681	173.123	−2432.054	−1968.696	85.695
1300	235.978	485.720	334.508	196.575	−2427.556	−1930.265	77.559
1400	237.860	503.284	345.943	220.277	−2423.029	−1892.182	70.598
1500	238.488	519.723	356.987	244.105	−2418.582	−1854.421	64.577

PREVIOUS: September 1962 CURRENT: March 1965

$S°(298.15\ K) = [342.45]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2357.0 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -2365.2 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[1233] (1)	1450 (2)	714 (1)
[790] (1)	1381 (2)	[170] (1)
[570] (1)	966 (2)	[630] (2)
[1280] (1)	[420] (2)	[185] (2)
[440] (1)	[220] (2)	

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: $[D_{3h}]$
Bond Distances: B–F = [1.3] Å; B–O = [1.36] Å
Bond Angles: F–B–O = [120]°; B–O–B = [120]°; O–B–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.925790 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy changes of the reaction $B_2O_3(l) + BF_3(g) = (BOF)_3(g)$ are derived by both the 2nd and 3rd law methods, using the equilibrium constant data reported by several investigators.

Source	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 3rd law	2nd law	$\Delta_f H°$(298.15 K) kcal mol^{-1}
Hildenbrand, *et al.*[1]	4.06	4.01 ± 0.3	−565.32 ± 1.0
Fisher, *et al.*[2]	3.41	6.45 ± 0.6	−565.97 ± 1.5
Smith and Lawrence[3]	4.03	—	−565.35 ± 1.3
Farber[4]	5.25	—	−565.13 ± 2.0
	2.56	7.58 ± 0.2	−565.82 ± 2.0
Porter, *et al.*[5]	—	4.33 ± 0.30	−565.05 ± 1.0

The adopted value of $\Delta_f H°$(298.15 K) for $(BOF)_3$(cr) is the weighted average of the six $\Delta_f H°$(298.15 K) values listed above.

Heat Capacity and Entropy

The infra-red spectrum has been reported by Smith and Lawrence[3] and by Fisher, Lehmann, and Shapiro[6] who also made a partial assignment. The unassigned bands at 1280 and 1233 from Fisher, *et al.*,[6] can be assigned to the A_2^1 and A_1^1 species which may be observed if the selection rules are not rigorously obeyed in the solid. All the unobserved frequencies were estimated by comparison with $B_3O_3(OH)_3$, $B_3O_3(OD)_3$ from Parsons[7] and $B_3O_3H_3$ and $B_3O_3D_3$ from Gupta and Porter[8] and Lee, Bauer and Wiberley.[9] The D_{3h} assumed symmetry has 14 vibrations of the type $3A_1^1$, $2A_2^1$, 5E', $2A_2^{11}$ and 2E" which are given in order above. The B–F bond distance was assumed to be the same as that in BF_3. The B–O bond distance was estimated by comparison with other related compounds. The principal moments of inertia are: $I_A = I_B = 45.8345 \times 10^{-39}$, and $I_C = 91.6691 \times 10^{-39}$ g·cm^2.

References

[1]D. L. Hildenbrand, L. P. Theard and A. M. Saul, J. Chem. Phys. **39**, 1973 (1963).
[2]H. D. Fisher, J. Kiehl and A. Cane, Report HTC-61-90, June 1961, Hughes Tool Company, Culver City, California.
[3]D. D. Smith and R. W. Lawrence, Aerojet Report No. 1952, February 1961, Aerojet-General Corporation.
[4]M. Farber, J. Chem. Phys. **36**, 661 (1962). The first $\Delta_f H°$(298.15 K) value was evaluated based on K(1000 K) = 11.8. The second $\Delta_f H°$(298.15 K) values refer to the reaction $B_2O_3(cr) + BF_3(g) = (BOF)_3(g)$.
[5]R. F. Porter, D. R. Bidinosti and K. F. Watterson, J. Chem. Phys. **36**, 2104 (1962). The $\Delta_f H°$(298.15 K) value was derived from $\Delta_f H°$(700 K) = 3.46 ± 0.30 kcal·mol^{-1}.
[6]H. D. Fisher, W. J. Lehmann, and I. Shapiro, J. Phys. Chem. **65**, 1166 (1961).
[7]J. L. Parsons, J. Chem. Phys. **33**, 1860 (1960).
[8]S. K. Gupta and R. F. Porter, J. Phys. Chem. **67**, 1286 (1963).
[9]G. H. Lee, W. H. Bauer, and S. E. Wiberley, J. Phys. Chem. **67**, 1742 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−21.691	−2357.002	−2357.002	INFINITE
100	57.998	251.201	426.907	−17.571	−2361.671	−2335.147	1219.756
200	89.987	301.683	352.202	−10.104	−2363.963	−2307.608	602.685
250	103.398	323.231	344.283	−5.263	−2364.676	−2293.432	479.187
298.15	115.012	342.454	342.454	0.	−2365.215	−2279.660	399.387
300	115.435	343.167	342.456	0.213	−2365.234	−2279.129	396.832
350	126.216	361.786	343.902	6.260	−2365.667	−2264.743	337.994
400	135.793	379.278	347.242	12.815	−2366.005	−2250.301	293.859
450	144.217	395.770	351.726	19.820	−2366.260	−2235.822	259.527
500	151.566	411.354	356.917	27.218	−2366.431	−2221.318	232.060
600	163.450	440.091	368.427	42.998	−2366.545	−2192.281	190.855
700	172.330	465.987	380.546	59.809	−2366.409	−2163.244	161.423
800	178.998	489.454	392.716	77.391	−2366.095	−2134.241	139.352
900	184.064	510.843	404.671	95.555	−2365.665	−2105.284	122.187
1000	187.969	530.447	416.282	114.165	−2365.170	−2076.379	108.459
1100	191.023	548.511	427.492	133.120	−2364.647	−2047.524	97.229
1200	193.448	565.240	438.283	152.349	−2364.128	−2018.718	87.873
1300	195.399	580.804	448.655	171.794	−2363.636	−1989.954	79.957
1400	196.988	595.345	458.619	191.416	−2363.189	−1961.227	73.174
1500	198.299	608.982	468.193	211.183	−2362.803	−1932.529	67.297
1600	199.390	621.815	477.397	231.069	−2362.490	−1903.855	62.154
1700	200.307	633.932	486.252	251.055	−2362.258	−1875.197	57.618
1800	201.086	645.404	494.778	271.126	−2362.115	−1846.552	53.586
1900	201.751	656.294	502.995	291.268	−2362.064	−1817.911	49.978
2000	202.325	666.657	510.921	311.473	−2362.107	−1789.271	46.731
2100	202.822	676.541	518.574	331.731	−2362.246	−1760.626	43.793
2200	203.255	685.987	525.971	352.035	−2362.479	−1731.972	41.122
2300	203.636	695.030	533.126	372.380	−2362.805	−1703.306	38.683
2400	203.972	703.704	540.054	392.761	−2513.999	−1671.417	36.377
2500	204.269	712.037	546.768	413.173	−2514.735	−1636.294	34.189
2600	204.534	720.054	553.279	433.613	−2515.458	−1601.143	32.167
2700	204.771	727.777	559.600	454.079	−2516.163	−1565.963	30.295
2800	204.983	735.228	565.740	474.567	−2516.848	−1530.757	28.557
2900	205.175	742.425	571.709	495.075	−2517.510	−1495.529	26.937
3000	205.348	749.384	577.517	515.601	−2518.146	−1460.277	25.426
3100	205.505	756.120	583.170	536.144	−2518.753	−1425.004	24.011
3200	205.647	762.646	588.677	556.702	−2519.330	−1389.713	22.685
3300	205.778	768.976	594.045	577.273	−2519.874	−1354.405	21.438
3400	205.897	775.121	599.281	597.857	−2520.383	−1319.079	20.265
3500	206.006	781.091	604.391	618.452	−2520.857	−1283.740	19.159
3600	206.106	786.896	609.380	639.058	−2521.293	−1248.387	18.114
3700	206.199	792.545	614.255	659.673	−2521.690	−1213.024	17.125
3800	206.284	798.045	619.019	680.297	−2522.050	−1177.648	16.188
3900	206.363	803.404	623.678	700.930	−2522.370	−1142.264	15.299
4000	206.436	808.630	628.237	721.570	−2522.652	−1106.874	14.454
4100	206.504	813.728	632.699	742.217	−2522.895	−1071.477	13.651
4200	206.568	818.705	637.069	762.870	−3962.649	−1015.001	12.623
4300	206.627	823.566	641.350	783.530	−3959.555	−944.855	11.478
4400	206.682	828.317	645.545	804.195	−3956.430	−874.783	10.385
4500	206.733	832.962	649.659	824.866	−3953.276	−804.781	9.342
4600	206.781	837.507	653.693	845.542	−3950.095	−734.850	8.344
4700	206.826	841.954	657.652	866.222	−3946.890	−664.987	7.391
4800	206.869	846.309	661.537	886.907	−3943.662	−595.194	6.477
4900	206.908	850.575	665.351	907.596	−3940.414	−525.467	5.602
5000	206.946	854.756	669.098	928.289	−3937.150	−455.807	4.762
5100	206.981	858.854	672.778	948.985	−3933.872	−386.212	3.956
5200	207.014	862.873	676.396	969.685	−3930.583	−316.684	3.181
5300	207.046	866.817	679.951	990.388	−3927.286	−247.216	2.436
5400	207.076	870.687	683.448	1011.094	−3923.986	−177.812	1.720
5500	207.104	874.487	686.887	1031.803	−3920.684	−108.470	1.030
5600	207.130	878.219	690.270	1052.515	−3917.386	−39.185	0.366
5700	207.156	881.886	693.600	1073.229	−3914.094	30.038	−0.275
5800	207.180	885.489	696.877	1093.946	−3910.813	99.206	−0.893
5900	207.202	889.030	700.104	1114.665	−3907.545	168.314	−1.490
6000	207.224	892.513	703.282	1135.386	−3904.296	237.370	−2.066

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K) = [167 \pm 42]\ J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = Unknown

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1262.3 \pm 42\ kJ \cdot mol^{-1}$
$\Delta_m H°$ = Unknown

Enthalpy of Formation

The value of $\Delta_f H°(298.15\ K)$ for $B_3O_3H_3$(cr) is calculated from the $\Delta_f H°(298.15\ K)$ for $B_3O_3H_3$(g) and $\Delta_{sub} H°(298.15\ K)$ for $B_3O_3H_3$(cr) reported by Porter and Gupta.[1]

Heat Capacity and Entropy

The heat capacities were estimated from those from B_2O_3(cr) and 1/2 B_2H_6Kubaschewski and Evans.[2] The value of $S°(298.15\ K)$ for $B_3O_3H_3$(cr) is calculated based on $\Delta_r S°(298.15\ K) = 6.6\ cal \cdot K^{-1} \cdot mol^{-1}$ for the reaction $B_3O_3H_3(cr) = B_2O_3(am) + 1/2\ B_2H_6(g)$, which was obtained from the calculated $\Delta_f H°(298.15\ K)$ and measured $\Delta_f G°(298.15\ K)$ evaluated from the vapor pressure reported by Sholette and Porter.[3]

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is taken from Porter and Gupta.[3]

References

[1]R. F. Porter and S. K. Gupta, J. Phys. Chem. **68**, 280 (1964).
[2]O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," 3rd ed., Pergamon Press, New York, 426 pp. (1958).
[3]W. P. Sholette and R. F. Porter, J. Phys. Chem. **67**, 177 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	98.324	167.360	167.360	0.	−1262.313	−1156.803	202.667
300	98.742	167.969	167.362	0.182	−1262.355	−1156.148	201.303
400	120.081	199.288	171.488	11.120	−1264.321	−1120.431	146.313
500	141.838	228.436	179.991	24.223	−1265.383	−1084.312	113.277
600	162.758	256.203	190.396	39.484	−1265.199	−1048.093	91.245
700	179.912	282.612	201.700	56.638	−1263.798	−1012.004	75.517
800	194.556	307.628	213.392	75.389	−1261.331	−976.191	63.739
900	205.591	331.204	225.186	95.416	−1258.019	−940.740	54.599
1000	214.221	353.333	236.906	116.427	−1254.093	−905.692	47.309
1100	219.730	374.016	248.442	138.132	−1249.799	−871.057	41.363
1200	224.262	393.337	259.720	160.340	−1245.299	−836.824	36.426
1300	226.786	411.389	270.701	182.895	−1240.725	−802.970	32.264
1400	229.022	428.279	281.360	205.688	−1236.168	−769.467	28.709
1500	230.970	444.148	291.688	228.690	−1231.642	−736.290	25.640
1600	232.630	459.109	301.689	251.872	−1227.166	−703.413	22.964
1700	234.003	473.255	311.369	275.206	−1222.759	−670.814	20.612
1800	235.088	486.662	320.738	298.663	−1218.440	−638.472	18.528
1900	235.886	499.396	329.809	322.214	−1214.232	−606.367	16.670
2000	236.396	511.509	338.594	345.831	−1210.157	−574.479	15.004

PREVIOUS: CURRENT: March 1965

$S°(298.15\ K)$ = [291.91] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1205 \pm 42\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1218 \pm 42\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
2530 (1)	2620 (2)	903 (1)
[920] (1)	1404 (2)	[300] (1)
[735] (1)	1335 (2)	1115 (2)
[1560] (1)	940 (2)	[230] (2)
[550] (1)	[400] (2)	

Ground State Quantum Weight: [1] σ = [6]
Point Group: [D_{3h}]
Bond Distances: B–O = [1.36] Å; B–H = [1.18] Å
Bond Angles: B–O–B = [120]°; O–B–H = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [5.454021 × 10^{-114}] $g^3·cm^6$

Enthalpy of Formation

The equilibrium constants (1290–1481 K) for the reaction (1) 3/2 $H_2(g)$ + B(am) + $B_2O_3(l)$ = $B_3O_3H_3(g)$ were determined by Sholette and Porter.[1] The equilibrium pressures of $B_2H_6(g)$ and $B_3O_3H_3(g)$ for the reaction (2) $B_3O_3H_3(g)$ = 1/2 $B_2H_6(g)$ + $B_2O_3(cr)$ were measured at 300 K by Porter and Gupta.[2] The equilibrium constants (1246–1326 K) for the reaction[3] $2B_3O_3FH_2(g) = B_3O_3H_3(g) + B_3O_3F_2H(g)$ were reported by Porter and Sholette.[3] Using these data the corresponding enthalpy changes were evaluated by both the 2nd and 3rd law methods.

Reaction	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 3rd law	2nd law	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
(1)	−5.90	+6.52 ± 4.5	−304.0 ± 5.0
(2)**	−11.11	—	−287.6 ± 2.0
	−12.21	—	−272.5 ± 2.0
(3)	−2.0	—	−314 ± 12.0

**The initial system for the first set of measurements was $B_2H_6(g)$ + $B(OH)_3(cr)$.
That for the second set was $B_2H_6(g)$ + $B_2O_3(gl)$.

The value of $\Delta_f H°(298.15\ K)$ for $B_3O_3H_3(g)$ adopted is a weighted average of these $\Delta_f H°(298.15\ K)$ values listed.

Heat Capacity and Entropy

The infrared spectrum os solid boroxin has been determined by Gupta and Porter[4] and a partial assignment was made. The infrared spectra of the gas has also been reported by Lee, Bauer, and Wiberley[5] and is in essential agreement with the solid. The assignment of the frequencies has been changed slightly due to the non–appearance of the band at 1115 cm^{-1} in the gas phase. The assumed D_{3h} symmetry has 14 vibrations of the type $3A_1'$, $2A_2'$, 5E', $2A_2''$, and 2E'', and 7 estimated frequencies were obtained by comparison with $B_3O_6H_3$, by Parsons.[6]

The point group, bond angles and bond lengths were assumed to be the same as for $(BOF)_3(g)$. The B–H bond length was taken as the sum of the single covalent radii of the atoms. The principal moments of inertia are: $I_A = I_B$ = 13.9710 × 10^{-39}, and I_C = 27.9421 × 10^{-39} $g·cm^2$.

References

[1]W. P. Sholette and R. F. Porter, J. Phys. Chem. **67**, 177 (1963).
[2]R. F. Porter and S. K. Gupta, J. Phys. Chem. **68**, 280 (1964).
[3]R. F. Porter and W. P. Sholette, J. Phys. Chem. **37**, 198 (1962).
[4]S. K. Gupta and R. F. Porter, J. Phys. Chem. **67**, 1286 (1963).
[5]G. H. Lee, W. H. Bauer,and S. E. Wiberley, J. Phys. Chem. **67**, 1742 (1963).
[6]J. L. Parsons, J. Phys. Chem. **33**, 1860 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.846	−1205.022	−1205.022	INFINITE
100	44.531	223.177	355.472	−13.230	−1210.334	−1191.454	622.352
200	67.194	261.217	299.274	−7.612	−1214.122	−1171.045	305.846
250	77.761	277.347	293.296	−3.987	−1215.892	−1160.070	242.383
298.15	87.831	291.907	291.907	0.	−1217.544	−1149.168	201.329
300	88.213	292.451	291.909	0.163	−1217.606	−1148.743	200.014
350	98.298	306.813	293.020	4.828	−1219.211	−1137.138	169.708
400	107.750	320.564	295.609	9.982	−1220.690	−1125.310	146.950
450	116.426	333.765	299.120	15.590	−1222.032	−1113.306	129.229
500	124.290	346.445	303.223	21.611	−1223.226	−1101.160	115.037
600	137.736	370.338	312.444	34.736	−1225.177	−1076.554	93.722
700	148.586	392.415	322.312	49.072	−1226.596	−1051.664	78.476
800	157.375	412.850	332.369	64.385	−1227.565	−1026.603	67.030
900	164.538	431.814	342.377	80.493	−1228.173	−1001.443	58.122
1000	170.415	449.464	352.214	97.250	−1228.501	−976.231	50.993
1100	175.270	465.941	361.812	114.542	−1228.621	−950.996	45.159
1200	179.307	481.370	371.139	132.277	−1228.594	−925.758	40.297
1300	182.687	495.859	380.182	150.381	−1228.469	−900.526	36.184
1400	185.535	509.505	388.936	168.796	−1228.290	−875.306	32.658
1500	187.952	522.390	397.408	187.474	−1228.089	−850.100	29.603
1600	190.014	534.588	405.604	206.375	−1227.895	−824.908	26.930
1700	191.786	546.162	413.534	225.467	−1227.729	−799.726	24.573
1800	193.316	557.169	421.211	244.724	−1227.611	−774.553	22.477
1900	194.646	567.657	428.645	264.124	−1227.554	−749.385	20.602
2000	195.807	577.671	435.848	283.648	−1227.571	−724.218	18.915
2100	196.826	587.250	442.831	303.280	−1227.673	−699.048	17.388
2200	197.725	596.428	449.605	323.009	−1227.866	−673.871	16.000
2300	198.521	605.235	456.182	342.822	−1228.157	−648.684	14.732
2400	199.228	613.699	462.570	362.710	−1379.331	−620.275	13.500
2500	199.860	621.845	468.779	382.665	−1380.068	−588.633	12.299
2600	200.427	629.695	474.818	402.680	−1380.819	−556.961	11.189
2700	200.936	637.269	480.695	422.748	−1381.588	−525.259	10.162
2800	201.396	644.585	486.418	442.865	−1382.377	−493.528	9.207
2900	201.812	651.659	491.995	463.026	−1383.188	−461.770	8.317
3000	202.190	658.507	497.432	483.227	−1384.024	−429.983	7.487
3100	202.534	665.143	502.735	503.463	−1384.886	−398.167	6.709
3200	202.848	671.578	507.912	523.732	−1385.775	−366.324	5.980
3300	203.136	677.825	512.966	544.032	−1386.692	−334.452	5.294
3400	203.399	683.893	517.905	564.359	−1387.639	−302.551	4.648
3500	203.642	689.792	522.732	584.711	−1388.614	−270.623	4.039
3600	203.865	695.532	527.453	605.086	−1389.620	−238.666	3.463
3700	204.071	701.121	532.071	625.483	−1390.656	−206.682	2.918
3800	204.262	706.566	536.592	645.900	−1391.723	−174.667	2.401
3900	204.439	711.874	541.019	666.335	−1392.821	−142.624	1.910
4000	204.604	717.052	545.355	686.788	−1393.951	−110.555	1.444
4100	204.756	722.106	549.605	707.256	−1395.112	−78.455	1.000
4200	204.899	727.042	553.771	727.739	−2835.853	−25.255	0.314
4300	205.032	731.865	557.857	748.235	−2833.817	41.641	−0.506
4400	205.156	736.580	561.865	768.745	−2831.818	108.488	−1.288
4500	205.272	741.192	565.799	789.266	−2829.858	175.290	−2.035
4600	205.381	745.704	569.661	809.799	−2827.938	242.049	−2.749
4700	205.484	750.122	573.454	830.342	−2826.059	308.768	−3.432
4800	205.580	754.450	577.180	850.895	−2824.222	375.448	−4.086
4900	205.670	758.689	580.841	871.458	−2822.428	442.089	−4.713
5000	205.755	762.845	584.440	892.029	−2820.679	508.695	−5.314
5100	205.836	766.921	587.978	912.609	−2818.975	575.265	−5.892
5200	205.912	770.918	591.458	933.196	−2817.319	641.801	−6.447
5300	205.983	774.841	594.881	953.791	−2815.711	708.309	−6.981
5400	206.051	778.692	598.249	974.393	−2814.154	774.784	−7.495
5500	206.115	782.474	601.564	995.001	−2812.647	841.231	−7.989
5600	206.176	786.188	604.828	1015.616	−2811.193	907.654	−8.466
5700	206.234	789.838	608.042	1036.236	−2809.794	974.049	−8.926
5800	206.289	793.425	611.207	1056.862	−2808.450	1040.422	−9.370
5900	206.341	796.952	614.326	1077.494	−2807.163	1106.767	−9.799
6000	206.391	800.420	617.399	1098.131	−2805.936	1173.096	−10.213

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K)$ = [347.57] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−2252 ± 13] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−2272 ± 13] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[550] (1)	[250] (1)	[600] (2)
[1150] (1)	[500] (1)	[450] (2)
[950] (1)	[350] (1)	[3500] (2)
[3500] (1)	[750] (2)	[350] (2)
[1100] (1)	[900] (2)	[200] (2)
[600] (1)	[1300] (2)	[1000] (2)
[500] (1)	[1000] (2)	

Ground State Quantum Weight: 1 σ = 3
Point Group: C_{3h}
Bond Distances: B–O = [1.36] Å; O–H = [1.1] Å
Bond Angles: H–O–B = [120]°; O–B–O = [120]°; B–O–B = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.776533 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

The equilibrium constant, K_f (1451 K) = 0.9 for the reaction $H_3BO_3(l) + B_2O_3(l) = (HBO_2)_3(g)$ was reported by Meschi, Chupka and Berkowitz,[1] which was determined by means of mass spectrometry. The equilibrium constants of the reactions between water vapor and liquid B_2O_3 were determined at 1147 K by Blauer and Farber[2] by use of a transpiration method. From the reported value, $1.5\ K_2 + 0.5\ K_3 = 0.0342 \pm 0.0095$, the equilibrium constant, K_2, for the reaction $1.5\ B_2O_3(l) + 1.5\ H_2O(g) = (HBO_2)_3($ derived as 0.0168, using $K_3 = 0.0181$ for the reaction $0.5\ B_2O_3(l) + 1.5\ H_2O(g) = H_3BO_3(g)$ evaluated by use of JANAF values of $\Delta_f G°$ for $B_2O_3(l)$, $H_2O(g)$ and $H_3BO_3(g)$. Employing the equilibrium constants obtained, the respective enthalpy changes for the two reactions were calculated by the 3rd law method. The corresponding values of $\Delta_f H°(298.15\ K)$ for $(HBO_2)_3(g)$ were also derived.

Source	Chemical Reaction	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$	$\Delta_f H°(298.15$ $kcal·mol^{-1}$
Meschi, *et al.*[1]	$H_3BO_3(l) + B_2O_3(l) = (HBO_2)_3(g)$	−7.31	−543.8
Blauer and Farber[2]	$1.5\ B_2O_3(l) + 1.5\ H_2O(g) = (HBO_2)_3(g)$	−6.67	−542.3

The adopted value of $\Delta_f H°(298.15\ K)$ for $(HBO_2)_3(g)$ is the average of these two listed in the above table. The equilibrium constants for the same reactions between $B_2O_3(l)$ and $H_2O(g)$ were also determined by a transpiration method in the temperature region 1000–1273 K by Randall and Margrave.[3] The reported value, $\Delta_f H°(0\ K) = -537.5 \pm 3$ $kcal·mol^{-1}$ for $(HBO_2)_3(g)$, is in good agreement with the value adopted.

Heat Capacity and Entropy

All the molecular and spectroscopic constants were estimated by White, Mann, Walsh, and Sommer.[4] The principal moments of inertia are: $I_A = 43.6915 \times 10^{-39}$, $I_B = 45.5585 \times 10^{-39}$, and $I_C = 89.2499 \times 10^{-39}$ $g·cm^2$. The infrared absorption spectra for $B_3O_3(OH)_3$(cr) in the 430 to 4000 cm^{-1} was reported by Parsons.[5] A partial Raman spectrum was also given.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$		kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.763	−2252.282	−2252.282	INFINITE
100	51.541	251.641	441.169	−18.953	−2261.757	−2219.727	1159.467
200	96.849	301.091	358.876	−11.557	−2268.134	−2174.986	568.048
250	118.479	325.060	349.724	−6.166	−2270.324	−2151.434	449.518
298.15	137.265	347.567	347.567	0.	−2271.912	−2128.384	372.884
300	137.941	348.418	347.570	0.255	−2271.964	−2127.493	370.430
350	154.896	370.988	349.313	7.586	−2273.117	−2103.317	313.903
400	169.352	392.642	353.386	15.702	−2273.876	−2079.004	271.490
450	181.535	413.313	358.906	24.483	−2274.320	−2054.616	238.494
500	191.764	432.985	365.338	33.823	−2274.508	−2030.192	212.093
600	207.660	469.433	379.702	53.839	−2274.309	−1981.336	172.491
700	219.256	502.359	394.912	75.213	−2273.571	−1932.560	144.209
800	228.061	532.236	410.239	97.597	−2272.474	−1883.916	123.007
900	235.010	559.514	425.332	120.764	−2271.132	−1835.424	106.525
1000	240.666	584.577	440.020	144.557	−2269.617	−1787.093	93.348
1100	245.378	607.742	454.228	168.866	−2267.983	−1738.918	82.574
1200	249.367	629.269	467.929	193.608	−2266.271	−1690.896	73.603
1300	252.782	649.367	481.121	218.720	−2264.515	−1643.019	66.017
1400	255.730	668.211	493.818	244.149	−2262.741	−1595.278	59.521
1500	258.293	685.944	506.042	269.853	−2260.976	−1547.665	53.894
1600	260.531	702.686	517.813	295.797	−2259.240	−1500.167	48.975
1700	262.495	718.541	529.159	321.950	−2257.550	−1452.777	44.638
1800	264.225	733.595	540.102	348.288	−2255.925	−1405.486	40.786
1900	265.756	747.923	550.666	374.788	−2254.376	−1358.282	37.342
2000	267.115	761.590	560.873	401.433	−2252.917	−1311.156	34.244
2100	268.325	774.652	570.744	428.206	−2251.556	−1264.102	31.443
2200	269.406	787.160	580.299	455.094	−2250.302	−1217.109	28.898
2300	270.376	799.157	589.555	482.084	−2249.163	−1170.173	26.575
2400	271.248	810.683	598.531	509.166	−2398.922	−1120.077	24.378
2500	272.034	821.772	607.240	536.331	−2398.262	−1066.805	22.290
2600	272.745	832.456	615.698	563.570	−2397.633	−1013.560	20.363
2700	273.389	842.761	623.918	590.877	−2397.039	−960.337	18.579
2800	273.975	852.715	631.912	618.246	−2396.482	−907.135	16.923
2900	274.509	862.338	639.693	645.671	−2395.966	−853.955	15.381
3000	274.997	871.653	647.271	673.146	−2395.492	−800.790	13.943
3100	275.444	880.677	654.655	700.669	−2395.062	−747.639	12.598
3200	275.854	889.429	661.856	728.234	−2394.676	−694.505	11.337
3300	276.231	897.923	668.881	755.839	−2394.335	−641.380	10.152
3400	276.578	906.175	675.740	783.479	−2394.038	−588.264	9.038
3500	276.899	914.197	682.439	811.153	−2393.788	−535.157	7.987
3600	277.196	922.002	688.985	838.858	−2393.583	−482.056	6.994
3700	277.471	929.600	695.386	866.592	−2393.424	−428.962	6.056
3800	277.726	937.003	701.648	894.352	−2393.311	−375.867	5.167
3900	277.963	944.220	707.775	922.136	−2393.242	−322.776	4.323
4000	278.184	951.261	713.775	949.944	−2393.220	−269.690	3.522
4100	278.390	958.132	719.651	977.773	−2393.243	−216.601	2.760
4200	278.583	964.843	725.410	1005.621	−3832.860	−142.439	1.771
4300	278.763	971.401	731.054	1033.489	−3829.713	−54.608	0.663
4400	278.931	977.811	736.590	1061.374	−3826.619	33.148	−0.394
4500	279.089	984.081	742.020	1089.275	−3823.576	120.834	−1.403
4600	279.238	990.217	747.349	1117.191	−3820.587	208.453	−2.367
4700	279.378	996.224	752.581	1145.122	−3817.655	296.011	−3.290
4800	279.509	1002.107	757.718	1173.066	−3814.779	383.505	−4.173
4900	279.633	1007.872	762.765	1201.024	−3811.962	470.942	−5.020
5000	279.750	1013.522	767.724	1228.993	−3809.206	558.321	−5.833
5100	279.860	1019.063	772.598	1256.973	−3806.514	645.645	−6.613
5200	279.964	1024.498	777.390	1284.965	−3803.886	732.913	−7.362
5300	280.063	1029.832	782.103	1312.966	−3801.326	820.138	−8.083
5400	280.157	1035.068	786.739	1340.977	−3798.837	907.310	−8.776
5500	280.245	1040.209	791.301	1368.997	−3796.420	994.437	−9.444
5600	280.329	1045.260	795.791	1397.026	−3794.079	1081.525	−10.088
5700	280.409	1050.222	800.211	1425.063	−3791.816	1168.568	−10.709
5800	280.485	1055.100	804.564	1453.108	−3789.635	1255.576	−11.308
5900	280.557	1059.895	808.851	1481.160	−3787.539	1342.538	−11.886
6000	280.626	1064.611	813.075	1509.219	−3785.531	1429.475	−12.445

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 288.72\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -484.5 \pm 13\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -510.0 \pm 13\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
3450 (1)	3400 (2)
[554] (1)	[339] (1)
[266] (1)	528 (1)

Ground State Quantum Weight: 1 $\sigma = 6$
Point Group: D_{3h}
Bond Distances: B–N = 1.44 Å; B–H = 1.20 Å; H–N = 1.02 Å
Bond Angles: N–B–N = 120°; B–N–B = 120°; N–B–H = 120°
Product of the Moments of Inertia: $I_A I_B I_C = 8.326395 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of combustion for the reaction $B_3N_3H_6(l) + 15/4\ O_2(g) + 3/2\ H_2O(l) = 3\ H_3BO_3(c) + 3/2\ N_2(g)$ was reported to be -552.9 ± 3.0 kcal·mol^{-1} by Kilday, Johnson and Prosen.[1] $\Delta_f H°(H_3BO_3, cr, 298.15\ K) = -261.47$ kcal·mol^{-1} from JANAF tables were used to calculate $\Delta_f H°(B_3N_3H_6, l, 298.15\ K) = -129.0 \pm 3.0$ kcal·mol^{-1}. Vapor pressure data on $B_3N_3H_6(l)$ reported by Stock and Pohland[3] were fitted to a linear least squares. ΔC_p(l–g) for borazine was approximated by benzene to calculate a 2nd law $\Delta_{vap} H°(298.15\ K) = 7.1 \pm 0.1$ kcal·mol^{-1}.

Heat Capacity and Entropy

The fundamental frequency assignment was made by Crawford and Edsall.[4] The three frequencies enclosed by brackets are calculated values. The principal moments of inertia are calculated from molecular constants given by Bauer.[5] The principal moments of inertia are: $I_A = I_B = 16.0870 \times 10^{-39}$, and $I_C = 32.1740 \times 10^{-39}\ g·cm^2$.

References

[1]M. V. Kilday, W. H. Johnson, and E. J. Prosen, J. Res. Nat. Bur. Stand. **65A**, 101 (1961).
[2]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1962).
[3]A. Stock and E. Pohland, Ber. **59**, 2215 (1926).
[4]B. L. Crawford, Jr. and J. T. Edsall, J. Chem. Phys. **7**, 223 (1939).
[5]S. H. Bauer, J. Am. Chem. Soc. **60**, 524 (1938).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.515	−484.495	−484.495	INFINITE
100	39.386	222.416	352.981	−13.056	−494.460	−462.420	241.543
200	65.053	256.820	296.554	−7.947	−502.796	−427.066	111.538
250	81.262	273.063	290.231	−4.292	−506.627	−407.685	85.181
298.15	96.927	288.723	288.723	0.	−510.030	−388.315	68.031
300	97.516	289.324	288.725	0.180	−510.154	−387.560	67.480
350	112.826	305.522	289.969	5.444	−513.304	−366.873	54.753
400	126.782	321.515	292.916	11.440	−516.075	−345.761	45.152
450	139.307	337.185	296.967	18.098	−518.480	−324.323	37.646
500	150.485	352.452	301.756	25.348	−520.537	−302.637	31.616
600	169.391	381.623	312.662	41.377	−523.714	−258.739	22.525
700	184.667	408.922	324.486	59.105	−525.828	−214.396	15.998
800	197.230	434.427	336.652	78.220	−527.084	−169.811	11.088
900	207.712	458.281	348.856	98.482	−527.656	−125.111	7.261
1000	216.552	480.636	360.928	119.708	−527.689	−80.378	4.198
1100	224.064	501.637	372.775	141.748	−527.300	−35.662	1.693
1200	230.486	521.416	384.346	164.484	−526.590	9.003	−0.392
1300	236.003	540.088	395.614	187.815	−525.636	53.598	−2.154
1400	240.763	557.756	406.571	211.659	−524.504	98.113	−3.661
1500	244.887	574.511	417.213	235.947	−523.246	142.543	−4.964
1600	248.475	590.433	427.546	260.619	−521.905	186.885	−6.101
1700	251.610	605.593	437.577	285.627	−520.514	231.142	−7.102
1800	254.359	620.054	447.316	310.928	−519.102	275.316	−7.989
1900	256.779	633.872	456.774	336.488	−517.691	319.412	−8.781
2000	258.918	647.099	465.962	362.274	−516.299	363.434	−9.492
2100	260.815	659.778	474.891	388.263	−514.942	407.387	−10.133
2200	262.503	671.951	483.574	414.430	−513.632	451.277	−10.715
2300	264.011	683.654	492.020	440.758	−512.379	495.108	−11.244
2400	265.363	694.919	500.241	467.228	−661.971	542.093	−11.798
2500	266.579	705.777	508.247	493.826	−661.093	592.244	−12.374
2600	267.675	716.254	516.047	520.539	−660.198	642.360	−12.905
2700	268.666	726.375	523.650	547.357	−659.291	692.441	−13.396
2800	269.565	736.162	531.066	574.269	−658.378	742.488	−13.851
2900	270.382	745.636	538.303	601.267	−657.465	792.503	−14.275
3000	271.128	754.815	545.367	628.343	−656.555	842.487	−14.669
3100	271.809	763.717	552.268	655.491	−655.652	892.439	−15.038
3200	272.433	772.356	559.012	682.703	−654.759	942.364	−15.383
3300	273.006	780.748	565.604	709.976	−653.880	992.261	−15.706
3400	273.534	788.906	572.053	737.303	−653.018	1042.130	−16.010
3500	274.020	796.843	578.362	764.681	−652.174	1091.975	−16.297
3600	274.469	804.568	584.539	792.106	−651.351	1141.796	−16.567
3700	274.885	812.094	590.588	819.574	−650.551	1191.595	−16.822
3800	275.270	819.430	596.514	847.082	−649.777	1241.373	−17.064
3900	275.628	826.585	602.322	874.627	−649.030	1291.130	−17.293
4000	275.961	833.568	608.016	902.207	−648.311	1340.868	−17.510
4100	276.272	840.386	613.601	929.818	−647.623	1390.589	−17.716
4200	276.561	847.047	619.080	957.460	−2086.514	1461.366	−18.175
4300	276.832	853.558	624.458	985.130	−2082.627	1545.794	−18.778
4400	277.086	859.925	629.737	1012.826	−2078.778	1630.131	−19.352
4500	277.323	866.154	634.922	1040.547	−2074.970	1714.381	−19.900
4600	277.546	872.252	640.015	1068.290	−2071.202	1798.547	−20.423
4700	277.756	878.223	645.020	1096.055	−2067.477	1882.632	−20.923
4800	277.953	884.073	649.940	1123.841	−2063.794	1966.639	−21.401
4900	278.138	889.806	654.776	1151.646	−2060.155	2050.567	−21.859
5000	278.313	895.427	659.533	1179.468	−2056.561	2134.424	−22.298
5100	278.478	900.940	664.213	1207.308	−2053.011	2218.207	−22.719
5200	278.635	906.349	668.818	1235.164	−2049.505	2301.923	−23.123
5300	278.782	911.658	673.350	1263.035	−2046.044	2385.571	−23.511
5400	278.922	916.870	677.811	1290.920	−2042.627	2469.155	−23.884
5500	279.055	921.990	682.204	1318.819	−2039.254	2552.674	−24.243
5600	279.180	927.019	686.531	1346.730	−2035.924	2636.134	−24.589
5700	279.299	931.961	690.794	1374.655	−2032.637	2719.535	−24.922
5800	279.413	936.820	694.994	1402.590	−2029.392	2802.878	−25.243
5900	279.521	941.597	699.133	1430.537	−2026.189	2886.164	−25.552
6000	279.623	946.296	703.214	1458.494	−2023.026	2969.398	−25.851

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K) = [208.4 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1088\ K$

$\Delta_f H°(0\ K) = Unknown$
$\Delta_f H°(298.15\ K) = -3334.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 104.5 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was recalculated from the experimental data of Shartsis and Capps.[1] They studied the enthalpy of solution of various alkali borates in 2N nitric acid. Average molecular weights were used for physical mixtures of the oxides B_2O_3 and R_2O (where R is either Li, Na, or K) rather than for the borate compounds $R_2O \cdot nB_2O_3$ present. These incorrect molecular weights led to spurious correlations and faulty conclusions. In reinterpreting the data, the steps followed were: (1) The calculation of the correct molecular weights and molar enthalpies of reaction; (2) The establishment that the enthalpy of formation of the borates from the oxides is linear with the mole fraction of B_2O_3 in the total original moles of oxides for the reactions

$$R_2O(cr) + nB_2O_3(gl) \rightarrow R_2O \cdot nB_2O_3(gls) \quad (I)$$
$$\text{and } R_2O(cr) + nB_2O_3(gl) \rightarrow R_2O \cdot nB_2O_3(cr) \quad (II)$$

With the enthalpy of formation being zero at 100 percent R_2O; (3) The evaluation of the least square fit of the line through the enthalpy of reaction data for reaction I and for reaction II: (4) The use of the proper weighting factors in applying least squares to adjust for both the sample size and the molecular weight of the mixture of borates used in each solution experiment.

Heat Capacity and Entropy

The enthalpy measurements of Smith,[2] in the range 298–973 K were smoothed graphically and were used to obtain a smooth set of C_p data. The heat capacity was extrapolated smoothly above this region. The entropy at 298.15 K is estimated from that of $Na_2B_4O_7$(cr) by using an average entropy change of $4.5 \pm 1.5\ cal \cdot K^{-1} \cdot mol^{-1}$ on substituting Na_2 by K_2.

Fusion Data

T_{fus} was given by Rollet.[3] The enthalpy of melting was obtained from the enthalpies of formation of the crystal and glass at 298.15 K combined with the enthalpy differences between 298.15 K and 1088 K. This involves a slight extrapolation of the crystal data and an uncertainty of about $1.0\ kcal \cdot mol^{-1}$.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]G. S. Smith, Ph. D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. Mic 59-2916 (1959).
[3]A. P. Rollet, Comp. Rend. **200**, 1763 (1935).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
90							
200							
250							
298.15	170.498	208.363	208.363	0.	−3334.230	−3136.756	549.547
300	171.335	209.420	208.366	0.316	−3334.297	−3135.531	545.944
400	206.271	263.696	215.530	19.267	−3342.152	−3067.880	400.624
500	232.798	312.737	230.150	41.293	−3343.971	−2999.075	313.311
600	250.538	356.839	247.657	65.509	−3344.817	−2930.004	255.080
700	262.379	396.388	266.130	91.181	−3345.149	−2860.838	213.478
800	271.123	432.022	284.677	117.876	−3345.218	−2791.644	182.276
900	277.399	464.322	302.871	145.306	−3345.200	−2722.448	158.007
1000	283.257	493.860	320.514	173.346	−3345.151	−2653.256	138.592
1088.000	287.723	517.940	335.520	198.474	--- CRYSTAL <--> LIQUID ---		
1100	288.282	521.099	337.527	201.930	−3503.006	−2574.848	122.269
1200	292.478	546.369	353.890	230.975	−3500.895	−2490.563	108.411
1300	295.842	569.918	369.612	260.398	−3498.737	−2406.456	96.693
1400	298.374	591.940	384.715	290.115	−3496.583	−2322.515	86.654
1500	300.076	612.589	399.226	320.045	−3494.495	−2238.727	77.959

PREVIOUS: CURRENT: March 1963

$S°(298.15\ K) = [237.120]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1088\ K$

$\Delta_f H°(298.15\ K) = [-3289.042]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 104.5 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is obtained form reaction (1), as given on the crystal table.

Heat Capacity and Entropy

The enthalpy measurements of Smith[1] in the range 298 to 1373 K on the glass and liquid were smoothed graphically and used to determine C_p. There is a discontinuity (glass transition) in the C_p curve at 676 K. Above 1373 K the C_p values were extrapolated smoothly.

The entropy at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}S°$ and the entropy differences, $S°(1088\ K)–S°(298.15\ K)$, between the crystal and liquid.

Fusion Data

Refer to the crystal table for details.

Reference

[1]G. S. Smith, Ph. D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. Mic 59–2916 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
250							
298.15	170.498	237.120	237.120	0.	−3289.042	−3100.143	543.132
300	171.335	238.177	237.124	0.316	−3289.110	−3098.971	539.579
400	206.271	292.453	244.287	19.266	−3296.965	−3034.195	396.225
500	232.840	341.499	258.908	41.296	−3298.781	−2968.266	310.093
600	250.538	385.610	276.416	65.516	−3299.623	−2902.072	252.648
676.000	259.821	416.068	290.428	84.933	GLASS <--> LIQUID		
676.000	369.237	416.068	290.428	84.933	TRANSITION		
700	375.221	429.053	294.959	93.866	−3297.277	−2835.830	211.612
800	402.501	480.977	315.000	132.781	−3285.126	−2770.715	180.909
900	426.266	529.790	336.181	174.249	−3271.070	−2707.239	157.124
1000	446.558	575.818	357.866	217.952	−3255.357	−2645.420	138.183
1088.000	457.879	613.958	377.052	257.753	--- CRYSTAL <--> LIQUID ---		
1100	459.361	618.988	379.664	263.257	−3396.492	−2576.011	122.325
1200	471.143	659.470	401.312	309.790	−3376.892	−2502.281	108.921
1300	481.913	697.614	422.651	357.452	−3356.496	−2430.219	97.647
1400	491.670	733.691	443.591	406.139	−3335.372	−2359.755	88.044
1500	500.406	767.916	464.082	455.752	−3313.601	−2290.825	79.774
1600	507.268	800.434	484.096	506.140	−3291.314	−2223.364	72.585
1700	513.544	831.378	503.622	557.186	−3268.619	−2157.310	66.286
1800	519.234	860.896	522.657	608.830	−3245.569	−2092.603	60.726
1900	524.339	888.108	541.207	661.013	−3222.218	−2029.185	55.786
2000	528.858	916.121	559.282	713.678	−3198.621	−1967.003	51.373
2100	532.188	942.006	576.895	766.732	−3174.868	−1906.006	47.409
2200	535.234	966.835	594.059	820.106	−3151.032	−1846.140	43.833
2300	537.995	990.689	610.789	873.770	−3127.143	−1787.363	40.592
2400	540.472	1013.639	627.099	927.696	−3304.266	−1725.350	37.551
2500	542.665	1035.747	643.005	981.855	−3280.672	−1660.046	34.685
2600	544.573	1057.069	658.523	1036.219	−3256.986	−1595.688	32.058
2700	546.196	1077.653	673.668	1090.760	−3233.240	−1532.242	29.643
2800	547.535	1097.542	688.453	1145.449	−3209.468	−1469.676	27.417
2900	548.589	1116.775	702.893	1200.257	−3185.701	−1407.963	25.360
3000	549.359	1135.387	717.001	1255.157	−3161.975	−1347.065	23.454

PREVIOUS: CURRENT: March 1963

298.15	to 1088 K	crystal
above	1088 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	170.498	208.363	208.363	0.	−3334.230	−3136.756	549.547
300	171.335	209.420	208.366	0.316	−3334.297	−3135.531	545.944
400	206.271	263.696	215.530	19.267	−3342.152	−3067.880	400.624
500	232.798	312.737	230.150	41.293	−3343.971	−2999.075	313.311
600	250.538	356.839	247.657	65.509	−3344.817	−2930.004	255.080
700	262.379	396.388	266.130	91.181	−3345.149	−2860.838	213.478
800	271.123	432.022	284.677	117.876	−3345.218	−2791.644	182.276
900	277.399	464.322	302.871	145.306	−3345.200	−2722.448	158.007
1000	283.257	493.860	320.514	173.346	−3345.151	−2653.256	138.592
1088.000	287.723	517.940	335.520	198.474	CRYSTAL <--> LIQUID		
1088.000	457.879	613.958	335.520	302.940	TRANSITION		
1100	459.361	618.988	338.585	308.444	−3396.492	−2576.011	122.325
1200	471.143	659.470	363.656	354.978	−3376.892	−2502.281	108.921
1300	481.913	697.614	387.892	402.639	−3356.496	−2430.219	97.647
1400	491.670	733.691	411.315	451.327	−3335.372	−2359.755	88.044
1500	500.406	767.916	433.957	500.939	−3313.601	−2290.825	79.774
1600	507.268	800.434	455.854	551.327	−3291.314	−2223.364	72.585
1700	513.544	831.378	477.041	602.373	−3268.619	−2157.310	66.286
1800	519.234	860.896	497.553	654.017	−3245.569	−2092.603	60.726
1900	524.339	889.108	517.424	706.200	−3222.218	−2029.185	55.786
2000	528.858	916.121	536.688	758.865	−3198.621	−1967.003	51.373
2100	532.188	942.006	555.377	811.920	−3174.868	−1906.006	47.409
2200	535.234	966.835	573.519	865.293	−3151.033	−1846.140	43.833
2300	537.995	990.689	591.142	918.957	−3127.143	−1787.363	40.592
2400	540.472	1013.639	608.271	972.883	−3304.266	−1725.350	37.551
2500	542.665	1035.747	624.931	1027.042	−3280.672	−1660.046	34.685
2600	544.573	1057.069	641.144	1081.406	−3256.986	−1595.688	32.058
2700	546.196	1077.653	656.932	1135.947	−3233.240	−1532.242	29.643
2800	547.535	1097.542	672.315	1190.636	−3209.468	−1469.676	27.417
2900	548.589	1116.775	687.311	1245.445	−3185.701	−1407.963	25.360
3000	549.359	1135.387	701.938	1300.344	−3161.975	−1347.065	23.454

PREVIOUS: CURRENT: March 1963

$S°(298.15\ K) = [155.6 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1190 \pm 2\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = -3362.3 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° \approx 120.5 \pm 6.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from $\Delta_r H°(298.15\ K) = -12.2$ kcal for the reaction $Li_2B_4O_7(cr) + 2\ HNO_3(aq) + 5\ H_2O(l) = 4\ H_3BO_3(aq) + 2\ LiNO_3(aq)$. Capps[1] Auxilliary data are from National Bureau of Standards Circular 500.[2]

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 1190 K were smoothed graphically and used to determine C_p. A linear extrapolation of C_p was used from 1190 to 2000 K.

$S°(298.15\ K)$ was estimated by three routes: (1) $S°(Li_2B_4O_7, cr, 298.15\ K) = 37.3\ cal \cdot K^{-1} \cdot mol^{-1}$ based on JANAF $S°(Na_2B_4O_7, cr, 298.15\ K) = 45.3$ and $\Delta S°(2Na–2Li, 298.15\ K) = 8\ cal \cdot K^{-1} \cdot mol^{-1}$ from Latimer;[4] (2) $S°(Li_2B_4O_7, cr, 298.15\ K) = 36.7\ cal\ K^{-1} \cdot mol^{-1}$ in a similar manner based on $\Delta_f S°(2Na^+–2Li^+, 298.15\ K) = 8.6\ cal \cdot K^{-1} \cdot mol^{-1}$ from Kelley,[5] and (3) $S°(Li_2B_4O_7, cr, 298.15\ K) = 37.6\ cal \cdot K^{-1} \cdot mol^{-1}$ based on addition of the JANAF entropies for $2LiBO_2$ and B_2O_3. The value adopted is an average of these estimates.

Fusion Data

The value for T_{fus} is from Sastry and Hummel.[6] Rollet and Bouaziz[7] earlier reported $T_{fus} = 1188$ K. $\Delta_{fus} H° = 28.8\ kcal \cdot mol^{-1}$ is from Smith.[3]

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[3]G. S. Smith, Ph. D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. Mic 59–2916 (1959).
[4]W. M. Latimer, J. Am. Chem. Soc. **73**, 1480 (1951).
[5]K. K. Kelley, U. S. Bur. Mines, personal communication, (June, 1960).
[6]B. S. R. Sastry and F. A. Hummel, J. Am. Chem. Soc. **42**, 216 (1959).
[7]A. P. Rollet and R. Bouaziz, Comp. Rend. **240**. 2417 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	183.050	155.645	155.645	0.	−3362.262	−3170.291	555.422
300	183.096	156.777	155.648	0.339	−3362.289	−3169.100	551.789
400	197.648	211.259	162.980	19.311	−3364.367	−3104.421	405.396
500	219.940	257.778	177.378	40.200	−3372.974	−3038.519	317.432
600	241.103	299.795	194.332	63.278	−3374.846	−2971.434	258.686
700	259.199	338.357	212.190	88.317	−3375.669	−2904.120	216.708
800	274.412	373.983	230.216	115.013	−3375.575	−2836.753	185.221
900	287.717	407.078	248.050	143.125	−3374.692	−2769.445	160.734
1000	300.424	438.042	265.517	172.525	−3373.030	−2702.277	141.152
1100	314.018	467.306	282.543	203.239	−3370.479	−2635.316	125.141
1190.000	327.010	492.501	297.475	232.080	--- CRYSTAL <--> LIQUID ---		
1200	327.180	495.378	299.118	235.511	−3366.736	−2568.641	111.810
1300	340.343	522.086	315.249	268.887	−3362.211	−2502.310	100.544
1400	353.506	547.790	330.947	303.580	−3356.657	−2436.365	90.902
1500	366.669	572.628	346.236	339.589	−3350.045	−2370.856	82.561
1600	379.832	596.712	361.141	376.914	−3342.359	−2305.821	75.277
1700	392.995	620.135	375.690	415.555	−3624.059	−2226.948	68.426
1800	406.158	642.970	389.908	455.513	−3612.686	−2145.089	62.249
1900	419.320	665.283	403.816	496.786	−3600.229	−2063.890	56.740
2000	432.483	687.126	417.437	539.377	−3586.685	−1983.375	51.800

PREVIOUS: December 1962 CURRENT: June 1965

$S°(298.15\ K) = [173.375]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1190 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-3317.715]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 120.5 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding the enthalpy of fusion and the difference in enthalpy, $H°$(1190 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The enthalpy measurements of Smith[1] in the range 296 to 1373 K were smoothed graphically and used to determine C_p. The C_p data have a discontinuity at about 756 K. A linear extrapolation of C_p was used from 1373 to 3000 K.

The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Reference

[1] G. S. Smith, Ph. D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. Mic. 59–2916 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	181.146	173.375	173.375	0.	−3317.715	−3131.030	548.543
300	181.586	174.497	173.379	0.336	−3317.745	−3129.872	544.959
400	205.225	229.974	180.784	19.676	−3319.455	−3066.995	400.508
500	228.869	278.308	195.547	41.381	−3327.246	−3003.056	313.727
600	252.513	322.126	213.043	65.450	−3328.127	−2938.114	255.786
700	276.157	362.827	231.565	91.883	−3327.555	−2873.135	214.396
756.115	289.425	384.627	242.119	107.752	GLASS <--> LIQUID TRANSITION		
756.115	455.516	384.627	242.119	107.752			
800	456.746	410.361	250.649	127.769	−3318.272	−2808.552	183.380
900	459.549	464.319	271.448	173.584	−3299.686	−2745.956	159.371
1000	462.352	512.883	293.204	219.679	−3281.329	−2685.416	140.272
1100	465.156	557.081	315.213	266.055	−3263.117	−2626.707	124.732
1190.000	467.680	593.760	334.910	308.032	--- CRYSTAL <--> LIQUID ---		
1200	467.959	597.675	337.083	312.710	−3244.989	−2569.652	111.854
1300	470.762	635.243	358.592	359.646	−3226.905	−2514.108	101.018
1400	473.444	670.231	379.616	406.861	−3208.828	−2459.955	91.782
1500	475.836	702.977	400.094	454.325	−3190.762	−2407.096	83.823
1600	478.294	733.765	419.995	502.031	−3172.695	−2355.440	76.897
1700	480.818	762.836	439.315	549.986	−3445.081	−2290.563	70.380
1800	483.408	790.392	458.061	598.196	−3425.455	−2223.218	64.516
1900	486.063	816.600	476.247	646.669	−3405.799	−2156.962	59.299
2000	488.785	841.600	493.895	695.411	−3386.104	−2091.743	54.631
2100	491.572	865.515	511.026	744.429	−3366.359	−2027.510	50.432
2200	494.425	888.449	527.663	793.728	−3346.557	−1964.217	46.636
2300	497.344	910.491	543.832	843.316	−3326.690	−1901.830	43.192
2400	500.328	931.721	559.554	893.199	−3507.788	−1836.032	39.960
2500	503.379	952.207	574.853	943.384	−3488.083	−1766.780	36.915
2600	506.495	972.010	589.750	993.877	−3468.163	−1698.320	34.120
2700	509.677	991.185	604.264	1044.685	−3448.023	−1630.630	31.546
2800	512.925	1009.779	618.417	1095.814	−3427.657	−1563.690	29.171
2900	516.239	1027.837	632.225	1147.275	−3407.059	−1497.485	26.973
3000	519.297	1045.390	645.706	1199.054	−3386.242	−1431.991	24.933

PREVIOUS: December 1962 CURRENT: June 1965

298.15	to	1190 K	crystal
above		1190 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
250							
298.15	183.050	155.645	155.645	0.	−3362.262	−3170.291	555.422
300	183.096	156.777	155.648	0.339	−3362.289	−3169.100	551.789
400	197.648	211.259	162.980	19.311	−3364.367	−3104.421	405.396
500	219.940	257.778	177.378	40.200	−3372.974	−3038.519	317.432
600	241.103	299.795	194.332	63.278	−3374.846	−2971.434	258.686
700	259.199	338.357	212.190	88.317	−3375.669	−2904.120	216.708
800	274.412	373.983	230.216	115.013	−3375.575	−2836.753	185.221
900	287.717	407.078	248.050	143.125	−3374.692	−2769.445	160.734
1000	300.424	438.042	265.517	172.525	−3373.030	−2702.277	141.152
1100	314.018	467.306	282.543	203.239	−3370.479	−2635.316	125.141
1190.000	327.010	492.501	297.475	232.080	CRYSTAL <--> LIQUID TRANSITION		
1190.000	467.680	593.760	297.475	352.579			
1200	467.960	597.675	299.961	357.257	−3244.989	−2569.652	111.854
1300	470.762	635.243	324.324	404.194	−3226.905	−2514.108	101.018
1400	473.444	670.231	347.797	451.408	−3208.828	−2459.955	91.782
1500	475.836	702.977	370.396	498.872	−3190.762	−2407.096	83.823
1600	478.294	733.765	392.154	546.578	−3172.695	−2355.440	76.897
1700	480.818	762.836	413.111	594.533	−3445.081	−2290.563	70.380
1800	483.408	790.392	433.312	642.744	−3425.455	−2223.218	64.516
1900	486.063	816.600	452.801	691.217	−3405.799	−2156.962	59.299
2000	488.785	841.600	471.621	739.958	−3386.104	−2091.743	54.631
2100	491.572	865.515	489.813	788.976	−3366.359	−2027.510	50.432
2200	494.425	888.449	507.415	838.275	−3346.557	−1964.217	46.636
2300	497.344	910.491	524.464	887.863	−3326.690	−1901.830	43.192
2400	500.328	931.721	540.993	937.746	−3507.788	−1836.032	39.960
2500	503.379	952.207	557.034	987.931	−3488.083	−1766.780	36.915
2600	506.495	972.010	572.616	1038.424	−3468.163	−1698.320	34.120
2700	509.677	991.185	587.766	1089.232	−3448.023	−1630.630	31.546
2800	512.925	1009.779	602.507	1140.361	−3427.657	−1563.690	29.171
2900	516.239	1027.837	616.864	1191.822	−3407.059	−1497.485	26.973
3000	519.297	1045.390	630.857	1243.601	−3386.242	−1431.991	24.933

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 51.92\ J·K^{-1}·mol^{-1}$
$T_{dcm} = [1100]\ K$

$\Delta_f H°(0\ K) = -104.7 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -105.0 \pm 8.4\ kJ·mol^{-1}$

Enthalpy of Formation

The equilibrium pressures (1169–1177 K) of the reaction $MgB_4(cr) \rightarrow Mg(g) + 4B(cr)$ were measured by Wright and Walsh.[1] The 3rd law value of $\Delta_r H°(298.15\ K)$ for this reaction is derived as $60.40 \pm 1.5\ kcal·mol^{-1}$. This leads to a $\Delta_f H°(298.15\ K) = -25.1 \pm 2.0\ kcal·mol^{-1}$ for $MgB_4(cr)$. The unit of equilibrium pressures reported should be in atmosphere not in mm Hg as printed. The diameter of the hole drilled through the center of the lid served as the effusion orifice should be 1/16 inch rather than the reported value 1/6 inch.

Heat Capacity and Entropy

The low temperature (17.34–299.53 K) heat capacities were measured by Swift and White.[2] Above 298.15 K the C_p values are estimated by comparison with those of other related borides. $S°(298.15\ K)$ was reported by Swift and White[2] using $S°(extrap., 20\ K) = 0.022\ cal·K^{-1}·mol^{-1}$.

Decomposition Data

T_{dcm} was estimated from the decomposition reaction reported by Wright and Walsh.[1]

References

[1]M. Wright and P. N. Walsh, Ohio State Univ. Research Foundation, 'Technical Research Report OMCC–HEF–55, (January 9, 1958).
[2]R. M. Swift and D. White, J. Am. Chem. Soc. **79**, 3641 (1957).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.519	−104.683	−104.683	INFINITE
100	17.238	8.033	97.487	−8.945	−104.848	−104.578	54.626
200	46.275	28.702	57.635	−5.786	−105.028	−104.205	27.215
298.15	70.333	51.923	51.923	0.	−105.018	−103.801	18.185
300	70.710	52.360	51.925	0.130	−105.018	−103.793	18.072
400	79.496	73.935	54.807	7.651	−105.503	−103.339	13.495
500	87.027	92.491	60.529	15.981	−106.763	−102.664	10.725
600	94.140	109.006	67.256	25.050	−108.386	−101.695	8.853
700	99.956	123.955	74.305	34.755	−110.174	−100.440	7.495
800	105.730	137.684	81.380	45.043	−112.005	−98.924	6.459
900	111.043	150.450	88.354	55.887	−113.807	−97.180	5.640
1000	115.729	162.403	95.167	67.235	−124.164	−94.526	4.938
1100	118.512	173.561	101.793	78.945	−126.005	−91.473	4.344
1200	121.629	184.004	108.213	90.949	−127.787	−88.254	3.842
1300	125.525	193.897	114.427	103.311	−129.422	−84.892	3.411
1400	128.867	203.325	120.443	116.036	−258.297	−78.244	2.919
1500	131.587	212.311	126.270	129.062	−258.286	−65.382	2.277
1600	133.888	220.879	131.917	142.339	−258.193	−52.525	1.715
1700	135.562	229.046	137.393	155.811	−258.064	−39.674	1.219
1800	137.235	236.842	142.703	169.451	−257.921	−26.832	0.779
1900	138.909	244.307	147.855	183.258	−257.759	−13.998	0.385
2000	140.582	251.475	152.858	197.233	−257.573	−1.173	0.031

PREVIOUS: March 1963 CURRENT: March 1965

$S°(298.15\ K) = 189.49\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1015.6\ K$

$\Delta_f H°(0\ K) = -3259.0 \pm 8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -3276.7 \pm 8\ kJ·mol^{-1}$
$\Delta_{fus} H° = 76.9 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of the reaction $Na_2O(cr) + 2B_2O_3(l) \rightarrow Na_2B_4O_7(cr)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpy of formation using JANAF values[2] for $B_2O_3(l)$ and for $Na_2O(cr)$. The above $\Delta_r H° = -85.2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

In the low temperature region (5–344 K) the C_p values are those determined by Westrum and Grenier.[3] The enthalpy measurements of Smith[4] in the range 296 to 1015.6 K were smoothed graphically and used to determine C_p; the values did not join smoothly with those of Westrum and Grenier and the low temperature values were given greater weight. Above T_{fus} the heat capacity was extrapolated. $S°(298.15\ K)$ was derived from low temperature heat capacities.

Fusion Data

The value for T_{fus} is from Morey and Merwin.[5] Other reported values are: 1008 ± 5 K by Coles, Scholes, and Amberg;[6] 1011 K by Menzel;[7] 1005 K by Ponomareff;[8] 1015 K by Day and Allen;[9] and 1064 K by Burgess and Holt.[10] $\Delta_{fus} H°$ was obtained from the values of $\Delta_f H°$ for $Na_2B_4O_7(cr)$ and $Na_2B_4O_7(l)$ at 298.15 K as described above and the difference between $H°(1015\ K)$–$H°(298.15\ K)$ for crystal and liquid.

References

[1] L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2] JANAF Thermochemical Tables: $B_2O_3(l)$, 12–31–64; $Na_2O(cr)$, 6–30–62.
[3] E. F. Westrum, Jr. and G. Grenier, J. Am. Chem. Soc. **79**, 1799 (1957).
[4] G. S. Smith, Ph. D. Thesis, Penn. Stae Univ., Univ. Microfilms, Order No. Mic 59–2916 (1959).
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[6] S. S. Coles, S. R. Scholes, and C. R. Amberg, J. Am. Ceram. Soc. **18**, 58 (1935).
[7] H. Menzel, Z. anorg. Chem. **224**, 1 (1935).
[8] J. F. Ponomareff, Z. anorg. Chem. **89**, 383 (1924).
[9] A. L. Day and E. T. Allen, Carnegie Inst. of Washington, Publ. No. 31, 29 (1905).
[10] C. H. Burgess and Q. Holt, Proc. Roy. Soc. (London) **74**, 285 (1904).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−30.382	−3258.983	−3258.983	INFINITE
100	76.525	50.814	321.976	−27.116	−3268.658	−3208.196	1675.790
200	139.746	124.566	205.130	−16.113	−3274.087	−3145.347	821.480
298.15	186.774	189.490	189.490	0.	−3276.741	−3081.522	539.870
300	187.447	190.648	189.494	0.346	−3276.774	−3080.310	536.330
400	213.802	248.460	197.196	20.505	−3283.707	−3014.160	393.609
500	228.534	297.784	212.510	42.637	−3285.408	−2946.574	307.826
600	241.500	340.624	230.368	66.154	−3286.907	−2878.661	250.610
700	252.697	378.715	248.889	90.878	−3288.098	−2810.522	209.724
800	262.128	413.077	267.299	116.622	−3288.983	−2742.233	179.049
900	271.215	444.482	285.266	143.294	−3289.531	−2673.853	155.186
1000	279.700	473.502	302.657	170.845	−3289.721	−2605.430	136.094
1015.600	280.970	477.841	305.314	175.218	--- CRYSTAL <---> LIQUID ---		
1100	287.583	500.534	319.431	199.214	−3289.570	−2537.005	120.472
1200	294.863	525.874	335.589	228.342	−3482.640	−2463.728	107.243
1300	301.541	549.743	351.153	258.167	−3480.079	−2378.921	95.586
1400	307.616	572.316	366.152	288.630	−3477.180	−2294.323	85.602
1500	313.089	593.718	380.616	319.653	−3473.995	−2209.943	76.957
1600	320.013	614.144	394.577	351.307	−3470.439	−2125.786	69.400
1700	327.017	633.755	408.074	383.658	−3466.432	−2041.866	62.739
1800	334.105	652.647	421.139	416.714	−3461.958	−1958.196	56.825
1900	341.276	670.903	433.807	450.482	−3457.003	−1874.786	51.541
2000	348.527	688.592	446.106	484.972	−3451.552	−1791.650	46.793

PREVIOUS: March 1963 CURRENT: March 1965

$S°(298.15\ K) = [194.636]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1015.6\ K$

$\Delta_f H°(298.15\ K) = [-3256.658]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 76.9 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction $Na_2O(cr) + 2B_2O_3(l) \rightarrow Na_2B_4O_7(l)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for B_2O_3(l) and Na_2O(cr). The above $\Delta_f H° = -80.4\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 1373 K, were smoothed graphically and used to determine C_p. These were joined smoothly with the low temperature data of Westrum and Grenier.[4] At 743 K a glass transition was observed and above this temperature the C_p adopted as constant.

The entropy at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}S°$ and the difference in entropy, $S°(1015\ K) - S°(298.15\ K)$, between the crystal and liquid.

Fusion Data

Refer to the crystal table for details.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]JANAF Thermochemical Tables: B_2O_3(l), 12-31-64; Na_2O(cr), 6-30-62.
[3]G. S. Smith, Ph. D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. Mic 59-2916 (1959).
[4]E. F. Westrum, Jr. and G. Grenier, J. Am. Chem. Soc. **79**, 1799 (1957).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	187.443	194.636	194.636	0.	−3256.658	−3062.973	536.620
300	188.141	195.798	194.640	0.347	−3256.690	−3061.771	533.102
400	221.752	254.719	202.445	20.909	−3263.220	−2996.176	391.260
500	247.274	307.021	218.230	44.396	−3263.566	−2929.350	306.027
600	268.613	353.997	237.008	70.194	−3262.784	−2862.562	249.208
700	289.533	396.980	256.831	98.104	−3260.789	−2795.998	208.640
743.010	298.402	414.507	265.454	110.748	GLASS <--> LIQUID		
743.010	444.885	414.507	265.454	110.748	TRANSITION		
800	444.885	447.385	277.257	136.102	−3249.420	−2730.116	178.258
900	444.885	499.785	299.129	180.591	−3232.152	−2666.246	154.745
1000	444.885	546.658	321.579	225.079	−3215.404	−2604.270	136.033
1015.600	444.885	553.544	325.089	232.019	--- CRYSTAL <--> LIQUID ---		
1100	444.885	589.060	343.999	269.567	−3199.134	−2543.947	121.802
1200	444.885	627.770	366.057	314.056	−3376.842	−2480.207	107.961
1300	444.885	663.380	387.577	358.544	−3359.618	−2406.188	96.682
1400	444.885	696.350	408.469	403.033	−3342.693	−2333.483	87.063
1500	444.885	727.043	428.696	447.521	−3326.043	−2261.980	78.769
1600	444.885	755.756	448.249	492.010	−3309.653	−2191.579	71.548
1700	444.885	782.727	467.139	536.498	−3293.508	−2122.194	65.207
1800	444.885	808.156	485.385	580.987	−3277.602	−2053.755	59.598
1900	444.885	832.209	503.012	625.475	−3261.926	−1986.192	54.604
2000	444.885	855.029	520.047	669.964	−3246.476	−1919.448	50.131
2100	444.885	876.735	536.519	714.452	−3231.250	−1853.472	46.103
2200	444.885	897.431	552.458	758.941	−3216.243	−1788.214	42.458
2300	444.885	917.207	567.890	803.429	−3201.454	−1723.637	39.145
2400	444.885	936.141	582.842	847.918	−3387.918	−1655.423	36.029
2500	444.885	954.302	597.340	892.406	−3373.872	−1583.525	33.086
2600	444.885	971.751	611.407	936.895	−3359.910	−1512.187	30.380
2700	444.885	988.541	625.066	981.383	−3346.033	−1441.383	27.885
2800	444.885	1004.720	638.337	1025.872	−3332.239	−1371.092	25.578
2900	444.885	1020.332	651.242	1070.360	−3318.532	−1301.296	23.439
3000	444.885	1035.414	663.798	1114.848	−3304.911	−1231.967	21.450

PREVIOUS: March 1963 CURRENT: March 1965

0	to	1015.6 K	crystal
above		1015.6 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−30.382	−3258.983	−3258.983	INFINITE
100	76.525	50.814	321.976	−27.116	−3268.658	−3208.196	1675.790
200	139.746	124.566	205.130	−16.113	−3274.087	−3145.347	821.480
298.15	186.774	189.490	189.490	0.	−3276.741	−3081.522	539.870
300	187.447	190.648	189.494	0.346	−3276.774	−3080.310	536.330
400	213.802	248.460	197.196	20.505	−3283.707	−3014.160	393.609
500	228.534	297.784	212.510	42.637	−3285.408	−2946.574	307.826
600	241.500	340.624	230.368	66.154	−3286.907	−2878.661	250.610
700	252.697	378.715	248.889	90.878	−3288.098	−2810.522	209.724
800	262.128	413.077	267.299	116.622	−3288.983	−2742.233	179.049
900	271.215	444.482	285.266	143.294	−3289.531	−2673.853	155.186
1000	279.700	473.502	302.657	170.845	−3289.721	−2605.430	136.094
1015.600	280.970	477.841	305.314	175.218	CRYSTAL <--> LIQUID TRANSITION		
1015.600	444.885	553.544	305.314	252.102			
1100	444.885	589.060	325.741	289.651	−3199.134	−2543.946	120.802
1200	444.885	627.770	349.320	334.139	−3376.842	−2480.206	107.961
1300	444.885	663.379	372.127	378.628	−3359.618	−2406.187	96.682
1400	444.893	696.349	394.123	423.117	−3342.693	−2333.483	87.063
1500	444.885	727.043	415.306	467.605	−3326.043	−2261.980	78.769
1600	444.885	755.756	435.697	512.094	−3309.652	−2191.578	71.548
1700	444.885	782.727	455.325	556.582	−3293.507	−2122.194	65.207
1800	444.885	808.156	474.227	601.071	−3277.601	−2053.754	59.598
1900	444.885	832.209	492.441	645.559	−3261.925	−1986.191	54.604
2000	444.885	855.029	510.005	690.048	−3246.476	−1919.447	50.131
2100	444.885	876.735	526.956	734.536	−3231.249	−1853.471	46.103
2200	444.885	897.431	543.329	779.025	−3216.242	−1788.213	42.458
2300	444.885	917.207	559.158	823.513	−3201.453	−1723.636	39.145
2400	444.885	936.141	574.473	868.002	−3387.917	−1655.422	36.029
2500	444.885	954.302	589.306	912.490	−3373.871	−1583.524	33.086
2600	444.885	971.751	603.682	956.979	−3359.909	−1512.186	30.380
2700	444.885	988.541	617.627	1001.467	−3346.032	−1441.382	27.885
2800	444.885	1004.720	631.165	1045.956	−3332.239	−1371.091	25.578
2900	444.885	1020.332	644.317	1090.444	−3318.531	−1301.295	23.439
3000	444.885	1035.414	657.103	1134.933	−3304.910	−1231.967	21.450

PREVIOUS: CURRENT: March 1965

$S°(298.15\ K)$ = [166.9 ± 13] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K)$ = [−2858 ± 6] $kJ·mol^{-1}$

Enthalpy of Formation

See the PbB_2O_4(cr) table for the complete writeup. Evans[1] analysed the enthalpies of formation of lead borate system based upon Shartsis and Newman's enthalpies of solution and Mazzetti and DeCarli's phase studies. From the Shartsis and Newman paper Evans obtained the following:

$$PbO(cr) + 2B_2O_3(cr) \rightarrow PbO·2B_2O_3(gl) \qquad \Delta_r H = -11.9\ kcal·mol^{-1}$$

and estimated a $\Delta_f H°(298.15\ K)$ value of 11.4 $kcal·mol^{-1}$ for the conversion to the $PbO·2B_2O_3$(cr). With auxiliary JANAF values $\Delta_f H°(298.15\ K)$ is calculated to be −683.00 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The heat capacity employed in this table is obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 K is obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by Kelley and King.[2] These indicate for the reaction:

$$MO·B_2O_3 + B_2O_3 \rightarrow MO·2B_2O_3$$

that the simple addition of entropies will give values at least 2.7 $cal·K^{-1}·mol^{-1}$ in case of Na borates and 5.7 $cal·K^{-1}·mol^{-1}$ for Ca borates too high for the reaction. The reason for this is probably structural, the $B_4O_7^{=}$ ion is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the average entropy difference of 4.2 for the reaction was assumed to hold for each additional mole of B_2O_3. Therefore the entropy at 298.15 K is obtained from $S°(298.15\ K)$ for PbB_2O_4 and B_2O_3 and the subtraction of 4.2 $cal·K^{-1}·mol^{-1}$.

References

[1]W. H. Evans, U. S. Nat. Bur. Stand. Report 7192, Ch. 6 (July 1, 1961); refer to pp. 80–1.
[2]K. K. Kelly and E. G. King, U. S. Bur. Mines, Bull. 592, 149 pp. (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	168.197	166.942	166.942	0.	−2857.672	−2667.096	467.264
300	169.034	167.985	166.945	0.312	−2857.684	−2665.914	464.177
400	206.522	221.877	174.039	19.135	−2857.439	−2601.980	339.784
500	238.572	271.498	188.634	41.432	−2855.586	−2538.298	265.174
600	265.558	317.462	206.323	66.683	−2852.207	−2475.133	215.480
700	287.148	360.073	225.282	94.354	−2852.370	−2411.845	179.974
800	304.512	399.590	244.632	123.967	−2846.584	−2349.295	153.393
900	318.277	436.271	263.912	155.123	−2839.860	−2287.529	132.765
1000	330.034	470.433	282.876	187.558	−2832.345	−2226.555	116.303
1100	339.490	502.348	301.393	221.050	−2824.179	−2166.366	102.872
1200	347.021	532.225	319.398	255.393	−2815.507	−2106.944	91.713
1300	352.502	560.226	336.858	290.378	−2806.499	−2048.261	82.300
1400	356.853	586.512	353.761	325.851	−2797.295	−1990.279	74.258
1500	360.577	611.264	370.111	361.730	−2787.962	−1932.961	67.312
1600	363.422	634.629	385.920	397.935	−2778.570	−1876.267	61.254
1700	365.682	656.732	401.206	434.395	−2769.182	−1820.160	55.927
1800	367.397	677.685	415.989	471.052	−2759.850	−1764.606	51.208
1900	368.694	697.585	430.290	507.859	−2750.617	−1709.567	46.999
2000	369.740	716.524	444.132	544.782	−2741.512	−1655.011	43.224

PREVIOUS: December 1962 CURRENT: March 1965

$S°(298.15\ K) = 184.33\ J·K^{-1}·mol^{-1}$
$T_{fus} = 226.34\ K$

$\Delta_f H°(298.15\ K) = 42.84 \pm 6.7\ kJ·mol^{-1}$
$\Delta_{fus}H° = 6.134\ kJ·mol^{-1}$

Enthalpy of Formation

The vapor pressures of B_5H_9(l) were measured by Wirth and Palmer[1] and Johnston, Kerr, Clarke and Hallett.[2] By use of both the 2nd and 3rd law methods, the respective enthalpies of vaporization are evaluated. The $\Delta_f H°$(298.15 K) values for B_5H_9(l) are calculated from $\Delta_f H°$(298.15 K) for B_5H_9(g) and $\Delta_{vap}H°$(298.15 K) for B_5H_9(l) obtained previously.

Source	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Wirth and Palmer[1]	7.26 ± 0.02	7.26	10.24 ± 1.6
Johnston, *et al.*[2]	7.23 ± 0.04	7.25	10.23 ± 1.6

The adopted value is the average of the two $\Delta_f H°$(298.15 K) values obtained.

Heat Capacity and Entropy

The heat capacities, 231.34–290.19 K, for B_5H_9(l) were measured by Johnston, Kerr, Clarke and Hallett.[2] The C_p values above 290.19 K are estimated by graphical extrapolation of the C_p curve plotted using the experimental data. The value of $S°$(298.15 K) was derived based on the low temperature C_p, 13.29–221.61 K, and $\Delta_{fus}H°$ for B_5H_9(cr) reported by Johnston, Kerr, Clarke and Hallett[2] and C_p values, 226.34–298.15 K, for B_5H_9(l), using $S°(13.29\ K) = 0.236\ cal·K^{-1}·mol^{-1}$ for B_5H_9(cr).

Fusion Data

The values of T_{fus} and $\Delta_{fus}H°$ were taken from Johnston, Kerr, Clarke and Hallett.[2]

Vaporization Data

The boiling point is calculated as the temperature at which the Gibbs energy change of the reaction $B_5H_9(l) \rightarrow B_5H_9(g)$ is zero. The enthalpy change of the reaction at T_{vap} is enthalpy of vaporization.

References

[1]H. E. Wirth and E. D. Palmer, J. Phys. Chem. **60**, 914 (1956).
[2]H. L. Johnston, E. c. Kerr, J. T. Clarke, and N. Cl Hallet, The Ohio State University, TR–6, (July 8, 1949).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	151.126	184.330	184.330	0.	42.844	171.913	−30.118
300	152.298	185.269	184.333	0.281	42.780	172.714	−30.072
400	185.351	233.939	190.744	17.278	39.888	216.489	−28.271
500	190.372	275.566	203.682	35.942	36.745	260.981	−27.264
600	210.037	311.791	218.723	55.841	33.557	306.142	−26.652
700	244.346	347.030	234.537	78.745	32.465	351.697	−26.244
800	256.479	380.470	250.719	103.801	32.820	397.284	−25.940
900	267.096	411.315	266.871	130.000	33.724	442.793	−25.699
1000	275.307	439.903	282.763	157.140	35.036	488.177	−25.500
1100	280.272	466.381	298.267	184.925	36.497	533.421	−25.330
1200	284.512	490.955	313.313	213.170	37.945	578.532	−25.183
1300	288.027	513.872	327.869	241.803	39.327	623.524	−25.054
1400	290.816	535.323	341.929	270.751	40.588	668.414	−24.939
1500	292.880	555.462	355.500	299.942	41.671	713.219	−24.837

PREVIOUS: December 1962 CURRENT: March 1965

$S°(298.15\ K) = 275.41\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 102.23 \pm 6.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 73.22 \pm 6.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies			
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
2600 (1)	[1450](1)	[1500](1)	1449 (2)
2600 (1)	[500](1)	[1100](1)	1034 (2)
1844 (1)	1870 (1)	738 (1)	882 (2)
1413 (1)	1387 (1)	470 (1)	700 (2)
1126 (1)	[900] (1)	2598 (2)	605 (2)
985 (1)	782 (1)	1802 (2)	568 (2)
799 (1)	2600 (1)	1621 (2)	

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: C_{4v}
Bond Distances: B–B = 1.800 ± 0.003 Å; B–B(apex) = 1.687 ± 0.005 Å
B–H = B(apex)–H = 1.22 Å; B–H(bridge) = 1.35 ± 0.02 Å
Bond Angles: B(apex)–B–H = 136° 10' ± 30'; H–B(apex)–B = 131°:
B–H(bridge)–B = 83° 37'; B–B–B = 90°
Angle between B(apex)BB plane and BBH(bridge) plane = 196 ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 2.366493 \times 10^{-114}\ g^3\ cm^6$

Enthalpy of Formation

The enthalpy change[2] of the reaction $B_5H_9(g) \rightarrow 5\ B(am) + 9/2\ H_2(g)$ was reported to be −12.99 ± 0.39 and −9.9 ± 1 kcal·mol^{-1} by Prosen, Johnson and Pergiel[1] and Gunn and Green,[2] respectively. Using $\Delta_f H°(298.15\ K) = 1.2 \pm 0.4$ kcal·mol^{-1} for the reaction $B(cr) \rightarrow B(am)$, the corresponding $\Delta_f H°(298.15\ K)$ values for $B_5H_9(g)$ were derived as 18.99 and 15.9 kcal·mol^{-1}. The adopted value is the average of these two.

Heat Capacity and Entropy

The molecular structure, a tetragonal pyramid of boron atoms, and constants were obtained from Hrostowski and Myers.[3] The vibrational frequencies were reported by Hrostowski and Pimentel.[4] The earlier models of pentaborane were assumed to have a hydrocarbon–like structure of low symmetry by Bauer and Pauling,[5] and Pitzer.[6] However, the electron diffraction and X–ray data by Hedberg, Jones and Schomaker,[7] and Dulmage and Lipscomb[8] revealed an unusual pyramidal structure of C_{4v} symmetry. The Raman spectrum of liquid B_5H_9 and the infrared spectrum of gaseous B_5H_9 from 3 to 25 microns have been obtained by Taylor, Beckett, Tung, Holden and Johnston.[9] The near infrared spectrum of $B_5H_9(l)$ have been examined at high resolution by Pondy and Beachell.[10] Ten bands were observed. The principal moments of inertia are: $I_A = 16.9101 \times 10^{-39}$, and $I_B = I_C = 11.8299 \times 10^{-39}$ g cm^2.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.163	102.230	102.230	INFINITE
100	34.678	216.114	334.297	−11.818	91.958	115.828	−60.502
200	57.782	245.727	282.800	−7.415	82.575	143.319	−37.431
250	75.771	260.522	276.853	−4.083	77.768	159.061	−33.234
298.15	93.818	275.410	275.410	0.	73.220	175.133	−30.683
300	94.509	275.993	275.412	0.174	73.049	175.766	−30.604
350	112.830	291.947	276.630	5.361	68.579	193.243	−28.840
400	130.205	308.160	279.557	11.441	64.427	211.339	−27.598
450	146.409	324.443	283.639	18.362	60.637	229.935	−26.690
500	161.367	340.654	288.531	26.061	57.240	248.932	−26.006
600	187.614	372.467	299.884	43.550	51.642	287.822	−25.057
700	209.395	403.077	312.455	63.435	47.531	327.530	−24.441
800	227.365	432.249	325.622	85.302	44.697	367.737	−24.011
900	242.175	459.912	339.020	108.803	42.903	408.234	−23.693
1000	254.403	486.081	352.430	133.651	41.923	448.886	−23.447
1100	264.538	510.819	365.715	159.614	41.561	489.604	−23.249
1200	272.980	534.209	378.791	186.502	41.653	530.334	−23.085
1300	280.052	556.347	391.605	214.164	42.064	571.043	−22.945
1400	286.013	577.325	404.128	242.476	42.688	611.711	−22.823
1500	291.069	597.235	416.344	271.337	43.441	652.330	−22.716
1600	295.384	616.162	428.246	300.665	44.258	692.895	−22.621
1700	299.088	634.183	439.834	330.393	45.084	733.410	−22.535
1800	302.287	651.371	451.113	360.466	45.882	773.877	−22.457
1900	305.064	667.791	462.088	390.836	46.617	814.300	−22.387
2000	307.488	683.502	472.769	421.467	47.264	854.688	−22.322
2100	309.615	698.557	483.165	452.324	47.805	895.045	−22.263
2200	311.489	713.005	493.286	483.381	48.222	935.379	−22.209
2300	313.149	726.888	503.143	514.615	48.503	975.698	−22.159
2400	314.625	740.247	512.745	546.005	−202.660	1021.352	−22.229
2500	315.942	753.118	522.104	577.535	−203.071	1072.361	−22.406
2600	317.122	765.533	531.230	609.189	−203.482	1123.386	−22.569
2700	318.183	777.522	540.131	640.955	−203.899	1174.427	−22.721
2800	319.141	789.111	548.817	672.822	−204.330	1225.484	−22.862
2900	320.007	800.325	557.298	704.780	−204.779	1276.557	−22.993
3000	320.793	811.187	565.581	736.821	−205.251	1327.645	−23.116
3100	321.509	821.718	573.674	768.936	−205.750	1378.749	−23.232
3200	322.163	831.936	581.586	801.121	−206.279	1429.871	−23.340
3300	322.761	841.859	589.323	833.367	−206.843	1481.010	−23.442
3400	323.309	851.502	596.893	865.671	−207.444	1532.165	−23.539
3500	323.814	860.882	604.302	898.028	−208.084	1583.339	−23.630
3600	324.278	870.010	611.557	930.432	−208.766	1634.532	−23.716
3700	324.707	878.901	618.663	962.882	−209.493	1685.745	−23.798
3800	325.104	887.566	625.626	995.373	−210.265	1736.978	−23.876
3900	325.472	896.016	632.451	1027.902	−211.086	1788.232	−23.951
4000	325.814	904.260	639.144	1060.466	−211.957	1839.507	−24.021
4100	326.131	912.309	645.708	1093.064	−212.878	1890.806	−24.089
4200	326.427	920.172	652.150	1125.692	−2613.099	1977.248	−24.591
4300	326.704	927.856	658.473	1158.349	−2608.690	2086.489	−25.346
4400	326.962	935.370	664.681	1191.032	−2604.344	2195.629	−26.065
4500	327.203	942.720	670.778	1223.740	−2600.062	2304.670	−26.752
4600	327.430	949.914	676.768	1256.472	−2595.847	2413.618	−27.407
4700	327.642	956.959	682.655	1289.226	−2591.698	2522.474	−28.034
4800	327.842	963.859	688.442	1322.000	−2587.617	2631.245	−28.634
4900	328.030	970.620	694.132	1354.794	−2583.605	2739.928	−29.208
5000	328.207	977.249	699.728	1387.606	−2579.661	2848.533	−29.758
5100	328.374	983.750	705.234	1420.435	−2575.787	2957.056	−30.286
5200	328.531	990.128	710.651	1453.280	−2571.983	3065.507	−30.793
5300	328.680	996.388	715.984	1486.141	−2568.247	3173.885	−31.281
5400	328.821	1002.533	721.233	1519.016	−2564.579	3282.193	−31.749
5500	328.955	1008.568	726.403	1551.905	−2560.978	3390.432	−32.200
5600	329.081	1014.496	731.495	1584.807	−2557.444	3498.608	−32.634
5700	329.201	1020.322	736.511	1617.721	−2553.975	3606.721	−33.052
5800	329.315	1026.048	741.454	1650.647	−2550.569	3714.775	−33.455
5900	329.423	1031.678	746.325	1683.584	−2547.226	3822.767	−33.844
6000	329.526	1037.216	751.127	1716.531	−2543.942	3930.705	−34.220

PREVIOUS: March 1965 (1 atm) CURRENT: March 1965 (1 bar)

$S°(298.15\ K) = [251 \pm 13]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{dcm} = 1098\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -4633.53 \pm 10.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction $K_2O(cr) + 3B_2O_3(l) \rightarrow K_2B_6O_{10}(cr)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for $B_2O_3(l)$ and for $K_2O(cr)$. The above $\Delta_r H° = -122.8\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 973 K were graphically smoothed and used to determine C_p. Above this range C_p is extrapolated.

The entropy at 298.15 K is obtained from a consideration of the entropies of sodium and calcium borates and those of the constituent oxides, as given by Kelley and King.[4] These indicate that for the reactions

$$MO + B_2O_3 \rightarrow MO \cdot B_2O_3 \qquad (1)$$

$$MO \cdot B_2O_3 + B_2O_3 \rightarrow MO \cdot 2B_2O_3 \qquad (2)$$

the simple addition of entropies will give values at least 2.7 $cal \cdot K^{-1} mol^{-1}$ too low for the reaction[1] and at least 2.7 $cal \cdot K^{-1} mol^{-1}$ too high for reaction[2]. The reason for this is probably structural, the $B_2O_4^{=}$ ion being a flexible chain while the $B_4O_7^{=}$ on probably is a rigid chain of rings. It was assumed that additional B_2O_3 would extend the ring structure into a rigid plane and thus the entropy difference for reaction[2] was assumed to hold for each additional mole of B_2O_3 added. Thus a value for $Na_2B_6O_{10}$ was estimated to be 55.5 ± 1.5 and then using an average value of 4.5 ± 1.5 $cal \cdot K^{-1} mol^{-1}$ for the difference between K_2 and Na_2 gave 60 ± 3 $cal \cdot K^{-1} \cdot mol^{-1}$ for the entropy fo $K_2B_6O_{10}$.

Decomposition Data

The incongruent melting point was given by Rollet[5] the decomposition products being $K_2B_4O_7(l)$ and $K_2B_8O_{13}(cr)$.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]JANAF Thermochemical Tables: $B_2O_3(l)$, 12-31-64; $K_2O(cr)$, 6-30-63.
[3]G. S. Smith, Ph.D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. Mic 59-2916 (1959).
[4]K. K. Kelley and E. G. King, U.S. Bur. Mines, Bull. 592, 149 pp. (1961).
[5]A.-P. Rollet, Comp. rend. **200**, 1763 (1935).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	261.918	251.040	251.040	0.	−4633.529	−4353.554	762.725
300	262.337	252.661	251.045	0.485	−4633.551	−4351.817	757.719
400	285.767	331.362	261.617	27.898	−4640.126	−4256.761	555.876
500	308.277	397.560	282.348	57.606	−4642.314	−4160.664	434.662
600	330.118	455.703	306.487	89.530	−4644.154	−4064.153	353.816
700	351.456	508.194	331.610	123.608	−4645.271	−3967.385	296.050
800	372.794	556.524	356.742	159.826	−4645.388	−3870.524	252.719
900	393.463	601.639	381.473	198.150	−4644.347	−3773.716	219.021
1000	412.835	644.176	405.636	238.539	−4642.067	−3677.091	192.072
1100	423.295	684.043	429.155	280.376	−4796.992	−3571.514	169.597
1200	430.073	721.173	451.961	323.055	−4791.748	−3460.337	150.625
1300	435.680	755.823	474.018	366.347	−4786.378	−3349.604	134.589
1400	440.659	788.294	495.318	410.167	−4780.923	−3239.287	120.859
1500	445.387	818.859	515.879	454.471	−4775.390	−3129.364	108.974
1600	449.864	847.747	535.726	499.234	−4769.782	−3019.811	98.587
1700	454.299	875.154	554.893	544.443	−4764.094	−2910.611	89.432
1800	458.622	901.244	573.416	590.090	−4758.324	−2801.750	81.305
1900	462.834	926.153	591.330	636.164	−4752.475	−2693.210	74.042
2000	466.934	949.998	608.672	682.653	−4746.552	−2584.980	67.513

PREVIOUS: March 1963 CURRENT: March 1965

$S°(298.15\ K)$ = [188.3 ± 4] $J·K^{-1}·mol^{-1}$
T_{dcm} = 1107 ± 4 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −4659.89 ± 5.6 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction $Li_2O(cr) + 3B_2O_3(l) \rightarrow Li_2B_6O_{10}(cr)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for $B_2O_3(l)$ and $Li_2O(cr)$. The above $\Delta_r H° = -72.80\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The enthalpy measurement of Smith[3] in the range 298 to 823 K were used to determine C_p. Above this range C_p is extrapolated. Entropy at 298.15 K is estimated from that of the component oxides and the difference from the oxides observed for twice $LiBO_2$(cr).

Decomposition Data

The incongruent melting point reported by Sastry and Hummel[4] is used here.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]JANAF Thermochemical Tables: B_2O_3(l) 12-31-64; Li_2O(cr), 3-31-64.
[3]G. S. Smith, Ph.D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. 59-2916 (1959).
[4]B.S.R. Sastry and F. A. Hummel, J. Am. Ceram. Soc. **42**, 216 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	293.215	188.280	188.280	0.	−4659.888	−4382.421	767.782
300	293.633	190.095	188.286	0.543	−4659.835	−4380.700	762.748
400	316.269	277.724	200.080	31.057	−4657.552	−4288.034	559.960
500	336.561	350.530	223.085	63.723	−4662.433	−4195.190	438.268
600	354.008	413.481	249.687	98.277	−4661.531	−4101.824	357.096
700	368.401	469.162	277.139	134.416	−4660.445	−4008.622	299.127
800	380.493	519.165	304.320	171.876	−4659.158	−3915.591	255.662
900	390.744	564.586	330.753	210.450	−4657.685	−3822.731	221.866
1000	399.572	606.219	356.247	249.972	−4656.018	−3730.046	194.838
1100	406.456	644.627	380.740	290.275	−4654.202	−3637.535	172.732
1200	413.157	680.281	404.234	331.257	−4652.249	−3545.196	154.318
1300	419.675	713.610	426.764	372.900	−4650.116	−3453.027	138.744
1400	426.012	744.944	448.383	415.186	−4647.768	−3361.029	125.402
1500	432.165	774.547	469.149	458.096	−4645.185	−3269.209	113.844
1600	438.137	802.630	489.122	501.613	−4642.361	−3177.568	103.737
1700	443.926	829.367	508.356	545.718	−4929.767	−3071.759	94.384
1800	449.532	854.900	526.905	590.392	−4924.960	−2962.603	85.973
1900	454.956	879.351	544.815	635.618	−4919.944	−2853.719	78.454
2000	460.198	902.822	562.133	681.377	−4914.730	−2745.104	71.695

PREVIOUS: December 1962 CURRENT: March 1965

Sodium Borate ($Na_2B_6O_{10}$) CRYSTAL M_r = 270.83354

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [232.2 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -4580.48 \pm 9.2\ kJ \cdot mol^{-1}$

$T_{dcm} = 1039\ K$

Enthalpy of Formation

The enthalpy of reaction $Na_2O(cr) + 3\ B_2O_3(l) \rightarrow Na_2B_6O_{10}(cr)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for $B_2O_3(l)$ and $Na_2O(cr)$. The above $\Delta_r H° = -97.52\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 1039 K were smoothed graphically and used to determine C_p. Above this range C_p was extrapolated. Entropy at 298.15 K was estimated as described in detail for $K_2B_6O_{10}(cr)$.

Decomposition Data

The incongruent melting point was reported by Morey and Merwin[4] the products are $Na_2B_4O_7(l)$ and $Na_2B_8O_{13}(cr)$.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).

[2]JANAF Thermochemical Tables: $B_2O_3(l)$, 12–31–64; $Na_2O(cr)$, 6–30–62.

[3]G. S. Smith, Ph.D. Thesis, Penn. State Univ., Univ. Microfilms, Order No. 59–2916 (1959).

[4]G. W. Morey and H. E. Merwin, J. Am. Chem. Soc. **58**, 2248 (1936).

Sodium Borate ($Na_2B_6O_{10}$) $B_6Na_2O_{10}(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	243.509	232.212	232.212	0.	−4580.476	−4302.768	753.827
300	244.346	233.721	232.217	0.451	−4580.527	−4301.045	748.878
400	283.173	309.380	242.270	26.844	−4588.408	−4207.071	549.387
500	319.992	376.581	262.525	57.028	−4590.107	−4111.507	429.526
600	353.757	437.950	286.718	90.739	−4590.114	−4015.757	349.603
700	384.677	494.845	312.434	127.687	−4588.273	−3920.150	292.525
800	412.375	548.063	338.597	167.572	−4584.587	−3824.935	249.743
900	436.182	598.047	364.677	210.033	−4579.219	−3730.284	216.500
1000	456.056	645.071	390.389	254.682	−4572.428	−3636.311	189.941
1100	471.453	689.291	415.572	301.090	−4564.561	−3543.071	168.246
1200	482.917	730.824	440.131	348.831	−4749.519	−3445.703	149.988
1300	491.746	769.840	464.008	397.582	−4738.691	−3337.488	134.102
1400	498.482	806.540	487.177	447.108	−4727.528	−3230.120	120.517
1500	503.461	841.109	509.632	497.217	−4716.188	−3123.559	108.772
1600	507.017	873.720	531.378	547.747	−4704.808	−3017.754	98.520
1700	509.737	904.543	552.431	598.590	−4693.479	−2912.661	89.495
1800	511.829	933.739	572.811	649.672	−4682.263	−2808.233	81.493
1900	513.544	961.459	592.542	700.941	−4671.198	−2704.422	74.350
2000	515.134	987.841	611.653	752.376	−4660.301	−2601.189	67.936

PREVIOUS: March 1963 CURRENT: March 1965

$S°(298.15\ K)$ = [203.3 ± 13] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = *Unknown*

$\Delta_f H°(298.15\ K)$ = −4197 ± 8 $kJ·mol^{-1}$

Enthalpy of Formation

See the PbB_2O_4(cr) table for the complete writeup. Evans[1] analysed the enthalpies of formation of lead borate system based upon Shartsis and Newman's enthalpies of solution and Mazzetti and De Carli's phase studies. From the Shartsis and Newman paper Evans obtained the following:

$$PbO(cr) + 3B_2O_3(cr) \rightarrow PbO.3B_2O_3(gls) \quad \Delta_r H = -24.5\ kcal·mol^{-1}$$

and estimated a $\Delta_r H°(298.15\ K)$ of 16.0 $kcal·mol^{-1}$ for the conversion to the $PbO·3B_2O_3$(cr). With auxiliary JANAF values the $\Delta_f H°(298.15\ K)$ is calculated to be −1003.00 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The heat capactiy employed in this table was obtained by graphically smoothing the summation of heat capacities of the constituent oxides.

The entropy at 298.15 K was obtained in the manner decribed in the PbB_4O_7 table from $S°(298.15\ K)$ for PbB_4O_7 and B_2O_3 and the subtraction of 4.2 $cal·K^{-1}·mol^{-1}$.

References

[1]W. H. Evans, U.S. Nat. Bur. Stand., Report 7192, Ch. 6 (July 1, 1961); refer to pp. 80–1.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	230.957	203.342	203.342	0.	−4196.552	−3921.603	687.049
300	231.794	204.774	203.347	0.428	−4196.572	−3919.897	682.515
400	286.186	279.058	213.108	26.380	−4196.379	−3827.635	499.838
500	334.218	348.197	233.290	57.454	−4193.800	−3735.697	390.266
600	375.849	412.869	257.889	92.988	−4188.839	−3644.504	317.282
700	413.714	473.741	284.419	132.526	−4186.327	−3553.532	265.168
800	444.466	531.083	311.705	175.503	−4176.749	−3463.763	226.161
900	467.060	584.797	339.098	221.129	−4165.426	−3375.304	195.898
1000	483.629	634.906	366.203	268.703	−4152.890	−3288.176	171.757
1100	495.469	681.590	392.778	317.694	−4139.548	−3202.344	152.067
1200	503.000	725.044	418.678	367.640	−4125.774	−3117.750	135.712
1300	507.812	765.511	443.819	418.199	−4111.850	−3034.313	121.920
1400	510.406	803.246	468.160	469.120	−4097.997	−2951.946	110.138
1500	511.787	838.510	491.688	520.234	−4084.360	−2870.563	99.962
1600	512.707	871.570	514.408	571.459	−4071.001	−2790.081	91.087
1700	513.502	902.678	536.342	622.771	−4057.931	−2710.424	83.281
1800	514.130	932.047	557.517	674.154	−4045.156	−2631.531	76.365
1900	514.590	959.857	577.968	725.591	−4032.686	−2553.337	70.196
2000	514.967	986.262	597.728	777.069	−4020.525	−2475.792	64.661

PREVIOUS: December 1962 CURRENT: March 1965

$S°(298.15\ K) = [293.7 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1130\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15) = -5945.13 \pm 5.9\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 149.8 \pm 4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction $K_2O(cr) + 4\ B_2O_3(l) \rightarrow K_2B_8O_{13}(cr)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for $B_2O_3(l)$ and $K_2O(cr)$.The above $\Delta_f H° = -137.00\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 1130 K were smoothed graphically and used to determine C_p. Above this range C_p is extrapolated.

$S°(298.15\ K)$ is obtained by estimating the entropy of $Na_2B_8O_{13}(cr)$ as $65.7 \pm 2.5\ cal \cdot K^{-1} \cdot mol^{-1}$ as described on the table for $K_2B_6O_{10}(cr)$ and then using an average value of $4.5 \pm 1.5\ cal \cdot K^{-1} \cdot mol^{-1}$ for the replacement of Na_2 by K_2.

Fusion Data

T_{fus} is given by Rollet.[4] $\Delta_{fus} H°$ was obtained from the values of $\Delta_f H°$ for $K_2B_8O_{13}(cr)$ and $K_2B_8O_{13}(l)$ at 298.15 K reported above and the enthalpy of the crystal and liquid at T_{fus}.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]JANAF Thermochemical Tables: $B_2O_3(l)$, 12–31–64; $K_2O(cr)$, 6–30–63.
[3]G. S. Smith, Ph.D. Thesis, Penn State Univ., Univ. Microfilms, Order No. 59–2916 (1959).
[4]A.–P. Rollet, Comp. rend. **200**, 1763 (1935).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	321.289	293.717	293.717	0.	−5945.129	−5582.653	978.058
300	322.042	295.707	293.723	0.595	−5945.165	−5580.404	971.635
400	360.493	393.657	306.819	34.735	−5952.194	−5457.589	712.688
500	397.313	478.036	332.801	72.617	−5954.258	−5333.683	557.206
600	435.136	553.841	363.420	114.252	−5955.089	−5209.463	453.524
700	471.453	623.739	395.677	159.643	−5954.085	−5085.245	379.466
800	500.406	688.630	428.291	208.272	−5951.363	−4961.293	323.939
900	525.092	749.032	460.612	259.578	−5947.212	−4837.770	280.777
1000	546.012	805.494	492.308	313.186	−5941.830	−4714.777	246.275
1100	560.656	858.271	523.206	368.571	−6093.530	−4583.146	217.635
1130.000	563.825	873.400	532.303	385.440	--- CRYSTAL <--> LIQUID ---		
1200	574.045	907.597	553.205	425.270	−6084.767	−4446.220	193.539
1300	586.178	954.032	582.269	483.292	−6075.326	−4310.053	173.180
1400	597.057	997.879	610.404	542.464	−6065.317	−4174.635	155.758
1500	606.680	1039.407	637.632	602.662	−6054.821	−4039.951	140.684
1600	615.048	1078.835	663.986	663.758	−6043.933	−3905.979	127.517
1700	622.161	1116.342	689.501	725.629	−6032.754	−3772.698	115.921
1800	628.018	1152.075	714.215	788.149	−6021.394	−3640.083	105.632
1900	632.621	1186.159	738.164	851.191	−6009.968	−3508.098	96.444
2000	635.968	1218.699	761.383	914.631	−5998.593	−3376.715	88.191

PREVIOUS: March 1963 CURRENT: March 1965

$S°(298.15\ K)$ = [302.212] $J·K^{-1}·mol^{-1}$
T_{fus} = 1130 K

$\Delta_f H°(0\ K)$ = [−5897.253] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 149.8 ± 4 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction $K_2O(cr) + 4B_2O_3(l) \rightarrow K_2B_8O_{13}(l)$ was reported by Shartsis and Capps[1] their enthalpies of solution measurments. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for $B_2O_3(l)$ and for $K_2O(cr)$. The above $\Delta_f H° = -119.65$ kcal·mol^{-1}.

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 1373 K on the glass and liquid were smoothed graphically and used to determine C_p. There is a discontinuity in the C_p curve, a glass transition at about 673 K. Above 673 K the C_p values were estimated to be constant.

The entropy is calculated from that of the crystal by adding $\Delta_{fus}S°$ and differences in entropy, $S°(1130\ K) - S°(298.15\ K)$, between the crystal and liquid.

Fusion Data

Refer to the crystal table for details.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]JANAF Thermochemical Tables: $B_2O_3(l)$, 12-31-64; $K_2O(cr)$, 6-30-63.
[3]G. S. Smith, Ph.D. Thesis, Penn State Univ., Univ. Microfilms, Order No. 59-2916 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
0							
100							
200							
250							
298.15	323.088	302.212	302.212	.000	−5897.253	−5537.309	970.114
300	324.511	304.215	302.218	.599	−5897.285	−5535.076	963.742
400	393.798	407.368	315.813	36.622	−5902.431	−5413.311	706.906
500	450.198	501.882	343.717	79.083	−5899.917	−5291.264	552.775
600	475.302	586.656	377.292	125.618	−5895.847	−5169.911	450.081
673.000	473.866	641.307	403.024	160.364	GLASS <--> LIQUID		
673.000	661.490	641.307	403.024	160.364	TRANSITION		
700	661.490	667.327	412.720	178.225	−5887.628	−5049.299	376.783
800	661.490	755.657	450.189	244.374	−5867.385	−4930.936	321.957
900	661.490	833.569	488.544	310.523	−5848.391	−4815.032	279.457
1000	661.490	903.264	526.592	376.672	−5830.468	−4701.185	245.565
1100	661.490	966.311	563.746	442.821	−5971.405	−4579.864	217.480
1130.000	661.490	984.110	574.671	462.666	--- CRYSTAL <--> LIQUID ---		
1200	661.490	1023.868	599.726	508.970	−5953.192	−4454.170	193.885
1300	661.490	1076.815	634.416	575.119	−5935.623	−4329.968	173.980
1400	661.490	1125.837	667.789	641.268	−5918.637	−4207.097	156.969
1500	661.490	1171.475	699.864	707.417	−5902.190	−4085.423	142.267
1600	661.490	1214.167	730.688	773.566	−5886.250	−3964.827	129.438
1700	661.490	1254.269	760.319	839.715	−5870.792	−3845.213	118.149
1800	661.490	1292.079	788.821	905.864	−5855.803	−3726.499	108.140
1900	661.490	1327.844	816.258	972.013	−5841.270	−3608.602	99.207
2000	661.490	1361.774	842.693	1038.162	−5827.186	−3491.459	91.188
2100	661.490	1394.048	868.186	1104.311	−5813.546	−3375.010	83.949
2200	661.490	1424.821	892.794	1170.460	−5800.347	−3259.196	77.383
2300	661.490	1454.225	916.569	1236.609	−5787.588	−3143.979	71.402
2400	661.490	1482.378	939.562	1302.758	−6177.341	−3020.757	65.745
2500	661.490	1509.381	961.818	1368.907	−6166.081	−2889.465	60.372
2600	661.490	1535.326	983.381	1435.056	−6154.999	−2758.619	55.421
2700	661.490	1560.290	1004.288	1501.206	−6144.097	−2628.195	50.845
2800	661.490	1584.347	1024.578	1567.355	−6133.377	−2498.171	46.604
2900	661.490	1607.560	1044.283	1633.504	−6122.843	−2368.534	42.662
3000	661.490	1629.985	1063.435	1699.653	−6112.499	−2239.249	38.989

PREVIOUS: March 1963 CURRENT: March 1965

298.15	to	1130 K	crystal
above		1130 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	321.289	293.717	293.717	0.	−5945.129	−5582.653	978.058
300	322.042	295.707	293.723	0.595	−5945.165	−5580.404	971.635
400	360.493	393.657	306.819	34.735	−5952.194	−5457.589	712.688
500	397.313	478.036	332.801	72.617	−5954.258	−5333.683	557.206
600	435.136	553.841	363.420	114.252	−5955.089	−5209.463	453.524
700	471.453	623.739	395.677	159.643	−5954.085	−5085.245	379.466
800	500.406	688.630	428.291	208.272	−5951.363	−4961.293	323.939
900	525.092	749.032	460.612	259.578	−5947.212	−4837.770	280.777
1000	546.012	805.494	492.308	313.186	−5941.830	−4714.777	246.275
1100	560.656	858.271	523.206	368.571	−6093.530	−4583.146	217.635
1130.000	563.825	873.400	532.303	385.440	CRYSTAL <--> LIQUID TRANSITION		
1130.000	661.490	1005.983	532.303	535.258			
1200	661.490	1023.868	559.830	556.846	−5953.192	−4454.170	193.885
1300	661.490	1076.815	597.589	622.995	−5935.623	−4329.968	173.980
1400	661.490	1125.837	633.591	689.144	−5918.637	−4207.097	156.969
1500	661.490	1171.475	667.947	755.293	−5902.190	−4085.422	142.267
1600	661.490	1214.167	700.766	821.442	−5886.250	−3964.827	129.438
1700	661.490	1254.269	732.157	887.591	−5870.792	−3845.213	118.149
1800	661.490	1292.079	762.224	953.740	−5855.803	−3726.499	108.140
1900	661.490	1327.844	791.060	1019.889	−5841.270	−3608.602	99.207
2000	661.490	1361.774	818.755	1086.038	−5827.186	−3491.458	91.188
2100	661.490	1394.048	845.388	1152.187	−5813.546	−3375.009	83.949
2200	661.490	1424.821	871.032	1218.336	−5800.347	−3259.196	77.383
2300	661.490	1454.225	895.753	1284.485	−5787.588	−3143.979	71.402
2400	661.490	1482.378	919.614	1350.634	−6177.341	−3020.757	65.745
2500	661.490	1509.381	942.668	1416.783	−6166.081	−2889.464	60.372
2600	661.490	1535.326	964.967	1482.932	−6154.999	−2758.619	55.421
2700	661.490	1560.290	986.557	1549.081	−6144.097	−2628.194	50.845
2800	661.490	1584.347	1007.479	1615.230	−6133.377	−2498.171	46.604
2900	661.490	1607.560	1027.774	1681.379	−6122.843	−2368.534	42.662
3000	661.490	1629.985	1047.476	1747.529	−6112.499	−2239.249	38.989

PREVIOUS: CURRENT: March 1965

$S°(298.15\ K) = [265.3 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{dcm} = 908 \pm 10\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15) = -5914.38 \pm 6.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of the reaction $Li_2O(cr) + 4\ B_2O_3(l) \rightarrow Li_2B_8O_{13}(cr)$ was reported by Shartsis and Capps[1] from their enthalpy of solution measurements. Their values for the enthalpy of reaction of the oxides have been converted to the enthalpies of formation using JANAF values[2] for $B_2O_3(l)$ and for $Li_2O(cr)$. The above $\Delta_f H° = -73.35\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The enthalpy measurements of Smith[3] in the range 298 to 823 K were used to determine C_p. Above this range C_p is extrapolated. The entropy at 298.15 K is estimated from that of the component oxides and the difference from the oxides observed for twice $LiBO_2$(cr).

Decomposition Data

The incongruent melting point reported by Sastry and Hummel[4] is used here.

References

[1]L. Shartsis and W. Capps, J. Am. Ceram. Soc. **37**, 27 (1954).
[2]JANAF Thermochemical Tables: B_2O_3(l), 12-31-64; Li_2O(cr), 3-31-64.
[3]G. S. Smith, Ph.D. Thesis, Penn State Univ., Univ. Microfilms, Order No. 59-2916 (1959).
[4]B. S. R. Sastry and T. A. Hummel, J. Am. Ceram. Soc. **42**, 216 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	325.515	265.266	265.266	0.	−5914.377	−5564.637	974.901
300	326.770	267.283	265.272	0.603	−5914.386	−5562.467	968.512
400	390.367	370.606	278.926	36.672	−5913.731	−5445.208	711.071
500	428.567	462.069	306.606	77.732	−5918.268	−5327.630	556.574
600	453.211	542.480	339.359	121.873	−5916.480	−5209.666	453.542
700	471.537	613.760	373.565	168.137	−5914.462	−5092.021	379.971
800	486.683	677.748	407.656	216.074	−5912.270	−4974.678	324.813
900	498.733	735.788	440.941	265.362	−5909.954	−4857.617	281.929
1000	508.649	788.860	473.117	315.743	−5907.545	−4740.819	247.635
1100	517.142	837.742	504.072	367.037	−5905.062	−4624.264	219.588
1200	524.623	883.062	533.789	419.127	−5902.502	−4507.941	196.226
1300	531.915	925.343	562.300	471.956	−5899.841	−4391.835	176.466
1400	539.016	965.023	589.664	525.504	−5897.031	−4275.938	159.537
1500	545.928	1002.448	615.947	579.752	−5894.040	−4160.251	144.873
1600	552.651	1037.897	641.221	634.683	−5890.855	−4044.767	132.048
1700	559.183	1071.599	665.554	690.276	−6177.943	−3915.137	120.298
1800	565.526	1103.741	689.012	746.513	−6172.856	−3782.179	109.756
1900	571.679	1134.483	711.654	803.375	−6167.596	−3649.505	100.332
2000	577.643	1163.959	733.538	860.843	−6162.172	−3517.113	91.858

PREVIOUS: December 1962 CURRENT: March 1965

$S°(298.15\ K) = 176.56\ J·K^{-1}·mol^{-1}$
$T_{fus} = 371.93\ K$

$\Delta_f H°(0\ K) = 14.3 \pm 19\ kJ·mol^{-1}$
$\Delta_f H°(298.15) = -28.9 \pm 19\ kJ·mol^{-1}$
$\Delta_{fus} H° = 21.966 \pm 0.04\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy change of the reaction $B_{10}H_{14}(cr) \rightarrow 10\ B(am) + 7H_2(g)$ was reported to be 19.8 ± 1.4 and 18.0 ± 1.0 kcal·mol^{-1} by Johnson, Kilday and Prosen[1] and Gal'chenko, Timofeev and Skuratov,[2] respectively. Using $\Delta_f H°(298.15\ K) = 1.2 \pm 0.4$ kcal·mol^{-1} for the reaction $B(cr) \rightarrow B(am)$, the corresponding $\Delta_f H°(298.15\ K)$ values for $B_{10}H_{14}(cr)$ are calculated to be −7.8 and −6.0 kcal·mol^{-1}. The adopted value $\Delta_f H°(298.15\ K)$ for $B_{10}H_{14}(cr)$ is the average of these two.

Heat Capacity and Entropy

C_p(60 to 371.93 K) was given by Furukawa and Park.[3] The heat capacity above 371.93 K is estimated by comparison with that of the liquid decarborane. Heat capacity (14 to 205 K) was also reported by Kerr, Hallett and Johnston.[4] The value of $S°(298.15\ K)$ was taken from Furukawa and Park.[3]

Fusion Data

T_{fus} and $\Delta_{fus} H°$ were obtained from Furukawa and Park.[3]

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated from Gibbs energy functions and vapor pressure reported by Furukawa and Park.[3] Refer to the ideal gas table for details.

References

[1]W. H. Johnson, M. V. Kilday, and E. J. Prosen, J. Res. Nat. Bur. Stand. **64A**, 521 (1960).
[2]G. L. Gal'chenko, B. I. Timofeev, and S. M. Skuratov, Dokl. Akad. Nauk SSSR **142**, 1077 (1962).
[3]G. T. Furukawa and R. P. Park, J. Res. Nat. Bur. Stand. **55**, 255 (1955).
[4]E. C. Kerr, N. C. Hallett, and H. L. Johnston, J. Am. Chem, Soc. **73**, 1117 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−28.292	14.248	14.248	INFINITE
100	55.580	53.212	305.968	−25.276	−3.969	61.527	−32.138
200	123.386	109.725	193.426	−16.740	−17.619	132.450	−34.592
298.15	217.953	176.565	176.565	0.	−28.870	208.617	−36.549
300	219.706	177.918	176.569	0.405	−29.048	210.091	−36.580
371.930	293.483	232.548	182.044	18.784	--- CRYSTAL <--> LIQUID ---		
400	305.014	254.416	186.360	27.222	−36.197	291.017	−38.003
500	326.352	324.505	207.161	58.672	−42.516	373.532	−39.023
600	364.845	387.498	232.030	93.281	−48.223	457.307	−39.812
700	397.480	446.265	258.485	131.446	−52.174	541.898	−40.437
800	421.538	500.946	285.418	172.423	−54.694	626.951	−40.936
900	442.458	551.835	312.225	215.649	−56.109	712.253	−41.338
1000	460.240	599.400	338.590	260.810	−56.596	797.660	−41.665
1100	474.884	643.978	364.348	307.592	−56.385	883.080	−41.934
1200	486.390	685.814	389.412	355.682	−55.733	968.459	−42.156
1300	494.758	725.097	413.739	404.766	−54.909	1053.776	−42.341
1400	499.988	761.974	437.310	454.529	−54.192	1139.030	−42.498
1500	502.080	796.559	460.119	504.659	−53.862	1224.246	−42.632

PREVIOUS: September 1962 CURRENT: December 1964

$S°(298.15\ K) = [234.935]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 371.93\ K$

$\Delta_f H°(298.15\ K) = [-7.133]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 21.966 \pm 0.04\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(B_{10}H_{14}, cl, 298.15\ K)$ is calculated from $\Delta_f H°(B_{10}H_{14}, cr, 298.15\ K)$, by adding $\Delta_{fus}H°$ reported by and Park[1] and the enthalpy difference, $H°(371.93\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

C_p (371.93 to 380 K) was measured by Furukawa and Park.[1] Heat capacities below 371.93 and above 380 K were estimated by comparison with that of the gaseous decarborane. $S°(298.15\ K)$ is calculated from that of crystal in a manner analogous to the used for the enthalpy of formation.

Fusion and Vaporization Data

T_{fus} and $\Delta_{fus}H°$ were obtained from Furukawa and Park.[1] T_{vap} and $\Delta_{vap}H°$ are calculated from functions for $B_{10}H_{14}$(1) and $B_{10}H_{14}$(g).

References

[1]G. T. Furukawa and R. P. Park, J. Res. Nat. Bur. Stand, **55**, 255 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	221.208	234.935	234.935	0.	−7.133	212.950	−37.308
300	222.924	236.309	234.939	0.411	−7.305	214.316	−37.316
371.930	296.720	291.607	240.487	19.013	--- CRYSTAL <--> LIQUID ---		
400	323.005	314.790	244.892	27.959	−13.724	289.341	−37.784
500	347.272	389.393	266.520	61.436	−18.015	365.589	−38.193
600	389.949	456.569	292.659	98.346	−21.421	442.666	−38.538
700	426.768	519.520	320.619	139.231	−22.652	520.141	−38.813
800	456.056	578.465	349.207	183.407	−21.973	597.656	−39.023
900	481.160	633.672	377.780	230.302	−19.718	674.990	−39.175
1000	502.080	685.486	405.987	279.499	−16.169	752.000	−39.280
1100	518.816	734.158	433.631	330.579	−11.661	828.605	−39.347
1200	531.368	779.869	460.600	383.123	−6.555	904.771	−39.384
1300	539.736	822.760	486.826	436.713	−1.225	980.499	−39.397
1400	543.920	862.937	512.272	490.931	3.947	1055.820	−39.393
1500	543.920	900.488	536.916	545.358	8.574	1130.788	−39.378

PREVIOUS: September 1962 CURRENT: December 1964

0	to	371.93 K	crystal
above		371.93 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−28.292	14.248	14.248	INFINITE
100	55.580	53.212	305.968	−25.276	−3.969	61.527	−32.138
200	123.386	109.725	193.426	−16.740	−17.619	132.450	−34.592
298.15	217.953	176.565	176.565	0.	−28.870	208.617	−36.549
300	219.706	177.918	176.569	0.405	−29.048	210.091	−36.580
371.930	293.483	232.548	182.044	18.784	____ CRYSTAL <-- --> LIQUID ____		
371.930	296.720	291.607	182.044	40.750	TRANSITION		
400	323.005	314.790	190.551	49.696	−13.724	289.340	−37.784
500	347.272	389.393	223.047	83.173	−18.015	365.589	−38.193
600	389.949	456.569	256.431	120.083	−21.421	442.666	−38.537
700	426.768	519.520	289.567	160.967	−22.653	520.141	−38.813
800	456.056	578.465	322.036	205.143	−21.973	597.656	−39.023
900	481.160	633.672	353.628	252.039	−19.718	674.990	−39.175
1000	502.080	685.486	384.250	301.236	−16.170	752.000	−39.280
1100	518.816	734.158	413.871	352.316	−11.661	828.605	−39.347
1200	531.368	779.869	442.486	404.860	−6.555	904.771	−39.384
1300	539.736	822.760	470.106	458.450	−1.225	980.499	−39.397
1400	543.920	862.937	496.746	512.667	3.946	1055.819	−39.393
1500	543.920	900.488	522.425	567.094	8.574	1130.787	−39.378

PREVIOUS: CURRENT: December 1964

$S°(298.15\ K) = 352.16\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 93.8 \pm 18.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 47.3 \pm 18.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies, υ, cm^{-1}							
230(1)	295(1)	344(1)	350(1)	387(1)	434(1)	446(1)	452(1)
464(1)	508(1)	588(1)	618(1)	635(1)	651(1)	690(1)	701(1)
709(1)	720(1)	747(1)	752(1)	767(1)	773(1)	814(1)	822(1)
832(1)	859(1)	862(1)	903(1)	915(1)	921(1)	924(1)	938(1)
942(1)	960(1)	967(1)	972(1)	1008(1)	1037(1)	1060(1)	1104(1)
1160(1)	1190(1)	1210(1)	1250(1)	1300(1)	1360(1)	1104(1)	1410(1)
1460(1)	1500(1)	1555(1)	1590(1)	1620(1)	1665(1)	1880(2)	1929(2)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distances: B–B = 1.762 Å; B–B(apex) = 1.773 Å; B–H(bridge) = 1.394 Å; B–H = 1.256 Å

Bond Angles: B–B–B = 108°; H–B(apex)–B = 59° 34'; B–B–B(apex) = 60° 13'; B–H(bridge)–B = 46° 17'; B(apex–B–H) = 87° 42'; B(center)–B(center)–H = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 8.657643 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The vapor pressures of decaborane were measured by Furukawa and Park[1] and Miller.[2] The enthalpies of vaporization were derived by both the 2nd and 3rd law methods. Using the average value of $\Delta_{vap}H°$, the respective of enthalpies of formation for $B_{10}H_{14}$(g) are calculated.

Source	Reaction	$\Delta_r H°(298.15)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15)$ kcal·mol^{-1}
1	$B_{10}H_{14}(cr) \rightarrow B_{10}H_{14}(g)$	16.63 ± 0.93	18.20	10.52 ± 4.5
	$B_{10}H_{14}(l) \rightarrow B_{10}H_{14}(g)$	13.28 ± 0.06	13.06	11.47 ± 4.5
2	$B_{10}H_{14}(cr) \rightarrow B_{10}H_{14}(g)$	17.81 ± 0.01	18.27	11.14 ± 4.5

The adopted value of $\Delta_f H°(298.15\ K)$ for $B_{10}H_{14}$(g) is the weighted average of the three $\Delta_f H°(298.15\ K)$ values listed in the above table.

Heat Capacity and Entropy

The molecular structure of $B_{10}H_{14}$(c) were reported by Kasper, Lucht and Harker,[3] Moore, Dickerson, and Lipscomb,[4] and Lipscomb.[5] For the calculation of the moments of inertia for $B_{10}H_{14}$(g) a simplified molecular model is adopted. The molecule is assumed to be composed of two regular pentagonal pyramids with a common base edge. The angle between the base planes of those pyramids is 73° 30'. Each of 10 H atoms is attached to a single B atom above the base plane. The remaining 4 H atoms, each bridge two B atoms. The vibrational frequencies were obtained from Evans,[6] which were derived based on the infrared and Raman spectra reported by Stewart[7] and Keller and Johnston.[8] The principal moments of inertia are: $I_A = 35.1322 \times 10^{-39}$, $I_B = 45.3594 \times 10^{-39}$, and $I_C = 54.3284 \times 10^{-39}\ g·cm^2$.

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[7]J. E. Stewart, U.S. Nat. Bur. Stand., personal communication, (1957).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−24.839	93.850	93.850	INFINITE
100	46.005	248.258	460.646	−21.239	76.216	122.208	−63.835
200	105.137	296.347	366.164	−13.963	61.306	174.051	−45.457
250	142.942	323.835	354.911	−7.769	54.016	203.084	−42.432
298.15	179.581	352.159	352.159	0.	47.279	232.412	−40.718
300	180.961	353.275	352.163	0.333	47.029	233.561	−40.667
350	216.949	383.907	354.500	10.292	40.573	265.169	−39.574
400	249.946	415.066	360.121	21.978	34.707	297.661	−38.871
450	279.729	446.256	367.960	35.233	29.462	330.852	−38.404
500	306.427	477.136	377.337	49.900	24.860	364.593	−38.089
600	351.663	537.156	399.010	82.888	17.533	433.268	−37.719
700	387.932	594.191	422.857	119.934	12.463	502.987	−37.533
800	417.186	647.970	447.669	160.241	9.273	573.299	−37.433
900	440.941	698.527	472.762	203.188	7.580	643.918	−37.372
1000	460.360	746.023	497.738	248.285	7.028	714.660	−37.330
1100	476.345	790.674	522.360	295.146	7.318	785.416	−37.296
1200	489.595	832.708	546.488	343.463	8.197	856.117	−37.266
1300	500.656	872.346	570.044	392.992	9.466	926.728	−37.236
1400	509.954	909.799	592.987	443.536	10.963	997.231	−37.207
1500	517.824	945.258	615.301	494.935	12.564	1067.623	−37.178
1600	524.530	978.897	636.983	547.062	14.169	1137.907	−37.149
1700	530.279	1010.873	658.044	599.809	15.700	1208.094	−37.120
1800	535.238	1041.327	678.498	653.091	17.099	1278.193	−37.092
1900	539.541	1070.384	698.365	706.835	18.318	1348.219	−37.065
2000	543.294	1098.156	717.666	760.981	19.318	1418.188	−37.039
2100	546.584	1124.745	736.422	815.479	20.073	1488.112	−37.015
2200	549.483	1150.240	754.656	870.285	20.557	1558.005	−36.992
2300	552.049	1174.723	772.391	925.364	20.752	1627.884	−36.970
2400	554.329	1198.268	789.649	980.685	−481.950	1708.449	−37.183
2500	556.363	1220.938	806.450	1036.222	−483.155	1799.741	−37.604
2600	558.185	1242.795	822.814	1091.951	−484.360	1891.079	−37.992
2700	559.824	1263.893	838.762	1147.853	−485.577	1982.465	−38.353
2800	561.301	1284.279	854.312	1203.910	−486.816	2073.897	−38.689
2900	562.638	1304.000	869.480	1260.108	−488.084	2165.374	−39.003
3000	563.852	1323.095	884.284	1316.434	−489.389	2256.895	−39.296
3100	564.956	1341.602	898.739	1372.875	−490.738	2348.459	−39.571
3200	565.964	1359.555	912.860	1429.422	−492.135	2440.067	−39.830
3300	566.886	1376.985	926.662	1486.065	−493.585	2531.722	−40.074
3400	567.732	1393.921	940.157	1542.796	−495.094	2623.420	−40.304
3500	568.510	1410.389	953.358	1599.609	−496.665	2715.164	−40.522
3600	569.226	1426.415	966.277	1656.496	−498.303	2806.953	−40.728
3700	569.887	1442.020	978.925	1713.452	−500.009	2898.790	−40.924
3800	570.499	1457.226	991.313	1770.472	−501.788	2990.673	−41.110
3900	571.066	1472.053	1003.450	1827.551	−503.643	3082.604	−41.287
4000	571.593	1486.518	1015.347	1884.684	−505.575	3174.582	−41.456
4100	572.082	1500.638	1027.011	1941.868	−507.587	3266.612	−41.617
4200	572.538	1514.429	1038.453	1999.099	−5308.175	3428.933	−42.645
4300	572.964	1527.906	1049.680	2056.375	−5299.480	3636.856	−44.179
4400	573.362	1541.083	1060.699	2113.691	−5290.888	3844.578	−45.641
4500	573.734	1553.972	1071.518	2171.046	−5282.400	4052.105	−47.036
4600	574.083	1566.586	1082.143	2228.437	−5274.020	4259.446	−48.368
4700	574.411	1578.936	1092.582	2285.862	−5265.751	4466.606	−49.641
4800	574.718	1591.033	1102.841	2343.319	−5257.594	4673.594	−50.859
4900	575.008	1602.886	1112.926	2400.805	−5249.551	4880.407	−52.026
5000	575.280	1614.505	1122.842	2458.320	−5241.623	5087.063	−53.144
5100	575.537	1625.900	1132.594	2515.861	−5233.812	5293.556	−54.217
5200	575.780	1637.078	1142.189	2573.427	−5226.117	5499.902	−55.247
5300	576.010	1648.048	1151.630	2631.016	−5218.540	5706.099	−56.237
5400	576.227	1658.817	1160.923	2688.628	−5211.080	5912.155	−57.189
5500	576.432	1669.392	1170.072	2746.261	−5203.735	6118.070	−58.105
5600	576.627	1679.780	1179.081	2803.914	−5196.507	6323.857	−58.987
5700	576.812	1689.988	1187.955	2861.586	−5189.393	6529.516	−59.836
5800	576.987	1700.021	1196.698	2919.276	−5182.391	6735.050	−60.656
5900	577.154	1709.886	1205.313	2976.983	−5175.501	6940.461	−61.446
6000	577.312	1719.588	1213.803	3034.707	−5168.720	7145.758	−62.209

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

Lead Borate ($Pb_2B_{10}O_{17}$) CRYSTAL $M_r = 794.4898$

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [352.7 \pm 13]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15) = -7087.7 \pm 13\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Refer to the PbB_2O_4(cr) table for the complete writeup. Evans[1] analysed the enthalpies of formation of lead borate system based upon Shartsis and Newman's enthalpies of solution and Mazzetti and DeCarli's phase studies. From the Shartsis and Newman paper Evans obtained the following:

$$2\ PbO(cr) + 5\ B_2O_3(cr) \rightarrow 2\ PbO \cdot 5B_2O_3(gls) \quad \Delta_r H = -45.2\ kcal \cdot mol^{-1}$$

and estimated a ΔH_{298} of 26.8 $kcal \cdot mol^{-1}$ for the conversion to the $2PbO \cdot 5B_2O_3$(cr). With auxiliary JANAF values the $\Delta_f H°(298.15\ K)$ is calculated to be $-1694.00\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacity employed in this table was obtained by graphically smoothing the summation of the heat capacities of the constituent oxides.

The entropy at 298.15 K was obtained in the manner described in the PbB_4O_7 table from the entropies of $PbO \cdot 2B_2O_3$ and $Pb \cdot 3B_2O_3$ and the subtraction of 4.2 $cal \cdot K^{-1} \cdot mol^{-1}$.

References

[1]W. H. Evans, U.S. Nat. Bur. Stand. Report 7192, Ch. 6 (July 1, 1961); refer to pp. 80–1.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	406.685	352.711	352.711	0.	−7087.696	−6616.932	1159.259
300	408.358	355.232	352.719	0.754	−7087.714	−6614.011	1151.602
400	502.917	486.150	369.928	46.489	−7086.317	−6456.200	843.093
500	576.974	606.499	405.379	100.560	−7081.183	−6299.195	658.072
600	641.826	717.604	448.275	161.597	−7072.593	−6143.547	534.843
700	694.962	820.629	494.201	228.499	−7070.549	−5987.999	446.830
800	740.568	916.489	541.065	300.339	−7055.936	−5834.313	380.942
900	778.642	1005.987	587.807	376.362	−7038.648	−5682.623	329.811
1000	809.186	1089.665	633.856	455.809	−7019.159	−5532.980	289.013
1100	833.034	1167.960	678.891	537.976	−6997.967	−5385.374	255.730
1200	850.189	1241.225	722.733	622.189	−6975.596	−5239.755	228.081
1300	861.067	1309.734	765.282	707.787	−6952.611	−5096.032	204.761
1400	867.762	1373.811	806.485	794.256	−6929.479	−4954.086	184.839
1500	871.109	1433.795	846.328	881.200	−6906.558	−4813.790	167.631
1600	874.456	1490.122	884.823	968.478	−6883.959	−4675.011	152.623
1700	877.803	1543.236	922.005	1056.091	−6861.659	−4537.635	139.425
1800	881.150	1593.504	957.927	1144.039	−6839.645	−4401.567	127.730
1900	884.498	1641.235	992.645	1232.321	−6817.903	−4266.712	117.300
2000	887.845	1686.689	1026.220	1320.938	−6796.422	−4132.994	107.943

PREVIOUS: December 1962 CURRENT: March 1965

Continued from page 222

There have been no measurements reported for HBO which provide direct experimental information on its structure. However, the millimeter-wave spectra of the related species HBS[14] have been observed. These results show that this molecule is linear and has a B=S bond length which is 0.01 Å less than that for BS.[1] We assume a similar decrease in r_e(B=O) for the HBO–BO pair, and we obtain r_e(HB–O) = 1.19 Å with r_e(B=O) = 1.20 Å.[1] The H–B bond length is assumed the same as that for HBS.[14] Ab– initio calculations[8] of bond lengths for HBO by an optimization procedure predict values only slightly lower (~0.01 Å) than our estimates. We note that bond lengths computed by this procedure are normally slightly lower (~0.005 Å) than the true values as indicated by the results for HCP[16] and HBS.[17] By analogy with HBS,[14] we assume HBO to be linear. This assumption is in agreement with predictions from the Walsh diagram[15] for HAB molecules with ten valence electrons. In direct evidence available from product rule calculations[2] also tend to support a linear configuration.

References

[1]JANAF Thermochemical Tables: H_2(g), 3–31–61; B_2O_3(l), 6–30–71; BO(g), 6–30–68; B_2O_2(g) and BH_3(g), 12–31–64; HCP(g) and HCN(g), 12–31–69; BS(g), 6–30–72.
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calculation on HCN led these workers to conclude that their υ_2 values were probably lower (~50 cm^{-1}) than the true values. They suggested a better estimate of υ_2 as 690 ± 30 cm^{-1}. Pearson and McCormick[8] estimated υ_2 = 680 cm^{-1} from the l–doubling constant determined from their microwave measurements. These latter two values support our selection of υ_2 = 715 cm^{-1}. Photoelectron spectrometric results[10, 11] have led to predictions of υ_3 = 1100 cm^{-1} from the changes observed in vibrational frequencies produced upon ionization. We believe our calculated frequencies are uncertain to no more than ±50 cm^{-1} which amounts to an $S°$(298.15 K) error of ± 0.1 cal·K^{-1}·mol^{-1}.

Evidence is available which suggests that the ground state configuration and excited states of HBS are similar to those for the isoelectronic molecule HCP. Theoretical calculations[7, 12] predict the same ordering of valence orbitals for these two molecules. This orbital order is corroborated by the results[10, 11, and 13] of photoelectron spectroscopy where the similarity[11] in their PE spectra has been noted. In addition, we note that the Zeeman parameters recently reported for HBS and HCP by Pearson *et al.*[14] are nearly identical. We assume the same ground state configuration ($^1\Sigma^+$) for HBS as that for HCP,[3] and we estimate the electronic levels by analogy with those observed for HCP.

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REFERENCE STATE

0	to	582.53 K	crystal, alpha
582.53	to	768.13 K	crystal, beta
768.13	to	1000 K	crystal, gamma
1000	to	2118.599 K	liquid
above		2118.599 K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.912	0.	0.	0.
100	24.301	34.083	86.220	−5.214	0.	0.	0.
200	26.368	51.643	64.988	−2.669	0.	0.	0.
298.15	28.096	62.475	62.475	0.	0.	0.	0.
300	28.142	62.649	62.476	0.052	0.	0.	0.
400	33.229	71.295	63.622	3.069	0.	0.	0.
500	43.744	79.771	65.997	6.887	0.	0.	0.
582.530	54.400	87.232	68.471	10.929	ALPHA <--> BETA		
582.530	32.468	87.232	68.471	10.929	TRANSITION		
600	33.941	88.213	69.031	11.509	0.	0.	0.
700	42.363	94.077	72.186	15.324	0.	0.	0.
768.130	48.103	98.274	74.313	18.406	BETA <--> GAMMA		
768.130	39.066	98.274	74.313	18.406	TRANSITION		
800	39.066	99.863	75.299	19.651	0.	0.	0.
900	39.066	104.464	78.289	23.557	0.	0.	0.
1000	39.066	108.580	81.116	27.464	0.	0.	0.
1000.000	39.066	108.580	81.116	27.464	GAMMA <--> LIQUID		
1000.000	43.304	116.592	81.116	35.476	TRANSITION		
1100	42.007	120.657	84.530	39.741	0.	0.	0.
1200	40.878	124.262	87.693	43.883	0.	0.	0.
1300	39.999	127.498	90.633	47.925	0.	0.	0.
1400	39.330	130.437	93.373	51.890	0.	0.	0.
1500	38.869	133.133	95.935	55.798	0.	0.	0.
1600	38.618	135.633	98.339	59.670	0.	0.	0.
1700	38.576	137.971	100.602	63.528	0.	0.	0.
1800	38.740	140.180	102.740	67.392	0.	0.	0.
1900	39.116	142.284	104.766	71.283	0.	0.	0.
2000	39.706	144.304	106.693	75.223	0.	0.	0.
2100	40.518	146.260	108.531	79.232	0.	0.	0.
2118.599	40.692	146.618	108.863	79.987	LIQUID <--> IDEAL GAS		
2118.599	30.938	212.831	108.863	220.265	FUGACITY = 1 bar		
2200	32.665	214.029	112.732	222.853	0.	0.	0.
2300	34.873	215.530	117.169	226.230	0.	0.	0.
2400	37.123	217.062	121.299	229.830	0.	0.	0.
2500	39.355	218.622	125.161	233.654	0.	0.	0.
2600	41.512	220.208	128.786	237.698	0.	0.	0.
2700	43.543	221.814	132.202	241.952	0.	0.	0.
2800	45.406	223.431	135.431	246.401	0.	0.	0.
2900	47.068	225.054	138.493	251.026	0.	0.	0.
3000	48.509	226.675	141.406	255.807	0.	0.	0.
3100	49.718	228.286	144.182	260.720	0.	0.	0.
3200	50.695	229.880	146.836	265.743	0.	0.	0.
3300	51.410	231.450	149.376	270.844	0.	0.	0.
3400	51.931	232.992	151.813	276.012	0.	0.	0.
3500	52.262	234.503	154.154	281.223	0.	0.	0.
3600	52.420	235.978	156.406	286.458	0.	0.	0.
3700	52.431	237.415	158.576	291.702	0.	0.	0.
3800	52.319	238.812	160.669	296.940	0.	0.	0.
3900	52.105	240.168	162.691	302.162	0.	0.	0.
4000	51.814	241.483	164.644	307.358	0.	0.	0.
4200	51.068	243.993	168.363	317.645	0.	0.	0.
4400	50.234	246.350	171.855	327.776	0.	0.	0.
4600	49.384	248.563	175.143	337.732	0.	0.	0.
4800	48.545	250.640	178.245	347.499	0.	0.	0.
5000	47.832	252.606	181.180	357.129	0.	0.	0.
5200	47.194	254.465	183.963	366.608	0.	0.	0.
5400	46.697	256.236	186.607	375.995	0.	0.	0.
5600	46.176	257.908	189.122	385.200	0.	0.	0.
5800	45.812	259.517	191.522	394.376	0.	0.	0.
6000	45.369	261.036	193.810	403.351	0.	0.	0.

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 62.475 \pm 0.8\ J·K^{-1}·mol^{-1}$
$T_{trs} = [582.53]\ K\ (\alpha \rightarrow \beta)$
$T_{trs} = [768.13]\ K\ (\beta \rightarrow \gamma)$
$T_{fus} = 1000 \pm 3\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{trs} H° = [0.0]\ kJ·mol^{-1}$
$\Delta_{trs} H° = [0.0]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 8.012 \pm 0.62\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted values below 298.15 K are based on $C_p°$(18–370 K) of Furukawa and Ishihara[1] and $C_p°$(1.5–20 K) of Roberts.[2] $S°$(298.15 K) is calculated from $C_p°$ based on an extrapolation of about 0.001 $cal·K^{-1}·mol^{-1}$ below 1.5 K. We estimate that $S°$(298.15 K) is uncertain by about 0.2 $cal·K^{-1}·mol^{-1}$, due mainly to possible effects of impurities. Furukawa and Ishihara[1] reported impurities (in mole %) of about 3% BaO, 1% Sr and 0.2% Ca. Further details on adjustment of the data for impurities are given in the original paper.[1]

Relative enthalpies were measured by Jauch,[3] Shpil'rain[4] and Ditmars and Douglas.[5] Earlier reviewers dismissed the abnormally high $C_p°$ values of Jauch as due to a very impure sample. The new data confirm this decision, but at least one new study[5] may also involve bias due to impurities. Separate portions from a common sample consisting of three Ba rods were used in the heat capacity study,[1] the enthalpy study[5] and the analytical studies.[1,5] The calorimetric data suggest variability in the impurity contents of the separate portions. The 2nd law study[4] used Ba which was not analyzed for O or N which are the most likely contaminants. Since the premelting effect in the enthalpy at 979 K appears to be 1/4 as large in[4] as in,[5] the sample of[4] may have been more pure; however, such a conclusion would be quite speculative. Liquid enthalpies are in reasonable agreement, but the crystal enthalpies of[4] are 4 to 20% lower than those of.[5] Another major difference is that[4] suggests a single "transition" near 650 K, while[5] suggests two "transitions" near 580 and 770 K. Further confusion arises because the enthalpies reported[4] for CsF(c, l) are unreasonably large.

We tentatively adopt the smoothed $C_p°$ of Ditmars and Douglas,[5] pending resolution of the transition discrepancy. The following alternative functions reproduce the enthalpies of Shpil'rain[4] and provide estimates of the possible bias in the adopted functions, Ba(α): $C_p°/cal·K^{-1}·mol^{-1} = 5.023 \pm 0.005657\ T$ (298–650 K), $\Delta_{trs} H° = 0.345\ kcal·mol^{-1}$ at 650 K; Ba(γ): $C_p°/cal·K^{-1}·mol^{-1} = 9.4$ (650–999.6 K), $\Delta_{fus} H° = 2.048\ kcal·mol^{-1}$ at 999.6 K; Ba(l): $C_p°/cal·K^{-1}·mol^{-1} = 10.0$ (999.6–1300 K). There is reasonable agreement between the alternative and adopted $C_p°$ for Ba(l) and Ba(γ), suggesting that the γ–phases are identical in the two studies. $C_p°(\alpha)$ from the equation is a reasonable extension of the data below 298.15 K;[1] $C_p°$ does not show the abnormally steep rise just above 300 K which appears in the enthalpy data[5] and to a lesser degree, in the $C_p°$ data.[1] The alternative functions suggest that the adopted γ–phase entropy may be biased by about +0.6 $cal·K^{-1}·mol^{-1}$ (about +6% in $S°(T)$–$S°$(298.15 K) due to impurities. Ditmars and Douglas stressed the possibility of such systematic errors[5] and estimated errors of up to 5% in $C_p°$ and $H°$. Our alternative functions suggest the maximum error in $C_p°(\alpha)$ may be much larger than 5%.

TransitionData

Recent data for Sr and Ca indicate that the pure metals exist in the fcc and bcc polymorphs but that impurities probably stabilize the hcp form. Although enthalpy data[4,5] suggest a similar controversy for Ba, the pure metal is usually reported to have the bcc form at all temperatures at atmospheric pressure.[6–9] Several high–pressure polymorphs are known.[10–12] Earlier literature[13] contains much evidence for a "transition" near 648 K at one atmosphere; this is consistent with new enthalpy data[4] and could correspond to the "transition" found by Bridgman[13] near 17 kbar at room temperature. Bridgman's "transition" is in dispute; it seems to involve a very small volume contraction[12,14] and no obvious change in X–ray pattern.[15] We speculate that these two "transitions" are identical; however, evidence for their being a property of pure Ba is inconclusive. The main support comes from the relatively small premelting effect in enthalpy.[4] The enthalpy data[4] are insufficient to distinguish whether the "transitions" is first or second order.

We tentatively adopt the two "transitions" with zero enthalpies selected by Ditmars and Douglas.[5] These values are placed in brackets to emphasize that there is no confirmatory evidence whatsoever. The authors suggest that these "transitions" may have resulted wholly from impurities. We speculate further the $T_{trs} = 582$ K could be due to impurity lowering of $T_{trs} = 650$ K, while $T_{trs} = 768$ K could result from crossing of a solid–solubility limit below the eutectic temperature of the Ba–BaO system. This case would favor the alternative functions given above. It is also possible that the Sr and Ca impurities could nucleate other polymorphs.

The adopted functions include $\Delta_{trs} H° = 0.97\ cal·mol^{-1}$ at 57 K from a small–anomaly observed between 50 and 60 K.[1]

Fusion and Sublimation Data

Refer to the liquid and ideal gas tables for details.

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Continued on page 358

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.912	0.	0.	0.
100	24.301	34.083	86.220	−5.214	0.	0.	0.
200	26.368	51.643	64.988	−2.669	0.	0.	0.
250	27.196	57.613	62.933	−1.330	0.	0.	0.
298.15	28.096	62.475	62.475	0.	0.	0.	0.
300	28.142	62.649	62.476	0.052	0.	0.	0.
350	29.898	67.105	62.824	1.498	0.	0.	0.
400	33.229	71.295	63.622	3.069	0.	0.	0.
450	38.031	75.475	64.706	4.846	0.	0.	0.
500	43.744	79.771	65.997	6.887	0.	0.	0.
582.530	54.400	87.232	68.471	10.929	ALPHA <--> BETA		
582.530	32.468	87.232	68.471	10.929	TRANSITION		
600	33.941	88.213	69.031	11.509	0.	0.	0.
700	42.363	94.077	72.186	15.324	0.	0.	0.
768.130	48.103	98.274	74.313	18.406	BETA <--> GAMMA		
768.130	39.066	98.274	74.313	18.406	TRANSITION		
800	39.066	99.863	75.299	19.651	0.	0.	0.
900	39.066	104.464	78.289	23.557	0.	0.	0.
1000	39.066	108.580	81.116	27.464	0.	0.	0.
1000.000	39.066	108.580	81.116	27.464	GAMMA <--> LIQUID		
1100	39.066	112.303	83.784	31.371	−8.370	0.820	−0.039
1200	39.066	115.702	86.305	35.277	−8.606	1.666	−0.073
1300	39.066	118.829	88.688	39.184	−8.741	2.528	−0.102
1400	39.066	121.724	90.946	43.090	−8.799	3.398	−0.127
1500	39.066	124.420	93.088	46.997	−8.801	4.269	−0.149

PREVIOUS: December 1970 CURRENT: December 1970

$S°(298.15\ K)$ = [66.328] $J·K^{-1}·mol^{-1}$
T_{fus} = 1000 ± 3 K

$\Delta_f H°(298.15\ K)$ = [4.985] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 8.012 ± 0.62 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1000\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is based on the parabolic equation derived by Douglas and Krause[1] from enthalpy data of Ditmars and Douglas.[2] The enthalpy data (1003 to 1173 K) may be biased due to impurities in the sample;[2] however, enthalpy data (1035 to 1253 K) of Shpil'rain[3] are in reasonable agreement. This suggests that the large discrepancies for Ba(cr) are partially compensated by different values of $\Delta_{fus}H°$. Detailed discussions of the discrepancies and possible alternative functions are given on the crystal table. The alternative functions, derived from the possibly purer sample of Shpil'rain,[3] suggest that the adopted liquid entropies may be biased by about +0.4 $cal·K^{-1}·mol^{-1}$.

Douglas and Krause emphasized the uncertain nature[1] of the parabolic extrapolation of $C_p°$ from 1200 to 2000 K. The extrapolation is reasonable provided that the temperature coefficient of $C_p°$ is not grossly biased due to effects of impurities on the observed enthalpies. Such bias seems unlikely because of the agreement in enthalpy between samples of different purity[2,3] and because the impurities[2] are present in amounts much below their solubility limits[2,4,5] in Ba(l). We note also that $S°(2000\ K)$ is not significantly changed when the parabolic fit is replaced by a two–constant fit in which $C_p°$ approaches a constant (8.48 $cal·K^{-1}·mol^{-1}$) at high temperature.

The parabolic $C_p°$ is extrapolated to 580 K, the assumed glass transition temperature. $C_p°$ below 580 K is taken to be the same as the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that of the enthalpy of formation.

Melting Data

Ditmars and Douglas[2] considered early melting point data and arbitrarily selected 991 K. Recent data yield higher values of 998 ± 1[6,7] and 1002 ± 1 K.[8,10] These values represent more carefully purified samples. We adopt 1000 ± 3 K and adjust $\Delta_{fus}H°$ slightly so that the result is consistent with the smoothed enthalpy[2] of the liquid. Alternative functions based on enthalpies of Shpil'rain[3] suggest that the adopted $\Delta_{fus}H°$ may be too small by about 0.15 $kcal·mol^{-1}$ (see the crystal table).

Vaporization Data

T_{vap} = 2118.599 K is calculated as the temperature at which $\Delta_r G° = 0$ for Ba(l) → Ba(g). $\Delta_{vap}H°$ = 140.278 $kJ·mol^{-1}$ is the difference between $\Delta_f H°$(g) and $\Delta_f H°$(l) at T_{vap}. Bohdansky and Schins[11] ported T_{vap} = 2063 K(1 atm) based on extrapolation of their vapor pressure data from 2024 K. Our calculated T_{vap} is some 60 K higher due to the entropy difference between the adopted functions and vapor pressure data[11] and to adoption of the mean 3rd law $\Delta_{sub}H°$ rather than the apparent value at 2024 K. Refer to the ideal gas table for further details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0						
100						
200						
250						
298.15	28.096	66.328	66.328	0.	4.985	3.837	−0.672
300	28.142	66.502	66.329	0.052	4.985	3.829	−0.667
350	29.898	70.958	66.677	1.498	4.985	3.636	−0.543
400	33.229	75.147	67.475	3.069	4.985	3.444	−0.450
450	38.031	79.327	68.559	4.846	4.985	3.251	−0.377
500	43.744	83.623	69.849	6.887	4.985	3.059	−0.320
580.000	54.057	90.849	72.242	10.792	GLASS <--> LIQUID		
580.000	51.120	90.849	72.242	10.792	TRANSITION		
600	50.664	92.574	72.891	11.809	5.286	2.669	−0.232
700	48.509	100.219	76.267	16.766	6.428	2.128	−0.159
800	46.564	106.567	79.670	21.518	6.853	1.489	−0.097
900	44.832	111.950	82.965	26.086	7.514	0.777	−0.045
1000	43.304	116.592	86.101	30.491	8.012	0.	0.
1000.000	43.304	116.592	86.101	30.491	GAMMA <--> LIQUID		
1100	42.007	120.657	89.062	34.755	0.	0.	0.
1200	40.878	124.262	91.848	38.898	0.	0.	0.
1300	39.999	127.498	94.468	42.940	0.	0.	0.
1400	39.330	130.437	96.933	46.904	0.	0.	0.
1500	38.869	133.133	99.258	50.813	0.	0.	0.
1600	38.618	135.633	101.454	54.685	0.	0.	0.
1700	38.576	137.971	103.534	58.543	0.	0.	0.
1800	38.740	140.180	105.509	62.407	0.	0.	0.
1900	39.116	142.284	107.390	66.298	0.	0.	0.
2000	39.706	144.304	109.185	70.238	0.	0.	0.
2100	40.518	146.260	110.905	74.247	0.	0.	0.
2118.599	40.692	146.618	111.217	75.002	FUGACITY = 1 bar		
2200	41.539	148.168	112.555	78.348	−139.520	5.375	−0.128
2300	42.769	150.041	114.144	82.562	−138.683	11.942	−0.271
2400	44.208	151.891	115.679	86.909	−137.935	18.475	−0.402
2500	45.857	153.728	117.164	91.410	−137.258	24.978	−0.522
2600	47.708	155.562	118.605	96.087	−136.626	31.455	−0.632
2700	49.771	157.400	120.008	100.959	−136.008	37.907	−0.733
2800	52.047	159.251	121.377	106.048	−135.368	44.337	−0.827
2900	54.536	161.120	122.715	111.376	−134.666	50.743	−0.914
3000	57.237	163.014	124.027	116.962	−133.860	57.123	−0.995
3100	60.151	164.938	125.315	122.830	−132.905	63.474	−1.070
3200	63.277	166.896	126.584	129.000	−131.758	69.791	−1.139
3300	66.616	168.894	127.836	135.493	−130.366	76.068	−1.204
3400	70.167	170.935	129.073	142.330	−128.696	82.299	−1.264
3500	73.931	173.023	130.299	149.533	−126.704	88.477	−1.320

PREVIOUS: December 1970 CURRENT: December 1970

0	to	582.53	K	crystal, alpha
582.53	to	768.13	K	crystal, beta
768.13	to	1000	K	crystal, gamma
above		1000	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−6.912	0.	0.	0.
100	24.301	34.083	86.220	−5.214	0.	0.	0.
200	26.368	51.643	64.988	−2.669	0.	0.	0.
250	27.196	57.613	62.933	−1.330	0.	0.	0.
298.15	28.096	62.475	62.475	0.	0.	0.	0.
300	28.142	62.649	62.476	0.052	0.	0.	0.
350	29.898	67.105	62.824	1.498	0.	0.	0.
400	33.229	71.295	63.622	3.069	0.	0.	0.
450	38.031	75.475	64.706	4.846	0.	0.	0.
500	43.744	79.771	65.997	6.887	0.	0.	0.
582.530	54.400	87.232	68.471	10.929	ALPHA <--> BETA TRANSITION		
582.530	32.468	87.232	68.471	10.929			
600	33.941	88.213	69.031	11.509	0.	0.	0.
700	42.363	94.077	72.186	15.324	0.	0.	0.
768.130	48.103	98.274	74.313	18.406	BETA <--> GAMMA TRANSITION		
768.130	39.066	98.274	74.313	18.406			
800	39.066	99.863	75.299	19.651	0.	0.	0.
900	39.066	104.464	78.289	23.557	0.	0.	0.
1000	39.066	108.580	81.116	27.464	0.	0.	0.
1000.000	39.066	108.580	81.116	27.464	GAMMA <--> LIQUID TRANSITION		
1000.000	43.304	116.592	81.116	35.476			
1100	42.007	120.657	84.530	39.741	0.	0.	0.
1200	40.878	124.262	87.693	43.883	0.	0.	0.
1300	39.999	127.498	90.633	47.925	0.	0.	0.
1400	39.330	130.437	93.373	51.890	0.	0.	0.
1500	38.869	133.133	95.935	55.798	0.	0.	0.
1600	38.618	135.633	98.339	59.670	0.	0.	0.
1700	38.576	137.971	100.602	63.528	0.	0.	0.
1800	38.740	140.180	102.740	67.392	0.	0.	0.
1900	39.116	142.284	104.766	71.283	0.	0.	0.
2000	39.706	144.304	106.693	75.223	0.	0.	0.
2100	40.518	146.260	108.531	79.232	0.	0.	0.
2118.599	40.692	146.618	108.863	79.987	----- FUGACITY = 1 bar -----		
2200	41.539	148.168	110.289	83.333	−139.520	5.375	−0.128
2300	42.769	150.041	111.977	87.547	−138.683	11.942	−0.271
2400	44.208	151.891	113.601	91.894	−137.935	18.475	−0.402
2500	45.857	153.728	115.170	96.396	−137.258	24.978	−0.522
2600	47.708	155.562	116.688	101.072	−136.626	31.455	−0.632
2700	49.771	157.400	118.162	105.944	−136.008	37.908	−0.733
2800	52.047	159.251	119.596	111.033	−135.368	44.337	−0.827
2900	54.536	161.120	120.996	116.361	−134.666	50.743	−0.914
3000	57.237	163.014	122.365	121.948	−133.860	57.123	−0.995
3100	60.151	164.938	123.707	127.815	−132.905	63.474	−1.070
3200	63.277	166.896	125.026	133.985	−131.758	69.791	−1.139
3300	66.616	168.894	126.325	140.478	−130.366	76.068	−1.204
3400	70.167	170.935	127.607	147.315	−128.696	82.299	−1.264
3500	73.931	173.023	128.874	154.518	−126.704	88.477	−1.320

PREVIOUS: December 1970 CURRENT: December 1970

IP (Ba, g) = 42035.14 ± 0.05 cm^{-1}
$S°(298.15\ K)$ = 170.245 ± 0.01 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 179.8 ± 5.0 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 179.1 ± 5.0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0.0	1	22947	7	25704	3	33188	15	39765	[21]	[42000]	33
9034.0	3	23757	9	25957	5	33837	8	39905	[9]	[36440]	1
9215.5	5	23068	10	26160	3	35142	10	40736	3	[40000]	63
9596.6	7	23209	1	26816	7	34649	28	40893	15	[20000]	21
11395.4	5	23480	3	28230	1	35658	20	41097	9	[24000]	9
12266.0	1	23919	5	28554	3	35893	3	42012	3	[25000]	1
12636.6	3	24192	3	30237	5	36400	55	42436	9	[19000]	20
13514.7	5	24532	5	30771	15	36974	56	43264	3	[39000]	20
18060	3	24980	7	30903	9	37425	58	35500	9	[42000]	120
22065	5	25642	1	32547	3	38031	37	37700	9		

Enthalpy of Formation

$\Delta_f H°$ is $\Delta_{sub} H°$, 42.8 ± 1.2 $kcal·mol^{-1}$, selected from 3rd law analyses of pressure data tubulated below. The adopted value is from the recent boiling-point study of Bohdansky and Schins.[1] Except for the very scattered effusion data of Zavitsanos,[4] the other studies differ by unusually large amounts: −2,[2] −6[3] and +3 $kcal·mol^{-1}$.[5] Data of Ruff and Hartmann[3] are readily dismissed due to the large entropy discrepancy; their data for other metals have similar discrepancies. Data of Rudberg and Lempert[5] for Ca and Ba show almost identical biases, presumably due to poor effusion geometry or to impurities. A similar bias seems to exist in the effusion–resonance–fluorescence data of Hinnov and Ohlendorf:[6] our analysis is not tabulated below since the graphical data include large discrepancies in temperature. Hartmann and Scheider's Ba data[2] deviate considereably more from the selected value than do their data for Li, Mg, Ca and Sr. The differences probably arise from impurity effects. Since Ba is the least volatile of the reactive metals studied,[1,2] purification by distillation presents special problems. Even Bohdansky and Schins[1] noted that their Ba data may be biased by impurities.

Analyses of the pressure data assume that the monatomic gas is the only significant species in the vapor and that gas imperfection is negligible. Evidence supporting the unimportance of the dimer was reviewed by Douglas and Krause.[7] Estimated bond energies for the dimers of Mg, Ca, Sr nd Ba are less than 8.6 $kcal·mol^{-1}$.[8,10]

Source	Method	T/K[a]	$\Delta_f H°$(298.15 K), $kcal·mol^{-1}$ 2nd law	3rd law	δS $cal·K^{-1}·mol^{-1}$
1	Boiling Point	1498–2027	46.7 ± 0.3	42.78 ± 0.04	2.2 ± 0.1
2	Boiling Point	1334–1421	41.4 ± 3.3	40.76 ± 0.33	0.4 ± 2.4
3	Boiling Point	1204–1404	92.6 ± 3.0	37.0 ± 6.1	43 ± 2.3
4	Effusion	1120–1210	65 ± 10	43.8 ± 1.6	18 ± 8.8
4	Torsion Effusion	1103–1216	36 ± 10	43.5 ± 1.9	−6.3 ± 8.4
5	Effusion	798–1024	43.2 ± 1.2	45.91 ± 0.77	−3.0 ± 1.3

[a]Temperature adjusted to IPTS–68 assuming published values to be IPTS–48.

Heat Capacity and Entropy

Observed energy levels and quantum weights are from Moore[11] as modified by Garton *et al.*[12,13] Additional levels above the cutoffs have been reported.[14,15] We adopt an energy–level cutoff which is about kTmax (Tmax = 6000 K) below each series limit. For Ba I this corresponds to omitting levels above 9s, 8p, 7d and 5f. Energies of unobserved but predicted terms[11] are estimated by comparison of Ca I, Sr I, Ba I and their isoelectronic ions. The most important are terms of the $5d^2$ configuration (20000–25000 cm^{-1}) and those of the 5d6s' configuration (estimated at 19000 ± 10000 cm^{-1}). Levels above 30000 cm^{-1} are averaged. The adopted functions are essentially identical with earlier tables up to 2000 K; however, the entropies at 6000 K differ as follows: Hilsenrath *et al.*,[16] 62.26; JANAF, 63.20; Gurvich *et al.*,[17] 63.65 $cal·K^{-1}·mol^{-1}$. These differences arise from different methods of cutoff and different degrees of accounting for the unobserved terms.

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Continued on page 358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	179.790	179.790	INFINITE
90	20.786	147.537	188.725	−4.119	180.170	168.825	−88.185
200	20.786	161.945	172.146	−2.040	179.704	157.644	−41.172
250	20.786	166.584	170.587	−1.001	179.404	152.162	−31.792
298.15	20.786	170.245	170.245	0.	179.075	146.944	−25.744
300	20.786	170.373	170.245	0.038	179.062	146.744	−25.550
350	20.786	173.577	170.498	1.078	178.654	141.389	−21.101
400	20.786	176.353	171.060	2.117	178.123	136.100	−17.773
450	20.786	178.801	171.787	3.156	177.386	130.889	−15.193
500	20.786	180.991	172.600	4.196	176.384	125.774	−13.139
600	20.786	184.781	174.324	6.274	173.841	115.900	−10.090
700	20.786	187.985	176.053	8.353	172.104	106.368	−7.937
800	20.788	190.761	177.721	10.432	169.856	97.137	−6.342
900	20.796	193.210	179.309	12.511	168.028	88.157	−5.117
1000	20.821	195.402	180.811	14.591	166.202	79.380	−4.146
1100	20.883	197.389	182.229	16.676	156.011	71.606	−3.400
1200	21.014	199.211	183.569	18.770	153.963	64.024	−2.787
1300	21.251	200.901	184.838	20.882	152.033	56.608	−2.275
1400	21.635	202.489	186.043	23.025	150.211	49.337	−1.841
1500	22.204	204.000	187.190	25.216	148.493	42.192	−1.469
1600	22.993	205.457	188.286	27.473	146.878	35.159	−1.148
1700	24.024	206.881	189.338	29.822	145.369	28.223	−0.867
1800	25.307	208.289	190.352	32.287	143.969	21.373	−0.620
1900	26.839	209.697	191.333	34.892	142.684	14.598	−0.401
2000	28.599	211.118	192.287	37.662	141.514	7.887	−0.206
2100	30.556	212.560	193.218	40.618	140.461	1.232	−0.031
2118.599	30.938	212.831	193.389	41.190	----- FUGACITY = 1 bar -----		
2200	32.665	214.029	194.130	43.778	0.	0.	0.
2300	34.873	215.530	195.028	47.155	0.	0.	0.
2400	37.123	217.062	195.914	50.754	0.	0.	0.
2500	39.355	218.622	196.791	54.579	0.	0.	0.
2600	41.512	220.208	197.661	58.623	0.	0.	0.
2700	43.543	221.814	198.526	62.877	0.	0.	0.
2800	45.406	223.431	199.386	67.326	0.	0.	0.
2900	47.068	225.054	200.243	71.951	0.	0.	0.
3000	48.509	226.675	201.098	76.732	0.	0.	0.
3100	49.718	228.286	201.949	81.645	0.	0.	0.
3200	50.695	229.880	202.797	86.668	0.	0.	0.
3300	51.410	231.450	203.641	91.769	0.	0.	0.
3400	51.931	232.992	204.482	96.936	0.	0.	0.
3500	52.262	234.503	205.318	102.148	0.	0.	0.
3600	52.420	235.978	206.149	107.383	0.	0.	0.
3700	52.431	237.415	206.975	112.627	0.	0.	0.
3800	52.319	238.812	207.794	117.865	0.	0.	0.
3900	52.105	240.168	208.607	123.087	0.	0.	0.
4000	51.814	241.483	209.413	128.283	0.	0.	0.
4100	51.463	242.758	210.211	133.445	0.	0.	0.
4200	51.068	243.993	211.000	138.570	0.	0.	0.
4300	50.656	245.190	211.782	143.656	0.	0.	0.
4400	50.234	246.350	212.554	148.701	0.	0.	0.
4500	49.812	247.474	213.318	153.703	0.	0.	0.
4600	49.384	248.563	214.072	158.657	0.	0.	0.
4700	48.932	249.614	214.817	163.550	0.	0.	0.
4800	48.545	250.640	215.552	168.423	0.	0.	0.
4900	48.171	251.636	216.278	173.254	0.	0.	0.
5000	47.832	252.606	216.995	178.054	0.	0.	0.
5100	47.483	253.545	217.702	182.799	0.	0.	0.
5200	47.194	254.465	218.401	187.533	0.	0.	0.
5300	46.933	255.361	219.089	192.239	0.	0.	0.
5400	46.697	256.236	219.769	196.920	0.	0.	0.
5500	46.442	257.084	220.439	201.547	0.	0.	0.
5600	46.176	257.908	221.100	206.125	0.	0.	0.
5700	46.000	258.724	221.753	210.734	0.	0.	0.
5800	45.812	259.517	222.397	215.301	0.	0.	0.
5900	45.508	260.272	223.029	219.733	0.	0.	0.
6000	45.369	261.036	223.656	224.276	0.	0.	0.

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

IP(Ba^+, g) = 80686.87 ± 0.05 cm^{-1}
$S°$(298.15 K) = 176.008 ± 0.05 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 682.6 ± 5.0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [688.126] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2
$^2D_{3/2}$	4873.85	4
$^2D_{5/2}$	5674.824	6
$^2P_{1/2}$	20261.562	2
$^2P_{3/2}$	21952.422	4
.	.	.
.	.	.
.	.	.
.	.	.
$^2G_{9/2}$	77628	10
IP	80686.87	

Enthalpy of Formation

$\Delta_f H°(Ba^+, g, 0 K)$ is calculated from $\Delta_f H°$(Ba, g, 0 K)[1] using the spectroscopic value of IP(Ba) = 42035.14 ± 0.05 cm^{-1} (502.8521 ± 0.0006 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ba^+, g, 298.15 K)$ is calculated from $\Delta_f H°$(Ba, g, 0 K) by using IP(Ba) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for Ba(g), Ba^+(g), and e^-(ref). $\Delta_f H°(Ba \rightarrow Ba^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ of it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first four excited states, the highest observed excited state, and the ionization potential for Ba^+(g), all levels listed by Moore,[2,6] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Ba^+(g), the thermodynamic functions are independent of the estimated missing levels (for n = 6), the cut–off procedure, and the inclusion of n = 12 levels up to 6000 K. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>12), and use of different fill and cut–off procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	682.643		
100	20.786	153.301	194.488	−4.119			
200	20.786	167.708	177.909	−2.040			
250	20.786	172.347	176.350	−1.001			
298.15	20.786	176.008	176.008	0.	688.126	648.021	−113.531
300	20.786	176.136	176.008	0.038	688.151	647.772	−112.787
350	20.786	179.341	176.261	1.078	688.783	640.991	−95.663
400	20.786	182.116	176.823	2.117	689.291	634.127	−82.809
450	20.787	184.564	177.550	3.156	689.593	627.211	−72.805
500	20.789	186.755	178.363	4.196	689.630	620.275	−64.800
600	20.811	190.546	180.087	6.275	689.166	606.457	−52.797
700	20.890	193.759	181.817	8.360	689.514	592.634	−44.223
800	21.081	196.560	183.488	10.457	689.363	578.810	−37.792
900	21.437	199.061	185.082	12.582	689.660	564.973	−32.790
1000	21.989	201.347	186.596	14.751	690.001	551.102	−28.787
1100	22.738	203.476	188.034	16.986	682.038	538.012	−25.548
1200	23.660	205.493	189.406	19.305	682.293	524.909	−22.849
1300	24.710	207.428	190.718	21.722	682.748	511.777	−20.563
1400	25.834	209.300	191.979	24.249	683.388	498.602	−18.603
1500	26.975	211.121	193.195	26.890	684.199	485.376	−16.902
1600	28.082	212.898	194.371	29.643	685.159	472.090	−15.412
1700	29.109	214.631	195.512	32.503	686.240	458.741	−14.095
1800	30.026	216.322	196.621	35.461	687.412	445.325	−12.923
1900	30.811	217.967	197.701	38.504	688.643	431.843	−11.872
2000	31.452	219.564	198.755	41.619	689.896	418.295	−10.925
2100	31.949	221.111	199.783	44.790	691.137	404.684	−10.066
2200	32.305	222.606	200.787	48.004	552.808	396.390	−9.412
2300	32.533	224.048	201.767	51.247	554.753	389.236	−8.840
2400	32.643	225.435	202.724	54.506	556.492	382.002	−8.314
2500	32.653	226.768	203.659	57.772	558.011	374.699	−7.829
2600	32.576	228.048	204.573	61.034	559.308	367.340	−7.380
2700	32.429	229.275	205.465	64.285	560.383	359.936	−6.963
2800	32.224	230.450	206.337	67.518	561.246	352.495	−6.576
2900	31.975	231.577	207.188	70.728	561.909	345.028	−6.215
3000	31.693	232.656	208.019	73.912	562.391	337.540	−5.877
3100	31.387	233.691	208.831	77.066	562.710	330.040	−5.561
3200	31.066	234.682	209.623	80.189	562.889	322.531	−5.265
3300	30.737	235.633	210.397	83.279	562.957	315.018	−4.986
3400	30.405	236.546	211.153	86.336	562.925	307.505	−4.724
3500	30.074	237.422	211.891	89.360	562.817	299.994	−4.477
3600	29.749	238.265	212.612	92.351	562.651	292.487	−4.244
3700	29.431	239.076	213.316	95.310	562.445	284.985	−4.023
3800	29.124	239.856	214.004	98.238	562.212	277.489	−3.814
3900	28.827	240.609	214.677	101.135	561.967	270.000	−3.616
4000	28.543	241.335	215.334	104.004	561.718	262.517	−3.428
4100	28.273	242.037	215.977	106.844	561.475	255.040	−3.249
4200	28.015	242.715	216.606	109.659	561.243	247.568	−3.079
4300	27.771	243.371	217.221	112.448	561.024	240.102	−2.917
4400	27.541	244.007	217.822	115.213	560.824	232.641	−2.762
4500	27.323	244.623	218.411	117.956	560.643	225.185	−2.614
4600	27.119	245.222	218.987	120.678	560.490	217.731	−2.472
4700	26.927	245.803	219.552	123.381	560.378	210.279	−2.337
4800	26.747	246.368	220.104	126.064	560.267	202.831	−2.207
4900	26.579	246.918	220.646	128.730	560.181	195.385	−2.083
5000	26.422	247.453	221.177	131.380	560.110	187.941	−1.963
5100	26.275	247.975	221.697	134.015	560.078	180.496	−1.849
5200	26.139	248.484	222.208	136.636	560.043	173.053	−1.738
5300	26.012	248.980	222.708	139.243	560.023	165.611	−1.632
5400	25.895	249.465	223.199	141.838	560.016	158.170	−1.530
5500	25.786	249.940	223.681	144.422	560.052	150.724	−1.431
5600	25.686	250.403	224.154	146.996	560.126	143.274	−1.336
5700	25.593	250.857	224.618	149.560	560.160	135.830	−1.245
5800	25.509	251.301	225.075	152.115	560.226	128.382	−1.156
5900	25.431	251.737	225.523	154.662	560.420	120.916	−1.071
6000	25.361	252.164	225.963	157.201	560.494	113.467	−0.988

\PREVIOUS: CURRENT: September 1983 (1 bar)

$S°(298.15\ K) = 270.4 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -101.6 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -110.6 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2	$D^2\Sigma$	25670.9	2
$[A^2\Pi]$	[13000]	[4]	$E^2\Sigma$	26865.9	2
$[B^2\Sigma]$	[13500]	[2]	$[F^2\Pi]$	[28000]	[4]
$C_1{}^2\Pi_{1/2}$	18650.9	2	$[G_1{}^2\Delta]$	[29000]	[4]
$C_2{}^2\Pi_{3/2}$	19192.5	2	$[H^2\Sigma]$	[30000]	[2]

$\omega_e = 193.2\ cm^{-1}$ $\omega_e x_e = 0.42\ cm^{-1}$ $\sigma = 1$
$B_e = [0.04052]\ cm^{-1}$ $\alpha_e = [0.000113]\ cm^{-1}$ $r_e = [2.87]$ Å

Enthalpy of Formation

The selected value, $\Delta_f H°(0\ K) = -24.3\ kcal \cdot mol^{-1}$, is obtained from an analysis of spectroscopic data. Herzberg[1] suggested $D_0° = 2.8$ eV for BaBr(g) which was derived from a linear Birge–Sponer extrapolation of the ground state vibrational levels. Our adopted vibrational constants give 2.74 eV by a similar extrapolation. Based on the ionicity correction developed by Hildenbrand,[2] this value adjusts to 4.14 eV (95.5 $kcal \cdot mol^{-1}$) which is adopted. Gaydon[3] has claimed that the spectroscopic data for BaBr(g) are insufficient to obtain a reliable extrapolation. However, our adopted value for $D_0°$ gives $D_0°(BaBr)/\Delta_{at}H°(BaBr_2) = 0.48$ which is quite consistent with values of this ratio for other alkaline earth halide systems.[4] $\Delta_f H°(298.15\ K)$ corresponds to $-26.4\ kcal \cdot mol^{-1}$.

Ionic model calculations[5,6] have led to $D_0°$ values of 4.9 eV[5] and 3.76 eV[6]. The latter result is believed to represent a minimum value. Two other experimental values, which bracket the selected value, have been reported. Flame studies[7] gave $D_0° = 3.79$ eV, and chemiluminescence[8] from reaction of Ba atoms with Br_2 gave a lower limit to $D_0°$ of 4.54 eV. We assign an uncertainty of $\pm 10\ kcal \cdot mol^{-1}$ to $\Delta_f H°(0\ K)$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $BaBr_2$[9] with $r_e(BaBr)/r_e(BaBr_2) = 0.96$. This value for the ratio is calculated from bond lengths[4] for several other alkaline earth halide systems. Two other estimates[5,6] of r_e agree with the adopted value to within 0.05 Å. The rotational constant is calculated from the estimated value for r_e. The value of α_e is obtained from a Morse potential function.

The vibrational constants are taken from the compilation of Rosen[10] and are corrected for the natural isotopic abundances of the elements. The observed electronic levels for BaBr(g) are from Rosen.[10] Also included are A, B, F, G, and H states. Their energies are estimated by analogy with those for SrBr(g).[9]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.200	−101.621	−101.621	INFINITE
100	33.690	231.368	302.718	−7.135	−101.651	−118.687	61.996
200	36.304	255.748	273.762	−3.603	−103.114	−135.193	35.309
250	36.742	263.900	271.003	−1.776	−104.033	−143.109	29.901
298.15	36.996	270.395	270.395	0.	−110.587	−149.888	26.260
300	37.004	270.624	270.396	0.068	−110.641	−150.132	26.140
350	37.177	276.342	270.847	1.923	−126.558	−155.829	23.256
400	37.300	281.315	271.852	3.785	−127.181	−159.970	20.890
450	37.394	285.714	273.152	5.653	−128.011	−164.022	19.039
500	37.469	289.658	274.609	7.524	−129.106	−167.967	17.547
600	37.586	296.500	277.704	11.277	−131.834	−175.474	15.276
700	37.677	302.301	280.814	15.041	−133.755	−182.607	13.626
800	37.756	307.337	283.822	18.812	−136.187	−189.413	12.367
900	37.826	311.788	286.687	22.592	−138.196	−195.946	11.372
1000	37.891	315.777	289.400	26.378	−140.204	−202.255	10.565
1100	37.954	319.392	291.964	30.170	−150.580	−207.543	9.855
1200	38.015	322.697	294.390	33.968	−152.819	−212.622	9.255
1300	38.075	325.742	296.686	37.773	−154.957	−217.518	8.740
1400	38.136	328.566	298.863	41.583	−157.016	−222.253	8.292
1500	38.199	331.199	300.932	45.400	−159.017	−226.843	7.899
1600	38.268	333.666	302.902	49.223	−160.981	−231.300	7.551
1700	38.343	335.989	304.780	53.054	−162.929	−235.635	7.240
1800	38.428	338.183	306.576	56.892	−164.882	−239.856	6.960
1900	38.526	340.263	308.294	60.740	−166.859	−243.967	6.707
2000	38.639	342.242	309.943	64.598	−168.883	−247.973	6.476
2100	38.769	344.130	311.526	68.468	−170.975	−251.877	6.265
2200	38.919	345.937	313.049	72.352	−312.674	−250.304	5.943
2300	39.091	347.671	314.517	76.253	−314.122	−247.437	5.619
2400	39.286	349.338	315.934	80.171	−315.787	−244.503	5.321
2500	39.504	350.946	317.302	84.111	−317.667	−241.495	5.046
2600	39.746	352.500	318.626	88.073	−319.756	−238.407	4.790
2700	40.013	354.005	319.909	92.061	−322.040	−235.236	4.551
2800	40.304	355.466	321.153	96.076	−324.501	−231.976	4.328
2900	40.619	356.886	322.361	100.122	−327.119	−228.626	4.118
3000	40.956	358.268	323.535	104.201	−329.869	−225.183	3.921
3100	41.314	359.617	324.677	108.314	−332.725	−221.647	3.735
3200	41.692	360.935	325.789	112.464	−335.660	−218.017	3.559
3300	42.089	362.223	326.874	116.653	−338.641	−214.295	3.392
3400	42.502	363.486	327.932	120.883	−341.652	−210.482	3.234
3500	42.930	364.724	328.966	125.154	−344.668	−206.580	3.083
3600	43.372	365.940	329.976	129.469	−347.666	−202.592	2.940
3700	43.824	367.134	330.964	133.829	−350.628	−198.521	2.803
3800	44.286	368.309	331.932	138.234	−353.539	−194.371	2.672
3900	44.756	369.466	332.879	142.687	−356.384	−190.145	2.547
4000	45.231	370.605	333.808	147.186	−359.153	−185.848	2.427
4100	45.710	371.727	334.719	151.733	−361.836	−181.482	2.312
4200	46.191	372.835	335.614	156.328	−364.428	−177.051	2.202
4300	46.673	373.927	336.492	160.971	−366.928	−172.560	2.096
4400	47.154	375.006	337.355	165.662	−369.330	−168.012	1.995
4500	47.632	376.071	338.204	170.402	−371.634	−163.411	1.897
4600	48.106	377.123	339.038	175.189	−373.834	−158.760	1.803
4700	48.575	378.162	339.860	180.023	−375.916	−154.064	1.712
4800	49.037	379.190	340.668	184.903	−377.924	−149.322	1.625
4900	49.491	380.206	341.465	189.830	−379.832	−144.540	1.541
5000	49.937	381.210	342.250	194.801	−381.655	−139.720	1.460
5100	50.373	382.203	343.024	199.817	−383.368	−134.866	1.381
5200	50.798	383.186	343.786	204.876	−385.016	−129.977	1.306
5300	51.211	384.157	344.539	209.976	−386.584	−125.057	1.233
5400	51.612	385.118	345.282	215.117	−388.076	−120.109	1.162
5500	52.001	386.069	346.015	220.298	−389.462	−115.137	1.093
5600	52.376	387.009	346.738	225.517	−390.750	−110.145	1.027
5700	52.737	387.939	347.453	230.773	−392.022	−105.122	0.963
5800	53.084	388.860	348.159	236.064	−393.205	−100.082	0.901
5900	53.417	389.770	348.856	241.389	−394.209	−95.038	0.841
6000	53.735	390.670	349.546	246.747	−395.282	−89.958	0.783

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [148.5 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1130 \pm 2\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -757.7 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{fus} H° = 31.96 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

The selected value is based on results obtained from solution calorimetry performed in aqueous acid media. Ehrlich *et al.*[1] reported measurements of the enthalpies of solution of Ba(cr) and $BaBr_2$(cr) in HBr(555 H_2O). These results lead to $\Delta_f H°(BaBr_2, cr, 298.15\ K) = -181.1 \pm 0.4\ kcal·mol^{-1}$ ($-757.7 \pm 1.7\ kJ·mol^{-1}$) when combined with the most recent thermal data[2,3] for aqueous HBr. This value is adopted and is essentially that ($-181.0\ kcal·mol^{-1}$) which has been selected by NBS.[4]

Two independent calorimetric values in $kcal·mol^{-1}$ of -180.7[5] and -181.7[6] bracket our adopted value. These values are based on results of early enthalpy of solution measurements[5,6] which are combined with $\Delta_f H°(Ba^{+2}, aq, 298.15\ K) = -128.5\ kcal·mol^{-1}$ [4] and $\Delta_f H°(Br^-, aq, 298.15\ K) = -29.039 \pm 0.035\ kcal·mol^{-1}$.[2] Use of the newly derived value (see BaO(cr) table) for $\Delta_f H°$ of Ba^{+2}(aq) makes these values less negative by 0.5 $kcal·mol^{-1}$.

Heat Capacity and Entropy

$C_p°$ data needed to define $S°(298.15\ K)$ are unavailable. The adopted value $S°(298.15\ K) = 35.5 \pm 1.0\ cal·K^{-1}·mol^{-1}$ is a compromise between several estimates. JANAF[7] entropies for the other three barium dihalides suggest a value of $S°(298.15\ K)$ near $35.3\ cal·K^{-1}·mol^{-1}$ for the bromide. Application of the Berthelot principle[8] to the process $SrBr_2(cr) + Ba(cr) \rightarrow BaBr_2(cr) + Sr(cr)$ gives $S°(298.15\ K) = 36.7 \pm 1.7\ cal·K^{-1}·mol^{-1}$. Literature estimates which were considered are (in $cal·K^{-1}·mol^{-1}$) 35.0,[4] 35.5 ± 5.0,[9] and 38.[10]

The adopted $C_p°$ data are obtained from JANAF curve fits of the relative enthalpies (825–1130 K) reported by Efremova and Matizen.[11] For 27 enthalpy points the average deviation of the fit is ±0.4%; the maximum deviation is −1.0% at 847 K. Two points (1129 and 1130 K) are omitted from the fit, since these points presumably involve pre-melting effects. The derived value of $C_p°(298.15\ K) = 18.41\ cal·K^{-1}·mol^{-1}$ is supported by the value ($18.48\ cal·K^{-1}·mol^{-1}$) obtained from the process $BaCl_2(cr) + 2\ KBr(cr) \rightarrow BaBr_2(cr) + 2\ KCl(cr)$ with $\Delta C_p° = 0$. Relative enthalpies (487–1126 K) reported in equation form by Janz et al.[12] suggest a somewhat lower value ($17.8\ cal·K^{-1}·mol^{-1}$) for $C_p°$ at 298.15 K. Their smoothed enthalpies show deviations from our adopted ones that are generally less than ±0.3% but show maximum deviations of ±1.0% at 500 K and 900 K. The enthalpy measurement of Dworkin and Bredig[13] at the melting point ($T_{fus} \approx 1130$ K) is roughly 1% lower than that which is adopted. The values of $C_p°$ above T_{fus} are obtained from the adopted enthalpy equation.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is the difference in the values of $\Delta_f H°$ for the gas and crystal at 298.15 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	77.015	148.532	148.532	0.000	−757.722	−738.000	129.295
300	77.053	149.009	148.533	0.143	−757.772	−737.877	128.476
400	79.216	171.471	151.582	7.956	−787.455	−725.089	94.687
500	81.379	189.380	157.409	15.986	−786.935	−709.575	74.129
600	83.542	204.409	164.022	24.232	−787.031	−694.082	60.425
700	85.701	217.449	170.743	32.694	−786.122	−678.671	50.643
800	87.864	229.034	177.319	41.372	−785.523	−663.354	43.313
900	90.027	239.507	183.656	50.267	−784.299	−648.154	37.618
1000	92.190	249.105	189.727	59.377	−782.869	−633.101	33.070
1100	94.353	257.993	195.534	68.705	−789.601	−617.382	29.317
1130.000	95.002	260.540	197.226	71.545	--- CRYSTAL <--> LIQUID ---		
1200	96.512	266.295	201.089	78.248	−787.992	−601.795	26.195
1300	98.675	274.106	206.408	88.007	−786.076	−586.354	23.560
1400	100.839	281.498	211.510	97.983	−783.874	−571.071	21.307
1500	103.002	288.528	216.412	108.175	−781.409	−555.956	19.360

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = [172.108]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1130 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-730.193]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 31.96 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ of the liquid is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1130\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ for the liquid is taken equal to 25.06 $cal·K^{-1}·mol^{-1}$ above the assumed glass transition temperature of 800 K. The constant value of $C_p°$ is derived from a curve fit of the relative enthalpies (1134–1963 K) reported by Efremova and Matizen.[1] For 11 enthalpy points the average deviation of the fit is ±0.3%; the maximum deviation occurs at 1386 K and amounts to −0.7%. Our adopted value for $C_p°$ is supported by the enthalpy measurements of Dworkin and Bredig[2] who found $C_p°(l) = 25.6\ cal·K^{-1}·mol^{-1}$. A considerably higher value (31 $cal·K^{-1}·mol^{-1}$) for $C_p°(l)$ is obtained from yet another enthalpy study;[3] however, these latter measurements extend over a relatively short temperature interval (~100 K) above T_{fus} and are probably insufficient to accurately establish $C_p°$ of the liquid. $C_p°$ data below the glass transition are those of the crystal.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is the value determined in two independent drop–calorimetric investigations.[1,2] Nine other reported values for T_{fus} lie within 11 K of the adopted value. These other values are 1126 K,[3–5] 1119 K,[6,7] 1128 K[8] and 1120 K.[9–11]

$\Delta_{fus}H°$ is calculated as the difference between JANAF values for the enthalpies of the liquid and crystal at T_{fus}. Our value for $\Delta_{fus}H°$ is in excellent agreement with another drop–calorimetric value ($\Delta_{fus}H° = 7.63\ kcal·mol$)[2] and is further supported by a value ($\Delta_{fus}H° = 7.7\ kcal·mol^{-1}$)[4] obtained by dynamic differential calorimetry. Other published values include (in $kcal·mol^{-1}$) 7.75 ± 0.08,[1] 7.25 ± 0.19,[3] 7.15 ± 0.4,[4] and 7.0.[5]

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G° = 0$ for the process $BaBr_2(l) = BaBr_2(g)$ at p = 1 bar. $\Delta_{vap}H°$ is the corresponding difference in the $\Delta_f H°$ values for the gas and liquid at T_{vap}. Petersen and Hutchison[12] calculated $T_{vap} = 2122$ K (p = 1 atm) from their measured vapor pressure data which covered the range 1175–1321 K. This value is considered somewhat uncertain due to the rather long extrapolation.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.015	172.108	172.108	0.000	−730.193	−717.500	125.703
300	77.053	172.585	172.109	0.143	−730.242	−717.421	124.914
400	79.216	195.047	175.158	7.956	−759.926	−706.990	92.323
500	81.379	212.956	180.985	15.986	−759.406	−693.834	72.484
600	83.542	227.985	187.598	24.232	−759.501	−680.698	59.260
700	85.701	241.025	194.319	32.694	−758.593	−667.645	49.820
800	87.866	252.610	200.895	41.372	−757.994	−654.685	42.747
800.000	87.866	252.610	200.895	41.372	GLASS <--> LIQUID		
800.000	104.851	252.610	200.895	41.372	TRANSITION		
900	104.851	264.959	207.340	51.857	−755.179	−641.940	37.257
1000	104.851	276.007	213.664	62.342	−752.375	−629.509	32.882
1100	104.851	286.000	219.793	72.827	−757.949	−616.538	29.277
1130.000	104.851	288.821	221.589	75.973	--- CRYSTAL <--> LIQUID ---		
1200	104.851	295.123	225.696	83.313	−755.398	−603.794	26.282
1300	104.851	303.516	231.364	93.798	−752.756	−591.267	23.757
1400	104.851	311.286	236.798	104.283	−750.045	−578.946	21.601
1500	104.851	318.520	242.008	114.768	−747.287	−566.821	19.738
1600	104.851	325.287	247.004	125.253	−744.504	−554.881	18.115
1700	104.851	331.643	251.798	135.738	−741.717	−543.114	16.688
1800	104.851	337.637	256.402	146.223	−738.950	−531.512	15.424
1900	104.851	343.306	260.828	156.708	−736.225	−520.062	14.298
2000	104.851	348.684	265.087	167.193	−733.565	−508.754	13.287
2100	104.851	353.799	269.191	177.678	−730.993	−497.577	12.377
2200	104.851	358.677	273.148	188.164	−868.053	−481.145	11.424
2300	104.851	363.338	276.969	198.649	−864.890	−463.630	10.529
2400	104.851	367.800	280.661	209.134	−861.972	−446.248	9.712
2500	104.851	372.081	284.233	219.619	−859.302	−428.981	8.963
2600	104.851	376.193	287.691	230.104	−856.874	−411.818	8.274
2700	104.851	380.150	291.043	240.589	−854.678	−394.742	7.637
2800	104.851	383.963	294.294	251.074	−852.699	−377.745	7.047
2900	104.851	387.643	297.450	261.559	−850.916	−360.814	6.499
3000	104.851	391.197	300.516	272.044	−849.307	−343.942	5.989

PREVIOUS: CURRENT: December 1974

0	to 1130 K	crystal
above	1130 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	77.015	148.532	148.532	0.000	−757.722	−738.000	129.295
300	77.053	149.009	148.533	0.143	−757.772	−737.877	128.476
400	79.216	171.471	151.582	7.956	−787.455	−725.089	94.687
500	81.379	189.380	157.409	15.986	−786.935	−709.575	74.129
600	83.542	204.409	164.022	24.232	−787.031	−694.082	60.425
700	85.701	217.449	170.743	32.694	−786.122	−678.671	50.643
800	87.864	229.034	177.319	41.372	−785.523	−663.354	43.313
900	90.027	239.507	183.656	50.267	−784.299	−648.154	37.618
1000	92.190	249.105	189.727	59.377	−782.869	−633.101	33.070
1100	94.353	257.993	195.534	68.705	−789.602	−617.382	29.317
1130.000	95.002	260.540	197.226	71.545	CRYSTAL <--> LIQUID TRANSITION		
1130.000	104.851	288.821	197.226	103.502			
1200	104.851	295.123	202.755	110.842	−755.398	−603.794	26.282
1300	104.851	303.516	210.187	121.327	−752.756	−591.267	23.757
1400	104.851	311.286	217.134	131.812	−750.045	−578.946	21.601
1500	104.851	318.520	223.655	142.297	−747.287	−566.821	19.738
1600	104.851	325.287	229.798	152.782	−744.504	−554.881	18.115
1700	104.851	331.644	235.604	163.268	−741.717	−543.114	16.688
1800	104.851	337.637	241.107	173.753	−738.950	−531.512	15.424
1900	104.851	343.306	246.338	184.238	−736.225	−520.062	14.298
2000	104.851	348.684	251.322	194.723	−733.565	−508.754	13.287
2100	104.851	353.799	256.081	205.208	−730.993	−497.577	12.377
2200	104.851	358.677	260.635	215.693	−868.053	−481.145	11.424
2300	104.851	363.338	265.000	226.178	−864.890	−463.630	10.529
2400	104.851	367.800	269.191	236.663	−861.972	−446.248	9.712
2500	104.851	372.081	273.221	247.148	−859.302	−428.982	8.963
2600	104.851	376.193	277.103	257.633	−856.874	−411.818	8.274
2700	104.851	380.150	280.847	268.119	−854.678	−394.742	7.637
2800	104.851	383.963	284.462	278.604	−852.699	−377.745	7.047
2900	104.851	387.643	287.957	289.089	−850.916	−360.814	6.499
3000	104.851	391.197	291.339	299.574	−849.307	−343.942	5.989

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = [342.1 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -408.5 \pm 12.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -424.7 \pm 12.6\ kJ·mol^{-1}$

Vibrational Fequencies and Degeneracies ν, cm^{-1}
[160] (1)
[28] (1)
[223] (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Ba–Br = 2.99 ± 0.03 Å
Bond Angle: Br–Ba–Br = [150 ± 30]°
Product of Moments of Inertia: $I_A I_B I_C$ = [3.718284 × 10^{-112}] $g^3\ cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from the selected value for the enthalpy of vaporization, ($\Delta_{vap}H°(298.15\ K) = 73.04 \pm 0.24$ kcal·mol^{-1}, and the adopted value for $\Delta_f H°$(l). The selected value of $\Delta_{vap}H°$ is obtained from a 3rd law analysis of the vapor pressures for the liquid (1175–1321 K) reported by Peterson and Hutchison.[1,2] These measurements were made by the Knudsen effusion method on a sample of anhydrous $BaBr_2$ which had been prepared by direct union of high purity elements. The 2nd law $\Delta_{vap}H° = 73.7$ kcal·mol^{-1} is in agreement with the 3rd law value; thus, the entropy deviation is small ($\Delta_{vap}S°$(2nd law)–$\Delta_{vap}S°$(3rd law) = 0.5 ± 0.8 cal·K^{-1}·mol^{-1}). The dominant vapor species is assumed to be the dihalide monomer. This assumption is supported by the fact that negligible concentrations of polymeric species have been observed for some of the other alkaline–earth dihalides by use of mass spectrometry (see $CaBr_2$(g) table.[9]

A 3rd law analysis of a single sublimation pressure reported by Stock and Heynemann[3] leads to $\Delta_f H°(298.15\ K) = 104.3$ kcal·mol^{-1}. This result suggests a possible uncertainty in the adopted value for $\Delta_f H°$ of as much as ±3 kcal·mol^{-1}. This also brings our value in agreement with the selection (−105 kcal·mol^{-1}) of NBS.[4]

Heat Capacity and Entropy

Experimental evidence which has been presented in favor of a linear or nonlinear structure for $BaBr_2$ is conflicting. Electron diffraction analysis by Akishin and Spiridonov[5] showed $BaBr_2$ to be linear (180 ± 30°). Later studies by Klemperer *et al.*,[6,7] using electric quadrupole deflection of molecular beams, have shown that this molecule possesses a permanent dipole moment and therefore must be bent. A simple explanation of the observed trends in the geometries of the alkaline–earth dihalides as established by the electric deflection experiments[6,7] has been presented by Hayes,[8] and it appears quite likely that $BaBr_2$ is probably bent. The bond angle is arbitrarily taken to be greater than that for $BaCl_2$ (100°)[9] but less than that for BaI_2 (170°).[9] The bond distance is that measured in the gas phase by an electron diffraction study of Akishin and Spiridonov.[5] The principal moments of inertia are: $I_A = 228.6976 \times 10^{-39}$, $I_B = 221.3525 \times 10^{-39}$, and $I_C = 7.3451 \times 10^{-39}$ g cm^2. stretching force constant (K = 1.117 × 10^5 dynes/cm) is taken equal to that for BaBr.[9] The ratio of the stretching to bending force constants is estimated as 125. This value for the ratio is to be compared with that for BaF_2 (93)[9] and $BaCl_2$(1199).[9] The uncertainty in the adopted value for ν_2 is believed to be no greater than ±20 cm^{-1} which corresponds to roughly 1 cal·K^{-1}·mol^{-1} in the value of $S°(298.15\ K)$. Other sets[11–13] of estimated vibrational frequencies compare faavorably with ours; the maximum deviation is 35 cm^{-1} in ν_3.[13] The ground state quantum weight of one is assigned by analogy with that for $BaCl_2$.[9] Our Gibbs energy functions differ by roughly 2 cal·K^{-1}·mol^{-1} in the range 298–2000 K from those given by Brewer *et al.*[11] However, their values are based on a linear structure for the bromide which now appears to be incorrect.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.255	−408.509	−408.509	INFINITE
100	50.661	282.411	391.697	−10.929	−408.675	−428.123	223.628
200	55.737	319.525	347.252	−5.545	−410.737	−446.830	116.700
250	56.566	332.061	343.004	−2.736	−412.082	−455.703	95.214
298.15	57.029	342.067	342.067	0.	−424.676	−462.656	81.055
300	57.043	342.420	342.068	0.106	−424.762	−462.891	80.597
350	57.340	351.237	342.764	2.966	−455.999	−467.523	69.774
400	57.536	358.908	344.313	5.838	−456.527	−469.135	61.263
450	57.673	365.693	346.319	8.718	−457.265	−470.669	54.634
500	57.772	371.775	348.566	11.604	−458.270	−472.107	49.321
600	57.901	382.320	353.339	17.389	−460.827	−474.626	41.320
700	57.980	391.252	358.133	23.183	−462.587	−476.798	35.579
800	58.031	398.998	362.768	28.984	−464.865	−478.667	31.254
900	58.067	405.835	367.181	34.789	−466.731	−480.280	27.875
1000	58.092	411.954	371.357	40.597	−468.603	−481.685	25.161
1100	58.111	417.492	375.304	46.407	−478.853	−482.083	22.892
1200	58.125	422.549	379.033	52.219	−480.975	−482.282	20.993
1300	58.136	427.202	382.562	58.032	−483.005	−482.308	19.379
1400	58.145	431.511	385.906	63.846	−484.965	−482.180	17.990
1500	58.152	435.522	389.082	69.661	−486.877	−481.915	16.782
1600	58.158	439.276	392.103	75.477	−488.763	−481.522	15.720
1700	58.163	442.802	394.983	81.293	−490.646	−481.012	14.780
1800	58.167	446.126	397.732	87.109	−492.547	−480.390	13.941
1900	58.171	449.271	400.363	92.926	−494.490	−479.662	13.187
2000	58.174	452.255	402.884	98.743	−496.498	−478.830	12.506
2100	58.176	455.094	405.303	104.561	−498.594	−477.896	11.887
2200	58.178	457.800	407.628	110.378	−640.321	−471.484	11.194
2300	58.180	460.386	409.866	116.196	−641.825	−463.777	10.533
2400	58.182	462.862	412.023	122.015	−643.574	−455.999	9.925
2500	58.183	465.237	414.104	127.833	−645.571	−448.143	9.363
2600	58.185	467.520	416.115	133.651	−647.810	−440.202	8.844
2700	58.186	469.715	418.060	139.470	−650.280	−432.171	8.361
2800	58.187	471.832	419.943	145.288	−652.968	−424.045	7.911
2900	58.188	473.873	421.768	151.107	−655.851	−415.818	7.490
3000	58.189	475.846	423.537	156.926	−658.908	−407.490	7.095
3100	58.190	477.754	425.256	162.745	−662.114	−399.057	6.724
3200	58.190	479.602	426.925	168.564	−665.444	−390.518	6.375
3300	58.191	481.392	428.549	174.383	−668.863	−381.874	6.045
3400	58.191	483.129	430.129	180.202	−672.357	−373.126	5.732
3500	58.192	484.816	431.667	186.021	−675.902	−364.273	5.436
3600	58.192	486.456	433.167	191.840	−679.474	−355.319	5.156
3700	58.193	488.050	434.628	197.660	−683.055	−346.265	4.888
3800	58.193	489.602	436.055	203.479	−686.629	−337.115	4.634
3900	58.194	491.113	437.447	209.298	−690.182	−327.871	4.391
4000	58.194	492.587	438.807	215.118	−693.703	−318.536	4.160
4100	58.194	494.024	440.137	220.937	−697.182	−309.114	3.938
4200	58.195	495.426	441.436	226.757	−700.612	−299.608	3.726
4300	58.195	496.795	442.708	232.576	−703.991	−290.020	3.523
4400	58.195	498.133	443.953	238.396	−707.315	−280.354	3.328
4500	58.195	499.441	445.171	244.215	−710.580	−270.614	3.141
4600	58.196	500.720	446.365	250.035	−713.780	−260.802	2.961
4700	58.196	501.972	447.535	255.854	−716.901	−250.923	2.789
4800	58.196	503.197	448.682	261.674	−719.984	−240.976	2.622
4900	58.196	504.397	449.806	267.493	−723.003	−230.966	2.462
5000	58.196	505.573	450.910	273.313	−725.972	−220.894	2.308
5100	58.197	506.725	451.993	279.133	−728.865	−210.765	2.159
5200	58.197	507.855	453.057	284.952	−731.725	−200.579	2.015
5300	58.197	508.964	454.101	290.772	−734.536	−190.337	1.876
5400	58.197	510.052	455.127	296.592	−737.300	−180.043	1.742
5500	58.197	511.119	456.136	302.412	−739.988	−169.703	1.612
5600	58.197	512.168	457.127	308.231	−742.605	−159.317	1.486
5700	58.198	513.198	458.101	314.051	−745.231	−148.878	1.364
5800	58.198	514.210	459.060	319.871	−747.794	−138.397	1.246
5900	58.198	515.205	460.003	325.691	−750.200	−127.888	1.132
6000	58.198	516.183	460.932	331.510	−752.697	−117.319	1.021

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 258.64 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -140.6 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -142.3 \pm 12.6\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X $^2\Sigma^+$	0.0	2	D $^2\Sigma$	25471.5	2
A $^2\Pi$	10351.1	2	E $^2\Sigma$	27064.6	2
	10995.3	2	F $^2\Sigma$	29493.6	2
B $^2\Sigma^+$	11880.0		G $^2\Sigma$	32511.4	2
C $^2\Pi$	19062.9	2			
	19450.1	2			

$\omega_e = 277.9\ cm^{-1}$ $\omega_e x_e = 0.88\ cm^{-1}$ $\sigma = 1$

$B_e = [0.08518 \pm 0.003] cm^{-1}$ $\alpha_e = [0.00035]\ cm^{-1}$ $r_e = [2.65 \pm 0.05]$Å

Enthalpy of Formation

$\Delta_f H°$ is based mainly on two sets of gas–phase equilibria measured mass spectrometrically by Hildenbrand[1] and, to a lesser extent, on the analogous data of Potter *et al.*[2] Analyses of the mass–spectrometric data[1-3] are summarized below. The results from Potter *et al.*[2] and Zmbov[3] are less negative by about 4 kcal·mol^{-1}, suggesting the approximate uncertainty in $\Delta_f H°$. From the adopted $\Delta_f H°$ we derive $D_0° = 106.4 \pm 3$ kcal·mol^{-1}. Independent methods yield $D_0° = 103 \pm 5$,[4] ≥ 110,[5] 106.8 ± 2[6] and 105 ± 6 kcal·mol^{-1}.[6]

Electron–impact data[4] gave $D_0°$ (ClBa–Cl) = 115.8 ± 3.3 kcal·mol^{-1} and we use $\Delta_{at}H°(BaCl_2) = 219 \pm 4$ kcal·mol^{-1} to derive $D_0° = 103 \pm 5$ kcal·mol^{-1}. Chemiluminescence from crossed beams of Ba atoms with Cl_2 gave an approximate lower limit to $D_0°$ of 110 kcal·mol^{-1}.[5] Flame studies[6] gave $D_0° = 106.8 \pm 2$ kcal·mol^{-1} and $D_0°$ (ClBa–Cl) = 114 ± 4; we derive $D_0° = 105 \pm 6$ kcal·mol^{-1} from the latter value using $\Delta_{at}H°(BaCl_2) = 219$ kcal·mol^{-1}. Ryabova[6] considered the flames to involve $BaCl_2$, BaOHCl, and BaOH as well as BaCl. Schofield and Sugden[7] inferred that the flames involved mainly $BaCl_2$ rather than BaCl as assumed in earlier flame studies. Gaydon[8] discounted the values derived from electronic spectra, but Hildenbrand[1] showed that ionicity corrections bring the Birge–Sponer extrapolation into reasonable agreement with $D_0°$.

Source	Reaction[a]	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$D_0°$
(1)	A	1234–1380	3.3 ± 3.6	6.76 ± 0.8	−2.6 ± 2.7	−34.82 ± 2.2	107.2
(2)	A	1507–1702	13.0 ± 5.4	13.34 ± 1.0	−0.2 ± 3.3	−31.53 ± 2.2	103.9
(3)[b]	A	974–1052	21.8 ± 9.4	5.89 ± 1.3	5.9 ± 9.3	−30.26 ± 2.2	102.7
(1)	B	1234–1380	10.3 ± 5.1	13.21 ± 1.1	−2.2 ± 3.9	−34.29 ± 2.6	106.7
(2)	B	1507–1702	9.7 ± 7.3	17.72 ± 1.5	−5.0 ± 4.5	−29.78 ± 2.8	102.2

[a]Reactions: (A) Ba(g) + $BaCl_2$(g) → 2BaCl(g); (B) Ba(g) + AlCl(g) → BaCl(g) + Al(g).
[b]Data given in Table 2[3] are assumed to be $10^3 \times K_p$ instead of $10^4 \times K_p$.

Heat Capacity and Entropy

Electronic levels and vibrational constants are taken from the review of Rosen.[9] The level at 10351.1 cm^{-1} is T_0 rather than T_e. Vibrational constants are adjusted for natural isotopic abundances. B_e is calculated from r_e which is estimated by comparison of the bond lengths of MX_2(M=Mg, Ca, Sr, Ba and X=F, Cl) with those of MgCl, CaCl and MF(M=Mg, Ca, Sr, Ba). The value of α_e is estimated from the Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.878	−140.631	−140.631	INFINITE
100	31.691	221.045	290.084	−6.904	−140.812	−150.058	78.382
200	35.235	244.313	261.945	−3.526	−141.498	−159.035	41.536
250	35.986	252.263	259.241	−1.744	−141.864	−163.379	34.136
298.15	36.436	258.643	258.643	0.	−142.256	−167.488	29.343
300	36.450	258.868	258.644	0.067	−142.272	−167.644	29.189
350	36.757	264.512	259.089	1.898	−142.747	−171.837	25.645
400	36.973	269.435	260.081	3.742	−143.350	−175.953	22.977
450	37.132	273.799	261.367	5.594	−144.162	−179.983	20.892
500	37.256	277.718	262.810	7.454	−145.241	−183.907	19.213
600	37.438	284.528	265.879	11.189	−147.944	−191.378	16.661
700	37.570	290.309	268.966	14.940	−149.844	−198.478	14.811
800	37.676	295.333	271.955	18.703	−152.258	−205.255	13.402
900	37.765	299.776	274.804	22.475	−154.253	−211.760	12.290
1000	37.846	303.759	277.504	26.255	−156.247	−218.043	11.389
1100	37.921	307.370	280.057	30.044	−166.610	−223.306	10.604
1200	37.995	310.673	282.473	33.840	−168.837	−228.361	9.940
1300	38.072	313.717	284.761	37.643	−170.962	−233.235	9.371
1400	38.156	316.541	286.931	41.454	−173.007	−237.948	8.878
1500	38.252	319.177	288.994	45.275	−174.990	−242.517	8.445
1600	38.364	321.649	290.959	49.105	−176.932	−246.955	8.062
1700	38.496	323.979	292.833	52.948	−178.851	−251.273	7.721
1800	38.652	326.184	294.625	56.805	−180.767	−255.478	7.414
1900	38.835	328.278	296.342	60.679	−182.698	−259.576	7.136
2000	39.046	330.275	297.989	64.573	−184.662	−263.571	6.884
2100	39.287	332.186	299.572	68.489	−186.679	−267.467	6.653
2200	39.557	334.020	301.097	72.431	−328.289	−265.891	6.313
2300	39.856	335.785	302.567	76.402	−329.632	−263.025	5.973
2400	40.183	337.488	303.986	80.404	−331.174	−260.097	5.661
2500	40.535	339.135	305.360	84.439	−332.915	−257.100	5.372
2600	40.909	340.732	306.689	88.511	−334.848	−254.030	5.104
2700	41.304	342.284	307.979	92.622	−336.962	−250.882	4.854
2800	41.716	343.793	309.231	96.773	−339.239	−247.653	4.620
2900	42.143	345.264	310.449	100.966	−341.661	−244.339	4.401
3000	42.581	346.700	311.633	105.202	−344.205	−240.940	4.195
3100	43.027	348.104	312.787	109.482	−346.846	−237.455	4.001
3200	43.478	349.477	313.912	113.807	−349.561	−233.883	3.818
3300	43.933	350.822	315.010	118.178	−352.319	−230.226	3.644
3400	44.387	352.140	316.083	122.594	−355.106	−226.485	3.480
3500	44.839	353.433	317.132	127.055	−357.898	−222.661	3.323
3600	45.287	354.703	318.158	131.561	−360.677	−218.758	3.174
3700	45.728	355.950	319.163	136.112	−363.425	−214.777	3.032
3800	46.161	357.175	320.147	140.707	−366.128	−210.724	2.897
3900	46.585	358.380	321.112	145.344	−368.775	−206.599	2.767
4000	46.998	359.564	322.058	150.023	−371.356	−202.408	2.643
4100	47.399	360.730	322.987	154.743	−373.864	−198.153	2.525
4200	47.787	361.877	323.900	159.503	−376.294	−193.838	2.411
4300	48.162	363.005	324.796	164.300	−378.646	−189.466	2.302
4400	48.523	364.117	325.677	169.135	−380.916	−185.040	2.197
4500	48.869	365.211	326.543	174.005	−383.103	−180.564	2.096
4600	49.200	366.289	327.396	178.908	−385.203	−176.040	1.999
4700	49.516	367.350	328.235	183.844	−387.203	−171.474	1.906
4800	49.817	368.396	329.060	188.811	−389.145	−166.863	1.816
4900	50.103	369.426	329.874	193.807	−391.005	−162.213	1.729
5000	50.374	370.441	330.675	198.831	−392.798	−157.526	1.646
5100	50.631	371.441	331.465	203.881	−394.499	−152.806	1.565
5200	50.873	372.427	332.243	208.957	−396.152	−148.050	1.487
5300	51.101	373.398	333.010	214.055	−397.741	−143.264	1.412
5400	51.315	374.355	333.767	219.176	−399.272	−138.448	1.339
5500	51.515	375.299	334.514	224.318	−400.714	−133.608	1.269
5600	51.703	376.229	335.250	229.479	−402.074	−128.746	1.201
5700	51.878	377.145	335.977	234.658	−403.433	−123.853	1.135
5800	52.040	378.049	336.695	239.854	−404.719	−118.940	1.071
5900	52.191	378.940	337.403	245.066	−405.840	−114.022	1.009
6000	52.331	379.818	338.103	250.292	−407.044	−109.066	0.950

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 123.666 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1198 \pm 1\ K\ (\alpha \rightarrow \beta)$
$T_{fus} = 1235 \pm 1\ K\ (\beta \rightarrow \gamma)$

$\Delta_f H°(0\ K) = -859.17 \pm 13$ (or ± 2.5) $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -858.6 \pm 13$ (or ± 2.5) $kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 16.90 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 15.991 \pm 0.33\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is from NBS Technical Note 270–6[1] and its selection was discussed in detail by Parker.[2] The adopted value was derived by Ehrlich *et al.*[3] from their measurements of ΔH_{sol} of Ba(cr) and $BaCl_2$(cr) in HCl (550 H_2O). Earlier solution data for Ba[4] and $BaCl_2$[5, 6] are in good agreement,[2] but a recent study by Vorob'ev *et al.*[7] of Ba in HCl (240 and 400 H_2O) yields $\Delta_f H° = -201.8\ kcal \cdot mol^{-1}$. The deviation (+3.4 $kcal \cdot mol^{-1}$) from the adopted value is confirmed by direct measurements[7] of $\Delta_f H°$ and $\Delta_{sol} H°$ of BaH_2(cr), yielding $-202.1\ kcal \cdot mol^{-1}$ for $BaCl_2$(cr). All authors reported difficulties in obtaining or maintaining Ba and BaH_2 free of impurities; this provides conceivable reasons for bias in either of the opposing results. We assign an uncertainty of $\pm 3\ kcal \cdot mol^{-1}$ to include the possibility that Vorob'ev *et al.*[7] are correct but add an alternative of $\pm 0.6\ kcal \cdot mol^{-1}$ if their data are biased.

Parker[2] rejected $\Delta_f H° = -219.3\ kcal \cdot mol^{-1}$ obtained by Siemonsen[8] by direct chlorination and $\Delta_f H° = -212.0\ kcal \cdot mol^{-1}$ which would result from BaO(cr) based on Mah's direct combustion.[9] Parker noted that these more negative values are incompatible with data for BaO_2, $Ba(OH)_2$ and $BaCO_3$. They are also incompatible with calorimetric data for BaH_2 noted above and equilibrium data as discussed on the tables for $BaCl_2$(l and g).

Heat Capacity and Entropy

$C_p°$ is based on adiabatic calorimetry (6–346 K) of Goodman and Westrum.[10] $S°$ is calculated from $C_p°$ using $S°(6\ K) = 0.012\ cal \cdot K^{-1} \cdot mol^{-1}$. $C_p°$ above 300 K is from constrained fitting of enthalpy data (340–1197 K for α–phase and 1201–1231 K for β–phase) measured in an ice calorimeter by Gardner and Taylor.[11] The sample studied at high temperatures was a portion of that used at low temperatures. Deviations of the H data[11] from the adopted values are <0.1% for most points but show a maximum of −0.3% for two points near 400 K.

Other enthalpy studies include those of Dworkin and Bredig,[12] Janz et al.[13] and Gant.[14] Deviations from the adopted values are about +2% for the smooth values (~1100–1230 K) of,[12] +1.8 to +2.9% for the equations (892–1235 K) of,[13] and −1.7 to +6.7% for the data (406–1230 K) of.[14] Popov and Gal'chenko[15] used a continuous heating method to obtain $C_p°$ values which deviate by +4 to +9% (443–973 K).

Transition Data

T_{trs} = 1198 K is from the enthalpy study of Gardner and Taylor.[11] Other enthalpy studies gave 1193[12] and 1198 K,[13] while thermal analysis gave 1199[16] and 1197 K.[17] $\Delta_{trs} H°$ is calculated from our adopted fits of the enthalpy data.[11] Published values include 4.04,[11] 4.10[12] and 4.15 ± 0.16.[13]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−16.707	−859.171	−859.171	INFINITE
100	56.961	49.346	187.175	−13.783	−860.857	−843.483	440.590
200	71.038	94.429	130.426	−7.199	−859.856	−826.420	215.839
298.15	75.140	123.666	123.666	0.000	−858.557	−810.290	141.959
300	75.195	124.131	123.668	0.139	−858.533	−809.990	141.032
400	77.329	146.082	126.646	7.774	−857.384	−793.994	103.685
500	78.857	163.505	132.335	15.585	−856.963	−778.216	81.300
600	80.425	178.018	138.772	23.547	−857.255	−762.428	66.375
700	82.233	190.548	145.293	31.678	−856.611	−746.684	55.718
800	84.299	201.661	151.657	40.003	−856.313	−730.992	47.729
900	86.624	211.721	157.780	48.546	−855.396	−715.380	41.520
1000	89.471	220.988	163.643	57.345	−854.241	−699.882	36.558
1100	93.531	229.692	169.256	66.480	−861.132	−683.694	32.466
1198.010	100.015	237.924	174.538	75.937	ALPHA <--> BETA		
1198.010	123.846	252.033	174.538	92.840	TRANSITION		
1200	123.846	252.239	174.666	93.087	−842.429	−667.664	29.063
1235.000	123.846	255.799	176.915	97.422	---- BETA <--> LIQUID ----		
1300	123.846	262.152	181.020	105.472	−837.859	−653.284	26.249
1400	123.846	271.330	187.147	117.856	−833.221	−639.260	23.851
1500	123.846	279.874	193.047	130.241	−828.535	−625.569	21.784
1600	123.846	287.867	198.726	142.625	−823.823	−612.191	19.986
1700	123.846	295.375	204.193	155.010	−819.105	−599.109	18.408
1800	123.846	302.454	209.457	167.395	−814.402	−586.304	17.014
1900	123.846	309.150	214.529	179.779	−809.736	−573.759	15.774
2000	123.846	315.503	219.421	192.164	−805.128	−561.459	14.664

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = [143.518]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1235 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-832.467]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 15.991 \pm 0.33\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1235\ K)-H°(298.15\ K)$, between crystal and liquid. Independent values of $\Delta_f H°$ for liquid (and crystal) may be derived from equilibrium data[1,2] for $Ca(l) + BaCl_2(l) \rightarrow Ba(l) + CaCl_2(l)$. Our 3rd-law analysis is summarized below; it shows that the data of Feschotte–Ostertag[1] are consistent with the adopted $\Delta_f H°(cr) = -205.2\ kcal·mol^{-1}$ from Ehrlich *et al.* (cf. $BaCl_2$, cr), while the data of Peterson and Hinkebein[2] are more consistent with the alternative $\Delta_f H°(cr) = -201.8\ kcal·mol^{-1}$ from Vorob'ev *et al.* Both are incompatible with $\Delta_f H°(cr) = -219.3$ from direct chlorination and $\Delta_f H°(cr) = -212.0$ derived from Mah's $\Delta_c H$ value for $\Delta_f H°$ of BaO(cr).

Source	Remarks	T/K	δS cal·K⁻¹·mol⁻¹	$\Delta_r H°(298.15\ K)$ kcal·mol⁻¹	$\Delta_f H°$(l) kcal·mol⁻¹	$\Delta_f H°$(cr) kcal·mol⁻¹
1	Direct measurement	1273	13.24 ± 1.6		−198.3 ± 2	−204.5 ± 2
1	Indirect via $SrCl_2$	1273	14.12 ± 1.8		−199.1 ± 2	−205.4 ± 2
2	Direct measurement	1173–1223	−2.5 ± 8.1	11.47 ± 0.6	−196.5 ± 1	−202.7 ± 1

Heat Capacity and Entropy

The constant $C_p° = 26.0\ cal·K^{-1}·mol^{-1}$ is based on enthalpy data (1238–1347 K) measured in an ice calorimeter by Gardner and Taylor.[3] Deviations of the data from the adopted fit are all less than 0.05%. Smoothed enthalpies of Dworkin and Bredig[4] deviate by +1.2% and those of Janz *et al.*[5] by +2.7 to 2.1%. Enthalpy data of Gant[6] deviate by +1.5%. $C_p°$ is taken equal to that of the crystal from 298 to 800 K, the assumed glass transition. $S°$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

T_{fus} is from the enthalpy study of Gardner and Taylor.[3] Some other reported values include 1233[4] and 1235 K[5,6] from enthalpy studies and 1234[7] and 1235 K[8] from thermal analysis. $\Delta_{fus}H°$ is obtained from the difference in the adopted enthalpy fits for liquid and β-phases. Published values include 3.82,[3] 3.90[4] and 4.13 ± 0.12[5] $kcal·mol^{-1}$.

Vaporization Data

T_{vap} is calculated as the temperature at which $\Delta_r G° = 0$ for $BaCl_2(l) \rightarrow BaCl_2(g)$ at p=1 bar. $\Delta_{vap}H°$ is calculated as the corresponding $\Delta_r H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K⁻¹mol⁻¹	$S°$ J·K⁻¹mol⁻¹	$-[G°-H°(T_r)]/T$ J·K⁻¹mol⁻¹	$H°-H°(T_r)$ kJ·mol⁻¹	$\Delta_f H°$ kJ·mol⁻¹	$\Delta_f G°$ kJ·mol⁻¹	log K_f
0							
100							
200							
298.15	75.140	143.518	143.518	0.000	−832.467	−790.119	138.426
300	75.195	143.983	143.520	0.139	−832.443	−789.857	137.526
400	77.329	165.934	146.498	7.774	−831.295	−775.846	101.315
500	78.857	183.357	152.187	15.585	−830.874	−762.052	79.611
600	80.425	197.869	158.624	23.547	−831.165	−748.249	65.141
700	82.233	210.399	165.145	31.678	−830.522	−734.491	54.808
800	84.299	221.512	171.509	40.003	−830.223	−720.784	47.062
800.010	84.299	221.513	171.509	40.004	GLASS <--> LIQUID		
800.010	108.784	221.513	171.509	40.004	TRANSITION		
900	108.784	234.325	177.791	50.881	−826.972	−707.300	41.051
1000	108.784	245.786	184.027	61.759	−823.737	−694.176	36.260
1100	108.784	256.155	190.120	72.638	−828.885	−680.557	32.317
1200	108.784	265.620	196.023	83.516	−825.911	−667.203	29.043
1235.000	108.784	268.748	198.040	87.324	---- BETA <--> LIQUID ----		
1300	108.784	274.328	201.716	94.395	−822.847	−654.101	26.282
1400	108.784	282.389	207.194	105.273	−819.715	−641.237	23.925
1500	108.784	289.895	212.460	116.151	−816.536	−628.600	21.890
1600	108.784	296.915	217.522	127.030	−813.330	−616.175	20.116
1700	108.784	303.510	222.388	137.908	−810.118	−603.951	18.557
1800	108.784	309.728	227.069	148.787	−806.921	−591.916	17.177
1900	108.784	315.610	231.576	159.665	−803.761	−580.058	15.947
2000	108.784	321.190	235.918	170.543	−800.659	−568.365	14.844
2100	108.784	326.497	240.106	181.422	−797.639	−556.824	13.850
2200	108.784	331.558	244.149	192.300	−934.242	−540.051	12.822
2300	108.784	336.394	248.055	203.179	−930.614	−522.215	11.860
2400	108.784	341.023	251.833	214.057	−927.225	−504.532	10.981
2500	108.784	345.464	255.490	224.935	−924.075	−486.986	10.175
2600	108.784	349.731	259.033	235.814	−921.163	−469.560	9.434
2700	108.784	353.836	262.469	246.692	−918.478	−452.242	8.749
2800	108.784	357.793	265.803	257.571	−916.008	−435.020	8.115
2900	108.784	361.610	269.041	268.449	−913.733	−417.883	7.527
3000	108.784	365.298	272.189	279.327	−911.633	−400.821	6.979

PREVIOUS: CURRENT: December 1972

0	to 1198 K	crystal, alpha
1198	to 1235 K	crystal, beta
above	1235 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−16.707	−859.171	−859.171	INFINITE
90	56.961	49.346	187.175	−13.783	−860.857	−843.483	440.590
200	71.038	94.429	130.426	−7.199	−859.856	−826.420	215.839
298.15	75.140	123.666	123.666	0.000	−858.557	−810.290	141.959
300	75.195	124.131	123.668	0.139	−858.533	−809.990	141.032
400	77.329	146.082	126.646	7.774	−857.384	−793.994	103.685
500	78.857	163.505	132.335	15.585	−856.963	−778.216	81.300
600	80.425	178.018	138.772	23.547	−857.255	−762.428	66.375
700	82.233	190.548	145.293	31.678	−856.611	−746.684	55.718
800	84.299	201.661	151.657	40.003	−856.313	−730.992	47.729
900	86.624	211.721	157.780	48.546	−855.396	−715.380	41.520
1000	89.471	220.988	163.643	57.345	−854.241	−699.882	36.558
1100	93.531	229.692	169.256	66.480	−861.132	−683.694	32.466
1198.010	100.015	237.924	174.538	75.937	ALPHA <--> BETA		
1198.010	123.846	252.033	174.538	92.840	TRANSITION		
1200	123.846	252.239	174.666	93.087	−842.429	−667.664	29.063
1235.000	123.846	255.799	176.915	97.422	BETA <--> LIQUID		
1235.000	108.784	268.748	176.915	113.413	TRANSITION		
1300	108.784	274.328	181.648	120.484	−822.847	−654.101	26.282
1400	108.784	282.389	188.559	131.362	−819.715	−641.237	23.925
1500	108.784	289.895	195.068	142.241	−816.536	−628.600	21.890
1600	108.784	296.915	201.216	153.119	−813.330	−616.175	20.116
1700	108.784	303.510	207.041	163.997	−810.118	−603.951	18.557
1800	108.784	309.728	212.575	174.876	−806.921	−591.916	17.177
1900	108.784	315.610	217.845	185.754	−803.761	−580.058	15.947
2000	108.784	321.190	222.874	196.633	−800.659	−568.365	14.844
2100	108.784	326.497	227.683	207.511	−797.639	−556.825	13.850
2200	108.784	331.558	232.290	218.389	−934.242	−540.051	12.822
2300	108.784	336.394	236.712	229.268	−930.615	−522.215	11.860
2400	108.784	341.023	240.963	240.146	−927.225	−504.532	10.981
2500	108.784	345.464	245.054	251.025	−924.075	−486.986	10.175
2600	108.784	349.731	248.999	261.903	−921.163	−469.560	9.434
2700	108.784	353.836	252.806	272.781	−918.479	−452.243	8.749
2800	108.784	357.793	256.486	283.660	−916.008	−435.021	8.115
2900	108.784	361.610	260.045	294.538	−913.733	−417.883	7.527
3000	108.784	365.298	263.492	305.417	−911.634	−400.821	6.979

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = 325.74 \pm 5.0\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -497.3 \pm 17 (or \pm 6.7)\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -498.7 \pm 17 (or \pm 6.7)\ kJ \cdot mol^{-1}$

Vibrational Fequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
255 (1)	[36] (1)	265 (1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Ba–Cl = 2.82 ± 0.03Å

Bond Angle: Cl–Ba–Cl = [100 ± 20]°

Product of the Moments of Inertia: $I_A I_B I_C = 1.128013 \times 10^{-112}\ g^3 cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $\Delta_f H°(cr)$ by addition of $\Delta_{sub} H° = 86.0 \pm 1.5\ kcal \cdot mol^{-1}$ derived from 3rd law analysis of the vapor–pressure equation of Hildenbrand *et al.*[1,2] The equation[1] summarized five torsion–effusion runs (83 total points) and is reasonably consistent with five boiling pressures in the mmHg range measured by Novikov.[3] Other vapor pressure data[4-6] reviewed below are considered less reliable. $\Delta_f H°(g)$ is assigned alternative uncertainties to reflect the discrepancies in $\Delta_f H°(cr)$. Equilibria derived from flame studies[7] yield $\Delta_f H°(g) = -119.1 \pm 3$ and $\Delta_f H°(cr) = -205.1 \pm 3\ kcal \cdot mol^{-1}$, which confirm the adopted values by an independent path. Mass spectra[8] at 1230 K showed that the saturated vapor consists predominantly of $BaCl_2$ with considerably less than 1% of dimer.

Source	Method	Points	T/K	$\Delta_{sub} H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	δS cal·K⁻¹·mol⁻¹
(1,2)	Torsion effusion	83[a]	1235–1440	85.1	86.01	−0.7
(3)	Boiling Point	5	1588–1710	75.6 ± 4.2	86.30 ± 0.7	−6.4 ± 2.5
(4)	Effusion	3	1244–1277	78.5 ± 1.6	85.3 ± 0.2	−5.4 ± 1.3
(5)	Boiling point	1	1819		>81	
(6)	Static	4	1343–1487	85.4 ± 3.8	76.6 ± 0.9	6.1 ± 2.7
(7)	Flame K_p[b]	8	2134–2535	−9.5 ± 8.7[b]	− 13.5 ± 2.4[b]	1.7 ± 3.7

[a]Pressures obtained from an equation summarizing 5 runs (83 total points).

[b]$\Delta_r H°$ for Ba(g) + 2 HCl(g) → BaCl(g) + 2 H(g) yields $\Delta_f H°(298.15\ K) = 119.1 \pm 3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Vibrations ν_1 and ν_2 are the values quoted by Hildenbrand[9] and derived from IR spectra of molecules in matrix isolation.[10] The bending mode was not observed; its value was calculated[10] from force–constant correlations as described for BaF_2.[11] Hastie *et al.*[12] assigned the bending mode to a band which they observed at 61 cm^{-1} in argon and 62 cm^{-1} in neon. This value would reduce $S°$ by about 1.0 $cal \cdot K^{-1} \cdot mol^{-1}$. Our assigned uncertainty includes this possibility. Agreement is better for $\nu_1 = 255$[9,10] or 262 cm^{-1} (in Ne)[12] and for $\nu_3 = 265 \pm 5$ (gas)[13], 260[9,10] or 268 cm^{-1} (in Ne).[12] We adopt the gas–phase value[13] for ν_3.

Bond length is from gas–phase electron diffraction[14] which also gave the bond angle 180° ± 40°. Later studies[15] of electric and magnetic deflection of molecular beams revealed a permanent electric dipole moment and suggested a bond angle of the order of roughly 120°. Hastie *et al.*[12] estimated an angle of 120° ± 10° from relative intensities of ν_1 and ν_3. The matrix spectra[9,10] were first interpreted to give an angle of 120° but reanalysis by Hemple[10] gave the angle 95.4°, estimated from the three fundamentals. We adopt 100° ± 20° and note that $S°$ changes by only 0.2 $cal \cdot K^{-1} \cdot mol^{-1}$ in the range 95° to 120°. The singlet ground state is based on magnetic deflection data.[15] The principal moments of inertia are $I_A = 25.5142 \times 10^{-39}$, $I_B = 54.9471 \times 10^{-39}$, and $I_C = 80.4613 \times 10^{-39}\ g \cdot cm^2$.

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Continued on page 358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−14.667	−497.307	−497.307	INFINITE
100	47.186	268.409	373.964	−10.556	−497.806	−502.338	262.394
200	54.049	303.691	330.820	−5.426	−498.258	−506.675	132.330
250	55.387	315.909	326.656	−2.687	−498.477	−508.755	106.299
298.15	56.160	325.736	325.736	0.	−498.733	−510.713	89.475
300	56.183	326.083	325.737	0.104	−498.744	−510.787	88.936
350	56.689	334.784	326.423	2.927	−499.086	−512.769	76.527
400	57.028	342.378	327.953	5.770	−499.565	−514.693	67.212
450	57.266	349.109	329.936	8.628	−500.260	−516.545	59.959
500	57.439	355.152	332.161	11.496	−501.228	−518.305	54.147
600	57.667	365.647	336.893	17.252	−503.726	−521.477	45.399
700	57.807	374.547	341.653	23.026	−505.439	−524.311	39.125
800	57.898	382.273	346.258	28.812	−507.680	−526.849	34.400
900	57.961	389.096	350.646	34.605	−509.514	−529.135	30.710
1000	58.006	395.205	354.802	40.403	−511.358	−531.216	27.748
1100	58.040	400.735	358.730	46.206	−521.583	−532.293	25.276
1200	58.066	405.787	362.444	52.011	−523.681	−533.173	23.208
1300	58.085	410.435	365.959	57.819	−525.688	−533.882	21.452
1400	58.101	414.740	369.292	63.628	−527.625	−534.439	19.940
1500	58.114	418.749	372.457	69.439	−529.513	−534.860	18.625
1600	58.125	422.500	375.469	75.251	−531.374	−535.155	17.471
1700	58.133	426.024	378.340	81.064	−533.228	−535.335	16.449
1800	58.141	429.348	381.082	86.877	−535.096	−535.405	15.537
1900	58.147	432.491	383.706	92.692	−536.999	−535.371	14.718
2000	58.152	435.474	386.221	98.507	−538.961	−535.235	13.979
2100	58.157	438.311	388.634	104.322	−541.004	−534.998	13.307
2200	58.160	441.017	390.954	110.138	−682.670	−529.288	12.567
2300	58.164	443.602	393.187	115.954	−684.104	−522.284	11.861
2400	58.167	446.078	395.340	121.771	−685.776	−515.214	11.213
2500	58.170	448.452	397.417	127.587	−687.688	−508.069	10.616
2600	58.172	450.734	399.424	133.405	−689.837	−500.842	10.062
2700	58.174	452.929	401.366	139.222	−692.214	−493.529	9.548
2800	58.176	455.045	403.245	145.039	−694.804	−486.123	9.069
2900	58.178	457.086	405.067	150.857	−697.590	−478.622	8.621
3000	58.179	459.059	406.834	156.675	−700.551	−471.021	8.201
3100	58.180	460.966	408.549	162.493	−703.664	−463.319	7.807
3200	58.182	462.814	410.216	168.311	−706.904	−455.515	7.436
3300	58.183	464.604	411.838	174.129	−710.241	−447.608	7.085
3400	58.184	466.341	413.415	179.948	−713.660	−439.598	6.754
3500	58.185	468.028	414.952	185.766	−717.139	−431.487	6.440
3600	58.186	469.667	416.449	191.585	−720.654	−423.276	6.142
3700	58.187	471.261	417.909	197.403	−724.190	−414.966	5.858
3800	58.187	472.813	419.333	203.222	−727.728	−406.562	5.589
3900	58.188	474.324	420.724	209.041	−731.256	−398.064	5.331
4000	58.189	475.797	422.082	214.859	−734.763	−389.476	5.086
4100	58.189	477.234	423.410	220.678	−738.238	−380.801	4.851
4200	58.190	478.636	424.708	226.497	−741.673	−372.041	4.627
4300	58.190	480.006	425.979	232.316	−745.066	−363.200	4.412
4400	58.191	481.343	427.222	238.135	−748.410	−354.281	4.206
4500	58.191	482.651	428.439	243.954	−751.704	−345.287	4.008
4600	58.192	483.930	429.631	249.774	−754.938	−336.220	3.818
4700	58.192	485.182	430.800	255.593	−758.097	−327.085	3.635
4800	58.192	486.407	431.946	261.412	−761.221	−317.882	3.459
4900	58.193	487.607	433.070	267.231	−764.285	−308.614	3.290
5000	58.193	488.782	434.172	273.051	−767.299	−299.284	3.127
5100	58.193	489.935	435.254	278.870	−770.236	−289.897	2.969
5200	58.194	491.065	436.317	284.689	−773.140	−280.450	2.817
5300	58.194	492.173	437.360	290.509	−775.992	−270.948	2.670
5400	58.194	493.261	438.385	296.328	−778.794	−261.393	2.528
5500	58.194	494.329	439.393	302.147	−781.515	−251.789	2.391
5600	58.195	495.377	440.383	307.967	−784.160	−242.141	2.259
5700	58.195	496.407	441.357	313.786	−786.808	−232.439	2.130
5800	58.195	497.419	442.315	319.606	−789.386	−222.693	2.006
5900	58.195	498.414	443.257	325.425	−791.800	−212.921	1.885
6000	58.195	499.392	444.185	331.245	−794.296	−203.088	1.768

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 246.23 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -320.2 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -322.2 \pm 8.4\ kJ·mol^{-1}$

State	Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$D\ ^2\Sigma^+$	24156.8	2
$A\ ^2\Pi_{1/2}$	11646.9	2	$D'^2\Sigma^+$	26222.3	2
$A\ ^2\Pi_{3/2}$	12278.2	2	$E\ ^2\Sigma^+$	28139.7	2
$B\ ^2\Sigma^+$	14062.5	2	$F\ ^2\Sigma^+$	29411.3	2
$C\ ^2\Pi$	19998.2	2	$G\ ^2\Sigma^+$	31451.9	2
	20197.2	2	$H\ ^2\Sigma^+$	31582.0	2

$\omega_e = 468.9\ cm^{-1}$ $\omega_e x_e = 1.79\ cm^{-1}$ $\sigma = 1$
$B_e = 0.2164\ cm^{-1}$ $\alpha_e = [0.00112]\ cm^{-1}$ $r_e = 2.152$ Å

Enthalpy of Formation

$\Delta_f H°$ is obtained from a 3rd law analysis of K_p data for three gaseous dissociation equilibria. The K_p data were derived from observations made on the condensed phase systems BaF_2–B^1 and BaF_2–Al^2 by the mass spectrometric–Knudsen effusion method. Results of a 2nd and 3rd law analysis of these data are given below. Also included below are results derived from two mass spectrometric studies[2, 3] of the heterogeneous reaction (D), and a value for the heat of dissociation of BaF which was determined from spectrophotometric studies[4, 5] of reaction equilibria in H_2–O_2–N_2 flames.

Source	Reaction	T/K	Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
1	A	1418–1512	8	−1.0	−6.6 ± 0.5	−3.8 ± 2.2	−78.0 ± 1.5
1	B	1418–1512	8	8.6	−3.5 ± 1.1	−3.5 ± 5.7	−77.3 ± 3.6
2	C	1175–1255	8[a]	26.0	23.0 ± 0.2	−2.5 ± 0.9	−75.6 ± 3.0
2	D	1175–1255	8	−118.8	−96.4 ± 1.1	18.4 ± 3.6	−74.9 ± 1.7
3	D	1428		−103.5			−71.3 ± 3.0
4,5	E			145 ± 6			−83.3 ± 8.0

Reactions: (A) $Ba(g) + BaF_2(g) \rightarrow 2\ BaF(g)$ (D) $2\ BaF(g) \rightarrow Ba(g) + BaF_2(cr)$
(B) $2Ba(g) + BF_3(g) \rightarrow 2\ BaF(g) + BF(g)$ (E) $BaF(g) \rightarrow Ba(g) + F(g)$
(C) $Ba(g) + AlF(g) \rightarrow BaF(g) + Al(g)$

[a]One point rejected due to failure of a statistical test.

It is believed that the K_p data for the three homogeneous reactions (A, B, and C) are more reliable than those for the heterogeneous reaction (D) due to the need for a machine calibration constant which appears in the equilibrium expression for the latter. Ehlert *et al.*[2] determined this constant from vaporization experiments performed with silver contained in their Knudsen cell. Further support for this belief is provided by the large positive drift that arises in the 3rd law analysis of these K_p's. Also, it is felt that the results otained from the flame–spectrophotometric studies[4, 5] are somewhat more uncertain than those derived from the K_p data for the three homogeneous reactions. Therefore, we choose to adopt a median value $\Delta_f H°(BaF, g, 298.15\ K) = -77.0 \pm 2.0\ kcal·mol^{-1}$ of the first three results. The adopted value corresponds to a dissociation energy of $D_0°$ (Ba–F) = 137.9 $kcal·mol^{-1}$ (5.98 eV).

Gaydon[7] has reported a spectroscopic value for $D_0°$ of 3.8 eV which is considerably lower than the adopted thermochemical value. The spectroscopic value is based on a linear Birge–Sponer extrapolation of the thirteen known vibrational levels for the ground state ($^2\Sigma^+$). However, Gaydon[7] and later Hildenbrand[8] have shown that the linear extrapolation generally under–estimates $D_0°$ when the bonding in the molecule is partially ionic. Correcting $D_0°$(LBX) for the ionic character of BaF with the ionicity parameter suggested by Hildenbrand,[8] we obtain $D_0°$ (Ba–F) = 6.9 eV which is somewhat high. Other values for $D_0°$ that have been reported are 5.94[1] and 5.68 eV.[9] Both of these values were calculated from the Rittner ionic model[10] for polarizable ions and show remarkably good agreement with the adopted value.

Heat Capacity and Entropy

The spectroscopic data, except for α_e, are given by Rosen[11] for ^{138}BaF. α_e is calculated from the Morse potential function. Corrections to these data to account for the natural isotopic abundances of barium were found to be negligible. The electronic states and levels are also taken from the compilation of Rosen.[11]

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Continued on page 358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.345	−320.188	−320.188	INFINITE
100	29.574	211.330	275.613	−6.428	−320.424	−329.630	172.181
200	32.669	232.752	249.349	−3.319	−321.324	−338.481	88.402
250	33.896	240.181	246.796	−1.654	−321.748	−342.721	71.608
298.15	34.748	246.228	246.228	0.	−322.168	−346.723	60.744
300	34.776	246.443	246.229	0.064	−322.185	−346.875	60.396
350	35.405	251.854	246.655	1.820	−322.670	−350.953	52.377
400	35.863	256.613	247.608	3.602	−323.274	−354.954	46.352
450	36.206	260.858	248.849	5.404	−324.082	−358.868	41.656
500	36.468	264.687	250.244	7.221	−325.155	−362.679	37.889
600	36.839	271.371	253.224	10.888	−327.847	−369.921	32.205
700	37.088	277.069	256.234	14.585	−329.741	−376.796	28.117
800	37.268	282.034	259.155	18.303	−332.154	−383.347	25.030
900	37.406	286.432	261.946	22.037	−334.154	−389.626	22.613
1000	37.517	290.379	264.595	25.783	−336.159	−395.682	20.668
1100	37.611	293.959	267.105	29.540	−346.539	−400.718	19.029
1200	37.694	297.235	269.481	33.305	−348.789	−405.543	17.653
1300	37.770	300.255	271.734	37.078	−350.943	−410.185	16.481
1400	37.843	303.057	273.872	40.859	−353.022	−414.663	15.471
1500	37.917	305.671	275.906	44.647	−355.048	−418.995	14.591
1600	37.995	308.120	277.843	48.443	−357.039	−423.193	13.816
1700	38.081	310.426	279.693	52.246	−359.016	−427.267	13.128
1800	38.179	312.605	281.461	56.059	−360.997	−431.225	12.514
1900	38.292	314.673	283.155	59.883	−363.001	−435.072	11.961
2000	38.421	316.640	284.781	63.718	−365.045	−438.813	11.461
2100	38.570	318.518	286.343	67.568	−367.149	−442.450	11.005
2200	38.740	320.316	287.847	71.433	−508.849	−440.610	10.461
2300	38.933	322.042	289.296	75.316	−510.286	−437.476	9.935
2400	39.148	323.704	290.695	79.220	−511.924	−434.276	9.452
2500	39.387	325.307	292.048	83.147	−513.759	−431.004	9.005
2600	39.649	326.857	293.357	87.098	−515.782	−427.655	8.592
2700	39.934	328.358	294.626	91.077	−517.981	−424.224	8.207
2800	40.240	329.816	295.857	95.086	−520.335	−420.709	7.848
2900	40.566	331.234	297.052	99.126	−522.823	−417.107	7.513
3000	40.911	332.615	298.215	103.200	−525.421	−413.418	7.198
3100	41.273	333.962	299.346	107.309	−528.102	−409.640	6.902
3200	41.651	335.278	300.449	111.455	−530.842	−405.775	6.624
3300	42.042	336.566	301.524	115.639	−533.606	−401.825	6.360
3400	42.445	337.827	302.573	119.864	−536.382	−397.790	6.111
3500	42.859	339.063	303.598	124.129	−539.144	−393.673	5.875
3600	43.280	340.276	304.600	128.436	−541.871	−389.478	5.651
3700	43.708	341.468	305.580	132.785	−544.548	−385.208	5.438
3800	44.140	342.639	306.540	137.177	−547.159	−380.867	5.235
3900	44.575	343.792	307.481	141.613	−549.693	−376.457	5.042
4000	45.012	344.926	308.403	146.092	−552.141	−371.984	4.858
4100	45.448	346.043	309.307	150.615	−554.495	−367.451	4.681
4200	45.883	347.143	310.195	155.182	−556.750	−362.861	4.513
4300	46.315	348.228	311.067	159.792	−558.907	−358.219	4.352
4400	46.742	349.297	311.923	164.445	−560.963	−353.528	4.197
4500	47.164	350.352	312.766	169.140	−562.919	−348.791	4.049
4600	47.579	351.394	313.594	173.877	−564.768	−344.013	3.906
4700	47.986	352.421	314.409	178.656	−566.499	−339.197	3.770
4800	48.385	353.436	315.212	183.474	−568.157	−334.344	3.638
4900	48.775	354.437	316.002	188.332	−569.716	−329.457	3.512
5000	49.155	355.427	316.781	193.229	−571.193	−324.538	3.390
5100	49.524	356.404	317.548	198.163	−572.563	−319.594	3.273
5200	49.882	357.369	318.305	203.133	−573.872	−314.621	3.160
5300	50.228	358.322	319.051	208.139	−575.105	−309.623	3.052
5400	50.563	359.264	319.787	213.179	−576.266	−304.603	2.946
5500	50.884	360.195	320.513	218.251	−577.328	−299.566	2.845
5600	51.193	361.115	321.230	223.355	−578.297	−294.514	2.747
5700	51.490	362.023	321.938	228.489	−579.255	−289.438	2.652
5800	51.773	362.921	322.636	233.653	−580.131	−284.349	2.561
5900	52.043	363.809	323.327	238.844	−580.833	−279.261	2.472
6000	52.299	364.686	324.009	244.061	−581.611	−274.144	2.387

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = [239.0 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 146.1 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 150.2 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$a^3\Pi$	[9000]	6
$A'^1\Pi$	[11000]	2
$B'^1\Delta$	[13000]	2
$b^3\Sigma^-$	[15000]	3
$A^1\Sigma^+$	[16000]	1
$B^1\Sigma^+$	[30000]	1

$\omega_e = [540]\ cm^{-1}$ $\omega_e x_e = [2.06]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.2371]\ cm^{-1}$ $\alpha_e = [0.00122]\ cm^{-1}$ $r_e = [2.064]$ Å

Enthalpy of Formation

The appearance potential (AP) of BaF^+ from BaF(g) has been measured mass spectrometrically as 4.9 eV[1] and 4.8 ± 0.3 eV.[2] This latter value has been confirmed by Zmbov and Margrave.[3] Combining these results with $\Delta_f H°$(BaF, g, 0 K) = −76.5 ± 2.0 kcal·mol^{-1},[4] we obtain $\Delta_f H°$(BaF^+, g, 0 K) equal to 36.5 and 34.2 ± 9.0 kcal·mol^{-1}.

Hildenbrand[2] also reported an AP for BaF^+ from BaF_2(g) as 13.5 ± 1.0 eV. Green *et al.*[5] obtained an ionization efficiency curve for BaF^+ which extrapolates (high-energy portion) to 12.9 eV at zero ion current. Assuming the process to be $e^- + BaF_2(g) \rightarrow BaF^+(g) + F(g) + 2e^-$, we obtain $\Delta_f H°$(BaF^+, g, 0 K) values of 101.3 ± 25 and 87.5 kcal·mol^{-1} by combining the above results with $\Delta_f H°$(BaF_2, g, 0 K) = −191.6 ± 1.5 kcal·mol^{-1} and $\Delta_f H°$(F, g, 0 K) = 18.36 ± 0.4 kcal·mol^{-1}.[4]

The two lower values for $\Delta H°$(0 K) are preferred here, since the dissociative ionization of BaF (g) most likely involved unknown kinetic energy factors. We choose to adopt $\Delta_f H°$(BaF^+, g, 0 K) = 35.0 ± 10.0 kcal·mol^{-1} which gives $\Delta_f H°$(BaF^+,g, 298.15 K) = 35.9 ± 10.0 kcal·mol^{-1}. The adopted heat of formation corresponds to an ionization potential for BaF(g) of 4.83 eV.

Heat Capacity and Entropy

The dissociation energy of BaF^+($D_0°$ = 145.4 kcal·mol^{-1}) is slightly greater than that for BaF($D_0°$ = 137.9 kcal·mol^{-1})[4] which implies somewhat stronger bonding in the ion. Thus, one would expect the internuclear distance (r_e) for the ground state of BaF^+ to be less than that for BaF. Barrow and Beale[6] postulated from a rotational analysis of the $F^2\Sigma^+$–$X^2\Sigma^+$ band system of SrF a r_e for SrF^+ which was some 4% lower than that for SrF. We assume a similar decrease in r_e for BaF^+ and obtain r_e = 2.064 Å from r_e(BaF) = 2.152 Å.[4] ω_e is calculated from Badger's rule[7] which can be written in the form $\omega_{e2} = 3.159 \times 10^6/\mu(r_e - d_{ij})$.[3] Molecular data for CsF,[4] BaF,[4] and BaO[8] were used to determine the constant d_{ij}. The product $x_e\mu^{1/2}$ has been shown to be constant within a group of similar molecules by Barrow and Caunt.[9] Since $\mu^{1/2}(BaF^+) \cong \mu^{1/2}$(BaF), we assume $x_e(BaF^+) = x_e$(BaF) and obtain $\omega_e x_e$ equal to 2.06 cm^{-1} with our estimated value for ω_e. α_e is obtained from the other constants assuming a Morse potential function.

BaF has eight valence electrons; thus, the ground state configuration ($^1\Sigma^+$) and electronic levels for the A and B states are estimated from those for the isoelectronic molecule BaS.[10] By analogy with the gaseous alkaline earth oxides,[11] C_2,[4] and BeS,[12] low-lying triplet states are to be expected. The two estimated triplet levels are based on those which have been observed directly in C_2,[4] BeS,[12] and indirectly (through perturbative effects) in BaS.[10] Also included are a $^1\Pi$ state at 11,000 cm^{-1} and $^1\Delta$ state at 13,000 cm^{-1}. These levels are also estimated by analogy with those for C_2[4] and BeS.[12] It is believed that our adopted electronic entropies for BaF^+ are most likely minimal values. Probable upper limits for the electronic contributions can be established by decreasing the triplet levels to 1000 cm^{-1} ($^3\Pi$) and 5000 cm^{-1} ($^3\Sigma$) and neglecting the other excited states. This increases the entropy (in cal·K^{-1}·mol^{-1}) by 3.8 and 2.1 at 2000 K and 4000 K, respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.205	146.127		
100	29.331	204.761	267.690	−6.293			
200	31.866	225.783	242.009	−3.245			
250	33.131	233.035	239.511	−1.619			
298.15	34.073	238.955	238.955	0.	150.206	121.564	−21.298
300	34.105	239.166	238.956	0.063	150.226	121.387	−21.135
350	34.831	244.480	239.374	1.787	150.749	116.538	−17.392
400	35.375	249.169	240.311	3.543	151.158	111.620	−14.576
450	35.787	253.360	241.532	5.323	151.367	106.663	−12.381
500	36.105	257.148	242.907	7.120	151.313	101.696	−10.624
600	36.557	263.773	245.848	10.755	150.668	91.843	−7.996
700	36.859	269.433	248.823	14.427	150.827	82.015	−6.120
800	37.074	274.369	251.714	18.124	150.471	72.215	−4.715
900	37.240	278.746	254.479	21.840	150.532	62.429	−3.623
1000	37.381	282.677	257.106	25.571	150.591	52.636	−2.749
1100	37.520	286.246	259.595	29.316	142.278	43.658	−2.073
1200	37.678	289.518	261.954	33.076	142.101	34.701	−1.510
1300	37.877	292.541	264.192	36.853	142.030	25.754	−1.035
1400	38.139	295.357	266.319	40.653	142.049	16.810	−0.627
1500	38.481	298.000	268.344	44.484	142.144	7.861	−0.274
1600	38.919	300.497	270.276	48.353	142.305	−1.096	0.036
1700	39.461	302.872	272.124	52.271	142.521	−10.065	0.309
1800	40.114	305.145	273.896	56.249	142.783	−19.048	0.553
1900	40.875	307.334	275.599	60.297	143.084	−28.046	0.771
2000	41.741	309.452	277.239	64.427	143.412	−37.061	0.968
2100	42.700	311.512	278.822	68.648	143.759	−46.094	1.147
2200	43.739	313.522	280.354	72.970	4.593	−49.767	1.182
2300	44.843	315.490	281.839	77.398	5.780	−52.265	1.187
2400	45.992	317.423	283.281	81.940	6.859	−54.813	1.193
2500	47.167	319.324	284.685	86.598	7.833	−57.403	1.199
2600	48.349	321.197	286.053	91.374	8.713	−60.030	1.206
2700	49.518	323.044	287.389	96.267	9.508	−62.689	1.213
2800	50.656	324.865	288.695	101.276	10.233	−65.376	1.220
2900	51.747	326.662	289.973	106.397	10.903	−68.089	1.226
3000	52.776	328.434	291.226	111.623	11.537	−70.823	1.233
3100	53.732	330.180	292.454	116.949	12.151	−73.579	1.240
3200	54.605	331.900	293.660	122.367	12.762	−76.354	1.246
3300	55.389	333.593	294.845	127.868	13.392	−79.149	1.253
3400	56.079	335.257	296.009	133.442	14.045	−81.963	1.259
3500	56.673	336.891	297.154	139.080	14.735	−84.797	1.266
3600	57.171	338.495	298.280	144.773	15.472	−87.651	1.272
3700	57.576	340.067	299.388	150.511	16.263	−90.526	1.278
3800	57.890	341.607	300.479	156.285	17.112	−93.424	1.284
3900	58.119	343.114	301.553	162.087	18.022	−96.344	1.290
4000	58.266	344.587	302.610	167.906	18.993	−99.289	1.297
4100	58.340	346.027	303.652	173.737	20.026	−102.259	1.303
4200	58.345	347.433	304.678	179.572	21.117	−105.255	1.309
4300	58.289	348.805	305.688	185.404	22.261	−108.277	1.315
4400	58.179	350.144	306.683	191.228	23.455	−111.326	1.322
4500	58.020	351.450	307.663	197.038	24.693	−114.403	1.328
4600	57.819	352.723	308.629	202.831	25.978	−117.509	1.334
4700	57.583	353.964	309.581	208.601	27.317	−120.645	1.341
4800	57.316	355.173	310.518	214.346	28.665	−123.807	1.347
4900	57.024	356.352	311.441	220.063	30.043	−126.999	1.354
5000	56.712	357.501	312.351	225.750	31.435	−130.218	1.360
5100	56.383	358.621	313.247	231.405	32.864	−133.467	1.367
5200	56.042	359.713	314.131	237.027	34.285	−136.742	1.374
5300	55.692	360.777	315.001	242.613	35.712	−140.045	1.380
5400	55.336	361.815	315.858	248.165	37.141	−143.374	1.387
5500	54.977	362.827	316.703	253.680	38.601	−146.735	1.394
5600	54.618	363.814	317.535	259.160	40.086	−150.124	1.400
5700	54.259	364.778	318.356	264.604	41.516	−153.534	1.407
5800	53.903	365.718	319.164	270.012	42.964	−156.972	1.414
5900	53.551	366.637	319.961	275.385	44.522	−160.451	1.421
6000	53.204	367.534	320.747	280.722	45.943	−163.937	1.427

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 96.40 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} \approx 1240\ K\ (\alpha \rightarrow \beta)$
$T_{trs} \approx 1480\ K\ (\beta \rightarrow \gamma)$
$T_{fus} \approx 1641\ K$

$\Delta_f H°(0\ K) = -1207.5 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1208.8 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° \approx 2.674 \pm 0.837\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 23.359 \pm 0.628\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Guntz[1] measured the heat of neutralization of $Ba(OH)_2$(aq) with HF(aq) as $\Delta H = -34.8\ kcal \cdot mol^{-1}$ at 284 K. We estimate $\Delta C_p = 106\ cal \cdot K^{-1} \cdot mol^{-1}$[2] for $Ba(OH)_2\ 660\ H_2O + 2(HF\ 110\ H_2O) \rightarrow BaF_2(cr) + 2\ H_2O(l)$ which gives $\Delta_r H°(298.15\ K) = -33.4\ kcal \cdot mol^{-1}$. This leads to $\Delta_f H°(298.15\ K) = -288.3\ kcal \cdot mol^{-1}$ when combined with auxiliary data.[3,4,5] Petersen[6] investigated the same reaction but with HF·200 H_2O and found that 16% of the BaF_2 remained dissolved. After correcting for incomplete precipitation his final result was $\Delta H°(292.15\ K) \approx -33.92\ kcal \cdot mol^{-1}$ which gives $\Delta_f H°(298.15\ K) = -288.2\ kcal \cdot mol^{-1}$.

In the same study, Petersen[6] measured the heat of precipitation of BaF_2 from $BaCl_2$(aq) with AgF(aq) as $\Delta H°(292\ K) = -35.02\ kcal \cdot mol^{-1}$. We estimate $\Delta C_p = 108\ cal \cdot K^{-1} \cdot mol^{-1}$[2] for $2\ (AgF \cdot 200\ H_2O) + BaCl_2 \cdot 400\ H_2O \rightarrow BaF_2(cr) + 2AgCl(cr)$ which gives $\Delta H°(298.15\ K) \approx -34.4\ kcal \cdot mol^{-1}$. Using auxiliary data,[4,7] we obtain $\Delta_f H°(BaF_2, cr, 298.15\ K) \approx -288.4\ kcal \cdot mol^{-1}$. Petersen[6] also reported the heat of solution of BaF_2 as $\Delta_{sol} H° = 1.88\ kcal \cdot mol^{-1}$. From this result, we obtain $\Delta_f H°(298.15\ K) \approx -290.3\ kcal \cdot mol^{-1}$.

Stephen and Stephen[9] have selected a "best" value for the solubility of BaF_2 of 1.614 g/l at 298.15 K which corresponds to $K_{sp} \approx 3.1196 \times 10^{-6}$. Using $\Delta_f G°$ (Ba^{+2}, ∞ aq, 298.15 K) = −134.02[4] and $\Delta_f G°(F^-, \infty\ aq, 298.15\ K) = -66.96\ kcal \cdot mol^{-1}$,[1,5] we calculate $\Delta_f G°(298.15\ K) = -275.45\ kcal \cdot mol^{-1}$. Based on the adopted functions, $\Delta_f H°(298.15\ K) = -287.5\ kcal \cdot mol^{-1}$.

Two equilibrium studies[10,11] have also been reported. 2nd and 3rd law analyses of these data are given below.

Source	Reaction	T/K	No. of Points	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Domangem[10]	A	1173–1373	3	41.0	62.5 ± 3.4	16.9 ± 1.0	−267.3
Hood and Woyski[11]	B	477–1033	9	5.9	5.8 ± 1.0	−0.1 ± 0.1	−279.8

Reaction: (A) $BaF_2(cr) + H_2O(g) \rightarrow 2\ HF(g) + BaO(cr)$ (B) $HF(g) + 0.5\ BaCl_2(cr) \rightarrow HCl(g) + 0.5\ BaF_2(cr)$

The large discrepancy which arises in the $\Delta_f H°$values obtained from the equilibrium and calorimetric results is not well understood. Domange[10] has measured similar equilibria for CoF_2, MgF_2, and CaF_2 which are very consistent with JANAF heats of formation. Very recently, Finch *et al.*[12] attempted to determine the heat of precipitation of BaF_2 form $BaCl_2$(aq) by dissolving a slight excess of NaF. X-ray diffraction studies of the precipitate showed the formation of BaClF and Ba_2ClF_3along with BaF_2. We believe the equilibrium results of Hood and Woyski[11] may have been influenced by the formation of mixed halides. Also, it seems quite likely that the calorimetric results of Petersen[6] on the precipitation of BaF_2 from $BaCl_2$(aq) with AgF(aq) would be similarly influenced. We adopt $\Delta_f H°(298.15\ K) = -288.9 \pm 1.0\ kcal \cdot mol^{-1}$ which is a weighted value of the calorimetric results of Guntz[1] and Petersen[6] on the heat of neutralization of $Ba(OH)_2$(aq), the heat of solution of BaF_2(cr)[6] and the K_{sp} value obtained from the solubility data of Stephen and Stephen.[9] Barany *et al.*[8] determined the heat of solution of BaO(cr) in HF(aq), which contained some dissolved silica, as $\Delta H° = -73.04\ kcal \cdot mol^{-1}$. We assume this value refers to the reaction $BaO(cr) + 2\ HF \cdot 4.41\ H_2O \rightarrow BaF_2(cr) + H_2O(l)$, and we calculate $\Delta_f H°(298.15\ K) = -290.2 \pm 2.0\ kcal \cdot mol^{-1}$with $\Delta_f H°(BaO, cr, 298.15\ K) = -132.3\ kcal \cdot mol^{-1}$.[5] These results substantiate our adopted $\Delta_f H°$ value.

Heat Capacity and Entropy

C_p below 298 K is based on the low temperature (14–300 K) heat capacities of Pitzer *et al.*[13] These data show an unusual leveling off of C_p above 274 K, and values in the range 274–300 K are obtained by graphical extrapolation of their low temperature data. $S°(298.15\ K)$ is based on the adopted C_p's with $S°(15\ K) = 0.09\ cal \cdot K^{-1} \cdot mol^{-1}$.

Relative enthalpies have been reported by Efremova and Matizen (757–2053 K)[14] and Krestovnikov and Karetnikov (288–1273 K).[15] The enthalpy data of Efremova and Matizen[14] indicated the existence of a second order phase transition at 1240 K. We adopt their smoothed C_p data for 800–1480 K. C_p's below 800 K are estimated graphically by comparison with those for $BaCl_2$, CaF_2, and SrF_2.[5] C_p (BaF_2, γ) are based on a JANAF curve fit of their relative enthalpies (1482–1596 K). The rapid rise in the enthalpy near the melting point is assumed to be due to premelting, and these points were not used in the fit. The maximum deviation of our adopted functions from those used in the fit is 0.5%. Kelley[16] analyzed the enthalpy data of Krestovnikov and Karetnikov.[15] His smoothed enthalpies are consistently 2–3% higher than those adopted. No second order phase transition was observed. These data are judged to be less reliable and are not used in our evaluation.

Transition Data

The transition temperatures are those reported by Efremova and Matizen.[14] We assume the transition at 1240 K is of the second order type, since no discontinuity appears in their enthalpy data at this temperature. The heat of the β–γ transition is calculated as the difference between the adopted enthalpies for these two phases at 1480 K.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.000	0.000	INFINITE	−14.454	−1207.475	−1207.475	INFINITE
100	43.897	29.894	155.326	−12.543	−1210.169	−1192.713	623.010
200	65.796	68.764	102.826	−6.812	−1209.912	−1175.206	306.932
298.15	72.204	96.397	96.397	0.000	−1208.758	−1158.410	202.949
300	72.304	96.844	96.398	0.134	−1208.734	−1158.097	201.643
400	75.940	118.170	99.281	7.556	−1207.548	−1141.405	149.052
500	78.450	135.397	104.837	15.280	−1207.007	−1124.951	117.523
600	80.333	149.864	111.167	23.218	−1207.165	−1108.515	96.505
700	82.383	162.395	117.610	31.350	−1206.400	−1092.143	81.497
800	84.935	173.549	123.917	39.705	−1205.980	−1075.841	70.245
900	88.701	183.750	130.005	48.370	−1204.877	−1059.636	61.500
1000	94.558	193.369	135.864	57.505	−1203.338	−1043.576	54.511
1100	104.182	202.789	141.520	67.396	−1209.444	−1026.882	48.763
1200	130.541	212.702	147.030	78.807	−1205.921	−1010.421	43.983
1240.000	194.914	217.601	149.222	84.790	ALPHA <--> BETA		
1240.000	194.713	217.601	149.222	84.790	TRANSITION		
1300	137.654	225.182	152.565	94.403	−1198.136	−994.440	39.957
1400	114.014	234.302	158.091	106.695	−1193.600	−978.956	36.525
1480.000	107.104	240.427	162.380	115.511	BETA <--> GAMMA		
1480.000	107.654	242.234	162.380	118.184	TRANSITION		
1500	107.654	243.679	163.454	120.337	−1187.676	−963.778	33.562
1600	107.654	250.627	168.687	131.103	−1184.612	−948.951	30.980
1641.000	107.654	253.351	170.769	135.517	--- GAMMA <--> LIQUID ---		
1700	107.654	257.153	173.701	141.868	−1181.550	−934.316	28.708
1800	107.654	263.307	178.510	152.634	−1178.508	−919.861	26.694
1900	107.654	269.127	183.128	163.399	−1175.506	−905.574	24.896
2000	107.654	274.649	187.567	174.164	−1172.561	−891.443	23.282

PREVIOUS: CURRENT: December 1972

Continued on page 358

$S°(298.15\ K) = [121.254]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1641\ K$

$\Delta_f H°(298.15\ K) = [-1171.294]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 23.359 \pm 0.628\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the liquid is calculated from that of the crystal by addition of $\Delta_{fus}H°$ the difference in enthalpy, $H°(1641\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1100 K below which $C_p°$ follows that of the crystal. $C_p°$ is assumed constant in the temperature range 1100–3500 K and is based on a JANAF curve fit of the relative enthalpies of Efremova and Matizen[1] for the liquid (1641–1900 K). Some scatter was observed in these data at the higher temperatures, and these points were not included in the fit. The maximum deviation of the observed enthalpies which were used in the fit from those adopted is 0.29%.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is the value selected by Efremova and Matizen[1] from their relative enthalpy data. These data show premelting starting near 1620 K and complete melting occurring at 1646 K. Other values for T_{fus} that have been reported are 1627,[2] 1628,[3] 1627,[4] 1617,[5] and 1593 K.[6] The selected T_{fus} was obtained from measurements made on samples of BaF_2 contained in steel and molybdenum capsules. There were no indications of any reaction between the sample and container. Three of the lower values given above were determined from measurements on BaF_2 contained in either graphite[3,4] or tantalum[2] crucibles. It has now been established by mass spectroscopy[7,8] that the alkaline earth difluorides can be appreciably reduced by these materials near 1400 K. Thus, we prefer the higher value.

$\Delta_{fus}H°$ is obtained as the difference in the adopted functions for the liquid and crystal at T_{fus}.

Vaporization Data

T_{vap} is the calculated temperature at which $\Delta_r G° = 0$ for $BaF_2(l) \rightarrow BaF_2(g)$. $\Delta_{vap}H°$ is calculated from the difference in $\Delta_f H°(T_{vap})$ for the gas and liquid. Ruff and Le Boucher[9] derived $T_{vap} = 2533$ K and $\Delta_{vap}H° = 69.8\ kcal·mol^{-1}$ from an analysis of their vapor pressures (1960–2206 K).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	72.203	121.254	121.254	0.000	−1171.294	−1128.357	197.684
300	72.304	121.701	121.256	0.134	−1171.270	−1128.091	196.418
400	75.940	143.027	124.139	7.555	−1170.085	−1113.885	145.458
500	78.450	160.253	129.694	15.280	−1169.544	−1099.916	114.907
600	80.333	174.720	136.024	23.218	−1169.702	−1085.965	94.542
700	82.383	187.251	142.467	31.349	−1168.937	−1072.079	80.000
800	84.935	198.405	148.774	39.705	−1168.517	−1058.263	69.097
900	88.701	208.606	154.862	48.369	−1167.414	−1044.544	60.624
1000	94.558	218.222	160.721	57.501	−1165.879	−1030.969	53.852
1100	104.182	227.655	166.377	67.407	−1171.970	−1016.761	48.282
1100.000	104.182	227.655	166.377	67.407	GLASS <--> LIQUID		
1100.000	99.826	227.655	166.377	67.407	TRANSITION		
1200	99.826	236.341	171.850	77.389	−1169.875	−1002.742	43.648
1300	99.826	244.332	177.123	87.372	−1167.704	−988.902	39.735
1400	99.826	251.730	182.191	97.354	−1165.476	−975.232	36.386
1500	99.826	258.617	187.059	107.337	−1163.213	−961.722	33.490
1600	99.826	265.060	191.735	117.320	−1160.931	−948.363	30.961
1641.000	99.826	267.585	193.598	121.413	--- GAMMA <--> LIQUID ---		
1700	99.826	271.111	196.228	127.302	−1158.652	−935.147	28.734
1800	99.826	276.817	200.548	137.285	−1156.393	−922.065	26.758
1900	99.826	282.215	204.705	147.267	−1154.174	−909.108	24.993
2000	99.826	287.335	208.710	157.250	−1152.011	−896.266	23.408
2100	99.826	292.206	212.571	167.233	−1149.925	−883.531	21.977
2200	99.826	296.850	216.297	177.215	−1287.453	−865.517	20.550
2300	99.826	301.287	219.897	187.198	−1284.735	−846.400	19.222
2400	99.826	305.536	223.377	197.181	−1282.236	−827.396	18.008
2500	99.826	309.611	226.745	207.163	−1279.952	−808.492	16.893
2600	99.826	313.526	230.008	217.146	−1277.876	−789.675	15.865
2700	99.826	317.293	233.172	227.128	−1275.994	−770.935	14.915
2800	99.826	320.924	236.241	237.111	−1274.288	−752.260	14.034
2900	99.826	324.427	239.222	247.094	−1272.736	−733.644	13.214
3000	99.826	327.811	242.119	257.076	−1271.316	−715.080	12.451
3100	99.826	331.084	244.936	267.059	−1270.001	−696.561	11.737
3200	99.826	334.254	247.678	277.041	−1268.767	−678.082	11.069
3300	99.826	337.326	250.349	287.024	−1267.581	−659.642	10.441
3400	99.826	340.306	252.951	297.007	−1266.430	−641.237	9.851
3500	99.826	343.199	255.488	306.989	−1265.291	−622.866	9.296

PREVIOUS: CURRENT: December 1972

0	to 1240 K	crystal, alpha
1240	to 1480 K	crystal, beta
1480	to 1641 K	crystal, gamma
above	1641 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−14.454	−1207.475	−1207.475	INFINITE
100	43.897	29.894	155.326	−12.543	−1210.169	−1192.713	623.010
200	65.796	68.764	102.826	−6.812	−1209.912	−1175.206	306.932
298.15	72.204	96.397	96.397	0.000	−1208.758	−1158.410	202.949
300	72.304	96.844	96.398	0.134	−1208.734	−1158.097	201.643
400	75.940	118.170	99.281	7.556	−1207.548	−1141.405	149.052
500	78.450	135.397	104.837	15.280	−1207.007	−1124.951	117.523
600	80.333	149.864	111.167	23.218	−1207.165	−1108.515	96.505
700	82.383	162.395	117.610	31.350	−1206.400	−1092.143	81.497
800	84.935	173.549	123.917	39.705	−1205.980	−1075.841	70.245
900	88.701	183.750	130.005	48.370	−1204.877	−1059.636	61.500
1000	94.558	193.369	135.864	57.505	−1203.338	−1043.576	54.511
1100	104.182	202.789	141.520	67.396	−1209.444	−1026.882	48.763
1200	130.541	212.702	147.030	78.807	−1205.921	−1010.421	43.983
1240.000	194.914	217.601	149.222	84.790	ALPHA <--> BETA TRANSITION		
1240.000	194.713	217.601	149.222	84.790			
1300	137.654	225.182	152.565	94.403	−1198.136	−994.440	39.957
1400	114.014	234.302	158.091	106.695	−1193.600	−978.956	36.525
1480.000	107.104	240.427	162.380	115.511	BETA <--> GAMMA TRANSITION		
1480.000	107.654	242.234	162.380	118.184			
1500	107.654	243.679	163.454	120.337	−1187.676	−963.778	33.562
1600	107.654	250.627	168.687	131.103	−1184.612	−948.951	30.980
1641.000	107.654	253.351	170.769	135.517	GAMMA <--> LIQUID TRANSITION		
1641.000	99.826	267.585	170.769	158.876			
1700	99.826	271.111	174.191	164.766	−1158.652	−935.148	28.734
1800	99.826	276.817	179.735	174.748	−1156.393	−922.066	26.758
1900	99.826	282.215	184.988	184.731	−1154.174	−909.108	24.993
2000	99.826	287.335	189.978	194.713	−1152.012	−896.266	23.408
2100	99.826	292.206	194.731	204.696	−1149.925	−883.531	21.977
2200	99.826	296.850	199.268	214.679	−1287.454	−865.517	20.550
2300	99.826	301.287	203.608	224.661	−1284.736	−846.400	19.222
2400	99.826	305.536	207.767	234.644	−1282.236	−827.396	18.008
2500	99.826	309.611	211.760	244.626	−1279.952	−808.492	16.893
2600	99.826	313.526	215.599	254.609	−1277.876	−789.675	15.865
2700	99.826	317.293	219.296	264.592	−1275.994	−770.935	14.915
2800	99.826	320.924	222.862	274.574	−1274.288	−752.261	14.034
2900	99.826	324.427	226.304	284.557	−1272.736	−733.645	13.214
3000	99.826	327.811	229.631	294.539	−1271.316	−715.080	12.451
3100	99.826	331.084	232.851	304.522	−1270.001	−696.561	11.737
3200	99.826	334.254	235.971	314.505	−1268.767	−678.082	11.069
3300	99.826	337.326	238.996	324.487	−1267.581	−659.642	10.441
3400	99.826	340.306	241.932	334.470	−1266.430	−641.237	9.851
3500	99.826	343.199	244.784	344.452	−1265.291	−622.866	9.296

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = 301.30 \pm 2.09\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -801.7 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -803.7 \pm 6.3\ kJ·mol^{-1}$

Vibrational Frequencies, ν/cm^{-1} and Degeneracies		
413(1)	[64](1)	390(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Ba–F = 2.32 ± 0.03 Å
Bond Angle: F–Ba–F = [95]°
Product of Moments of Inertia: $I_A I_B I_C = [6.858791 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(BaF_2, g, 298.15\ K) = -192.1 \pm 1.5\ kcal·mol^{-1}$ ($-803.7 \pm 6.3\ kJ·mol^{-1}$) is obtained from that of the crystal by addition of $\Delta_{sub}H° = 96.83 \pm 0.50\ kcal·mol^{-1}$. The selected $\Delta_{sub}H°$ is based on an analysis of six sets of vapor pressure data.[1-5] The results of our analysis are given below. A weighted value of these six results is adopted.

Source	Method	T/K	Data Points	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
Ruff and Le Boucher[1]	Dynamic B.P.	2061–2206	9	97.0[a]	86.79 ± 0.88[a]	−4.9 ± 0.8	−193.2 ± 2.0
Green *et al.*[2]	Knudsen–Mass Spec.	1232–1503	20	96.5	98.17 ± 0.45	1.2 ± 0.6	−190.7 ± 1.5
Bautista and Margrave[3]	Langmuir	1130–1250	10[b]	96.4	97.68 ± 0.19	1.1 ± 0.9	−191.2 ± 1.2
Hart and Searcy[4]	Torsion–Effusion	1261–1548	49[c]	93.2	96.12 ± 0.68	2.1 ± 0.7	−192.8 ± 1.7
Hart and Searcy[4]	Torsion–Langmuir	1315–1492	25[d]	93.7	96.47 ± 0.38	2.0 ± 0.8	−192.4 ± 1.4
Hildenbrand *et al.*[5]	Torsion–Effusion	1265–1550	Equation	94.2	94.74 ± 0.13	0.4	−194.2 ± 1.1

[a] $\Delta_{vap}H°$, 2[b], 4[c], and 3[d] points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The bond length is taken from the high-temperature electron diffraction studies of Akishin and Spiridonov.[6] Although Akishin and Spiridonov[6] interpreted their results in terms of a linear configuration for BaF_2, recent electric-deflection experiments[7] and matrix isolation infrared studies[8,9] clearly indicate that BaF_2 is bent. Calder *et al.*[8] estimated the bond angle as 100° from the changes in the bond angles with mass of the central atom for other alkaline earth difluorides. Baikov[10] estimated the angle as 115°. We prefer a slightly lower value (95°) than these, since there are indications that other heavy metal halides have bond angles below 100°. For example, bond angles for PbF_2 and $PbCl_2$ have been reported as 90°[11] and 96 ± 3°,[12] respectively.

The symmetric (ν_1) and antisymmetric (ν_3) stretching frequencies are those observed by Calder *et al.*[8] in their study of infrared spectra of BaF_2 trapped in a krypton matrix. Other matrix frequencies in excellent agreement with the adopted ones have been reported by Snelson.[9] Further confirmation of the adopted ν_3 is provided by observations of Baikov.[13] He reported $\nu_3 = 415 \pm 7\ cm^{-1}$ which was observed in the infrared spectra of BaF_2 vapor at 1950 K. The bending frequency (ν_2) is that estimated by Calder *et al.*[8] This value is considerably less than that observed by Baikov[10] ($\nu_2 = 100\ cm^{-1}$). However, only the high frequency portion of this rather broad band was recorded. We have used our adopted frequencies in a valence bond calculation with the result k/(k δ/l²) = 11.8. This ratio of the stretching to bending force constants appears quite reasonable in comparison with those for other alkaline earth difluorides.[14] Also, our adopted frequencies give thermodynamic functions which show good compatibility with the vapor pressure data (see Enthalpy of Formation section).

The principal moments of inertia are: $I_A = 30.6016 \times 10^{-39}$, $I_B = 18.4604 \times 10^{-39}$, and $I_C = 12.1412 \times 10^{-39}\ g·cm^2$.

References

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[3]R. G. Bautista and J. L. Margrave, J. Phys. Chem. **69**, 1770 (1965).
[4]P. E. Hart and A. W. Searcy, J. Phys. Chem. **70**, 2763 (1966).

Continued on page 358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−13.649	−801.659	−801.659	INFINITE
100	42.748	248.473	346.341	−9.787	−802.402	−806.804	421.431
200	50.089	280.512	306.118	−5.121	−803.210	−810.853	211.773
250	52.332	291.947	302.175	−2.557	−803.487	−812.732	169.811
298.15	53.780	301.297	301.297	0.	−803.746	−814.489	142.695
300	53.826	301.630	301.298	0.100	−803.757	−814.556	141.827
350	54.840	310.008	301.957	2.818	−804.074	−816.332	121.831
400	55.551	317.380	303.434	5.579	−804.514	−818.055	106.827
450	56.064	323.954	305.355	8.370	−805.167	−819.711	95.150
500	56.444	329.882	307.516	11.183	−806.094	−821.280	85.799
600	56.957	340.222	312.130	16.855	−808.517	−824.081	71.743
700	57.276	349.027	316.788	22.568	−810.171	−826.557	61.678
800	57.487	356.690	321.307	28.307	−812.368	−828.742	54.111
900	57.634	363.470	325.622	34.063	−814.172	−830.680	48.211
1000	57.740	369.548	329.716	39.832	−816.000	−832.417	43.481
1100	57.819	375.055	333.592	45.610	−826.218	−833.150	39.563
1200	57.879	380.089	337.260	51.395	−828.321	−833.686	36.289
1300	57.926	384.724	340.735	57.185	−830.342	−834.051	33.513
1400	57.964	389.018	344.032	62.980	−832.303	−834.262	31.127
1500	57.994	393.018	347.166	68.778	−834.224	−834.335	29.054
1600	58.019	396.762	350.150	74.579	−836.125	−834.280	27.236
1700	58.040	400.280	352.997	80.382	−838.025	−834.107	25.629
1800	58.057	403.598	355.716	86.186	−839.944	−833.821	24.197
1900	58.072	406.737	358.320	91.993	−841.900	−833.428	22.913
2000	58.084	409.716	360.816	97.801	−843.913	−832.930	21.754
2100	58.095	412.550	363.212	103.610	−846.001	−832.330	20.703
2200	58.104	415.253	365.517	109.420	−987.701	−826.253	19.618
2300	58.113	417.836	367.736	115.231	−989.155	−818.883	18.597
2400	58.120	420.310	369.875	121.042	−990.827	−811.444	17.661
2500	58.126	422.682	371.941	126.854	−992.713	−803.932	16.797
2600	58.132	424.962	373.936	132.667	−994.807	−796.340	15.999
2700	58.137	427.156	375.867	138.481	−997.094	−788.664	15.258
2800	58.141	429.271	377.737	144.295	−999.556	−780.900	14.568
2900	58.145	431.311	379.549	150.109	−1002.173	−773.045	13.924
3000	58.149	433.282	381.308	155.924	−1004.920	−765.098	13.322
3100	58.152	435.189	383.015	161.739	−1007.773	−757.057	12.756
3200	58.155	437.035	384.675	167.554	−1010.706	−748.923	12.225
3300	58.158	438.825	386.288	173.370	−1013.687	−740.696	11.724
3400	58.160	440.561	387.859	179.186	−1016.703	−732.379	11.252
3500	58.163	442.247	389.389	185.002	−1019.730	−723.972	10.805
3600	58.165	443.885	390.880	190.818	−1022.748	−715.479	10.381
3700	58.167	445.479	392.335	196.635	−1025.740	−706.902	9.980
3800	58.168	447.030	393.754	202.452	−1028.692	−698.246	9.598
3900	58.170	448.541	395.139	208.268	−1031.593	−689.512	9.235
4000	58.172	450.014	396.493	214.086	−1034.434	−680.704	8.889
4100	58.173	451.451	397.816	219.903	−1037.208	−671.827	8.559
4200	58.174	452.852	399.110	225.720	−1039.910	−662.882	8.244
4300	58.176	454.221	400.375	231.538	−1042.540	−653.874	7.943
4400	58.177	455.559	401.614	237.355	−1045.096	−644.806	7.655
4500	58.178	456.866	402.828	243.173	−1047.577	−635.680	7.379
4600	58.179	458.145	404.016	248.991	−1049.978	−626.501	7.114
4700	58.180	459.396	405.181	254.809	−1052.287	−617.272	6.860
4800	58.181	460.621	406.324	260.627	−1054.547	−607.992	6.616
4900	58.181	461.821	407.444	266.445	−1056.734	−598.667	6.382
5000	58.182	462.996	408.543	272.263	−1058.862	−589.297	6.156
5100	58.183	464.148	409.622	278.081	−1060.907	−579.888	5.939
5200	58.184	465.278	410.682	283.900	−1062.914	−570.436	5.730
5300	58.184	466.386	411.723	289.718	−1064.866	−560.947	5.528
5400	58.185	467.474	412.745	295.536	−1066.768	−551.421	5.334
5500	58.185	468.542	413.750	301.355	−1068.591	−541.864	5.146
5600	58.186	469.590	414.738	307.174	−1070.341	−532.278	4.965
5700	58.186	470.620	415.709	312.992	−1072.098	−522.655	4.790
5800	58.187	471.632	416.664	318.811	−1073.791	−513.004	4.620
5900	58.187	472.626	417.605	324.630	−1075.327	−503.340	4.456
6000	58.188	473.604	418.530	330.448	−1076.953	−493.632	4.297

PREVIOUS: December 1972 (a atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K)$ = [252.9 ± 8] J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = −221.75 ± 29.3 kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = −226.44 ± 29.3 kJ·mol^{-1}

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[19500]	[2]
[11800]	[4]	[20500]	[2]
[13500]	[2]		

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[469] (1)
[431] (2)
[3650] (1)

Bond Distances: Ba–O = [2.17] Å Ba–O = [2.173] Å; O–H=[0.96] Å
Bond Angle: Ba–O–H = [180]°
Rotational Constant: B_o = [0.222044] cm^{-1} σ = [1]

Enthalpy of Formation

The adopted $\Delta_f H°$(BaOH, g, 0 K) = −53.0 ± 7.0 kcal·mol^{-1} is based on an assessment of dissociation energies derived from Knudsen–cell mass–spectrometric measurements of Stafford and Berkowitz[1] and Newbury[2] and flame spectral work.[3–6]

Source	Reaction	No. Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$D°_0$(Ba–OH) kcal·mol^{-1}
	1	2	1755–1785	115.23 ± 3.55	−83.6	−51.58 ± 6	102.8
1	2	1	1785	62.11	—	−55.82	108.1
2	3	1	1851	77.33	—	−53.67	104.8
5	4	2	1570–1800	2.40 ± 2.39	7.3	−64.70	115.9

Reactions 1) BaO(cr) + BaO(g) + H_2O(g) → 2BaOH(g) + 0.5 O_2(g)
2) 2BaO(g) + H_2O(g) → 2BaOH(g) + O(g)
3) BaO(cr) + 0.5 H_2(g) = BaOH(g)
4) Ba(g) + H_2O(g) → BaOH(g) + H(g)

Ryabova and Gurvich[3] considered the reaction Ba(g) + H_2O(g) → BaOH(g) + H(g) to be dominant and derived $D°_0$ (as defined in the table above) = 111 ± 8 kcal·mol^{-1}. Sugden and Schofield[4] considered the reaction Ba(g) + 2H_2O(g) → Ba(OH)$_2$(g) + 2H(g) to be dominant. Cotton and Jenkins[5] found both the mono– and dihydroxide to be present in significant amounts in fuel–rich hydrogen–oxygen–nitrogen flames and derived $D°_0$ = 114 ± 5 kcal·mol^{-1}. Cotton and Jenkins[5] recalculated the work of Ryabova and Gurvich[3] and of Sugden and Schofield[4] considering both BaOH and Ba(OH)$_2$ to be present and obtained recalculated values of $D°_0$ = 110 and 114 kcal·mol^{-1}, respectively. Ryabova *et al.*[6] made further measurements, considered BaOH as dominant, and reported $D°_0$ = 109 ± 3 kcal·mol^{-1}. The $D°_0$ calculation from the 3rd law analysis of Cotton and Jenkins[5] data above, using auxiliary data,[7] is about 2 kcal·mol^{-1} higher than theirs. Applying this correction to the values from Ryabova and Gurvich[3] and Sugden and Schofield[4] as recalculated by Cotton and Jenkins,[5] gives 112 and 116 kcal·mol^{-1}, respectively. The value $D°_0$ = 109 ± 3 kcal·mol^{-1} given by Ryabova *et al.*[6] is an average of four calculations with two sets of molecular constants assumed for BaOH. This value, if recalculated with the present auxiliary data, would probably be higher.

The dissociation energies derived from flame spectra are higher, as a group, than those derived from the Knudsen cell mass spectrometric measurements. The ratio of $D°_0$ (monohydroxide)/$D°_0$(dihydroxide), where $D°_0$ of the dihydroxide is defined by the reaction Ba(OH)$_2$(g) → Ba(g) + 2 OH(g) and is 209.6 kcal·mol^{-1},[7] is approximately 0.53–0.55 for the flame spectral measurements and 0.50 for the average $D°_0$ = 105.3 kcal·mol^{-1} for the Knudsen–cell mass spectrometric measurements. The ratio for the barium mono– and difluoride[7] is 0.51, and the ratio for the other alkaline earth halides fall in the 0.40 to 0.51 range[7] with an average close to 0.46.[8] The similarity of the halides and hydroxides, particularly the fluorides, has been established.[1,9–11] $D°_0$ = 105.3 kcal·mol^{-1} is adopted from which is calculated $\Delta_f H°(0\ K)$ = −53.0 ± 7.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh[12] and the evidence that gaseous alkali metal hydroxides are linear.[13–15] The ground state is assumed to be $^2\Sigma^+$ by analogy with BaF and BaCl.[7] The electronic levels are estimated from the observed band spectra[16–20] and the comparison with BaF and BaCl.[7]

The Ba–O bond distance is estimated to be slightly larger, 0.02 Å, than the Ba–F distance[7] after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[7] The Ba–O stretching frequency, 469 cm^{-1}, is estimated

Continued on page 358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.799	−221.752	−221.752	INFINITE
90	30.847	211.167	289.791	−7.862	−223.465	−227.472	118.819
200	40.469	235.500	256.974	−4.295	−225.245	−230.727	60.260
250	43.984	244.931	253.644	−2.178	−225.894	−232.020	48.478
298.15	46.356	252.893	252.893	0.	−226.440	−233.150	40.847
300	46.432	253.180	252.894	0.086	−226.460	−233.191	40.602
350	48.141	260.474	253.466	2.453	−227.003	−234.271	34.963
400	49.361	266.986	254.757	4.892	−227.610	−235.269	30.723
450	50.257	272.854	256.447	7.383	−228.384	−236.182	27.415
500	50.937	278.186	258.358	9.914	−229.396	−236.997	24.759
600	51.916	287.565	262.466	15.060	−231.917	−238.270	20.743
700	52.641	295.625	266.641	20.289	−233.599	−239.207	17.850
800	53.266	302.695	270.715	25.585	−235.775	−239.854	15.661
900	53.855	309.003	274.625	30.941	−237.515	−240.259	13.944
1000	54.427	314.707	278.352	36.355	−239.241	−240.471	12.561
1100	54.983	319.921	281.898	41.826	−249.320	−239.691	11.382
1200	55.519	324.728	285.269	47.351	−251.251	−238.730	10.392
1300	56.029	329.192	288.478	52.929	−253.067	−237.612	9.547
1400	56.512	333.363	291.537	58.556	−254.793	−236.358	8.819
1500	56.968	337.277	294.457	64.230	−256.452	−234.983	8.183
1600	57.398	340.968	297.250	69.949	−258.065	−233.499	7.623
1700	57.807	344.460	299.925	75.709	−259.656	−231.915	7.126
1800	58.199	347.775	302.492	81.509	−261.244	−230.237	6.681
1900	58.578	350.932	304.959	87.348	−262.852	−228.471	6.281
2000	58.951	353.946	307.334	93.225	−264.501	−226.619	5.919
2100	59.320	356.831	309.622	99.138	−266.213	−224.683	5.589
2200	59.689	359.599	311.832	105.089	−407.527	−217.288	5.159
2300	60.063	362.261	313.967	111.076	−408.587	−208.618	4.738
2400	60.442	364.825	316.033	117.102	−409.858	−199.898	4.351
2500	60.828	367.300	318.034	123.165	−411.342	−191.120	3.993
2600	61.223	369.694	319.975	129.268	−413.030	−182.278	3.662
2700	61.627	372.012	321.860	135.410	−414.913	−173.368	3.354
2800	62.040	374.260	323.691	141.593	−416.972	−164.384	3.067
2900	62.460	376.445	325.473	147.818	−419.188	−155.325	2.798
3000	62.888	378.570	327.208	154.086	−421.539	−146.186	2.545
3100	63.321	380.639	328.898	160.396	−423.999	−136.967	2.308
3200	63.759	382.656	330.547	166.750	−426.546	−127.668	2.084
3300	64.200	384.625	332.156	173.148	−429.146	−118.289	1.872
3400	64.642	386.548	333.727	179.590	−431.787	−108.829	1.672
3500	65.083	388.428	335.263	186.076	−434.447	−99.292	1.482
3600	65.522	390.268	336.766	192.607	−437.104	−89.678	1.301
3700	65.957	392.069	338.236	199.181	−439.743	−79.991	1.129
3800	66.386	393.833	339.676	205.798	−442.351	−70.233	0.965
3900	66.807	395.563	341.087	212.458	−444.915	−60.407	0.809
4000	67.220	397.260	342.470	219.159	−447.428	−50.516	0.660
4100	67.622	398.925	343.827	225.901	−449.884	−40.562	0.517
4200	68.013	400.559	345.158	232.683	−452.277	−30.550	0.380
4300	68.391	402.164	346.465	239.503	−454.608	−20.481	0.249
4400	68.755	403.740	347.749	246.361	−456.876	−10.359	0.123
4500	69.104	405.289	349.011	253.254	−459.081	−0.186	0.002
4600	69.438	406.812	350.251	260.181	−461.217	10.034	−0.114
4700	69.756	408.309	351.470	267.141	−463.275	20.299	−0.226
4800	70.057	409.780	352.670	274.132	−465.298	30.610	−0.333
4900	70.342	411.228	353.850	281.152	−467.262	40.961	−0.437
5000	70.610	412.652	355.012	288.200	−469.182	51.353	−0.536
5100	70.860	414.052	356.156	295.273	−471.036	61.779	−0.633
5200	71.093	415.431	357.282	302.371	−472.869	72.244	−0.726
5300	71.309	416.787	358.392	309.491	−474.665	82.745	−0.816
5400	71.509	418.122	359.486	316.632	−476.430	93.279	−0.902
5500	71.691	419.436	360.564	323.793	−478.136	103.840	−0.986
5600	71.857	420.729	361.627	330.970	−479.790	114.430	−1.067
5700	72.007	422.002	362.675	338.163	−481.473	125.056	−1.146
5800	72.142	423.256	363.709	345.371	−483.114	135.709	−1.222
5900	72.261	424.490	364.729	352.591	−484.622	146.371	−1.296
6000	72.366	425.705	365.735	359.823	−486.244	157.080	−1.368

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$\Delta_f H°(0\ K) = 269.36 \pm 62.8\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [247.26 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = 270.90 \pm 62.8\ kJ \cdot mol^{-1}$

Vibrational Fequencies and Degeneracies υ, cm^{-1}
[460] (1)
[430] (2)
[3650] (1)

Ground State Quantum Weight: [1] σ = [1]
Point Group:[$C_{\infty v}$]
Bond Distances: Ba–O = [2.17] Å; O–H = [0.96] Å
Bond Angle: Ba–O–H = [180]°
Rotational Constant: B_o = [0.222053] cm^{-1}

Enthalpy of Formation

The ionization potential of BaOH(g) was deduced by Kelly and Padley[1] to be 5.25 ± 0.1 eV. These authors quantitatively examined the total positive ion concentrations produced from Ba aqueous salt additives in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data,[2] we recalculate the ionization potential to be 5.36 eV.

Jensen[3] determined the enthalpy of reaction $\Delta_r H° = 6 \pm 10\ kcal \cdot mol^{-1}$ for $Ba(g) + OH(g) = BaOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for $BaOH^+$. The value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data,[2] we derive an ionization potential of 4.83 eV, which is not in good agreement with the value derived from the data of Kelly and Padley.[1]

We adopt an ionization potential of 5.09 eV (117.38 $kcal \cdot mol^{-1}$) which is an average of the above two studies.[1, 3] This leads to $\Delta_f H°(0\ K) = 64.38\ kcal \cdot mol^{-1}$ and $\Delta_f H°(298.15\ K) = 64.75\ kcal \cdot mol^{-1}$ for $BaOH^+(g)$. We assign an uncertainty of ±15 $kcal \cdot mol^{-1}$.

For comparison, the ionization potential of BaF(g) is 4.83 eV[2] while that of Ba(g) is 5.21 eV.[4]
The average of these two values is very close to the ionization potential adopted for $BaOH^+$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[2, 5, 6, 7] In addition, Walsh[8] had predicted tha BAH molecules (H = hydrogen atom) with ten or less valence electrons ($BaOH^+$ has eight valence electrons) will be linear in their ground state. The molecule $BaOH^+$ is isoelectronic with CsOH.

The bond dissociation energy for $BaOH^+$ ($D_0° = 108.2\ kcal \cdot mol^{-1}$),[4, 2] for the process $BaOH^+(g) = Ba^+(g) + OH(g)$ is nearly the same as that for BaOH ($D_0° = 105.3\ kcal \cdot mol^{-1}$).[2] This suggests that the bonding in these two molecules is quite similar. Thus, the bond distances are assumed to be the same as those adopted for BaOH(g).[2] The vibrational frequencies are assumed to be similar to those adopted for BaOH(g).[2] The ground state quantum weight is assumed to be the same as that of CsOH(g).[2]

References

[1]R. Kelly and P. J. Padley, Trans. Faraday Soc. **67**, 1384 (1971).
[2]JANAF Thermochemical Tables: e^- (ref st), 3–31–65; $H_2(g)$ and $H_2O(g)$, 3–31–61; OH(g) and Ba(g), 12–31–70; H(g), 6–30–74; BaOH(g) and $Ba(OH)_2(g)$, 12–31–75; BaF(g), 12–31–72; CsOH(g), 6–30–71.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.823	269.364		
100	30.902	205.415	284.269	−7.885			
200	40.603	229.824	251.356	−4.306			
250	44.104	239.283	248.018	−2.184			
298.15	46.458	247.265	247.265	0.	270.897	259.611	−45.483
300	46.533	247.552	247.266	0.086	270.916	259.541	−45.190
350	48.225	254.860	247.839	2.457	271.417	257.605	−38.445
400	49.430	261.383	249.132	4.900	271.853	255.601	−33.378
450	50.315	267.258	250.825	7.395	272.122	253.551	−29.431
500	50.986	272.596	252.739	9.928	272.151	251.483	−26.272
600	51.952	281.983	256.852	15.078	271.713	247.401	−21.538
700	52.668	290.047	261.032	20.311	272.113	243.306	−18.156
800	53.287	297.121	265.110	25.609	272.018	239.203	−15.618
900	53.872	303.431	269.023	30.967	272.358	235.081	−13.644
1000	54.440	309.137	272.754	36.383	272.713	230.920	−12.062
1100	54.994	314.351	276.302	41.855	264.713	227.543	−10.805
1200	55.526	319.159	279.675	47.381	264.862	224.158	−9.757
1300	56.031	323.624	282.886	52.959	265.125	220.757	−8.870
1400	56.505	327.794	285.947	58.586	265.477	217.331	−8.109
1500	56.945	331.707	288.868	64.259	265.895	213.877	−7.448
1600	57.351	335.396	291.662	69.974	266.357	210.395	−6.869
1700	57.723	338.884	294.338	75.728	266.839	206.882	−6.357
1800	58.064	342.193	296.906	81.517	267.319	203.342	−5.901
1900	58.375	345.341	299.373	87.339	267.772	199.775	−5.492
2000	58.658	348.343	301.747	93.191	268.177	196.185	−5.124
2100	58.917	351.211	304.034	99.070	268.510	192.577	−4.790
2200	59.152	353.957	306.242	104.974	129.227	194.331	−4.614
2300	59.366	356.591	308.374	110.900	130.185	197.267	−4.480
2400	59.562	359.122	310.436	116.846	130.913	200.167	−4.357
2500	59.740	361.557	312.433	122.812	131.410	203.042	−4.242
2600	59.903	363.903	314.367	128.794	131.680	205.901	−4.137
2700	60.053	366.167	316.244	134.792	131.732	208.754	−4.039
2800	60.190	368.354	318.066	140.804	131.580	211.609	−3.948
2900	60.316	370.468	319.837	146.830	131.243	214.473	−3.863
3000	60.432	372.515	321.559	152.867	130.741	217.351	−3.784
3100	60.539	374.498	323.235	158.916	130.097	220.248	−3.711
3200	60.637	376.422	324.867	164.975	129.334	223.168	−3.643
3300	60.729	378.289	326.458	171.043	128.483	226.113	−3.579
3400	60.813	380.103	328.009	177.120	127.555	229.085	−3.519
3500	60.891	381.867	329.523	183.205	126.573	232.085	−3.464
3600	60.964	383.584	331.001	189.298	125.557	235.114	−3.411
3700	61.032	385.255	332.445	195.398	124.523	238.172	−3.362
3800	61.094	386.883	333.856	201.504	123.483	241.258	−3.316
3900	61.153	388.471	335.236	207.617	122.450	244.371	−3.273
4000	61.208	390.020	336.586	213.735	121.431	247.509	−3.232
4100	61.259	391.532	337.908	219.858	120.436	250.674	−3.194
4200	61.307	393.009	339.203	225.987	119.468	253.862	−3.157
4300	61.352	394.452	340.471	232.120	118.528	257.073	−3.123
4400	61.395	395.863	341.714	238.257	117.619	260.305	−3.090
4500	61.434	397.243	342.932	244.398	116.741	263.558	−3.059
4600	61.472	398.594	344.128	250.544	115.901	266.829	−3.030
4700	61.507	399.916	345.301	256.693	115.111	270.117	−3.002
4800	61.540	401.211	346.452	262.845	114.329	273.423	−2.975
4900	61.571	402.481	347.583	269.001	113.578	276.745	−2.950
5000	61.601	403.725	348.693	275.159	112.848	280.083	−2.926
5100	61.629	404.945	349.784	281.321	112.160	283.432	−2.903
5200	61.655	406.142	350.856	287.485	111.473	286.796	−2.881
5300	61.680	407.317	351.911	293.652	110.801	290.175	−2.860
5400	61.704	408.470	352.947	299.821	110.143	293.565	−2.840
5500	61.727	409.602	353.967	305.992	109.527	296.964	−2.820
5600	61.748	410.715	354.971	312.166	108.948	300.371	−2.802
5700	61.768	411.808	355.958	318.342	108.326	303.794	−2.784
5800	61.788	412.882	356.930	324.520	107.734	307.226	−2.767
5900	61.806	413.939	357.888	330.700	107.264	310.650	−2.750
6000	61.824	414.977	358.831	336.881	106.670	314.102	−2.735

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [107.11 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{,fus} = 681.15 \pm 1\ K$
$T_{trs} = 521 \pm 2\ K$ (β–α)

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-946.30]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 16.74 \pm 1.26\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°$ = Unknown

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -226.17 \pm 1.5\ kcal \cdot mol^{-1}$ is obtained from the enthalpy of formation of the liquid[1] minus the enthalpy of fusion and the enthalpy difference of the liquid and the crystal between the melting point and 298.15 K. Using auxiliary data,[1] our 2nd and 3rd law analysis of the dissociation pressure equation of Kondakov *et al.*[2] for the reaction Ba(OH)$_2$(cr) = BaO(cr) + H$_2$O(g) is given below.

	$\Delta_r H°(298.15\ K)$, $kcal^{-1} \cdot mol^{-1}$		Drift	$\Delta_f H°(298.15\ K)$
T/K	2nd law	3rd law	$cal \cdot K^{-1} \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
559–682	46.4	38.04 ± 1.63	−13.5 ± 0.2	−226.84 ± 2

While this is in good agreement with the adopted value, there is an inconsistency in the measurements of Kondakov *et al.*[2] for the crystal and the liquid and the adopted enthalpy of fusion. The liquid state dissociation pressures are in good agreement with other measurements (see the liquid table)[1] and are judged more reliable than the solid state measurements. The adopted value for the alpha crystal is also in good agreement with −225.8 kcal from another recent evaluation.[4]

Heat Capacity and Entropy

The heat capacities at 298.15 K and above are derived from the drop–ice–calorimeter enthalpy measurements of Powers and Blalock,[3] 425–681 K) combined with a graphical comparison of the heat capacities of Mg(OH)$_2$(cr) and Ca(OH)$_2$(cr)[1] From the information referenced in the Transition Data Section below, it is concluded tha the α–form is maintained on cooling to 273.15 K. This JANAF Table is a single–phase alpha–crystal table.

The adopted entropy, $S°(298.15\ K) = [25.6 \pm 2]\ cal \cdot K^{-1} \cdot mol^{-1}$, is calculated from Kelley's additive entropy constants for cations and anions.[5]

Fusion Data

Seward[6] determined a melting point of 408 ± 1°C and a cryoscopic enthalpy of fusion of 3400 ± 100 cal·mol^{-1}. Powers and Blalock[3] chose a melting point of 395°C where they found $\Delta_{fus}H° = 24$ cal/g (4113 $cal \cdot mol^{-1}$) by drop calorimetry. However, their enthalpy measurements show a possible melting range of 395 to 421°C. (At the adopted temperature of melting, 408°C, our smoothing of Powers and Blalock's experimental enthalpies[3] leads to $\Delta_{fus}H° = 4051\ cal \cdot mol^{-1}$). Kondakov *et al.* observed barium hydroxide to melt at 682 K (ca. 409°C) while investigating the dissociation pressures of the crystal and liquid states. Michaud[7,8] determined a melting point of 409 ± 1°C and a cryoscopic enthalpy of fusion of 3720 ± 200 $cal \cdot mol^{-1}$.[8] From a consideration of all of these data, a melting point of 681.15 ± 1 K (408 ± 1°C) and a enthalpy of fusion of 4000 ± 300 $cal \cdot mol^{-1}$ are adopted.

Transition Data

Michaud has observed a β to α crystal transition, on heating anhydrous barium dihydroxide, at 250°C[7] and at 246°C[8] by both thermal and dilatometric techniques. In the absence of water vapor, the high temperature α–form is maintained on cooling to room temperature.[7] This "metastable" state has been confirmed by others.[9,10] This present JANAF Table considers only the α–form. A transition temperature of 521 ± 2 K (248 ± 2°C) is adopted.

References

[1]JANAF Thermochemical Tables: Ba(OH)$_2$(l), 12–31–75; BaO(cr), 6–30–74; H$_2$O(g), 3–31–61; Mg(OH)$_2$(cr), 12–31–75; Ca(OH)$_2$(cr), 12–31–75.
[2]B. V. Kondakov, P. V. Kovtunenko, and A. A. Bundel, Zh. Fiz. Khim. **38**, 190 (1964).
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Enthalpy Reference Temperature = T_r = 298.15 K *Standard State Pressure = $p°$ = 0.1 MPa*

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
90							
200							
250							
298.15	101.629	107.110	107.110	0.000	−946.295	−859.476	150.577
300	101.797	107.740	107.112	0.188	−946.267	−858.938	149.554
400	112.633	138.679	111.257	10.969	−944.380	−830.099	108.400
500	118.658	164.520	119.399	22.560	−942.589	−801.748	83.758
600	122.717	186.510	128.797	34.628	−941.231	−773.693	67.356
681.150	126.022	202.280	136.628	44.719	--- CRYSTAL <--> LIQUID ---		
700	126.775	205.731	138.443	47.102	−938.765	−745.972	55.665
800	130.834	222.924	147.947	59.982	−936.501	−718.575	46.918
900	134.892	238.569	157.159	73.268	−933.501	−691.511	40.134
1000	138.951	252.991	166.030	86.961	−930.182	−664.799	34.726

PREVIOUS: CURRENT: December 1975

$S°(298.15\ K) = [123.357]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 681.15 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-934.123]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 16.74 \pm 1.26\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -223.26 \pm 1.0\ kcal·mol^{-1}$ is the average of values derived from the 3rd law analysis of dissociation pressure measurements of Tamaru and Shiomi[1] and of Kondakov *et al.*[2] Auxiliary data used in the analysis are from the JANAF Thermochemical Tables.[3] Johnston[4] has also determined pressures for the dissociation reaction $Ba(OH)_2(l) = BaO(cr) + H_2O(g)$.

Source	No. of Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15)$ kcal·mol^{-1}
Tamaru and Shiomi[1]	7	788–1018	32.1	34.56 ± 0.48	2.8 ± 0.5	−223.35 ± 1
Kondakov *et al.*[2]	Equation	682–993	34.0	34.37 ± 0.21	0.4	−223.17 ± 0.7
Johnston[4]	11	918–1263	34.4	33.86 ± 0.38	−0.5 ± 0.5	−222.66 ± 0.9

The enthalpy of formation derived from Johnston's measurements is in good agreement with the adopted value but is not averaged in because, as indicated by Kondakov *et al.*,[2] the measurements are believed less accurate.

Heat Capacity and Entropy

$C_p°$ is based on the enthalpy measurements of Powers and Blalock[5] and is assumed constant at 33.7 cal·K^{-1}·mol^{-1} over the range of 450 to 1600 K. A glass transition is assumed at 450 K below which $C_p°$ is that of the alpha crystal. The entropy at 298.15 K is derived from the value adopted for the alpha crystal.

Decomposition Data

T_{dcm} is calculated as the temperature at which $\Delta_r G° = 0$ for the reaction $Ba(OH)_2(l) = BaO(cr) + H_2O(g)$.

References

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[3]JANAF Thermochemical Tables: BaO(cr), 6–30–74; H_2O(g), 3–31–61.
[4]J. Johnston, Z. physik. Chem. **62**, 330 (1908).
[5]W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm., ORNL–1653 (1954).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
90							
200							
250							
298.15	101.629	123.357	123.357	0.000	−934.123	−852.148	149.293
300	101.797	123.987	123.359	0.188	−934.095	−851.640	148.284
400	112.633	154.926	127.504	10.969	−932.208	−824.426	107.659
450.010	116.065	168.404	131.312	16.692	GLASS <--> LIQUID TRANSITION		
450.010	141.001	168.404	131.312	16.692			
500	141.001	183.256	135.776	23.740	−929.236	−797.764	83.342
600	141.001	208.964	145.896	37.841	−925.847	−771.780	67.189
681.150	141.001	226.850	154.498	49.283	--- CRYSTAL <--> LIQUID ---		
700	141.001	230.699	156.498	51.941	−921.754	−746.439	55.700
800	141.001	249.527	166.976	66.041	−918.270	−721.627	47.117
900	141.001	266.135	177.090	80.141	−914.457	−697.277	40.469
1000	141.001	280.991	186.750	94.241	−910.729	−673.346	35.172
1100	141.001	294.430	195.938	108.341	−915.454	−648.965	30.817
1200	141.001	306.698	204.664	122.441	−912.123	−624.886	27.201
1300	141.001	317.984	212.953	136.541	−908.769	−601.085	24.152
1400	141.001	328.434	220.833	150.641	−905.411	−577.543	21.548
1500	141.001	338.162	228.334	164.741	−902.068	−554.241	19.300
1600	141.001	347.262	235.486	178.841	−898.759	−531.161	17.341
1700	141.001	355.810	242.315	192.941	−895.502	−508.286	15.618
1800	141.001	363.869	248.846	207.041	−892.316	−485.601	14.092
1900	141.001	371.493	255.102	221.142	−889.219	−463.090	12.731
2000	141.001	378.725	261.104	235.242	−886.231	−440.740	11.511

PREVIOUS: CURRENT: December 1975

0	to	681.15 K	crystal, alpha*
above		681.15 K	liquid

*A low temperature beta form does exist but is not included in this table, $T_{trs}(\beta \rightarrow \alpha) = 521 \pm 2$ K.

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	101.629	107.110	107.110	0.000	−946.295	−859.476	150.577
300	101.797	107.740	107.112	0.188	−946.267	−858.938	149.554
400	112.633	138.679	111.257	10.969	−944.380	−830.099	108.400
500	118.658	164.520	119.399	22.560	−942.589	−801.748	83.758
600	122.717	186.510	128.797	34.628	−941.231	−773.693	67.356
681.150	126.022	202.280	136.628	44.719	____ CRYSTAL <---> LIQUID ____		
681.150	141.001	226.850	136.628	61.455	TRANSITION		
700	141.001	230.699	139.110	64.113	−921.754	−746.439	55.700
800	141.001	249.527	151.761	78.213	−918.270	−721.627	47.117
900	141.001	266.135	163.565	92.313	−914.457	−697.277	40.469
1000	141.001	280.991	174.578	106.413	−910.729	−673.346	35.172
1100	141.001	294.430	184.872	120.513	−915.454	−648.965	30.817
1200	141.001	306.698	194.521	134.613	−912.123	−624.886	27.201
1300	141.001	317.984	203.590	148.713	−908.769	−601.085	24.152
1400	141.001	328.434	212.138	162.813	−905.411	−577.543	21.548
1500	141.001	338.162	220.219	176.913	−902.068	−554.241	19.300
1600	141.001	347.262	227.878	191.013	−898.759	−531.161	17.341
1700	141.001	355.810	235.155	205.113	−895.502	−508.286	15.618
1800	141.001	363.869	242.084	219.214	−892.316	−485.601	14.092
1900	141.001	371.493	248.696	233.314	−889.219	−463.090	12.731
2000	141.001	378.725	255.018	247.414	−886.231	−440.740	11.511

PREVIOUS: CURRENT: December 1975

$S°(298.15\ K) = [315.0 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) \approx -619.09 \pm 37.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) \approx -626.56 \pm 37.7\ kJ \cdot mol^{-1}$

Vibrational Fequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[413] (1)	[3650] (2)
[64] (1)	[431] (4)
[390] (1)	

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Ba–O = [2.34] Å; O–H = [0.96] Å
Bond Angles: O–Ba–O = [95]°; Ba–O–H = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [6.366076 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -149.75 \pm 9.0\ kcal \cdot mol^{-1}$ is derived from the Knudsen–cell mass–spectrometric equilibrium study of Newbury.[1] Tabulated below are the results of a 2nd and 3rd law analysis of this study,[1] the Knudsen–cell mass–spectrometric work of Stafford and Berkowitz,[2] and the flame–spectral work of Cotton and Jenkins.[3]

Source	Rxn No.	No. of Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	$D_0°$ kcal·mol^{-1}
Stafford and Berkowitz[2]	A	24[a]	1485–1727	56.4	45.37 ± 1.82	−6.7 ± 1.7	−143.43 ± 2.5	203.3
Newbury[1]	A	44[a]	1428–1899	39.0	39.05 ± 0.17	0.0 ± 0.1	−149.75 ± 0.7	209.6
Cotton and Jenkin[3]	B	2	1570–1800	8.1	23.04 ± 2.98	8.8 ± 0.0	−153.96 ± 4.0	213.8

Reactions: A) $BaO(cr) + H_2O(g) = Ba(OH)_2(g)$ B) $Ba(g) + 2H_2O(g) = Ba(OH)_2(g) + 2H(g)$

a. Two points rejected by a statistical test.

b. $D_0°$ is the dissociation energy for the reaction $Ba(OH)_2(g) = Ba(g) + 2OH(g)$.

In addition to the three investigations above, dissociation energies ($D_0°$ as defined in the table above) have been derived from flame spectra by Ryabova and Gurvich[5] and by Sugden and Schofield.[6] Ryabova and Gurvich[5] believed the dominant reaction to be $Ba(g) + H_2O(g) = BaOH(g) + H(g)$, but they also considered the possibility that the reaction $Ba(g) + 2H_2O(g) = Ba(OH) + 2H(g)$ was dominant and derived $D_0° = 205 \pm 20\ kcal \cdot mol^{-1}$. Sugden and Schofield[6] considered the dihydroxide to be the domiant product and derived $D_0° = 229 \pm 12\ kcal \cdot mol^{-1}$. Cotton and jenkins[3] found both BaOH and $Ba(OH)_2$ to be present and obtained recalculated $D_0°$ values of 208 and 212 $kcal \cdot mol^{-1}$, respectively.

The 3rd law analysis of the data of Cotton and Jenkins[3] above combined with current JANAF Thermochemical Table data[4] leads to $D_0° = 213.8\ kcal \cdot mol^{-1}$ which is 0.8 $kcal \cdot mol^{-1}$ higher than the 213 $kcal \cdot mol^{-1}$ derived by Cotton and Jenkins.[3] Applying this difference to the values of Ryabova and Gurvich[5] and of Sugden and Schofield[6] as recalculated by Cotton and Jenkins[3] gives $D_0° = 208.8$ and 212.8 $kcal \cdot mol^{-1}$, respectively.

The average of the dissociation energies from the flame–spectral measurements (208.8, 212.8, and 213.8) and the dissociation energy from the Knudsen–cell mass–spectrometric work of Stafford and Berkowitz (203.3) is 209.7 $kcal \cdot mol^{-1}$ which happens to be in agreement with the 209.6 $kcal \cdot mol^{-1}$ calculated from Newbury's data.

$\Delta_f H°(298.15\ K) = -149.75 \pm 9.0\ kcal \cdot mol^{-1}$ is adopted because of the excellent agreement in the 2nd and 3rd law enthalpies of reaction from Newbury's data[1] and because of the larger uncertainty associated with dissociation energies derived from flame spectra.

The enthalpy of dissociation listed by Jackson[9] leads to $\Delta_f H°(298.15\ K) = -151.22\ kcal \cdot mol^{-1}$. Another recent compilation[10] lists $\Delta_f H°(298.15\ K) = -140\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The analogy between gaseous mono– and dihydroxides and gaseous mono– and dihalides, particularly the mono– and difluorides, has been recognized.[2,7–9] The O–Ba–O bond angle is assumed to be the same as the F–Ba–F bond angle;[4] the Ba–O–H bond angle is considered to be linear as in BaOH.[4] The Ba–O bond distance is estimated to slightly larger, 0.02 Å, than the Ba–F distance in BaF_2[4] after noting the close similarity in the bond distance of the alkale metal fluorides and hydroxides. The O–H bond distance is taken to be the same as in water.[4]

The vibrational frequencies are assumed to be the same as in BaF_2[4] (O–Ba–O symmetrical and asymmetrical stretch, and bend) and as in BaOH[4] (O–H stretch and Ba–O–H bend). The principal moments of inertial are: $I_A = 29.8004 \times 10^{-39}$, $I_B = 17.7971 \times 10^{-39}$, and $I_C = 12.0033 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 359

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.594	−619.094	−619.094	INFINITE
100	45.351	248.363	375.259	−12.690	−622.792	−616.816	322.192
200	65.873	286.310	321.778	−7.094	−625.345	−609.699	159.237
250	72.732	301.794	316.265	−3.618	−626.062	−605.700	126.554
298.15	77.256	315.016	315.016	0.	−626.562	−601.731	105.421
300	77.399	315.494	315.017	0.143	−626.579	−601.576	104.744
350	80.612	327.681	315.973	4.098	−626.996	−597.376	89.153
400	82.884	338.602	318.131	8.189	−627.428	−593.116	77.453
450	84.542	348.465	320.962	12.376	−627.994	−588.795	68.346
500	85.798	357.440	324.168	16.636	−628.780	−584.399	61.052
600	87.607	373.254	331.067	25.312	−630.814	−575.322	50.086
700	88.958	386.863	338.088	34.143	−631.991	−565.991	42.235
800	90.141	398.820	344.947	43.098	−633.652	−556.443	36.332
900	91.271	409.503	351.537	52.169	−634.868	−546.718	31.731
1000	92.380	419.177	357.825	61.352	−636.057	−536.860	28.043
1100	93.465	428.033	363.810	70.644	−645.589	−526.064	24.981
1200	94.513	436.210	369.507	80.044	−646.959	−515.137	22.423
1300	95.510	443.815	374.934	89.545	−648.204	−504.100	20.255
1400	96.447	450.928	380.111	99.144	−649.348	−492.972	18.393
1500	97.319	457.612	385.057	108.833	−650.416	−481.765	16.777
1600	98.124	463.919	389.791	118.605	−651.435	−470.488	15.360
1700	98.864	469.890	394.328	128.455	−652.428	−459.148	14.108
1800	99.540	475.561	398.685	138.376	−653.421	−447.750	12.993
1900	100.158	480.959	402.874	148.361	−654.439	−436.297	11.995
2000	100.721	486.111	406.908	158.406	−655.506	−424.788	11.094
2100	101.234	491.038	410.798	168.504	−656.648	−413.224	10.278
2200	101.702	495.759	414.554	178.651	−797.410	−396.228	9.408
2300	102.128	500.289	418.183	188.843	−797.936	−377.982	8.584
2400	102.517	504.644	421.696	199.075	−798.697	−359.709	7.829
2500	102.873	508.836	425.098	209.345	−799.697	−341.397	7.133
2600	103.198	512.877	428.397	219.649	−800.931	−323.042	6.490
2700	103.495	516.778	431.598	229.984	−802.391	−304.634	5.894
2800	103.768	520.547	434.708	240.347	−804.064	−286.169	5.339
2900	104.019	524.192	437.731	250.737	−805.932	−267.641	4.821
3000	104.250	527.723	440.673	261.150	−807.973	−249.044	4.336
3100	104.463	531.145	443.536	271.586	−810.166	−230.377	3.882
3200	104.659	534.464	446.326	282.042	−812.488	−211.638	3.455
3300	104.841	537.688	449.046	292.517	−814.908	−192.825	3.052
3400	105.009	540.820	451.699	303.010	−817.416	−173.936	2.672
3500	105.165	543.866	454.289	313.519	−819.987	−154.973	2.313
3600	105.309	546.831	456.819	324.043	−822.602	−135.936	1.972
3700	105.444	549.718	459.291	334.580	−825.247	−116.826	1.649
3800	105.569	552.532	461.708	345.131	−827.907	−97.643	1.342
3900	105.686	555.275	464.072	355.694	−830.571	−78.390	1.050
4000	105.796	557.953	466.386	366.268	−833.231	−59.071	0.771
4100	105.898	560.566	468.651	376.853	−835.879	−39.684	0.506
4200	105.993	563.119	470.870	387.447	−838.509	−20.233	0.252
4300	106.083	565.614	473.044	398.051	−841.123	−0.718	0.009
4400	106.167	568.054	475.176	408.664	−843.716	18.855	−0.224
4500	106.246	570.441	477.267	419.285	−846.289	38.488	−0.447
4600	106.321	572.777	479.318	429.913	−848.834	58.176	−0.661
4700	106.391	575.064	481.330	440.549	−851.342	77.919	−0.866
4800	106.457	577.305	483.307	451.191	−853.851	97.718	−1.063
4900	106.519	579.501	485.248	461.840	−856.341	117.568	−1.253
5000	106.578	581.653	487.154	472.495	−858.822	137.469	−1.436
5100	106.634	583.764	489.028	483.155	−861.271	157.417	−1.612
5200	106.687	585.835	490.870	493.821	−863.732	177.414	−1.782
5300	106.736	587.868	492.681	504.492	−866.188	197.461	−1.946
5400	106.784	589.864	494.462	515.169	−868.644	217.552	−2.104
5500	106.829	591.823	496.214	525.849	−871.068	237.684	−2.257
5600	106.872	593.749	497.939	536.534	−873.468	257.860	−2.405
5700	106.912	595.641	499.636	547.223	−875.922	278.083	−2.548
5800	106.951	597.500	501.308	557.917	−878.359	298.348	−2.687
5900	106.988	599.329	502.954	568.614	−880.687	318.635	−2.821
6000	107.023	601.127	504.575	579.314	−883.151	338.985	−2.951

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = 278.74 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -39.29 \pm 84\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -42.42 \pm 84\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X[^2\Sigma^+]$	0	2
$C[^2\Pi]$	17816.3	2
	18568.8	2
$D[^2\Sigma^+]$	25764.4	2
$E[^2\Sigma^+]$	26753.3	2

$\omega_e = 152.2\ cm^{-1}$ $\omega_e x_e = 0.29\ cm^{-1}$ $\sigma = 1$
$B_e = [0.0250]\ cm^{-1}$ $\alpha_e = [0.000059]\ cm^{-1}$ $r_e = [3.20]$ Å

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -9.39 \pm 20\ kcal·mol^{-1}$ is calculated from $D_0° = 3.37$ eV (77.7 $kcal·mol^{-1}$) calculated by a linear Birge–Sponer extrapolation of $\omega_e x_e$ data[1] with a correction for the ionic character of the molecule as described by Hildenbrand.[2] Other values, in $kcal·mol^{-1}$, are 55[3] predicted from a correlation of binding energies of Group II and Group III diatomic hydrides and halides, 71.7[4] as a lower bound from a consideration of ionic bonding forces and 66[5] derived as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. $D_0° = 77.7\ kcal·mol^{-1}$ is adopted because the ratio of $D_0°(BaI)/\Delta_{at}H°(BaI_2) = 0.47$ which is nearly the same as the ratio of 0.46 found for a series of mono- and difluorides[6] and for other alkaline earth halides systems.[8]

$\Delta_f H°(298.15\ K) = -10.14 \pm 20\ kcal·mol^{-1}$ is calculated from the adopted $\Delta_f H°(0\ K) = -9.39 \pm 20\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen.[1] The adopted value of $r_e = 3.20$ Å was estimated by Margrave[3] and is also the bond distance in $BaI_2(g)$.[7] B_e is calculated from the adopted r_e; α_e is calculated assuming a Morse potential function.

The electronic levels and their probable designation are those given by Rosen.[1]

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[8]JANAF Thermochemical Tables; refer to all alkaline earth halide tables.

Enthalpy Reference Temperature = T_r = 298.15 K *Standard State Pressure = $p°$ = 0.1 MPa*

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.381	−39.287	−39.287	INFINITE
100	34.820	239.050	311.435	−7.239	−39.368	−56.815	29.677
200	36.747	263.961	282.130	−3.634	−40.774	−73.742	19.259
250	37.046	272.196	279.349	−1.788	−41.582	−81.893	17.111
298.15	37.221	278.737	278.737	0.	−42.417	−89.582	15.694
300	37.227	278.967	278.738	0.069	−42.451	−89.875	15.649
350	37.349	284.716	279.192	1.933	−43.439	−97.703	14.581
400	37.439	289.709	280.201	3.803	−52.553	−105.106	13.725
450	37.510	294.123	281.507	5.677	−54.472	−111.562	12.950
500	37.569	298.078	282.970	7.554	−76.718	−115.892	12.107
600	37.666	304.937	286.077	11.316	−79.455	−123.460	10.748
700	37.747	310.749	289.197	15.087	−81.383	−130.654	9.749
800	37.820	315.794	292.213	18.865	−83.821	−137.520	8.979
900	37.887	320.253	295.086	22.650	−85.838	−144.111	8.364
1000	37.952	324.248	297.806	26.442	−87.853	−150.478	7.860
1100	38.015	327.868	300.376	30.241	−98.239	−155.823	7.399
1200	38.076	331.178	302.807	34.045	−100.493	−160.957	7.006
1300	38.137	334.229	305.109	37.856	−102.652	−165.908	6.666
1400	38.197	337.057	307.291	41.673	−104.744	−170.695	6.369
1500	38.256	339.694	309.364	45.495	−106.793	−175.334	6.106
1600	38.315	342.165	311.338	49.324	−108.826	−179.837	5.871
1700	38.374	344.490	313.220	53.158	−110.867	−184.213	5.660
1800	38.433	346.685	315.019	56.999	−112.941	−188.468	5.469
1900	38.493	348.764	316.741	60.845	−115.071	−192.606	5.295
2000	38.554	350.740	318.392	64.697	−117.278	−196.630	5.135
2100	38.616	352.623	319.977	68.556	−119.583	−200.541	4.988
2200	38.680	354.421	321.502	72.421	−261.525	−198.965	4.724
2300	38.746	356.142	322.971	76.292	−263.243	−196.084	4.453
2400	38.816	357.792	324.388	80.170	−265.199	−193.123	4.203
2500	38.889	359.378	325.756	84.055	−267.391	−190.076	3.971
2600	38.968	360.905	327.079	87.948	−269.805	−186.936	3.756
2700	39.051	362.377	328.359	91.849	−272.426	−183.700	3.554
2800	39.140	363.799	329.600	95.758	−275.234	−180.363	3.365
2900	39.236	365.174	330.803	99.677	−278.203	−176.922	3.187
3000	39.339	366.506	331.971	103.606	−281.307	−173.377	3.019
3100	39.450	367.798	333.106	107.545	−284.517	−169.727	2.860
3200	39.569	369.052	334.209	111.496	−287.807	−165.972	2.709
3300	39.696	370.272	335.284	115.459	−291.141	−162.114	2.566
3400	39.832	371.459	336.330	119.436	−294.505	−158.153	2.430
3500	39.977	372.615	337.351	123.426	−297.872	−154.094	2.300
3600	40.130	373.744	338.346	127.431	−301.221	−149.938	2.176
3700	40.293	374.845	339.318	131.452	−304.534	−145.690	2.057
3800	40.465	375.922	340.267	135.490	−307.795	−141.353	1.943
3900	40.646	376.976	341.195	139.546	−310.992	−136.932	1.834
4000	40.835	378.007	342.102	143.620	−314.116	−132.429	1.729
4100	41.033	379.018	342.990	147.713	−317.157	−127.849	1.629
4200	41.239	380.009	343.860	151.826	−320.111	−123.196	1.532
4300	41.453	380.982	344.712	155.961	−322.976	−118.473	1.439
4400	41.674	381.937	345.547	160.117	−325.750	−113.685	1.350
4500	41.902	382.876	346.366	164.296	−328.432	−108.835	1.263
4600	42.137	383.800	347.170	168.498	−331.016	−103.927	1.180
4700	42.377	384.709	347.959	172.724	−333.489	−98.966	1.100
4800	42.623	385.603	348.734	176.974	−335.894	−93.950	1.022
4900	42.874	386.485	349.495	181.248	−338.206	−88.886	0.948
5000	43.130	387.354	350.244	185.549	−340.439	−83.776	0.875
5100	43.389	388.210	350.980	189.874	−342.570	−78.623	0.805
5200	43.651	389.055	351.704	194.226	−344.641	−73.427	0.738
5300	43.916	389.889	352.417	198.605	−346.638	−68.193	0.672
5400	44.184	390.713	353.118	203.010	−348.563	−62.921	0.609
5500	44.452	391.526	353.809	207.442	−350.388	−57.618	0.547
5600	44.722	392.329	354.490	211.900	−352.119	−52.286	0.488
5700	44.992	393.123	355.161	216.386	−353.836	−46.916	0.430
5800	45.262	393.908	355.822	220.899	−355.467	−41.521	0.374
5900	45.532	394.684	356.474	225.438	−356.920	−36.114	0.320
6000	45.800	395.452	357.117	230.005	−358.442	−30.664	0.267

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 165.14 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 984 \pm 2\ K$

$\Delta_f H°(0\ K) = -604.5 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -605.4 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 26.53 \pm 0.54\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Ehrlich, Peik, and Koch[1] derived $\Delta_f H°(BaI_2, cr, 298.15\ K) = -144.7 \pm 0.4\ kcal \cdot mol^{-1}$ from enthalpy of solution measurements of Ba(cr) and BaI_2(cr) in 0.1 N HI. An auxiliary HI enthalpy of solution value, $-13.22\ kcal \cdot mol^{-1}$, calculated from data in reference[2] was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA key value of $\Delta_f H°(I^-, aq, 298.15\ K) = -13.60\ kcal \cdot mol^{-1}$[3] in the $\Delta_f H°$(HI, aq, 298.15 K) table, so that the above derived enthalpy of formation of BaI_2(cr) will be approximately $-145.1\ kcal \cdot mol^{-1}$.

Combining $\Delta_f H°(Ba^{+2}, aq, 298.15\ K) = -128.5\ kcal \cdot mol^{-1}$, selected by Parker,[4] with the CODATA value for $I^-(aq)$[3] gives $\Delta_f H°(BaI_2, aq, 298.15\ K) = -155.7\ kcal \cdot mol^{-1}$. Further combination with the enthalpy of solution, $-10.98\ kcal \cdot mol^{-1}$,[5, 11] gives $\Delta_f H°(BaI_2, cr, 298.15\ K) = -144.7\ kcal \cdot mol^{-1}$. This enthalpy of solution value was based on several sets of data, one of which was that of Ehrlich *et al.*[1,11]

We adopt $-144.7 \pm 0.8\ kcal \cdot mol^{-1}$ ($-605.425 \pm 3.347\ kJ \cdot mol^{-1}$) because of the correlation of $\Delta_f H°(Ba^{+2}, aq, 298.15\ K)$ with the evaluation of data for several barium compounds.[4] See also the updated discussion in the enthalpy of formation section for BaO(cr).[12]

Heat Capacity and Entropy

$C_p°$ (13.08–300.17 K) has been measured by Paukov, Khriplovich, and Smirnova.[6] Our T^3 extrapolation agrees with their $S°(13) = 0.619\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(13\ K) - H°(0\ K) = 6.01\ cal \cdot K^{-1} \cdot mol^{-1}$, and our smoothing and integration of their $C_p°$ data agrees with their $S°(298.15\ K) = 39.47 \pm 0.1\ cal \cdot K^{-1} \cdot mol^{-1}$ which is adopted.

The low-temperature heat capacities join smoothly with a linear extrapolation from $C_p°(298.15\ K) = 18.52\ cal \cdot K^{-1} \cdot mol^{-1}$ to Dworkin and Bredig's reported $C_p°$ of 21.8 $cal \cdot K^{-1} \cdot mol^{-1}$ at the adopted T_{fus} of 984 K.[7] This gives $H°(984\ K) - H°(298.15\ K) = 13.83\ kcal \cdot mol^{-1}$, in fair agreement with Dworkin and Bredig's drop calorimeter value of $13.9\ kcal \cdot mol^{-1}$.[7]

Fusion Data

Dworkin and Bredit[7] report $\Delta_{fus} H° = 6.34\ kcal \cdot mol^{-1}$ (±2%) at T_{fus} of 984 K from drop calorimetry; Emons and Loeffelholz[8] found 6.050 $kcal \cdot mol^{-1}$ (±5%) at a reported , T_{fus} of 981 K by high temperature cryoscopy. Hutchison[9] determined T_{fus} to be 983 K, while Kubaschewski *et al.*[10] listed 985 K. We adopt $\Delta_{fus} H° = 6.34 \pm 0.13\ kcal \cdot mol^{-1}$ and $T_{fus} = 984 \pm 2$ K.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference between the enthalpies of formation of the ideal gas and the crystal at 298.15 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.000	0.000	INFINITE	−19.230	−604.544	−604.544	INFINITE
100	68.952	84.559	232.338	−14.778	−604.841	−603.789	315.387
200	75.228	134.767	172.276	−7.502	−605.042	−602.675	157.403
298.15	77.488	165.142	165.142	0.000	−605.425	−601.407	105.364
300	77.530	165.622	165.144	0.143	−605.434	−601.382	104.710
400	79.538	188.201	168.209	7.997	−622.236	−599.374	78.270
500	81.546	206.166	174.063	16.051	−666.196	−589.434	61.578
600	83.513	221.207	180.700	24.304	−666.319	−574.057	49.976
700	85.521	234.231	187.437	32.756	−665.450	−558.758	41.695
800	87.529	245.782	194.022	41.408	−664.904	−543.545	35.490
900	89.538	256.207	200.361	50.262	−663.747	−528.443	30.670
984.000	91.211	264.271	205.477	57.853	--- CRYSTAL <---> LIQUID ---		
1000	91.546	265.743	206.429	59.314	−662.403	−513.479	26.821
1100	93.617	274.566	212.227	68.573	−669.237	−497.840	23.640
1200	95.653	282.799	217.769	78.036	−667.748	−482.322	20.995
1300	97.653	290.535	223.072	87.702	−665.980	−466.940	18.762
1400	99.617	297.844	228.154	97.566	−663.968	−451.703	16.853
1500	101.546	304.783	233.033	107.624	−661.745	−436.618	15.204

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [183.669]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 984 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-585.884]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 26.53 \pm 0.54\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(BaI_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in ethalpy, $H°(984\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, 27.0 $cal·K^{-1}·mol^{-1}$, was determined by Dworkin and Bredig[1] from drop calorimetric measurements. This value is adopted and assumed constant over a 700–2800 K range. A glass transition is assumed at 700 K below which the heat capacity is that of the crystal.

$S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Vaporization Data

The temperature at which $\Delta_r G° = 0$ for the reaction $BaI_2(l) = BaI_2(g)$ is the adopted T_{vap}. Peterson and Hutchison[2] have extrapolated Knudsen effusion cell measurements in the 1154–1301 K range to obtain a normal boiling point (1 atm) of 2300 K.

$\Delta_{vap} H°(T_{vap})$ is the calculated difference between the enthalpies of formation of the ideal gas and the liquid at T_{vap}. Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
0							
100							
200							
298.15	77.488	183.669	183.669	0.000	−585.884	−587.390	102.908
300	77.530	184.149	183.671	0.143	−585.893	−587.399	102.275
400	79.538	206.728	186.736	7.997	−602.695	−587.244	76.686
500	81.546	224.693	192.590	16.051	−646.655	−579.156	60.504
600	83.513	239.733	199.227	24.304	−646.778	−565.632	49.243
699.990	85.521	252.756	205.963	32.754	GLASS <--> LIQUID		
699.990	112.968	252.756	205.963	32.754	TRANSITION		
700	112.968	252.758	205.964	32.756	−645.910	−552.186	41.205
800	112.968	267.842	212.777	44.052	−642.719	−539.009	35.194
900	112.968	281.148	219.649	55.349	−639.119	−526.261	30.543
984.000	112.968	291.228	225.336	64.838	--- CRYSTAL <--> LIQUID ---		
1000	112.968	293.051	226.405	66.646	−635.530	−513.914	26.844
1100	112.968	303.818	232.960	77.943	−640.325	−501.106	23.796
1200	112.968	313.647	239.281	89.240	−637.003	−488.595	21.268
1300	112.968	322.689	245.354	100.536	−633.605	−476.365	19.141
1400	112.968	331.061	251.180	111.833	−630.159	−464.399	17.327
1500	112.968	338.855	256.768	123.130	−626.698	−452.680	15.764
1600	112.968	346.146	262.129	134.427	−623.251	−441.191	14.403
1700	112.968	352.995	267.275	145.724	−619.848	−429.917	13.210
1800	112.968	359.452	272.218	157.020	−616.516	−418.841	12.154
1900	112.968	365.559	276.972	168.317	−613.281	−407.948	11.215
2000	112.968	371.354	281.547	179.614	−610.164	−397.222	10.374
2100	112.968	376.866	285.956	190.911	−607.184	−386.649	9.617
2200	112.968	382.121	290.208	202.208	−743.879	−370.839	8.805
2300	112.968	387.143	294.315	213.504	−740.384	−353.962	8.039
2400	112.968	391.950	298.283	224.801	−737.157	−337.231	7.340
2500	112.968	396.562	302.123	236.098	−734.189	−320.629	6.699
2600	112.968	400.993	305.841	247.395	−731.462	−304.141	6.110
2700	112.968	405.256	309.445	258.692	−728.956	−287.754	5.567
2800	112.968	409.365	312.940	269.988	−726.644	−271.456	5.064

PREVIOUS: CURRENT: June 1974

0	to	984 K	crystal
above		984 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−19.230	−604.544	−604.544	INFINITE
100	68.952	84.559	232.338	−14.778	−604.841	−603.789	315.387
200	75.228	134.767	172.276	−7.502	−605.042	−602.675	157.403
298.15	77.488	165.142	165.142	0.000	−605.425	−601.407	105.364
300	77.530	165.622	165.144	0.143	−605.434	−601.382	104.710
400	79.538	188.201	168.209	7.997	−622.236	−599.374	78.270
500	81.546	206.166	174.063	16.051	−666.196	−589.434	61.578
600	83.513	221.207	180.700	24.304	−666.319	−574.057	49.976
700	85.521	234.231	187.437	32.756	−665.450	−558.758	41.695
800	87.529	245.782	194.022	41.408	−664.904	−543.545	35.490
900	89.538	256.207	200.361	50.262	−663.747	−528.443	30.670
984.000	91.211	264.271	205.477	57.853	CRYSTAL <--> LIQUID		
984.000	112.968	291.228	205.477	84.380	TRANSITION		
1000	112.968	293.051	206.863	86.187	−635.530	−513.913	26.844
1100	112.968	303.818	215.196	97.484	−640.325	−501.105	23.796
1200	112.968	313.647	222.996	108.781	−637.003	−488.595	21.268
1300	112.968	322.689	230.322	120.078	−633.604	−476.365	19.141
1400	112.968	331.061	237.222	131.374	−630.159	−464.399	17.327
1500	112.968	338.855	243.741	142.671	−626.698	−452.679	15.764
1600	112.968	346.146	249.916	153.968	−623.251	−441.191	14.403
1700	112.968	352.995	255.780	165.265	−619.848	−429.916	13.210
1800	112.968	359.452	261.362	176.562	−616.516	−418.841	12.154
1900	112.968	365.559	266.687	187.858	−613.280	−407.947	11.215
2000	112.968	371.354	271.776	199.155	−610.163	−397.222	10.374
2100	112.968	376.866	276.650	210.452	−607.184	−386.648	9.617
2200	112.968	382.121	281.326	221.749	−743.879	−370.839	8.805
2300	112.968	387.143	285.818	233.046	−740.384	−353.961	8.039
2400	112.968	391.950	290.141	244.342	−737.157	−337.231	7.340
2500	112.968	396.562	294.306	255.639	−734.188	−320.629	6.699
2600	112.968	400.993	298.325	266.936	−731.462	−304.141	6.110
2700	112.968	405.256	302.207	278.233	−728.956	−287.754	5.567
2800	112.968	409.365	305.961	289.530	−726.644	−271.456	5.064

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [348.14 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -298.5 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -302.9 \pm 16.7\ kJ·mol^{-1}$

Vibrational Fequencies and Degeneracies ν, cm^{-1}
[111] (1)
[26] (1)
[185] (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Ba–I = 3.20 ± 0.03 Å
Bond Angle: I–Ba–I = [170]°
Product of Moments of Inertia: $I_A I_B I_C = 2.117174 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

Winchell[1] has reported ΔH, ΔG, and ΔS for the vaporization of BaI_2(l) at 1150 K derived from a mass spectrometric Knudsen effusion cell investigation (28 unpublished points in the range of 1019–1278 K). The spectra showed no evidence of BaI_2 polymers; also it was consluded that BaI_2(l) = BaI_2(g) is the important vaporization. Peterson and Hutchison[2,3] used a weight loss Knudsen effusion technique to observe vapor presured at 18 temperatures in the range of 1154–1301 K. Their enthalpy of vaporization, 53.6 ± 1.3 kcal·mol^{-1}, is in good agreement with Winchell's value, 54 ± 4 kcal·mol^{-1}.

Source	No. of Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Winchell[1]	3[a]	1019–1278	62.16	68.07	5.1
Peterson and Hutchison[2]	18[b]	1154–1301	64.35 ±1.5	67.61 ±0.5	2.6 ±1.2

[a]ΔG calculated at 1019 K and 1278 K from ΔH, ΔG, and ΔS values given at 1150 K to permit use of 2nd law.
[b]one point rejected by statistical tests.

We select $\Delta_{vap}H°(298.15\ K) = 67.6 \pm 3$ kcal·mol^{-1} and combine this with $\Delta_f H°$(I, 298.15 K) = −140.029 ± 0.9 kcal·mol^{-1} to give the adopted $\Delta_f H°$(g, 298.15 K) = −72.4 ± 4 kcal·mol^{-1}.

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from the work of Akishin *et al.*[4] who also judged the bond angle to be 180 ± 20°. The later electric deflection study of Buechler *et al.*[5] showed that all of the barium dihalide molecules are bent. Noting the trend in the magnitude of the bond angle in the alkaline earth–halide series, we have assumed a bond angle of 170°. The principal moments of inertia are: $I_A = 429.4543 \times 10^{-39}$, $I_B = 428.3033 \times 10^{-39}$, and $I_C = 1.1510 \times 10^{-39}$ g cm^2.

In estimating the vibrational frequencies, the stretching force constants for gaseous BaF, BaF_2, BaCl, and $BaCl_2$ are calculated from their vibrational frequencies,[6] using the valence force model. The trend in the ratio k(monohalide)/k_1(dihalide) indicates that k(BaI)/k_1(BaI_2) = 1 is a reasonable approximation, an approximation used by Brewer *et al.*[7] The stretching force constant for BaI(g) is calculated from the ground state vibrational frequency given by Rosen.[8] The bending force constant is assumed to be 0.01 times the stretching force constant.[7] The adopted vibrational frequencies are calculated from these estimated force constants. Other estimates for ν_1, ν_2, and ν_3 where a linear molecule was assumed, are 109, 26, 184[7] and 106, 37, 178.[9]

We assign an uncertainty of ±2 cal·K^{-1}·mol^{-1} to the entropy to allow for error in the estimation of bond angle and of the vibrational frequencies.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.651	−298.463	−298.463	INFINITE
100	52.981	287.151	398.518	−11.137	−298.697	−317.904	166.056
200	56.623	325.343	353.375	−5.606	−300.643	−336.392	87.856
250	57.165	338.042	349.083	−2.760	−301.764	−345.202	72.126
298.15	57.463	348.139	348.139	0.	−302.922	−353.464	61.925
300	57.472	348.494	348.140	0.106	−302.968	−353.778	61.598
350	57.661	357.369	348.840	2.985	−304.348	−362.141	54.047
400	57.785	365.077	350.399	5.871	−321.858	−369.746	48.284
450	57.871	371.888	352.415	8.763	−324.777	−375.560	43.594
500	57.933	377.989	354.673	11.658	−368.086	−377.235	39.410
600	58.014	388.559	359.466	17.456	−370.664	−378.814	32.979
700	58.063	397.506	364.278	23.260	−372.443	−380.043	28.359
800	58.096	405.262	368.927	29.068	−374.741	−380.966	24.875
900	58.118	412.106	373.352	34.879	−376.627	−381.631	22.149
1000	58.133	418.230	377.539	40.691	−378.523	−382.086	19.958
1100	58.145	423.771	381.494	46.505	−388.801	−381.530	18.117
1200	58.154	428.831	385.231	52.320	−390.961	−380.773	16.575
1300	58.161	433.486	388.766	58.136	−393.043	−379.839	15.262
1400	58.166	437.796	392.116	63.952	−395.078	−378.747	14.131
1500	58.171	441.810	395.297	69.769	−397.097	−377.510	13.146
1600	58.174	445.564	398.322	75.586	−399.129	−376.138	12.280
1700	58.177	449.091	401.206	81.404	−401.205	−374.638	11.511
1800	58.180	452.416	403.960	87.222	−403.352	−373.014	10.825
1900	58.182	455.562	406.594	93.040	−405.596	−371.267	10.207
2000	58.184	458.546	409.117	98.858	−407.957	−369.400	9.648
2100	58.186	461.385	411.539	104.677	−410.456	−367.411	9.139
2200	58.187	464.092	413.867	110.495	−552.629	−359.925	8.546
2300	58.188	466.679	416.107	116.314	−554.612	−351.122	7.974
2400	58.189	469.155	418.266	122.133	−556.863	−342.228	7.448
2500	58.190	471.530	420.350	127.952	−559.372	−333.234	6.963
2600	58.191	473.813	422.362	133.771	−562.124	−324.135	6.512
2700	58.192	476.009	424.309	139.590	−565.095	−314.925	6.093
2800	58.192	478.125	426.193	145.409	−568.261	−305.603	5.701
2900	58.193	480.167	428.019	151.229	−571.592	−296.164	5.334
3000	58.193	482.140	429.791	157.048	−575.056	−286.607	4.990
3100	58.194	484.048	431.510	162.867	−578.624	−276.934	4.666
3200	58.194	485.896	433.181	168.687	−582.263	−267.144	4.361
3300	58.195	487.687	434.806	174.506	−585.938	−257.240	4.072
3400	58.195	489.424	436.387	180.326	−589.631	−247.224	3.798
3500	58.195	491.111	437.926	186.145	−593.315	−237.100	3.539
3600	58.196	492.750	439.427	191.965	−596.969	−226.871	3.292
3700	58.196	494.345	440.890	197.784	−600.573	−216.540	3.057
3800	58.196	495.897	442.317	203.604	−604.113	−206.113	2.833
3900	58.196	497.408	443.710	209.423	−607.577	−195.594	2.620
4000	58.197	498.882	445.071	215.243	−610.957	−184.988	2.416
4100	58.197	500.319	446.401	221.063	−614.243	−174.298	2.221
4200	58.197	501.721	447.702	226.882	−617.433	−163.529	2.034
4300	58.197	503.091	448.974	232.702	−620.528	−152.685	1.855
4400	58.197	504.429	450.219	238.522	−623.524	−141.770	1.683
4500	58.198	505.736	451.438	244.342	−626.423	−130.788	1.518
4600	58.198	507.016	452.633	250.161	−629.221	−119.744	1.360
4700	58.198	508.267	453.803	255.981	−631.906	−108.641	1.207
4800	58.198	509.492	454.951	261.801	−634.522	−97.480	1.061
4900	58.198	510.692	456.076	267.621	−637.046	−86.265	0.920
5000	58.198	511.868	457.180	273.441	−639.493	−75.001	0.784
5100	58.198	513.021	458.264	279.260	−641.841	−63.689	0.652
5200	58.198	514.151	459.328	285.080	−644.134	−52.330	0.526
5300	58.198	515.259	460.373	290.900	−646.358	−40.929	0.403
5400	58.199	516.347	461.399	296.720	−648.518	−29.485	0.285
5500	58.199	517.415	462.408	302.540	−650.584	−18.006	0.171
5600	58.199	518.464	463.400	308.360	−652.565	−6.493	0.061
5700	58.199	519.494	464.375	314.180	−654.542	5.062	−0.046
5800	58.199	520.506	465.334	319.999	−656.443	16.647	−0.150
5900	58.199	521.501	466.277	325.819	−658.176	28.248	−0.250
6000	58.199	522.479	467.206	331.639	−659.990	39.898	−0.347

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 72.069 \pm 0.38\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2286 \pm 15\ K$

$\Delta_f H°(0\ K) = -546.8 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -548.1 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [59]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is rounded from -130.98 ± 0.47 kcal·mol^{-1} derived by Fitzgibbon *et al.*[1] from calorimetric reactions of HCl(aq) with Ba(cr) and BaO(cr). Combination of their two reactions yields $\Delta_f H°(298.15\ K) = -62.66 \pm 0.47$ kcal·mol^{-1} for Ba(cr) + H_2O(l) → BaO(cr) + H_2(g). Although the resulting $\Delta_f H°$ is 1.3 kcal·mol^{-1} less negative than that of NBS Technical Note 270–6,[2] it confirms Parker's selection[2] of key values for BaO and $BaCl_2$ from calorimetry involving aqueous HCl[3–5] instead of discrepant values derived from other reactions.[6–8] Earlier HCl calorimetry gave $\Delta_f H°$(BaO, cr) = -132.0[3,2] and -132.1 kcal·mol^{-1}.[4,5] The new value[1] is preferred since both reactions were run in the same calorimeter on samples that were well characterized. The latter is particulaly important since impurities were a major problem in studies of BaO[3,4,9–14] and Ba.[2,5–7]

Direct measurements of $\Delta_c H$ of Ba(cr) by Mah[6] gave -139.06 ± 0.7 kcal·mol^{-1}. Combustion studies of Fitzgibbon *et al.*[1] suggest that the negative bias of 8 kcal·mol^{-1} was due to partial dissolution of the crucible lining (MgO) in molten BaO formed in the combustion. Dissolution was eliminated in combustions on sintered MgO disks, but large amounts of BaO_2 were formed both in this case and with the use of BaO crucibles.[1] This led the authors[1] to dismiss combustion calorimetry in favor of solution calorimetry. Parker[2] noted earlier that the combustion result was incompatible with data for $BaCl_2$(aq), $Ba(OH)_2$(aq and cr), BaO_2(cr) and $BaCO_3$(cr); also a similar discrepancy existed for SrO(cr). We find that the combustion value is incompatible with equilibrium data[19] for $BaCl_2$(l and g).

$\Delta_f H°(BaCl_2, cr)$ and $\Delta_f H°(Ba^{2+}, aq)$ deserve an updated discussion. We combine $\Delta_f H° = -127.95 \pm 0.41$ kcal·mol^{-1} [1] for Ba(cr) + 2HCl(54.3 H_2O) = H_2(g) + $BaCl_2$ [in 149.9 HCl (55.0 H_2O)] with $\Delta_f H°$(HCl, 54.3 H_2O) = -39.52 ± 0.02 kcal·mol^{-1} [16] and $\Delta_{sol} H° = -2.09 \pm 0.2$ kcal·mol^{-1} [17,18,2] for $BaCl_2$(cr) in HCl(55 H_2O) to give $\Delta_f H°(BaCl_2, cr) = -204.9 \pm 0.5$ kcal·mol^{-1}. This confirms the JANAF[19] $\Delta_f H°(BaCl_2)$ of -205.2 kcal·mol^{-1} based on the selection of Parker;[2] the alternative uncertainty of ± 0.6 kcal·mol^{-1} should now be used instead of ± 3 kcal·mol^{-1}.[19] The new $\Delta_f H°$ for $BaCl_2$[1] yields $\Delta_f H°(Ba^{2+}, aq) = -128.0 \pm 0.6$ kcal·mol^{-1}, assuming $\Delta_{sol} H°(BaCl_2, cr) = -3.0 \pm 0.2$ kcal·mol^{-1} (many references) and $\Delta_f H°(Cl^-, aq) = -39.933 \pm 0.021$ kcal·mol^{-1}.[16] This is consistent with Parker's selection of $\Delta_f H°(Ba^{2+}, aq) = -128.5$ kcal·mol^{-1}.[2]

Heat Capacity and Entropy

$C_p°$ is based on data (1.4–310 K) of Gmelin[12] who reported smoothed values only in the range 4 to 300 K. Based on Gmelin's graphs, we have corrected several typographical errors and resmoothed $C_p°$ above 240 K where the scatter increases rapidly. The entropy is obtained by integration of our adopted $C_p°$ using $S° = 0.0015$ cal·K^{-1}·mol^{-1} at 4 K. The value $S° = 15.75 \pm 0.02$ cal·K^{-1}·mol^{-1} reported by Gmelin[12] corresponds to neither 273.15 K nor 298.15 K and must be erroneous. $C_p°$ data (56–299 K) of Anderson[13] differ by $\pm 1.6\%$ but average about 1.0% higher from 150 to 260 K.

$C_p°$ above 300 K is from constrained fitting of enthalpy data (391–1299 K) of Lander.[14] This calorimetry is subject to bias from a calibration based on Pt and from impurities in the two samples. Information is insufficient to assess the bias due to minor changes in the enthalpy of Pt.[15] We apply crude corrections to the observed enthalpies for 27 mole % SrO in one sample and for about 2.8 mole % SiO_2 in the other sample. Deviations from the adopted curve are $\pm 0.9\%$ (first sample) and $\pm 1.0\%$ (second sample) except for -2.0% at 421 K.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°$ is calculated as the difference in $\Delta_f H°$ between gas and crystal.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−9.983	−546.833	−546.833	INFINITE
100	31.941	27.301	111.119	−8.382	−548.383	−539.039	281.565
200	43.493	53.898	76.289	−4.478	−548.479	−529.582	138.313
298.15	47.279	72.069	72.069	0.000	−548.104	−520.382	91.169
300	47.329	72.362	72.070	0.088	−548.096	−520.210	90.577
400	49.898	86.347	73.960	4.955	−547.731	−510.977	66.727
500	51.785	97.694	77.607	10.044	−547.990	−501.778	52.420
600	53.220	107.267	81.773	15.296	−548.939	−492.436	42.870
700	54.396	115.561	86.021	20.678	−548.999	−483.025	36.044
800	55.405	122.892	90.180	26.169	−549.503	−473.558	30.920
900	56.312	129.471	94.186	31.756	−549.526	−464.063	26.934
1000	57.153	135.448	98.018	37.429	−549.490	−454.569	23.744
1100	57.948	140.932	101.674	43.185	−557.766	−444.261	21.096
1200	58.706	146.007	105.159	49.018	−557.850	−433.937	18.889
1300	59.442	150.735	108.485	54.925	−557.776	−423.613	17.021
1400	60.162	155.167	111.663	60.905	−557.567	−413.300	15.420
1500	60.869	159.342	114.704	66.957	−557.244	−403.006	14.034
1600	61.563	163.292	117.618	73.079	−556.829	−392.737	12.822
1700	62.250	167.045	120.416	79.269	−556.342	−382.496	11.753
1800	62.927	170.623	123.107	85.528	−555.805	−372.285	10.803
1900	63.605	174.043	125.698	91.855	−555.239	−362.105	9.955
2000	64.275	177.323	128.198	98.249	−554.665	−351.955	9.192
2100	64.940	180.475	130.613	104.710	−554.107	−341.833	8.503
2200	65.605	183.511	132.949	111.237	−693.105	−326.362	7.749
2286.000	66.177	186.038	134.899	116.904	--- CRYSTAL <--> LIQUID ---		
2300	66.270	186.442	135.211	117.831	−691.803	−309.721	7.034
2400	66.927	189.276	137.405	124.491	−690.669	−293.134	6.380
2500	67.588	192.022	139.535	131.216	−689.705	−276.591	5.779
2600	68.245	194.686	141.605	138.008	−688.906	−260.082	5.225
2700	68.898	197.273	143.620	144.865	−688.261	−243.602	4.713
2800	69.555	199.791	145.581	151.788	−687.756	−227.142	4.237
2900	70.208	202.243	147.493	158.776	−687.372	−210.699	3.795
3000	70.860	204.634	149.358	165.830	−687.088	−194.267	3.382

PREVIOUS: December 1972 CURRENT: June 1974

Continued on page 359

$S°(298.15\ K)$ = [96.553] $J·K^{-1}·mol^{-1}$
T_{fus} = 2286 ± 15 K

$\Delta_f H°(298.15\ K)$ = [−491.627] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [59] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2286\ K)-H°(298.15\ K)$, between crystal and liquid.

Heat Capacity and Entropy

$C_p°$ of the liquid is estimated as 8 $cal·K^{-1}$ g-$atom^{-1}$ by comparison with other oxides. $C_p°$ is taken from the crystal in the range 298.15 K up to the glass transition assumed at 1600 K. $S°$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Foex[1] obtained T_{fus} = 2010°C from a solar-furnace study using BaO as its own container. We adopt this result but increase it by 3° for conversion to IPTS-68. Foex showed that the much lower value (1918°C) of Schumacher[2,3] probably resulted from contamination by WO_3 from tungsten supports of the sample. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ is 6 $cal·K^{-1}·mol^{-1}$.

Vaporization Data

Unlike the other alkaline-earth oxides, BaO(cr) vaporizes mainly to BaO(g) with traces of Ba_2O_2 and Ba_2O. Mass-spectrometric studies[4] suggest that decomposition to Ba(g) and O(g) is not a major contributor even though the observed intensities of Ba^+ are almost comparable with those of BaO^+. T_{vap} is the calculated temperature at which $\Delta_f G° = 0$ for BaO(l) = BaO(g); $\Delta_{vap}H°$ is the corresponding difference in $\Delta_f H°$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	47.279	96.553	96.553	0.000	−491.627	−471.205	82.553
300	47.329	96.845	96.554	0.088	−491.618	−471.078	82.022
400	49.898	110.831	98.443	4.955	−491.253	−464.293	60.631
500	51.785	122.178	102.090	10.044	−491.512	−457.543	47.799
600	53.220	131.750	106.257	15.296	−492.461	−450.649	39.232
700	54.396	140.045	110.504	20.678	−492.522	−443.686	33.108
800	55.405	147.375	114.664	26.169	−493.026	−436.668	28.511
900	56.312	153.954	118.670	31.756	−493.049	−429.621	24.935
1000	57.153	159.931	122.502	37.429	−493.013	−422.575	22.073
1100	57.948	165.416	126.157	43.185	−501.289	−414.716	19.693
1200	58.706	170.491	129.643	49.018	−501.372	−406.840	17.709
1300	59.442	175.219	132.969	54.925	−501.298	−398.965	16.031
1400	60.162	179.650	136.146	60.905	−501.090	−391.100	14.592
1500	60.869	183.825	139.187	66.957	−500.767	−383.254	13.346
1600	61.563	187.776	142.102	73.079	−500.351	−375.433	12.257
1600.010	61.563	187.776	142.102	73.079	GLASS <--> LIQUID		
1600.010	66.944	187.776	142.102	73.079	TRANSITION		
1700	66.944	191.834	144.909	79.773	−499.361	−367.656	11.297
1800	66.944	195.661	147.623	86.468	−498.388	−359.937	10.445
1900	66.944	199.280	150.248	93.162	−497.455	−352.271	9.685
2000	66.944	202.714	152.786	99.856	−496.581	−344.653	9.001
2100	66.944	205.980	155.242	106.551	−495.789	−337.076	8.384
2200	66.944	209.094	157.619	113.245	−634.620	−324.159	7.697
2286.000	66.944	211.661	159.604	119.002	--- CRYSTAL <--> LIQUID ---		
2300	66.944	212.070	159.923	119.940	−633.217	−310.080	7.042
2400	66.944	214.919	162.155	126.634	−632.049	−296.057	6.444
2500	66.944	217.652	164.321	133.328	−631.116	−282.077	5.894
2600	66.944	220.278	166.423	140.023	−630.414	−268.130	5.387
2700	66.944	222.804	168.465	146.717	−629.932	−254.206	4.918
2800	66.944	225.239	170.449	153.412	−629.655	−240.296	4.483
2900	66.944	227.588	172.379	160.106	−629.565	−226.392	4.078
3000	66.944	229.857	174.257	166.800	−629.640	−212.489	3.700
3100	66.944	232.053	176.086	173.495	−629.857	−198.580	3.346
3200	66.944	234.178	177.869	180.189	−630.192	−184.663	3.014
3300	66.944	236.238	179.607	186.884	−630.614	−170.735	2.703
3400	66.944	238.236	181.302	193.578	−631.111	−156.792	2.409
3500	66.944	240.177	182.956	200.272	−631.660	−142.833	2.132
3600	66.944	242.063	184.572	206.967	−632.240	−128.859	1.870
3700	66.944	243.897	186.151	213.661	−632.837	−114.868	1.622
3800	66.944	245.682	187.694	220.356	−633.435	−100.860	1.386
3900	66.944	247.421	189.203	227.050	−634.023	−86.837	1.163
4000	66.944	249.116	190.680	233.744	−634.593	−72.800	0.951
4100	66.944	250.769	192.125	240.439	−635.135	−58.748	0.748
4200	66.944	252.382	193.541	247.133	−635.646	−44.684	0.556
4300	66.944	253.957	194.928	253.828	−636.125	−30.608	0.372
4400	66.944	255.496	196.287	260.522	−636.568	−16.521	0.196
4500	66.944	257.001	197.619	267.216	−636.975	−2.425	0.028
4600	66.944	258.472	198.926	273.911	−637.339	11.680	−0.133
4700	66.944	259.912	200.209	280.605	−637.649	25.790	−0.287
4800	66.944	261.321	201.467	287.300	−637.946	39.909	−0.434
4900	66.944	262.702	202.703	293.994	−638.206	54.034	−0.576
5000	66.944	264.054	203.916	300.688	−638.442	68.164	−0.712

PREVIOUS: December 1972 CURRENT: June 1974

0	to 2286 K	crystal
above	2286 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−9.983	−546.833	−546.833	INFINITE
100	31.941	27.301	111.119	−8.382	−548.383	−539.039	281.565
200	43.493	53.898	76.289	−4.478	−548.479	−529.582	138.313
298.15	47.279	72.069	72.069	0.000	−548.104	−520.382	91.169
300	47.329	72.362	72.070	0.088	−548.096	−520.210	90.577
400	49.898	86.347	73.960	4.955	−547.731	−510.977	66.727
500	51.785	97.694	77.607	10.044	−547.990	−501.778	52.420
600	53.220	107.267	81.773	15.296	−548.939	−492.436	42.870
700	54.396	115.561	86.021	20.678	−548.999	−483.025	36.044
800	55.405	122.892	90.180	26.169	−549.503	−473.558	30.920
900	56.312	129.471	94.186	31.756	−549.526	−464.063	26.934
1000	57.153	135.448	98.018	37.429	−549.490	−454.569	23.744
1100	57.948	140.932	101.674	43.185	−557.766	−444.261	21.096
1200	58.706	146.007	105.159	49.018	−557.850	−433.937	18.889
1300	59.442	150.735	108.485	54.925	−557.776	−423.613	17.021
1400	60.162	155.167	111.663	60.905	−557.567	−413.300	15.420
1500	60.869	159.342	114.704	66.957	−557.244	−403.006	14.034
1600	61.563	163.292	117.618	73.079	−556.829	−392.737	12.822
1700	62.250	167.045	120.416	79.269	−556.342	−382.496	11.753
1800	62.927	170.623	123.107	85.528	−555.805	−372.285	10.803
1900	63.605	174.043	125.698	91.855	−555.239	−362.105	9.955
2000	64.275	177.323	128.198	98.249	−554.665	−351.955	9.192
2100	64.940	180.475	130.613	104.710	−554.107	−341.833	8.503
2200	65.605	183.511	132.949	111.237	−693.105	−326.362	7.749
2286.000	66.177	186.038	134.899	116.904	CRYSTAL <--> LIQUID TRANSITION		
2286.000	66.944	211.661	134.899	175.480			
2300	66.944	212.070	135.367	176.417	−633.217	−310.080	7.042
2400	66.944	214.919	138.623	183.111	−632.049	−296.057	6.444
2500	66.944	217.652	141.730	189.806	−631.116	−282.077	5.894
2600	66.944	220.278	144.701	196.500	−630.414	−268.130	5.387
2700	66.944	222.804	147.547	203.194	−629.932	−254.206	4.918
2800	66.944	225.239	150.278	209.889	−629.655	−240.296	4.483
2900	66.944	227.588	152.904	216.583	−629.565	−226.392	4.078
3000	66.944	229.857	155.432	223.278	−629.640	−212.489	3.700
3100	66.944	232.053	157.868	229.972	−629.857	−198.580	3.346
3200	66.944	234.178	160.220	236.666	−630.192	−184.663	3.014
3300	66.944	236.238	162.492	243.361	−630.614	−170.735	2.703
3400	66.944	238.236	164.691	250.055	−631.111	−156.792	2.409
3500	66.944	240.177	166.820	256.750	−631.660	−142.833	2.132
3600	66.944	242.063	168.884	263.444	−632.240	−128.859	1.870
3700	66.944	243.897	170.887	270.138	−632.837	−114.868	1.622
3800	66.944	245.682	172.832	276.833	−633.435	−100.860	1.386
3900	66.944	247.421	174.722	283.527	−634.023	−86.837	1.163
4000	66.944	249.116	176.561	290.222	−634.593	−72.800	0.951
4100	66.944	250.769	178.351	296.916	−635.135	−58.748	0.748
4200	66.944	252.382	180.094	303.610	−635.646	−44.684	0.556
4300	66.944	253.957	181.794	310.305	−636.125	−30.608	0.372
4400	66.944	255.496	183.451	316.999	−636.568	−16.521	0.196
4500	66.944	257.001	185.069	323.694	−636.975	−2.425	0.028
4600	66.944	258.472	186.649	330.388	−637.339	11.680	−0.133
4700	66.944	259.912	188.192	337.082	−637.649	25.790	−0.287
4800	66.944	261.321	189.701	343.777	−637.946	39.909	−0.434
4900	66.944	262.702	191.177	350.471	−638.206	54.034	−0.576
5000	66.944	264.054	192.621	357.166	−638.442	68.163	−0.712

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = 235.457 \pm 0.33\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -121.6 \pm 8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -123.8 \pm 8\ kJ\cdot mol^{-1}$

Source	State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm	α_e, cm^{-1}	ω_e, cm	$\omega_e x_e$, cm^{-1}
		Electronic and Molecular Constants (σ = 1)						
[1-4]	$X^1\Sigma$	0.0	1	1.9397	0.31261	0.00139	669.81	2.054
[1]	$a^3\Pi$	17372.	6	2.289	0.2244	0.0014	448.3	2.4
[1]	$A'^1\Pi$	17568.	2	2.289	0.2244	0.0014	448.3	2.4
[5]	$^3\Sigma^+$	[14000]	3	[2.133]	[0.2583]	[0.0011]	[499.7]	[1.64]
[1,6,2]	$A^1\Sigma^+$	16722.	1	2.133	0.25832	0.00107	499.7	1.64
[5]	$^3\Sigma^+$	[22000]	3	[2.26]	[0.230]	[0.001]	[480]	[2]
[5]	$^3\Delta$	[22000]	6	"	"	"	"	"
[5]	$^1\Delta$	[24000]	2	"	"	"	"	"
[5]	$^3\Sigma^-$	[24000]	3	"	"	"	"	"
[5]	$^1\Sigma^-$	[24000]	1	"	"	"	"	"
[5]	$^1\Sigma^+$	[28000]	1	"	"	"	"	"
[5]	$^3\Pi$	[32000]	6	[2.20]	[0.243]	"	[488]	[3.6]
[2]	$B^1\Pi$	32775.	2	"	"	"	488.	3.6

Enthalpy of Formation

We adopt $D_0° = 131.0 \pm 2$ kcal·mol^{-1} and $\Delta_f H°(298.15\ K) = -29.6 \pm 2$ kcal·mol^{-1} based on equilibria and vaporization data analyzed below. The results are in excellent agreement, even though δS varies widely. The dissociation energy is confirmed also by values of 132 ± 5(electron impact),[17] ≥ 131.4 (crossed-beam chemiluminescence),[18] and 131 kcal·mol^{-1} (flame study, 1973).[7] We have adjusted the latter value to make it roughly consistent with our Gibbs energy functions. Less reliable data were reviewed by Schofield.[19] Our analysis supports the conclusions of Brewer and Rosenblatt.[20]

Source	Method	Reaction[a]	T/K	Points	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$, $D_0°$ kcal·mol^{-1}
[7]Kalff (1970)	Flame photometric	A	~2680–2860	12	19. ± 4	49. ± 11	−4.7 ± 2.5	−29.6 ± 3 131.0
[8]Colin (1964)	Knudsen mass spec.	B	1934–2069	3	−11. ± 10	−29. ± 20	−6.8 ± 2.0	−29.1 ± 3 130.5
[9]Semenov (1972)	" " "	C	1423–1723	Eqn.	3.7	108.1	102.2 ± 1.0	−28.8 ± 2 130.2
[10]Newbury (1968)	Knudsen thermobal.	C	1563–1853	17	5.9 ± 0.9	111.8 ± 1.5	101.8 ± 1.3	−29.2 ± 2 130.6
	" " "	C	1503–1862	45	4.2 ± 0.5	109.2 ± 0.8	102.1 ± 1.0	−28.9 ± 2 130.3
	Knudsen mass spec.	C	1590–1892	11	4.8 ± 0.2	110.1 ± 0.3	101.7 ± 1.1	−29.3 ± 2 130.8
	" " "	C	1481–1917	38	5.6 ± 0.3	111.4 ± 0.5	101.8 ± 1.4	−29.2 ± 2 130.6
	" " "	C	1365–1910	29	6.1 ± 0.4	112.1 ± 0.6	102.1 ± 1.6	−28.9 ± 2 130.3
[11]Inghram (1955)	" " "	C	1530–1758	4	−2.8 ± 6.1	99. ± 10	103.2 ± 1.7	−27.8 ± 2 129.2
[12]Shchukarev (1957)	Langmuir mass spec.	C	~1173–1473	Eqn.	−6.1	93.3	101.4 ± 0.6	−29.6 ± 2 131.0
[13]Novikov (1961)	Knudsen effusion	C	~1140–1470	Eqn.	−2.0	97.2	99.8 ± 1.5	−31.2 ± 2 132.6
[14]Blewett (1939)	" "	C	1526–1800	12	−0.5 ± 2.5	103.1 ± 4.1	103.9 ± 4.3	−27.1 ± 3 128.5
[15]Herrmann (1937)	Langmuir	C	~1200–1560	Eqn.	16.	124.	101.8 ± 1.6	−29.2 ± 3 130.7
[16]Claassen (1933)	"	C	1223–1475	7	−4.5 ± 1.5	95.9 ± 2.1	101.9 ± 1.0	−29.1 ± 2 130.5

[a]Reactions: A) Ba(g) + CO_2(g) = BaO(g) + CO(g); B) Ba(g) + SO(g) = BaO(g) + S(g); C) BaO(cr) = BaO(g).

Heat Capacity and Entropy

Electronic levels (T_e) and vibrational–rotational constants of the observed states are from Field[1] and Rosen.[2] The long-sought $a^3\Pi$ and $A'^1\Pi$ states of CaO, SrO and BaO were characterized by Field[1] using a new method for assignment of perturbations. This study resolved the long-standing controversy over low-lying electronic levels and confirmed[1] that $X^1\Sigma^+$is the ground state.[4] We estimate the other potentially low-lying state ($^3\Sigma^+$) at 14000 cm^{-1} by assuming that it lies 3000 ± 2500 cm^{-1} [1,5] below the isoconfigurational A state. Other predicted states and their vibrational–rotational constants are estimated in isoconfigurational groups by comaprison with BeO, MgO, CaO and SrO.[5] Comparisons are facilitated by listing the states in the isoconfigurational order of MgO.[5] Our thermodynamic functions correspond to an "effective" ground state with $g = 1$ instead of $g = 6$.[10,19] Our functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

Continued on page 359

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.014	−121.607	−121.607	INFINITE
100	29.160	202.190	263.233	−6.104	−121.848	−129.993	67.901
200	30.735	222.767	238.400	−3.127	−122.870	−137.747	35.976
298.15	32.897	235.457	235.457	0.	−123.846	−144.839	25.375
300	32.932	235.661	235.458	0.061	−123.865	−144.969	25.241
400	34.443	245.359	236.770	3.435	−124.993	−151.844	19.829
500	35.385	253.154	239.293	6.930	−126.845	−158.363	16.544
600	35.988	259.662	242.160	10.501	−129.476	−164.410	14.313
700	36.393	265.242	245.068	14.122	−131.298	−170.100	12.693
800	36.679	270.121	247.901	17.776	−133.639	−175.478	11.458
900	36.889	274.454	250.616	21.455	−135.569	−180.592	10.481
1000	37.049	278.350	253.197	25.152	−137.510	−185.491	9.689
1100	37.177	281.887	255.647	28.864	−147.829	−189.375	8.993
1200	37.281	285.126	257.971	32.587	−150.023	−193.054	8.403
1300	37.370	288.114	260.176	36.319	−152.124	−196.554	7.898
1400	37.448	290.886	262.272	40.060	−154.154	−199.895	7.458
1500	37.520	293.472	264.267	43.809	−156.135	−203.093	7.072
1600	37.593	295.896	266.169	47.564	−158.085	−206.160	6.730
1700	37.671	298.178	267.985	51.327	−160.026	−209.105	6.425
1800	37.762	300.333	269.723	55.099	−161.977	−211.936	6.150
1900	37.873	302.378	271.388	58.880	−163.956	−214.658	5.901
2000	38.014	304.324	272.987	62.675	−165.982	−217.274	5.675
2100	38.195	306.183	274.523	66.485	−168.074	−219.787	5.467
2200	38.427	307.965	276.003	70.315	−309.769	−216.824	5.148
2300	38.720	309.679	277.430	74.172	−311.204	−212.568	4.828
2400	39.086	311.335	278.809	78.062	−312.841	−208.245	4.532
2500	39.535	312.939	280.142	81.992	−314.672	−203.850	4.259
2600	40.079	314.500	281.434	85.972	−316.684	−199.378	4.006
2700	40.725	316.024	282.687	90.011	−318.858	−194.825	3.769
2800	41.483	317.519	283.904	94.121	−321.166	−190.190	3.548
2900	42.357	318.989	285.089	98.312	−323.579	−185.470	3.341
3000	43.353	320.442	286.243	102.596	−326.064	−180.665	3.146
3100	44.471	321.881	287.369	106.986	−328.585	−175.777	2.962
3200	45.711	323.312	288.470	111.494	−331.106	−170.807	2.788
3300	47.069	324.739	289.548	116.132	−333.585	−165.760	2.624
3400	48.539	326.166	290.604	120.912	−335.997	−160.638	2.468
3500	50.112	327.595	291.640	125.844	−338.308	−155.447	2.320
3600	51.777	329.030	292.659	130.937	−340.490	−150.191	2.179
3700	53.519	330.472	293.661	136.201	−342.516	−144.877	2.045
3800	55.323	331.924	294.649	141.643	−344.367	−139.509	1.918
3900	57.172	333.384	295.624	147.268	−346.025	−134.096	1.796
4000	59.044	334.855	296.586	153.078	−347.479	−128.643	1.680
4100	60.922	336.337	297.537	159.077	−348.717	−123.157	1.569
4200	62.784	337.827	298.479	165.262	−349.737	−117.643	1.463
4300	64.609	339.326	299.411	171.632	−350.540	−112.107	1.362
4400	66.380	340.832	300.336	178.182	−351.127	−106.555	1.265
4500	68.076	342.342	301.252	184.906	−351.505	−100.992	1.172
4600	69.681	343.856	302.162	191.794	−351.675	−95.423	1.084
4700	71.180	345.371	303.065	198.838	−351.636	−89.855	0.999
4800	72.561	346.885	303.962	206.026	−351.439	−84.287	0.917
4900	73.812	348.394	304.854	213.346	−351.073	−78.725	0.839
5000	74.928	349.896	305.740	220.784	−350.565	−73.172	0.764
5100	75.901	351.390	306.620	228.327	−349.905	−67.632	0.693
5200	76.729	352.872	307.495	235.960	−349.151	−62.105	0.624
5300	77.413	354.340	308.365	243.668	−348.300	−56.593	0.558
5400	77.953	355.793	309.230	251.437	−347.371	−51.098	0.494
5500	78.354	357.227	310.090	259.254	−346.348	−45.624	0.433
5600	78.620	358.641	310.944	267.104	−345.252	−40.173	0.375
5700	78.759	360.034	311.793	274.974	−344.175	−34.735	0.318
5800	78.777	361.404	312.637	282.851	−343.058	−29.318	0.264
5900	78.684	362.750	313.475	290.725	−341.820	−23.939	0.212
6000	78.489	364.071	314.307	298.585	−340.718	−18.560	0.162

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 78.4 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -462.7 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -463.6 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Sabatier[1] measured the enthalpy of solution of BaS in hydrochloric acid solution as $\Delta_r H°(284\ K) = -27.0 \pm 1.0\ kcal \cdot mol^{-1}$ for $BaS(cr) + 2HCl(100\ H_2O, aq) \rightarrow BaCl_2(100\ H_2O, aq) + H_2S(aq)$. We derive $\Delta_f H°(298.15\ K) = -111.0 \pm 2.0\ kcal \cdot mol^{-1}$ based on the following auxiliary data: $\Delta_f H°(HCl \cdot 100\ H_2O, aq, 298.15\ K) = -39.657\ kcal \cdot mol^{-1}$,[2] $\Delta_f H°(H_2S, aq, 298.15\ K) = -9.5\ kcal \cdot mol^{-1}$,[2] and $\Delta_f H°(BaCl_2 \cdot 100\ H_2O, aq, 298.15\ K) = -207.803\ kcal \cdot mol^{-1}$.[3] Mourlot[4] also measured the enthalpy of solution of BaS in hydrochloric acid solution as $\Delta_r H° = -27.35 \pm 1.0\ kcal \cdot mol^{-1}$ from which we calculate $\Delta_f H°(298.15\ K) = -110.6 \pm 2\ kcal \cdot mol^{-1}$ using the same auxiliary data. The uncertainties quoted reflect the correction to 298.15 K and the ambiguity of the exact solution composition.

Our analyses of equilibrium studies of Okuno,[5] Culver and Hamdorf,[6] Nikonov,[7] Schenck and Hammerschmidt,[8] and Colin *et al.*,[9] are listed below. The calculated 3rd law $\Delta_f H°(298.15\ K)$ may have an uncertainty of 0.5 $kcal \cdot mol^{-1}$ since the JANAF Gibbs energy functions are partially based on the estimated $C_p°$ data (above 300 K). The enthalpy of formation of BaS(cr) derived from equilibrium studies is in good agreement with that derived from enthalpy of solution studies.[1,4] We discount the studies of Nikonov[7] and of Colin *et al.*[9] More information is given in the SrS(cr) table.[10]

A weighted average, $\Delta_f H°(BaS, cr, 298.15\ K) = -110.8 \pm 0.5\ kcal \cdot mol^{-1}$, is adopted in the tabulation.

Source	Method	Reaction[a]	T/K	No. of Points	δS $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
[5]Okuno (1935)	Equilibrium	A	973–1173	5	0.85 ± 0.75	−6.27 ± 0.81	−7.18 ± 0.25	−110.29 ± 1.0
[6]Culver (1955)	Equilibrium	B	1073–1373	Equation	−2.89	6.14	9.68 ± 0.75	−111.23 ± 2.5
[7]Nikonov (1961)	Vaporization	C	1400–1600	Equation	2.2	−106.38	−109.74 ± 0.6	−100.7 ± 4
[8]Schenck (1933)	Equilibrium	C	1355–1399	2	−11.4	52.6	68.31 ± 0.7	−111.05 ± 4.0
[9]Colin *et al.* (1964)	Mass Spec	E	1846–2120	10	−17.6 ± 7.5	−59.4 ± 15.0	−24.2 ± 4.2	−118.6 ± 12

[a]Reactions:
A) $BaSO_4(cr) + 4CO(g) = BaS(cr) + 4CO_2(g)$
B) $BaSO_4(cr) + 4H_2(g) = BaS(cr) + 4H_2O(g)$
C) $BaS(g) = BaS(cr)$
D) $BaSO_4(cr) + S_2(g) = BaS(cr) + 2SO_2(g)$
E) $Ba(g) + 2S_2(g) = BaS(cr) + 3S(g)$

Heat Capacity and Entropy

King and Weller[11] measured the low temperature heat capacities from 54–296 K. Their smooth values are adopted in the tabulation. The entropy, $S°(298.15\ K) = 18.7 \pm 0.2\ cal \cdot K^{-1} \cdot mol^{-1}$, is based on $S°(51\ K) = 2.60\ cal \cdot K^{-1} \cdot mol^{-1}$ as extrapolated by King and Weller using Debye and Einstein functions ($\theta_D = 159$, $\theta_E = 267$). The $C_p°$ values above 300 K are estimated by graphical extrapolation combined with method B of Kubaschewski *et al.*[12]

Fusion Data

Literature melting data for BaS(cr) are not available. It has been reported[13,14] that BaS melts above 2500 K but this value must be looked upon as a lower limit.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.000	0.000	INFINITE	−10.458	−462.722	−462.722	INFINITE
100	36.317	29.938	120.037	−9.010	−463.661	−461.995	241.321
200	46.610	59.176	82.843	−4.733	−463.571	−460.350	120.231
298.15	49.374	78.395	78.395	0.000	−463.587	−458.776	80.376
300	49.407	78.701	78.396	0.091	−463.590	−458.746	79.875
400	51.128	93.153	80.355	5.119	−466.176	−457.002	59.678
500	52.718	104.737	84.110	10.314	−468.728	−454.445	47.476
600	54.057	114.473	88.380	15.655	−471.593	−451.302	39.289
700	55.061	122.882	92.722	21.112	−473.298	−447.793	33.415
800	55.982	130.296	96.965	26.665	−475.283	−444.006	28.991
900	56.777	136.935	101.043	32.302	−529.809	−438.930	25.475
1000	57.656	142.963	104.938	38.025	−529.849	−428.829	22.400
1100	58.430	148.494	108.650	43.829	−538.193	−417.908	19.845
1200	59.204	153.612	112.186	49.710	−538.341	−406.965	17.715
1300	59.983	158.381	115.558	55.670	−538.326	−396.017	15.912
1400	60.752	162.855	118.778	61.707	−538.172	−385.075	14.367
1500	61.500	167.071	121.859	67.819	−537.901	−374.148	13.029
1600	62.258	171.065	124.810	74.007	−537.534	−363.243	11.859
1700	63.037	174.862	127.644	80.272	−537.090	−352.363	10.827
1800	63.806	178.487	130.369	86.614	−536.588	−341.511	9.910
1900	64.554	181.957	132.993	93.032	−536.051	−330.688	9.091
2000	65.312	185.288	135.525	99.525	−535.498	−319.894	8.355
2100	66.086	188.493	137.971	106.095	−534.950	−309.127	7.689
2200	66.860	191.585	140.339	112.742	−673.947	−293.011	6.957
2300	67.640	194.574	142.632	119.467	−672.630	−275.725	6.262
2400	68.408	197.469	144.857	126.270	−671.468	−258.494	5.626
2500	69.156	200.277	147.018	133.148	−670.463	−241.308	5.042
2600	69.915	203.004	149.119	140.102	−669.609	−224.159	4.503
2700	70.694	205.657	151.164	147.132	−668.895	−207.041	4.005
2800	71.463	208.242	153.157	154.240	−668.304	−189.946	3.543
2900	72.221	210.763	155.100	161.424	−667.818	−172.871	3.114
3000	72.969	213.224	156.996	168.684	−667.418	−155.811	2.713

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 248.861 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 39.55 \pm 12.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 37.78 \pm 12.6\ kJ·mol^{-1}$

Source	State	ϵ_i, cm^{-1}	Electronic and Molecular Constants (σ = 1) g_i	r_e, g	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
1, 2	$X^1\Sigma^+$	0.0	1	2.5067	0.103160	0.000314	379.117	0.8828
8	$^3\Sigma^+$	[12000.]	3	[2.635]	[0.09339]	[0.000713]	[294.1]	[3.075]
1, 8	$^3\Pi$	[14000.]	6	[2.88]	[0.0784]	[0.0004]	[234.8]	[0.9]
8	$^1\Pi$	[14200.]	2	[2.88]	[0.0784]	[0.0004]	[234.8]	[0.9]
1	$A^1\Sigma^+$	14450.	1	2.635	0.09339	0.000713	294.06	3.075
1	$B^1\Sigma^+$	26997.74	1	2.7468	0.08591	0.000439	253.90	0.4373

Enthalpy of Formation

The adopted value of the enthalpy of formation, $\Delta_f H°(BaS, g, 298.15\ K) = 9.03 \pm 3.0\ kcal·mol^{-1}$, is based on the Knudsen mass-spectrometric study of Colin *et al.*[3] Our reanalysis of their ion intensity data is given below. Although the large drift would suggest a larger uncertainty in the derived quantities ($\Delta_f H°$, $D_0°$), our experience with related work on other alkaline earth sulfides and oxides by the same authors indicates that results derived from a 3rd law analysis are preferred. Our value of the enthalpy of formation is intermediate between $\Delta_f H°(298.15\ K) = 7.3 \pm 5\ kcal·mol^{-1}$ obtained by Mills[6] (using different Gibbs energy functions) in a recent critical compilation and $\Delta_f H°(298.15\ K) = 12.0\ kcal·mol^{-1}$ preferred by NBS.[7] Using auxiliary JANAF data,[8] and the recommended value for $D_0°$ (S_2, g) = 100.69 ± 0.01 $kcal·mol^{-1}$,[8] we calculate $D_0°$ (BaS, g) = 99.3 ± 3 $kcal·mol^{-1}$. A linear Birge–Sponer extrapolation of the $X^1\Sigma^+$ ground state based on the data of Barrow *et al.*,[1] after an ionic correction due to Hildenbrand,[4] yields the dissociation energy of 99.8 $kcal·mol^{-1}$ for the products $Ba(^1S) + S(^1D)$. The $X^1\Sigma^+$ ground state cannot dissociate to ground state atoms. If the dissociation products are instead $Ba(^3D) + S(^3P)$, analogous to the work of Field *et al.*[5] on BaO, the dissociation energy becomes $D_0° = 100.4\ kcal·mol^{-1}$. Both of these values are uncertain due to the very long vibrational extrapolation.

Source	Method	Reaction[a]	T/K	No. of Points	δS $cal·K^{-1}mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$, $D_0°$ $kcal·mol^{-1}$
[3]Colin (1964)	Mass Spec.	A	1846–2120	10	−2.5 ± 4.9	−3.37 ± 9.8	1.68 ± 2.5	9.03 ± 3.0 99.2 ± 3.0

[a]Reaction: A) $Ba(g) + S_2(g) = BaS(g) + S(g)$

Heat Capacity and Entropy

Electronic levels (T_{oo}) and vibrational–rotational constants of the observed states are from the optical study of Barrow *et al.*[1] and the microwave work of Tiemann *et al.*[2] Other low-lying electronic states and their vibrational–rotational constants are estimated in isoconfigurational groups by analogy with BaO[8] and from trends observed in the known states of the other alkaline-earth oxides and sulfides. Thermodynamic functions are calculated using first-order anharmonic corrections to Q_t^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_t^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$. Uncertainty in the energy and molecular constants for the estimated states may contribute as much as 2–3 $cal·K^{-1}·mol^{-1}$ to $S°$ at 3000 K. The molecular constants have been corrected to the natural isotopic abundances.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.556	39.549	39.549	INFINITE
100	30.195	212.875	279.140	−6.627	40.091	23.464	−12.256
200	33.796	234.997	252.065	−3.414	39.117	7.174	−1.874
298.15	35.531	248.861	248.861	0.	37.782	−8.232	1.442
300	35.552	249.081	248.862	0.066	37.753	−8.517	1.483
400	36.360	259.433	250.267	3.666	33.740	−23.599	3.082
500	36.789	267.597	252.946	7.326	29.653	−37.494	3.917
600	37.047	274.329	255.965	11.018	25.139	−50.484	4.395
700	37.219	280.053	259.007	14.732	21.691	−62.824	4.688
800	37.342	285.032	261.956	18.461	17.881	−74.630	4.873
900	37.438	289.436	264.769	22.200	−38.543	−84.914	4.928
1000	37.515	293.384	267.437	25.947	−40.558	−89.959	4.699
1100	37.581	296.963	269.961	29.702	−50.951	−93.981	4.463
1200	37.643	300.236	272.349	33.464	−53.219	−97.792	4.257
1300	37.705	303.251	274.612	37.231	−55.396	−101.418	4.075
1400	37.776	306.048	276.759	41.005	−57.505	−104.879	3.913
1500	37.867	308.657	278.799	44.787	−59.565	−108.190	3.768
1600	37.990	311.105	280.743	48.579	−61.593	−111.366	3.636
1700	38.161	313.413	282.597	52.386	−63.607	−114.415	3.516
1800	38.399	315.600	284.370	56.214	−65.620	−117.346	3.405
1900	38.721	317.685	286.069	60.069	−67.645	−120.164	3.304
2000	39.146	319.681	287.700	63.961	−69.693	−122.875	3.209
2100	39.691	321.604	289.269	67.902	−71.774	−125.484	3.121
2200	40.370	323.465	290.782	71.904	−213.416	−122.616	2.911
2300	41.193	325.277	292.242	75.981	−214.748	−118.460	2.690
2400	42.168	327.051	293.656	80.148	−216.221	−114.242	2.486
2500	43.296	328.794	295.026	84.420	−217.822	−109.961	2.298
2600	44.576	330.517	296.358	88.812	−219.530	−105.613	2.122
2700	45.998	332.225	297.655	93.340	−221.318	−101.198	1.958
2800	47.551	333.926	298.920	98.016	−223.159	−96.715	1.804
2900	49.216	335.623	300.157	102.853	−225.020	−92.167	1.660
3000	50.972	337.321	301.367	107.862	−226.871	−87.554	1.524
3100	52.795	339.022	302.554	113.050	−228.680	−82.880	1.397
3200	54.657	340.728	303.721	118.422	−230.418	−78.149	1.276
3300	56.529	342.438	304.868	123.982	−232.051	−73.365	1.161
3400	58.384	344.153	305.998	129.728	−233.569	−68.534	1.053
3500	60.193	345.872	307.113	135.657	−234.951	−63.659	0.950
3600	61.930	347.592	308.213	141.764	−236.184	−58.747	0.852
3700	63.570	349.312	309.301	148.040	−237.261	−53.803	0.760
3800	65.093	351.027	310.376	154.474	−238.178	−48.832	0.671
3900	66.482	352.736	311.441	161.054	−238.936	−43.839	0.587
4000	67.723	354.436	312.494	167.765	−239.543	−38.829	0.507
4100	68.809	356.122	313.538	174.593	−240.004	−33.805	0.431
4200	69.733	357.791	314.572	181.522	−240.331	−28.772	0.358
4300	70.494	359.441	315.596	188.534	−240.541	−23.732	0.288
4400	71.094	361.069	316.611	195.615	−240.647	−18.688	0.222
4500	71.539	362.672	317.617	202.748	−240.663	−13.644	0.158
4600	71.835	364.248	318.613	209.918	−240.600	−8.600	0.098
4700	71.991	365.795	319.601	217.110	−240.459	−3.560	0.040
4800	72.020	367.311	320.579	224.312	−240.296	1.479	−0.016
4900	71.931	368.795	321.548	231.510	−240.099	6.513	−0.069
5000	71.737	370.246	322.508	238.695	−239.892	11.544	−0.121
5100	71.451	371.664	323.458	245.855	−239.662	16.568	−0.170
5200	71.085	373.048	324.398	252.982	−239.460	21.590	−0.217
5300	70.650	374.398	325.329	260.069	−239.277	26.609	−0.262
5400	70.158	375.715	326.250	267.110	−239.123	31.624	−0.306
5500	69.619	376.997	327.161	274.100	−238.973	36.632	−0.348
5600	69.043	378.246	328.062	281.033	−238.837	41.635	−0.388
5700	68.439	379.463	328.953	287.907	−238.799	46.643	−0.427
5800	67.814	380.648	329.834	294.720	−238.788	51.648	−0.465
5900	67.175	381.802	330.705	301.470	−238.713	56.636	−0.501
6000	66.529	382.925	331.566	308.155	−238.821	61.643	−0.537

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

Continued from page 320

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Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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Continued from page 341

to be the same as in BaF.[7, 11] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 431 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[11, 15]

The entropy in the present table is lower by 1.25 cal·K^{-1}·mol^{-1} at 298 K and 1.77 cal·K^{-1}·mol^{-1} at 1000 K than that proposed by Jackson;[11] the vibrational frequencies and electronic levels adopted here differ from those of Jackson.[11] The moment of inertia in Jackson[11] appears to be in error.

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Jackson[9] used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K) = 78.045\ cal \cdot K^{-1} \cdot mol^{-1}$. We assign uncertainty of $\pm 3\ cal \cdot K^{-1} \cdot mol^{-1}$ to the adopted entropy.

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REFERENCE STATE

0	to	1527	K crystal, alpha
1527	to	1560	K crystal, beta
1560	to	2741.437	K liquid
above		2741.437	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−1.932	0.	0.	0.
100	1.819	0.503	19.434	−1.893	0.	0.	0.
200	9.984	4.174	10.751	−1.315	0.	0.	0.
298.15	16.380	9.440	9.440	0.	0.	0.	0.
300	16.472	9.542	9.440	0.030	0.	0.	0.
400	19.965	14.817	10.136	1.872	0.	0.	0.
500	21.943	19.501	11.551	3.975	0.	0.	0.
600	23.336	23.630	13.227	6.242	0.	0.	0.
700	24.463	27.314	14.981	8.634	0.	0.	0.
800	25.458	30.647	16.734	11.130	0.	0.	0.
900	26.384	33.699	18.452	13.723	0.	0.	0.
1000	27.274	36.525	20.119	16.406	0.	0.	0.
1100	28.147	39.166	21.732	19.177	0.	0.	0.
1200	29.016	41.652	23.290	22.035	0.	0.	0.
1300	29.886	44.009	24.793	24.980	0.	0.	0.
1400	30.763	46.256	26.247	28.013	0.	0.	0.
1500	31.650	48.409	27.653	31.133	0.	0.	0.
1527.000	31.892	48.975	28.025	31.991	ALPHA <--> BETA TRANSITION		
1527.000	30.000	53.461	28.025	38.840			
1560.000	30.000	54.102	28.570	39.830	BETA <--> LIQUID TRANSITION		
1560.000	28.788	59.163	28.570	47.725			
1600	28.874	59.893	29.344	48.879	0.	0.	0.
1700	29.089	61.650	31.193	51.777	0.	0.	0.
1800	29.304	63.319	32.932	54.696	0.	0.	0.
1900	29.519	64.909	34.573	57.638	0.	0.	0.
2000	29.734	66.429	36.128	60.600	0.	0.	0.
2100	29.949	67.884	37.606	63.584	0.	0.	0.
2200	30.164	69.283	39.014	66.590	0.	0.	0.
2300	30.379	70.628	40.360	69.617	0.	0.	0.
2400	30.594	71.926	41.648	72.666	0.	0.	0.
2500	30.809	73.179	42.885	75.736	0.	0.	0.
2600	31.024	74.391	44.073	78.828	0.	0.	0.
2700	31.239	75.566	45.218	81.941	0.	0.	0.
2741.437	31.328	76.043	45.680	83.237	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
2741.437	20.883	182.400	45.680	374.809			
2800	20.905	182.842	48.545	376.032	0.	0.	0.
2900	20.949	183.576	53.188	378.125	0.	0.	0.
3000	21.006	184.287	57.546	380.223	0.	0.	0.
3100	21.075	184.977	61.646	382.327	0.	0.	0.
3200	21.159	185.648	65.511	384.438	0.	0.	0.
3300	21.259	186.300	69.161	386.559	0.	0.	0.
3400	21.376	186.937	72.616	388.691	0.	0.	0.
3500	21.512	187.558	75.891	390.835	0.	0.	0.
3600	21.668	188.166	79.001	392.994	0.	0.	0.
3700	21.844	188.762	81.960	395.169	0.	0.	0.
3800	22.041	189.347	84.778	397.363	0.	0.	0.
3900	22.259	189.923	87.467	399.578	0.	0.	0.
4000	22.500	190.489	90.035	401.816	0.	0.	0.
4100	22.761	191.048	92.492	404.079	0.	0.	0.
4200	23.045	191.600	94.845	406.369	0.	0.	0.
4300	23.349	192.146	97.102	408.688	0.	0.	0.
4400	23.674	192.686	99.268	411.039	0.	0.	0.
4500	24.019	193.222	101.350	413.424	0.	0.	0.
4600	24.383	193.754	103.353	415.844	0.	0.	0.
4700	24.764	194.282	105.282	418.301	0.	0.	0.
4800	25.162	194.808	107.142	420.797	0.	0.	0.
4900	25.576	195.331	108.936	423.334	0.	0.	0.
5000	26.003	195.852	110.669	425.913	0.	0.	0.
5200	26.894	196.889	113.965	431.202	0.	0.	0.
5400	27.822	197.921	117.056	436.673	0.	0.	0.
5600	28.776	198.950	119.962	442.332	0.	0.	0.
5800	29.743	199.977	122.704	448.184	0.	0.	0.
6000	30.711	201.001	125.297	454.229	0.	0.	0.

PREVIOUS: September 1961 (1 atm) CURRENT: September 1983 (1 bar)

$S°(298.15\ K) = 9.44 \pm 0.15\ J·K^{-1}·mol^{-1}$
$\Delta_{trs}H° = 1527 \pm 25\ K\ (\alpha \rightarrow \beta)$
$T_{fus} = 1560 \pm 5\ K\ (\beta \rightarrow l)$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{trs}H° = 6.849 \pm 0.5\ kJ·mol^{-1}$
$\Delta_{fus}H° = 7.895 \pm 0.5\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions for Be(α, β, cr) are derived from the studies of Ahlers (1.4–30 K)[1], Hill and Smith (4–300 K),[2] Ginnings *et al.* (367–1169 K),[3] and Kantor *et al.* (600–3200 K).[4] The mathematical and graphical treatment of these four studies yields a continuous and smooth heat capacity curve for α–Be(cr).

There are no heat capacity or enthalpy measurements for β–Be(cr). We assume a constant value of $C_p = 30.0\ J·K^{-1}·mol^{-1}$ for the β–region.

The entropy at 298.15 K is 0.06 $J·K^{-1}·mol^{-1}$ less than that recommended by CODATA.[5] This is undoubtedly due to the manner in which the data of Ahlers[1] and Hill and Smith[2] were merged. A detailed discussion of the heat capacities of all alkaline earth metals is in preparation.

Phase and Fusion Data

Cannon[6] has summarized the data on the polymorphic phase changes and the variation of the melting temperature of beryllium with pressure. His critical evaluation results in the recommendation that at ambient pressure there are two stable phases. His recommendations are entirely attributable to the resistance studies of Francois and Contre.[7] The phases are denoted alpha(hcp) and beta(bcc).

The melting point of beryllium is fairly well defined. We adopt $T_{fus} = 1560 \pm 5$ K based on the studies of Kantor *et al.*,[4] Martin and Moore,[8] Teitel and Cohen,[9] and Loasby and Dearden.[10]

The alpha–beta transition is ill–defined. There are many conflicting studies as to the value of the transition temperature and the value and sign of the derivative (dT/dP) for this transition. We adopt $T_{trs} = 1527 \pm 25$ K based on the study of Ammonenko, *et al.*[11]

The enthalpies of transition and fusion are also poorly defined. Kantor, *et al.*[4] has measured the enthalpy of the crystal and liquid. No data points were obtained in the beta phase region. As a result, we can only derive a combined value for the enthalpy of transition and fusion. Following the suggestion of Abey,[12] the enthalpy values of Loasby and Dearden[10] and Abey[12] have the same value for the ratio of the transition enthalpy to fusion enthalpy, even though the actual values for each enthalpy are quite different. Thus, using this ratio and the sum of the enthalpies, as determined by Kantor *et al.*,[4] we calculate the individual enthalpies of transition and fusion. A much more detailed discussion is in progress.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−1.932	0.	0.	0.
100	1.819	0.503	19.434	−1.893	0.	0.	0.
200	9.984	4.174	10.751	−1.315	0.	0.	0.
250	13.574	6.801	9.695	−0.723	0.	0.	0.
298.15	16.380	9.440	9.440	0.	0.	0.	0.
300	16.472	9.542	9.440	0.030	0.	0.	0.
350	18.520	12.245	9.649	0.909	0.	0.	0.
400	19.965	14.817	10.136	1.872	0.	0.	0.
450	21.061	17.235	10.792	2.899	0.	0.	0.
500	21.943	19.501	11.551	3.975	0.	0.	0.
600	23.336	23.630	13.227	6.242	0.	0.	0.
700	24.463	27.314	14.981	8.634	0.	0.	0.
800	25.458	30.647	16.734	11.130	0.	0.	0.
900	26.384	33.699	18.452	13.723	0.	0.	0.
1000	27.274	36.525	20.119	16.406	0.	0.	0.
1100	28.147	39.166	21.732	19.177	0.	0.	0.
1200	29.016	41.652	23.290	22.035	0.	0.	0.
1300	29.886	44.009	24.793	24.980	0.	0.	0.
1400	30.763	46.256	26.247	28.013	0.	0.	0.
1500	31.650	48.409	27.653	31.133	0.	0.	0.
1527.000	31.892	48.975	28.025	31.991	ALPHA <--> BETA		
1527.000	30.000	53.461	28.025	38.840	TRANSITION		
1560.000	30.000	54.102	28.570	39.830	---- BETA <--> LIQUID ----		
1600	30.000	54.862	29.218	41.030	−7.848	0.202	−0.007
1700	30.000	56.680	30.780	44.030	−7.747	0.702	−0.022
1800	30.000	58.395	32.267	47.030	−7.666	1.196	−0.035
1900	30.000	60.017	33.685	50.030	−7.607	1.687	−0.046
2000	30.000	61.556	35.041	53.030	−7.570	2.175	−0.057

PREVIOUS: September 1961 CURRENT: September 1983

$S°(298.15\ K) = [19.539]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1560 \pm 5\ K\ (\beta \rightarrow l)$

$\Delta_f H°(298.15\ K) = [15.508]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 7.895 \pm 0.05\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of liquid beryllium is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1560\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is derived from the measured enthalpy data of Kantor *et al.*,[1] 17 data points in the liquid region, 1560 to 2200 K. The data was presented graphically. We adopt the reported equation: $C_p° = 6.079 + 5.138 \times 10^{-4}\ T\ cal·K^{-1}·mol^{-1}$. This equation is used to calculate extrapolated values from 2200 K to 3500 K and from 1150 K to 1560 K.

A glass transition temperature is assumed at 1150 K, below which the heat capacity values of crystalline beryllium are adopted. The entropy at 298.15 K is calculated in a mannner analogous to that used for the enthalpy of formation.

Transition and Fusion Data

Refer to the crystal table for details.

Vaporization Data

There is only one reported vaporization study for Be(l): Baur and Brunner (926–1283 K).[2] This study was not considered in the analysis as it had an incorrect temperature dependence, as was also noted by Hultgren *et al.*[3]

The boiling point (f = 1 bar), T_{vap} = 2741.437 K, is calculated as the temperature for which $\Delta_r G° = 0$ for Be(l) = Be(g). The difference in the enthalpy of formation ofa Be(l) and Be(g) at T_{vap} is the enthalpy of vaporization, $\Delta_{vap}H° = 291.572\ kJ·mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	16.380	19.539	19.539	0.	15.508	12.497	−2.189
300	16.472	19.641	19.540	0.030	15.508	12.478	−2.173
350	18.520	22.344	19.749	0.909	15.508	11.973	−1.787
400	19.965	24.917	20.235	1.872	15.508	11.468	−1.498
450	21.061	27.334	20.891	2.899	15.508	10.963	−1.273
500	21.943	29.600	21.650	3.975	15.508	10.458	−1.093
600	23.336	33.730	23.326	6.242	15.508	9.448	−0.823
700	24.463	37.414	25.080	8.634	15.508	8.438	−0.630
800	25.458	40.746	26.833	11.130	15.508	7.428	−0.485
900	26.384	43.799	28.551	13.723	15.508	6.418	−0.372
1000	27.274	46.625	30.219	16.406	15.508	5.408	−0.282
1100	28.147	49.265	31.832	19.177	15.508	4.398	−0.209
1150.000	28.582	50.526	32.617	20.595	GLASS <--> LIQUID		
1150.000	27.907	50.526	32.617	20.595	TRANSITION		
1200	28.014	51.716	33.388	21.993	15.466	3.389	−0.148
1300	28.229	53.967	34.886	24.805	15.333	2.388	−0.096
1400	28.444	56.067	36.325	27.639	15.134	1.399	−0.052
1500	28.659	58.037	37.707	30.494	14.869	0.427	−0.015
1560.000	28.788	59.163	38.511	32.218	BETA <--> LIQUID		
1600	28.874	59.893	39.036	33.371	0.	0.	0.
1700	29.089	61.650	40.315	36.269	0.	0.	0.
1800	29.304	63.319	41.547	39.189	0.	0.	0.
1900	29.519	64.909	42.735	42.130	0.	0.	0.
2000	29.734	66.429	43.882	45.093	0.	0.	0.
2100	29.949	67.884	44.991	48.077	0.	0.	0.
2200	30.164	69.283	46.063	51.082	0.	0.	0.
2300	30.379	70.628	47.102	54.110	0.	0.	0.
2400	30.594	71.926	48.110	57.158	0.	0.	0.
2500	30.809	73.179	49.088	60.228	0.	0.	0.
2600	31.024	74.391	50.038	63.320	0.	0.	0.
2700	31.239	75.566	50.962	66.433	0.	0.	0.
2741.437	31.328	76.043	51.337	67.729	FUGACITY = 1 bar		
2800	31.454	76.706	51.861	69.568	−290.957	6.223	−0.116
2900	31.669	77.814	52.737	72.724	−289.894	16.817	−0.303
3000	31.884	78.891	53.591	75.901	−288.814	27.375	−0.477
3100	32.099	79.940	54.424	79.101	−287.718	37.897	−0.639
3200	32.314	80.963	55.237	82.321	−286.609	48.383	−0.790
3300	32.529	81.960	56.032	85.563	−285.488	58.834	−0.931
3400	32.744	82.934	56.809	88.827	−284.356	69.251	−1.064
3500	32.959	83.887	57.569	92.112	−283.215	79.635	−1.188

PREVIOUS: September 1961 CURRENT: September 1983

0	to 1527 K	crystal, alpha
1527	to 1560 K	crystal, beta
above	1560 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−1.932	0.	0.	0.
100	1.819	0.503	19.434	−1.893	0.	0.	0.
200	9.984	4.174	10.751	−1.315	0.	0.	0.
250	13.574	6.801	9.695	−0.723	0.	0.	0.
298.15	16.380	9.440	9.440	0.	0.	0.	0.
300	16.472	9.542	9.440	0.030	0.	0.	0.
350	18.520	12.245	9.649	0.909	0.	0.	0.
400	19.965	14.817	10.136	1.872	0.	0.	0.
450	21.061	17.235	10.792	2.899	0.	0.	0.
500	21.943	19.501	11.551	3.975	0.	0.	0.
600	23.336	23.630	13.227	6.242	0.	0.	0.
700	24.463	27.314	14.981	8.634	0.	0.	0.
800	25.458	30.647	16.734	11.130	0.	0.	0.
900	26.384	33.699	18.452	13.723	0.	0.	0.
1000	27.274	36.525	20.119	16.406	0.	0.	0.
1100	28.147	39.166	21.732	19.177	0.	0.	0.
1200	29.016	41.652	23.290	22.035	0.	0.	0.
1300	29.886	44.009	24.793	24.980	0.	0.	0.
1400	30.763	46.256	26.247	28.013	0.	0.	0.
1500	31.650	48.409	27.653	31.133	0.	0.	0.
1527.000	31.892	48.975	28.025	31.991	ALPHA <~–> BETA TRANSITION		
1527.000	30.000	53.461	28.025	38.840			
1560.000	30.000	54.102	28.570	39.830	BETA <–~> LIQUID TRANSITION		
1560.000	28.788	59.163	28.570	47.725			
1600	28.874	59.893	29.344	48.879	0.	0.	0.
1700	29.089	61.650	31.193	51.777	0.	0.	0.
1800	29.304	63.319	32.932	54.696	0.	0.	0.
1900	29.519	64.909	34.573	57.638	0.	0.	0.
2000	29.734	66.429	36.128	60.600	0.	0.	0.
2100	29.949	67.884	37.606	63.584	0.	0.	0.
2200	30.164	69.283	39.014	66.590	0.	0.	0.
2300	30.379	70.628	40.360	69.617	0.	0.	0.
2400	30.594	71.926	41.648	72.666	0.	0.	0.
2500	30.809	73.179	42.885	75.736	0.	0.	0.
2600	31.024	74.391	44.073	78.828	0.	0.	0.
2700	31.239	75.566	45.218	81.941	0.	0.	0.
2741.437	31.328	76.043	45.680	83.237	----- FUGACITY = 1 bar -----		
2800	31.454	76.706	46.322	85.075	−290.957	6.223	−0.116
2900	31.669	77.814	47.389	88.232	−289.894	16.817	−0.303
3000	31.884	78.891	48.421	91.409	−288.814	27.375	−0.477
3100	32.099	79.940	49.421	94.608	−287.718	37.897	−0.639
3200	32.314	80.963	50.391	97.829	−286.609	48.383	−0.790
3300	32.529	81.960	51.333	101.071	−285.488	58.834	−0.931
3400	32.744	82.934	52.248	104.335	−284.356	69.251	−1.064
3500	32.959	83.887	53.138	107.620	−283.215	79.635	−1.188

PREVIOUS: CURRENT: September 1983

IP(Be, g) = 75192.07 ± 0.1 cm^{-1}
$S°(298.15\ K)$ = 136.274 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 320 ± 5 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 324 ± 5 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1
$^3P_0$	21978.28	1
$^3P_1$	21978.92	3
$^3P_2$	21981.27	5
$^1P_1$	42565.35	3
.	.	.
.	.	.
.	.	.
$^1D_2$	74443.20	5
IP	75192.29	

Enthalpy of Formation

The enthalpy of formation is derived from the sublimation studies of Holden *et al.* (1172–1552 K),[1] Gulbranson and Andrew (1103–1229 K),[2] and Hildenbrand and Murad (1400–1500 K).[4] The adopted value, $\Delta_f H°(Be, g, 298.15\ K) = 324 \pm 5\ kJ·mol^{-1}$, is that recommended by CODATA.[5] There are additional vapor pressure studies (~20), but they have been omitted in this analysis.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6,7] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[8] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the three levels at ~22000 cm^{-1}; the next excited state is approximately 42565 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[8]

The thermal functions at 298.15 K agree with the CODATA recommendations[5] except that the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$, since this table uses a standard state pressure of 1 bar (CODATA recommendations are based on 1 atm).

References

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	319.735	319.735	INFINITE
90	20.786	113.567	154.755	−4.119	321.774	310.468	−162.172
200	20.786	127.975	138.176	−2.040	323.275	298.515	−77.964
250	20.786	132.613	136.617	−1.001	323.723	292.269	−61.066
298.15	20.786	136.274	136.274	0.	324.000	286.184	−50.138
300	20.786	136.403	136.275	0.038	324.008	285.950	−49.788
350	20.786	139.607	136.528	1.078	324.169	279.592	−41.727
400	20.786	142.383	137.090	2.117	324.245	273.218	−35.679
450	20.786	144.831	137.817	3.156	324.257	266.839	−30.974
500	20.786	147.021	138.630	4.196	324.221	260.460	−27.210
600	20.786	150.811	140.354	6.274	324.032	247.724	−21.566
700	20.786	154.015	142.082	8.353	323.719	235.029	−17.538
800	20.786	156.791	143.751	10.431	323.301	222.386	−14.520
900	20.786	159.239	145.339	12.510	322.787	209.802	−12.177
1000	20.786	161.429	146.840	14.589	322.183	197.279	−10.305
1100	20.786	163.410	148.258	16.667	321.490	184.822	−8.776
1200	20.786	165.219	149.597	18.746	320.711	172.431	−7.506
1300	20.786	166.882	150.863	20.824	319.844	160.109	−6.433
1400	20.786	168.423	152.063	22.903	318.890	147.857	−5.517
1500	20.786	169.857	153.202	24.982	317.848	135.676	−4.725
1600	20.786	171.198	154.286	27.060	302.182	124.093	−4.051
1700	20.786	172.458	155.318	29.139	301.362	112.988	−3.472
1800	20.787	173.647	156.303	31.218	300.521	101.931	−2.958
1900	20.787	174.770	157.246	33.296	299.659	90.922	−2.500
2000	20.789	175.837	158.149	35.375	298.775	79.958	−2.088
2100	20.791	176.851	159.016	37.454	297.870	69.040	−1.717
2200	20.795	177.818	159.849	39.533	296.943	58.165	−1.381
2300	20.801	178.743	160.650	41.613	295.996	47.332	−1.075
2400	20.811	179.628	161.423	43.694	295.028	36.541	−0.795
2500	20.824	180.478	162.168	45.775	294.039	25.791	−0.539
2600	20.844	181.295	162.888	47.859	293.031	15.081	−0.303
2700	20.870	182.082	163.584	49.944	292.003	4.410	−0.085
2741.437	20.883	182.400	163.867	50.809	----- FUGACITY = 1 bar -----		
2800	20.905	182.842	164.259	52.033	0.	0.	0.
2900	20.949	183.576	164.912	54.126	0.	0.	0.
3000	21.006	184.287	165.546	56.223	0.	0.	0.
3100	21.075	184.977	166.162	58.327	0.	0.	0.
3200	21.159	185.648	166.761	60.439	0.	0.	0.
3300	21.259	186.300	167.343	62.559	0.	0.	0.
3400	21.376	186.937	167.910	64.691	0.	0.	0.
3500	21.512	187.558	168.462	66.835	0.	0.	0.
3600	21.668	188.166	169.001	68.994	0.	0.	0.
3700	21.844	188.762	169.527	71.170	0.	0.	0.
3800	22.041	189.347	170.041	73.364	0.	0.	0.
3900	22.259	189.923	170.544	75.578	0.	0.	0.
4000	22.500	190.489	171.035	77.816	0.	0.	0.
4100	22.761	191.048	171.516	80.079	0.	0.	0.
4200	23.045	191.600	171.988	82.369	0.	0.	0.
4300	23.349	192.146	172.451	84.689	0.	0.	0.
4400	23.674	192.686	172.904	87.040	0.	0.	0.
4500	24.019	193.222	173.350	89.424	0.	0.	0.
4600	24.383	193.754	173.788	91.844	0.	0.	0.
4700	24.764	194.282	174.218	94.301	0.	0.	0.
4800	25.162	194.808	174.642	96.798	0.	0.	0.
4900	25.576	195.331	175.058	99.334	0.	0.	0.
5000	26.003	195.852	175.469	101.913	0.	0.	0.
5100	26.443	196.371	175.874	104.535	0.	0.	0.
5200	26.894	196.889	176.273	107.202	0.	0.	0.
5300	27.354	197.405	176.667	109.914	0.	0.	0.
5400	27.822	197.921	177.056	112.673	0.	0.	0.
5500	28.296	198.436	177.440	115.479	0.	0.	0.
5600	28.776	198.950	177.819	118.333	0.	0.	0.
5700	29.258	199.464	178.195	121.234	0.	0.	0.
5800	29.743	199.977	178.566	124.184	0.	0.	0.
5900	30.227	200.489	178.933	127.183	0.	0.	0.
6000	30.711	201.001	179.296	130.230	0.	0.	0.

PREVIOUS: September 1961 (1 atm) CURRENT: Septmeber 1983 (1 bar)

IP(Be^+, g) = 146882.86 ± 0.1 cm^{-1}
$S°$(298.15 K) = 142.037 ± 0.02 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 1208.77 ± 5.0 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [1219.232] kJ·mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.0	2
$^2P_{1/2}$	31928.8	2
$^2P_{3/2}$	31935.4	4

Enthalpy of Formation

$\Delta_f H°(Be^+, g, 0\ K)$ is calculated from $\Delta_f H°(Be, g, 0\ K)$[1] using the spectroscopic value of IP(Be) = 75192.07 ± 0.1 cm^{-1} (899.497 ± 0.001 kJ·mol^{-1}) from Moore.[2] The ionization limit is converted from cm^{-1} to kJ·mol^{-1} using the factor, 1 cm^{-1} = 0.01196266 kJ·mol^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rossenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Be^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Be, g, 0\ K)$ by using IP(Be) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for Be(g), Be^+(g), and e^-(ref). $\Delta_f H°(Be \rightarrow Be^+ e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first two excited states; the next excited state is 88231.2 cm^{-1} above the ground state and the first two excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1208.770		
100	20.786	119.330	160.517	−4.119			
200	20.786	133.737	143.938	−2.040			
250	20.786	138.376	142.379	−1.001			
298.15	20.786	142.037	142.037	0.	1219.232	1173.444	−205.582
300	20.786	142.165	142.037	0.038	1219.279	1173.159	−204.265
350	20.786	145.370	142.290	1.078	1220.479	1165.376	−173.923
400	20.786	148.145	142.852	2.117	1221.594	1157.428	−151.145
450	20.786	150.593	143.579	3.156	1222.646	1149.343	−133.412
500	20.786	152.783	144.392	4.196	1223.648	1141.144	−119.215
600	20.786	156.573	146.116	6.274	1225.539	1124.464	−97.893
700	20.786	159.777	147.845	8.353	1227.304	1107.477	−82.641
800	20.786	162.553	149.514	10.431	1228.965	1090.244	−71.186
900	20.786	165.001	151.101	12.510	1230.529	1072.809	−62.264
1000	20.786	167.191	152.602	14.589	1232.003	1055.205	−55.118
1100	20.786	169.172	154.020	16.667	1233.390	1037.457	−49.265
1200	20.786	170.981	155.359	18.746	1234.689	1019.587	−44.381
1300	20.786	172.645	156.626	20.824	1235.901	1001.612	−40.245
1400	20.786	174.185	157.826	22.903	1237.026	983.547	−36.697
1500	20.786	175.619	158.965	24.982	1238.062	965.405	−33.618
1600	20.786	176.961	160.048	27.060	1224.474	947.722	−30.940
1700	20.786	178.221	161.080	29.139	1225.733	930.386	−28.587
1800	20.786	179.409	162.066	31.217	1226.971	912.977	−26.494
1900	20.786	180.533	163.008	33.296	1228.187	895.500	−24.619
2000	20.786	181.599	163.912	35.375	1229.381	877.959	−22.930
2100	20.786	182.613	164.778	37.453	1230.554	860.359	−21.400
2200	20.786	183.580	165.611	39.532	1231.706	842.703	−20.008
2300	20.786	184.504	166.412	41.610	1232.836	824.996	−18.736
2400	20.786	185.389	167.185	43.689	1233.944	807.240	−17.569
2500	20.786	186.237	167.930	45.768	1235.031	789.438	−16.494
2600	20.786	187.052	168.650	47.846	1236.097	771.594	−15.502
2700	20.786	187.837	169.346	49.925	1237.141	753.708	−14.581
2800	20.787	188.593	170.020	52.004	947.207	742.007	−13.842
2900	20.787	189.322	170.673	54.082	949.271	734.642	−13.232
3000	20.787	190.027	171.307	56.161	951.331	727.206	−12.662
3100	20.788	190.709	171.922	58.240	953.384	719.701	−12.127
3200	20.789	191.369	172.519	60.319	955.430	712.130	−11.624
3300	20.790	192.008	173.100	62.398	957.467	704.496	−11.151
3400	20.792	192.629	173.665	64.477	959.493	696.799	−10.705
3500	20.795	193.232	174.216	66.556	961.507	689.044	−10.283
3600	20.798	193.818	174.752	68.636	963.506	681.231	−9.884
3700	20.802	194.388	175.275	70.716	965.490	673.362	−9.506
3800	20.806	194.942	175.785	72.796	967.454	665.441	−9.147
3900	20.812	195.483	176.284	74.877	969.399	657.468	−8.806
4000	20.820	196.010	176.770	76.958	971.322	649.445	−8.481
4100	20.829	196.524	177.246	79.041	973.220	641.374	−8.171
4200	20.839	197.026	177.711	81.124	975.092	633.258	−7.876
4300	20.851	197.517	178.166	83.209	976.935	625.097	−7.593
4400	20.865	197.996	178.611	85.295	978.749	616.894	−7.323
4500	20.882	198.465	179.047	87.382	980.530	608.650	−7.065
4600	20.900	198.924	179.474	89.471	982.278	600.366	−6.817
4700	20.921	199.374	179.893	91.562	983.990	592.045	−6.580
4800	20.945	199.815	180.303	93.655	985.666	583.688	−6.352
4900	20.972	200.247	180.706	95.751	987.304	575.297	−6.133
5000	21.001	200.671	181.101	97.850	988.902	566.872	−5.922
5100	21.033	201.087	181.489	99.951	990.460	558.416	−5.719
5200	21.069	201.496	181.870	102.057	991.977	549.930	−5.524
5300	21.108	201.898	182.244	104.165	993.452	541.415	−5.336
5400	21.150	202.292	182.611	106.278	994.885	532.872	−5.155
5500	21.195	202.681	182.973	108.396	996.275	524.304	−4.979
5600	21.244	203.063	183.328	110.517	997.622	515.710	−4.810
5700	21.297	203.440	183.678	112.644	998.926	507.093	−4.647
5800	21.353	203.811	184.022	114.777	1000.187	498.453	−4.489
5900	21.412	204.176	184.360	116.915	1001.405	489.792	−4.336
6000	21.475	204.537	184.693	119.059	1002.581	481.111	−4.188

PREVIOUS: June 1965 (1 atm) CURRENT: September 1983 (1 bar)

$S°(298.15\ K) = [228.5 \pm 0.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 125.3 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 120.1 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1{}^2\Pi_{1/2}$	26353.2	2
$A_2{}^2\Pi_{3/2}$	26550.2	2
$B[^2\Sigma]$	[27000]	[2]
$C[^2\Pi]$	[40000]	[4]

$\omega_e = 715.06\ cm^{-1}$ $\omega_e x_e = 4.30\ cm^{-1}$ $\sigma = 1$
$B_e = [0.62155]\ cm^{-1}$ $\alpha_e = [0.005285]\ cm^{-1}$ $r_e = [1.83]$ Å

Enthalpy of Formation

No thermochemical measurement of the enthalpy of formation has been made. The selected value, $\Delta_f H°$(BeBr, g, 0 K) = 30.0 ± 10.0 kcal·mol^{-1}, is obtained from an analysis of spectroscopic data. The adopted values for the ground state vibrational constants give $D_0^\circ = 3.64_1$ eV by a linear Birge–Sponer extrapolation.[1] Based on the ionicity correction developed by Hildenbrand,[2] this value adjusts to $D_0^\circ = 3.27_2$ eV(75.46 kcal·mol^{-1}) which is adopted. $\Delta_f H°$(298.15 K) corresponds to 28.7 kcal·mol^{-1}.

Ionic model calculations[4,6] and bond energy correlations[5] have led to D_0° values of (in eV) 1.2,[4] 4.1,[5] and 2.1.[6] The latter value which is based on a Rittner potential[7] is believed to represent a minimum value for D_0°. Additional support for the adopted value of $\Delta_f H°$ is provided by a comparison of values for the ratio D_0°(MX, 298.15 K)/$\Delta_{at} H°(MX_2, 298.15\ K)$ for the alkaline–earth halides.[3] We find D_0°(BeBr, 298.15 K)/$\Delta_{at} H°(BeBr_2, 298.15\ K) = 0.41$ which is quite consistent with values of this ratio for other alkaline–earth halides.

Heat Capacity and Entropy

We estimate r_e to be 0.08 Å less than that for $BeBr_2$.[3] *This estimation is made based on the observation that the ratio* $r_e(MX)/r_e(MX_2)$ is near 0.96 for several alkaline–earth halides.[3] The value of B_e is calculated from r_e. The value of α_e is obtained from the other constants by assuming a Morse potential function.

The ground state vibrational constants are taken from the results of a recent vibrational analysis of the $A^2\Pi$–$X^2\Sigma$ system by Reddy *et al.*[8] Other values[9] for these constants are slightly different than ours, but we consider them to be less accurate. It should also be noted that the values for $\omega_e x_e$ tabulated by Rosen[9] for the ground and first excited states have been inadvertently reversed. The electronic level for the $A_{12}\Pi_{1/2}$ state is also taken from Reddy *et al.*[8] The doublet splitting of this state is assumed to be 197 cm^{-1} as was observed in the emission spectrum of BeBr by Reddy and Rao.[10,11] We also include a $B^2\Sigma$ level at 27000 cm^{-1} and a $C^2\Pi$ level at 40000 cm^{-1}. These levels are estimated by analogy with those for CaBr, SrBr, and BaBr.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.971	125.326	125.326	INFINITE
100	29.145	195.462	256.089	−6.063	126.799	109.995	−57.455
200	30.486	215.960	231.450	−3.098	126.735	93.120	−24.320
250	31.597	222.881	229.065	−1.546	126.287	84.763	−17.710
298.15	32.598	228.534	228.534	0.	120.110	77.477	−13.574
300	32.633	228.736	228.535	0.060	120.070	77.213	−13.444
350	33.508	233.834	228.935	1.715	104.521	70.926	−10.585
400	34.218	238.357	229.836	3.408	104.336	66.139	−8.637
450	34.787	242.421	231.012	5.134	104.114	61.377	−7.124
500	35.246	246.111	232.340	6.885	103.865	56.642	−5.917
600	35.922	252.601	235.191	10.446	103.298	47.249	−4.113
700	36.386	258.175	238.086	14.063	102.654	37.957	−2.832
800	36.721	263.057	240.908	17.719	101.938	28.763	−1.878
900	36.973	267.397	243.615	21.404	101.148	19.663	−1.141
1000	37.170	271.303	246.192	25.112	100.286	10.654	−0.557
1100	37.330	274.854	248.638	28.837	99.348	1.736	−0.082
1200	37.465	278.108	250.960	32.577	98.334	−7.094	0.309
1300	37.580	281.111	253.166	36.329	97.241	−15.836	0.636
1400	37.681	283.900	255.262	40.092	96.067	−24.490	0.914
1500	37.772	286.503	257.259	43.865	94.810	−33.058	1.151
1600	37.854	288.943	259.164	47.646	78.931	−41.014	1.339
1700	37.931	291.240	260.984	51.436	77.902	−48.479	1.490
1800	38.002	293.410	262.726	55.232	76.852	−55.883	1.622
1900	38.069	295.467	264.395	59.036	75.780	−63.228	1.738
2000	38.134	297.421	265.998	62.846	74.685	−70.516	1.842
2100	38.195	299.283	267.539	66.663	73.565	−77.748	1.934
2200	38.255	301.061	269.023	70.485	72.420	−84.927	2.016
2300	38.312	302.763	270.453	74.313	71.248	−92.053	2.091
2400	38.369	304.395	271.834	78.147	70.050	−99.128	2.157
2500	38.424	305.962	273.168	81.987	68.824	−106.152	2.218
2600	38.479	307.470	274.458	85.832	67.571	−113.126	2.273
2700	38.533	308.924	275.708	89.683	66.291	−120.052	2.323
2800	38.586	310.326	276.919	93.539	−225.973	−120.707	2.252
2900	38.640	311.681	278.095	97.400	−226.243	−116.943	2.106
3000	38.694	312.992	279.236	101.267	−226.522	−113.169	1.970
3100	38.749	314.262	280.346	105.139	−226.809	−109.386	1.843
3200	38.805	315.493	281.425	109.017	−227.106	−105.593	1.724
3300	38.862	316.688	282.475	112.900	−227.412	−101.791	1.611
3400	38.921	317.849	283.499	116.789	−227.727	−97.980	1.505
3500	38.982	318.978	284.497	120.684	−228.052	−94.159	1.405
3600	39.045	320.077	285.470	124.586	−228.388	−90.329	1.311
3700	39.111	321.148	286.420	128.494	−228.734	−86.489	1.221
3800	39.180	322.191	287.347	132.408	−229.091	−82.640	1.136
3900	39.252	323.210	288.254	136.330	−229.459	−78.781	1.055
4000	39.328	324.205	289.140	140.259	−229.840	−74.913	0.978
4100	39.408	325.177	290.007	144.195	−230.234	−71.035	0.905
4200	39.492	326.128	290.856	148.140	−230.642	−67.147	0.835
4300	39.581	327.058	291.687	152.094	−231.064	−63.249	0.768
4400	39.674	327.969	292.501	156.057	−231.502	−59.342	0.704
4500	39.772	328.862	293.300	160.029	−231.955	−55.424	0.643
4600	39.876	329.737	294.082	164.011	−232.426	−51.496	0.585
4700	39.984	330.596	294.850	168.004	−232.914	−47.557	0.529
4800	40.098	331.439	295.603	172.008	−233.420	−43.608	0.475
4900	40.218	332.267	296.343	176.024	−233.946	−39.648	0.423
5000	40.342	333.080	297.070	180.052	−234.491	−35.677	0.373
5100	40.473	333.880	297.784	184.093	−235.056	−31.696	0.325
5200	40.609	334.668	298.486	188.147	−235.642	−27.703	0.278
5300	40.751	335.443	299.176	192.215	−236.248	−23.698	0.234
5400	40.898	336.206	299.854	196.297	−236.876	−19.682	0.190
5500	41.051	336.957	300.522	200.395	−237.525	−15.654	0.149
5600	41.209	337.699	301.179	204.507	−238.195	−11.614	0.108
5700	41.372	338.429	301.826	208.636	−238.886	−7.561	0.069
5800	41.541	339.150	302.464	212.782	−239.598	−3.497	0.031
5900	41.714	339.862	303.092	216.945	−240.331	0.580	−0.005
6000	41.892	340.564	303.710	221.125	−241.084	4.670	−0.041

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K) = [100.4 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 781 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-355.6 \pm 12.6]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [9.83 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

A direct measurement of the enthalpy of formation has not been made. An estimate of $\Delta_f H°$ is obtained by a method suggested by Parker.[1] Biltz and Messerknecht[2] have measured the enthalpies of solution of $BeCl_2$(cr) and $BeBr_2$(cr) in aqueous HCl (18.69%). Samples[3] of the dihalides were prepared from reactions of BeO–C mixtures with the halogens at elevated temperatures. We assume that the two dihalides had similar structures, i.e. α form. $\Delta_f H°(BeBr_2$, in 18.7% HCl, 298.15 K) is estimated as $-140.1\ kcal·mol^{-1}$ by combining $\Delta_{sol} H°$ of $BeCl_2$(cr) with $\Delta_f H°$(α–$BeCl_2$, cr, 298.15 K) = $-117.3 \pm 0.8\ kcal·mol^{-1}$ [4] and twice the difference in $\Delta_f H°$(HCl·8.8H_2O, 298.15 K) and $\Delta_f H°$(HBr·8.8H_2O, 298.15 K) which is $-21.2\ kcal·mol^{-1}$.[5] The heat associated with the interchange of the aqueous anions is assumed to be negligible. Combination of the estimated value for $\Delta_f H°(BeBr_2$, in 18.7% HCl, 298.15 K) with $\Delta_{sol} H° = -55.7\ kcal·mol^{-1}$ [2] gives $\Delta_f H°(BeBr_2$, cr, 298.15 K) = $-84.4\ kcal·mol^{-1}$ which is essentially the value adopted by NBS.[6] Subsequent measurements by Biltz *et al.*[7] in less concentrated HCl(1.48%) solutions lead to $\Delta_f H°(298.15\ K)$ equal to $-85.6\ kcal·mol^{-1}$ by a similar route. We adopt an average value of $-85.0\ kcal·mol^{-1}$($-355.64\ kJ·mol^{-1}$) but emphasize that the uncertainty in $\Delta_f H°$ is much greater than that indicated ($-1.0\ kcal·mol^{-1}$) by the agreement of these two results. A combined total uncertainty of $\pm 3.0\ kcal·mol^{-1}$ ($\pm 12.552\ kJ·mol^{-1}$) is believed to be more realistic.

Heat Capacity and Entropy

No low–temperature heat capacity or high–temperature enthalpy measurements have been reported. We estimate $C_p°(298.15\ K) = 15.78\ cal·K^{-1}·mol^{-1}$ from the reaction BeF_2(cr) + 2LiBr(cr) = $BeBr_2$(cr) + 2LiF(cr) by assuming $\Delta C_p° = 0$. Comparison of this value with $C_p°$ data for α,β–$BeCl_2$[4] suggests that our estimate is reasonable. $C_p°$ data above 298 K are estimated graphically by comparison with those for α,β–$BeCl_2$ and $MgCl_2$.[4]

Several methods of estimation predict that the value of $S°(298.15\ K)$ should lie near $24.0\ cal·K^{-1}·mol^{-1}$. Application of the Berthelot principle[8] to the process $SrBr_2$(cr) + Be(cr) = Sr(cr) + $BeBr_2$(cr) and additive entropy constants[9] give values of 24.1 and $24.0\ cal·K^{-1}·mol^{-1}$, respectively. A graphical comparison of the standard entropies for other alkaline–earth dihalides[4] suggests values for $S°(298.15\ K)$ in the range 23.5–24.5 $cal·K^{-1}·mol^{-1}$. Literature estimates have included (in $cal·K^{-1}·mol^{-1}$) 29[10] and 22.[11] We adopt $S°(298.15\ K) = 24.0 \pm 1.0\ cal·K^{-1}·mol^{-1}$ ($100.416 \pm 4.184\ J·K^{-1}·mol^{-1}$).

Fusion Data

The reported melting points for $BeBr_2$ show an unusual amount of scatter. Values of T_{fus} include 761 K,[12] 763 K,[13] and 779–781 K.[14] Semenenko and Naumova[14] reported encountering difficulties in handling $BeBr_2$ due to its hygroscopic nature and susceptibility to oxidation by traces of oxygen. These factors could account for the discrepancies in the T_{fus}values. We tentatively adopt the highest value of 781 K[14] but believe that T_{fus} is more uncertain (±15 K) than the accuracy (±5 K) claimed in their temperature measurements.

A thermal analysis[14] of $BeBr_2$ up to temperatures near the melting point showed no polymorphic modifications. Also, the interpretation of electron–diffraction patterns for freshly sublimed $BeBr_2$ indicated that it is isostructural with the α form of $BeCl_2$. Thus, we estimate $\Delta_{fus} H° = 2.35 \pm 2.0\ kcal·mol^{-1}$ from $\Delta_{fus} S° = 3.0\ cal·K^{-1}·mol^{-1}$ which is calculated for α–$BeCl_2$.[4]

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is obtained from an analysis of the sublimation pressures reported by Rahlfs and Fischer.[12] Further details of the analysis are given on the gas–phase table. The value, $T_{sub} = 752$ K, is the temperature at which ΔG approaches zero for the process $BeBr_2$(cr) = $BeBr_2$(g). T_{sub} has been measured as 746 K.[12] The good agreement between the calculated and observed values of T_{sub} is believed to indicate the presence of only small amounts of dimer in the saturated vapor of $BeBr_2$ near the melting point. However, this conflicts with other evidence which is discussed on the gas–phase table. Our results show that $T_{sub} < T_{fus}$ which implies that the liquid phase is thermodynamically unstable under ordinary conditions.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	66.024	100.416	100.416	0.	−355.640	−337.384	59.108
300	66.149	100.825	100.417	0.122	−355.688	−337.271	58.724
400	70.626	120.475	103.066	6.963	−385.169	−324.995	42.440
500	74.810	136.710	108.216	14.247	−383.680	−310.120	32.398
600	77.613	150.608	114.151	21.874	−382.039	−295.560	25.731
700	79.705	162.735	120.244	29.744	−380.299	−281.283	20.990
800	81.337	173.487	126.240	37.798	−378.495	−267.260	17.450
900	82.634	183.144	132.035	45.998	−376.651	−253.467	14.711
1000	83.764	191.909	137.591	54.318	−374.788	−239.879	12.530
1100	84.810	199.942	142.899	62.747	−372.913	−226.479	10.755
1200	85.856	207.366	147.966	71.280	−371.030	−213.250	9.283
1300	86.902	214.280	152.804	79.919	−369.137	−200.178	8.043
1400	87.864	220.755	157.429	88.656	−367.241	−187.252	6.986
1500	88.910	226.852	161.856	97.494	−365.343	−174.462	6.075

PREVIOUS: June 1965 CURRENT: June 1975

$S°(298.15\ K)$ = [273.9 ± 2.1] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−215.8 ± 16.7] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−229.3 ± 16.7] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[227] (1)
220 (2)
1010 (1)

Ground State Quantum Weight: [1] σ = 2
Point Group: $D_{\infty h}$
Bond Distance: Be–Br = 1.91 ± 0.02 Å
Bond Angle: Br–Be–Br = 180°
Rotational Constant: B_o = [0.028916] cm^{-1}

Enthalpy of Formation

Rahlfs and Fischer[1] have reported measurements of the sublimation pressures (624–695 K) and vapor densities (736–799 K) for $BeBr_2$. Both measurements were complicated by significant reaction of the dibromide with the quartz apparatus. Assuming the reaction to be $2BeBr_2(cr) + SiO_2(cr) = SiBr_4(g) + 2BeO(cr)$, Rahlfs and Fischer[1] corrected their measured total pressure for the partial pressure of the tetrabromide. Results of a 2nd and 3rd law analyses of their data are tabulated below.

Measurement	No. of Points	T/K	$\Delta_{sub}H°$(298.15 K), kcal mol^{-1} 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal·mol^{-1}$
Sublimation Pressures[a]	8[b]	624–695	31.0	30.2 ± 0.1	−1.0 ± 0.8	−54.8
Vapor Densities–Total Pressures[c]	4	736–799	23.9	33.4 ± 1.0	12.4 ± 9.0	−51.6

[a]Pressures assigned to monomer. [b]One point rejected due to failure of a statistical test. [c]Pressures corrected for dimer.

The vapor density measurements[1] predict about 50% dimerization at temperatures near the melting point (T_{fus} = 781 K). This value appears to be unusually high when compared with dimerization data which are available for $BeCl_2$, $MgBr_2$, $MgCl_2$, and MgF_2.[2] Mass spectral studies of these alkaline–earth dihalides show the presence of only small amounts (1–5%) of dimer in the saturated vapors up to temperatures near their melting points. Electron–diffraction experiments on $BeBr_2$ vapor are also inconsistent with high concentrations of dimer. It is quite likely that the monomer and dimer pressures reported by Rahlfs and Fischer[1] from their vapor density measurements are unreliable. Thus, we choose to adopt $\Delta_f H°(298.15\ K) = -54.8\ kcal·mol^{-1}$ rather than the average value (−53.2 $kcal·mol^{-1}$) of these two results. The sublimation pressures[1] are assigned solely to the monomer pending resolution of the dimerization problem. Also, $\Delta_f H°(g)$ is placed in brackets to emphasize the uncertainties in $\Delta_f H°(cr)$.

Heat Capacity and Entropy

Information available on the structure of $BeBr_2$ tend to indicate that the molecule is linear. Electron–diffraction patterns[3,4] for $BeBr_2$ vapor have been successfully interpreted in terms of a linear configuration. Buchler *et al.*,[5] using electric quadrupole deflection of molecular beams to detect permanent dipole moments in molecules, have shown that for the gaseous alkaline–earth dihalides the linear form is favored by a light metal–heavy halogen combination. The matrix– isolation spectrum[6] of $BeBr_2$ shows the two infrared–active vibrations which would be expected for a linear molecule. We adopt the linear configuration. The bond length is taken from the electron–diffraction studies of Akishin.[3,4]

The asymmetric stretching (ν_3) and bending (ν_2) frequencies ahve been observed in the matrix–isolation spectrum of BeBr by Snelson.[6] The adopted frequencies are gas–phase values which were estimated by Snelson[6] from the matrix data. The infrared–inactive symmetrical stretching frequency (ν_1) is calculated from an estimated force constant by a simple valence force field approximation.[7] The stretching force constant (K = 2.430 × 10^5 dynes/cm) is assumed equal to that for BeBr.[2] Literature estimates of ν_1 include (in cm^{-1}) 230[6,8] and 209.[9] The ground state quantum weight of one is assigned by analogy with $BaCl_2$.[2]

Brewer *et al.*[8] have tabulated Gibbs energy functions for $BeBr_2$ up to 1500 K. Their values are consistently lower than ours by about 2.5 $cal·K^{-1}·mol^{-1}$. These differences are due entirely to the higher bending frequency (ν_2 = 446 cm^{-1}) which was used by Brewer *et al.*[8] This estimated value is now known to be incorrect.

References

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[2]JANAF Thermochemical Tables: $Be_2Cl_4(g)$, 6–30–65; $Mg_2Br_4(g)$, 6–30–74; $Mg_2Cl_4(g)$, 12–31–69; $Mg_2F_4(g)$, 3–31–66; BeBr(g), 6–30–75; $BaCl_2(g)$, 12–31–72.

Continued on page 428

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.917	−215.758	−215.758	INFINITE
100	40.423	221.826	318.498	−9.667	−215.341	−232.089	121.231
200	49.650	253.339	278.680	−5.068	−216.221	−248.570	64.920
250	51.746	264.655	274.778	−2.531	−217.091	−256.564	53.606
298.15	53.315	273.909	273.909	0.	−229.283	−262.754	46.033
300	53.369	274.239	273.910	0.099	−229.355	−262.962	45.786
350	54.705	282.569	274.564	2.802	−260.180	−266.871	39.828
400	55.816	289.949	276.035	5.565	−260.210	−267.826	34.974
450	56.740	296.578	277.955	8.380	−260.264	−268.774	31.199
500	57.507	302.597	280.123	11.237	−260.333	−269.716	28.177
600	58.673	313.191	284.776	17.049	−260.507	−271.578	23.643
700	59.490	322.301	289.501	22.960	−260.726	−273.406	20.402
800	60.075	330.285	294.110	28.940	−260.996	−275.200	17.969
900	60.504	337.387	298.531	34.970	−261.322	−276.956	16.074
1000	60.826	343.779	302.742	41.037	−261.712	−278.673	14.556
1100	61.072	349.588	306.741	47.132	−262.171	−280.347	13.313
1200	61.265	354.911	310.536	53.250	−262.704	−281.977	12.274
1300	61.418	359.821	314.141	59.384	−263.315	−283.559	11.394
1400	61.542	364.377	317.568	65.532	−264.009	−285.091	10.637
1500	61.643	368.627	320.832	71.692	−264.789	−286.570	9.979
1600	61.726	372.608	323.945	77.860	−280.195	−287.468	9.385
1700	61.796	376.352	326.919	84.037	−280.757	−287.906	8.846
1800	61.855	379.886	329.764	90.219	−281.348	−288.309	8.367
1900	61.906	383.232	332.491	96.407	−281.970	−288.679	7.936
2000	61.949	386.408	335.108	102.600	−282.626	−289.015	7.548
2100	61.986	389.432	337.624	108.797	−283.317	−289.318	7.196
2200	62.018	392.316	340.045	114.997	−284.047	−289.587	6.876
2300	62.047	395.073	342.378	121.200	−284.816	−289.822	6.582
2400	62.072	397.715	344.629	127.406	−285.626	−290.022	6.312
2500	62.094	400.249	346.803	133.615	−286.478	−290.188	6.063
2600	62.114	402.685	348.906	139.825	−287.372	−290.319	5.833
2700	62.131	405.029	350.941	146.037	−288.309	−290.414	5.618
2800	62.147	407.289	352.914	152.251	−580.243	−284.252	5.303
2900	62.161	409.470	354.827	158.467	−580.198	−273.682	4.930
3000	62.174	411.578	356.683	164.683	−580.174	−263.113	4.581
3100	62.185	413.617	358.487	170.901	−580.171	−252.544	4.255
3200	62.196	415.591	360.241	177.120	−580.189	−241.975	3.950
3300	62.205	417.505	361.947	183.341	−580.227	−231.406	3.663
3400	62.214	419.362	363.609	189.562	−580.284	−220.835	3.393
3500	62.222	421.166	365.228	195.783	−580.359	−210.262	3.138
3600	62.230	422.919	366.806	202.006	−580.451	−199.686	2.897
3700	62.236	424.624	368.346	208.229	−580.560	−189.108	2.670
3800	62.243	426.284	369.849	214.453	−580.685	−178.526	2.454
3900	62.249	427.901	371.317	220.678	−580.826	−167.942	2.249
4000	62.254	429.477	372.751	226.903	−580.983	−157.353	2.055
4100	62.259	431.014	374.153	233.129	−581.156	−146.760	1.870
4200	62.264	432.514	375.525	239.355	−581.345	−136.163	1.693
4300	62.268	433.979	376.868	245.581	−581.550	−125.561	1.525
4400	62.272	435.411	378.182	251.808	−581.772	−114.954	1.365
4500	62.276	436.810	379.469	258.036	−582.012	−104.341	1.211
4600	62.279	438.179	380.731	264.263	−582.270	−93.724	1.064
4700	62.283	439.519	381.967	270.491	−582.547	−83.100	0.924
4800	62.286	440.830	383.180	276.720	−582.843	−72.471	0.789
4900	62.289	442.114	384.370	282.949	−583.160	−61.835	0.659
5000	62.291	443.373	385.537	289.178	−583.499	−51.192	0.535
5100	62.294	444.606	386.683	295.407	−583.859	−40.542	0.415
5200	62.296	445.816	387.809	301.636	−584.242	−29.885	0.300
5300	62.299	447.003	388.915	307.866	−584.649	−19.220	0.189
5400	62.301	448.167	390.001	314.096	−585.081	−8.548	0.083
5500	62.303	449.310	391.069	320.326	−585.537	2.133	−0.020
5600	62.305	450.433	392.119	326.557	−586.019	12.822	−0.120
5700	62.307	451.536	393.152	332.787	−586.528	23.520	−0.216
5800	62.308	452.619	394.168	339.018	−587.062	34.227	−0.308
5900	62.310	453.684	395.168	345.249	−587.624	44.944	−0.398
6000	62.312	454.732	396.152	351.480	−588.213	55.670	−0.485

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K) = [217.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 58.3 \pm 12.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 60.7 \pm 12.6\ kJ·mol^{-1}$

Electronic levels and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
A^2	27970	4

$\omega_e = 845.29\ cm^{-1}$ $\omega_e x_e = 4.831\ cm^{-1}$ $\sigma = 1$
$B_e = [0.769]\ cm^{-1}$ $\alpha_e = [0.0063]\ cm^{-1}$ $r_e = [1.75]$ Å

Enthalpy of Formation

Novikov[1] measured 39 bands in the ultraviolet spectrum of BeCl(g). A linear extrapolation leads to a ground state dissociation energy of 36,555 cm^{-1}. The authors assumed that the non–crossing rule applied and that the ground and first excited states had a common dissociation limit. However, in the analogous case of BeF, treated in the same way by the above authors, it was shown by Mann[2] that these assumptions were not correct. If it is assumed that the excited state dissociates $A^2\Pi \rightarrow Be(^3P) + F(^2P)$ and the ground state $X^2\Sigma \rightarrow Be(^1S_0) + F(^2P)$ then ν_{oo} + D' should equal D" + Excitation energy of Be atom. We find ν_{oo} + D' = 27,960 + 30,390 = 58,350 and D" + E_{Be} = 36,555 + 21,981 = 58,536 which is excellent agreement. Thus, the dissociation energy to ground state atoms is taken as 104.5 $kcal·mol^{-1}$ which leads to a enthalpy of formation of 3 $kcal·mol^{-1}$using reaction a.

Greenbaum *et al.*[3] report equilibrium constants for reaction b in the temperature range 1573–1724 K using the molecular flow effusion method. Also Hildenbrand *et al.*[4] report equilibrium constants for reaction c and d which were calculated from mass spectrometric ion intensities. The $\Delta_f H°(298.15\ K)$ values by 2nd and 3rd law analysis for these data and the corresponding $\Delta_f H°(298.15\ K)$ values are listed below.

Author	Method	Reaction	T/K	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Novikov	Spectroscopic	(a) BeCl(g) → Be(g) + Cl(g)		104.5			2.677
Greenbaum	K_p	(b) BeCl2(g) + Be(l) →	1573–1724	93.56 ± 7			5.2
		2 BeCl(g)			85.87	−4.521	1.3
Hildenbrand	K_p from Mass	(c) Be(g) + AlCl(g) → BeCl(g)	1382–1554	27.5 ± 2			16.5 ± 3
	Spectroscopy	+ Al(g)			26.25	−.779	15.3 ± 2
		(d) Be(g) + BeCl(g) → 2 BeCl(g)	1382–1536	33.41 ± 8			12.8 ± 5
					36.08	2.198	14.1 ± 2.5

The equilibrium data of Greenbaum *et al.*[3] was not weighted, since calculations indicated the possiblility of reaction of BeCl(g) with the Al_2O_3 tube at the temperatures and pressures used. The data of Hildenbrand *et al.*[4] which reflect the true gas phase equilibria and appear consistent with each other were adopted yielding $\Delta_f H°(298.15\ K) = 14.5\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The vibrational constants used to calculate the functions were derived by Novikov[1] from a two constant equation $[\omega_o'' - (2\nu'' + 1)\omega_o''x_o'' = \Delta G_o''(\nu'')]$. The electronic levels were obtained from Herzberg.[5] B_e was obtained from the estimated bond length, which was taken to be slightly less than that in $BeCl_2$(g) and α_e was estimated from the Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.860	58.331	58.331	INFINITE
100	29.118	185.044	244.568	−5.952	59.743	50.739	−26.504
200	29.867	205.369	220.449	−3.016	60.583	41.340	−10.797
250	30.735	212.124	218.131	−1.502	60.696	36.513	−7.629
298.15	31.642	217.615	217.615	0.	60.668	31.856	−5.581
300	31.677	217.811	217.615	0.059	60.665	31.677	−5.516
350	32.554	222.761	218.004	1.665	60.533	26.856	−4.008
400	33.316	227.159	218.879	3.312	60.341	22.057	−2.880
450	33.957	231.121	220.023	4.994	60.109	17.285	−2.006
500	34.490	234.727	221.315	6.706	59.847	12.541	−1.310
600	35.301	241.092	224.095	10.198	59.256	3.134	−0.273
700	35.872	246.579	226.924	13.758	58.589	−6.168	0.460
800	36.285	251.397	229.688	17.367	57.851	−15.370	1.004
900	36.596	255.690	232.343	21.012	57.043	−24.475	1.420
1000	36.836	259.558	234.875	24.684	56.164	−33.486	1.749
1100	37.029	263.079	237.281	28.378	55.211	−42.405	2.014
1200	37.187	266.308	239.567	32.089	54.183	−51.235	2.230
1300	37.319	269.289	241.740	35.814	53.077	−59.975	2.410
1400	37.433	272.059	243.808	39.552	51.892	−68.627	2.561
1500	37.533	274.646	245.779	43.300	50.624	−77.192	2.688
1600	37.622	277.071	247.659	47.058	34.737	−85.144	2.780
1700	37.702	279.354	249.457	50.824	33.700	−92.605	2.845
1800	37.776	281.511	251.179	54.598	32.646	−100.004	2.902
1900	37.844	283.555	252.829	58.379	31.572	−107.345	2.951
2000	37.908	285.498	254.415	62.167	30.478	−114.628	2.994
2100	37.968	287.349	255.939	65.961	29.364	−121.856	3.031
2200	38.025	289.117	257.407	69.760	28.228	−129.030	3.064
2300	38.080	290.808	258.823	73.566	27.069	−136.152	3.092
2400	38.133	292.430	260.190	77.376	25.886	−143.224	3.117
2500	38.184	293.988	261.511	81.192	24.680	−150.245	3.139
2600	38.233	295.486	262.789	85.013	23.448	−157.218	3.159
2700	38.282	296.930	264.027	88.839	22.190	−164.143	3.176
2800	38.329	298.323	265.227	92.669	−270.050	−164.798	3.074
2900	38.376	299.669	266.392	96.505	−270.297	−161.035	2.901
3000	38.423	300.971	267.523	100.345	−270.553	−157.263	2.738
3100	38.469	302.232	268.622	104.189	−270.821	−153.482	2.586
3200	38.515	303.454	269.692	108.038	−271.101	−149.693	2.443
3300	38.562	304.639	270.733	111.892	−271.395	−145.894	2.309
3400	38.609	305.791	271.747	115.751	−271.704	−142.087	2.183
3500	38.656	306.911	272.736	119.614	−272.027	−138.270	2.064
3600	38.705	308.001	273.700	123.482	−272.368	−134.443	1.951
3700	38.754	309.062	274.642	127.355	−272.725	−130.607	1.844
3800	38.805	310.096	275.561	131.233	−273.101	−126.761	1.742
3900	38.857	311.105	276.460	135.116	−273.495	−122.905	1.646
4000	38.911	312.089	277.338	139.004	−273.909	−119.038	1.554
4100	38.967	313.051	278.198	142.898	−274.343	−115.161	1.467
4200	39.025	313.991	279.039	146.798	−274.799	−111.273	1.384
4300	39.085	314.910	279.862	150.703	−275.276	−107.374	1.304
4400	39.148	315.809	280.669	154.615	−275.775	−103.464	1.228
4500	39.212	316.689	281.460	158.533	−276.296	−99.542	1.155
4600	39.280	317.552	282.235	162.458	−276.841	−95.608	1.086
4700	39.350	318.397	282.995	166.389	−277.410	−91.662	1.019
4800	39.423	319.227	283.742	170.328	−278.002	−87.704	0.954
4900	39.499	320.040	284.474	174.274	−278.619	−83.733	0.893
5000	39.578	320.839	285.193	178.228	−279.261	−79.749	0.833
5100	39.660	321.624	285.900	182.190	−279.927	−75.752	0.776
5200	39.745	322.394	286.595	186.160	−280.618	−71.742	0.721
5300	39.833	323.152	287.277	190.139	−281.334	−67.719	0.667
5400	39.923	323.898	287.948	194.126	−282.075	−63.681	0.616
5500	40.017	324.631	288.609	198.123	−282.841	−59.630	0.566
5600	40.114	325.353	289.258	202.130	−283.631	−55.564	0.518
5700	40.213	326.064	289.898	206.146	−284.446	−51.485	0.472
5800	40.316	326.764	290.528	210.173	−285.285	−47.390	0.427
5900	40.421	327.454	291.148	214.210	−286.147	−43.281	0.383
6000	40.529	328.135	291.758	218.257	−287.032	−39.158	0.341

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = [213.0 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [970 \pm 84]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [979 \pm 84]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma_g^+$	0	1
$^3\Pi_u$	[10000]	6
$^1\Pi_u$	[15000]	2
$^3\Sigma_g^-$	[30000]	3
$^1\Delta$	[35000]	2
$^1\Sigma^+$	[40000]	1

$\omega_e = [700]\ cm^{-1}$ $\omega_e x_e = [4.8]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.7241]\ cm^{-1}$ $\alpha_e = [0.0071]\ cm^{-1}$ $r_e = [1.8]$Å

Enthalpy of Formation

Krasnow[1] has reported calculations of the ionization potentials (IP) for the monohalides (MX, where X = F, Cl, Br, and I) of Group IIA elements (M = Mg, Ca, Sr, and Ba). Based on his data we obtain graphically the value IP(BeCl, g) = 8.9 ± 0.5 eV. The value of $\Delta_f H°(298.15\ K)$ is derived as 219 ± 15 kcal·mol^{-1}, using $\Delta_f H°$(BeCl, g, 0 K) = 13.9 kcal·mol^{-1}. Beckett[2] reported the ionization potential of BeCl(g) to be approximately 9 ± 1 eV, yielding $\Delta_f H°(298.15\ K) = 222 \pm 23$ kcal·mol^{-1}. Hildenbrand[9] measured the appearance potential (AP) of $BeCl^+$(g) to be 9.5 ± 0.7 cal·K^{-1}·mol^{-1} which is on the same order of the above IP values, and assumed that IP($BeCl^+$, g) = AP($BeCl^+$, g) = 9.5 ± 0.7 eV. Using this IP value, we obtain $\Delta_f H°(298.15\ K) = 234 \pm 20$ kcal·mol^{-1} which is adopted.

Heat Capacity and Entropy

The six electronic states are obtained from Fougere.[3] The electronic levels are estimated by comparison with those of the isoelectronic molecules, BeS,[4] BeO,[5,6] and MgO.[5,7] The values of ω_e, $\omega_e x_e$ are estimated by comparison with those for BeCl(g) and LiCl(g). B_e and α_e are calculated using the method suggested by Herzberg.[5] The bond distance is estimated.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.990	970.392		
100	29.155	179.796	240.610	−6.081			
200	30.594	200.327	215.883	−3.111			
250	31.734	207.277	213.488	−1.553			
298.15	32.744	212.955	212.955	0.	979.056	945.379	−165.626
300	32.780	213.157	212.955	0.061	979.093	945.170	−164.569
350	33.652	218.278	213.358	1.722	980.057	939.439	−140.204
400	34.356	222.820	214.262	3.423	980.957	933.574	−121.912
450	34.918	226.900	215.443	5.155	981.814	927.599	−107.673
500	35.370	230.603	216.777	6.913	982.638	921.531	−96.272
600	36.036	237.115	219.639	10.486	984.206	909.161	−79.149
700	36.495	242.706	222.544	14.113	985.685	896.535	−66.900
800	36.828	247.602	225.377	17.780	987.084	883.703	−57.700
900	37.082	251.955	228.093	21.476	988.406	870.700	−50.534
1000	37.287	255.873	230.678	25.195	989.652	857.554	−44.794
1100	37.463	259.435	233.133	28.933	990.822	844.287	−40.092
1200	37.628	262.702	235.463	32.687	991.916	830.917	−36.169
1300	37.800	265.721	237.676	36.459	992.934	817.459	−32.846
1400	37.993	268.529	239.780	40.248	993.879	803.925	−29.995
1500	38.224	271.158	241.785	44.059	994.752	790.326	−27.522
1600	38.503	273.633	243.699	47.894	981.021	777.197	−25.373
1700	38.842	275.977	245.530	51.761	982.164	764.422	−23.488
1800	39.247	278.209	247.284	55.665	983.318	751.581	−21.810
1900	39.722	280.343	248.968	59.613	984.490	738.675	−20.308
2000	40.267	282.394	250.588	63.612	985.686	725.706	−18.954
2100	40.881	284.373	252.150	67.669	986.913	712.677	−17.727
2200	41.558	286.290	253.659	71.790	988.177	699.589	−16.610
2300	42.290	288.154	255.118	75.982	989.483	686.442	−15.590
2400	43.068	289.970	256.533	80.250	990.836	673.238	−14.653
2500	43.883	291.744	257.906	84.597	992.240	659.976	−13.789
2600	44.722	293.482	259.241	89.027	993.696	646.657	−12.991
2700	45.575	295.186	260.541	93.542	995.206	633.281	−12.252
2800	46.431	296.859	261.808	98.142	705.814	626.070	−11.679
2900	47.278	298.503	263.045	102.828	708.496	623.175	−11.225
3000	48.108	300.120	264.254	107.597	711.248	620.186	−10.798
3100	48.910	301.710	265.437	112.448	714.065	617.104	−10.398
3200	49.677	303.275	266.595	117.378	716.944	613.931	−10.021
3300	50.403	304.815	267.730	122.382	719.879	610.666	−9.666
3400	51.082	306.330	268.843	127.457	722.866	607.312	−9.330
3500	51.709	307.820	269.935	132.597	725.897	603.870	−9.012
3600	52.283	309.285	271.008	137.797	728.968	600.340	−8.711
3700	52.802	310.724	272.062	143.052	732.070	596.724	−8.424
3800	53.264	312.139	273.098	148.355	735.199	593.024	−8.152
3900	53.670	313.528	274.117	153.703	738.348	589.242	−7.892
4000	54.022	314.891	275.119	159.088	741.509	585.378	−7.644
4100	54.320	316.229	276.106	164.505	744.677	581.436	−7.408
4200	54.568	317.541	277.077	169.950	747.845	577.416	−7.181
4300	54.768	318.827	278.033	175.417	751.009	573.321	−6.964
4400	54.922	320.088	278.974	180.902	754.161	569.152	−6.757
4500	55.034	321.324	279.902	186.400	757.298	564.912	−6.557
4600	55.108	322.534	280.815	191.908	760.415	560.602	−6.366
4700	55.147	323.720	281.716	197.421	763.507	556.225	−6.182
4800	55.154	324.881	282.603	202.936	766.569	551.782	−6.005
4900	55.132	326.018	283.477	208.450	769.599	547.276	−5.834
5000	55.085	327.132	284.339	213.962	772.594	542.709	−5.670
5100	55.016	328.222	285.189	219.467	775.550	538.082	−5.511
5200	54.928	329.289	286.027	224.964	778.464	533.397	−5.358
5300	54.822	330.335	286.853	230.452	781.336	528.656	−5.210
5400	54.703	331.358	287.668	235.928	784.162	523.862	−5.067
5500	54.572	332.361	288.471	241.392	786.941	519.016	−4.929
5600	54.431	333.343	289.264	246.842	789.673	514.120	−4.796
5700	54.282	334.305	290.046	252.278	792.357	509.176	−4.666
5800	54.127	335.248	290.817	257.698	794.991	504.185	−4.541
5900	53.968	336.172	291.578	263.103	797.575	499.148	−4.419
6000	53.805	337.077	292.329	268.492	800.109	494.069	−4.301

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [246.49]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-574 \pm 42]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-573 \pm 42]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[500] (1)
[270] (2)
[1300] (1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: $C_{\infty v}$

Bond Distances: Be–Cl = [1.77] Å; Be–F = [1.43] Å

Bond Angle: Cl–Be–F = [180]°

Rotational Constant: $B_o = [0.129706]\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation was estimated by assuming $\Delta_f H° = 0$ for the reaction $BeF_2 + BeCl_2 \rightarrow 2BeClF$.

Heat Capacity and Entropy

The structure, bond lengths and frequencies were all estimated from the properties of $BeCl_2$ and BeF_2.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.704	−573.977	−573.977	INFINITE
100	34.801	200.224	286.766	−8.654	−573.876	−575.879	300.808
200	44.537	227.702	250.869	−4.633	−573.416	−578.060	150.974
250	47.364	237.961	247.289	−2.332	−573.267	−579.240	121.026
298.15	49.413	246.486	246.486	0.	−573.208	−580.397	101.683
300	49.483	246.792	246.487	0.091	−573.207	−580.442	101.064
350	51.183	254.552	247.096	2.609	−573.221	−581.647	86.806
400	52.601	261.482	248.469	5.205	−573.280	−582.847	76.112
450	53.805	267.748	250.268	7.866	−573.368	−584.038	67.793
500	54.832	273.472	252.307	10.583	−573.474	−585.218	61.137
600	56.463	283.621	256.701	16.152	−573.725	−587.544	51.150
700	57.663	292.419	261.189	21.861	−574.019	−589.824	44.013
800	58.556	300.180	265.588	27.674	−574.357	−592.060	38.658
900	59.231	307.118	269.824	33.565	−574.746	−594.250	34.489
1000	59.749	313.387	273.872	39.515	−575.192	−596.394	31.152
1100	60.152	319.101	277.727	45.511	−575.702	−598.490	28.420
1200	60.472	324.349	281.397	51.543	−576.283	−600.536	26.141
1300	60.729	329.200	284.890	57.603	−576.938	−602.531	24.210
1400	60.938	333.708	288.218	63.687	−577.673	−604.473	22.553
1500	61.109	337.919	291.392	69.789	−578.491	−606.359	21.115
1600	61.252	341.867	294.425	75.908	−593.933	−607.662	19.838
1700	61.373	345.584	297.326	82.039	−594.527	−608.502	18.697
1800	61.474	349.095	300.106	88.182	−595.142	−609.307	17.682
1900	61.562	352.421	302.772	94.334	−595.781	−610.077	16.772
2000	61.636	355.581	305.334	100.494	−596.443	−610.812	15.953
2100	61.701	358.590	307.799	106.661	−597.128	−611.514	15.211
2200	61.758	361.462	310.174	112.834	−597.836	−612.182	14.535
2300	61.808	364.208	312.464	119.012	−598.566	−612.818	13.918
2400	61.851	366.840	314.675	125.195	−599.318	−613.422	13.351
2500	61.890	369.365	316.812	131.382	−600.090	−613.993	12.829
2600	61.925	371.793	318.881	137.573	−600.883	−614.534	12.346
2700	61.956	374.131	320.884	143.767	−601.696	−615.044	11.899
2800	61.983	376.385	322.826	149.964	−893.483	−609.300	11.367
2900	62.008	378.560	324.711	156.163	−893.268	−599.155	10.792
3000	62.031	380.663	326.541	162.365	−893.054	−589.017	10.256
3100	62.051	382.697	328.320	168.570	−892.839	−578.886	9.754
3200	62.070	384.667	330.050	174.776	−892.626	−568.761	9.284
3300	62.087	386.578	331.734	180.984	−892.413	−558.644	8.843
3400	62.102	388.431	333.375	187.193	−892.203	−548.533	8.427
3500	62.117	390.232	334.973	193.404	−891.995	−538.428	8.036
3600	62.130	391.982	336.533	199.616	−891.790	−528.329	7.666
3700	62.142	393.684	338.055	205.830	−891.589	−518.235	7.316
3800	62.153	395.342	339.540	212.045	−891.393	−508.148	6.985
3900	62.163	396.956	340.992	218.261	−891.203	−498.065	6.671
4000	62.173	398.530	342.411	224.477	−891.020	−487.986	6.372
4100	62.182	400.066	343.798	230.695	−890.845	−477.913	6.089
4200	62.190	401.564	345.156	236.914	−890.678	−467.843	5.818
4300	62.198	403.028	346.485	243.133	−890.522	−457.778	5.561
4400	62.205	404.457	347.786	249.353	−890.377	−447.716	5.315
4500	62.211	405.855	349.061	255.574	−890.244	−437.657	5.080
4600	62.218	407.223	350.311	261.795	−890.125	−427.600	4.856
4700	62.224	408.561	351.536	268.017	−890.020	−417.547	4.641
4800	62.229	409.871	352.738	274.240	−889.930	−407.495	4.434
4900	62.234	411.154	353.917	280.463	−889.858	−397.445	4.237
5000	62.239	412.412	355.074	286.687	−889.802	−387.397	4.047
5100	62.244	413.644	356.211	292.911	−889.765	−377.349	3.865
5200	62.248	414.853	357.327	299.136	−889.748	−367.302	3.690
5300	62.252	416.039	358.423	305.361	−889.750	−357.255	3.521
5400	62.256	417.202	359.501	311.586	−889.773	−347.207	3.359
5500	62.260	418.345	360.561	317.812	−889.817	−337.160	3.202
5600	62.263	419.467	361.603	324.038	−889.883	−327.111	3.051
5700	62.266	420.569	362.627	330.264	−889.971	−317.061	2.906
5800	62.270	421.652	363.636	336.491	−890.082	−307.008	2.765
5900	62.272	422.716	364.628	342.718	−890.215	−296.954	2.629
6000	62.275	423.763	365.605	348.946	−890.372	−286.898	2.498

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K) = 82.68 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 688\ K$

$\Delta_f H°(0\ K) = -491.8 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -490.9 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 8.66 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Johnson and Gilliland[1] have directly reacted beryllium and chlorine and obtained $\Delta_f H° = -118.03 \pm 0.56\ kcal \cdot mol^{-1}$ though the crystal form of the product was unknown. Gross, Heyman, Greene and Bingha[2] also by direct combustion of the elements obtain $\Delta_f H° = -117.1 \pm 0.4\ kcal \cdot mol^{-1}$. The crystal form of the sample was deduced to be α' by a comparison experiment, the assumption is made here that α and α' are identical. Thompson, Sinke and Stull[3] by solution calorimetry report a $\Delta_f H° = -118.25 \pm 0.5\ kcal \cdot mol^{-1}$. Initially this sample was reported to be of unknown crystal form. However, Sinke[4] reports that an x–ray of the sample used has been reinterpreted, in the light of more recent data, as being approximately 50% α' and 50% β. Using the enthalpies of transition adopted for these tables, enthalpies of formation of $-117.3 \pm 0.8\ kcal \cdot mol^{-1}$ for α and $-118.6 \pm 0.8\ kcal \cdot mol^{-1}$ for β have been adopted as being the most consistent with all measurements.

Heat Capacity and Entropy

McDonald and Oetting[5] have measured the heat capacity of the α' form from 13 and 304 K and the enthalpy (relative to the α' form) from 676 to 688 K. The assumption has been made that the α and α' forms are identical and the heat capacity curve between 304 and 676 K has been estimated graphically. The entropy was obtained by integration of the heat capacity curve assuming $S°(13\ K) = 0.16\ cal \cdot K^{-1} \cdot mol^{-1}$. The sample was identified as α' by x–ray diffraction both before and after the experiments.

Fusion Data

The temperature and enthalpy of melting were reported by McDonald and Oetting.[5] Several investigations of the melting point are in disagreement mainly due to the uncertainty of the crystal form of the material and a solid state transition just below the pure α–liquid melting point.

Sublimation Data

The adopted enthalpy of sublimation was calculated from that of the β form and enthalpy of the α–β transition at 298.15 K.

References

[1]W. H. Johnson and A. A. Gilliland, J. Res. Nat. Bur. Stand. **65A,** 59 (1961).
[2]P. Gross, C. Hayman, P. D. Greene and J. T. Bingham, Fulmer Research Institute, Report R. 163/SR.1/Sept. 1964 under Contract AF61 (052)–447.
[3]C J. Thompson, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 380 (1962).
[4]G. C. Sinke, personal communication, (February 1965)
[5]R. A. McDonald and F. L. Oetting, J. Phys. Chem., **69**, 3839 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.979	−491.795	−491.795	INFINITE
100	33.660	28.974	131.942	−10.297	−493.064	−477.011	249.165
200	53.555	59.036	88.261	−5.845	−492.228	−461.208	120.455
298.15	64.852	82.676	82.676	0.	−490.930	−446.254	78.182
300	65.019	83.078	82.677	0.120	−490.903	−445.977	77.651
400	72.760	102.907	85.329	7.031	−489.303	−431.234	56.313
500	77.530	119.678	90.566	14.556	−487.453	−416.927	43.556
600	80.082	134.040	96.644	22.437	−485.471	−403.007	35.085
688.000	81.278	145.083	102.148	29.539	---- ALPHA <--> LIQUID ----		
700	81.358	146.489	102.896	30.515	−483.457	−389.422	29.059
800	82.257	157.413	109.042	38.697	−481.471	−376.125	24.558
900	83.023	167.146	114.967	46.961	−479.519	−363.074	21.072
1000	83.680	175.929	120.631	55.297	−477.603	−350.239	18.295
1100	84.230	183.931	126.027	63.694	−475.728	−337.593	16.031
1200	84.672	191.280	131.163	72.140	−473.902	−325.117	14.152
1300	85.007	198.071	136.052	80.625	−472.134	−312.790	12.568
1400	85.234	204.380	140.710	89.138	−470.435	−300.597	11.215
1500	85.354	210.265	145.153	97.668	−468.817	−288.523	10.047

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 75.81 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [682]\ K$
$T_{trs} = 676\ K\ (\beta \rightarrow \alpha)$

$\Delta_f H°(0\ K) = -496.5 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -496.2 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [15.27 \pm 0.63]\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = [6.82 \pm 0.63]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

See the α–crystal table for details.

Heat Capacity and Entropy

McDonald and Oetting[1] have measured the heat capacity of the β–form from 13 to 304 K and the enthalpy of the β–form from 298 to 676 K. The entropy was obtained by integration of the heat capacity curve based on $S°(13\ K) = 0.06\ cal \cdot K^{-1} \cdot mol^{-1}$. The sample was identified as β–$BeCl_2$ both before and after the low temperature experiments.

Fusion Data

The temperature and enthalpy of melting were obtained from cross over point of the tables for β–$BeCl_2$ and liquid $BeCl_2$.

Transition Data

The temperature of the β → α transition was obtained from McDonald and Oetting.[1] The enthalpy of the transiton is a function of the heat capacity curve chosen for α–$BeCl_2$ between 298 and 676 K. A straight line interpolation was used by McDonald and Oetting, which gives a different result (1.49 $kcal \cdot mol^{-1}$) than the curve employed here. It should also be noted that the transitional enthalpy is not included in this table, which is for β–$BeCl_2$ only.

Sublimation Data

The enthalpy of sublimation was determined by 2nd and 3rd law analysis of vapor pressure data as described fully on the table for $BeCl_2$(g).

References

[1]R. A. McDonald and F. L. Oetting, J. Phys. Chem., **69**, 3839 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.418	−496.527	−496.527	INFINITE
100	31.777	24.104	127.616	−10.351	−498.412	−481.871	251.704
200	51.798	52.928	81.211	−5.657	−497.332	−465.090	121.469
298.15	62.425	75.814	75.814	0.	−496.222	−449.501	78.751
300	62.593	76.201	75.815	0.116	−496.200	−449.211	78.215
400	68.701	95.099	78.350	6.700	−494.928	−433.736	56.640
500	72.802	110.900	83.324	13.788	−493.514	−418.599	43.731
600	75.814	124.449	89.075	21.224	−491.977	−403.758	35.150
700	78.157	136.327	94.995	28.933	−490.331	−389.184	29.041
800	79.956	146.885	100.833	36.841	−488.619	−374.851	24.475
900	81.379	156.387	106.487	44.910	−486.863	−360.735	20.936
1000	82.550	165.025	111.915	53.109	−485.084	−346.816	18.116
1100	83.387	172.934	117.108	61.408	−483.306	−333.075	15.816
1200	84.015	180.217	122.068	69.780	−481.555	−319.495	13.907
1300	84.475	186.961	126.803	78.205	−479.846	−306.060	12.298
1400	84.782	193.234	131.327	86.669	−478.196	−292.754	10.923
1500	84.935	199.089	135.652	95.157	−476.621	−279.564	9.735

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = [79.727]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 688\ K$

$\Delta_f H°(298.15\ K) = [-491.313]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 8.66 \pm 0.25\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the α–$BeCl_2$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(688\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

McDonald and Oetting[1] have measured the enthalpy of the liquid, relative to α–$BeCl_2$, from 688 to 713 K. The heat capacity was assumed constant above this point and also below the melting point to 460 K where a glass transition was assumed. Below 416 K the heat capacity was assumed to be that of β–$BeCl_2$. The entropy is calculated in a manner analagous to that used for the enthalpy of formation.

Fusion

Refer to the α–crystal table for details.

Vaporization Data

The boiling point and enthalpy of vaporization are calculated from the cross over point of the $BeCl_2$ (l) and (g) tables. The analysis of the liquid vapor pressure data is given on the table for $BeCl_2$(g).

References

[1] R. A. McDonald and F. L. Oetting, J. Phys. Chem., **69**, 3839 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	62.425	79.727	79.727	0.	−491.313	−445.758	78.095
300	62.593	80.114	79.728	0.116	−491.291	−445.475	77.564
400	68.701	99.012	82.263	6.700	−490.019	−430.392	56.203
460.100	71.356	108.819	85.103	10.912	GLASS <--> LIQUID		
460.100	121.420	108.819	85.103	10.912	TRANSITION		
500	121.420	118.917	87.404	15.757	−486.636	−415.729	43.431
600	121.420	141.054	94.557	27.898	−480.393	−402.138	35.009
688.000	121.420	157.671	101.591	38.583	---- ALPHA <--> LIQUID		----
700	121.420	159.771	102.570	40.040	−474.314	−389.578	29.071
800	121.420	175.984	110.756	52.182	−468.369	−377.880	24.673
900	121.420	190.286	118.814	64.324	−462.540	−366.920	21.295
1000	121.420	203.078	126.612	76.466	−456.817	−356.603	18.627
1100	121.420	214.651	134.098	88.608	−451.197	−346.854	16.471
1200	121.420	225.216	141.257	100.750	−445.675	−337.613	14.696
1300	121.420	234.935	148.094	112.892	−440.250	−328.829	13.213
1400	121.420	243.933	154.623	125.034	−434.922	−320.458	11.956
1500	121.420	252.310	160.859	137.176	−429.692	−312.465	10.881
1600	121.420	260.146	166.822	149.318	−439.095	−304.293	9.934
1700	121.420	267.507	172.531	161.460	−433.660	−296.034	9.096
1800	121.420	274.447	178.002	173.602	−428.255	−288.095	8.360
1900	121.420	281.012	183.252	185.744	−422.881	−280.455	7.710
2000	121.420	287.240	188.297	197.886	−417.540	−273.097	7.133

PREVIOUS: September 1961 CURRENT: June 1965

0	to	676 K	crystal, beta
676	to	688	crystal, alpha
above		688	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.979	−491.795	−491.795	INFINITE
100	33.660	28.974	131.942	−10.297	−493.064	−477.011	249.165
200	53.555	59.036	88.261	−5.845	−492.228	−461.208	120.455
298.15	64.852	82.676	82.676	0.	−490.930	−446.254	78.182
300	65.019	83.078	82.677	0.120	−490.903	−445.977	77.651
400	72.760	102.907	85.329	7.031	−489.303	−431.234	56.313
500	77.530	119.678	90.566	14.556	−487.453	−416.927	43.556
600	80.082	134.040	96.644	22.437	−485.471	−403.007	35.085
688.000	81.278	145.083	102.148	29.539	ALPHA <- -> LIQUID		
688.000	121.420	157.671	102.148	38.200	TRANSITION		
700	121.420	159.771	103.118	39.657	−474.314	−389.578	29.071
800	121.420	175.984	111.235	51.799	−468.369	−377.880	24.673
900	121.420	190.286	119.240	63.941	−462.540	−366.920	21.295
1000	121.420	203.078	126.995	76.083	−456.817	−356.603	18.627
1100	121.420	214.651	134.446	88.225	−451.197	−346.854	16.471
1200	121.420	225.216	141.577	100.367	−445.675	−337.613	14.696
1300	121.420	234.935	148.389	112.509	−440.250	−328.829	13.212
1400	121.420	243.933	154.896	124.651	−434.922	−320.458	11.956
1500	121.420	252.310	161.115	136.793	−429.692	−312.465	10.881
1600	121.420	260.146	167.062	148.935	−439.095	−304.293	9.934
1700	121.420	267.507	172.756	161.077	−433.660	−296.034	9.096
1800	121.420	274.447	178.215	173.219	−428.255	−288.095	8.360
1900	121.420	281.012	183.454	185.361	−422.881	−280.455	7.710
2000	121.420	287.240	188.489	197.503	−417.540	−273.097	7.133

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K)$ = [252 ± 4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -361.5 \pm 10.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -360.2 \pm 10.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[375] (1)
[230] (2)
1113 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Be–Cl = [1.77] Å
Bond Angle: Cl–Be–F = [180]°
Rotational Constant: $B_o = 0.075887\ cm^{-1}$

Enthalpy of Formation

The vapor pressure data over the crystal was assumed to be for the β–form. The 2nd and 3rd law analyses of the data are summarized below after conversion to a common process. The data were also analyzed using gaseous Gibbs energy functions based on a bending frequency of 170 cm^{-1} but no significant improvement of the results was noted.

Source	T/K	$\Delta_{sub}H°(298.15\ K)$, 2nd law, $kcal·mol^{-1}$	3rd law	Drift $cal·K^{-1}·mol^{-1}$
1	680–740*	33.5 ± 0.6	31.38	−3.4 ± 0.7
2	680–740	34.3	31.22	−4.7
1	613–663	31.6 ± 1.6	30.91	−1.3 ± 2.6
2	638–668	35.6	31.07	−7.0
3	441–518	31.4 ± 0.8	32.45	2.5 ± 1.7
3	510–600*	31.8 ± 0.3	32.07	0.40 ± 0.5
4	460–504*	32.45 ± 0.4	32.48	0.14 ± 0.8

*Points rejected due to failure of a statistical test.

It is obvious that there is no real agreement between the data sets, and some of this is undoubtedly due to the difficulty of keeping a single crystal form throughout a series of measurements. It is also doubtful that water vapor was adequately excluded in some experiments. We have adopted the only piece of work which shows adequate 2nd and 3rd law agreement, and no 3rd law trend, that is $\Delta_{sub}H° = 32.5 \pm 1\ kcal·mol^{-1}$ from.[4] It is interesting to note that all the other data can be made much more precise and its drift removed if a constant pressure is added to all points. The addition which varied from 20–30% of the lowest pressure in each data set serves to indicate the magnitude of possible systematic errors.

Heat Capacity and Entropy

The linear structure of $BeCl_2(g)$ has been confirmed by the electric deflection experiments of Buchler.[5] The bond length was obtained from the electron diffraction data of Akishin, Spirodinov and Sobelev.[6] Buchler and Klemperer[7] have reported the infra–red spectrum and assigned 1113 as the asymmetric stretch ν_3 and 482 as the bending frequency ν_2. However, Snelson[8] using matrix isolation experiments, has shown this second band to be due to beryllium chloride solid. The unobserved frequencies were estimated from a valence force field treatment by assuming that the ratio of stretching to bending force constant was 50:1, the same as for $BeF_2(g)$. This gives 230 cm^{-1} for ν_2 and 375 cm^{-1} for the symmetric stretch.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.322	−361.451	−361.451	INFINITE
100	37.378	202.989	294.816	−9.183	−361.263	−362.611	189.409
200	47.267	232.467	256.831	−4.873	−360.568	−364.234	95.128
250	49.785	243.300	253.072	−2.443	−360.350	−365.179	76.300
298.15	51.622	252.232	252.232	0.	−360.242	−366.120	64.143
300	51.685	252.552	252.233	0.096	−360.240	−366.156	63.753
350	53.221	260.638	252.868	2.719	−360.213	−367.145	54.793
400	54.497	267.831	254.297	5.413	−360.234	−368.135	48.073
450	55.563	274.313	256.167	8.166	−360.285	−369.119	42.846
500	56.455	280.215	258.281	10.967	−360.355	−370.098	38.664
600	57.830	290.636	262.828	16.685	−360.536	−372.030	32.388
700	58.809	299.629	267.458	22.520	−360.764	−373.928	27.903
800	59.517	307.530	271.983	28.438	−361.043	−375.790	24.537
900	60.042	314.572	276.331	34.417	−361.376	−377.614	21.916
1000	60.438	320.920	280.478	40.442	−361.771	−379.398	19.818
1100	60.744	326.695	284.421	46.502	−362.233	−381.139	18.099
1200	60.983	331.991	288.167	52.588	−362.766	−382.835	16.664
1300	61.174	336.880	291.729	58.697	−363.375	−384.483	15.449
1400	61.329	341.419	295.118	64.822	−364.064	−386.081	14.405
1500	61.455	345.655	298.347	70.961	−364.836	−387.628	13.498
1600	61.560	349.625	301.430	77.112	−380.230	−388.594	12.686
1700	61.648	353.360	304.376	83.273	−380.776	−389.100	11.956
1800	61.722	356.885	307.196	89.441	−381.345	−389.573	11.305
1900	61.785	360.224	309.900	95.617	−381.938	−390.014	10.722
2000	61.840	363.395	312.496	101.798	−382.557	−390.424	10.197
2100	61.887	366.413	314.992	107.985	−383.203	−390.801	9.721
2200	61.928	369.293	317.395	114.175	−383.879	−391.147	9.287
2300	61.964	372.047	319.712	120.370	−384.585	−391.462	8.890
2400	61.995	374.685	321.948	126.568	−385.325	−391.745	8.526
2500	62.023	377.216	324.108	132.769	−386.099	−391.997	8.190
2600	62.048	379.649	326.198	138.972	−386.909	−392.217	7.880
2700	62.070	381.991	328.221	145.178	−387.756	−392.405	7.592
2800	62.090	384.249	330.182	151.386	−679.599	−386.339	7.207
2900	62.108	386.428	332.084	157.596	−679.460	−375.868	6.770
3000	62.124	388.534	333.931	163.808	−679.343	−365.401	6.362
3100	62.139	390.571	335.726	170.021	−679.251	−354.938	5.981
3200	62.152	392.544	337.470	176.236	−679.184	−344.477	5.623
3300	62.164	394.457	339.168	182.451	−679.143	−334.018	5.287
3400	62.176	396.313	340.822	188.668	−679.128	−323.560	4.971
3500	62.186	398.115	342.433	194.887	−679.140	−313.102	4.673
3600	62.195	399.867	344.005	201.106	−679.179	−302.644	4.391
3700	62.204	401.571	345.537	207.326	−679.244	−292.183	4.125
3800	62.212	403.230	347.034	213.546	−679.336	−281.721	3.873
3900	62.219	404.846	348.496	219.768	−679.455	−271.256	3.633
4000	62.226	406.422	349.924	225.990	−679.600	−260.788	3.406
4100	62.232	407.958	351.321	232.213	−679.771	−250.315	3.189
4200	62.238	409.458	352.687	238.436	−679.967	−239.838	2.983
4300	62.244	410.923	354.025	244.661	−680.188	−229.357	2.786
4400	62.249	412.354	355.334	250.885	−680.433	−218.869	2.598
4500	62.253	413.753	356.617	257.110	−680.703	−208.376	2.419
4600	62.258	415.121	357.874	263.336	−680.997	−197.877	2.247
4700	62.262	416.460	359.106	269.562	−681.314	−187.371	2.082
4800	62.266	417.771	360.315	275.788	−681.653	−176.858	1.925
4900	62.270	419.055	361.501	282.015	−682.016	−166.338	1.773
5000	62.273	420.313	362.664	288.242	−682.400	−155.810	1.628
5100	62.277	421.546	363.807	294.470	−682.807	−145.274	1.488
5200	62.280	422.755	364.929	300.698	−683.235	−134.730	1.353
5300	62.283	423.942	366.031	306.926	−683.684	−124.178	1.224
5400	62.285	425.106	367.114	313.154	−684.155	−113.617	1.099
5500	62.288	426.249	368.179	319.383	−684.646	−103.046	0.979
5600	62.290	427.371	369.226	325.612	−685.157	−92.467	0.863
5700	62.293	428.474	370.256	331.841	−685.688	−81.879	0.750
5800	62.295	429.557	371.269	338.070	−686.239	−71.281	0.642
5900	62.297	430.622	372.266	344.300	−686.810	−60.674	0.537
6000	62.299	431.669	373.247	350.530	−687.399	−50.056	0.436

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

Ground State Configuration: $^2\Sigma^+$
$S°(298.15\ K) = [205.75 \pm 0.04]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -172.2 \pm 8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -169.9 \pm 8\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	50419	2
33180	4	63916	[4]
49573	2	66373	[4]

$\omega_e = 1265.9\ cm^{-1}$ $\omega_e x_e = 9.35\ cm^{-1}$ $\sigma = 1$
$B_e = 1.489\ cm^{-1}$ $\alpha_e = 0.0176\ cm^{-1}$ $r_e = 1.361$ Å

Enthalpy of Formation

$\Delta_f H°$ is based on 3rd law analysis of K_p data for three gas–phase reactions observed mass spectrometrically by Hildenbrand *et al.*[1,2] Our analysis is summarized below. Also included are data for heterogeneous reaction of Be(cr, l) with BeF_2(g), observed with a molecular–flow–effusion method by Greenbaum *et al.*[3] The mutual consistency of the gas–phase results prompts us to adopt a weighted average of -40.6 ± 2 kcal·mol^{-1} rather than the mean value of -53.1 kcal·mol^{-1} derived from the heterogeneous reaction.

Analogous studies of BeCl(g) gave a similar discrepancy which was reaffirmed by new transport studies of Gross and Lewin.[4] These authors suggested that transport via $(BeCl)_2$ provides a possible, but inconclusive, explanation of the discrepancy. This explanation may also apply to BeF, but new data would be needed to establish this.

The adopted $\Delta_f H°$ yields $D_0° = 5.98 \pm 0.1$ eV which is consistent with spectroscopic results within their probable uncertainties.[5] Spectroscopic values[1,5] include 6.3 or 6.0 ± 0.5 eV (from $A^2\Pi$) and 5.3 cal·K^{-1}·mol^{-1} (from $X^2\Sigma$). Rationales have been given[5–8] for the lowness of the value derived from the ground state. Recent calculations[13] showed that the ground–state potential energy curve is consistent with $D_0° = 5.85$ eV. The flow–effusion data[3] yield 6.52 cal·K^{-1}mol^{-1}.

Source	Method	Reaction[a]	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Hildenbrand[1]	Mass Spec.	A	1458–1609	25.9 ± 9	28.28 ± 2	−1.6 ± 5.7	−41.86 ± 1.3
		A	1321–1518	31.2 ± 2	29.09 ± 2	1.5 ± 1.5	−41.46 ± 1.3
		A	1423–1443	−4.1	30.4 ± 3	24.	−40.8 ± 1.7
		B	1321–1503	−6.7 ± 3	−7.86 ± 2	−0.8 ± 2.1	−37.46 ± 3.0
		B	1423–1443	−38.	−8.7 ± 3	20.	−38.3 ± 3.8
		C	1423–1443	12.7	24.2 ± 3	8.	−38.9 ± 3.4
Greenbaum[3]	Flow Eff.	D	1420–1525	97. ± 10	84.7 ± 3	8.2 ± 7.3	−52.8 ± 1.6
		E	1570–1675	83. ± 6	80.7 ± 3	−1.2 ± 3.7	−53.4 ± 1.6

[a] A) $Be(g) + BeF_2(g) \rightarrow 2BeF(g)$; B) $Be(g) + CaF(g) \rightarrow BeF(g) + Ca(g)$;
C) $Be(g) + AlF(g) \rightarrow BeF(g) + Al(g)$; D) $BeF_2(g) + Be(cr) \rightarrow 2BeF(g)$;
E) $BeF_2(g) + Be(l) \rightarrow 2BeF(g)$.

Heat Capacity and Entropy

Rotational constants are from a new analysis of the A–X system by Walker and Barrow.[9] Vibrational constants are those derived by Novikov and Gurvich[10] from data of Tatevskii et. al.[11] Excited states are from Novikov and Gurvich.[10] We assume that the two highest states are $^2\Pi$ as postulated by Walker and Barrow[9] from comparison with quantum calculations.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.711	−172.237	−172.237	INFINITE
100	29.109	173.800	231.865	−5.807	−170.825	−179.636	93.832
200	29.204	193.990	208.457	−2.893	−169.954	−188.852	49.323
250	29.454	200.530	206.241	−1.428	−169.831	−193.594	40.449
298.15	29.872	205.751	205.751	0.	−169.870	−198.170	34.719
300	29.891	205.936	205.752	0.055	−169.874	−198.345	34.535
350	30.461	210.586	206.118	1.564	−170.039	−203.079	30.308
400	31.091	214.694	206.938	3.102	−170.279	−207.783	27.134
450	31.725	218.393	208.009	4.673	−170.569	−212.454	24.661
500	32.327	221.767	209.218	6.274	−170.893	−217.091	22.679
600	33.379	227.757	211.821	9.561	−171.609	−226.265	19.698
700	34.217	232.968	214.478	12.943	−172.395	−235.313	17.559
800	34.872	237.581	217.083	16.399	−173.241	−244.244	15.948
900	35.387	241.720	219.595	19.913	−174.146	−253.066	14.688
1000	35.795	245.470	221.998	23.472	−175.115	−261.783	13.674
1100	36.124	248.898	224.289	27.069	−176.149	−270.401	12.840
1200	36.393	252.053	226.473	30.695	−177.254	−278.921	12.141
1300	36.617	254.975	228.555	34.346	−178.433	−287.346	11.546
1400	36.806	257.696	230.540	38.018	−179.689	−295.677	11.032
1500	36.968	260.241	232.436	41.707	−181.026	−303.916	10.583
1600	37.109	262.631	234.250	45.411	−196.982	−311.537	10.171
1700	37.233	264.885	235.986	49.128	−198.085	−318.663	9.791
1800	37.343	267.016	237.651	52.857	−199.206	−325.723	9.452
1900	37.442	269.038	239.250	56.596	−200.344	−332.721	9.147
2000	37.532	270.961	240.788	60.345	−201.498	−339.659	8.871
2100	37.615	272.794	242.269	64.102	−202.668	−346.538	8.620
2200	37.691	274.545	243.697	67.868	−203.853	−353.361	8.390
2300	37.762	276.222	245.075	71.640	−205.052	−360.130	8.179
2400	37.829	277.831	246.406	75.420	−206.263	−366.847	7.984
2500	37.892	279.377	247.694	79.206	−207.484	−373.513	7.804
2600	37.951	280.864	248.942	82.998	−208.715	−380.130	7.637
2700	38.008	282.297	250.151	86.796	−209.953	−386.699	7.481
2800	38.063	283.681	251.323	90.600	−502.155	−387.000	7.220
2900	38.115	285.017	252.462	94.409	−502.341	−382.884	6.896
3000	38.166	286.310	253.569	98.223	−502.516	−378.762	6.595
3100	38.215	287.562	254.646	102.042	−502.678	−374.634	6.313
3200	38.263	288.776	255.693	105.866	−502.828	−370.501	6.048
3300	38.310	289.955	256.714	109.694	−502.968	−366.364	5.799
3400	38.356	291.099	257.708	113.528	−503.099	−362.222	5.565
3500	38.402	292.211	258.678	117.366	−503.221	−358.077	5.344
3600	38.446	293.294	259.625	121.208	−503.337	−353.928	5.135
3700	38.491	294.348	260.549	125.055	−503.448	−349.776	4.938
3800	38.535	295.375	261.452	128.906	−503.556	−345.622	4.751
3900	38.579	296.377	262.335	132.762	−503.663	−341.464	4.573
4000	38.623	297.354	263.198	136.622	−503.772	−337.304	4.405
4100	38.667	298.308	264.043	140.487	−503.884	−333.141	4.244
4200	38.712	299.240	264.870	144.356	−504.003	−328.975	4.091
4300	38.758	300.152	265.680	148.229	−504.130	−324.806	3.946
4400	38.804	301.043	266.474	152.107	−504.267	−320.634	3.806
4500	38.850	301.916	267.252	155.990	−504.417	−316.459	3.673
4600	38.898	302.770	268.014	159.877	−504.582	−312.280	3.546
4700	38.947	303.607	268.763	163.769	−504.764	−308.098	3.424
4800	38.997	304.428	269.497	167.667	−504.965	−303.911	3.307
4900	39.049	305.233	270.218	171.569	−505.187	−299.721	3.195
5000	39.102	306.022	270.927	175.477	−505.431	−295.525	3.087
5100	39.157	306.797	271.622	179.389	−505.700	−291.324	2.984
5200	39.213	307.558	272.306	183.308	−505.994	−287.118	2.884
5300	39.271	308.305	272.978	187.232	−506.314	−282.906	2.788
5400	39.331	309.040	273.639	191.162	−506.662	−278.687	2.696
5500	39.393	309.762	274.290	195.098	−507.039	−274.462	2.607
5600	39.458	310.472	274.929	199.041	−507.446	−270.230	2.521
5700	39.524	311.171	275.559	202.990	−507.882	−265.990	2.438
5800	39.593	311.859	276.179	206.946	−508.348	−261.742	2.357
5900	39.664	312.537	276.790	210.909	−508.845	−257.486	2.280
6000	39.738	313.204	277.391	214.879	−509.373	−253.222	2.204

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 53.354 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 500$ K (low quartz → high quartz)
$T_{fus} = 825$ K

$\Delta_f H°(0\ K) = -1024.5 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1026.8 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.2201\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 4.757\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is the value selected by Parker,[1] based on a thorough review of data for BeF_2(cr, vitreous, aq) and BeO(cr). Parker's analysis remains essentially unchanged for BeO(cr) and BeF_2(cr), even though the results for BeF_2(HF, aq) become more negative by 0.93 $kcal \cdot mol^{-1}$ due to JANAF selections for HF(aq). Three values derived by Parker for BeF_2(cr) from PbF_2(cr) are changed due to JANF auxiliary data; these values become −246.9, −246.0 and −247.2 for the three paths used by Parker.

The adopted $\Delta_f H°$ was derived by combination of calorimetric data for Be(cr) + F_2(g) → BeF_2(vitreous) and BeF_2(cr) → BeF_2(vitreous). Churney and Armstrong[2] obtained $\Delta_f H°(298.15\ K) = -244.32 \pm 0.8\ kcal \cdot mol^{-1}$ for vitreous BeF_2 by combustion in fluorine of polytetrafluoroethylene and mixtures of Be(cr) with polytetrafluoroethylene. $\Delta_r H°(298.15\ K,$ cr → vitreous) = $1.125 \pm 0.016\ kcal \cdot mol^{-1}$ was measured via solution calorimetry by Taylor and Gardner.[3]

Heat Capacity and Entropy

$C_p°$ is based on JANAF curve fits of measurements by adiabatic calorimetry (8–300 K) and by ice calorimetry (354–776 K) as reported by Taylor and Gardner.[3] The sample was estimated as approximately 99.5% BeF_2. Analyses indicated that the major impurity was about 0.3% oxygen, mainly in the form of absorbed water. Petrographic examination and x-ray diffraction showed the sample to be composed almost completely of quartz-type crystals. The entropy is derived from the smoothed $C_p°$ based on the extrapolation $S°(8\ K) = 0.0065\ cal \cdot K^{-1} \cdot mol^{-1}$. The adopted $C_p°$ above 300 K agrees closely with the relative enthalpy data and shows a remarkable similarity to that of SiO_2 (low quartz, high quartz).

Transition Data

T_{trs} is the value selected by Taylor and Gardner[3] from their relative enthalpy data. $\Delta_{trs} H°$ is the corresponding difference in relative enthalpy from the JANAF curve fits for the two crystalline forms. Levina[4] studied the polymorphism of BeF_2 by observing the peaks in C_p near the transition temperatures. For low quartz → high quartz, Levina's peak began near 438 K, was complete near 503 K, and gave $\Delta_{trs} H° = 0.17\ kcal \cdot mol^{-1}$. Levina found a 2nd transition attributed to a form analogous to tridymite; this began above 670 K, was complete by 740 K, and gave $\Delta_{trs} H° = 0.24\ kcal \cdot mol^{-1}$. There is no evidence for this transition in the relative enthalpy data, so we suspect that its occurrence may be due to impurities in Levina's sample. Levina also found that the cristobalite-like phase transformed in the region 380 to 420 K with $\Delta_{trs} H° = 1.27\ kcal \cdot mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

References

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[3]A. R. Taylor and T. Estelle Gardner, U. S. Bur. Mines RI-6664, 15 pp. (1965).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.468	−1024.465	−1024.465	INFINITE
100	21.004	14.753	90.253	−7.550	−1026.493	−1010.881	528.030
200	39.083	35.271	57.702	−4.486	−1026.935	−995.024	259.874
298.15	51.819	53.354	53.354	0.	−1026.754	−979.385	171.584
300	52.028	53.676	53.355	0.096	−1026.746	−979.091	170.475
400	62.522	70.077	55.522	5.822	−1026.081	−963.292	125.793
500	76.048	85.392	59.971	12.710	−1024.661	−947.738	99.009
500.000	76.048	85.392	59.971	12.710	II <--> I		
500.000	64.099	85.832	59.971	12.930	TRANSITION		
600	67.446	97.814	65.302	19.508	−1023.604	−932.474	81.179
700	70.793	108.463	70.720	26.420	−1022.636	−917.360	68.454
800	74.140	118.134	76.051	33.666	−1021.495	−902.396	58.920
825.000	74.977	120.428	77.362	35.530	----- I <--> LIQUID -----		
900	77.488	127.060	81.229	41.248	−1020.160	−887.587	51.514
1000	80.835	135.397	86.234	49.164	−1018.617	−872.937	45.598
1100	84.182	143.259	91.064	57.415	−1016.858	−858.453	40.765
1200	87.529	150.727	95.727	66.000	−1014.876	−844.138	36.744
1300	90.876	157.865	100.234	74.920	−1012.670	−829.998	33.350

PREVIOUS: June 1964 CURRENT: June 1970

$S°(298.15\ K) = [59.920]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-1022.048]\ kJ·mol^{-1}$

$T_{fus} = 825\ K$ $\Delta_{fus}H° = 4.757\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by means of $\Delta_r H° = 1.125 \pm 0.016\ kcal·mol^{-1}$ for $\rightarrow BeF_2$(vitreous) at 298.15 K. Further details are given in the section on Fusion Data. $\Delta_f H°$(l) actually is based on the direct determination of $\Delta_f H°$(virteous) by Churney and Armstrong[1] as discussed on the crystal table.

Heat Capacity and Entropy

C_p^o is based on a JANAF curve fit of relative enthalpies of Taylor and Gardner[2] for the liquid (828–1183 K) and vitreous (320–473 K) forms of BeF_2. The combined data yeild a normal C_p^o curve and reveal no need for a glass transition. Scatter in the data is somewhat larger than for the crystal, presumably due to minor variations in the vitreous state at the conclusion of each drop. $S°$(298.15 K, l) is calculated from that of the crystal by addition of $\Delta_{fus}S°$ and the difference for crystal and liquid of $S°$(825 K)–$S°$(298.15 K).

Fusion Data

T_{fus} is the value selected by Taylor and Gardner[2] from their relative enthalpy data. These showed premelting starting near 804 K and complete melting above 828 K. Cooling of the liquid produced the vitreous state. T_{fus} has also been reported as 815,[3] 821,[4] 818,[5] and 816 ± 5 K.[6]

Solution calorimetry[2] gave $\Delta_r H° = 1.125 \pm 0.016\ kcal·mol^{-1}$ for BeF_2(low quartz) $\rightarrow BeF_2$(vitreous) at 298.15 K. Confirmation of ths result came from transposed temperature–drop calorimetry[7] and calorimetric conversion.[8] These gave 1.1 ± 0.2 and 1.1 ± 0.5 $kcal·mol^{-1}$, respectively. Combination of $\Delta_r H° = 1.125$ with JANAF enthalpies yields $\Delta_{vap}H° = 1.137\ kcal·mol^{-1}$.

Vaporization Data

T_{vap} is the calculated temperature at which $\Delta_r G° = 0$ for BeF_2(l) $\rightarrow BeF_2$(g); $\Delta_{vap}H°$ is the corresponding value of $\Delta_r H°$ at T_{vap}. These calculations neglect the presence of dimer, which is assumed to be negligible based on extrapolation of the equations of Belousov.[9] Cantor[10] obtained T_{vap} = 1442 K by extrapolation of his vapor pressures (1146–1372 K).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	C_p^o	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	49.903	59.920	59.920	0.	−1022.048	−976.637	171.103
300	50.112	60.229	59.921	0.093	−1022.044	−976.355	169.998
400	59.208	75.979	62.006	5.589	−1021.608	−961.180	125.517
500	65.559	89.906	66.222	11.842	−1020.823	−946.157	98.844
600	70.551	102.314	71.222	18.655	−1019.751	−931.320	81.079
700	74.810	113.516	76.477	25.928	−1018.421	−916.684	68.404
800	78.647	123.761	81.756	33.604	−1016.851	−902.254	58.911
825.000	79.538	126.195	83.066	35.582	----- I <--> LIQUID -----		
900	82.228	133.232	86.956	41.648	−1015.054	−888.035	51.540
1000	85.642	142.073	92.030	50.043	−1013.032	−874.028	45.655
1100	88.943	150.391	96.961	58.773	−1010.793	−860.234	40.849
1200	92.165	158.269	101.745	67.829	−1008.342	−846.654	36.854
1300	95.332	165.771	106.383	77.204	−1005.681	−833.286	33.482
1400	98.458	172.950	110.884	86.894	−1002.814	−820.131	30.599
1500	101.550	179.849	115.253	96.894	−999.744	−807.188	28.109
1600	104.621	186.501	119.499	107.203	−1011.010	−793.931	25.919
1700	107.671	192.935	123.631	117.818	−1007.139	−780.481	23.981
1800	110.709	199.175	127.655	128.737	−1002.999	−767.266	22.265
1900	113.734	205.242	131.580	139.959	−998.590	−754.289	20.737
2000	116.750	211.153	135.411	151.483	−993.909	−741.551	19.367

PREVIOUS: June 1964 CURRENT: June 1970

0	to	500 K	crystal, low quartz
500	to	825 K	crystal, high quartz
above		825 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.468	−1024.465	−1024.465	INFINITE
100	21.004	14.753	90.253	−7.550	−1026.493	−1010.881	528.030
200	39.083	35.271	57.702	−4.486	−1026.935	−995.024	259.874
298.15	51.819	53.354	53.354	0.	−1026.754	−979.385	171.584
300	52.028	53.676	53.355	0.096	−1026.746	−979.091	170.475
400	62.522	70.077	55.522	5.822	−1026.081	−963.292	125.793
500	76.048	85.392	59.971	12.710	−1024.661	−947.738	99.009
500.000	76.048	85.392	59.971	12.710	II <--> I		
500.000	64.099	85.832	59.971	12.930	TRANSITION		
600	67.446	97.814	65.302	19.508	−1023.604	−932.474	81.179
700	70.793	108.463	70.720	26.420	−1022.636	−917.360	68.454
800	74.140	118.134	76.051	33.666	−1021.495	−902.396	58.920
825.000	74.977	120.428	77.362	35.530	I <--> LIQUID		
900	82.228	133.232	81.727	46.354	−1015.054	−888.035	51.540
1000	85.642	142.073	87.324	54.749	−1013.032	−874.028	45.655
1100	88.943	150.391	92.683	63.479	−1010.793	−860.234	40.849
1200	92.165	158.268	97.823	72.535	−1008.342	−846.653	36.854
1300	95.332	165.771	102.763	81.910	−1005.681	−833.286	33.482
1400	98.458	172.950	107.522	91.600	−1002.814	−820.131	30.599
1500	101.550	179.849	112.115	101.600	−999.744	−807.188	28.109
1600	104.621	186.501	116.558	111.909	−1011.010	−793.931	25.919
1700	107.671	192.935	120.862	122.524	−1007.139	−780.481	23.981
1800	110.709	199.175	125.041	133.443	−1002.999	−767.266	22.265
1900	113.734	205.242	129.103	144.665	−998.590	−754.289	20.737
2000	116.750	211.153	133.058	156.189	−993.909	−741.551	19.367

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = [227.56 \pm 1.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -796.19 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -796.01 \pm 4.2\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[670](1)	345 (2)	1530 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Be–F = 1.40 ± 0.03 Å
Bond Angle: F–Be–F = 180°
Rotational Constant: $B_0 = 0.226357\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by means of $\Delta_f H°(298.15\ K) = 55.15 \pm 0.1\ kcal \cdot mol^{-1}$. The selected value of $\Delta_{sub} H°$ is an average of those obtained by 3rd law analysis of vapor pressures measured by manometry,[3] torsion effusion[4] and entrainment.[8–10] Mass–spectrometric data[1,2] are in reasonable agreement and so is the average of two Knudsen–effusion studies.[6,7] Several techniques[2,4,6] were used to show that the amount of dimer in the vapor is negligible up to at least 1000 K. JANAF analyses of the vaporization data are summarized as follows:

Source	Method	T/K	δS $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_{sub} H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law
[1] Efimenko (1968)	Mass Spectrometry	705– 819	—	56.14 ± 0.43	—
[2] Belousov (1967)	Mass Spectrometry	815– 977	−1.0	54.51	55.44
[3] Cantor (1965)	Manometry	1146–1372	0.65 ± 0.08	55.96 ± 0.10	55.14
[4] Hildenbrand (1965)	Torsion Effusion				
	Cell 13	891– 942	4.2 ± 0.4	58.87 ± 0.34	54.98
	Cell 27	872– 907	0.9 ± 0.3	55.82 ± 0.22	54.98
	Cell 12	821– 921	−0.8 ± 0.3	54.42 ± 0.27	55.12
	Cell 14	840– 921	3.4 ± 0.3	58.13 ± 0.29	55.13
[5] Blauer (1965)	Torsion Effusion				
	Cells A & B	713– 795	6.2 ± 0.9	58.07 ± 0.66	53.44
[6] Greenbaum (1963)	Effusion	823–1053	2.4 ± 0.6	56.75 ± 0.59	54.50
[7] Khandamirova (1959)	Effusion	846– 950	3.4 ± 2.4	58.82 ± 2.20	55.75
[6] Greenbaum (1963)	Entrainment	1123–1223	1.5 ± 3.0	55.88 ± 3.50	54.17
[8] Ozhigov (1961)	Entrainment	1019–1241	1.4 ± 0.8	56.64 ± 0.94	55.04
[9] Sense (1958)	Entrainment	1075–1298	−0.06 ± 0.43	55.11 ± 0.51	55.18
[10] Novoselova (1958)	Entrainment	1095–1376	−2.1 ± 0.5	52.64 ± 0.56	55.25

Heat Capacity and Entropy

The bond length and angle are those derived by Akishin *et al.*[11] from electron–diffraction data for the vapor. Linearity of BeF_2 was confirmed by electric–deflection studies[12] of the vapor and by infrared studies[13] of matrix–isolated BeF_2. Infrared absorptions were found near 330 and 1540 cm^{-1} in neon matrices, leading to gas–phase estimates of 345 and 1555 cm^{-1}.[13] The latter absorption was observed[14] at 1520 cm^{-1} in the infrared spectra of the vapor at 1000°C. We adopt a compromise of 1530 cm^{-1} and use this value in the valence–force–field approximation to estimate 670 cm^{-1} for the symmetric stretching mode.

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Continued on page 428

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−10.942	−796.191	−796.191	INFINITE
100	32.054	185.038	264.782	−7.974	−796.169	−797.586	416.616
200	40.895	210.117	231.640	−4.305	−796.006	−799.064	208.694
250	44.021	219.594	228.306	−2.178	−795.974	−799.834	167.116
298.15	46.364	227.556	227.556	0.	−796.006	−800.576	140.258
300	46.444	227.843	227.556	0.086	−796.008	−800.604	139.398
350	48.393	235.153	228.129	2.458	−796.103	−801.363	119.597
400	50.020	241.725	229.425	4.920	−796.236	−802.106	104.744
450	51.407	247.698	231.128	7.456	−796.393	−802.830	93.190
500	52.606	253.178	233.063	10.057	−796.566	−803.536	83.945
600	54.553	262.950	237.250	15.420	−796.945	−804.895	70.072
700	56.034	271.475	241.543	20.953	−797.355	−806.188	60.159
800	57.168	279.035	245.766	26.615	−797.799	−807.420	52.719
900	58.044	285.821	249.846	32.378	−798.283	−808.595	46.930
1000	58.728	291.973	253.756	38.217	−798.816	−809.712	42.295
1100	59.270	297.597	257.490	44.118	−799.406	−810.774	38.500
1200	59.704	302.774	261.050	50.068	−800.061	−811.779	35.336
1300	60.055	307.567	264.447	56.056	−800.786	−812.726	32.656
1400	60.344	312.028	267.688	62.077	−801.589	−813.615	30.356
1500	60.582	316.200	270.784	68.124	−802.473	−814.444	28.361
1600	60.782	320.116	273.746	74.192	−817.979	−814.685	26.597
1700	60.951	323.807	276.584	80.279	−818.636	−814.459	25.025
1800	61.094	327.295	279.305	86.381	−819.313	−814.194	23.627
1900	61.217	330.601	281.918	92.497	−820.010	−813.891	22.375
2000	61.323	333.744	284.432	98.624	−820.727	−813.550	21.248
2100	61.415	336.738	286.852	104.761	−821.461	−813.174	20.227
2200	61.496	339.597	289.185	110.907	−822.210	−812.762	19.297
2300	61.566	342.332	291.437	117.060	−822.973	−812.315	18.448
2400	61.629	344.954	293.612	123.220	−823.745	−811.835	17.669
2500	61.684	347.471	295.717	129.386	−824.524	−811.323	16.952
2600	61.734	349.891	297.754	135.556	−825.307	−810.779	16.289
2700	61.778	352.222	299.728	141.732	−826.091	−810.206	15.674
2800	61.818	354.469	301.644	147.912	−1117.830	−803.380	14.987
2900	61.853	356.639	303.503	154.095	−1117.545	−792.155	14.268
3000	61.886	358.737	305.309	160.282	−1117.237	−780.940	13.597
3100	61.915	360.766	307.066	166.473	−1116.905	−769.736	12.970
3200	61.942	362.732	308.775	172.665	−1116.550	−758.542	12.382
3300	61.966	364.639	310.439	178.861	−1116.171	−747.360	11.830
3400	61.989	366.489	312.060	185.059	−1115.769	−736.190	11.310
3500	62.009	368.286	313.641	191.259	−1115.345	−725.032	10.821
3600	62.028	370.033	315.183	197.460	−1114.901	−713.886	10.358
3700	62.045	371.733	316.689	203.664	−1114.437	−702.753	9.921
3800	62.061	373.388	318.159	209.869	−1113.956	−691.633	9.507
3900	62.076	375.000	319.596	216.076	−1113.461	−680.526	9.115
4000	62.090	376.572	321.001	222.285	−1112.952	−669.431	8.742
4100	62.103	378.105	322.375	228.494	−1112.434	−658.350	8.387
4200	62.115	379.602	323.720	234.705	−1111.908	−647.281	8.050
4300	62.126	381.064	325.037	240.917	−1111.377	−636.225	7.729
4400	62.136	382.492	326.326	247.130	−1110.844	−625.181	7.422
4500	62.146	383.889	327.590	253.344	−1110.311	−614.149	7.129
4600	62.155	385.255	328.829	259.559	−1109.781	−603.129	6.849
4700	62.163	386.591	330.044	265.775	−1109.256	−592.120	6.581
4800	62.171	387.900	331.235	271.992	−1108.740	−581.123	6.324
4900	62.179	389.182	332.405	278.209	−1108.234	−570.136	6.078
5000	62.186	390.439	333.553	284.428	−1107.740	−559.160	5.842
5100	62.192	391.670	334.681	290.647	−1107.262	−548.193	5.615
5200	62.199	392.878	335.788	296.866	−1106.800	−537.235	5.397
5300	62.205	394.063	336.877	303.086	−1106.357	−526.286	5.187
5400	62.210	395.225	337.946	309.307	−1105.935	−515.346	4.985
5500	62.215	396.367	338.998	315.528	−1105.534	−504.413	4.791
5600	62.220	397.488	340.033	321.750	−1105.156	−493.486	4.603
5700	62.225	398.589	341.050	327.972	−1104.802	−482.567	4.422
5800	62.230	399.672	342.052	334.195	−1104.474	−471.654	4.248
5900	62.234	400.735	343.037	340.418	−1104.172	−460.745	4.079
6000	62.238	401.781	344.008	346.642	−1103.897	−449.843	3.916

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 89.24 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = [650 K]

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1651.8 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [27.196]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Interpolation of the calorimetric enthalpies of mixing of Holm and Kleppa[1] yields $\Delta_r H° = -0.56 \pm 0.1$ kcal·mol^{-1} for LiF(l) + BeF_2(l) → $LiBeF_3$(l) at 1135 K. Reduction with the estimated JANAF functions yields $\Delta_r H° = -3.07 \pm 1.0$ kcal·mol^{-1} at 298.15 K for LiF(cr) + BeF_2(l) → $LiBeF_3$(cr), where BeF_2(l) is the supercooled liquid. $\Delta_r H°$(298.15 K) for the latter reaction may also be calculated as -2.77 ± 0.2 kcal·mol^{-1} from the difference of two calorimetric reactions measured by Gross.[2] These results at 298.15 K were $\Delta_r H° = -2.28 \pm 0.12$ kcal·mol^{-1} for LiF(cr) + $LiBeF_3$(cr) → Li_2BeF_4(cr) and $\Delta_r H° = -5.06 \pm 0.06$ kcal·mol^{-1} for 2LiF(cr) + BeF_2(l) → Li_2BeF_4(cr). We adopt the high-temperature results of Holm and Kleppa since the entropy must be calculated by combination of $\Delta_r H°$ with $\Delta_r G°$ obtained at high temperature.

Heat Capacity and Entropy

$C_p°$ is estimated from $C_p°$ of Li_2BeF_4(cr) minus $C_p°$ of LiF(cr). Existing information leads to three values for $S°$ at 298.15 K; namely 21.41 cal·K^{-1}·mol^{-1} from $\Delta_r G°$ and $\Delta_r H°$ for mixing of molten LiF and BeF_2, 21.33 cal·K^{-1}·mol^{-1} from $\Delta_r G° = 552$ K for disproportionation of $LiBeF_3$(cr) to Li_2BeF_4(cr) and BeF_2(cr), and 21.28 cal·K^{-1}·mol^{-1} estimated from $S°$ of LiF(cr) and BeF_2(cr). We adopt the intermediate value but emphasize that $S°(298.15\ K)$ is much more uncertain than indicated by the consistency of the three values. There is less uncertainty in $S°(900)$ since it does not involve large contributions from the estimated values of $C_p°$ and $\Delta_{fus} H°$.

Hitch and Baes[3] reported emf data and activity coefficients which yield $\Delta_r G° = -5.91$ kcal·mol^{-1} at 900 K for LiF(l) + BeF_2(l) → $LiBeF_3$(l). Combining $\Delta_r G°$ with $\Delta_r H° = -1.05$ kcal·mol^{-1} derived with JANAF functions from data of Holm and Kleppa,[1] we obtain $\Delta_r S° = 5.4$ and $S°(LiBeF_3, l) = 64.46$ cal·K^{-1}·mol^{-1}, both at 900 K. The corresponding values from the adoped tables are $\Delta_r G° - 5.84$ kcal·mol^{-1} and $S(LiBeF_3, l) = 64.38$ cal·K^{-1}·mol^{-1}.

Disproportionation Data

No transitions are known between room temperature and T_{fus}, but $LiBeF_3$(cr) does disproportionate into Li_2BeF_4(cr) and BeF_2 (high quartz). Disporportionation occurs at 553 K according to the latest phase diagrams[4,5] or at 573 k according to Roy *et al.*[6] The adopted tables yield $\Delta_r G° = 0$ at 552 K, but this temperature is very sensitive to the value selected for $S°$, which in turn depends on the estimates of $C_p°$ and $\Delta_{fus} H°$.

Fusion Data

Refer to the liquid table for details.

References

[1]J. L. Holm and O. J. Kleppa, Inorg. Chem. **8**, 207 (1969).
[2]P. Gross, Fulmer Res. Inst. Report, R.163/23/May 1966 and R.163/22/Jan. 1966, contract AF 61(052)-863; R.163/18/Dec. 1964, contract AF 61(052)-447.
[3]B. F. Hitch and C. F. Baes, Inorg. Chem. **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL-4257, 46 pp., (1968).
[4]K. A. Romberger, J. Braunstein and R. E. Thoma, J. Phys. Chem., **76**, 1154 (1972).
[5]R. Thoma, H. Insley, H. A. Friedman, and G. M. Hebert, J. Nucl. Materials **27**, 166 (1968).
[6]D. M. Roy, R. Roy and E. F. Osborn, J. Amer. Ceram. Soc. **37**, 300 (1954).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
0						
100						
200						
298.15	91.816	89.245	0.	−1651.843	−1576.273	276.156
300	92.048	89.813	0.170	−1651.836	−1575.804	274.372
400	104.600	118.013	10.002	−1651.275	−1550.535	202.479
500	117.152	142.702	21.090	−1653.272	−1525.148	159.331
600	129.704	165.171	33.433	−1651.389	−1499.682	130.559
650.0	135.980	175.801	114.147	40.075	− − − CRYSTAL <− −> LIQUID − − −	
700	142.256	186.108	118.921	47.031	−1648.435	−1474.616	110.037
800	154.808	205.923	128.568	61.884	−1644.389	−1450.048	94.678
900	167.360	224.881	138.223	77.992	−1639.246	−1426.053	82.766
1000	179.912	243.164	147.808	95.356	−1632.986	−1402.690	73.269
1100	192.464	260.900	157.286	113.975	−1625.600	−1380.009	65.531
1200	205.016	278.185	166.644	133.849	−1617.079	−1358.049	59.114

PREVIOUS: June 1966 CURRENT: December 1971

$S°(298.15\ K) = [111.681]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [650]\ K$

$\Delta_f H°(298.15\ K) = [-1634.323]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [27.2]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of $\Delta_{fus} H°$ and the difference in enthalpy, $H°(650\ K)–H°(298.15\ K)$, between the crystal and liquid. Note that the result is based on direct measurements of the enthalpy of mixing of molten LiF and BeF_2 at 1135 K.[1]

Heat Capacity and Entropy

$C_p°$ is estimated on the basis of 7.6 $cal·K^{-1}·mol^{-1}$ by comparison with the liquid phases of LiF, BeF_2 and Li_2BeF_4. A glass transition is assumed at 400 K and below this temperature $C_p°$ is obtained from that of the crystal. The entropy is calculated in a manner analogous to that used for $\Delta_f H°$. Note that the resulting value of $S°(900\ K)$ differs by only 0.08 $cal·K^{-1}·mol^{-1}$ from that based on measurements of $\Delta_f H°(1135\ K)$[1] and $\Delta_f G°(900\ K)$[2] for mixing of molten LiF and BeF_2.

Fusion Data

The composition corresponding to $LiBeF_3$ melts incongruently,[3] starting with the eutectic composition of 53 mole percent BeF_2 at 636.6 ± 0.5 K and finishing at a liquidus temperature near 653 K. Just below the melting region, the solid consists of an equimolar mixture of Li_2BeF_4(cr) and BeF_2(high quartz). We arbitrarily adopt 650 K as the hypothetical, congruent melting point of metastable $LiBeF_3$. We estimate $\Delta_{fus} H°$ on the basis of $\Delta_{fus} S° = 2.0\ cal·K^{-1}\ g\text{-}atom^{-1}$ by comparison with Li_2BeF_4.

Vaporization Data

Mass–spectrometric data[4,5] for the LiF–BeF_2 system suggest that the vapor consists mainly of BeF_2(g), some $LiBeF_3$(g), and traces of other molecules.

References

[1] J. L. Holm and O. J. Kleppa, Inorg. Chem. **8**, 207 (1969).
[2] B. F. Hitch and C. F. Baes, Inorg. Chem. **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL–4257, 46 pp., (1968).
[3] K. A. Romberger, J. Braunstien and R. E. Thoma, J. Phys. Chem., **76**, 1154 (1972).
[4] A. Buchler and J. L. Stauffer, Thermodynamics, Proc. Symp., Vienna, 1965, **1**, 271, Intl. At. Energy Agency, Vienna, (1966).
[5] J. Berkowitz, and W. A. Chupka, Ann. New York Acad. Sci. **79**, Art. 11, 1073 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.816	111.681	111.681	0.	−1634.323	−1565.442	274.259
300	92.048	112.249	111.683	0.170	−1634.315	−1565.014	272.493
400	104.600	140.449	115.443	10.002	−1633.755	−1541.988	201.363
400.001	104.600	140.449	115.443	10.003	GLASS <--> LIQUID		
400.001	158 .992	140.449	115.443	10.003	TRANSITION		
500	158.992	175.927	124.124	25.902	−1630.939	−1519.428	158.734
600	158.992	204.915	135.247	41.801	−1625.501	−1497.640	130.381
650.000	158.992	217.641	141.102	49.750	--- CRYSTAL <--> LIQUID ---		
700	158.992	229.423	146.995	57.700	−1620.246	−1476.748	110.196
800	158.992	250.654	158.655	73.599	−1615.154	−1456.597	95.106
900	158.992	269.380	169.938	89.498	−1610.219	−1437.076	83.406
1000	158.992	286.132	180.734	105.398	−1605.424	−1418.096	74.074
1100	158.992	301.285	191.015	121.297	−1600.757	−1399.590	66.461
1200	158.992	315.119	200.789	137.196	−1596.211	−1381.503	60.135
1300	158.992	327.846	210.080	153.095	−1591.783	−1363.792	54.798
1400	158.992	339.628	218.918	168.994	−1587.468	−1346.417	50.235
1500	158.992	350.597	227.335	184.894	−1583.263	−1329.346	46.292
1600	158.992	360.859	235.363	200.793	−1593.702	−1312.027	42.833
1700	158.992	370.497	243.032	216.692	−1734.546	−1287.380	39.556
1800	158.992	379.585	250.368	232.591	−1729.437	−1261.224	36.600
1900	158.992	388.181	257.397	248.490	−1724.368	−1235.351	33.962
2000	158.992	396.337	264.142	264.390	−1719.337	−1209.743	31.595

PREVIOUS: CURRENT: December 1971

0	to	650 K	crystal
above		650 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.816	89.245	89.245	0.	−1651.843	−1576.273	276.156
300	92.048	89.813	89.246	0.170	−1651.836	−1575.804	274.372
400	104.600	118.013	93.007	10.002	−1651.275	−1550.535	202.479
500	117.152	142.702	100.522	21.090	−1653.272	−1525.148	159.331
600	129.704	165.171	109.450	33.433	−1651.389	−1499.682	130.559
650.000	135.980	175.801	114.147	40.075	CRYSTAL <--> LIQUID TRANSITION		
650.000	158.992	217.641	114.147	67.271			
700	158.992	229.423	121.965	75.221	−1620.246	−1476.748	110.196
800	158.992	250.654	136.754	91.120	−1615.154	−1456.597	95.106
900	158.992	269.380	150.470	107.019	−1610.219	−1437.076	83.406
1000	158.992	286.132	163.214	122.918	−1605.424	−1418.096	74.074
1100	158.992	301.285	175.088	138.817	−1600.757	−1399.590	66.461
1200	158.992	315.119	186.189	154.717	−1596.211	−1381.503	60.135
1300	158.992	327.846	196.603	170.616	−1591.783	−1363.792	54.798
1400	158.992	339.628	206.403	186.515	−1587.468	−1346.417	50.235
1500	158.992	350.597	215.655	202.414	−1583.263	−1329.346	46.292
1600	158.992	360.859	224.413	218.313	−1593.702	−1312.027	42.833
1700	158.992	370.497	232.725	234.213	−1734.546	−1287.380	39.556
1800	158.992	379.585	240.634	250.112	−1729.437	−1261.224	36.600
1900	158.992	388.181	248.176	266.011	−1724.368	−1235.351	33.962
2000	158.992	396.337	255.382	281.910	−1719.337	−1209.743	31.595

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = [267.42]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -880\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -887\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[1530] (1)	[485] (2)
[820] (2)	[800] (3)
[700] (1)	

Point Group: $[C_{3v}]$ $\sigma = [3]$
Bond Distances: Be–F = [1.40] Å; Li–Be = [1.209] Å; Li–F = [1.85] Å
Bond Angles: F–Be F = [120]°; Li–Be–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.1635 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $\Delta_f H°(900\ K) = 53\ kcal·mol^{-1}$ for the reaction: $LiF(g) + BeF_2(g) = LiBeF_3(g)$ reported by Hildenbrand, et al.[1]

Heat Capacity and Entropy

The molecular structure was assumed to be pyramidal with Li atom at the top and BeF_3 located at the bottom. Beryllium atom was taken at the center of the equilateral triangle formed by the three F atoms. The Be–F distance was estimated from that of BeF(g). The bond distance of Li–F was taken from Porter and Zeller.[2] Vibrational frequencies were estimated by comparison with related fluorides. The principal moments of inertia are: $I_A = I_B = 10.7996 \times 10^{-39}$ and $I_C = 18.5503 \times 10^{-39}\ g·cm^2$.

References

[1]D. L. Hildenbrand, et. al., Aeronutronic, Division of Ford Motor Co., Publication No. U–1734, (June 1962).
[2]R. F. Porter and E. E. Zeller, J. Chem. Phys., **33**, 858 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.459	−879.675	−879.675	INFINITE
100	34.100	219.860	311.078	−9.122	−881.233	−876.878	458.034
200	45.467	246.303	272.513	−5.242	−884.166	−871.430	227.594
250	53.629	257.324	268.384	−2.765	−885.662	−868.072	181.374
298.15	61.090	267.419	267.419	0.	−887.008	−864.560	151.467
300	61.360	267.798	267.420	0.113	−887.058	−864.421	150.509
350	68.105	277.777	268.193	3.354	−888.341	−860.545	128.429
400	73.789	287.253	269.988	6.906	−889.536	−856.492	111.846
450	78.517	296.226	272.410	10.717	−890.676	−852.292	98.932
500	82.442	304.708	275.219	14.744	−894.782	−847.661	88.555
600	88.434	320.301	281.458	23.306	−896.681	−838.052	72.959
700	92.663	334.269	288.022	32.373	−898.258	−828.152	61.797
800	95.721	346.853	294.603	41.800	−899.638	−818.041	53.413
900	97.986	358.264	301.052	51.491	−900.912	−807.764	46.881
1000	99.700	368.681	307.302	61.379	−902.128	−797.349	41.649
1100	101.024	378.248	313.323	71.418	−903.322	−786.813	37.363
1200	102.064	387.085	319.106	81.574	−904.518	−776.169	33.786
1300	102.895	395.288	324.655	91.824	−905.740	−765.424	30.755
1400	103.568	402.939	329.976	102.148	−907.000	−754.583	28.154
1500	104.121	410.104	335.082	112.533	−908.309	−743.651	25.896
1600	104.579	416.839	339.983	122.969	−924.211	−732.104	23.901
1700	104.963	423.191	344.693	133.447	−1070.477	−712.890	21.904
1800	105.288	429.200	349.222	143.960	−1070.753	−691.847	20.077
1900	105.566	434.900	353.583	154.503	−1071.041	−670.789	18.441
2000	105.804	440.321	357.785	165.071	−1071.340	−649.716	16.969
2100	106.011	445.488	361.839	175.662	−1071.650	−628.627	15.636
2200	106.190	450.424	365.755	186.273	−1071.970	−607.523	14.424
2300	106.348	455.148	369.539	196.900	−1072.298	−586.404	13.318
2400	106.487	459.677	373.201	207.542	−1072.631	−565.271	12.303
2500	106.610	464.027	376.748	218.197	−1072.967	−544.125	11.369
2600	106.719	468.210	380.186	228.863	−1073.303	−522.964	10.506
2700	106.817	472.240	383.521	239.540	−1073.638	−501.791	9.708
2800	106.905	476.126	386.759	250.226	−1364.926	−474.383	8.850
2900	106.984	479.879	389.906	260.921	−1364.188	−442.591	7.972
3000	107.055	483.507	392.966	271.623	−1363.426	−410.825	7.153
3100	107.120	487.018	395.944	282.332	−1362.642	−379.084	6.388
3200	107.179	490.420	398.843	293.047	−1361.835	−347.369	5.670
3300	107.232	493.719	401.668	303.767	−1361.006	−315.680	4.997
3400	107.281	496.921	404.423	314.493	−1360.159	−284.016	4.363
3500	107.326	500.032	407.111	325.223	−1359.295	−252.377	3.767
3600	107.368	503.056	409.734	335.958	−1358.417	−220.763	3.203
3700	107.406	505.998	412.296	346.697	−1357.527	−189.174	2.671
3800	107.441	508.863	414.800	357.439	−1356.630	−157.609	2.166
3900	107.473	511.654	417.248	368.185	−1355.728	−126.068	1.688
4000	107.503	514.375	419.642	378.934	−1354.827	−94.549	1.235
4100	107.531	517.030	421.985	389.685	−1353.929	−63.054	0.803
4200	107.557	519.622	424.279	400.440	−1353.040	−31.579	0.393
4300	107.581	522.153	426.526	411.197	−1352.164	−0.127	0.002
4400	107.604	524.626	428.727	421.956	−1351.284	31.304	−0.372
4500	107.625	527.045	430.885	432.718	−1350.437	62.717	−0.728
4600	107.645	529.411	433.002	443.481	−1349.618	94.111	−1.069
4700	107.663	531.726	435.078	454.247	−1348.828	125.489	−1.395
4800	107.681	533.993	437.115	465.014	−1348.071	156.849	−1.707
4900	107.697	536.213	439.115	475.783	−1347.353	188.194	−2.006
5000	107.712	538.389	441.078	486.553	−1346.677	219.524	−2.293
5100	107.727	540.522	443.007	497.325	−1346.041	250.842	−2.569
5200	107.741	542.614	444.903	508.099	−1345.460	282.148	−2.834
5300	107.754	544.667	446.766	518.873	−1344.934	313.443	−3.089
5400	107.766	546.681	448.598	529.649	−1344.464	344.728	−3.335
5500	107.777	548.658	450.399	540.426	−1344.057	376.005	−3.571
5600	107.788	550.600	452.171	551.205	−1343.713	407.276	−3.799
5700	107.799	552.508	453.915	561.984	−1343.438	438.541	−4.019
5800	107.808	554.383	455.631	572.764	−1343.233	469.802	−4.231
5900	107.818	556.226	457.320	583.546	−1343.101	501.060	−4.436
6000	107.827	558.038	458.984	594.328	−1343.046	532.316	−4.634

PREVIOUS: December 1962 (1 atm) CURRENT: December 1962 (1 bar)

$S°(298.15\ K) = 130.58 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 732.2 \pm 0.2\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -2273.6 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 43.995 \pm 2.09\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Interpolation of the calorimetric enthalpies of mixing of Holm and Kleppa[1] yields $\Delta_r H° = -3.2 \pm 0.1$ kcal·mol^{-1} for $2LiF(l) + BeF_2(l) \rightarrow Li_2BeF_4(l)$ at 1135 K. Reduction with the estimated JANAF functions yields $\Delta_r H° = -4.24 \pm 0.2$ kcal·mol^{-1} at 298.15 K for $2LiF(cr) + BeF_2(l) \rightarrow Li_2BeF_4(cr)$, where $BeF_2(l)$ is the supercooled liquid. Gross[2] studied the latter reaction calorimetrically and obtained $\Delta_r H° = -5.05 \pm 0.06$ kcal·mol^{-1} at 298.15 K. The difference of 0.8 kcal·mol^{-1} between the two results is greater than the combined uncertainties but probably is not unreasonable in this case. We adopt the high–temperature results of Holm and Kleppa since the entropy must be calculated by combination of $\Delta_r H°$ with $\Delta_r G°$ obtained at high temperature.

Heat Capacity and Entropy

$C_p°$ is taken from the enthalpy study (323–873 K) of Douglas and Payne.[3] Their sample was only 98.6% pure and extensive premelting corrections were necessary above 650 K. Thus, $C_p°$ may be more uncertain than usual in this region. The premelting corrections could also be affected by new phase data which show that pure Li_2BeF_4 melts congruently at a temperature 12° lower than assumed in the premelting analysis. The magnitude of the adopted $C_p°$ is confirmed by data by Levina *et al.*[4] for samples prepared by fusion.

Hitch and Baes[5] reported emf data and activity coefficients which yield $\Delta_r G° = -9.33$ kcal·mol^{-1} at 900 K for $2LiF(l) + BeF_2(l) \rightarrow Li_2BeF_4(l)$. Combining $\Delta_r G°$ with $\Delta_r H° = -4.19$ kcal·mol^{-1} derived from data of Holm and Kleppa,[1] we obtain $\Delta_r S° = 5.71$ cal·K^{-1}·mol^{-1} at 900 K and $S° = 31.21 \pm 0.5$ cal·K^{-1}·mol^{-1} for Li_2BeF_4(cr) at 298.15 K. This experimental entropy may be compared with 29.8 ± 2 cal·K^{-1}·mol^{-1} estimated by assuming $\Delta_r S° = 0$ cal·K^{-1}·mol^{-1} for formation form LiF(cr) and BeF_2(cr).

Transition Data

Li_2BeF_4 has a hexagonal unit cell (space group $R\bar{3}$) isotypic with phenacite.[6] This structure shows no phase transitions between room temperature and T_{fus},[3,4,7] but exposure to traces of moisture at elevated temperatures causes decomposition to LiF and BeO.[7,8] Metastable forms have been reported[4] but not confirmed or identified.

Fusion Data

New electrochemical measurements[9] of the liquidus in the LiF–BeF_2 system show that Li_2BeF_4 melts congruently at 459.1 ± 0.2°C with the eutectic point at 458.9 ± 0.2°C and 32.8 mole percent BeF_2. The close proximity of the eutectic explains previous conflicting reports of incongruent[8] and congruent[4,8] melting. We adopt $T_{fus} = 732.2 \pm 0.2$ K and derive $\Delta_{fus} H° = 10.515$ kcal·mol^{-1} from the difference in smoothed enthalpies for liquid and crystal.[3] The uncertainty estimated for $\Delta_{fus} H°$ emphasized the nature of the premelting corrections.

References

[1] J. L. Holm and O. J. Kleppa, Inorg. Chem. **8**, 207 (1969).
[2] P. Gross, Fulmer Res. inst. Report R.163/23/May 1966 and R.163/22/Jan. 1966, Contract AF 61(052)–863; R.163/18/December 1964, Contract AF 61(052)–447.
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[4] M. W. Levina, V. I. Kalitin and V. T. Kalinnikov, Vestnik Moskov. Univ., Khim. Ser. II16, No. 4, 43 (1961).
[5] B. F. Hitch and C. F. Baes, Inorg. Chem. **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL–4257, 46 pp., (1968).
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[7] T. Hahn, H. Bielen, W. Eysel and F. Weber, Chem. Erde **22**, 175 (1962).
[8] R. Thoma, H. Insley, H. A. Friedman, and G. M. Hebert, J. Nucl. Materials **27**, 166 (1968).
[9] K. A. Romberger, J. Braunstein and R. E. Thoma, J. Phys. Chem., **76**, 1154 (1972).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S° - [G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0						
100						
200						
298.15	135.269	130.583	0.	−2273.586	−2171.438	380.427
300	135.520	131.420	0.250	−2273.573	−2170.804	377.971
400	150.457	172.453	14.550	−2272.755	−2136.665	279.020
500	165.352	207.627	30.340	−2277.665	−2102.147	219.610
600	180.247	239.090	47.620	−2275.565	−2067.220	179.967
700	195.184	267.997	66.391	−2272.139	−2032.747	151.685
732.200	199.995	276.882	177.519	72.753	--- CRYSTAL <---> LIQUID ---	
800	210.100	295.034	186.715	86.656	−2267.383	−1998.858	130.512
900	225.004	320.641	200.184	108.411	−2261.310	−1965.643	114.083
1000	239.911	345.119	213.462	131.657	−2253.900	−1933.176	100.979
1100	254.819	368.684	226.509	156.393	−2245.137	−1901.516	90.295
1200	269.729	391.495	239.312	182.620	−2235.011	−1870.714	81.430
1300	284.640	413.674	251.875	210.339	−2223.521	−1840.813	73.965
1400	299.554	435.314	264.208	239.549	−2210.657	−1811.848	67.601
1500	314.469	456.490	276.323	270.250	−2196.413	−1783.850	62.119

PREVIOUS: June 1966 CURRENT: December 1971

$S°(298.15\ K) = [171.395]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 732.2 \pm 0.2\ K$

$\Delta_f H°(298.15\ K) = [-2241.068]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 43.995 \pm 2.09\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of $\Delta_{fus} H°$ and the difference in enthalpy, $H°(732.2\ K) - H°(298.15\ K)$, between the crystal and liquid. Note that the result is based on direct measurements of the enthalpy of mixing of molten LiF and BeF_2 at 1135 K.[1]

Heat Capacity and Entropy

The constant $C_p°$ is derived from enthalpy data (743–873 K) of Douglas and Payne.[2] A glass transition is assumed at 500 K and below this temperature $C_p°$ is obtained from that of the crystal. The entropy is calculated in a manner analogous to that used for $\Delta_f H°$. Note that the result is based on measurements of $\Delta_f H°(1135\ K)$[1] and $\Delta_f G°(900\ K)$[3] for mixing of molten LiF and BeF_2.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Mass spectra of vapor effusing from twin–crucible Knudsen cells[4] suggest that the vapor consists of BeF_2, $LiBeF_3$ and traces of other molecules.

References

[1] J. L. Holm and O. J. Kleppa, Inorg. Chem. **8**, 207 (1969).
[2] T. B. Douglas and W. H. Payne, J. Res. Nat. Bur. Stand. **73A**, 479 (1969).
[3] B. F. Hitch and C. F. Baes, Inorg. Chem. **8**, 201 (1969); U. S. Atomic Energy Comm., ORNL–4257, 46 pp., (1968).
[4] A. Buchler and J. L. Stauffer, "Thermodynamics, Proc. Symp., Vienna, 1965," **1**, 271, Intl. At. Energy Agency, Vienna, (1966).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	135.269	171.395	171.395	0.	−2241.068	−2151.088	376.862
300	135.520	172.232	171.397	0.250	−2241.055	−2150.530	374.441
400	150.457	213.265	176.891	14.550	−2240.238	−2120.472	276.905
500	165.352	248.440	187.759	30.340	−2245.147	−2090.036	218.345
500.001	165.352	248.440	187.759	30.341	GLASS <--> LIQUID		
500.001	232.086	248.440	187.759	30.341	TRANSITION		
600	232.086	290.754	201.506	53.549	−2237.119	−2059.771	179.319
700	232.086	326.530	216.877	76.758	−2229.255	−2030.837	151.543
732.200	232.086	336.968	221.930	84.231	--- CRYSTAL <--> LIQUID ---		
800	232.086	357.521	232.563	99.966	−2221.555	−2003.019	130.784
900	232.086	384.857	247.996	123.175	−2214.029	−1976.156	114.693
1000	232.086	409.310	262.926	146.384	−2206.655	−1950.122	101.864
1100	232.086	431.430	277.255	169.592	−2199.420	−1924.820	91.402
1200	232.086	451.624	290.957	192.801	−2192.313	−1900.171	82.712
1300	232.086	470.201	304.040	216.010	−2185.333	−1876.110	75.383
1400	232.086	487.400	316.530	239.218	−2178.470	−1852.582	69.121
1500	232.086	503.413	328.461	262.427	−2171.718	−1829.540	63.710
1600	232.086	518.391	339.869	285.635	−2179.611	−1806.420	58.974
1700	232.086	532.461	350.788	308.844	−2463.146	−1768.956	54.353
1800	232.086	545.727	361.253	332.053	−2454.737	−1728.364	50.156
1900	232.086	558.275	371.296	355.261	−2446.377	−1688.238	46.413
2000	232.086	570.180	380.945	378.470	−2438.061	−1648.551	43.056
2100	232.086	581.503	390.228	401.679	−2429.783	−1609.280	40.029
2200	232.086	592.300	399.169	424.887	−2421.540	−1570.402	37.286
2300	232.086	602.617	407.792	448.096	−2413.325	−1531.897	34.790
2400	232.086	612.494	416.117	471.305	−2405.134	−1493.750	32.511
2500	232.086	621.968	424.163	494.513	−2396.963	−1455.944	30.420

PREVIOUS: June 1966 CURRENT: December 1971

0	to	732.2 K	crystal
above		732.2 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	135.269	130.583	130.583	0.	−2273.586	−2171.438	380.427
300	135.520	131.420	130.585	0.250	−2273.573	−2170.804	377.971
400	150.457	172.453	136.079	14.550	−2272.755	−2136.665	279.020
500	165.352	207.627	146.947	30.340	−2277.665	−2102.147	219.610
600	180.247	239.090	159.724	47.620	−2275.565	−2067.220	179.967
700	195.184	267.997	173.152	66.391	−2272.139	−2032.747	151.685
732.200	199.995	276.882	177.519	72.753	CRYSTAL <--> LIQUID TRANSITION		
732.200	232.086	336.968	177.519	116.748			
800	232.086	357.521	191.917	132.484	−2221.555	−2003.019	130.784
900	232.086	384.857	211.866	155.692	−2214.029	−1976.156	114.693
1000	232.086	409.310	230.409	178.901	−2206.655	−1950.122	101.864
1100	232.086	431.430	247.694	202.110	−2199.420	−1924.820	91.402
1200	232.086	451.624	263.859	225.318	−2192.313	−1900.171	82.712
1300	232.086	470.201	279.026	248.527	−2185.333	−1876.110	75.383
1400	232.086	487.400	293.304	271.736	−2178.470	−1852.582	69.121
1500	232.086	503.413	306.783	294.944	−2171.718	−1829.540	63.710
1600	232.086	518.391	319.546	318.153	−2179.611	−1806.420	58.974
1700	232.086	532.461	331.660	341.361	−2463.146	−1768.956	54.353
1800	232.086	545.727	343.188	364.570	−2454.737	−1728.364	50.156
1900	232.086	558.275	354.181	387.779	−2446.377	−1688.238	46.413
2000	232.086	570.180	364.686	410.987	−2438.061	−1648.551	43.056
2100	232.086	581.503	374.743	434.196	−2429.783	−1609.280	40.029
2200	232.086	592.300	384.389	457.405	−2421.540	−1570.402	37.286
2300	232.086	602.617	393.654	480.613	−2413.325	−1531.897	34.790
2400	232.086	612.494	402.568	503.822	−2405.134	−1493.750	32.511
2500	232.086	621.968	411.156	527.031	−2396.963	−1455.944	30.420

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = 176.822\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 319 \pm 29\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 321 \pm 29\ kJ·mol^{-1}$

Electronic Levels and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma^+$	0	2

$\omega_e = 2058.6\ cm^{-1}$ $\omega_e x_e = 35.5\ cm^{-1}$ $\sigma = 1$
$B_e = 10.308\ cm^{-1}$ $\alpha_e = 0.300\ cm^{-1}$ $r_e = 1.3431$ Å

Enthalpy of Formation

Gaydon[1] selected a value of 2.3 ± 0.3 eV (53 ± 7 kcal·mol^{-1}) for $D_0°$. Herzberg[2] estimated $D_0°$ as being 2.2 eV (50.7 kcal·mol^{-1}). Gaydon's[1] value was used in this table.

Heat Capacity and Entropy

Molecular constants were found in Herzberg.[2]

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall Ltd., London, 261 pp. (1953); refer to p. 221.
[2]G. Herzberg, "Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules," D. Van Nostrand Co. Inc., New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.648	318.716	318.716	INFINITE
100	29.128	144.978	202.751	−5.777	320.047	310.636	−162.260
200	29.149	165.173	179.492	−2.864	321.036	300.778	−78.555
250	29.171	171.680	177.303	−1.406	321.204	295.689	−61.781
298.15	29.224	176.822	176.822	0.	321.197	290.773	−50.942
300	29.227	177.003	176.822	0.054	321.194	290.585	−50.595
350	29.344	181.516	177.179	1.518	321.056	285.493	−42.607
400	29.538	185.446	177.972	2.990	320.835	280.426	−36.620
450	29.809	188.940	179.000	4.473	320.561	275.391	−31.967
500	30.144	192.098	180.154	5.972	320.253	270.389	−28.247
600	30.932	197.661	182.620	9.025	319.574	260.479	−22.677
700	31.769	202.492	185.122	12.160	318.849	250.686	−18.706
800	32.570	206.788	187.566	15.377	318.093	241.000	−15.736
900	33.296	210.667	189.921	18.671	317.307	231.410	−13.431
1000	33.937	214.209	192.175	22.033	316.485	221.910	−11.591
1100	34.496	217.470	194.328	25.456	315.617	212.494	−10.090
1200	34.982	220.493	196.384	28.930	314.694	203.159	−8.843
1300	35.404	223.310	198.348	32.450	313.708	193.904	−7.791
1400	35.774	225.947	200.227	36.009	312.653	184.728	−6.892
1500	36.098	228.427	202.025	39.603	311.522	175.629	−6.116
1600	36.385	230.766	203.749	43.228	295.776	167.134	−5.456
1700	36.641	232.980	205.404	46.879	294.882	159.121	−4.889
1800	36.871	235.081	206.994	50.555	293.972	151.162	−4.387
1900	37.079	237.080	208.526	54.253	293.042	143.253	−3.938
2000	37.269	238.987	210.001	57.970	292.092	135.394	−3.536
2100	37.443	240.809	211.425	61.706	291.120	127.583	−3.173
2200	37.603	242.555	212.801	65.458	290.128	119.819	−2.845
2300	37.752	244.230	214.131	69.226	289.113	112.100	−2.546
2400	37.892	245.839	215.419	73.008	288.076	104.426	−2.273
2500	38.023	247.389	216.667	76.804	287.017	96.795	−2.022
2600	38.146	248.883	217.878	80.613	285.935	89.208	−1.792
2700	38.264	250.324	219.053	84.433	284.830	81.662	−1.580
2800	38.376	251.718	220.195	88.265	−7.255	80.381	−1.500
2900	38.483	253.067	221.305	92.108	−7.341	83.512	−1.504
3000	38.585	254.373	222.386	95.962	−7.434	86.646	−1.509
3100	38.684	255.640	223.438	99.825	−7.534	89.784	−1.513
3200	38.780	256.869	224.464	103.698	−7.644	92.925	−1.517
3300	38.872	258.064	225.464	107.581	−7.764	96.070	−1.521
3400	38.962	259.226	226.440	111.473	−7.896	99.218	−1.524
3500	39.049	260.357	227.393	115.373	−8.042	102.371	−1.528
3600	39.135	261.458	228.324	119.283	−8.204	105.527	−1.531
3700	39.218	262.531	229.234	123.200	−8.384	108.689	−1.534
3800	39.300	263.578	230.124	127.126	−8.584	111.856	−1.538
3900	39.380	264.600	230.995	131.060	−8.806	115.028	−1.541
4000	39.459	265.598	231.848	135.002	−9.053	118.206	−1.544
4100	39.536	266.573	232.683	138.952	−9.327	121.391	−1.547
4200	39.613	267.527	233.501	142.909	−9.629	124.583	−1.549
4300	39.688	268.460	234.303	146.874	−9.962	127.783	−1.552
4400	39.762	269.373	235.090	150.847	−10.329	130.990	−1.555
4500	39.835	270.268	235.862	154.827	−10.730	134.206	−1.558
4600	39.908	271.144	236.619	158.814	−11.168	137.432	−1.561
4700	39.980	272.003	237.363	162.808	−11.644	140.667	−1.563
4800	40.051	272.846	238.093	166.810	−12.161	143.914	−1.566
4900	40.121	273.672	238.811	170.819	−12.719	147.171	−1.569
5000	40.191	274.483	239.517	174.834	−13.319	150.440	−1.572
5100	40.261	275.280	240.210	178.857	−13.964	153.721	−1.574
5200	40.329	276.062	240.892	182.886	−14.654	157.016	−1.577
5300	40.398	276.831	241.563	186.923	−15.389	160.324	−1.580
5400	40.466	277.587	242.223	190.966	−16.170	163.647	−1.583
5500	40.533	278.330	242.873	195.016	−16.998	166.984	−1.586
5600	40.600	279.061	243.512	199.072	−17.873	170.337	−1.589
5700	40.667	279.780	244.142	203.136	−18.794	173.706	−1.592
5800	40.733	280.488	244.763	207.206	−19.762	177.092	−1.595
5900	40.800	281.185	245.374	211.282	−20.777	180.494	−1.598
6000	40.865	281.871	245.977	215.366	−21.837	183.915	−1.601

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 170.65\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1147.8 \pm 42\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 1156.5 \pm 42\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1
$^3\Sigma$	[20000]	[3]

$\omega_e = 2221.7\ cm^{-1}$ $\omega_e x_e = 39.79\ cm^{-1}$ $\sigma = 1$
$B_e = 10.7996\ cm^{-1}$ $\alpha_e = 0.2935\ cm^{-1}$ $r_e = 1.31216$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from the equation $BeH(g) \rightarrow BeH^+(g) + e^-$ with the JANAF auxiliary data for BeH(g)[1] using an ionization potential of 8.6 ± 0.4 eV (198.34 ± 9.23 $kcal\cdot mol^{-1}$) obtained from Beckett and Cassidy.[2]

The dissociation energy, $D_0°(Be^+–H) = 3.2 \pm 0.2$ eV (73.8 $kcal\cdot mol^{-1}$), has been reported by Gaydon.[3] This yields $\Delta_f H°(BeH^+, g, 0\ K) = 270.0\ kcal\cdot mol^{-1}$ which is in agreement with the value adopted.

Heat Capacity and Entropy

The molecular constants were obtained from the ultraviolet spectroscopic studies by Watson and Humphrey.[4] The ground state configuration was given by Herzberg.[5] The estimated electronic level and quantum weight were obtained by assuming a $^3\Sigma$ level lies below the first observed excited state ($^1\Sigma$) at 40,000 cm^{-1}.

References

[1]JANAF Thermochemical Tables: BeH(g), 3–31–63.
[2]C. W. Beckett and E. C. Cassidy, NBS Report 8628, 111 pp. (January 1965); refer to App. IV, p. 109.
[3]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd. ed., Chapman and Hall Ltd., London, 261 pp. (1953); refer to p. 221.
[4]W. W. Watson and R. F. Humphreys, Phys. Rev. **52**, 318 (1937).
[5]G. Herzberg, "Molecular Spectra and Molecular Structure of Diatomic Molecules," 2nd ed., D. Van Nostrand Company, New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.644	1147.782		
100	29.126	138.816	196.573	−5.776			
200	29.144	159.009	173.321	−2.862			
250	29.159	165.514	171.133	−1.405			
298.15	29.193	170.653	170.653	0.	1156.458	1121.618	−196.503
300	29.195	170.833	170.653	0.054	1156.493	1121.402	−195.253
350	29.274	175.339	171.009	1.515	1157.391	1115.481	−166.476
400	29.413	179.256	171.800	2.982	1158.205	1109.438	−144.878
450	29.621	182.732	172.825	4.458	1158.963	1103.296	−128.067
500	29.892	185.866	173.975	5.946	1159.683	1097.072	−114.610
600	30.571	191.374	176.428	8.968	1161.052	1084.419	−94.407
700	31.339	196.144	178.911	12.063	1162.365	1071.543	−79.960
800	32.105	200.379	181.335	15.235	1163.643	1058.481	−69.112
900	32.823	204.203	183.667	18.482	1164.889	1045.260	−60.665
1000	33.471	207.695	185.898	21.797	1166.098	1031.903	−53.901
1100	34.046	210.913	188.027	25.174	1167.262	1018.427	−48.361
1200	34.551	213.897	190.060	28.604	1168.374	1004.847	−43.740
1300	34.994	216.681	192.002	32.082	1169.425	991.177	−39.826
1400	35.384	219.289	193.859	35.601	1170.408	977.428	−36.468
1500	35.728	221.742	195.637	39.157	1171.318	963.611	−33.556
1600	36.033	224.057	197.341	42.746	1157.614	950.262	−31.023
1700	36.304	226.250	198.978	46.363	1158.765	937.267	−28.799
1800	36.549	228.332	200.552	50.006	1159.900	924.205	−26.820
1900	36.770	230.314	202.066	53.672	1161.017	911.081	−25.047
2000	36.971	232.206	203.526	57.359	1162.115	897.898	−23.451
2100	37.156	234.014	204.935	61.065	1163.193	884.660	−22.005
2200	37.328	235.747	206.297	64.790	1164.251	871.372	−20.689
2300	37.489	237.409	207.614	68.531	1165.288	858.036	−19.487
2400	37.642	239.008	208.889	72.287	1166.304	844.655	−18.383
2500	37.788	240.548	210.124	76.059	1167.299	831.233	−17.368
2600	37.930	242.033	211.323	79.845	1168.273	817.771	−16.429
2700	38.069	243.467	212.487	83.645	1169.226	804.272	−15.560
2800	38.207	244.854	213.619	87.458	879.202	796.960	−14.867
2900	38.345	246.197	214.719	91.286	881.179	793.988	−14.301
3000	38.484	247.499	215.790	95.127	883.153	790.948	−13.772
3100	38.627	248.763	216.833	98.983	885.123	787.842	−13.275
3200	38.773	249.992	217.851	102.853	887.089	784.672	−12.808
3300	38.924	251.187	218.843	106.738	889.050	781.442	−12.369
3400	39.080	252.352	219.811	110.638	891.005	778.151	−11.955
3500	39.242	253.487	220.757	114.554	892.953	774.804	−11.563
3600	39.410	254.595	221.682	118.486	894.893	771.401	−11.193
3700	39.586	255.677	222.586	122.436	896.823	767.944	−10.841
3800	39.768	256.735	223.471	126.404	898.743	764.435	−10.508
3900	39.958	257.770	224.337	130.390	900.652	760.875	−10.191
4000	40.154	258.784	225.186	134.395	902.547	757.267	−9.889
4100	40.358	259.778	226.017	138.421	904.428	753.612	−9.601
4200	40.568	260.754	226.833	142.467	906.293	749.911	−9.327
4300	40.785	261.711	227.633	146.535	908.141	746.166	−9.064
4400	41.008	262.651	228.418	150.624	909.970	742.378	−8.813
4500	41.237	263.575	229.189	154.737	911.780	738.548	−8.573
4600	41.472	264.484	229.946	158.872	913.569	734.679	−8.343
4700	41.712	265.378	230.691	163.031	915.336	730.771	−8.122
4800	41.956	266.259	231.423	167.214	917.080	726.826	−7.909
4900	42.204	267.127	232.142	171.422	918.800	722.844	−7.706
5000	42.455	267.982	232.851	175.655	920.495	718.828	−7.510
5100	42.709	268.825	233.548	179.913	922.164	714.778	−7.321
5200	42.966	269.657	234.234	184.197	923.807	710.695	−7.139
5300	43.224	270.478	234.910	188.507	925.424	706.581	−6.964
5400	43.484	271.288	235.577	192.842	927.013	702.437	−6.795
5500	43.744	272.088	236.233	197.204	928.576	698.264	−6.632
5600	44.004	272.879	236.881	201.591	930.110	694.063	−6.474
5700	44.264	273.660	237.519	206.004	931.618	689.834	−6.322
5800	44.522	274.432	238.149	210.444	933.097	685.580	−6.174
5900	44.779	275.195	238.770	214.909	934.550	681.299	−6.032
6000	45.035	275.950	239.384	219.399	935.976	676.995	−5.894

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = [209.59 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -113.7 \pm 37.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -114.6 \pm 37.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm	g_i
0	[2]
[30000]	[4]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[1266](1)
[606](2)
[3650](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
Bond Distances: Be–O = [1.38] Å; O–H = [0.96] Å
Bond Angle: Be–O–H = [180]°
Rotational Constant: $B_O = [1.29312]\ cm^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -27.4 \pm 10\ kcal \cdot mol^{-1}$, which corresponds to $D_0°(Be–OH) = 113.9 \pm 10\ kcal \cdot mol^{-1}$, is derived from 3rd law analysis of Knudsen-cell mass-spectrometric studies and Knudsen-cell weight-loss studies of several BeOH(g) producing reactions.[1-3] The earlier Knudsen-cell mass-spectrometric measurement by Hildenbrand *et al.*[4] had indicated a minimum absolute value of $\Delta_f H°$(BeOH, g, 298.15 K) = $-25 \pm 10\ kcal \cdot mol^{-1}$.

Source	Reaction	Data Points	T/K	$\Delta_r H°(298.15\ K)$, 3rd law kcal·mol^{-1}	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Inami and Ju[1]	A	3	2422–2485	9.73 ± 0.93	−13.0 ± 2.0	−27.2
	B	3	2422–2485	0.82 ± 0.59	6.2 ± 5.5	−37.3
	C	3	2422–2485	75.56 ± 1.3	−5.3 ± 17	−16.1
	D	3	2422–2485	12.09 ± 1.8	3.6 ± 25	−29.0
Inami and Ju[2]	E	3	2425–2518	22.11 ± 2.1	−21.3 ± 8.6	−27.1
Ko, Greenbaum, and Farber[3]	F	3	2107–2368	106.01 ± 1.40	5.1 ± 1.7	−39.4

Reactions:
A) BeO(g) + OH(g) = BeOH(g) + O(g)
B) Be_2O(g) + OH(g) = BeOH(g) + BeO(g)
C) BeO(cr, β) + H(g) = BeOH(g)
D) Be_2O(g) + H(g) = BeOH(g) + Be(g)
E) BeCl(g) + OH(g) = BeOH(g) + Cl(g)
F) BeO(cr, α) + $0.5H_2$(g) = BeOH(g)

The average $\Delta_f H°$(BeOH, g, 298.15 K) from the measurements of Inami and Ju[1, 2] is −27.4 kcal·mol^{-1}. The $\Delta_{at} H°$(Be–OH, g, 298.15 K) = 115 kcal·mol^{-1} from $\Delta_f H°(298.15\ K)$ of −27.4 kcal·mol^{-1} appears more reasonable than a $\Delta_{at} H°$(Be–OH, g, 298.15 K) = 127 kcal·mol^{-1} from the $\Delta_f H°(298.15\ K)$ of −39.4 kcal·mol^{-1}, derived from Ko, Greenbaum, and Farber[3] above. This is based on a comparison *of the trends in* $D_0°$ values of the alkaline earth monofluorides and monochlorides and in the adopted $D_0°$ values for the other alkaline earth monohydroxides.[5] The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has already been recognized.[6-9] Accordingly, $\Delta_f H°$(BeOH, g, 298.15 K) = $-27.4 \pm 10\ kcal \cdot mol^{-1}$ is adopted.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh[10] and the evidence that the gaseous alkali metal monohydroxides are linear.[11-13] By analogy with BeF and BeCl[5] the ground state is assumed to be $^2\Sigma^+$ and the first excited state is estimated at 30000 cm^{-1}.

The Be–O bond distance is estimated to be slightly larger, 0.02 Å, than the Be–F bond distance[5] after noting the close similiarity in bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[5]

The Be–O stretching frequency, 1266 cm^{-1}, is estimated to be the same as the Be–F stretching frequency.[5, 9] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali metal hydroxides series. The bending frequency, 606 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides, by Acquista and Abramowitz.[9, 13]

Continued on page 428

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.528	−113.662	−113.662	INFINITE
100	29.307	174.021	240.225	−6.620	−113.745	−117.396	61.321
200	33.323	195.328	212.944	−3.523	−114.028	−120.970	31.594
250	35.983	203.052	210.212	−1.790	−114.314	−122.673	25.631
298.15	38.321	209.594	209.594	0.	−114.642	−124.254	21.769
300	38.405	209.831	209.595	0.071	−114.655	−124.314	21.645
350	40.511	215.914	210.070	2.045	−115.022	−125.895	18.789
400	42.314	221.444	211.152	4.117	−115.390	−127.423	16.640
450	43.849	226.519	212.581	6.272	−115.750	−128.905	14.963
500	45.157	231.208	214.212	8.498	−116.102	−130.348	13.617
600	47.250	239.636	217.763	13.123	−116.788	−133.133	11.590
700	48.862	247.045	221.428	17.932	−117.467	−135.803	10.134
800	50.175	253.658	225.051	22.886	−118.155	−138.376	9.035
900	51.295	259.634	228.566	27.961	−118.862	−140.861	8.175
1000	52.281	265.090	231.950	33.140	−119.598	−143.267	7.483
1100	53.162	270.115	235.194	38.413	−120.371	−145.596	6.914
1200	53.956	274.776	238.301	43.770	−121.186	−147.854	6.436
1300	54.672	279.123	241.276	49.202	−122.051	−150.041	6.029
1400	55.319	283.199	244.126	54.702	−122.972	−152.160	5.677
1500	55.901	287.036	246.860	60.264	−123.955	−154.211	5.370
1600	56.426	290.661	249.485	65.881	−139.543	−155.669	5.082
1700	56.898	294.096	252.009	71.547	−140.267	−156.655	4.813
1800	57.324	297.360	254.439	77.259	−141.000	−157.598	4.573
1900	57.708	300.470	256.780	83.011	−141.746	−158.499	4.357
2000	58.053	303.439	259.040	88.799	−142.506	−159.361	4.162
2100	58.366	306.279	261.222	94.620	−143.285	−160.185	3.984
2200	58.648	309.001	263.332	100.471	−144.083	−160.971	3.822
2300	58.904	311.614	265.375	106.349	−144.903	−161.721	3.673
2400	59.136	314.126	267.355	112.251	−145.747	−162.434	3.535
2500	59.347	316.544	269.274	118.175	−146.615	−163.111	3.408
2600	59.540	318.876	271.137	124.120	−147.509	−163.754	3.290
2700	59.715	321.126	272.947	130.083	−148.430	−164.361	3.180
2800	59.876	323.301	274.707	136.063	−440.336	−158.711	2.961
2900	60.024	325.404	276.419	142.058	−440.249	−148.655	2.678
3000	60.159	327.442	278.086	148.067	−440.174	−138.601	2.413
3100	60.284	329.416	279.710	154.089	−440.114	−128.550	2.166
3200	60.400	331.332	281.294	160.123	−440.069	−118.500	1.934
3300	60.507	333.192	282.838	166.169	−440.042	−108.452	1.717
3400	60.606	335.000	284.346	172.224	−440.034	−98.404	1.512
3500	60.700	336.758	285.818	178.290	−440.047	−88.356	1.319
3600	60.787	338.470	287.257	184.364	−440.083	−78.307	1.136
3700	60.869	340.136	288.664	190.447	−440.145	−68.257	0.964
3800	60.947	341.760	290.040	196.538	−440.235	−58.204	0.800
3900	61.021	343.345	291.387	202.636	−440.354	−48.149	0.645
4000	61.092	344.890	292.705	208.742	−440.505	−38.091	0.497
4100	61.160	346.400	293.996	214.855	−440.690	−28.028	0.357
4200	61.226	347.874	295.262	220.974	−440.911	−17.961	0.223
4300	61.290	349.316	296.502	227.100	−441.170	−7.887	0.096
4400	61.353	350.726	297.718	233.232	−441.470	2.192	−0.026
4500	61.415	352.105	298.912	239.370	−441.811	12.279	−0.143
4600	61.477	353.456	300.083	245.515	−442.197	22.373	−0.254
4700	61.538	354.778	301.232	251.666	−442.628	32.478	−0.361
4800	61.598	356.075	302.362	257.823	−443.107	42.591	−0.463
4900	61.660	357.345	303.471	263.985	−443.635	52.716	−0.562
5000	61.721	358.592	304.561	270.154	−444.212	62.851	−0.657
5100	61.784	359.814	305.632	276.330	−444.842	72.999	−0.748
5200	61.847	361.015	306.686	282.511	−445.524	83.158	−0.835
5300	61.911	362.194	307.722	288.699	−446.259	93.333	−0.920
5400	61.977	363.351	308.741	294.893	−447.048	103.521	−1.001
5500	62.043	364.489	309.745	301.094	−447.892	113.724	−1.080
5600	62.111	365.608	310.732	307.302	−448.791	123.944	−1.156
5700	62.181	366.708	311.705	313.517	−449.746	134.179	−1.230
5800	62.252	367.790	312.662	319.738	−450.756	144.433	−1.301
5900	62.324	368.854	313.606	325.967	−451.822	154.703	−1.370
6000	62.399	369.903	314.535	332.203	−452.943	164.993	−1.436

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [203.9 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 754.70 \pm 50\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 759.93 \pm 50\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1260] (1)
[600] (2)
[3650] (1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Be–O = [1.38] Å; O–H = [0.96] Å
Bond Angle: Be–O–H = [180]°
Rotational Constant: B_O = [1.2932] cm^{-1}

Enthalpy of Formation

Using mass spectrometric techniques, Inami and Ju[1] determined the appearance potential of BeOH(g) to be 9.0 ± 0.5 eV (207.55 ± 11.53 $kcal \cdot mol^{-1}$). In the same study, Porter[2] was reported to have said that the appearance potential of a metal hydroxide is expected to be about the same as the corresponding fluoride. In this case, the appearance potential of BeF(g) is 9.1 eV,[1] which is within 0.1 eV of the value for BeOH(g). It is also interesting to note that the ionization potential of Be(g) is 9.32 eV.[3] We adopt the experimentally determined appearance potential of 9.0 ± 0.5 eV which refers to the process $BeOH(g) + e^- = BeOH^+(g) + 2e^-$. Using auxiliary data,[3] we calculate $\Delta_f H°(0\ K) = 180.39 \pm 12.0\ kcal \cdot mol^{-1}$ for $BeOH^+(g)$. This leads to $\Delta_f H°(298.15\ K) = 181.63 \pm 12.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[3,4,5,6] In addition, Walsh[7] had predicted that BAH molecules (H=hydrogen atom) with ten or less valence electrons ($BeOH^+$ has 8 valence electrons) will be linear in their ground state. The molecule $BeOH^+$ is isoelectronic with LiOH.

The bond dissociation energy for $BeOH^+$(121.2 $kcal \cdot mol^{-1}$)[3] for the process $BeOH^+(g) = Be^+(g) + OH(g)$ is fairly close to that for BeOH(113.9 $kcal \cdot mol^{-1}$).[3] This suggests a similar bonding in these two molecules. Thus, bond distances are assumed to be the same as those adopted for BeOH(g).[3] The vibrational frequencies are assumed to be similar to those adopted for BeOH(g).[3] The ground state quantum weight is assumed to be the same as that of LiOH(g).[3]

References

[1]Y. H. Inami and F. Ju, Philco–Ford Corp., Aeronutronic Dev., Report U–4307, Contract F 04611–68–C–0012, (February 1, 1968).
[2]R. F. Porter, personal communication, as referenced by Inami and Ju.[1]
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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.546	754.698		
100	29.321	168.260	234.642	−6.638			
200	33.428	189.606	207.280	−3.535			
250	36.103	197.356	204.539	−1.796			
298.15	38.441	203.919	203.919	0.	759.934	745.758	−130.654
300	38.525	204.157	203.920	0.071	759.959	745.670	−129.833
350	40.625	210.257	204.397	2.051	760.638	743.235	−110.922
400	42.420	215.803	205.481	4.129	761.314	740.703	−96.726
450	43.946	220.889	206.914	6.289	761.998	738.085	−85.675
500	45.245	225.589	208.550	8.519	762.690	735.391	−76.826
600	47.323	234.031	212.109	13.153	764.091	729.800	−63.535
700	48.922	241.450	215.782	17.968	765.497	723.974	−54.024
800	50.224	248.071	219.411	22.927	766.894	717.946	−46.877
900	51.336	254.052	222.933	28.007	768.269	711.745	−41.309
1000	52.316	259.512	226.322	33.190	769.615	705.392	−36.846
1100	53.192	264.540	229.571	38.466	770.925	698.906	−33.188
1200	53.982	269.203	232.682	43.826	772.191	692.303	−30.135
1300	54.695	273.553	235.660	49.260	773.407	685.596	−27.548
1400	55.338	277.630	238.514	54.762	774.567	678.797	−25.326
1500	55.918	281.468	241.251	60.326	775.664	671.918	−23.398
1600	56.441	285.094	243.879	65.944	762.156	665.493	−21.726
1700	56.912	288.530	246.405	71.612	763.512	659.410	−20.261
1800	57.336	291.795	248.837	77.325	764.859	653.248	−18.957
1900	57.719	294.906	251.180	83.078	766.193	647.010	−17.788
2000	58.063	297.875	253.441	88.868	767.512	640.704	−16.733
2100	58.375	300.716	255.625	94.690	768.813	634.331	−15.778
2200	58.657	303.438	257.737	100.542	770.095	627.897	−14.908
2300	58.912	306.051	259.781	106.420	771.354	621.405	−14.113
2400	59.143	308.563	261.762	112.323	772.590	614.859	−13.382
2500	59.354	310.982	263.683	118.248	773.801	608.262	−12.709
2600	59.546	313.314	265.547	124.193	774.986	601.617	−12.087
2700	59.721	315.564	267.358	130.157	776.144	594.927	−11.510
2800	59.881	317.739	269.119	136.137	486.318	594.417	−11.089
2900	60.027	319.843	270.832	142.132	488.483	598.239	−10.775
3000	60.162	321.880	272.500	148.142	490.637	601.987	−10.482
3100	60.285	323.855	274.125	154.164	492.776	605.664	−10.205
3200	60.399	325.771	275.709	160.199	494.900	609.271	−9.945
3300	60.505	327.631	277.254	166.244	497.005	612.813	−9.700
3400	60.602	329.439	278.763	172.299	499.092	616.291	−9.468
3500	60.692	331.197	280.236	178.364	501.157	619.708	−9.249
3600	60.775	332.908	281.675	184.438	503.198	623.066	−9.040
3700	60.853	334.574	283.082	190.519	505.213	626.368	−8.843
3800	60.925	336.198	284.459	196.608	507.200	629.616	−8.655
3900	60.992	337.781	285.806	202.704	509.157	632.812	−8.476
4000	61.055	339.326	287.125	208.806	511.081	635.958	−8.305
4100	61.113	340.835	288.416	214.915	512.971	639.056	−8.142
4200	61.168	342.308	289.682	221.029	514.823	642.109	−7.986
4300	61.220	343.748	290.923	227.148	516.636	645.118	−7.837
4400	61.268	345.156	292.139	233.273	518.407	648.085	−7.694
4500	61.313	346.533	293.333	239.402	520.135	651.013	−7.557
4600	61.355	347.881	294.504	245.535	521.817	653.902	−7.425
4700	61.395	349.201	295.654	251.673	523.451	656.756	−7.299
4800	61.433	350.494	296.783	257.814	525.035	659.576	−7.178
4900	61.469	351.761	297.892	263.959	526.569	662.363	−7.061
5000	61.502	353.003	298.982	270.108	528.049	665.119	−6.948
5100	61.534	354.222	300.053	276.260	529.475	667.846	−6.840
5200	61.564	355.417	301.106	282.415	530.845	670.546	−6.736
5300	61.593	356.590	302.142	288.572	532.158	673.220	−6.635
5400	61.620	357.741	303.161	294.733	533.414	675.870	−6.538
5500	61.645	358.872	304.164	300.896	534.611	678.496	−6.444
5600	61.670	359.983	305.151	307.062	535.748	681.102	−6.353
5700	61.693	361.075	306.122	313.230	536.826	683.688	−6.265
5800	61.715	362.148	307.079	319.401	537.843	686.256	−6.180
5900	61.735	363.203	308.021	325.573	538.800	688.806	−6.098
6000	61.755	364.241	308.950	331.748	539.695	691.341	−6.019

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K)$ = [173.1] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(\ K)$ = [127.21] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [125.52] $kJ·mol^{-1}$

Vibrational Frequencies and Multiplicities υ, cm^{-1}
[2200] (1)
[1500] (2)
[1300] (1)

Ground State Quantum Weight: 1 σ = 2
Point Group: [$D_{\infty h}$]
Bond Distance: Be–H = [1.34] Å
Bond Angle: H–Be–H = [180]°
Rotational constant: B_o = [4.657172] cm^{-1}

Enthalpy of Formation

Estimated by O'Brien, Perrin and Perrine.[1]

Heat Capacity and Entropy

Molecular and spectroscopic parameters estimated.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.714	127.206	127.206	INFINITE
100	29.101	141.109	199.331	−5.822	127.059	123.071	−64.286
200	29.204	161.292	175.842	−2.910	126.700	119.159	−31.121
250	29.588	167.843	173.610	−1.442	126.180	117.329	−24.515
298.15	30.370	173.115	173.115	0.	125.520	115.682	−20.267
300	30.408	173.303	173.115	0.056	125.492	115.622	−20.131
350	31.659	178.079	173.490	1.606	124.715	114.037	−17.019
400	33.233	182.406	174.338	3.227	123.916	112.566	−14.700
450	34.999	186.421	175.460	4.933	123.134	111.195	−12.907
500	36.842	190.204	176.747	6.729	122.392	109.908	−11.482
600	40.446	197.244	179.585	10.595	121.062	107.540	−9.362
700	43.678	203.727	182.577	14.805	119.943	105.378	−7.863
800	46.434	209.744	185.601	19.315	119.003	103.363	−6.749
900	48.733	215.351	188.599	24.077	118.198	101.458	−5.888
1000	50.634	220.587	191.539	29.048	117.482	99.637	−5.204
1100	52.204	225.489	194.405	34.192	116.816	97.885	−4.648
1200	53.505	230.088	197.189	39.480	116.167	96.192	−4.187
1300	54.589	234.415	199.887	44.886	115.508	94.554	−3.799
1400	55.496	238.495	202.501	50.392	114.817	92.968	−3.469
1500	56.262	242.351	205.030	55.981	114.078	91.433	−3.184
1600	56.912	246.003	207.478	61.640	98.740	90.475	−2.954
1700	57.467	249.470	209.847	67.360	98.268	89.973	−2.765
1800	57.944	252.769	212.140	73.131	97.786	89.499	−2.597
1900	58.357	255.913	214.362	78.947	97.287	89.052	−2.448
2000	58.716	258.916	216.515	84.801	96.769	88.632	−2.315
2100	59.030	261.788	218.603	90.688	96.227	88.238	−2.195
2200	59.306	264.541	220.629	96.605	95.659	87.871	−2.086
2300	59.550	267.183	222.596	102.548	95.065	87.530	−1.988
2400	59.766	269.722	224.507	108.514	94.441	87.215	−1.898
2500	59.958	272.165	226.365	114.501	93.787	86.928	−1.816
2600	60.131	274.520	228.172	120.505	93.102	86.667	−1.741
2700	60.285	276.793	229.931	126.526	92.386	86.433	−1.672
2800	60.425	278.988	231.644	132.562	−199.320	92.448	−1.725
2900	60.551	281.110	233.313	138.611	−199.037	102.864	−1.853
3000	60.665	283.165	234.941	144.672	−198.771	113.270	−1.972
3100	60.768	285.156	236.529	150.743	−198.524	123.667	−2.084
3200	60.863	287.087	238.079	156.825	−198.295	134.056	−2.188
3300	60.950	288.961	239.593	162.916	−198.089	144.439	−2.286
3400	61.029	290.782	241.071	169.015	−197.906	154.816	−2.378
3500	61.102	292.552	242.517	175.121	−197.748	165.188	−2.465
3600	61.169	294.274	243.931	181.235	−197.619	175.555	−2.547
3700	61.231	295.951	245.314	187.355	−197.519	185.920	−2.625
3800	61.288	297.585	246.669	193.481	−197.451	196.282	−2.698
3900	61.341	299.177	247.995	199.612	−197.418	206.643	−2.768
4000	61.390	300.731	249.294	205.749	−197.421	217.003	−2.834
4100	61.436	302.247	250.567	211.890	−197.463	227.365	−2.897
4200	61.478	303.728	251.815	218.036	−197.547	237.727	−2.957
4300	61.518	305.175	253.039	224.186	−197.674	248.092	−3.014
4400	61.555	306.590	254.240	230.339	−197.847	258.461	−3.068
4500	61.590	307.974	255.419	236.497	−198.067	268.834	−3.121
4600	61.622	309.328	256.576	242.657	−198.337	279.212	−3.171
4700	61.653	310.653	257.713	248.821	−198.658	289.597	−3.219
4800	61.681	311.952	258.829	254.988	−199.031	299.990	−3.265
4900	61.708	313.224	259.926	261.157	−199.458	310.390	−3.309
5000	61.734	314.471	261.005	267.329	−199.940	320.800	−3.351
5100	61.758	315.693	262.065	273.504	−200.478	331.220	−3.392
5200	61.780	316.893	263.108	279.681	−201.072	341.651	−3.432
5300	61.802	318.070	264.134	285.860	−201.724	352.094	−3.470
5400	61.822	319.225	265.144	292.041	−202.433	362.550	−3.507
5500	61.841	320.360	266.137	298.224	−203.200	373.019	−3.543
5600	61.859	321.474	267.115	304.409	−204.024	383.504	−3.577
5700	61.876	322.569	268.079	310.596	−204.905	394.003	−3.611
5800	61.893	323.646	269.028	316.785	−205.842	404.519	−3.643
5900	61.908	324.704	269.962	322.975	−206.836	415.050	−3.675
6000	61.923	325.744	270.883	329.166	−207.884	425.599	−3.705

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = [53.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) =$ Unknown

$\Delta_f H°(298.15\ K) = -902.9 \pm 2.0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Bear and Turnbull[1] measured the enthalpy of solution of α–Be(OH)$_2$ and Be in 22.6% HF(aq) at 21°C. Combining these results, adjusting to 25°C, and correcting for the small HF concentration differences in the two systems, we calculate $\Delta_r H°(298.15\ K) = -79.16\ kcal \cdot mol^{-1}$ for the reaction Be(cr) + 2H$_2$O(l) = Be(OH)$_2$(α, cr) + H$_2$(g). Using auxiliary data,[2,3] we derive $\Delta_f H°(298.15\ K) = -215.8\ kcal \cdot mol^{-1}$ for α–Be(OH)$_2$. Since this adopted value is calorimetrically determined and based on well characterized samples, we assign an uncertainty of ± 0.5 $kcal \cdot mol^{-1}$.

Parker[4] recently reviewed data pertaining to the enthalpy of formation of the beryllium hydroxides. Her analyses were intended to give additional support to the thermochemical values chosen for BeO(cr). Our interpretation would differ slightly due to the fact that our $\Delta_f H°$ value for BeO(cr) is different (by 0.3 $kcal \cdot mol^{-1}$ at 298.15 K) from that adopted by Parker.[4] Discussed in her review were the enthalpy of solution studies by Fricks and Wullhorst[5] [involving BeO and α–Be(OH)$_2$ in 11.59% HF] and Matignon and Marchal[6,7] [amorphous Be(OH)$_2$ in 30% HF]. In addition there is also an earlier study by Mulert[8] involving amorphous Be(OH)$_2$ in 20% HF. All these studies are in fair agreement with our adopted value for $\Delta_f H°(298.15\ K)$. These latter studies are thought to be less reliable, however, due to incomplete characterization of the beryllium compounds.

Heat Capacity and Entropy

The heat capacity is assumed to be identical to that of the β–phase. The entropy difference between the α and β phases may be obtained from the solubility data of Fricke and Humme.[9] Both crystalline forms of Be(OH)$_2$ were dissolved in varying concentrations of aqueous NaOH. By relating the quantities dissolved, we calculate $\Delta_r G°(303\ K) = -0.5\ (\pm 0.2)\ kcal \cdot mol^{-1}$ for the process α–Be(OH)$_2$ = β–Be(OH)$_2$. Using auxiliary data,[2] we find $\Delta_r S°(303\ K) = -0.8\ cal \cdot K^{-1} \cdot mol^{-1}$, from which we calculate and adopt $S°(298.15\ K) = 12.8\ cal \cdot K^{-1} \cdot mol^{-1}$ for α–Be(OH)$_2$. We assign an uncertainty of ±2 $cal \cdot K^{-1} \cdot mol^{-1}$ to reflect the possible error in this calculation of $\Delta_r S°(303\ K)$.

Phase Data

The structural information for α–Be(OH)$_2$ via x–ray techniques is not complete.[1,9–11] A tetragonal unit cell has been suggested by Guillemat and Lecocq[11] without supporting data. Bear and Turnbull,[1] following this suggestion and using their x–ray data, calculated a crystal density which was consistent with the two experimentally determined values of Fricke and Severin[12] (helium densitometry and a pycnometric method). This lends support to the premise that α–Be(OH)$_2$ has a tetragonal unit cell. The alpha phase is metastable.

Decomposition Data

T_{dcm} is calculated as the temperature at which $\Delta_r G°$ is zero for the reaction Be(OH)$_2$(α, cr) = BeO(α, cr) + H$_2$O(g).

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[1] I. J. Bear and A. G. Turnbull, J. Phys. Chem. **69**, 2828 (1965).
[2] JANAF Thermochemical Tables: Be(cr), 9–30–61; H$_2$(g) and H$_2$O(g), 3–31–61; BeO(aq, cr), 6–30–75; Be(OH)$_2$(β, cr), 12–31–75.
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[11] A. Guillemat and A. Lecocq, Compt. Rend. **257**, 1260 (1963).
[12] R. Fricke and H. Severin, Z. anorg. allgem. Chem. **205**, 287 (1932).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	65.701	53.555	53.555	0.	−902.907	−815.933	142.948
300	66.053	53.963	53.556	0.122	−902.923	−815.394	141.973
400	82.902	75.434	56.369	7.626	−903.139	−786.150	102.661
500	92.994	95.086	62.183	16.451	−902.397	−756.975	79.081
600	99.387	112.633	69.157	26.086	−901.119	−728.004	63.378
700	103.956	128.310	76.508	36.261	−899.527	−699.274	52.180
800	107.495	142.430	83.881	46.839	−897.735	−670.787	43.798
900	110.399	155.262	91.110	57.737	−895.810	−642.532	37.292
1000	112.905	167.027	98.121	68.906	−893.790	−614.498	32.098

PREVIOUS: December 1966 CURRENT: December 1975

$S°(298.15\ K) = [50.2 \pm 4.2]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(0\ K) =$ Unknown

$T_{dcm} = [366]$ K $\Delta_f H°(298.15\ K) \approx -905.8 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

Bear and Turnbull[1] measured the enthalpy of solution of β–Be(OH)$_2$ and Be in 22.6% HF(aq) at 21°C. Combining these results, adjusting to 25°C, and correcting for the small HF concentration differences in the two systems, we calculate $\Delta_f H°(298.15\ K) = -79.89\ kcal·mol^{-1}$ for the reaction Be(cr) + 2H$_2$O(l) = Be(OH)$_2$(β, cr) + H$_2$(g). Using auxiliary data,[2,3] we derive $\Delta_f H°(298.15\ K) = -216.5\ kcal·mol^{-1}$ for β–Be(OH)$_2$. Since this adopted value is calorimetrically determined and based on well characterized samples, we assign an uncertainty of ±0.5 kcal·mol^{-1}.

Parker[4] recently reviewed data pertaining to the enthalpy of formation of the beryllium hydroxides. Her analyses were intended to give additional support to the thermochemical values chosen for BeO(cr). Our interpretation would differ slightly due to the fact that our $\Delta_f H°$ value for BeO(cr) is different (by 0.3 kcal·mol^{-1} at 298.15 K) from that adopted by Parker.[4] Discussed in her review were the enthalpy of solution studies by Fricke and Wullhorst[5] [involving BeO and β–Be(OH)$_2$ in 11.59% HF] and Matignon and Marchal[6,7] [amorphous Be(OH)$_2$ in 30% HF]. In addition there is also an earlier study by Mulert[8] involving amorphous Be(OH)$_2$ in 20% HF. These latter three studies are in fair agreement with our adopted value for $\Delta_f H°(298.15\ K)$ but are thought to be less reliable, however, due to incomplete characterization of the beryllium compounds.

Fricke and Severin[9] and Baur and Lecocq[10] measured the deomposition pressure of water vapor over β–Be(OH)$_2$. Fricke and Severin[9] observed a decomposition temperature at 105°C at a pressure of 100 mm Hg while Baur and Lecocq[10] observed 223°C for the equilibrium with saturated water vapor at 24.2 atm. We reduce the latter data to a standard state value $\Delta_r G°(496\ K) = -3028\ cal·mol^{-1}$ for the decomposition reaction Be(OH)$_2$(β, cr) → BeO(α, cr) + H$_2$O(g). The 3rd law analyses for these two decomposition studies are given below where $\Delta_f H°(298.15\ K)$ refers to the enthalpy of formation of β–Be(OH)$_2$.

			kcal·mol^{-1}	
Source	T/K	Method	$\Delta_r H°(298.15\ K)$	$\Delta_f H°(298.15\ K)$
Fricke and Severin[9]	378	K_p	15.27	≥−218.5
Baur and Lecocq[10]	496	K_p	14.88	≥−218.1

These values are within 2 kcal·mol^{-1} of our adopted $\Delta_f H°(298.15\ K)$ value. The difference may be due to the formation of metastable BeO. Fricke and Severin[9] reported that BeO had a distorted lattice which would suggest a $\Delta_f H°$ value more positive than −145.4 kcal·mol^{-1}. Thus, we conclude that these two studies[9,10] are consistent with our adopted value but are not sufficiently definitive for further consideration.

Heat Capacity and Entropy

The heat capacity is estimated from that for Mg(OH)$_2$ by subtracting the values for MgO(cr) and adding those for BeO(α, cr).[2] The entropy is estimated to be $S°(298.15\ K) = 12.0\ cal·K^{-1}·mol^{-1}$. This value is a compromise of values suggested by two different paths. Additive entropy constants of Kelley[11] yield $S°(298.15\ K) = 13.20\ cal·K^{-1}·mol^{-1}$ whereas a comparison of entropy differences for the alkali metal and alkaline earth chlorides and hydroxides sugggest values in the range 10.2 to 12.4 cal·K^{-1}·mol^{-1}. Our adopted value is the same as that selected by NBS.[12]

Phase Data

Bear and Turnbull[1] and Seitz *et al.*,[13] using x–ray powder techniques, determined that β–Be(OH)$_2$ has an orthorhombic structure, the ϵ–Zn(OH)$_2$ structure. The β–structure is the stable crystalline form for Be(OH)$_2$ whereas the α–structure is metastable.

Decomposition Data

T_{dcm} is calculated as the temperature at which $\Delta_r G°$ is zero for the reaction Be(OH)$_2$(β, cr) → BeO(α, cr) + H$_2$O(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	65.701	50.208	50.208	0.	−905.836	−817.864	143.286
300	66.053	50.615	50.209	0.122	−905.852	−817.318	142.308
400	82.902	72.087	53.022	7.626	−906.067	−787.740	102.868
500	92.994	91.739	58.836	16.451	−905.326	−758.230	79.212
600	99.387	109.286	65.810	26.086	−904.047	−728.924	63.458
700	103.956	124.963	73.161	36.261	−902.456	−699.859	52.224
800	107.495	139.082	80.533	46.839	−900.664	−671.038	43.814
900	110.399	151.915	87.763	57.737	−898.739	−642.449	37.287
1000	112.905	163.680	94.774	68.906	−896.719	−614.080	32.076

PREVIOUS: December 1966 CURRENT: December 1975

$S°(298.15\ K)$ = [233.97 ± 12.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -670 \pm 38\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -677 \pm 38\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[670](1)	[3650](2)
[345](2)	[606](4)
[1530](1)	

Ground State Quantum Weight: [1] σ = 2
Point Group: [$C_{\infty v}$]
Bond Distances: Be–O = [1.42] Å; O–H = [0.96] Å
Bond Angles: Be–O–H = [180]°; O–Be–O = [180]°
Rotational Constant: B_o = [0.22198] cm^{-1}

Enthalpy of Formation

The equilibrium reaction $BeO(\alpha, cr) + H_2O(g) = Be(OH)_2(g)$ has been studied by several investigators;[1-6] all inferred that $Be(OH)_2$ was the major product, but there was no direct proof of this. A 2nd and 3rd law analysis is given below.

Investigator	Data Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Stuart and Price[1]	15**	1338–1653	40.66 ± 0.70	41.76 ± 0.26	0.7 ± 0.4	−161.74
Young[2]	7	1576–1839	42.25 ± 1.46	41.58 ± 0.43	−0.4 ± 0.9	−161.92
Grossweiner and Seifert[3]	24**	1472–1873	42.23 ± 0.17	42.27 ± 0.69	0.0 ± 0.7	−161.23
	11	1673		41.09 ± 1.47		−161.81
Blauer *et al.*[4]	4	1567–1808	38.2 ± 4.3	35.26 ± 0.82	−1.8 ± 2.5	−168.24
Brewer and Elliott[5]	6	1527–1583	74.8 ± 68.8	44.12 ± 4.4	−20 ± 44	−159.38
Morize *et al.*[6]	eqn		49.1	37.7	−6.9	−165.80

**One (or two) point(s) rejected due to a statistical test.

Three of these studies[1-3] were conducted under similar conditions. Each of these investigations[1-3] varied the $H_2O(g)$ flow rate without a detectable change in K_p value. However, one study[3] used a considerable larger flow rate than the others.[1,2] The residence times in all cases were quite comparable. Blauer *et al.*[4] studied the same system using molecular flow effusion techniques. They reported a larger variation of K_p with surface area, operated at pressures near the upper limits of the molecular flow regime, and encountered unexpected variations of the blank experiments with sample size. Brewer and Elliot[5] also studied the same system but details of the sample are not available and the results show considerable drift. Baur and Lecocq[7] cited a study by Morize *et al.*[6] No details are given and the results are presented in equation form. It is presumed that the results were obtained in the vicinity of 1673 K.

We adopt $\Delta_f H°(298.15\ K) = -161.7\ kcal·mol^{-1}$ for $Be(OH)_2(g)$ which is an average value of three studies.[1-3] We assign an uncertainty of ±9.0 $kcal·mol^{-1}$. The remaining studies are in reasonable agreement with our adopted value (and its uncertainty). As is suggested by Blauer *et al.*,[4] the results of the transpiration studies are greatly affected by surface effects. The larger $\Delta_f H°$ value derived from Blauer *et al.*[4] is due to a consideration of sample size and surface effects. Thus, it is possible that the earlier studies[1,2,3] had not achieved equilibrium.

Hildenbrand *et al.*[8] examined the $BeO–H_2O$ system at 2300°C mass-spectrometrically and detected BeOH and $Be(OH)_2$. They reported a maximum value for the equilibrium constant for the reaction $BeO(g) + H_2O(g) = Be(OH)_2(g)$. From this maximum value, we calculate $\Delta_f H°(298.15\ K) \geq -161.3\ kcal·mol^{-1}$ for $Be(OH)_2(g)$. This gives additional support for our adopted value. Qualitative support is found by comparing the dissociation energies of BeOH(g) and $Be(OH)_2(g)$ into Be(g) and OH(g); the ratio for the mono- to dihydroxide dissociation is (113.9/256.1) = 0.445; a value which is consistent with similar ratios for the other alkaline earth hydroxides and halides.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized.[9-11] The O–Be–O angle is assumed to be the same as the F–Be–F angle,[12] i.e. 180°; the Be–O–H angle is assumed to be linear as in MgOH(g).[12] The Be–O bond distance is estimated to be slightly larger, 0.02 Å, than the Be–F distance in BeF_2[12] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is taken to be the same as in water.[12]

The vibrational frequencies are estimated to be the same as in BeF_2[12] (O–Be–O symmetrical and antisymmetrical stretch and bend) and as in BeOH[12] (O–H stretch and Be–O–H bend).

Jackson[13] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K)$ = 59.076 cal·K^{-1}·mol^{-1}. We assign an uncertainty of ±3 cal·K^{-1}·mol^{-1} to the adopted entropy.

Continued on page 428

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.588	−670.058	−670.058	INFINITE
100	32.467	184.150	280.300	−9.615	−673.028	−663.989	346.832
200	49.187	211.481	239.353	−5.575	−675.170	−654.052	170.821
250	57.182	223.343	234.979	−2.909	−675.951	−648.679	135.534
298.15	63.419	233.968	233.968	0.	−676.553	−643.369	112.716
300	63.631	234.361	233.970	0.118	−676.573	−643.163	111.985
350	68.713	244.567	234.764	3.431	−677.063	−637.554	95.150
400	72.738	254.016	236.587	6.971	−677.439	−631.883	82.516
450	75.976	262.776	239.017	10.692	−677.722	−626.171	72.684
500	78.628	270.923	241.805	14.559	−677.935	−620.431	64.816
600	82.730	285.641	247.911	22.638	−678.212	−608.902	53.010
700	85.823	298.636	254.248	31.072	−678.362	−597.337	44.574
800	88.333	310.265	260.536	39.783	−678.437	−585.756	38.246
900	90.482	320.796	266.655	48.726	−678.466	−574.169	33.324
1000	92.385	330.429	272.558	57.872	−678.470	−562.580	29.386
1100	94.095	339.316	278.228	67.197	−678.464	−550.991	26.164
1200	95.642	347.571	283.667	76.685	−678.461	−539.403	23.480
1300	97.044	355.283	288.882	86.321	−678.474	−527.814	21.208
1400	98.311	362.522	293.886	96.089	−678.515	−516.224	19.261
1500	99.456	369.344	298.692	105.979	−678.596	−504.629	17.573
1600	100.490	375.796	303.311	115.977	−693.262	−492.502	16.079
1700	101.421	381.917	307.756	126.073	−693.048	−479.961	14.747
1800	102.262	387.738	312.039	136.258	−692.833	−467.433	13.565
1900	103.019	393.288	316.171	146.523	−692.622	−454.916	12.507
2000	103.703	398.590	320.160	156.860	−692.420	−442.410	11.555
2100	104.321	403.665	324.016	167.261	−692.234	−429.914	10.694
2200	104.881	408.531	327.748	177.722	−692.066	−417.427	9.911
2300	105.387	413.204	331.363	188.236	−691.921	−404.947	9.197
2400	105.847	417.699	334.867	198.798	−691.801	−392.473	8.542
2500	106.266	422.029	338.267	209.404	−691.711	−380.002	7.940
2600	106.647	426.204	341.570	220.050	−691.650	−367.535	7.384
2700	106.995	430.236	344.780	230.732	−691.622	−355.070	6.869
2800	107.313	434.133	347.902	241.448	−982.586	−336.382	6.275
2900	107.604	437.904	350.940	252.194	−981.564	−313.322	5.644
3000	107.872	441.556	353.900	262.968	−980.562	−290.296	5.055
3100	108.118	445.097	356.785	273.767	−979.581	−267.303	4.504
3200	108.345	448.534	359.599	284.591	−978.625	−244.342	3.988
3300	108.554	451.871	362.345	295.436	−977.695	−221.411	3.505
3400	108.747	455.114	365.026	306.301	−976.794	−198.506	3.050
3500	108.926	458.269	367.645	317.185	−975.923	−175.628	2.621
3600	109.093	461.340	370.205	328.086	−975.085	−152.775	2.217
3700	109.247	464.331	372.709	339.003	−974.282	−129.944	1.834
3800	109.390	467.247	375.159	349.935	−973.517	−107.134	1.473
3900	109.524	470.090	377.556	360.881	−972.791	−84.343	1.130
4000	109.649	472.865	379.905	371.839	−972.108	−61.572	0.804
4100	109.766	475.573	382.205	382.810	−971.470	−38.817	0.495
4200	109.875	478.220	384.460	393.792	−970.878	−16.076	0.200
4300	109.977	480.807	386.670	404.785	−970.336	6.651	−0.081
4400	110.073	483.336	388.839	415.788	−969.846	29.365	−0.349
4500	110.163	485.811	390.966	426.799	−969.410	52.069	−0.604
4600	110.248	488.233	393.055	437.820	−969.030	74.764	−0.849
4700	110.327	490.605	395.105	448.849	−968.708	97.452	−1.083
4800	110.402	492.928	397.119	459.885	−968.446	120.134	−1.307
4900	110.473	495.205	399.097	470.929	−968.247	142.811	−1.522
5000	110.540	497.438	401.042	481.980	−968.111	165.484	−1.729
5100	110.603	499.628	402.954	493.037	−968.041	188.155	−1.927
5200	110.663	501.776	404.833	504.100	−968.037	210.825	−2.118
5300	110.720	503.884	406.683	515.169	−968.102	233.497	−2.301
5400	110.774	505.954	408.502	526.244	−968.236	256.169	−2.478
5500	110.825	507.987	410.292	537.324	−968.440	278.844	−2.648
5600	110.873	509.985	412.055	548.409	−968.715	301.526	−2.813
5700	110.919	511.948	413.790	559.499	−969.062	324.211	−2.971
5800	110.963	513.877	415.499	570.593	−969.482	346.905	−3.124
5900	111.004	515.774	417.183	581.691	−969.974	369.603	−3.272
6000	111.044	517.640	418.841	592.793	−970.540	392.313	−3.415

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = 237.30 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 169.5 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 170.0 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1{}^2\Pi_{1/2}$	23541	2
$A_2{}^2\Pi_{3/2}$	23898	2

$\omega_e = 611.7\ cm^{-1}$ $\omega_e x_e = [3.36]\ cm^{-1}$ $\sigma = 1$
$B_e = 0.4406\ cm^{-1}$ $\alpha_e = [0.0042]\ cm^{-1}$ $r_e = 2.132$ Å

Enthalpy of Formation

No thermochemical measurements of the enthalpy of formation has been made. The selected value, $\Delta_f H°(BeI, g, 0\ K) = 40.5\ kcal \cdot mol^{-1}$, is obtained from an analysis of spectroscopic data. The adopted values for the ground state vibrational constants give $D_0° = 3.41_4$ eV (78.73 $kcal \cdot mol^{-1}$) via a linear Berge–Sponer extrapolation.[1] Based on the ionicity correction developed by Hildenbrand,[2] this value adjusts to $D_0° = 2.70_7$ eV (62.43 $kcal \cdot mol^{-1}$). We adopt $D_0° = 62.4 \pm 10\ kcal \cdot mol^{-1}$ which corresponds to $\Delta_f H°(0\ K) = 40.5 \pm 10.0\ kcal \cdot mol^{-1}$.

Support for the adopted $D_0°$ value is provided by an examination of the trends in the dissociation energies for all alkaline earth monohalides and a comparison of the values for the ratio $\Delta_{at}H°(MX, 298.15\ K)/\Delta_{at}H°(MX_2, 298.15\ K)$ for the alkaline earth halides.[3] For the beryllium iodides this ratio is 0.44 which is consistent with the values of this ratio for other alkaline earth halides.

Heat Capacity and Entropy

The ground state vibrational and rotational constants are derived from spectroscopic studies by Murty and Rao.[4,5,6] The reported value for $\omega_e x_e$ (1.6 cm^{-1}) appears to be inconsistent with the values obtained for other alkaline earth monohalides. By a comparison of $(\omega_e/\omega_e x_e)$ and $x_e u^{1/2}$ values, we estimate $\omega_e x_e = 3.36\ cm^{-1}$ and adopt this value. The reported B_o value is converted to B_e by using a calculated value for α_e. We calculate α_e from the relation $\alpha_e/B_e = 13.2\ (B_e/\omega_e)$ as suggested by Calder and Ruedenberg.[7] Initially we use the B_o value in this relationship and then iterate to obtain consistent values for B_e and α_e. We calculate $r_e = 2.132$ Å from B_e. This corresponds well with the 2.12 Å Be–I distance for $BeI_2(g)$ obtained via the electron diffraction study of Akishin *et al.*[8]

The electronic levels are also from the study by Murty and Rao.[4,5,6] The possibility of additional levels ($^2\Pi$ and $^2\Sigma^+$) near 15000 cm^{-1} is suggested by a comparison with CaI, SrI, and BaI.[3] Including these levels does not change the entropy at 298.15 K but does increase the entropy at 6000 K by 0.7 $cal \cdot K^{-1} \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.098	169.452	169.452	INFINITE
100	29.217	203.629	265.506	−6.188	170.798	153.535	−80.198
200	31.228	224.384	240.293	−3.182	170.760	136.214	−35.575
250	32.473	231.489	237.843	−1.589	170.447	127.610	−26.663
298.15	33.475	237.297	237.297	0.	170.018	119.397	−20.918
300	33.509	237.505	237.298	0.062	170.000	119.083	−20.734
350	34.321	242.734	237.709	1.759	169.412	110.641	−16.512
400	34.949	247.359	238.632	3.491	160.767	102.563	−13.393
450	35.437	251.505	239.836	5.251	159.484	95.364	−11.070
500	35.821	255.259	241.193	7.033	138.109	90.209	−9.424
600	36.377	261.843	244.102	10.645	137.576	80.678	−7.024
700	36.755	267.481	247.048	14.302	136.959	71.242	−5.316
800	37.028	272.407	249.917	17.992	136.262	61.901	−4.042
900	37.236	276.781	252.663	21.706	135.488	52.652	−3.056
1000	37.401	280.713	255.275	25.438	134.636	43.492	−2.272
1100	37.538	284.284	257.752	29.185	133.705	34.422	−1.635
1200	37.655	287.556	260.102	32.945	132.690	25.441	−1.107
1300	37.758	290.574	262.331	36.716	131.588	16.547	−0.665
1400	37.850	293.376	264.450	40.496	130.393	7.742	−0.289
1500	37.934	295.990	266.466	44.286	129.098	−0.974	0.034
1600	38.012	298.441	268.389	48.083	113.161	−9.074	0.296
1700	38.085	300.747	270.225	51.888	112.050	−16.680	0.513
1800	38.155	302.926	271.982	55.700	110.892	−24.219	0.703
1900	38.222	304.991	273.665	59.519	109.684	−31.693	0.871
2000	38.286	306.953	275.281	63.344	108.427	−39.102	1.021
2100	38.349	308.823	276.834	67.176	107.120	−46.446	1.155
2200	38.410	310.608	278.329	71.014	105.767	−53.727	1.276
2300	38.470	312.317	279.770	74.858	104.372	−60.946	1.384
2400	38.530	313.955	281.160	78.708	102.938	−68.103	1.482
2500	38.588	315.529	282.504	82.564	101.472	−75.200	1.571
2600	38.647	317.044	283.803	86.426	99.979	−82.237	1.652
2700	38.706	318.504	285.062	90.293	98.465	−89.217	1.726
2800	38.765	319.912	286.281	94.167	−194.021	−89.917	1.677
2900	38.825	321.274	287.465	98.046	−194.497	−86.191	1.552
3000	38.886	322.591	288.614	101.932	−194.960	−82.448	1.436
3100	38.949	323.867	289.730	105.824	−195.409	−78.691	1.326
3200	39.014	325.105	290.817	109.722	−195.841	−74.919	1.223
3300	39.080	326.306	291.874	113.626	−196.253	−71.133	1.126
3400	39.149	327.474	292.904	117.538	−196.646	−67.336	1.034
3500	39.221	328.610	293.908	121.456	−197.018	−63.527	0.948
3600	39.295	329.716	294.887	125.382	−197.370	−59.708	0.866
3700	39.373	330.793	295.843	129.315	−197.702	−55.880	0.789
3800	39.454	331.844	296.777	133.257	−198.015	−52.042	0.715
3900	39.539	332.870	297.689	137.207	−198.312	−48.197	0.646
4000	39.628	333.872	298.581	141.165	−198.592	−44.344	0.579
4100	39.721	334.852	299.454	145.132	−198.860	−40.485	0.516
4200	39.818	335.810	300.308	149.109	−199.116	−36.619	0.455
4300	39.919	336.749	301.145	153.096	−199.362	−32.747	0.398
4400	40.024	337.667	301.964	157.093	−199.602	−28.869	0.343
4500	40.134	338.568	302.768	161.101	−199.837	−24.986	0.290
4600	40.247	339.451	303.556	165.120	−200.070	−21.098	0.240
4700	40.365	340.318	304.329	169.151	−200.302	−17.205	0.191
4800	40.486	341.169	305.087	173.193	−200.537	−13.307	0.145
4900	40.612	342.005	305.832	177.248	−200.776	−9.404	0.100
5000	40.742	342.827	306.564	181.316	−201.020	−5.496	0.057
5100	40.875	343.635	307.283	185.396	−201.273	−1.583	0.016
5200	41.012	344.430	307.990	189.491	−201.535	2.335	−0.023
5300	41.152	345.213	308.685	193.599	−201.808	6.258	−0.062
5400	41.295	345.983	309.368	197.721	−202.093	10.187	−0.099
5500	41.442	346.743	310.041	201.858	−202.392	14.121	−0.134
5600	41.591	347.491	310.703	206.010	−202.706	18.060	−0.168
5700	41.742	348.228	311.355	210.176	−203.035	22.005	−0.202
5800	41.896	348.955	311.997	214.358	−203.380	25.956	−0.234
5900	42.052	349.673	312.630	218.556	−203.741	29.913	−0.265
6000	42.210	350.381	313.253	222.769	−204.120	33.877	−0.295

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [120.5 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 753 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-188.7 \pm 21]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [20.9 \pm 12.6]\ kJ·mol^{-1}$

Enthalpy of Formation

A direct measurement of the enthalpy of formation has not been made. An estimate of $\Delta_f H°$ is obtained by a method suggested by Parker[1] and used in the $BeBr_2$(cr) table.[2] Biltz and Messerknecht[3] have measured the enthalpies of solution of $BeCl_2$(cr) and BeI_2(cr) is aqueous HCl (18.69%). Samples[4] of the dihalides were prepared from reactions of BeO–C mixtures with the halogens at elevated temperatures. We assume that the two dihalides had similar structures, i.e. the α–form (orthorhombic). $\Delta_f H°(BeI_2$, in 18.7% HCl, 298.15 K) is estimated at −109.1 $kcal·mol^{-1}$ by combing $\Delta_f H°$ of $BeCl_2$(cr) with $\Delta_f H°(BeCl_2$, cr, α, 298.15 K) = $-117.3 \pm 0.8\ kcal·mol^{-1}$ [2] and twice the difference in $\Delta_f H°(HCl8H_2O$, 298.15 K) and $\Delta_f H°$(298.15 K, $HI8H_2O$) which is $-52.3\ kcal·mol^{-1}$.[5] The enthalpy associated with the aqueous anions is assumed to be negligible. Combination of the estimated value for $\Delta_f H°(BeI_2$, in 18.8% HCl, 298.15 K) with $\Delta_f H° = -62.5\ kcal·mol^{-1}$ [3] gives $\Delta_f H°(BeI_2$, cr, 298.15 K) = −46.6 $kcal·mol^{-1}$ which is within 0.6 $kcal·mol^{-1}$ of the value suggested by NBS.[6] Subsequent measurements by Biltz *et al.*[7] in less concentrated HCl (1.48%) solution leads to $\Delta_f H°(298.15\ K) = -43.6\ kcal·mol^{-1}$ by a similar route. We adopt an average value of $-45.1\ kcal·mol^{-1}$ but emphasize that the uncertainty in $\Delta_f H°$ is much greater than indicated (3 $kcal·mol^{-1}$) by the closeness of these two values. An uncertainty of ±0.5 $kcal·mol^{-1}$ is believed to be more realistic.

Heat Capacity and Entropy

No low–temperature heat capacity or high–temperature enthalpy measurements have been reported. We estimate $C_p°(298.15\ K)$ = 16.482 $cal·K^{-1}·mol^{-1}$ from the reaction $BeCl_2$(cr, α) + 2LiI(cr) = BeI_2(cr) + 2LiCl(cr) by assuming $\Delta C_p° = 0$. Similar results are obtained using BeF_2(cr). $C_p°$ values above 298.15 K are assumed to parallel those for α–$BeCl_2$.[2]

Application of the Berthelot principle[8] to the process BaI_2(cr) + Be(cr) → Ba(cr) + BeI_2(cr) suggests $S°(298.15\ K) = 26.8\ cal·K^{-1}·mol^{-1}$. A graphical comparison of the standard entropies for other alkaline–earth dihalides[2] indicates that this value is reasonable. Other estimated values are given by additive entropy constants (27.4 $cal·K^{-1}·mol^{-1}$),[9] Brewer (31.0 $cal·K^{-1}·mol^{-1}$),[10] and Brewer *et al.* (25 $cal·K^{-1}mol^{-1}$).[11]

For additional information of the heat capacity and entropy, refer to the enthalpy of formation discussion for gaseous BeI_2.[2]

Fusion Data

Refer to the liquid table for details.

Phase Data

Semenenko and Naumova[12] studied the BeI_2 crystal modifications by thermal and x–ray techniques. The study was complicated by the extreme hygroscopicity, high vapor pressures near the melting point, and susceptibility to oxidation on heating by traces of oxygen. As stated by Semenenko and Naumova,[12] the sequence of polymorphic conversion and the character of the resulting modifications of BeI_2, which are largely dependent on the heating and cooling conditions, parallel those of $BeCl_2$.[13] They detected thermally transitions at 290°C, 370°C, 470°C, and a melting at 490°C. However, this data does not appear to be fully consistent in terms of crystallographic structures with that proposed by Johnson, Staritzky, and Douglas[14] and Messerknecht and Biltz.[15] These latter works suggested two structures with a transition at 350°C.

We assume the similarity with $BeCl_2$ with a transition in the vicinity of 350–370°C. Further study is necessary to resolve all possible phases and their structures.

Sublimation Data

Refer to the ideal gas table for details.

References

[1]V. B. Parker, personal communication, Nat. Bur. Stand., (March, 1975).
[2]JANAF Thermochemical Tables: $BeBr_2$(cr), 6–30–75; BeI_2(l) and BeI_2(g), 12–31–75; $BeCl_2$(cr, α), 6–30–75.
[3]W. Biltz and C. Messerknecht. Z. Anorg. Chem. **148**, 157 (1925).
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[5]U. S. Nat. Bur. Stand. Tech. Note 270–3, 264 pp. (1968).
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[15]C. Messerknecht and W. Biltz, Z. anorg. allgem. Chem. **48**, 152 (1925).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	68.961	120.499	120.499	0.	−188.698	−187.183	32.794
300	69.128	120.926	120.501	0.128	−188.702	−187.174	32.590
400	76.868	141.944	123.314	7.452	−204.858	−186.084	24.300
500	81.638	159.651	128.858	15.396	−247.213	−177.328	18.525
600	84.190	174.780	135.283	23.698	−244.932	−163.563	14.239
700	85.467	187.860	141.881	32.185	−242.604	−150.186	11.207
753.000	85.944	194.116	145.340	36.728	--- CRYSTAL <-> LIQUID ---		
800	86.366	199.331	148.360	40.777	−240.288	−137.142	8.954
900	87.132	209.549	154.602	49.453	−237.995	−124.386	7.219
1000	87.789	218.764	160.565	58.200	−235.733	−111.885	5.844
1100	88.337	227.158	166.243	67.007	−233.512	−99.608	4.730
1200	88.780	234.864	171.645	75.864	−231.346	−87.531	3.810
1300	89.115	241.984	176.785	84.759	−229.252	−75.632	3.039
1400	89.341	248.597	181.681	93.683	−227.247	−63.891	2.384
1500	89.462	254.766	186.350	102.624	−225.354	−52.289	1.821

PREVIOUS: June 1965 CURRENT: December 1975

$S°(298.15\ K) = [128.999]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-178.377]\ kJ·mol^{-1}$

$T_{fus} = 753 \pm 15\ K$ $\Delta_{fus}H° = [20.9 \pm 12.6]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the differnce enthalpy, $H°(753\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with the measured value for $BeCl_2$.[1] A glass transition is assumed at 400 K below which the heat capacity is that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Rahlfs and Fischer[2] reported a melting point of 753 K. Semenenko and Naumova,[3] using thermal analysis techniques, implied a melting point of 763 K. Since this latter value was derived from a thermogram, it is probable that this value represents a maximum, with the true melting point somewhat lower. We adopt $T_{fus} = 753 \pm 15$ K.

We estimate the enthalpy of melting, $\Delta_{fus}H° = 5.0 \pm 3.0\ kcal·mol^{-1}$. This estimate includes a contribution for melting (based on the entropy of melting for other alkaline earth dihalides) and a contribution for a phase transition. There is no experimental data available pertaining to the enthalpy of melting.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G° = 0$ for the process $BeI_2(l) = BeI_2(g)$. $\Delta_{vap}H°$ is the corresponding difference in the $\Delta_f H°$ values for the liquid and gas at T_{vap}.

References

[1]JANAF Thermochemical Table: $BeCl_2$(l), 6–30–65.

[2]O. Rahlfs and W. Fischer, Z. Anorg. Chem. **211**, 349 (1933).

[3]K. N. Semenenko and J. N. Naumova, Russ. J. Structural Chem. **4**, 59 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	68.961	128.999	128.999	0.	−178.377	−179.396	31.429
300	69.128	129.426	129.000	0.128	−178.380	−179.402	31.237
400	76.868	150.434	131.812	7.449	−194.539	−179.162	23.396
400.000	76.868	150.434	131.812	7.449	GLASS <-- -> LIQUID		
400.000	112.968	150.434	131.812	7.449	TRANSITION		
500	112.968	175.643	138.151	18.746	−233.542	−171.653	17.932
600	112.968	196.239	146.168	30.043	−228.266	−159.773	13.909
700	112.968	213.653	154.597	41.339	−223.128	−148.765	11.101
753.000	112.968	221.898	159.047	47.327	--- CRYSTAL <--> LIQUID ---		
800	112.968	228.738	162.943	52.636	−218.107	−138.486	9.042
900	112.968	242.044	171.007	63.933	−213.193	−128.830	7.477
1000	112.968	253.946	178.716	75.230	−208.381	−119.715	6.253
1100	112.968	264.713	186.053	86.527	−203.671	−111.077	5.275
1200	112.968	274.542	193.023	97.823	−199.065	−102.863	4.478
1300	112.968	283.585	199.646	109.120	−194.569	−95.030	3.818
1400	112.968	291.957	205.944	120.417	−190.192	−87.538	3.266
1500	112.968	299.751	211.941	131.714	−185.943	−80.355	2.798

PREVIOUS: June 1965 CURRENT: December 1975

0	to	753 K	crystal
above		753 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	68.961	120.499	120.499	0.	−188.698	−187.183	32.794
300	69.128	120.926	120.501	0.128	−188.702	−187.174	32.590
400	76.868	141.944	123.314	7.452	−204.858	−186.084	24.300
500	81.638	159.651	128.858	15.396	−247.213	−177.328	18.525
600	84.190	174.780	135.283	23.698	−244.932	−163.563	14.239
700	85.467	187.860	141.881	32.185	−242.604	−150.186	11.207
753.000	85.944	194.116	145.340	36.728	CRYSTAL <--> LIQUID		
753.000	112.968	221.898	145.340	57.648	TRANSITION		
800	112.968	228.738	150.041	62.958	−218.107	−138.486	9.042
900	112.968	242.044	159.539	74.254	−213.193	−128.830	7.477
1000	112.968	253.946	168.395	85.551	−208.381	−119.715	6.253
1100	112.968	264.713	176.669	96.848	−203.671	−111.077	5.275
1200	112.968	274.542	184.422	108.145	−199.065	−102.863	4.478
1300	112.968	283.585	191.707	119.442	−194.569	−95.030	3.818
1400	112.968	291.957	198.572	130.738	−190.192	−87.538	3.266
1500	112.968	299.751	205.060	142.035	−185.943	−80.354	2.798

PREVIOUS: CURRENT: December 1975

$S°(298.15\ K) = [291.52 \pm 2.1]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -62.5 \pm 33.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -64.0 \pm 33.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[160] (1)
[175] (2)
873 (1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: $D_{\infty h}$

Bond Distance: Be–I = 2.12 ± 0.05 Å

Bond Angle: I–Be–I = 180° ± 10°

Rotational Constant: $B_o = 0.014778\ cm^{-1}$

Enthalpy of Formation

Rahlfs and Fischer[1] have reported measurements of the sublimaiton pressures (578–703 K, 9 pts) for BeI_2. The measurements were complicated by reaction of the diiodide with the quartz apparatus. Assuming the reaction to be $BeI_2(cr) + SiO_2(cr) = SiI_4(g) + 2BeO(cr)$, Rahlfs and Fischer[1] corrected their measured total pressure for the partial pressure of the tetraiodide. A 2nd and 3rd law analysis of their corrected data yields $\Delta_{sub}H°(298.15\ K) = 29.81 \pm 0.29\ kcal·mol^{-1}$ (3rd law) and $28.34 \pm 0.74\ kcal·mol^{-1}$ (2nd law) with a drift of $2.2 \pm 1.1\ cal·K^{-1}·mol^{-1}$. We adopt $\Delta_{sub}H°(298.15\ K) = 29.8 \pm 2.0\ kcal·mol^{-1}$. We have assumed negligible dimer formation. $\Delta_f H°(298.15\ K) = -15.3\ kcal·mol^{-1}$ for $BeI_2(g)$ when the adopted $\Delta_{sub}H°(298.15\ K)$ value is added to the $\Delta_f H°(298.15\ K)$ value for $BeI_2(cr)$.

The drift could be reduced by further adjusting the Gibbs energy functions for the crystal. These functions may be changed by altering the $C_p°$ values and/or the $S°(298.15\ K)$ value. Such changes would yield values which are unreasonable when compared to other alkaline earth dihalides. Note also that a similar sublimation study for $BeCl_2$[2] gives a drift of $-1.3 \pm 2.6\ cal·K^{-1}·mol^{-1}$. We tentatively assume the drift is due to the data rather than our choice of functions.

Heat Capacity and Entropy

Electron diffraction patterns for BeI_2 vapor[3,4] have been interpreted in terms of a linear configuration, with the latter study reporting the Be–I bond distance as 2.12 Å. Other studies also suggest a linear molecule. For example, the electric deflection of mass spectrometricaly detected molecular beams[5] showed that all the beryllium dihalides are linear.

Snelson[6] observed the infrared spectra of BeI_2 in the spectral range 4000–200 cm^{-1} using a matrix isolation technique. Assuming a linear geometry, υ_3 was assigned as 873 cm^{-1}. Snelson[6] estimated a value for υ_2 based on force constant values for the other three beryllium dihalides. The values of υ_1 were calculated using a simple valence force field approximation. We adopt the two estimated and one measured vibrational frequency as reported by Snelson.[6] The ground state quantum weight of one is assigned by analogy with $BaCl_2$.[2]

Brewer *et al.*[7] have tabulated Gibbs energy functions for BeI_2 up to 2000 K. Their values are consistently lower than ours due primarily to their use of a higher bending frequency ($\upsilon_2 = 395\ cm^{-1}$).

References

[1]O. Rahlfs and W. Fischer, Z. Anorg. Chem. **211**, 349 (1933).

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[3]P. S. Akishin and V. P. Spiridonov, Kristallografiya **2**, 472 (1957).

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[7]L. Brewer, G. R. Somoyajulu, and E. Brackett, Chem. Revs. **63**, 111 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.633	−62.517	−62.517	INFINITE
100	44.605	236.565	337.992	−10.143	−62.117	−79.624	41.591
200	51.767	270.220	296.456	−5.247	−62.731	−96.949	25.320
250	53.542	281.970	292.421	−2.613	−63.316	−105.439	22.030
298.15	54.939	291.524	291.524	0.	−64.015	−113.491	19.883
300	54.988	291.864	291.525	0.102	−64.045	−113.798	19.814
350	56.181	300.433	292.199	2.882	−64.955	−122.021	18.211
400	57.156	308.001	293.710	5.716	−81.910	−129.559	16.919
450	57.948	314.780	295.681	8.594	−84.092	−135.385	15.715
500	58.591	320.920	297.903	11.508	−126.417	−137.167	14.330
600	59.544	331.692	302.662	17.418	−126.529	−139.307	12.128
700	60.192	340.923	307.484	23.407	−126.699	−141.425	10.553
800	60.648	348.992	312.179	29.450	−126.931	−143.513	9.370
900	60.977	356.155	316.675	35.532	−127.232	−145.569	8.449
1000	61.222	362.593	320.950	41.643	−127.606	−147.587	7.709
1100	61.408	368.437	325.005	47.775	−128.061	−149.563	7.102
1200	61.552	373.787	328.851	53.923	−128.604	−151.495	6.594
1300	61.667	378.718	332.499	60.084	−129.243	−153.377	6.163
1400	61.759	383.292	335.966	66.256	−129.991	−155.206	5.791
1500	61.834	387.555	339.265	72.436	−130.859	−156.978	5.466
1600	61.895	391.548	342.409	78.622	−146.395	−158.162	5.163
1700	61.947	395.302	345.411	84.814	−147.137	−158.875	4.882
1800	61.990	398.844	348.282	91.011	−147.961	−159.542	4.630
1900	62.027	402.197	351.032	97.212	−148.871	−160.161	4.403
2000	62.059	405.379	353.671	103.417	−149.870	−160.730	4.198
2100	62.086	408.408	356.206	109.624	−150.955	−161.246	4.011
2200	62.110	411.296	358.645	115.834	−152.121	−161.710	3.839
2300	62.131	414.058	360.994	122.046	−153.361	−162.118	3.682
2400	62.149	416.702	363.261	128.260	−154.666	−162.471	3.536
2500	62.165	419.240	365.450	134.476	−156.025	−162.768	3.401
2600	62.180	421.678	367.566	140.693	−157.425	−163.010	3.275
2700	62.193	424.025	369.614	146.911	−158.856	−163.198	3.157
2800	62.204	426.287	371.598	153.131	−451.264	−157.110	2.931
2900	62.214	428.470	373.521	159.352	−451.660	−146.597	2.641
3000	62.224	430.580	375.388	165.574	−452.039	−136.071	2.369
3100	62.232	432.620	377.202	171.797	−452.394	−125.533	2.115
3200	62.240	434.596	378.965	178.021	−452.718	−114.984	1.877
3300	62.247	436.511	380.680	184.245	−453.008	−104.425	1.653
3400	62.253	438.370	382.349	190.470	−453.259	−93.858	1.442
3500	62.259	440.174	383.976	196.696	−453.471	−83.284	1.243
3600	62.265	441.928	385.561	202.922	−453.641	−72.705	1.055
3700	62.270	443.634	387.108	209.149	−453.769	−62.122	0.877
3800	62.274	445.295	388.617	215.376	−453.858	−51.535	0.708
3900	62.278	446.913	390.091	221.603	−453.907	−40.947	0.548
4000	62.282	448.489	391.532	227.831	−453.920	−30.358	0.396
4100	62.286	450.027	392.940	234.060	−453.898	−19.770	0.252
4200	62.289	451.528	394.317	240.289	−453.844	−9.182	0.114
4300	62.292	452.994	395.664	246.518	−453.763	1.404	−0.017
4400	62.295	454.426	396.984	252.747	−453.656	11.989	−0.142
4500	62.298	455.826	398.276	258.977	−453.528	22.570	−0.262
4600	62.301	457.196	399.542	265.207	−453.381	33.148	−0.376
4700	62.303	458.535	400.783	271.437	−453.220	43.723	−0.486
4800	62.305	459.847	402.000	277.667	−453.048	54.295	−0.591
4900	62.308	461.132	403.193	283.898	−452.867	64.863	−0.691
5000	62.310	462.391	404.365	290.129	−452.683	75.427	−0.788
5100	62.311	463.625	405.515	296.360	−452.496	85.987	−0.881
5200	62.313	464.835	406.644	302.591	−452.311	96.544	−0.970
5300	62.315	466.022	407.753	308.822	−452.129	107.097	−1.056
5400	62.316	467.186	408.843	315.054	−451.954	117.647	−1.138
5500	62.318	468.330	409.914	321.286	−451.788	128.193	−1.217
5600	62.319	469.453	410.967	327.518	−451.633	138.737	−1.294
5700	62.321	470.556	412.003	333.750	−451.490	149.278	−1.368
5800	62.322	471.640	413.022	339.982	−451.362	159.817	−1.439
5900	62.323	472.705	414.025	346.214	−451.250	170.353	−1.508
6000	62.324	473.752	415.011	352.446	−451.154	180.888	−1.575

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K)$ = [208.77] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [424] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [427] $kJ·mol^{-1}$

Electronic Levels and Multiplicities		
state	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	[4]

ω_e = [1194] cm^{-1} $\omega_e x_e$ = [12.4] cm^{-1} σ = 1
B_e = [1.555] cm^{-1} α_e = [0.019] r_e = [1.406] Å

Enthalpy of Formation

The enthalpy of formation was taken from Gordon.[1]

Heat Capacity and Entropy

The molecular constants were taken from Gordon.[1]

Reference

[1] J. S. Gordon, personal communication, (April, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.725	424.231	424.231	INFINITE
100	29.111	176.758	234.965	−5.821	425.645	416.010	−217.301
200	29.254	196.957	211.487	−2.906	426.527	405.969	−106.028
250	29.583	203.516	209.260	−1.436	426.677	400.808	−83.744
298.15	30.089	208.768	208.768	0.	426.688	395.823	−69.347
300	30.111	208.954	208.768	0.056	426.687	395.632	−68.886
350	30.757	213.643	209.137	1.577	426.602	390.461	−58.273
400	31.439	217.794	209.964	3.132	426.462	385.308	−50.316
450	32.102	221.536	211.046	4.721	426.292	380.173	−44.129
500	32.716	224.951	212.268	6.341	426.099	375.059	−39.182
600	33.761	231.012	214.900	9.667	425.667	364.891	−31.767
700	34.574	236.280	217.586	13.086	425.172	354.800	−26.475
800	35.203	240.939	220.219	16.576	424.611	344.784	−22.512
900	35.693	245.115	222.758	20.122	423.976	334.843	−19.434
1000	36.081	248.897	225.185	23.711	423.262	324.977	−16.975
1100	36.395	252.351	227.500	27.336	422.467	315.186	−14.967
1200	36.653	255.529	229.705	30.988	421.587	305.471	−13.297
1300	36.869	258.471	231.806	34.665	420.622	295.833	−11.887
1400	37.052	261.211	233.810	38.361	419.569	286.273	−10.681
1500	37.211	263.772	235.723	42.074	418.427	276.791	−9.639
1600	37.351	266.179	237.552	45.803	402.661	267.914	−8.747
1700	37.475	268.447	239.303	49.544	401.741	259.521	−7.974
1800	37.587	270.592	240.982	53.297	400.800	251.182	−7.289
1900	37.689	272.627	242.595	57.061	399.838	242.896	−6.678
2000	37.783	274.563	244.145	60.835	398.855	234.661	−6.129
2100	37.870	276.408	245.638	64.617	397.851	226.476	−5.633
2200	37.951	278.172	247.077	68.408	396.826	218.339	−5.184
2300	38.027	279.860	248.466	72.207	395.781	210.249	−4.775
2400	38.100	281.480	249.808	76.014	394.716	202.206	−4.401
2500	38.169	283.037	251.106	79.827	393.632	194.206	−4.058
2600	38.236	284.535	252.363	83.648	392.527	186.251	−3.742
2700	38.300	285.980	253.582	87.474	391.403	178.339	−3.450
2800	38.361	287.374	254.764	91.307	99.302	176.691	−3.296
2900	38.421	288.721	255.912	95.147	99.202	179.457	−3.232
3000	38.479	290.024	257.027	98.992	99.100	182.226	−3.173
3100	38.536	291.287	258.112	102.842	98.994	184.998	−3.117
3200	38.592	292.511	259.168	106.699	98.882	187.774	−3.065
3300	38.646	293.700	260.197	110.561	98.764	190.554	−3.016
3400	38.700	294.854	261.199	114.428	98.638	193.337	−2.970
3500	38.752	295.977	262.177	118.301	98.501	196.125	−2.927
3600	38.804	297.069	263.131	122.178	98.353	198.916	−2.886
3700	38.855	298.133	264.063	126.061	98.190	201.712	−2.848
3800	38.906	299.170	264.973	129.949	98.012	204.512	−2.811
3900	38.956	300.181	265.863	133.843	97.816	207.317	−2.777
4000	39.005	301.168	266.733	137.741	97.600	210.127	−2.744
4100	39.054	302.132	267.585	141.644	97.362	212.944	−2.713
4200	39.102	303.074	268.419	145.551	97.099	215.766	−2.683
4300	39.151	303.994	269.235	149.464	96.810	218.594	−2.655
4400	39.198	304.895	270.035	153.381	96.492	221.430	−2.629
4500	39.246	305.776	270.820	157.304	96.143	224.274	−2.603
4600	39.293	306.639	271.589	161.231	95.763	227.125	−2.579
4700	39.340	307.485	272.344	165.162	95.348	229.985	−2.556
4800	39.387	308.314	273.085	169.099	94.896	232.855	−2.534
4900	39.433	309.126	273.812	173.040	94.408	235.734	−2.513
5000	39.479	309.923	274.526	176.985	93.880	238.623	−2.493
5100	39.525	310.706	275.228	180.935	93.311	241.524	−2.474
5200	39.571	311.474	275.918	184.890	92.701	244.436	−2.455
5300	39.617	312.228	276.596	188.850	92.048	247.360	−2.438
5400	39.662	312.969	277.262	192.814	91.352	250.297	−2.421
5500	39.708	313.697	277.918	196.782	90.612	253.247	−2.405
5600	39.753	314.413	278.564	200.755	89.826	256.211	−2.390
5700	39.798	315.117	279.199	204.733	88.995	259.189	−2.375
5800	39.843	315.809	279.824	208.715	88.119	262.183	−2.361
5900	39.888	316.491	280.440	212.701	87.196	265.192	−2.348
6000	39.933	317.162	281.046	216.692	86.227	268.217	−2.335

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 13.770 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{trs} = 2373 \pm 15$ K (α–β)
$T_{fus} = [2821.2 \pm 100]$ K (β–l)
$T_{fus} = 2780 \pm 100$ K (α–l)

$\Delta_f H°(0\ K) = -604.9 \pm 0.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -608.4 \pm 3.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = [6.694 \pm 1.7]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [79.057 \pm 6.3]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 84.9 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

Parker[1] thoroughly reviewed the data as of 1969 and selected -145.4 ± 0.8 kcal·mol^{-1}. She later revised[1] this value to -145.7 ± 0.6 kcal·mol^{-1} due to new HF–solution calorimtry on BeF_2(amorphous) performed by Kilday *et al.*[2] Values of $\Delta_f H°$ from Parker's revised analysis[1] are summarized below. We adopt -145.4 ± 0.8, rather than the revised selection, as a compromise between the indirect results based on Be(cr) and those based on BeF_2(am). The latter depend on $\Delta_f H°$ for HF(n H_2O). Use of the JANAF $\Delta_f H°$[4] in place of the NBS value[3] causes a change of ±0.9 kcal·mol^{-1} in the results based on BeF_2(am). Recent data for HF suggest that the change could be even larger.

Direct Determination of $\Delta_f H°$		Indirect Determinations of $\Delta_f H°$	
kcal·mol^{-1}	Source	kcal·mol^{-1}	Source
−136.2	Mielenz & Von Wartenberg (1921)	−144.9	Neumann *et al.* (1934, 1932), $\Delta_c H°$ & $\Delta_f H°$ of Be_3N_2
−134.4	Moose & Parr (1924)	−141.1	Smirnov & Chukreev (1958), emf data
−145.3	Neumann *et al.* (1934)	−145.7 ± 1.5	Kilday *et al.* (1969), Thomson *et al.* (1962)[a]
−147.3	Roth *et al.* (1938)	−143.9 ± 1.5	Kilday *et al.* (1969), Armstrong & Coyle (1965)[b]
−143.1	Cosgrove & Snyder (1953)	−145.7 ± 0.6	Kolesov *et al.* (1959), Bear & Turnbull (1965)[b]
		−146.2, −145.65, −145.65, −145.3 ± 0.6	Kilday *et al.* (1959), Bear & Turnbull (1969)[b]
		−144.7(−145.6)[d], −144.5(−145.4)[d] ± 1.2	Kilday *et al.* (1971), Churney & Armstrong (1969)[c]

[a]HCl–solution calorimetry of BeO(cr) and Be(cr). [b]HF–solution calorimetry of BeO(cr) and Be(cr). [c]HF–solution calorimetry of BeO(cr) and BeF_2(am) and $\Delta_f H°$ of the latter. [d]Values in parentheses based on $\Delta_f H°$ of HF(n H_2O) from NBS[3] instead of JANAF.[4]

Heat Capacity and Entropy

The adopted $C_p°$ and $S°$ below 298.15 K are taken from Furukawa and Reilly[5] who measured $C_p°$ from 16 to 370 K. The authors give a detailed comparison with the earlier data of Gmelin[6](5 to 75 K) and Kelley[7](56 to 292 K). Gmelin's results deviate by roughly +20% from 15 to 75 and Kelley's results deviate by about +50% at 56 K, +8% at 100 K and +1% at 200 K. The deviation of Kelley are probably due to the sensitivity limit of his calorimeter and to non–standard state effects of finely powdered BeO.

The adopted $C_p°$ above 298.15 K is from a constrained fit of the $C_p°$ data[5] and enthalpy data of Victor and Douglas[8](323 to 1173 K), Conway and Hein[9](2161 to 2365 K) and Shpil'rain *et al.*,[10](2023 to 2708 K). The latter data show no evidence of transition even though they extend more than 300 K above T_{trs} = 2373 K. Deviations of the data[8] from the adopted enthalpies are < ±0.15 % above 373 K and −0.4% at 323 K. Deviations above 2000 K are −0.3 to +0.8%[9] and −1.8 to +0.4%[10] excluding the point at 2266 K.[10] Enthalpy measurements not used in the fit deviate by −2.1 to +2.9%[11](1142 to 2697 K), −17 ± 8%[12](2273 to 2523 K), −2.1 ± 0.8%[13](400 to 1100 K) and +0.4 to −0.7%[14](363 to 1128 K). $C_p°$ data from the cooling–rate method[15] deviate by <2% (1300 to 1700 K) but by −5% at 2000 K.

Transition Data

Refer to the β–crystal table for details.

Fusion Data

Refer to the liquid table for details.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−2.835	−604.914	−604.914	INFINITE
100	2.636	0.824	28.539	−2.771	−606.343	−597.709	312.211
200	14.159	5.887	15.759	−1.974	−607.579	−588.573	153.719
298.15	25.560	13.770	13.770	0.	−608.354	−579.062	101.449
300	25.744	13.928	13.770	0.047	−608.364	−578.880	100.792
400	33.757	22.513	14.886	3.051	−608.688	−568.992	74.303
500	38.920	30.641	17.235	6.703	−608.668	−559.065	58.405
600	42.376	38.061	20.098	10.778	−608.440	−549.163	47.809
700	44.823	44.786	23.152	15.144	−608.092	−539.310	40.244
800	46.656	50.897	26.244	19.722	−607.680	−529.511	34.574
900	48.091	56.478	29.298	24.462	−607.235	−519.767	30.166
1000	49.262	61.607	32.276	29.331	−606.780	−510.073	26.643
1100	50.254	66.350	35.161	34.308	−606.329	−500.424	23.763
1200	51.116	70.760	37.946	39.377	−605.892	−490.815	21.365
1300	51.882	74.882	40.630	44.527	−605.478	−481.243	19.337
1400	52.580	78.753	43.216	49.751	−605.094	−471.701	17.599
1500	53.225	82.403	45.708	55.042	−604.744	−462.185	16.095
1600	53.827	85.857	48.111	60.394	−618.971	−452.166	14.762
1700	54.396	89.138	50.428	65.806	−618.303	−441.761	13.574
1800	54.944	92.262	52.666	71.273	−617.614	−431.396	12.519
1900	55.467	95.247	54.829	76.794	−616.904	−421.069	11.576
2000	55.974	98.105	56.922	82.366	−616.176	−410.781	10.729
2100	56.467	100.848	58.949	87.988	−615.430	−400.530	9.963
2200	56.948	103.486	60.914	93.659	−614.669	−390.314	9.267
2300	57.421	106.028	62.820	99.378	−613.893	−380.133	8.633
2373.001	57.756	107.827	64.177	103.582	---- ALPHA <--> BETA ----		
2400	57.881	108.482	64.672	105.143	−613.103	−369.987	8.053
2500	58.338	110.854	66.472	110.954	−612.300	−359.873	7.519
2600	58.789	113.151	68.224	116.810	−611.483	−349.792	7.027
2700	59.233	115.378	69.929	122.711	−610.654	−339.743	6.573
2800	59.676	117.540	71.591	128.657	−900.769	−323.502	6.035
2900	60.112	119.641	73.212	134.646	−898.851	−302.919	5.456
3000	60.547	121.687	74.794	140.679	−896.904	−282.403	4.917
3100	60.978	123.679	76.339	146.755	−894.930	−261.952	4.414
3200	61.404	125.622	77.849	152.874	−892.929	−241.565	3.943
3300	61.831	127.518	79.325	159.036	−890.903	−221.242	3.502
3400	62.254	129.370	80.770	165.240	−888.855	−200.979	3.088
3500	62.676	131.181	82.184	171.487	−886.784	−180.778	2.698

PREVIOUS: December 1974 CURRENT: June 1975

$S°(298.15\ K) = [16.591]\ J·K^{-1}·mol^{-1}$
$T_{trs} = 2373 \pm 15\ K\ (\alpha \rightarrow \beta)$
$T_{fus} = [2821.2 \pm 100]\ K\ (\beta \rightarrow l)$

$\Delta_f H°(298.15\ K) = [-601.659]\ kJ·mol^{-1}$
$\Delta_{trs}H° = 6.694 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{fus}H° = [79.057 \pm 6.3]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of BeO(α, cr) by addition of $\Delta_{trs}H°$, since the difference in enthalpy, $H°(2373\ K)–H°(298.15\ K)$, between the α–and β–phases is zero according to the adopted functions.

Heat Capacity and Entropy

$C_p°$ is taken to be the same as that of BeO(α, cr). Enthalpy data for β–BeO[1] extend from 2377 to 2501 K, a range too short for obtaining an accurate $C_p°$ curve. The enthalpy data deviate from the adopted functions by −0.2 to ± 1.4%. Other enthalpy data[2–4] show no obvious transition to β–BeO; this suggests that experimental uncertainties masked the transition or that these samples failed to transform. $S°$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Transition Data

Studies of x–ray diffraction,[5–7] optical properties,[6, 8] thermal expansion,[1, 9] thermal analysis,[10–14] enthalpy,[1] and decrepitation of single crystals[6, 9, 15] indicate the existence of a reversible transition near 2100°C. β–BeO is tetragonal with a structure related to rutile,[5] while α–BeO is hexagonal close–packed with a wurtzite–type structure.[16, 17]

T_{trs} is lower on cooling than on heating. Earlier studies gave temperature differences of about 40°,[11, 12] 50°[7] and 80°,[14] but a recent DTA study[10] gave T_{trs} values on cooling which were only ≈15° below those on heating. $T_{trs} = 2107 \pm 7$°C (IPTS–68) was proposed as a DTA standard temperature because it is reproducible and relatively unchanged by oxide impurities.[10] Reported values of T_{trs} on heating include 2100 ± 10°C,[1] 2107 ± 7°C,[10] 2095°C,[11] 2075 ± 15°C.[12] 2050–2100°C,[7] 2100–2250°C,[7] 2144 ± 40°C,[14] and 2050 ± 25°C.[6] We adopt 2100 ± 15°C.

Reported values of $\Delta_{trs}H°$ include 1.35 ± 0.1,[1] 1.40 ± 0.25,[10] 1.25 ± 0.25,[14] and 0.95 ± 0.3 $kcal·mol^{-1}$.[13] The first value is from enthalpy data and the others are from thermal analysis. It is not clear why the transition fails to appear in two other enthalpy studies.[2,3] We adopt $\Delta_{trs}H° = 1.60 \pm 0.4\ kcal·mol^{-1}$ derived from the difference between the enthalpy data for β–BeO[1] and the JANAF enthalpy for α–BeO.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0						
100						
200						
298.15	25.560	16.591	0.	−601.659	−573.209	100.424
300	25.744	16.749	0.047	−601.669	−573.032	99.774
400	33.757	25.335	3.051	−601.993	−563.426	73.576
500	38.920	33.462	6.703	−601.974	−553.781	57.853
600	42.376	40.882	10.778	−601.746	−544.161	47.373
700	44.823	47.608	15.144	−601.398	−534.590	39.892
800	46.656	53.718	19.722	−600.986	−525.074	34.284
900	48.091	59.299	24.462	−600.541	−515.611	29.925
1000	49.262	64.428	29.331	−600.086	−506.199	26.441
1100	50.254	69.171	34.308	−599.635	−496.832	23.593
1200	51.116	73.581	39.377	−599.198	−487.506	21.221
1300	51.882	77.703	44.527	−598.784	−478.216	19.215
1400	52.580	81.574	49.751	−598.399	−468.956	17.497
1500	53.225	85.224	55.042	−598.050	−459.722	16.009
1600	53.827	88.678	60.394	−612.276	−449.985	14.691
1700	54.396	91.959	65.806	−611.609	−439.862	13.515
1800	54.944	95.083	71.273	−610.919	−429.779	12.472
1900	55.467	98.068	76.794	−610.210	−419.735	11.539
2000	55.974	100.926	82.366	−609.481	−409.729	10.701
2100	56.467	103.669	87.988	−608.736	−399.760	9.943
2200	56.948	106.307	93.659	−607.975	−389.826	9.256
2300	57.421	108.849	99.378	−607.199	−379.927	8.628
2373.001	57.758	110.649	103.582	---- ALPHA <--> BETA ----		
2400	57.881	111.303	105.143	−606.409	−370.063	8.054
2500	58.338	113.675	110.954	−605.605	−360.232	7.527
2600	58.789	115.972	116.810	−604.789	−350.433	7.040
2700	59.233	118.199	122.711	−603.959	−340.666	6.591
2800	59.676	120.361	128.657	−894.074	−324.707	6.057
2821.220	59.770	120.812	129.924	---- BETA <--> LIQUID ----		
2900	60.112	122.463	134.646	−892.156	−304.406	5.483
3000	60.547	124.508	140.679	−890.210	−284.172	4.948
3100	60.978	126.500	146.755	−888.235	−264.003	4.448
3200	61.404	128.443	152.874	−886.235	−243.899	3.981
3300	61.831	130.339	159.036	−884.209	−223.857	3.543
3400	62.254	132.191	165.240	−882.160	−203.877	3.132
3500	62.676	134.002	171.487	−880.090	−183.957	2.745

PREVIOUS: June 1971 CURRENT: December 1974

$S°(298.15\ K) = [35.931]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [2821.2 \pm 100]\ K\ (\beta - l)$
$T_{fus} = 2780 \pm 100\ K\ (\alpha \rightarrow l)$

$\Delta_f H°(298.15\ K) = [-542.705]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [79.057 \pm 6.3]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 84.9 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–BeO by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2780\ K)–H°(298.15\ K)$, between the α and liquid phases.

Heat Capacity and Entropy

$C_p°$ is taken to be 19 $cal·K^{-1}·mol^{-1}$ based on the lower two of three enthalpy points (2867–3159 K) measured by Shpil'rain *et al.*[1] The upper two points yield 24.9 $cal·K^{-1}·mol^{-1}$, which is too large in our opinion. Earlier enthalpy data[2,3] are inadequate for deriving $C_p°$. Below the assumed glass transition at 1900 K, $C_p°$ is taken to be the same as that of the crystal. $S°$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Conflicting evidence suggests that the melting points of α– and β–Beo are quite uncertain. Schneider's review[4] listed C six values (T_{fus}/°C, IPTS–48, with dates in parentheses): 2410(1916), 2452(1956), 2508(1937), 2557(1930), 2570(1948) and 2573° . 1913). Subsequent T_{fus} values include 2430 ± 10,[5] 2560 ± 10,[6] 2444 ± 30,[7] 2547 ± 9,[2] 2450 ± 30 and 2470 ± 30°C.[8] The reported values fall roughly into two groups near 2450°C and 2560°C. Three enthalpy studies[1-3] avoided the region from 2435°C to 2547°C. Part of the conflict arises because, in most cases, the measurement of T_{fus} of BeO was only an incidental part of the study. Such values are more likely to be in error due to temperature measurement, detection of melting, impurities, volatilization and reaction with the surroundings. The actual discrepancies may be even larger than they appear, since one of the higher T_{fus} values seems to refer to α–BeO which should melt ≈40 below β–BeO. Enthalpy data of Kandyba *et al.*[2] suggest that their sample may have remained as α–BeO, yet they reported T_{fus} = 2547 ± 9°C. In contrast T_{fus} = 2430 ± 10°C was found for β–BeO by Latta *et al.*;[5] their thermal analysis showed both T_{trs} and T_{fus}.

The conflict is epitomized by the two most recent values of T_{fus}, 2430 ± 10°C[5] and 2560 ± 10°C.[6] These studies[5,6] seem to be more satisfactory than their predecessors yet at least one of them has a large bias. They agree[5,6] on T_{fus} for Al_2O_3, Mo and Ta but differ in opposite directions for BeO and UO_2. Non–stoichiometry could explain the lower $T_{fus}(UO_2)$ reported by Riley,[6] but analogous evidence for BeO is lacking. As a compromise, we adopt $T_{fus}(\alpha)$ = 2507°C = 2780 K and calculate $T_{fus}(\beta)$ = 2548°C = 2821.2 K from $\Delta_r G° = 0$ for $BeO(\beta) \rightarrow BeO(l)$.

$\Delta_{fus}H°(\alpha) = 20.3\ kcal·mol^{-1}$ is calculated by difference from enthalpies (2867–3159 K) of Shpil'rain *et al.*[1] and the JANAF enthalpy for α–BeO. We assume that BeO(l) reverted to α–BeO and that β–BeO did not form during the drop calorimetry.[1] $\Delta_{fus}H°(\beta) = 13.895\ kcal·mol^{-1}$ is calculated from $BeO(\beta) \rightarrow BeO(l)$ at the corresponding T_{fus} using the adopted tables. Enthalpy data of Greenbaum *et al.*[3] gave $\Delta_{fus}H°$ 19.3 $kcal·mol^{-1}$ (phase uncertain) even though both the crystal and liquid data have large negative bias. Ohta and Sata[9] derived $\Delta_{fus}H° = 7.6 \pm 2.1$ $kcal·mol^{-1}$ from liquidus data in the binary system BeO–ThO_2. This can be discounted along with other binary data[10,11] due to the uncertainty in T_{fus}.

Vaporization Data

The vapor over BeO is composed mainly of trimer, tetramer and individual atoms, along with minor amounts of several other molecules.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$				$kJ·mol^{-1}$		
0							
100							
200							
298.15	25.560	35.931	35.931	0.	−542.705	−520.021	91.105
300	25.744	36.089	35.931	0.047	−542.715	−519.880	90.519
400	33.757	44.675	37.047	3.051	−543.039	−512.208	66.887
500	38.920	52.802	39.396	6.703	−543.019	−504.497	52.704
600	42.376	60.222	42.259	10.778	−542.791	−496.811	43.251
700	44.823	66.948	45.313	15.144	−542.444	−489.174	36.503
800	46.656	73.058	48.405	19.722	−542.031	−481.591	31.445
900	48.091	78.639	51.459	24.462	−541.586	−474.063	27.514
1000	49.262	83.768	54.437	29.331	−541.131	−466.585	24.372
1100	50.254	88.511	57.322	34.308	−540.680	−459.152	21.803
1200	51.116	92.921	60.107	39.377	−540.243	−451.760	19.665
1300	51.882	97.043	62.791	44.527	−539.830	−444.403	17.856
1400	52.580	100.914	65.377	49.751	−539.445	−437.077	16.308
1500	53.225	104.564	67.869	55.042	−539.096	−429.778	14.966
1600	53.827	108.018	70.272	60.394	−553.322	−421.975	13.776
1700	54.396	111.299	72.589	65.806	−552.655	−413.786	12.714
1800	54.944	114.423	74.827	71.273	−551.965	−405.637	11.771
1900	55.467	117.408	76.990	76.794	−551.255	−397.527	10.929
1900.001	55.467	117.408	76.990	76.794	GLASS <--> LIQUID		
1900.001	79.496	117.408	76.990	76.794	TRANSITION		
2000	79.496	121.486	79.114	84.743	−548.149	−389.516	10.173
2100	79.496	125.364	81.225	92.693	−545.077	−381.660	9.493
2200	79.496	129.063	83.316	100.643	−542.037	−373.950	8.879
2300	79.496	132.596	85.382	108.592	−539.030	−366.377	8.321
2400	79.496	135.980	87.421	116.542	−536.055	−358.934	7.812
2500	79.496	139.225	89.428	124.491	−533.113	−351.615	7.347
2600	79.496	142.343	91.404	132.441	−530.203	−344.412	6.919
2700	79.496	145.343	93.346	140.391	−527.326	−337.321	6.526
2800	79.496	148.234	95.255	148.340	−815.436	−324.113	6.046
2821.220	79.496	148.834	95.656	150.027	---- BETA <--> LIQUID ----		
2900	79.496	151.024	97.131	156.290	−811.558	−306.635	5.523
3000	79.496	153.719	98.972	164.239	−807.695	−289.290	5.037
3100	79.496	156.325	100.780	172.189	−803.847	−272.073	4.584
3200	79.496	158.849	102.556	180.139	−800.016	−254.980	4.162
3300	79.496	161.295	104.299	188.088	−796.202	−238.007	3.767
3400	79.496	163.669	106.010	196.038	−792.408	−221.149	3.398
3500	79.496	165.973	107.691	203.987	−788.635	−204.402	3.051
3600	79.496	168.213	109.341	211.937	−784.884	−187.763	2.724
3700	79.496	170.391	110.962	219.887	−781.157	−171.228	2.417
3800	79.496	172.511	112.554	227.836	−777.455	−154.792	2.128
3900	79.496	174.576	114.118	235.786	−773.782	−138.454	1.854
4000	79.496	176.588	115.654	243.735	−770.138	−122.211	1.596
4100	79.496	178.551	117.165	251.685	−766.525	−106.057	1.351
4200	79.496	180.467	118.649	259.635	−762.946	−89.992	1.119
4300	79.496	182.337	120.109	267.584	−759.403	−74.011	0.899
4400	79.496	184.165	121.544	275.534	−755.897	−58.112	0.690
4500	79.496	185.952	122.955	283.483	−752.431	−42.293	0.491
4600	79.496	187.699	124.344	291.433	−749.007	−26.550	0.301
4700	79.496	189.408	125.710	299.383	−745.626	−10.881	0.121
4800	79.496	191.082	127.055	307.332	−742.290	4.717	−0.051
4900	79.496	192.721	128.378	315.282	−739.001	20.246	−0.216
5000	79.496	194.327	129.681	323.231	−735.761	35.708	−0.373

PREVIOUS: December 1971 CURRENT: December 1974

0	to	2373 K	crystal, alpha
2373	to	2821.2 K	crystal, beta
above		2821.2 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−2.835	−604.914	−604.914	INFINITE
100	2.636	0.824	28.539	−2.771	−606.343	−597.709	312.211
200	14.159	5.887	15.759	−1.974	−607.579	−588.573	153.719
298.15	25.560	13.770	13.770	0.	−608.354	−579.062	101.449
300	25.744	13.928	13.770	0.047	−608.364	−578.880	100.792
400	33.757	22.513	14.886	3.051	−608.688	−568.992	74.303
500	38.920	30.641	17.235	6.703	−608.668	−559.065	58.405
600	42.376	38.061	20.098	10.778	−608.440	−549.163	47.809
700	44.823	44.786	23.152	15.144	−608.092	−539.310	40.244
800	46.656	50.897	26.244	19.722	−607.680	−529.511	34.574
900	48.091	56.478	29.298	24.462	−607.235	−519.767	30.166
1000	49.262	61.607	32.276	29.331	−606.780	−510.073	26.643
1100	50.254	66.350	35.161	34.308	−606.329	−500.424	23.763
1200	51.116	70.760	37.946	39.377	−605.892	−490.815	21.365
1300	51.882	74.882	40.630	44.527	−605.478	−481.243	19.337
1400	52.580	78.753	43.216	49.751	−605.094	−471.701	17.599
1500	53.225	82.403	45.708	55.042	−604.744	−462.185	16.095
1600	53.827	85.857	48.111	60.394	−618.971	−452.166	14.762
1700	54.396	89.138	50.428	65.806	−618.303	−441.761	13.574
1800	54.944	92.262	52.666	71.273	−617.614	−431.396	12.519
1900	55.467	95.247	54.829	76.794	−616.904	−421.069	11.576
2000	55.974	98.105	56.922	82.366	−616.176	−410.781	10.729
2100	56.467	100.848	58.949	87.988	−615.430	−400.530	9.963
2200	56.948	103.486	60.914	93.659	−614.669	−390.314	9.267
2300	57.421	106.028	62.820	99.378	−613.893	−380.133	8.633
2373.001	57.756	107.827	64.177	103.582	ALPHA <--> BETA		
2373.001	57.758	110.649	64.177	110.276	TRANSITION		
2400	57.881	111.303	64.704	111.837	−606.409	−370.063	8.054
2500	58.338	113.675	66.616	117.648	−605.605	−360.232	7.527
2600	58.789	115.972	68.470	123.504	−604.789	−350.433	7.040
2700	59.233	118.199	70.271	129.406	−603.959	−340.665	6.591
2800	59.676	120.361	72.021	135.351	−894.074	−324.707	6.057
2821.220	59.770	120.812	72.386	136.618	BETA <--> LIQUID		
2821.220	79.496	148.834	72.386	215.676	TRANSITION		
2900	79.496	151.024	74.493	221.939	−811.558	−306.635	5.523
3000	79.496	153.719	77.089	229.888	−807.695	−289.290	5.037
3100	79.496	156.325	79.603	237.838	−803.847	−272.073	4.584
3200	79.496	158.849	82.041	245.787	−800.016	−254.980	4.162
3300	79.496	161.295	84.405	253.737	−796.202	−238.007	3.767
3400	79.496	163.669	86.702	261.687	−792.408	−221.149	3.398
3500	79.496	165.973	88.934	269.636	−788.635	−204.402	3.051
3600	79.496	168.213	91.105	277.586	−784.884	−187.763	2.724
3700	79.496	170.391	93.219	285.535	−781.157	−171.228	2.417
3800	79.496	172.511	95.278	293.485	−777.455	−154.792	2.128
3900	79.496	174.576	97.285	301.435	−773.782	−138.454	1.854
4000	79.496	176.588	99.242	309.384	−770.138	−122.211	1.596
4100	79.496	178.551	101.153	317.334	−766.525	−106.057	1.351
4200	79.496	180.467	103.018	325.283	−762.946	−89.992	1.119
4300	79.496	182.337	104.841	333.233	−759.403	−74.011	0.899
4400	79.496	184.165	106.624	341.183	−755.897	−58.112	0.690
4500	79.496	185.952	108.367	349.132	−752.431	−42.293	0.491
4600	79.496	187.699	110.072	357.082	−749.007	−26.550	0.301
4700	79.496	189.408	111.742	365.031	−745.626	−10.881	0.121
4800	79.496	191.082	113.378	372.981	−742.290	4.717	−0.051
4900	79.496	192.721	114.980	380.931	−739.001	20.246	−0.216
5000	79.496	194.327	116.551	388.880	−735.761	35.708	−0.373

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 197.625 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 134.0 \pm 13\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 136.4 \pm 13\ kJ·mol^{-1}$

Source	State	Electronic and Molecular Constants (σ = 1) ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
[1]	$X^1\Sigma^+$	0.0	1	1.3310	1.6510	0.0190	1487.3	11.83
[1-7]	$^3\Pi$	[8000]	6	[1.463]	[1.366]	[0.0163]	1130.8	8.2
[1]	$A^1\Pi$	9234.8	2	1.4632	1.3661	0.0163	1144.2	8.42
[4-7]	$^3\Sigma^+$	[16000]	3	[1.362]	[1.576]	[0.015]	[1370]	[7.8]
[1]	$B^1\Sigma^+$	21197.	1	1.3623	1.5758	0.0154	1370.8	7.75
[4]	$^3\Sigma^+$	[37000]	3	[1.49]	[1.31]	[0.01]	[1082]	[9.]
[4]	$^3\Delta$	[38000]	6	[1.49]	[1.31]	[0.01]	[1082]	[9.]
[1]	$D^1\Delta$	38918.	2	1.49	1.31	0.01	1081.5	9.1
[1,4]	$^3\Sigma^-$	[40000]	3	[1.49]	[1.31]	[0.01]	1012.2	8.4
[1,4]	$^1\Sigma^-$	38956.	1	[1.49]	[1.31]	[0.01]	[1082]	[9.]
[4]	$^1\Sigma^+$	[47000]	1	[1.49]	[1.31]	[0.01]	[1082]	[9.]

Enthalpy of Formation

We adopt $D_0°$ = 104.2 ± 3 and $\Delta_f H°(298.15\ K)$ = 32.6 ± 3 $kcal·mol^{-1}$ based on two mass–spectrometric studies,[8,9] analyzed below. The adopted values correspond to the average of the two results for reaction A and also to the average for reaction B. Improved agreement between reactions A and B is due to recalculation of K_p of reaction B using the current table[4] for BeO(α). Our analysis should be compared to the analysis of Brewer and Rosenblatt,[10] using "functions based upon calculated levels."

The controversy over $D_0°$ of alkaline earth oxides has been reviewed in detail.[10-12] Uncertainty in the electronic partition function of BeO due to triplet states now is much reduced.[2] Gaydon[12] derived spectroscopic values for $D_0°$ of 91 and 111 $kcal·mol^{-1}$ from the X and A states, respectively. $D_0°$ = 101 $kcal·mol^{-1}$ was derived[13] by fitting an electro– negativity potential function to the X state.

Source	Method	Reaction[a]	T/K	Data Points	δS $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$	$D_0°$
[8] Chupka (1959)	Knudsen mass spec.	A	2100–2474	8	1.6 ± 2.3	−8.4 ± 5	−11.9 ± 3	30.6	106.2
[9] Theard (1964)	Knudsen mass spec.	A	2380	1	–	–	−15.9 ± 3	34.6	102.2
[8] Chupka (1959)	Knudsen mass spec.	B[b]	1914–2304	6	0.7 ± 0.9	107.3 ± 2	105.9 ± 3	31.9	104.9
[9] Theard (1964)	Knudsen mass spec.	B[b]	2380	1	–	–	104.5 ± 3	33.3	103.5

[a]Reactions: A) BeO(g) + O(g) = Be(g) + O_2(g); B) BeO(g) = Be(g) + O(g).
[b]Recalculated as in Chupka *et al.*[8] assuming $P_{Be} = P_O$ and JANAF values for BeO(α) = Be(g) + O(g).

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational–rotational constants of the observed states are from Rosen.[1] Field[2] concluded that calculations[3,5-7] of the isoconfigurational $A^1\Pi - {}^3\Pi$ separation should be adequate for estimating the low–lying $^3\Pi$ state. The adopted separation of 1200 cm^{-1} is consistent with analysis[3] of perturbations. We estimate $^3\Sigma^+$ at 16000 cm^{-1} by assuming that it lies 5200 ± 4000 cm^{-1} [4-7] below the isoconfigurational B state. Other predicted states and their vibrational–rotational constants are facilitated by listing the states in the isconfigurational order of MgO.[4] Our thermodynamic functions correspond to an "effective" ground state with $1<g<2$ instead of g = 3 or 6.[10,11] This comparison is only approximate since our functions are calculated using first–order anharmonic corrections to Q_t^i and Q_v^i in the partition function $Q = Q_t^i \Sigma\ Q_r^i\ Q_v^i\ g_i \exp(-c_2\epsilon_i/T)$.

Sublimation and Vaporization Data

Mass spectra[8,9] at 1900–2400 K showed the vapor to consist mainly of Be, O, $(BeO)_3$, and $(BeO)_4$ with small amounts of O_2, Be_2O, BeO and other polymer of BeO. Tetramer, trimer and pentamer become dominant at higher temperatures.

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Continued on page 428

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ $J·K^{-1}·mol^{-1}$	$S° - [G°-H°(T_r)]/T$ $J·K^{-1}·mol^{-1}$	$H°-H°(T_r)$ $kJ·mol^{-1}$	$\Delta_f H°$ $kJ·mol^{-1}$	$\Delta_f G°$ $kJ·mol^{-1}$	log K_f
0	0.	0.	INFINITE	−8.688	133.984	133.984	INFINITE
100	29.108	165.763	223.605	−5.784	135.397	127.536	−66.618
200	29.139	185.943	200.307	−2.873	136.275	119.270	−31.150
298.15	29.481	197.625	197.625	0.	136.398	110.873	−19.425
300	29.493	197.807	197.626	0.055	136.395	110.715	−19.277
400	30.348	206.400	198.791	3.043	136.056	102.198	−13.346
500	31.421	213.286	201.023	6.131	135.513	93.793	−9.799
600	32.454	219.108	203.564	9.326	134.860	85.509	−7.444
700	33.345	224.179	206.155	12.617	134.133	77.340	−5.771
800	34.084	228.682	208.694	15.990	133.340	69.280	−4.524
900	34.704	232.733	211.144	19.430	132.485	61.324	−3.559
1000	35.252	236.418	213.490	22.928	131.569	53.465	−2.793
1100	35.784	239.803	215.730	26.480	130.595	45.702	−2.170
1200	36.357	242.941	217.869	30.086	129.569	38.029	−1.655
1300	37.023	245.876	219.911	33.755	128.501	30.444	−1.223
1400	37.825	248.648	221.866	37.496	127.403	22.942	−0.856
1500	38.788	251.290	223.740	41.325	126.291	15.519	−0.540
1600	39.927	253.829	225.542	45.259	110.646	8.696	−0.284
1700	41.236	256.288	227.278	49.316	109.959	2.346	−0.072
1800	42.698	258.685	228.957	53.511	109.377	−3.967	0.115
1900	44.285	261.036	230.584	57.860	108.914	−10.250	0.282
2000	45.956	263.350	232.164	62.371	108.582	−16.513	0.431
2100	47.670	265.633	233.704	67.052	108.386	−22.762	0.566
2200	49.379	267.890	235.206	71.905	108.329	−29.005	0.689
2300	51.042	270.122	236.676	76.927	108.408	−35.249	0.801
2400	52.616	272.328	238.116	82.110	108.617	−41.499	0.903
2500	54.070	274.506	239.528	87.446	108.944	−47.761	0.998
2600	55.375	276.653	240.915	92.919	109.378	−54.037	1.086
2700	56.514	278.765	242.277	98.515	109.902	−60.332	1.167
2800	57.475	280.838	243.618	104.216	−180.457	−60.425	1.127
2900	58.255	282.869	244.936	110.004	−178.741	−56.168	1.012
3000	58.856	284.854	246.234	115.861	−176.970	−51.972	0.905
3100	59.286	286.792	247.511	121.770	−175.163	−47.834	0.806
3200	59.556	288.679	248.768	127.713	−173.338	−43.757	0.714
3300	59.681	290.514	250.006	133.676	−171.511	−39.735	0.629
3400	59.676	292.295	251.223	139.645	−169.698	−35.769	0.550
3500	59.559	294.024	252.422	145.608	−167.911	−31.856	0.475
3600	59.345	295.699	253.601	151.554	−166.164	−27.994	0.406
3700	59.051	297.321	254.760	157.474	−164.466	−24.180	0.341
3800	58.691	298.891	255.901	163.362	−162.827	−20.410	0.281
3900	58.279	300.410	257.023	169.210	−161.254	−16.682	0.223
4000	57.827	301.880	258.126	175.016	−159.754	−12.995	0.170
4100	57.347	303.302	259.211	180.775	−158.332	−9.344	0.119
4200	56.848	304.678	260.277	186.485	−156.993	−5.726	0.071
4300	56.337	306.010	261.325	192.144	−155.740	−2.139	0.026
4400	55.822	307.299	262.356	197.752	−154.576	1.419	−0.017
4500	55.308	308.548	263.368	203.309	−153.503	4.952	−0.057
4600	54.801	309.758	264.364	208.814	−152.523	8.462	−0.096
4700	54.303	310.931	265.342	214.269	−151.636	11.952	−0.133
4800	53.818	312.069	266.304	219.675	−150.844	15.424	−0.168
4900	53.348	313.174	267.249	225.033	−150.146	18.881	−0.201
5000	52.895	314.247	268.178	230.345	−149.544	22.324	−0.233
5100	52.460	315.291	269.092	235.613	−149.035	25.756	−0.264
5200	52.044	316.305	269.990	240.838	−148.621	29.179	−0.293
5300	51.647	317.293	270.873	246.022	−148.301	32.595	−0.321
5400	51.271	318.255	271.742	251.168	−148.073	36.006	−0.348
5500	50.914	319.192	272.596	256.277	−147.937	39.413	−0.374
5600	50.577	320.106	273.436	261.351	−147.892	42.819	−0.399
5700	50.259	320.999	274.263	266.393	−147.936	46.225	−0.424
5800	49.961	321.870	275.076	271.404	−148.069	49.633	−0.447
5900	49.681	322.722	275.877	276.386	−148.289	53.042	−0.470
6000	49.418	323.555	276.665	281.340	−148.596	56.458	−0.492

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 77.971\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 863\ K\ (\alpha \rightarrow \beta)$
$T_{trs2} = 908\ K\ (\beta \rightarrow \gamma)$

$\Delta_f H°(0\ K) = -1190.1 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1200.8 \pm 3.3\ kJ·mol^{-1}$
$\Delta_{trs1} H° = [1.113]\ kJ·mol^{-1}$
$\Delta_{trs2} H° = [19.552]\ kJ·mol^{-1}$

Enthalpy of Formation

Bear *et al.*[1] measured the enthalpies of solution of Be(cr) and $BeSO_4$(cr,α) in concentrated HF and the enthalpy of reaction of H_2SO_4(aq) with $BeSO_4$(aq HF). Combination of these yields reaction (a) below. Taylor *et al.*[2] measured enthalpies of solution of Be(cr) and $BeSO_4$(cr,α) in H_2SO_4(aq) which yields reaction (b). Marchal[3] measured the total vapor pressure of $BeSO_4$(cr) in the temperature range 863–1103 K. Partial pressures of SO_3(g) were calculated from Marchal's[3] data using JANAF[4] values for the SO_3–SO_2 equilibrium. 3rd law analysis of these data yields $\Delta_f H°$ for reaction (c) as given below. This was converted to $\Delta_f H°$ for α–$BeSo_4$ using JANAF[4] enthalpies of transitions.

Source	Method	Reaction	T/K	$\Delta_{fus}H_r$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	Calorimetric	(a) Be(cr) + H_2SO_4(109 H_2O) = H_2(g) + α–$BeSO_4$	294	−74.47	−286.65 ± 0.5
2	Calorimetric	(b) Be(cr) + H_2SO_4(47.849 H_2O) = H_2(g) + α–$BeSO_4$	298	−76.38	−287.55 ± 0.13
3	K_p (973–1083 K)	(c) $BeSO_4$(γ) → BeO(cr) + SO_3(g)	298	43.92	−286.55 ± 0.5

The adopted $\Delta_f H°(298.15\ K) = -287.0 \pm 0.8$ is an average value of reaction (a) and (b). This value is for relatively finely divided crystals of $BeSO_4$ as was indicated by Bear *et al.*[1]

Heat Capacity and Entropy

Low temperature heat capacities (12–301 K) and high temperature enthalpies (366–864 K) were measured by Taylor, Gardner and Smith.[5] These data were joined smoothly at 298.15 K and extrapolated graphically above 864 K. The entropy was obtained from the heat capacities using $S°(12.56\ K) = 0.034\ cal·K^{-1}·mol^{-1}$.

Transition Data

Bosik, Novoselova and Simanov[6] observed two endothermic effects at 863–883 K and 908–913 K on the heating and cooling curves of $BeSO_4$(cr); thus we have adopted $T_{trs1}(\alpha \rightarrow \beta) = 863\ K$ and $T_{trs2}(\beta \rightarrow \alpha) = 908\ K$. $\Delta_{trs1}H°(\alpha \rightarrow \beta) = 0.266\ kcal·mol^{-1}$ was obtained from the single enthalpy point at 863.9 K observed by Taylor, Gardner and Smith.[5] $\Delta_{trs2}H°(\beta \rightarrow \gamma) = 4.673\ kcal·mol^{-1}$ was chosen in order to give good agreement with the equilibrium data of Marchal.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.979	−1190.076	−1190.076	INFINITE
100	29.320	18.630	136.399	−11.777	−1195.412	−1161.311	606.607
200	60.675	48.883	85.043	−7.232	−1198.909	−1125.730	294.010
298.15	85.697	77.971	77.971	0.	−1200.808	−1089.354	190.850
300	86.111	78.502	77.973	0.159	−1200.830	−1088.662	189.553
400	103.880	105.869	81.583	9.714	−1203.656	−1051.063	137.255
500	116.357	130.457	88.944	20.756	−1204.763	−1012.781	105.805
600	126.817	152.591	97.737	32.913	−1204.777	−974.366	84.826
700	137.988	172.967	107.046	46.145	−1203.793	−936.028	69.847
800	149.787	192.159	116.496	60.531	−1201.788	−897.901	58.627
900	162.046	210.506	125.928	76.120	−1251.860	−859.007	49.855
1000	174.431	228.245	135.278	92.967	−1246.475	−815.635	42.604
1100	183.088	245.296	144.510	110.864	−1240.239	−772.847	36.699
1200	189.209	261.502	153.591	129.494	−1233.452	−730.653	31.805
1300	193.543	276.827	162.487	148.643	−1226.317	−689.041	27.686
1400	196.581	291.287	171.175	168.157	−1218.980	−647.986	24.177
1500	198.656	304.925	179.642	187.925	−1211.549	−607.460	21.154
1600	200.004	317.792	187.878	207.863	−1218.639	−566.905	18.508
1700	200.706	329.941	195.881	227.903	−1210.843	−526.410	16.175
1800	200.832	341.418	203.650	247.981	−1203.093	−486.374	14.114
1900	200.832	352.276	211.189	268.065	−1195.419	−446.766	12.282
2000	200.832	362.577	218.504	288.148	−1187.825	−407.560	10.644
2100	200.832	372.376	225.599	308.231	−1180.309	−368.732	9.172
2200	200.832	381.719	232.485	328.314	−1172.870	−330.259	7.841
2300	200.832	390.646	239.169	348.397	−1165.508	−292.124	6.634

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [79.258]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs1} = 863\ K\ (\alpha \rightarrow \beta)$
$T_{trs2} = 908\ K\ (\beta \rightarrow \gamma)$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-1199.695]\ kJ\cdot mol^{-1}$
$\Delta_{trs1} H° = [1.113]\ kJ\cdot mol^{-1}$
$\Delta_{trs2} H° = [19.552]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the alpha phase by adding $\Delta_{trs1}H°$; since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy

The heat capacity was assumed to be the same as that of alpha phase. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

Refer to the α–crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	85.697	79.258	79.258	0.	−1199.695	−1088.624	190.722
300	86.111	79.789	79.259	0.159	−1199.717	−1087.935	189.426
400	103.880	107.156	82.870	9.714	−1202.543	−1050.464	137.177
500	116.357	131.743	90.231	20.756	−1203.650	−1012.312	105.755
600	126.817	153.878	99.024	32.913	−1203.664	−974.025	84.796
700	137.988	174.253	108.332	46.145	−1202.680	−935.816	69.831
800	149.787	193.446	117.782	60.531	−1200.675	−897.818	58.621
900	162.046	211.792	127.215	76.120	−1250.747	−859.052	49.858
1000	174.431	229.532	136.564	92.967	−1245.362	−815.809	42.613
1100	183.088	246.583	145.797	110.864	−1239.126	−773.149	36.714
1200	189.209	262.789	154.877	129.494	−1232.339	−731.084	31.823
1300	193.543	278.114	163.773	148.643	−1225.204	−689.601	27.708
1400	196.581	292.574	172.462	168.157	−1217.867	−648.675	24.202
1500	198.656	306.211	180.928	187.925	−1210.436	−608.277	21.182
1600	200.004	319.079	189.164	207.863	−1217.526	−567.851	18.538
1700	200.706	331.228	197.167	227.903	−1209.730	−527.485	16.208
1800	200.832	342.704	204.937	247.981	−1201.980	−487.577	14.149
1900	200.832	353.563	212.476	268.065	−1194.306	−448.098	12.319
2000	200.832	363.864	219.790	288.148	−1186.712	−409.020	10.683
2100	200.832	373.663	226.886	308.231	−1179.196	−370.321	9.211
2200	200.832	383.005	233.772	328.314	−1171.757	−331.976	7.882
2300	200.832	391.933	240.456	348.397	−1164.395	−293.970	6.676

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [100.784]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs1} = 863\ K\ (\alpha \rightarrow \beta)$
$T_{trs2} = 908\ K\ (\beta \rightarrow \gamma)$

$\Delta_f H°(0\ K)$ Unknown
$\Delta_f H°(298.15\ K) = [-1180.143]\ kJ\cdot mol^{-1}$
$\Delta_{trs1} H° = [1.113]\ kJ\cdot mol^{-1}$
$\Delta_{trs2} H° = [19.552]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the beta phase by adding $\Delta_{trs2}H°$; since the heat capacities of both phases are assumed the same.

Heat Capacity and Entropy

The heat capacity was assumed to be the same as that of alpha phase. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

Refer to the α–crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	85.697	100.784	100.784	0.	−1180.143	−1075.491	188.422
300	86.111	101.316	100.786	0.159	−1180.166	−1074.841	187.147
400	103.880	128.682	104.396	9.714	−1182.991	−1039.523	135.748
500	116.357	153.270	111.757	20.756	−1184.098	−1003.523	104.837
600	126.817	175.405	120.550	32.913	−1184.113	−967.389	84.219
700	137.988	195.780	129.859	46.145	−1183.128	−931.333	69.497
800	149.787	214.973	139.309	60.531	−1181.123	−895.487	58.469
900	162.046	233.319	148.742	76.120	−1231.195	−858.874	49.848
1000	174.431	251.058	158.091	92.967	−1225.810	−817.784	42.717
1100	183.088	268.110	167.324	110.864	−1219.574	−777.277	36.910
1200	189.209	284.316	176.404	129.494	−1212.787	−737.364	32.097
1300	193.543	299.640	185.300	148.643	−1205.652	−698.033	28.047
1400	196.581	314.101	193.988	168.157	−1198.316	−659.260	24.597
1500	198.656	327.738	202.455	187.925	−1190.884	−621.016	21.626
1600	200.004	340.606	210.691	207.863	−1197.974	−582.742	19.025
1700	200.706	352.755	218.694	227.903	−1190.178	−544.528	16.731
1800	200.832	364.231	226.464	247.981	−1182.428	−506.773	14.706
1900	200.832	375.089	234.003	268.065	−1174.754	−469.446	12.906
2000	200.832	385.391	241.317	288.148	−1167.160	−432.522	11.296
2100	200.832	395.189	248.413	308.231	−1159.644	−395.975	9.849
2200	200.832	404.532	255.298	328.314	−1152.206	−359.783	8.542
2300	200.832	413.459	261.982	348.397	−1144.843	−323.930	7.357

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [88.37 \pm 8.4]\ J·K^{-1}·mol^{-1}$
T_{fus} = Unknown

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-1513.4 \pm 63]\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(BeWO_4, cr, 298.15\ K) = -361.7\ kcal·mol^{-1}$, is calculated from $\Delta_r H°(298.15\ K) = -17.1\ kcal·mol^{-1}$ for $BeO(cr) + WO_3(cr) \rightarrow BeWO_4(cr)$. The value of $\Delta_r H°(298.15\ K)$ is assumed to be the same as that for $MgO(cr) + WO_3(cr) \rightarrow MgWO_4(cr)$, using −143.7, −143.1, −201.5, and −362.3 $kcal·mol^{-1}$ for the enthalpies of formation of MgO(cr), BeO(cr), WO_3(cr) and $MgWO_4$(cr), respectively.

Heat Capacity and Entropy

Heat capacities are estimated by comparison with those of $CaWO_4$(cr),[1] BeO(cr),[2] and CaO(cr).[3]

The entropy, $S°(298.15\ K) = 21.12\ cal·K^{-1}·mol^{-1}$, is calculated from $\Delta S°(298.15\ K) = -0.4\ cal·K^{-1}·mol^{-1}$ for $BeO(cr) + WO_3(cr) \rightarrow BeWO_4(cr)$. The value of $\Delta S°(298.15\ K)$ is assumed to be the same as that for $MgO(cr) + WO_3(cr) \rightarrow MgWO_4(cr)$, using 6.44, 3.38, 18.14 and 24.18 $cal·K^{-1}·mol^{-1}$ for MgO(cr), BeO(cr), WO_3(cr) and $MgWO_4$(cr), respectively.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	97.278	88.366	88.366	0.	−1513.353	−1404.818	246.118
300	97.696	88.969	88.368	0.180	−1513.357	−1404.145	244.483
400	112.968	119.279	92.397	10.753	−1513.032	−1367.762	178.611
500	123.512	145.670	100.471	22.600	−1511.920	−1331.561	139.107
600	131.336	168.909	109.980	35.357	−1510.306	−1295.634	112.795
700	137.319	189.609	119.904	48.794	−1508.371	−1260.005	94.023
800	142.884	208.312	129.804	62.806	−1506.174	−1224.671	79.963
900	148.114	225.447	139.492	77.359	−1503.714	−1189.628	69.044
1000	153.009	241.307	148.890	92.417	−1500.997	−1154.873	60.324
1100	157.737	256.114	157.972	107.956	−1498.026	−1120.401	53.203
1200	162.256	270.033	166.736	123.956	−1494.806	−1086.212	47.282
1300	166.649	283.193	175.193	140.401	−1491.342	−1052.302	42.282
1400	171.126	295.708	183.358	157.291	−1487.628	−1018.667	38.007
1500	175.435	307.661	191.249	174.618	−1483.667	−985.307	34.311
1600	179.912	319.126	198.885	192.386	−1493.988	−951.693	31.070
1700	184.305	330.165	206.285	210.596	−1489.116	−917.947	28.205
1800	188.698	340.824	213.465	229.247	−1483.922	−884.498	25.667
1900	193.092	351.144	220.441	248.336	−1478.405	−851.345	23.405
2000	197.485	361.160	227.228	267.865	−1472.565	−818.492	21.377

PREVIOUS: June 1963 CURRENT: March 1967

$S°(298.15\ K) = [37.03 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 863\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -234.3 \pm 8.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Von Wartenberg[1] has measured the enthalpy of solution of Be and BeS in H_2SO_4. The difference between these two enthalpies gives $\Delta_r H°(353\ K) = -51.35 \pm 2.1\ kcal \cdot mol^{-1}$ for the reaction $Be(cr) + H_2S(g) \rightarrow BeS(cr) + H_2(g)$. Using auxiliary JANAF[2] data we calculate $\Delta_f H°(BeS, cr, 298.15\ K) = -56.0 \pm 2.1\ kcal \cdot mol^{-1}$. This is in agreement with the value for the enthalpy of formation preferred by NBS.[3]

Heat Capacity and Entropy

No low-temperature heat capacity or high-temperature enthalpy measurements have been reported. We estimate $C_p°(298.15\ K) = 8.13\ cal \cdot K^{-1} \cdot mol^{-1}$ from the reaction BeO(cr, α) + MgS(cr) = BeS(cr) by assuming $\Delta C_p° = 0$.[2] Comparison of this value with $C_p°$ data for all the alkaline earth oxides and sulfides[2] suggests that our estimate is reasonable. $C_p°$ data above 298.15 K are estimated graphically by comparison with α- and β-BeO.[2]

Several methods of estimation predict that the value of $S°(298.15\ K)$ should lie near 8.85 $cal \cdot K^{-1} \cdot mol^{-1}$. A graphical comparison of the standard entropies for other alkaline-earth oxides and sulfides suggest values for $S°(298.15\ K)$ in the range 9–10 $cal \cdot K^{-1} \cdot mol^{-1}$ while additive entropy constants[4] give 6.8 (Kelly's) and 9.3 (Latimer's) $cal \cdot K^{-1} \cdot mol^{-1}$. Literature estimates have included (in $cal \cdot K^{-1} \cdot mol^{-1}$) 7.4,[5] 8.0,[6] and 8.4.[7] We adopt $S°(298.15\ K) = 8.85 \pm 1.0\ cal \cdot K^{-1} \cdot mol^{-1}$based on cation increments for a series of beryllium and magnesium compounds.

Fusion Data

No literature melting data are available. BeO and BeS have a different crystal structure (cubic, zincblende type) than the remaining alkaline-earth oxides and sulfides (cubic, NaCl type).

References

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[2]JANAF Thermochemical Tables: H_2S(g), 6–30–77; H_2(g), 3–31–74; MgO(cr), 12–31–74; SrO(cr), 12–31–72; CaO(cr), 6–30–73; BaO(cr), 8–30–74; BeO(cr), 12–31–74; BaS(cr), SrS(cr), CaS(cr), and MgS(cr), 9–30–77.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	34.016	37.028	37.028	0.	−234.304	−232.972	40.816
300	34.309	37.240	37.029	0.063	−234.313	−232.964	40.563
400	42.551	48.313	38.483	3.932	−236.884	−232.365	30.344
500	47.698	58.394	41.475	8.459	−238.387	−231.067	24.139
600	51.045	67.402	45.060	13.405	−239.293	−229.509	19.981
700	53.346	75.450	48.837	18.629	−239.807	−227.834	17.001
800	55.145	82.694	52.624	24.056	−240.088	−226.102	14.763
900	56.651	89.278	56.336	29.648	−293.346	−223.264	12.958
1000	57.907	95.314	59.936	35.377	−292.155	−215.540	11.259
1100	58.968	100.883	63.409	41.222	−290.953	−207.937	9.874
1200	59.915	106.056	66.750	47.167	−289.753	−200.443	8.725
1300	60.762	110.886	69.961	53.202	−288.566	−193.049	7.757
1400	61.463	115.415	73.048	59.315	−287.404	−185.745	6.930
1500	61.955	119.673	76.016	65.486	−286.287	−178.523	6.217
1600	62.425	123.686	78.871	71.705	−299.761	−170.848	5.578
1700	62.859	127.484	81.620	77.969	−298.358	−162.834	5.003
1800	63.304	131.089	84.269	84.277	−296.946	−154.903	4.495
1900	63.769	134.525	86.824	90.631	−295.523	−147.050	4.043
2000	64.224	137.807	89.292	97.031	−294.087	−139.273	3.637
2100	64.664	140.951	91.678	103.475	−292.639	−131.568	3.273
2200	65.103	143.970	93.986	109.963	−291.179	−123.932	2.943
2300	65.542	146.873	96.223	116.496	−289.706	−116.363	2.643
2400	65.982	149.672	98.392	123.072	−288.219	−108.858	2.369
2500	66.421	152.374	100.498	129.692	−286.718	−101.415	2.119
2600	66.860	154.988	102.543	136.356	−285.201	−94.033	1.889
2700	67.300	157.520	104.533	143.064	−283.668	−86.710	1.677
2800	67.739	159.975	106.469	149.816	−573.076	−73.220	1.366
2900	68.178	162.360	108.356	156.612	−570.446	−55.415	0.998
3000	68.618	164.679	110.195	163.452	−567.783	−37.700	0.656

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 210.29 \pm 0.42\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [261 \pm 63]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [264 \pm 63]\ kJ\cdot mol^{-1}$

Source	State	Electronic and Molecular Constants (σ = 1) ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
1	$X^1\Sigma^+$	0.0	1	1.7415	0.79059	0.0064	997.94	6.137
1,2,7	$^3\Pi$	[6600.]	6	[1.9075]	[0.6590]	[0.00605]	[762.46]	[4.12]
1	$A^1\Pi$	7842.9	2	1.9075	0.6590	0.00605	762.46	4.12
1	$^1\Delta$	[13048.4]	2	[2.000]	[0.5997]	[0.0069]	[671.6]	[5.48]
1,2	$^3\Sigma^+$	[21000.]	3	[1.8137]	[0.72894]	[0.00604]	[851.35]	[4.85]
1	$B^1\Sigma^+$	25868.6	1	1.8137	0.72894	0.00604	851.35	4.85

Enthalpy of Formation

No experimental data are available on BeS(g). We estimate $D_0°$(BeS, g) by the method of Hauge and Margrave[1] based on data involving known bond energies and force constants of the gaseous diatomic oxides and sulfides. Based on dissociation energies of the alkaline earth monoxides, taken from Srivastava,[2] dissociation energies of the alkaline earth sulfides and force constants calculated from JANAF data,[3] we calculate $D_0°$(BeS, g) = 80 ± 10 kcal·mol^{-1}. A normal linear–Birge–Sponer extrapolation of the ground state yields $D_0°$(BeS, g) = 115 kcal·mol^{-1}. After correcting for ionic character[8] and for excited state products $D_0°$(BeS, g) = 76 kcal·mol^{-1}. These values are very uncertain. See the discussion of MgS(g).[3] We adopte $D_0°$(BeS, g) = 80 ± 15 kcal·mol^{-1}. Using auxiliary JANAF data,[3] we calculate $\Delta_f H°$(BeS, g, 298.15 K) = 63 ± 15 kcal·mol^{-1}.

Heat Capacity and Entropy

The spectroscopic constants of the observed states taken from Cheetham *et al.*[4] are corrected to account for the natural abundances of the elements. Other low-lying electronic states and their vibrational–rotational constants are estimated in isoconfigurational groups by analogy with BeO[5] and from trends observed in the known states of the other alkaline–earth oxides and sulfides.[3] Uncertainty in the energy and molecular constants for the estimated states may contribute as much as 2–3 cal·K^{-1}·mol^{-1} to the entropy above 3000 K.

The splitting between the $A^1\Pi$ and a $^3\Pi$ states, ~1200 cm^{-1}, is based on trends in the triplet–singlet splitting observed by Field[6] for the alkaline–earth oxides. The Hartree–Fock calculations of Verhaegen and Richards[7] support this. Their theoretical signlet–triplet splitting should be reasonably accurate even though the absolute energies are biased. The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r and Q_v in the partition function $Q = Q_e^1\Sigma\ Q_t^1\ Q_r^1\ Q_v^1\ g_i \exp(-c_2\epsilon_i/T)$.

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[1] R. H. Hauge and J. L. Margrave, High Temp. Sci. **4**, 170 (1972).

[2] R. D. Srivastava, High Temp. Sci. **8**, 225 (1976).

[3] JANAF Thermochemical Tables: Be(g), 9–30–61; S(g) 6–30–71; S_2(g), 12–31–65; BaO(g) and SrO(g), 6–30–74; BeO(g), MgO(g), and CaO(g), 12–31–74; MgS(g), CaS(g), SrS(g), and BaS(g), 9–30–77.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.780	261.156	261.156	INFINITE
100	29.109	178.064	236.789	−5.872	263.335	246.831	−128.931
200	29.468	198.299	213.056	−2.951	264.036	229.939	−60.054
298.15	30.786	210.288	210.288	0.	263.592	213.267	−37.363
300	30.816	210.478	210.289	0.057	263.577	212.954	−37.079
400	32.371	219.561	211.516	3.218	260.298	196.318	−25.636
500	33.636	226.926	213.884	6.521	257.571	180.624	−18.870
600	34.575	233.146	216.590	9.934	255.132	165.469	−14.405
700	35.273	238.531	219.348	13.428	252.888	150.704	−11.246
800	35.834	243.279	222.049	16.984	250.736	136.254	−8.896
900	36.363	247.530	224.648	20.594	195.496	123.152	−7.148
1000	36.960	251.391	227.132	24.259	194.622	115.160	−6.015
1100	37.713	254.947	229.501	27.991	193.712	107.258	−5.093
1200	38.688	258.269	231.761	31.809	192.784	99.439	−4.328
1300	39.919	261.412	233.922	35.737	191.865	91.698	−3.684
1400	41.407	264.423	235.994	39.801	190.979	84.026	−3.135
1500	43.124	267.338	237.987	44.026	190.150	76.416	−2.661
1600	45.017	270.180	239.910	48.432	174.862	69.385	−2.265
1700	47.016	272.969	241.773	53.033	174.602	62.801	−1.930
1800	49.044	275.714	243.583	57.836	174.509	56.228	−1.632
1900	51.023	278.419	245.345	62.840	174.583	49.656	−1.365
2000	52.883	281.084	247.066	68.037	174.815	43.075	−1.125
2100	54.566	283.706	248.748	73.411	175.193	36.480	−0.907
2200	56.030	286.279	250.396	78.943	175.696	29.863	−0.709
2300	57.248	288.797	252.011	84.609	176.303	23.221	−0.527
2400	58.209	291.255	253.595	90.384	176.989	16.551	−0.360
2500	58.918	293.647	255.150	96.242	177.728	9.851	−0.206
2600	59.386	295.967	256.675	102.159	178.498	3.120	−0.063
2700	59.635	298.214	258.172	108.112	179.276	−3.640	0.070
2800	59.690	300.384	259.641	114.080	−110.916	−4.206	0.078
2900	59.580	302.477	261.083	120.045	−109.117	−0.427	0.008
3000	59.333	304.493	262.496	125.991	−107.347	3.291	−0.057
3100	58.975	306.433	263.882	131.907	−105.618	6.950	−0.117
3200	58.531	308.299	265.241	137.783	−103.942	10.555	−0.172
3300	58.023	310.092	266.574	143.611	−102.326	14.108	−0.223
3400	57.471	311.816	267.879	149.386	−100.779	17.613	−0.271
3500	56.890	313.474	269.158	155.105	−99.305	21.073	−0.314
3600	56.293	315.068	270.412	160.764	−97.909	24.492	−0.355
3700	55.693	316.602	271.639	166.363	−96.594	27.874	−0.394
3800	55.097	318.080	272.842	171.903	−95.361	31.222	−0.429
3900	54.512	319.503	274.020	177.383	−94.213	34.538	−0.463
4000	53.943	320.876	275.175	182.806	−93.150	37.825	−0.494
4100	53.393	322.201	276.306	188.172	−92.173	41.087	−0.523
4200	52.866	323.482	277.414	193.485	−91.281	44.326	−0.551
4300	52.363	324.720	278.500	198.746	−90.476	47.546	−0.578
4400	51.884	325.918	279.564	203.958	−89.756	50.747	−0.602
4500	51.430	327.079	280.607	209.124	−89.122	53.933	−0.626
4600	51.001	328.204	281.629	214.245	−88.574	57.106	−0.648
4700	50.597	329.297	282.632	219.325	−88.110	60.267	−0.670
4800	50.217	330.358	283.615	224.365	−87.731	63.420	−0.690
4900	49.859	331.390	284.580	229.369	−87.435	66.566	−0.710
5000	49.524	332.394	285.526	234.338	−87.222	69.707	−0.728
5100	49.210	333.371	286.455	239.274	−87.093	72.844	−0.746
5200	48.916	334.324	287.366	244.181	−87.044	75.979	−0.763
5300	48.641	335.253	288.261	249.058	−87.077	79.114	−0.780
5400	48.384	336.160	289.140	253.909	−87.190	82.251	−0.796
5500	48.143	337.045	290.003	258.736	−87.383	85.390	−0.811
5600	47.919	337.911	290.850	263.539	−87.653	88.534	−0.826
5700	47.709	338.757	291.683	268.320	−88.001	91.683	−0.840
5800	47.513	339.585	292.502	273.081	−88.425	94.839	−0.854
5900	47.331	340.396	293.307	277.823	−88.923	98.003	−0.868
6000	47.160	341.190	294.099	282.547	−89.496	101.176	−0.881

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$D_0^\circ = 8.535 \pm 0.879$ kJ·mol^{-1}
$S°(298.15\ K) \approx 206.4 \pm 4.0$ J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = 631.1 \pm 6.3$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = 637.2 \pm 7.0$ kJ·mol^{-1}

Spectroscopic Constants for Be_2 in cm^{-1} (ground state)

v/	0	1	2	3	4	5	6	7	8
G(v)–G(O)	0	224	328.6	405.1	459.7	508	547.9	578.2	600.7
B(v)*	0.548	0.457	0.366	0.317	0.296	0.275	0.254	0.233	0.212
$10^6 \times$ D(v)*	10.13	10.13	10.13	31.64	31.64	31.64	31.64	31.64	31.64

*Estimated as explained below.

Enthalpy of Formation

The adopted value of the ground state dissociation energy for Be_2(g), $D_0^\circ = 8.535 \pm 0.879$ kJ·mol^{-1}, was determined via a high level *quantum mechanical calculation by Lengsfield, et al.*[1] Using this value and the recommended value for $\Delta_f H°$(Be, g, 0 K) = 319.8 kJ·mol^{-1} from CODATA,[2] we calculate the adopted value of $\Delta_f H°(Be_2, g, 0\ K) = 631.1 \pm 6.3$ kJ·mol^{-1}.

Heat Capacity and Entropy

The thermal functions were calculated using a direct summation technique analogous to the alkali dimers and diatomic halogens.[12] As in the diatomic fluorine case, the values of G(v), B_v, and D_v were directly input into the calculation. Values of 9 bound vibrational energy levels for the $^1\Sigma_g^+$ ground state were determined from a high level *ab initio* quantum mechanical calculation (including full configuration interaction).[3] However, a recent spectroscopic determination by Bondybey[4] gave a value for $\Delta G_{1/2} = 224$ cm^{-1} which is 1.21 times larger than the corresponding value from the theoretical calculation. We therefore adopt $\Delta G_{1/2} = 224$ cm^{-1} and increase the rest of the theoretically determined vibrational spacings by the same factor. These scaled G(v) are given in the table above. Since the theoretical binding energy of Harrison and Handy[3] may also be too small, we adopt the value calculated by Lengsfield *et al.*[1] The adopted values of B_v are estimated using the correlation of Calder and Ruedenberg.[5] Since a plot of $\Delta G_{v+1/2}$ vs. v exhibits two linear regions ($0 \le v \le 3$ and $4 \le v \le 8$), the value of B_e used to estimate α_e in the $4 \le v \le 8$ region is reduced from 0.593 to 0.39. This is done in order to assure a smoothly decreasing B_v as v increases. The D_v parameters are determined from the estimation method of Herzberg[6] where we use the first order D_e term only.

The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[7] who proposed a simpler form of Wooley's method.[8] The rotational levels are weighted in accordance with the nuclear spin–rotation interaction[9] as follows: even J weight = 0.625, odd J weight = 0.375. The so–called quasibound rotational levels were not included in the calculation. No suitable spectroscopic information exists for any of the excited states of Be_2. It should be noted that the inclusion of $^3\Sigma_u^+$ and $^3\Pi_g$ states in the range $T_e \ge 5000$ cm^{-1} as proposed by Jones[10] would cause our calculated thermal functions to be deficient at temperatures greater than about 2000 K.[13] Due to the extremely shallow well of the ground state, most Be_2 molecules will probably exist in an excited state at temperatures T ≥ 1000 K. The calculated $S°(298.15\ K)$ is 5.41 J·K^{-1}·mol^{-1} smaller than the value adopted by Glushko, *et al.*[11]

References

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[9] Reference 6, Chapter 5.
[10] R. O. Jones, J. Chem. Phys. **71**, 1300 (1979).
[11] V. P. Glushko, V. Medvedev, *et al.*, "Thermal Constants of Substances," Volume IX, Moscow, (1979).
[12] JANAF Thermochemical Tables, Li_2(g), 12–31–83; F_2(r), 6–30–82.
[13] See for example JANAF Thermochemical Tables, Mg_2(g), 9–30–83.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.960	631.065	631.065	INFINITE
100	37.037	167.734	235.643	−6.791	634.156	617.483	−322.540
200	34.597	194.091	209.116	−3.005	636.787	599.638	−156.609
298.15	27.492	206.410	206.410	0.	637.161	581.249	−101.832
300	27.405	206.580	206.411	0.051	637.151	580.902	−101.144
400	24.295	213.975	207.440	2.614	636.030	562.294	−73.428
500	22.893	219.227	209.297	4.965	634.176	544.063	−56.838
600	22.173	223.331	211.306	7.215	631.891	526.249	−45.814
700	21.763	226.715	213.273	9.410	629.303	508.843	−37.970
800	21.509	229.603	215.138	11.572	626.472	491.825	−32.113
900	21.341	232.126	216.888	13.714	623.429	475.175	−27.578
1000	21.226	234.368	218.526	15.842	620.191	458.874	−23.969
1100	21.142	236.387	220.060	17.960	616.767	442.906	−21.032
1200	21.081	238.224	221.498	20.071	613.162	427.258	−18.598
1300	21.033	239.910	222.850	22.177	609.377	411.919	−16.551
1400	20.997	241.467	224.125	24.278	605.414	396.877	−14.808
1500	20.968	242.915	225.330	26.377	601.271	382.125	−13.307
1600	20.944	244.267	226.472	28.472	567.876	368.707	−12.037
1700	20.925	245.536	227.556	30.566	564.173	356.372	−10.950
1800	20.909	246.732	228.589	32.657	560.425	344.256	−9.990
1900	20.896	247.862	229.574	34.747	556.633	332.350	−9.137
2000	20.884	248.933	230.515	36.836	552.797	320.644	−8.374
2100	20.875	249.952	231.417	38.924	548.916	309.132	−7.689
2200	20.866	250.923	232.281	41.011	544.992	297.805	−7.071
2300	20.859	251.850	233.112	43.098	541.024	286.658	−6.510
2400	20.853	252.738	233.912	45.183	537.012	275.685	−6.000
2500	20.847	253.589	234.682	47.268	532.957	264.879	−5.534
2600	20.843	254.407	235.425	49.353	528.858	254.237	−5.108
2700	20.838	255.193	236.142	51.437	524.716	243.753	−4.716
2800	20.834	255.951	236.836	53.521	−61.384	245.869	−4.587
2900	20.831	256.682	237.508	55.604	−63.485	256.879	−4.627
3000	20.828	257.388	238.159	57.687	−65.598	267.962	−4.666
3100	20.825	258.071	238.791	59.769	−67.723	279.116	−4.703
3200	20.823	258.732	239.403	61.852	−69.864	290.338	−4.739
3300	20.820	259.373	239.999	63.934	−72.023	301.628	−4.774
3400	20.818	259.994	240.578	66.016	−74.204	312.983	−4.808
3500	20.816	260.598	241.141	68.098	−76.411	324.403	−4.841
3600	20.815	261.184	241.690	70.179	−78.647	335.887	−4.874
3700	20.813	261.755	242.225	72.261	−80.917	347.432	−4.905
3800	20.812	262.310	242.746	74.342	−83.223	359.040	−4.935
3900	20.810	262.850	243.255	76.423	−85.572	370.709	−4.965
4000	20.809	263.377	243.751	78.504	−87.967	382.439	−4.994
4100	20.808	263.891	244.236	80.585	−90.411	394.230	−5.023
4200	20.807	264.392	244.710	82.666	−92.911	406.080	−5.050
4300	20.806	264.882	245.173	84.746	−95.469	417.991	−5.078
4400	20.805	265.360	245.627	86.827	−98.091	429.962	−5.104
4500	20.804	265.828	246.071	88.907	−100.779	441.994	−5.131
4600	20.803	266.285	246.505	90.988	−103.539	454.085	−5.156
4700	20.803	266.732	246.931	93.068	−106.373	466.238	−5.182
4800	20.802	267.170	247.348	95.148	−109.285	478.452	−5.207
4900	20.801	267.599	247.757	97.228	−112.279	490.727	−5.231
5000	20.801	268.019	248.158	99.308	−115.356	503.064	−5.255
5100	20.800	268.431	248.551	101.388	−118.520	515.464	−5.279
5200	20.799	268.835	248.937	103.468	−121.774	527.927	−5.303
5300	20.799	269.231	249.317	105.548	−125.119	540.453	−5.326
5400	20.798	269.620	249.689	107.628	−128.556	553.043	−5.350
5500	20.798	270.002	250.055	109.708	−132.088	565.697	−5.373
5600	20.798	270.377	250.414	111.788	−135.715	578.417	−5.395
5700	20.797	270.745	250.768	113.868	−139.439	591.203	−5.418
5800	20.797	271.106	251.115	115.947	−143.259	604.054	−5.440
5900	20.796	271.462	251.457	118.027	−147.177	616.972	−5.462
6000	20.796	271.811	251.794	120.107	−151.191	629.958	−5.484

PREVIOUS: CURRENT: September 1983 (1 bar)

$S°(298.15\ K) = [381.47]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-752]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-749]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[220] (1)	[185] (1)	[250] (1)
[110] (1)	[100] (1)	[200] (1)
[180] (1)	860 (1)	[400] (1)
[105] (1)	[300] (1)	640 (1)

Ground State Quantum Weight: 1 $\alpha = 4$

Point Group: $[D_{2h}]$

Bond Distances: Be–Cl = [1.7] Å; Be–Cl' (in ring) = [1.8]Å

Bond Angles: Cl'–Be–Cl' (in ring) = [88]°; Cl'–Be–Cl = [136]°

Product of the Moments of Inertia: $I_A I_B I_C = [2.6276 \times 10^{-112}]\ g^3\ cm^6$

Enthalpy of Formation

The enthalpy of formation was estimated by assuming that the concentration of dimer in equilibrium with the monomer was −5% at 500 K as reported by Hildenbrand, Theard, Murad and Ju,[1] giving an effective $K_p = 5.5 \times 10^{-4}$ for $2BeCl_2(g) \rightarrow Be_2Cl_4(g)$ at 500 K.

Heat Capacity and Entropy

The structure was assumed planar with a D_{2h} symmetry, the bond lengths were estimated from the values for $BeCl_2(g)$, a lengthening being assumed in the ring. The frequencies were estimated using K_2Cl_2 as a basis for the ring vibrations. Two polymeric frequencies had been observed by Snelson.[2] These were observed in matrix isolated $BeCl_2$ gas and were ascribed to polymeric species on account of thier warm up behavior. They are here assigned to the B_{3u} asymmetric stretching mode and the B_{1u} symmetric out of plane wag of the non–ring chlorines. The order of the frequencies listed above is arbitrary and not related to their species type. The principal moments of inertia are: $I_A = [18.4088 \times 10^{-39}]$, $I_B = [110.6214 \times 10^{-39}]$, and $I_C = [129.0303 \times 10^{-39}]$ g cm^2.

References

[1]D. L. Hildenbrand, L. P. Theard, E. Murad and F. Ju, Aeronutronic Div. of Philco Corp. Report U-3068, April 1965, under contract AF 04 (611)–8523.

[2]A. Snelson, IIT Research Institute, Report No. IITRI–C 6013–4, May 1964, under contract No. DA–31–124–ARO (D)–111.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−25.305	−752.015	−752.015	INFINITE
100	77.971	273.932	475.560	−20.163	−752.775	−742.266	387.720
200	104.193	337.542	391.721	−10.836	−750.678	−732.532	191.318
250	110.809	361.547	383.350	−5.451	−749.715	−728.110	152.130
298.15	115.368	381.475	381.475	0.	−748.936	−724.021	126.846
300	115.517	382.189	381.477	0.214	−748.909	−723.867	126.036
350	118.970	400.268	382.897	6.080	−748.236	−719.748	107.417
400	121.557	416.331	386.091	12.096	−747.650	−715.719	93.463
450	123.529	430.768	390.266	18.225	−747.127	−711.760	82.619
500	125.056	443.865	394.982	24.442	−746.652	−707.856	73.949
600	127.217	466.871	405.099	37.063	−745.829	−700.176	60.956
700	128.625	486.595	415.366	49.860	−745.159	−692.623	51.684
800	129.587	503.837	425.370	62.774	−744.638	−685.155	44.736
900	130.270	519.142	434.955	75.769	−744.269	−677.743	39.335
1000	130.771	532.894	444.073	88.822	−744.055	−670.364	35.016
1100	131.149	545.377	452.723	101.919	−744.001	−662.999	31.483
1200	131.440	556.801	460.927	115.049	−744.111	−655.632	28.539
1300	131.669	567.331	468.712	128.205	−744.390	−648.248	26.047
1400	131.852	577.096	476.110	141.381	−744.842	−640.837	23.910
1500	132.001	586.198	483.149	154.574	−745.472	−633.387	22.057
1600	132.123	594.721	489.859	167.780	−775.356	−624.838	20.399
1700	132.225	602.734	496.265	180.998	−775.552	−615.425	18.910
1800	132.311	610.295	502.392	194.225	−775.800	−605.999	17.586
1900	132.384	617.450	508.261	207.459	−776.102	−596.558	16.401
2000	132.446	624.242	513.892	220.701	−776.460	−587.099	15.333
2100	132.500	630.706	519.302	233.948	−776.878	−577.621	14.368
2200	132.546	636.871	524.507	247.201	−777.359	−568.121	13.489
2300	132.587	642.763	529.521	260.457	−777.904	−558.598	12.686
2400	132.623	648.407	534.358	273.718	−778.519	−549.051	11.950
2500	132.655	653.822	539.029	286.982	−779.205	−539.476	11.272
2600	132.683	659.025	543.545	300.249	−779.965	−529.872	10.645
2700	132.708	664.033	547.915	313.518	−780.802	−520.237	10.065
2800	132.731	668.860	552.149	326.790	−1363.631	−498.125	9.293
2900	132.751	673.518	556.254	340.064	−1362.499	−467.234	8.416
3000	132.769	678.019	560.238	353.340	−1361.413	−436.381	7.598
3100	132.786	682.372	564.108	366.618	−1360.378	−405.564	6.834
3200	132.801	686.588	567.870	379.897	−1359.393	−374.780	6.118
3300	132.814	690.675	571.530	393.178	−1358.462	−344.025	5.445
3400	132.827	694.640	575.093	406.460	−1357.584	−313.298	4.813
3500	132.838	698.491	578.564	419.744	−1356.760	−282.596	4.218
3600	132.849	702.233	581.947	433.028	−1355.991	−251.916	3.655
3700	132.858	705.873	585.248	446.313	−1355.277	−221.257	3.124
3800	132.867	709.416	588.469	459.600	−1354.617	−190.617	2.620
3900	132.875	712.868	591.615	472.887	−1354.010	−159.994	2.143
4000	132.883	716.232	594.688	486.175	−1353.456	−129.385	1.690
4100	132.890	719.513	597.693	499.463	−1352.955	−98.789	1.259
4200	132.897	722.715	600.632	512.753	−1352.505	−68.206	0.848
4300	132.903	725.843	603.507	526.043	−1352.105	−37.632	0.457
4400	132.909	728.898	606.322	539.333	−1351.755	−7.067	0.084
4500	132.914	731.885	609.080	552.624	−1351.454	23.491	−0.273
4600	132.919	734.806	611.781	565.916	−1351.200	54.042	−0.614
4700	132.924	737.665	614.429	579.208	−1350.994	84.588	−0.940
4800	132.928	740.464	617.026	592.501	−1350.834	115.131	−1.253
4900	132.932	743.204	619.573	605.794	−1350.719	145.671	−1.553
5000	132.936	745.890	622.073	619.087	−1350.649	176.208	−1.841
5100	132.940	748.523	624.526	632.381	−1350.623	206.745	−2.118
5200	132.943	751.104	626.936	645.675	−1350.641	237.282	−2.384
5300	132.946	753.636	629.303	658.970	−1350.702	267.819	−2.640
5400	132.950	756.122	631.628	672.264	−1350.804	298.358	−2.886
5500	132.952	758.561	633.914	685.559	−1350.948	328.900	−3.124
5600	132.955	760.957	636.161	698.855	−1351.134	359.444	−3.353
5700	132.958	763.310	638.371	712.150	−1351.359	389.992	−3.574
5800	132.960	765.622	640.545	725.446	−1351.624	420.545	−3.787
5900	132.963	767.895	642.685	738.743	−1351.927	451.102	−3.994
6000	132.965	770.130	644.790	752.039	−1352.269	481.664	−4.193

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K)$ = [298.9] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1204.1 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1204.6 \pm 21\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[1200] (1)	[1500] (1)
[600] (1)	[900] (1)
[400] (1)	[300] (1)
[100] (1)	[300] (1)
[300] (1)	

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Be–O = [1.33] Å; Be–F = [1.43] Å
Bond Angles: O–Be–F = [180]°; Be–O–Be = [150]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.5549×10^{-114}] $g^3·cm^6$

Enthalpy of Formation

Efimenko[1] has studied mass spectrometrically the reaction BeO(cr) + BeF_2(g) → Be_2OF_2(g) and also reported two sets of equilibrium constants. Uning JANAF thermal functions, the enthalpy of reaction has been calculated from those reported equilibrium constants by the 2nd law and the 3rd law methods.

Number of Measurements	T/K	$\Delta_r H°$(298.15K), kcal·mol 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
1st Set 13	1570–1891	41.448 ± 3.04	41.981	0.408 ± 1.726
2nd Set 21*	1872–2195	42.553 ± 0.70	42.714	0.015 ± 0.359

*There are 4 points rejected due to failure of statistical test.

A weighted average value, $\Delta_r H°(298.15\ K) = 42.70\ kcal·mol^{-1}$, was chosen for the enthalpy of reaction. The enthalpy of formation $\Delta_f H°(Be_2OF_2, g, 298.15\ K) = 287.9 \pm 5\ kcal·mol^{-1}$ was calculated from the selected enthalpy of reaction, using $\Delta_f H°$(BeO, cr, 298.15 K) = 143.1 $kcal·mol^{-1}$ and $\Delta_f H°(BeF_2, g, 298.15\ K) = 187.5\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The adopted "V" shape molecular structure with nine fundamental vibrational frequencies was obtained from an estimation by Mann.[3] The bond distance Be–O and Be–F were estimated to be the same as those in BeO(g) and BeF_2(g), respectively. The principal moments of inertia are: $I_A = 1.0103 \times 10^{-39}$, $I_B = 49.7842 \times 10^{-39}$, and $I_C = 50.7946 \times 10^{-39}\ g·cm^2$.

References

[1]J. Efimenko, NBS Report 8186, Ch. 13 (January, 1964); refer to pp. 103–112.
[2]D. E. Mann, NBS Report 8186, Ch. 15 (January, 1964); refer to pp. 118–121.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−16.585	−1204.127	−1204.127	INFINITE
100	47.638	231.587	358.833	−12.725	−1204.705	−1202.060	627.892
200	65.525	270.625	305.569	−6.989	−1204.509	−1199.485	313.273
250	71.486	285.913	300.144	−3.558	−1204.493	−1198.233	250.357
298.15	76.151	298.915	298.915	0.	−1204.574	−1197.022	209.713
300	76.314	299.387	298.916	0.141	−1204.578	−1196.975	208.412
350	80.365	311.463	299.861	4.061	−1204.742	−1195.696	178.448
400	83.817	322.426	302.007	8.168	−1204.941	−1194.390	155.971
450	86.772	332.473	304.842	12.434	−1205.153	−1193.059	138.487
500	89.304	341.750	308.074	16.838	−1205.371	−1191.703	124.496
600	93.336	358.407	315.107	25.980	−1205.816	−1188.928	103.505
700	96.312	373.030	322.359	35.470	−1206.288	−1186.077	88.506
800	98.534	386.043	329.521	45.217	−1206.812	−1183.154	77.252
900	100.216	397.750	336.462	55.159	−1207.413	−1180.162	68.495
1000	101.510	408.378	343.131	65.248	−1208.111	−1177.098	61.485
1100	102.521	418.103	349.511	75.451	−1208.924	−1173.958	55.747
1200	103.324	427.059	355.605	85.745	−1209.867	−1170.738	50.961
1300	103.969	435.356	361.424	96.111	−1210.952	−1167.435	46.908
1400	104.494	443.080	366.984	106.535	−1212.190	−1164.042	43.431
1500	104.927	450.305	372.301	117.007	−1213.590	−1160.555	40.414
1600	105.288	457.089	377.390	127.518	−1244.232	−1155.918	37.737
1700	105.591	463.481	382.268	138.062	−1245.176	−1150.369	35.347
1800	105.849	469.524	386.949	148.635	−1246.160	−1144.764	33.220
1900	106.069	475.253	391.447	159.231	−1247.188	−1139.104	31.316
2000	106.258	480.699	395.775	169.847	−1248.259	−1133.387	29.601
2100	106.422	485.887	399.943	180.482	−1249.373	−1127.617	28.048
2200	106.566	490.841	403.963	191.131	−1250.528	−1121.791	26.635
2300	106.691	495.581	407.844	201.794	−1251.723	−1115.913	25.343
2400	106.802	500.124	411.595	212.469	−1252.956	−1109.982	24.158
2500	106.901	504.486	415.224	223.154	−1254.223	−1103.999	23.067
2600	106.988	508.681	418.739	233.849	−1255.522	−1097.965	22.058
2700	107.066	512.720	422.145	244.551	−1256.850	−1091.880	21.124
2800	107.137	516.615	425.450	255.262	−1840.120	−1073.300	20.023
2900	107.200	520.376	428.659	265.979	−1839.373	−1045.927	18.839
3000	107.257	524.011	431.777	276.701	−1838.615	−1018.579	17.735
3100	107.309	527.529	434.809	287.430	−1837.847	−991.257	16.703
3200	107.356	530.936	437.760	298.163	−1837.069	−963.961	15.735
3300	107.399	534.240	440.634	308.901	−1836.284	−936.688	14.827
3400	107.438	537.447	443.435	319.643	−1835.494	−909.439	13.972
3500	107.475	540.562	446.165	330.388	−1834.700	−882.214	13.166
3600	107.508	543.590	448.830	341.138	−1833.907	−855.011	12.406
3700	107.538	546.536	451.431	351.890	−1833.117	−827.831	11.687
3800	107.566	549.404	453.972	362.645	−1832.335	−800.671	11.006
3900	107.593	552.199	456.455	373.403	−1831.564	−773.532	10.360
4000	107.617	554.923	458.882	384.164	−1830.809	−746.413	9.747
4100	107.639	557.581	461.257	394.926	−1830.075	−719.312	9.164
4200	107.660	560.175	463.582	405.691	−1829.365	−692.229	8.609
4300	107.680	562.708	465.858	416.458	−1828.686	−665.162	8.080
4400	107.698	565.184	468.087	427.227	−1828.041	−638.111	7.575
4500	107.715	567.605	470.272	437.998	−1827.434	−611.074	7.093
4600	107.731	569.972	472.414	448.770	−1826.872	−584.051	6.632
4700	107.746	572.289	474.514	459.544	−1826.358	−557.038	6.191
4800	107.760	574.558	476.575	470.319	−1825.897	−530.036	5.768
4900	107.773	576.780	478.597	481.096	−1825.493	−503.043	5.363
5000	107.785	578.957	480.583	491.874	−1825.149	−476.058	4.973
5100	107.797	581.092	482.533	502.653	−1824.870	−449.079	4.600
5200	107.808	583.185	484.448	513.433	−1824.658	−422.105	4.240
5300	107.818	585.239	486.331	524.214	−1824.518	−395.134	3.894
5400	107.828	587.254	488.181	534.997	−1824.452	−368.166	3.561
5500	107.837	589.233	490.000	545.780	−1824.462	−341.198	3.240
5600	107.846	591.176	491.790	556.564	−1824.551	−314.228	2.931
5700	107.854	593.085	493.550	567.349	−1824.721	−287.257	2.632
5800	107.862	594.961	495.282	578.135	−1824.973	−260.282	2.344
5900	107.870	596.805	496.988	588.922	−1825.310	−233.302	2.065
6000	107.877	598.618	498.666	599.709	−1825.732	−206.315	1.796

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = [220.8]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -64 \pm 42\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -63 \pm 42\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	g_i
[1100]	(1)
[500]	(2)
[1600]	(1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Be–O = [1.4] Å
Bond Angle: Be–O–Be = [180]°
Rotational Constant: $B_O = [0.477178]\ cm^{-1}$

Enthalpy of Formation

Hildenbrand, Theard, and Ju[1] have reported the enthalpy of formation. Equilibrium constants were determined in a mass spectrometer for the reactions $2BeO(cr) \rightarrow Be_2O(g) + O(g)$ − (1); $2BeO(g) \rightarrow Be_2O(g) + O(g)$ − (2); and $Be_2O_2(g) \rightarrow Be_2O(g) + O(g)$ − (3). Using our own Gibbs energy functions we obtain $\Delta_f H°(Be_2O, g, 298.15\ K)$ = 13.1, −14.5, and −16.7 $kcal·mol^{-1}$, all ±10; the 2nd law treatment of reaction 1 gives $-18.3 \pm 10\ kcal·mol^{-1}$. We adopt a median value $-15 \pm 10\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Buchler, Stauffer, Klemperer and Wharton[2] have shown Li_2O to be linear. Also Walsh[3] predicted that AB_2 molecules with less than 16 bonding electrons would be linear. Thus Be_2O was taken to be linear and symmetrical, with a Be–O bond length of 1.4 Å, which is a little longer than in BeO(g). The vibrational frequencies were estimated by taking ν_3 to be larger than the stretch in BeO(g) and then calculating ν_1 from the valence force field assumption. The bending force constant was estimated as 1/20th of the stretching force constant. The two outermost electrons were considered unpaired and so gave a $^3\Sigma$ ground state.

References

[1]D. L. Hildenbrand, L. P. Theard, and F. Ju, Ford Motor Co., Aeronutronic Division, Third Quarterly Technical Report U-2231, (April–June 1963).
[2]A. Buchler, J. L. Stauffer, W. Klemperer and C. Wharton, A. D. Little, Inc., Interim Technical Report No. 5, (1963).
[3]A. D. Walsh, J. Chem. Soc. London **1953**, 2269.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.925	−64.479	−64.479	INFINITE
100	29.748	183.340	253.419	−7.008	−63.092	−72.660	37.954
200	35.536	205.584	224.408	−3.765	−62.460	−82.559	21.562
250	38.466	213.835	221.488	−1.913	−62.521	−87.581	18.299
298.15	40.952	220.827	220.827	0.	−62.760	−92.388	16.186
300	41.041	221.081	220.828	0.076	−62.772	−92.572	16.118
350	43.322	227.582	221.336	2.186	−63.156	−97.510	14.553
400	45.354	233.502	222.492	4.404	−63.614	−102.387	13.370
450	47.163	238.951	224.022	6.718	−64.112	−107.204	12.444
500	48.767	244.004	225.771	9.117	−64.636	−111.964	11.697
600	51.429	253.141	229.588	14.132	−65.734	−121.327	10.562
700	53.482	261.230	233.541	19.382	−66.894	−130.502	9.738
800	55.063	268.480	237.463	24.813	−68.126	−139.506	9.109
900	56.290	275.039	241.280	30.383	−69.443	−148.350	8.610
1000	57.250	281.021	244.959	36.062	−70.861	−157.043	8.203
1100	58.011	286.515	248.491	41.826	−72.394	−165.588	7.863
1200	58.620	291.590	251.874	47.659	−74.052	−173.988	7.573
1300	59.115	296.302	255.112	53.547	−75.846	−182.244	7.323
1400	59.520	300.698	258.213	59.479	−77.785	−190.357	7.102
1500	59.856	304.816	261.184	65.448	−79.877	−198.326	6.906
1600	60.138	308.689	264.033	71.449	−111.202	−205.098	6.696
1700	60.375	312.342	266.769	77.474	−112.818	−210.917	6.481
1800	60.577	315.799	269.397	83.522	−114.467	−216.641	6.287
1900	60.750	319.079	271.926	89.589	−116.153	−222.271	6.111
2000	60.899	322.198	274.363	95.671	−117.877	−227.812	5.950
2100	61.029	325.173	276.712	101.768	−119.641	−233.265	5.802
2200	61.142	328.015	278.980	107.877	−121.448	−238.634	5.666
2300	61.242	330.735	281.171	113.996	−123.298	−243.919	5.540
2400	61.330	333.343	283.291	120.125	−125.193	−249.123	5.422
2500	61.408	335.848	285.344	126.262	−127.134	−254.247	5.312
2600	61.478	338.258	287.333	132.406	−129.121	−259.293	5.209
2700	61.540	340.580	289.262	138.557	−131.155	−264.261	5.112
2800	61.596	342.819	291.135	144.714	−715.150	−256.707	4.789
2900	61.647	344.981	292.955	150.876	−715.152	−240.335	4.329
3000	61.692	347.072	294.724	157.043	−715.169	−223.961	3.900
3100	61.734	349.095	296.446	163.214	−715.203	−207.587	3.498
3200	61.771	351.056	298.122	169.390	−715.258	−191.212	3.121
3300	61.806	352.957	299.755	175.569	−715.336	−174.834	2.767
3400	61.837	354.803	301.347	181.751	−715.441	−158.454	2.434
3500	61.866	356.596	302.900	187.936	−715.576	−142.070	2.120
3600	61.893	358.339	304.416	194.124	−715.746	−125.682	1.824
3700	61.917	360.035	305.896	200.314	−715.953	−109.288	1.543
3800	61.940	361.687	307.343	206.507	−716.203	−92.888	1.277
3900	61.961	363.296	308.757	212.702	−716.498	−76.481	1.024
4000	61.980	364.865	310.140	218.899	−716.845	−60.067	0.784
4100	61.998	366.395	311.493	225.098	−717.246	−43.642	0.556
4200	62.015	367.890	312.818	231.299	−717.706	−27.208	0.338
4300	62.030	369.349	314.116	237.501	−718.230	−10.761	0.131
4400	62.045	370.775	315.388	243.705	−718.821	5.698	−0.068
4500	62.059	372.170	316.634	249.910	−719.484	22.172	−0.257
4600	62.071	373.534	317.856	256.117	−720.222	38.661	−0.439
4700	62.083	374.869	319.055	262.324	−721.040	55.167	−0.613
4800	62.095	376.176	320.232	268.533	−721.941	71.691	−0.780
4900	62.105	377.457	321.387	274.743	−722.929	88.236	−0.941
5000	62.115	378.711	322.521	280.954	−724.006	104.801	−1.095
5100	62.124	379.941	323.634	287.166	−725.175	121.389	−1.243
5200	62.133	381.148	324.729	293.379	−726.440	138.000	−1.386
5300	62.142	382.332	325.805	299.593	−727.802	154.637	−1.524
5400	62.149	383.493	326.862	305.807	−729.265	171.300	−1.657
5500	62.157	384.634	327.902	312.023	−730.828	187.991	−1.785
5600	62.164	385.754	328.925	318.239	−732.495	204.712	−1.909
5700	62.171	386.854	329.932	324.455	−734.266	221.463	−2.029
5800	62.177	387.935	330.923	330.673	−736.142	238.247	−2.146
5900	62.183	388.998	331.898	336.891	−738.125	255.063	−2.258
6000	62.189	390.043	332.858	343.109	−740.214	271.915	−2.367

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K) = [247.61]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) \approx -409 \pm 50\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) \approx -410 \pm 50\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[1120] (1)	[460] (1)
[630] (1)	[920] (1)
[760] (1)	[1480] (1)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: [V_h]

Bond Distance: Be–O = [1.63] Å

Bond Angles: Be–O–Be = [90]°; O–Be–O = [90]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.0972 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

Chupka, Berkowitz, and Giese[1] studied the temperature dependence of the $(BeO)_2^+$ ion in a mass spectrometer and obtained a 2nd law enthalpy of vaporization of 172 ± 8 kcal·mol^{-1} at 2150 K. No correction was made for fragmentation of higher polymers and this is reflected in the uncertainty. We adopted an enthalpy of sublimation of 178 kcal·mol^{-1} in order to match more closely the equilibrium constant found by Chupka, *et al.*[1] However, it was not possible to alter either the enthalpy or entropy sufficiently to obtain exact agreement, the predicted pressure being too high by a factor of 20.

Heat Capacity and Entropy.

A planar ring configuration was assumed which has six vibrational frequencies of the type $2A_{1g}$, B_{1g}, B_{1u}, B_{2u}, and B_{3u}. These were estimated by comparison with $(LiO)_2$ for which values have been calculated by White, Seshadri, Dever, Mann, and Linevsky.[2] It seems unlikely that any other structure than that of a ring is possible, as, in order to approach the observed equilibrium constant an even lower entropy is needed. A non–linear chain would have a higher entropy due to the change in symmetry number and the two odd electrons. A linear chain would have approximately the same entropy due to cancellation of opposite effects. The vibrational frequencies were also made as high as possible by normalizing them using B_{3u} equal to the BeO stretch in BeO(g). The bond length was taken as the sum of the covalent radii of O and Be, which is in general agreement with other polymeric structures which generally increase in bond length by 10–20% in going from monomer to polymer. The bond angle was chosen arbitrarily, however, changes in the angle would change the entropy less than 1 cal·K^{-1}·mol^{-1}.

The principal moments of inertia are: $I_A = 7.0589 \times 10^{-39}$, $I_B = 3.9761 \times 10^{-39}$, and $I_C = 11.0350 \times 10^{-39}$ g·cm^2.

References

[1]W. A. Chupka, J. Berkowitz and C. F. Giese, J. Chem. Phys. **30**, 827 (1959).

[2]D. White, K. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, prepublication communication, (July 1963).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.409	−408.893	−408.893	INFINITE
100	33.845	204.646	285.396	−8.075	−408.542	−411.575	214.985
200	40.459	229.794	251.839	−4.409	−408.942	−414.535	108.265
250	45.019	239.309	248.400	−2.273	−409.448	−415.877	86.893
298.15	49.339	247.611	247.611	0.	−410.032	−417.064	73.068
300	49.499	247.917	247.612	0.091	−410.056	−417.107	72.625
350	53.618	255.862	248.230	2.671	−410.709	−418.231	62.418
400	57.274	263.266	249.652	5.445	−411.357	−419.261	54.750
450	60.456	270.200	251.554	8.391	−411.982	−420.211	48.777
500	63.197	276.715	253.748	11.484	−412.583	−421.093	43.991
600	67.555	288.643	258.589	18.033	−413.728	−422.687	36.798
700	70.753	299.310	263.658	24.956	−414.842	−424.092	31.646
800	73.124	308.920	268.725	32.156	−415.973	−425.337	27.772
900	74.910	317.641	273.683	39.561	−417.157	−426.437	24.750
1000	76.277	325.607	278.483	47.124	−418.423	−427.401	22.325
1100	77.342	332.929	283.105	54.807	−419.791	−428.233	20.335
1200	78.185	339.696	287.542	62.585	−421.278	−428.936	18.671
1300	78.861	345.982	291.799	70.438	−422.898	−429.510	17.258
1400	79.410	351.847	295.881	78.353	−424.662	−429.953	16.042
1500	79.863	357.342	299.797	86.317	−426.580	−430.265	14.983
1600	80.239	362.508	303.556	94.323	−457.732	−429.393	14.018
1700	80.555	367.382	307.169	102.363	−459.180	−427.577	13.138
1800	80.823	371.994	310.643	110.432	−460.666	−425.676	12.353
1900	81.051	376.371	313.988	118.526	−462.194	−423.690	11.648
2000	81.248	380.533	317.212	126.641	−463.767	−421.623	11.012
2100	81.419	384.501	320.323	134.775	−465.387	−419.476	10.434
2200	81.568	388.293	323.327	142.924	−467.057	−417.251	9.907
2300	81.698	391.921	326.231	151.088	−468.778	−414.949	9.424
2400	81.813	395.401	329.041	159.263	−470.553	−412.571	8.979
2500	81.915	398.743	331.763	167.450	−472.382	−410.118	8.569
2600	82.006	401.957	334.401	175.646	−474.265	−407.590	8.189
2700	82.087	405.054	336.961	183.851	−476.204	−404.989	7.835
2800	82.160	408.041	339.446	192.063	−1060.112	−389.869	7.273
2900	82.226	410.925	341.862	200.283	−1060.036	−365.934	6.591
3000	82.285	413.713	344.211	208.508	−1059.983	−342.000	5.955
3100	82.339	416.412	346.496	216.740	−1059.955	−318.068	5.359
3200	82.388	419.027	348.722	224.976	−1059.955	−294.137	4.801
3300	82.432	421.563	350.891	233.217	−1059.987	−270.205	4.277
3400	82.473	424.025	353.006	241.462	−1060.053	−246.270	3.783
3500	82.510	426.416	355.070	249.711	−1060.156	−222.335	3.318
3600	82.545	428.741	357.084	257.964	−1060.300	−198.395	2.879
3700	82.576	431.003	359.051	266.220	−1060.489	−174.451	2.463
3800	82.605	433.205	360.974	274.479	−1060.726	−150.500	2.069
3900	82.632	435.351	362.854	282.741	−1061.016	−126.543	1.695
4000	82.657	437.444	364.692	291.006	−1061.363	−102.578	1.340
4100	82.681	439.485	366.492	299.273	−1061.770	−78.604	1.001
4200	82.702	441.478	368.254	307.542	−1062.242	−54.618	0.679
4300	82.722	443.424	369.979	315.813	−1062.784	−30.621	0.372
4400	82.741	445.326	371.670	324.086	−1063.399	−6.610	0.078
4500	82.759	447.186	373.328	332.361	−1064.091	17.415	−0.202
4600	82.775	449.005	374.953	340.638	−1064.864	41.456	−0.471
4700	82.791	450.785	376.548	348.916	−1065.723	65.516	−0.728
4800	82.805	452.528	378.113	357.196	−1066.670	89.595	−0.975
4900	82.819	454.236	379.649	365.477	−1067.710	113.695	−1.212
5000	82.832	455.909	381.157	373.760	−1068.846	137.817	−1.440
5100	82.844	457.550	382.639	382.044	−1070.081	161.962	−1.659
5200	82.855	459.158	384.095	390.329	−1071.418	186.132	−1.870
5300	82.866	460.737	385.526	398.615	−1072.860	210.330	−2.073
5400	82.876	462.286	386.934	406.902	−1074.409	234.555	−2.269
5500	82.886	463.807	388.318	415.190	−1076.066	258.810	−2.458
5600	82.895	465.300	389.679	423.479	−1077.836	283.097	−2.641
5700	82.903	466.767	391.019	431.769	−1079.718	307.415	−2.817
5800	82.912	468.209	392.337	440.060	−1081.715	331.769	−2.988
5900	82.919	469.627	393.635	448.351	−1083.828	356.156	−3.153
6000	82.927	471.020	394.913	456.643	−1086.057	380.582	−3.313

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K) = 64.190 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1833\ K$

$\Delta_f H°(0\ K) = [-2105 \pm 29]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-2117 \pm 29]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The $\Delta_f H°(298.15\ K)$ was estimated from the $\Delta_r H°(298.15\ K)$ of Mg, Ca and Ba oxides with SiO_2 given by Kelley[1] and from the $\Delta_f H°(298.15\ K)$ of BeO(cr) and SiO_2(cr) in the JANAF tables.[2] The $\Delta_r H°(298.15\ K) = 0 \pm 7\ kcal \cdot mol^{-1}$ was estimated for the reaction $2BeO(cr) + SiO_2(cr) \rightarrow Be_2SiO_4(cr)$.

Heat Capacity and Entropy

At low temperatures C_p was used from Kelley.[4] Above 298.15 K, C_p values were estimated by summation of the component oxides using the JANAF tables,[2] BeO and SiO_2. The entropy was calculated at 54.7 K using the Debye and Planck–Einstein functions D(422/T) + 2E(527/T) given by Kelley.[4] The value of $S°(54.7\ K) = 13.59\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The incongruent melting point was taken from Kubaschewski and Evans.[4]

References

[1]K. K. Kelley, U.S. Bur. Mines, RI–5901, 32 pp. (1962).
[2]JANAF Thermochemical Table: BeO(cr), 9–30–63; SiO2(cr), 12–30–62.
[3]K. K. Kelley, J. Am. Chem. Soc., **61**, 1217 (1939).
[4]O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry" 3rd, edition, Pergamon Press., New York, 426 pp. (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.227	−2105.003	−2105.003	INFINITE
100	18.794	7.470	124.264	−11.679	−2110.609	−2076.211	1084.501
200	60.433	33.245	71.847	−7.720	−2114.806	−2040.059	532.809
298.15	95.563	64.190	64.190	0.	−2117.225	−2002.794	350.881
300	96.098	64.782	64.191	0.177	−2117.255	−2002.084	348.594
400	120.750	96.007	68.281	11.090	−2118.090	−1963.528	256.411
500	136.942	124.764	76.748	24.008	−2117.773	−1924.906	201.094
600	149.160	150.850	86.960	38.334	−2116.676	−1886.425	164.228
700	158.866	174.605	97.810	53.757	−2114.993	−1848.175	137.913
800	166.021	196.312	108.786	70.021	−2112.905	−1810.198	118.194
900	170.749	216.154	119.630	86.872	−2110.613	−1772.496	102.873
1000	174.054	234.324	130.204	104.120	−2108.265	−1735.053	90.630
1100	176.356	251.025	140.439	121.644	−2105.957	−1697.844	80.624
1200	178.197	266.451	150.305	139.375	−2103.739	−1660.841	72.295
1300	179.636	280.773	159.797	157.268	−2101.643	−1624.019	65.254
1400	180.916	294.134	168.921	175.298	−2099.687	−1587.353	59.225
1500	181.887	306.649	177.690	193.439	−2097.894	−1550.822	54.004
1600	182.849	318.418	186.121	211.676	−2125.349	−1513.353	49.406
1700	183.803	329.532	194.233	230.008	−2173.281	−1474.725	45.313
1800	184.749	340.065	202.045	248.436	−2170.844	−1433.704	41.605
1900	185.686	350.079	209.575	266.958	−2168.403	−1392.819	38.291
2000	186.606	359.627	216.841	285.572	−2165.958	−1352.061	35.312
2100	187.493	368.753	223.859	304.277	−2163.512	−1311.427	32.620
2200	188.380	377.496	230.645	323.071	−2161.066	−1270.907	30.175
2300	189.267	385.889	237.213	341.954	−2158.618	−1230.501	27.946
2400	190.154	393.963	243.578	360.925	−2156.170	−1190.202	25.904
2500	191.041	401.743	249.750	379.984	−2153.720	−1150.003	24.028
2600	191.928	409.253	255.741	399.133	−2151.267	−1109.903	22.298
2700	192.815	416.513	261.562	418.370	−2148.810	−1069.896	20.698
2800	193.702	423.542	267.222	437.696	−2728.262	−1017.536	18.982
2900	194.589	430.354	272.730	457.111	−2723.668	−956.521	17.229
3000	195.476	436.966	278.095	476.614	−2719.034	−895.663	15.595

PREVIOUS: September 1961 CURRENT: June 1965

$S°(298.15\ K) = 34.129\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2473$ K

$\Delta_f H°(0\ K) = -580.9 \pm 1.3$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = -588.3 \pm 1.3$ kJ·mol^{-1}
$\Delta_{fus} H° = [129.3]$ kJ·mol^{-1}

Enthalpy of Formation

Gross, Hayman, Greene and Bingham[1] have measured the enthalpy of Chlorination of α–Be_3N_2 to α–$BeCl_2$, and the enthalpy of reaction of Be with ammonia. The chlorination reaction (A) α–Be_3N_2(cr) + 3Cl_2(g) → 3 α–$BeCl_2$(cr) + N_2(g) had a $\Delta_f H°(298.15\ K) = -210.3 \pm 0.4$ kcal·mol^{-1} which, combined with the value of $-117.1 + 0.4$ kcal·mol^{-1} for α–$BeCl_2$ reported in the same paper, yields $\Delta_f H°$(α–Be_3N_2, cr, 298.15 K) = -141.0 ± 1.6 kcal·mol^{-1}. Reaction (B) 3Be(cr) + 2 NH_3(g) → α–Be_3N_2(cr) + 3 H_2(g) had a $\Delta_f H°(298.15\ K) = -214.6 \pm 0.3$ kcal·mol^{-1}, which, combined with the JANAF[2] value for NH_3(g), yields $\Delta_f H°$(α–Be_3N_2, cr, 298.15 K) = -140.3 ± 0.3 kcal·mol^{-1}. A weighted mean value of the above two determinations is adopted.

The decomposition Be_3N_2(cr) = 3 Be(g) + N_2(g) has been studied by Yates, Greenbaum and Farber[3] using the torsion effusion technique. The same decomposition has also been investigated by Hoenig[4] using the Knudsen technique. An analysis of these data sets by 2nd and 3rd law methods is given below.

Source	T/K	Points	$\Delta_f H°$(298.15 K) 2nd law kcal·mol^{-1}	3rd law kcal·mol^{-1}	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[3]–1	1478–1592	9*	364.5 ± 5.9	374.00	6.0 ± 3.8	−139.23
[3]–2	1541–1652	15*	369.6 ± 8.3	376.51	4.0 ± 5.3	−141.74
[3]–3	1438–1661	14	347.7 ± 3.7	374.54	16.9 ± 2.4	−139.77
[3]–4	1450–1646	17*	366.7 ± 8.9	375.28	4.8 ± 5.7	−140.51
[3]	1473–1661	52*	358.9 ± 5.1	375.41	10.3 ± 3.3	−140.64
[4]–1	1767–1946	14	355.8 ± 3.3	377.77	11.9 ± 1.8	−143.00
[4]–2	1660–1891	10	395.0 ± 5.6	378.69	−9.1 ± 3.1	−143.92
[4]–3	1648–1893	10	416.9 ± 8.4	383.15	−19.5 ± 4.6	−148.38

*Points rejected due to failure of statistical test.
The data of Yates *et al.* [3] are seen to be in good agreement with the adopted $\Delta_f H°$(298.15 K).

Heat Capacity and Entropy

The low temperature heat capacity of α–Be_3N_2 has been measured, 25–310 K, by Justice.[5] These measurements are joined smoothly with the high temperature enthalpies reported by Douglas and Payne.[6] Above 1200 K the values were smoothly extrapolated to a limiting value of 6.2 cal·K^{-1} g–atom^{-1}. The entropy at 298.15 K was calculated by integration of the low temperature data based on $S°(25\ K) = 0.002$ cal·K^{-1}·mol^{-1}.

Fusion Data

Refer to the liquid table for details.

References

[1]P. Gross, C. Hayman, P. D. Greene and J. T. Bingham, Trans. Faraday Soc. **62**, 2719 (1966).
[2]JANAF Thermochemical Tables: NH_3(g), 9–30–65.
[3]R. E. Yates, M. A. Greenbaum and M. Farber, J. Phys. Chem. **68**, 2682 (1964).
[4]C. L. Hoenig, UCRL–7521, (April 1964).
[5]B. H. Justice, The Dow Chemical Co., 1st. Quarterly Report under contract AFO4611–67–C–0009, (April 1967).
[6]T. B. Douglas and W. H. Payne, U. S. Nat. Bur. Stand. Report 7587, (July 1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S° - [G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−7.075	−580.879	−580.879	INFINITE
100	6.109	1.845	71.174	−6.933	−583.756	−567.809	296.593
200	35.489	14.313	39.125	−4.962	−586.429	−550.790	143.852
298.15	64.358	34.129	34.129	0.	−588.270	−532.874	93.357
300	64.668	34.528	34.130	0.119	−588.296	−532.530	92.722
400	84.433	56.036	36.928	7.643	−589.216	−513.778	67.092
500	97.512	76.374	42.811	16.782	−589.325	−494.891	51.701
600	106.516	94.995	49.981	27.009	−588.882	−476.039	41.443
700	112.922	111.922	57.640	37.998	−588.110	−457.290	34.123
800	117.591	127.321	65.402	49.535	−587.172	−438.664	28.642
900	121.043	141.381	73.075	61.475	−586.186	−420.159	24.385
1000	123.612	154.273	80.559	73.714	−585.237	−401.763	20.986
1100	125.520	166.148	87.807	86.174	−584.387	−383.458	18.209
1200	126.922	177.132	94.799	98.800	−583.685	−365.224	15.898
1300	127.926	187.333	101.530	111.545	−583.169	−347.041	13.944
1400	128.616	196.840	108.002	124.374	−582.871	−328.890	12.271
1500	129.047	205.730	114.224	137.259	−582.816	−310.752	10.821
1600	129.269	214.066	120.206	150.176	−626.634	−291.033	9.501
1700	129.319	221.905	125.960	163.106	−625.924	−270.080	8.299
1800	129.366	229.298	131.498	176.040	−625.298	−249.166	7.231
1900	129.411	236.293	136.831	188.979	−624.753	−228.285	6.276
2000	129.452	242.932	141.971	201.922	−624.286	−207.431	5.418
2100	129.490	249.249	146.931	214.869	−623.896	−186.598	4.641
2200	129.526	255.274	151.720	227.820	−623.582	−165.782	3.936
2300	129.559	261.032	156.348	240.774	−623.343	−144.978	3.293
2400	129.588	266.547	160.826	253.731	−623.176	−124.184	2.703
2473.000	129.606	270.430	164.004	263.192	--- CRYSTAL <---> LIQUID ---		
2500	129.615	271.838	165.161	266.692	−623.083	−103.395	2.160
2600	129.639	276.922	169.362	279.654	−623.062	−82.608	1.660
2700	129.659	281.815	173.437	292.619	−623.112	−61.820	1.196
2800	129.677	286.530	177.393	305.586	−1496.105	−22.362	0.417
2900	129.692	291.081	181.235	318.555	−1493.106	30.219	−0.544
3000	129.704	295.478	184.970	331.524	−1490.129	82.696	−1.440

PREVIOUS: September 1964 CURRENT: March 1967

$S°(298.15\ K) = [39.457]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2473\ K$

$\Delta_f H°(298.15\ K) = [-486.979]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [129.3]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Be_3N_2(l) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2473\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated to be constant and slightly greater than the maximum for Be_3N_2(cr). The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point was reported by Fichter and Brunner.[1] The enthalpy of melting is calculated on the assumption that each g–atom contributed 2.5 $cal·K^{-1}·mol^{-1}$ to $\Delta_{fus}S°$.

References

[1] F. Fichter and E. Brunner, Z. anorg. allgem. Chem. **93**, 84 (1915).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	133.888	39.457	39.457	0.	−486.979	−433.172	75.890
300	133.888	40.285	39.459	0.248	−486.877	−432.838	75.364
400	133.888	78.802	44.711	13.636	−481.931	−415.600	54.272
500	133.888	108.678	54.628	27.025	−477.790	−399.509	41.736
600	133.888	133.089	65.732	40.414	−474.185	−384.199	33.447
700	133.888	153.728	76.867	53.803	−471.014	−369.457	27.569
800	133.888	171.606	87.617	67.192	−468.225	−355.144	23.189
900	133.888	187.376	97.842	80.580	−465.790	−341.159	19.800
1000	133.888	201.482	107.513	93.969	−463.691	−327.426	17.103
1100	133.888	214.243	116.645	107.358	−461.913	−313.889	14.905
1200	133.888	225.893	125.271	120.747	−460.447	−300.499	13.080
1300	133.888	236.610	133.429	134.136	−459.287	−287.219	11.541
1400	133.888	246.532	141.157	147.524	−458.429	−274.017	10.224
1500	133.888	255.769	148.494	160.913	−457.870	−260.866	9.084
1600	133.888	264.410	155.471	174.302	−501.217	−246.166	8.036
1700	133.888	272.527	162.121	187.691	−500.048	−230.261	7.075
1800	133.888	280.180	168.469	201.080	−498.967	−214.423	6.222
1900	133.888	287.419	174.541	214.468	−497.972	−198.643	5.461
2000	133.888	294.287	180.358	227.857	−497.060	−182.913	4.777
2100	133.888	300.819	185.940	241.246	−496.228	−167.226	4.160
2200	133.888	307.047	191.304	254.635	−495.476	−151.577	3.599
2300	133.888	312.999	196.467	268.024	−494.802	−135.961	3.088
2400	133.888	318.697	201.442	281.412	−494.204	−120.372	2.620
2473.000	133.888	322.709	204.963	291.186	--- CRYSTAL <--> LIQUID ---		
2500	133.888	324.163	206.242	294.801	−493.682	−104.807	2.190
2600	133.888	329.414	210.879	308.190	−493.235	−89.261	1.793
2700	133.888	334.467	215.364	321.579	−492.861	−73.731	1.426
2800	133.888	339.336	219.705	334.968	−1365.432	−39.545	0.738
2900	133.888	344.034	223.911	348.356	−1362.013	7.747	−0.140
3000	133.888	348.573	227.992	361.745	−1358.617	54.923	−0.956
3100	133.888	352.964	231.953	375.134	−1355.246	101.985	−1.718
3200	133.888	357.214	235.801	388.523	−1351.905	148.939	−2.431
3300	133.888	361.334	239.543	401.912	−1348.597	195.789	−3.099
3400	133.888	365.331	243.184	415.300	−1345.327	242.539	−3.726
3500	133.888	369.212	246.730	428.689	−1342.101	289.194	−4.316
3600	133.888	372.984	250.185	442.078	−1338.923	335.758	−4.872
3700	133.888	376.652	253.553	455.467	−1335.801	382.234	−5.396
3800	133.888	380.223	256.840	468.856	−1332.738	428.626	−5.892
3900	133.888	383.701	260.048	482.244	−1329.743	474.938	−6.361
4000	133.888	387.091	263.182	495.633	−1326.820	521.175	−6.806

PREVIOUS: September 1964 CURRENT: March 1967

0	to	2473 K	crystal, alpha
above		2473 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K *Standard State Pressure = $p°$ = 0.1 MPa*

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.075	−580.879	−580.879	INFINITE
100	6.109	1.845	71.174	−6.933	−583.756	−567.809	296.593
200	35.489	14.313	39.125	−4.962	−586.429	−550.790	143.852
298.15	64.358	34.129	34.129	0.	−588.270	−532.874	93.357
300	64.668	34.528	34.130	0.119	−588.296	−532.530	92.722
400	84.433	56.036	36.928	7.643	−589.216	−513.778	67.092
500	97.512	76.374	42.811	16.782	−589.325	−494.891	51.701
600	106.516	94.995	49.981	27.009	−588.882	−476.039	41.443
700	112.922	111.922	57.640	37.998	−588.110	−457.290	34.123
800	117.591	127.321	65.402	49.535	−587.172	−438.664	28.642
900	121.043	141.381	73.075	61.475	−586.186	−420.159	24.385
1000	123.612	154.273	80.559	73.714	−585.237	−401.763	20.986
1100	125.520	166.148	87.807	86.174	−584.387	−383.458	18.209
1200	126.922	177.132	94.799	98.800	−583.685	−365.224	15.898
1300	127.926	187.333	101.530	111.545	−583.169	−347.041	13.944
1400	128.616	196.840	108.002	124.374	−582.871	−328.890	12.271
1500	129.047	205.730	114.224	137.259	−582.816	−310.752	10.821
1600	129.269	214.066	120.206	150.176	−626.634	−291.033	9.501
1700	129.319	221.905	125.960	163.106	−625.924	−270.080	8.299
1800	129.366	229.298	131.498	176.040	−625.298	−249.166	7.231
1900	129.411	236.293	136.831	188.979	−624.753	−228.285	6.276
2000	129.452	242.932	141.971	201.922	−624.286	−207.431	5.418
2100	129.490	249.249	146.931	214.869	−623.896	−186.598	4.641
2200	129.525	255.274	151.720	227.820	−623.582	−165.782	3.936
2300	129.558	261.032	156.348	240.774	−623.343	−144.978	3.293
2400	129.587	266.547	160.826	253.731	−623.177	−124.184	2.703
2473.000	129.606	270.430	164.004	263.192	CRYSTAL <--> LIQUID TRANSITION		
2473.000	133 .888	322.709	164.004	392.477			
2500	133.888	324.163	165.726	396.092	−493.682	−104.807	2.190
2600	133.888	329.414	171.921	409.481	−493.235	−89.261	1.793
2700	133.888	334.467	177.848	422.870	−492.861	−73.731	1.426
2800	133.888	339.336	183.529	436.259	−1365.432	−39.545	0.738
2900	133.888	344.034	188.984	449.647	−1362.013	7.747	−0.140
3000	133.888	348.573	194.228	463.036	−1358.617	54.923	−0.956
3100	133.888	352.964	199.278	476.425	−1355.246	101.985	−1.718
3200	133.888	357.214	204.148	489.814	−1351.905	148.939	−2.431
3300	133.888	361.334	208.849	503.203	−1348.597	195.789	−3.099
3400	133.888	365.331	213.393	516.591	−1345.327	242.539	−3.726
3500	133.888	369.212	217.789	529.980	−1342.101	289.194	−4.316
3600	133.888	372.984	222.048	543.369	−1338.923	335.758	−4.872
3700	133.888	376.653	226.177	556.758	−1335.801	382.233	−5.396
3800	133.888	380.223	230.184	570.147	−1332.738	428.626	−5.892
3900	133.888	383.701	234.076	583.535	−1329.743	474.938	−6.361
4000	133.888	387.091	237.860	596.924	−1326.820	521.175	−6.806

PREVIOUS: CURRENT: March 1967

$S°(298.15\ K) = [273.3]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1049 \pm 38\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1054 \pm 38\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[730] (1)	[1380] (2)
[990] (1)	[1450] (2)
[1480] (1)	[610] (2)
[1100] (1)	[320] (2)

Ground State Quantum Weight: [1] $\sigma = [6]$

Point Group: $[D_{3h}]$

Bond Distance: Be–O = [1.63] Å

Bond Angles: Be–O–Be = [120]°; O–Be–O [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [9.0703 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

Chupka, Berkowitz, and Giese[1] measured the change in the intensity of the $(BeO)_3^+$ ion with temperature and obtained a 2nd law enthalpy of vaporization of 161 ± 6 kcal·mol^{-1} at 2150 K. The uncertainty is large because of an approximate correction of 8 kcal·mol^{-1} and the neglect of fragmentation effects. We adopted an enthalpy of sublimation at 2150 K of 163 kcal·mol^{-1} in order to bring the equilibrium vapor pressure into agreement with that measured by Chupka *et al.*[1]

Heat Capacity and Entropy

The assumed D_{3h} symmetry implies eight vibrational frequencies of the types $2A_1'$, A_2', A_2'', $3E'$ and E_2''. The frequencies were estimated by comparison with the values for the $B_3O_3(O^-)_3$ skeleton as given by Parsons[2] and the partial assignment of boroxine by Gupta and Porter.[3] The bond length was taken as that in $Be_2O_2(g)$, while the bond angle was arbitrarily taken as 120°. The principal moments of inertia are: $I_A = I_B = 16.5525 \times 10^{-39}$, and $I_C = 33.1050 \times 10^{-39}\ g·cm^2$.

References

[1] W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. **30**, 827 (1959).

[2] J. L. Parsons, J. Chem. Phys. **33**, 1860 (1960).

[3] S. K. Gupta and R. F. Porter, J. Phys. Chem. **67**, 1286 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.325	−1048.871	−1048.871	INFINITE
100	37.082	221.244	320.437	−9.919	−1049.940	−1045.917	546.331
200	50.124	250.834	278.710	−5.575	−1051.695	−1041.313	271.963
250	56.935	262.750	274.345	−2.899	−1052.982	−1038.572	216.998
298.15	63.458	273.337	273.337	0.	−1054.368	−1035.673	181.446
300	63.706	273.731	273.339	0.118	−1054.423	−1035.557	180.306
350	70.315	284.051	274.139	3.469	−1055.921	−1032.294	154.061
400	76.597	293.854	275.995	7.144	−1057.380	−1028.818	134.350
450	82.418	303.217	278.504	11.121	−1058.758	−1025.165	118.998
500	87.701	312.179	281.426	15.376	−1060.043	−1021.362	106.701
600	96.611	328.989	287.973	24.610	−1062.350	−1013.404	88.225
700	103.530	344.425	294.950	34.632	−1064.384	−1005.082	75.000
800	108.857	358.612	302.034	45.263	−1066.249	−996.482	65.064
900	112.975	371.682	309.056	56.363	−1068.035	−987.653	57.322
1000	116.187	383.758	315.930	67.828	−1069.812	−978.627	51.118
1100	118.723	394.955	322.612	79.578	−1071.639	−969.420	46.034
1200	120.750	405.376	329.079	91.556	−1073.559	−960.044	41.790
1300	122.389	415.108	335.327	103.715	−1075.609	−950.502	38.192
1400	123.730	424.229	341.355	116.024	−1077.818	−940.797	35.102
1500	124.840	432.804	347.168	128.454	−1080.212	−930.927	32.418
1600	125.766	440.892	352.776	140.985	−1126.417	−919.315	30.013
1700	126.547	448.540	358.186	153.602	−1128.033	−906.321	27.848
1800	127.210	455.793	363.409	166.291	−1129.677	−893.233	25.921
1900	127.778	462.686	368.454	179.041	−1131.359	−880.051	24.194
2000	128.268	469.253	373.331	191.844	−1133.088	−866.780	22.638
2100	128.694	475.522	378.049	204.692	−1134.870	−853.421	21.228
2200	129.065	481.517	382.617	217.581	−1136.711	−839.974	19.944
2300	129.391	487.262	387.043	230.504	−1138.615	−826.445	18.769
2400	129.679	492.775	391.334	243.458	−1140.587	−812.830	17.691
2500	129.935	498.074	395.499	256.439	−1142.629	−799.132	16.697
2600	130.162	503.175	399.542	269.444	−1144.743	−785.351	15.778
2700	130.366	508.091	403.472	282.470	−1146.932	−771.486	14.925
2800	130.549	512.835	407.294	295.516	−2022.067	−738.872	13.784
2900	130.713	517.419	411.013	308.579	−2021.218	−693.059	12.483
3000	130.862	521.853	414.634	321.658	−2020.398	−647.274	11.270
3100	130.997	526.147	418.162	334.751	−2019.610	−601.516	10.135
3200	131.120	530.307	421.602	347.857	−2018.860	−555.784	9.072
3300	131.232	534.344	424.958	360.975	−2018.151	−510.075	8.074
3400	131.335	538.263	428.233	374.104	−2017.489	−464.384	7.134
3500	131.429	542.072	431.431	387.242	−2016.879	−418.715	6.249
3600	131.516	545.775	434.556	400.389	−2016.327	−373.060	5.413
3700	131.595	549.380	437.611	413.545	−2015.839	−327.422	4.622
3800	131.669	552.890	440.599	426.708	−2015.420	−281.793	3.874
3900	131.737	556.311	443.522	439.878	−2015.078	−236.176	3.163
4000	131.800	559.647	446.384	453.055	−2014.817	−190.567	2.489
4100	131.859	562.903	449.186	466.238	−2014.646	−144.963	1.847
4200	131.914	566.081	451.932	479.427	−2014.569	−99.362	1.236
4300	131.964	569.185	454.622	492.621	−2014.594	−53.761	0.653
4400	132.012	572.220	457.261	505.820	−2014.728	−8.160	0.097
4500	132.056	575.187	459.848	519.023	−2014.975	37.446	−0.435
4600	132.098	578.090	462.388	532.231	−2015.342	83.058	−0.943
4700	132.137	580.931	464.880	545.443	−2015.836	128.682	−1.430
4800	132.173	583.714	467.326	558.658	−2016.461	174.316	−1.897
4900	132.208	586.439	469.730	571.877	−2017.224	219.966	−2.345
5000	132.240	589.111	472.091	585.100	−2018.130	265.632	−2.775
5100	132.271	591.730	474.411	598.325	−2019.182	311.318	−3.189
5200	132.299	594.298	476.692	611.554	−2020.387	357.023	−3.586
5300	132.326	596.819	478.935	624.785	−2021.747	402.757	−3.969
5400	132.352	599.292	481.141	638.019	−2023.266	448.516	−4.339
5500	132.376	601.721	483.311	651.255	−2024.949	494.304	−4.695
5600	132.399	604.106	485.447	664.494	−2026.798	540.126	−5.038
5700	132.421	606.450	487.549	677.735	−2028.815	585.981	−5.370
5800	132.442	608.753	489.619	690.978	−2031.003	631.875	−5.691
5900	132.462	611.017	491.658	704.224	−2033.364	677.804	−6.001
6000	132.480	613.244	493.665	717.471	−2035.900	723.779	−6.301

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K)$ = [302.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1581 \pm 50\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1590 \pm 50\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[700] (1)	[200] (2)
[850] (1)	[900] (1)
[1400] (1)	[400] (1)
[1000] (1)	[500] (1)
[800] (1)	[1150] (2)
[1000] (1)	[1200] (2)
[800] (1)	[600] (2)

Ground State Quantum Weight: [1] σ = [8]
Point Group: [D_{4h}]
Bond Distance: Be–O = [1.63] Å
Bond Angles: Be–O–Be = [115]°; O–Be–O = [155]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.1171 × 10^{-112}] $g^3\ cm^6$

Enthalpy of Formation

Chupka, Berkowitz, and Giese[1] measured the variation of intensity of the $(BeO)_4^+$ ion with temperature in a mass spectrometer. They reported a 2nd law enthalpy of vaporization of 177 ± 8 $kcal·mol^{-1}$ at 2150 K, which included an approximate correction of 9 $kcal·mol^{-1}$, and this value was adopted here.

Heat Capacity and Entropy

The assumed D_{4h} structure has 14 vibrational frequencies of the type $2A_{1g}$, A_{2g}, $2B_{2g}$, E_g, A_{2u}, B_{2u}, B_{1u}, and $3E_u$. The frequencies were estimated by comparison with $(BeO)_3$ and cyclobutane from Rathjens, Freeman, Gwinn, and Pitzer.[2] The estimated structure and frequencies gave an entropy which was in excellent agreement with the experimental enthalpy and equilibrium constant determined by Chupka *et al.*[1]

The bond lengths were taken equal to those in $Be_2O_2(g)$ and the angles were chosen so that O–Be–O was almost linear. The principal moments of inertia are: $I_A = I_B = 38.2258 \times 10^{-39}$, and $I_C = 76.4515 \times 10^{-39}$ $g·cm^2$.

References

[1]W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. **30**, 827 (1959).
[2]G. W. Rathjens, N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, J. Am. Chem. Soc. **75**, 5634 (1953).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−16.529	−1581.354	−1581.354	INFINITE
100	43.449	235.990	364.943	−12.895	−1583.686	−1572.422	821.349
200	64.574	272.167	309.947	−7.556	−1586.479	−1560.180	407.477
250	77.225	287.926	303.979	−4.013	−1588.220	−1553.405	324.566
298.15	89.389	302.575	302.575	.000	−1589.920	−1546.545	270.948
300	89.844	303.129	302.577	.166	−1589.985	−1546.276	269.231
350	101.591	317.876	303.714	4.956	−1591.659	−1538.857	229.662
400	112.062	332.140	306.381	10.303	−1593.157	−1531.209	199.955
450	121.155	345.877	310.012	16.140	−1594.463	−1523.385	176.830
500	128.942	359.056	314.262	22.397	−1595.592	−1515.425	158.315
600	141.187	383.708	323.813	35.937	−1597.439	−1499.211	130.518
700	150.034	406.173	333.999	50.522	−1598.930	−1482.718	110.642
800	156.507	426.652	344.320	65.865	−1600.247	−1466.026	95.722
900	161.327	445.377	354.524	81.768	−1601.525	−1449.171	84.108
1000	164.987	462.573	364.481	98.092	−1602.858	−1432.173	74.809
1100	167.817	478.436	374.129	114.738	−1604.314	−1415.034	67.194
1200	170.043	493.137	383.441	131.635	−1605.947	−1397.757	60.843
1300	171.821	506.821	392.412	148.732	−1607.797	−1380.334	55.463
1400	173.262	519.608	401.045	165.988	−1609.897	−1362.760	50.845
1500	174.443	531.604	409.354	183.375	−1612.275	−1345.026	46.838
1600	175.423	542.894	417.350	200.870	−1673.096	−1325.021	43.258
1700	176.245	553.555	425.052	218.455	−1674.488	−1303.224	40.043
1800	176.940	563.649	432.474	236.115	−1675.938	−1281.344	37.184
1900	177.533	573.232	439.632	253.839	−1677.457	−1259.381	34.623
2000	178.043	582.351	446.542	271.619	−1679.053	−1237.336	32.316
2100	178.484	591.049	453.218	289.446	−1680.734	−1215.209	30.227
2200	178.869	599.361	459.673	307.314	−1682.505	−1192.999	28.325
2300	179.205	607.320	465.921	325.218	−1684.371	−1170.708	26.588
2400	179.502	614.953	471.972	343.154	−1686.335	−1148.334	24.993
2500	179.765	622.286	477.839	361.117	−1688.402	−1125.875	23.524
2600	179.998	629.341	483.531	379.106	−1690.573	−1103.332	22.166
2700	180.207	636.138	489.058	397.116	−1692.849	−1080.702	20.907
2800	180.394	642.696	494.429	415.146	−2859.061	−1033.096	19.273
2900	180.563	649.029	499.652	433.194	−2857.299	−967.916	17.434
3000	180.715	655.153	504.733	451.258	−2855.580	−902.793	15.719
3100	180.853	661.081	509.682	469.337	−2853.908	−837.727	14.116
3200	180.979	666.825	514.503	487.429	−2852.290	−772.716	12.613
3300	181.093	672.395	519.204	505.532	−2850.731	−707.755	11.203
3400	181.198	677.803	523.789	523.647	−2849.238	−642.837	9.876
3500	181.294	683.057	528.265	541.772	−2847.819	−577.965	8.626
3600	181.382	688.166	532.636	559.905	−2846.479	−513.131	7.445
3700	181.463	693.136	536.907	578.048	−2845.226	−448.334	6.329
3800	181.538	697.977	541.083	596.198	−2844.069	−383.567	5.272
3900	181.607	702.693	545.166	614.355	−2843.015	−318.830	4.270
4000	181.671	707.292	549.162	632.519	−2842.074	−254.121	3.318
4100	181.731	711.779	553.074	650.689	−2841.252	−189.432	2.413
4200	181.787	716.158	556.905	668.865	−2840.559	−124.763	1.552
4300	181.838	720.437	560.658	687.047	−2840.003	−60.107	.730
4400	181.886	724.618	564.337	705.233	−2839.593	4.536	−.054
4500	181.931	728.706	567.945	723.424	−2839.336	69.171	−.803
4600	181.974	732.705	571.483	741.619	−2839.241	133.803	−1.519
4700	182.013	736.619	574.955	759.818	−2839.316	198.435	−2.205
4800	182.050	740.451	578.363	778.021	−2839.567	263.071	−2.863
4900	182.085	744.205	581.710	796.228	−2840.003	327.715	−3.493
5000	182.118	747.884	584.996	814.438	−2840.630	392.368	−4.099
5100	182.149	751.491	588.226	832.652	−2841.454	457.036	−4.681
5200	182.178	755.028	591.400	850.868	−2842.482	521.720	−5.241
5300	182.205	758.499	594.520	869.087	−2843.717	586.430	−5.780
5400	182.231	761.905	597.588	887.309	−2845.167	651.162	−6.299
5500	182.256	765.249	600.606	905.533	−2846.835	715.922	−6.799
5600	182.279	768.533	603.576	923.760	−2848.725	780.718	−7.282
5700	182.301	771.759	606.498	941.989	−2850.841	845.547	−7.749
5800	182.322	774.930	609.375	960.220	−2853.185	910.418	−8.199
5900	182.342	778.047	612.207	978.454	−2855.760	975.326	−8.635
6000	182.361	781.112	614.997	996.689	−2858.569	1040.285	−9.056

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K)$ = [323.28] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2101 \pm 75\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -2113 \pm 75\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[700] (1)	[1200] (2)
[850] (1)	[600] (2)
[1400] (1)	[500] (2)
[1100] (2)	[900] (1)
[900] (2)	[200] (2)
[1000] (2)	[400] (2)
[1200] (2)	[500] (2)

Ground State Quantum Weight: [1] σ = [10]
Point Group: [D_{5h}]
Bond Distance: Be–O = [1.63] Å
Bond Angles: Be–O–Be = [110]°: O–Be–O = [178]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [6.9690 X 10^{-112}] $g^3\ cm^6$

Enthalpy of Formation

Chupka, Berkowitz, and Giese[1] measured the variation in intensity of the $(BeO)_5^+$ ion with temperature in a mass spectrometer. They calculated a 2nd law enthalpy of vaporization of 193 ± 12 $kcal·mol^{-1}$ at 2150 K; the uncertainty reflects the inclusion of an approximate correction of 10 $kcal·mol^{-1}$. This value was adopted here.

Heat Capacity and Entropy

The assumed D_{5h} structure has 14 vibrations of the type $2A_1'$, A_2'', $3E_1'$, $4E_2'$, A_2'', E_1'', and $2E_2$''. These were estimated by comparison with similar motions in other ring structures including $(BeO)_3$ and $(BeO)_4$. The estimated structure and frequencies gave an entropy in good agreement with the experimental enthalpy and equilibrium constant determined by Chupka *et al.*[1]

The bond length was assumed to be the same as in Be_2O_2(g) and the angles were chosen so as to make O–Be–O almost linear. The principal moments of inertia are: $I_A = I_B = 70.3689 \times 10^{-39}$, and $I_C = 140.7378 \times 10^{-39}$ $g·cm^2$.

References

[1]W. A. Chupka, J. Berkowitz, and C. F. Giese, J. Chem. Phys. **30**, 827 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.090	−2100.640	−2100.640	INFINITE
100	45.283	244.859	399.133	−15.427	−2104.435	−2085.343	1089.271
200	77.909	285.714	332.441	−9.345	−2108.519	−2064.746	539.256
250	95.670	305.013	325.031	−5.005	−2110.783	−2053.541	429.064
298.15	112.018	323.278	323.278	0.	−2112.920	−2042.321	357.806
300	112.622	323.973	323.280	0.208	−2113.000	−2041.883	355.523
350	128.074	342.516	324.709	6.232	−2115.057	−2029.864	302.941
400	141.704	360.528	328.067	12.985	−2116.862	−2017.567	263.467
450	153.478	377.916	332.646	20.372	−2118.401	−2005.060	232.741
500	163.529	394.621	338.014	28.304	−2119.703	−1992.395	208.144
600	179.296	425.909	350.095	45.488	−2121.752	−1966.731	171.219
700	190.665	454.448	362.996	64.017	−2123.317	−1940.765	144.822
800	198.973	480.478	376.079	83.520	−2124.641	−1914.595	125.010
900	205.156	504.288	389.021	103.741	−2125.896	−1888.263	109.592
1000	209.847	526.157	401.656	124.501	−2127.206	−1861.791	97.250
1100	213.474	546.335	413.903	145.675	−2128.660	−1835.180	87.145
1200	216.326	565.037	425.728	167.170	−2130.328	−1808.428	78.719
1300	218.603	582.445	437.121	188.921	−2132.260	−1781.527	71.583
1400	220.447	598.715	448.089	210.877	−2134.500	−1754.465	65.460
1500	221.960	613.978	458.645	232.999	−2137.083	−1727.232	60.148
1600	223.215	628.344	468.807	255.260	−2212.718	−1697.186	55.407
1700	224.267	641.909	478.594	277.636	−2214.062	−1664.925	51.157
1800	225.157	654.754	488.027	300.108	−2215.478	−1632.583	47.376
1900	225.916	666.948	497.126	322.663	−2216.978	−1600.159	43.991
2000	226.568	678.553	505.909	345.288	−2218.572	−1567.654	40.943
2100	227.132	689.621	514.396	367.973	−2220.271	−1535.067	38.183
2200	227.624	700.199	522.603	390.712	−2222.081	−1502.394	35.671
2300	228.055	710.327	530.546	413.496	−2224.009	−1469.640	33.377
2400	228.435	720.041	538.241	436.321	−2226.060	−1436.798	31.271
2500	228.771	729.373	545.701	459.182	−2228.237	−1403.868	29.332
2600	229.070	738.352	552.939	482.074	−2230.544	−1370.848	27.541
2700	229.337	747.002	559.967	504.995	−2232.982	−1337.736	25.880
2800	229.577	755.347	566.797	527.941	−3690.339	−1273.419	23.756
2900	229.792	763.407	573.438	550.909	−3687.727	−1187.149	21.383
3000	229.987	771.201	579.901	573.898	−3685.169	−1100.965	19.169
3100	230.164	778.745	586.194	596.906	−3682.670	−1014.865	17.100
3200	230.324	786.055	592.326	619.931	−3680.238	−928.847	15.162
3300	230.471	793.145	598.305	642.971	−3677.879	−842.904	13.342
3400	230.605	800.027	604.137	666.024	−3675.602	−757.028	11.630
3500	230.727	806.713	609.830	689.091	−3673.417	−671.221	10.017
3600	230.840	813.215	615.390	712.170	−3671.330	−585.473	8.495
3700	230.944	819.541	620.822	735.259	−3669.353	−499.784	7.056
3800	231.040	825.701	626.133	758.358	−3667.496	−414.142	5.693
3900	231.128	831.704	631.328	781.466	−3665.767	−328.550	4.400
4000	231.210	837.556	636.410	804.583	−3664.178	−243.002	3.173
4100	231.287	843.266	641.386	827.708	−3662.738	−157.491	2.006
4200	231.357	848.841	646.260	850.841	−3661.460	−72.013	0.896
4300	231.424	854.285	651.034	873.980	−3660.353	13.438	−0.163
4400	231.485	859.606	655.714	897.125	−3659.427	98.862	−1.174
4500	231.543	864.809	660.303	920.277	−3658.693	184.268	−2.139
4600	231.597	869.899	664.805	943.434	−3658.162	269.660	−3.062
4700	231.647	874.880	669.222	966.596	−3657.842	355.045	−3.946
4800	231.695	879.758	673.557	989.763	−3657.743	440.424	−4.793
4900	231.739	884.536	677.814	1012.935	−3657.875	525.805	−5.605
5000	231.781	889.218	681.996	1036.111	−3658.245	611.190	−6.385
5100	231.821	893.808	686.104	1059.291	−3658.862	696.585	−7.134
5200	231.858	898.310	690.142	1082.475	−3659.732	781.991	−7.855
5300	231.893	902.727	694.111	1105.662	−3660.864	867.422	−8.549
5400	231.926	907.062	698.015	1128.853	−3662.262	952.872	−9.217
5500	231.958	911.317	701.854	1152.048	−3663.933	1038.351	−9.861
5600	231.988	915.497	705.632	1175.245	−3665.882	1123.867	−10.483
5700	232.016	919.604	709.350	1198.445	−3668.112	1209.416	−11.083
5800	232.043	923.639	713.010	1221.648	−3670.628	1295.011	−11.663
5900	232.068	927.606	716.614	1244.854	−3673.433	1380.645	−12.223
6000	232.093	931.506	720.163	1268.062	−3676.530	1466.335	−12.766

PREVIOUS: September1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K)$ = [343.2] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2645 \pm 92\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ $-2661 \pm 92\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies			
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[700] (1)	[600] (2)	[900] (1)	[1100] (2)
[850] (1)	[750] (2)	[1100] (1)	[1200] (2)
[400] (1)	[850] (2)	[1000] (1)	[500] (2)
[500] (1)	[850] (2)	[800] (1)	[200] (2)
[400] (1)	[950] (2)	[1400] (1)	[250] (2)

Ground State Quantum Weight: [1] σ = [12]
Point Group: [D_{6h}]
Bond Distance: Be–O = [1.63] Å
Bond Angles: Be–O–Be = [110]°; O–Be–O = [190]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.1282 X 10^{-111}] $g^3\ cm^6$

Enthalpy of Formation

Chupka, Berkowitz, and Giese[1] measured the temperature dependence of the $(BeO)_6^+$ ion in a mass spectrometer. They calculated a 2nd law enthalpy of vaporizaion of 203 ± 15 $kcal \cdot mol^{-1}$ which was adopted here. The uncertainty reflects in part an approximate correction of 10 $kcal \cdot mol^{-1}$ and the small observed intensities.

Heat Capacity and Entropy

The assumed symmetry D_{6h} has 20 vibrational frequencies of the type $2A_{1g}$, A_{2g}, B_{1g}, B_{2g}, E_{1g}, $4E_{2g}$, A_{2u}, $2B_{1u}$, $2B_{2u}$, $3E_{1u}$, and $2E_{2u}$. The frequencies were estimated by comparison with similar motions in other ring molecules including benzene, $(BeO)_3$ and $(BeO)_4$. The assumed structure and vibrational frequencies gave an entropy in good agreement with the experimental enthalpy and equilibrium constant determined by Chupka *et al.*[1] The bond length was taken equal to that in Be_2O_2(g). The angles were chosen so that the O–Be–O angle was almost linear but with the Be–O–Be angle less than 120°. The principal moments of inertia are: $I_A = I_B$ = 116.0793 × 10^{-39}, and I_C = 232.1586 × 10^{-39} $g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.479	−2644.860	−2644.860	INFINITE
100	50.386	253.784	430.456	−17.667	−2649.997	−2623.081	1370.157
200	88.526	299.761	353.847	−10.817	−2655.345	−2594.199	677.535
250	110.694	321.887	345.242	−5.839	−2658.293	−2578.570	538.763
298.15	131.624	343.191	343.191	0.	−2661.024	−2562.965	449.021
300	132.400	344.008	343.194	0.244	−2661.125	−2562.357	446.146
350	152.248	365.937	344.880	7.370	−2663.698	−2545.687	379.923
400	169.665	387.432	348.861	15.428	−2665.907	−2528.673	330.211
450	184.604	408.302	354.313	24.295	−2667.752	−2511.405	291.516
500	197.270	428.426	360.724	33.851	−2669.277	−2493.948	260.541
600	216.981	466.236	375.205	54.619	−2671.589	−2458.651	214.045
700	231.084	500.802	390.716	77.061	−2673.260	−2423.023	180.808
800	241.334	532.364	406.479	100.708	−2674.605	−2387.181	155.867
900	248.936	561.249	422.094	125.240	−2675.844	−2351.178	136.459
1000	254.690	587.789	437.355	150.434	−2677.134	−2315.036	120.925
1100	259.130	612.280	452.158	176.134	−2678.588	−2278.757	108.209
1200	262.617	634.983	466.459	202.228	−2680.289	−2242.336	97.606
1300	265.398	656.117	480.245	228.634	−2682.303	−2205.761	88.629
1400	267.649	675.871	493.520	255.290	−2684.682	−2169.017	80.927
1500	269.494	694.401	506.301	282.150	−2687.469	−2132.090	74.246
1600	271.024	711.844	518.608	309.179	−2777.915	−2091.808	68.291
1700	272.306	728.315	530.464	336.347	−2779.211	−2048.886	62.955
1800	273.389	743.911	541.892	363.633	−2780.590	−2005.888	58.209
1900	274.313	758.718	552.918	391.019	−2782.069	−1962.809	53.961
2000	275.107	772.809	563.563	418.491	−2783.660	−1919.649	50.136
2100	275.795	786.248	573.850	446.037	−2785.376	−1876.407	46.673
2200	276.393	799.092	583.798	473.647	−2787.224	−1833.078	43.523
2300	276.918	811.390	593.428	501.314	−2789.213	−1789.665	40.645
2400	277.379	823.186	602.757	529.029	−2791.348	−1746.162	38.004
2500	277.788	834.518	611.802	556.788	−2793.635	−1702.566	35.573
2600	278.152	845.420	620.579	584.585	−2796.076	−1658.875	33.327
2700	278.477	855.924	629.103	612.417	−2798.675	−1615.087	31.246
2800	278.768	866.056	637.385	640.279	−4547.176	−1533.865	28.615
2900	279.030	875.843	645.440	668.169	−4543.714	−1426.310	25.691
3000	279.267	885.307	653.279	696.084	−4540.316	−1318.870	22.964
3100	279.482	894.468	660.912	724.022	−4536.989	−1211.542	20.414
3200	279.677	903.344	668.350	751.980	−4533.742	−1104.324	18.026
3300	279.855	911.953	675.602	779.957	−4530.582	−997.205	15.784
3400	280.018	920.310	682.677	807.951	−4527.521	−890.177	13.676
3500	280.167	928.429	689.583	835.960	−4524.569	−783.241	11.689
3600	280.304	936.324	696.328	863.984	−4521.736	−676.385	9.814
3700	280.430	944.005	702.919	892.021	−4519.034	−569.609	8.041
3800	280.547	951.486	709.362	920.069	−4516.475	−462.900	6.363
3900	280.654	958.774	715.664	948.130	−4514.070	−356.257	4.772
4000	280.754	965.881	721.831	976.200	−4511.833	−249.677	3.260
4100	280.847	972.815	727.868	1004.280	−4509.776	−143.149	1.824
4200	280.933	979.584	733.781	1032.369	−4507.911	−36.669	0.456
4300	281.013	986.195	739.575	1060.467	−4506.252	69.770	−0.848
4400	281.088	992.656	745.254	1088.572	−4504.811	176.171	−2.091
4500	281.158	998.974	750.822	1116.684	−4503.599	282.541	−3.280
4600	281.224	1005.154	756.284	1144.803	−4502.631	388.888	−4.416
4700	281.285	1011.203	761.644	1172.929	−4501.916	495.218	−5.504
4800	281.343	1017.126	766.905	1201.060	−4501.467	601.535	−6.546
4900	281.397	1022.927	772.071	1229.197	−4501.294	707.847	−7.546
5000	281.448	1028.613	777.145	1257.339	−4501.407	814.157	−8.505
5100	281.496	1034.187	782.130	1285.487	−4501.817	920.473	−9.428
5200	281.541	1039.653	787.030	1313.638	−4502.530	1026.795	−10.314
5300	281.584	1045.016	791.848	1341.795	−4503.556	1133.141	−11.168
5400	281.624	1050.280	796.585	1369.955	−4504.904	1239.504	−11.990
5500	281.663	1055.448	801.245	1398.120	−4506.577	1345.895	−12.782
5600	281.699	1060.524	805.829	1426.288	−4508.584	1452.324	−13.547
5700	281.733	1065.510	810.342	1454.459	−4510.930	1558.787	−14.285
5800	281.766	1070.410	814.783	1482.634	−4513.617	1665.299	−14.998
5900	281.797	1075.227	819.157	1510.812	−4516.652	1771.853	−15.687
6000	281.826	1079.963	823.464	1538.994	−4520.037	1878.469	−16.354

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

Continued from page 369

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Continued from page 392

The entropy in the present table is higher by 1.83 $cal \cdot K^{-1} \cdot mol^{-1}$ at 298.15 K and 1.76 $cal \cdot K^{-1} \cdot mol^{-1}$ at 1000 K than that proposed by Jackson;[9] the moment of inertia as calculated by Jackson[9] appears to be in error.

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Continued from page 397

One vibrational frequency, 649 cm^{-1}, was reported by Farber *et al.*[14] based on infrared spectral data. We do not adopt this value for the following reasons. It is within 21 cm^{-1} of an adopted value and will not drastically change the entropy. For consistency we estimate all the vibrational frequencies for the alkaline earth dihydroxides in the same manner since the result of Farber *et al.*[14] is the only reported value.

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IP(Br, g) = 95284.8 ± 0.5 cm^{-1}
$S°(298.15\ K)$ = 175.017 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 117.92 ± 0.06 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 111.86 ± 0.06 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P°_{3/2}$	0.0	4
$^2P°_{1/2}$	3685.24	2

Enthalpy of Formation

The adopted value for the enthalpy of formation of Br(g) is derived from the spectroscopically determined dissociation energy of $Br_2(g)$ as reported by Barrow *et al.*[1,2] This value is also recommended by Brewer and Winn[3] and Huber and Herzberg.[4] The adopted value, $D_0°$ = 15895.6 ± 0.02 cm^{-1} (190.154 ± 0.001 $kJ·mol^{-1}$), has been corrected for the natural isotopic abundance from the dissociation energies of $^{79}Br_2$ and $^{81}Br_2$. The convergence limit in the absorption spectrum of the $^3\Pi_{0^+_u} - {}^1\Sigma^+_g$ system corresponds to dissociation to a ground state bromine atom ($^2P_{3/2}$) and a bromine atom in the $^2P_{1/2}$ excited state.

Using earlier data, the CODATA recommended value[5] was calculated using $D_0°$ (^{79}Br–^{81}Br) = 15893.1 ± 2 cm^{-1} based on Horsley and Barrow[6] and Sitterly.[7] LeRoy[8] recalculated the dissociation energy from these data; his result is correct only if Horsley and Barrow[6] missed many upper rotational levels of higher vibrational states in their interpretation of the absorption spectra. Subsequent to these initial CODATA evaluation, LeRoy and Bernstein,[9] using the band origins obtained by Horsley and Barrow,[6] derived $D_0°$ (^{79}Br–^{81}Br) = 15895.5 ± 0.5 cm^{-1}.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[10, 11] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 63430 cm^{-1}. Our calculations indicate that any reasonable method of filling in the missing levels and cutting off the summation in the partition function[12] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels. Therefore, we list only the ground state and the first excited state. Extension to higher temperatures may require consideration of the higher excited states and utilization of different fill and cutoff procedures.

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations[13] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the monatomic halogens arise due to the use of slightly different values for the relative atomic mass and for R; this table uses R = 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*[14] Gurvich *et al.*[15] and Wagman *et al.*[16] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[17] and the 1973 values,[18] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	117.917	117.917	INFINITE
100	20.786	152.310	193.497	−4.119	118.599	106.061	−55.400
200	20.786	166.717	176.918	−2.040	118.227	93.626	−24.453
250	20.786	171.356	175.359	−1.001	117.859	87.515	−18.285
298.15	20.786	175.017	175.017	0.	111.860	82.369	−14.431
300	20.786	175.145	175.017	0.038	111.828	82.186	−14.310
350	20.786	178.350	175.270	1.078	96.543	78.082	−11.653
400	20.787	181.125	175.832	2.117	96.667	75.436	−9.851
450	20.790	183.574	176.559	3.157	96.786	72.775	−8.447
500	20.798	185.765	177.372	4.196	96.900	70.100	−7.323
600	20.833	189.559	179.097	6.277	97.122	64.720	−5.634
700	20.908	192.776	180.827	8.364	97.339	59.302	−4.425
800	21.027	195.575	182.499	10.461	97.560	53.853	−3.516
900	21.184	198.060	184.093	12.571	97.788	48.376	−2.808
1000	21.365	200.301	185.603	14.698	98.028	42.873	−2.239
1100	21.559	202.347	187.034	16.844	98.283	37.345	−1.773
1200	21.752	204.231	188.389	19.010	98.552	31.794	−1.384
1300	21.937	205.979	189.676	21.195	98.837	26.219	−1.054
1400	22.107	207.611	190.899	23.397	99.134	20.622	−0.769
1500	22.258	209.142	192.065	25.615	99.443	15.004	−0.522
1600	22.388	210.583	193.178	27.848	99.761	9.364	−0.306
1700	22.497	211.943	194.242	30.092	100.085	3.704	−0.114
1800	22.586	213.232	195.262	32.346	100.412	−1.975	0.057
1900	22.657	214.455	196.240	34.609	100.740	−7.672	0.211
2000	22.710	215.619	197.180	36.877	101.066	−13.386	0.350
2100	22.748	216.728	198.085	39.150	101.387	−19.117	0.476
2200	22.772	217.786	198.956	41.426	101.701	−24.862	0.590
2300	22.785	218.799	199.797	43.704	102.006	−30.622	0.695
2400	22.788	219.769	200.609	45.983	102.301	−36.395	0.792
2500	22.782	220.699	201.394	48.262	102.585	−42.180	0.881
2600	22.769	221.592	202.154	50.539	102.856	−47.976	0.964
2700	22.750	222.451	202.890	52.815	103.114	−53.782	1.040
2800	22.727	223.278	203.603	55.089	103.360	−59.598	1.112
2900	22.699	224.075	204.296	57.360	103.592	−65.421	1.178
3000	22.669	224.844	204.968	59.629	103.813	−71.253	1.241
3100	22.635	225.587	205.621	61.894	104.023	−77.092	1.299
3200	22.600	226.305	206.256	64.156	104.222	−82.938	1.354
3300	22.564	227.000	206.875	66.414	104.411	−88.790	1.405
3400	22.526	227.673	207.476	68.669	104.593	−94.647	1.454
3500	22.489	228.325	208.063	70.919	104.767	−100.510	1.500
3600	22.450	228.958	208.634	73.166	104.936	−106.377	1.543
3700	22.412	229.573	209.192	75.409	105.101	−112.249	1.585
3800	22.374	230.170	209.736	77.649	105.263	−118.126	1.624
3900	22.336	230.751	210.268	79.884	105.423	−124.006	1.661
4000	22.298	231.316	210.787	82.116	105.582	−129.891	1.696
4100	22.261	231.866	211.294	84.344	105.743	−135.780	1.730
4200	22.225	232.402	211.791	86.568	105.904	−141.673	1.762
4300	22.189	232.925	212.276	88.789	106.069	−147.569	1.793
4400	22.154	233.434	212.751	91.006	106.237	−153.470	1.822
4500	22.120	233.932	213.216	93.220	106.409	−159.374	1.850
4600	22.087	234.418	213.672	95.430	106.587	−165.283	1.877
4700	22.055	234.892	214.118	97.637	106.770	−171.195	1.903
4800	22.023	235.356	214.556	99.841	106.960	−177.111	1.927
4900	21.992	235.810	214.985	102.042	107.156	−183.031	1.951
5000	21.962	236.254	215.406	104.239	107.359	−188.955	1.974
5100	21.933	236.689	215.819	106.434	107.570	−194.883	1.996
5200	21.905	237.114	216.225	108.626	107.789	−200.816	2.017
5300	21.878	237.531	216.623	110.815	108.016	−206.753	2.038
5400	21.851	237.940	217.014	113.002	108.251	−212.694	2.057
5500	21.825	238.341	217.398	115.186	108.495	−218.640	2.076
5600	21.800	238.734	217.775	117.367	108.746	−224.590	2.095
5700	21.776	239.119	218.146	119.546	109.007	−230.545	2.113
5800	21.752	239.498	218.511	121.722	109.275	−236.504	2.130
5900	21.730	239.870	218.870	123.896	109.552	−242.468	2.147
6000	21.708	240.235	219.223	126.068	109.838	−248.437	2.163

PREVIOUS: June 1974 (1 atm) CURRENT: June 1982 (1 bar)

IP(Br^+, g) = 175870 ± 10 cm^{-1}
$S°$(298.15 K) = 176.872 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1256.95 ± 0.13 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1257.091] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	3136.4	3
$^3P_0$	3837.5	1
$^1D_2$	12089.1	5
$^1S_0$	27867.1	1

Enthalpy of Formation

$\Delta_f H°(Br^+, g, 0 K)$ is calculated from $\Delta_f H°(Br, g, 0 K)$[1] using the spectroscopic value of IP(Br) = 95284.8 ± 0.5 cm^{-1}(1139.86 ± 0.01 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization potential and appearance potential data.

$\Delta_f H°(Br^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Br, g, 0 K)$ by using IP(Br) with JANAF[1] enthalpies, $H°(0 K)–H°(298.15 K)$, for Br(g), $Br^+(g)$, and e^-(ref). $\Delta_f H°(Br \rightarrow Br^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the lowest four excited states; the next lowest level is approximately 93927 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and four excited states, with the energy of these states taken from recent study by Moore.[2] The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, fundamental constants, and the position of the four lowest excited states. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1256.951		
100	20.786	154.165	195.352	−4.119			
200	20.786	168.573	178.773	−2.040			
250	20.786	173.211	177.214	−1.001			
298.15	20.786	176.872	176.872	0.	1257.091	1220.792	−213.878
300	20.786	177.001	176.872	0.038	1257.098	1220.567	−212.520
350	20.788	180.205	177.125	1.078	1242.852	1215.232	−181.364
400	20.794	182.981	177.688	2.117	1244.016	1211.207	−158.167
450	20.809	185.431	178.415	3.157	1245.175	1207.037	−140.109
500	20.838	187.625	179.228	4.199	1246.330	1202.737	−125.649
600	20.953	191.433	180.954	6.287	1248.638	1193.802	−103.930
700	21.153	194.677	182.688	8.392	1250.952	1184.480	−88.387
800	21.426	197.519	184.368	10.520	1253.282	1174.825	−76.708
900	21.746	200.060	185.973	12.679	1255.637	1164.877	−67.608
1000	22.084	202.369	187.499	14.870	1258.020	1154.665	−60.313
1100	22.415	204.490	188.948	17.095	1260.432	1144.212	−54.334
1200	22.720	206.453	190.326	19.352	1262.872	1133.540	−49.342
1300	22.990	208.283	191.638	21.638	1265.336	1122.662	−45.109
1400	23.220	209.995	192.889	23.949	1267.821	1111.594	−41.474
1500	23.409	211.604	194.083	26.281	1270.322	1100.348	−38.318
1600	23.560	213.120	195.226	28.629	1272.835	1088.934	−35.550
1700	23.677	214.552	196.321	30.992	1275.355	1077.363	−33.103
1800	23.765	215.908	197.372	33.364	1277.879	1065.644	−30.924
1900	23.829	217.194	198.382	35.744	1280.403	1053.784	−28.971
2000	23.874	218.418	199.353	38.129	1282.924	1041.792	−27.209
2100	23.904	219.583	200.289	40.518	1285.440	1029.673	−25.612
2200	23.923	220.696	201.192	42.909	1287.948	1017.435	−24.157
2300	23.935	221.760	202.063	45.302	1290.447	1005.083	−22.826
2400	23.942	222.778	202.905	47.696	1292.935	992.623	−21.604
2500	23.946	223.756	203.720	50.091	1295.413	980.059	−20.477
2600	23.948	224.695	204.508	52.485	1297.880	967.396	−19.435
2700	23.950	225.599	205.273	54.880	1300.336	954.638	−18.469
2800	23.952	226.470	206.014	57.275	1302.781	941.790	−17.569
2900	23.955	227.310	206.734	59.671	1305.216	928.854	−16.730
3000	23.959	228.123	207.434	62.066	1307.643	915.835	−15.946
3100	23.964	228.908	208.114	64.462	1310.062	902.735	−15.211
3200	23.971	229.669	208.776	66.859	1312.474	889.557	−14.521
3300	23.979	230.407	209.420	69.257	1314.882	876.303	−13.871
3400	23.988	231.123	210.048	71.655	1317.286	862.977	−13.258
3500	23.997	231.818	210.660	74.054	1319.687	849.580	−12.679
3600	24.008	232.495	211.257	76.455	1322.088	836.114	−12.132
3700	24.018	233.153	211.840	78.856	1324.490	822.582	−11.613
3800	24.029	233.793	212.409	81.258	1326.893	808.985	−11.120
3900	24.040	234.418	212.966	83.662	1329.300	795.324	−10.652
4000	24.051	235.026	213.510	86.066	1331.711	781.602	−10.207
4100	24.061	235.620	214.042	88.472	1334.127	767.819	−9.782
4200	24.071	236.200	214.562	90.878	1336.550	753.977	−9.377
4300	24.080	236.767	215.072	93.286	1338.980	740.078	−8.990
4400	24.088	237.320	215.572	95.694	1341.418	726.122	−8.620
4500	24.095	237.862	216.061	98.104	1343.864	712.110	−8.266
4600	24.101	238.391	216.541	100.513	1346.320	698.044	−7.927
4700	24.107	238.910	217.011	102.924	1348.785	683.925	−7.601
4800	24.111	239.417	217.473	105.335	1351.260	669.753	−7.288
4900	24.114	239.915	217.926	107.746	1353.746	655.529	−6.988
5000	24.116	240.402	218.370	110.157	1356.242	641.254	−6.699
5100	24.116	240.879	218.807	112.569	1358.748	626.930	−6.421
5200	24.116	241.348	219.236	114.981	1361.265	612.556	−6.153
5300	24.114	241.807	219.658	117.392	1363.793	598.133	−5.895
5400	24.111	242.258	220.072	119.803	1366.332	583.663	−5.646
5500	24.107	242.700	220.479	122.214	1368.881	569.146	−5.405
5600	24.102	243.134	220.880	124.625	1371.440	554.582	−5.173
5700	24.096	243.561	221.274	127.035	1374.010	539.973	−4.948
5800	24.089	243.980	221.662	129.444	1376.590	525.318	−4.731
5900	24.081	244.392	222.044	131.853	1379.181	510.618	−4.521
6000	24.072	244.796	222.420	134.260	1381.780	495.875	−4.317

PREVIOUS: CURRENT: June 1982 (1 bar)

EA(Br, g) = 3.365 ± 0.003 eV
$S°$(298.15 K) = 163.491 ± 0.005 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −206.8 ± 0.5 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [−219.008] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(Br^-, g, 0 K)$ is calculated from $\Delta_f H°(Br,g, 0 K)$[1] using the adopted electron affinity of EA(Br) = 3.363 ± 0.003 eV (324.671 ± 0.289 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[10] is based on plasma absorption and plasma emission studies.[5, 6] Additional information on $Br^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H°(Br^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Br, g, 0 K)$ by using EA(Br) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for $Br^-(g)$, Br(g), and e^-(ref). $\Delta_f H°(Br^- \rightarrow Br + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°(298.15 K)$ should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for $Br^-(g)$ is given by Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

The entropy at all temperatures (0–6000 K) agrees within 0.001 J·K^{-1}·mol^{-1} with the values of Gurvich *et al.*[8] except for one minor difference. The entropy differs by 0.1094 J·K^{-1}·mol^{-1} because this table uses a standard-state pressure of 1 bar, whereas the tabulation of Gurvich *et al.*[8] is based on 1 atm. The estimated uncertainty is due to uncertainties in the relative ionic mass and the fundamental constants which are based on the 1981 scale[9] and the 1973 values,[7] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	−206.753		
100	*20.786*	*140.783*	*181.971*	*−4.119*			
200	20.786	155.191	165.392	−2.040			
250	20.786	159.829	163.833	−1.001			
298.15	20.786	163.491	163.491	0.	−219.008	−238.808	41.838
300	20.786	163.619	163.491	0.038	−219.078	−238.930	41.601
350	20.786	166.823	163.744	1.078	−235.403	−241.321	36.015
400	20.786	169.599	164.306	2.117	−236.318	−242.104	31.616
450	20.786	172.047	*165.033*	*3.156*	−237.239	−242.772	28.180
500	20.786	174.237	165.846	4.196	−238.164	−243.337	25.421
600	20.786	178.027	167.570	6.274	−240.023	−244.198	21.259
700	20.786	181.231	169.299	8.353	−241.893	−244.746	18.263
800	20.786	184.007	170.967	10.431	−243.769	−245.025	15.999
900	20.786	186.455	172.555	12.510	−245.651	−245.069	14.223
1000	20.786	188.645	174.056	14.589	−247.538	−244.904	12.792
1100	*20.786*	*190.626*	*175.474*	*16.667*	−249.429	−244.549	*11.613*
1200	20.786	192.435	176.813	18.746	−251.325	−244.021	10.622
1300	20.786	194.099	178.080	20.824	−253.226	−243.335	9.777
1400	20.786	195.639	179.280	22.903	−255.130	−242.503	9.048
1500	20.786	197.073	180.419	24.982	−257.040	−241.535	8.411
1600	20.786	198.415	181.502	27.060	−258.954	−240.439	7.850
1700	20.786	199.675	182.534	29.139	−260.875	−239.223	7.350
1800	20.786	200.863	183.520	31.217	−262.802	−237.893	6.903
1900	20.786	201.987	184.462	33.296	−264.736	−236.457	6.501
2000	20.786	203.053	185.365	35.375	−266.679	−234.918	6.135
2100	20.786	204.067	186.232	37.453	−268.631	−233.282	5.803
2200	20.786	205.034	187.065	39.532	−270.593	−231.553	5.498
2300	20.786	205.958	187.866	41.610	−272.566	−229.734	5.217
2400	20.786	206.843	188.639	43.689	−274.550	−227.830	4.959
2500	20.786	207.691	189.384	45.768	−276.545	−225.842	4.719
2600	20.786	208.506	190.104	47.846	−278.551	−223.774	4.496
2700	20.786	209.291	190.800	49.925	−280.569	−221.629	4.288
2800	20.786	210.047	191.474	52.004	−282.597	−219.409	4.093
2900	20.786	210.776	192.127	54.082	−284.636	−217.117	3.911
3000	20.786	211.481	192.761	56.161	−286.684	−214.754	3.739
3100	20.786	212.162	193.375	58.239	−288.739	−212.322	3.578
3200	20.786	212.822	193.973	60.318	−290.802	−209.824	3.425
3300	20.786	213.462	*194.554*	62.397	−292.871	−207.261	3.281
3400	20.786	214.082	195.119	64.475	−294.944	−204.636	3.144
3500	20.786	214.685	195.670	66.554	−297.020	−201.950	3.014
3600	20.786	215.271	196.206	68.632	−299.098	−199.204	2.890
3700	20.786	215.840	196.729	70.711	−301.176	−196.401	2.773
3800	20.786	216.394	197.239	72.790	−303.254	−193.541	2.660
3900	20.786	216.934	197.737	74.868	−305.329	−190.627	2.553
4000	20.786	217.461	198.224	76.947	−307.401	−187.659	2.451
4100	20.786	217.974	198.699	79.025	−309.469	−184.640	2.352
4200	20.786	218.475	199.164	81.104	−311.532	−181.571	2.258
4300	20.786	218.964	199.619	83.183	−313.588	−178.452	2.168
4400	20.786	219.442	200.064	85.261	−315.637	−175.286	2.081
4500	20.786	219.909	200.500	87.340	−317.678	−172.073	1.997
4600	20.786	220.366	200.927	89.418	−319.711	−168.815	1.917
4700	20.786	220.813	201.345	91.497	−321.735	−165.513	1.839
4800	20.786	221.250	201.755	93.576	−323.749	−162.167	1.765
4900	20.786	221.679	202.158	95.654	−325.754	−158.780	1.693
5000	20.786	222.099	202.552	97.733	−327.748	−155.352	1.623
5100	20.786	222.510	202.940	99.811	−329.732	−151.885	1.556
5200	20.786	222.914	203.320	101.890	−331.705	−148.378	1.490
5300	20.786	223.310	203.693	103.969	−333.667	−144.834	1.427
5400	20.786	223.699	204.060	106.047	−335.618	−141.253	1.366
5500	20.786	224.080	204.421	108.126	−337.559	−137.635	1.307
5600	20.786	224.454	204.775	110.204	−339.488	−133.983	1.250
5700	20.786	224.822	205.124	112.283	−341.407	−130.296	1.194
5800	20.786	225.184	205.466	114.362	−343.314	−126.576	1.140
5900	20.786	225.539	205.804	116.440	−345.212	−122.823	1.087
6000	20.786	225.889	206.135	118.519	−347.098	−119.038	1.036

PREVIOUS: CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 252.89 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -41.3 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -49.4 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$D\ ^2\Sigma$	30190.6	2
$A_1\ ^2\Pi_{1/2}$	15922.5	2	$E\ ^2\Sigma$	33942.2	2
$A_2\ ^2\Pi_{3/2}$	15985.8	2	[F $^2\Pi$]	[35000]	[4]
$B\ ^2\Sigma$	16380.0	2	[G $^2\Delta$]	[36000]	[4]
$C_1\ ^2\Pi$	25314.0	2	[H $^2\Sigma$]	36798.7	[2]
$C_2\ ^2\Pi_{3/2}$	25537.5	2			

$\omega_e = 284.56\ cm^{-1}$ $\omega_e x_e = 0.86\ cm^{-1}$ $\sigma = 1$

$B_e = [0.09637]\ cm^{-1}$ $\alpha_e = [0.000389]\ cm^{-1}$ $r_e = [2.56]$ Å

Enthalpy of Formation

The selected value, $\Delta_f H°(0\ K) = -41.258\ kJ \cdot mol^{-1}$, is obtained from an analysis of spectroscopic data. The adopted values of the ground state vibrational constants, ω_e and $\omega_e x_e$, give $D_0^\circ = 2.90$ eV for CaBr(g) by a linear Birge–Sponer extrapolation. Based on the ionicity correction suggested by Hildenbrand,[1] this value adjusts to 3.50 eV (337.696 $kJ \cdot mol^{-1}$) which is adopted. The adopted value for D_0° gives $D_0^\circ(CaBr)/\Delta_a H°(CaBr_2) = 0.43$ which is quite consistent with values of this ratio for other alkaline earth halide systems.[2] Also, Hildenbrand[3,4] found that the ionicity parameter brings thermochemical and spectroscopic dissociation energies for CaF(g) and CaCl(g) into reasonable agreement. $\Delta_f H°(298.15\ K)$ corresponds to $-49.4\ kJ \cdot mol^{-1}$.

Ionic model calculations have led to D_0° values of 5.29 eV[5] and 3.4 eV.[6] The latter result is believed to represent a minimum value for D_0°. Two other experimental values, which bracket the selected value, have also been reported. Flame studies[7] gave $D_0^\circ = 3.29$ eV and chemiluminescence[8] from reaction of Ca atoms with Br gave a lower limit to D_0° of 4.22 eV. We assign an uncertainty of $\pm 41.8\ kJ \cdot mol^{-1}$ to $\Delta_f H°(0\ K)$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $CaBr_2$[9] with $r_e(CaBr)/r_e(CaBr_2) = 0.96$. The value of this ratio is calculated from bond lengths[2] for several other alkaline earth halide systems. Our adopted value for r_e is supported by an estimate ($r_e = 2.6$ Å) of Krasnov and Karaseva[6] while another etimated value[5] is only 0.14 Å larger than ours. The rotational constant is calculated from the estimated value of r_e. The value of α_e is obtained from a Morse potential function.

The vibrational constants are those recently determined from a complete vibrational analysis of the D $^2\Sigma$–X $^2\Sigma$ system by Shah.[10] These two values are corrected for the natural isotopic abundances of Br. The electronic levels with the exception of those for the D, F, G, and H states are from the compilation of Rosen.[11] The D state energy is from Shah.[10] The two doublet states (F and G) are estimated by analogy with those for SrBr.[9] Recently, Reddy *et al.*[12] reported observing a new system of bands in the visible emission spectrum of CaBr which was associated with $^2\Sigma$ – A $^2\Pi$ transition. The upper state of this system is assigned the H $^2\Sigma$ state by analogy with SrBr.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.854	−41.259	−41.259	INFINITE
100	31.560	215.410	284.258	−6.885	−40.667	−57.919	30.254
200	35.141	238.594	256.190	−3.519	−42.021	−74.700	19.510
250	35.915	246.526	253.491	−1.741	−42.901	−82.771	17.294
298.15	36.381	252.894	252.894	0.	−49.396	−89.707	15.716
300	36.395	253.119	252.895	0.067	−49.447	−89.957	15.663
350	36.713	258.755	253.339	1.896	−65.250	−95.832	14.302
400	36.935	263.673	254.330	3.737	−65.652	−100.174	13.081
450	37.100	268.033	255.615	5.588	−66.084	−104.463	12.126
500	37.227	271.949	257.056	7.446	−66.554	−108.703	11.356
600	37.413	278.754	260.122	11.179	−67.624	−117.035	10.189
700	37.548	284.532	263.207	14.927	−68.883	−125.173	9.341
800	37.654	289.553	266.193	18.688	−71.193	−133.014	8.685
900	37.743	293.993	269.040	22.458	−72.831	−140.646	8.163
1000	37.822	297.974	271.738	26.236	−74.760	−148.080	7.735
1100	37.894	301.582	274.289	30.022	−76.988	−155.307	7.375
1200	37.962	304.882	276.703	33.815	−87.252	−161.695	7.038
1300	38.026	307.923	278.989	37.614	−88.852	−167.834	6.744
1400	38.088	310.744	281.158	41.420	−90.451	−173.849	6.486
1500	38.149	313.373	283.219	45.232	−92.049	−179.750	6.259
1600	38.209	315.837	285.181	49.050	−93.646	−185.545	6.057
1700	38.269	318.156	287.054	52.873	−95.242	−191.240	5.876
1800	38.331	320.345	288.843	56.703	−245.513	−194.630	5.648
1900	38.395	322.419	290.556	60.540	−245.698	−191.798	5.273
2000	38.463	324.390	292.199	64.383	−245.889	−188.956	4.935
2100	38.536	326.268	293.777	68.232	−246.091	−186.104	4.629
2200	38.615	328.063	295.295	72.090	−246.306	−183.243	4.351
2300	38.703	329.781	296.757	75.956	−246.539	−180.371	4.096
2400	38.800	331.430	298.168	79.831	−246.792	−177.489	3.863
2500	38.908	333.016	299.530	83.716	−247.071	−174.596	3.648
2600	39.028	334.545	300.848	87.613	−247.381	−171.691	3.449
2700	39.161	336.020	302.123	91.522	−247.726	−168.773	3.265
2800	39.307	337.447	303.359	95.445	−248.113	−165.842	3.094
2900	39.468	338.829	304.559	99.384	−248.545	−162.896	2.934
3000	39.644	340.170	305.723	103.340	−249.030	−159.935	2.785
3100	39.835	341.473	306.856	107.313	−249.573	−156.956	2.645
3200	40.041	342.741	307.957	111.307	−250.178	−153.959	2.513
3300	40.262	343.976	309.030	115.322	−250.852	−150.942	2.389
3400	40.498	345.182	310.076	119.360	−251.600	−147.903	2.272
3500	40.748	346.359	311.096	123.422	−252.427	−144.842	2.162
3600	41.013	347.511	312.091	127.510	−253.338	−141.755	2.057
3700	41.291	348.638	313.064	131.625	−254.336	−138.642	1.957
3800	41.582	349.743	314.015	135.769	−255.426	−135.501	1.863
3900	41.885	350.827	314.945	139.942	−256.610	−132.330	1.772
4000	42.199	351.892	315.855	144.146	−257.892	−129.127	1.686
4100	42.524	352.938	316.747	148.382	−259.272	−125.891	1.604
4200	42.858	353.966	317.621	152.651	−260.751	−122.620	1.525
4300	43.201	354.979	318.478	156.954	−262.332	−119.313	1.449
4400	43.552	355.976	319.319	161.291	−264.009	−115.968	1.377
4500	43.910	356.959	320.144	165.664	−265.770	−112.584	1.307
4600	44.274	357.928	320.955	170.074	−267.634	−109.160	1.240
4700	44.643	358.884	321.752	174.519	−269.594	−105.694	1.175
4800	45.016	359.828	322.536	179.002	−271.643	−102.185	1.112
4900	45.394	360.760	323.306	183.523	−273.778	−98.633	1.051
5000	45.773	361.681	324.064	188.081	−275.993	−95.036	0.993
5100	46.155	362.591	324.811	192.677	−278.285	−91.395	0.936
5200	46.538	363.491	325.546	197.312	−280.642	−87.708	0.881
5300	46.921	364.381	326.271	201.985	−283.068	−83.974	0.828
5400	47.303	365.261	326.984	206.696	−285.553	−80.194	0.776
5500	47.685	366.133	327.688	211.446	−288.090	−76.368	0.725
5600	48.065	366.996	328.383	216.233	−290.664	−72.496	0.676
5700	48.442	367.850	329.067	221.059	−293.286	−68.577	0.628
5800	48.817	368.695	329.743	225.921	−295.942	−64.612	0.582
5900	49.188	369.533	330.411	230.822	−298.626	−60.601	0.537
6000	49.555	370.363	331.070	235.759	−301.330	−56.544	0.492

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 240.001\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 22.087 \pm 1.25\ kJ·mol^{-1}$
$\Delta H°(298.15\ K) = 14.644 \pm 1.25\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 443.1\ cm^{-1}$ $\omega_e x_e = 1.8\ cm^{-1}$ $\sigma = 1$
$B_e = 0.150797\ cm^{-1}$ $\alpha_e = 0.0007597\ cm^{-1}$ $r_e = 2.136$ Å

Enthalpy of Formation

The average $\Delta_r H°(298.15\ K) = 0.406\ kcal·mol^{-1}$ for the reaction $Br_2(g) + Cl_2(g) = 2BrCl(g)$ and the $\Delta_f H°(298.15\ K) = 3.694\ kcal·mol^{-1}$ for 1/2 $Br_2(g)$ from JANAF tables were used to calculate the $\Delta_f H°(298.15\ K) = 3.5 \pm 0.3\ kcal·mol^{-1}$ ($14.644 \pm 1.25\ kJ·mol^{-1}$). Other equilibrium measurements not included below have been summarized by Beeson and Yost.[3]

Source	T, K	Method	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$
[1]	301	Light absorption	.51
[2]	298	Light absorption	0.34
[3]	372–492	Total pressure Run III	0.39
[3]	372–492	Total pressure Run II	0.47
[4]	313 ± 5	Mass spectrometric	0.32
		Average	0.406

Heat Capacity and Entropy

All spectroscopic and molecular constants were obtained from Evans *et al.*[5] except r_e which was calculated from B_e. The value of r_e was reported to be 2.13 Å and 2.11 Å by Beeson and Yost[3] and Cole and Elverum,[6] respectively. Ground state configuration was taken from Herzberg.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.402	22.087	22.087	INFINITE
100	29.709	204.809	269.641	−6.483	22.153	13.815	−7.216
200	32.987	226.411	243.147	−3.347	21.320	5.776	−1.509
250	34.180	233.907	240.573	−1.666	20.783	1.950	−0.407
298.15	34.990	240.001	240.001	0.	14.644	−0.967	0.169
300	35.015	240.218	240.002	0.065	14.607	−1.063	0.185
350	35.604	245.662	240.430	1.831	−0.811	−2.829	0.422
400	36.029	250.445	241.389	3.622	−0.810	−3.117	0.407
450	36.344	254.708	242.637	5.432	−0.809	−3.405	0.395
500	36.586	258.550	244.039	7.256	−0.808	−3.694	0.386
600	36.927	265.253	247.032	10.932	−0.807	−4.271	0.372
700	37.157	270.964	250.053	14.637	−0.807	−4.848	0.362
800	37.323	275.937	252.984	18.362	−0.809	−5.426	0.354
900	37.452	280.340	255.784	22.101	−0.812	−6.003	0.348
1000	37.557	284.292	258.441	25.851	−0.817	−6.579	0.344
1100	37.646	287.876	260.956	29.612	−0.823	−7.155	0.340
1200	37.724	291.155	263.338	33.380	−0.832	−7.730	0.336
1300	37.793	294.177	265.596	37.156	−0.842	−8.305	0.334
1400	37.858	296.980	267.738	40.939	−0.855	−8.878	0.331
1500	37.918	299.594	269.776	44.727	−0.871	−9.451	0.329
1600	37.974	302.043	271.717	48.522	−0.891	−10.022	0.327
1700	38.028	304.347	273.569	52.322	−0.916	−10.592	0.325
1800	38.081	306.522	275.340	56.128	−0.946	−11.160	0.324
1900	38.131	308.583	277.036	59.938	−0.984	−11.727	0.322
2000	38.180	310.540	278.663	63.754	−1.029	−12.291	0.321
2100	38.229	312.404	280.225	67.574	−1.085	−12.853	0.320
2200	38.276	314.183	281.729	71.400	−1.152	−13.412	0.318
2300	38.323	315.886	283.177	75.230	−1.232	−13.967	0.317
2400	38.369	317.518	284.574	79.064	−1.326	−14.519	0.316
2500	38.414	319.085	285.923	82.903	−1.434	−15.066	0.315
2600	38.460	320.592	287.228	86.747	−1.558	−15.609	0.314
2700	38.504	322.045	288.491	90.595	−1.698	−16.147	0.312
2800	38.549	323.446	289.714	94.448	−1.853	−16.680	0.311
2900	38.593	324.799	290.901	98.305	−2.023	−17.206	0.310
3000	38.637	326.108	292.053	102.166	−2.208	−17.726	0.309
3100	38.681	327.376	293.172	106.032	−2.407	−18.240	0.307
3200	38.724	328.605	294.260	109.903	−2.617	−18.748	0.306
3300	38.768	329.797	295.319	113.777	−2.838	−19.248	0.305
3400	38.811	330.955	296.350	117.656	−3.068	−19.742	0.303
3500	38.854	332.081	297.355	121.539	−3.303	−20.230	0.302
3600	38.897	333.176	298.335	125.427	−3.543	−20.710	0.300
3700	38.940	334.242	299.291	129.319	−3.784	−21.183	0.299
3800	38.983	335.281	300.225	133.215	−4.025	−21.650	0.298
3900	39.026	336.294	301.137	137.115	−4.263	−22.111	0.296
4000	39.068	337.283	302.028	141.020	−4.495	−22.566	0.295
4100	39.111	338.248	302.900	144.929	−4.719	−23.015	0.293
4200	39.154	339.191	303.752	148.842	−4.933	−23.458	0.292
4300	39.196	340.113	304.587	152.760	−5.135	−23.897	0.290
4400	39.239	341.015	305.405	156.682	−5.322	−24.331	0.289
4500	39.281	341.897	306.206	160.608	−5.493	−24.761	0.287
4600	39.323	342.761	306.992	164.538	−5.645	−25.187	0.286
4700	39.366	343.607	307.762	168.472	−5.777	−25.611	0.285
4800	39.408	344.436	308.517	172.411	−5.888	−26.032	0.283
4900	39.450	345.249	309.258	176.354	−5.975	−26.450	0.282
5000	39.492	346.046	309.986	180.301	−6.039	−26.868	0.281
5100	39.535	346.829	310.701	184.252	−6.077	−27.284	0.279
5200	39.577	347.597	311.403	188.208	−6.089	−27.700	0.278
5300	39.619	348.351	312.093	192.168	−6.074	−28.115	0.277
5400	39.661	349.092	312.772	196.132	−6.032	−28.531	0.276
5500	39.703	349.820	313.439	200.100	−5.961	−28.948	0.275
5600	39.745	350.536	314.095	204.072	−5.861	−29.367	0.274
5700	39.788	351.240	314.740	208.049	−5.732	−29.788	0.273
5800	39.830	351.932	315.375	212.030	−5.574	−30.212	0.272
5900	39.872	352.614	316.001	216.015	−5.387	−30.638	0.271
6000	39.914	353.284	316.617	220.004	−5.170	−31.068	0.270

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 228.967\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -50.815 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -58.463 \pm 1.7\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 673\ cm^{-1}$ $\omega_e x_e = 4\ cm^{-1}$ $\sigma = 1$
$B_e = 0.356319\ cm^{-1}$ $\alpha_e = 0.005206\ cm^{-1}$ $r_e = 1.7555$ Å

Enthalpy of Formation

The equilibrium constant for the reaction $Br_2(g) + BrF_3(g) = 3BrF(g)$ has been measured over the temperature range 328–380 K by Steunenberg *et al.*[1] 3rd law analysis of the data yields a $\Delta_f H°(298.15\ K) = 11.785 \pm 0.2$ kcal·mol^{-1}, with a drift of -0.6 ± 1.2 cal·K^{-1}·mol^{-1}. 2nd law analysis yields $\Delta_f H°(298.15\ K) = 11.98 \pm 0.45$ kcal·mol^{-1}, thus it is obvious that the data is thermodynamically self consistent. There is an uncertainty in the entropy of BrF_3(g) of ± 1 cal·K^{-1}·mol^{-1} but this corresponds only to ± 0.35 kcal·mol^{-1} in $\Delta_f H°(298.15\ K)$, thus a best value of $\Delta_f H°(298.15\ K) = 11.78 \pm 0.5$ kcal·mol^{-1} is adopted. This yields $\Delta_f H°$(BrF, g, 298.15 K) = -13.973 ± 0.4 kcal·mol^{-1} (-58.463 ± 1.7 kJ·mol^{-1}), the uncertainty in the enthalpy of formation being a maximum value comprising the sum of the uncertainties in Br_2, BrF_3 and $\Delta_f H°$.

Attempts have been made to analyze the spectra of BrF to obtain a dissociation energy. Brodersen and Sicre,[2] obtained two dissociation limits for BrF of 65.62 kcal·mol^{-1} and 54.98 kcal·mol^{-1}. The difference corresponds to the Br($^2P_{1/2}$) – Br($^2P_{3/2}$) excitation energy, indicating that the upper state goes to F($^2P_{3/2}$) and Br($^2P_{1/2}$). This yields an enthalpy of formation of BrF of -10.23 kcal·mol^{-1}. Since this value is well outside the possible uncertainty limits of the equilibrium data we must conclude that the extrapolation is in error. Evans *et al.*[3] have also analyzed the spectra and conclude that an enthalpy of formation of -14.4 kcal·mol^{-1} is possible. However, Evans[4] now believes that the dissociating state was too strongly perturbed for meaningful extrapolation.

Heat Capacity and Entropy

All molecular constants were obtained from Evans *et al.*,[3] except r_e and the ground state configuration which were taken from Herzberg.[5]

References

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[4]W. H. Evans, U. S. Nat. Bur. Stand., personal communication, Nov. (1965).
[5]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.019	−50.815	−50.815	INFINITE
100	29.162	195.677	256.772	−6.109	−50.755	−59.112	30.877
200	30.760	216.261	231.914	−3.131	−51.692	−67.137	17.534
250	31.940	223.252	229.504	−1.563	−52.283	−70.931	14.820
298.15	32.956	228.967	228.967	0.	−58.463	−73.809	12.931
300	32.991	229.171	228.968	0.061	−58.501	−73.904	12.868
350	33.852	234.324	229.373	1.733	−73.949	−75.622	11.286
400	34.537	238.891	230.283	3.443	−73.968	−75.859	9.906
450	35.080	242.991	231.471	5.184	−73.982	−76.095	8.833
500	35.513	246.710	232.812	6.949	−73.991	−76.329	7.974
600	36.148	253.245	235.688	10.535	−74.002	−76.796	6.686
700	36.584	258.852	238.606	14.172	−74.009	−77.261	5.765
800	36.900	263.759	241.450	17.847	−74.015	−77.725	5.075
900	37.140	268.119	244.175	21.550	−74.022	−78.188	4.538
1000	37.330	272.043	246.769	25.274	−74.030	−78.651	4.108
1100	37.487	275.608	249.231	29.015	−74.041	−79.112	3.757
1200	37.620	278.876	251.567	32.770	−74.054	−79.573	3.464
1300	37.736	281.892	253.785	36.538	−74.071	−80.032	3.216
1400	37.840	284.692	255.894	40.317	−74.092	−80.490	3.003
1500	37.934	287.306	257.902	44.106	−74.118	−80.946	2.819
1600	38.021	289.757	259.817	47.903	−74.149	−81.400	2.657
1700	38.102	292.064	261.647	51.710	−74.186	−81.852	2.515
1800	38.179	294.244	263.398	55.524	−74.229	−82.302	2.388
1900	38.252	296.311	265.076	59.345	−74.278	−82.749	2.275
2000	38.323	298.275	266.688	63.174	−74.332	−83.193	2.173
2100	38.391	300.146	268.237	67.010	−74.392	−83.635	2.080
2200	38.457	301.933	269.728	70.852	−74.457	−84.073	1.996
2300	38.522	303.644	271.166	74.701	−74.524	−84.509	1.919
2400	38.585	305.285	272.553	78.556	−74.595	−84.942	1.849
2500	38.647	306.862	273.894	82.418	−74.665	−85.371	1.784
2600	38.708	308.379	275.192	86.286	−74.735	−85.798	1.724
2700	38.769	309.841	276.448	90.160	−74.802	−86.222	1.668
2800	38.828	311.252	277.666	94.040	−74.865	−86.644	1.616
2900	38.887	312.615	278.848	97.925	−74.920	−87.064	1.568
3000	38.946	313.934	279.995	101.817	−74.967	−87.482	1.523
3100	39.003	315.212	281.111	105.714	−75.003	−87.898	1.481
3200	39.061	316.452	282.196	109.618	−75.025	−88.314	1.442
3300	39.118	317.654	283.252	113.527	−75.033	−88.729	1.404
3400	39.175	318.823	284.282	117.441	−75.023	−89.144	1.370
3500	39.232	319.960	285.285	121.362	−74.995	−89.560	1.337
3600	39.288	321.065	286.263	125.288	−74.946	−89.977	1.306
3700	39.344	322.143	287.219	129.219	−74.875	−90.395	1.276
3800	39.400	323.193	288.152	133.156	−74.781	−90.816	1.248
3900	39.455	324.217	289.063	137.099	−74.662	−91.239	1.222
4000	39.511	325.216	289.955	141.047	−74.517	−91.666	1.197
4100	39.566	326.193	290.827	145.001	−74.345	−92.097	1.173
4200	39.622	327.147	291.680	148.961	−74.145	−92.532	1.151
4300	39.677	328.080	292.516	152.926	−73.917	−92.973	1.129
4400	39.732	328.993	293.334	156.896	−73.660	−93.419	1.109
4500	39.786	329.886	294.137	160.872	−73.374	−93.871	1.090
4600	39.841	330.761	294.923	164.853	−73.058	−94.330	1.071
4700	39.896	331.619	295.695	168.840	−72.712	−94.796	1.054
4800	39.951	332.459	296.452	172.832	−72.336	−95.270	1.037
4900	40.005	333.283	297.196	176.830	−71.930	−95.752	1.021
5000	40.060	334.092	297.925	180.833	−71.494	−96.242	1.005
5100	40.114	334.886	298.642	184.842	−71.029	−96.742	0.991
5200	40.168	335.665	299.347	188.856	−70.533	−97.251	0.977
5300	40.223	336.431	300.039	192.876	−70.008	−97.769	0.964
5400	40.277	337.183	300.720	196.901	−69.454	−98.298	0.951
5500	40.331	337.923	301.390	200.931	−68.871	−98.838	0.939
5600	40.385	338.650	302.049	204.967	−68.260	−99.388	0.927
5700	40.439	339.365	302.697	209.008	−67.621	−99.950	0.916
5800	40.494	340.069	303.336	213.055	−66.955	−100.523	0.905
5900	40.548	340.762	303.964	217.107	−66.261	−101.107	0.895
6000	40.602	341.444	304.583	221.164	−65.541	−101.704	0.885

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 292.397\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -244.37 \pm 2.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -255.59 \pm 2.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
674 (1)	613 (1)
[528](1)	[384](1)
[300](1)	[289](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: $Br–F_1 = Br–F_3 = 1.8061$Å; $Br–F_2 = 1.721$Å
Bond Angles: $F_1–Br–F_2 = 86°12.6'$; $F_2–Br–F_3 = 86°12.6'$; $F_3–Br–F_1 = 187°4.8'$
Product of the Moment of Inertia: $I_A I_B I_C = 4.48703 \times 10^{-114}\ g^3·cm^6$

Enthalpy for Formation

$\Delta_f H°(298.15\ K) = -255.588 \pm 2.9\ kJ·mol^{-1}$ is from Stein[1] and was derived from enthaply of reaction of F_2 with Br_2 which were measured in an adiabatic calorimeter. Stein's value for the $\Delta_f H°(298.15\ K) = -271.040\ kJ·mol^{-1}$ was based upon gaseous Br_2, which has been adjusted to the liquid Br_2 reference state at 298.15 K.

Heat Capacity and Entropy

Magnuson[2] determined the moments of inertia and quadrupole coupling coefficients of both $^{79}BrF_3$ and $^{81}BrF_3$ from a number f microwave transitions. From the moment of inertia the bromine trifluoride molecule was found to have a distorted "T" structure with one short, 1.721 Å, and two long, 1.810 Å Br–F bonds. The FBrF angle was found to be 86°12.6'.

Claasen *et al.*,[3] observed two of the six vibrational levels in the vapor, and calculated the other four levels from a normal coordinate treatment of the molecule. They also obtained a measured entropy of BrF_3(g), from low temperature data combined with vapor pressure data and an approximate correction for dimerization. This value is 300.9 $J·K^{-1}·mol^{-1}$ at 316.27 K compared with a value of 296.42 $J·K^{-1}·mol^{-1}$ from this table, the difference is probably within the uncertainty of the data. The principal moments of inertia are: $I_A = 7.7525 \times 10^{-39}$, $I_B = 20.4920 \times 10^{-39}$, and $I_C = 28.2445 \times 10^{-39}\ g·cm^2$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.275	−244.370	−244.370	INFINITE
100	39.106	235.530	343.752	−10.822	−246.675	−241.980	126.398
200	55.795	267.920	298.179	−6.052	−248.749	−236.395	61.740
250	62.017	281.071	293.468	−3.099	−249.458	−233.222	48.729
298.15	66.497	292.397	292.397	0.	−255.588	−229.383	40.187
300	66.644	292.808	292.398	0.123	−255.622	−229.221	39.911
350	70.048	303.351	293.223	3.545	−270.908	−223.983	33.428
400	72.571	312.877	295.094	7.113	−270.700	−217.293	28.376
450	74.468	321.539	297.558	10.791	−270.444	−210.632	24.450
500	75.918	329.464	300.358	14.553	−270.155	−204.002	21.312
600	77.935	343.498	306.409	22.253	−269.525	−190.829	16.613
700	79.228	355.616	312.593	30.116	−268.859	−177.765	13.265
800	80.100	366.255	318.649	38.085	−268.180	−164.798	10.760
900	80.713	375.727	324.475	46.127	−267.501	−151.916	8.817
1000	81.160	384.256	330.034	54.222	−266.828	−139.110	7.266
1100	81.495	392.007	335.321	62.355	−266.166	−126.370	6.001
1200	81.752	399.110	340.345	70.518	−265.518	−113.690	4.949
1300	81.954	405.662	345.120	78.704	−264.887	−101.063	4.061
1400	82.115	411.741	349.664	86.908	−264.274	−88.485	3.301
1500	82.246	417.411	353.994	95.126	−263.680	−75.949	2.645
1600	82.353	422.723	358.125	103.356	−263.108	−63.453	2.072
1700	82.443	427.718	362.073	111.596	−262.557	−50.991	1.567
1800	82.518	432.433	365.853	119.844	−262.025	−38.561	1.119
1900	82.581	436.896	369.475	128.099	−261.512	−26.161	0.719
2000	82.636	441.133	372.953	136.360	−261.016	−13.787	0.360
2100	82.683	445.166	376.297	144.626	−260.533	−1.438	0.036
2200	82.723	449.014	379.515	152.897	−260.058	10.889	−0.259
2300	82.759	452.692	382.617	161.171	−259.589	23.195	−0.527
2400	82.790	456.214	385.611	169.448	−259.121	35.480	−0.772
2500	82.818	459.595	388.503	177.729	−258.647	47.745	−0.998
2600	82.842	462.843	391.300	186.012	−258.164	59.991	−1.205
2700	82.864	465.970	394.008	194.297	−257.666	72.218	−1.397
2800	82.884	468.984	396.633	202.584	−257.149	84.427	−1.575
2900	82.901	471.893	399.178	210.874	−256.606	96.617	−1.740
3000	82.917	474.704	401.649	219.165	−256.035	108.787	−1.894
3100	82.931	477.423	404.050	227.457	−255.430	120.937	−2.038
3200	82.944	480.056	406.384	235.751	−254.788	133.068	−2.172
3300	82.956	482.609	408.655	244.046	−254.105	145.179	−2.298
3400	82.967	485.085	410.867	252.342	−253.379	157.267	−2.416
3500	82.977	487.490	413.022	260.639	−252.605	169.334	−2.527
3600	82.986	489.828	415.123	268.937	−251.783	181.378	−2.632
3700	82.995	492.102	417.173	277.236	−250.909	193.398	−2.730
3800	83.002	494.315	419.174	285.536	−249.983	205.394	−2.823
3900	83.010	496.471	421.129	293.837	−249.002	217.365	−2.911
4000	83.016	498.573	423.039	302.138	−247.966	229.310	−2.994
4100	83.022	500.623	424.906	310.440	−246.875	241.229	−3.073
4200	83.028	502.624	426.733	318.743	−245.727	253.120	−3.148
4300	83.033	504.578	428.520	327.046	−244.522	264.983	−3.219
4400	83.038	506.487	430.271	335.349	−243.261	276.817	−3.286
4500	83.043	508.353	431.985	343.653	−241.943	288.623	−3.350
4600	83.047	510.178	433.665	351.958	−240.569	300.398	−3.411
4700	83.051	511.964	435.312	360.263	−239.139	312.143	−3.469
4800	83.055	513.713	436.928	368.568	−237.654	323.857	−3.524
4900	83.059	515.425	438.512	376.874	−236.115	335.539	−3.577
5000	83.062	517.103	440.067	385.180	−234.522	347.189	−3.627
5100	83.065	518.748	441.594	393.486	−232.877	358.807	−3.675
5200	83.068	520.361	443.093	401.793	−231.180	370.393	−3.721
5300	83.071	521.943	444.566	410.100	−229.433	381.945	−3.764
5400	83.074	523.496	446.013	418.407	−227.636	393.464	−3.806
5500	83.076	525.021	447.436	426.715	−225.790	404.948	−3.846
5600	83.079	526.517	448.835	435.023	−223.898	416.399	−3.884
5700	83.081	527.988	450.211	443.331	−221.959	427.816	−3.920
5800	83.083	529.433	451.564	451.639	−219.975	439.198	−3.955
5900	83.085	530.853	452.896	459.947	−217.948	450.546	−3.989
6000	83.087	532.250	454.207	468.256	−215.878	461.859	−4.021

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 323.682\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -413.58 \pm 2.1\ kJ·mol^{-1}$
$(298.15\ K) = -428.72 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
683 (1)	535 (1)	644 (2)
587 (1)	[281](1)	415 (2)
369 (1)	312 (1)	245 (2)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: C_{4v}
Bond Distances: Br–F = 1.79 Å; Br–F* = 1.68 Å
Bond Angles: F–Br–F = [90]° and F*–Br–F = [90]°
(* axial)
Product of the Moments of Inertia: $I_A I_B I_C = 3.20483 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = -428.718 \pm 2.1\ kJ·mol^{-1}$ is from Stein[1] and was derived from enthalpies of reaction of F_2 with Br_2 which were measured in an adiabatic calorimeter. Stein's value for the $\Delta_f H°(298.15\ K) = -444.17\ kJ·mol^{-1}$ was based upon gaseous Br_2 which has been adjusted to the liquid Br_2 reference state at 298.15 K.

Heat Capacity and Entropy

Begun *et al.*[2] report the infrared (gas phase) and Raman (liquid phase) spectra and correlate the observations by means of normal coordinate calculations for the similar molecules BrF_5, IF_5, ClF_5 and $XeOF_4$. The fundamental frequencies are taken from Begun *et al.*[2] except for υ_9 which was beyond the range of their infrared measurements. The value $\upsilon_9 = 245\ cm^{-1}$ for the gas has been observed by McDowell and Asprey[3] and is confirmed by 237 cm^{-1} found in the Raman spectra of the liquid. Raman values from the liquid were used for the infrared inactive fundamentals υ_4 and υ_6. One Raman active frequency, persumably , υ_5 is not observed in any of the four molecules. The value $\upsilon_5 = 281\ cm^{-1}$ was obtained from the normal coordinate calculation. Previous Raman studies were reported by Stephenson and Jones.[4]

A tetragonal pyramidal structure (C_{4v} symmetry) with the above parameters was used by Begun *et al.*[2] in the analysis of the spectra. This symmetry is consistent with the NMR spectra of Gutowsky and Hoffman,[5] with the dipole moment determined by Rogers *et al.*,[6] and with the X–ray crystal structure obtained by Robinson and Bensey.[7] Bond distances were based on those in the crystal and the bond angle was assumed to be 90°, slightly larger than those in the crystal (80.5–86.5°). Begun *et al.*[2] indicate that the angle in the gaseous molecule is probably not exactly 90° but that the normal coordinate calculations are not sensitive to this angle. The three principal moments of inertia are: $I_A = 40.4333 \times 10^{-39}$ and $I_B = I_C = 28.1536 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.180	−413.581	−413.581	INFINITE
100	47.334	243.616	398.823	−15.521	−418.586	−397.662	207.717
200	80.797	287.176	332.382	−9.041	−421.879	−375.246	98.004
250	92.816	306.562	325.307	−4.686	−422.688	−363.487	75.946
298.15	101.404	323.682	323.682	0.	−428.718	−351.379	61.560
300	101.685	324.310	323.684	0.188	−428.745	−350.899	61.097
350	108.182	340.499	324.948	5.443	−443.787	−337.105	50.310
400	112.985	355.274	327.829	10.978	−443.243	−321.901	42.036
450	116.590	368.799	331.640	16.721	−442.588	−306.771	35.609
500	119.343	381.232	335.986	22.623	−441.858	−291.719	30.476
600	123.169	403.356	345.417	34.763	−440.261	−261.839	22.795
700	125.618	422.540	355.095	47.211	−438.561	−232.235	17.330
800	127.270	439.429	364.603	59.861	−436.812	−202.879	13.247
900	128.431	454.490	373.768	72.649	−435.041	−173.744	10.084
1000	129.277	468.067	382.531	85.537	−433.265	−144.806	7.564
1100	129.911	480.420	390.877	98.497	−431.496	−116.046	5.511
1200	130.398	491.745	398.817	111.514	−429.740	−87.447	3.806
1300	130.780	502.198	406.373	124.573	−428.004	−58.993	2.370
1400	131.085	511.902	413.568	137.667	−426.291	−30.672	1.144
1500	131.332	520.954	420.429	150.789	−424.606	−2.472	0.086
1600	131.535	529.437	426.979	163.932	−422.948	25.616	−0.836
1700	131.704	537.416	433.243	177.094	−421.320	53.601	−1.647
1800	131.846	544.949	439.242	190.272	−419.719	81.491	−2.365
1900	131.966	552.080	444.995	203.463	−418.142	109.293	−3.005
2000	132.069	558.852	450.520	216.665	−416.586	137.013	−3.578
2100	132.158	565.298	455.833	229.876	−415.044	164.654	−4.096
2200	132.235	571.448	460.950	243.096	−413.510	192.223	−4.564
2300	132.302	577.327	465.883	256.323	−411.976	219.723	−4.990
2400	132.361	582.959	470.644	269.556	−410.435	247.155	−5.379
2500	132.413	588.364	475.246	282.795	−408.878	274.522	−5.736
2600	132.460	593.558	479.697	296.038	−407.297	301.827	−6.064
2700	132.501	598.558	484.007	309.287	−405.682	329.071	−6.366
2800	132.538	603.377	488.185	322.539	−404.028	356.253	−6.646
2900	132.571	608.029	492.238	335.794	−402.325	383.377	−6.905
3000	132.601	612.524	496.173	349.053	−400.567	410.440	−7.146
3100	132.628	616.872	499.997	362.314	−398.748	437.443	−7.371
3200	132.653	621.083	503.715	375.578	−396.861	464.387	−7.580
3300	132.676	625.166	507.334	388.845	−394.903	491.271	−7.776
3400	132.696	629.127	510.858	402.113	−392.868	518.095	−7.960
3500	132.715	632.973	514.292	415.384	−390.753	544.857	−8.132
3600	132.732	636.712	517.641	428.656	−388.555	571.559	−8.293
3700	132.748	640.349	520.909	441.930	−386.271	598.197	−8.445
3800	132.763	643.890	524.099	455.206	−383.900	624.772	−8.588
3900	132.776	647.338	527.215	468.483	−381.439	651.285	−8.723
4000	132.789	650.700	530.260	481.761	−378.889	677.733	−8.850
4100	132.800	653.979	533.238	495.040	−376.248	704.115	−8.971
4200	132.811	657.180	536.151	508.321	−373.516	730.433	−9.084
4300	132.821	660.305	539.002	521.603	−370.695	756.684	−9.192
4400	132.831	663.358	541.794	534.885	−367.783	782.869	−9.294
4500	132.839	666.344	544.528	548.169	−364.782	808.987	−9.390
4600	132.848	669.263	547.208	561.453	−361.693	835.036	−9.482
4700	132.855	672.120	549.836	574.738	−358.518	861.018	−9.569
4800	132.862	674.918	552.413	588.024	−355.256	886.932	−9.652
4900	132.869	677.657	554.941	601.311	−351.911	912.776	−9.730
5000	132.876	680.342	557.422	614.598	−348.483	938.551	−9.805
5100	132.882	682.973	559.858	627.886	−344.975	964.257	−9.876
5200	132.887	685.553	562.250	641.174	−341.387	989.894	−9.944
5300	132.893	688.085	564.601	654.463	−337.723	1015.461	−10.008
5400	132.898	690.569	566.911	667.753	−333.983	1040.957	−10.069
5500	132.902	693.007	569.181	681.043	−330.169	1066.383	−10.128
5600	132.907	695.402	571.414	694.333	−326.285	1091.741	−10.183
5700	132.911	697.754	573.610	707.624	−322.330	1117.027	−10.236
5800	132.915	700.066	575.770	720.916	−318.308	1142.243	−10.287
5900	132.919	702.338	577.896	734.207	−314.220	1167.392	−10.335
6000	132.923	704.572	579.989	747.499	−310.068	1192.468	−10.381

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K)$ = [333.648 ± 2.1] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−953.5 ± 59] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−972.8 ± 59] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
848 (1)	621 (1)	580 (2)
694 (1)	[325](1)	423 (2)
597 (1)	502 (1)	225 (2)
279 (1)	892 (2)	

Ground State Quantum Weight: 1 σ = 4
Point Group: C_{4v}
Bond Distances: S–F = 1.597 Å; S-Br = 2.1902 Å
Bond Angles: Br–S–F* = [92°]; F*-S-F* = 90°
(* equatorial)
Product of Moments of Inertia: $I_A I_B I_C$ = [1.66563 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(BrSF_5, g, 0\ K)$ = −953.529 ± 59 $kJ·mol^{-1}$ is calculated from a S–Br bond energy of 173.0 ± 42 $kJ·mol^{-1}$ by combining $D_0°$ with JANAF enthalpies of formation[1] for SF_5 and Br. We estimate the strength of the S–Br bond in $BrSF_5$ from bond energy correlations. In the case of related sulfur chlorine molecules, we calculate that the ratio of the S–Cl bond strength in $ClSF_5$[1] is 1.1 times the mean S–Cl bond energy in $SOCl_2$.[2] Assuming that this relationship holds for $BrSF_5$ and $SOBr_2$, we obtain the adopted value for $D_0°(SF_5–Br)$ from $D_0°(SOBr–Br)$, 157.3 $kJ·mol^{-1}$.

The enthalpy of atomization and mean S–F bond energy are calculated to be 1730.5 ± 67 $kJ·mol^{-1}$ and 311.3 $kJ·mol^{-1}$, respectively. The latter value is identical with that found for $ClSF_5$, indicating that the sulfur fluorine bonding is very similar in these two molecules. This conclusion is supported by spectroscopic data.[1,3,4]

Heat Capacity and Entropy

Microwave[3] and vibrational spectroscopic[4] measurements indicate that $BrSF_5$ is a symmetrical top molecule possessing C_{4v} symmetry. We adopt the structural parameters proposed by Neuvar and Jache[3] from an analysis of the observed rotational spectrum. The adopted bond lengths were calculated assuming that the Br–S–F* bond angle was 92° which was estimated from the value (91.6°) for the Cl–S–F* angle in $ClSF_5$ reported by Kewley *et al.*[5] A more plausible value for the Cl–S–F* angle is 90.7 ± 0.2,[1] indicating that the bond lengths reported by Neuvar and Jache[3] may be slightly biased. We place the values of $S°(298.15\ K)$ and $I_A I_B I_C$ in brackets to emphasize this uncertainty.

The vibrational frequencies are based on the infrared and laser-excited Raman spectra of $BrSF_5$ recorded under matrix (argon) isolation conditions by Smardzewski *et al.*[4] We adjust their reported frequencies for a matrix effect which is estimated as 5 cm^{-1} from gas phase[1] and argon–matrix[4] spectral data for $ClSF_5$. Evidence available for ClS_5[1] indicates that ν_6 = 220 cm^{-1} by Smardzewski *et al.*[4] should be reassigned. We believe that this Raman band is the low frequency mode (S–Br wag) and that ν_6 has not been resolved. We estimate ν_6 = 325 cm^{-1} from the force-field value for $ClSF_5$.[1]

The principal moments of inertia are: I_A = 32.1450 × 10^{-39} g cm^2 and $I_B = I_C$ = 71.9835 × 10^{-39} $g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−19.433	−953.526	−953.526	INFINITE
100	47.160	252.860	410.417	−15.756	−959.203	−937.951	489.936
200	81.206	296.049	342.686	−9.327	−964.189	−914.603	238.870
250	95.727	315.781	335.351	−4.893	−965.938	−901.996	188.462
298.15	107.073	333.648	333.648	0.	−972.822	−888.897	155.731
300	107.459	334.312	333.650	0.198	−972.880	−888.376	154.680
350	116.682	351.599	334.995	5.811	−988.731	−873.408	130.349
400	123.876	367.669	338.087	11.833	−991.131	−856.830	111.891
450	129.504	382.598	342.213	18.173	−991.805	−840.009	97.506
500	133.940	396.481	346.954	24.763	−992.388	−823.108	85.990
600	140.315	421.507	357.341	38.499	−992.781	−789.203	68.706
700	144.531	443.474	368.109	52.755	−992.620	−755.280	56.360
800	147.434	462.974	378.772	67.362	−992.125	−721.405	47.103
900	149.507	480.466	389.116	82.215	−1044.546	−686.525	39.845
1000	151.033	496.301	399.055	97.245	−1042.483	−646.855	33.788
1100	152.186	510.752	408.562	112.409	−1040.383	−607.393	28.843
1200	153.077	524.034	417.639	127.674	−1038.265	−568.124	24.730
1300	153.779	536.315	426.302	143.018	−1036.147	−529.031	21.257
1400	154.341	547.733	434.572	158.425	−1034.040	−490.102	18.286
1500	154.798	558.397	442.476	173.882	−1031.951	−451.322	15.716
1600	155.175	568.400	450.037	189.382	−1029.886	−412.681	13.473
1700	155.488	577.817	457.279	204.915	−1027.849	−374.168	11.497
1800	155.753	586.713	464.225	220.478	−1025.840	−335.774	9.744
1900	155.977	595.140	470.895	236.065	−1023.857	−297.492	8.179
2000	156.169	603.145	477.309	251.672	−1021.896	−259.312	6.773
2100	156.335	610.769	483.485	267.297	−1019.953	−221.232	5.503
2200	156.479	618.045	489.437	282.938	−1018.020	−183.243	4.351
2300	156.605	625.004	495.181	298.593	−1016.091	−145.341	3.301
2400	156.715	631.671	500.730	314.259	−1014.158	−107.524	2.340
2500	156.813	638.071	506.096	329.935	−1012.212	−69.787	1.458
2600	156.900	644.223	511.291	345.621	−1010.244	−32.129	0.645
2700	156.977	650.146	516.325	361.315	−1008.246	5.453	−0.105
2800	157.047	655.856	521.207	377.016	−1006.210	42.960	−0.801
2900	157.109	661.368	525.946	392.724	−1004.128	80.394	−1.448
3000	157.166	666.695	530.549	408.438	−1001.994	117.755	−2.050
3100	157.217	671.849	535.024	424.157	−999.800	155.044	−2.612
3200	157.263	676.841	539.379	439.881	−997.541	192.261	−3.138
3300	157.305	681.681	543.618	455.609	−995.213	229.407	−3.631
3400	157.344	686.378	547.748	471.342	−992.810	266.480	−4.094
3500	157.379	690.940	551.774	487.078	−990.330	303.482	−4.529
3600	157.412	695.373	555.702	502.818	−987.769	340.413	−4.939
3700	157.441	699.687	559.535	518.560	−985.125	377.271	−5.326
3800	157.469	703.886	563.279	534.306	−982.397	414.055	−5.692
3900	157.494	707.977	566.937	550.054	−979.582	450.768	−6.037
4000	157.518	711.964	570.513	565.805	−976.681	487.407	−6.365
4100	157.540	715.854	574.011	581.558	−973.693	523.972	−6.675
4200	157.560	719.651	577.433	597.313	−970.618	560.464	−6.970
4300	157.579	723.358	580.784	613.070	−967.457	596.880	−7.251
4400	157.597	726.981	584.066	628.828	−964.211	633.223	−7.517
4500	157.613	730.523	587.281	644.589	−960.880	669.491	−7.771
4600	157.629	733.987	590.433	660.351	−957.467	705.684	−8.013
4700	157.643	737.378	593.523	676.115	−953.971	741.802	−8.244
4800	157.657	740.697	596.555	691.880	−950.396	777.845	−8.465
4900	157.670	743.948	599.530	707.646	−946.742	813.812	−8.675
5000	157.682	747.133	602.450	723.414	−943.011	849.704	−8.877
5100	157.693	750.256	605.318	739.182	−939.207	885.521	−9.070
5200	157.704	753.318	608.135	754.952	−935.329	921.262	−9.254
5300	157.714	756.322	610.902	770.723	−931.381	956.928	−9.431
5400	157.723	759.270	613.623	786.495	−927.364	992.519	−9.601
5500	157.732	762.164	616.297	802.268	−923.280	1028.034	−9.763
5600	157.741	765.006	618.928	818.041	−919.132	1063.476	−9.920
5700	157.749	767.798	621.515	833.816	−914.922	1098.842	−10.070
5800	157.757	770.542	624.061	849.591	−910.650	1134.133	−10.214
5900	157.764	773.239	626.566	865.367	−906.320	1169.352	−10.353
6000	157.771	775.890	629.033	881.144	−901.933	1204.496	−10.486

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 198.699 \pm 0.033\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -28.60 \pm 0.25\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -36.44 \pm 0.17\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 2649.1816 \pm 0.007\ cm^{-1}$ $\omega_e x_e = 45.2245 \pm 0.003\ cm^{-1}$ $\sigma = 1$

$B_e = 8.466203 \pm 0.000025\ cm^{-1}$ $\alpha_e = 0.233332 \pm 0.00004\ cm^{-1}$ $r_e = 1.414435$ Å

Enthaply of Formation

For HBr(g), CODATA[1] recommended the key value $\Delta_f H°(298.15\ K) = -36.38 \pm 0.17\ kJ·mol^{-1}$ which is adopted. References 2–9 were cited by CODATA.

Heat Capacity and Entropy

The values of ω_e, $\omega_e x_e$, B_e, and α_e are taken from Rank *et al.*[10] after correction to the averge isotopic species. See also James and Thibault,[11] Jones and Gordy,[12] Plyler,[13] and Mould *et al.*[14] The ground state configuration is from Huber and Herzberg[15] where molecular constants for HBr(g) are also given.

Our evaluations lead to $S°(298.15\ K) = 198.589\ J·K^{-1}·mol^{-1}$ in agreement with the CODATA recommended value[1] of $198.585 \pm 0.033\ J·K^{-1}·mol^{-1}$, both values based on a reference pressure of one atm. The value adopted, $S°(298.15\ K) = 198.694 \pm 0.033\ J·K^{-1}·mol^{-1}$, is the CODATA value corrected, by $0.109\ J·K^{-1}·mol^{-1}$, to a reference pressure of one bar.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.648	−28.603	−28.603	INFINITE
100	29.115	166.884	224.595	−5.771	−28.622	−37.581	19.630
200	29.124	187.067	201.363	−2.859	−29.507	−46.237	12.076
250	29.130	193.567	199.178	−1.403	−30.157	−50.348	10.520
298.15	29.141	198.699	198.699	0.	−36.443	−53.513	9.375
300	29.141	198.879	198.699	0.054	−36.485	−53.619	9.336
350	29.167	203.373	199.054	1.512	−52.077	−55.615	8.300
400	29.220	207.270	199.843	2.971	−52.261	−56.108	7.327
450	29.313	210.717	200.863	4.434	−52.449	−56.577	6.567
500	29.453	213.812	202.006	5.903	−52.636	−57.026	5.957
600	29.870	219.216	204.437	8.868	−52.996	−57.869	5.038
700	30.427	223.861	206.887	11.882	−53.320	−58.655	4.377
800	31.055	227.965	209.270	14.956	−53.599	−59.398	3.878
900	31.698	231.660	211.556	18.093	−53.830	−60.109	3.489
1000	32.319	235.032	213.737	21.294	−54.018	−60.796	3.176
1100	32.897	238.140	215.816	24.556	−54.168	−61.466	2.919
1200	33.425	241.025	217.798	27.872	−54.287	−62.124	2.704
1300	33.902	243.720	219.690	31.239	−54.381	−62.773	2.522
1400	34.329	246.248	221.497	34.651	−54.455	−63.416	2.366
1500	34.711	248.630	223.228	38.103	−54.517	−64.054	2.231
1600	35.053	250.881	224.886	41.592	−54.568	−64.688	2.112
1700	35.360	253.015	226.479	45.113	−54.614	−65.319	2.007
1800	35.635	255.044	228.010	48.663	−54.658	−65.947	1.914
1900	35.884	256.978	229.484	52.239	−54.703	−66.573	1.830
2000	36.109	258.824	230.905	55.838	−54.751	−67.196	1.755
2100	36.313	260.591	232.277	59.460	−54.805	−67.817	1.687
2200	36.500	262.285	233.603	63.101	−54.865	−68.436	1.625
2300	36.672	263.911	234.885	66.759	−54.935	−69.051	1.568
2400	36.830	265.475	236.128	70.434	−55.014	−69.663	1.516
2500	36.976	266.982	237.332	74.125	−55.104	−70.272	1.468
2600	37.111	268.435	238.500	77.829	−55.205	−70.877	1.424
2700	37.238	269.838	239.635	81.547	−55.317	−71.477	1.383
2800	37.357	271.194	240.738	85.277	−55.440	−72.074	1.345
2900	37.468	272.507	241.811	89.018	−55.574	−72.665	1.309
3000	37.573	273.779	242.856	92.770	−55.719	−73.252	1.275
3100	37.673	275.013	243.873	96.532	−55.872	−73.834	1.244
3200	37.767	276.210	244.865	100.304	−56.034	−74.411	1.215
3300	37.857	277.374	245.833	104.086	−56.203	−74.983	1.187
3400	37.943	278.505	246.777	107.876	−56.378	−75.549	1.161
3500	38.025	279.606	247.699	111.674	−56.558	−76.110	1.136
3600	38.104	280.678	248.601	115.481	−56.742	−76.666	1.112
3700	38.181	281.724	249.482	119.295	−56.928	−77.217	1.090
3800	38.254	282.743	250.344	123.117	−57.116	−77.763	1.069
3900	38.325	283.737	251.187	126.946	−57.304	−78.304	1.049
4000	38.394	284.709	252.013	130.782	−57.492	−78.840	1.030
4100	38.461	285.657	252.822	134.624	−57.677	−79.372	1.011
4200	38.526	286.585	253.615	138.474	−57.860	−79.898	0.994
4300	38.589	287.492	254.392	142.329	−58.039	−80.421	0.977
4400	38.651	288.380	255.155	146.191	−58.214	−80.940	0.961
4500	38.711	289.249	255.903	150.059	−58.384	−81.454	0.945
4600	38.770	290.101	256.637	153.934	−58.548	−81.965	0.931
4700	38.828	290.935	257.358	157.814	−58.705	−82.472	0.917
4800	38.885	291.753	258.066	161.699	−58.856	−82.976	0.903
4900	38.941	292.556	258.762	165.591	−58.999	−83.478	0.890
5000	38.996	293.343	259.446	169.487	−59.134	−83.975	0.877
5100	39.050	294.116	260.118	173.390	−59.260	−84.471	0.865
5200	39.103	294.875	260.779	177.297	−59.378	−84.964	0.853
5300	39.155	295.620	261.429	181.210	−59.487	−85.455	0.842
5400	39.207	296.352	262.069	185.128	−59.585	−85.944	0.831
5500	39.258	297.072	262.699	189.052	−59.675	−86.432	0.821
5600	39.309	297.780	263.319	192.980	−59.753	−86.917	0.811
5700	39.359	298.476	263.930	196.913	−59.822	−87.402	0.801
5800	39.408	299.161	264.531	200.852	−59.879	−87.885	0.791
5900	39.457	299.835	265.124	204.795	−59.925	−88.368	0.782
6000	39.506	300.499	265.708	208.743	−59.960	−88.850	0.774

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 262.47 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-61.84 \pm 17]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-78.24 \pm 17]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2200 (1)	2209.2(2)
930.3 (1)	946.3(2)
430.6 (1)	632.6(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.486 ± 0.008 Å; Si–Br = 2.210 Å
Bond Angles: H–Si–H = 110.42° ± 0.5°; H–Si–Br = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 3.79963 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy for Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of $SiBr_4$(g) and SiH_4(g). The only experimental value for $SiHBr_3$(g) appears to be too uncertain to justify a nonlinear interpolation such as that adopted for SiH_3Cl.[1] ormally we would seek a comparison with $\Delta_f H°$ values of CH_nBr_{4-n}. These were recently reviewed by Kudchadker and Kudchadker.[2] They adopted a cubic variation of $\Delta_f H°$ with n, based on $\Delta_f H°$ values of $CHBr_3$ and CBr_4 selected by Wagman *et al.*[3] We presume that Wagman's values are calculated rather than experimental. Uncertainty in these values[4–6] precludes their use as a comparison for SiH_nBr_{4-n}. We conclude, as did Hunt and Sirtl,[15] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley *et al.*[7] for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structural determinations.[8] The principal moments of inertia are $I_A = 0.9971 \times 10^{-39}$ and $I_B = I_C = 19.5210 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are from gas–phase infrared spectra[9] measured with a grating spectrometer by Buerger *et al.*[9] Assignments were based on analysis of band contours and rotational fine structure. These results supersede Shimanouchi's selected frequencies[10] which derive from lower resolution spectra. The new data agree with unpublished data cited by Ball *et al.*[11]

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3Br.[12] SiH_3Br has several high–lying electronic absorptions and a diffuse band with a maximum at ~52000 cm^{-1}.[13] Comparison[12,13] with CH_3Br[12,14] suggests that the lowest excited state in SiH_3Br is near 40000 cm^{-1}. Contributions due to excited states should be unimportant.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−11.769	−61.836	−61.836	INFINITE
100	34.071	217.875	302.187	−8.431	−64.660	−68.263	35.657
200	42.240	243.595	266.964	−4.674	−68.572	−70.393	18.385
250	47.756	253.612	263.308	−2.424	−70.675	−70.606	14.752
298.15	52.865	262.466	262.466	0.	−78.241	−69.751	12.220
300	53.052	262.794	262.467	0.098	−78.330	−69.698	12.135
350	57.817	271.337	263.131	2.872	−95.089	−67.304	10.045
400	62.019	279.337	264.662	5.870	−96.278	−63.252	8.260
450	65.736	286.861	266.715	9.066	−97.318	−59.060	6.856
500	69.060	293.962	269.088	12.437	−98.219	−54.760	5.721
600	74.795	307.077	274.345	19.639	−99.646	−45.926	3.998
700	79.577	318.976	279.884	27.365	−100.645	−36.888	2.753
800	83.586	329.872	285.461	35.529	−101.295	−27.732	1.811
900	86.942	339.917	290.961	44.060	−101.669	−18.512	1.074
1000	89.747	349.227	296.328	52.899	−101.834	−9.261	0.484
1100	92.092	357.894	301.535	61.994	−101.845	−0.002	0.
1200	94.058	365.993	306.573	71.304	−101.747	9.252	−0.403
1300	95.712	373.589	311.439	80.795	−101.577	18.496	−0.743
1400	97.111	380.735	316.136	90.438	−101.368	27.724	−1.034
1500	98.299	387.476	320.669	100.210	−101.141	36.937	−1.286
1600	99.315	393.854	325.046	110.092	−100.917	46.135	−1.506
1700	100.188	399.902	329.273	120.069	−150.886	55.766	−1.713
1800	100.942	405.650	333.358	130.126	−150.476	67.911	−1.971
1900	101.597	411.126	337.308	140.254	−150.062	80.032	−2.200
2000	102.169	416.352	341.130	150.443	−149.650	92.132	−2.406
2100	102.671	421.349	344.832	160.685	−149.247	104.211	−2.592
2200	103.114	426.136	348.420	170.975	−148.858	116.271	−2.761
2300	103.505	430.728	351.899	181.306	−148.485	128.314	−2.914
2400	103.854	435.141	355.276	191.675	−148.132	140.341	−3.054
2500	104.165	439.387	358.556	202.076	−147.801	152.354	−3.183
2600	104.443	443.478	361.744	212.506	−147.493	164.353	−3.302
2700	104.694	447.424	364.845	222.964	−147.209	176.342	−3.412
2800	104.920	451.236	367.863	233.444	−146.951	188.321	−3.513
2900	105.124	454.921	370.802	243.947	−146.717	200.291	−3.608
3000	105.310	458.488	373.665	254.469	−146.508	212.253	−3.696
3100	105.478	461.944	376.458	265.008	−146.324	224.208	−3.778
3200	105.633	465.295	379.182	275.564	−146.164	236.158	−3.855
3300	105.774	468.548	381.841	286.134	−146.027	248.104	−3.927
3400	105.903	471.708	384.438	296.718	−145.912	260.045	−3.995
3500	106.022	474.779	386.975	307.314	−145.818	271.984	−4.059
3600	106.132	477.767	389.456	317.922	−529.897	294.381	−4.271
3700	106.233	480.677	391.882	328.540	−529.430	317.271	−4.479
3800	106.326	483.511	394.256	339.168	−528.983	340.148	−4.676
3900	106.413	486.274	396.580	349.806	−528.555	363.015	−4.862
4000	106.494	488.969	398.857	360.451	−528.145	385.870	−5.039
4100	106.569	491.600	401.087	371.104	−527.752	408.716	−5.207
4200	106.638	494.169	403.272	381.764	−527.374	431.552	−5.367
4300	106.704	496.679	405.416	392.432	−527.010	454.379	−5.520
4400	106.764	499.133	407.518	403.105	−526.660	477.198	−5.665
4500	106.821	501.532	409.580	413.784	−526.323	500.009	−5.804
4600	106.875	503.881	411.605	424.469	−525.997	522.813	−5.937
4700	106.925	506.180	413.593	435.159	−525.683	545.610	−6.064
4800	106.972	508.432	415.545	445.854	−525.378	568.400	−6.185
4900	107.016	510.638	417.463	456.553	−525.082	591.184	−6.302
5000	107.058	512.800	419.349	467.257	−524.795	613.962	−6.414
5100	107.097	514.921	421.202	477.965	−524.515	636.734	−6.521
5200	107.134	517.000	423.024	488.677	−524.243	659.501	−6.625
5300	107.169	519.042	424.817	499.392	−523.976	682.263	−6.724
5400	107.203	521.045	426.580	510.110	−523.715	705.020	−6.820
5500	107.234	523.012	428.316	520.832	−523.457	727.771	−6.912
5600	107.264	524.945	430.024	531.557	−523.204	750.519	−7.001
5700	107.292	526.844	431.706	542.285	−522.953	773.262	−7.086
5800	107.319	528.710	433.362	553.016	−522.705	796.001	−7.169
5900	107.345	530.545	434.994	563.749	−522.457	818.734	−7.249
6000	107.369	532.349	436.602	574.484	−522.209	841.464	−7.326

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 112.84\ J·K^{-1}·mol^{-1}$
$T_{trs} = 411\ K$
$T_{fus} = 815.2\ K$

$\Delta_f H°(0\ K) = -255.0 \pm 1.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -271.5 \pm 1.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 3.222\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The equilibrium pressures for the reaction $NH_4Br(cr) \rightarrow NH_3(g) + HBr(g)$ have been measured by several investigators. Using the densi-tensimeter, Smits and Purcell,[2] determined both the equilibrium pressures and vapor densities of the decomposition products, simultaneously, at several temperatures. In order to check the density values obtained, the authors applied the "extrapolation method," from which it was calculated that the corresponding vapor density agreed with complete dissociation. Based on this conclusion, the reported equilibrium pressures were employed to evaluate the enthalpy changes ($\Delta_r H°$) of the decomposition reaction by both the 2nd and 3rd law methods. The results obtained are presented as follows.

Source	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Equipment Used
Smith and Calvert[1]	576.40–676.02	45.12 ± 0.13	44.93	Isoteniscope
Smits and Purcell[2]	604.95–668.15	45.50 ± 0.17	45.08	Densi-tensimeter
Johnson[3]	573.15–667.75	45.41 ± 0.44	44.85	Spiral Manometer

The value of $\Delta_f H°(298.15\ K)$ adopted is 45.2 ± 0.2 kcal·mol^{-1}. Using $\Delta_f H°(298.15\ K) = -10.97$ and -8.71 kcal·mol^{-1} for $NH_3(g)$ and HBr(g), respectively, the value of $\Delta_f H°(298.15\ K)$ for $NH_4Br(cr)$ is evaluated as -64.9 ± 0.3 kcal·mol^{-1} (-271.542 ± 1.3 kJ·mol^{-1}). The corresponding $\Delta_f H°(298.15\ K)$ value evaluated from solution data, selected by Parker[4] is 45.5 ± 0.2 kcal·mol^{-1}.

The vapor densities (573–661 K) of dissociation products of $NH_4Br(cr)$ were also measured by Smith and Lombard.[5] Using the equilibrium pressures reported by Smith and Calvert,[1] they derived the corresponding degrees of dissociation of $NH_4Br(cr)$ at different temperatures. The calculated results indicated that only 48% of $NH_4Br(cr)$ decomposed at 573 K and as reaction temperatures increased to 661 K the degree of dissocation decreased to 10%. This conclusion was stated to be erroneous by Smits and Purcell[2] probably because of incorrect density determinations.

Heat Capacity and Entropy

The low temperature (13–305 K) heat capacities and $S°(298.15\ K)$ were obtained from Sorai *et al.*[6] The $C_p°$ values above 305 K were estimated by comparison with those for NaCl(cr), NaBr(cr) and $NH_4Cl(cr)$. The low temperature heat capacities were also measured by Ewald,[7] 139–301 K, and by Simon *et al.*,[8] 201.2–277.1 K.

Transition Data

The temperature (T_{trs}) and enthalpy of transition ($\Delta_{trs} H°$) were given by Bridgman.[9] $T_{trs} = 419.5 \pm 0.6$ K was reported Markowitz and Boryta,[10] which was determined by differential thermal analysis. According to Sorai *et al.*,[6] there are three solid phase transitions, namely Phase IV (CsCl) → Phase III (tetragonal) at 108 K, Phase III (tetragonal) → Phase II (CsCl) at 235 K and Phase II (CsCl) → Phase I (NaCl) at 411 K.

Fusion Data

The value of T_{fus} was taken from Rassow,[11] determined under pressure.

Decomposition Data

The temperature of decomposition was calculated as 670 K, i.e. the temperature at which the total pressure of the decomposition products for the reaction $NH_4Br(cr) \rightarrow NH_3(g) + HBr(g)$ equals 1 atm. Values of 674 and 668.4 K were reported by Luft[12] and Markowitz and Boryta,[10] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.954	−254.971	−254.971	INFINITE
100	44.283	35.690	183.887	−14.820	−261.683	−234.424	122.450
200	78.680	77.864	120.813	−8.590	−264.747	−205.814	53.753
298.15	88.676	112.842	112.842	0.	−271.542	−176.007	30.836
300	88.893	113.392	112.844	0.164	−271.581	−175.414	30.542
400	92.717	139.666	116.401	9.306	−286.950	−140.189	18.307
411.000	92.844	142.183	117.057	10.327	II <--> I		
411.000	72.867	150.022	117.057	13.548	TRANSITION		
500	87.195	165.676	124.323	20.677	−284.740	−104.074	10.873
600	102.424	182.959	132.660	30.179	−284.447	−67.944	5.915
700	115.060	199.708	141.050	41.061	−282.832	−31.971	2.386
800	126.775	215.856	149.397	53.167	−280.062	3.690	−0.241
900	136.817	231.376	157.650	66.353	−276.295	38.943	−2.260
1000	146.022	246.276	165.772	80.503	−271.660	73.728	−3.851
1100	154.102	260.577	173.745	95.515	−266.266	108.012	−5.129
1200	161.502	274.308	181.557	111.301	−260.207	141.775	−6.171
1300	168.127	287.500	189.203	127.787	−253.560	175.007	−7.032
1400	174.264	300.187	196.680	144.910	−246.386	207.708	−7.750
1500	179.912	312.406	203.990	162.623	−238.733	239.879	−8.353

PREVIOUS: March 1962 CURRENT: September 1965

$S°(298.15\ K) = 271.538\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 115.5 \pm 38\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 104.2 \pm 38\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma^+$	0	2

$\omega_e = 187.29\ cm^{-1}$ $\omega_e x_e = 0.9665\ cm^{-1}$ $\sigma = 1$
$B_e = [0.0545]\ cm^{-1}$ $\alpha_e = [0.0003]\ cm^{-1}$ $r_e = [2.33]$ Å

Enthalpy of Formation

Gaydon[1] gives 0.7 ± 0.4 eV for the dissociation energy into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from Wieland[2] were weighted according to their natural isotopic abundances. The bond length was estimated to be 0.965 of the mercuric bond length by analogy with the mercury chlorides. Rotational constants were estimated.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.252	115.527	115.527	INFINITE
100	33.918	232.289	304.036	−7.175	115.502	98.688	−51.549
200	36.493	256.811	274.923	−3.622	114.019	82.403	−21.522
250	36.940	265.007	272.149	−1.786	110.751	74.762	−15.621
298.15	37.210	271.538	271.538	0.	104.182	68.581	−12.015
300	37.218	271.768	271.538	0.069	104.129	68.360	−11.902
350	37.413	277.521	271.992	1.935	88.280	63.279	−9.444
400	37.561	282.526	273.003	3.809	87.864	59.736	−7.801
450	37.681	286.958	274.312	5.690	87.457	56.245	−6.529
500	37.783	290.933	275.779	7.577	87.058	52.798	−5.516
600	37.956	297.837	278.897	11.364	86.271	46.020	−4.006
700	38.105	303.700	282.032	15.168	26.732	45.945	−3.428
800	38.242	308.797	285.066	18.985	26.594	48.699	−3.180
900	38.372	313.309	287.958	22.816	26.464	51.470	−2.987
1000	38.497	317.358	290.699	26.659	26.342	54.255	−2.834
1100	38.619	321.033	293.292	30.515	26.228	57.051	−2.709
1200	38.738	324.399	295.746	34.383	26.121	59.858	−2.606
1300	38.857	327.504	298.071	38.263	26.022	62.674	−2.518
1400	38.974	330.388	300.278	42.154	25.930	65.497	−2.444
1500	39.090	333.081	302.376	46.057	25.845	68.326	−2.379
1600	39.206	335.607	304.375	49.972	25.767	71.161	−2.323
1700	39.322	337.988	306.283	53.899	25.694	74.000	−2.274
1800	39.437	340.238	308.107	57.837	25.627	76.843	−2.230
1900	39.552	342.374	309.855	61.786	25.563	79.690	−2.191
2000	39.666	344.405	311.532	65.747	25.503	82.541	−2.156
2100	39.780	346.343	313.144	69.719	25.444	85.394	−2.124
2200	39.895	348.197	314.695	73.703	25.388	88.250	−2.095
2300	40.009	349.973	316.191	77.698	25.331	91.109	−2.069
2400	40.123	351.678	317.634	81.705	25.276	93.970	−2.045
2500	40.237	353.318	319.029	85.723	25.220	96.834	−2.023
2600	40.350	354.898	320.378	89.752	25.164	99.699	−2.003
2700	40.464	356.423	321.685	93.793	25.108	102.567	−1.984
2800	40.578	357.897	322.952	97.845	25.054	105.437	−1.967
2900	40.691	359.323	324.182	101.908	25.000	108.309	−1.951
3000	40.805	360.704	325.377	105.983	24.948	111.182	−1.936
3100	40.919	362.044	326.538	110.069	24.900	114.057	−1.922
3200	41.032	363.345	327.668	114.167	24.856	116.934	−1.909
3300	41.146	364.609	328.768	118.276	24.818	119.812	−1.896
3400	41.259	365.839	329.841	122.396	24.787	122.691	−1.885
3500	41.372	367.037	330.886	126.527	24.763	125.571	−1.874
3600	41.486	368.204	331.907	130.670	24.750	128.452	−1.864
3700	41.599	369.342	332.903	134.825	24.747	131.332	−1.854
3800	41.713	370.453	333.877	138.990	24.756	134.213	−1.845
3900	41.826	371.538	334.829	143.167	24.778	137.093	−1.836
4000	41.939	372.599	335.760	147.355	24.815	139.972	−1.828
4100	42.053	373.635	336.671	151.555	24.868	142.851	−1.820
4200	42.166	374.650	337.563	155.766	24.936	145.728	−1.812
4300	42.279	375.644	338.437	159.988	25.022	148.603	−1.805
4400	42.393	376.617	339.294	164.222	25.126	151.475	−1.798
4500	42.506	377.571	340.134	168.467	25.249	154.346	−1.792
4600	42.619	378.506	340.958	172.723	25.391	157.213	−1.785
4700	42.733	379.424	341.767	176.991	25.552	160.077	−1.779
4800	42.846	380.325	342.561	181.270	25.733	162.937	−1.773
4900	42.959	381.210	343.340	185.560	25.934	165.794	−1.767
5000	43.072	382.079	344.106	189.861	26.156	168.646	−1.762
5100	43.186	382.933	344.859	194.174	26.398	171.493	−1.756
5200	43.299	383.772	345.600	198.499	26.660	174.336	−1.751
5300	43.412	384.598	346.328	202.834	26.942	177.173	−1.746
5400	43.525	385.411	347.044	207.181	27.244	180.005	−1.741
5500	43.639	386.211	347.749	211.539	27.565	182.831	−1.736
5600	43.752	386.998	348.443	215.909	27.906	185.651	−1.732
5700	43.865	387.773	349.126	220.290	28.265	188.464	−1.727
5800	43.978	388.537	349.799	224.682	28.643	191.271	−1.723
5900	44.092	389.290	350.462	229.085	29.039	194.072	−1.718
6000	44.205	390.032	351.115	233.500	29.452	196.866	−1.714

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

$S°(298.15\ K) = 258.95\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 49.815 \pm 0.08\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 40.878 \pm 0.08\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^1\Sigma^+$	0	1	$B'\ 0^+$	16880	1
$A\ ^3\Pi_1$	12230	6	C ($\Pi_{1,2}$)	[51677]	2
$B\ ^3\Pi_{0+}$	[16155]	5	D ($\Pi_{1,0}$)	[56349]	2

$\omega_e = 267.38\ cm^{-1}$ $\omega_e x_e = 0.774\ cm^{-1}$ $\sigma = 1$
$B_e = 0.05568\ cm^{-1}$ $\alpha_e = 0.00034\ cm^{-1}$ $r_e = 2.485$ Å

Enthalpy for Formation

The equilibrium constants for the reaction (A) $I_2(g) + Br_2(g) = 2\ IBr(g)$ were determined to be 0.01124 and 0.01303 at 547.7 and 578 K, respectively, by Muller[1] who studied the rate of reaction between $H_2(g)$ and $Br_2(g)$ in the presence of $I_2(g)$. Bodenstein and Schmidt[2] derived two values of the equilibrium constants at 1495 K for the same reaction by vapor density studies on the system I_2, I, Br_2, Br and BrI. The equilibrium between $CuBr_2(cr)$, $I_2(g)$, CuBr(cr) and IBr(g) was investigated by McMorris and Yost[3] and the equilibrium constants at 115.0, 151.2 and 176.0°C for reaction (A) were evaluated. Based on these reported equilibrium constants, the corresponding enthalpy changes for reaction (A) are calculated by both the 2nd and 3rd law methods.

Badger and Yost[4] observed the infrared bands of IBr and classified them as the $A^3\Pi_2$–$X^1\Sigma$ transition. They have shown that the dissociation products of the upper state are normal atoms. Brown[5] assigned a faint set of bands in the red as the $B^3\Pi_0$–$X^1\Sigma$ system. By means of a vibrational analysis he found that the absorption spectrum of IBr is analogous to that of ICl. The dissociation energy for IBr was evaluated to be 14,660 ± 5 cm^{-1} or 1.817 eV. Hence the enthalpy change for the reaction (B) IBr(g) = I(g) + Br(g) is calculated as 41.92 $kcal·mol^{-1}$.

The enthaplies of formation for IBr(g) derived from the enthalpy changes for reaction (A) and (B) are presented in the following table. The value of $\Delta_f H°$(IBr, g, 298.15 K) adopted is 9.77 ± 0.02 $kcal·mol^{-1}$ (40.878 ± 0.08 $kJ·mol^{-1}$).

Source	Reaction	T/K	Data Points	$\Delta_r H°$(298.15 K), $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°$(298.15K) $kcal·mol^{-1}$
Muller[1]	A	547.7, 578	2	−3.07	−3.38	−0.55	9.47
Bodenstein and Schmidt[2]	A	1495	1	–	−2.92	–	9.70
McMorris and Yost[3]	A	388.2–449.2	14	−2.46	−2.85	−0.9 ± 0.4	9.73
Brown[5]	B	298	–	–	41.92**	–	9.77**

**The value is derived from $D_0°$(I–Br).

Heat Capacity and Entropy

The ground state configuration, electronic levels, quantum weights, ω_e and $\omega_e x_e$ are obtained from Herzberg.[6] The values of B_e, α_e(corrected to the average isotopic species) and r_e were reported by Jaseja[7] who analyzed the microwave spectrum of IBr, corresponding to the transitions $J = 4 \rightarrow 5$ and $J = 5 \rightarrow 6$, for the two isotopic species, $^{127}I^{79}Br$ and $^{127}I\ ^{81}Br$.

The infrared absorption spectrum of IBr at 8000–6800 Å, associated with a $^3\Pi_1$–$X^1\Sigma^+$ transition, was observed by Selin.[8] The derived rotational constants are different from those reported by Jaseja.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.917	49.815	49.815	INFINITE
100	31.904	221.168	290.519	−6.935	49.875	33.500	−17.499
200	35.387	244.574	262.265	−3.538	48.355	17.678	−4.617
250	36.103	252.554	259.552	−1.749	47.422	10.114	−2.113
298.15	36.531	258.952	258.952	0.	40.878	3.675	−0.644
300	36.544	259.178	258.953	0.068	40.825	3.444	−0.600
350	36.836	264.835	259.399	1.903	24.929	−1.903	0.284
400	37.042	269.768	260.394	3.750	16.448	−5.428	0.709
450	37.196	274.140	261.683	5.606	15.367	−8.098	0.940
500	37.316	278.066	263.128	7.469	−5.777	−8.748	0.914
600	37.494	284.886	266.203	11.210	−5.773	−9.342	0.813
700	37.627	290.676	269.296	14.966	−5.769	−9.937	0.742
800	37.734	295.708	272.290	18.734	−5.767	−10.533	0.688
900	37.827	300.158	275.144	22.513	−5.766	−11.129	0.646
1000	37.911	304.147	277.848	26.300	−5.767	−11.724	0.612
1100	37.989	307.764	280.406	30.095	−5.771	−12.320	0.585
1200	38.066	311.073	282.825	33.897	−5.781	−12.915	0.562
1300	38.143	314.123	285.117	37.708	−5.798	−13.509	0.543
1400	38.227	316.953	287.291	41.526	−5.828	−14.101	0.526
1500	38.323	319.593	289.358	45.354	−5.874	−14.690	0.512
1600	38.437	322.070	291.326	49.191	−5.939	−15.276	0.499
1700	38.576	324.405	293.203	53.042	−6.027	−15.857	0.487
1800	38.748	326.614	294.999	56.908	−6.139	−16.432	0.477
1900	38.962	328.715	296.718	60.793	−6.273	−17.000	0.467
2000	39.223	330.720	298.369	64.702	−6.427	−17.561	0.459
2100	39.538	332.641	299.955	68.639	−6.596	−18.114	0.451
2200	39.911	334.488	301.483	72.611	−6.771	−18.658	0.443
2300	40.347	336.272	302.957	76.624	−6.944	−19.194	0.436
2400	40.845	337.999	304.382	80.683	−7.104	−19.724	0.429
2500	41.408	339.678	305.760	84.795	−7.239	−20.247	0.423
2600	42.033	341.314	307.096	88.966	−7.337	−20.765	0.417
2700	42.718	342.913	308.393	93.203	−7.386	−21.280	0.412
2800	43.457	344.480	309.654	97.512	−7.374	−21.795	0.407
2900	44.245	346.018	310.882	101.896	−7.290	−22.311	0.402
3000	45.076	347.532	312.078	106.362	−7.124	−22.832	0.398
3100	45.942	349.024	313.246	110.913	−6.866	−23.359	0.394
3200	46.834	350.497	314.387	115.551	−6.508	−23.897	0.390
3300	47.745	351.952	315.503	120.280	−6.044	−24.447	0.387
3400	48.664	353.391	316.597	125.101	−5.469	−25.013	0.384
3500	49.585	354.815	317.668	130.013	−4.779	−25.597	0.382
3600	50.497	356.224	318.720	135.017	−3.972	−26.203	0.380
3700	51.393	357.620	319.752	140.112	−3.046	−26.833	0.379
3800	52.264	359.002	320.767	145.295	−2.001	−27.490	0.378
3900	53.105	360.371	321.765	150.564	−0.839	−28.176	0.377
4000	53.909	361.726	322.747	155.915	0.439	−28.893	0.377
4100	54.671	363.066	323.714	161.344	1.829	−29.643	0.378
4200	55.386	364.392	324.667	166.847	3.327	−30.429	0.378
4300	56.050	365.704	325.606	172.420	4.929	−31.251	0.380
4400	56.661	366.999	326.532	178.056	6.630	−32.112	0.381
4500	57.217	368.279	327.446	183.750	8.425	−33.012	0.383
4600	57.717	369.542	328.347	189.497	10.307	−33.954	0.386
4700	58.161	370.788	329.237	195.292	12.272	−34.937	0.388
4800	58.548	372.017	330.115	201.127	14.312	−35.963	0.391
4900	58.881	373.228	330.983	206.999	16.423	−37.032	0.395
5000	59.159	374.420	331.840	212.902	18.598	−38.145	0.398
5100	59.387	375.594	332.686	218.829	20.830	−39.302	0.403
5200	59.565	376.749	333.522	224.777	23.116	−40.503	0.407
5300	59.696	377.885	334.349	230.741	25.448	−41.749	0.411
5400	59.782	379.001	335.165	236.715	27.822	−43.039	0.416
5500	59.828	380.099	335.972	242.696	30.233	−44.373	0.421
5600	59.836	381.177	336.770	248.679	32.675	−45.751	0.427
5700	59.809	382.236	337.558	254.662	35.145	−47.174	0.432
5800	59.749	383.276	338.338	260.640	37.639	−48.640	0.438
5900	59.661	384.296	339.108	266.611	40.152	−50.149	0.444
6000	59.546	385.298	339.869	272.571	42.681	−51.701	0.450

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 95.94 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1007\ K$

$\Delta_f H°(0\ K) = -386.674 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -393.798 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 25.5\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution, $\Delta_{sol}H$, of KBr(cr) in H_2O(l) has been measured by many investigators. The results were reviewed in detail by Parker.[1] Eight pertinent $\Delta_{sol}H°$(aq, ∞) values are reproduced in the table below. Adopting the best value, $\Delta_f H°(298.15\ K) = 4.75 \pm 0.02$ kcal·mol^{-1}, for the reaction KBr(cr) = K^+(aq, ∞) + Br^-(aq, ∞), we derive $\Delta_f H°(298.15\ K) = -94.12$ kcal·mol^{-1} for KBr(cr) (−393.798 kJ·mol^{-1}). The auxiliary values $\Delta_f H°(298.15\ K) = -60.32$ and −29.05 kcal·mol^{-1} for K^+(aq, ∞) and Br^-(∞H_2O), respectively, are obtained from reference.[2]

$\Delta_{sol}H°$(aq, ∞)* kcal·mol^{-1}	T/°C	m**	Source
4.727	16.6	0.28	Walden[3]
4.777	25	0.37	Wust and Lange[4]
7.753	25	0.09	Chipman *et al.*[5]
4.684	20	0.19	Popov *et al.*[6]
4.889	23.5	0.14	Fedorov and Sil'chenko[7]
4.783	25	0.13	Lange and Martin[8]
4.542	20.5	0.12	Popov *et al.*[9]
4.739	25	0.28	Hietala[10]

*Values are adjusted to 298.15 K and to infinite dilution.
**Lowest experimental molality.

Heat Capacity and Entropy

The low temperature heat capacities, 2.9–272.2 K, were measured by Berg and Morrison[11] using an adiabatic calorimeter. The high temperature heat capacities, 325.25–711.75 K, are taken from Mustajoki.[12] These two sets of $C_p°$ data are joined smoothly at 298.15 K. The $C_p°$ values at temperatures, 720–1007 K, are extrapolated graphically, so that the derived enthalpy change $H°(1007\ K) - H°(298.15\ K) = 9.9$ kcal·mol^{-1} agrees with that determined by Dworkin.[13] The derived enthalpies at 700, 800 and 900 K are also in good agreement with those measured by Skuratov and Lapushkin.[14] The $C_p°$ values above 1007 K are obtained by graphical extrapolation.

The $S°(298.15\ K)$ is calculated from the adopted low temperature $C_p°$, based on $S°(2.9\ K) = 0.006276\ J \cdot K^{-1} \cdot mol^{-1}$.

The heat capacities of KBr(cr) were also measured by Nernst and Lindemann,[15] 78.7–89.2 K; Koref,[16] 137–234 K; and Clusius *et al.*[17] The enthalpies of KBr(cr) were determined by Magnus[18] and by Cooper.[19] The results are in reasonable agreement with the adopted functions except for those reported by Cooper.[14]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The heats of sublimation to monomer and dimer are calculated as the enthalpy changes for the following two reactions: KBr(cr) = KBr(g) and 2 KBr(cr) = K_2Br_2(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.213	−386.674	−386.674	INFINITE
100	43.145	42.949	140.561	−9.761	−387.351	−385.394	201.309
200	49.873	75.509	100.634	−5.025	−387.660	−383.321	100.113
298.15	52.379	95.939	95.939	0.	−393.798	−380.431	66.650
300	52.300	96.263	95.940	0.097	−393.826	−380.348	66.224
400	53.806	111.525	98.011	5.406	−411.235	−372.297	48.617
500	55.250	123.669	101.968	10.850	−410.744	−362.615	37.882
600	56.358	133.837	106.456	16.429	−410.065	−353.050	30.736
700	58.084	142.647	111.010	22.146	−409.212	−343.612	25.641
800	60.417	150.546	115.466	28.064	−408.148	−334.311	21.828
900	63.687	157.840	119.773	34.260	−406.816	−325.158	18.872
1000	68.011	164.764	123.928	40.836	−405.141	−316.171	16.515
1007.000	68.367	165.240	124.214	41.313	--- CRYSTAL <--> LIQUID ---		
1100	73.053	171.491	127.948	47.897	−481.989	−302.762	14.377
1200	76.860	178.018	131.850	55.402	−478.460	−286.622	12.476
1300	79.622	184.283	135.644	63.231	−474.610	−270.790	10.880
1400	81.797	190.265	139.333	71.304	−470.520	−255.263	9.524
1500	83.680	195.974	142.921	79.580	−466.233	−240.036	8.359

PREVIOUS: December 1961 CURRENT: March 1967

$S°(298.15\ K) = [105.540]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-376.492]\ kJ·mol^{-1}$

$T_{fus} = 1007\ K$ $\Delta_{fus}H° = 25.522\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1007\ K)–H°(298.15\ K)$, between the crystal and liquid.

Toguri *et al.*[1] studied the chemical equilibrium for the reaction KBr(l) + HCl(g) = KCl(l) + HBr(g). They obtained $\Delta_r G°(1073\ K) = 3.50 \pm 0.08$ and 3.54 kcal·mol^{-1} from partial pressure data and emf data, respectively. The corresponding value calculated from these tables is 3.78 kcal·mol^{-1}. Combination of the experimental results with JANAF auxiliary data leads to −89.70 and −89.74 kcal·mol^{-1} for $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

The heat capacity of 16.7 cal·K^{-1}·mol^{-1} (69.873 J·K^{-1}·mol^{-1}) was derived by Dworkin[2] from enthalpy data in the range 1010–1100 K. This $C_p°$ value is adopted here for the temperature range 298–2500 K.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted $T_{fus} = 1007\ K$ and $\Delta_{fus}H° = 6.1$ kcal·mol^{-1} (25.522 kJ·mol^{-1}) were determined by Johnson and Bredig[3] and Dworkin and Bredig,[4] respectively.

Enthalpies of melting of 6.2 kcal·mol^{-1} from phase diagram studies and 6.7 kcal·mol^{-1} from calorimetric measurements were obtained by Aukrust *et al.*[5]

Vaporization Data

The boiling point, $T_{vap} = 1671\ K$, is calculated as the temperature at which the sum of the partial pressures of KBr(g) and K_2Br_2(g) over KBr(l) equals one atmosphere. The value of $\Delta_{vap}H°$ is calculated as the enthalpy required to produce one mole of vapor mixture, which contains 19.5% dimer (K_2Br_2) and 80.5% monomer (KBr).

T_{vap} was reported to be 1648 and 1668 K by von Wartenberg and Albrecht[6] and Ruff and Mugdan,[7] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	69.873	105.540	105.540	0.	−376.492	−365.987	64.119
300	69.873	105.972	105.541	0.129	−376.487	−365.922	63.713
400	69.873	126.073	108.282	7.117	−392.218	−359.099	46.894
500	69.873	141.665	113.457	14.104	−390.185	−351.053	36.674
600	69.873	154.404	119.252	21.091	−388.097	−343.422	29.898
700	69.873	165.175	125.063	28.078	−385.974	−336.144	25.083
800	69.873	174.505	130.673	35.066	−383.840	−329.171	21.493
900	69.873	182.735	136.010	42.053	−381.718	−322.465	18.715
1000	69.873	190.097	141.057	49.040	−379.630	−315.994	16.506
1100	69.873	196.757	145.823	56.027	−456.553	−305.119	14.489
1200	69.873	202.836	150.324	63.015	−453.541	−291.485	12.688
1300	69.873	208.429	154.581	70.002	−450.532	−278.103	11.174
1400	69.873	213.607	158.615	76.989	−447.529	−264.951	9.885
1500	69.873	218.428	162.444	83.977	−444.531	−252.015	8.776
1600	69.873	222.938	166.085	90.964	−441.539	−239.278	7.812
1700	69.873	227.174	169.555	97.951	−438.554	−226.728	6.967
1800	69.873	231.167	172.868	104.938	−435.579	−214.354	6.220
1900	69.873	234.945	176.037	111.926	−432.615	−202.144	5.557
2000	69.873	238.529	179.073	118.913	−429.665	−190.091	4.965
2100	69.873	241.938	181.986	125.900	−426.731	−178.184	4.432
2200	69.873	245.189	184.785	132.888	−423.816	−166.417	3.951
2300	69.873	248.295	187.480	139.875	−420.923	−154.782	3.515
2400	69.873	251.269	190.076	146.862	−418.055	−143.272	3.118
2500	69.873	254.121	192.581	153.849	−415.215	−131.881	2.756

PREVIOUS: December 1961 CURRENT: March 1967

0 to	1007 K	crystal
above	1007 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.213	−386.674	−386.674	INFINITE
100	43.145	42.949	140.561	−9.761	−387.351	−385.394	201.309
200	49.873	75.509	100.634	−5.025	−387.660	−383.321	100.113
298.15	52.379	95.939	95.939	0.	−393.798	−380.431	66.650
300	52.300	96.263	95.940	0.097	−393.826	−380.348	66.224
400	53.806	111.525	98.011	5.406	−411.235	−372.297	48.617
500	55.250	123.669	101.968	10.850	−410.744	−362.615	37.882
600	56.358	133.837	106.456	16.429	−410.065	−353.050	30.736
700	58.084	142.647	111.010	22.146	−409.212	−343.612	25.641
800	60.417	150.546	115.466	28.064	−408.148	−334.311	21.828
900	63.687	157.840	119.773	34.260	−406.816	−325.158	18.872
1000	68.011	164.764	123.928	40.836	−405.141	−316.171	16.515
1007.000	68.367	165.240	124.214	41.313	CRYSTAL <--> LIQUID TRANSITION		
1007.000	69.873	190.585	124.214	66.835			
1100	69.873	196.757	130.090	73.333	−456.553	−305.119	14.489
1200	69.873	202.836	135.902	80.321	−453.541	−291.485	12.688
1300	69.873	208.429	141.269	87.308	−450.532	−278.103	11.174
1400	69.873	213.607	146.254	94.295	−447.529	−264.951	9.885
1500	69.873	218.428	150.906	101.283	−444.531	−252.015	8.776
1600	69.873	222.938	155.269	108.270	−441.539	−239.278	7.812
1700	69.873	227.174	159.375	115.257	−438.554	−226.728	6.967
1800	69.873	231.167	163.254	122.244	−435.579	−214.354	6.220
1900	69.873	234.945	166.929	129.232	−432.615	−202.144	5.557
2000	69.873	238.529	170.420	136.219	−429.665	−190.091	4.965
2100	69.873	241.938	173.745	143.206	−426.731	−178.184	4.432
2200	69.873	245.189	176.919	150.194	−423.816	−166.417	3.951
2300	69.873	248.295	179.955	157.181	−420.923	−154.782	3.515
2400	69.873	251.269	182.865	164.168	−418.055	−143.272	3.118
2500	69.873	254.121	185.659	171.155	−415.215	−131.881	2.756

PREVIOUS: CURRENT: March 1967

$S°(298.15) = 250.532\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -170.85 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -180.08 \pm 2.1\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 218.47\ cm^{-1}$ $\omega_e x_e = 0.7533\ cm^{-1}$ $\sigma = 1$
$B_e = 0.0807\ cm^{-1}$ $\alpha_e = 0.000401\ cm^{-1}$ $r_e = 2.821$ Å

Enthalpy of Formation

The enthalpy of formation is derived from the sublimation and vaporization data analyzed below. Numerous investigators have obtained total pressures by static methods or "apparent" pressures by effusion or transpiration. These pressures are converted to monomer pressures by use of functions [see $K_2Br_2(g)$ table] which are consistent with the dimer–monomer equilibrium data of Hagemark *et al.*[6] 2nd and 3rd law analyses of the monomer pressures show remarkable consistency over temperatures from 637 to 1668 K. The selected value of $\Delta_f H°(298\ K) = -43.04 \pm 0.5\ kcal·mol^{-1}$ ($-180.079 \pm 2.1\ kJ·mol^{-1}$) may be compared with $-43.8\ kcal·mol^{-1}$derived from $D°_0 = 3.95$ eV [which is reported by Gaydon[14]] based on atomic fluorescence data.

Source	Reaction	T/K	Data Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Wartenberg–Albrecht[1]	A	1368.15–1654.15	14	48.28 ± 0.31	46.70	−1.1 ± 0.2	−43.28
Ruff–Mugdan[2]	"	1361.15–1668.15	10	49.06 ± 0.56	47.16	−1.4 ± 0.4	−42.82
Fiock–Rodebush[3]	"	1179.15–1335.75	10	47.80 ± 0.05	46.95	−0.7 ± 0.1	−43.03
Hintz–Jellinek[4]	"	1523.15	1	–	47.34	–	−42.64
Murgulescu–Marta[5]	"	1373.15–1473.15	5	46.20 ± 1.15	47.69	1.1 ± 0.8	−42.29
Hagemark *et al.*[6]	"	1138.95–1416.02	26	47.15 ± 0.49	46.94	−0.2 ± 0.4	−43.04
Niwa[7]	B	823.15–923.15	6	48.04 ± 0.51	51.67	4.1 ± 0.6	−42.45
Mayer–Wintner[8]	"	884.90–929.40	6	56.15 ± 3.17	51.49	−5.2 ± 3.5	−42.63
Zimm–Mayer[9]	"	636.94–900.09	15	50.71 ± 0.21	50.58	−0.1 ± 0.2	−43.54

Reactions: (A) KBr(l) = KBr(g) (B) KBr(cr) = KBr(g)

Heat Capacity and Entropy

Rusk and Gordy[10] have investigated the pure rotational spectra of KBr in the 1.5 to 5.0 mm range of the microwave region by millimeter wave molecular beam spectroscopy. The reported values of ω_e, $\omega_e x_e$, B_e and r_e are adopted here and corrected to the average isotopic species. The value of α_e is obtained from Fabricand *et al.*[11] Molecular constants for KBr(g) have also been reported by Hertzberg[12] and Rice and Klemperer.[13] They are in good agreement with the values adopted. Herzberg[12] also lists an A state in 31770 cm^{-1} based on observed electronic spectra.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.109	−170.852	−170.852	INFINITE
100	33.058	211.876	282.656	−7.078	−170.949	−185.884	97.096
200	36.056	235.946	253.888	−3.588	−172.505	−200.253	52.301
250	36.600	244.056	251.138	−1.771	−173.469	−207.082	43.267
298.15	36.922	250.532	250.532	0.	−180.079	−212.804	37.282
300	36.932	250.761	250.533	0.068	−180.136	−213.007	37.088
350	37.155	256.471	250.983	1.921	−198.500	−217.498	32.460
400	37.316	261.444	251.987	3.783	−199.139	−220.168	28.751
450	37.440	265.846	253.287	5.652	−199.755	−222.760	25.857
500	37.541	269.796	254.744	7.526	−200.349	−225.284	23.535
600	37.701	276.656	257.841	11.289	−201.486	−230.163	20.037
700	37.829	282.477	260.955	15.066	−202.575	−234.856	17.525
800	37.940	287.536	263.968	18.854	−203.639	−239.394	15.631
900	38.041	292.011	266.840	22.653	−204.705	−243.800	14.150
1000	38.136	296.024	269.562	26.462	−205.796	−248.086	12.959
1100	38.226	299.663	272.135	30.280	−285.888	−247.650	11.760
1200	38.314	302.992	274.570	34.107	−286.036	−244.167	10.628
1300	38.400	306.063	276.876	37.943	−286.179	−240.672	9.670
1400	38.484	308.911	279.063	41.787	−286.318	−237.167	8.849
1500	38.568	311.569	281.143	45.640	−286.455	−233.651	8.136
1600	38.650	314.061	283.123	49.501	−286.589	−230.126	7.513
1700	38.732	316.407	285.013	53.370	−286.723	−226.593	6.962
1800	38.814	318.623	286.819	57.247	−286.858	−223.052	6.473
1900	38.895	320.724	288.549	61.132	−286.996	−219.504	6.035
2000	38.975	322.721	290.208	65.026	−287.139	−215.948	5.640
2100	39.056	324.624	291.802	68.927	−287.291	−212.385	5.283
2200	39.136	326.443	293.335	72.837	−287.454	−208.814	4.958
2300	39.216	328.184	294.813	76.755	−287.631	−205.236	4.661
2400	39.296	329.855	296.238	80.680	−287.824	−201.649	4.389
2500	39.376	331.461	297.615	84.614	−288.037	−198.054	4.138
2600	39.456	333.007	298.947	88.556	−288.273	−194.450	3.907
2700	39.535	334.497	300.236	92.505	−288.533	−190.837	3.692
2800	39.615	335.937	301.486	96.463	−288.822	−187.213	3.493
2900	39.694	337.328	302.698	100.428	−289.140	−183.579	3.307
3000	39.774	338.675	303.875	104.401	−289.491	−179.933	3.133
3100	39.853	339.981	305.018	108.383	−289.877	−176.275	2.970
3200	39.932	341.247	306.131	112.372	−290.301	−172.603	2.817
3300	40.012	342.477	307.214	116.369	−290.757	−168.919	2.674
3400	40.091	343.673	308.269	120.374	−291.260	−165.219	2.538
3500	40.170	344.836	309.297	124.387	−291.806	−161.505	2.410
3600	40.249	345.969	310.300	128.408	−292.401	−157.773	2.289
3700	40.328	347.073	311.279	132.437	−293.047	−154.025	2.174
3800	40.408	348.149	312.235	136.474	−293.747	−150.259	2.065
3900	40.487	349.200	313.169	140.519	−294.504	−146.473	1.962
4000	40.566	350.226	314.083	144.571	−295.315	−142.667	1.863
4100	40.645	351.229	314.977	148.632	−296.192	−138.841	1.769
4200	40.724	352.209	315.852	152.700	−297.140	−134.992	1.679
4300	40.803	353.168	316.708	156.777	−298.160	−131.119	1.593
4400	40.882	354.107	317.548	160.861	−298.978	−127.249	1.511
4500	40.961	355.027	318.370	164.953	−300.084	−123.334	1.432
4600	41.040	355.928	319.177	169.053	−301.262	−119.393	1.356
4700	41.119	356.811	319.969	173.161	−302.492	−115.428	1.283
4800	41.198	357.678	320.745	177.277	−303.687	−111.448	1.213
4900	41.277	358.528	321.508	181.401	−305.060	−107.429	1.145
5000	41.356	359.363	322.256	185.532	−306.507	−103.381	1.080
5100	41.435	360.183	322.992	189.672	−308.031	−99.304	1.017
5200	41.514	360.988	323.715	193.819	−309.630	−95.196	0.956
5300	41.593	361.779	324.426	197.975	−311.305	−91.056	0.897
5400	41.672	362.558	325.125	202.138	−313.057	−86.884	0.840
5500	41.751	363.323	325.812	206.309	−314.885	−82.679	0.785
5600	41.830	364.076	326.489	210.488	−316.787	−78.440	0.732
5700	41.909	364.817	327.155	214.675	−318.418	−74.214	0.680
5800	41.988	365.547	327.810	218.870	−320.421	−69.913	0.630
5900	42.067	366.265	328.456	223.073	−322.491	−65.576	0.581
6000	42.146	366.973	329.092	227.283	−324.625	−61.204	0.533

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = [74.06]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 823\ K$

$\Delta_f H°(0\ K)$ = unknown
$\Delta_f H°(298.15\ K) = -350.9 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.656\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiBr, cr, 298.15 K) = −83.87 kcal·mol^{-1}(−350.912 kJ·mol^{-1}) was calculated from the enthalpy of solution of lithium bromide (cr) at infinite dilution and the ionic enthalpies of formation of Li^+(aq,∞) and Br^-(aq, ∞).

Parker[1] reviewed the enthalpy of solution data in the literature and gave the "best" value, $\Delta_{sol}H^\infty = -11{,}670 \pm 50$ cal·mol^{-1} for LiBr(cr) → LiBr(aq,∞) at 298.15 K. The ionic enthalpy of formation, $\Delta_f H°(Li^+, aq, \infty\ 298.15\ K) = -66.49$ kcal·mol^{-1}, was calculated from $\Delta_f H°$(LiOH, aq, ∞ 298.15 K) = −121.46 kcal·mol^{-1} [2] with $\Delta_f H°(OH^-, aq, \infty\ 298.15\ K) = -54.97$ kcal·mol^{-1}.[3] The v$\Delta_f H°$(Br, aq, ∞, 298.15 K) = −29.05 kcal·mol^{-1} was also obtained from.[3] Combination of the ionic enthalpies of formation of Li^+(aq, ∞) and Br^-(aq, ∞) gives the enthalpy of formation of LiBr(aq, ∞), $\Delta_f H°(298.15\ K) = -95.54$ kcal·mol^{-1}.

Heat Capacity and Entropy

Dworkin[4] has measured the enthalpy changes by the drop method (723–883 K), yielding $H°(823;298) = 7.0$ kcal·mol^{-1} for the crystal at the melting point. Heat capacities derived from his data were $C_p°(773\ K) = 15.1$ and $C_p°(853\ K) = 15.6$ cal·K^{-1}·mol^{-1} for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of LiCl(cr), NaCl(cr) and NaBr(cr).

$S°(298.15\ K) = 17.7$ cal·K^{-1}·mol^{-1}(74.06 J·K^{-1}·mol^{-1}) was estimated by adding the entropy difference between NaBr(cr) and NaCl(cr) to the entropy of lithium chloride (cr) at 298.15 K. Comparisons with other alkali halides give results within ± 0.5 cal·K^{-1}·mol^{-1} of this value. Kelley[5] has estimated $C_p° = 11.50 + 3.02 \times 10^{-3}$ T cal·K^{-1}·mol^{-1} and $S°(298.15\ K) = 16.0 \pm 0.5$ cal·K^{-1}mol^{-1}.

Fusion Data

The selected enthalpy of fusion, $\Delta_{fus}H°(823\ K) = 4.22$ kcal·mol^{-1}(17.656 kJ·mol^{-1}), was obtained from enthalpy measurements in a drop calorimeter by Dworkin and Bredig.[6]

Kelley[7] reviewed some phase diagram studies of the lithium bromide system in the literature, and gave the enthalpy of fusion $\Delta_{fus}H°(825\ K) = 2.90$ kcal·mol^{-1}. Blanc[8] reported the enthalpy of fusion $\Delta_{fus}H°(819\ K) = 3.095$ kcal·mol^{-1} by a cryoscopic method. Both values are too low.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	48.919	74.057	74.057	0.	−350.912	−341.630	59.852
300	48.995	74.360	74.058	0.091	−350.937	−341.573	59.473
400	51.233	88.767	76.007	5.104	−365.764	−335.373	43.795
500	53.430	100.430	79.760	10.335	−368.312	−327.524	34.216
600	56.087	110.394	84.054	15.804	−367.686	−319.419	27.808
700	59.768	119.300	88.463	21.586	−366.698	−311.447	23.240
800	64.455	127.583	92.840	27.794	−365.263	−303.647	19.826
823.000	65.333	129.422	93.837	29.287	− − − CRYSTAL <− −> LIQUID − − −		
900	68.471	135.414	97.139	34.447	−363.383	−296.053	17.182
1000	71.379	142.787	101.339	41.448	−361.155	−288.689	15.080
1100	73.555	149.695	105.425	48.698	−358.678	−281.560	13.370
1200	75.228	156.172	109.387	56.142	−356.005	−274.666	11.956
1300	76.442	162.244	113.222	63.730	−353.191	−268.001	10.768
1400	77.278	167.942	116.929	71.418	−350.273	−261.557	9.759
1500	77.822	173.293	120.510	79.175	−347.283	−255.325	8.891
1600	78.199	178.329	123.968	86.977	−344.245	−249.293	8.139
1700	78.408	183.076	127.307	94.808	−486.412	−236.276	7.260
1800	78.576	187.563	130.531	102.658	−482.570	−221.673	6.433
1900	78.701	191.815	133.645	110.522	−478.721	−207.284	5.699
2000	78.743	195.853	136.655	118.395	−474.875	−193.097	5.043

PREVIOUS: September 1961 CURRENT: June 1966

$S°(298.15\ K) = [84.603]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-338.226]\ kJ·mol^{-1}$

$T_{fus} = 823\ K$ $\Delta_{fus}H° = 17.656\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding the $\Delta_{fus}H°$ and the difference in enthalpy, $H°(823\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Dworkin[1] has derived the heat capacity $C_p = 15.6\ cal·K^{-1}·mol^{-1}$ from enthalpy measurements (823–883 K) by the drop method. The liquid heat capacity was assumed to be constant as $15.6\ cal·K^{-1}·mol^{-1}$. $S°(298.15\ K)$ is obtained in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap}(l→monomer) is taken as the temperature at which the calculated Gibbs energy change is zero for LiBr(l) → LiBr(g), while $\Delta_{vap}H°$(l→monomer) is the corresponding enthalpy of vaporization.

T_{vap}(l→equilibrium mixture) is taken as the temperature at which the sum of the calculated partial vapor pressures of LiBr(g) and Li_2Br_2(g) reaches one bar (trimer and higher polymers have been neglected in calculation). This value (1562 K) is in good agreement with the boiling point (at 1 atm) of 1583 K obtained from total vapor pressure measurements by von Wartenberg and Schulz[2] and also the boiling point of 1538 K by Ruff and Mugdan.[3] $\Delta_{vap}H°$(l→equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 29.23 mole percent of dimer. For detailed information see LiBr(g) and Li_2Br_2(g) tables.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0.							
100							
200							
298.15	65.270	84.603	84.603	0.	−338.226	−332.088	58.181
300	65.270	85.007	84.605	0.121	−338.221	−332.050	57.815
400	65.270	103.784	87.165	6.648	−351.534	−327.150	42.721
500	65.270	118.349	91.999	13.175	−352.786	−320.957	33.530
600	65.270	130.249	97.413	19.702	−351.102	−314.748	27.401
700	65.270	140.311	102.841	26.229	−349.369	−308.825	23.045
800	65.270	149.026	108.081	32.756	−347.614	−303.153	19.794
900	65.270	156.714	113.066	39.283	−345.861	−297.701	17.278
1000	65.270	163.591	117.781	45.810	−344.107	−292.444	15.276
1100	65.270	169.812	122.233	52.337	−342.352	−287.363	13.646
1200	65.270	175.491	126.438	58.864	−340.597	−282.441	12.294
1300	65.270	180.715	130.415	65.391	−338.843	−277.666	11.157
1400	65.270	185.552	134.182	71.918	−337.086	−273.026	10.187
1500	65.270	190.056	137.759	78.445	−335.326	−268.511	9.350
1600	65.270	194.268	141.160	84.972	−333.563	−264.115	8.622
1700	65.270	198.225	144.402	91.499	−477.034	−252.652	7.763
1800	65.270	201.956	147.497	98.026	−474.514	−239.526	6.951
1900	65.270	205.485	150.457	104.553	−472.004	−226.539	6.228
2000	65.270	208.833	153.293	111.080	−469.503	−213.685	5.581

PREVIOUS: September 1961 CURRENT: June 1966

298.15	to	823	K	crystal
above		823	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0.							
100.							
200.							
298.15	48.919	74.057	74.057	0.	−350.912	−341.630	59.852
300	48.995	74.360	74.058	0.091	−350.937	−341.573	59.473
400	51.233	88.767	76.007	5.104	−365.764	−335.373	43.795
500	53.430	100.430	79.760	10.335	−368.312	−327.524	34.216
600	56.087	110.394	84.054	15.804	−367.686	−319.419	27.808
700	59.768	119.300	88.463	21.586	−366.698	−311.447	23.240
800	64.455	127.583	92.840	27.794	−365.263	−303.647	19.826
823.000	65.333	129.422	93.837	29.287	CRYSTAL <-> LIQUID TRANSITION		
823.000	65.270	150.876	93.837	46.944			
900	65.270	156.714	98.970	51.969	−345.861	−297.701	17.278
1000	65.270	163.591	105.094	58.496	−344.107	−292.444	15.276
1100	65.270	169.812	110.700	65.023	−342.352	−287.363	13.646
1200	65.270	175.491	115.866	71.550	−340.597	−282.441	12.294
1300	65.270	180.715	120.656	78.078	−338.843	−277.666	11.157
1400	65.270	185.552	125.121	84.605	−337.086	−273.026	10.187
1500	65.270	190.056	129.301	91.132	−335.326	−268.511	9.350
1600	65.270	194.268	133.231	97.659	−333.563	−264.115	8.622
1700	65.270	198.225	136.939	104.186	−477.034	−252.652	7.763
1800	65.270	201.956	140.449	110.713	−474.514	−239.526	6.951
1900	65.270	205.485	143.780	117.240	−472.004	−226.539	6.228
2000	65.270	208.833	146.949	123.767	−469.503	−213.685	5.581

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 224.345\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -146.3 \pm 13\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -154.0 \pm 13\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 563.16\ cm^{-1}$ $\omega_e x_e = 3.53\ cm^{-1}$ $\sigma = 1$

$B_e = 0.56112\ cm^{-1}$ $\alpha_e = 0.00573\ cm^{-1}$ $r_e = 2.1704$ Å

Enthalpy of Formation

$\Delta_f H°$(LiBr, g, 298.15 K) = -36.8 ± 3 kcal·mol^{-1} (-153.971 ± 13 kJ·mol^{-1}) is calculated from the selected enthalpy of vaporization and the enthalpy of formation for lithium bromide (l). Lithium bromide vaporizes to a mixture of monomeric and dimeric gases. (Higher polymers have been neglected in the calculation.) The enthalpies of vaporization to monomer and to dimer were chosen to satisfy (1) the total vapor pressure data measured by von Wartenberg and Schulz[1] and by Ruff and Mugdan;[2] the partial vapor pressures of monomer and dimer derived from Miller and Kusch[3] in an analysis of the velocity distribution of molecules in alkali halide vapor. The selected enthalpies of vaporization are $\Delta_{vap}H°$(larwrt|monomer, 298.15 K) = 44.0 ± 3 kcal·mol^{-1} and $\Delta_{vap}H°$(l→dimer, 298.15 K) = 42.0 ± 5 kcal·mol^{-1} which combine with the enthalpy of formation of lithium bromide (l), $\Delta_f H°(298.15\ K) = -80.84$ kcal·mol^{-1}, to give the standard enthaply of formation of LiBr(g) and $Li_2Br_2(g)$ − 36.8 and −119.7 kcal·mol^{-1} (−153.971 and −500.825 kJ·mol^{-1}), respectively. The derived enthaply of dissociation is $\Delta_d H°(298.15\ K) = 46.0$ kcal·mol^{-1} for $Li_2Br_2(g) \rightarrow 2LiBr(g)$.

Berkowitz *et al.*[4] have measured mass-spectrometrically the enthaply of dissociation $\Delta_r H°(850\ K) = 45.9$ kcal·mol^{-1}($\Delta_r H°(298.15\ K) = 46.9$ kcal·mol^{-1}) for $Li_2Br_2(g) \rightarrow 2LiBr(g)$ in a double oven apparatus by the 2nd law method. Hildenbrand *et al.*[5] have determined mass-spectrometrically the enthaply of sublimation of lithium bromide by the 2nd law method as $\Delta_{sub}H°$(cr → monomer, 740 K) = 46.9 and $\Delta_{sub}H°$(cr → dimer, 740 K) = 45.0 kcal·mol^{-1} (equivalent to $\Delta_{vap}H°$(l → monomer, 298.15 K) = 45.82 kcal·mol^{-1} and $\Delta_{vap}H°$(l → dimer, 298.15 K) = 41.93 kcal·mol^{-1}). These values are in reasonable agreement with those selected in the tabulation.

Heat Capacity and Entropy

The bond distance (r_e) was obtained from the microwave studies by Honig *et al.*[6] The vibrational constants (ω_e and $\omega_e x_e$) were determined from the infrared spectrum by Klemperer *et al.*[7] The rotational constants which have been corrected to the average isotopic species were obtained by Herbert *et al.*[8] using microwave spectra. Their data are in good agreement with those reported by Honig *et al.*[6] and Rusk and Gordy.[9]

The tabulated thermodynamic functions are in reasonable agreement with those calculated by Wilkins[10] who used slightly different molecular constants.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.177	−146.271	−146.271	INFINITE
100	29.297	190.290	252.948	−6.266	−145.252	−160.854	84.022
200	31.695	211.235	227.385	−3.230	−146.508	−176.048	45.979
250	32.974	218.450	224.899	−1.612	−147.426	−183.330	38.305
298.15	33.952	224.345	224.345	0.	−153.971	−189.498	33.199
300	33.985	224.555	224.345	0.063	−154.024	−189.718	33.033
350	34.753	229.854	224.762	1.782	−169.893	−194.785	29.070
400	35.336	234.534	225.697	3.535	−170.392	−198.308	25.896
450	35.785	238.724	226.916	5.314	−170.958	−201.764	23.420
500	36.136	242.513	228.289	7.112	−174.594	−204.847	21.400
600	36.646	249.149	231.228	10.753	−175.796	−210.783	18.350
700	36.995	254.826	234.204	14.436	−176.908	−216.525	16.157
800	37.252	259.784	237.098	18.149	−177.967	−222.112	14.502
900	37.451	264.183	239.867	21.884	−179.005	−227.568	13.208
1000	37.614	268.138	242.500	25.638	−180.024	−232.909	12.166
1100	37.752	271.729	244.996	29.406	−181.029	−238.148	11.309
1200	37.873	275.020	247.363	33.188	−182.019	−243.297	10.590
1300	37.981	278.055	249.609	36.980	−182.999	−248.364	9.979
1400	38.081	280.874	251.743	40.784	−183.966	−253.356	9.453
1500	38.174	283.504	253.773	44.596	−184.921	−258.279	8.994
1600	38.261	285.971	255.709	48.418	−185.863	−263.139	8.591
1700	38.345	288.293	257.559	52.248	−332.030	−260.764	8.012
1800	38.425	290.487	259.327	56.087	−332.199	−256.567	7.445
1900	38.503	292.567	261.023	59.933	−332.369	−252.360	6.938
2000	38.579	294.543	262.650	63.788	−332.541	−248.145	6.481
2100	38.653	296.428	264.214	67.649	−332.718	−243.920	6.067
2200	38.726	298.227	265.719	71.518	−332.901	−239.688	5.691
2300	38.798	299.950	267.170	75.394	−333.093	−235.447	5.347
2400	38.869	301.603	268.571	79.278	−333.295	−231.197	5.032
2500	38.939	303.191	269.924	83.168	−333.508	−226.938	4.742
2600	39.008	304.720	271.233	87.065	−333.736	−222.671	4.474
2700	39.077	306.193	272.501	90.970	−333.978	−218.395	4.225
2800	39.145	307.616	273.730	94.881	−334.236	−214.109	3.994
2900	39.213	308.990	274.922	98.799	−334.512	−209.814	3.779
3000	39.280	310.321	276.080	102.723	−334.806	−205.509	3.578
3100	39.347	311.610	277.205	106.655	−335.119	−201.194	3.390
3200	39.414	312.860	278.300	110.593	−335.451	−196.869	3.214
3300	39.480	314.074	279.366	114.537	−335.803	−192.533	3.048
3400	39.546	315.254	280.404	118.489	−336.175	−188.186	2.891
3500	39.612	316.401	281.416	122.447	−336.568	−183.828	2.743
3600	39.678	317.518	282.404	126.411	−336.981	−179.458	2.604
3700	39.744	318.606	283.367	130.382	−337.415	−175.076	2.472
3800	39.810	319.667	284.309	134.360	−337.870	−170.683	2.346
3900	39.875	320.702	285.229	138.344	−338.346	−166.277	2.227
4000	39.940	321.712	286.128	142.335	−338.843	−161.858	2.114
4100	40.005	322.699	287.008	146.332	−339.363	−157.427	2.006
4200	40.071	323.664	287.870	150.336	−339.905	−152.983	1.903
4300	40.136	324.607	288.713	154.346	−340.470	−148.526	1.804
4400	40.201	325.531	289.539	158.363	−341.038	−144.057	1.710
4500	40.265	326.435	290.349	162.386	−341.641	−139.574	1.620
4600	40.330	327.321	291.143	166.416	−342.270	−135.077	1.534
4700	40.395	328.189	291.922	170.452	−342.925	−130.566	1.451
4800	40.460	329.040	292.687	174.495	−343.605	−126.040	1.372
4900	40.524	329.875	293.437	178.544	−344.311	−121.500	1.295
5000	40.589	330.694	294.174	182.600	−345.046	−116.946	1.222
5100	40.653	331.499	294.898	186.662	−345.805	−112.377	1.151
5200	40.718	332.289	295.610	190.731	−346.598	−107.792	1.083
5300	40.782	333.065	296.309	194.806	−347.424	−103.192	1.017
5400	40.847	333.828	296.997	198.887	−348.283	−98.575	0.954
5500	40.911	334.578	297.673	202.975	−349.177	−93.943	0.892
5600	40.976	335.316	298.339	207.069	−350.108	−89.294	0.833
5700	41.040	336.041	298.994	211.170	−351.077	−84.628	0.776
5800	41.104	336.756	299.639	215.277	−352.086	−79.945	0.720
5900	41.169	337.459	300.274	219.391	−353.137	−75.244	0.666
6000	41.233	338.151	300.900	223.511	−354.231	−70.525	0.614

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 244.95 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -27.7 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -35.3 \pm 41.8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A_1{}^2\Pi_{1/2}$	25765.2	2
$A_2{}^2\Pi_{3/2}$	25876.3	2
$B[^2\Sigma]$	[26500]	2
$C[^2\Sigma]$	39285.9	2

$\omega_e = 373.2\ cm^{-1}$ $\omega_e x_e = 1.34\ cm^{-1}$ $\sigma = 1$
$B_e = 0.16241\ cm^{-1}$ $\alpha_e = [0.00079]\ cm^{-1}$ $r_e = 2.36 \pm 0.10$ Å

Enthaply of Formation

No thermochemical measurement of the enthaply of formation has been made. The selected value, $\Delta_f H°(MgBr, g, 0\ K) = -6.611 \pm 10.0$ kcal·mol^{-1} (-27.660 kJ·mol^{-1}), is based on an analysis of spectroscopic data. Herzberg[1] obtained the value $D_0° \leq 3.35$ eV from predissociation which sets in above v_3 = of A Π^2 state. Gaydon[2] recommended $D_0° = 3.2 \pm 1.0$ eV which was obtained from a linear Birge–Sponer extrapolation of the ground state vibrational levels (v, 0–6). Our adopted vibrational constants give this same value by a similar extrapolation. The linear Birge–Sponer $D_0°$ value adjusts to 3.03 eV (69.79 kcal·mol^{-1}) when corrected for the ionic character of the Mg–Br bond by the method suggested by Hildenbrand.[3] This adjusted $D_0°$ value is adopted and corresponds to $\Delta_f H°(298.15\ K)$ of -35.3 kJ·mol^{-1}.

Two lower values of $D_0°$ have been reported from results of ionic model calculations.[4,5] Margrave[4] calculated an ionic binding energy of 135 kcal·mol^{-1} which gives $D_0° = 1.75$ eV. Krasnov and Karaseva,[5] using a Rittner potential function[6], found $D_0° = 2.39$ eV which probably represents a minimum value. In addition, we find $D_0°(MgBr, g, 298.15\ K)/\Delta_{at}H°(MgBr_2, g, 298.15\ K) = 0.44$ which is quite consistent with values of this ratio for other alkaline–earth halides.[7] This consistency provides further support for our adopted results. An estimated uncertainty of ± 10.0 kcal·mol^{-1} (41.8 kJ·mol^{-1}) is believed to be realistic.

Heat Capacity and Entropy

Values for the ground state vibrational constants and bond length are taken from the tabulation of Rosen.[8] The adopted value of r_e which was obtained from a rotational analysis of the (0,0) bands of the $A^2\Pi$–$X^2\Sigma$ system by Patel and Patel[9,10] gives $r_e(MgBr)/r_e(MgBr_2) = 1.01$. Comparison of values for this ratio for several alkaline–earth halides[7] shows that $r_e(MX)/r_e(MX_2)$ is generally slightly less than one (~0.96). This suggests that the uncertainty in $r_e(MgBr)$ may be as high as 0.1 Å, assuming r_e for $MgBr_2$ is correct.[7] The value of B_e is calculated from r_e. α_e is obtained from the other constants assuming a Morse potential function.

The electronic levels except for the two uppe most states are from Rosen.[8] We estimate a $^2\Sigma$ state to lie at 26500 cm^{-1} by analogy with those observed for CaBr and SrBr.[7] The assignment o the level at 39285.9 cm^{-1} is rather uncertain. Rosen[8] has assigned this level as a $C^2\Pi$ state. Very recently, Reddy and Rao[11] observed that the bands were single-headed, and they attributed the system to a $C^2\Sigma$–$X^2\Sigma$ transition by analogy with that for MgF. Comparison of the observed spectra for MgCl, CaBr, SrBr, and BaBr[7] suggests yet another assignment. It appears likely that the observed level near 40000 cm^{-1} arises from a $D^2\Sigma$–$X^2\Sigma$ transition, and the $C^2\Pi$ state, estimated to lie near 30000 cm^{-1}, has gone unobserved. We tentatively adopt the assignment of Reddy and Rao.[11] However, thermodynamic functions based on the alternate assignments are not significantly different from those adopted, below 4500 K.

References

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[11] B. R. K. Reddy and P. T. Rao, Curr. Sci. **39**, 509 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.580	−27.670	−27.670	INFINITE
100	30.272	208.838	275.326	−6.649	−26.777	−44.018	22.993
200	33.916	231.036	248.160	−3.425	−28.011	−60.847	15.892
250	34.967	238.726	245.529	−1.701	−28.865	−68.960	14.408
298.15	35.639	244.946	244.946	0.	−35.342	−75.942	13.305
300	35.660	245.166	244.947	0.066	−35.392	−76.194	13.266
350	36.132	250.701	245.383	1.861	−51.184	−82.118	12.255
400	36.467	255.549	246.357	3.677	−51.577	−86.511	11.297
450	36.715	259.859	247.622	5.507	−51.988	−90.853	10.546
500	36.904	263.738	249.043	7.347	−52.418	−95.148	9.940
600	37.173	270.491	252.071	11.052	−53.341	−103.609	9.020
700	37.359	276.236	255.123	14.779	−54.355	−111.908	8.351
800	37.498	281.235	258.081	18.522	−55.476	−120.055	7.839
900	37.609	285.658	260.904	22.278	−56.721	−128.054	7.432
1000	37.703	289.625	263.582	26.044	−66.699	−135.195	7.062
1100	37.785	293.223	266.115	29.818	−68.247	−141.969	6.742
1200	37.860	296.514	268.513	33.601	−69.791	−148.603	6.469
1300	37.928	299.547	270.785	37.390	−71.333	−155.108	6.232
1400	37.993	302.360	272.941	41.186	−200.282	−158.328	5.907
1500	38.054	304.983	274.991	44.989	−200.467	−155.324	5.409
1600	38.113	307.441	276.943	48.797	−200.652	−152.309	4.972
1700	38.171	309.754	278.806	52.611	−200.837	−149.282	4.587
1800	38.227	311.937	280.586	56.431	−201.023	−146.244	4.244
1900	38.281	314.005	282.291	60.256	−201.210	−143.195	3.937
2000	38.335	315.970	283.927	64.087	−201.401	−140.137	3.660
2100	38.389	317.842	285.497	67.923	−201.596	−137.069	3.409
2200	38.441	319.629	287.009	71.765	−201.796	−133.992	3.181
2300	38.493	321.339	288.464	75.612	−202.001	−130.905	2.973
2400	38.545	322.978	289.868	79.464	−202.214	−127.809	2.782
2500	38.597	324.553	291.225	83.321	−202.434	−124.705	2.606
2600	38.649	326.068	292.536	87.183	−202.662	−121.591	2.443
2700	38.702	327.527	293.805	91.051	−202.898	−118.468	2.292
2800	38.755	328.936	295.034	94.924	−203.142	−115.337	2.152
2900	38.808	330.297	296.227	98.802	−203.396	−112.197	2.021
3000	38.863	331.613	297.385	102.685	−203.658	−109.047	1.899
3100	38.919	332.888	298.510	106.574	−203.930	−105.889	1.784
3200	38.976	334.125	299.603	110.469	−204.211	−102.722	1.677
3300	39.035	335.325	300.668	114.370	−204.501	−99.546	1.576
3400	39.097	336.491	301.704	118.276	−204.801	−96.361	1.480
3500	39.161	337.626	302.715	122.189	−205.111	−93.168	1.390
3600	39.228	338.730	303.700	126.108	−205.431	−89.965	1.305
3700	39.298	339.806	304.661	130.035	−205.761	−86.753	1.225
3800	39.372	340.855	305.600	133.968	−206.103	−83.532	1.148
3900	39.450	341.878	306.517	137.909	−206.457	−80.302	1.076
4000	39.531	342.878	307.413	141.858	−206.823	−77.062	1.006
4100	39.618	343.855	308.290	145.816	−207.203	−73.813	0.940
4200	39.708	344.811	309.149	149.782	−207.597	−70.555	0.877
4300	39.804	345.746	309.989	153.757	−208.006	−67.288	0.817
4400	39.905	346.663	310.812	157.743	−208.432	−64.010	0.760
4500	40.011	347.561	311.619	161.739	−208.874	−60.723	0.705
4600	40.123	348.441	312.410	165.745	−209.334	−57.426	0.652
4700	40.239	349.305	313.186	169.763	−209.814	−54.118	0.601
4800	40.362	350.154	313.947	173.793	−210.314	−50.800	0.553
4900	40.490	350.987	314.694	177.836	−210.835	−47.472	0.506
5000	40.623	351.807	315.428	181.891	−211.379	−44.132	0.461
5100	40.762	352.612	316.150	185.961	−211.946	−40.782	0.418
5200	40.907	353.405	316.858	190.044	−212.538	−37.420	0.376
5300	41.056	354.186	317.555	194.142	−213.155	−34.046	0.336
5400	41.212	354.955	318.241	198.256	−213.799	−30.661	0.297
5500	41.372	355.713	318.915	202.385	−214.470	−27.263	0.259
5600	41.537	356.459	319.579	206.530	−215.170	−23.853	0.222
5700	41.707	357.196	320.233	210.692	−215.899	−20.430	0.187
5800	41.882	357.923	320.876	214.872	−216.659	−16.995	0.153
5900	42.062	358.641	321.510	219.069	−217.450	−13.546	0.120
6000	42.245	359.349	322.135	223.284	−218.273	−10.083	0.088

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15)$ = [269.52 ± 8] J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = [464.4 ± 42] kJ·mol^{-1}
$\Delta_f H°(298.15)$ = [457.3 ± 42] kJ·mol^{-1}

Electronic Levels and Quantum Weights					
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[15199]	[6]	[15890]	[2]
[11783]	[2]	[15331]	[8]	[16796]	[2]
[12034]	[4]	[15428]	[10]	[16947]	[8]
[12417]	[6]	[15447]	[12]	[17174]	[4]
[12900]	[8]	[15691]	[6]	[17344]	[6]
[13461]	[10]	[15699]	[4]		

ω_e = [300] cm^{-1} $\omega_e x_e$ = [0.7] cm^{-1} σ = 1
B_e = [0.066] cm^{-1} α_e = [0.0002] cm^{-1} r_e = [2.42] Å

Enthaply of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ is that estimated by Brewer[1] using bonding models. The value of $\Delta_f H°(0\ K)$ combined with JANAF data[2] for Mo(g) and Br(g) gives $D°_0$(Mo–Br) = 310.87 ± 42 kJ·mol^{-1}. This value of the bond dissociation energy agrees favorably with the mean Mo–Br bond energy $\Delta_{at} H°(MoBr_4, g, 0\ K)/4$ = 317.98 kJ·mol^{-1}.[2]

Enthaply Capacity and Entropy

The Mo–Br bond length of 2.42 Å and the ground state vibrational frequency of 300 cm^{-1} are estimates from Brewer.[1] The electronic contributions are assumed to be the same as those of the free gaseous ion, Mo^+, as suggested by Brewer.[1] All states up to 17,344 cm^{-1} as listed by Moore[3] are included in the calculation. Our thermodynamic functions differ slightly from those reported by Brewer[1] due to the use of non–zero values for $\omega_e x_e$ and α_e. Estimates for α_e and $\omega_e x_e$ are based on the empirical correlations of Calder and Ruedenberg.[4]

References

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[2]JANAF Thermochemical Tables: Mo(g), 3–31–78; Br(g), 9–30–61; $MoBr_4$(g), 9–30–78.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.796	464.355	464.355	INFINITE
100	31.264	232.325	300.685	−6.836	465.427	445.589	−232.752
200	34.897	255.303	272.802	−3.500	464.470	426.047	−111.272
250	35.718	263.186	270.117	−1.733	463.711	416.526	−87.028
298.15	36.214	269.523	269.523	0.	457.311	408.172	−71.510
300	36.229	269.747	269.524	0.067	457.264	407.867	−71.016
350	36.566	275.359	269.966	1.887	441.545	400.504	−59.772
400	36.800	280.258	270.953	3.722	441.223	394.663	−51.538
450	36.971	284.603	272.233	5.566	440.882	388.863	−45.138
500	37.101	288.505	273.668	7.418	440.525	383.102	−40.022
600	37.285	295.287	276.723	11.138	439.769	371.687	−32.358
700	37.413	301.044	279.796	14.874	438.962	360.404	−26.894
800	37.509	306.047	282.772	18.620	438.111	349.239	−22.803
900	37.587	310.469	285.608	22.375	437.217	338.183	−19.628
1000	37.653	314.433	288.296	26.137	436.280	327.229	−17.093
1100	37.712	318.024	290.838	29.905	435.294	316.371	−15.023
1200	37.768	321.308	293.242	33.679	434.254	305.605	−13.303
1300	37.822	324.333	295.519	37.459	433.152	294.929	−11.850
1400	37.880	327.138	297.679	41.244	431.982	284.340	−10.609
1500	37.945	329.754	299.731	45.035	430.739	273.837	−9.536
1600	38.024	332.205	301.685	48.833	429.415	263.419	−8.600
1700	38.123	334.513	303.549	52.640	428.007	253.087	−7.776
1800	38.251	336.696	305.330	56.459	426.507	242.841	−7.047
1900	38.416	338.768	307.036	60.292	424.911	232.680	−6.397
2000	38.627	340.744	308.672	64.144	423.213	222.606	−5.814
2100	38.891	342.635	310.245	68.019	421.410	212.620	−5.289
2200	39.216	344.451	311.759	71.924	419.497	202.722	−4.813
2300	39.610	346.203	313.218	75.864	417.471	192.913	−4.381
2400	40.075	347.898	314.628	79.848	415.328	183.195	−3.987
2500	40.617	349.545	315.992	83.882	413.063	173.569	−3.627
2600	41.236	351.150	317.313	87.974	410.663	164.036	−3.296
2700	41.931	352.719	318.596	92.132	408.096	154.599	−2.991
2800	42.701	354.257	319.842	96.363	405.307	145.260	−2.710
2900	43.541	355.770	321.055	100.674	366.340	136.076	−2.451
3000	44.445	357.261	322.237	105.073	364.925	128.160	−2.231
3100	45.406	358.734	323.391	109.565	363.596	120.290	−2.027
3200	46.414	360.192	324.518	114.156	362.358	112.461	−1.836
3300	47.460	361.636	325.621	118.849	361.217	104.670	−1.657
3400	48.534	363.069	326.701	123.649	360.178	96.912	−1.489
3500	49.623	364.491	327.761	128.557	359.244	89.182	−1.331
3600	50.717	365.904	328.801	133.574	358.418	81.478	−1.182
3700	51.805	367.309	329.822	138.700	357.700	73.796	−1.042
3800	52.875	368.705	330.827	143.934	357.091	66.131	−0.909
3900	53.916	370.092	331.816	149.274	356.590	58.481	−0.783
4000	54.920	371.469	332.790	154.716	356.194	50.842	−0.664
4100	55.877	372.837	333.751	160.256	355.901	43.212	−0.551
4200	56.781	374.195	334.697	165.890	355.707	35.588	−0.443
4300	57.624	375.541	335.632	171.611	355.606	27.968	−0.340
4400	58.401	376.875	336.554	177.412	355.593	20.349	−0.242
4500	59.109	378.195	337.465	183.289	355.662	12.729	−0.148
4600	59.744	379.502	338.364	189.232	355.807	5.107	−0.058
4700	60.306	380.793	339.253	195.235	356.020	−2.520	0.028
4800	60.793	382.067	340.132	201.290	356.296	−10.151	0.110
4900	61.205	383.325	341.001	207.391	356.626	−17.788	0.190
5000	61.545	384.565	341.860	213.529	−234.380	−19.702	0.206
5100	61.815	385.787	342.709	219.698	−235.641	−15.396	0.158
5200	62.016	386.989	343.549	225.890	−237.013	−11.064	0.111
5300	62.153	388.172	344.380	232.099	−238.501	−6.705	0.066
5400	62.229	389.335	345.202	238.318	−240.111	−2.317	0.022
5500	62.248	390.477	346.014	244.543	−241.844	2.102	−0.020
5600	62.214	391.598	346.818	250.766	−243.706	6.554	−0.061
5700	62.131	392.699	347.614	256.984	−245.697	11.041	−0.101
5800	62.004	393.778	348.400	263.191	−247.820	15.563	−0.140
5900	61.837	394.837	349.178	269.383	−250.074	20.123	−0.178
6000	61.634	395.874	349.948	275.557	−252.464	24.722	−0.215

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = 235.48 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 308.4 \pm 21\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 300.8 \pm 21\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^3\Sigma^-$	0	3

$\omega_e = 699.1\ cm^{-1}$ $\omega_e x_e = 4.7\ cm^{-1}$ $\sigma = 1$
$B_e = 0.443\ cm^{-1}$ $\alpha_e = 0.00399\ cm^{-1}$ $r_e = 1.79$ Å

Enthaply of Formation

Miller and Dunford[1] have extrapolated the ground state vibrational levels and obtain $D_0^\circ = 67 \pm 5$ kcal·mol^{-1} or $\Delta_f H°(0\ K) = 73.7 \pm 5$ kcal·mol^{-1} (308.361 ± 21 kJ·mol^{-1}).

Heat Capacity and Entropy

Miller and Dunford[1] give all the vibrational and rotational constants, which have been adjusted to the normally occurring isotopic mixture for bromine.

Reference

[1]R. V. Miller and H. B. Dunford, J. Chem. Phys. **35**, 1202 (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.989	308.359	308.359	INFINITE
100	29.149	202.331	263.129	−6.080	308.421	298.871	−156.114
200	30.586	222.859	238.409	−3.110	307.484	289.653	−75.650
250	31.724	229.806	236.015	−1.552	306.907	285.261	−59.602
298.15	32.730	235.482	235.482	0.	300.758	281.804	−49.371
300	32.766	235.685	235.483	0.061	300.722	281.686	−49.046
350	33.634	240.803	235.885	1.721	285.329	279.359	−41.692
400	34.334	245.342	236.789	3.421	285.384	278.502	−36.369
450	34.892	249.419	237.969	5.152	285.462	277.638	−32.227
500	35.339	253.119	239.302	6.909	285.556	276.763	−28.913
600	35.997	259.625	242.162	10.478	285.774	274.985	−23.940
700	36.449	265.209	245.065	14.101	286.007	273.168	−20.384
800	36.774	270.099	247.895	17.763	286.237	271.318	−17.715
900	37.019	274.445	250.608	21.453	286.457	269.440	−15.638
1000	37.211	278.356	253.190	25.165	286.662	267.538	−13.975
1100	37.368	281.910	255.642	28.894	286.851	265.617	−12.613
1200	37.499	285.167	257.969	32.638	287.024	263.678	−11.478
1300	37.613	288.173	260.178	36.394	287.183	261.726	−10.516
1400	37.713	290.964	262.279	40.160	287.328	259.763	−9.692
1500	37.803	293.569	264.279	43.936	287.460	257.789	−8.977
1600	37.885	296.012	266.187	47.720	287.580	255.807	−8.351
1700	37.961	298.311	268.009	51.513	287.690	253.818	−7.799
1800	38.032	300.483	269.754	55.312	287.788	251.822	−7.308
1900	38.100	302.541	271.425	59.119	287.875	249.822	−6.868
2000	38.165	304.497	273.031	62.932	287.951	247.817	−6.472
2100	38.226	306.360	274.574	66.752	288.016	245.809	−6.114
2200	38.286	308.140	276.059	70.577	288.070	243.798	−5.788
2300	38.345	309.843	277.491	74.409	288.112	241.784	−5.491
2400	38.401	311.476	278.874	78.246	288.143	239.769	−5.218
2500	38.457	313.045	280.209	82.089	288.163	237.753	−4.968
2600	38.511	314.554	281.501	85.938	288.171	235.737	−4.736
2700	38.565	316.009	282.753	89.791	288.170	233.720	−4.522
2800	38.617	317.412	283.966	93.651	288.158	231.703	−4.322
2900	38.670	318.768	285.142	97.515	288.138	229.688	−4.137
3000	38.721	320.080	286.285	101.384	288.110	227.672	−3.964
3100	38.772	321.351	287.396	105.259	288.076	225.658	−3.802
3200	38.823	322.582	288.476	109.139	288.036	223.646	−3.651
3300	38.873	323.778	289.528	113.024	287.993	221.634	−3.508
3400	38.923	324.939	290.553	116.913	287.948	219.624	−3.374
3500	38.972	326.068	291.551	120.808	287.901	217.615	−3.248
3600	39.021	327.167	292.525	124.708	287.856	215.607	−3.128
3700	39.070	328.236	293.476	128.612	287.812	213.601	−3.016
3800	39.119	329.279	294.405	132.522	287.772	211.596	−2.909
3900	39.168	330.296	295.312	136.436	287.737	209.592	−2.807
4000	39.216	331.288	296.199	140.355	287.707	207.589	−2.711
4100	39.264	332.257	297.067	144.279	287.685	205.586	−2.619
4200	39.312	333.204	297.916	148.208	287.671	203.584	−2.532
4300	39.360	334.129	298.747	152.142	287.666	201.582	−2.449
4400	39.408	335.035	299.562	156.080	287.671	199.580	−2.369
4500	39.456	335.921	300.360	160.023	287.687	197.577	−2.293
4600	39.503	336.789	301.143	163.971	287.714	195.575	−2.221
4700	39.551	337.639	301.910	167.924	287.753	193.571	−2.151
4800	39.598	338.472	302.663	171.882	287.805	191.567	−2.085
4900	39.646	339.289	303.402	175.844	287.870	189.561	−2.021
5000	39.693	340.090	304.128	179.811	287.948	187.554	−1.959
5100	39.740	340.877	304.841	183.782	288.039	185.546	−1.900
5200	39.787	341.649	305.541	187.759	288.144	183.535	−1.844
5300	39.834	342.407	306.230	191.740	288.263	181.522	−1.789
5400	39.881	343.152	306.907	195.726	288.396	179.507	−1.736
5500	39.928	343.884	307.572	199.716	288.543	177.489	−1.686
5600	39.975	344.604	308.227	203.711	288.704	175.468	−1.637
5700	40.022	345.312	308.872	207.711	288.879	173.445	−1.589
5800	40.069	346.009	309.506	211.716	289.067	171.418	−1.544
5900	40.116	346.694	310.130	215.725	289.268	169.388	−1.500
6000	40.163	347.369	310.746	219.739	289.483	167.354	−1.457

PREVIOUS: December 1962 (1 atm) CURRENT: December 1962 (1 bar)

$S°(298.15\ K) = 273.52\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 91.41 \pm 0.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 82.13 \pm 0.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1801(1)
542 (1)
[265](1)

Ground State Quantum Weight: 1 σ = 1
Point Group: C_s
Bond Distances: O–N = 1.15 ± 0.04 Å; N–Br = 2.14 ± 0.02 Å
Bond Angle: O–N–Br = 117 ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 5.16414 \times 10^{-115}\ g^3·cm^6$

Enthaply of Formation

The chemical equilibrium of the reaction $2NO(g) + Br_2(g) = 2NOBr(g)$ has been studied by Trautz and Dalal,[1] Blair *et al.*,[2] and Krauss.[3] Using the reported equilibrium constants, the enthalpy changes $\Delta_r H°(298.15\ K)$, of this reaction are evaluated by both the 2nd and 3rd law methods. Based on the 3rd law $\Delta_r H°(298.15\ K)$ values, the enthaplies of formation for NOBr(g) are derived. The results obtained are presented in the table below. The value of $\Delta_f H°(NOBr, g, 298.15\ K)$ adopted is 19.63 ± 0.2 kcal·mol^{-1} (82.132 ± 0.8 kJ·mol^{-1}).

Source	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Trautz and Dalal[1]	*	258.2 – 603.2	−11.11	−11.30	−0.4	19.62
Blair *et al.*[2]	30	296.9 – 502.9	−11.74 + 0.07	−11.26	1.3 ± 0.2	19.64
Krauss[3]	23	264.0 – 290.1	−13.46 + 0.30	−9.62	−13.7 ± 1.1	20.46

*The data points employed for evaluation are calculated from a given equation.

Heat Capacity and Entropy

The molecular structure of NOBr(g) has been determined by electron diffraction by Ketelaar and Palmer.[4] The results were confirmed later by Weatherly and Williams,[5] who studied the microwave spectrum of NOBr(g) in the region 20000–40000 Mc/sec and analyzed the J = 2 → 3 transition. The values of bond length and angle adopted are obtained from Ketelaar and Palmer.[4] The infrared absorption spectrum of NOBr(g) has been examined from 400 to 5303 cm^{-1} by Burns and Bernstein.[6] The authors observed the first two fundamental vibrational frequencies and obtained the third from combination and overtones. These assignments are adopted. The principal moments of inertia are: $I_A = 0.9405 \times 10^{-39}$, $I_B = 22.9668 \times 10^{-39}$, and $I_C = 23.9093 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−11.654	91.410	91.410	INFINITE
100	36.257	228.950	311.488	−8.254	90.510	86.963	−45.425
200	42.124	256.017	277.590	−4.315	89.087	83.973	−21.931
250	44.073	265.637	274.266	−2.157	88.380	82.775	−17.295
298.15	45.473	273.525	273.525	0.	82.132	82.417	−14.439
300	45.520	273.806	273.526	0.084	82.092	82.419	−14.350
350	46.660	280.912	274.084	2.390	66.605	83.326	−12.436
400	47.623	287.207	275.339	4.747	66.571	85.717	−11.194
450	48.480	292.866	276.977	7.150	66.562	88.111	−10.228
500	49.264	298.015	278.827	9.594	66.573	90.505	−9.455
600	50.656	307.124	282.804	14.592	66.639	95.286	−8.295
700	51.831	315.023	286.855	19.718	66.748	100.053	−7.466
800	52.807	322.010	290.821	24.951	66.881	104.802	−6.843
900	53.609	328.278	294.640	30.274	67.031	109.533	−6.357
1000	54.266	333.961	298.293	35.668	67.187	114.247	−5.968
1100	54.804	339.159	301.775	41.123	67.347	118.945	−5.648
1200	55.248	343.947	305.092	46.626	67.506	123.629	−5.381
1300	55.615	348.385	308.254	52.170	67.660	128.300	−5.155
1400	55.922	352.518	311.270	57.747	67.809	132.959	−4.961
1500	56.179	356.385	314.150	63.352	67.951	137.607	−4.792
1600	56.397	360.018	316.904	68.982	68.082	142.247	−4.644
1700	56.583	363.443	319.542	74.631	68.202	146.878	−4.513
1800	56.742	366.681	322.072	80.297	68.309	151.503	−4.396
1900	56.880	369.753	324.501	85.979	68.402	156.122	−4.292
2000	57.000	372.674	326.837	91.673	68.477	160.737	−4.198
2100	57.104	375.457	329.087	97.378	68.535	165.349	−4.113
2200	57.196	378.116	331.255	103.093	68.575	169.958	−4.035
2300	57.276	380.660	333.349	108.817	68.594	174.566	−3.965
2400	57.348	383.099	335.371	114.548	68.592	179.173	−3.900
2500	57.412	385.442	337.327	120.286	68.569	183.781	−3.840
2600	57.469	387.695	339.222	126.030	68.525	188.390	−3.785
2700	57.520	389.864	341.057	131.780	68.461	193.002	−3.734
2800	57.566	391.957	342.838	137.534	68.375	197.616	−3.687
2900	57.607	393.978	344.567	143.293	68.271	202.233	−3.643
3000	57.645	395.932	346.247	149.055	68.147	206.855	−3.602
3100	57.679	397.822	347.880	154.821	68.007	211.481	−3.563
3200	57.710	399.654	349.469	160.591	67.850	216.111	−3.528
3300	57.739	401.430	351.017	166.363	67.679	220.747	−3.494
3400	57.765	403.154	352.525	172.139	67.495	225.388	−3.463
3500	57.789	404.829	353.996	177.916	67.300	230.034	−3.433
3600	57.811	406.457	355.431	183.696	67.095	234.687	−3.405
3700	57.831	408.042	356.831	189.478	66.882	239.345	−3.379
3800	57.850	409.584	358.199	195.262	66.662	244.010	−3.354
3900	57.867	411.087	359.536	201.048	66.437	248.680	−3.331
4000	57.884	412.552	360.843	206.836	66.208	253.355	−3.308
4100	57.899	413.982	362.122	212.625	65.977	258.037	−3.287
4200	57.913	415.377	363.374	218.416	65.744	262.724	−3.267
4300	57.926	416.740	364.599	224.207	65.510	267.417	−3.248
4400	57.938	418.072	365.799	230.001	65.277	272.115	−3.230
4500	57.949	419.374	366.975	235.795	65.045	276.818	−3.213
4600	57.960	420.648	368.128	241.590	64.815	281.527	−3.197
4700	57.970	421.895	369.259	247.387	64.587	286.240	−3.181
4800	57.979	423.115	370.368	253.184	64.361	290.959	−3.166
4900	57.988	424.311	371.457	258.983	64.138	295.682	−3.152
5000	57.996	425.482	372.526	264.782	63.918	300.410	−3.138
5100	58.004	426.631	373.576	270.582	63.701	305.142	−3.125
5200	58.012	427.757	374.607	276.383	63.486	309.878	−3.113
5300	58.019	428.862	375.620	282.184	63.274	314.619	−3.101
5400	58.025	429.947	376.616	287.986	63.064	319.363	−3.089
5500	58.032	431.012	377.595	293.789	62.856	324.111	−3.078
5600	58.037	432.057	378.559	299.593	62.650	328.863	−3.068
5700	58.043	433.085	379.506	305.397	62.444	333.618	−3.057
5800	58.048	434.094	380.439	311.201	62.238	338.378	−3.047
5900	58.054	435.086	381.357	317.006	62.032	343.140	−3.038
6000	58.058	436.062	382.260	322.812	61.825	347.907	−3.029

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 86.82 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1020\ K$

$\Delta_f H°(0\ K) = -354.30 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -361.41 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 26.108\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution of NaBr(cr) in water has been measured by Askew *et al.*[1] and Wallace[2] to be +0.01 and −0.144 kcal·mol^{-1}, respectively. Using $\Delta_f H°(Na^+, aq, 298.15\ K) = -57.39$ and $\Delta_f H°(Br^-, aq, 298.15\ K) = -29.05$ kcal·mol^{-1}, from Wagman,[3] the respective value of $\Delta_f H°(298.15\ K)$ for NaBr(cr) was found to be −86.3 and −86.45 kcal·mol^{-1}. The adopted value is the average of these two.

Heat Capacity and Entropy

The low temperature heat capacities (7.21–301.73 K) were measured by Gardner and Taylor.[4] The high temperature enthalpy changes (290–645, 290–816 K) were determined by Magnus.[5] Based upon the latter data, the high temperature heat capacities were derived. The two sets of $C_p°$ data were joined smoothly at 298.15 K by graphical method. $S°(298.15\ K)$ was obtained from Gardner and Taylor[4] using $S°(10\ K) = 0.034\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were reported by Dworkin and Bredig.[6] The values, $T_{fus} = 1014$ K and $\Delta_{fus}H° = 5.52$ kcal·mol^{-1}, reported by Blanc[7] were not used.

Sublimation Data

The value of $\Delta_{sub}H°(298.15\ K)$ was derived from six sets of vapor pressure data by both the 2nd and 3rd law methods. See the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.590	−354.302	−354.302	INFINITE
100	40.166	35.606	130.332	−9.473	−354.921	−353.408	184.601
200	48.744	66.818	91.420	−4.920	−355.275	−351.758	91.870
298.15	51.400	86.818	86.818	0.	−361.414	−349.267	61.190
300	51.442	87.136	86.819	0.095	−361.441	−349.192	60.800
400	53.451	102.226	88.863	5.345	−379.052	−341.804	44.635
500	54.852	114.311	92.784	10.764	−378.581	−332.542	34.740
600	56.066	124.419	97.236	16.310	−377.911	−323.394	28.154
700	57.321	133.156	101.757	21.979	−377.063	−314.372	23.459
800	58.576	140.892	106.175	27.774	−376.054	−305.484	19.946
900	59.831	147.864	110.426	33.694	−374.903	−296.730	17.222
1000	61.086	154.232	114.492	39.740	−373.631	−288.111	15.049
1020.000	61.337	155.445	115.284	40.964	--- CRYSTAL <---> LIQUID ---		
1100	62.342	160.113	118.376	45.911	−372.260	−279.625	13.278
1200	63.597	165.592	122.085	52.208	−467.569	−268.827	11.702
1300	64.852	170.732	125.631	58.631	−465.125	−252.364	10.140
1400	66.107	175.584	129.027	65.179	−462.561	−236.093	8.809
1500	67.345	180.187	132.286	71.851	−459.877	−220.010	7.661
1600	68.618	184.573	135.418	78.649	−457.072	−204.109	6.663
1700	69.925	188.772	138.434	85.576	−454.144	−188.388	5.788
1800	71.267	192.807	141.343	92.635	−451.091	−172.843	5.016
1900	72.645	196.697	144.155	99.830	−447.910	−157.471	4.329
2000	74.057	200.459	146.876	107.165	−444.598	−142.270	3.716

PREVIOUS: CURRENT: September 1964

$S°(298.15\ K) = [104.363]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1020\ K$

$\Delta_f H°(298.15\ K) = [-339.343]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 26.108\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(1020 K)–$H°$(298.15 K), between the crystal and liquid. The equilibrium constant of the reaction NaBr(l) + HCl(g) = NaCl(l) + HBr(g) has been determined by Toguri *et al.*[1] From the reported data, ln K(800°C) = −1.19 ± 0.01, the enthalpy of reaction ($\Delta_r H°$(298.15 K)) was derived to be 2.11 kcal·mol^{-1}. Using $\Delta_f H°$(HCl, g, 298.15 K) = −22.062, $\Delta_f H°$(NaCl, l, 298.15 K) = −92.24 and $\Delta_f H°$(HBr, g, 298.15 K) = 8.70 kcal·mol^{-1}, the value of $\Delta_f H°$(298.15 K) for NaBr(l) was evaluated to be −81.0 ± 0.5 kcal·mol^{-1} which is in reasonable agreement with the value adopted. The values of $\Delta_f H°$(298.15 K) for HCl(g) and HBr(g) were obtained from Wagman.[2]

Heat Capacity and Entropy

Heat capacity for NaBr(l) is estimated by comparison with those for NaCl(cr), NaCl(l), AgCl(cr), and AgCl(l). The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were reported by Dworkin and Bredig.[3] The values, T_{fus} = 1014 K and $\Delta_{fus}H°$ = 5.52 kcal·mol^{-1}, reported by Blanc,[4] were not used.

Vaporization Data

The boiling point, T_{vap}(l → monomer), is calculated as the temperature at which the value of $\Delta_r G° = 0$ for the reaction NaBr(l) → NaBr(g). The difference between $\Delta_f H°$ for NaBr(l) and NaBr(g) at T_{vap}(l → monomer) is the enthalpy of vaporization, $\Delta_{vap}H°$(l → monomer).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200.							
298.15	62.342	104.363	104.363	0.	−339.343	−332.427	58.240
300	62.342	104.749	104.364	0.115	−339.350	−332.384	57.873
400	62.342	122.683	106.810	6.349	−355.977	−326.912	42.690
500	62.342	136.594	111.427	12.584	−354.690	−319.792	33.408
600	62.342	147.961	116.598	18.818	−353.332	−312.939	27.244
700	62.342	157.571	121.782	25.052	−351.919	−306.318	22.858
800	62.342	165.895	126.787	31.286	−350.470	−299.903	19.582
900	62.342	173.238	131.549	37.520	−349.005	−293.670	17.044
1000	62.342	179.806	136.052	43.754	−347.545	−287.600	15.023
1100	62.342	185.748	140.304	49.989	−346.111	−281.675	13.376
1200	62.342	191.172	144.320	56.223	−441.483	−273.439	11.902
1300	62.342	196.162	148.119	62.457	−439.228	−259.526	10.428
1400	62.342	200.782	151.717	68.691	−436.977	−245.788	9.170
1500	62.342	205.084	155.133	74.925	−434.731	−232.210	8.086
1600	62.342	209.107	158.382	81.159	−432.490	−218.781	7.142
1700	62.342	212.886	161.478	87.394	−430.256	−205.493	6.314
1800	62.342	216.450	164.434	93.628	−428.027	−192.336	5.581
1900	62.342	219.820	167.262	99.862	−425.807	−179.303	4.929
2000	62.342	223.018	169.970	106.096	−423.596	−166.386	4.346
2100	62.342	226.060	172.569	112.330	−421.395	−153.580	3.820
2200	62.342	228.960	175.067	118.564	−419.205	−140.878	3.345
2300	62.342	231.731	177.471	124.799	−417.028	−128.276	2.913
2400	62.342	234.384	179.787	131.033	−414.864	−115.768	2.520
2500	62.342	236.929	182.023	137.267	−412.716	−103.349	2.159

PREVIOUS: CURRENT: September 1964

0	to 1020	K	crystal
above	1020	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.590	−354.302	−354.302	INFINITE
100	40.166	35.606	130.332	−9.473	−354.921	−353.408	184.601
200	48.744	66.818	91.420	−4.920	−355.275	−351.758	91.870
298.15	51.400	86.818	86.818	0.	−361.414	−349.267	61.190
300	51.442	87.136	86.819	0.095	−361.441	−349.192	60.800
400	53.451	102.226	88.863	5.345	−379.052	−341.804	44.635
500	54.852	114.311	92.784	10.764	−378.581	−332.542	34.740
600	56.066	124.419	97.236	16.310	−377.911	−323.394	28.154
700	57.321	133.156	101.757	21.979	−377.063	−314.372	23.459
800	58.576	140.892	106.175	27.774	−376.054	−305.484	19.946
900	59.831	147.864	110.426	33.694	−374.903	−296.730	17.222
1000	61.086	154.232	114.492	39.740	−373.631	−288.111	15.049
1020.000	61.337	155.445	115.284	40.964	CRYSTAL <--> LIQUID		
1020.000	62.342	181.041	115.284	67.072	TRANSITION		
1100	62.342	185.748	120.239	72.060	−346.111	−281.675	13.376
1200	62.342	191.172	125.928	78.294	−441.483	−273.439	11.902
1300	62.342	196.162	131.141	84.528	−439.228	−259.526	10.428
1400	62.342	200.782	135.952	90.762	−436.977	−245.788	9.170
1500	62.342	205.084	140.419	96.996	−434.731	−232.210	8.086
1600	62.342	209.107	144.588	103.230	−432.490	−218.781	7.142
1700	62.342	212.886	148.496	109.465	−430.256	−205.493	6.314
1800	62.342	216.450	152.173	115.699	−428.027	−192.336	5.581
1900	62.342	219.820	155.645	121.933	−425.807	−179.303	4.929
2000	62.342	223.018	158.935	128.167	−423.596	−166.386	4.346
2100	62.342	226.060	162.059	134.401	−421.395	−153.580	3.820
2200	62.342	228.960	165.035	140.635	−419.205	−140.878	3.345
2300	62.342	231.731	167.875	146.870	−417.028	−128.276	2.913
2400	62.342	234.384	170.591	153.104	−414.864	−115.768	2.520
2500	62.342	236.929	173.194	159.338	−412.716	−103.349	2.159

PREVIOUS: CURRENT: September 1964

$S°(298.15\ K) = 241.218\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -135.04 \pm 2.09\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -143.93 \pm 2.09\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 302.1 \pm 4\ cm^{-1}$ $\omega_e x_e = 1.50\ cm^{-1}$ $\sigma = 1$
$B_e = 0.1495\ cm^{-1}$ $\alpha_e = 0.000939\ cm^{-1}$ $r_e = 2.5020 \pm 0.0001$ Å

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from $\Delta_f H°(298.15\ K)$ and $\Delta_{sub} H°(298.15\ K)$ for NaBr(cr). The latter was derived by both the 2nd and 3rd law methods from six sets of vapor pressure data, corrected for the presence of dimer species in the vapor. The results are listed as follows.

Source	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$[a] kcal·mol^{-1}
Niwa[1]	NaBr(cr) → NaBr(g)	50.31	51.97	−35.24
Cogin and Kimball[2]	NaBr(cr) → NaBr(g)	52.14	52.26	−34.18
Mayer and Wintner[3]	NaBr(cr) → NaBr(g)	65.30	52.59	−33.79[b]
Ruff and Mugdan[4]	NaBr(l) → NaBr(g)	47.48	46.43	−34.15
Wartenberg and Albrecht[5]	NaBr(l) → NaBr(g)	47.54	46.38	−34.15
Bloom *et al.*[6]	NaBr(l) → NaBr(g)	51.53	46.23	−34.88[b]

[a]Based on the average of the 2nd and 3rd law values.
[b]Only the 3rd law value being used.

The value of $\Delta_f H°$(NaBr, g, 298.15 K) = −34.40 ± 0.50 kcal·mol^{-1} (−143.930 kJ·mol^{-1}) adopted is the average value of the six $\Delta_f H°(298.15\ K)$ values listed in the above table. The dissociation energy was calculated to be 86.28 kcal·mol^{-1} or 3.74 eV which is in good agreement with the values, 3.84 ± 1 and 3.85 eV, reported by Gaydon[7] and Herzberg,[8] respectively. According to Brewer,[9] Gaydon's original reported value, $D_0° = 3.8$, is an average of the value of 3.84 eV from atomic fluorescence and the value of 3.75 eV calculated for Gaydon by Brewer from pressure data available at that time.

Heat Capacity and Entropy

The values of ω_e, $\omega_e x_e$, B_e and α_e were taken from Rice and Klemperer.[10] The adopted bond distance (r_e) reported by Honing *et al.*[11] was derived from microwave spectrum. By electron–diffraction method, the Na–Br bond distance was determined as 2.64 ± 0.01 Å by Maxwell *et al.*[12] The discrepancy may be due to the presence of a large proportion of dimer at the higher pressures used in the electron–diffraction determination. The ground state configuration was reported by G. Herzberg.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.807	−135.035	−135.035	INFINITE
100	31.273	203.967	272.441	−6.847	−134.812	−150.135	78.422
200	34.956	226.965	244.505	−3.508	−136.379	−164.890	43.065
250	35.803	234.864	241.813	−1.737	−137.340	−171.910	35.919
298.15	36.323	241.218	241.218	0.	−143.930	−177.817	31.153
300	36.339	241.443	241.219	0.067	−143.984	−178.027	30.997
350	36.699	247.073	241.663	1.894	−159.936	−182.814	27.283
400	36.957	251.991	242.653	3.735	−163.178	−185.836	24.268
450	37.150	256.356	243.937	5.588	−163.808	−188.630	21.896
500	37.301	260.278	245.379	7.450	−164.411	−191.355	19.991
600	37.529	267.100	248.447	11.192	−165.545	−196.636	17.119
700	37.699	272.899	251.536	14.954	−166.604	−201.733	15.054
800	37.837	277.942	254.529	18.731	−167.612	−206.682	13.495
900	37.957	282.405	257.383	22.520	−168.592	−211.507	12.276
1000	38.065	286.410	260.089	26.322	−169.565	−216.223	11.294
1100	38.165	290.043	262.649	30.133	−170.553	−220.841	10.487
1200	38.260	293.368	265.073	33.954	−268.339	−222.928	9.704
1300	38.351	296.434	267.369	37.785	−268.487	−219.138	8.805
1400	38.440	299.279	269.547	41.625	−268.631	−215.337	8.034
1500	38.526	301.934	271.619	45.473	−268.770	−211.525	7.366
1600	38.611	304.423	273.592	49.330	−268.907	−207.704	6.781
1700	38.695	306.767	275.476	53.195	−269.041	−203.875	6.264
1800	38.778	308.981	277.276	57.069	−269.173	−200.038	5.805
1900	38.860	311.080	279.000	60.950	−269.305	−196.193	5.394
2000	38.941	313.075	280.655	64.840	−269.438	−192.342	5.023
2100	39.022	314.977	282.244	68.739	−269.573	−188.484	4.688
2200	39.103	316.794	283.774	72.645	−269.711	−184.619	4.383
2300	39.183	318.534	285.247	76.559	−269.854	−180.748	4.105
2400	39.263	320.203	286.669	80.481	−270.002	−176.871	3.849
2500	39.342	321.808	288.043	84.412	−270.158	−172.987	3.614
2600	39.422	323.352	289.371	88.350	−270.321	−169.097	3.397
2700	39.501	324.841	290.658	92.296	−270.492	−165.201	3.196
2800	39.580	326.279	291.904	96.250	−270.674	−161.298	3.009
2900	39.660	327.670	293.114	100.212	−270.865	−157.388	2.835
3000	39.739	329.016	294.288	104.182	−271.066	−153.472	2.672
3100	39.817	330.320	295.430	108.160	−271.279	−149.548	2.520
3200	39.896	331.585	296.540	112.146	−271.502	−145.618	2.377
3300	39.975	332.814	297.621	116.139	−271.737	−141.681	2.243
3400	40.054	334.009	298.673	120.141	−271.985	−137.736	2.116
3500	40.132	335.171	299.700	124.150	−272.246	−133.784	1.997
3600	40.211	336.303	300.701	128.167	−272.519	−129.824	1.884
3700	40.289	337.405	301.678	132.192	−272.807	−125.856	1.777
3800	40.368	338.481	302.632	136.225	−273.110	−121.880	1.675
3900	40.446	339.530	303.565	140.265	−273.429	−117.897	1.579
4000	40.524	340.555	304.477	144.314	−273.766	−113.904	1.487
4100	40.603	341.557	305.369	148.370	−274.121	−109.903	1.400
4200	40.681	342.536	306.243	152.434	−274.494	−105.894	1.317
4300	40.759	343.495	307.098	156.506	−274.892	−101.875	1.238
4400	40.837	344.433	307.936	160.586	−275.271	−97.850	1.162
4500	40.916	345.351	308.757	164.674	−275.695	−93.813	1.089
4600	40.994	346.251	309.562	168.769	−276.153	−89.767	1.019
4700	41.072	347.134	310.352	172.873	−276.638	−85.710	0.953
4800	41.150	347.999	311.128	176.984	−277.153	−81.642	0.888
4900	41.228	348.849	311.889	181.103	−277.700	−77.563	0.827
5000	41.307	349.682	312.636	185.230	−278.273	−73.474	0.768
5100	41.385	350.501	313.371	189.364	−278.888	−69.371	0.711
5200	41.463	351.305	314.093	193.506	−279.543	−65.257	0.656
5300	41.541	352.096	314.802	197.657	−280.239	−61.129	0.602
5400	41.619	352.873	315.500	201.815	−280.979	−56.988	0.551
5500	41.697	353.638	316.187	205.981	−281.766	−52.833	0.502
5600	41.775	354.390	316.862	210.154	−282.601	−48.664	0.454
5700	41.853	355.130	317.527	214.336	−283.488	−44.478	0.408
5800	41.931	355.858	318.182	218.525	−284.428	−40.277	0.363
5900	42.010	356.576	318.826	222.722	−285.424	−36.059	0.319
6000	42.088	357.282	319.461	226.927	−286.319	−31.842	0.277

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

D_0^o = 19332 ± 200 cm^{-1}
S^o(298.15 K) = 232.97 ± 0.1 J·K^{-1}·mol^{-1}

$\Delta_f H^o$(0 K) = 133.3 ± 2.4 kJ·mol^{-1}
$\Delta_f H^o$(298.15 K) = 125.8 ± 2.4 kJ·mol^{-1}

Electronic Levels and Molecular Constants ($^{79}Br^{16}O$), cm^{-1}

State	T_e	g_i	ω_e	$\omega_e x_e$	$\omega_e y_e$	B_e	α_e	$D_e \cdot 10^6$	r_e/Å
$X^2\Pi_{3/2}$	0	2	727.05	4.932	–	0.4299	0.003639	0.594	1.717
$X^2\Pi_{1/2}$	968	2	727.05	4.932	–	0.4299	0.003639	0.594	1.717
$A^2\Pi_{3/2}$	27871	2	511.3	4.83	−0.074	0.314	0.0034	0.474	1.95
$A^2\Pi_{1/2}$	[29321]	2	511.3	4.8	−0.074	0.314	0.0034	0.474	1.95

Point Group: $C_{\infty v}$ σ=1

Enthalpy of Formation

The two existing spectroscopic studies by Coleman and Gaydon[1] and Durie and Ramsay[2] yield dissociation energy values for BrO(g). One should note, with respect to those studies, that the first bound excited state $A^2\Pi$ of BrO(g) dissociates to $Br(^2P_{3/2}) + O(^1D_2)$. A linear Birge–Sponer extrapolation of the Coleman and Gaydon[1] data gave 17800 cm^{-1} or 213.2 kJ·mol^{-1} for the ground state dissociation energy. Assuming the extrapolation was high by up to 20%, they recommended 1.75 ± 0.3 eV or 170 ± 29 kJ·mol^{-1}. Durie and Ramsay,[2] from a graphical Birge–Sponer extrapolation, calculated a dissociation energy of D_0^o = 19332 ± 200 cm^{-1} or 231.6 ± 2.4 kJ·mol^{-1}. The latter value leads to the present adopted value for $\Delta_f H^o$(298.15 K) for BrO(g) of 125.8 ± 2.4 kJ·mol^{-1}. Additional data needed for the calculations presented here, e.g. thermal functions for the Br(g), and Br_2(ref), O(g), and O_2(ref), are taken from the JANAF Thermochemical Tables.[3]

Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{79}Br^{16}O$ isotopomer. Isotopic relationships[4] are used to convert the above constants to those for the normally occurring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X and A states are included in the calculation of the thermal functions; a sum–over–states technique is used.

Values of ω_e and $\omega_e x_e$ given in the table above for the ground state are from Butler *et al.*,[5] while those for the first excited state are from Barnett *et al.*[6] These values in fact described an average $^2\Pi$ state; there are differences in the vibrational constants for the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ states but they are not considered in this calculation. The B_e value for the ground state is from Amano *et al.*[7] The internuclear distance and value for B_e for the A state are from Barnett *et al.*[6] The value of D_e for the excited state was estimated.[4] Barnett *et al.*[6] gave a dissociation energy of 8960 cm^{-1} for the A state which is used in conjunction with T_e to provide an energy cutoff from the sum–over–states calculation on the excited state.

Previously, the value of the spin orbit constant, A_o, for the inverted doublet $X^2\Pi$ ground state adopted by Huber and Herzberg[8] was an average based on two values derived from the EPR spectra studies: A_o = −815 cm^{-1} of Carrington *et al.*[9] and A_o = −980 cm^{-1} of Brown *et al.*[10] The recent measured value of McKellar,[11] A_o = −968 cm^{-1}, for the spin–orbit splitting of the ground state is adopted here. For ClO the spin–orbit splitting of the A state is approximately 1.5 times the value found for the ground state.[12] Using the same factor of 1.5, the spin–orbit splitting for the A state in BrO is estimated to be 1450 cm^{-1}.

Numerous excited states have been estimated by Monks *et al.*[13] and observed by Duignan and Hudgens.[14] These states are not fully characterized in terms of vibrational and rotational constants and do not contribute significantly to the thermal functions below 6000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p^o = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	C_p^o	S^o	$-[G^o-H^o(T_r)]/T$	$H^o-H^o(T_r)$	$\Delta_f H^o$	$\Delta_f G^o$	log K_f
0	0.0	0.0	INFINITE	−9.061	133.305	133.305	INFINITE
50	29.103	179.334	331.631	−7.615	133.611	129.149	−134.918
100	29.139	199.511	261.104	−6.159	133.358	124.765	−65.169
150	29.592	211.388	242.681	−4.694	132.932	120.555	−41.980
200	30.805	220.050	235.985	−3.187	132.424	116.505	−30.427
250	32.493	227.101	233.523	−1.606	131.869	112.588	−23.523
298.15	34.182	232.970	232.970	0.000	125.770	109.582	−19.198
300	34.244	233.182	232.971	0.063	125.736	109.482	−19.062
400	37.062	243.447	234.351	3.638	110.586	107.200	−13.999
500	38.719	251.915	237.042	7.436	111.008	106.307	−11.105
600	39.525	259.055	240.132	11.354	111.486	105.321	−9.169
700	39.839	265.176	243.283	15.325	111.960	104.256	−7.780
800	39.901	270.502	246.360	19.313	112.405	103.125	−6.733
900	39.846	275.199	249.308	23.301	112.808	101.940	−5.916
1000	39.746	279.392	252.111	27.281	113.170	100.713	−5.261
1100	39.634	283.175	254.766	31.250	113.493	99.451	−4.722
1200	39.528	286.619	257.279	35.208	113.780	98.162	−4.273
1300	39.437	289.779	259.659	39.156	114.036	96.850	−3.891
1400	39.361	292.699	261.916	43.096	114.265	95.519	−3.564
1500	39.301	295.412	264.060	47.029	114.467	94.173	−3.279
1600	39.256	297.947	266.099	50.957	114.647	92.814	−3.030
1700	39.225	300.326	268.043	54.881	114.805	91.445	−2.810
1800	39.2 05	302.568	269.900	58.802	114.942	90.066	−2.614
1900	39.194	304.687	271.675	62.722	115.057	88.681	−2.438
2000	39.189	306.697	273.377	66.641	115.153	87.291	−2.280
2100	39.189	308.609	275.009	70.560	115.226	85.895	−2.136
2200	39.189	310.432	276.578	74.479	115.279	84.497	−2.006
2300	39.188	312.174	278.088	78.398	115.310	83.098	−1.887
2400	39.182	313.842	279.544	82.316	115.318	81.697	−1.778
2500	39.168	315.441	280.948	86.234	115.303	80.296	−1.678
2600	39.145	316.977	282.304	90.150	115.264	78.897	−1.585
2700	39.110	318.454	283.616	94.062	115.201	77.498	−1.499
2800	39.061	319.875	284.886	97.971	115.112	76.103	−1.420
2900	38.996	321.245	286.116	101.874	114.998	74.711	−1.346
3000	38.915	322.566	287.309	105.770	114.858	73.325	−1.277
3100	38.817	323.840	288.467	109.656	114.690	71.945	−1.212
3200	38.701	325.071	289.592	113.532	114.496	70.568	−1.152
3300	38.568	326.260	290.685	117.396	114.276	69.198	−1.095
3400	38.418	327.409	291.748	121.245	114.028	67.836	−1.042
3500	38.251	328.520	292.783	125.079	113.755	66.483	−0.992
3600	38.068	329.595	293.791	128.895	113.453	65.136	−0.945
3700	37.871	330.635	294.773	132.692	113.124	63.796	−0.901
3800	37.661	331.643	295.730	136.469	112.769	62.471	−0.859
3900	37.439	332.618	296.663	140.224	112.389	61.150	−0.819
4000	37.205	333.563	297.574	143.956	111.980	59.840	−0.781
4100	36.%3	334.479	298.463	147.665	111.547	58.545	−0.746
4200	36.712	335.366	299.331	151.349	111.088	57.255	−0.712
4300	36.454	336.227	300.179	155.007	110.603	55.980	−0.680
4400	36.191	337.062	301.008	158.639	110.093	54.717	−0.650
4500	35.924	337.873	301.818	162.245	109.559	53.463	−0.621
4600	35.654	338.659	302.611	165.824	108.999	52.222	−0.593
4700	35.382	339.423	303.386	169.376	108.416	50.994	−0.567
4800	35.108	340.165	304.144	172.900	107.809	49.780	−0.542
4900	34.835	340.886	304.887	176.397	107.177	48.579	−0.518
5000	34.562	341.587	305.614	179.867	106.523	47.388	−0.495
5100	34.291	342.269	306.326	183.310	105.844	46.213	−0.473
5200	34.021	342.932	307.024	186.725	105.143	45.048	−0.452
5300	33.755	343.578	307.707	190.114	104.418	43.900	−0.433
5400	33.491	344.206	308.377	193.476	103.669	42.765	−0.414
5500	33.232	344.818	309.034	196.813	102.898	41.646	−0.396
5600	32.976	345.415	309.679	200.123	102.103	40.537	−0.378
5700	32.724	345.996	310.311	203.408	101.285	39.445	−0.361
5800	32.477	346.563	310.931	206.668	100.444	38.367	−0.346
5900	32.235	347.116	311.540	209.903	99.579	37.305	−0.330
6000	31.998	347.656	312.137	213.115	98.690	36.256	−0.316

PREVIOUS CURRENT: March 1996 (1 bar)

Bromine Oxide (OBrO) — Ideal Gas — M_r = 111.9028

$\Delta_{at}H°(0\ K)$ = [450 ± 25] kJ·mol^{-1}
$S°(298.15\ K)$ = 271.1 ± 2 J·K^{-1}·mol^{-1}

$\Delta_fH°(0\ K)$ = [161.5 ± 25] kJ·mol^{-1}
$\Delta_fH°(298.15\ K)$ = [152.0 ± 25] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
X^2B_1	0.0	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
800 (1)
300 (1)
852 (1)

Point Group: C_{2v} σ = 2
Bond Distance: Br–O = 1.649 Å
Bond Angle: O–Br–O = 114.4°
Product of the Moments of Inertia: $I_AI_BI_C$ = 409.0844 × 10^{-117} g^3·cm^6

Enthalpy of Formation

For the series OXO(g) [where X = F, Cl, Br, I], there is only reliable experimental data for OClO(g). Assuming that the values $\Delta_{at}H°$(OClO,g) and $D_0°$(ClO) are reasonable, we adopt the ratio of the numbers (~1.94) to apply for a similar relationship between BrO(g) and OBrO(g). Thus we calculate $\Delta_{at}H°$(OBrO, g, 0 K) = 1.94×$D_0°$ (BrO) = 450 ± 25 kJ·mol^{-1}.

Cottrell[1] reported D(O–BrO) ≥ 70 ± 10 kcal·mol^{-1}. This converts to $\Delta_fH°$(0 K) = 87 kJ·mol^{-1}. This value was based on the enthalpy of formation of BrO_2(cr) reported by Pflugmacher *et al.*[2] and a $D_0°$(BrO) = 2.25 eV or 52 kcal·mol^{-1}. Cottrell expressed doubt as to the validity of this value based on comparison with ClO_2. The enthalpy of dissociation reported by Vedeneyev *et al.*[3] was ΔH(298 K) ≥ 70 kcal·mol^{-1} for the reaction $BrO_2 \rightarrow BrO + O$. This is an estimated value based on the work by Cottrell (1954) although a different temperature was given.

In contrast, Huie and Laszlo[4] have estimated the enthalpy of formation of OBrO(g) in the following manner. According to Stanbury,[5] the enthalpy of formation of OBrO in the gas phase can be estimated by assuming that the difference in the Δ_fG for Cl_2(g) and ClO_2(aq) also applies for the bromine species. Using a value of 2.9 kJ·mol^{-1} recommended by Wagman *et al.*[6] as this difference and $\Delta G(BrO_2, aq)$ = 144.0 kJ·mol^{-1}, we obtain $\Delta G°$ = 146.9 kJ·mol^{-1} for OBrO(g) and $\Delta_fH°$ = 122.5 kJ·mol^{-1}. In comparison $D_0°$(BrO) = 231.6 kJ·mol^{-1}.

Heat Capacity and Entropy

Mueller *et al.*[7] have measured the microwave spectra of OBrO(g). Preliminary analysis of the data suggested a bent structure (r_o = 1.649 Å and <(OBrO) = 114.4°). This structure is adopted and is consistent with the expected trends in the corresponding chlorine and iodine oxide molecules. The principal moments of inertia (in g·cm^2) are: I_A = 3.0275 × 10^{-39}, I_B = 10.2087 × 10^{-39}, and I_C = 13.2361 × 10^{-39}.

In support of this study, Byberg and Spanget-Larsen[8] used modified extended Huckel theory to calculate nuclear quadrupole coupling constants for a series of oxygen halogen compounds. The comparison of calculated values with observed values helped confirm the geometry of BrO_2: C_{2v} symmetry with a bond length of 1.625 Å and a bond angle of 117.6°. This geometry was assumed to be similar to that of ClO_2, using a 0.15 Å difference between the covalent radii of the chlorine and bromine atoms.

Tevault *et al.*[9] observed the infrared spectra of BrO_2 in a solid argon matrix. Assuming the proper identification of the antisymmetric stretching ν_3 to be 852 cm^{-1}, the apex angle was calculated to be 110 ± 2°. This was close to the value observed for the analogous matrix isolated ClO_2.

The recommended vibrational frequency (ν_3) is that suggested by Jacox.[10] This data is based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*[9] Preliminary microwave studies by Mueller *et al.*[7] suggested an approximate value for ν_2 (300 cm^{-1}). The unobserved vibrational frequency (ν_1) is estimated from those which describe the other halogen oxide molecules.[11] Maier and Bothur,[12] using flash photolysis, trapped OBrO in a matrix and measured ν_1 and ν_3 for two isotopes. Their values for ν_3 are within a few wave numbers of the values derived by Tevault *et al.*[9] ν_1 values are of the order of 791–799 cm^{-1}, depending on the concentration of the pyrolized mixture (Br_2/O_2/Ar).

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Continued on page 548

Bromine oxide (OBrO) — Br_1O_2(g)

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−11.395	161.500	161.500	INFINITE
50	33.368	204.239	398.861	−9.731	161.299	159.420	−166.544
100	35.399	227.876	308.078	−8.020	160.573	157.809	−82.431
150	37.993	242.726	283.956	−6.185	159.790	156.596	−54.531
200	40.539	254.003	275.111	−4.222	159.010	155.649	−40.651
250	43.088	263.324	271.846	−2.131	158.236	154.898	−32.364
298.15	45.364	271.112	271.112	.000	151.957	154.979	−27.152
300	45.446	271.393	271.113	.084	151.916	154.998	−26.988
400	49.171	285.010	272.944	4.826	136.447	159.211	−20.791
500	51.674	296.270	276.516	9.877	136.594	164.888	−17.226
600	53.335	305.848	280.626	15.133	136.830	170.525	−14.846
700	54.463	314.160	284.836	20.526	137.100	176.120	−13.142
800	55.253	321.487	288.969	26.015	137.375	181.675	−11.862
900	55.823	328.030	292.952	31.570	137.643	187.196	−10.865
1000	56.246	333.934	296.760	37.174	137.898	192.688	−10.065
1100	56.567	339.311	300.387	42.816	138.139	198.156	−9.410
1200	56.817	344.244	303.839	48.485	138.364	203.602	−8.863
1300	57.013	348.800	307.125	54.177	138.572	209.030	−8.399
1400	57.172	353.031	310.254	59.887	138.764	214.442	−8.001
1500	57.301	356.980	313.239	65.611	138.937	219.842	−7.656
1600	57.407	360.681	316.090	71.346	139.090	225.230	−7.353
1700	57.495	364.164	318.816	77.091	139.223	230.610	−7.086
1800	57.570	367.453	321.428	82.845	139.334	235.982	−6.848
1900	57.634	370.567	323.933	88.605	139.420	241.349	−6.635
2000	57.688	373.525	326.339	94.371	139.481	246.712	−6.443
2100	57.735	376.341	328.654	100.142	139.515	252.073	−6.270
2200	57.776	379.028	330.883	105.918	139.520	257.433	−6.112
2300	57.812	381.597	333.032	111.698	139.497	262.792	−5.968
2400	57.843	384.058	335.108	117.480	139.443	268.154	−5.836
2500	57.871	386.420	337.113	123.266	139.358	273.519	−5.715
2600	57.896	388.690	339.053	129.054	139.244	278.887	−5.603
2700	57.918	390.875	340.933	134.845	139.100	284.261	−5.499
2800	57.937	392.982	342.754	140.638	138.926	289.640	−5.403
2900	57.955	395.015	344.521	146.433	138.725	295.026	−5.314
3000	57.971	396.980	346.237	152.229	138.496	300.420	−5.231
3100	57.986	398.881	347.905	158.027	138.243	305.822	−5.153
3200	57.999	400.723	349.527	163.826	137.965	311.231	−5.080
3300	58.011	402.508	351.106	169.626	137.666	316.650	−5.012
3400	58.022	404.240	352.643	175.428	137.347	322.079	−4.948
3500	58.032	405.922	354.141	181.231	137.010	327.517	−4.888
3600	58.041	407.557	355.602	187.035	136.657	332.965	−4.831
3700	58.050	409.147	357.028	192.839	136.289	338.423	−4.778
3800	58.058	410.695	358.420	198.644	135.908	343.892	−4.727
3900	58.065	412.203	359.780	204.451	135.517	349.370	−4.679
4000	58.072	413.673	361.109	210.257	135.116	354.858	−4.634
4100	58.078	415.107	362.409	216.065	134.707	360.357	−4.591
4200	58.084	416.507	363.680	221.873	134.291	365.866	−4.550
4300	58.089	417.874	364.925	227.682	133.870	371.385	−4.511
4400	58.094	419.209	366.143	233.491	133.444	376.913	−4.475
4500	58.099	420.515	367.337	239.300	133.014	382.451	−4.439
4600	58.103	421.792	368.507	245.111	132.581	387.998	−4.406
4700	58.107	423.042	369.654	250.921	132.145	393.556	−4.374
4800	58.111	424.265	370.779	256.732	131.707	399.122	−4.343
4900	58.115	425.463	371.883	262.543	131.266	404.698	−4.314
5000	58.118	426.637	372.966	268.355	130.823	410.283	−4.286
5100	58.121	427.788	374.030	274.167	130.377	415.877	−4.259
5200	58.125	428.917	375.075	279.979	129.928	421.479	−4.234
5300	58.127	430.024	376.101	285.792	129.475	427.091	−4.209
5400	58.130	431.111	377.110	291.605	129.018	432.710	−4.186
5500	58.133	432.177	378.101	297.418	128.557	438.338	−4.163
5600	58.135	433.225	379.076	303.231	128.089	443.975	−4.141
5700	58.137	434.254	380.035	309.045	127.615	449.620	−4.120
5800	58.140	435.265	380.979	314.859	127.134	455.273	−4.100
5900	58.142	436.259	381.907	320.673	126.644	460.934	−4.081
6000	58.144	437.236	382.821	326.487	126.143	466.605	−4.062

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [288.8 \pm 3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [116.1 \pm 40]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [108.0 \pm 40]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$X[^2A'']$	0.0	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1487 (1)
[250] (1)
[160] (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Br–O = [2.0] Å; O–O = [1.25] Å
Bond Angle: Br–O–O = [115]°
Product of the Moments of Inertia: $I_A I_B I_C = [588.4497 \times 10^{-117}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Ip and Burns[1] determined the recombination rate constants of bromine atoms in the presence of six different third bodies (helium, neon, argon, krypton, oxygen and nitrogen) over the temperature range of 300 and 1273° K. The authors refer to two earlier studies: Rabinowitch and Wood[2] and Strong *et al.*[3] Based on these data, Blake *et al.*[4] calculated interaction potentials between atomic bromine, oxygen and an inert third body (such as a rare gas). A value is given for $Br–O_2$. BrOO was thought to be unstable with a bond energy (Br–OO) of approximately 1 $kcal \cdot mol^{-1}$ (at 298.15 K) which translated to an enthalpy of formation of 108.0 kJ mol^{-1}.

Heat Capacity and Entropy

Butkovskaya *et al.*[5] estimated the structure of this molecule to be bent with a Br–O–O angle of [115]° and bond lengths, r(Br–O) = [2.0] Å and r(O–O) = [1.25] Å. Butkovskaya *et al.* assumed this structure in an attempt to explain the formation of BrO_2 from the reaction of O + Br_2 in a flow discharge system. Under the experimental conditions studied, OBrO was actually formed. The principal moments of inertia (in $g \cdot cm^2$) are: $I_A = [1.2011 \times 10^{-39}]$, $I_B = [21.5417 \times 10^{-39}]$, and $I_C = [22.7428 \times 10^{-39}]$.

The recommended vibrational frequency for ν_1 is that suggested by Jacox.[6] In addition, we adopt ν_2=[250] and ν_3=[160] cm^{-1} based on an assumed trend of the FOO(g) and ClOO(g) vibrational frequencies.[7] ν_1 is based on the infrared spectra of the argon matrix isolated radical as studied by Tevault and Smardzewski.[8] Michael and Payne[9] calculated (BEBO method) a stretching frequency of 872 cm^{-1} for ν_1 which is in conflict with the observed frequency by Tevault and Smardzewski[8] and the corresponding value for ClOO. FOO(g) and ClOO(g) have ν_1(O–O stretch) values of 1487 and 1443 cm^{-1}, respectively.[7] Thus, ν_1=1487 cm^{-1} for BrOO appears reasonable. The authors suggested that the bending frequency of 100 cm^{-1} was consistent with their kinetic data. The recent study by Maier and Bothur[10] suggested a ν_1 value in agreement with the adopted value.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.851	116.087	116.087	INFINITE
50	35.382	212.021	435.344	−11.166	115.907	113.639	−118.718
100	41.818	238.630	330.908	−9.228	115.409	111.569	−58.278
150	45.376	256.347	303.261	−7.037	114.981	109.743	−38.216
200	47.128	269.668	293.267	−4.720	114.555	108.061	−28.223
250	48.143	280.301	289.646	−2.336	114.073	106.491	−22.250
298.15	48.875	288.845	288.845	.000	108.000	105.736	−18.524
300	48.901	289.148	288.846	.090	107.966	105.722	−18.408
400	50.265	303.404	290.781	5.049	92.714	108.119	−14.119
500	51.562	314.761	294.479	10.141	92.901	111.949	−11.695
600	52.707	324.266	298.672	15.356	93.097	115.741	−10.076
700	53.657	332.465	302.928	20.676	93.293	119.499	−8.917
800	54.421	339.682	307.080	26.082	93.485	123.230	−8.046
900	55.031	346.128	311.067	31.555	93.671	126.936	−7.367
1000	55.517	351.952	314.869	37.084	93.851	130.623	−6.823
1100	55.907	357.263	318.485	42.656	94.022	134.292	−6.377
1200	56.222	362.141	321.922	48.263	94.184	137.946	−6.005
1300	56.480	366.652	325.192	53.898	94.336	141.586	−5.689
1400	56.692	370.845	328.305	59.557	94.477	145.215	−5.418
1500	56.869	374.763	331.273	65.235	94.605	148.835	−5.183
1600	57.017	378.438	334.107	70.930	94.717	152.446	−4.977
1700	57.142	381.899	336.817	76.638	94.813	156.051	−4.795
1800	57.249	385.168	339.414	82.358	94.890	159.651	−4.633
1900	57.341	388.266	341.904	88.087	94.946	163.247	−4.488
2000	57.421	391.209	344.296	93.825	94.979	166.841	−4.357
2100	57.490	394.012	346.597	99.571	94.987	170.434	−4.239
2200	57.550	396.688	348.814	105.323	94.969	174.028	−4.132
2300	57.603	399.247	350.951	111.081	94.923	177.622	−4.034
2400	57.650	401.700	353.015	116.843	94.849	181.219	−3.944
2500	57.692	404.054	355.010	122.611	94.746	184.820	−3.862
2600	57.729	406.318	356.940	128.382	94.614	188.425	−3.786
2700	57.763	408.497	358.810	134.156	94.454	192.036	−3.715
2800	57.792	410.598	360.622	139.934	94.266	195.654	−3.650
2900	57.819	412.627	362.380	145.715	94.050	199.278	−3.589
3000	57.844	414.587	364.088	151.498	93.809	202.911	−3.533
3100	57.866	416.484	365.748	157.283	93.543	206.553	−3.480
3200	57.886	418.322	367.362	163.071	93.254	210.202	−3.431
3300	57.905	420.104	368.934	168.861	92.944	213.861	−3.385
3400	57.922	421.832	370.464	174.652	92.614	217.531	−3.342
3500	57.937	423.512	371.956	180.445	92.267	221.209	−3.301
3600	57.951	425.144	373.411	186.239	91.905	224.899	−3.263
3700	57.965	426.732	374.831	192.035	91.528	228.598	−3.227
3800	57.977	428.278	376.217	197.832	91.139	232.308	−3.193
3900	57.988	429.784	377.571	203.630	90.740	236.028	−3.161
4000	57.998	431.252	378.895	209.430	90.331	239.759	−3.131
4100	58.008	432.685	380.189	215.230	89.915	243.499	−3.102
4200	58.017	434.083	381.456	221.031	89.493	247.250	−3.075
4300	58.025	435.448	382.696	226.833	89.065	251.012	−3.049
4400	58.033	436.782	383.910	232.636	88.633	254.783	−3.025
4500	58.040	438.086	385.099	238.440	88.197	258.563	−3.001
4600	58.047	439.362	386.265	244.244	87.759	262.354	−2.979
4700	58.054	440.610	387.408	250.049	87.317	266.154	−2.958
4800	58.060	441.833	388.529	255.855	86.874	269.964	−2.938
4900	58.065	443.030	389.630	261.661	86.428	273.784	−2.919
5000	58.071	444.203	390.709	267.468	85.979	277.612	−2.900
5100	58.076	445.353	391.769	273.276	85.529	281.449	−2.883
5200	58.081	446.481	392.811	279.083	85.075	285.294	−2.866
5300	58.085	447.587	393.834	284.892	84.618	289.150	−2.850
5400	58.089	448.673	394.839	290.700	84.157	293.013	−2.834
5500	58.093	449.739	395.828	296.510	83.692	296.884	−2.820
5600	58.097	450.786	396.800	302.319	83.220	300.766	−2.805
5700	58.101	451.814	397.756	308.129	82.743	304.654	−2.792
5800	58.104	452.824	398.697	313.939	82.258	308.552	−2.779
5900	58.107	453.818	399.623	319.750	81.764	312.457	−2.766
6000	58.111	454.794	400.534	325.561	81.260	316.372	−2.754

PREVIOUS: CURRENT: March 1996 (1 bar)

$\Delta_{at}H°(298.15\ K) = [625 \pm 50]\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [284.5 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [233 \pm 50]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [221 \pm 50]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
$[^2A_1]$	0.0	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[442](1)
[800](1)
[350](2)
[828](2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Br–O = [1.68]Å
Bond Angle: O–Br–O = [89]°
Product of the Moments of Inertia: $I_A I_B I_C = 2198.7927 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt an enthalpy of formation value which is based on an assumed relationship of $\Delta_{at}H°(BrO_3,g)/3 = 0.9D°_0(BrO)$.

An enthalpy of formation value (at 298.15 K) has been reported by Farkas and Klein.[1] This value, 23 $kcal \cdot mol^{-1}$ (96 $kJ \cdot mol^{-1}$), was derived from absorption spectra measurements of bromate ions in solutions. There is considerable uncertainty in this value, both in terms of the experimental measurements and the fact that the authors have interchanged BrO_3 and BrO_3^-. This corresponds to an average bond energy of 254 $kJ \cdot mol^{-1}$. In comparison $D°_0(BrO) = 231\ kJ \cdot mol^{-1}$.

Heat Capacity and Entropy

The structure of this molecule is estimated to be pyramidal with a O–Br–O angle of [89]° and a bond length of [1.68] Å, in analogy with the corresponding chlorine and iodine oxide molecules. Venkateswarlu and Sundaram,[2] Venkateswarlu and Rajalakshmi,[3] Rao and Santhamma,[4] Rao,[5] and Thirugnanasambandam and Mohan[6] assumed the same structure and bond angle for ClO_3, BrO_3, and IO_3. Using Badgers' rule, the authors examined the relationship between the vibrational frequencies and force constants for the three pyramidal molecules -- ClO_3, BrO_3, and IO_3. Although these authors refer to early measurements of the vibrational frequencies, the values appear to be in part, those of the ion BrO_3^-. The vibrational frequencies are derived from the force constants which describe the other halogen oxide molecules. The principal moments of inertia (in $g \cdot cm^2$) are: $I_A = 12.2156 \times 10^{-39}$, $I_B = 12.2156 \times 10^{-39}$, and $I_C = 14.7352 \times 10^{-39}$.

Byberg,[7] in an EPR study, suggested the molecule had C_{3v} symmetry with a bond angle of 112° and bond length of 1.57 Å. In contrast, Begum *et al.*,[8] in a radiolysis study, suggested a bond length of 114° with C_{3v} symmetry. In calculating atomic phase shifts, Lee and Beni[9] calculated a bond length of 1.66 Å in solution. In these cases, there is no definitive evidence as to the geometry. Values were suggested which would be consistent with experimental observations.

References

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[2] K. Venkateswarlu and S. Sundaram, Proc. Phys. Soc. (London) **A69**, 180 (1956).
[3] K. Venkateswarlu and K. V. Rajalakshmi, Indian J. Pure Appl. Phys. **1**, 380 (1963).
[4] C. G. R. Rao and C. Santhamma, Current Sci. **33**(22), 677 (1964).
[5] C. G. R. Rao, Sci. Cult. **38**(12), 522 (1972).
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[7] J. R. Byberg, J. Chem. Phys. **83**(3), 919 (1985).
[8] A. Begum, S. Subramanuan, and M. C. R. Symons, J. Chem. Soc. **6**, 918 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	0.000	.000	INFINITE	−13.101	233.000	233.000	INFINITE
50	33.333	209.520	438.271	−11.438	232.073	233.759	−244.206
100	36.646	233.329	330.438	−9.711	230.636	235.992	−123.269
150	43.085	249.376	300.850	−7.721	229.279	238.971	−83.217
200	49.535	262.667	289.684	−5.403	228.126	242.381	−63.303
250	55.297	274.354	285.471	−2.779	227.156	246.060	−51.411
298.15	59.999	284.509	284.509	.000	220.821	250.432	−43.875
300	60.162	284.880	284.510	.111	220.781	250.616	−43.636
400	67.300	303.241	286.965	6.511	205.483	263.728	−34.439
500	71.849	318.785	291.815	13.485	206.024	278.233	−29.067
600	74.791	332.164	297.452	20.827	206.767	292.607	−25.474
700	76.759	343.850	303.263	28.411	207.599	306.849	−22.897
800	78.125	354.194	308.995	36.159	208.466	320.969	−20.957
900	79.105	363.456	314.541	44.023	209.340	334.979	−19.442
1000	79.829	371.830	319.858	51.972	210.208	348.892	−18.224
1100	80.377	379.465	324.935	59.983	211.065	362.719	−17.224
1200	80.801	386.478	329.775	68.043	211.905	376.469	−16.387
1300	81.136	392.959	334.389	76.140	212.728	390.149	−15.676
1400	81.404	398.982	338.791	84.268	213.530	403.767	−15.065
1500	81.623	404.606	342.993	92.420	214.311	417.327	−14.533
1600	81.803	409.880	347.010	100.591	215.067	430.837	−14.065
1700	81.953	414.844	350.856	108.779	215.797	444.300	−13.652
1800	82.080	419.532	354.542	116.981	216.498	457.721	−13.283
1900	82.187	423.972	358.080	125.195	217.168	471.104	−12.952
2000	82.279	428.190	361.481	133.418	217.805	484.452	−12.653
2100	82.358	432.207	364.754	141.650	218.406	497.770	−12.381
2200	82.428	436.040	367.908	149.889	218.971	511.060	−12.134
2300	82.488	439.705	370.951	158.135	219.499	524.324	−11.908
2400	82.541	443.217	373.889	166.387	219.987	537.566	−11.700
2500	82.588	446.587	376.730	174.643	220.436	550.790	−11.508
2600	82.630	449.827	379.480	182.904	220.846	563.996	−11.331
2700	82.667	452.947	382.143	191.169	221.217	577.187	−11.166
2800	82.700	455.954	384.726	199.437	221.551	590.365	−11.013
2900	82.730	458.856	387.232	207.709	221.847	603.531	−10.871
3000	82.757	461.661	389.667	215.983	222.108	616.688	−10.737
3100	82.781	464.375	392.033	224.260	222.336	629.838	−10.613
3200	82.804	467.004	394.335	232.539	222.532	642.979	−10.496
3300	82.824	469.552	396.576	240.821	222.698	656.115	−10.385
3400	82.843	472.025	398.759	249.104	222.837	669.247	−10.282
3500	82.859	474.427	400.887	257.389	222.950	682.374	−10.184
3600	82.875	476.761	402.962	265.676	223.040	695.500	−10.091
3700	82.889	479.032	404.988	273.964	223.109	708.622	−10.004
3800	82.903	481.243	406.965	282.254	223.158	721.745	−9.921
3900	82.915	483.396	408.898	290.545	223.190	734.865	−9.842
4000	82.926	485.496	410.786	298.837	223.207	747.984	−9.768
4100	82.937	487.543	412.634	307.130	223.209	761.104	−9.697
4200	82.946	489.542	414.441	315.424	223.199	774.223	−9.629
4300	82.956	491.494	416.210	323.719	223.178	787.343	−9.564
4400	82.964	493.401	417.943	332.015	223.145	800.463	−9.503
4500	82.972	495.266	419.641	340.312	223.104	813.584	−9.444
4600	82.979	497.089	421.305	348.609	223.053	826.706	−9.388
4700	82.986	498.874	422.936	356.908	222.994	839.830	−9.334
4800	82.993	500.621	424.537	365.207	222.926	852.955	−9.282
4900	82.999	502.333	426.107	373.506	222.849	866.082	−9.233
5000	83.005	504.009	427.648	381.807	222.764	879.210	−9.185
5100	83.010	505.653	429.162	390.107	222.670	892.340	−9.139
5200	83.015	507.265	430.648	398.409	222.565	905.471	−9.096
5300	83.020	508.846	432.109	406.710	222.451	918.606	−9.053
5400	83.025	510.398	433.544	415.013	222.324	931.741	−9.013
5500	83.029	511.922	434.955	423.315	222.185	944.879	−8.974
5600	83.033	513.418	436.343	431.618	222.032	958.022	−8.936
5700	83.037	514.888	437.708	439.922	221.863	971.165	−8.900
5800	83.041	516.332	439.052	448.226	221.678	984.313	−8.865
5900	83.044	517.751	440.373	456.530	221.474	997.462	−8.831
6000	83.048	519.147	441.675	464.835	221.250	1010.617	−8.798

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [249.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [170.7]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [162.6]\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^3\Sigma$	0	[3]

$\omega_e = [400]\ cm^{-1}$ $\omega_e x_e = [1.5]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.1519]\ cm^{-1}$ $\alpha_e = [0.0008]\ cm^{-1}$ $r_e = [2.23]$ Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as 40.8 kcal·mol^{-1} by Gordon[1] with white (α) phosphorus as the reference state.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1]

Reference

[1] J. S. Gordon, Astrosystems International, Livingston, New Jersey, personal communication, (August 25, 1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.508	170.707	170.707	INFINITE
100	30.017	213.468	279.294	−6.583	171.349	154.463	−80.683
200	33.551	235.417	252.392	−3.395	169.823	137.906	−36.017
250	34.666	243.032	249.783	−1.688	169.030	130.016	−27.165
298.15	35.394	249.204	249.204	0.	162.601	123.238	−21.591
300	35.417	249.423	249.205	0.065	162.552	122.994	−21.415
350	35.935	254.924	249.638	1.850	146.076	117.345	−17.513
400	36.304	259.748	250.606	3.657	145.651	113.270	−14.791
450	36.578	264.040	251.865	5.479	145.237	109.247	−12.681
500	36.786	267.905	253.279	7.313	144.830	105.270	−10.997
600	37.083	274.640	256.294	11.008	144.032	97.433	−8.482
700	37.285	280.373	259.335	14.727	143.249	89.729	−6.696
800	37.434	285.362	262.283	18.463	142.476	82.136	−5.363
900	37.552	289.778	265.097	22.212	141.711	74.639	−4.332
1000	37.649	293.739	267.767	25.973	140.952	67.228	−3.512
1100	37.734	297.332	270.294	29.742	140.197	59.892	−2.844
1200	37.810	300.618	272.686	33.519	75.873	53.703	−2.338
1300	37.879	303.648	274.953	37.304	75.900	51.854	−2.084
1400	37.943	306.457	277.104	41.095	75.924	50.004	−1.866
1500	38.004	309.077	279.149	44.892	75.945	48.152	−1.677
1600	38.062	311.532	281.097	48.695	75.963	46.298	−1.511
1700	38.118	313.841	282.956	52.504	75.978	44.444	−1.366
1800	38.173	316.021	284.733	56.319	75.989	42.588	−1.236
1900	38.226	318.086	286.434	60.139	75.996	40.732	−1.120
2000	38.278	320.048	288.066	63.964	75.997	38.876	−1.015
2100	38.329	321.917	289.634	67.794	75.992	37.021	−0.921
2200	38.380	323.701	291.142	71.630	75.980	35.165	−0.835
2300	38.430	325.409	292.595	75.470	75.961	33.310	−0.756
2400	38.479	327.045	293.997	79.316	75.933	31.456	−0.685
2500	38.529	328.617	295.351	83.166	75.898	29.604	−0.619
2600	38.577	330.129	296.659	87.021	75.854	27.753	−0.558
2700	38.626	331.586	297.926	90.882	75.802	25.904	−0.501
2800	38.674	332.992	299.153	94.747	75.743	24.057	−0.449
2900	38.722	334.350	300.344	98.616	75.677	22.212	−0.400
3000	38.770	335.663	301.499	102.491	75.605	20.370	−0.355
3100	38.817	336.935	302.622	106.370	75.528	18.530	−0.312
3200	38.865	338.168	303.714	110.254	75.448	16.692	−0.272
3300	38.912	339.365	304.776	114.143	75.366	14.857	−0.235
3400	38.959	340.527	305.810	118.037	75.282	13.025	−0.200
3500	39.007	341.657	306.819	121.935	75.198	11.195	−0.167
3600	39.054	342.757	307.802	125.838	75.116	9.368	−0.136
3700	39.100	343.827	308.761	129.746	75.038	7.543	−0.106
3800	39.147	344.871	309.698	133.658	74.963	5.719	−0.079
3900	39.194	345.888	310.613	137.575	74.894	3.898	−0.052
4000	39.241	346.881	311.507	141.497	74.831	2.078	−0.027
4100	39.288	347.851	312.382	145.424	74.776	0.260	−0.003
4200	39.334	348.798	313.237	149.355	74.731	−1.557	0.019
4300	39.381	349.724	314.075	153.290	74.694	−3.373	0.041
4400	39.427	350.630	314.896	157.231	74.668	−5.188	0.062
4500	39.474	351.517	315.700	161.176	74.654	−7.002	0.081
4600	39.520	352.385	316.488	165.126	74.651	−8.817	0.100
4700	39.567	353.235	317.261	169.080	74.661	−10.632	0.118
4800	39.613	354.069	318.019	173.039	74.684	−12.447	0.135
4900	39.660	354.886	318.763	177.003	74.720	−14.262	0.152
5000	39.706	355.688	319.493	180.971	74.770	−16.078	0.168
5100	39.753	356.474	320.211	184.944	74.834	−17.896	0.183
5200	39.799	357.247	320.916	188.922	74.912	−19.715	0.198
5300	39.845	358.005	321.608	192.904	75.004	−21.536	0.212
5400	39.892	358.750	322.289	196.891	75.110	−23.358	0.226
5500	39.938	359.483	322.959	200.882	75.231	−25.183	0.239
5600	39.984	360.203	323.618	204.878	75.367	−27.010	0.252
5700	40.030	360.911	324.266	208.879	75.516	−28.839	0.264
5800	40.077	361.608	324.903	212.884	75.680	−30.671	0.276
5900	40.123	362.293	325.531	216.894	75.858	−32.507	0.288
6000	40.169	362.968	326.150	220.909	76.051	−34.345	0.299

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = 272.47 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 79.91 \pm 42\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 70.92 \pm 42\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	[8300]	2
$A[^2\Sigma]$	20884.3	[2]
$B[^2\Sigma]$	34523.7	[2]

$\omega_e = 206.56\ cm^{-1}$ $\omega_e x_e = 0.495\ cm^{-1}$ $\sigma = 1$

$B_e = 0.0451\ cm^{-1}$ $\alpha_e = [0.00014]\ cm^{-1}$ $r_e = 2.546$ Å

Enthalpy of Formation

$\Delta_f H°(0\ K) = -19.10 \pm 10\ kcal \cdot mol^{-1}$ ($79.914 \pm 42\ kJ \cdot mol^{-1}$) is calculated and rounded from the $D_0° = 2.43$ eV ($56.04\ kcal \cdot mol^{-1}$) determined by Singh from emission spectra,[1] $\Delta_f H°(Pb, g, 0\ K) = 46.91 \pm 0.13\ kcal \cdot mol^{-1}$,[2] and $\Delta_f H°(Br, g, 0\ K) = 28.188\ kcal \cdot mol^{-1}$.[2] Rosen[3] and Gaydon[4] recommended $57 \pm 9\ kcal \cdot mol^{-1}$ and $58 \pm 9\ kcal \cdot mol^{-1}$, respectively, for $D_0°$. A linear Birge–Sponer extrapolation of the ground state vibrational constants, as derived from absorption spectra (v, 0–11) observed by Morgan,[5] gives a dissociation energy of 2.66 eV. Correction for the ionic character of PbBr as proposed by Hildenbrand[6] gives $D_0° = 2.44$ eV which is in good agreement with the value determined by Singh.[1] $\Delta_f H°(298.15\ K) = -16.95 \pm 10\ kcal \cdot mol^{-1}$ is calculated from the adopted $\Delta_f H°(0\ K) = -19.10 \pm 10\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational constants are from the compilation of Rosen,[3] corrected for the natural isotopic abundance of ^{79}Br and ^{81}Br. Analogous to PbF[2] and PbCl,[2] a $^2\Pi_{3/2}$ state at 8300 cm^{-1} is added to the electronic states and levels listed by Rosen.[3] The assignment of the first excited state remains uncertain; the choice appears to be between $^2\Sigma$ state, tentatively assigned to PbF[2] and PbCl,[2] and $^2\Delta$, tentatively assigned to PbI.[2] The $^2\Sigma$ state is adopted. The entropy is increased by $0.009\ cal \cdot K^{-1} \cdot mol^{-1}$ at 4000 K and $0.012\ cal \cdot K^{-1} \cdot mol^{-1}$ at 6000 K if the $^2\Delta$ state is used. The adopted value of B_e was determined by Lal and Khanna[7] and is adjusted for the natural abundance of the bromine isotopes. The value of r_e is calculated from the adopted B_e. The value of α_e is calculated assuming a Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.146	79.910	79.910	INFINITE
100	33.337	233.663	304.665	−7.100	79.793	62.802	−32.804
200	36.150	257.867	275.829	−3.592	78.326	46.349	−12.105
250	36.638	265.991	273.077	−1.771	77.433	38.455	−8.035
298.15	36.922	272.471	272.471	0.	70.923	31.692	−5.552
300	36.930	272.699	272.471	0.068	70.872	31.448	−5.476
350	37.123	278.407	272.922	1.920	55.044	25.756	−3.844
400	37.260	283.374	273.925	3.780	54.614	21.602	−2.821
450	37.363	287.769	275.223	5.645	54.162	17.502	−2.032
500	37.446	291.710	276.678	7.516	53.691	13.454	−1.405
600	37.572	298.549	279.770	11.267	52.693	5.499	−0.479
700	37.671	304.348	282.878	15.029	46.764	−1.485	0.111
800	37.754	309.384	285.883	18.801	45.642	−8.301	0.542
900	37.830	313.835	288.746	22.580	44.554	−14.978	0.869
1000	37.904	317.825	291.458	26.367	43.499	−21.536	1.125
1100	37.980	321.441	294.022	30.161	42.477	−27.990	1.329
1200	38.062	324.749	296.447	33.963	41.489	−34.352	1.495
1300	38.155	327.799	298.743	37.773	40.529	−40.633	1.633
1400	38.262	330.631	300.920	41.594	39.582	−46.841	1.748
1500	38.385	333.274	302.990	45.426	38.641	−52.981	1.845
1600	38.524	335.756	304.961	49.272	37.699	−59.058	1.928
1700	38.680	338.096	306.842	53.132	36.753	−65.077	2.000
1800	38.852	340.312	308.641	57.008	35.801	−71.039	2.062
1900	39.038	342.417	310.363	60.903	34.841	−76.949	2.115
2000	39.237	344.425	312.017	64.816	33.872	−82.807	2.163
2100	39.446	346.344	313.606	68.750	−144.328	−81.502	2.027
2200	39.663	348.184	315.136	72.706	−144.927	−78.497	1.864
2300	39.886	349.952	316.612	76.683	−145.603	−75.462	1.714
2400	40.112	351.655	318.037	80.683	−146.359	−72.397	1.576
2500	40.339	353.297	319.414	84.706	−147.195	−69.298	1.448
2600	40.566	354.883	320.748	88.751	−148.109	−66.165	1.329
2700	40.791	356.418	322.041	92.819	−149.101	−62.994	1.219
2800	41.012	357.906	323.295	96.909	−150.165	−59.786	1.115
2900	41.230	359.349	324.514	101.021	−151.297	−56.538	1.018
3000	41.441	360.750	325.699	105.155	−152.492	−53.251	0.927
3100	41.648	362.112	326.851	109.309	−153.743	−49.922	0.841
3200	41.848	363.438	327.974	113.484	−155.042	−46.553	0.760
3300	42.041	364.728	329.068	117.678	−156.382	−43.142	0.683
3400	42.228	365.986	330.136	121.892	−157.756	−39.689	0.610
3500	42.407	367.213	331.178	126.124	−159.155	−36.197	0.540
3600	42.581	368.410	332.195	130.373	−160.574	−32.663	0.474
3700	42.747	369.579	333.190	134.640	−162.003	−29.091	0.411
3800	42.907	370.721	334.163	138.922	−163.438	−25.479	0.350
3900	43.061	371.838	335.114	143.221	−164.870	−21.830	0.292
4000	43.210	372.930	336.046	147.534	−166.295	−18.144	0.237
4100	43.352	373.999	336.959	151.863	−167.707	−14.423	0.184
4200	43.489	375.045	337.853	156.205	−169.101	−10.668	0.133
4300	43.621	376.070	338.730	160.560	−170.473	−6.879	0.084
4400	43.749	377.074	339.590	164.929	−171.820	−3.059	0.036
4500	43.872	378.059	340.434	169.310	−173.137	0.791	−0.009
4600	43.991	379.024	341.263	173.703	−174.422	4.671	−0.053
4700	44.106	379.971	342.076	178.108	−175.674	8.578	−0.095
4800	44.217	380.901	342.875	182.524	−176.889	12.511	−0.136
4900	44.325	381.814	343.661	186.951	−178.067	16.469	−0.176
5000	44.430	382.711	344.433	191.389	−179.207	20.451	−0.214
5100	44.531	383.591	345.192	195.837	−180.308	24.455	−0.250
5200	44.631	384.457	345.939	200.295	−181.369	28.480	−0.286
5300	44.727	385.308	346.674	204.763	−182.390	32.526	−0.321
5400	44.821	386.145	347.397	209.240	−183.372	36.590	−0.354
5500	44.914	386.968	348.109	213.727	−184.315	40.672	−0.386
5600	45.004	387.778	348.810	218.223	−185.219	44.771	−0.418
5700	45.092	388.576	349.501	222.728	−186.085	48.886	−0.448
5800	45.178	389.361	350.181	227.241	−186.914	53.015	−0.477
5900	45.263	390.134	350.852	231.763	−187.706	57.159	−0.506
6000	45.346	390.895	351.513	236.294	−188.463	61.315	−0.534

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 247.42 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 240.8 \pm 46.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 235.3 \pm 46.0\ kJ·mol^{-1}$

Electronic States and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X\ ^2\Pi_{1/2}$	0	2	423.2	1.5	0.1669	0.0019	2.210	(5)
$^2\Pi_{3/2}$	419.2	2	423.2	1.5	0.1669	0.0019	2.210	(5)
$A\ ^2\Sigma$	20937.6	2	249.6	0.5	[0.1669]	[0.0019]	[2.210]	(6)
$B'\ ^2\Delta$	23920	4	394	4	[0.1669]	[0.0019]	[2.210]	(1)
$B\ ^2\Sigma$	33572.7	2	573.6	4.0	0.1793	[0.0019]	2.132	(5)
$C\ ^2\Pi$	41057	4	529.2	2.0	[0.1669]	[0.0019]	[2.210]	(10)

Enthalpy of Formation

Kuznetsova and Kuzyakov[1] suggested a value of $D_0° = 85.8 \pm 11.4\ kcal·mol^{-1}$ based on linear Birge–Sponer extrapolations of the ground state and $B'\ ^2\Delta$ state vibrational data. We correct this value for the ionic character of the bond according to Hildenbrand[2] and obtain $D_0° = 77.3 \pm 10.3\ kcal·mol^{-1}$. With auxiliary JANAF data[3] this yields the adopted $\Delta_f H°(0\ K) = 57.543\ kcal·mol^{-1}$ (240.760 $kJ·mol^{-1}$). Tandon and Tandon[4] obtained $D_0° = 85.3\ kcal·mol^{-1}$ from a theoretical treatment based on Sutherland's potential function in good agreement with the adopted value. The value of $D_0°$ may be compared to the average (per bond) enthalpy of atomization of 80.58 and 77.89 $kcal·mol^{-1}$ for $SiBr_2(g)$ and $SiBr_4(g)$, respectively.[3]

Heat Capacity and Entropy

Molecular constant data for the ground state are from Mishra and Khanna.[5] The vibrational data is in good agreement with data from Rao and Haranath,[6] Kuznetsova *et al.*,[7] and Jevons and Bashford.[8] Data for the $A\ ^2\Sigma$ and $B'\ ^2\Delta$ states are from Rao and Haranath[6] and Kuznetsova and Kuzyakov,[1] respectively. The $B\ ^2\Sigma$ state data are from Mishra and Khanna[5] and the vibrational data agree well with Jevons and Bashford.[8] Slightly different values for the rotational constants for both this state and the ground state have been obtained by Kuznetsova and Kuzyakov.[9] Data for the $C\ ^2\Pi$ state is from Oldershaw and Robinson[10] who also reported data for several higher states; these are not included due to uncertainties in their assignments and degeneracies. Splittings of 18 and 12 cm^{-1} for the $B'\ ^2\Delta$ and $C\ ^2\Pi$ states,[1,10] respectively, have not been included in our calculations. The $^4\Sigma$ state observed for SiF and SiI has not been observed for SiBr. It is expected to lie near 24000 cm^{-1} by analogy with SiF and SiI[3] which is very near the $B'\ ^2\Delta$ state. This raises the possibility that this state may have been missed, or the $^2\Delta$ state misassigned, due to the large number of lines in this region[1]. A high resolution re-examination of this region of the spectrum is desirable to clarify the situation. We have assigned an uncertainty of $\pm 0.05\ cal·K^{-1}·mol^{-1}$ to $S°(298.15\ K)$ in view of these uncertainties. All molecular constant data has been corrected to the natural abundances of Si and Br assuming the observed data was for $^{28}Si\ ^{79}Br$. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant ($A = 419.2\ cm^{-1}$). This approximation gives slightly biased results at low temperature: the stated uncertainty in $S°(298.15\ K)$ should account for this.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.040	240.758	240.758	INFINITE
100	30.564	209.105	280.168	−7.106	242.029	224.194	−117.107
200	36.635	232.296	250.917	−3.724	241.782	206.398	−53.906
298.15	38.731	247.418	247.418	0.	235.325	189.859	−33.262
300	38.746	247.658	247.419	0.072	235.290	189.577	−33.008
400	39.025	258.862	248.945	3.967	219.824	177.510	−23.180
500	38.903	267.559	251.831	7.864	219.597	166.955	−17.442
600	38.742	274.638	255.060	11.746	219.244	156.458	−13.621
700	38.615	280.600	258.294	15.614	218.794	146.028	−10.897
800	38.529	285.750	261.412	19.471	218.266	135.668	−8.858
900	38.477	290.285	264.373	23.321	217.672	125.379	−7.277
1000	38.449	294.337	267.170	27.167	217.020	115.158	−6.015
1100	38.440	298.001	269.809	31.011	216.317	105.006	−4.986
1200	38.446	301.346	272.300	34.855	215.566	94.919	−4.132
1300	38.462	304.424	274.654	38.701	214.771	84.897	−3.411
1400	38.486	307.275	276.884	42.548	213.931	74.938	−2.796
1500	38.517	309.931	278.999	46.398	213.048	65.041	−2.265
1600	38.552	312.418	281.011	50.252	212.120	55.204	−1.802
1700	38.591	314.757	282.928	54.109	160.972	45.873	−1.409
1800	38.634	316.964	284.758	57.970	160.187	39.125	−1.135
1900	38.679	319.054	286.509	61.836	159.398	32.421	−0.891
2000	38.726	321.039	288.186	65.706	158.606	25.758	−0.673
2100	38.775	322.930	289.796	69.581	157.810	19.135	−0.476
2200	38.826	324.735	291.343	73.461	157.008	12.550	−0.298
2300	38.879	326.462	292.833	77.346	156.201	6.002	−0.136
2400	38.933	328.117	294.269	81.237	155.388	−0.511	0.011
2500	38.989	329.708	295.655	85.133	154.570	−6.990	0.146
2600	39.047	331.238	296.994	89.035	153.745	−13.436	0.270
2700	39.107	332.713	298.290	92.942	152.916	−19.850	0.384
2800	39.170	334.136	299.545	96.856	152.082	−26.234	0.489
2900	39.235	335.512	300.761	100.777	151.244	−32.587	0.587
3000	39.304	336.843	301.942	104.704	150.403	−38.912	0.678
3100	39.376	338.133	303.089	108.638	149.562	−45.209	0.762
3200	39.451	339.385	304.204	112.579	148.721	−51.478	0.840
3300	39.530	340.600	305.288	116.528	147.882	−57.721	0.914
3400	39.614	341.781	306.344	120.485	147.046	−63.939	0.982
3500	39.702	342.931	307.373	124.451	146.216	−70.133	1.047
3600	39.796	344.050	308.377	128.426	−238.758	−65.841	0.955
3700	39.894	345.142	309.356	132.410	−239.158	−61.033	0.862
3800	39.998	346.207	310.311	136.405	−239.548	−56.213	0.773
3900	40.107	347.248	311.245	140.410	−239.927	−51.384	0.688
4000	40.223	348.265	312.158	144.426	−240.292	−46.545	0.608
4100	40.344	349.259	313.051	148.455	−240.642	−41.697	0.531
4200	40.471	350.233	313.925	152.495	−240.975	−36.840	0.458
4300	40.604	351.187	314.780	156.549	−241.289	−31.976	0.388
4400	40.743	352.122	315.618	160.616	−241.582	−27.105	0.322
4500	40.888	353.039	316.440	164.698	−241.853	−22.227	0.258
4600	41.040	353.939	317.245	168.794	−242.100	−17.344	0.197
4700	41.197	354.824	318.035	172.906	−242.323	−12.456	0.138
4800	41.360	355.693	318.811	177.034	−242.520	−7.563	0.082
4900	41.529	356.547	319.572	181.178	−242.690	−2.666	0.028
5000	41.703	357.388	320.320	185.340	−242.832	2.234	−0.023
5100	41.883	358.216	321.055	189.519	−242.945	7.137	−0.073
5200	42.069	359.031	321.778	193.717	−243.029	12.041	−0.121
5300	42.259	359.834	322.488	197.933	−243.084	16.947	−0.167
5400	42.454	360.626	323.187	202.169	−243.108	21.853	−0.211
5500	42.654	361.406	323.875	206.424	−243.101	26.760	−0.254
5600	42.859	362.177	324.552	210.700	−243.064	31.666	−0.295
5700	43.067	362.937	325.219	214.996	−242.995	36.572	−0.335
5800	43.280	363.688	325.875	219.313	−242.896	41.475	−0.374
5900	43.496	364.430	326.523	223.652	−242.766	46.377	−0.411
6000	43.716	365.163	327.161	228.013	−242.603	51.276	−0.446

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 263.8 \pm 0.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -80.4 \pm 42\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -89.1 \pm 42\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2	$E\ ^2\Sigma$	32052.5	2
$A_1\ ^2\Pi_{1/2}$	14699.4	2	$F_1\ ^2\Pi_{1/2}$	33131.7	2
$A_2\ ^2\Pi_{3/2}$	15000.7	2	$F_2\ ^2\Pi_{3/2}$	33215.0	2
$B\ ^2\Sigma$	15352.0	2	$G_1\ ^2\Delta_{3/2}$	34257.0	2
$C_1\ ^2\Pi_{1/2}$	24343.7	2	$G_2\ ^2\Delta_{3/2}$	34282.8	2
$C_2\ ^2\Pi_{3/2}$	24665.8	2	$H\ ^2\Sigma$	34357.7	2
$D\ ^2\Sigma$	28958.2	2			

$\omega_e = 216.5\ cm^{-1}$ $\omega_e x_e = 0.51\ cm^{-1}$ $\sigma = 1$

$B_e = [0.054924]\ cm^{-1}$ $\alpha_e = [0.000171]\ cm^{-1}$ $r_e = [2.71]$ Å

Enthalpy of Formation

The selected value, $\Delta_f H°(298.15\ K) = -21.3\ kcal\cdot mol^{-1}$ ($-89.119\ kJ\cdot mol^{-1}$), is obtained from an analysis of spectroscopic data. Herzberg[1] suggested $D_0° = 2.8$ eV for SrBr(g) which was derived from a linear Birge–Sponer extrapolation of the ground state vibrational levels. Later, Gaydon[2] claimed that this value is unreliable and suggested that the true value may be much higher. The adopted ground state vibrational constants give $D_0° = 2.84$ eV by a similar extrapolation. We note that JANAF analyses[3] of the spectroscopic and thermochemical data for SrF(g) and SrCl(g) show that the ionicity corrections of Hildenbrand[4] bring the Birge–Sponer extrapolations into reasonable agreement with adopted $D_0°$ values. Based on this correction for SrBr(g), we obtain $D_0° = 3.76$ eV ($86.7\ kcal\cdot mol^{-1}$) which is adopted. The adopted value of $D_0°$ corresponds to $\Delta_f H°(298.15\ K) = 21.3\ kcal\cdot mol^{-1}$. We also find $D_0°(SrBr)/\Delta_{at}H°(SrBr_2) = 0.46$ which is quite consistent with values of this ratio for other alkaline earth halide systems.[5]

Ionic model calculations[6,7] have led to $D_0°$ values of 5.07 eV[6] and 3.53 eV.[7] The latter result is believed to represent a minimum value for $D_0°$. Two other experimental values for $D_0°$ which bracket the selected value, have been reported. Flame studies[8] gave $D_0° = 3.4$ eV, and chemiluminescence[9] from reaction of Sr atoms with Br_2 gave a lower limit to $D_0°$ of 4.1 eV. We assign an uncertainty of $\pm 10\ kcal\cdot mol^{-1}$ to $\Delta_f H°(298.15\ K)$ to include the possibility that these studies are correct.

Heat Capacity and Entropy

The value of r_e is obtained from that for gaseous $SrBr_2$[3] with $r_e(SrBr)/r_e(SrBr_2) = 0.96$. This value for the ratio is calculated from bond lengths[5] for several other alkaline earth halide systems. Our adopted value for r_e agrees with that (2.74 Å) estimated by Krasnov and Karaseva,[7] while two other estimated values[6,10] lie somewhat higher (~0.2 Å). The rotational constant is calculated from the estimated value for r_e. The value of α_e is obtained from a Morse potential function. The vibrational constants and first seven electronic states and levels are taken from the compilation of Rosen.[11] The E state energy has been measured by Reddy and Rao,[12] while the F, G, and H state energies are due to Reddy *et al.*[13] The five uppermost states were associated with transitions between the excited states of SrBr, and their assignments[13] were made by analogy with the observed spectrum for SrCl(g).

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.105	−80.401	−80.401	INFINITE
100	33.079	225.114	295.842	−7.073	−80.265	−97.279	50.813
200	36.028	249.184	267.101	−3.584	−81.715	−113.767	29.713
250	36.551	257.285	264.356	−1.768	−82.609	−121.685	25.425
298.15	36.856	263.751	263.751	0.	−89.119	−128.461	22.506
300	36.866	263.979	263.751	0.068	−89.171	−128.705	22.410
350	37.073	269.678	264.201	1.917	−105.000	−134.416	20.060
400	37.219	274.639	265.202	3.774	−105.433	−138.589	18.098
450	37.329	279.029	266.500	5.638	−105.892	−142.706	16.565
500	37.416	282.967	267.953	7.507	−106.375	−146.771	15.333
600	37.548	289.801	271.042	11.255	−107.416	−154.754	13.473
700	37.649	295.597	274.146	15.015	−108.559	−162.554	12.130
800	37.733	300.630	277.149	18.785	−109.805	−170.184	11.112
900	37.808	305.078	280.010	22.562	−111.784	−177.579	10.306
1000	37.877	309.065	282.719	26.346	−112.921	−184.829	9.655
1100	37.941	312.678	285.281	30.137	−121.958	−191.600	9.098
1200	38.003	315.982	287.704	33.934	−124.003	−197.841	8.612
1300	38.063	319.027	289.998	37.738	−126.046	−203.911	8.193
1400	38.122	321.849	292.173	41.547	−128.088	−209.824	7.829
1500	38.181	324.482	294.240	45.362	−130.128	−215.591	7.508
1600	38.241	326.948	296.208	49.183	−132.168	−221.222	7.222
1700	38.303	329.268	298.085	53.010	−271.122	−225.546	6.930
1800	38.368	331.459	299.879	56.844	−271.301	−222.860	6.467
1900	38.438	333.535	301.596	60.684	−271.487	−220.163	6.053
2000	38.515	335.509	303.243	64.531	−271.682	−217.457	5.679
2100	38.601	337.390	304.825	68.387	−271.890	−214.741	5.341
2200	38.696	339.188	306.346	72.252	−272.115	−212.014	5.034
2300	38.803	340.910	307.812	76.127	−272.363	−209.277	4.753
2400	38.924	342.564	309.226	80.013	−272.640	−206.528	4.495
2500	39.059	344.156	310.591	83.912	−272.951	−203.767	4.257
2600	39.209	345.691	311.912	87.825	−273.305	−200.993	4.038
2700	39.376	347.173	313.190	91.754	−273.706	−198.205	3.834
2800	39.559	348.609	314.430	95.701	−274.164	−195.400	3.645
2900	39.760	350.000	315.633	99.667	−274.686	−192.578	3.469
3000	39.977	351.352	316.801	103.653	−275.279	−189.737	3.304
3100	40.212	352.667	317.937	107.663	−275.951	−186.875	3.149
3200	40.463	353.947	319.042	111.696	−276.709	−183.989	3.003
3300	40.730	355.196	320.119	115.756	−277.559	−181.079	2.866
3400	41.012	356.416	321.168	119.843	−278.508	−178.141	2.737
3500	41.309	357.609	322.193	123.959	−279.562	−175.174	2.614
3600	41.619	358.777	323.193	128.105	−280.725	−172.175	2.498
3700	41.942	359.922	324.170	132.283	−282.000	−169.143	2.388
3800	42.277	361.045	325.126	136.494	−283.392	−166.074	2.283
3900	42.622	362.148	326.061	140.739	−284.901	−162.968	2.183
4000	42.977	363.231	326.977	145.018	−286.528	−159.821	2.087
4100	43.341	364.297	327.874	149.334	−288.274	−156.632	1.996
4200	43.712	365.346	328.754	153.687	−290.132	−153.399	1.908
4300	44.089	366.379	329.617	158.077	−292.108	−150.120	1.824
4400	44.472	367.397	330.464	162.505	−294.194	−146.794	1.743
4500	44.859	368.400	331.296	166.971	−296.386	−143.420	1.665
4600	45.250	369.391	332.113	171.477	−298.614	−140.001	1.590
4700	45.643	370.368	332.917	176.021	−300.984	−136.527	1.517
4800	46.037	371.333	333.707	180.605	−303.437	−133.002	1.447
4900	46.433	372.286	334.485	185.229	−305.969	−129.426	1.380
5000	46.828	373.228	335.250	189.892	−308.564	−125.797	1.314
5100	47.222	374.160	336.004	194.594	−311.201	−122.117	1.251
5200	47.614	375.080	336.747	199.336	−313.909	−118.384	1.189
5300	48.004	375.991	337.478	204.117	−316.661	−114.597	1.129
5400	48.391	376.892	338.200	208.937	−319.447	−110.758	1.071
5500	48.774	377.783	338.912	213.795	−322.260	−106.868	1.015
5600	49.153	378.666	339.614	218.692	−325.092	−102.926	0.960
5700	49.527	379.539	340.306	223.626	−327.934	−98.934	0.907
5800	49.895	380.404	340.990	228.597	−330.780	−94.892	0.855
5900	50.257	381.260	341.666	233.605	−333.411	−90.824	0.804
6000	50.613	382.107	342.333	238.648	−336.211	−86.689	0.755

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [260.25 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [219.7 \pm 42]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [212.5 \pm 42]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ, cm^{-1}	g_i
[$^4\Sigma$]	0	[4]
	[1000]	[4]
	[2000]	[4]
	[4000]	[4]
	[6000]	[4]
	[8000]	[4]
	[10000]	[4]

$\omega_e = [295]\ cm^{-1}$ $\omega_e x_e = [2.21]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.0904]\ cm^{-1}$ $\alpha_e = [0.00067]\ cm^{-1}$ $r_e = [2.5]$ Å

Enthalpy of Formation

$\Delta_f H°$(TiBr, g, 298.15 K) is calculated from the dissociation energy which is estimated as 104 kcal·mol^{-1}. This estimate is obtained from the relation $\Delta_{at}H°(TiBr_4) < D°_0(TiBr) < \Delta_{at}H°(TiBr_3)$, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF_2(g) by Zmbov and Margrave.[1]

Heat Capacity and Entropy

The vibrational frequency, ω_e, and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenhemier's relation.[2] B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+.[3] α_e is estimated from the Morse potential function.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.938	219.694	219.694	INFINITE
100	31.427	222.442	292.172	−6.973	220.702	201.976	−105.501
200	35.424	245.604	263.646	−3.608	219.699	183.565	−47.942
250	36.809	253.660	260.868	−1.802	218.934	174.618	−36.484
298.15	38.020	260.249	260.249	0.	212.547	166.815	−29.225
300	38.065	260.484	260.249	0.070	212.501	166.531	−28.996
350	39.192	266.438	260.717	2.002	196.821	159.737	−23.839
400	40.173	271.737	261.769	3.987	196.564	154.457	−20.170
450	41.000	276.518	263.147	6.017	196.316	149.209	−17.320
500	41.678	280.874	264.705	8.085	196.076	143.988	−15.042
600	42.651	288.566	268.058	12.305	195.611	133.614	−11.632
700	43.232	295.189	271.472	16.602	195.150	123.317	−9.202
800	43.559	300.985	274.806	20.943	194.690	113.087	−7.384
900	43.734	306.127	278.006	25.309	194.183	102.916	−5.973
1000	43.829	310.740	281.053	29.687	193.553	92.807	−4.848
1100	43.887	314.920	283.945	34.073	192.733	82.771	−3.930
1200	43.933	318.741	286.687	38.464	187.733	72.938	−3.175
1300	43.980	322.259	289.290	42.860	187.248	63.391	−2.547
1400	44.034	325.520	291.763	47.260	186.685	53.884	−2.010
1500	44.097	328.561	294.116	51.667	186.032	44.420	−1.547
1600	44.169	331.409	296.359	56.080	185.276	35.003	−1.143
1700	44.249	334.089	298.500	60.501	184.404	25.637	−0.788
1800	44.336	336.621	300.548	64.930	183.402	16.326	−0.474
1900	44.426	339.020	302.510	69.368	182.258	7.075	−0.195
2000	44.519	341.301	304.393	73.816	166.270	−1.659	0.043
2100	44.612	343.475	306.203	78.272	164.051	−10.001	0.249
2200	44.704	345.553	307.945	82.738	161.831	−18.237	0.433
2300	44.794	347.542	309.624	87.213	159.610	−26.372	0.599
2400	44.881	349.450	311.244	91.697	157.386	−34.410	0.749
2500	44.965	351.284	312.809	96.189	155.159	−42.356	0.885
2600	45.044	353.049	314.323	100.689	152.929	−50.213	1.009
2700	45.119	354.751	315.789	105.198	150.696	−57.984	1.122
2800	45.190	356.393	317.210	109.713	148.460	−65.672	1.225
2900	45.256	357.980	318.588	114.235	146.220	−73.280	1.320
3000	45.318	359.515	319.927	118.764	143.977	−80.810	1.407
3100	45.376	361.002	321.228	123.299	141.732	−88.266	1.487
3200	45.430	362.444	322.494	127.839	139.486	−95.650	1.561
3300	45.481	363.842	323.726	132.385	137.239	−102.963	1.630
3400	45.528	365.201	324.926	136.935	134.993	−110.208	1.693
3500	45.572	366.521	326.095	141.490	132.748	−117.387	1.752
3600	45.614	367.806	327.236	146.050	130.506	−124.502	1.806
3700	45.653	369.056	328.350	150.613	−280.831	−123.767	1.747
3800	45.690	370.274	329.437	155.180	−281.831	−119.508	1.643
3900	45.726	371.461	330.499	159.751	−282.880	−115.223	1.543
4000	45.760	372.619	331.538	164.325	−283.977	−110.910	1.448
4100	45.793	373.750	332.554	168.903	−285.119	−106.570	1.358
4200	45.825	374.854	333.548	173.484	−286.303	−102.201	1.271
4300	45.856	375.932	334.521	178.068	−287.527	−97.803	1.188
4400	45.887	376.987	335.474	182.655	−288.788	−93.376	1.109
4500	45.918	378.018	336.408	187.245	−290.084	−88.920	1.032
4600	45.949	379.028	337.324	191.839	−291.412	−84.435	0.959
4700	45.980	380.016	338.222	196.435	−292.769	−79.921	0.888
4800	46.011	380.985	339.103	201.035	−294.154	−75.378	0.820
4900	46.042	381.934	339.967	205.637	−295.564	−70.806	0.755
5000	46.074	382.864	340.816	210.243	−296.996	−66.204	0.692
5100	46.106	383.777	341.649	214.852	−298.447	−61.574	0.631
5200	46.140	384.673	342.468	219.464	−299.917	−56.915	0.572
5300	46.173	385.552	343.273	224.080	−301.402	−52.228	0.515
5400	46.208	386.415	344.064	228.699	−302.901	−47.513	0.460
5500	46.244	387.263	344.841	233.322	−304.411	−42.769	0.406
5600	46.280	388.097	345.606	237.948	−305.930	−37.998	0.354
5700	46.318	388.916	346.359	242.578	−307.458	−33.200	0.304
5800	46.356	389.722	347.100	247.212	−308.991	−28.376	0.256
5900	46.395	390.515	347.829	251.849	−310.528	−23.524	0.208
6000	46.436	391.295	348.547	256.491	−312.068	−18.647	0.162

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [272.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [593.7 \pm 84]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [586.2 \pm 84]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Delta]$	0	[4]
	[5000]	[2]
	[15000]	[20]

$\omega_e = [321.4]\ cm^{-1}$ $\omega_e x_e = [0.80]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.05254]\ cm^{-1}$ $\alpha_e = [0.00015]\ cm^{-1}$ $r_e = [2.40]$ Å

Enthalpy of Formation

$\Delta_f H°$(WBr, g, 298.15 K) = 140.1 kcal·mol^{-1} (586.178 kJ·mol^{-1}) is calculated from the bond dissociation energy, $\Delta_{at}H°$(W−Br, 298.15 K) = 90 ± 20 kcal·mol^{-1}. This value is estimated to be slightly higher than the average bond dissociation energy of WBr_6(g), by analogy with the WCl_x system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WBr_6(g). The distance is then used with Guggenheimer's relation[1] for polar molecules to calculate the fundamental vibrational freqency, ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/(D° + 0.5\ \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond istance. The value of α_e is calculated from the Morse potential function. The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for WF(g).[2]

References

[1]K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
[2]JANAF Thermochemical Table: WF(g), 3-31-67.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.726	593.680	593.680	INFINITE
100	30.915	235.768	303.535	−6.777	594.581	574.657	−300.170
200	34.595	258.493	275.876	−3.477	593.422	555.121	−144.983
250	35.487	266.317	273.208	−1.723	592.612	545.636	−114.004
298.15	36.032	272.617	272.617	0.	586.178	537.325	−94.137
300	36.049	272.840	272.618	0.067	586.130	537.022	−93.504
350	36.421	278.427	273.058	1.879	570.393	529.709	−79.055
400	36.681	283.308	274.041	3.707	570.067	523.919	−68.417
450	36.870	287.640	275.316	5.546	569.733	518.171	−60.148
500	37.013	291.533	276.746	7.393	569.393	512.460	−53.536
600	37.218	298.300	279.791	11.105	568.688	501.139	−43.628
700	37.366	304.049	282.856	14.835	567.947	489.939	−36.560
800	37.494	309.047	285.824	18.578	567.169	478.847	−31.266
900	37.622	313.471	288.655	22.334	566.354	467.856	−27.154
1000	37.761	317.441	291.339	26.103	565.502	456.957	−23.869
1100	37.914	321.048	293.878	29.886	564.615	446.145	−21.186
1200	38.082	324.354	296.282	33.686	563.695	435.415	−18.953
1300	38.260	327.409	298.560	37.503	562.741	424.764	−17.067
1400	38.445	330.251	300.723	41.338	561.756	414.187	−15.453
1500	38.635	332.910	302.782	45.192	560.738	403.681	−14.057
1600	38.824	335.409	304.743	49.065	559.686	393.245	−12.838
1700	39.013	337.769	306.617	52.957	558.600	382.876	−11.764
1800	39.200	340.004	308.411	56.868	557.480	372.571	−10.812
1900	39.386	342.128	310.130	60.797	556.322	362.330	−9.961
2000	39.572	344.153	311.781	64.745	555.126	352.150	−9.197
2100	39.760	346.088	313.369	68.712	553.891	342.032	−8.508
2200	39.952	347.943	314.898	72.697	552.616	331.973	−7.882
2300	40.151	349.723	316.374	76.702	551.299	321.973	−7.312
2400	40.358	351.436	317.799	80.728	549.942	312.031	−6.791
2500	40.576	353.088	319.178	84.774	548.546	302.147	−6.313
2600	40.806	354.684	320.513	88.843	547.113	292.319	−5.873
2700	41.050	356.228	321.808	92.936	545.618	282.548	−5.466
2800	41.307	357.726	323.064	97.054	544.029	272.833	−5.090
2900	41.578	359.180	324.284	101.198	542.308	263.177	−4.740
3000	41.863	360.594	325.471	105.370	540.431	253.584	−4.415
3100	42.162	361.972	326.626	109.571	538.356	244.056	−4.112
3200	42.473	363.315	327.752	113.803	536.055	234.598	−3.829
3300	42.795	364.627	328.850	118.066	533.504	225.216	−3.565
3400	43.126	365.910	329.921	122.362	530.671	215.916	−3.317
3500	43.465	367.165	330.967	126.691	527.494	206.704	−3.085
3600	43.810	368.394	331.990	131.055	523.879	197.589	−2.867
3700	44.159	369.599	332.990	135.453	484.961	188.771	−2.665
3800	44.510	370.781	333.969	139.887	483.760	180.782	−2.485
3900	44.861	371.942	334.928	144.355	482.597	172.824	−2.315
4000	45.210	373.082	335.867	148.859	481.472	164.896	−2.153
4100	45.556	374.203	336.789	153.397	480.386	156.995	−2.000
4200	45.896	375.305	337.693	157.970	479.340	149.120	−1.855
4300	46.230	376.389	338.580	162.576	478.334	141.270	−1.716
4400	46.555	377.455	339.452	167.216	477.368	133.442	−1.584
4500	46.870	378.505	340.308	171.887	476.441	125.636	−1.458
4600	47.174	379.538	341.149	176.589	475.554	117.851	−1.338
4700	47.466	380.556	341.977	181.321	474.706	110.084	−1.223
4800	47.746	381.558	342.791	186.082	473.896	102.334	−1.114
4900	48.012	382.546	343.592	190.870	473.123	94.602	−1.008
5000	48.264	383.518	344.381	195.684	472.386	86.884	−0.908
5100	48.501	384.476	345.158	200.522	471.685	79.181	−0.811
5200	48.723	385.420	345.923	205.384	471.017	71.491	−0.718
5300	48.931	386.350	346.677	210.267	470.381	63.815	−0.629
5400	49.123	387.267	347.421	215.169	469.776	56.149	−0.543
5500	49.301	388.170	348.153	220.091	469.200	48.495	−0.461
5600	49.463	389.060	348.876	225.029	468.653	40.851	−0.381
5700	49.611	389.936	349.588	229.983	468.132	33.216	−0.304
5800	49.744	390.800	350.292	234.951	467.635	25.590	−0.230
5900	49.863	391.652	350.985	239.931	467.162	17.973	−0.159
6000	49.969	392.491	351.670	244.923	466.711	10.363	−0.090

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = [265.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [309.3 \pm 42]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [301.2 \pm 2]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^4\Sigma]$	0	[4]
	[3000]	[4]
	[6000]	[4]
	[12000]	[4]
	[18000]	[4]
	[24000]	[4]
	[30000]	[4]

$\omega_e = [317]\ cm^{-1}$ $\omega_e x_e = [0.69]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.065]\ cm^{-1}$ $\alpha_e = [0.00018]\ cm^{-1}$ $r_e = [2.47]$ Å

Enthalpy of Formation

$\Delta_f H°$(ZrBr, g, 298.15 K) = 72 kcal·mol^{-1} (301.248 kJ·mol^{-1}) is derived from the estimated bond dissociation energy, $\Delta_{at}H°$ (Zr–Br, 298.15 K) = 103.5 ± 10 kcal·mol^{-1}. This value of is calculated from the relation $\Delta_{at}H°$(Zr–Br, 298.15 K)/$\Delta_{at}H°$(Ti–Br, 298.15 K) = $\Delta_{at}H°$(ZrBr4, 298.15 K)/$\Delta_{at}H°$(TiBr4, 298.15 K) where the average bond dissociation energies, $\Delta_{at}H°(ZrBr_4, 298.15\ K)$ = 102.2 kcal·mol^{-1}, $\Delta_{at}H°(TiBr_4, 298.15\ K)$ = 87.9 kcal·mol^{-1} and $\Delta_{at}H°$(TiBr, 298.15 K) = 89.0 kcal·mol^{-1}, all calculated from JANAF $\Delta_f H°$(298.15 K) for $ZrBr_4$(g), $TiBr_4$(g), TiBr(g), Zr(g), Ti(g) and Br(g).

Heat Capacity and Entropy

The bond distance is assumed to be the same as that in $ZrBr_4$(g), which was estiamted as 2.47 Å by Godnev *et al.*[1] The estimated bond distance is then used with Guggenheimer's[2] relation for polar molecules to calculate the fundamental frequency ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4\ (\Delta_{at}H° + 0.5\ \omega_e) = 0.0021$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by Moore.[3] The electronic levels and quantum weights are estimated to be the same as those of ZrF(g).

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.739	309.261	309.261	INFINITE
100	30.981	228.641	296.521	−6.788	309.929	291.163	−152.088
200	34.653	251.415	268.819	−3.481	308.592	272.862	−71.264
250	35.530	259.250	266.148	−1.725	307.725	264.027	−55.165
298.15	36.065	265.557	265.557	0.	301.248	256.351	−44.912
300	36.082	265.780	265.557	0.067	301.198	256.073	−44.586
350	36.451	271.371	265.998	1.881	285.416	249.427	−37.225
400	36.719	276.257	266.982	3.710	285.042	244.311	−31.904
450	36.936	280.595	268.258	5.552	284.658	239.243	−27.771
500	37.133	284.496	269.690	7.403	284.265	234.218	−24.469
600	37.542	291.302	272.741	11.137	283.447	224.284	−19.526
700	38.018	297.124	275.818	14.914	282.589	214.491	−16.006
800	38.558	302.235	278.807	18.743	281.691	204.824	−13.374
900	39.134	306.810	281.669	22.627	280.746	195.272	−11.333
1000	39.714	310.963	284.394	26.569	279.746	185.828	−9.707
1100	40.274	314.775	286.985	30.569	278.682	176.487	−8.381
1200	40.798	318.302	289.449	34.623	273.839	167.468	−7.290
1300	41.277	321.587	291.796	38.727	273.174	158.630	−6.374
1400	41.705	324.662	294.035	42.877	272.508	149.844	−5.591
1500	42.082	327.552	296.174	47.067	271.825	141.106	−4.914
1600	42.410	330.279	298.222	51.292	271.108	132.415	−4.323
1700	42.691	332.858	300.184	55.547	270.342	123.769	−3.803
1800	42.929	335.306	302.068	59.828	269.511	115.171	−3.342
1900	43.129	337.632	303.879	64.131	268.599	106.621	−2.931
2000	43.295	339.849	305.622	68.453	267.591	98.122	−2.563
2100	43.432	341.964	307.303	72.789	266.472	89.675	−2.231
2200	43.543	343.988	308.925	77.138	243.906	82.031	−1.948
2300	43.633	345.925	310.492	81.497	242.108	74.713	−1.697
2400	43.705	347.784	312.007	85.864	240.308	67.473	−1.469
2500	43.763	349.569	313.474	90.238	238.502	60.309	−1.260
2600	43.808	351.286	314.895	94.616	236.690	53.217	−1.069
2700	43.844	352.940	316.274	98.999	234.871	46.195	−0.894
2800	43.872	354.535	317.612	103.385	233.044	39.240	−0.732
2900	43.894	356.075	318.912	107.773	231.210	32.351	−0.583
3000	43.911	357.564	320.176	112.164	229.369	25.525	−0.444
3100	43.926	359.004	321.405	116.555	227.521	18.761	−0.316
3200	43.938	360.399	322.602	120.949	225.667	12.056	−0.197
3300	43.948	361.751	323.768	125.343	223.809	5.410	−0.086
3400	43.958	363.063	324.905	129.738	221.947	−1.181	0.018
3500	43.968	364.337	326.013	134.134	220.083	−7.716	0.115
3600	43.977	365.576	327.095	138.532	218.219	−14.198	0.206
3700	43.988	366.781	328.151	142.930	216.355	−20.628	0.291
3800	43.999	367.954	329.183	147.329	214.492	−27.009	0.371
3900	44.011	369.097	330.192	151.730	212.633	−33.340	0.447
4000	44.024	370.212	331.179	156.131	210.779	−39.623	0.517
4100	44.038	371.299	332.144	160.535	208.930	−45.860	0.584
4200	44.053	372.360	333.089	164.939	207.088	−52.052	0.647
4300	44.070	373.397	334.015	169.345	205.254	−58.201	0.707
4400	44.088	374.411	334.921	173.753	203.429	−64.306	0.763
4500	44.107	375.402	335.810	178.163	201.613	−70.371	0.817
4600	44.127	376.371	336.681	182.574	199.808	−76.395	0.867
4700	44.148	377.320	337.536	186.988	198.014	−82.380	0.916
4800	44.171	378.250	338.374	191.404	−364.705	−76.710	0.835
4900	44.194	379.161	339.197	195.822	−366.127	−70.695	0.754
5000	44.219	380.054	340.006	200.243	−367.553	−64.651	0.675
5100	44.244	380.930	340.799	204.666	−368.982	−58.579	0.600
5200	44.270	381.789	341.580	209.092	−370.412	−52.479	0.527
5300	44.296	382.633	342.346	213.520	−371.842	−46.351	0.457
5400	44.323	383.461	343.100	217.951	−373.269	−40.196	0.389
5500	44.351	384.275	343.841	222.385	−374.694	−34.015	0.323
5600	44.379	385.074	344.570	226.821	−376.113	−27.808	0.259
5700	44.408	385.860	345.288	231.261	−377.527	−21.576	0.198
5800	44.437	386.633	345.994	235.703	−378.933	−15.319	0.138
5900	44.466	387.392	346.689	240.148	−380.331	−9.038	0.080
6000	44.495	388.140	347.374	244.596	−381.720	−2.733	0.024

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

REFERENCE STATE

0	to	265.90 K	crystal
265.90	to	332.62 K	liquid
above		332.62 K	ideal diatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−24.509	0.	0.	0.
100	43.587	53.847	271.009	−21.716	0.	0.	0.
200	53.761	87.421	171.496	−16.815	0.	0.	0.
265.900	61.630	103.687	152.725	−13.039	CRYSTAL <--> LIQUID TRANSITION		
265.900	77.724	143.445	152.725	−2.468			
298.15	75.674	152.206	152.206	0.	0.	0.	0.
300	75.624	152.674	152.208	0.140	0.	0.	0.
332.503	75.302	160.429	152.639	2.590	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
332.503	36.332	249.341	152.639	32.153			
400	36.723	256.093	169.543	34.620	0.	0.	0.
500	37.077	264.329	187.706	38.312	0.	0.	0.
600	37.301	271.110	201.058	42.031	0.	0.	0.
700	37.460	276.873	211.488	45.770	0.	0.	0.
800	37.586	281.883	219.981	49.522	0.	0.	0.
900	37.692	286.316	227.110	53.286	0.	0.	0.
1000	37.787	290.293	233.233	57.060	0.	0.	0.
1100	37.876	293.898	238.586	60.843	0.	0.	0.
1200	37.962	297.198	243.335	64.635	0.	0.	0.
1300	38.049	300.240	247.597	68.436	0.	0.	0.
1400	38.140	303.063	251.459	72.245	0.	0.	0.
1500	38.239	305.697	254.988	76.064	0.	0.	0.
1600	38.348	308.169	258.236	79.893	0.	0.	0.
1700	38.471	310.497	261.242	83.734	0.	0.	0.
1800	38.611	312.700	264.040	87.588	0.	0.	0.
1900	38.769	314.792	266.657	91.457	0.	0.	0.
2000	38.945	316.785	269.114	95.342	0.	0.	0.
2100	39.137	318.690	271.429	99.246	0.	0.	0.
2200	39.345	320.515	273.619	103.170	0.	0.	0.
2300	39.563	322.269	275.697	107.116	0.	0.	0.
2400	39.789	323.957	277.673	111.083	0.	0.	0.
2500	40.018	325.586	279.557	115.074	0.	0.	0.
2600	40.244	327.160	281.358	119.087	0.	0.	0.
2700	40.463	328.683	283.082	123.122	0.	0.	0.
2800	40.672	330.158	284.737	127.179	0.	0.	0.
2900	40.864	331.589	286.328	131.256	0.	0.	0.
3000	41.038	332.977	287.860	135.351	0.	0.	0.
3100	41.190	334.326	289.338	139.463	0.	0.	0.
3200	41.318	335.635	290.764	143.589	0.	0.	0.
3300	41.420	336.908	292.143	147.726	0.	0.	0.
3400	41.496	338.146	293.478	151.872	0.	0.	0.
3500	41.545	339.350	294.772	156.024	0.	0.	0.
3600	41.567	340.521	296.026	160.180	0.	0.	0.
3700	41.563	341.659	297.244	164.337	0.	0.	0.
3800	41.533	342.767	298.428	168.492	0.	0.	0.
3900	41.480	343.846	299.578	172.642	0.	0.	0.
4000	41.404	344.895	300.698	176.787	0.	0.	0.
4100	41.306	345.916	301.789	180.922	0.	0.	0.
4200	41.190	346.910	302.851	185.047	0.	0.	0.
4300	41.056	347.878	303.887	189.160	0.	0.	0.
4400	40.907	348.820	304.898	193.258	0.	0.	0.
4500	40.744	349.738	305.884	197.341	0.	0.	0.
4600	40.569	350.631	306.847	201.407	0.	0.	0.
4700	40.383	351.502	307.788	205.454	0.	0.	0.
4800	40.189	352.350	308.708	209.483	0.	0.	0.
4900	39.987	353.176	309.607	213.492	0.	0.	0.
5000	39.780	353.982	310.486	217.480	0.	0.	0.
5100	39.568	354.768	311.347	221.448	0.	0.	0.
5200	39.353	355.534	312.189	225.394	0.	0.	0.
5300	39.136	356.282	313.014	229.318	0.	0.	0.
5400	38.917	357.011	313.822	233.221	0.	0.	0.
5500	38.698	357.723	314.614	237.102	0.	0.	0.
5600	38.480	358.419	315.390	240.961	0.	0.	0.
5700	38.263	359.098	316.151	244.798	0.	0.	0.
5800	38.047	359.761	316.897	248.613	0.	0.	0.
5900	37.834	360.410	317.629	252.407	0.	0.	0.
6000	37.624	361.044	318.347	256.180	0.	0.	0.

PREVIOUS: September 1961 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 152.21 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 265.90 \pm 0.05\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 10.571 \pm 0.008\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity for crystalline and liquid bromine was measured by Hildenbrand *et al.*,[1] 179 data points in the range 15–310 K. The reported values are corrected for the current relative molecular weight and converted to joules. The liquid phase heat capacity is extrapolated to a constant value of 18.0 cal $K^{-1} \cdot mol^{-1}$ for temperatures above 320 K. The value recommended by CODATA[2] for $S°(Br_2, l, 298.15\ K)$ is the same as adopted here and is based on the same study. References to earlier work are given by Hildenbrand *et al.*[1] They are not used in this analysis.

Fusion Data

The adopted values for the fusion point and the enthalpy of fusion are from the study of Hildenbrand *et al.*[1]

Vaporization Data

The enthalpy of vaporization of bromine at 25°C was measured by Hildenbrand *et al.*[1] Six vaporization determinations were made using 14 to 18 gram samples of bromine. Correcting their reported values for the current relative atomic mass and converting to Joules yields $\Delta_{vap}H(Br_2, l, 298.15\ K) = 30.91 \pm 0.11\ kJ \cdot mol^{-1}$. CODATA[2] has recommended the same value based on the same study.

Vapor pressure studies include: Fischer and Bingle (298–389 K),[3] Frey and Gregory (177–195 K),[4] Henglein, *et al.* (177–241 K),[5] Ramsay and Young (256–329 K)[6] and Scheffer and Voogd (253–362 K).[7] For the liquid region, the data of Fischer and Bingle[3] and Scheffer and Voogd[7] show a decided decrease of $\Delta_{vap}H°$ with increasing temperature. The data of Ramsey and Young[6] show only a small temperature trend and are in good agreement with the adopted calorimetric study. For the crystal region, the data are too scattered to be conclusive.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−24.509	0.	0.	0.
100	43.587	53.847	271.009	−21.716	0.	0.	0.
200	53.761	87.421	171.496	−16.815	0.	0.	0.
250	59.225	99.965	155.962	−13.999	0.	0.	0.
265.900	61.630	103.687	152.725	−13.039	CRYSTAL <--> LIQUID TRANSITION		
265.900	77.724	143.445	152.725	−2.468			
298.15	75.674	152.206	152.206	0.	0.	0.	0.
300	75.624	152.674	152.208	0.140	0.	0.	0.
332.503	75.302	160.429	152.639	2.590	----- FUGACITY = 1 bar -----		
350	75.302	164.291	153.126	3.908	−28.882	1.538	−0.230
400	75.302	174.347	155.164	7.673	−26.947	5.752	−0.751
450	75.302	183.216	157.798	11.438	−25.023	9.723	−1.129
500	75.302	191.150	160.743	15.203	−23.108	13.481	−1.408

PREVIOUS: September 1961 CURRENT: June 1982

D_0° = 191.154 ± 0.001 kJ·mol^{-1} (natural abundance)
S°(298.15 K) = 245.394 ± 0.050 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 45.70 ± 0.121 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 30.911 ± 0.11 kJ·mol^{-1}

Spectroscopic Data for $^{79}Br_2$ in cm^{-1}

State	T_e	D°	ω_e	$\omega_e x_e$	B_e	$10^3 \cdot \alpha_e$	$10^7 \cdot D_e$	r_e, Å	Reference
$^1\Sigma_g^+$	0	15894.6	325.3213	1.07742[a]	0.082107	0.31873	0.2092	2.28107	1
$^3\Pi_{2u}$	13400	15894.6	160	2.4	0.057	0.5	0.29	2.74	2
$^3\Pi_{1u}$	13904	15894.6	153.8	2.78	0.0588	0.72	0.34	2.695	3
$^3\Pi_{o_u^-}$	15850	15894.6	70	6.2	0.06	2.8	1.76	2.67	2
$^3\Pi_{o_u^+}$	15902.47	19579.76	166.546	1.61517[b]	0.059589	0.489095[c]	0.3013	2.6776	4d

(a) $-2.29798 \times 10^{-3}(v + 1/2)^3$
(b) $-7.53588 \times 10^{-3}(v + 1/2)^3 - 2.44989 \times 10^{-4}(v + 1/2)^4 + 0.991688 \times 10^{-5}(v + 1/2)^5 - 6.97853 \times 10^{-8}(v + 1/2)^6$
(c) $-6.6369 \times 10^{-6}(v + 1/2)^2$
(d) $^3\Pi_{o_u^+}$ constants for natural abundance Br_2, actual coefficients for $^{79}Br_2$ will differ slightly from these according to the scaling method of Herzberg.[5]
(e) *The dissociation energy of each state is relative to the lowest level of the ground state.*

Enthalpy of Formation

We adopt the enthalpy of formation values of CODATA[6] as follows: $\Delta_f H^\circ$(298.15 K) = 30.91 ± 0.11 kJ·mol^{-1} and $\Delta_f H^\circ$(0 K) = 45.71 ± 0.12 kJ·mol^{-1}. These values were based on the heat capacity and enthalpy of vaporization measurements of Hildenbrand *et al.*[7] Note that the latter value of $\Delta_f H^\circ$ is deduced from the former using the CODATA values of H°(298.15 K)–H°(0 K) for $Br_2(g)$ and $Br_2(l)$. Our calculated value of H°(298.15 K)–H°(0 K) for $Br_2(g)$ is only 1.3 J·mol^{-1} smaller than the recommended value of CODATA. Our adopted dissociation energy for the natural abundance mixture is derived from the isotopic values reported by Barrow *et al.*[1] as given by Huber and Herzberg.[3] The CODATA value for $D_0^\circ(Br_2, g)$, as deduced from the $\Delta_f H^\circ$(0 K) data for $Br_2(g)$ and Br(g), is 190.14 kJ·mol^{-1}. The 0.01 kJ·mol^{-1} discrepancy is due to CODATA's adoption of D_0° for $^{79}Br^{81}Br$ based on earlier work of Horsley and Barrow.[8] Refer to the monatomic bromine gas table for additional discussion of the dissociation energy.

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique. Included in the calculation are the ground state plus the four lowest lying excited states. Spectroscopic constants for the ground state are taken from Barrow, *et al.*[1] for $^{79}Br_2$ while the excited state constants are from Gurvich *et al.*[2-4] Note that Barrow, *et al.*[1] presented constants for the $^3\Pi_{o_u^+}$ state of $^{79}Br_2$ for v ≤10 only. Therefore for this state we adopted the constants of Gurvich, *et al.*[2] which are fit to the experimental data up to the dissociation limit. For the ground state and the $^3\Pi_{1u}$ and $^3\Pi_{o_u^+}$ excited states, the calculation is performed including the quasi-bound rotational levels above the dissociation limit (see $Cl_2(g)$ table) using J_{lim} and v_{max} given by Gurvich *et al.*[2] Splitting of the rotational levels due to the rotational–electronic interaction in the $^3\Pi_{2u}$ and $^3\Pi_{1u}$ states is taken into account only insofar as the statistical weight of the rotational levels is doubled. The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[9] who proposed a simpler form of Wooley's method.[10] The spectroscopic constants for the hypothetical natural abundance species are determined from the $^{79}Br_2$ constants using a standard reduced mass scaling scheme. The calculated value of S°(298.15 K) is 0.07 J·mol^{-1}·K^{-1} smaller than that adopted by CODATA[6] and also by Gurvich *et al.*[2] For this comparison, the entropy value reported by CODATA and Gurvich is increased by 0.1094 J·K^{-1}·mol^{-1} to account for a change in the standard state pressure from 1 atm to 1 bar.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−9.722	45.697	45.697	INFINITE
100	30.884	208.563	276.306	−6.774	45.852	30.380	−15.869
200	34.582	231.269	248.653	−3.477	44.248	15.479	−4.043
250	35.489	239.092	245.984	−1.723	43.186	8.404	−1.756
298.15	36.048	245.394	245.394	0.	30.910	3.126	−0.548
300	36.066	245.617	245.394	0.067	30.837	2.954	−0.514
332.503	36.332	249.341	245.601	1.243	----- FUGACITY = 1 bar -----		
350	36.451	251.207	245.835	1.880	0.	0.	0.
400	36.723	256.093	246.818	3.710	0.	0.	0.
450	36.923	260.431	248.094	5.551	0.	0.	0.
500	37.077	264.329	249.526	7.402	0.	0.	0.
600	37.301	271.110	252.575	11.121	0.	0.	0.
700	37.460	276.873	255.645	14.860	0.	0.	0.
800	37.586	281.883	258.618	18.612	0.	0.	0.
900	37.692	286.316	261.454	22.376	0.	0.	0.
1000	37.787	290.293	264.143	26.150	0.	0.	0.
1100	37.876	293.898	266.686	29.933	0.	0.	0.
1200	37.962	297.198	269.093	33.725	0.	0.	0.
1300	38.049	300.240	271.374	37.526	0.	0.	0.
1400	38.140	303.063	273.538	41.335	0.	0.	0.
1500	38.239	305.697	275.595	45.154	0.	0.	0.
1600	38.348	308.169	277.554	48.983	0.	0.	0.
1700	38.471	310.497	279.424	52.824	0.	0.	0.
1800	38.611	312.700	281.212	56.678	0.	0.	0.
1900	38.769	314.792	282.925	60.547	0.	0.	0.
2000	38.945	316.785	284.569	64.432	0.	0.	0.
2100	39.137	318.690	286.148	68.336	0.	0.	0.
2200	39.345	320.515	287.669	72.260	0.	0.	0.
2300	39.563	322.269	289.136	76.206	0.	0.	0.
2400	39.789	323.957	290.552	80.173	0.	0.	0.
2500	40.018	325.586	291.921	84.164	0.	0.	0.
2600	40.244	327.160	293.246	88.177	0.	0.	0.
2700	40.463	328.683	294.530	92.212	0.	0.	0.
2800	40.672	330.158	295.777	96.269	0.	0.	0.
2900	40.864	331.589	296.987	100.346	0.	0.	0.
3000	41.038	332.977	298.164	104.441	0.	0.	0.
3100	41.190	334.326	299.308	108.553	0.	0.	0.
3200	41.318	335.635	300.423	112.679	0.	0.	0.
3300	41.420	336.908	301.510	116.816	0.	0.	0.
3400	41.496	338.146	302.569	120.962	0.	0.	0.
3500	41.545	339.350	303.603	125.114	0.	0.	0.
3600	41.567	340.521	304.612	129.270	0.	0.	0.
3700	41.563	341.659	305.598	133.427	0.	0.	0.
3800	41.533	342.767	306.562	137.582	0.	0.	0.
3900	41.480	343.846	307.504	141.732	0.	0.	0.
4000	41.404	344.895	308.426	145.877	0.	0.	0.
4100	41.306	345.916	309.328	150.012	0.	0.	0.
4200	41.190	346.910	310.211	154.137	0.	0.	0.
4300	41.056	347.878	311.076	158.250	0.	0.	0.
4400	40.907	348.820	311.923	162.348	0.	0.	0.
4500	40.744	349.738	312.753	166.431	0.	0.	0.
4600	40.569	350.631	313.567	170.497	0.	0.	0.
4700	40.383	351.502	314.365	174.544	0.	0.	0.
4800	40.189	352.350	315.147	178.573	0.	0.	0.
4900	39.987	353.176	315.915	182.582	0.	0.	0.
5000	39.780	353.982	316.668	186.570	0.	0.	0.
5100	39.568	354.768	317.408	190.538	0.	0.	0.
5200	39.353	355.534	318.133	194.484	0.	0.	0.
5300	39.136	356.282	318.846	198.408	0.	0.	0.
5400	38.917	357.011	319.546	202.311	0.	0.	0.
5500	38.698	357.723	320.234	206.192	0.	0.	0.
5600	38.480	358.419	320.910	210.051	0.	0.	0.
5700	38.263	359.098	321.574	213.888	0.	0.	0.
5800	38.047	359.761	322.226	217.703	0.	0.	0.
5900	37.834	360.410	322.868	221.497	0.	0.	0.
6000	37.624	361.044	323.499	225.270	0.	0.	0.

PREVIOUS: December 1961 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = [129.7 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1015\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -683.2 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = 29.079 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is the mean of three values derived from two independent paths. One path involves the enthalpy of solution of Ca(cr) and $CaBr_2$(cr) in HBr·555 H_2O which were measured by Ehrlich *et al.*[1] Recalculation of their results using recent thermal data[2,3] for aqueous HBr yields $\Delta_f H°(CaBr_2, cr, 298.15\ K) = -164.0\ kcal·mol^{-1}$. The uncertainty in this value could approach $\pm 1.0\ kcal·mol^{-1}$ due primarily to the rather impure metal (99.3% free Ca) used in these measurements.

An alternate path used to obtain values for $\Delta_f H°$ involves the results of measurements on the enthalpy of solution of $CaBr_2$(cr) in aqueous solution. The work[4-6] reported in this area has been reviewed by Bichowsky and Rossini.[7] Recalculation of these results using $\Delta_f H°(Ca^{+2}, \infty\ aq, 298.15\ K) = -129.74\ kcal·mol^{-1}$[8] and $\Delta_f H°(Br^-, \infty\ aq, 298.15\ K) = -29.039 \pm 0.036\ kcal·mol^{-1}$[12] yields values for $\Delta_f H°$ of $CaBr_2$(cr) in $kcal·mol^{-1}$ of −162.3,[4] −160.2,[5] and −163.6.[6] The disagreement in these values is disturbing but can be mostly accounted for when one considers the difficulties involved in the preparation[6] of "pure" anhydrous $CaBr_2$.

A mean value ($-163.3\ kcal·mol^{-1}$, $683.247\ kJ·mol^{-1}$) for $\Delta_f H°(CaBr_2, cr, 298.15\ K)$ of three results[1,4,6] is preferred because of the difficulties reported in obtaining and keeping samples free of impurities. NBS[8] has selected essentially the same value ($-163.2\ kcal·mol^{-1}$) from their analysis of the available data.

Heat Capacity and Entropy

No low temperature $C_p°$ data have been reported for $CaBr_2$; thus, the value of $S°(298.15\ K)$ must be estimated. Application of the Berthelot principle[9] to the process $SrBr_2(cr) + Ca(cr) = CaBr_2(cr) + Sr(cr)$ gives $S°(298.15\ K) = 31.7 \pm 1.5\ cal·K^{-1}mol^{-1}$ for $CaBr_2$. Auxiliary entropies are taken from the JANAF Tables.[10] Also, JANAF entropies[10] for the other three calcium dihalides suggest a value near $30.5\ cal·K^{-1}·mol^{-1}$ for $CaBr_2$. We adopt $S°(298.15\ K) = 31 \pm 1\ cal·K^{-1}·mol^{-1}$ which is the value selected by NBS.[8] Other reported estimates for $S°(298.15\ K)$ in $cal·K^{-1}·mol^{-1}$ are 32.0 ± 2.8,[11] 32.2 ± 0.7,[12] and 33.[13]

$C_p°$ at 298.15 K has not been measured. However, Janz *et al.*[14] measured relative enthalpies (434–1013 K) for $CaBr_2$ and reported the results in equation form. Their equation gives $C_p° = 16.3\ cal·K^{-1}·mol^{-1}$ at 298.15 K which appears to be too low by about 2 units when compared with JANAF $C_p°$ data for several other alkaline earth dihalides. The only other enthalpy study that has been reported is that of Dworkin and Bredig[15] who measured $H°(1015\ K)-H°(298.15\ K) = 14.00\ kcal·mol^{-1}$ in a copper block drop–calorimeter. We adopt this result. JANAF data[10] are used to obtain $C_p°$ at 298.15 K from the process $CaCl_2(cr) + 2\ KBr(cr) = CaBr_2(cr) + 2\ KCl(cr)$ by assuming $\Delta C_p° = 0$. Data in the temperature range 300–1013 K are estimated by comparison with those for CaF_2 and $CaCl_2$.[10] More weight is given to the results for $CaCl_2$, since it has the same crystal structure[15] as $CaBr_2$ and nearly the same melting temperature (1045 K)[10] and enthalpy $H°(1045\ K)-H°(298.15\ K) = 14.2\ kcal·mol^{-1}$[10] at T_{fus} as does $CaBr_2$. The $C_p°$ estimates are also made so as to reproduce as closely as possible the adopted enthalpy at 1015 K. Our estimated $C_p°$ data give a value of $H°(1015\ K)-H°(298.15\ K) = 13.994\ kcal·mol^{-1}$ which agrees with the measured value[15] to within 6 $cal·mol^{-1}$. $C_p°$ data above 1015 K are obtained by graphical extrapolation. The enthalpies obtained from the equation of Janz *et al.*[14] are systematically lower than our adopted values. The deviation is −0.4% at 1015 K; it increases at lower temperatures and reaches a maximum value of −2.7% at 600 K.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference in the adopted enthalpies of formation for the ideal gas and crystal at 298.15 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
100							
200							
298.15	75.040	129.704	129.704	0.	−683.247	−664.139	116.354
300	75.124	130.168	129.705	0.139	−683.296	−664.020	115.616
400	77.990	152.206	132.691	7.806	−712.744	−651.460	85.072
500	79.454	169.774	138.410	15.682	−711.325	−636.304	66.474
600	80.500	184.352	144.887	23.679	−709.990	−621.427	54.100
700	81.630	196.836	151.437	31.780	−708.767	−606.765	45.277
800	83.471	207.851	157.813	40.030	−708.463	−592.168	38.665
900	85.856	217.816	163.935	48.493	−707.289	−577.703	33.529
1000	88.617	227.004	169.788	57.216	−706.160	−563.365	29.427
1015.000	89.036	228.327	170.643	58.549	--- CRYSTAL <--> LIQUID ---		
1100	91.922	235.601	175.384	66.238	−705.045	−549.139	26.076
1200	95.563	243.753	180.745	75.611	−711.624	−534.394	23.262
1300	99.412	251.554	185.893	85.358	−709.177	−519.722	20.883
1400	103.387	259.067	190.853	95.499	−706.346	−505.252	18.851
1500	107.320	266.334	195.644	106.034	−703.129	−490.998	17.098

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [147.861]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1015\ K$

$\Delta_f H°(298.15\ K) = [-662.989]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 29.079 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1015\ K)–H°(298.15\ K)$, between the crystal and liquid. Toguri *et al.*[1] have reported a K_p value for the anion exchange equilibrium $0.5\ CaBr_2(l) + HCl(g) = 0.5\ CaCl_2(l) + HBr(g)$ at 1073 K. A 3rd law analysis of this single value gives $\Delta_f H°(298.15\ K) = -0.22\ kcal·mol^{-1}$ with JANAF functions. The 3rd law enthalpy leads to $\Delta_f H°(l, 298.15\ K) = -157.9\ kcal·mol^{-1}$ which supports our adopted value by an independent path.

Heat Capacity and Entropy

$C_p°$ of the liquid above 700 K is the value ($27.0\ cal·K^{-1}·mol^{-1}$) determined by Dworkin and Bredig[2] from enthalpy measurements in the vicinity of the melting point. A similar enthalpy study (1013–1132 K) by Janz *et al.*[3] suggests only a slightly higher value ($27.38\ cal·K^{-1}·mol^{-1}$) for $C_p°$ of $CaBr_2(l)$. A glass transition is assumed at 700 K below which $C_p°$ is that of the crystal.

The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted value of T_{fus} is that measured calorimetrically by Dworkin and Bredig.[2] Similar measurements by Janz *et al.*[3] gave essentially the same value (1013 K). Other reported values for T_{fus} are 1018 K,[4] 1003 K,[5–7] and 1016 K.[8]

$\Delta_{fus}H°$ is that measured by Dworkin and Bredig[2] in a copper block drop–calorimeter. Another calorimetrically eternined value[3] ($\Delta_{fus}H° = 6.86 \pm 0.09\ kcal·mol^{-1}$) and one based on cryoscopic measurements[4] ($\Delta_{fus}H° = 7.03 \pm 0.35\ kcal·mol^{-1}$) bracket the selected value.

Vaporization Data

T_{vap} (f = 1 bar) is the temperature at which $\Delta_r G°$ for the process $CaBr_2(l) = CaBr_2(g)$ approaches zero. $\Delta_{vap}H°$ is the difference in the enthalpies of formation of the gas and liquid at T_{vap}. Peterson and Hutchison[9] obtained $T_{vap} = 2088$ K (at 1 atm) from vapor pressure measurements on the liquid (1149–1321 K). This value is nearly identical to our result.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	75.040	147.861	147.861	0.	−662.989	−649.294	113.754
300	75.124	148.325	147.862	0.139	−663.038	−649.209	113.037
400	77.990	170.363	150.847	7.806	−692.486	−638.465	83.375
500	79.454	187.931	156.567	15.682	−691.067	−625.125	65.306
600	80.500	202.508	163.043	23.679	−689.732	−612.063	53.285
700	81.631	215.001	169.594	31.785	−688.503	−599.217	44.714
700.000	81.631	215.001	169.594	31.785	GLASS <-> LIQUID TRANSITION		
700.000	112.968	215.001	169.594	31.785			
800	112.968	230.086	176.234	43.082	−685.153	−586.647	38.304
900	112.968	243.392	182.971	54.378	−681.146	−574.578	33.348
1000	112.968	255.294	189.619	65.675	−677.444	−562.938	29.405
1100	112.968	266.061	196.087	76.972	−674.053	−551.654	26.196
1200	112.968	275.891	202.333	88.269	−678.708	−540.043	23.507
1300	112.968	284.933	208.344	99.566	−674.712	−528.650	21.241
1400	112.968	293.305	214.117	110.862	−670.724	−517.564	19.311
1500	112.968	301.099	219.659	122.159	−666.746	−506.763	17.647
1600	112.968	308.389	224.979	133.456	−662.779	−496.226	16.200
1700	112.968	315.238	230.089	144.753	−658.823	−485.938	14.931
1800	112.968	321.695	235.001	156.050	−803.554	−473.671	13.746
1900	112.968	327.803	239.726	167.346	−798.212	−455.490	12.522
2000	112.968	333.598	244.276	178.643	−792.893	−437.590	11.429
2100	112.968	339.109	248.662	189.940	−787.600	−419.955	10.446
2200	112.968	344.365	252.893	201.237	−782.338	−402.572	9.558
2300	112.968	349.386	256.980	212.534	−777.112	−385.427	8.753
2400	112.968	354.194	260.931	223.830	−771.927	−368.508	8.020
2500	112.968	358.806	264.755	235.127	−766.790	−351.805	7.351

PREVIOUS: CURRENT: June 1974

209.15	to	1015 K	crystal
above		1015 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	75.040	129.704	129.704	0.	−683.247	−664.139	116.354
300	75.124	130.168	129.705	0.139	−683.296	−664.020	115.616
400	77.990	152.206	132.691	7.806	−712.744	−651.460	85.072
500	79.454	169.774	138.410	15.682	−711.325	−636.304	66.474
600	80.500	184.352	144.887	23.679	−709.990	−621.427	54.100
700	81.630	196.836	151.437	31.780	−708.767	−606.765	45.277
800	83.471	207.851	157.813	40.030	−708.463	−592.168	38.665
900	85.856	217.816	163.935	48.493	−707.289	−577.703	33.529
1000	88.617	227.004	169.788	57.216	−706.160	−563.365	29.427
1015.000	89.036	228.327	170.643	58.549	CRYSTAL <--> LIQUID TRANSITION		
1015.000	112.968	256.976	170.643	87.628			
1100	112.968	266.061	177.670	97.230	−674.053	−551.654	26.196
1200	112.968	275.891	185.452	108.527	−678.708	−540.043	23.507
1300	112.968	284.933	192.761	119.824	−674.712	−528.650	21.241
1400	112.968	293.305	199.647	131.120	−670.724	−517.564	19.311
1500	112.968	301.099	206.154	142.417	−666.746	−506.763	17.647
1600	112.968	308.389	212.318	153.714	−662.779	−496.226	16.200
1700	112.968	315.238	218.173	165.011	−658.823	−485.938	14.931
1800	112.968	321.695	223.747	176.308	−803.554	−473.671	13.746
1900	112.968	327.803	229.064	187.604	−798.212	−455.490	12.522
2000	112.968	333.598	234.147	198.901	−792.893	−437.590	11.429
2100	112.968	339.109	239.015	210.198	−787.600	−419.955	10.446
2200	112.968	344.365	243.685	221.495	−782.338	−402.572	9.558
2300	112.968	349.386	248.172	232.792	−777.112	−385.427	8.753
2400	112.968	354.194	252.491	244.088	−771.927	−368.508	8.020
2500	112.968	358.806	256.652	255.385	−766.790	−351.805	7.351

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [314.8 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -370.5 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -384.9 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[148](1)
[47](2)
330 (1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: $D_{\infty h}$

Bond Distance: Ca–Br = 2.67 ± 0.03 Å;

Bond Angle: Br–Ca–Br = 180°

Rotational Constant: $B_o = 0.014797\ cm^{-1}$

Enthalpy of Formation

The selection of $\Delta_f H°(298.15\ K) = -92.0 \pm 2.0\ kcal·mol^{-1}$ ($-384.928 \pm 8.4\ kJ·mol^{-1}$) for $CaBr_2(g)$ is based on results derived from two independent means. Peterson and Hutchison[1,2] have reported results of an extensive study of the vapor pressures (1149–1321 K) for liquid $CaBr_2$. Measurements were made by the Knudsen effusion method on a sample which had been prepared by direct union of high purity elements. X-ray diffraction patterns on the final product showed no metal or oxide lines. Schofield and Sugden[3] investigated the equilibrium $Ca(g) + 2\ HBr(g) = CaBr_2(g) + 2\ H(g)$ in H_2–O_2–N_2 flames and reported K_p data for temperatures in the range 2137–2532 K. Results of our 2nd and 3rd law analysis of these data are tabulated below. We assume that the dibromide monomer is the only vapor species produced in the volatilization of $CaBr_2(l)$. Support for this assumption is provided by mass spectra for some of the other alkaline earth dihalides.[4] These studies indicate that the saturated vapors consist predominately of the metal dihalide monomer and agree with predictions which were made by Brewer *et al.*[5] for these dihalide molecules. Included in the table for comparison are results of our analysis of older vapor pressure data[6,7] which have been reviewed by Brewer *et al.*[5]

Source	Method	Reaction	Data Points	T/K	$\Delta_r H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Peterson and Hutchison[1,2]	Knudsen Effusion	A	18(a)	1149–1321	65.7	67.70 ± 0.60	1.6 ± 1.3	−90.8 ± 1.6
Brewer[5,6]		B	1	990		68.9		−94.4
Brewer[5,7]	Boiling Point	A	2	1180;1480	62.5	64.76 ± 0.7	1.7	−93.7 ± 1.7
Schofield and Sugden[3]	Flame K_p	C	8(a)	2137–2532	−9.4	−14.38 ± 1.7	−2.1 ± 3.2	−93.2 ± 2.0

Reactions: (A) $CaBr_2(l) = CaBr_2(g)$ (B) $CaBr_2(cr) = CaBr_2(g)$ (C) $Ca(g) + 2\ HBr(g) = CaBr_2(g) + 2\ H(g)$

[a]One point rejected due to failure of a statistical test.

In the selection of $\Delta_f H°$, no weight is given to those measurements made prior to 1965. Also, we note that Schofield and Sugden[3] reported in the same paper similar results for $SrCl_2$ and $BaCl_2$ which lead to $\Delta_f H°$ values that are quite consistent with JANAF enthalpies of formation.[4] We, therefore, choose to select an average value of the results of Peterson and Hutchison[1,2] and Schofield and Sugden.[3] An earlier analysis[14] of the vapor pressure data[1,2] with older functions[5] gave $\Delta_f H°$ of $-95.2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The bond length is from the high-temperature electron diffraction work of Akishin and Spiridonov.[8] Electron diffraction patterns[8] were satisfactorily explained on the basis of a linear model (180° ± 10°). Later studies by Wharton *et al.*,[9] using electric deflection of molecular beams to detect dipole moments, showed no polarity in the $CaBr_2$ molecule. The absence of dipolar character is most reasonably explained by a linear and centrosymmetric configuration.

The antisymmetric stretching frequency (ν_3) was observed in the high-temperature infrared spectra of $CaBr_2$ vapor by Baikov.[10] The symmetric stretching (ν_1) and bending (ν_2) frequencies are calculated from force constants by the valence force method.[11] The observed value of ν_3 gives $k = 1.028 \times 10^5$ dynes/cm which leads to $\nu_1 = 148\ cm^{-1}$. Other estimates that have been reported for ν_1 (in cm^{-1}) are 148,[10] 164,[5] and 172.[13] A comparison of values for the ratio of the stretch to bend force constants for the linear molecules $CaCl_2$[4][(ratio = 81)] and $SrBr_2$[4][(ratio = [100])] suggests a value near 100 for $CaBr_2$. This value for the ratio gives $k\delta/l^2 = 1.028 \times 10^3$ dynes/cm, or $\nu_2 = 47\ cm^{-1}$. However, similar data for $BeBr_2$[12] indicate that the value of the ratio could be as low as 41. This leads to a $\nu_2 = 73\ cm^{-1}$ which agrees with the value (85 cm^{-1}) recommended by Krasnov and Svettsov.[13] Brewer *et al.*[5] choose $\nu_2 = 52\ cm^{-1}$ We prefer the lowest value of ν_2(47 cm^{-1}) at this time but include in the uncertainty (±2.0 cal·K^{-1}mol^{-1}) assigned to the value of $S°(298.15\ K)$ the possibility that the highest value (85 cm^{-1}) is correct. The singlet ground state is assigned by analogy with that for $BaCl_2$.[4]

Continued on page 548

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.799	−370.482	−370.482	INFINITE
100	52.538	252.373	366.898	−11.452	−369.908	−388.164	202.756
200	58.448	290.991	320.226	−5.847	−371.473	−405.889	106.007
250	59.666	304.176	315.742	−2.892	−372.583	−414.370	86.578
298.15	60.387	314.752	314.752	0.	−384.928	−420.991	73.756
300	60.409	315.125	314.753	0.112	−385.004	−421.215	73.340
350	60.889	324.476	315.490	3.145	−415.927	−425.550	63.510
400	61.214	332.629	317.134	6.198	−416.033	−426.918	55.750
450	61.443	339.853	319.264	9.265	−416.170	−428.271	49.712
500	61.611	346.336	321.653	12.341	−416.346	−429.606	44.881
600	61.833	357.590	326.732	18.515	−416.835	−432.216	37.628
700	61.970	367.133	331.840	24.705	−417.522	−434.728	32.440
800	62.059	375.414	336.780	30.907	−419.266	−437.023	28.535
900	62.121	382.727	341.487	37.116	−420.347	−439.181	25.489
1000	62.166	389.275	345.944	43.331	−421.727	−441.202	23.046
1100	62.199	395.201	350.157	49.549	−423.415	−443.070	21.040
1200	62.224	400.615	354.139	55.770	−433.145	−444.149	19.333
1300	62.244	405.596	357.909	61.994	−434.222	−445.022	17.881
1400	62.260	410.209	361.482	68.219	−435.307	−445.813	16.633
1500	62.272	414.505	364.875	74.445	−436.399	−446.525	15.549
1600	62.283	418.525	368.104	80.673	−437.500	−447.164	14.598
1700	62.291	422.301	371.182	86.902	−438.613	−447.734	13.757
1800	62.298	425.861	374.122	93.131	−588.411	−446.027	12.943
1900	62.304	429.230	376.934	99.362	−588.136	−438.125	12.045
2000	62.310	432.426	379.630	105.592	−587.883	−430.236	11.237
2100	62.314	435.466	382.217	111.823	−587.655	−422.359	10.506
2200	62.318	438.365	384.704	118.055	−587.458	−414.493	9.841
2300	62.321	441.135	387.097	124.287	−587.297	−406.635	9.235
2400	62.324	443.788	389.405	130.519	−587.177	−398.782	8.679
2500	62.327	446.332	391.631	136.752	−587.104	−390.934	8.168
2600	62.329	448.776	393.782	142.985	−587.084	−383.088	7.696
2700	62.331	451.129	395.863	149.218	−587.124	−375.241	7.259
2800	62.333	453.396	397.877	155.451	−587.228	−367.392	6.854
2900	62.335	455.583	399.830	161.684	−587.405	−359.538	6.476
3000	62.337	457.696	401.724	167.918	−587.659	−351.677	6.123
3100	62.338	459.740	403.562	174.152	−587.997	−343.805	5.793
3200	62.339	461.720	405.349	180.386	−588.425	−335.921	5.483
3300	62.340	463.638	407.086	186.620	−588.949	−328.023	5.192
3400	62.341	465.499	408.777	192.854	−589.574	−320.107	4.918
3500	62.342	467.306	410.424	199.088	−590.305	−312.171	4.659
3600	62.343	469.062	412.028	205.322	−591.147	−304.212	4.414
3700	62.344	470.770	413.593	211.556	−592.105	−296.229	4.182
3800	62.345	472.433	415.120	217.791	−593.181	−288.219	3.962
3900	62.345	474.052	416.610	224.025	−594.380	−280.178	3.753
4000	62.346	475.631	418.066	230.260	−595.703	−272.105	3.553
4100	62.347	477.170	419.489	236.495	−597.152	−263.997	3.363
4200	62.347	478.673	420.880	242.729	−598.728	−255.853	3.182
4300	62.348	480.140	422.241	248.964	−600.433	−247.669	3.009
4400	62.348	481.573	423.573	255.199	−602.262	−239.445	2.843
4500	62.348	482.974	424.878	261.434	−604.203	−231.178	2.683
4600	62.349	484.345	426.156	267.669	−606.274	−222.866	2.531
4700	62.349	485.686	427.408	273.903	−608.469	−214.508	2.384
4800	62.350	486.998	428.636	280.138	−610.780	−206.102	2.243
4900	62.350	488.284	429.840	286.373	−613.205	−197.646	2.107
5000	62.350	489.544	431.022	292.608	−615.738	−189.140	1.976
5100	62.351	490.778	432.181	298.843	−618.374	−180.581	1.850
5200	62.351	491.989	433.320	305.078	−621.105	−171.971	1.727
5300	62.351	493.177	434.438	311.314	−623.930	−163.307	1.609
5400	62.351	494.342	435.537	317.549	−626.842	−154.589	1.495
5500	62.352	495.486	436.616	323.784	−629.834	−145.816	1.385
5600	62.352	496.610	437.678	330.019	−632.890	−136.989	1.278
5700	62.352	497.713	438.721	336.254	−636.021	−128.106	1.174
5800	62.352	498.798	439.748	342.489	−639.212	−119.168	1.073
5900	62.352	499.864	440.758	348.725	−642.458	−110.174	0.975
6000	62.353	500.912	441.752	354.960	−645.751	−101.124	0.880

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 140.67 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{trs} = 650\ K$
$T_{fus} = 964\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -248.9 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0.4184\ kJ·mol^{-1}$
$\Delta_{fus} H° = [50.208 \pm 13]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of Fe(cr), Br_2(l) and $FeBr_2$(cr) in Br_2–KBr aqueous solution were measured by use of an ice calorimeter by Hieber and Woerner.[1] From the results obtained, the enthalpy of formation for $FeBr_2$(cr) was reported to be $-59.87\ kcal·mol^{-1}$. The enthalpies of solution of $FeBr_2$(cr) in water were determined by Li and Gregory[2] and by Paoletti[3] to be -20.1 ± 0.4 and $-20.06 \pm 0.06\ kcal·mol^{-1}$, respectively. Using $\Delta_f H°(298.15\ K) = -29.05$ and $-21.3\ kcal·mol^{-1}$ for Br^-(aq, ∞) and Fe^{++}(aq, ∞), the corresponding $\Delta_f H°(298.15\ K)$ for $FeBr_2$(cr) were calculated as -59.3 and $-59.34\ kcal·mol^{-1}$. The value of $\Delta_f H°(Br^-, aq, ∞, 298.15\ K)$ was taken from.[4] The value of $\Delta_f H°(Fe^{++}, aq, ∞, 298.15\ K)$ was derived from enthalpies of solution and formation for $FeCl_2$(cr) using $\Delta_f H°(Cl^-, aq, ∞, 298.15\ K) = -39.952\ kcal·mol^{-1}$ from.[4]

The value of $\Delta_f H°(FeBr_2, cr, 298.15\ K)$ adopted is $-59.5 \pm 0.5\ kcal·mol^{-1}$ $(-248.948 \pm 2.1\ kJ·mol^{-1})$.

Heat Capacity and Entropy

The heat capacities, 323–633 K, were measured by Gregory and O'Neal.[5] Those for temperatures below 232 K and above 633 K were estimated by linear extrapolation. Low temperature $C_p°$, 12–110 K, were reported by Miljutin and Nachimowitsch.[6] However, these data are inadequate for obtaining an accurate entropy at 298.15 K. The adopted $S°(298.15\ K)$ value was reported by Gregory and MacLaren[7] and was obtained from Westrum.[8] A magnetic transition at 11 K was reported by Bizette *et al.*[9]

Transition Data

T_{trs} and $\Delta_{trs} H°$ were taken from Gregory and O'Neal.[5]

Fusion Data

T_{fus} adopted was reported by MacLaren and Gregory.[10] The value was calculated from the vapor pressure equations and is slightly above 684°C (957 K) reported by Ferrari *et al.*[11] However, it agrees well with 962 ± 2 K obtained by the differential thermocouple cooling curve analysis.[10] The $\Delta_{fus} H°$ value was estimated from the vapor pressure data in order to obtain good agreement between the 2nd and 3rd law heats of vaporization. See the $FeBr_2$(g) table for details.

Sublimation Data

$\Delta_{sub} H°$(monomer → 298.15 K) is calculated as the difference between $\Delta_f H°(298.15\ K)$ for $FeBr_2$(g) and $FeBr_2$(cr). $\Delta_{sub} H°$(dimer → 298.15 K) is calculated as the difference between those for Fe_2Br_4(g) and 2 $FeBr_2$(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	80.232	140.666	140.666	0.	−248.948	−237.362	41.585
300	80.274	141.163	140.668	0.148	−248.986	−237.290	41.316
400	82.500	164.560	143.843	8.287	−277.955	−227.334	29.687
500	84.726	183.209	149.912	16.648	−276.138	−214.890	22.449
600	86.952	198.853	156.799	25.232	−274.360	−202.807	17.656
650.000	88.061	205.857	160.306	29.608		I <--> II	
650.000	88.069	206.500	160.306	30.026		TRANSITION	
700	89.178	213.067	163.843	34.457	−272.199	−191.053	14.257
800	91.404	225.121	170.763	43.486	−270.537	−179.575	11.725
900	93.630	236.015	177.417	52.738	−269.078	−168.295	9.768
964.000	95.054	242.495	181.525	58.776	----- II <--> LIQUID -----		
1000	95.855	245.995	183.783	62.212	−268.125	−157.156	8.209
1100	98.081	255.236	189.864	71.909	−267.854	−146.056	6.936
1200	100.307	263.865	195.675	81.828	−266.817	−135.047	5.878
1300	102.533	271.982	201.235	91.970	−263.919	−124.183	4.990
1400	104.759	279.662	206.565	102.335	−260.891	−113.547	4.236
1500	106.985	286.965	211.684	112.922	−257.733	−103.132	3.591

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [169.376]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-211.005]\ kJ·mol^{-1}$

$T_{fus} = 964\ K$ $\Delta_{fus}H° = [50.208 \pm 13]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(964\ K)-H°(298.15\ K)$, between $FeBr_2$(cr) and $FeBr_2$(l).

Heat Capacity and Entropy

The heat capacity is assumed to be constant in the temperature range from 298.15 to 2000 K and is estimated on the basis of 8.5 $cal·K^{-1}·mol^{-1}$ per atom. $S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the total pressure of $FeBr_2$(g) and Fe_2Br_4(g) over $FeBr_2$(l) equals one bar. Based on the vapor composition and the values of $\Delta_{vap}H°$ for both the monomer and dimer at T_{vap} for both the monomer and dimer at T_{vap}, the enthalpy of vaporization is derived.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	106.692	169.376	169.376	0.	−211.005	−207.978	36.437
300	106.692	170.036	169.378	0.197	−210.994	−207.960	36.209
400	106.692	200.729	173.563	10.867	−237.433	−201.279	26.284
500	106.692	224.537	181.465	21.536	−233.308	−192.723	20.134
600	106.692	243.989	190.314	32.205	−229.444	−184.974	16.103
700	106.692	260.436	199.187	42.874	−225.839	−177.850	13.271
800	106.692	274.683	207.753	53.543	−222.537	−171.224	11.180
900	106.692	287.249	215.902	64.213	−219.661	−164.988	9.576
1000	106.692	298.490	223.608	74.882	−217.513	−159.039	8.307
1100	106.692	308.659	230.885	85.551	−216.269	−153.237	7.277
1200	106.692	317.942	237.759	96.220	−214.482	−147.605	6.425
1300	106.692	326.482	244.260	106.889	−211.057	−142.172	5.713
1400	106.692	334.389	250.419	117.559	−207.724	−136.998	5.111
1500	106.692	341.750	256.265	128.228	−204.485	−132.060	4.599
1600	106.692	348.636	261.825	138.897	−201.339	−127.335	4.157
1700	106.692	355.104	267.124	149.566	−199.239	−122.785	3.773
1800	106.692	361.202	272.183	160.235	−196.620	−118.364	3.435
1900	106.692	366.971	277.021	170.905	−208.198	−113.383	3.117
2000	106.692	372.443	281.657	181.574	−206.017	−108.449	2.832

PREVIOUS: CURRENT: September 1966

298.15	to	650 K	crystal, I
650	to	964 K	crystal, II
above		964 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	80.232	140.666	140.666	0.	−248.948	−237.362	41.585
300	80.274	141.163	140.668	0.148	−248.986	−237.290	41.316
400	82.500	164.560	143.843	8.287	−277.955	−227.334	29.687
500	84.726	183.209	149.912	16.648	−276.138	−214.890	22.449
600	86.952	198.853	156.799	25.232	−274.360	−202.807	17.656
650.000	88.061	205.857	160.306	29.608	I <-–> II		
650.000	88.069	206.500	160.306	30.026	TRANSITION		
700	89.178	213.067	163.843	34.457	−272.199	−191.053	14.257
800	91.404	225.121	170.763	43.486	−270.537	−179.575	11.725
900	93.630	236.015	177.417	52.738	−269.078	−168.295	9.768
964.000	95.054	242.495	181.525	58.776	II <-–> LIQUID		
964.000	106.692	294.578	181.525	108.984	TRANSITION		
1000	106.692	298.490	185.666	112.825	−217.513	−159.039	8.307
1100	106.692	308.659	196.392	123.494	−216.269	−153.237	7.277
1200	106.692	317.942	206.140	134.163	−214.482	−147.605	6.425
1300	106.692	326.482	215.073	144.832	−211.057	−142.172	5.713
1400	106.692	334.389	223.317	155.501	−207.724	−136.998	5.111
1500	106.692	341.750	230.970	166.171	−204.485	−132.060	4.599
1600	106.692	348.636	238.111	176.840	−201.339	−127.335	4.157
1700	106.692	355.104	244.805	187.509	−199.239	−122.785	3.773
1800	106.692	361.202	251.103	198.178	−196.620	−118.364	3.435
1900	106.692	366.971	257.051	208.847	−208.198	−113.383	3.117
2000	106.692	372.443	262.685	219.517	−206.017	−108.449	2.832

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K)$ = [337.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−28.43 ± 2.1] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−41.42 ± 2.1] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i
0	[10]
[4450]	[10]
[6900]	[5]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[150](1)
[35](2)
[300](1)

Point Group [$D_{\infty h}$] σ = [2]
Bond Distance: Fe–Br = [2.24] Å
Bond Angle: Br–Fe–Br = [180]°
Rotational Constant: B_o = [0.021023] cm^{-1}

Enthalpy of Formation

The vapor pressures of $FeBr_2$(cr) and $FeBr_2$(l) have been measured in the temperature range from 623.15 to 962.15 K.[1,2] Using the reported data the corresponding enthalpy changes for the reactions (A) $FeBr_2$(cr) = $FeBr_2$(g) and (B) $FeBr_2$(l) = $FeBr_2$(g) were evaluated by both the 2nd and 3rd law methods. The results obtained are presented in the following table. The values of $\Delta_f H°$(298.15 K) for $FeBr_2$(g) are calculated based on the 3rd law values for $\Delta_r H°$(298.15 K). The value of $\Delta_f H°$(298.15 K) for $FeBr_2$(g) adopted is − 9.9 ± 0.5 $kcal·mol^{-1}$ (−41.422 $kJ·mol^{-1}$).

Source	Method	Reaction	T/K	$\Delta_r H°$(298.15 K), $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal·mol^{-1}$
1	Transpiration	(A)	673.15– 962.15	50.04	49.56	− 0.75	−9.94
1	Effusion	(A)	623.15– 718.15	49.21	50.14	+ 1.37	−9.36
1	Diaphragm	(A)	873.15– 962.15	59.20	49.95	−10.09	−9.55
2	Torsion–Effusion	(A)	670.0 – 740.0	49.11	49.59	+ 0.71	−9.91
1	Diaphragm	(B)	962.15–1182.15	39.77	40.84	+ 0.93	−9.59

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The electronic levels and quantum weights were estimated by comparison with those for $FeCl_2$(g) reported by DeKock and Gruen.[3] The bond distance was estimated by Brewer *et al.*[4] The vibrtional frequencies were estimated in order to obtain good agreement between the 2nd and 3rd law enthalpies of sublimation and vaporization.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J·K^{-1}·mol^{-1}$)	$S°-[G°-H°(T_r)]/T$ ($J·K^{-1}·mol^{-1}$)	$H°-H°(T_r)$ ($kJ·mol^{-1}$)	$\Delta_f H°$ ($kJ·mol^{-1}$)	$\Delta_f G°$ ($kJ·mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−16.019	−28.425	−28.425	INFINITE
100	53.226	274.411	389.883	−11.547	−27.169	−48.619	25.396
200	58.914	313.454	342.863	−5.882	−28.174	−69.790	18.227
250	60.014	326.729	338.354	−2.906	−29.151	−80.088	16.733
298.15	60.653	337.359	337.359	0.	−41.422	−88.479	15.501
300	60.672	337.734	337.360	0.112	−41.496	−88.771	15.456
350	61.093	347.120	338.100	3.157	−72.387	−94.953	14.171
400	61.376	355.298	339.750	6.219	−72.497	−98.170	12.820
450	61.575	362.539	341.887	9.293	−72.661	−101.370	11.767
500	61.722	369.035	344.283	12.376	−72.884	−104.548	10.922
600	61.932	380.307	349.375	18.559	−73.506	−110.827	9.648
700	62.102	389.867	354.494	24.761	−74.369	−116.982	8.729
800	62.284	398.171	359.446	30.980	−75.517	−122.995	8.031
900	62.506	405.520	364.165	37.219	−77.071	−128.842	7.478
1000	62.777	412.119	368.636	43.483	−79.328	−134.483	7.025
1100	63.094	418.117	372.866	49.776	−82.461	−139.832	6.640
1200	63.445	423.622	376.869	56.103	−85.016	−144.954	6.310
1300	63.819	428.715	380.664	62.466	−85.897	−149.913	6.024
1400	64.202	433.458	384.267	68.867	−86.832	−154.803	5.776
1500	64.582	437.901	387.696	75.306	−87.823	−159.624	5.559
1600	64.949	442.080	390.966	81.783	−88.870	−164.377	5.366
1700	65.295	446.028	394.090	88.295	−90.926	−169.043	5.194
1800	65.614	449.770	397.080	94.841	−92.431	−173.596	5.038
1900	65.902	453.325	399.948	101.417	−108.102	−177.360	4.876
2000	66.158	456.712	402.702	108.020	−109.987	−180.956	4.726
2100	66.380	459.945	405.351	114.648	−111.866	−184.459	4.588
2200	66.570	463.038	407.904	121.295	−113.744	−187.871	4.461
2300	66.728	466.001	410.366	127.960	−115.627	−191.199	4.342
2400	66.855	468.843	412.743	134.640	−117.518	−194.444	4.232
2500	66.955	471.575	415.042	141.331	−119.420	−197.610	4.129
2600	67.029	474.202	417.268	148.030	−121.336	−200.700	4.032
2700	67.080	476.733	419.423	154.736	−123.268	−203.716	3.941
2800	67.110	479.173	421.514	161.445	−125.218	−206.660	3.855
2900	67.121	481.528	423.543	168.157	−127.185	−209.534	3.774
3000	67.116	483.804	425.514	174.869	−129.171	−212.340	3.697
3100	67.096	486.004	427.430	181.580	−131.174	−215.079	3.624
3200	67.065	488.134	429.294	188.288	−481.494	−210.330	3.433
3300	67.023	490.197	431.108	194.992	−481.628	−201.854	3.195
3400	66.971	492.197	432.876	201.692	−481.809	−193.373	2.971
3500	66.913	494.138	434.599	208.386	−482.035	−184.887	2.759
3600	66.848	496.022	436.279	215.074	−482.305	−176.393	2.559
3700	66.778	497.852	437.918	221.756	−482.617	−167.891	2.370
3800	66.704	499.632	439.519	228.430	−482.970	−159.380	2.191
3900	66.626	501.364	441.083	235.096	−483.364	−150.860	2.021
4000	66.546	503.050	442.611	241.755	−483.796	−142.328	1.859
4100	66.465	504.692	444.105	248.405	−484.265	−133.786	1.704
4200	66.382	506.293	445.567	255.048	−484.772	−125.232	1.557
4300	66.299	507.854	446.997	261.682	−485.315	−116.665	1.417
4400	66.215	509.377	448.398	268.308	−485.894	−108.085	1.283
4500	66.132	510.864	449.769	274.925	−486.507	−99.492	1.155
4600	66.049	512.317	451.113	281.534	−487.156	−90.884	1.032
4700	65.966	513.736	452.431	288.135	−487.840	−82.262	0.914
4800	65.885	515.124	453.723	294.727	−488.558	−73.625	0.801
4900	65.805	516.482	454.990	301.312	−489.312	−64.973	0.693
5000	65.726	517.810	456.233	307.888	−490.102	−56.305	0.588
5100	65.648	519.111	457.453	314.457	−490.928	−47.621	0.488
5200	65.572	520.385	458.651	321.018	−491.791	−38.921	0.391
5300	65.497	521.633	459.828	327.571	−492.692	−30.203	0.298
5400	65.424	522.857	460.983	334.117	−493.634	−21.468	0.208
5500	65.352	524.057	462.119	340.656	−494.616	−12.715	0.121
5600	65.283	525.234	463.236	347.188	−495.641	−3.944	0.037
5700	65.215	526.389	464.334	353.713	−496.711	4.846	−0.044
5800	65.148	527.522	465.414	360.231	−497.828	13.654	−0.123
5900	65.083	528.635	466.476	366.742	−498.994	22.483	−0.199
6000	65.020	529.729	467.521	373.248	−500.213	31.332	−0.273

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = [310.05 \pm 1.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-168.4 \pm 17]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-190.4 \pm 17]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
2206(1)	2232(1)
942(1)	556(1)
407(1)	843(1)
122(1)	471(1)
688(1)	

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Si–H = [1.49] Å; Si–Br = [2.19] Å
Bond Angles: H–Si–H = [111]°; Br–Si–Br = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [6.36266 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of $SiBr_4$(g) and SiH_4(g). The only experimental $\Delta_f H°$ for $SiHBr_3$(g) appears to be too uncertain to justify a nonlinear interpolation such as that adopted for SiH_3Cl.[1] Normally we would seek a comparison with $\Delta_f H°$ values of CH_nBr_{4-n}. These were recently reviewed by Kudchadker and Kudchadker.[2] They adopted a cubic variation of $\Delta_f H°$ with n, based on $\Delta_f H°$ values of $CHBr_3$ and CBr_4 selected by Wagman *et al.*[3] We presume that Wagman's values are calculated rather than experimental. Uncertainty in these values[4–6] precludes their use as a comparison for SiH_nBr_{4-n}. We conclude, as did Hunt and Sirtl,[7] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3Br, $SiHBr_3$ and the chlorosilanes.[1] Bond distances are assumed to be intermediate between those of SiH_3Br and $SiHBr_3$.[1] The principal moments of inertia are $I_A = 7.9748 \times 10^{-39}$, $I_B = 85.9075 \times 10^{-39}$, and $I_C = 92.8728 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are those selected by Shimanouchi[8] based on gas–phase infrared spectra[9] and liquid–phase Raman spectra.[10] Gas–phase frequencies are adopted except for $\upsilon_4 = 122\ cm^{-1}$ and infrared inactive $\upsilon_5 = 688\ cm^{-1}$.

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: Br_4Si(g), Br_3HSi(g), BrH_3Si(g), ClH_3Si(g), Cl_2H_2Si(g), Cl3HSi(g)12–31–76; H_4Si(g) 6–30–76.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−14.272	−168.449	−168.449	INFINITE
100	41.215	253.984	360.165	−10.618	−170.854	−180.412	94.237
200	53.911	286.243	315.696	−5.891	−174.900	−188.449	49.218
250	60.273	298.971	311.102	−3.033	−177.104	−191.584	40.029
298.15	65.545	310.051	310.051	0.	−190.372	−192.860	33.788
300	65.730	310.457	310.053	0.121	−190.481	−192.875	33.583
350	70.258	320.941	310.870	3.525	−222.212	−191.509	28.581
400	74.012	330.575	312.739	7.134	−222.976	−187.069	24.429
450	77.170	339.480	315.222	10.916	−223.620	−182.541	21.189
500	79.882	347.754	318.066	14.844	−224.158	−177.947	18.590
600	84.357	362.730	324.289	23.065	−224.962	−168.624	14.680
700	87.937	376.013	330.747	31.686	−225.465	−159.190	11.879
800	90.864	387.952	337.164	40.631	−225.734	−149.702	9.775
900	93.276	398.798	343.419	49.841	−225.824	−140.191	8.136
1000	95.273	408.733	349.461	59.272	−225.782	−130.677	6.826
1100	96.931	417.893	355.271	68.885	−225.647	−121.172	5.754
1200	98.315	426.389	360.848	78.649	−225.452	−111.683	4.861
1300	99.476	434.305	366.197	88.540	−225.222	−102.211	4.107
1400	100.455	441.714	371.329	98.538	−224.981	−92.758	3.461
1500	101.285	448.674	376.256	108.626	−224.743	−83.322	2.902
1600	101.994	455.234	380.989	118.791	−224.525	−73.901	2.413
1700	102.603	461.436	385.541	129.022	−274.514	−64.046	1.968
1800	103.128	467.316	389.922	139.309	−274.134	−51.677	1.500
1900	103.584	472.904	394.143	149.645	−273.759	−39.328	1.081
2000	103.982	478.228	398.216	160.024	−273.396	−26.999	0.705
2100	104.331	483.309	402.148	170.440	−273.049	−14.688	0.365
2200	104.638	488.170	405.948	180.889	−272.722	−2.393	0.057
2300	104.910	492.828	409.625	191.366	−272.420	9.888	−0.225
2400	105.152	497.298	413.185	201.870	−272.145	22.156	−0.482
2500	105.368	501.595	416.636	212.396	−271.899	34.414	−0.719
2600	105.561	505.731	419.984	222.943	−271.683	46.662	−0.937
2700	105.735	509.718	423.234	233.508	−271.497	58.902	−1.140
2800	105.892	513.567	426.392	244.089	−271.342	71.136	−1.327
2900	106.034	517.285	429.462	254.686	−271.216	83.366	−1.502
3000	106.162	520.882	432.450	265.295	−271.118	95.591	−1.664
3100	106.280	524.365	435.359	275.918	−271.047	107.813	−1.817
3200	106.387	527.741	438.194	286.551	−271.001	120.033	−1.959
3300	106.484	531.016	440.957	297.195	−270.977	132.253	−2.093
3400	106.574	534.196	443.653	307.848	−270.974	144.472	−2.220
3500	106.656	537.287	446.284	318.509	−270.989	156.691	−2.338
3600	106.732	540.293	448.854	329.179	−655.172	179.372	−2.603
3700	106.803	543.218	451.365	339.855	−654.802	202.548	−2.859
3800	106.867	546.067	453.820	350.539	−654.445	225.715	−3.103
3900	106.928	548.844	456.221	361.229	−654.098	248.873	−3.333
4000	106.983	551.552	458.571	371.924	−653.759	272.021	−3.552
4100	107.035	554.194	460.871	382.625	−653.425	295.162	−3.760
4200	107.084	556.774	463.124	393.331	−653.095	318.294	−3.959
4300	107.129	559.294	465.331	404.042	−652.765	341.418	−4.147
4400	107.171	561.757	467.494	414.757	−652.435	364.535	−4.328
4500	107.210	564.166	469.616	425.476	−652.103	387.644	−4.500
4600	107.247	566.523	471.697	436.199	−651.767	410.746	−4.664
4700	107.282	568.830	473.739	446.926	−651.426	433.840	−4.822
4800	107.315	571.089	475.744	457.655	−651.078	456.928	−4.972
4900	107.345	573.302	477.713	468.388	−650.724	480.007	−5.117
5000	107.374	575.471	479.646	479.124	−650.361	503.080	−5.256
5100	107.402	577.598	481.546	489.863	−649.989	526.145	−5.389
5200	107.427	579.683	483.413	500.605	−649.607	549.203	−5.517
5300	107.452	581.730	485.249	511.349	−649.215	572.254	−5.640
5400	107.475	583.739	487.054	522.095	−648.811	595.296	−5.758
5500	107.496	585.711	488.830	532.844	−648.395	618.331	−5.872
5600	107.517	587.648	490.578	543.594	−647.968	641.359	−5.982
5700	107.537	589.551	492.297	554.347	−647.528	664.379	−6.088
5800	107.555	591.422	493.990	565.102	−647.075	687.391	−6.191
5900	107.573	593.260	495.657	575.858	−646.609	710.394	−6.289
6000	107.590	595.068	497.299	586.616	−646.128	733.390	−6.385

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [170.314 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 514\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -169.45 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 17.908 \pm 0.33\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is taken from.[1]

Heat Capacity and Entropy

$C_p°$ is assumed to be a linear function of temperature and is fitted to the data of Guinchant[2] and Janz and Goodkin.[3] The entropy is estimated by adjusting its value until the melting, sublimation, and vaporization data are in agreement.

Fusion Data

T_{fus} is from NBS;[1] $\Delta_{fus} H°$ is from Janz and Goodkin.[3]

References

[1]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2]M. Guinchant, Comp. Rend. **145**, 320 (1907).
[3]G.J. Janz and J. Goodkin, J. Phys. Chem. **63**, 1975 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	75.312	170.314	170.314	0.	−169.452	−152.183	26.662
300	75.366	170.780	170.315	0.139	−169.504	−152.076	26.479
400	78.321	192.861	173.306	7.822	−199.068	−140.110	18.297
500	81.206	210.688	179.055	15.816	−197.492	−125.547	13.116
600	84.157	225.738	185.612	24.076	−195.666	−111.325	9.692
700	87.086	238.931	192.305	32.638	−252.316	−90.860	6.780
800	90.015	250.751	198.885	41.493	−249.292	−67.998	4.440
900	92.943	261.522	205.255	50.641	−245.987	−45.531	2.643
1000	95.872	271.466	211.385	60.082	−242.399	−23.448	1.225
1100	98.801	280.741	217.273	69.815	−238.527	−1.738	0.083
1200	101.730	289.464	222.929	79.842	−234.371	19.607	−0.853
1300	104.659	297.722	228.367	90.161	−229.931	40.593	−1.631
1400	107.587	305.585	233.604	100.774	−225.206	61.227	−2.284
1500	110.516	313.108	238.655	111.679	−220.199	81.514	−2.839

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = [192.172]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 514\ K$

$\Delta_f H°(298.15\ K) = [-156.626]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 17.908 \pm 0.33\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(514\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is obtained from the data of Janz and Goodkin[1] in the range 507–544 K; it is assumed constant above and below this range. $S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion and Vaporization Data

T_{fus} and T_{vap} (1 atm) are from.[2] $\Delta_{fus}H°$ is the value given by Janz and Goodkin,[1] and $\Delta_{vap}H$ (1 atm) is obtained from the data of Prideaux[3] and Johnson.[4]

References

[1]G. J. Janz and J. Goodkin, J. Phys. Chem. **63**, 1975 (1959).
[2]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[3]E. B. R. Prideaux, J. Chem. Soc. (London) **97**, 2032 (1910).
[4]F. M. G. Johnson, J. Am. Chem. Soc. **33**, 777 (1911).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.090	192.172	192.172	0.	−156.626	−145.874	25.557
300	102.090	192.804	192.174	0.189	−156.629	−145.807	25.387
400	102.090	222.173	196.179	10.398	−183.665	−136.433	17.816
500	102.090	244.954	203.740	20.607	−179.875	−125.064	13.065
600	102.090	263.567	212.207	30.816	−176.100	−114.456	9.964
700	102.090	279.304	220.697	41.025	−231.103	−97.908	7.306
800	102.090	292.936	228.894	51.234	−226.726	−79.179	5.170
900	102.090	304.961	236.691	61.443	−222.359	−60.998	3.540
1000	102.090	315.717	244.065	71.652	−218.003	−43.303	2.262
1100	102.090	325.447	251.028	81.861	−213.656	−26.043	1.237
1200	102.090	334.330	257.605	92.070	−209.317	−9.179	0.400
1300	102.090	342.502	263.826	102.278	−204.987	7.323	−0.294
1400	102.090	350.067	269.719	112.487	−200.666	23.493	−0.877
1500	102.090	357.111	275.313	122.696	−196.355	39.354	−1.370

PREVIOUS: CURRENT: March 1962

298.15	to	514 K	crystal
above		514 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	75.312	170.314	170.314	0.	−169.452	−152.183	26.662
300	75.366	170.780	170.315	0.139	−169.504	−152.076	26.479
400	78.321	192.861	173.306	7.822	−199.068	−140.110	18.297
500	81.206	210.688	179.055	15.816	−197.492	−125.547	13.116
514.000	81.437	212.933	179.948	16.955	CRYSTAL <--> LIQUID TRANSITION		
514.000	102.090	247.773	179.948	34.862			
600	102.090	263.567	190.830	43.642	−176.100	−114.456	9.964
700	102.090	279.304	202.374	53.851	−231.103	−97.908	7.306
800	102.090	292.936	212.861	64.060	−226.726	−79.179	5.170
900	102.090	304.961	222.440	74.269	−222.359	−60.998	3.540
1000	102.090	315.717	231.239	84.478	−218.003	−43.303	2.262
1100	102.090	325.447	239.368	94.687	−213.656	−26.043	1.237
1200	102.090	334.330	246.917	104.896	−209.317	−9.179	0.400
1300	102.090	342.502	253.960	115.105	−204.987	7.323	−0.294
1400	102.090	350.067	260.557	125.314	−200.666	23.493	−0.877
1500	102.090	357.111	266.762	135.523	−196.355	39.354	−1.370

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = 320.223\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -67.26 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -85.45 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
225(1)
41(2)
293(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Hg–Br = 2.4 Å
Bond Angle: Br–Hg–Br = 180°
Rotational Constant: $B_o = 0.018162\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°$(cr, 298.15 K)[1] is combined with the 3rd law $\Delta_{sub} H°$(298.15 K) derived from the data of Niwa and Shibata[2] and Johnson.[3]

Heat Capacity and Entropy

The vibrational constants are those given by Klemperer and Lindeman.[4] The bond length is an average of the values given by Braune and Knoke,[5] Gregg *et al.*,[6] and Akishin *et al.*[7]

References

[1]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2]K. Niwa and Z. Shibata, J. Fac. Sci. Hokkaido, Imp. Univ. Ser. III **2**, 183 (1938).
[3]F. M. G. Johnson, J. Am. Chem. Soc. **33**, 777 (1911).
[4]W. Klemperer and L. Lindeman, J. Chem. Phys. **25**, 397 (1956).
[5]H. Braune and S. Knoke, Z. Phys. Chem. **B23**, 163 (1933).
[6]A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, Trans. Faraday Soc. **33**, 852 (1937).
[7]P. A. Akishin, V. P. Spiridinov, and A. N. Khodchenkov, Zh. Fiz. Khim. **33**, 20 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.658	−67.260	−67.260	INFINITE
100	51.210	258.441	372.093	−11.365	−67.466	−84.203	43.983
200	58.139	296.540	325.684	−5.829	−69.415	−100.235	26.179
250	59.492	309.672	321.212	−2.885	−72.984	−107.644	22.491
298.15	60.276	320.223	320.223	0.	−85.454	−112.881	19.776
300	60.300	320.596	320.225	0.112	−85.534	−113.051	19.684
350	60.814	329.933	320.961	3.140	−116.545	−115.929	17.302
400	61.160	338.078	322.602	6.190	−116.701	−115.831	15.126
450	61.403	345.296	324.730	9.255	−116.845	−115.713	13.432
500	61.579	351.775	327.116	12.329	−116.981	−115.580	12.075
600	61.812	363.025	332.191	18.500	−117.244	−115.275	10.036
700	61.955	372.565	337.295	24.689	−176.267	−108.354	8.086
800	62.048	380.844	342.232	30.889	−175.898	−98.678	6.443
900	62.113	388.156	346.937	37.097	−175.532	−89.047	5.168
1000	62.159	394.703	351.392	43.311	−175.171	−79.457	4.150
1100	62.193	400.629	355.603	49.529	−174.815	−69.903	3.319
1200	62.219	406.042	359.584	55.750	−174.465	−60.381	2.628
1300	62.240	411.023	363.351	61.973	−174.121	−50.888	2.045
1400	62.256	415.636	366.923	68.197	−173.785	−41.421	1.545
1500	62.269	419.932	370.316	74.424	−173.456	−31.978	1.114
1600	62.280	423.951	373.544	80.651	−173.136	−22.557	0.736
1700	62.289	427.727	376.621	86.880	−172.827	−13.155	0.404
1800	62.296	431.287	379.560	93.109	−172.531	−3.772	0.109
1900	62.303	434.656	382.372	99.339	−172.248	5.596	−0.154
2000	62.308	437.851	385.067	105.569	−171.982	14.950	−0.390
2100	62.313	440.891	387.653	111.800	−171.733	24.290	−0.604
2200	62.317	443.790	390.139	118.032	−171.504	33.619	−0.798
2300	62.320	446.561	392.533	124.264	−171.296	42.938	−0.975
2400	62.323	449.213	394.840	130.496	−171.110	52.248	−1.137
2500	62.326	451.757	397.066	136.728	−170.947	61.552	−1.286
2600	62.328	454.202	399.217	142.961	−170.806	70.849	−1.423
2700	62.331	456.554	401.297	149.194	−170.687	80.141	−1.550
2800	62.333	458.821	403.311	155.427	−170.589	89.429	−1.668
2900	62.334	461.008	405.263	161.661	−170.511	98.714	−1.778
3000	62.336	463.121	407.157	167.894	−170.452	107.996	−1.880
3100	62.337	465.165	408.995	174.128	−170.408	117.277	−1.976
3200	62.338	467.145	410.782	180.362	−170.379	126.557	−2.066
3300	62.340	469.063	412.519	186.595	−170.361	135.836	−2.150
3400	62.341	470.924	414.209	192.829	−170.351	145.114	−2.229
3500	62.342	472.731	415.856	199.064	−170.348	154.392	−2.304
3600	62.343	474.487	417.460	205.298	−170.349	163.671	−2.375
3700	62.343	476.195	419.025	211.532	−170.350	172.949	−2.442
3800	62.344	477.858	420.551	217.766	−170.349	182.227	−2.505
3900	62.345	479.477	422.041	224.001	−170.345	191.506	−2.565
4000	62.346	481.056	423.497	230.235	−170.334	200.784	−2.622
4100	62.346	482.595	424.920	236.470	−170.314	210.062	−2.676
4200	62.347	484.098	426.311	242.705	−170.284	219.339	−2.728
4300	62.347	485.565	427.672	248.939	−170.242	228.615	−2.777
4400	62.348	486.998	429.004	255.174	−170.186	237.890	−2.824
4500	62.348	488.399	430.308	261.409	−170.115	247.164	−2.869
4600	62.349	489.770	431.586	267.644	−170.028	256.436	−2.912
4700	62.349	491.111	432.838	273.879	−169.923	265.706	−2.953
4800	62.349	492.423	434.066	280.114	−169.800	274.973	−2.992
4900	62.350	493.709	435.270	286.349	−169.658	284.238	−3.030
5000	62.350	494.968	436.452	292.584	−169.498	293.499	−3.066
5100	62.350	496.203	437.611	298.819	−169.318	302.758	−3.101
5200	62.351	497.414	438.750	305.054	−169.118	312.012	−3.134
5300	62.351	498.602	439.868	311.289	−168.898	321.263	−3.166
5400	62.351	499.767	440.966	317.524	−168.660	330.509	−3.197
5500	62.351	500.911	442.046	323.759	−168.402	339.750	−3.227
5600	62.352	502.035	443.107	329.994	−168.125	348.987	−3.255
5700	62.352	503.138	444.151	336.229	−167.829	358.218	−3.283
5800	62.352	504.223	445.177	342.464	−167.516	367.444	−3.309
5900	62.352	505.288	446.187	348.700	−167.186	376.665	−3.335
6000	62.352	506.336	447.181	354.935	−166.839	385.880	−3.359

PREVIOUS: March 1962 (1 atm) CURRENT: March 1962 (1 bar)

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = 218.75 \pm 3.2\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -204.18 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The average of the values obtained from the cell measurements of Dakin and Ewing[1] and Ishikawa and Ueda[2] is adopted.

Heat Capacity and Entropy

The heat capacity is estimated by analogy with Hg_2Cl_2(cr). The entropy was obtained from the Gibbs energy and enthalpy of formation.[1,2]

Sublimation Data

According to Jung and Ziegler,[3] the vapor pressure over Hg_2Br_2(cr) reaches one atmosphere at 666 K where the vapor is dissociated into Hg(g) and $HgBr_2$(g).

References

[1]T. W. Dakin and D. T. Ewing, J. Am. Chem. Soc. **62**, 2280 (1940).
[2]F. Ishikawa and Y. Ueda, J. Chem. Soc. Japan **51**, 59 (1930).
[3]G. Jung and W. Ziegler, Z. Phys. Chem. **A150**, 139 (1930).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.600	218.752	218.752	0.	−204.179	−178.684	31.305
300	104.703	219.399	218.754	0.194	−204.229	−178.526	31.084
400	109.621	250.226	222.924	10.921	−233.513	−163.837	21.395
500	113.052	275.074	230.948	22.063	−231.518	−146.642	15.320
600	115.604	295.921	240.086	33.501	−229.227	−129.878	11.307
700	117.529	313.890	249.376	45.160	−344.254	−100.372	7.490
800	119.118	329.691	258.447	56.995	−340.329	−65.797	4.296
900	120.416	343.797	267.161	68.973	−336.272	−31.723	1.841
1000	121.545	356.544	275.472	81.072	−332.104	1.893	−0.099
1100	122.539	368.176	283.379	93.277	−327.840	35.087	−1.666
1200	123.470	378.878	290.897	105.578	−323.488	67.889	−2.955
1300	124.209	388.789	298.050	117.960	−319.064	100.325	−4.031
1400	125.143	398.027	304.865	130.426	−314.564	132.417	−4.941
1500	126.273	406.698	311.368	142.995	−309.971	164.185	−5.717

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = [376.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -522.9 \pm 17\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -540.6 \pm 17\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[135](1)	[80](1)
[80](1)	[125](1)
[130](1)	[150](1)

Ground State Quantum Weight: 1 σ = [4]
Point Group: [D_{2h}]
Bond Distances: K–Br = [3.07] Å; K–K = [1.94] Å: Br–Br = [2.39] Å
Bond Angles: Br–K–Br = [102]°; K–Br–K = [78]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.46082 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

Vapor densities and vapor pressures of KBr were measured, using a liquid gold isoteniscope, by Hagemark *et al.*,[1] and Hagemark.[2] Based on the equilibrium constants for the reaction $2KBr(g) = K_2Br_2(g)$ in the temperature range 1267–1434 K, the enthalpy change $\Delta_r H°(298.15\ K)$ of this reaction is evaluated by the 2nd and 3rd law methods to be -42.80 ± 4.26 and -43.12 kcal·mol^{-1}, respectively. The enthalpy of formation for $K_2Br_2(g)$ is calculated to be -129.2 ± 4 kcal·mol^{-1}, using the 3rd law $\Delta_r H°(298.15\ K)$ value and $\Delta_f H°(KBr, g, 298.15\ K) = -43.04$ kcal·mol^{-1}. The drift in the 3rd law $\Delta_r H°(298.15\ K)$ values is 0.01 ± 3.2 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The molecular structure and bond distances were estimated by Berkowitz,[3] and are tentatively adopted. Berkowitz[4] has calculated vibrational frequencies on the basis of the potential function for an ionic model. These values are adjusted so that the 3rd law $\Delta_r H°(298.15\ K)$ value for the reaction $2KBr(g) = K_2Br_2(g)$ agrees with the 2nd law value. The prinicpal moments of inertia are: $I_A = 48.4690 \times 10^{-39}$, $I_B = 151.0555 \times 10^{-39}$, and $I_C = 199.5245 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.014	−522.913	−522.913	INFINITE
100	72.670	290.395	447.575	−15.718	−523.875	−540.409	282.281
200	80.188	343.855	383.672	−7.964	−526.211	−556.100	145.238
250	81.223	361.872	377.574	−3.926	−527.737	−563.402	117.717
298.15	81.782	376.230	376.230	0.	−540.573	−568.802	99.652
300	81.799	376.736	376.231	0.151	−540.671	−568.977	99.068
350	82.151	389.374	377.229	4.251	−577.004	−571.752	85.329
400	82.381	400.359	379.448	8.364	−577.894	−570.940	74.557
450	82.540	410.072	382.322	12.488	−578.740	−570.020	66.166
500	82.654	418.775	385.540	16.618	−579.548	−569.007	59.444
600	82.803	433.859	392.374	24.891	−581.073	−566.754	49.340
700	82.893	446.630	399.236	33.176	−582.518	−564.253	42.105
800	82.952	457.703	405.867	41.469	−583.932	−561.547	36.665
900	82.992	467.476	412.180	49.766	−585.364	−558.663	32.424
1000	83.021	476.222	418.155	58.067	−586.863	−555.617	29.022
1100	83.042	484.135	423.799	66.370	−746.380	−543.196	25.794
1200	83.058	491.362	429.132	74.675	−746.024	−524.740	22.841
1300	83.071	498.010	434.178	82.982	−745.676	−506.314	20.344
1400	83.081	504.167	438.960	91.289	−745.336	−487.914	18.204
1500	83.089	509.899	443.501	99.598	−745.006	−469.539	16.351
1600	83.096	515.262	447.820	107.907	−744.687	−451.185	14.730
1700	83.101	520.300	451.937	116.217	−744.383	−432.850	13.300
1800	83.106	525.050	455.868	124.527	−744.097	−414.533	12.029
1900	83.110	529.543	459.629	132.838	−743.833	−396.231	10.893
2000	83.113	533.806	463.232	141.149	−743.596	−377.942	9.871
2100	83.116	537.862	466.690	149.461	−743.391	−359.665	8.946
2200	83.119	541.728	470.013	157.772	−743.224	−341.396	8.106
2300	83.121	545.423	473.212	166.084	−743.101	−323.135	7.339
2400	83.123	548.961	476.295	174.397	−743.027	−304.877	6.635
2500	83.124	552.354	479.270	182.709	−743.008	−286.621	5.989
2600	83.126	555.614	482.144	191.021	−743.050	−268.365	5.392
2700	83.127	558.751	484.924	199.334	−743.157	−250.106	4.839
2800	83.128	561.775	487.615	207.647	−743.336	−231.842	4.325
2900	83.129	564.692	490.223	215.960	−743.590	−213.570	3.847
3000	83.130	567.510	492.752	224.273	−743.926	−195.288	3.400
3100	83.131	570.236	495.208	232.586	−744.348	−176.994	2.982
3200	83.132	572.875	497.594	240.899	−744.862	−158.684	2.590
3300	83.133	575.433	499.914	249.212	−745.453	−140.358	2.222
3400	83.133	577.915	502.172	257.526	−746.157	−122.011	1.874
3500	83.134	580.325	504.371	265.839	−746.961	−103.643	1.547
3600	83.135	582.667	506.513	274.152	−747.880	−85.250	1.237
3700	83.135	584.945	508.602	282.466	−748.916	−66.829	0.943
3800	83.136	587.162	510.641	290.779	−750.076	−48.380	0.665
3900	83.136	589.321	512.631	299.093	−751.366	−29.898	0.400
4000	83.136	591.426	514.574	307.407	−752.781	−11.381	0.149
4100	83.137	593.479	516.474	315.720	−754.341	7.172	−0.091
4200	83.137	595.482	518.331	324.034	−756.061	25.766	−0.320
4300	83.137	597.438	520.148	332.348	−757.939	44.403	−0.539
4400	83.138	599.350	521.927	340.661	−759.431	63.031	−0.748
4500	83.138	601.218	523.668	348.975	−761.514	81.746	−0.949
4600	83.138	603.045	525.374	357.289	−763.755	100.510	−1.141
4700	83.139	604.833	527.046	365.603	−766.117	119.319	−1.326
4800	83.139	606.584	528.684	373.917	−768.425	138.157	−1.503
4900	83.139	608.298	530.292	382.231	−771.105	157.072	−1.674
5000	83.139	609.978	531.869	390.544	−773.949	176.043	−1.839
5100	83.139	611.624	533.416	398.858	−776.961	195.073	−1.998
5200	83.140	613.238	534.936	407.172	−780.140	214.162	−2.151
5300	83.140	614.822	536.428	415.486	−783.488	233.316	−2.299
5400	83.140	616.376	537.895	423.800	−787.005	252.533	−2.443
5500	83.140	617.902	539.335	432.114	−790.688	271.818	−2.582
5600	83.140	619.400	540.752	440.428	−794.536	291.170	−2.716
5700	83.140	620.871	542.145	448.742	−797.858	310.498	−2.845
5800	83.140	622.317	543.514	457.056	−801.941	329.978	−2.972
5900	83.141	623.738	544.862	465.370	−806.172	349.530	−3.095
6000	83.141	625.136	546.188	473.684	−810.546	369.155	−3.214

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = [314.53]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°K) = -483.8 \pm 21\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -500.8 \pm 21\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[202](1)	[327](1)
[203](1)	413 (1)
[353](1)	295 (1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Li–Br = 2.35 Å; Li–Li = 2.70 Å
Bond Angle: Br–Li–Br = 110°
Product of the Moments of Inertia: $I_A I_B I_C = 4.22259 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

This was obtained from the enthalpy of formation of the liquid and the selected enthalpy of vaporization to the dimer, which derivation has been given in the LiBr(g) table.

Heat Capacity and Entropy

Berkowitz[1] has calculated the molecular structure and vibrational frequencies based on an ionic model. The planar rhombic structure for dimeric lithium bromide, proposed by Berkowitz, has been confirmed by the lack of polarity in electric deflection by Buchler *et al.*[2] The selected bond distances and angle were obtained from the electron diffraction studies of monomer–dimer vapor by Akischin and Rambidi.[3] The bond distances (r_{Br-Br} = 4.20 Å and r_{Li-Li} = 2.60 Å) calculated by Berkowitz are in reasonable agreement with those selected. The principal moments of inertia are: $I_A = 4.1882 \times 10^{-39}$, $I_B = 98.3375 \times 10^{-39}$, and $I_C = 102.5257 \times 10^{-39}$ g·cm^2.

Bauer *et al.*[4] have estimated six vibrational frequencies (576, 576, 202, 230, 329 and 365 cm^{-1}) for $Li_2Br_2(g)$ in the electron diffraction studies of $Li_2Cl_2(g)$. Klemperer and Norris[5] have observed two fundamental vibrational frequencies (413 and 295 cm^{-1}) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes; and these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from Berkowitz[1] because his model and derivation are self-consistent.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.696	−483.767	−483.767	INFINITE
100	47.860	245.752	375.407	−12.966	−483.820	−501.542	261.979
200	67.533	285.942	321.206	−7.053	−486.491	−518.265	135.357
250	72.201	301.555	315.755	−3.550	−488.060	−526.031	109.908
298.15	75.049	314.534	314.534	0.	−500.825	−531.879	93.183
300	75.136	314.998	314.535	0.139	−500.917	−532.072	92.642
350	77.065	326.735	315.458	3.947	−532.285	−535.530	79.923
400	78.388	337.117	317.529	7.835	−532.902	−535.953	69.988
450	79.329	346.407	320.231	11.780	−533.645	−536.291	62.251
500	80.020	354.803	323.275	15.764	−540.530	−535.925	55.988
600	80.943	369.481	329.787	23.816	−542.164	−534.847	46.563
700	81.513	382.005	336.374	31.941	−543.628	−533.510	39.811
800	81.888	392.915	342.775	40.112	−545.002	−531.970	34.734
900	82.148	402.576	348.893	48.315	−546.345	−530.260	30.775
1000	82.335	411.242	354.702	56.540	−547.667	−528.402	27.601
1100	82.474	419.096	360.205	64.780	−548.972	−526.412	24.997
1200	82.580	426.277	365.416	73.033	−550.263	−524.304	22.822
1300	82.663	432.890	370.355	81.296	−551.545	−522.089	20.978
1400	82.729	439.018	375.043	89.565	−552.817	−519.775	19.393
1500	82.782	444.728	379.501	97.841	−554.076	−517.371	18.016
1600	82.826	450.072	383.746	106.121	−555.323	−514.883	16.809
1700	82.862	455.094	387.797	114.406	−847.035	−497.965	15.301
1800	82.892	459.832	391.669	122.693	−846.762	−477.440	13.855
1900	82.918	464.314	395.375	130.984	−846.503	−456.929	12.562
2000	82.940	468.568	398.929	139.277	−846.263	−436.431	11.398
2100	82.959	472.615	402.343	147.572	−846.045	−415.945	10.346
2200	82.975	476.475	405.625	155.869	−845.853	−395.469	9.390
2300	82.990	480.163	408.786	164.167	−845.690	−375.001	8.517
2400	83.002	483.696	411.834	172.466	−845.561	−354.539	7.716
2500	83.013	487.084	414.777	180.767	−845.468	−334.082	6.980
2600	83.023	490.340	417.621	189.069	−845.416	−313.628	6.301
2700	83.032	493.474	420.373	197.372	−845.406	−293.174	5.672
2800	83.040	496.493	423.038	205.675	−845.441	−272.721	5.088
2900	83.047	499.407	425.621	213.980	−845.524	−252.265	4.544
3000	83.053	502.223	428.128	222.285	−845.656	−231.806	4.036
3100	83.059	504.946	430.562	230.590	−845.839	−211.342	3.561
3200	83.064	507.584	432.928	238.897	−846.074	−190.870	3.116
3300	83.069	510.140	435.230	247.203	−846.360	−170.391	2.697
3400	83.073	512.620	437.469	255.510	−846.700	−149.902	2.303
3500	83.077	515.028	439.651	263.818	−847.094	−129.403	1.931
3600	83.081	517.368	441.778	272.126	−847.541	−108.891	1.580
3700	83.084	519.644	443.851	280.434	−848.043	−88.366	1.248
3800	83.087	521.860	445.875	288.743	−848.599	−67.827	0.932
3900	83.090	524.018	447.851	297.052	−849.211	−47.272	0.633
4000	83.093	526.122	449.782	305.361	−849.878	−26.701	0.349
4100	83.095	528.174	451.669	313.670	−850.603	−6.113	0.078
4200	83.098	530.176	453.515	321.980	−851.384	14.494	−0.180
4300	83.100	532.132	455.320	330.290	−852.225	35.119	−0.427
4400	83.102	534.042	457.088	338.600	−853.084	55.762	−0.662
4500	83.104	535.910	458.819	346.910	−854.027	76.428	−0.887
4600	83.105	537.736	460.514	355.220	−855.035	97.116	−1.103
4700	83.107	539.524	462.177	363.531	−856.105	117.826	−1.309
4800	83.109	541.273	463.806	371.842	−857.240	138.560	−1.508
4900	83.110	542.987	465.405	380.153	−858.441	159.318	−1.698
5000	83.111	544.666	466.973	388.464	−859.711	180.102	−1.882
5100	83.113	546.312	468.513	396.775	−861.041	200.910	−2.058
5200	83.114	547.926	470.025	405.086	−862.454	221.746	−2.227
5300	83.115	549.509	471.509	413.398	−863.944	242.611	−2.391
5400	83.116	551.063	472.968	421.709	−865.513	263.504	−2.549
5500	83.117	552.588	474.402	430.021	−867.166	284.426	−2.701
5600	83.118	554.085	475.812	438.333	−868.904	305.380	−2.848
5700	83.119	555.557	477.198	446.645	−870.732	326.366	−2.991
5800	83.120	557.002	478.561	454.957	−872.653	347.383	−3.129
5900	83.121	558.423	479.903	463.269	−874.670	368.436	−3.262
6000	83.121	559.820	481.223	471.581	−876.786	389.523	−3.391

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = [117.2 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 984 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -524.26 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus} H° = [39.330 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

The selected value for $\Delta_f H°(298.15\ K)$ is that given by NBS.[1] This value is derived from the solution calorimetric measurements of Finch *et al.*[2] Their enthalpies for the reaction of crystalline MgO with aqueous HBr and solution of anhydrous $MgBr_2$ in the same solvent are combined to give $\Delta_r H°(298.15\ K) = 7.77 \pm 0.40\ kcal·mol^{-1}$ for the process $MgO(cr) + 2\ HBr(aq) = MgBr_2(cr) + H_2O(l)$. When this result is combined with auxiliary data,[1,3-4] the selected value is obtained. This value is confirmed by an independent means. Bichowsky and Rossini[5] give the enthalpy of solution of $MgBr_2$ in 800 H_2O as $-43.3\ kcal·mol^{-1}$ based on measurements by Beketoff.[6] Correction of this value to 298.15 K and infinite dilution gives a value for $\Delta_{sol} H°$ which leads to $\Delta_f H°(298.15\ K) = -125.4\ kcal·mol^{-1}$ when combined with $\Delta_f H°(Mg^{+2}, aq, \infty, 298.15\ K) = -111.58\ kcal·mol^{-1}$[11] and $\Delta_f H°(Br^-, aq, \infty, 298.15\ K) = -29.039 \pm 0.035\ kcal·mol^{-1}$.[4]

Two emf studies[7,8] on the potential of the magnesium electrode in ether solution give results in disagreement with the calorimetric values. From these cell data we derive $\Delta_f H°(298.15\ K)$ values of $-118.8\ kcal·mol^{-1}$[7] and $-115.0\ kcal·mol^{-1}$.[8] These rather large discrepancies are taken as an indication that the electrodes are probably irreversible under these conditions. In fact one study[8] reported that from 10 to 20 hours were required before stable emf values were obtained.

Heat Capacity and Entropy

$C_p°$ at 298.15 K is obtained from the process $MgCl_2(cr) + 2\ NaBr(cr) = MgBr_2(cr) + 2\ NaCl(cr)$ by assuming $\Delta C_p°$ is zero. A comparison of the $C_p°$ value ($17.49\ cal·K^{-1}·mol^{-1}$) with those for other alkaline earth dihalides shows that it is reasonable. $C_p°$ data above 300 K are estimated by comparison with similar data for $MgCl_2$ and CaI_2.[3]

Several estimates[9-12] lying in the range 27–30 $cal·K^{-1}·mol^{-1}$ for $S°(298.15\ K)$ have been reported. Available experimental data for several other alkaline earth dihalides suggest a value for $S°(298.15\ K)$ of $MgBr_2(cr)$ near 28 $cal·K^{-1}·mol^{-1}$ ($117.152\ J·K^{-1}·mol^{-1}$). We tentatively adopt this value. It is also the value recommended by Kelley and King[10] and NBS.[1]

Fusion Data

The value of T_{fus} is that determined from cooling curves by Kellner.[13,14] The uncertainty in these measurements is probably near ±15 K. $\Delta_{fus} H°$ is calculated from a $\Delta_{fus} S° = 9.5\ cal·K^{-1}·mol^{-1}$ by multiplication of T_{fus}. $\Delta_{fus} S°$ is assumed the same as that for CaI_2[3] which also has the hexagonal CdI_2 structure.[15] Kelley[16] obtained a value of $\Delta_{fus} H°$ equal to 8.3 $kcal·mol^{-1}$ from an analysis of phase diagrams for the systems $MgBr_2$–MBr(M = Na, K)[14] and $MgBr_2$–$LiBr$.[17] However, he implied that the value was somewhat uncertain. Furthermore, it is noted that several $\Delta_{fus} H°$ values listed by Kelley for other alkaline earth dihalides deviate considerably (1–3 $kcal·mol^{-1}$) from those measured calorimetrically.[18] Thus, we prefer the estimated value at this time. (See also $MgBr_2$(l) table Enthalpy of Formation Section).

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	73.161	117.152	117.152	0.	−524.255	−504.063	88.310
300	73.387	117.605	117.153	0.136	−524.306	−503.937	87.743
400	77.278	139.284	120.083	7.681	−553.796	−491.005	64.119
500	79.743	156.808	125.731	15.538	−552.296	−475.479	49.673
600	81.429	171.498	132.168	23.598	−550.723	−460.263	40.069
700	82.969	184.165	138.712	31.818	−549.114	−445.313	33.230
800	84.554	195.346	145.106	40.193	−547.480	−430.595	28.115
900	86.270	205.403	151.256	48.733	−545.822	−416.084	24.149
1000	88.136	214.586	157.136	57.450	−552.735	−401.046	20.948
1100	90.144	223.079	162.749	66.363	−551.036	−385.957	18.328
1200	92.257	231.013	168.111	75.483	−549.140	−371.032	16.151
1300	94.433	238.484	173.240	84.817	−547.036	−356.274	14.315
1400	96.567	245.560	178.155	94.367	−672.136	−338.518	12.630
1500	98.701	252.295	182.875	104.131	−668.270	−314.822	10.963

PREVIOUS: June 1966 CURRENT: June 1974

$S°(298.15\ K) = [150.500]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 984 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-490.408]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [39.330 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(984\ K)–H°(298.15\ K)$, between the crystal and liquid. The derived value is supported by results obtained from an equilibrium study[1] of the anion exchange reaction 0.5 $MgBr_2(l) + HCl(g) = 0.5\ MgCl_2(l) + HBr(g)$. A third law analysis of the K_p value reported for the equilibrium at 1073 K gives $\Delta_r H°(298.15\ K) = 0.05\ kcal·mol^{-1}$ which leads to $\Delta_f H°(l, 298.15\ K) = -117.2\ kcal·mol^{-1}$. In the same paper, Toguri *et al.*[1] reported similar data for the chloride–bromide salts of Ca, K, and Na. These results lead to $\Delta_f H°(298.15\ K)$ values for the molten bromides which show deviations from adopted JANAF values[2] of no more than 0.6 $kcal·mol^{-1}$. Thus, although the exact agreement in the $\Delta_f H°(298.15\ K)$ values for $MgBr_2(l)$ is fortuitous, it does tend to substantiate our thermal data.

Heat Capacity and Entropy

$C_p°$ for the liquid is estimated as 25.0 $cal·K^{-1}·mol^{-1}$ by analogy with measured $C_p°$ data for molten $CaBr_2$ and $SrBr_2$.[2] The value is taken to be constant above the assumed glass transition at 700 K. Below 700 K, $C_p°$ is that of the crystal.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G° = 0$ at 1 bar for the process $MgBr_2(l) = MgBr_2(g)$. $\Delta_{vap} H°$ is the difference in the enthalpies of formation of the gas and liquid at T_{vap}.

References

[1]J. Toguri, H. Flood, and T. Forland, Acta Chem. Scand. **17**, 502 (1963).
[2]JANAF Thermochemical Tables: $CaBr_2(l)$ and $SrBr_2(l)$, 6–30–74; KBr(l), 3–31–67; NaBr(l), 6–30–64.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.161	150.500	150.500	0.	−490.408	−480.158	84.122
300	73.387	150.954	150.502	0.136	−490.458	−480.094	83.592
400	77.278	172.633	153.431	7.681	−519.948	−470.497	61.441
500	79.743	190.156	159.080	15.538	−518.449	−458.306	47.879
600	81.429	204.846	165.516	23.598	−516.876	−446.424	38.865
700	82.970	217.516	172.060	31.819	−515.265	−434.809	32.446
700.000	82.970	217.516	172.060	31.819	GLASS <-- -> LIQUID		
700.000	104.600	217.516	172.060	31.819	TRANSITION		
800	104.600	231.484	178.635	42.279	−511.546	−423.571	27.656
900	104.600	243.804	185.205	52.739	−507.968	−412.790	23.958
1000	104.600	254.824	191.625	63.199	−513.139	−401.687	20.982
1100	104.600	264.794	197.831	73.659	−509.893	−390.699	18.553
1200	104.600	273.895	203.796	84.119	−506.655	−380.006	16.541
1300	104.600	282.268	209.514	94.579	−503.427	−369.583	14.850
1400	104.600	290.019	214.991	105.039	−627.616	−356.242	13.292
1500	104.600	297.236	220.237	115.499	−623.054	−337.017	11.736
1600	104.600	303.987	225.262	125.959	−618.502	−318.096	10.385
1700	104.600	310.328	230.082	136.419	−613.961	−299.460	9.201
1800	104.600	316.307	234.707	146.879	−609.434	−281.091	8.157
1900	104.600	321.962	239.152	157.339	−604.921	−262.972	7.230
2000	104.600	327.328	243.428	167.799	−600.426	−245.091	6.401

PREVIOUS: June 1966 CURRENT: June 1974

298.15 to 984 K crystal
above 984 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.161	117.152	117.152	0.	−524.255	−504.063	88.310
300	73.387	117.605	117.153	0.136	−524.306	−503.937	87.743
400	77.278	139.284	120.083	7.681	−553.796	−491.005	64.119
500	79.743	156.808	125.731	15.538	−552.296	−475.479	49.673
600	81.429	171.498	132.168	23.598	−550.723	−460.263	40.069
700	82.969	184.165	138.712	31.818	−549.114	−445.313	33.230
800	84.554	195.346	145.106	40.193	−547.480	−430.595	28.115
900	86.270	205.403	151.256	48.733	−545.822	−416.084	24.149
984.000	87.811	213.168	156.213	56.044	CRYSTAL <--> LIQUID TRANSITION		
984.000	104.600	253.137	156.213	95.373			
1000	104.600	254.824	157.778	97.047	−513.139	−401.687	20.982
1100	104.600	264.794	167.060	107.507	−509.893	−390.699	18.553
1200	104.600	273.895	175.590	117.967	−506.655	−380.006	16.541
1300	104.600	282.268	183.478	128.427	−503.427	−369.583	14.850
1400	104.600	290.019	190.815	138.887	−627.616	−356.242	13.292
1500	104.600	297.236	197.672	149.347	−623.054	−337.017	11.736
1600	104.600	303.987	204.108	159.807	−618.502	−318.096	10.385
1700	104.600	310.328	210.171	170.267	−613.961	−299.460	9.201
1800	104.600	316.307	215.903	180.727	−609.434	−281.091	8.157
1900	104.600	321.962	221.338	191.187	−604.921	−262.973	7.230
2000	104.600	327.328	226.504	201.647	−600.426	−245.091	6.401

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [301.0 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -288.4 \pm 10.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -302.9 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[179](1)
[70](2)
490(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point group: $[D_{\infty h}]$
Bond Distance: Mg–Br = 2.34 ± 0.03 Å
Bond Angle: Br–Mg–Br = [180]°
Rotational Constant: B = [0.019265] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of the gas is obtained from that of the crystal by addition of $\Delta_{sub} H°(298.15\ K) = 52.9 \pm 2.0\ kcal \cdot mol^{-1}$ (221.334 ± 8.4 $kJ \cdot mol^{-1}$). The selected value for the enthalpy of sublimation is derived from results of a mass spectrometric–Knudsen effusion study by Berkowitz and Marquart.[1] The presence of ~2% dimer in the vapor phase over the solid at near 800 K was revealed by the mass spectral results. Berkowitz and Marquart,[1] using $MgBr_2^+$–ion intensity as a measure of the monomer concentration, obtained a 2nd law $\Delta_{sub} H = 50.3\ kcal \cdot mol^{-1}$ at 751 K. This value when corrected to 298.15 K gives $\Delta_{sub} H°(298.15\ K) = 52.4\ kcal \cdot mol^{-1}$. Absolute partial pressures were also determined at 798 and 842 K by integrating the ion current during complete volatilization of the sample. A 3rd law analysis of these two pressures gives a enthalpy of sublimation equal to 53.4 $kcal \cdot mol^{-1}$ which is in good agreement with the value obtained from the ion intensities by the 2nd law. The drift in the 3rd law analysis is 1.0 $cal \cdot K^{-1} \cdot mol^{-1}$. The selected value of $\Delta_{sub} H°(298.15\ K)$ is an average of these two results.

Heat Capacity and Entropy

The bond length is from the electron–diffraction measurements of Akishin and Spiridonov.[3] Their diffraction patterns for $MgBr_2$ were satisfactorily explained on the basis of a linear model. Klemperer *et al.*[4,5] have performed electronic quadrupole deflection experiments on several symmetrical triatomic dihalides in an attempt to determine which molecules possess permanent dipole moments. Their results on the geometrics of the alkaline earth dihalides have been summarized by Hayes[6] who pointed out that the linear form is favored by the light metal–heavy halogen combination. Thus, one would expect $MgBr_2$ to be linear, and we adopt this configuration.

The antisymmetric stretching frequency ($\nu_3 = 490\ cm^{-1}$) has been observed in the infrared absorption spectrum of gaseous $MgBr_2$ by Randall *et al.*[7] The symmetric stretching (ν_1) and bending (ν_2) frequencies are calculated from force constants by the valence force method.[8] The observed υ_3 frequency leads to $k = 1.5 \times 10^5$ dynes/cm, or $\nu_1 = 179\ cm^{-1}$. A comparison of values for the ratio of the stretch to bend force constants for the linear molecules $MgCl_2$[9](ratio = 88)], $CaBr_2$[9](ratio = [100])], and $SrBr_2$[9](ratio = [100])] suggests a value near 100 for $MgBr_2$. This value for the ratio gives $k\delta/l^2 = 1.5 \times 10^3$ dynes/cm, or $\nu_2 = 70\ cm^{-1}$ Based on similar data for linear $BeBr_2$,[10] it is possible that the value of the ratio could be as low as 41. This ratio corresponds to a bending frequency of 109 cm^{-1}. We prefer the lower value of ν_2, since it is consistent with the observed value for [$MgCl_2$[9]($\nu_2 = 88\ cm^{-1}$)]. However, we do include in the uncertainty of the value for $S°(298.15\ K)$ the possibility that the higher value is correct. Brewer *et al.*[2] used a value for the ratio of 10 and obtained $\nu_2 = 220\ cm^{-1}$. By comparison with the observed frequencies for $MgCl_2$ and [$BeBr_2$[10]($\nu_2 = 220\ cm^{-1}$)] it is unlikely that the value for $MgBr_2$ is this high. Krasnov and Svettsov[11] have reported $\nu_1 = 188\ cm^{-1}$ and $\nu_2 = 148\ cm^{-1}$ based on force constant correlations. The ground state is assumed to be singlet by analogy with that for $BaCl_2$.[9]

References

[1] J. Berkowitz and J. R. Marquart, J. Chem. Phys. **37**, 1853 (1962).
[2] L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Revs. **63**, 111 (1963).
[3] P. A. Akishin and V. P. Spiridonov, Kristallografiya **2**, 472 (1957).
[4] L. Wharton, R. A. Berg, and W. Klemperer, J. Chem. Phys. **39**, 2023 (1963).
[5] A. Buchler, J. L. Stauffer, and W. Klemperer, J. Am. Chem. Soc. **86**, 4544 (1964).
[6] E. F. Hayes, J. Phys. Chem. **70**, 3740 (1966).
[7] S. P. Randall, F. T. Greene, and J. L. Margrave, J. Phys. Chem. **63**, 758 (1959).
[8] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, (1962).
[9] JANAF Thermochemical Tables: $MgCl_2$(g), 12–31–69; $CaBr_2$(g) and $SrBr_2$(g), 6–30–74; $BaCl_2$(g), 12–31–72.
[10] A. Snelson, J. Phys. Chem. **72**, 250 (1968).
[11] K. S. Krasnov and V. I. Svettsov, Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol. **6**, 167 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.012	−288.427	−288.427	INFINITE
100	49.669	241.523	351.095	−10.957	−287.807	−305.624	159.641
200	55.867	278.131	306.332	−5.640	−289.398	−322.911	84.336
250	57.579	290.793	301.998	−2.801	−290.546	−331.162	69.192
298.15	58.711	301.038	301.038	0.	−302.922	−337.555	59.138
300	58.747	301.401	301.039	0.109	−302.999	−337.769	58.811
350	59.557	310.521	301.757	3.067	−333.953	−341.862	51.020
400	60.134	318.514	303.363	6.061	−334.082	−342.984	44.789
450	60.555	325.622	305.448	9.078	−334.226	−344.088	39.941
500	60.870	332.019	307.791	12.114	−334.387	−345.175	36.060
600	61.299	343.158	312.784	18.224	−334.763	−347.299	30.235
700	61.568	352.629	317.817	24.369	−335.230	−349.353	26.069
800	61.747	360.863	322.694	30.535	−335.804	−351.332	22.940
900	61.872	368.143	327.347	36.716	−336.505	−353.233	20.501
1000	61.962	374.667	331.759	42.908	−345.943	−354.335	18.509
1100	62.030	380.576	335.932	49.108	−346.958	−355.125	16.863
1200	62.081	385.976	339.881	55.314	−347.975	−355.822	15.489
1300	62.122	390.946	343.620	61.524	−348.996	−356.435	14.322
1400	62.154	395.551	347.167	67.738	−477.432	−353.802	13.201
1500	62.180	399.841	350.538	73.954	−477.113	−344.982	12.013
1600	62.201	403.854	353.746	80.174	−476.801	−336.184	10.975
1700	62.219	407.626	356.805	86.395	−476.500	−327.404	10.060
1800	62.234	411.182	359.728	92.617	−476.210	−318.643	9.247
1900	62.247	414.548	362.526	98.841	−475.933	−309.896	8.520
2000	62.258	417.741	365.207	105.067	−475.672	−301.164	7.866
2100	62.267	420.779	367.782	111.293	−475.429	−292.445	7.274
2200	62.275	423.675	370.257	117.520	−475.205	−283.737	6.737
2300	62.282	426.444	372.640	123.748	−475.003	−275.038	6.246
2400	62.288	429.095	374.938	129.976	−474.822	−266.348	5.797
2500	62.294	431.637	377.155	136.205	−474.665	−257.665	5.384
2600	62.298	434.081	379.298	142.435	−474.532	−248.988	5.002
2700	62.303	436.432	381.371	148.665	−474.424	−240.315	4.649
2800	62.307	438.698	383.378	154.896	−474.339	−231.646	4.321
2900	62.310	440.884	385.324	161.126	−474.278	−222.980	4.016
3000	62.313	442.997	387.211	167.358	−474.241	−214.315	3.732
3100	62.316	445.040	389.044	173.589	−474.226	−205.651	3.465
3200	62.319	447.019	390.825	179.821	−474.233	−196.987	3.215
3300	62.321	448.936	392.557	186.053	−474.260	−188.323	2.981
3400	62.323	450.797	394.242	192.285	−474.307	−179.657	2.760
3500	62.325	452.603	395.884	198.517	−474.373	−170.990	2.552
3600	62.327	454.359	397.484	204.750	−474.458	−162.321	2.355
3700	62.329	456.067	399.045	210.983	−474.561	−153.649	2.169
3800	62.330	457.729	400.567	217.216	−474.681	−144.975	1.993
3900	62.332	459.348	402.054	223.449	−474.818	−136.296	1.825
4000	62.333	460.926	403.506	229.682	−474.972	−127.614	1.666
4100	62.334	462.465	404.925	235.915	−475.144	−118.928	1.515
4200	62.335	463.968	406.313	242.149	−475.333	−110.238	1.371
4300	62.336	465.434	407.671	248.382	−475.541	−101.543	1.233
4400	62.337	466.867	409.000	254.616	−475.767	−92.842	1.102
4500	62.338	468.268	410.302	260.850	−476.012	−84.137	0.977
4600	62.339	469.639	411.577	267.084	−476.278	−75.426	0.856
4700	62.340	470.979	412.827	273.318	−476.566	−66.708	0.741
4800	62.341	472.292	414.052	279.552	−476.876	−57.985	0.631
4900	62.341	473.577	415.253	285.786	−477.210	−49.254	0.525
5000	62.342	474.837	416.433	292.020	−477.570	−40.517	0.423
5100	62.343	476.071	417.590	298.254	−477.956	−31.772	0.325
5200	62.343	477.282	418.726	304.488	−478.370	−23.020	0.231
5300	62.344	478.469	419.842	310.723	−478.813	−14.258	0.141
5400	62.344	479.635	420.939	316.957	−479.287	−5.489	0.053
5500	62.345	480.779	422.016	323.192	−479.794	3.290	−0.031
5600	62.345	481.902	423.076	329.426	−480.334	12.078	−0.113
5700	62.346	483.005	424.118	335.661	−480.909	20.876	−0.191
5800	62.346	484.090	425.142	341.895	−481.522	29.684	−0.267
5900	62.346	485.155	426.150	348.130	−482.172	38.504	−0.341
6000	62.347	486.203	427.143	354.364	−482.862	47.334	−0.412

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = [321.7 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 739.2 \pm 25.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [731.363]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Pi$	[25000]	4
$^2\Sigma$	[30000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[150](1)
[50](2)
[450](1)

Point Group: $[D_{\infty h}]$ $\sigma = 2$
Bond Distance: Mg–Br = [2.6] Å
Bond Angle: Br–Mg–Br = [180]°
Rotational Constant: B_o = [0.015605] cm^{-1}

Enthalpy of Formation

Berkowitz and Marquart[1] have reported the appearance potential of $MgBr_2^+$ as $10.6 \pm 0.1_5$ eV(245.6 $kcal \cdot mol^{-1}$). Assuming this value refers to the direct ionization process $MgBr_2(g) + e^- = MgBr_2^+(g) + 2e^-$, we obtain $\Delta_f H°(MgBr_2^+, g, 0\ K) = 176.7 \pm 6.0\ kcal \cdot mol^{-1}$ by combining the appearance potential with $\Delta_f H°(MgBr_2, g, 0\ K) = -68.9 \pm 2.5\ kcal \cdot mol^{-1}$.[2] The former value corresponds to $\Delta_f H°(298.15\ K) = 174.8\ kcal \cdot mol^{-1}$ (731.363 $kJ \cdot mol^{-1}$) which is adopted.

Heat Capacity and Entropy

A comparison of the dissociation energy, $\Delta_a H° = 91.0\ kcal \cdot mol^{-1}$, for $MgBr_2^+$ with that for $MgBr_2$,[2] $\Delta_a H° = 160.3\ kcal \cdot mol^{-1}$, suggests the existence of somewhat weaker bonding in the ion relative to the molecule. Thus, one would expect the bond length in the ion to be greater than that for $MgBr_2$. We assume a 10% increase in r_e for the ion. The correlation diagrams of Walsh[3] predict a linear configuration for $MgBr_2^+$(fifteen valence electrons). This prediction is supported by the fact that several other fifteen valence electron molecules (BO_2, N_3, NCO, and NNO^+) are now known to be linear.[2] We adopt a linear configuration for the ion.

The vibrational frequencies are estimated to be slightly less than those for $MgBr_2$.[2] The ground state electronic configuration is assumed to be $^2\Pi$ by analogy with those for the isoelectronic molecules[2] BO_2, N_3, NCO, and N_2O^+. Two excited states are also included based on those observed for BO_2.[2] The enthalpy at 0 K is $-15.441\ kJ \cdot mol^{-1}$.

References

[1] J. Berkowitz and J. R. Marquart, J. Chem. Phys. **37**, 1853 (1962).
[2] JANAF Thermochemical Tables: $MgBr_2$(g), 6-30-74; BO_2(g), 6-30-68; CNO(g), N_2O^+(g), and N_3(g), 12-31-70.
[3] A. D. Walsh, J. Chem. Soc. **1953**, 2266.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.442	739.231		
100	51.289	261.045	372.577	−11.153			
200	56.811	298.524	327.095	−5.714			
250	58.322	311.375	322.708	−2.833			
298.15	59.303	321.737	321.737	0.	731.363	684.304	−119.887
300	59.334	322.104	321.738	0.110	731.325	684.012	−119.097
350	60.027	331.305	322.463	3.095	701.437	677.744	−101.148
400	60.514	339.354	324.082	6.109	702.368	674.296	−88.054
450	60.868	346.503	326.183	9.144	703.280	670.732	−77.857
500	61.131	352.931	328.542	12.194	704.174	667.067	−69.688
600	61.487	364.110	333.566	18.327	705.898	659.482	−57.413
700	61.710	373.607	338.625	24.487	707.527	651.616	−48.624
800	61.857	381.857	343.524	30.666	709.043	643.524	−42.018
900	61.960	389.149	348.196	36.857	710.431	635.249	−36.869
1000	62.034	395.681	352.624	43.057	703.079	627.540	−32.779
1100	62.090	401.596	356.811	49.264	704.150	619.935	−29.438
1200	62.132	407.001	360.772	55.475	705.217	612.232	−26.650
1300	62.165	411.975	364.522	61.690	706.279	604.440	−24.287
1400	62.191	416.583	368.078	67.908	579.926	599.734	−22.376
1500	62.213	420.875	371.456	74.128	582.327	601.064	−20.931
1600	62.230	424.891	374.672	80.350	584.720	602.236	−19.661
1700	62.245	428.664	377.738	86.574	587.103	603.257	−18.536
1800	62.257	432.222	380.667	92.799	589.474	604.139	−17.532
1900	62.267	435.588	383.470	99.025	591.831	604.889	−16.630
2000	62.276	438.782	386.156	105.252	594.173	605.516	−15.814
2100	62.284	441.821	388.735	111.480	596.496	606.026	−15.074
2200	62.290	444.719	391.214	117.709	598.800	606.426	−14.398
2300	62.296	447.488	393.601	123.938	601.083	606.721	−13.779
2400	62.302	450.139	395.902	130.168	603.343	606.918	−13.209
2500	62.306	452.682	398.123	136.398	605.580	607.021	−12.683
2600	62.311	455.126	400.269	142.629	607.793	607.035	−12.195
2700	62.315	457.478	402.344	148.861	609.982	606.964	−11.742
2800	62.320	459.744	404.354	155.092	612.146	606.812	−11.320
2900	62.324	461.931	406.302	161.325	614.287	606.584	−10.926
3000	62.329	464.044	408.192	167.557	616.404	606.282	−10.556
3100	62.335	466.088	410.027	173.791	618.500	605.910	−10.210
3200	62.341	468.067	411.810	180.024	620.574	605.471	−9.883
3300	62.348	469.986	413.544	186.259	622.627	604.967	−9.576
3400	62.355	471.847	415.231	192.494	624.662	604.401	−9.285
3500	62.364	473.655	416.875	198.730	626.677	603.776	−9.011
3600	62.374	475.412	418.476	204.967	628.676	603.094	−8.751
3700	62.386	477.121	420.038	211.205	630.657	602.356	−8.504
3800	62.399	478.785	421.563	217.444	632.622	601.564	−8.269
3900	62.414	480.406	423.051	223.685	634.571	600.721	−8.046
4000	62.431	481.986	424.504	229.927	636.504	599.829	−7.833
4100	62.450	483.528	425.925	236.171	638.422	598.888	−7.630
4200	62.471	485.033	427.315	242.417	640.324	597.901	−7.436
4300	62.494	486.503	428.674	248.665	642.209	596.868	−7.251
4400	62.519	487.940	430.005	254.916	644.079	595.793	−7.073
4500	62.547	489.346	431.308	261.169	645.932	594.674	−6.903
4600	62.577	490.721	432.585	267.425	647.766	593.515	−6.740
4700	62.610	492.067	433.836	273.685	649.583	592.316	−6.583
4800	62.645	493.385	435.063	279.947	651.380	591.078	−6.432
4900	62.683	494.677	436.266	286.214	653.157	589.804	−6.287
5000	62.723	495.944	437.447	292.484	654.912	588.493	−6.148
5100	62.765	497.187	438.607	298.758	656.644	587.148	−6.014
5200	62.810	498.406	439.745	305.037	658.353	585.768	−5.884
5300	62.857	499.603	440.863	311.320	660.038	584.356	−5.759
5400	62.907	500.778	441.962	317.609	661.696	582.913	−5.639
5500	62.959	501.933	443.042	323.902	663.327	581.439	−5.522
5600	63.013	503.068	444.103	330.201	664.930	579.935	−5.409
5700	63.069	504.184	445.148	336.505	666.503	578.403	−5.300
5800	63.127	505.281	446.175	342.814	668.044	576.844	−5.195
5900	63.188	506.361	447.186	349.130	669.553	575.259	−5.093
6000	63.250	507.423	448.181	355.452	671.029	573.648	−4.994

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

Molybdenum Bromide ($MoBr_2$) CRYSTAL M_r = 255.748

$S°(298.15\ K) = [124.7 \pm]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = unknown

$\Delta_f H°(298.15\ K) = -202.9 \pm 25\ kJ·mol^{-1}$

Enthalpy of Formation

Shukurov *et al.*[1] (determined the enthalpies of combustion of $MoBr_2$(cr) and $MoBr_3$(cr)). Dellien *et al.*[2] used the combustion values of Shukurov to obtain $\Delta_f H°(MoBr_2, cr, 298.15\ K) = -54\ kcal·mol^{-1}$ and $\Delta_f H°(MoBr_3, cr, 298.15\ K) = -64\ kcal·mol^{-1}$. Oppermann[3] carried out equilibrium experiments on the mixed phases $MoBr_2$(cr) + $MoBr_3$(cr). Brewer[4] re-evaluated the data of Oppermann (see the discussion in the $MoBr_4$(g) table[5]) and supplemented the combustion data with other data on $MoBr_4$(cr). For this reason we believe Brewer's value of $\Delta_f H°(MoBr_2, cr, 298.15\ K) = -48.5 \pm 6\ kcal·mol^{-1}(-202.924 \pm 25\ kJ·mol^{-1})$ to be the most reliable among all the data and is our adopted value. Note that the enthalpy of formation listed in NBS 270-4,[6] $\Delta_f H°(298.15\ K) = -62.4\ kcal·mol^{-1}$, is much more negative.

Heat Capacity and Entropy

Brewer[4] estimated $S°(298.15\ K) = 29.8 \pm 4\ cal·K^{-1}·mol^{-1}$ ($124.683 \pm 17\ J·K^{-1}·mol^{-1}$) and derived $C_p° = 18.30 + 2.50 \times 10^{-3}T$ $cal·K^{-1}·mol^{-1}$ (298-1353 K) from the heat capacities estimated by Opperman.[3] Other estimates are $C_p°(15\ K) = 17.1\ cal·K^{-1}·mol^{-1}$ from the ionic contributions of Kubaschewski and Unal[7] and $S°(298.15\ K) = 30.4\ cal·K^{-1}·mol^{-1}$ from the additive entropy constants of Stull and Prophet.[8] The heat capacity at 298.15 K listed in NBS 270-4[6] is 18.3 $cal·K^{-1}·mol^{-1}$.

Decomposition Data

T_{dcm} is the calculated temperature at which the pressure of $MoBr_4$(g) is one atmosphere for the reaction 2 $MoBr_2$(cr) = Mo(cr) + $MoBr_4$(g).

References

[1] A. Shukurov, T. Nikol'skaya, I. V. Vasil'kova and S. A. Shchukarev, Izv. Akad. Nauk Tadzhsk. SSR, Otd. Geol.-Khim. Tekhn. Nauk, No. 4, 23 (1961).

[2] I. Dellien, F. M. Hall, and L. G. Hepler, Chem. Rev. **76**, 283 (1976).

[3] H. Oppermann, Z. anorg. allg. Chem. **395**, 249 (1973).

[4] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978; preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.

[5] JANAF Thermochemical Tables: $MoBr_4$(g), 9-30-78.

[6] U. S. Nat. Bur. Stand. Tech. Note 270-4, 141 pp. (1969).

[7] O. Kubaschewski and H. Unal, High Temp.-High Pressures **9**, 361 (1977).

[8] D. R. Stull and H. Prophet, Chap. 13 in "The Characterization of High Temperature Vapors" ed. by J. L. Margrave, John Wiley, (1967).

Molybdenum Bromide ($MoBr_2$) Br_2Mo_1(cr)

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	79.684	124.683	124.683	0.	−202.924	−186.189	32.620
300	79.705	125.176	124.685	0.147	−202.961	−186.085	32.400
400	80.751	148.249	127.824	8.170	−231.874	−174.412	22.776
500	81.797	166.381	133.785	16.298	−229.986	−160.265	16.743
600	82.843	181.387	140.504	24.530	−228.091	−146.499	12.754
700	83.889	194.235	147.284	32.866	−226.165	−133.052	9.928
800	84.935	205.506	153.871	41.308	−224.197	−119.884	7.828
900	85.981	215.570	160.177	49.853	−222.182	−106.965	6.208
1000	87.027	224.683	166.179	58.504	−220.118	−94.273	4.924
1100	88.073	233.027	171.882	67.259	−218.009	−81.790	3.884
1200	89.119	240.735	177.303	76.118	−215.860	−69.501	3.025
1300	90.165	247.909	182.461	85.083	−213.677	−57.393	2.306
1400	91.211	254.630	187.379	94.152	−211.468	−45.454	1.696
1500	92.257	260.958	192.075	103.325	−209.238	−33.674	1.173
1600	93.303	266.946	196.569	112.603	−206.997	−22.043	0.720
1700	94.349	272.634	200.878	121.986	−204.750	−10.552	0.324
1800	95.395	278.056	205.016	131.473	−202.508	0.807	−0.023

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K)$ = [321.0 ± 8] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [179.2 ± 84] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [167.4 ± 84] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[1]
[243.10]	[3]
[669.60]	[5]
[1225.20]	[7]
[1873.80]	[9]
[11271]	[1]
[12510]	[3]
[12630]	[9]
[13201]	[11]
[13742]	[13]

Vibrational Frequencies and Degeneracies
ν_i, cm^{-1}
[300](1)
[60](2)
[300](1)

Ground State Quantum Weight: 1 σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: Mo–Br = [2.42] Å
Bond Angle: Br–Mo–Br = [180]°
Rotational Constant: B_o = [0.018012] cm^{-1}

Enthaply of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ = 40.0 ± 20 $kcal·mol^{-1}$ (167.360 ± 84 $kJ·mol^{-1}$) is that estimated by Brewer[1] using bonding models. The value is consistent with sublimation data for $MoBr_2$ at 1023 K and 1273 K reported by Schafer, *et al.*[2] Brewer gave no weight to the partial pressures of $MoBr_2$ obtained by Oppermann[3] by difference (see the discussion on the $MoBr_4$(g) table[4]). The value of $\Delta_f H°(0\ K)$ combined with JANAF data[4] for Mo(g) and Br(g) gives $\Delta_{at} H°(MoBr_2, g)$ = 171 ± 20 $kcal·mol^{-1}$ (715.5 ± 84 $kJ·mol^{-1}$). This yields a mean bond energy $\Delta_{at} H°(MoBr_2, g)/2$ = 85.5 $kcal·mol^{-1}$, somewhat higher than that found in $MoBr_4$(g), 76.0 $kcal·mol^{-1}$.[4]

Heat Capacity and Entropy

The linear structure of $MoBr_2$(g), bond length, and the ground state vibrational frequencies are estimates from Brewer.[1] The electronic contributions are assumed to be the same as the free ion, Mo^{++}, as suggested by Brewer.[1] All states up to 13,742 cm^{-1} as listed by Rico[5] are included in the calculation.

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of September 29, 1978; preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]H. Schafer, T. Grofe, and M. Trenkel, J. Solid State Chem. **8**, 14 (1973).
[3]H. Oppermann, Z. anorg. allg. Chem. **395**, 249 (1973).
[4]JANAF Thermochemical Tables: Mo(g), 3-31-78; Br(g), 9-30-61, $MoBr_4$(g), 9-30-78.
[5]F. R. Rico, Anales. Real Soc. Espan. Fys. Quim., Ser. A, **61**, 103 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.293	179.161	179.161	INFINITE
100	56.960	250.449	380.393	−12.994	180.175	161.218	−84.211
200	66.592	293.789	327.229	−6.688	179.738	142.360	−37.181
250	68.260	308.843	322.096	−3.313	179.179	133.075	−27.805
298.15	69.291	320.960	320.960	0.	167.360	125.575	−22.000
300	69.322	321.389	320.962	0.128	167.304	125.315	−21.819
350	70.005	332.131	321.809	3.613	136.924	119.974	−17.905
400	70.409	341.508	323.697	7.124	137.364	117.522	−15.347
450	70.590	349.813	326.147	10.650	137.784	115.017	−13.351
500	70.590	357.252	328.892	14.180	138.180	112.466	−11.749
600	70.206	370.094	334.722	21.223	138.887	107.254	−9.337
700	69.536	380.868	340.566	28.212	139.465	101.935	−7.606
800	68.771	390.104	346.195	35.127	139.906	96.541	−6.304
900	68.020	398.160	351.531	41.966	140.215	91.101	−5.287
1000	67.333	405.291	356.557	48.733	140.395	85.633	−4.473
1100	66.728	411.679	361.283	55.436	140.452	80.153	−3.806
1200	66.204	417.462	365.727	62.082	140.387	74.673	−3.250
1300	65.756	422.743	369.913	68.679	140.203	69.204	−2.781
1400	65.375	427.602	373.862	75.235	139.900	63.753	−2.379
1500	65.053	432.101	377.597	81.756	139.477	58.328	−2.031
1600	64.783	436.290	381.136	88.247	138.932	52.935	−1.728
1700	64.559	440.211	384.497	94.714	138.262	47.580	−1.462
1800	64.377	443.896	387.695	101.161	137.464	42.268	−1.227
1900	64.232	447.372	390.745	107.591	136.530	37.004	−1.017
2000	64.122	450.664	393.660	114.008	135.456	31.793	−0.830
2100	64.043	453.790	396.449	120.416	134.233	26.640	−0.663
2200	63.993	456.769	399.124	126.818	132.855	21.548	−0.512
2300	63.970	459.613	401.693	133.216	131.313	16.522	−0.375
2400	63.972	462.335	404.163	139.613	129.599	11.567	−0.252
2500	63.996	464.947	406.543	146.011	127.704	6.688	−0.140
2600	64.040	467.458	408.837	152.413	125.607	1.888	−0.038
2700	64.103	469.876	411.054	158.820	123.271	−2.827	0.055
2800	64.182	472.208	413.196	165.234	120.637	−7.451	0.139
2900	64.275	474.462	415.270	171.657	81.743	−11.924	0.215
3000	64.380	476.643	417.280	178.089	80.314	−15.129	0.263
3100	64.496	478.756	419.229	184.533	78.881	−18.287	0.308
3200	64.620	480.805	421.121	190.989	77.445	−21.399	0.349
3300	64.750	482.796	422.960	197.457	76.011	−24.465	0.387
3400	64.886	484.731	424.749	203.939	74.581	−27.489	0.422
3500	65.025	486.614	426.490	210.434	73.159	−30.470	0.455
3600	65.167	488.448	428.185	216.944	71.747	−33.411	0.485
3700	65.309	490.235	429.838	223.468	70.349	−36.312	0.513
3800	65.452	491.979	431.451	230.006	68.966	−39.177	0.539
3900	65.593	493.681	433.025	236.558	67.602	−42.005	0.563
4000	65.732	495.343	434.562	243.124	66.258	−44.798	0.585
4100	65.868	496.968	436.064	249.704	64.937	−47.558	0.606
4200	66.000	498.557	437.533	256.298	63.640	−50.286	0.625
4300	66.128	500.111	438.971	262.904	62.368	−52.984	0.644
4400	66.252	501.633	440.377	269.523	61.123	−55.652	0.661
4500	66.370	503.123	441.755	276.154	59.906	−58.292	0.677
4600	66.483	504.583	443.105	282.797	58.717	−60.905	0.692
4700	66.590	506.014	444.429	289.451	57.558	−63.493	0.706
4800	66.691	507.417	445.726	296.115	56.428	−66.057	0.719
4900	66.786	508.793	446.999	302.789	55.327	−68.597	0.731
5000	66.875	510.143	448.249	309.472	−537.129	−65.384	0.683
5100	66.958	511.468	449.475	316.163	−539.850	−55.922	0.573
5200	67.034	512.769	450.680	322.863	−542.688	−46.406	0.466
5300	67.105	514.047	451.864	329.570	−545.640	−36.834	0.363
5400	67.169	515.302	453.027	336.284	−548.707	−27.205	0.263
5500	67.227	516.535	454.170	343.004	−551.885	−17.519	0.166
5600	67.280	517.747	455.295	349.729	−555.175	−7.774	0.073
5700	67.327	518.938	456.401	356.460	−558.571	2.031	−0.019
5800	67.369	520.109	457.489	363.194	−562.074	11.896	−0.107
5900	67.405	521.261	458.561	369.933	−565.679	21.823	−0.193
6000	67.436	522.394	459.615	376.675	−569.388	31.812	−0.277

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = [348.949]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -468.33 \pm 3.77\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -486.35 \pm 3.77\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[182](1)	[134](1)
[120](1)	[188](1)
[207](1)	[228](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: [D_{2h}]
Bond Distance: Na–Br = [2.75] Å
Bond Angles: Na–Br–Na = [71]°; Br–Na–Br = [109]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.94920 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The temperature dependence of the equilibrium constants (1293–1434 K) for the reaction $(NaBr)_2(g) = 2NaBr(g)$ has been studied by Datz *et al.*[1] The dissociation energy ($\Delta_r E°$(1300 K) was evaluated to be 42.9 ± 1.3 kcal·mol^{-1}. The vapor mixture contains 37 to 17% of dimers in the temperature range of 1293 to 1434 K. Hence the vapor pressure data on NaBr(g) reported by the previous investigators were reexamined. In other words, the reported vapor pressures of NaBr(g) is the sum of the partial pressures of both the monomer (NaBr) and the dimer (Na_2Br_2). The partial pressures of Na_2Br_2(g) thus obtained were used to evaluate the enthaply of vaporization by both the 2nd and 3rd law methods. The values of $\Delta_f H°(Na_2Br_2, g, 298.15\ K)$ were then calculated. The results are as follows.

Source	Reaction	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K)* kcal·mol^{-1}
Niwa[2]	$2NaBr(cr) \rightarrow Na_2Br_2(g)$	54.84	56.51	−117.08
Cogin and Kimball[3]	$2NaBr(cr) \rightarrow Na_2Br_2(g)$	56.69	56.80	−116.01
Mayer and Wintner[4]	$2NaBr(cr) \rightarrow Na_2Br_2(g)$	68.78	57.13	−115.63**
Ruff and Mugdan[5]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	46.71	45.70	−116.00
Wartenberg and Albrecht[6]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	46.77	45.64	−116.00
Bloom *et al.*[7]	$2NaBr(l) \rightarrow Na_2Br_2(g)$	51.17	45.49	−116.72**

*Based on the average of the 2nd and 3rd law values.
**Only the third law value being used.

The value of $\Delta_f H°(Na_2Br_2, g, 298.15\ K) = -116.24$ kcal·mol^{-1} (−486.348 kJ·mol^{-1}) adopted is the average of the six $\Delta_f H°$(298.15 K) values listed in the above table.

Heat Capacity and Entropy

Bond distance and angles were calculated based on the related data reported by Berkowitz.[8] The vibrational frequencies were calculated by Berkowitz,[9] from an assumed model. The ground state quantum weight was estimated. The principal moments of inertia are $I_A = 19.4713 \times 10^{-39}$, $I_B = 133.0124 \times 10^{-39}$, and $I_C = 152.4836 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−19.383	−468.328	−468.328	INFINITE
100	63.244	268.362	417.381	−14.902	−469.320	−486.008	253.865
200	76.762	317.552	356.196	−7.729	−471.959	−501.707	131.032
250	78.921	334.937	350.262	−3.831	−473.526	−508.967	106.343
298.15	80.121	348.949	348.949	0.	−486.348	−514.324	90.108
300	80.157	349.445	348.950	0.148	−486.444	−514.498	89.582
350	80.925	361.863	349.929	4.177	−517.971	−517.428	77.222
400	81.432	372.704	352.113	8.236	−524.079	−516.883	67.498
450	81.785	382.317	354.945	12.317	−524.965	−515.930	59.888
500	82.039	390.948	358.121	16.413	−525.797	−514.881	53.789
600	82.373	405.937	364.879	24.635	−527.326	−512.551	44.622
700	82.576	418.652	371.675	32.884	−528.721	−509.977	38.055
800	82.708	429.687	378.252	41.148	−530.027	−507.210	33.117
900	82.799	439.435	384.519	49.424	−531.290	−504.281	29.268
1000	82.865	448.162	390.455	57.707	−532.555	−501.213	26.181
1100	82.913	456.062	396.066	65.996	−533.866	−498.016	23.649
1200	82.950	463.278	401.370	74.289	−728.786	−489.816	21.321
1300	82.978	469.919	406.391	82.586	−728.447	−469.916	18.881
1400	83.001	476.069	411.151	90.885	−728.114	−450.041	16.791
1500	83.020	481.796	415.672	99.186	−727.790	−430.190	14.981
1600	83.035	487.155	419.974	107.489	−727.473	−410.361	13.397
1700	83.047	492.189	424.076	115.793	−727.168	−390.550	12.000
1800	83.058	496.936	427.993	124.098	−726.875	−370.758	10.759
1900	83.066	501.427	431.741	132.404	−726.596	−350.981	9.649
2000	83.074	505.688	435.332	140.711	−726.335	−331.219	8.651
2100	83.081	509.741	438.780	149.019	−726.093	−311.469	7.747
2200	83.086	513.607	442.094	157.327	−725.873	−291.730	6.927
2300	83.091	517.300	445.284	165.636	−725.679	−272.001	6.177
2400	83.095	520.836	448.359	173.946	−725.511	−252.280	5.491
2500	83.099	524.229	451.326	182.255	−725.372	−232.565	4.859
2600	83.103	527.488	454.193	190.565	−725.265	−212.855	4.276
2700	83.106	530.624	456.967	198.876	−725.190	−193.148	3.737
2800	83.108	533.647	459.651	207.187	−725.150	−173.444	3.236
2900	83.111	536.563	462.254	215.498	−725.145	−153.740	2.769
3000	83.113	539.381	464.778	223.809	−725.176	−134.036	2.334
3100	83.115	542.106	467.229	232.120	−725.246	−114.330	1.926
3200	83.117	544.745	469.610	240.432	−725.353	−94.622	1.545
3300	83.118	547.302	471.926	248.743	−725.499	−74.909	1.186
3400	83.120	549.784	474.179	257.055	−725.685	−55.192	0.848
3500	83.121	552.193	476.374	265.367	−725.912	−35.468	0.529
3600	83.122	554.535	478.513	273.680	−726.182	−15.737	0.228
3700	83.124	556.812	480.598	281.992	−726.495	4.001	−0.056
3800	83.125	559.029	482.633	290.304	−726.855	23.749	−0.326
3900	83.126	561.188	484.620	298.617	−727.262	43.507	−0.583
4000	83.127	563.293	486.561	306.929	−727.719	63.276	−0.826
4100	83.127	565.346	488.457	315.242	−728.229	83.057	−1.058
4200	83.128	567.349	490.312	323.555	−728.791	102.851	−1.279
4300	83.129	569.305	492.126	331.868	−729.417	122.659	−1.490
4400	83.130	571.216	493.902	340.181	−730.022	142.476	−1.691
4500	83.130	573.084	495.641	348.494	−730.734	162.312	−1.884
4600	83.131	574.911	497.344	356.807	−731.527	182.166	−2.069
4700	83.131	576.699	499.014	365.120	−732.391	202.038	−2.245
4800	83.132	578.449	500.651	373.433	−733.329	221.929	−2.415
4900	83.132	580.163	502.256	381.746	−734.347	241.841	−2.578
5000	83.133	581.843	503.831	390.059	−735.434	261.773	−2.735
5100	83.133	583.489	505.377	398.373	−736.621	281.729	−2.885
5200	83.134	585.103	506.895	406.686	−737.902	301.708	−3.031
5300	83.134	586.687	508.385	415.000	−739.282	321.714	−3.171
5400	83.134	588.241	509.850	423.313	−740.764	341.747	−3.306
5500	83.135	589.766	511.289	431.626	−742.356	361.808	−3.436
5600	83.135	591.264	512.704	439.940	−744.060	381.899	−3.562
5700	83.135	592.736	514.095	448.253	−745.882	402.021	−3.684
5800	83.136	594.182	515.463	456.567	−747.827	422.176	−3.802
5900	83.136	595.603	516.809	464.881	−749.899	442.366	−3.916
6000	83.136	597.000	518.134	473.194	−751.786	462.556	−4.027

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

$\Delta_{at}H°(0\ K) = 358 \pm 5\ kJ·mol^{-1}$
$S°(298.15\ K) = 290.8 \pm 2\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = 124.1 \pm 3.5\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = 107.6 \pm 3.5\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
X^1A	0.0	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
526.1 (1)
180 (1)
623.4 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Br–O = 1.8429 Å
Bond Angle: Br–O–Br = 112.24°
Product of the Moments of Inertia: $I_AI_BI_C = 10238.8084 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

Thorn *et al.*[3] using experimental results from photoionization efficiency spectrum of Br_2O, along with the ionization and appearance energy, have derived a value of the enthalpy of formation $\Delta_fH(Br_2O, 0\ K) = 124.1 \pm 3.5\ kJ·mol^{-1}$, which we adopt.

There are three other related studies leading to an enthalpy of formation. Orlando and Burkholder[1] measured the equilibrium constant for the reaction: $Br_2O + H_2O = 2HOBr$. They determined $\Delta_rG°(298\ K) = 9.70\ kJ·mol^{-1}$. Using the thermal functions presented in this table and thermal functions for HOBr(g) given by JANAF,[2] we calculate $\Delta_fH°(Br_2O,g, 298.15) = 107.6 \pm 3.5\ kJ·mol^{-1}$. This value supports our adopted value. Assuming that the values D_0^0(ClO) and $\Delta_{at}H°$(OClO,g) are reasonable, we would anticipate the ratio of the numbers (1.52) to apply for a similar relationship between BrO(g) and BrOBr(g). This would yield a value of 114 $kJ·mol^{-1}$ which is in good agreement with our adopted value. Using the estimation scheme of Novak[4] (in part based on ab initio calculations and an extended basis set), the enthalpy of formation was calculated to be $83 \pm 8\ kJ·mol^{-1}$ at 0 K.

Heat Capacity and Entropy

Mueller and Cohen,[5] from the microwave spectra of three isotopomers of BrOBr(g), have determined $r_o = 1.8429$ Å and <(BrOBr) = 112.24°, which we adopt. Supporting evidence was derived from bromine K-edge EXAFS study of Levason *et al.*[6] The structure of this molecule was bent with a Br–O–Br angle of 112 ± 2° and the Br–O bond length was 1.85 ± 0.01 Å. The bond angle is in good agreement with the value derived from matrix IR studies[7] where a value of 113° was estimated from isotope shifts. In comparison, Novak,[4] with the aid of ab initio calculations, determined a bond length of 1.809 Å and a bond angle of 115.7°. The principal moments of inertia (in $g·cm^2$) are: $I_A = 2.5488 \times 10^{-39}$, $I_B = 62.1189 \times 10^{-39}$, and $I_C = 64.6677 \times 10^{-39}$.

The recommended vibrational frequencies (ν_1, ν_3) are those suggested by Jacox.[8] These results are based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*,[9] Allen *et al.*,[7] and Levason *et al.*[6] A value of $\nu_2 = 197\ cm^{-1}$ reported in the solid IR spectra study of Campbell *et al.*[10] However, the Mueller and Cohen[5] study implied $\nu_2 = 180\ cm^{-1}$ (± 5). Lee,[11] using ab initio calculations – CCSD(T)-derived vibrational frequencies (513, 180 and 613 cm^{-1}) which are in reasonable agreement with our adopted values. Similar calculations by Lee yielded a structure in agreement with our recommendations (112.9° and 1.865 Å).

All specific studies (condensed or matrix)[5–12] yielded values for ν_1 and ν_3 which are in reasonable agreement. Although Tevault *et al.*[9] stated that the values for ν_1 and ν_3 reported by Campbell *et al.*[10] are reversed, this does not affect the thermal functions.

Anthar and Dostrovsky[13] measured the ultraviolet absorption spectra of Br_2O in CCl_4. A strong absorption band was observed at 2800 Å (35714 cm^{-1}). We assume this refers to the position of the first excited electronic state. This state is not included in the calculations.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−12.399	124.100	124.100	INFINITE
50	34.529	217.773	432.252	−10.724	124.219	118.511	−123.808
100	38.480	242.978	331.921	−8.894	123.359	113.112	−59.083
150	41.918	259.228	305.126	−6.885	122.314	108.209	−37.682
200	45.264	271.753	295.272	−4.704	121.193	103.675	−27.077
250	48.075	282.168	291.638	−2.367	119.985	99.433	−20.775
298.15	50.168	290.823	290.823	.000	107.648	96.902	−16.977
300	50.238	291.133	290.824	.093	107.574	96.835	−16.861
400	53.068	306.013	292.833	5.272	76.787	99.594	−13.006
500	54.685	318.044	296.711	10.667	76.961	105.277	−10.998
600	55.664	328.108	301.128	16.188	77.183	110.920	−9.656
700	56.293	336.739	305.614	21.788	77.417	116.524	−8.695
800	56.717	344.285	309.986	27.440	77.648	122.095	−7.972
900	57.016	350.984	314.176	33.127	77.869	127.637	−7.408
1000	57.234	357.003	318.163	38.840	78.077	133.156	−6.955
1100	57.397	362.466	321.946	44.572	78.271	138.654	−6.584
1200	57.523	367.466	325.534	50.318	78.451	144.135	−6.274
1300	57.621	372.074	328.939	56.076	78.616	149.602	−6.011
1400	57.700	376.347	332.174	61.842	78.766	155.057	−5.785
1500	57.763	380.330	335.254	67.615	78.900	160.501	−5.589
1600	57.816	384.060	338.189	73.394	79.016	165.938	−5.417
1700	57.859	387.566	340.991	79.178	79.113	171.367	−5.265
1800	57.896	390.875	343.671	84.966	79.189	176.791	−5.130
1900	57.927	394.006	346.239	90.757	79.242	182.212	−5.009
2000	57.953	396.978	348.702	96.551	79.269	187.631	−4.900
2100	57.976	399.806	351.069	102.347	79.269	193.049	−4.802
2200	57.996	402.503	353.346	108.146	79.239	198.468	−4.712
2300	58.014	405.082	355.540	113.947	79.179	203.889	−4.630
2400	58.029	407.551	357.656	119.749	79.087	209.313	−4.556
2500	58.042	409.920	359.699	125.552	78.963	214.741	−4.487
2600	58.054	412.197	361.675	131.357	78.807	220.175	−4.423
2700	58.065	414.388	363.587	137.163	78.618	225.616	−4.365
2800	58.074	416.500	365.439	142.970	78.400	231.064	−4.311
2900	58.083	418.538	367.235	148.778	78.152	236.521	−4.260
3000	58.091	420.507	368.978	154.587	77.877	241.986	−4.213
3100	58.098	422.412	370.671	160.396	77.577	247.462	−4.170
3200	58.104	424.257	372.317	166.206	77.254	252.947	−4.129
3300	58.110	426.045	373.918	172.017	76.912	258.442	−4.091
3400	58.115	427.780	375.477	177.828	76.554	263.949	−4.055
3500	58.120	429.464	376.996	183.640	76.181	269.465	−4.022
3600	58.125	431.102	378.476	189.452	75.798	274.994	−3.990
3700	58.129	432.694	379.920	195.265	75.407	280.532	−3.960
3800	58.132	434.245	381.329	201.078	75.011	286.081	−3.932
3900	58.136	435.755	382.706	206.891	74.612	291.641	−3.906
4000	58.139	437.227	384.050	212.705	74.214	297.211	−3.881
4100	58.142	438.662	385.365	218.519	73.818	302.791	−3.858
4200	58.145	440.063	386.651	224.334	73.427	308.380	−3.835
4300	58.148	441.432	387.909	230.148	73.042	313.979	−3.814
4400	58.150	442.768	389.140	235.963	72.666	319.586	−3.794
4500	58.152	444.075	390.347	241.778	72.299	325.202	−3.775
4600	58.154	445.353	391.529	247.593	71.944	330.826	−3.757
4700	58.156	446.604	392.687	253.409	71.600	336.458	−3.739
4800	58.158	447.828	393.823	259.225	71.270	342.097	−3.723
4900	58.160	449.028	394.938	265.041	70.953	347.743	−3.707
5000	58.162	450.203	396.031	270.857	70.650	353.395	−3.692
5100	58.163	451.354	397.105	276.673	70.362	359.053	−3.677
5200	58.165	452.484	398.159	282.489	70.088	364.715	−3.664
5300	58.166	453.592	399.194	288.306	69.829	370.384	−3.650
5400	58.167	454.679	400.212	294.123	69.583	376.057	−3.638
5500	58.169	455.746	401.212	299.939	69.352	381.734	−3.625
5600	58.170	456.794	402.195	305.756	69.134	387.416	−3.614
5700	58.171	457.824	403.162	311.573	68.930	393.102	−3.602
5800	58.172	458.836	404.113	317.390	68.738	398.791	−3.591
5900	58.173	459.830	405.049	323.208	68.557	404.482	−3.581
6000	58.174	460.808	405.970	329.025	68.388	410.178	−3.571

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [312.7 \pm 2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [183.7 \pm 20]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [168 \pm 20]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
[^{3}A"]	0.0	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
804 (1)
[150] (1)
236 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Br–O = [1.69] Å; Br–Br = [2.51] Å
Bond Angle: Br–Br–O = [113.1]°
Product of the Moments of Inertia: $I_A I_B I_C = [13784.9110 \times 10^{-117}]\ g^3 \cdot cm^6$

Enthalpy of Formation

For the four halogen oxide species, XXO(g) where X = F, Cl, Br, I, there is no experimental data related to the enthalpy of formation. Lee[1] determined the enthalpies of formation of many triatomic bromine compounds using a combination of theoretical isomeric, homodesmic and isodesmic reaction energies. The calculated results suggested that BrBrO is less stable than BrOBr by 14.6 kcal·mol^{-1} (61.1 kJ·mol) at 298.15 K.

Heat Capacity and Entropy

Lee,[1] using ab initio calculations–CCSD(T)–derived a bond angle of 113.1° and bond distances r(Br–Br) = 2.510 Å and r(Br–O) = 1.690 Å, which we adopt. The principal moments of inertia (in g·cm^2) are: $I_A = 4.7079 \times 10^{-39}$, $I_B = 51.8084 \times 10^{-39}$, and $I_C = 56.5163 \times 10^{-39}$.

The recommended vibrational frequencies are those suggested by Jacox.[2] These results are based on the infrared spectra of the argon matrix isolated radical as studied by Tevault *et al.*[3] ν_2 is estimated based on comparisons of the vibrational frequencies with ClOO. Lee,[1] using ab initio calculations, derived the vibrational frequencies to be 793, 153 and 215 cm^{-1}. These are in excellent agreement with our recommendations.

Tevault *et al.*[3] observed very intense bands at 804 and 236 cm^{-1} which appeared when Ar–Br_2–O_3 matrices were photolyzed with 632.8 nm light. The assignments for BrBrO were assumed to be $\nu_1 = 804\ cm^{-1}$ (Br–O stretch), $\nu_3 = 236\ cm^{-1}$ (Br–Br stretch) and the ν_2 value (the bending mode) was expected to be below 200 cm^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.138	183.713	183.713	INFINITE
50	35.814	234.286	463.229	−11.447	183.848	177.315	−185.239
100	42.429	261.298	356.090	−9.479	183.126	171.047	−89.346
150	46.014	279.255	327.647	−7.259	182.292	165.183	−57.522
200	48.247	292.815	317.312	−4.899	181.349	159.619	−41.688
250	49.997	303.775	313.543	−2.442	180.262	154.309	−32.241
298.15	51.385	312.704	312.704	.000	168.000	150.730	−26.407
300	51.433	313.022	312.705	.095	167.928	150.623	−26.226
400	53.530	328.128	314.750	5.351	137.218	151.179	−19.742
500	54.868	340.228	318.676	10.776	137.422	154.646	−16.156
600	55.735	350.313	323.132	16.309	137.656	158.069	−13.761
700	56.316	358.951	327.647	21.913	137.895	161.453	−12.048
800	56.719	366.499	332.041	27.566	138.127	164.802	−10.760
900	57.008	373.197	336.249	33.253	138.347	168.123	−9.758
1000	57.222	379.215	340.250	38.965	138.554	171.420	−8.954
1100	57.384	384.677	344.044	44.696	138.747	174.698	−8.296
1200	57.509	389.676	347.642	50.441	138.925	177.958	−7.746
1300	57.608	394.283	351.054	56.197	139.089	181.204	−7.281
1400	57.687	398.555	354.297	61.962	139.238	184.438	−6.881
1500	57.752	402.537	357.381	67.734	139.371	187.662	−6.535
1600	57.805	406.266	360.321	73.512	139.486	190.877	−6.231
1700	57.849	409.772	363.128	79.295	139.582	194.086	−5.964
1800	57.887	413.080	365.812	85.081	139.657	197.290	−5.725
1900	57.918	416.210	368.383	90.872	139.708	200.490	−5.512
2000	57.946	419.182	370.849	96.665	139.735	203.689	−5.320
2100	57.969	422.010	373.219	102.461	139.734	206.886	−5.146
2200	57.989	424.707	375.498	108.259	139.704	210.085	−4.988
2300	58.007	427.285	377.694	114.059	139.643	213.285	−4.844
2400	58.023	429.754	379.812	119.860	139.550	216.488	−4.712
2500	58.037	432.123	381.858	125.663	139.426	219.697	−4.590
2600	58.049	434.400	383.835	131.467	139.269	222.910	−4.478
2700	58.060	436.591	385.749	137.273	139.080	226.131	−4.375
2800	58.070	438.702	387.602	143.079	138.861	229.359	−4.279
2900	58.079	440.740	389.400	148.887	138.613	232.595	−4.189
3000	58.087	442.709	391.144	154.695	138.337	235.841	−4.106
3100	58.094	444.614	392.838	160.504	138.037	239.096	−4.029
3200	58.101	446.459	394.485	166.314	137.714	242.361	−3.956
3300	58.107	448.246	396.088	172.124	137.372	245.636	−3.888
3400	58.112	449.981	397.647	177.935	137.013	248.922	−3.824
3500	58.117	451.666	399.167	183.747	136.640	252.219	−3.764
3600	58.122	453.303	400.648	189.559	136.256	255.527	−3.708
3700	58.126	454.896	402.093	195.371	135.865	258.845	−3.654
3800	58.130	456.446	403.503	201.184	135.469	262.175	−3.604
3900	58.134	457.956	404.880	206.997	135.070	265.514	−3.556
4000	58.137	459.428	406.225	212.811	134.671	268.864	−3.511
4100	58.140	460.863	407.540	218.624	134.275	272.224	−3.468
4200	58.143	462.264	408.827	224.438	133.884	275.593	−3.427
4300	58.146	463.632	410.085	230.253	133.499	278.972	−3.389
4400	58.148	464.969	411.318	236.068	133.122	282.359	−3.352
4500	58.150	466.276	412.524	241.883	132.756	285.755	−3.317
4600	58.153	467.554	413.707	247.698	132.400	289.158	−3.283
4700	58.155	468.805	414.866	253.513	132.056	292.570	−3.252
4800	58.157	470.029	416.002	259.329	131.726	295.989	−3.221
4900	58.158	471.228	417.117	265.144	131.409	299.415	−3.192
5000	58.160	472.403	418.211	270.960	131.106	302.846	−3.164
5100	58.162	473.555	419.285	276.776	130.817	306.284	−3.137
5200	58.163	474.684	420.340	282.593	130.543	309.727	−3.111
5300	58.165	475.792	421.376	288.409	130.284	313.176	−3.087
5400	58.166	476.880	422.393	294.226	130.038	316.629	−3.063
5500	58.167	477.947	423.394	300.042	129.807	320.086	−3.040
5600	58.168	478.995	424.377	305.859	129.589	323.548	−3.018
5700	58.170	480.025	425.345	311.676	129.384	327.013	−2.997
5800	58.171	481.036	426.296	317.493	129.192	330.482	−2.976
5900	58.172	482.031	427.232	323.310	129.012	333.954	−2.957
6000	58.173	483.008	428.154	329.127	128.842	337.429	−2.938

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = 161.13 \pm 2.1\ J·K^{-1}·mol^{-1}$
$T_{fus} = 644 \pm 5\ K$

$\Delta_f H°(0\ K) = -265.2 \pm 2.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -277.4 \pm 2.5\ kJ·mol^{-1}$
$\Delta_{fus} H° = 16.443 \pm 0.8\ kJ·mol^{-1}$

Enthaply of Formation

$\Delta_f H°(PbBr_2, cr, 298.15\ K) = -66.3 \pm 0.6\ kcal·mol^{-1}$ ($-277.399\ kJ·mol^{-1}$) is the rounded average of $-66.350\ kcal·mol^{-1}$ calorimetrically determined by Braune and Koref[1] at about 293.15 K and five other values obtained from a 2nd and 3rd law analysis of electromotive force data.[2,3,4] The auxiliary value $\Delta_f H°(AgBr, cr, 298.15\ K) = -23.99\ kcal·mol^{-1}$ [5] is used in the analysis.

Source	Reaction*	Data Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
Krahmer[2]	A	5	273–292	17.88 ± 0.06	18.52 ± 0.04	−2.2 ± 0.2	−65.86	−66.50
Cann and Sumner[3]	A	1	298		18.57			−66.57
Jahn–Held and Jellinek[4]	B	3	288–308	66.68 ± 0.06	66.09 ± 0.04	2.0 ± 0.2	−66.68	−66.09

*Reactions: (A) $Pb(cr) + 2\ AgBr(cr) = PbBr_2(cr) + 2\ Ag(cr)$ (B) $Pb(cr) + Br_2(l) = PbBr_2(cr)$

Heat Capacity and Entropy

$C_p°$ (18.4–297.0 K) has been measured by Latimer and Hoenshel.[6] The enthalpy data of Ehrhardt (273–786 K)[7] and of Goodwin and Kalmus (298–860 K)[8] are discarded because the observed high T_{fus} shows their samples were not pure. (See melting data discussion.) Linsey[16] measured the enthalpy (39 points) of $PbBr_2$ in the range 319–424 K using an ice calorimeter. The heat capacity data of Latimer and Hoenshel[6] is smoothed graphically. The enthalpy data was analyzed by Linsey[16] to yield heat capacity values from 273–644 K. Both sets of heat capacity values are adjusted graphically in the region 200–400 K so as to yield a smooth curve in the vicinity of 298 K. The adjustments are quite small such that the resulting enthalpy at 600 K differs by about 7 cal·mol^{-1} from the smooth enthalpies reported by Linsey.[16] The data of Linsey[16] did not indicate any transitions other than the solid–liquid transition at 644 K.

Latimer and Hoenshel[6] obtained $S°(15.85\ K) = 2.4\ cal·K^{-1}·mol^{-1}$ after allowing for an approach to the T^3 rule. Kelley and King[10] later derived $S°(17.80\ K) = 1.64\ cal·K^{-1}·mol^{-1}$ from the same data; this value is adopted. Combining this with $S°(298.15;17.80) = 36.871\ cal·K^{-1}·mol^{-1}$ derived from the adopted $C_p°$ value gives $S°(298.15\ K) = 38.511 \pm 0.5\ cal·K^{-1}·mol^{-1}$ ($161.128\ J·K^{-1}·mol^{-1}$). A graphical extrapolation and integration of $C_p°$ gives $H°(17.80;0) = 0.0252\ kcal·mol^{-1}$. This value may not be entirely consistent with the adopted $S°(17.80\ K)$ value, but the error involved is undoubtedly small.

Fusion Data

The older reported values of T_{fus} have been summarized by Mellor.[11] Seven determinations fall in the 636–653 K range and four more range from 753 to 772 K. Included in the high melting range are $T_{fus} = 763$ K by Ehrhardt[7] and $T_{fus} = 761$ K by Goodwin and Kalmus.[8] Knowles,[12] suggested that contamination of the $PbBr_2$ by PbO probably caused the high melting temperatures. The enthalpy measurements of Ehrhardt[7] and of Goodwin and Kalmus[8] are therefore judged not to represent $PbBr_2$. More recently, Blanc and Petit[13] have reported $T_{fus} = 640$ K and $\Delta_{fus} H = 4.96\ kcal·mol^{-1}$ from a cryoscopic investigation. A visual polytherm technique was employed by Il'yasov[14] who found $T_{fus} = 649$ K. Cola *et al.*[15] determined $T_{fus} = 644$ K by differential thermal analysis and $\Delta_{fus} H° = 4.41 \pm 0.07\ kcal·mol^{-1}$ by differential scanning calorimetry. The enthalpy study by Linsey[16] gave $T_{fus} = 644$ K and $\Delta_{fus} H° = 3.93\ kcal·mol^{-1}$ ($16.443\ kJ·mol^{-1}$). We adopt these latter two values.

Sublimation Data

$\Delta_{sub} H°(298.15\ K) = 41.35\ kcal·mol^{-1}$ ($173.008\ kJ·mol^{-1}$) is the sum of the heat of fusion, the enthalpy difference of crystal and liquid between the melting point and 298.15 K, and $\Delta_{vap} H°(298.15\ K)$. See the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−19.235	−265.247	−265.247	INFINITE
100	68.199	79.592	229.504	−14.991	−265.562	−264.454	138.136
200	76.567	129.902	168.330	−7.686	−265.682	−263.324	68.773
298.15	79.578	161.128	161.128	0.	−277.399	−260.743	45.681
300	79.613	161.620	161.129	0.147	−277.442	−260.640	45.381
400	81.253	184.747	164.272	8.190	−306.608	−248.951	32.510
500	84.684	203.229	170.271	16.479	−304.824	−234.739	24.523
600	88.784	219.026	177.110	25.149	−302.762	−220.910	19.232
700	93.061	233.033	184.116	34.242	−305.230	−206.654	15.421
800	97.341	245.739	191.037	43.762	−302.480	−192.754	12.586
900	101.621	257.451	197.774	53.710	−299.281	−179.226	10.402
1000	105.901	268.380	204.294	64.086	−295.634	−166.078	8.675

PREVIOUS: March 1962 CURRENT: December 1973

$S°(298.15\ K) = [173.878]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-267.412]\ kJ·mol^{-1}$

$T_{fus} = 644 \pm 5\ K$ $\Delta_{fus}H° = 16.443 \pm 0.8\ kJ·mol^{-1}$

Enthaply of Formationo

$\Delta_f H°(PbBr_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(644\ K)–H°(298.15\ K)$, between the crystal and liquid. $\Delta_f H°(l)$ can also be obtained from a 2nd and 3rd law analysis of emf measurements for the cell reaction $Pb(l) + Br_2(g) = PbBr_2(l)$. Results from three investigations are tabulated below. The auxiliary values, $\Delta_f H°(Pb, l, 298.15\ K) = 1.025\ kcal·mol^{-1}$ and $\Delta_f H°(Br_2, g, 298.15\ K) = 7.387\ kcal·mol^{-1}$, are used. The average result or $\Delta_f H°(l, 298.15\ K)$ is $-63.80\ kcal·mol^{-1}$, in good agreement with the adopted value.

Source	Data Points	T/K	$-\Delta_r H°(298.15\ K)$, kcal·mol 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
Salstrom and Hildebrand[2]	16	711–849	73.60 ± 0.10	72.10 ± 0.13	1.9 ± 0.1	−65.19	−63.69
Lantratov and Shevlyakova[3]	1	862		72.36			−63.95
Bloom and Welch[4]	4	723–1000	74.22 ± 0.33	68.79 ± 1.63	6.3 ± 0.4	−65.80	−60.38

Heat Capacity and Entropy

Ehrhardt[5] and Goodwin and Kalmus[6] have reported enthalpy measurements in the liquid temperature range. Their data are rejected because the high melting points observed indicated the samples were not entirely $PbBr_2$. See the $PbBr_2$(cr) table discussion. Bizouard and Paulty[7] have measured 26.3 ± 0.6 cal·K^{-1}·mol^{-1} for the heat capacity of the molten salt. Linsey[9] reported a heat capacity value of 26.8 cal·K^{-1}·mol^{-1} based on enthalpy measurements from T_{fus} to 924 K. This value is adopted and is assumed to represent the heat capacity up to 2000 K. A glass transition is assumed at 400 K below which the heat capacity is that of the crystal.

$S°(PbBr_2, l, 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Vaporization Data

$T_{vap} = 1185$ K is calculated as the temperature at which $\Delta_r G° = 0$ for the reaction $PbBr_2(l) = PbBr_2(g)$ at one atm. $\Delta_{vap}H° = 28.23\ kcal·mol^{-1}$ (118.114 kJ·mol^{-1}) is calculated as the difference between $\Delta_f H°$ at T_{vap} for the gas and the liquid. Bloom and Anthony[8] found an average value of $\Delta_{vap}H° = 29.8 \pm 2.0\ kcal·mol^{-1}$ from mass spectrometric studies in the 660–735 K range. The present table gives $\Delta_{vap}H°(700) = 34.50\ kcal·mol^{-1}$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	79.580	173.878	173.878	0.	−267.412	−254.558	44.598
300	79.613	174.370	173.879	0.147	−267.455	−254.478	44.309
400	81.254	197.507	177.023	8.194	−296.617	−244.065	31.872
400.000	81.254	197.507	177.023	8.194	GLASS <--> LIQUID		
400.000	112 .131	197.507	177.023	8.194	TRANSITION		
500	112.131	222.528	183.715	19.407	−291.910	−231.474	24.182
600	112.131	242.972	191.939	30.620	−287.305	−219.820	19.137
700	112.131	260.257	200.496	41.833	−287.652	−208.133	15.531
800	112.131	275.230	208.923	53.046	−283.209	−197.076	12.868
900	112.131	288.437	217.038	64.259	−278.745	−186.577	10.829
1000	112.131	300.252	224.779	75.472	−274.261	−176.576	9.223
1100	112.131	310.939	232.134	86.685	−269.755	−167.026	7.931
1200	112.131	320.696	239.113	97.899	−265.228	−157.886	6.873
1300	112.131	329.671	245.739	109.112	−260.686	−149.125	5.992
1400	112.131	337.981	252.034	120.325	−256.145	−140.714	5.250
1500	112.131	345.717	258.025	131.538	−251.615	−132.627	4.618
1600	112.131	352.954	263.734	142.751	−247.104	−124.842	4.076
1700	112.131	359.752	269.184	153.964	−242.617	−117.338	3.605
1800	112.131	366.161	274.396	165.177	−238.159	−110.098	3.195
1900	112.131	372.223	279.386	176.390	−233.735	−103.104	2.835
2000	112.131	377.975	284.173	187.604	−229.347	−96.342	2.516

PREVIOUS: March 1962 CURRENT: December 1973

0	to	644 K	crystal
above		644 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.235	−265.247	−265.247	INFINITE
100	68.199	79.592	229.504	−14.991	−265.562	−264.454	138.136
200	76.567	129.902	168.330	−7.686	−265.682	−263.324	68.773
298.15	79.578	161.128	161.128	0.	−277.399	−260.743	45.681
300	79.613	161.620	161.129	0.147	−277.442	−260.640	45.381
400	81.253	184.747	164.272	8.190	−306.608	−248.951	32.510
500	84.684	203.229	170.271	16.479	−304.824	−234.739	24.523
600	88.784	219.026	177.110	25.149	−302.762	−220.910	19.232
644.000	90.667	225.375	180.193	29.097	CRYSTAL <- -> LIQUID TRANSITION		
644.000	112.131	250.908	180.193	45.540			
700	112.131	260.257	186.229	51.820	−287.652	−208.133	15.531
800	112.131	275.230	196.439	63.033	−283.209	−197.076	12.868
900	112.131	288.437	205.942	74.246	−278.745	−186.577	10.829
1000	112.131	300.252	214.792	85.459	−274.261	−176.576	9.223
1100	112.131	310.939	223.055	96.672	−269.755	−167.026	7.931
1200	112.131	320.696	230.791	107.885	−265.228	−157.886	6.873
1300	112.131	329.671	238.057	119.098	−260.686	−149.125	5.992
1400	112.131	337.981	244.901	130.312	−256.145	−140.714	5.250
1500	112.131	345.717	251.367	141.525	−251.615	−132.627	4.618
1600	112.131	352.954	257.493	152.738	−247.104	−124.842	4.076
1700	112.131	359.752	263.310	163.951	−242.617	−117.338	3.605
1800	112.131	366.161	268.847	175.164	−238.159	−110.098	3.195
1900	112.131	372.223	274.130	186.377	−233.735	−103.104	2.835
2000	112.131	377.975	279.180	197.590	−229.347	−96.342	2.516

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 339.39 \pm 2.9\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -87.99 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -104.39 \pm 6.3\ kJ·mol^{-1}$

Vibrational Freqencies and Degeneracies ν, cm^{-1}
208 (1)
64 (1)
189 (1)

Ground State Quantum Weight : [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Pb–Br = 2.6 ± 0.3 Å
Bond Angle: Br–Pb–Br = [95]°
Product of Moments of Inertia: $I_A I_B I_C = [6.47916 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = -24.95 \pm 1.5\ kcal·mol^{-1}$ ($-104.391\ kJ·mol^{-1}$) is the sum of $\Delta_f H°$(l, 298.15 K) = $-63.913 \pm 0.8\ kcal·mol^{-1}$ and $\Delta_{vap}H°$(l, 298.15 K) = $39.96\ kcal·mol^{-1}$. The adopted enthaply of vaporization is from the 2nd and 3rd law analyses, tabulated below, of seven sets of liquid vapor pressure measurements, $PbBr_2(l) = PbBr_2(g)$. The overall average for $\Delta_{vap}H°(298.15\ K)$ is $39.23\ kcal·mol^{-1}$. The average value of the 3rd law $\Delta_{vap}H°(298.15\ K)$ is $38.96\ kcal·mol^{-1}$. This is in good agreement with both the 2nd and 3rd law values from the data of Wartenberg and Bosse.[1] The adopted enthalpy of formation for $PbBr_2(g)$ yields an atomization energy of $\Delta_{at}H° = 5.42$ eV for the process $PbBr_2(g) = Pb(g) + 2\ Br(g)$.

Source	Data Points	T/K	$\Delta_{vap}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
Wartenberg and Bosse[1]	7[a]	1008–1191	38.05 ± 0.19	39.02 ± 0.12	0.9 ± 0.2
Volmer[2]	11	684–841	39.36 ± 0.11	38.93 ± 0.08	−0.6 ± 0.1
Greiner and Jellinek[3]	1	1043		38.90	
Jahn–Held and Jellinek[4]	3	1045–1153	41.85 ± 6.54	38.68 ± 0.73	−2.9 ± 5.9
Bloom, *et al.*[5]	Equation	796–1133	39.56 ± 0.48	38.81 ± 0.30	−0.8 ± 0.5
Murgulescu and Marta[6]	1	973		39.13	
Bloom and Hastie[7]	1	973		39.27	

[a]One point rejected by statistical test.

Heat Capacity and Entropy

Molecular dimensions are those given by Sutton.[8] Beattie and Perry[9] observed the frequencies $\nu_1 = 200\ cm^{-1}$ and $\nu_2 = 64\ cm^{-1}$ in a gas phase Raman study of $PbBr_2$ in the presence of excess bromine; the $PbBr_2$ spectrum was superimposed on the resonance fluorescence spectrum of Br_2. The matrix isolation laser Raman spectroscopic study by Ozin and Vander Voet[10] gave $\nu_1 = 208\ cm^{-1}$ and $\nu_3 = 189\ cm^{-1}$. Experimental conditions prevented observations below 90 cm^{-1} so ν_2 expected about 65 cm^{-1} was not confirmed. The principal moments of inertia are: $I_A = 46.2255 \times 10^{-39}$, $I_B = 97.5131 \times 10^{-39}$, and $I_C = 143.7386 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−14.989	−87.992	−87.992	INFINITE
100	49.793	280.145	388.803	−10.866	−88.428	−107.375	56.087
200	55.493	316.912	344.558	−5.529	−90.518	−125.561	32.793
250	56.408	329.404	340.321	−2.729	−91.839	−134.174	28.034
298.15	56.918	339.386	339.386	0.	−104.391	−140.883	24.682
300	56.933	339.739	339.388	0.105	−104.475	−141.109	24.569
350	57.259	348.541	340.082	2.961	−135.624	−145.497	21.714
400	57.474	356.202	341.629	5.829	−135.960	−146.885	19.181
450	57.624	362.981	343.632	8.707	−136.320	−148.229	17.206
500	57.732	369.058	345.876	11.591	−136.704	−149.532	15.622
600	57.873	379.597	350.644	17.372	−137.531	−152.022	13.235
700	57.960	388.525	355.434	23.164	−143.300	−153.568	11.459
800	58.016	396.269	360.065	28.963	−144.271	−154.968	10.118
900	58.054	403.104	364.475	34.766	−145.216	−156.248	9.068
1000	58.082	409.222	368.649	40.573	−146.138	−157.425	8.223
1100	58.103	414.759	372.593	46.383	−147.036	−158.509	7.527
1200	58.118	419.816	376.321	52.194	−147.911	−159.514	6.943
1300	58.131	424.468	379.848	58.006	−148.770	−160.446	6.447
1400	58.140	428.776	383.191	63.820	−149.628	−161.312	6.019
1500	58.148	432.788	386.365	69.634	−150.497	−162.116	5.645
1600	58.154	436.541	389.385	75.449	−151.384	−162.862	5.317
1700	58.160	440.067	392.264	81.265	−152.294	−163.551	5.025
1800	58.164	443.391	395.013	87.081	−153.234	−164.187	4.765
1900	58.168	446.536	397.642	92.898	−154.206	−164.769	4.530
2000	58.171	449.520	400.162	98.715	−155.215	−165.299	4.317
2100	58.174	452.358	402.581	104.532	−333.483	−158.662	3.947
2200	58.176	455.064	404.905	110.350	−334.182	−150.321	3.569
2300	58.178	457.650	407.143	116.167	−334.991	−141.946	3.224
2400	58.180	460.126	409.299	121.985	−335.912	−133.534	2.906
2500	58.182	462.501	411.380	127.803	−336.947	−125.080	2.613
2600	58.183	464.783	413.390	133.622	−338.096	−116.584	2.342
2700	58.185	466.979	415.335	139.440	−339.354	−108.040	2.090
2800	58.186	469.095	417.217	145.258	−340.719	−99.449	1.855
2900	58.187	471.137	419.042	151.077	−342.183	−90.806	1.636
3000	58.188	473.110	420.811	156.896	−343.740	−82.112	1.430
3100	58.188	475.018	422.529	162.715	−345.382	−73.364	1.236
3200	58.189	476.865	424.198	168.534	−347.100	−64.562	1.054
3300	58.190	478.656	425.822	174.352	−348.884	−55.705	0.882
3400	58.191	480.393	427.401	180.172	−350.726	−46.793	0.719
3500	58.191	482.080	428.940	185.991	−352.614	−37.827	0.565
3600	58.192	483.719	430.439	191.810	−354.541	−28.806	0.418
3700	58.192	485.313	431.900	197.629	−356.496	−19.730	0.279
3800	58.193	486.865	433.326	203.448	−358.471	−10.603	0.146
3900	58.193	488.377	434.719	209.267	−360.459	−1.422	0.019
4000	58.193	489.850	436.079	215.087	−362.450	7.809	−0.102
4100	58.194	491.287	437.408	220.906	−364.438	17.090	−0.218
4200	58.194	492.689	438.707	226.726	−366.418	26.420	−0.329
4300	58.194	494.059	439.979	232.545	−368.382	35.796	−0.435
4400	58.195	495.397	441.223	238.364	−370.327	45.218	−0.537
4500	58.195	496.705	442.441	244.184	−372.247	54.684	−0.635
4600	58.195	497.984	443.635	250.003	−374.139	64.193	−0.729
4700	58.195	499.235	444.805	255.823	−376.000	73.742	−0.820
4800	58.196	500.460	445.951	261.643	−377.826	83.330	−0.907
4900	58.196	501.660	447.076	267.462	−379.616	92.956	−0.991
5000	58.196	502.836	448.180	273.282	−381.368	102.618	−1.072
5100	58.196	503.988	449.263	279.101	−383.081	112.315	−1.150
5200	58.196	505.119	450.326	284.921	−384.754	122.045	−1.226
5300	58.197	506.227	451.370	290.741	−386.386	131.807	−1.299
5400	58.197	507.315	452.396	296.560	−387.977	141.599	−1.370
5500	58.197	508.383	453.405	302.380	−389.527	151.421	−1.438
5600	58.197	509.431	454.396	308.200	−391.036	161.269	−1.504
5700	58.197	510.461	455.370	314.019	−392.506	171.145	−1.568
5800	58.197	511.474	456.329	319.839	−393.937	181.046	−1.630
5900	58.197	512.468	457.272	325.659	−395.328	190.972	−1.691
6000	58.198	513.447	458.200	331.479	−396.682	200.920	−1.749

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [305.22 \pm 2.13]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) \approx -37.9 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) \approx -52.3 \pm 16.7\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1A_1]$	0	[1]
$[^3B_1]$	[20000]	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
402 (1)
[120](1)
398.9(1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Si–Br – [2.19] Å
Bond Angle: Br–Si–Br = 109° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = [4.91229 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The equilibrium reaction Si(cr) + $SiBr_4$(g) = 2 $SiBr_2$(g) was studied by Schafer *et al.*[1] and Wolf and Herbst.[2] Both investigators used a flow technique in an argon atmosphere. A 2nd and 3rd law analysis of their results (reported only in equation form) is summarized below. As in the case of $SiCl_2$,[3] there is acceptable agreement between these two studies. Using the mean $\Delta_f H°(298.15\ K)$ from the 3rd law results and auxiliary data,[3] we calculate and adopt $\Delta_f H°(298.15\ K) = -12.5\ kcal·mol^{-1}$ (52.300 $kJ·mol^{-1}$) for $SiBr_2$(g).

Source	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Schafer *et al.*[1]	1320–1475 K	71.61	73.26	1.18
Wolf and Herbst[2]	1200–1550 K	77.33	75.21	−1.54

The adopted enthalpy of formation leads to a $\Delta_{at}H°$ value which implies that the average bond energy is roughly 10% larger in $SiBr_2$(g) than in SiBr(g) or $SiBr_4$(g).[3]

Heat Capacity and Entropy

Maass, Hauge, and Margrave[4] observed the infrared spectra of $SiBr_2$ in nitrogen and argon matrices in the Si–Br stretching region. Attempts to observe the bending fundamental in the region between 90 cm^{-1} and 150 cm^{-1} were unsuccessful. Maass *et al.*[4] measured and assigned υ_1 and υ_3. The bond angle was calculated to be 109 ± 3° from the isotopic splittings due to three silicon isotopes. The authors also assumed $\upsilon_2 = 120\ cm^{-1}$. This bending frequency is consistent with the analogous $SiBr_2$ "bending mode" in SiH_2Br_2.[3] We adopt the frequencies and bond angles as suggested by Maass *et al.*[4]

We assume the Si–Br bond distance to be the same as that in SiH_2Br_2[3]. By observing the trends in SiF_2 and $SiCl_2$,[3] we assume a $^1A_1$ ground electronic state and a $^3B_1$ excited state at ~20000 cm^{-1}. Additional support for this assignment comes from the luminescense spectrum of a glow discharge in $SiBr_4$ vapors observed by Kuznetsova and Kuzyokov.[5] They states that the complex spectral structure of the 16800–23500 cm^{-1} band could be attributed to the oscillation and deformation of the nonlinear $SiBr_2$ molecule. The inclusion of this triplet electronic state increases the entropy by 0.0004 cal·K^{-1}·mol^{-1} at 3000K. The principal moments of inertia are: $I_A = 6.4154 \times 10^{-39}$, $I_B = 84.3558 \times 10^{-39}$, and $I_C = 90.7711 \times 10^{-39}$ g·cm^2.

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[3] JANAF Thermochemical Tables: $SiBr_4$(g), SiBr(g), and SiH_2Br_2(g), 12–31–76; Si(g), 3–31–67; Br(g), 6–30–74; $SiCl_2$(g) and SiF_2(g), 12–31–77
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.368	−37.941	−37.941	INFINITE
100	41.529	252.970	349.983	−9.701	−37.333	−56.862	29.702
200	49.762	284.529	310.029	−5.100	−38.812	−75.900	19.823
250	52.126	295.906	306.100	−2.549	−39.926	−85.050	17.770
298.15	53.637	305.225	305.225	0.	−52.300	−92.311	16.173
300	53.684	305.557	305.226	0.099	−52.378	−92.559	16.116
350	54.738	313.916	305.884	2.811	−83.351	−97.553	14.559
400	55.473	321.276	307.357	5.568	−83.511	−99.571	13.003
450	56.003	327.843	309.275	8.355	−83.689	−101.568	11.790
500	56.395	333.764	311.433	11.166	−83.882	−103.545	10.817
600	56.923	344.097	316.040	16.834	−84.310	−107.438	9.353
700	57.251	352.898	320.693	22.544	−84.786	−111.255	8.302
800	57.468	360.558	325.208	28.280	−85.311	−115.001	7.509
900	57.619	367.336	329.519	34.035	−85.882	−118.679	6.888
1000	57.728	373.413	333.610	39.803	−86.499	−122.290	6.388
1100	57.809	378.919	337.483	45.580	−87.162	−125.838	5.976
1200	57.871	383.952	341.148	51.364	−87.868	−129.323	5.629
1300	57.919	388.586	344.621	57.154	−88.619	−132.747	5.334
1400	57.958	392.879	347.917	62.947	−89.417	−136.112	5.078
1500	57.989	396.879	351.049	68.745	−90.263	−139.418	4.855
1600	58.014	400.623	354.032	74.545	−91.158	−142.666	4.658
1700	58.036	404.140	356.877	80.348	−142.281	−145.410	4.468
1800	58.054	407.458	359.596	86.152	−143.051	−145.572	4.224
1900	58.070	410.597	362.198	91.958	−143.833	−145.691	4.005
2000	58.084	413.576	364.693	97.766	−144.630	−145.768	3.807
2100	58.098	416.411	367.089	103.575	−145.445	−145.805	3.627
2200	58.111	419.114	369.393	109.385	−146.278	−145.803	3.462
2300	58.125	421.697	371.611	115.197	−147.131	−145.762	3.310
2400	58.140	424.171	373.750	121.010	−148.005	−145.684	3.171
2500	58.157	426.545	375.815	126.825	−148.900	−145.569	3.041
2600	58.178	428.826	377.810	132.642	−149.816	−145.418	2.921
2700	58.202	431.022	379.740	138.461	−150.752	−145.231	2.810
2800	58.230	433.139	381.610	144.283	−151.707	−145.009	2.705
2900	58.264	435.183	383.422	150.107	−152.679	−144.752	2.607
3000	58.304	437.159	385.181	155.936	−153.665	−144.462	2.515
3100	58.351	439.072	386.888	161.768	−154.664	−144.139	2.429
3200	58.405	440.925	388.548	167.606	−155.672	−143.784	2.347
3300	58.466	442.723	390.163	173.449	−156.685	−143.396	2.270
3400	58.536	444.470	391.735	179.299	−157.700	−142.979	2.197
3500	58.614	446.168	393.266	185.157	−158.715	−142.531	2.127
3600	58.701	447.820	394.758	191.023	−543.876	−131.593	1.909
3700	58.797	449.430	396.214	196.897	−544.464	−120.133	1.696
3800	58.901	450.999	397.635	202.782	−545.041	−108.657	1.494
3900	59.014	452.530	399.023	208.678	−545.605	−97.166	1.301
4000	59.136	454.026	400.380	214.585	−546.152	−85.660	1.119
4100	59.266	455.488	401.706	220.505	−546.678	−74.141	0.945
4200	59.405	456.918	403.004	226.439	−547.181	−62.610	0.779
4300	59.551	458.317	404.274	232.387	−547.657	−51.067	0.620
4400	59.704	459.688	405.518	238.349	−548.104	−39.513	0.469
4500	59.864	461.031	406.736	244.328	−548.519	−27.949	0.324
4600	60.031	462.349	407.931	250.322	−548.901	−16.377	0.186
4700	60.203	463.642	409.103	256.334	−549.248	−4.797	0.053
4800	60.380	464.911	410.252	262.363	−549.557	6.791	−0.074
4900	60.562	466.158	411.381	268.410	−549.829	18.384	−0.196
5000	60.749	467.383	412.488	274.476	−550.061	29.983	−0.313
5100	60.938	468.588	413.577	280.560	−550.253	41.586	−0.426
5200	61.131	469.773	414.646	286.663	−550.405	53.192	−0.534
5300	61.325	470.940	415.697	292.786	−550.515	64.801	−0.639
5400	61.522	472.088	416.731	298.929	−550.584	76.412	−0.739
5500	61.719	473.219	417.748	305.091	−550.611	88.023	−0.836
5600	61.917	474.332	418.748	311.272	−550.597	99.634	−0.929
5700	62.114	475.430	419.733	317.474	−550.542	111.245	−1.019
5800	62.311	476.512	420.703	323.695	−550.446	122.854	−1.106
5900	62.507	477.579	421.658	329.936	−550.311	134.462	−1.190
6000	62.702	478.631	422.598	336.197	−550.135	146.067	−1.272

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 143.4 \pm 4.2\ J·K^{-1}·mol^{-1}$
$T_{trs} = 918\ K$
$T_{fus} = 930\ K$

$\Delta_f H°(0\ K) = -704.96 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -717.97 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{trs} H° = 12.217 \pm 0.21\ kJ·mol^{-1}$
$\Delta_{fus} H° = 10.125 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

The selected value for $\Delta_f H°$ is derived from results of solution calorimetric measurements in aqueous acids performed by Ehrlich *et al.*[1] Their results on the enthalpy of solution of Sr(cr) and $SrBr_2$(cr) in HBr·555 H_2O are combined with data for HBr(aq)[2, 3] in a thermochemical cycle to give $\Delta_f H°(SrBr_2, cr, 298.15\ K) = -171.6 \pm 0.4\ kcal·mol^{-1}$ ($-717.974 \pm 1.7\ kJ·mol^{-1}$). In the same paper, Ehrlich *et al.*[1] reported similar results for three (Ca, Sr, and Ba) of the alkaline earth dichlorides; these results have been the basis for adopted JANAF enthalpies of formation[4] for these dichlorides.

Independent values for $\Delta_f H°$ can be obtained from measurements of the enthalpy of solution of $SrBr_2$(cr) in aqueous solution[5–7] as summarized by Bichowsky and Rossini.[8] Combining these results with $\Delta_f H°(Sr^{+2}, \infty\ aq, 298.15\ K) = -130.45\ kcal·mol^{-1}$ [9] and $\Delta_f H°(Br^-, \infty\ aq, 298.15\ K) = -29.039 \pm 0.036\ kcal·mol^{-1}$,[2] we derive $\Delta_f H°$ values for $SrBr_2$(cr) in $kcal·mol^{-1}$ of −171.5,[5] −172.2,[6] and −171.6.[7] Deviations from our adopted value are at worst only 0.6 $kcal·mol^{-1}$, and the results of two studies[5,7] provide additional support for the selected value of $\Delta_f H°$. Also, our value for $\Delta_f H°$ is essentially that ($-171.5\ kcal·mol^{-1}$) selected by NBS.[9]

Heat Capacity and Entropy

$C_p°$ data below 300 K are based primarily on the adiabatic calorimetry (60–302 K) of Taylor and Smith.[10] These $C_p°$ data show an unusual leveling off at near 18.0 $cal·K^{-1}·mol^{-1}$ above 245 K. We adopt their $C_p°$ data in the temperature range 60–245 K; values above 245 K are estimated by comparison with similar data for $SrCl_2$ and $BaCl_2$.[4] Our value for $C_p°$ at 298.15 K (18.37 $cal·K^{-1}·mol^{-1}$) is roughly 0.4 $cal·K^{-1}·mol^{-1}$ higher than the measured value of Taylor and Smith.[10] Huttig and Slonim[11] have reported mean heat capacity values over three temperature intervals (85–198, 196–271, and 276–368 K). Their measurements suggest a slightly higher value (18.8 $cal·K^{-1}·mol^{-1}$) for $C_p°$ at 298.15 K than is adopted.

Taylor and Smith[10] reported $S°(298.15\ K) = 32.29\ cal·K^{-1}·mol^{-1}$ based on $S°(60\ K) = 6.68\ cal·K^{-1}·mol^{-1}$ obtained from Debye–Einstein functions which represented their $C_p°$ data to only ±1.8 percent from 60 to 100 K. A comparison of their extrapolated $C_p°$ data with those which have been measured for $SrCl_2$, $BaCl_2$, and CaI_2[4] indicates that the values for $SrBr_2$ decrease much more rapidly with temperature below 50 K than would be expected. We have made our own extrapolation to 0 K for $SrBr_2$ by comparison with the measured data for $SrCl_2$ (7.4 to 60 K), $BaCl_2$(6 to 60 K), and CaI (13.1 to 60 K). Our extrapolation gives $S°(60\ K) = 8.7\ cal·K^{-1}·mol^{-1}$, or $S°(298.15\ K) = 34.28\ cal·K^{-1}·mol^{-1}$ (143.438 $J·K^{-1}·mol^{-1}$) based on the adopted $C_p°$ data (60–300 K). Our value for $S°(298.15\ K)$ is consistent with the estimates of 35 $cal·K^{-1}·mol^{-1}$ [12] and 33.8 $cal·K^{-1}·mol^{-1}$,[13] suggesting a possible uncertainty of ±1 $cal·K^{-1}·mol^{-1}$ in the adopted value.

Taylor and Smith[10] measured relative enthalpy data (293–902 K) on a portion of the same sample used for their $C_p°$ measurements. This sample was reported to contain less than 0.1% oxide and was investigated in a Bunsen ice calorimeter. Our analysis of their relative enthalpies by curve fitting techniques reveals the existence of considerable scatter in the data, and no weight is given to their results. The average deviation of 36 points in a Shomate type fit is 2.5%; the maximum deviation is −9.3% at 397 K. Also, these workers[10] were apparently unaware of the transition in $SrBr_2$ at 918 K, since their data set contains only two enthalpy points between 902–927 K. Relative enthalpies have also been measured by Dworkin and Bredig,[14] and the results were reported in graphical form. The short temperature interval (846–902 K) over which these measurements were made for the α phase preclude derivation of accurate heat capacities. Dworkin and Bredig[14] also reported in the same paper enthalpy data for three (Ca, Sr, and Ba) of the alkaline earth dichlorides. A comparison of these enthalpies with those adopted by JANAF[4] indicates that their results are probably reliable to better than ±2%. We adopt their measured value for $H°(918;298.15) = 12.37\ kcal·mol^{-1}$ of the α phase at the transition temperature. $C_p°$ values (300–918 K) are then estimated by comparison with those for $SrCl_2$ and $BaCl_2$.[4] These estimates are made so as to reproduce as closely as possible the adopted enthalpy at 918 K. Our estimated $C_p°$ data give a value of $H°(918;298.15) = 12.35\ kcal·mol^{-1}$ which agrees with the measured value of Dworkin and Bredig to within 20 calories. The enthalpies of Taylor and Smith[10] are roughly 2.5% higher than the adopted values at temperatures near the transition. $C_p°$ data for the β phase (918–930 K) are taken from Dworkin and Bredig[14] and extrapolated above the melting point.

TransitionData

Existence of two forms of $SrBr_2$ has been shown by thermal analysis[15–18] and drop calorimetry.[14] Values of T_{trs}reported are 915 K,[15–16] 920 K,[17] 919 K,[18] and 918 K.[14] We adopt the last value which is based on the drop calorimetry of Dworkin and Bredig.[14] Several other investigators[10,19–21] have mistakenly interpreted the transition as due to melting.

$\Delta_{trs} H°$ of 2.92 $kcal·mol^{-1}$ (12.217 $kJ·mol^{-1}$) is derived from the enthalpy data of Dworkin and Bredig.[14]

FusionData

Refer to the liquid table for details.

SublimationData

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference in the adopted gas and crystal enthalpies of formation at 298.15 K.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.064	−704.960	−704.960	INFINITE
100	64.337	64.952	209.316	−14.436	−705.626	−703.931	367.696
200	73.645	113.388	150.374	−7.397	−705.976	−702.127	183.377
298.15	76.853	143.438	143.438	0.	−717.974	−698.755	122.419
300	76.902	143.913	143.439	0.142	−718.022	−698.636	121.643
400	79.036	166.337	146.482	7.942	−747.431	−686.047	89.589
500	80.835	184.166	152.295	15.935	−745.957	−670.871	70.085
600	82.676	199.060	158.881	24.107	−744.434	−655.995	57.109
700	84.893	211.966	165.563	32.482	−742.832	−641.381	47.860
800	87.571	223.468	172.094	41.099	−741.107	−627.004	40.939
900	91.002	233.971	178.394	50.020	−739.825	−612.781	35.565
918.000	91.717	235.781	179.501	51.664	ALPHA <--> BETA		
918.000	115.060	249.098	179.501	63.890	TRANSITION		
930.000	115.060	250.593	180.409	65.271	---- BETA <--> LIQUID ----		
1000	115.060	258.943	185.617	73.325	−723.327	−599.967	31.339
1100	115.060	269.909	192.790	84.831	−726.540	−587.492	27.898
1200	115.060	279.920	199.640	96.337	−722.773	−575.018	25.030
1300	115.060	289.130	206.174	107.843	−719.013	−562.857	22.616
1400	115.060	297.657	212.408	119.349	−715.263	−550.986	20.558
1500	115.060	305.595	218.359	130.855	−711.522	−539.383	18.783

PREVIOUS: CURRENT: June 1974

Continued on page 548

$S°(298.15\ K) = [154.843]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 930\ K$

$\Delta_f H°(298.15\ K) = [-705.098]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 10.125 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(SrBr_2, l)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(930\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ for the liquid in the temperature range 600–3000 K is assumed constant at 27.818 $cal·K^{-1}·mol^{-1}$. This value is based on JANAF curve fits (deviations ±0.1%) of the relative enthalpies (931–1002 K) reported by Dworkin and Bredig.[1] Taylor and Smith[2] have also reported enthalpies (927–1118 K) for the liquid. These results suggest a somewhat higher value (28.36 $cal·K^{-1}·mol^{-1}$) for $C_p°$; however, the data are considered less reliable. (See $SrBr_2$(cr) table for further discussion). The average deviation of the data of Taylor and Smith[2] from our adopted enthalpies is ±0.4%; the maximum deviation is 1.2% at 1067 K. A glass transition is assumed at 600 K below which $C_p°$ is that of the crystal.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is that observed by Dworkin and Bredig[1] from drop calorimetry. Other reported values for T_{fus} are 926 K,[3] 931 K,[4] 924 K,[5] and 928 K.[6] Four other investigators[2, 7–10] have reported values of T_{fus} near 916 K, but they have mistakenly interpreted the transition in $SrBr_2$ as that due to melting.

$\Delta_{fus}H°$ is calculated as the difference in the enthalpies of the liquid and β phase at T_{fus}. The enthalpy of the liquid at T_{fus} is based on JANAF curve fits of the enthalpy data reported by Dworkin and Bredig.[1] We adopted their measured value of 15.6 $kcal·mol^{-1}$ for $H°(930; 298.15)$ of the β phase at T_{fus}. A cryoscopic[4] determination of $\Delta_{fus}H°$ gave 2.6 ± 1.3 $kcal·mol^{-1}$which agrees well with the adopted calorimetric value. Taylor and Smith[2] reported a calorimetric value of $\Delta_{fus}H° = 5.25\ kcal·mol^{-1}$; however, this value also includes the heat of transition. Addition of our values for $\Delta_{trs}H°$ and $\Delta_{vap}H°$ gives 5.34 $kcal·mol^{-1}$.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G°$ for the process $SrBr_2(l) = SrBr_2(g)$ approaches zero. $\Delta_{vap}H°$ is the difference in the heats of formation of the gas and liquid at T_{vap}. Peterson and Hutchinson[10] obtained $T_{vap} = 2318$ K from vapor pressure measurements on the liquid (1114–1304 K). However, the value is based on a rather long extrapolation and is probably uncertain to at least ±100 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	76.852	154.843	154.843	0.	−705.098	−689.280	120.759
300	76.902	155.319	154.845	0.142	−705.146	−689.181	119.997
400	79.036	177.742	157.888	7.942	−734.555	−677.733	88.503
500	80.835	195.571	163.701	15.935	−733.082	−663.697	69.336
600	82.678	210.471	170.287	24.110	−731.556	−649.963	56.584
600.000	82.678	210.471	170.287	24.110	GLASS <--> LIQUID TRANSITION		
600.000	116.391	210.471	170.287	24.110			
700	116.391	228.413	177.342	35.749	−726.689	−636.751	47.515
800	116.391	243.955	184.719	47.388	−721.942	−624.228	40.758
900	116.391	257.664	192.077	59.027	−717.941	−612.220	35.532
1000	116.391	269.926	199.260	70.667	−713.110	−600.733	31.379
1100	116.391	281.020	206.196	82.306	−716.190	−589.363	27.987
1200	116.391	291.147	212.860	93.945	−712.289	−578.006	25.160
1300	116.391	300.463	219.245	105.584	−708.397	−566.974	22.781
1400	116.391	309.089	225.358	117.223	−704.513	−556.241	20.754
1500	116.391	317.119	231.211	128.862	−700.640	−545.785	19.006
1600	116.391	324.630	236.817	140.501	−696.776	−535.587	17.485
1700	116.391	331.687	242.193	152.140	−829.838	−524.451	16.114
1800	116.391	338.339	247.351	163.779	−824.139	−506.652	14.703
1900	116.391	344.632	252.307	175.418	−818.460	−489.169	13.448
2000	116.391	350.602	257.074	187.057	−812.806	−471.984	12.327
2100	116.391	356.281	261.664	198.696	−807.183	−455.081	11.320
2200	116.391	361.695	266.089	210.335	−801.596	−438.446	10.410
2300	116.391	366.869	270.359	221.974	−796.053	−422.063	9.585
2400	116.391	371.823	274.484	233.613	−790.561	−405.921	8.835
2500	116.391	376.574	278.473	245.252	−785.127	−390.006	8.149
2600	116.391	381.139	282.335	256.891	−779.761	−374.307	7.520
2700	116.391	385.532	286.076	268.530	−774.471	−358.813	6.942
2800	116.391	389.764	289.704	280.169	−769.265	−343.514	6.408
2900	116.391	393.849	293.225	291.809	−764.152	−328.399	5.915
3000	116.391	397.795	296.645	303.448	−759.140	−313.459	5.458

PREVIOUS: CURRENT: June 1974

0	to	918 K	crystal, I
918	to	930 K	crystal, II
above		930 K	liquid

Refer to the individ ual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−18.064	−704.960	−704.960	INFINITE
100	64.337	64.952	209.316	−14.436	−705.626	−703.931	367.696
200	73.645	113.388	150.374	−7.397	−705.976	−702.127	183.377
298.15	76.853	143.438	143.438	0.	−717.974	−698.755	122.419
300	76.902	143.913	143.439	0.142	−718.022	−698.636	121.643
400	79.036	166.337	146.482	7.942	−747.431	−686.047	89.589
500	80.835	184.166	152.295	15.935	−745.957	−670.871	70.085
600	82.676	199.060	158.881	24.107	−744.434	−655.995	57.109
700	84.893	211.966	165.563	32.482	−742.832	−641.381	47.860
800	87.571	223.468	172.094	41.099	−741.107	−627.004	40.939
900	91.002	233.971	178.394	50.020	−739.825	−612.781	35.565
918.000	91.717	235.781	179.501	51.664	ALPHA <--> BETA TRANSITION		
918.000	115.060	249.098	179.501	63.890			
930.000	115.060	250.593	180.409	65.271	BETA <--> LIQUID TRANSITION		
930.000	116.391	261.480	180.409	75.396			
1000	116.391	269.926	186.383	83.543	−713.108	−600.732	31.379
1100	116.391	281.020	194.490	95.182	−716.189	−589.362	27.986
1200	116.391	291.147	202.129	106.822	−712.288	−578.005	25.160
1300	116.391	300.463	209.340	118.461	−708.396	−566.973	22.781
1400	116.391	309.089	216.160	130.100	−704.512	−556.240	20.754
1500	116.391	317.119	222.626	141.739	−700.639	−545.784	19.006
1600	116.391	324.630	228.769	153.378	−696.775	−535.586	17.485
1700	116.391	331.687	234.618	165.017	−829.837	−524.450	16.114
1800	116.391	338.339	240.197	176.656	−824.138	−506.651	14.703
1900	116.391	344.632	245.530	188.295	−818.459	−489.168	13.448
2000	116.391	350.602	250.635	199.934	−812.805	−471.983	12.327
2100	116.391	356.281	255.532	211.573	−807.182	−455.080	11.320
2200	116.391	361.695	260.235	223.212	−801.595	−438.445	10.410
2300	116.391	366.869	264.760	234.851	−796.052	−422.062	9.585
2400	116.391	371.823	269.118	246.490	−790.560	−405.920	8.835
2500	116.391	376.574	273.322	258.129	−785.126	−390.005	8.149
2600	116.391	381.139	277.382	269.768	−779.760	−374.306	7.520
2700	116.391	385.532	281.307	281.407	−774.470	−358.812	6.942
2800	116.391	389.764	285.105	293.046	−769.264	−343.513	6.408
2900	116.391	393.849	288.785	304.685	−764.151	−328.398	5.915
3000	116.391	397.795	292.353	316.324	−759.139	−313.458	5.458

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [323.4 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -392.1 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -407.1 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[157](1)
[37](2)
[263](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Sr–Br = 2.82 ± 0.03 Å
Bond Angle: Br–Sr–Br = 180°
Rotational Constant: $B_0 = 0.013265\ cm^{-1}$

Enthalpy of Formation

Peterson and Hutchison[1,2] have measured vapor pressures (1114–1304 K) for liquid $SrBr_2$ by the Knudsen effusion method. Results of 2nd and 3rd law analysis of these pressures are tabulated below. We assume that the dibromide monomer was the only vapor species present. Mass spectra for some of the other alkaline earth dihalides[3] indicate that the saturated vapor consist predominantly of the metal dihalide monomer which agrees with predictions which were made by Brewer *et al.*[4] for the dihalide molecules. Included in the table is a value for $\Delta_f H°$ derived from a 3rd law analysis of a single vapor pressure point determined by Stock and Heynemann[5] and tabulated by Brewer *et al.*[4]

Source	Reaction[a]	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1,2	A	13[a]	1147–1304	69.9	71.24 ± 0.86	1.1 ± 2.5	97.3 ± 2.5
4,5	A	1	1040		66.9		101.6

[a]Reaction: (A) SrBr (l) = SrBr (g); [b]Two points rejected due to failure of a statistical test.

The value $\Delta_f H°(SrBr_2, g, 298.15\ K) = -97.3 \pm 3.0\ kcal^{-1} \cdot mol^{-1} (-407.103 \pm 12.6\ kJ \cdot mol^{-1})$ is preferred here rather than an average (−99.5 kcal·mol^{-1}) of the two results, since it is impossible to assess the reliability of the measurement by Stock and Heynemann.[5] However, our value does compare favorably with that (−98.0 kcal·mol^{-1}) selected by NBS.[6]

Heat Capacity and Entropy

The value of the bond length is that measured by Akishin and Spiridonov[7] in a high-temperature electron diffraction study. Electron diffraction patterns[7] for $SrBr_2$ were satisfactorily explained on the basis of a linear model (180° ± 10°). Later studies by Wharton *et al.*,[8] using electric deflection of molecular beams to detect dipole moments, showed no polarity in the $SrBr_2$ molecule; this is most reasonably explained by a linear and centrosymmetric configuration.

Few infrared spectral studies[9–11] have been reported for the gaseous alkaline earth dibromides. The antisymmetric stretch (ν_3) and bending (ν_2) frequencies for BeBr ν_2 were observed by Snelson[9] in a neon matrix. Baikov[10] observed a band at 330 ± 5 cm^{-1} in the high-temperature infrared spectra of $CaBr_2$ vapor and assigned this band to ν_3. In a similar study on $MgBr_2$(g) by Randall *et al.*[11] ν_3 was observed at 490 cm^{-1}. The only frequencies available for SrBr ν_2 are estimates[4, 10, and 12] which have been obtained by force constant calculations. The adopted vibrational frequencies are derived from force constants estimated by the valence force method.[13] A comparison of values for the ratio of the stretching force constants for diatomic and triatomic strontium fluorides (ratio = 1.33)[3] and chlorides (ratio = 1.15)[3] suggests a value of near unity for the ratio of the bromides. Therefore, the stretching force constant for $SrBr_2$ is taken equal to that for SrBr(k = 1.154 × 10^5 dynes/cm).[4] Our values for ν_1 and ν_3 compare favorably with those estimated by a similar procedure[4] (ν_1 = 156 cm and ν_3 = 262 cm^{-1}) and with those given by Krasnov and Svettsov[12] (ν_1 = 158 cm^{-1} and ν_3 = 265 cm^{-1}). The estimated frequencies of Baikov[10] are roughly 12% lower than ours. A comparison of values for the ratio of the stretch to bend force constants for the bent molecules SrF_2(ratio = 50)[3] and $SrCl_2$(ratio = 78)[3] suggests a value near 100 for $SrBr_2$. Brewer[4] used this same value in his force constant calculations. This value for the ratio gives $k\delta/l^2 = 1.154 \times 10^3$ dynes/cm, or ν_2 = 37 cm^{-1}. A comparison of similar data for the linear molecule $BeBr_2$[9] indicates that the value of the ratio could be as low as 41. This leads to a ν_2 = 58 cm^{-1} which is in excellent agreement with the value (56 cm^{-1} recommended by Krasnov and Svettsov.[12] We prefer the lower value of ν_2 at this time but include in the uncertainty ±2.0 cal·K^{-1}·mol^{-1} assigned to the value of S°(298.15 K) the possibility that the higher value is the correct one. The singlet ground state is assigned by analogy with that for $BaCl_2$.[3] Our adopted functions agree with those tabulated by Brewer *et al.*[4] to within 0.1 cal·K^{-1}·mol^{-1} in the range 298–2000 K.

Continued on page 548

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°-[G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.092	−392.118	−392.118	INFINITE
100	53.702	259.975	376.278	−11.630	−391.949	−409.756	214.035
200	59.338	299.377	328.945	−5.914	−393.621	−426.971	111.513
250	60.331	312.735	324.413	−2.920	−394.746	−435.188	90.928
298.15	60.896	323.413	323.413	0.	−407.103	−441.544	77.357
300	60.913	323.790	323.415	0.113	−407.180	−441.757	76.917
350	61.279	333.209	324.158	3.168	−438.128	−445.818	66.535
400	61.523	341.409	325.813	6.239	−438.263	−446.908	58.360
450	61.693	348.666	327.957	9.319	−438.425	−447.979	52.000
500	61.817	355.173	330.358	12.407	−438.614	−449.031	46.910
600	61.979	366.459	335.463	18.598	−439.073	−451.073	39.269
700	62.079	376.021	340.591	24.801	−439.642	−453.029	33.805
800	62.144	384.315	345.550	31.012	−440.323	−454.897	29.702
900	62.188	391.637	350.272	37.229	−441.744	−456.600	26.500
1000	62.220	398.191	354.742	43.449	−442.331	−458.220	23.935
1100	62.244	404.123	358.965	49.673	−450.827	−459.414	21.816
1200	62.262	409.539	362.958	55.898	−452.340	−460.128	20.029
1300	62.276	414.523	366.735	62.125	−453.860	−460.715	18.512
1400	62.288	419.139	370.315	68.353	−455.388	−461.185	17.207
1500	62.297	423.437	373.715	74.583	−456.923	−461.546	16.072
1600	62.304	427.458	376.950	80.813	−458.469	−461.804	15.076
1700	62.310	431.235	380.033	87.043	−596.940	−460.785	14.158
1800	62.315	434.797	382.977	93.275	−596.648	−452.784	13.139
1900	62.320	438.166	385.794	99.506	−596.377	−444.799	12.228
2000	62.323	441.363	388.493	105.739	−596.130	−436.828	11.409
2100	62.327	444.404	391.084	111.971	−595.913	−428.868	10.668
2200	62.329	447.303	393.574	118.204	−595.732	−420.918	9.994
2300	62.332	450.074	395.971	124.437	−595.595	−412.976	9.379
2400	62.334	452.727	398.281	130.670	−595.508	−405.038	8.815
2500	62.336	455.271	400.510	136.904	−595.480	−397.102	8.297
2600	62.338	457.716	402.663	143.137	−595.520	−389.167	7.818
2700	62.339	460.069	404.746	149.371	−595.635	−381.228	7.375
2800	62.340	462.336	406.763	155.605	−595.834	−373.284	6.964
2900	62.342	464.524	408.717	161.839	−596.125	−365.330	6.580
3000	62.343	466.637	410.613	168.074	−596.519	−357.366	6.222
3100	62.344	468.681	412.453	174.308	−597.021	−349.386	5.887
3200	62.345	470.661	414.241	180.542	−597.641	−341.388	5.573
3300	62.345	472.579	415.980	186.777	−598.385	−333.369	5.277
3400	62.346	474.440	417.672	193.011	−599.259	−325.326	4.998
3500	62.347	476.248	419.320	199.246	−600.270	−317.254	4.735
3600	62.347	478.004	420.926	205.481	−601.423	−309.152	4.486
3700	62.348	479.712	422.492	211.715	−602.720	−301.016	4.250
3800	62.348	481.375	424.020	217.950	−604.165	−292.843	4.025
3900	62.349	482.994	425.511	224.185	−605.759	−284.630	3.812
4000	62.349	484.573	426.968	230.420	−607.504	−276.374	3.609
4100	62.350	486.113	428.392	236.655	−609.398	−268.072	3.415
4200	62.350	487.615	429.784	242.890	−611.437	−259.723	3.230
4300	62.351	489.082	431.146	249.125	−613.623	−251.324	3.053
4400	62.351	490.516	432.479	255.360	−615.951	−242.871	2.883
4500	62.351	491.917	433.785	261.595	−618.416	−234.365	2.720
4600	62.352	493.287	435.063	267.830	−620.948	−225.807	2.564
4700	62.352	494.628	436.316	274.066	−623.651	−217.188	2.414
4800	62.352	495.941	437.545	280.301	−626.467	−208.510	2.269
4900	62.352	497.227	438.750	286.536	−629.391	−199.773	2.130
5000	62.353	498.486	439.932	292.771	−632.409	−190.975	1.995
5100	62.353	499.721	441.092	299.006	−635.497	−182.118	1.865
5200	62.353	500.932	442.231	305.242	−638.685	−173.197	1.740
5300	62.353	502.120	443.350	311.477	−641.944	−164.214	1.618
5400	62.353	503.285	444.449	317.712	−645.266	−155.169	1.501
5500	62.353	504.429	445.530	323.948	−648.643	−146.063	1.387
5600	62.354	505.553	446.591	330.183	−652.065	−136.894	1.277
5700	62.354	506.656	447.636	336.418	−655.524	−127.664	1.170
5800	62.354	507.741	448.662	342.654	−659.013	−118.373	1.066
5900	62.354	508.807	449.673	348.889	−662.314	−109.045	0.965
6000	62.354	509.855	450.667	355.125	−665.808	−99.639	0.867

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$\Delta_f H°(0\ K)$ = unknown

$S°(298.15\ K) = [108.4 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -405.43 \pm 20.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiBr_2$ crystal is derived from the data of Hall and Blocher[1] for the reaction $2\ TiBr_3(cr) = TiBr_4(g) + TiBr_2(cr)$. 2nd and 3rd law analyses of these data are not useful because of the formation of solid solutions in the above process. Hall and Blocher[1] obtained a value of $\Delta_r H°(800\ K)$ of 31.3 $kcal \cdot mol^{-1}$ for the reaction by integrating the incremental Gibbs energy changes over varying compositions of the solid solutions. The corresponding $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(298.15\ K)$ are calculated as 34.6 $kcal \cdot mol^{-1}$ and −96.9 $kcal \cdot mol^{-1}$ (−405.430 $kJ \cdot mol^{-1}$), respectively, using auxiliary JANAF enthalpy of formation and enthalpy data.

Heat Capacity and Entropy

The heat capacity of $TiBr_2(cr)$ was estimated by Kell.ey[2] The value of $S°(298.15\ K)$ is estimated from that of $TiCl_2(cr)$ and the difference between ionic entropy contribution of Cl^- and Br^-.

Sublimation Data

The enthalpy sublimation of $TiBr_2(cr)$ is taken as the difference in the enthalpies of formation of $TiBr_2(cr)$ and $TiBr_2(g)$ at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_r G° = 0$ for the reaction $TiBr_2(cr)$ $TiBr_2(g)$. The enthalpy of formation of $TiBr_2(g)$, upon which these quantities depend, is an estimated quantity.

References

[1]E. H. Hall and J. M. Blocher, Jr., J. Phys. Chem. **63**, 1525 (1959).
[2]K. K. Kelley, U.S. Bur. Mines Bull. 584, 232 pp. (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	78.688	108.366	108.366	0.	−405.430	−383.188	67.133
300	78.709	108.852	108.367	0.146	−405.471	−383.050	66.695
400	79.856	131.653	111.468	8.074	−434.636	−369.491	48.251
500	81.002	149.595	117.362	16.117	−433.025	−353.391	36.919
600	82.149	164.465	124.008	24.274	−431.412	−337.615	29.392
700	83.295	177.214	130.719	32.546	−429.767	−322.112	24.036
800	84.441	188.412	137.245	40.933	−428.057	−306.849	20.035
900	85.588	198.424	143.496	49.435	−426.311	−291.802	16.936
1000	86.734	207.501	149.450	58.051	−424.590	−276.950	14.466
1100	87.881	215.821	155.110	66.782	−422.957	−262.266	12.454
1200	89.027	223.517	160.494	75.627	−425.398	−247.606	10.778
1300	90.174	230.688	165.621	84.587	−423.219	−232.878	9.357
1400	91.320	237.413	170.511	93.662	−421.013	−218.319	8.146
1500	92.466	243.752	175.185	102.851	−418.793	−203.919	7.101

PREVIOUS: June 1964 CURRENT: June 1968

$S°(298.15\ K) = [308.7 \pm 12.6]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [-164.9 \pm 20.9]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [-179.1 \pm 20.9]\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequences and Degeneracies
υ, cm^{-1}
[160](1)
[105](2)
[333](1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Ti–Br = [2.4] Å
Bond Angle: Br–Ti–Br = [180°]
Rotational Constant: B_0 = [0.018314] cm^{-1}

Enthalpy of Formation

The enthalpy of formation of $TiBr_2$(g) is calculated from the estimated Ti–Br bond energy. The bond energy is estimated as being the same as the average Ti–Cl bond energy of $TiCl_2$(g). This estimate is used because the measured average bond energies of $TiBr_3$(g) and $TiCl_3$(g) and those of $TiBr_4$(g) and $TiCl_4$(g) are very nearly equal.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2$(g), $TiCl_4$(g) and $TiBr_4$(g). The vibrational frequencies are estimated from a valence force field model. The force constant k is estimated as 1.2 millidynes $Å^{-1}$, and the constant k_δ/l^2 is assumed to be 0.06 millidynes $Å^{-1}$. These values are derived by a correlation with other dihalides.

The electronic levels are assumed to be the same as $TiCl_2$(g). The levels of $TiCl_2$(g) are estimated by assuming that they correspond to the inverted states of $NiCl_2$(g).[1] The linear configuration is adopted since experimental evidence indicates that other transition metal dihalides are linear.[2–5]

References

[1]C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).
[2]R. A. Berg and O. Sinanoglu, J. Chem. Phys. **32**, 1082 (1960).
[3]J. T. Hougen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1670 (1961).
[4]G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. **36**, 2879 (1962).
[5]A. Buchler, J. L. Stauffer and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J{\cdot}K^{-1}{\cdot}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.127	−164.863	−164.863	INFINITE
100	49.952	247.576	360.164	−11.259	−164.348	−182.895	95.535
200	57.678	285.140	314.116	−5.795	−165.703	−201.001	52.496
250	59.160	298.185	309.669	−2.871	−166.758	−209.710	43.816
298.15	60.026	308.685	308.685	0.	−179.075	−216.558	37.940
300	60.052	309.056	308.686	0.111	−179.151	−216.791	37.747
350	60.624	318.359	309.419	3.129	−210.070	−221.365	33.037
400	61.009	326.481	311.055	6.170	−210.185	−222.971	29.117
450	61.281	333.684	313.177	9.228	−210.326	−224.561	26.066
500	61.479	340.151	315.556	12.297	−210.490	−226.134	23.624
600	61.741	351.385	320.619	18.459	−210.873	−229.228	19.956
700	61.904	360.916	325.712	24.642	−211.317	−232.253	17.331
800	62.016	369.189	330.641	30.839	−211.798	−235.211	15.358
900	62.109	376.499	335.338	37.045	−212.346	−238.106	13.819
1000	62.204	383.048	339.788	43.260	−213.026	−240.933	12.585
1100	62.319	388.982	343.994	49.486	−213.898	−243.684	11.572
1200	62.466	394.410	347.973	55.725	−218.946	−246.226	10.718
1300	62.655	399.417	351.740	61.981	−219.471	−248.478	9.984
1400	62.887	404.069	355.313	68.258	−220.063	−250.688	9.353
1500	63.163	408.417	358.710	74.560	−220.730	−252.853	8.805
1600	63.478	412.503	361.946	80.892	−221.482	−254.970	8.324
1700	63.825	416.362	365.034	87.256	−222.330	−257.038	7.898
1800	64.198	420.020	367.988	93.657	−223.287	−259.052	7.518
1900	64.587	423.502	370.819	100.097	−224.365	−261.010	7.176
2000	64.986	426.825	373.537	106.575	−240.264	−262.455	6.855
2100	65.387	430.005	376.151	113.094	−242.373	−263.512	6.555
2200	65.784	433.056	378.669	119.653	−244.462	−264.470	6.279
2300	66.171	435.989	381.097	126.250	−246.533	−265.333	6.026
2400	66.546	438.813	383.444	132.886	−248.588	−266.106	5.792
2500	66.904	441.537	385.713	139.559	−250.630	−266.794	5.574
2600	67.246	444.168	387.911	146.267	−252.659	−267.401	5.372
2700	67.568	446.712	390.042	153.007	−254.677	−267.929	5.183
2800	67.872	449.175	392.110	159.780	−256.686	−268.384	5.007
2900	68.157	451.561	394.119	166.581	−258.685	−268.766	4.841
3000	68.425	453.876	396.073	173.410	−260.675	−269.080	4.685
3100	68.675	456.124	397.974	180.266	−262.655	−269.327	4.538
3200	68.911	458.308	399.826	187.145	−264.625	−269.511	4.399
3300	69.132	460.432	401.630	194.047	−266.583	−269.633	4.268
3400	69.341	462.499	403.390	200.971	−268.530	−269.696	4.143
3500	69.538	464.512	405.108	207.915	−270.462	−269.703	4.025
3600	69.726	466.474	406.785	214.878	−272.378	−269.654	3.913
3700	69.904	468.387	408.424	221.860	−683.375	−261.763	3.695
3800	70.074	470.253	410.027	228.859	−684.021	−250.360	3.441
3900	70.238	472.075	411.595	235.874	−684.701	−238.939	3.200
4000	70.395	473.856	413.129	242.906	−685.412	−227.500	2.971
4100	70.547	475.596	414.632	249.953	−686.152	−216.044	2.752
4200	70.694	477.298	416.103	257.015	−686.917	−204.568	2.544
4300	70.836	478.963	417.546	264.092	−687.705	−193.075	2.345
4400	70.974	480.593	418.960	271.183	−688.512	−181.562	2.155
4500	71.108	482.189	420.348	278.287	−689.335	−170.031	1.974
4600	71.237	483.754	421.709	285.404	−690.172	−158.482	1.800
4700	71.362	485.287	423.046	292.534	−691.020	−146.915	1.633
4800	71.484	486.791	424.358	299.676	−691.876	−135.329	1.473
4900	71.601	488.266	425.647	306.831	−692.739	−123.725	1.319
5000	71.714	489.713	426.914	313.996	−693.605	−112.104	1.171
5100	71.822	491.135	428.160	321.173	−694.473	−100.465	1.029
5200	71.926	492.530	429.384	328.361	−695.340	−88.810	0.892
5300	72.026	493.901	430.588	335.558	−696.205	−77.137	0.760
5400	72.120	495.249	431.773	342.766	−697.067	−65.448	0.633
5500	72.210	496.573	432.940	349.982	−697.924	−53.744	0.510
5600	72.294	497.875	434.088	357.207	−698.774	−42.024	0.392
5700	72.373	499.155	435.218	364.441	−699.616	−30.289	0.278
5800	72.447	500.414	436.331	371.682	−700.449	−18.539	0.167
5900	72.516	501.653	437.428	378.930	−701.273	−6.775	0.060
6000	72.579	502.873	438.508	386.185	−702.086	5.003	−0.044

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [115.9 \pm 13]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [900]\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = [-404.6 \pm 42]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [62.760 \pm 42]\ kJ·mol^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(ZrBr_2, cr, 298.15\ K) = -96.7\ kcal·mol^{-1}$ ($-404.593\ kJ·mol^{-1}$) is calculated from the estimated $\Delta_{sub} H°(298.15\ K) = 55 \pm 5\ kcal·mol^{-1}$ for $ZrBr_2(cr) \rightarrow ZrBr_2(g)$, using $\Delta_f H°(ZrBr_2, g, 298.15\ K) = -41.7\ kcal·mol^{-1}$.[1] The estimated $\Delta_{sub} H°(298.15\ K)$ is obtained as an average of the enthalpies of sublimation at 298°K for $CrBr_2$, $MnBr_2$, $CoBr_2$ and $NiBr_2$ given by Brewer, Somayajulu and Brackett[2] and $TiBr_2$ and $FeBr_2$ listed in JANAF tables.[1]

Heat Capacity and Entropy

The heat capacities of $ZrBr_2(cr)$ are estimated from $TiBr_2(cr)$,[1] based on the assumption $C_p°(ZrBr_2) = C_p°(TiBr_2) + 3/2\ R\ln[A_r\ of\ Zr)/(A_r\ of\ Ti)]$. The entropy, $S°(298.15\ K) = 27.7\ cal·K^{-1}·mol^{-1}$ ($115.897\ J·K^{-1}·mol^{-1}$) is estimated in a similar manner based on $TiCl_2(cr)$[1] and $TiBr_2(cr)$.[1]

Fusion Data

The enthalpy of fusion is roughly estimated, so that the entropy of vaporization is about $20\ cal·K^{-1}·mol^{-1}$. The melting point was estimated by Brewer.[3]

References

[1]JANAF Thermochemical Tables: $ZrBr_2(g)$, 6–30–70; $TiBr_2(cr)$, $FeBr_2(cr)$, 9–30–66;$TiCl_2(cr)$, 12–31–68.
[2]L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).
[3]L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill Ed., McGraw–Hill Book Company, New York, (1949).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	86.722	115.897	115.897	0.	−404.593	−382.178	66.956
300	86.743	116.433	115.898	0.160	−404.619	−382.039	66.519
400	87.889	141.545	119.315	8.892	−432.927	−368.554	48.128
500	89.036	161.280	125.803	17.738	−430.397	−352.753	36.852
600	90.182	177.614	133.116	26.699	−427.847	−337.464	29.379
700	91.328	191.602	140.495	35.775	−425.276	−322.603	24.073
800	92.475	203.872	147.666	44.965	−422.688	−308.111	20.118
900	93.621	214.830	154.530	54.270	−420.095	−293.945	17.060
900.000	93.621	214.830	154.530	54.270	--- CRYSTAL <---> LIQUID ---		
1000	94.768	224.753	161.064	63.689	−417.506	−280.067	14.629
1100	95.914	233.839	167.273	73.223	−414.926	−266.448	12.653
1200	97.060	242.234	173.174	82.872	−416.071	−252.842	11.006
1300	98.207	250.048	178.791	92.635	−412.977	−239.365	9.618
1400	99.353	257.368	184.145	102.513	−409.819	−226.128	8.437
1500	100.500	264.262	189.258	112.506	−406.609	−213.119	7.421

PREVIOUS: March 1962 CURRENT: June 1970

$S°(298.15\ K) = [184.024]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [900]\ K$

$\Delta_f H°(298.15\ K) = [-342.333]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [62.760 \pm 42]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrBr_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(900\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 $cal·K^{-1}\ g·atom^{-1}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change approaches zero for the process $ZrBr_2(l) \rightarrow ZrBr_2(g)$ at one bar. The difference between $\Delta_f H°$ for ZrBr(l) and $ZrBr_2(g)$ at T_{vap} is $\Delta_{vap}H°$.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.002	184.024	184.024	0.	−342.333	−340.230	59.607
300	91.002	184.587	184.026	0.168	−342.351	−340.217	59.237
400	91.002	210.767	187.596	9.269	−370.290	−333.606	43.565
500	91.002	231.074	194.336	18.369	−367.506	−324.760	33.927
600	91.002	247.665	201.884	27.469	−364.817	−316.464	27.551
700	91.002	261.693	209.452	36.569	−362.222	−308.612	23.029
800	91.002	273.845	216.758	45.669	−359.724	−301.125	19.661
900	91.002	284.563	223.708	54.770	−357.335	−293.945	17.060
1000	91.002	294.151	230.282	63.870	−355.065	−287.025	14.993
1100	91.002	302.825	236.488	72.970	−352.919	−280.325	13.312
1200	91.002	310.743	242.351	82.070	−354.613	−273.594	11.909
1300	91.002	318.027	247.896	91.170	−352.182	−266.942	10.726
1400	91.002	324.771	253.149	100.271	−349.802	−260.475	9.718
1500	91.002	331.049	258.136	109.371	−347.484	−254.175	8.851
1600	91.002	336.923	262.878	118.471	−345.240	−248.028	8.097
1700	91.002	342.440	267.398	127.571	−343.081	−242.019	7.436
1800	91.002	347.641	271.713	136.671	−341.020	−236.134	6.852
1900	91.002	352.561	275.839	145.772	−339.070	−230.361	6.333
2000	91.002	357.229	279.793	154.872	−337.242	−224.687	5.868

PREVIOUS: March 1962 CURRENT: June 1970

298.15	to	900 K	crystal
above		900 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
298.15	86.722	115.897	115.897	0.	−404.593	−382.178	66.956
300	86.743	116.433	115.898	0.160	−404.619	−382.039	66.519
400	87.889	141.545	119.315	8.892	−432.927	−368.554	48.128
500	89.036	161.280	125.803	17.738	−430.397	−352.753	36.852
600	90.182	177.614	133.116	26.699	−427.847	−337.464	29.379
700	91.328	191.602	140.495	35.775	−425.276	−322.603	24.073
800	92.475	203.872	147.666	44.965	−422.688	−308.111	20.118
900	93.621	214.830	154.530	54.270	−420.095	−293.945	17.060
900.000	93.621	214.830	154.530	54.270	CRYSTAL <--> LIQUID TRANSITION		
900.000	91.002	284.563	154.530	117.030			
1000	91.002	294.151	168.022	126.130	−355.065	−287.025	14.993
1100	91.002	302.825	179.888	135.230	−352.919	−280.325	13.312
1200	91.002	310.743	190.468	144.330	−354.613	−273.594	11.909
1300	91.002	318.027	200.004	153.430	−352.182	−266.942	10.726
1400	91.002	324.771	208.678	162.531	−349.802	−260.475	9.718
1500	91.002	331.049	216.629	171.631	−347.484	−254.175	8.851
1600	91.002	336.923	223.966	180.731	−345.240	−248.028	8.097
1700	91.002	342.440	230.774	189.831	−343.081	−242.019	7.436
1800	91.002	347.641	237.124	198.931	−341.020	−236.134	6.852
1900	91.002	352.561	243.071	208.032	−339.070	−230.361	6.333
2000	91.002	357.229	248.663	217.132	−337.242	−224.687	5.868

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = [316.8 \pm 13]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-160.0 \pm 42]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-174.5 \pm 42]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[160](1)
[84](2)
[265](1)

Ground State Quantum Weight: [3] σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: Zr–Br = [2.47] Å
Bond Angle: Br–Zr–Br = [180]°
Rotational Constant: B_0 = [0.017290] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(ZrBr_2, g, 298.15\ K) = -41.7\ kcal\cdot mol^{-1}(-174.473\ kJ\cdot mol^{-1})$ is derived from the estimated $\Delta_r H°(298.15\ K) = 243.5 \pm 10\ kcal\cdot mol^{-1}$ for $ZrBr_2(g \rightarrow Zr(g) + 2\ Br(g)$. The value of $\Delta_r H°(298.15\ K)$ is twice the average bond dissociation energy, $\Delta_{at}H°(298.15\ K)/2 = 121.75\ kcal\cdot mol^{-1}$, which is calculated from the proportion of the average bond dissociation energies at 298.15 K for $ZrBr_2/TiBr_2 = ZrBr_4/TiBr_4$. The average bond dissociation energies at 298.15 K, $\Delta_{at}H°(ZrBr_4)/_4 = 102.2\ kcal\cdot mol^{-1}$, $\Delta_{at}H°(TiBr_4)/_4 = 87.9\ kcal\cdot mol^{-1}$, and $\Delta_{at}H°(TiBr_2)/2 = 104.6\ kcal\cdot mol^{-1}$, are all calculated from JANAF $\Delta_f H°(298.15\ K)$ for $ZrBr_4$(g), $TiBr_4$(g), $TiBr_2$(g), Zr(g), Ti(g), and Br(g).

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the transition metal dihalides are generally linear[1–5] even though a few fluorides are bent.[6] The bond distance is assumed to be the same as that in $ZrBr_4$(g) which was estimated as 2.47 Å by Godnev *et al.*[7]

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 1.2 millidyne $Å^{-1}$ and the bending force constant 0.06 millidyne $Å^{-1}$. These values are derived from force constants of transition metal dihalides listed by Brewer, Somayajulu and Brackett.[8] The electronic levels and quantum weights are estimated to be the same as those of gaseous $TiCl_2$.[9]

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[9]JANAF Thermochemical Tables: $TiCl_2$(g), 12-31-68.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.564	−160.030	−160.030	INFINITE
100	52.080	254.108	369.245	−11.514	−159.659	−178.280	93.124
200	58.882	292.867	322.284	−5.883	−161.123	−196.402	51.295
250	60.034	306.143	317.773	−2.908	−162.179	−205.105	42.854
298.15	60.685	316.777	316.777	0.	−174.473	−211.951	37.133
300	60.704	317.152	316.778	0.112	−174.547	−212.183	36.944
350	61.125	326.544	317.519	3.159	−205.422	−216.760	32.350
400	61.404	334.725	319.169	6.222	−205.477	−218.376	28.517
450	61.599	341.970	321.308	9.298	−205.547	−219.984	25.535
500	61.741	348.468	323.705	12.381	−205.634	−221.584	23.149
600	61.927	359.742	328.799	18.566	−205.860	−224.754	19.567
700	62.042	369.298	333.920	24.765	−206.166	−227.880	17.005
800	62.123	377.588	338.871	30.973	−206.560	−230.956	15.080
900	62.193	384.909	343.588	37.189	−207.056	−233.977	13.580
1000	62.273	391.465	348.053	43.412	−207.663	−236.936	12.376
1100	62.375	397.405	352.274	49.644	−208.385	−239.830	11.389
1200	62.514	402.838	356.265	55.888	−212.935	−242.431	10.553
1300	62.695	407.849	360.042	62.148	−213.344	−244.872	9.839
1400	62.922	412.503	363.625	68.429	−213.783	−247.281	9.226
1500	63.194	416.853	367.030	74.734	−214.260	−249.658	8.694
1600	63.505	420.941	370.273	81.069	−214.782	−252.001	8.227
1700	63.849	424.802	373.368	87.436	−215.356	−254.310	7.814
1800	64.219	428.461	376.328	93.840	−215.992	−256.583	7.446
1900	64.607	431.944	379.165	100.281	−216.701	−258.819	7.115
2000	65.003	435.268	381.887	106.761	−217.493	−261.016	6.817
2100	65.403	438.449	384.505	113.282	−218.380	−263.170	6.546
2200	65.798	441.501	387.027	119.842	−240.697	−264.535	6.281
2300	66.184	444.434	389.460	126.441	−242.227	−265.584	6.032
2400	66.558	447.259	391.810	133.078	−243.741	−266.567	5.802
2500	66.916	449.983	394.082	139.752	−245.242	−267.487	5.589
2600	67.256	452.614	396.283	146.461	−246.730	−268.348	5.391
2700	67.578	455.159	398.417	153.202	−248.208	−269.151	5.207
2800	67.881	457.622	400.488	159.975	−249.676	−269.900	5.035
2900	68.165	460.009	402.499	166.778	−251.134	−270.596	4.874
3000	68.432	462.324	404.455	173.608	−252.583	−271.243	4.723
3100	68.683	464.572	406.358	180.464	−254.023	−271.841	4.580
3200	68.918	466.757	408.212	187.344	−255.453	−272.393	4.446
3300	69.139	468.881	410.018	194.247	−256.871	−272.900	4.320
3400	69.347	470.948	411.780	201.171	−258.276	−273.365	4.200
3500	69.544	472.961	413.499	208.116	−259.668	−273.788	4.086
3600	69.731	474.923	415.178	215.080	−261.044	−274.172	3.978
3700	69.909	476.836	416.819	222.062	−262.403	−274.518	3.875
3800	70.079	478.702	418.423	229.061	−263.742	−274.828	3.778
3900	70.243	480.525	419.992	236.077	−265.061	−275.102	3.685
4000	70.400	482.305	421.528	243.110	−266.357	−275.343	3.596
4100	70.551	484.046	423.032	250.157	−267.629	−275.552	3.511
4200	70.698	485.747	424.505	257.220	−268.876	−275.730	3.429
4300	70.840	487.413	425.948	264.297	−270.095	−275.879	3.351
4400	70.978	489.043	427.364	271.388	−271.287	−275.999	3.277
4500	71.111	490.639	428.752	278.492	−272.449	−276.093	3.205
4600	71.240	492.204	430.115	285.610	−273.581	−276.162	3.136
4700	71.366	493.737	431.452	292.740	−274.682	−276.206	3.070
4800	71.487	495.241	432.765	299.883	−836.689	−264.610	2.880
4900	71.604	496.716	434.056	307.037	−837.379	−252.684	2.694
5000	71.717	498.164	435.323	314.203	−838.054	−240.745	2.515
5100	71.825	499.585	436.569	321.380	−838.713	−228.792	2.343
5200	71.929	500.981	437.795	328.568	−839.354	−216.827	2.178
5300	72.028	502.352	439.000	335.766	−839.976	−204.849	2.019
5400	72.123	503.699	440.186	342.974	−840.578	−192.860	1.866
5500	72.212	505.023	441.352	350.190	−841.160	−180.859	1.718
5600	72.296	506.325	442.501	357.416	−841.720	−168.849	1.575
5700	72.376	507.606	443.632	364.649	−842.258	−156.828	1.437
5800	72.449	508.865	444.746	371.891	−842.773	−144.799	1.304
5900	72.518	510.104	445.843	379.139	−843.265	−132.761	1.175
6000	72.581	511.323	446.924	386.394	−843.733	−120.714	1.051

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 348.05 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-276.5 \pm 17]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-302.9 \pm 17]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2239.2(1)	774. (2)
362. (1)	483.5(2)
168.5 (1)	116.8(2)

Ground State Quantum Weight: [1] $\sigma = 3$

Point Group: C_{3v}

Bond Distances: Si–H = 1.494 Å; Si–Br = 2.170 Å

Bond Angles: H–Si–Br = 107.51°; Br–Si–Br = 111.36°

Product of the Moments of Inertia: $I_A I_B I_C = 1.31228 \times 10^{-111}\ g \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of $SiBr_4$(g) and SiH_4(g). In adopting linear estimate for SiH_nBr_{4-n} (n=1,2,3), we dismiss the solution calorimetry of Wolf *et al.*[2] because of possible negative bias. These authors reported $\Delta_f H$(g, 298.15 K) = −69.3 ± 2.0 kcal·mol^{-1} derived from enthalpies of solution in dilute aqueous NaOH. Wagman *et al.*[3] changed this value to −75.9 kcal·mol^{-1} due to revised auxiliary data, especially $\Delta_f H°$ of Na_2SiO_3(cr) and Na_2SiO_5(sln). The calorimetric result is 3.5 kcal·mol^{-1} more negative than our linear estimate. This could imply a cubic variation of $\Delta_f H°(SiH_nBr_{4-n})$ with n, such as we adopt for the chlorosilanes.[1] We tentatively reject this hypothesis ecause the solution results[2] for $SiHCl_3$(g), $SiCl_4$(g), $SiBr_4$(l) and SiI_4(cr) are also more negative than our adopted values.[1] It is conceivable that the hydrolysis reactions did not proceed to equal degrees in the different calorimetric studies. We conclude, as did Hunt and Sirtl,[4] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Mitzlaff *et al.*[5] for eight isotopic forms of $SiHBr_3$ and $SiDBr_3$. Structural parameters are presumably substitutional (r_s) values. The principal moments of inertia are: $I_A = I_B = 87.7371 \times 10^{-39}$ and $I_C = 170.4749 \times 10^{-39}$ g cm^2. Vibrational frequencies are from gas-phase infrared spectra of Buerger and Cichon.[6] Assignments are based on band contour analysis and are consistent with Shimanouchi's values[7] derived from liquid–phase Raman spectra.[8]

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: Br_4Si(l, g), Br_2H_2Si(g), BrH_3Si(g), ClH_3Si(g), Cl_2H_2Si(g), Cl3HSi(g)l2–31–76; H_4Si(g), I_4Si(cr) 6–30–76.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.823	−276.529	−276.529	INFINITE
100	53.723	275.599	411.866	−13.627	−278.288	−292.351	152.709
200	69.766	318.044	355.097	−7.411	−281.949	−305.058	79.673
250	75.812	334.287	349.349	−3.765	−284.076	−310.594	64.895
298.15	80.410	348.049	348.049	0.	−302.922	−313.530	54.929
300	80.565	348.547	348.051	0.149	−303.046	−313.595	54.602
350	84.261	361.256	349.046	4.273	−349.657	−312.784	46.681
400	87.163	372.704	351.299	8.562	−349.928	−307.498	40.155
450	89.488	383.109	354.265	12.980	−350.126	−302.181	35.076
500	91.398	392.640	357.632	17.504	−350.263	−296.846	31.011
600	94.380	409.581	364.914	26.800	−350.386	−286.148	24.911
700	96.632	424.307	372.370	36.356	−350.355	−275.443	20.554
800	98.399	437.330	379.691	46.111	−350.214	−264.749	17.286
900	99.818	449.004	386.755	56.024	−349.996	−254.079	14.746
1000	100.970	459.583	393.518	66.065	−349.728	−243.435	12.716
1100	101.915	469.252	399.969	76.211	−349.433	−232.820	11.056
1200	102.697	478.155	406.119	86.443	−349.127	−222.232	9.674
1300	103.348	486.401	411.981	96.746	−348.825	−211.670	8.505
1400	103.894	494.081	417.574	107.109	−348.541	−201.131	7.504
1500	104.356	501.265	422.917	117.522	−348.284	−190.611	6.638
1600	104.748	508.013	428.026	127.978	−348.064	−180.106	5.880
1700	105.085	514.373	432.920	138.470	−398.065	−169.168	5.198
1800	105.374	520.388	437.614	148.993	−397.709	−155.714	4.519
1900	105.625	526.092	442.122	159.544	−397.368	−142.279	3.912
2000	105.844	531.516	446.457	170.117	−397.047	−128.861	3.366
2100	106.036	536.685	450.632	180.712	−396.751	−115.459	2.872
2200	106.205	541.622	454.656	191.324	−396.484	−102.071	2.423
2300	106.354	546.346	458.541	201.952	−396.249	−88.694	2.014
2400	106.486	550.875	462.294	212.594	−396.049	−75.326	1.639
2500	106.604	555.225	465.925	223.249	−395.884	−61.966	1.295
2600	106.710	559.408	469.441	233.914	−395.757	−48.612	0.977
2700	106.805	563.437	472.848	244.590	−395.666	−35.263	0.682
2800	106.891	567.323	476.153	255.275	−395.610	−21.916	0.409
2900	106.968	571.075	479.362	265.968	−395.589	−8.570	0.154
3000	107.039	574.703	482.480	276.669	−395.600	4.776	−0.083
3100	107.103	578.213	485.512	287.376	−395.640	18.122	−0.305
3200	107.161	581.615	488.462	298.089	−395.706	31.470	−0.514
3300	107.214	584.913	491.335	308.808	−395.794	44.821	−0.709
3400	107.263	588.115	494.135	319.532	−395.901	58.175	−0.894
3500	107.308	591.224	496.864	330.260	−396.023	71.531	−1.068
3600	107.350	594.248	499.528	340.993	−780.307	95.353	−1.384
3700	107.388	597.190	502.128	351.730	−780.033	119.673	−1.689
3800	107.423	600.054	504.667	362.471	−779.765	143.986	−1.979
3900	107.456	602.845	507.149	373.215	−779.497	168.291	−2.254
4000	107.486	605.566	509.575	383.962	−779.228	192.590	−2.515
4100	107.515	608.220	511.949	394.712	−778.952	216.882	−2.763
4200	107.541	610.812	514.272	405.465	−778.667	241.167	−2.999
4300	107.566	613.342	516.547	416.220	−778.371	265.446	−3.225
4400	107.589	615.815	518.775	426.978	−778.059	289.717	−3.439
4500	107.610	618.234	520.958	437.738	−777.731	313.981	−3.645
4600	107.630	620.599	523.099	448.500	−777.384	338.237	−3.841
4700	107.649	622.914	525.198	459.264	−777.015	362.486	−4.029
4800	107.667	625.180	527.258	470.030	−776.625	386.727	−4.208
4900	107.684	627.401	529.279	480.797	−776.210	410.959	−4.381
5000	107.699	629.576	531.263	491.566	−775.771	435.183	−4.546
5100	107.714	631.709	533.212	502.337	−775.305	459.397	−4.705
5200	107.728	633.801	535.126	513.109	−774.813	483.602	−4.858
5300	107.742	635.853	537.007	523.883	−774.294	507.798	−5.005
5400	107.754	637.867	538.856	534.657	−773.748	531.983	−5.146
5500	107.766	639.844	540.675	545.433	−773.173	556.158	−5.282
5600	107.777	641.786	542.463	556.211	−772.571	580.322	−5.413
5700	107.788	643.694	544.222	566.989	−771.941	604.476	−5.539
5800	107.798	645.569	545.953	577.768	−771.283	628.617	−5.661
5900	107.808	647.412	547.658	588.548	−770.598	652.748	−5.779
6000	107.817	649.224	549.335	599.330	−769.884	676.866	−5.893

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [174.5 \pm 17]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -283.7 \pm 25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Shukurov et al.[1] determined the enthalpy of combustion of $MoBr_3$(cr). Dellien *et al.*[2] obtained $\Delta_f H°(298.15\ K) = -64 \pm 5\ kcal \cdot mol^{-1}$ from the calorimetric result. Brewer[3] re-examined the equilibrium measurements of Oppermann[4] on the mixed solids $MoBr_2 + MoBr_3$ (see the discussion on the $MoBr_4$(g) table[5]) and obtained $\Delta_f H°(298.15\ K) = -67.8 \pm 6\ kcal \cdot mol^{-1}(-283.675 \pm 25\ kJ \cdot mol^{-1})$ which is the value adopted here.

Heat Capacity and Entropy

Brewer[3] estimated $S°(298.15\ K) = 41.7 \pm 4\ cal \cdot K^{-1} \cdot mol^{-1}(174.473 \pm 17\ J \cdot K^{-1} \cdot mol^{-1})$ and derived $C_p° = 24.14 + 3.50 \times 10^{-3} T\ cal \cdot K^{-1} \cdot mol^{-1}$(298–963 K) from the heat capacities estimated by Opperman.[4] Other estimates are $S°(298.15\ K) = 40.9\ cal \cdot K^{-1} \cdot mol^{-1}$ from the additive entropy constants of Stull and Prophet[6] and $C_p°(298.15\ K) = 23.3\ cal \cdot K^{-1} \cdot mol^{-1}$ from the ionic contributions of Kubaschewski and Unal.[7] We adopt the estimates of Brewer.[3]

Decomposition Data

T_{dcm} is the calculated temperature at which $\Delta_r G° = 0$ for the reaction 2 $MoBr_3$(cr) = $MoBr_2$(cr) + $MoBr_4$(g) at one bar.

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[5] JANAF Thermochemical Tables: $MoBr_4$(g), 9–30–78.

[6] D. R. Stull and H. Prophet, *in* "The Characterization of High-Temperature Vapors," J. L. Margrave (ed.), John Wiley, (1967).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	105.370	174.473	174.473	0.	−283.675	−259.095	45.392
300	105.395	175.125	174.475	0.195	−283.734	−258.942	45.086
400	106.859	205.645	178.626	10.808	−327.297	−241.576	31.547
500	108.324	229.648	186.514	21.567	−324.624	−220.454	23.031
600	109.788	249.527	195.406	32.472	−321.915	−199.874	17.401
700	111.253	266.561	204.383	43.524	−319.143	−179.752	13.413
800	112.717	281.512	213.108	54.723	−316.294	−160.032	10.449
900	114.181	294.873	221.464	66.068	−313.362	−140.675	8.165
1000	115.646	306.979	229.420	77.559	−310.344	−121.648	6.354
1100	117.110	318.070	236.982	89.197	−307.244	−102.928	4.888
1200	118.575	328.322	244.171	100.981	−304.066	−84.494	3.678
1300	120.039	337.871	251.016	112.912	−300.817	−66.327	2.665
1400	121.503	346.821	257.543	124.989	−297.504	−48.414	1.806
1500	122.968	355.254	263.778	137.213	−294.134	−30.739	1.070

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K) = [375.0 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [13.1 \pm 33]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-8.4 \pm 33]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[3505.43]	[2]
[10860.95]	[4]
[11062]	[4]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[170](1)	[260](2)
[95](1)	[90](2)

Point Group: [D_{3h}] σ = [6]
Bond Distance: Mo–Br = [2.42] Å
Bond Angle: Br–Mo–Br = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.16715 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K) = -2.0 \pm 8\ kcal \cdot mol^{-1}$ ($-8.368 \pm 33\ kJ \cdot mol^{-1}$) is that estimated by Brewer[1] who used bonding models to estimate the enthalpy of formation of MoBr(g), $MoBr_2$(g), and $MoBr_3$(g). The value of $\Delta_f H°(0\ K)$ combined with JANAF data[2] for Mo(g) and Br(g) leads to $\Delta_{at} H°(MoBr_3, g) = 238.6 \pm 8\ kcal \cdot mol^{-1}$. The mean bond energy $\Delta_{at} H°(MoBr_3, g)/3 = 79.5 \pm 3\ kcal \cdot mol^{-1}$ compared to $\Delta_{at} H°(MoBr_4, g)/4 = 76.0\ kcal \cdot mol^{-1}$.[4] The enthalpy of formation of $MoBr_4$(g) is based on the experimental measurements of Oppermann,[3] providing some confidence in the estimate of Brewer.

Heat Capacity and Entropy

Brewer[1] used a slight modification of the vibrational frequencies and internuclear distance estimated by Lofgren.[4] The Mo–Br distance was taken as 2.42 Å. Drake and Rosenblatt[5] predicted that $MoBr_3$ would be planar. The electronic contributions are taken to be the same as those for MoF_3(g)[2] which are estimated from TaO(g).[2] The principal moments of inertia are $I_A = I_B = 116.5591 \times 10^{-39}$ g cm^2 and $I_C = 233.1183 \times 10^{-39}\ g \cdot cm^2$.

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[2]JANAF Thermochemical Tables: $MoBr_4$(g) and MoF_3(g), 9–30–78; TaO(g), 12–31–73, Br(g), 9–30–61; Mo(g), 3–31–78.
[3]H. Oppermann, Z. anorg. allg. Chem. **395**, 249 (1973).
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[5]M. C. Drake and G. M. Rosenblatt, paper 388, The Electrochemical Society, Atlanta, Georgia, (October, 1977).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.910	13.071	13.071	INFINITE
100	65.839	293.440	443.828	−15.039	13.261	−7.303	3.815
200	77.191	343.488	382.257	−7.754	11.352	−27.224	7.110
250	79.157	360.945	376.306	−3.840	9.924	−36.710	7.670
298.15	80.270	374.990	374.990	0.	−8.368	−43.572	7.634
300	80.303	375.487	374.992	0.149	−8.474	−43.790	7.625
350	81.025	387.924	375.972	4.183	−54.628	−47.145	7.036
400	81.509	398.777	378.159	8.247	−54.551	−46.082	6.018
450	81.853	408.398	380.995	12.332	−54.493	−45.027	5.227
500	82.117	417.036	384.174	16.431	−54.453	−43.977	4.594
600	82.533	432.046	390.939	24.664	−54.416	−41.886	3.647
700	82.916	444.797	397.745	32.937	−54.423	−39.798	2.970
800	83.325	455.895	404.335	41.248	−54.462	−37.706	2.462
900	83.766	465.735	410.621	49.603	−54.520	−35.609	2.067
1000	84.222	474.584	416.582	58.002	−54.594	−33.504	1.750
1100	84.672	482.633	422.226	66.447	−54.686	−31.390	1.491
1200	85.099	490.019	427.572	74.936	−54.804	−29.267	1.274
1300	85.491	496.846	432.642	83.466	−54.956	−27.133	1.090
1400	85.845	503.195	437.457	92.033	−55.153	−24.986	0.932
1500	86.161	509.128	442.039	100.633	−55.406	−22.823	0.795
1600	86.445	514.698	446.408	109.264	−55.726	−20.641	0.674
1700	86.703	519.947	450.581	117.921	−56.125	−18.436	0.566
1800	86.943	524.909	454.574	126.604	−56.615	−16.206	0.470
1900	87.172	529.616	458.401	135.310	−57.207	−13.945	0.383
2000	87.395	534.093	462.074	144.038	−57.914	−11.650	0.304
2100	87.617	538.363	465.606	152.789	−58.746	−9.317	0.232
2200	87.841	542.444	469.007	161.562	−59.714	−6.941	0.165
2300	88.067	546.354	472.285	170.357	−60.832	−4.518	0.103
2400	88.297	550.106	475.450	179.175	−62.108	−2.043	0.044
2500	88.531	553.716	478.509	188.016	−63.556	0.489	−0.010
2600	88.766	557.192	481.469	196.881	−65.196	3.083	−0.062
2700	89.001	560.547	484.336	205.770	−67.068	5.743	−0.111
2800	89.235	563.788	487.116	214.681	−69.233	8.479	−0.158
2900	89.464	566.923	489.814	223.616	−107.653	11.347	−0.204
3000	89.688	569.960	492.435	232.574	−108.604	15.467	−0.269
3100	89.904	572.905	494.984	241.554	−109.558	19.618	−0.331
3200	90.110	575.762	497.464	250.555	−110.511	23.800	−0.388
3300	90.305	578.538	499.879	259.576	−111.461	28.012	−0.443
3400	90.487	581.237	502.232	268.615	−112.406	32.253	−0.496
3500	90.656	583.862	504.527	277.673	−113.343	36.521	−0.545
3600	90.810	586.418	506.766	286.746	−114.269	40.816	−0.592
3700	90.949	588.908	508.953	295.834	−115.182	45.137	−0.637
3800	91.072	591.335	511.089	304.935	−116.079	49.481	−0.680
3900	91.180	593.702	513.177	314.048	−116.958	53.850	−0.721
4000	91.272	596.012	515.219	323.171	−117.817	58.241	−0.761
4100	91.350	598.267	517.218	332.302	−118.655	62.652	−0.798
4200	91.412	600.469	519.174	341.440	−119.470	67.084	−0.834
4300	91.459	602.620	521.089	350.584	−120.260	71.535	−0.869
4400	91.493	604.723	522.966	359.731	−121.026	76.005	−0.902
4500	91.513	606.780	524.806	368.882	−121.765	80.491	−0.934
4600	91.521	608.791	526.610	378.034	−122.477	84.994	−0.965
4700	91.517	610.759	528.380	387.186	−123.162	89.511	−0.995
4800	91.502	612.686	530.116	396.337	−123.820	94.043	−1.023
4900	91.476	614.573	531.820	405.486	−124.450	98.589	−1.051
5000	91.441	616.420	533.494	414.632	−716.437	108.878	−1.137
5100	91.397	618.231	535.138	423.774	−718.691	125.407	−1.284
5200	91.345	620.005	536.753	432.911	−721.065	141.980	−1.426
5300	91.285	621.744	538.340	442.042	−723.555	158.601	−1.563
5400	91.219	623.450	539.900	451.168	−726.162	175.270	−1.695
5500	91.147	625.123	541.435	460.286	−728.882	191.988	−1.823
5600	91.069	626.765	542.944	469.397	−731.715	208.756	−1.947
5700	90.987	628.376	544.429	478.500	−734.658	225.577	−2.067
5800	90.900	629.958	545.890	487.594	−737.709	242.448	−2.183
5900	90.810	631.511	547.328	496.680	−740.864	259.375	−2.296
6000	90.716	633.036	548.744	505.756	−744.125	276.355	−2.406

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = 359.83\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-362.5]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-389.1]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
118 (2)	340 (1)
173 (1)	488 (2)
267 (2)	1261 (1)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: P–O = 1.41 ± 0.07 Å; P–Br = 2.06 ± 0.03 Å
Bond Angle: Br–P–Br = 108° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 1.11121 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(POBr_3, g, 298.15\ K)$ is calculated from the enthalpy of formation of the crystal and the enthalpy of sublimation. The enthalpy of sublimation is obtained by combining the $\Delta_{vap}H°$ and an estimated $\Delta_{fus}H°$.The enthalpy of formation of the crystal is derived from the enthalpies observed for the reaction:$POBr_3(cr) + (n+3)H_2O(l) \rightarrow [H_3PO_4 + 3\ HBr]$ in $n H_2O(l)$. The data used in these calculations may be summarized as follows:

Data	Source
$\Delta_f H°(H_3PO_4, aq, 298.15\ K)$	Obtained graphically from Holmes[1]
$\Delta_f H°(HBr, aq, 298.15\ K)$	Obtained graphically from[2]
$\Delta_f H°(H_2O, l, 298.15\ K) = -68.3174\ kcal·mol^{-1}$	Obtained from[2]
$\Delta_f H°(POBr_3, cr, 298.15\ K) = -109.1\ kcal·mol^{-1}$	Recalculated from data of Charnley and Skinner[3]
$\Delta_{fus}H°(298.15\ K) = [3.7]\ kcal·mol^{-1}$	Estimated from comparison with $POCl_3$
$\Delta_{vap}H°(298.15\ K) = [12.1]\ kcal·mol^{-1}$	Estimated from the $\Delta_{vap}H°$ at T_{vap}(10.6 $kcal·mol^{-1}$ at 464.9 K).Δ_{vap}H was calculated from a least squares treatment of the vapor pressure data of Driel[4]

Heat Capacity and Entropy

The molecular constants used were calculated from electron diffraction measurements by Secrist and Brockway.[5] The principal moments of inertia are: $I_A = I_B = 86.8222 \times 10^{-39}\ g·cm^2$ and $I_C = 147.4125 \times 10^{-39}\ g·cm^2$.

From the Raman spectra of $POBr_3$ the vibrational frequencies were measured and assigned by Gerding and Driel.[6] The Raman spectra was studied and the vibrational frequencies were listed by Delwaulle and Francois.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	.000	.000	INFINITE	−19.850	−362.496	−362.496	INFINITE
100	59.241	277.279	432.506	−15.523	−364.698	−373.915	195.313
150	71.868	303.845	385.347	−12.225	−366.394	−378.155	131.685
200	80.331	325.763	367.792	−8.406	−368.652	−381.805	99.717
250	85.998	344.337	361.291	−4.239	−370.529	−384.880	80.416
298.15	89.862	359.832	359.832	.000	−389.112	−385.496	67.537
300	89.989	360.388	359.834	.166	−389.227	−385.473	67.117
350	92.960	374.494	360.941	4.743	−436.299	−382.228	57.044
400	95.267	387.063	363.435	9.451	−436.399	−374.496	48.904
450	97.107	398.394	366.700	14.262	−436.425	−366.756	42.572
500	98.602	408.706	370.393	19.156	−436.394	−359.016	37.506
600	100.851	426.894	378.334	29.136	−436.206	−343.555	29.909
700	102.423	442.566	386.417	39.304	−435.905	−328.136	24.486
800	103.555	456.320	394.313	49.606	−435.533	−312.765	20.421
900	104.391	468.568	401.895	60.005	−435.115	−297.444	17.263
1000	105.022	479.601	409.123	70.477	−434.668	−282.171	14.739
1100	105.508	489.634	415.993	81.005	−434.202	−266.944	12.676
1200	105.890	498.832	422.519	91.576	−497.298	−250.681	10.912
1300	106.194	507.320	428.719	102.180	−496.044	−230.181	9.249
1400	106.441	515.199	434.618	112.813	−494.795	−209.777	7.827
1500	106.643	522.550	440.238	123.467	−493.556	−189.462	6.598
1600	106.810	529.438	445.600	134.140	−492.331	−169.229	5.525
1700	106.950	535.917	450.724	144.828	−491.124	−149.072	4.580
1800	107.069	542.034	455.629	155.529	−489.938	−128.986	3.743
1900	107.170	547.826	460.330	166.241	−488.778	−108.964	2.996
2000	107.257	553.325	464.844	176.963	−487.647	−89.003	2.325
2100	107.332	558.560	469.183	187.692	−486.549	−69.098	1.719
2200	107.398	563.555	473.360	198.429	−485.488	−49.244	1.169
2300	107.455	568.330	477.386	209.172	−484.466	−29.438	.669
2400	107.506	572.904	481.271	219.920	−483.485	−9.676	.211
2500	107.551	577.294	485.025	230.673	−482.546	10.047	−.210
2600	107.590	581.513	488.655	241.430	−481.650	29.733	−.597
2700	107.626	585.574	492.170	252.191	−480.795	49.385	−.955
2800	107.658	589.489	495.576	262.955	−479.980	69.006	−1.287
2900	107.687	593.267	498.880	273.722	−479.205	88.599	−1.596
3000	107.712	596.918	502.088	284.492	−478.465	108.166	−1.883
3100	107.736	600.450	505.204	295.264	−477.758	127.709	−2.152
3200	107.757	603.871	508.234	306.039	−477.080	147.228	−2.403
3300	107.777	607.187	511.183	316.816	−476.427	166.728	−2.639
3400	107.795	610.405	514.054	327.594	−475.796	186.208	−2.861
3500	107.811	613.530	516.852	338.375	−475.182	205.669	−3.069
3600	107.826	616.567	519.580	349.157	−474.580	225.114	−3.266
3700	107.840	619.522	522.241	359.940	−473.987	244.542	−3.452
3800	107.853	622.398	524.839	370.725	−473.399	263.954	−3.628
3900	107.864	625.200	527.377	381.510	−472.811	283.350	−3.795
4000	107.875	627.931	529.856	392.297	−472.221	302.731	−3.953
4100	107.885	630.595	532.281	403.085	−471.624	322.098	−4.104
4200	107.895	633.195	534.653	413.874	−471.017	341.449	−4.247
4300	107.904	635.733	536.974	424.664	−470.399	360.787	−4.383
4400	107.912	638.214	539.247	435.455	−469.765	380.109	−4.512
4500	107.920	640.639	541.473	446.247	−469.115	399.417	−4.636
4600	107.927	643.011	543.655	457.039	−468.446	418.710	−4.755
4700	107.933	645.333	545.794	467.832	−467.756	437.989	−4.868
4800	107.940	647.605	547.891	478.626	−467.045	457.253	−4.976
4900	107.946	649.831	549.949	489.420	−466.311	476.502	−5.080
5000	107.951	652.012	551.969	500.215	−465.553	495.735	−5.179
5100	107.957	654.149	553.951	511.010	−464.772	514.954	−5.274
5200	107.962	656.246	555.898	521.806	−463.966	534.155	−5.366
5300	107.966	658.302	557.811	532.603	−463.135	553.343	−5.454
5400	107.971	660.320	559.691	543.399	−462.281	572.514	−5.538
5500	107.975	662.302	561.539	554.197	−461.402	591.668	−5.619
5600	107.979	664.247	563.355	564.994	−460.500	610.807	−5.697
5700	107.983	666.158	565.142	575.792	−459.574	629.929	−5.773
5800	107.986	668.036	566.900	586.591	−458.627	649.035	−5.845
5900	107.989	669.882	568.630	597.390	−457.657	668.123	−5.915
6000	107.993	671.697	570.333	608.189	−456.667	687.197	−5.983

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = 348.234\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -121.7 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -146.0 \pm 6.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
392 (1)	392.2 (2)
161.3 (1)	115.7 (2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distance: P–Br = 2.20 ± 0.03 Å
Bond Angle: Br–P–Br = 106° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 1.18987 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of PBr gas from white (α) phosphorus, −34.9 kcal·mol^{-1}, was obtained by Charnley and Skinner.[1] To obtain their value (−34.9 kcal·mol^{-1}), Charnley and Skinner[1] measured the enthalpy of formation of the liquid, and combined it and their estimate of the liquid enthalpy with the enthalpy of vaporization (9.5 kcal·mol^{-1}) calculated by Driel and Gerding.[2] For the liquid enthalpy of formation Charnley and Skinner[1] observed the $\Delta_r H° = -67.2 \pm 0.6$ kcal·mol^{-1} for $PBr_3(l) + (n+3)H_2O(l) \rightarrow [H_3PO_3 + 3HBr]$ in $nH_2O(l)$. Driel and Gerding[2] measured the vapor pressure over $PBr_3(l)$ and calculated the enthalpy of vaporization with the aid of a modified Claperyron equation. The uncertainties on the enthalpy of formation are estimates.

Heat Capacity and Entropy

Williams and Gordy[3] have reported moments of inertia from the microwave spectrum of PBr_3. From this data Whiffen[4] has calculated the selected molecular constants. The principal moments of inertia are: $I_A = I_B = 85.2188 \times 10^{-39}$ g cm^2 and $I_C = 163.8427 \times 10^{-39}$ g◀cm^2.

Lister and Sutton[5] have reported P–Br = 2.23 ± 0.04 Å and the angle Br–P–Br = 100 ± 2. Swingle[6] has measured P–Br = 2.18 ± 0.03 Å and the angle Br–P–Br = 101.5 ± 1.5. Swingle's data as well as that of Lister and Sutton were obtained by electron diffraction. The 106° angle was selected since 101.5° and 100° give imaginary force constants with the ranges allowed for the type A, 392 cm^{-1} frequency and the form of the potential function assumed by Davis and Oetjen.[7]

The vibrational frequencies were measured and assigned in the infrared by Davis and Oetjen.[7] Raman measurements and assignments by Cabannes and Rausset[8] were also listed by Delwaulle.[9] The Raman assignments were as follows: type A, 380 cm^{-1} and 162 cm^{-1} and type E, 400 cm^{-1} and 116 cm^{-1}.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.753	−121.651	−121.651	INFINITE
100	54.768	275.812	411.024	−13.521	−122.496	−140.231	73.249
200	69.764	319.032	355.025	−7.199	−125.788	−156.943	40.989
250	73.619	335.046	349.473	−3.607	−127.512	−164.539	34.378
298.15	76.033	348.234	348.234	0.	−146.022	−169.530	29.701
300	76.108	348.704	348.235	0.141	−146.135	−169.675	29.543
350	77.770	360.569	349.168	3.990	−193.196	−170.981	25.518
400	78.922	371.034	351.260	7.909	−193.338	−167.797	21.912
450	79.748	380.380	353.986	11.877	−193.449	−164.598	19.106
500	80.357	388.815	357.054	15.881	−193.537	−161.387	16.860
600	81.176	403.545	363.610	23.961	−193.669	−154.944	13.489
700	81.683	416.099	370.234	32.105	−193.764	−148.482	11.080
800	82.018	427.029	376.665	40.292	−193.840	−142.007	9.272
900	82.250	436.704	382.809	48.506	−193.904	−135.525	7.866
1000	82.417	445.379	388.640	56.739	−193.964	−129.035	6.740
1100	82.542	453.240	394.161	64.988	−194.023	−122.539	5.819
1200	82.637	460.427	399.388	73.247	−257.656	−114.959	5.004
1300	82.711	467.044	404.341	81.514	−256.947	−103.097	4.142
1400	82.771	473.176	409.041	89.789	−256.250	−91.288	3.406
1500	82.818	478.888	413.509	98.068	−255.566	−79.529	2.769
1600	82.858	484.234	417.764	106.352	−254.896	−67.816	2.214
1700	82.890	489.259	421.824	114.639	−254.243	−56.143	1.725
1800	82.918	493.997	425.703	122.930	−253.610	−44.508	1.292
1900	82.941	498.481	429.416	131.223	−252.999	−32.908	0.905
2000	82.960	502.736	432.977	139.518	−252.414	−21.340	0.557
2100	82.977	506.784	436.396	147.815	−251.856	−9.800	0.244
2200	82.992	510.644	439.684	156.113	−251.329	1.714	−0.041
2300	83.005	514.334	442.850	164.413	−250.835	13.205	−0.300
2400	83.016	517.867	445.903	172.714	−250.374	24.675	−0.537
2500	83.026	521.256	448.849	181.016	−249.948	36.126	−0.755
2600	83.035	524.512	451.697	189.319	−249.558	47.561	−0.956
2700	83.043	527.646	454.453	197.623	−249.201	58.982	−1.141
2800	83.050	530.667	457.121	205.928	−248.877	70.390	−1.313
2900	83.057	533.581	459.707	214.233	−248.585	81.788	−1.473
3000	83.062	536.397	462.217	222.539	−248.320	93.175	−1.622
3100	83.067	539.121	464.654	230.846	−248.081	104.554	−1.762
3200	83.072	541.758	467.023	239.153	−247.864	115.926	−1.892
3300	83.076	544.314	469.326	247.460	−247.666	127.291	−2.015
3400	83.080	546.794	471.568	255.768	−247.481	138.651	−2.130
3500	83.084	549.203	473.752	264.076	−247.307	150.005	−2.239
3600	83.087	551.543	475.881	272.385	−247.139	161.355	−2.341
3700	83.090	553.820	477.957	280.694	−246.974	172.700	−2.438
3800	83.093	556.036	479.982	289.003	−246.806	184.039	−2.530
3900	83.096	558.194	481.960	297.312	−246.634	195.375	−2.617
4000	83.098	560.298	483.893	305.622	−246.453	206.707	−2.699
4100	83.100	562.350	485.781	313.932	−246.260	218.033	−2.778
4200	83.102	564.353	487.628	322.242	−246.052	229.355	−2.852
4300	83.104	566.308	489.435	330.552	−245.826	240.671	−2.924
4400	83.106	568.219	491.204	338.863	−245.580	251.983	−2.991
4500	83.108	570.086	492.936	347.174	−245.312	263.288	−3.056
4600	83.109	571.913	494.634	355.485	−245.019	274.587	−3.118
4700	83.111	573.700	496.297	363.796	−244.700	285.879	−3.177
4800	83.112	575.450	497.928	372.107	−244.354	297.165	−3.234
4900	83.113	577.164	499.527	380.418	−243.979	308.442	−3.288
5000	83.115	578.843	501.097	388.729	−243.574	319.712	−3.340
5100	83.116	580.489	502.638	397.041	−243.139	330.974	−3.390
5200	83.117	582.103	504.150	405.353	−242.673	342.226	−3.438
5300	83.118	583.686	505.636	413.664	−242.176	353.470	−3.484
5400	83.119	585.240	507.096	421.976	−241.647	364.704	−3.528
5500	83.120	586.765	508.531	430.288	−241.087	375.927	−3.570
5600	83.121	588.262	509.941	438.600	−240.494	387.140	−3.611
5700	83.121	589.734	511.328	446.912	−239.871	398.343	−3.650
5800	83.122	591.179	512.692	455.224	−239.215	409.533	−3.688
5900	83.123	592.600	514.035	463.537	−238.529	420.713	−3.725
6000	83.124	593.997	515.356	471.849	−237.812	431.880	−3.760

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = 372.828\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-238.2]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-263.6]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
299 (1)
438 (2)
718 (1)
115 (2)
165 (1)
179 (2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: P–Br = 2.13 ± 0.03 Å; P–S = 1.89 ± 0.06 Å
Bond Angle: Br–P–Br = 106° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 1.94531 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(PSBr_3, g, 298.15\ K)$ was calculated from the $\Delta_f H°(POBr_3, g, 298.15\ K)$ and estimated strengths for P–S and P–O bonds.

The difference in the P–S and P–O bond strengths was assumed to be the same for $POF_3 - PSF_3$ and $POBr_3 - PSBr_3$. For the P–S bond strength in PSF_3, Henderson and Scheffee[1] estimated 91 kcal from a consideration of unpublished data. The P–O bond was estimated to be 115 kcal by Neale and Williams[2] and Neale *et al.*[3]

Auxiliary data for $POBr_3$(g), O(g), and S(g) are from the JANAF tables.[4]

Heat Capacity and Entropy

The molecular constants were determined from electron diffraction data by Secrist and Brockway.[5] The principal moments of inertia are: $I_A = I_B = 112.5445 \times 10^{-39}\ g\ cm^2$ and $I_C = 153.5823 \times 10^{-39}\ g·cm^2$.

The vibrational frequencies obtained from the Raman spectra of $PSBr_3$ were reported by Delwaulle and Francois.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	.000	.000	INFINITE	−21.191	−238.247	−238.247	INFINITE
100	65.087	284.297	450.202	−16.591	−239.413	−256.745	134.110
150	77.458	313.212	399.905	−13.004	−240.831	−265.111	92.320
200	85.612	336.689	381.258	−8.914	−242.994	−272.953	71.288
250	91.175	356.429	374.371	−4.486	−244.900	−280.228	58.550
298.15	94.934	372.828	372.828	.000	−263.592	−284.875	49.909
300	95.055	373.415	372.829	.176	−263.712	−285.007	49.624
350	97.818	388.287	373.998	5.001	−310.964	−285.923	42.672
400	99.831	401.487	376.624	9.945	−313.512	−282.235	36.856
450	101.330	413.336	380.056	14.976	−314.485	−278.276	32.301
500	102.468	424.074	383.930	20.072	−315.483	−274.196	28.645
600	104.045	442.907	392.234	30.404	−316.948	−265.793	23.139
700	105.051	459.026	400.652	40.862	−318.077	−257.175	19.191
800	105.728	473.101	408.847	51.403	−319.008	−248.409	16.219
900	106.204	485.583	416.693	62.001	−372.945	−238.454	13.840
1000	106.551	496.792	424.152	72.640	−372.457	−223.537	11.676
1100	106.810	506.960	431.225	83.309	−371.967	−208.668	9.909
1200	107.010	516.262	437.929	94.000	−435.055	−192.766	8.391
1300	107.166	524.834	444.289	104.709	−433.807	−172.626	6.936
1400	107.291	532.781	450.329	115.432	−432.579	−152.582	5.693
1500	107.392	540.187	456.076	126.167	−431.373	−132.624	4.618
1600	107.475	547.120	461.552	136.910	−430.192	−112.746	3.681
1700	107.544	553.638	466.779	147.661	−429.038	−92.941	2.856
1800	107.602	559.787	471.777	158.419	−427.914	−73.204	2.124
1900	107.652	565.606	476.563	169.181	−426.823	−53.527	1.472
2000	107.694	571.129	481.155	179.949	−425.767	−33.907	.886
2100	107.730	576.384	485.565	190.720	−424.747	−14.340	.357
2200	107.762	581.397	489.808	201.495	−423.767	5.180	−.123
2300	107.789	586.187	493.895	212.272	−422.826	24.657	−.560
2400	107.813	590.775	497.837	223.052	−421.928	44.093	−.960
2500	107.835	595.177	501.643	233.835	−421.070	63.493	−1.327
2600	107.854	599.407	505.322	244.619	−420.254	82.859	−1.665
2700	107.871	603.477	508.883	255.405	−419.477	102.195	−1.977
2800	107.886	607.401	512.332	266.193	−418.738	121.502	−2.267
2900	107.899	611.187	515.676	276.982	−418.035	140.784	−2.536
3000	107.912	614.845	518.921	287.773	−417.365	160.042	−2.787
3100	107.923	618.384	522.072	298.565	−416.724	179.279	−3.021
3200	107.933	621.810	525.136	309.358	−416.109	198.494	−3.240
3300	107.942	625.132	528.116	320.151	−415.516	217.692	−3.446
3400	107.950	628.354	531.017	330.946	−414.941	236.871	−3.639
3500	107.958	631.483	533.843	341.741	−414.380	256.034	−3.821
3600	107.965	634.525	536.598	352.538	−413.829	275.181	−3.993
3700	107.972	637.483	539.285	363.334	−413.284	294.312	−4.155
3800	107.978	640.363	541.907	374.132	−412.741	313.429	−4.308
3900	107.983	643.167	544.467	384.930	−412.197	332.532	−4.454
4000	107.988	645.901	546.969	395.728	−411.649	351.621	−4.592
4100	107.993	648.568	549.415	406.528	−411.093	370.695	−4.723
4200	107.998	651.170	551.807	417.327	−410.527	389.756	−4.847
4300	108.002	653.712	554.147	428.127	−409.948	408.804	−4.966
4400	108.006	656.195	556.438	438.927	−409.353	427.838	−5.079
4500	108.009	658.622	558.682	449.728	−408.742	446.858	−5.187
4600	108.012	660.996	560.881	460.529	−408.112	465.865	−5.290
4700	108.016	663.319	563.036	471.331	−407.461	484.857	−5.389
4800	108.019	665.593	565.149	482.132	−406.789	503.836	−5.483
4900	108.021	667.820	567.221	492.934	−406.095	522.800	−5.573
5000	108.024	670.003	569.255	503.737	−405.377	541.750	−5.660
5100	108.026	672.142	571.252	514.539	−404.636	560.685	−5.743
5200	108.029	674.239	573.212	525.342	−403.870	579.605	−5.822
5300	108.031	676.297	575.138	536.145	−403.080	598.511	−5.899
5400	108.033	678.316	577.030	546.948	−402.265	617.401	−5.972
5500	108.035	680.299	578.889	557.751	−401.426	636.276	−6.043
5600	108.037	682.245	580.718	568.555	−400.562	655.136	−6.111
5700	108.039	684.158	582.516	579.359	−399.673	673.980	−6.176
5800	108.040	686.037	584.284	590.163	−398.761	692.807	−6.239
5900	108.042	687.884	586.025	600.967	−397.825	711.620	−6.300
6000	108.043	689.699	587.738	611.771	−396.866	730.416	−6.359

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = [351.77 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-179.1 \pm 63]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-201.7 \pm 63]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[362] (1)
[168] (1)
[483.5](2)
[116.8](2)

Ground State Quantum Weight: [2] σ = [3]
Point Group: [C_{3v}]
Bond Distance: Si–Br = [2.17] Å
Bond Angle: Br–Si–Br = [111.36]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.29082 \times 10^{111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of $SiBr_3$(g) is based on an assumed average bond energy of 78 ± 5 $kcal \cdot mol^{-1}$.[1] This average bond energy is that of $SiBr_4$(g), i.e. $\Delta_a H°(SiBr_4, g)/4$. The rationale for this assumption is based on the same relationship existing for the silicon chloride and fluoride species.[1]

Heat Capacity and Entropy

The molecular structure is assumed to be identical to the $SiBr_3$ group in $SiHBr_3$.[1] From this structure we estimate the following principal moments of inertia: $I_A = I_B = 87.0168 \times 10^{-39}$, and $I_C = 170.479 \times 10^{-39}$ $g \cdot cm^2$. The vibrational requencies are assumed to be those of the $SiBr_3$ group in $SiHBr_3$(g).

Reference

[1]JANAF Thermochemical Tables: $SiCl_3$(g) and SiF_3(g), 12–31–77; $SiBr_4$(g) and $SiHBr_3$(g), 12–31–76.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.370	−179.082	−179.082	INFINITE
100	53.692	281.244	412.980	−13.174	−179.341	−199.005	103.950
200	67.782	323.273	358.414	−7.028	−181.727	−217.822	56.889
250	71.881	338.868	352.988	−3.530	−183.302	−226.671	47.360
298.15	74.578	351.774	351.774	0.	−201.694	−232.894	40.802
300	74.663	352.236	351.776	0.138	−201.803	−233.087	40.584
350	76.584	363.898	352.692	3.922	−248.029	−235.764	35.186
400	77.944	374.218	354.750	7.787	−247.995	−234.014	30.559
450	78.934	383.459	357.436	11.710	−247.958	−232.268	26.961
500	79.673	391.816	360.463	15.676	−247.921	−230.527	24.083
600	80.677	406.438	366.941	23.698	−247.855	−227.055	19.767
700	81.305	418.925	373.497	31.799	−247.809	−223.592	16.685
800	81.723	429.811	379.871	39.952	−247.794	−220.134	14.373
900	82.014	439.454	385.966	48.140	−247.815	−216.675	12.576
1000	82.224	448.107	391.754	56.352	−247.874	−213.213	11.137
1100	82.381	455.951	397.240	64.583	−247.974	−209.742	9.960
1200	82.501	463.125	402.435	72.827	−248.116	−206.260	8.978
1300	82.595	469.732	407.361	81.082	−248.302	−202.765	8.147
1400	82.670	475.856	412.038	89.346	−248.536	−199.254	7.434
1500	82.731	481.562	416.485	97.616	−248.818	−195.724	6.816
1600	82.780	486.903	420.721	105.892	−249.152	−192.174	6.274
1700	82.822	491.923	424.763	114.172	−299.718	−188.154	5.781
1800	82.856	496.658	428.627	122.456	−299.935	−181.586	5.269
1900	82.886	501.138	432.326	130.743	−300.171	−175.004	4.811
2000	82.911	505.390	435.874	139.033	−300.429	−168.410	4.398
2100	82.932	509.436	439.281	147.325	−300.712	−161.802	4.025
2200	82.951	513.294	442.559	155.619	−301.023	−155.180	3.684
2300	82.967	516.982	445.715	163.915	−301.365	−148.543	3.374
2400	82.982	520.514	448.758	172.212	−301.739	−141.891	3.088
2500	82.994	523.901	451.697	180.511	−302.145	−135.222	2.825
2600	83.006	527.157	454.537	188.811	−302.584	−128.537	2.582
2700	83.016	530.289	457.285	197.112	−303.056	−121.834	2.357
2800	83.025	533.309	459.946	205.414	−303.559	−115.113	2.147
2900	83.033	536.222	462.527	213.717	−304.091	−108.373	1.952
3000	83.040	539.037	465.030	222.021	−304.650	−101.615	1.769
3100	83.047	541.760	467.462	230.325	−305.232	−94.838	1.598
3200	83.053	544.397	469.825	238.630	−305.835	−88.041	1.437
3300	83.058	546.953	472.124	246.936	−306.455	−81.225	1.286
3400	83.063	549.432	474.361	255.242	−307.088	−74.391	1.143
3500	83.068	551.840	476.541	263.548	−307.729	−67.538	1.008
3600	83.072	554.180	478.665	271.855	−692.528	−50.205	0.728
3700	83.076	556.457	480.737	280.163	−692.761	−32.359	0.457
3800	83.079	558.672	482.759	288.470	−692.993	−14.508	0.199
3900	83.082	560.830	484.733	296.778	−693.220	3.350	−0.045
4000	83.086	562.934	486.662	305.087	−693.438	21.214	−0.277
4100	83.088	564.985	488.547	313.396	−693.643	39.082	−0.498
4200	83.091	566.988	490.391	321.705	−693.833	56.956	−0.708
4300	83.093	568.943	492.195	330.014	−694.003	74.834	−0.909
4400	83.096	570.853	493.961	338.323	−694.153	92.716	−1.101
4500	83.098	572.720	495.691	346.633	−694.278	110.601	−1.284
4600	83.100	574.547	497.385	354.943	−694.378	128.488	−1.459
4700	83.102	576.334	499.046	363.253	−694.450	146.377	−1.627
4800	83.103	578.084	500.675	371.563	−694.493	164.268	−1.788
4900	83.105	579.797	502.272	379.874	−694.505	182.159	−1.942
5000	83.107	581.476	503.839	388.184	−694.487	200.050	−2.090
5100	83.108	583.122	505.378	396.495	−694.436	217.940	−2.232
5200	83.109	584.736	506.889	404.806	−694.353	235.829	−2.369
5300	83.111	586.319	508.372	413.117	−694.238	253.716	−2.501
5400	83.112	587.872	509.830	421.428	−694.089	271.601	−2.627
5500	83.113	589.397	511.263	429.739	−693.907	289.482	−2.749
5600	83.114	590.895	512.672	438.050	−693.693	307.360	−2.867
5700	83.115	592.366	514.057	446.362	−693.446	325.234	−2.980
5800	83.116	593.812	515.420	454.674	−693.168	343.103	−3.090
5900	83.117	595.232	516.760	462.985	−692.859	360.967	−3.196
6000	83.118	596.629	518.080	471.297	−692.518	378.825	−3.298

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 176.4 \pm 3.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 179.9\ K$

$\Delta_f H°(0\ K) = -531.6 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -550.2 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiBr_3$(cr) is based on the vapor pressure data reported by Hall and Blocher[1] for the process $1/2Hg_2Br_2(cr) + TiBr_3(cr) = TiBr_4(g) + Hg(l)$ over the temperature range 430 to 546 K. 2nd and 3rd law analyses of these data give values for the enthalpy of reaction of 24.2 ± 0.3 and 24.4 kcal·mol^{-1}, respectively, for seventy three points, with ten points rejected due to failure of a statistical test. The 3rd law drift in the data is calculated as 0.6 ± 0.8 cal·K^{-1}mol^{-1}. The 3rd law value of 24.4 kcal·mol^{-1} is combined with the JANAF enthalpies of formation of $TiBr_4$(g) and $HgBr_2$(cr) to obtain the adopted enthalpy of formation, $\Delta_f H°$(cr, 298.15 K) = −131.5 ± 2.0 kcal·mol^{-1} (−550.196 ± 8.4 kJ·mol^{-1}).

Heat Capacity and Entropy

The heat capacity and entropy of $TiBr_3$(cr) have been measured over the temperature range 51 to 800 K by King *et al.*[2] Heat capacities above 800 K are estimated from graphical extrapolation. The value of $S°(298.15\ K)$ is derived from these data, based on $S°(51\ K) = 8.60$ cal·K^{-1}·mol^{-1}. The value of $S°(51\ K)$ is estimated from a Debye–Einstein extrapolation of the measured heat capacities, the equation being $C_p° = D(70.0/T) + E(120/T) + 2E(306/T)$. It is assumed that all electronic entropy is contained within the measured and extrapolated heat capacities.

Transition Data

A second order transition at 179.9 K was observed by King *et al.*[2] The heat capacity at this temperature is in excess of 56.1 cal·K^{-1}·mol^{-1}. King *et al.*[2] measured the value of $H°(188\ K) - H°(160\ K)$ as 0.773 kcal·mol^{-1}.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $TiBr_3$(cr) and $TiBr_3$(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_f G = 0$ for the process $TiBr_3(cr) = TiBr_3(g)$ at one bar.

References

[1]E. H. Hall and J. M. Blocher, Jr., J. Electrochem. Soc. **105**, 40 (1958).
[2]E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−22.970	−531.572	−531.572	INFINITE
100	70.655	74.136	264.466	−19.033	−532.385	−530.896	277.312
200	97.818	137.244	185.506	−9.652	−532.274	−529.251	138.226
298.15	101.705	176.443	176.443	0.	−550.196	−525.561	92.076
300	101.776	177.073	176.445	0.188	−550.264	−525.408	91.482
400	105.818	206.789	180.471	10.527	−594.259	−507.949	66.331
500	114.709	231.322	188.246	21.538	−591.526	−486.673	50.842
600	125.507	253.176	197.274	33.541	−587.928	−466.024	40.571
700	137.210	273.423	206.722	46.691	−583.274	−446.060	33.285
800	147.277	292.463	216.262	60.961	−577.557	−426.837	27.870
900	151.879	310.075	225.722	75.918	−571.237	−408.372	23.701
1000	156.673	326.329	234.980	91.349	−564.588	−390.630	20.404
1100	161.084	341.471	243.980	107.240	−557.687	−373.567	17.739
1200	165.111	355.663	252.702	123.553	−554.556	−357.021	15.541
1300	168.755	369.025	261.141	140.250	−546.541	−340.883	13.697
1400	172.015	381.653	269.302	157.291	−538.272	−325.372	12.140
1500	174.891	393.621	277.195	174.640	−529.802	−310.459	10.811

PREVIOUS: June 1964 CURRENT: June 1968

$S°(298.15\ K) = [359.1 \pm 5.0]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -351.4 \pm 10.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -374.9 \pm 10.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[380](1)	[427](2)
[162](1)	[103](2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Ti–Br = [2.4] Å
Bond Angle: Br–Ti–Br = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.72305 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiBr_3$(g) is calculated from the enthalpy of sublimation of $TiBr_3$(cr). A tentative equation for the vapor pressure of $TiBr_3$(cr) was reported by Hall and Blocher.[1] 2nd and 3rd law analyses of the equation over the temperature range 700 to 900 K give values of $\Delta_{sub}H°(298.15\ K)$ of 45.2 and 41.9 $kcal·mol^{-1}$, respectively, with a 3nd law drift of $-4.2\ cal·K^{-1}·mol^{-1}$. The chosen value of $\Delta_f H°(298.15\ K)$, $-89.6 \pm 2.5\ kcal·mol^{-1}$ ($-374.886 \pm 10.5\ kJ\ mol^{-1}$), is based on the 3rd law $\Delta_{sub}H°(298.15\ K)$.

Heat Capacity and Entropy

The interatomic distance is estimated from those of $TiCl_4$, $TiCl_3$ and $TiBr_4$. The pyramidal bond angle is estimated assuming that $TiBr_3$(g) is similar to the group V trihalides. The principal moments of inertia are: $I_A = I_B = 98.0035 \times 10^{-39}\ g\ cm^2$ and $I_C = 179.3970 \times 10^{-39}\ g·cm^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3}.[2]

References

[1]E. H. Hall and J. M Blocher, J. Phys. Chem. **63**, 1525 (1959).
[2]C. E. Moore, U. S. Nat. Bur. Stand., Circ. 467, (1949).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.122	−351.415	−351.415	INFINITE
100	55.060	285.335	423.540	−13.820	−351.863	−371.494	194.048
200	71.226	328.902	366.106	−7.441	−354.752	−390.061	101.873
250	76.150	345.361	360.354	−3.748	−356.447	−398.697	83.303
298.15	79.334	359.064	359.064	0.	−374.886	−404.700	70.902
300	79.433	359.555	359.066	0.147	−374.996	−404.885	70.497
350	81.623	371.976	360.042	4.177	−421.229	−407.328	60.790
400	83.104	382.978	362.234	8.297	−421.179	−405.345	52.933
450	84.118	392.829	365.096	12.480	−421.117	−403.370	46.822
500	84.816	401.730	368.322	16.704	−421.050	−401.401	41.934
600	85.616	417.274	375.222	25.231	−420.928	−397.483	34.604
700	85.968	430.502	382.198	33.813	−420.842	−393.583	29.370
800	86.103	441.992	388.970	42.417	−420.791	−389.693	25.444
900	86.137	452.136	395.436	51.030	−420.815	−385.806	22.392
1000	86.128	461.211	401.568	59.643	−420.984	−381.908	19.949
1100	86.102	469.419	407.369	68.255	−421.362	−377.984	17.949
1200	86.068	476.909	412.856	76.863	−425.936	−373.896	16.275
1300	86.033	483.797	418.052	85.469	−426.013	−369.557	14.849
1400	85.996	490.171	422.978	94.070	−426.184	−365.209	13.626
1500	85.958	496.103	427.658	102.668	−426.465	−360.844	12.566
1600	85.921	501.649	432.111	111.262	−426.870	−356.457	11.637
1700	85.884	506.857	436.356	119.852	−427.413	−352.040	10.817
1800	85.847	511.765	440.411	128.438	−428.111	−347.587	10.087
1900	85.812	516.406	444.289	137.021	−428.980	−343.091	9.432
2000	85.779	520.806	448.006	145.601	−444.720	−338.090	8.830
2100	85.748	524.991	451.573	154.177	−446.724	−332.710	8.276
2200	85.718	528.979	455.002	162.750	−448.760	−327.233	7.769
2300	85.691	532.789	458.302	171.321	−450.832	−321.663	7.305
2400	85.665	536.435	461.482	179.889	−452.939	−316.001	6.878
2500	85.641	539.932	464.550	188.454	−455.083	−310.252	6.482
2600	85.619	543.290	467.515	197.017	−457.263	−304.416	6.116
2700	85.598	546.521	470.381	205.578	−459.479	−298.495	5.775
2800	85.578	549.634	473.156	214.137	−461.730	−292.492	5.457
2900	85.560	552.637	475.846	222.693	−464.012	−286.407	5.159
3000	85.542	555.537	478.454	231.249	−466.323	−280.244	4.879
3100	85.525	558.342	480.986	239.802	−468.661	−274.002	4.617
3200	85.508	561.057	483.446	248.354	−471.022	−267.686	4.370
3300	85.492	563.688	485.838	256.904	−473.401	−261.294	4.136
3400	85.475	566.239	488.165	265.452	−475.796	−254.831	3.915
3500	85.459	568.717	490.432	273.999	−478.201	−248.297	3.706
3600	85.443	571.124	492.640	282.544	−480.614	−241.694	3.507
3700	85.426	573.465	494.793	291.087	−892.127	−227.236	3.208
3800	85.410	575.743	496.893	299.629	−893.307	−209.251	2.876
3900	85.393	577.961	498.944	308.169	−894.538	−191.233	2.561
4000	85.376	580.123	500.946	316.707	−895.815	−173.183	2.262
4100	85.358	582.231	502.903	325.244	−897.134	−155.101	1.976
4200	85.340	584.288	504.816	333.779	−898.489	−136.987	1.704
4300	85.322	586.296	506.688	342.312	−899.876	−118.839	1.444
4400	85.304	588.257	508.520	350.844	−901.291	−100.659	1.195
4500	85.285	590.174	510.313	359.373	−902.730	−82.447	0.957
4600	85.266	592.048	512.070	367.901	−904.190	−64.203	0.729
4700	85.247	593.882	513.791	376.426	−905.666	−45.926	0.510
4800	85.228	595.676	515.478	384.950	−907.155	−27.618	0.301
4900	85.208	597.433	517.133	393.472	−908.655	−9.279	0.099
5000	85.188	599.154	518.756	401.992	−910.161	9.091	−0.095
5100	85.168	600.841	520.349	410.509	−911.671	27.492	−0.282
5200	85.147	602.495	521.913	419.025	−913.184	45.921	−0.461
5300	85.127	604.116	523.449	427.539	−914.695	64.380	−0.635
5400	85.106	605.707	524.957	436.051	−916.204	82.867	−0.802
5500	85.086	607.269	526.440	444.560	−917.708	101.382	−0.963
5600	85.065	608.802	527.897	453.068	−919.205	119.925	−1.119
5700	85.044	610.307	529.330	461.573	−920.694	138.494	−1.269
5800	85.023	611.786	530.738	470.076	−922.173	157.088	−1.415
5900	85.002	613.239	532.125	478.578	−923.640	175.709	−1.556
6000	84.981	614.668	533.488	487.077	−925.095	194.354	−1.692

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [172.05]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-616.1 \pm 67]\ kJ·mol^{-1}$

$\Delta\ H°(298.15\ K) = [-636.0 \pm 67]\ kJ·mol^{-1}$

Enthalpy of Formation

Larsen and Leddy[1] studied the reaction Zr(cr) + 3 $ZrBr_4$(g) = 4 $ZrBr_3$(cr) in the temperature range 473 to 973 K and pressure range 5 to 15 atm. They present a plot of the fractional reaction, for a series of temperatures, as a function of the reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The Gibbs energy function change for this reaction was calculated at 100 K invervals from 500 to 1100 K. At each temperature, the equilibrium constant was assumed to be 1, and $\Delta_r H$(298.15 K) accordingly calculated. These values and the enthalpy of formation of $ZrBr_4$(g) [Refer to the $ZrBr_4$ table] were used to compute a series of values for the standard enthalpy of formation of $ZrBr_3$(cr). The following table gives representative values at four temperatures.

T/K	K_p	$\Delta_r H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$($ZrBr_3$, cr, 298.15 K) kcal·mol^{-1}
500	1	−70.26	−132.8
700	1	−96.48	−139.3
900	1	−121.75	−145.6
1100	1	−146.28	−151.8

If one assumes an initial pressure of from 0 to 10 atm for $ZrBr_4$ and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of $ZrBr_4$ to attain a value of 1 atm and hence an equilibrium constant of 1. The data of Larsen and Leddy[1] indicate about 82% reaction at 973 K. It was assumed that around 1100 K the equilibrium constant attains a value of 1 giving −152 kcal·mol^{-1} (−635.968 kJ·mol^{-1}) for the enthaply of formation of $ZrBr_3$(cr) at 298.15 K. The limits of error were taken to be ±16 kcal·mol^{-1} which corresponds to a ±500 K temperature spread in the above table.

A 2nd law calculation of their data was carried out but the results are of doubtful value in view of the uncertainty in the attainment of equilibrium at the lower temperatures.

Heat Capacity and Entropy

The heat capacity was estimated in the same manner as for $ZrBr_4$(cr) [see $ZrBr_4$(cr) table]. The values for θ_D and θ_E were taken to be the same as those estimated for $ZrBr_4$(cr). The internal contribution was obtained from the estimated $ZrBr_3$vibrational frequencies and the anharmonicity factor "a" was taken to be 2.5×10^{-3}. The specific heat above 300 K was obtained by graphical extrapolation.

It was assumed, in the above estimation, that the crystalline lattice is made up of $ZrBr_3$ molecules. However, Holze[2] concluded that crystalline ZrI_3 was composed of a chain lattice of $(Zr_2I_6)_n$ units. A chain lattice of $(Zr_2Br_6)_n$ units is probably a better representation of the solid state structure of $ZrBr_3$. Until more quantitative data becomes available, however, it is felt that the above analysis gives a fair approximation to the heat capacity of $ZrBr_3$.

Disproportionation Data

As detailed above, this was assumed to be 1100 ± 500 K.

Liquid Phase

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data

The enthalpy of sublimation at 298.15 K was obtained from the difference in the enthalpy of formation of the gas and solid at 298.15 K. The sublimation point was obtained from the Gibbs energy crossover between gas and solid at one bar.

References

[1]E. M. Larsen and J. J. Leddy, J. Am. Chem. Soc. **78**, 5983 (1956).
[2]E. Holze in R. F. Rolsten, "Iodide Metals and Metal Iodides," John Wiley and Sons, Inc., New York, p. 46 (1961).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−22.372	−616.078	−616.078	INFINITE
100	74.421	74.693	255.609	−18.092	−616.874	−614.861	321.170
200	93.232	133.499	180.987	−9.498	−617.825	−612.489	159.966
298.15	99.483	172.054	172.054	0.	−635.968	−607.607	106.450
300	99.562	172.670	172.056	0.184	−636.040	−607.430	105.763
400	102.508	201.756	176.002	10.302	−680.202	−588.696	76.876
500	103.763	224.773	183.535	20.619	−678.047	−566.068	59.137
600	104.600	243.771	192.037	31.040	−675.896	−543.874	47.348
700	105.018	259.927	200.611	41.521	−673.790	−522.038	38.955
800	105.437	273.978	208.922	52.044	−671.745	−500.500	32.679
900	105.855	286.422	216.855	62.610	−669.773	−479.213	27.813
1000	106.064	297.587	224.380	73.207	−667.892	−458.142	23.931
1100	106.148	307.700	231.502	83.818	−666.128	−437.253	20.763
1200	106.232	316.940	238.242	94.437	−668.199	−416.298	18.121
1300	106.315	325.447	244.628	105.065	−666.140	−395.390	15.887
1400	106.357	333.327	250.685	115.698	−664.132	−374.639	13.978
1500	106.399	340.666	256.442	126.336	−662.185	−354.029	12.328
1600	106.441	347.534	261.923	136.978	−660.314	−333.547	10.889
1700	106.483	353.989	267.151	147.624	−658.530	−313.179	9.623
1800	106.525	360.076	272.146	158.275	−656.846	−292.913	8.500
1900	106.566	365.837	276.927	168.929	−655.276	−272.738	7.498
2000	106.608	371.304	281.510	179.588	−653.832	−252.642	6.598

PREVIOUS: March 1962 CURRENT: June 1964

$S°(298.15\ K) = [371.58]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-408]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-431]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[255](1)
[120](1)
[273](2)
[95](2)

Ground State Quantum Weight: [2] $\sigma = [3]$

Point Group: [C_{3v}]

Bond Distance: Zr–Br = [2.39] Å

Bond Angle: Br–Zr–Br = [98]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.77605 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpies of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides are computed from data issued in these JANAF tables. The zirconium–halide bond energy, taken as 1/4 of this enthaply of formation, is found to be linear with internuclear separation. From gaseous titanium tri– and tetrachloride, it is found that the bond energy of the trichloride is around 7 $kcal·mol^{-1}$ greater than that for titanium tetrachloride. This amount is added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, is found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium is determined from this curve and their estimated bond distances.

For zirconium tribromide, the enthaply of formation from the gaseous atoms is −329 $kcal·mol^{-1}$ and from the elements in their standard state, −103 $kcal·mol^{-1}$ (−430.952 $kJ·mol^{-1}$).

Heat Capacity and Entropy

The measured internuclear distances for the tribromides of P, As, and Sb are plotted as a function of the atomic weight of these atoms and a smooth curve is drawn through the points. The internuclear distance for $ZrBr_3$ is taken from this plot. The bond angle is assumed to be intermediate between the bond angles of $AsBr_3$ and $SbBr_3$; it is taken to be 98°. The principal moments of inertia are: $I_A = I_B = 101.4161 \times 10^{-39}$ gm cm^2, $I_C = 172.6792 \times 10^{-39}$ $g·cm^2$.

The measured vibrational frequencies for the tribromides of phosphorus, arsenic, and antimony are plotted as a function of internuclear distance. Smooth curves through these points are obtained for υ_1, υ_2, and υ_4; these curves and the estimated $ZrBr_3$ bond distance are used to obtain correlation values of υ_1, υ_2, and υ_4 for $ZrBr_3$. Force constants, assuming a valence force field and a Br–Zr–Br angle of 98°, are derived from the above values for υ_1 and υ_2. These force constants are then used to derive values for υ_3 and υ_4. By a process of successive approximation, a set of force constants are obtained which give frequencies in good agreement with the three correlation values. The three correlation frequencies and the derived frequency are used in this table.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.302	−407.993	−407.993	INFINITE
100	62.307	292.306	439.075	−14.677	−408.444	−428.192	223.664
200	75.575	340.557	378.756	−7.640	−410.951	−447.026	116.751
250	78.032	357.710	372.886	−3.794	−412.545	−455.867	95.248
298.15	79.443	371.585	371.585	0.	−430.952	−462.081	80.955
300	79.486	372.076	371.586	0.147	−431.062	−462.274	80.489
350	80.406	384.403	372.558	4.146	−477.309	−464.937	69.388
400	81.022	395.183	374.726	8.183	−477.306	−463.169	60.484
450	81.453	404.752	377.541	12.245	−477.310	−461.402	53.558
500	81.766	413.351	380.699	16.326	−477.324	−459.634	48.018
600	82.180	428.299	387.424	24.525	−477.396	−456.090	39.706
700	82.432	440.987	394.192	32.757	−477.538	−452.529	33.768
800	82.597	452.006	400.745	41.009	−477.765	−448.942	29.313
900	82.711	461.742	406.992	49.274	−478.093	−445.321	25.846
1000	82.793	470.460	412.911	57.550	−478.534	−441.657	23.070
1100	82.853	478.354	418.507	65.832	−479.098	−437.943	20.796
1200	82.900	485.566	423.799	74.120	−483.500	−433.950	18.889
1300	82.936	492.203	428.809	82.412	−483.777	−429.810	17.270
1400	82.964	498.350	433.559	90.707	−484.107	−425.647	15.881
1500	82.987	504.075	438.072	99.004	−484.501	−421.458	14.676
1600	83.006	509.431	442.366	107.304	−484.972	−417.240	13.621
1700	83.022	514.464	446.461	115.606	−485.533	−412.990	12.690
1800	83.035	519.210	450.372	123.909	−486.197	−408.704	11.860
1900	83.046	523.700	454.114	132.213	−486.977	−404.378	11.117
2000	83.056	527.960	457.701	140.518	−487.886	−400.008	10.447
2100	83.064	532.012	461.144	148.824	−488.940	−395.589	9.840
2200	83.071	535.876	464.453	157.130	−511.472	−390.370	9.269
2300	83.077	539.569	467.640	165.438	−513.267	−384.825	8.740
2400	83.083	543.105	470.711	173.746	−515.094	−379.202	8.253
2500	83.088	546.497	473.675	182.054	−516.955	−373.501	7.804
2600	83.092	549.756	476.539	190.363	−518.850	−367.726	7.388
2700	83.096	552.892	479.309	198.673	−520.778	−361.877	7.001
2800	83.099	555.914	481.991	206.983	−522.737	−355.956	6.640
2900	83.102	558.830	484.591	215.293	−524.727	−349.965	6.304
3000	83.105	561.647	487.113	223.603	−526.743	−343.904	5.988
3100	83.107	564.372	489.561	231.914	−528.784	−337.776	5.691
3200	83.110	567.011	491.941	240.224	−530.846	−331.582	5.413
3300	83.112	569.568	494.254	248.535	−532.924	−325.322	5.149
3400	83.114	572.049	496.506	256.847	−535.016	−319.000	4.901
3500	83.115	574.459	498.699	265.158	−537.117	−312.616	4.666
3600	83.117	576.800	500.836	273.470	−539.223	−306.172	4.442
3700	83.118	579.077	502.920	281.782	−541.330	−299.669	4.231
3800	83.120	581.294	504.954	290.093	−543.435	−293.110	4.029
3900	83.121	583.453	506.939	298.405	−545.533	−286.495	3.837
4000	83.122	585.557	508.878	306.718	−547.622	−279.826	3.654
4100	83.123	587.610	510.773	315.030	−549.697	−273.106	3.479
4200	83.124	589.613	512.627	323.342	−551.756	−266.335	3.312
4300	83.125	591.569	514.440	331.655	−553.796	−259.515	3.152
4400	83.126	593.480	516.215	339.967	−555.815	−252.648	2.999
4500	83.127	595.348	517.953	348.280	−557.811	−245.735	2.852
4600	83.127	597.175	519.655	356.593	−559.781	−238.778	2.711
4700	83.128	598.963	521.324	364.905	−561.723	−231.779	2.576
4800	83.129	600.713	522.959	373.218	−1124.574	−213.121	2.319
4900	83.129	602.427	524.564	381.531	−1126.110	−194.117	2.069
5000	83.130	604.107	526.138	389.844	−1127.632	−175.081	1.829
5100	83.131	605.753	527.683	398.157	−1129.139	−156.015	1.598
5200	83.131	607.367	529.200	406.470	−1130.628	−136.920	1.375
5300	83.132	608.951	530.690	414.783	−1132.097	−117.796	1.161
5400	83.132	610.504	532.153	423.096	−1133.545	−98.644	0.954
5500	83.132	612.030	533.592	431.410	−1134.971	−79.466	0.755
5600	83.133	613.528	535.006	439.723	−1136.372	−60.263	0.562
5700	83.133	614.999	536.396	448.036	−1137.749	−41.034	0.376
5800	83.134	616.445	537.764	456.350	−1139.100	−21.782	0.196
5900	83.134	617.866	539.110	464.663	−1140.424	−2.506	0.022
6000	83.134	619.263	540.434	472.976	−1141.720	16.791	−0.146

PREVIOUS: June 1964 (1 atm) CURRENT: June 1964 (1 bar)

$S°(298.15\ K) = [516.0]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -228.3 \pm 8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -253.1 \pm 8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[5]
[4450]	[5]
[6900]	[5]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[110](1)	[75](1)	[95](2)
[70](1)	[100](1)	[24](2)
[110](1)	[115](1)	[190](2)

Point Group: $[D_{2h}]$ σ = [4]
Bond Distance: Fe–Br = [2.24] Å
Bond Angles: $Fe–Br_{bridge}–Fe$ = [90]°; $Br_{bridge}–Fe–Br_{bridge}$ = [90]°; $Br–Fe–Br_{bridge}$ = [135]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.44991 \times 10^{-110}]\ g^3·cm^6$

Enthaply of Formation

The chemical equilibria, 622–665 K, for the reaction $Fe_2Br_4(g) = 2\ FeBr_2(g)$ were studied by Porter and Schoonmaker,[1] using a mass spectrometer. Based on the reported partial pressures for the two species, the enthalpy change $\Delta_r H°(298.15\ K)$ for the reaction is evaluated by both the 2nd and 3rd law method to be 40.36 ± 2.0 and 40.75 ± 0.2 kcal·mol^{-1}, respectively. Using the 3rd law $\Delta_r H°$ value and $\Delta_f H°(FeBr_2, g, 298.15\ K) = -9.9 \pm 0.5$ kcal·mol^{-1}, the enthaply of formation $\Delta_f H°(Fe_2Br_4, g, 298.15\ K)$ is calculated as −60.5 ± 2.0 kcal·mol^{-1} (−253.132 kJ·mol^{-1}) and is adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be planar. The two Fe atoms are at the two opposite corners of a square. The other two corners of the square are occupied by two Br atoms. The two remaining Br atoms are situated outside the square on a straight line joining the two Fe atoms. The Fe–Br bond distance was estimated to be the same as that in the $FeBr_2$(g) molecule. The first six vibrational frequencies were estimated by comparison with those for K_2Br_2(g) calculated by Berkowitz[2]. The last three degenerate frequencies were assigned arbitrarily *in order to give good second and third law agreement for the heats of dissociation of dimer to monomer. The order of the frequencies* listed above is arbitrary and not related to their species types.

The electronic levels and quantum weights were estimated by comparison with those for $FeBr_2$(g). The principal moments of inertia are: $I_A = 66.5764 \times 10^{-39}$, $I_B = 434.5679 \times 10^{-39}$, and $I_C = 501.1443 \times 10^{-39}$ g·cm^2.

References

[1] R. F. Porter and R. C. Schoonmaker, J. Phys. Chem. **63**, 626 (1959).
[2] J. Berkowitz, J. Chem. Phys. **32**, 1519 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−33.210	−228.310	−228.310	INFINITE
100	115.643	379.131	629.897	−25.077	−226.608	−252.539	131.913
200	127.972	464.315	527.906	−12.718	−227.590	−278.305	72.686
250	129.727	493.080	518.165	−6.271	−229.050	−290.829	60.765
298.15	130.683	516.018	516.018	0.	−253.132	−299.931	52.547
300	130.711	516.827	516.021	0.242	−253.263	−300.221	52.273
350	131.315	537.025	517.614	6.794	−314.584	−304.690	45.473
400	131.711	554.587	521.162	13.370	−314.351	−303.294	39.606
450	131.986	570.117	525.755	19.963	−314.236	−301.920	35.046
500	132.185	584.034	530.900	26.567	−314.242	−300.553	31.399
600	132.461	608.160	541.826	39.801	−314.620	−297.787	25.925
700	132.671	628.595	552.799	53.057	−315.491	−294.920	22.007
800	132.880	646.325	563.406	66.335	−316.948	−291.890	19.058
900	133.125	661.989	573.506	79.635	−319.234	−288.631	16.752
1000	133.420	676.030	583.069	92.961	−322.950	−285.051	14.890
1100	133.765	688.762	592.108	106.320	−328.442	−280.967	13.342
1200	134.155	700.418	600.655	119.716	−332.810	−276.496	12.036
1300	134.577	711.172	608.748	133.152	−333.862	−271.761	10.920
1400	135.018	721.162	616.425	146.632	−335.056	−266.941	9.960
1500	135.466	730.492	623.722	160.156	−336.391	−262.030	9.125
1600	135.908	739.249	630.671	173.725	−337.869	−257.025	8.391
1700	136.335	747.501	637.303	187.337	−341.395	−251.885	7.739
1800	136.737	755.306	643.644	200.991	−343.842	−246.550	7.155
1900	137.110	762.709	649.717	214.684	−374.643	−239.671	6.589
2000	137.448	769.750	655.544	228.412	−377.891	−232.483	6.072
2100	137.749	776.464	661.144	242.172	−381.144	−225.132	5.600
2200	138.012	782.878	666.533	255.960	−384.408	−217.627	5.167
2300	138.238	789.018	671.726	269.773	−387.691	−209.973	4.769
2400	138.426	794.906	676.736	283.607	−390.997	−202.175	4.400
2500	138.579	800.560	681.577	297.457	−394.332	−194.239	4.058
2600	138.699	805.997	686.258	311.321	−397.699	−186.169	3.740
2700	138.789	811.234	690.791	325.196	−401.100	−177.968	3.443
2800	138.850	816.282	695.183	339.078	−404.536	−169.642	3.165
2900	138.886	821.155	699.443	352.965	−408.008	−161.191	2.903
3000	138.899	825.864	703.579	366.855	−411.514	−152.621	2.657
3100	138.892	830.418	707.598	380.744	−415.052	−143.933	2.425
3200	138.867	834.828	711.505	394.632	−1115.220	−120.283	1.963
3300	138.828	839.100	715.307	408.517	−1115.013	−89.194	1.412
3400	138.774	843.244	719.009	422.397	−1114.894	−58.111	0.893
3500	138.710	847.266	722.617	436.272	−1114.860	−27.030	0.403
3600	138.636	851.172	726.134	450.139	−1114.908	4.052	−0.059
3700	138.555	854.970	729.565	463.999	−1115.036	35.136	−0.496
3800	138.467	858.664	732.914	477.850	−1115.239	66.224	−0.910
3900	138.373	862.259	736.184	491.692	−1115.517	97.318	−1.303
4000	138.276	865.761	739.380	505.524	−1115.865	128.421	−1.677
4100	138.175	869.174	742.504	519.347	−1116.284	159.533	−2.032
4200	138.072	872.503	745.560	533.159	−1116.769	190.656	−2.371
4300	137.968	875.751	748.550	546.961	−1117.321	221.792	−2.694
4400	137.863	878.921	751.477	560.753	−1117.938	252.941	−3.003
4500	137.757	882.018	754.344	574.534	−1118.620	284.105	−3.298
4600	137.652	885.045	757.153	588.304	−1119.365	315.285	−3.580
4700	137.547	888.004	759.905	602.064	−1120.173	346.481	−3.851
4800	137.443	890.899	762.604	615.814	−1121.046	377.696	−4.110
4900	137.341	893.732	765.252	629.553	−1121.984	408.930	−4.359
5000	137.240	896.505	767.849	643.282	−1122.987	440.183	−4.599
5100	137.140	899.222	770.398	657.001	−1124.057	471.457	−4.829
5200	137.042	901.884	772.901	670.710	−1125.196	502.752	−5.050
5300	136.946	904.494	775.360	684.410	−1126.407	534.071	−5.264
5400	136.852	907.053	777.775	698.099	−1127.691	565.412	−5.469
5500	136.760	909.563	780.148	711.780	−1129.052	596.779	−5.668
5600	136.671	912.026	782.481	725.452	−1130.495	628.170	−5.859
5700	136.583	914.444	784.775	739.114	−1132.021	659.589	−6.044
5800	136.497	916.819	787.032	752.768	−1133.637	691.033	−6.223
5900	136.414	919.152	789.251	766.414	−1135.348	722.508	−6.397
6000	136.333	921.444	791.435	780.051	−1137.158	754.012	−6.564

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K)$ = [461.3 ± 20.9] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -739.7 \pm 2.09\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -767.8 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[182](1)	[188](1)	[100](1)
[120](1)	[228](1)	[100](1)
[207](1)	[125](1)	[75](1)
[134](1)	[125](1)	[75](1)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: [D_{2h}]

Bond Distances: Mg–Br = [2.34] Å; Mg–Br'(bridge) = [2.60] Å

Bond Angles: Mg–Br'_{bridge}–Mg = [90]°; Br'_{bridge}–Mg–Br'_{bridge} = [90]°

Br–Mg–Br'(bridge) = [135]°

Product of Moments of Inertia: $I_A I_B I_C$ = [2.55371 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°$ of the dimer is based on an analysis of mass spectrometric data reported by Berkowitz and Marquart[1] These studies have revealed the presence of approximately 2% dimer in the equilibrium vapor over $MgBr_2$(cr) at around 800 K. The existence of the dimer was inferred from the observed ion intensities for $Mg_2Br_3^+$. Berkowitz and Marquart[1] reported a 2nd law $\Delta_r H$(803 K) of 12.9 $kcal·mol^{-1}$ for the process $MgBr_2(cr) + MgBr_2(g) = Mg_2Br_4(g)$. When corrected to 298.15 K this value gives $\Delta_r H° = 14.0\ kcal·mol^{-1}$ which leads to $\Delta_f H°(Mg_2Br_4, g, 298.15\ K) = -183.7\ kcal·mol^{-1}$. The absolute pressure of Mg_2Br_4(g) was also measured at 798 K by integrating the ion current during complete volatilization of a previously weighed sample. A 3rd law analysis of the reported pressure gives $\Delta_{sub} H°(298.15\ K) = 67.4\ kcal·mol^{-1}$ for 2 $MgBr_2(cr) = Mg_2Br_4(g)$. This value for the enthalpy of sublimation leads to $\Delta_f H°(Mg_2Br_4, g, 298.15\ K) = -183.2\ kcal·mol^{-1}$ which is in excellent agreement with the 2nd law result. We adopt an average value ($-183.5\ kcal·mol^{-1}$, $-767.764\ kJ·mol^{-1}$) of these two results. The uncertainty in $\Delta_f H°$ is estimated as $\pm 5.0\ kcal·mol^{-1}$, and the adopted $\Delta_f H°$ value value corresponds to a dimerization energy for $MgBr_2$(g) of 38.7 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The dimer molecule is assumed to have a bridge–bond structure of D_{2h} symmetry similar to that suggested by Thompson and Carlson[2] for the dimers of several transition metal dichlorides. The two outer Mg–Br bond lengths are assumed to be the same as that for $MgBr_2$[3](2.34 Å). The four ring Mg–Br'(bridge) bond lengths are taken to be somewhat longer (2.6 Å). The four atoms which lie in the ring form a square. The Br'(bridge)–Mg–Br bond angle is estimated as 135°. The principal moments of inertia are: $I_A = 89.6957 \times 10^{-39}$, $I_B = 490.6138 \times 10^{-39}$, and $I_C = 580.3094 \times 10^{-39}\ g·cm^2$.

The vibratonal frequencies of the ring (first six listed) are taken equal to those for Na_2Br_2.[3] These frequencies were obtained by Berkowitz[4] from ionic model calculations. The remaining six frequencies are estimated by analogy with those for $MgBr_2$ and Mg_2Cl_4.[3] Following the observations made by Thompson and Carlson,[2] all of the dimer frequencies are assumed to lie above the bending frequency ($\nu_2 = 70\ cm^{-1}$) of the monomer.[3] Our adopted functions for the monomer and dimer reproduce the pressures measured by Berkowitz and Marquart[1] and show that the dimer becomes an increasingly important vapor species with rising temperatures.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−30.967	−739.716	−739.716	INFINITE
100	105.171	329.984	572.231	−24.225	−739.844	−760.172	397.073
200	124.475	410.634	473.038	−12.481	−741.917	−779.818	203.668
250	127.401	438.757	463.463	−6.176	−743.586	−789.111	164.876
298.15	129.013	461.347	461.347	0.	−767.764	−795.072	139.293
300	129.061	462.145	461.349	0.239	−767.897	−795.241	138.464
350	130.087	482.123	462.925	6.719	−829.242	−796.439	118.862
400	130.763	499.540	466.436	13.242	−828.965	−791.773	103.395
450	131.231	514.971	470.988	19.792	−828.738	−787.138	91.369
500	131.569	528.816	476.090	26.363	−828.560	−782.526	81.750
600	132.011	552.846	486.940	39.544	−828.353	−773.342	67.325
700	132.280	573.218	497.847	52.759	−828.359	−764.175	57.023
800	132.455	590.893	508.398	65.996	−828.602	−754.993	49.296
900	132.575	606.502	518.448	79.248	−829.116	−745.764	43.283
1000	132.661	620.474	527.964	92.510	−847.114	−735.037	38.394
1100	132.725	633.122	536.958	105.780	−848.273	−723.773	34.369
1200	132.774	644.672	545.460	119.055	−849.443	−712.403	31.010
1300	132.812	655.302	553.506	132.334	−850.626	−700.935	28.164
1400	132.842	665.145	561.133	145.617	−1106.643	−683.042	25.485
1500	132.866	674.311	568.376	158.903	−1105.152	−652.837	22.734
1600	132.886	682.887	575.268	172.190	−1103.681	−622.731	20.330
1700	132.903	690.943	581.838	185.480	−1102.230	−592.716	18.212
1800	132.916	698.540	588.112	198.771	−1100.804	−562.786	16.332
1900	132.928	705.727	594.115	212.063	−1099.407	−532.934	14.651
2000	132.938	712.546	599.868	225.356	−1098.042	−503.155	13.141
2100	132.947	719.032	605.389	238.650	−1096.714	−473.443	11.776
2200	132.954	725.217	610.696	251.945	−1095.426	−443.794	10.537
2300	132.961	731.127	615.805	265.241	−1094.180	−414.203	9.407
2400	132.966	736.786	620.729	278.538	−1092.980	−384.664	8.372
2500	132.971	742.214	625.480	291.834	−1091.828	−355.175	7.421
2600	132.976	747.429	630.071	305.132	−1090.724	−325.731	6.544
2700	132.980	752.448	634.511	318.430	−1089.669	−296.328	5.733
2800	132.983	757.284	638.810	331.728	−1088.663	−266.964	4.980
2900	132.987	761.951	642.976	345.026	−1087.704	−237.634	4.280
3000	132.989	766.459	647.018	358.325	−1086.793	−208.337	3.627
3100	132.992	770.820	650.941	371.624	−1085.927	−179.070	3.017
3200	132.994	775.042	654.754	384.923	−1085.104	−149.830	2.446
3300	132.997	779.135	658.461	398.223	−1084.323	−120.614	1.909
3400	132.999	783.105	662.069	411.523	−1083.582	−91.422	1.405
3500	133.000	786.961	665.583	424.823	−1082.880	−62.252	0.929
3600	133.002	790.707	669.006	438.123	−1082.214	−33.100	0.480
3700	133.004	794.351	672.345	451.423	−1081.585	−3.966	0.056
3800	133.005	797.898	675.603	464.724	−1080.990	25.150	−0.346
3900	133.006	801.353	678.783	478.024	−1080.430	54.251	−0.727
4000	133.007	804.721	681.890	491.325	−1079.905	83.339	−1.088
4100	133.009	808.005	684.926	504.626	−1079.414	112.414	−1.432
4200	133.010	811.210	687.894	517.926	−1078.959	141.477	−1.760
4300	133.011	814.340	690.799	531.227	−1078.540	170.530	−2.072
4400	133.011	817.398	693.641	544.529	−1078.158	199.574	−2.369
4500	133.012	820.387	696.425	557.830	−1077.815	228.610	−2.654
4600	133.013	823.311	699.152	571.131	−1077.514	257.638	−2.926
4700	133.014	826.171	701.824	584.432	−1077.255	286.660	−3.186
4800	133.014	828.972	704.444	597.734	−1077.043	315.677	−3.435
4900	133.015	831.714	707.013	611.035	−1076.878	344.690	−3.674
5000	133.016	834.401	709.534	624.337	−1076.764	373.701	−3.904
5100	133.016	837.036	712.008	637.638	−1076.703	402.710	−4.125
5200	133.017	839.618	714.438	650.940	−1076.698	431.717	−4.337
5300	133.017	842.152	716.824	664.242	−1076.751	460.726	−4.541
5400	133.018	844.639	719.168	677.544	−1076.866	489.736	−4.737
5500	133.018	847.079	721.471	690.845	−1077.046	518.749	−4.927
5600	133.019	849.476	723.736	704.147	−1077.293	547.765	−5.109
5700	133.019	851.831	725.962	717.449	−1077.611	576.787	−5.286
5800	133.020	854.144	728.152	730.751	−1078.003	605.814	−5.456
5900	133.020	856.418	730.307	744.053	−1078.471	634.849	−5.621
6000	133.020	858.654	732.428	757.355	−1079.019	663.893	−5.780

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K)$ = [209.2 ± 17] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -304.2 \pm 8\ kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev *et al.*[1] have measured the enthalpy of solution of $MoBr_4$(cr) from which Dellien *et al.*[2] have obtained $\Delta_f H°(MoBr_4, cr, 298.15\ K) = -70.35\ kcal·mol^{-1}$. Brewer[3] has reviewed the equilibrium data of Oppermann[4] (see the discussion on the $MoBr_4$(g) table[5] as well as the above measurements and obtained $\Delta_f H°(298.15\ K) = -72.7 \pm 2\ kcal·mol^{-1}$ ($-304.177\ kJ·mol^{-1}$) which is the value adopted here. This differs from the value $\Delta_f H°(298.15\ K) = -76.8\ kcal·mol^{-1}$ adopted by NBS.[6]

Heat Capacity and Entropy

Brewer[3] estimated $C_p°(298.15\ K) = 31.8 \pm 2\ cal·K^{-1}·mol^{-1}$ and $S°(298.15\ K) = 50.0\ cal·K^{-1}·mol^{-1}$ ($209.200\ kJ·mol^{-1}$). Other estimates are $C_p°(298.15\ K) = 29.5\ cal·K^{-1}·mol^{-1}$ from the ionic contributions of Kubaschewski and Unal[7] and $S°(298.15\ K) = 51.4\ cal·K^{-1}·mol^{-1}$ from the additive entropy constants of Stull and Prophet.[8] We adopt Brewer's values[3] of $C_p°$ and $S°$ at 298.15 K and estimate $C_p°$ at higher temperatures by comparison with $MoBr_2$(cr) and $MoBr_3$(cr).[5]

Decomposition Data

T_{dcm} is the calculated temperature at which $\Delta_r G° = 0$ for the reaction $MoBr_4(cr) = MoBr_3(cr) + 0.5\ Br_2(g)$. Carnell *et al.*[9] have given conditions for the formation of $MoBr_4$(cr) and its dissociation to $MoBr_3$(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	133.051	209.200	209.200	0.	−304.177	−267.261	46.823
300	133.093	210.023	209.203	0.246	−304.255	−267.031	46.494
400	135.143	248.601	214.449	13.661	−362.256	−242.498	31.667
500	136.817	278.930	224.418	27.256	−358.593	−212.982	22.250
600	138.909	304.061	235.656	41.043	−354.861	−184.208	16.037
700	140.844	325.621	247.004	55.032	−351.022	−156.068	11.646
800	142.674	344.549	258.038	69.208	−347.071	−128.486	8.389
900	144.400	361.454	268.606	83.563	−343.011	−101.405	5.885
1000	146.022	376.753	278.668	98.085	−338.850	−74.782	3.906

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K) = 418.89 \pm 8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -142.4 \pm 8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -171.1 \pm 8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[15000]	[11]
[20000]	[9]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[230](1)	[80](3)
[70](2)	[390](3)

Point Group: T_d
Bond Distance: Mo–Br = 2.39 ± 0.02
Bond Angle: Br–Mo–Br = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 8.25596 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

Oppermann[1] made careful pressure measurements on the systems $MoBr_3$(cr) + Br_2(g), $MoBr_{2+x}$(cr) + $MoBr_{3-y}$(cr) and $MoBr_2$(cr) + Mo(cr). Brewer,[2] by comparison with the tungsten–bromide system, indicated the possibility of intermediate phases between $MoBr_2$ and $MoBr_3$ and thus modified the treatment of the data. Brewer used a 3rd law treatment combined with independent data on the enthalpies of formation of $MoBr_2$(cr), $MoBr_3$(cr) and $MoBr_4$(cr) and removed the restriction that $x = 0$ and $y = 0$. For this reason we adopt the value of $\Delta_f H°(298.15\ K)$ obtained by Brewer, $-40.9 \pm 2\ kcal \cdot mol^{-1}$ ($-171.126\ kJ \cdot mol^{-1}$), rather than the value of $-36.7\ kcal \cdot mol^{-1}$ reported by Dellien *et al.*[7]

Heat Capacity and Entropy

Brewer[2] used a slight modification of the vibrational frequencies and internuclear distance estimated by Lofgren.[3] He assumed an Mo–Br distance of 2.42 Å in all the molybdenum bromides. The electron diffraction study of Spiridonov and Romanov[4] established the structure of $MoBr_4$(g) to be a regular tetrahedron with an Mo–Br distance of 2.39 ± 0.02 Å.[5] This is the value adopted here. Our value for the product of the moments of inertia $I_A I_B I_C = 8.256 \times 10^{-111}\ g^3 \cdot cm^6$ is 8% lower than Brewer's value ($8.898 \times 10^{-111}\ g^3 \cdot cm^6$). This reduces $S°$ by 0.1 $cal \cdot K^{-1} \cdot mol^{-1}$ at all temperatures. Electronic levels are assumed to be the same as the MoF_4 levels,[6] which Brewer[2] estimated from crystal field theory.

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[6] JANAF Thermochemical Tables: $MoCl_6$(g), $MoCl_5$(g) and $MoCl_4$(g), 12–31–68; MoF_4(g), 12–30–78.
[7] I. Dellien, F. M. Hall, and L. G. Hepler, Chem. Rev. **76**, 283 (1976).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−24.839	−142.361	−142.361	INFINITE
100	80.869	316.427	506.136	−18.971	−142.571	−162.741	85.007
200	97.616	378.758	428.168	−9.882	−145.126	−182.014	47.537
250	100.942	400.931	420.574	−4.911	−146.904	−191.039	39.915
298.15	102.884	418.889	418.889	0.	−171.126	−196.728	34.466
300	102.942	419.526	418.891	0.190	−171.259	−196.887	34.281
350	104.222	435.498	420.150	5.372	−232.592	−197.799	29.520
400	105.084	449.474	422.960	10.606	−232.260	−192.851	25.184
450	105.690	461.888	426.609	15.876	−231.937	−187.944	21.816
500	106.131	473.048	430.704	21.172	−231.625	−183.073	19.126
600	106.716	492.454	439.426	31.817	−231.036	−173.419	15.097
700	107.074	508.934	448.208	42.508	−230.495	−163.859	12.227
800	107.308	523.248	456.713	53.228	−230.001	−154.374	10.080
900	107.470	535.897	464.822	63.967	−229.556	−144.948	8.413
1000	107.587	547.226	472.506	74.720	−229.164	−135.569	7.081
1100	107.673	557.485	479.772	85.483	−228.829	−126.226	5.994
1200	107.739	566.856	486.645	96.254	−228.561	−116.911	5.089
1300	107.791	575.482	493.151	107.031	−228.366	−107.615	4.324
1400	107.832	583.472	499.321	117.812	−228.254	−98.331	3.669
1500	107.867	590.913	505.181	128.597	−228.232	−89.053	3.101
1600	107.899	597.875	510.760	139.385	−228.309	−79.772	2.604
1700	107.929	604.418	516.078	150.177	−228.495	−70.483	2.166
1800	107.960	610.587	521.159	160.971	−228.800	−61.180	1.775
1900	107.995	616.426	526.021	171.769	−229.234	−51.857	1.426
2000	108.037	621.966	530.681	182.570	−229.810	−42.507	1.110
2100	108.089	627.238	535.154	193.377	−230.538	−33.125	0.824
2200	108.153	632.268	539.455	204.189	−231.430	−23.704	0.563
2300	108.232	637.077	543.596	215.008	−232.496	−14.238	0.323
2400	108.328	641.686	547.587	225.836	−233.747	−4.723	0.103
2500	108.444	646.110	551.440	236.674	−235.192	4.849	−0.101
2600	108.581	650.366	555.164	247.525	−236.853	14.482	−0.291
2700	108.741	654.467	558.766	258.391	−238.765	24.185	−0.468
2800	108.924	658.425	562.255	269.274	−240.987	33.963	−0.634
2900	109.132	662.250	565.638	280.177	−279.479	43.877	−0.790
3000	109.365	665.954	568.920	291.101	−280.510	55.045	−0.958
3100	109.623	669.544	572.109	302.050	−281.550	66.247	−1.116
3200	109.904	673.029	575.208	313.027	−282.591	77.483	−1.265
3300	110.209	676.416	578.224	324.032	−283.625	88.751	−1.405
3400	110.536	679.710	581.161	335.069	−284.646	100.051	−1.537
3500	110.884	682.920	584.022	346.140	−285.645	111.380	−1.662
3600	111.251	686.048	586.813	357.247	−286.616	122.737	−1.781
3700	111.635	689.102	589.537	368.391	−287.550	134.121	−1.893
3800	112.035	692.084	592.196	379.574	−288.443	145.529	−2.000
3900	112.447	695.000	594.795	390.798	−289.286	156.961	−2.102
4000	112.870	697.852	597.336	402.064	−290.075	168.413	−2.199
4100	113.301	700.644	599.822	413.372	−290.803	179.885	−2.292
4200	113.738	703.380	602.255	424.724	−291.467	191.373	−2.380
4300	114.178	706.061	604.638	436.120	−292.062	202.876	−2.464
4400	114.620	708.691	606.973	447.560	−292.584	214.393	−2.545
4500	115.061	711.272	609.262	459.044	−293.031	225.920	−2.622
4600	115.498	713.806	611.507	470.572	−293.400	237.457	−2.696
4700	115.931	716.294	613.710	482.144	−293.689	249.000	−2.767
4800	116.356	718.739	615.873	493.758	−293.898	260.549	−2.835
4900	116.772	721.143	617.997	505.414	−294.025	272.102	−2.901
5000	117.177	723.506	620.084	517.112	−885.455	289.387	−3.023
5100	117.570	725.830	622.134	528.849	−887.097	312.901	−3.205
5200	117.949	728.117	624.151	540.625	−888.805	336.446	−3.380
5300	118.313	730.367	626.134	552.439	−890.575	360.026	−3.548
5400	118.662	732.582	628.084	564.288	−892.410	383.639	−3.711
5500	118.993	734.762	630.004	576.170	−894.306	407.287	−3.868
5600	119.307	736.909	631.894	588.086	−896.265	430.970	−4.020
5700	119.603	739.024	633.755	600.031	−898.283	454.689	−4.167
5800	119.880	741.106	635.588	612.006	−900.362	478.442	−4.309
5900	120.139	743.158	637.394	624.007	−902.498	502.232	−4.446
6000	120.378	745.179	639.174	636.033	−904.696	526.060	−4.580

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = [426.20 \pm 12.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-426.4 \pm 84]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-456.4 \pm 84]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[207](1)
[59](2)
[231](3)
[73](3)

Ground State Quantum Weight: [1] σ = 12
Point Group: [T_d]
Bond Distance: Pb–Br = [2.58] Å
Bond Angle: Br–Pb–Br = [109.4712]°
Product of Moments of Inertia: $I_A I_B I_C = [1.30647 \times 10^{-110}]\ g^3·cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -101.9 \pm 20\ kcal·mol^{-1}$ ($-426.350 \pm 84\ kJ·mol^{-1}$) is derived from the dissociation energy for the process $PbBr_4(g) = Pb(g) + 4\ Br(g)$. $D_0° = 11.34$ eV is estimated from an intercomparison of the lead mono–, di–, and tetra– halides.[1] This adopted $D_0°$ value for $PbBr_4$(g) is greater than the $D_0°$ value for $PbBr_2$(g) by a factor of 2.09. The auxiliary values $\Delta_f H°$(Pb, g, 0 K) = 46.91 $kcal·mol^{-1}$ and $\Delta_f H°$(Br, g, 0 K) = 28.188 $kcal·mol^{-1}$ are used[1]. $\Delta_f H°(PbBr_4, g, 298.15\ K) = -109.1 \pm 20\ kcal·mol^{-1}$ ($-456.361 \pm 84\ kJ·mol^{-1}$) is calculated from $\Delta_f H°(0\ K)$.

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya *et al.*[2] Later works[3–5] mistakenly cite this work as observed data and use a bond distance of 2.54 Å rather than the 2.58 Å originally published.[2]

The principal moments of inertia are $I_A = I_B = I_C = 23.5227 \times 10^{-39}\ g·cm^2$.

References

[1]JANAF Thermochemical Tables: PbF(g), PbF_2(g), PbF_4(g), PbBr(g), $PbBr_2$(g), PbI(g), and PbI2(g), 12–31–73; PbCl(g) and $PbCl_2$(g), 6–30–73; Pb(g), 3–31–62;Br(g), 9–30–61.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−25.895	−426.359	−426.359	INFINITE
100	86.541	319.504	516.117	−19.661	−427.478	−444.976	232.432
200	100.868	385.092	435.680	−10.118	−430.262	−461.457	120.520
250	103.277	407.885	427.917	−5.008	−432.089	−469.054	98.003
298.15	104.631	426.201	426.201	0.	−456.361	−473.357	82.930
300	104.671	426.849	426.203	0.194	−456.497	−473.462	82.437
350	105.543	443.054	427.481	5.451	−517.895	−472.925	70.580
400	106.122	457.188	430.330	10.743	−517.637	−466.519	60.921
450	106.525	469.711	434.023	16.060	−517.400	−460.144	53.412
500	106.816	480.951	438.163	21.394	−517.183	−453.794	47.408
600	107.199	500.463	446.969	32.096	−516.809	−441.152	38.406
700	107.433	517.006	455.823	42.829	−521.375	−427.769	31.921
800	107.585	531.363	464.388	53.580	−521.146	−414.412	27.058
900	107.690	544.041	472.547	64.344	−520.895	−401.085	23.278
1000	107.765	555.391	480.274	75.117	−520.625	−387.788	20.256
1100	107.821	565.665	487.577	85.896	−520.337	−374.518	17.784
1200	107.863	575.048	494.481	96.681	−520.030	−361.275	15.726
1300	107.896	583.683	501.015	107.469	−519.714	−348.058	13.985
1400	107.922	591.680	507.209	118.260	−519.404	−334.865	12.494
1500	107.944	599.127	513.092	129.053	−519.113	−321.694	11.202
1600	107.961	606.094	518.689	139.848	−518.849	−308.542	10.073
1700	107.975	612.640	524.025	150.645	−518.619	−295.405	9.077
1800	107.987	618.812	529.121	161.443	−518.430	−282.280	8.192
1900	107.998	624.651	533.997	172.243	−518.289	−269.165	7.400
2000	108.006	630.190	538.669	183.043	−518.200	−256.055	6.687
2100	108.014	635.460	543.154	193.844	−695.388	−235.834	5.866
2200	108.020	640.485	547.464	204.645	−695.027	−213.960	5.080
2300	108.026	645.287	551.614	215.448	−694.797	−192.099	4.363
2400	108.031	649.885	555.613	226.251	−694.701	−170.245	3.705
2500	108.036	654.295	559.473	237.054	−694.741	−148.392	3.100
2600	108.039	658.532	563.202	247.858	−694.917	−126.535	2.542
2700	108.043	662.610	566.809	258.662	−695.225	−104.669	2.025
2800	108.046	666.539	570.301	269.466	−695.660	−82.789	1.544
2900	108.049	670.330	573.685	280.271	−696.216	−60.891	1.097
3000	108.051	673.993	576.968	291.076	−696.882	−38.972	0.679
3100	108.054	677.537	580.155	301.881	−697.649	−17.030	0.287
3200	108.056	680.967	583.252	312.687	−698.506	4.939	−0.081
3300	108.058	684.292	586.264	323.493	−699.441	26.936	−0.426
3400	108.059	687.518	589.195	334.298	−700.441	48.963	−0.752
3500	108.061	690.650	592.049	345.104	−701.495	71.019	−1.060
3600	108.062	693.695	594.831	355.911	−702.590	93.107	−1.351
3700	108.064	696.655	597.543	366.717	−703.715	115.225	−1.627
3800	108.065	699.537	600.189	377.523	−704.858	137.373	−1.888
3900	108.066	702.344	602.773	388.330	−706.009	159.552	−2.137
4000	108.067	705.080	605.296	399.136	−707.158	181.761	−2.374
4100	108.068	707.749	607.763	409.943	−708.294	203.998	−2.599
4200	108.069	710.353	610.174	420.750	−709.411	226.262	−2.814
4300	108.070	712.896	612.534	431.557	−710.501	248.553	−3.019
4400	108.071	715.380	614.843	442.364	−711.556	270.869	−3.216
4500	108.071	717.809	617.104	453.171	−712.571	293.208	−3.403
4600	108.072	720.184	619.320	463.978	−713.541	315.570	−3.583
4700	108.073	722.509	621.490	474.786	−714.462	337.952	−3.756
4800	108.073	724.784	623.619	485.593	−715.329	360.353	−3.921
4900	108.074	727.012	625.706	496.400	−716.141	382.771	−4.080
5000	108.074	729.196	627.754	507.208	−716.893	405.206	−4.233
5100	108.075	731.336	629.764	518.015	−717.586	427.656	−4.380
5200	108.075	733.435	631.738	528.823	−718.217	450.117	−4.521
5300	108.076	735.493	633.676	539.630	−718.785	472.591	−4.658
5400	108.076	737.513	635.580	550.438	−719.291	495.075	−4.789
5500	108.077	739.496	637.452	561.245	−719.734	517.567	−4.915
5600	108.077	741.444	639.292	572.053	−720.114	540.067	−5.038
5700	108.077	743.357	641.100	582.861	−720.433	562.573	−5.155
5800	108.078	745.236	642.880	593.669	−720.691	585.083	−5.269
5900	108.078	747.084	644.630	604.476	−720.888	607.599	−5.379
6000	108.078	748.900	646.353	615.284	−721.028	630.116	−5.486

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [278.24 \pm 1.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 278.4 \pm 1.0\ K$

$\Delta_f H°(298.15\ K) = -457.31 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

Schafer and Heine[1] measured the enthalpy of solution of Si(cr) in an HF solution containing AgF. For the overall reaction $SiBr_4(l) + 4\ Ag(cr) = Si(cr) + 4\ AgBr(cr)$, they reported $\Delta_r H°(298.15\ K) = +13.3\ kcal \cdot mol^{-1}$.Using auxiliary data for AgBr,[2] we calculate $\Delta_f H°(298.15\ K) = -109.3\ kcal \cdot mol^{-1}$ ($-457.311\ kJ \cdot mol^{-1}$) for $SiBr_4$(l). We adopt this value and assign an uncertainty of $\pm 2.0\ kcal \cdot mol^{-1}$. Wolf *et al.*[3] studied the enthalpies of solution of $SiBr_4$(l) and Na_2SiO_3(cr) in caustic solution. The net reaction of interest, $SiBr_4(l) + 6\ NaOH(cr) = Na_2SiO_3(cr) + 4\ NaBr(cr) + 3\ H_2O(l)$, yielded $\Delta_r H°(298.15\ K) = -199.32\ kcal \cdot mol^{-1}$ based on the appropriate combination of results from five solution studies. Using current auxiliary data,[4,5] we update this value to $\Delta_r H°(298.15\ K) = -198.06\ kcal \cdot mol^{-1}$ and calculate $\Delta_f H°(298.15\ K) = -114.8\ kcal \cdot mol^{-1}$ for $SiBr_4$(l). This data is suspect due to uncertainties in the conversion of data from Na_2SiO_3 (calorimetric solution) to Na_2SiO_3(cr). The final state of the calorimetric solution is not well defined or well known and thus large uncertainties result.

Heat Capacity and Entropy

The heat capacity from 25–100°C was determined calorimetrically within 2% by Sladkov.[6] The constant value of 35.0 $cal \cdot K^{-1} \cdot mol^{-1}$ is extrapolated to 800 K. The entropy at 298.15 K is chosen so as to bring the 2nd and 3rd law analysis of the vapor pressure data into agreement.

Fusion Data

Pohland[7] reported the melting point of $SiBr_4$ to be 5.2°C (±1°C). No data are available on the enthalpy of fusion.

Vaporization Data

T_{vap} is calculated as that temperature for which $\Delta_r G° = 0$ for the process $SiBr_4(l) = SiBr_4(g)$ [f = 1 bar]. $\Delta_{vap} H°$ is calculated as the difference between the $\Delta_f H°$ values for the ideal gas and the liquid at T_{vap}. Normal boiling points (p = 1 atm) reported in the literature are 426.0 K[7] and 426.6 K,[8] and 427.8 K (766 mm Hg).[9] A normal boiling point (p = 1 bar) should be slightly lower than our calculated T_{vap} which corresponds to f = 1 bar. Refer to the $SiBr_4$(g) table for a possible explanation of this discrepancy.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	146.440	278.236	278.236	0.	−457.311	−443.896	77.769
300	146.440	279.142	278.239	0.271	−457.357	−443.812	77.275
400	146.440	321.270	283.983	14.915	−513.795	−427.415	55.815
500	146.440	353.947	294.829	29.559	−508.812	−406.401	42.456
600	146.440	380.646	306.975	44.203	−503.983	−386.374	33.637
700	146.440	403.220	319.153	58.847	−499.264	−367.147	27.397
800	146.440	422.774	330.911	73.491	−494.634	−348.591	22.761

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = 379.36 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -385.55 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -415.47 \pm 16.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
246.7(1)	494 (3)
84.8(2)	133.6(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Si–Br = 2.15 ± 0.02 Å
Bond Angle: Br–Si–Br = 109.47122°
Product of the Moments of Inertia: $I_A I_B I_C = 4.37533 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

Pohland[1] has studied the vaporization of $SiBr_4$ from 260–426 K (0.8–755.5 mm Hg). This vapor pressure data (20 points) is corrected for vapor non-ideality by means of the equation $\Delta G°/T \approx -R \ln p - Bp/T$. The Berthelot equation of state and critical constants T_c = 656 K and P_c = 41.3 atm as suggested in the review article by Lapidus *et al.*[2] are used to calculate B. The recent study on orthobaric densities by Nisel'son *et al.*[3] reported T_c = 663 K. The use of this latter value does not signficantly affect the results.

A 2nd and 3rd law analysis of this corrected data[1] yields $\Delta_{vap}H°(298.15\ K) = 10.0\ kcal \cdot mol^{-1}$. The entropy of the liquid at 298.15 K is adjusted so as to bring the 2nd and 3rd law results into agreement. This treatment suggests that the five lowest pressure data points (260–345 K, 0.8–60.3 mm Hg) are biased. These five points are not included in the above analysis. Any vapor pressure equation used to represent this data will be significantly altered in neglecting these five data points.

We adopt $\Delta_{vap}H°(298.15\ K) = 10.0\ kcal \cdot mol^{-1}$ which leads to $\Delta_f H°(298.15\ K) = -99.3\ kcal \cdot mol^{-1}$ ($-415.471\ kJ \cdot mol^{-1}$).[4] Using auxiliary data,[4] we calculate $\Delta_{at}H°(SiBr_4, g) = 311.54\ kcal \cdot mol^{-1}$ (1303.48 $kJ \cdot mol^{-1}$). This value is 4.03 times the dissociation energy of SiBr(g).[4]

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark and Rippon,[5] who recorded the Raman spectra in the vapor phase (210°C). The spectral data were interpreted in terms of a tetrahedral structure. This structure is consistent with the electron diffraction data of Lister and Sutton,[6] Yamasaki *et al.*,[7] and Spitzer *et al.*,[8] which suggested a tetrahedral structure with a Si–Br bond distance of 2.15 ± 0.02 Å. We adopt this bond distance. The principal moments of inertia are: $I_A = I_B = I_C = 163.5574 \times 10^{-39}\ g \cdot cm^2$. Shimanouchi, in a recent compilation of molecular vibrational frequencies,[9] suggested somewhat different values (249, 90, 487, 137 cm^{-1}) based on earlier infrared and Raman studies by Trumpy,[10] Delwaulle,[11] and Radhakrishnan,[12] and Long *et al.*[13] These frequencies would lead to a $S°(298.15\ K)$ value of 90.3 $cal \cdot K^{-1} \cdot mol^{-1}$ (377.9 $J \cdot K^{-1} \cdot mol^{-1}$). Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of this work was published prior to the Clark and Rippon study,[5] it will not be further discussed or referenced. The same situation exists for temperature dependent thermochemical tabulations of $SiBr_4$(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.313	−385.548	−385.548	INFINITE
100	70.691	287.079	459.223	−17.214	−386.301	−403.857	210.953
200	88.479	342.240	388.009	−9.154	−389.222	−420.368	109.789
250	93.599	362.569	380.944	−4.594	−391.143	−427.942	89.414
298.15	97.009	379.365	379.365	0.	−415.471	−432.207	75.721
300	97.117	379.965	379.367	0.180	−415.609	−432.311	75.272
350	99.568	395.131	380.559	5.100	−477.023	−431.728	64.432
400	101.316	408.547	383.235	10.125	−476.745	−425.276	55.535
450	102.594	420.558	386.726	15.224	−476.453	−418.860	48.620
500	103.552	431.419	390.661	20.379	−476.152	−412.477	43.091
600	104.857	450.424	399.083	30.805	−475.541	−399.799	34.806
700	105.676	466.654	407.605	41.334	−474.936	−387.224	28.895
800	106.222	480.803	415.889	51.931	−474.354	−374.733	24.468
900	106.603	493.337	423.811	62.573	−473.801	−362.314	21.028
1000	106.879	504.584	431.336	73.248	−473.285	−349.955	18.280
1100	107.085	514.781	438.466	83.947	−472.809	−337.645	16.033
1200	107.243	524.106	445.219	94.664	−472.375	−325.377	14.163
1300	107.366	532.695	451.622	105.394	−471.986	−313.143	12.582
1400	107.464	540.655	457.701	116.136	−471.645	−300.938	11.228
1500	107.544	548.072	463.481	126.886	−471.357	−288.755	10.055
1600	107.609	555.015	468.987	137.644	−471.123	−276.590	9.030
1700	107.663	561.540	474.242	148.408	−521.126	−263.990	8.111
1800	107.709	567.696	479.264	159.177	−520.785	−248.874	7.222
1900	107.747	573.520	484.073	169.949	−520.470	−233.777	6.427
2000	107.780	579.048	488.685	180.726	−520.184	−218.695	5.712
2100	107.809	584.307	493.114	191.505	−519.932	−203.627	5.065
2200	107.833	589.323	497.374	202.287	−519.717	−188.570	4.477
2300	107.855	594.117	501.477	213.072	−519.543	−173.522	3.941
2400	107.874	598.707	505.433	223.858	−519.412	−158.480	3.449
2500	107.890	603.111	509.253	234.647	−519.324	−143.443	2.997
2600	107.905	607.343	512.945	245.436	−519.280	−128.410	2.580
2700	107.918	611.416	516.517	256.228	−519.279	−113.376	2.193
2800	107.930	615.341	519.977	267.020	−519.320	−98.342	1.835
2900	107.941	619.128	523.331	277.814	−519.400	−83.306	1.500
3000	107.950	622.788	526.585	288.608	−519.515	−68.267	1.189
3100	107.959	626.328	529.746	299.404	−519.663	−53.222	0.897
3200	107.967	629.756	532.818	310.200	−519.837	−38.173	0.623
3300	107.974	633.078	535.806	320.997	−520.034	−23.118	0.366
3400	107.981	636.301	538.715	331.795	−520.248	−8.057	0.124
3500	107.987	639.432	541.548	342.593	−520.474	7.010	−0.105
3600	107.992	642.474	544.309	353.392	−904.858	32.546	−0.472
3700	107.997	645.433	547.003	364.192	−904.677	58.583	−0.827
3800	108.002	648.313	549.631	374.992	−904.495	84.614	−1.163
3900	108.006	651.118	552.197	385.792	−904.305	110.640	−1.482
4000	108.010	653.853	554.705	396.593	−904.103	136.662	−1.785
4100	108.014	656.520	557.156	407.394	−903.883	162.679	−2.073
4200	108.017	659.123	559.552	418.196	−903.643	188.689	−2.347
4300	108.021	661.665	561.898	428.998	−903.377	214.694	−2.608
4400	108.024	664.148	564.193	439.800	−903.083	240.693	−2.857
4500	108.026	666.576	566.442	450.602	−902.756	266.684	−3.096
4600	108.029	668.950	568.644	461.405	−902.396	292.667	−3.323
4700	108.031	671.273	570.803	472.208	−901.999	318.643	−3.541
4800	108.034	673.548	572.920	483.011	−901.563	344.610	−3.750
4900	108.036	675.775	574.997	493.815	−901.087	370.567	−3.950
5000	108.038	677.958	577.034	504.618	−900.570	396.514	−4.142
5100	108.040	680.097	579.034	515.422	−900.010	422.450	−4.327
5200	108.042	682.195	580.998	526.226	−899.407	448.374	−4.504
5300	108.043	684.253	582.927	537.031	−898.760	474.288	−4.674
5400	108.045	686.273	584.822	547.835	−898.070	500.188	−4.838
5500	108.047	688.255	586.685	558.640	−897.335	526.075	−4.996
5600	108.048	690.202	588.516	569.444	−896.557	551.948	−5.148
5700	108.049	692.115	590.317	580.249	−895.735	577.807	−5.295
5800	108.051	693.994	592.088	591.054	−894.871	603.650	−5.436
5900	108.052	695.841	593.831	601.859	−893.966	629.479	−5.573
6000	108.053	697.657	595.546	612.665	−893.018	655.292	−5.705

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 243.6 \pm 6.7\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 311.4\ K$

$\Delta_f H°(0\ K) = -592.68 \pm 4.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -617.98 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 12.887\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TiBr_4, cr, 298.15\ K)$ has been determined calorimetrically by several investigators as follows.

Source	Reaction	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Nelson *et al.*[1]	$Ti(cr) + 2\ Br_2(g) = TiBr_4(cr)$	−147.3 ± 1.1
Johnson *et al.*[2]	$TiCl_4(l) + 2\ Br_2(l) = TiBr_4(cr) + 2\ Cl_2(g)$	−147.6 ± 1.3
Schlafer and Schmidtke[3]	$Ti(cr) + 2\ Br_2(l) = TiBr_4(cr)$	−147.7 ± 0.3
Gross, *et al.*[4]	$Ti(cr) + 2\ Br_2(l) = TiBr_4(cr)$	−148.1 ± 0.3

The chosen value of $\Delta_f H°(298.15\ K) = -147.7 \pm 1.0\ kcal \cdot mol^{-1}$ ($617.977 \pm 4.2\ kJ \cdot mol^{-1}$) is the average of these determinations. The value from the work of Nelson *et al.*[1] is obtained from their enthalpy of reaction and the JANAF value for the enthalpy of vaporization of bromine. The value obtained from Johnson *et al.*[2] is a combination of their enthalpy of reaction and the JANAF value for the enthalpy of formation of $TiCl_4(l)$.

Heat Capacity and Entropy

The heat capacity of $TiBr_4(cr)$ has been measured over the temperature range 51 to 298.15 K by King *et al.*[5] They reported a value of 42.74 $cal \cdot K^{-1} \cdot mol^{-1}$ for $S°(298.15\ K) - S°(51\ K)$ based on their measurements. The value of $S°(51\ K)$ is estimated as 15.46 $cal \cdot K^{-1} \cdot mol^{-1}$. King *et al.*[5] reported an estimate of $14.75 \pm 1.60\ cal \cdot K^{-1} \cdot mol^{-1}$ for the same quantity. The former estimate is used so that the values of $\Delta_{sub} H°(298.15\ K)$ obtained by both 2nd and 3rd law methods are in agreement. See $TiBr_4(g)$ table for details. The value of $H°(51\ K) - H°(0\ K)$ is estimated as 0.372 $kcal \cdot mol^{-1}$. This estimate is based on a Debye–Einstein extrapolation of the measured heat capacity with vibrational contributions removed.

Fusion Data

The melting temperature and heat of melting were reported by King *et al.*[5]

References

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[5]E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 20 pp. (1961).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−28.556	−592.684	−592.684	INFINITE
100	94.098	120.922	349.954	−22.903	−593.178	−593.675	310.104
200	117.273	194.146	255.191	−12.209	−594.203	−593.819	155.090
298.15	131.503	243.622	243.622	0.	−617.977	−590.681	103.485
300	131.815	244.436	243.624	0.244	−618.060	−590.512	102.817
311.400	133.779	249.388	243.745	1.757	--- CRYSTAL <--> LIQUID ---		
400	133.779	282.886	248.860	13.611	−676.266	−569.177	74.327
500	133.779	312.738	258.761	26.989	−673.012	−542.785	56.704
600	133.779	337.129	269.852	40.366	−669.899	−517.034	45.012
700	133.779	357.751	280.974	53.744	−666.885	−491.796	36.698
800	133.779	375.615	291.712	67.122	−663.937	−466.985	30.491
900	133.779	391.372	301.927	80.500	−661.078	−442.539	25.684
1000	133.779	405.467	311.589	93.878	−658.370	−418.404	21.855
1100	133.779	418.218	320.712	107.256	−655.873	−394.530	18.735
1200	133.779	429.858	329.329	120.634	−657.574	−370.753	16.138
1300	133.779	440.566	337.480	134.012	−654.777	−346.966	13.941
1400	133.779	450.480	345.202	147.390	−652.077	−323.390	12.066
1500	133.779	459.710	352.531	160.768	−649.487	−300.004	10.447

PREVIOUS: June 1964 CURRENT: June 1968

$S°(298.15\ K)$ = [284.168] $J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = 311.4 K

$\Delta_f H°(298.15\ K)$ = [−605.345] $kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = 12.887 $kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(311.4\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

King *et al.*[1] reported the heat capacity of $TiBr_4$(l) between the melting point and normal boiling point. $S°(TiBr_4, l, 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The melting temperature and heat of melting were reported by King *et al.*[1]

Vaporization Data

The boiling temperature, T_{vap}, is taken as the point at which $K_p = 1$ for the reaction $TiBr_4(l) = TiBr_4(g)$ at one bar. The enthalpy of vaporization is calculated as the difference between $\Delta_f H°$ of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $TiBr_4$(g).

Reference

[1] E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, 20 pp. (1961).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	151.879	284.168	284.168	0.	−605.345	−590.138	103.390
300	151.879	285.107	284.171	0.281	−605.391	−590.044	102.736
400	151.879	328.800	290.128	15.469	−661.776	−573.053	74.833
500	151.879	362.691	301.377	30.657	−656.712	−551.461	57.611
600	151.879	390.382	313.974	45.845	−651.789	−530.876	46.217
700	151.879	413.794	326.605	61.033	−646.966	−511.106	38.139
800	151.879	434.075	338.799	76.221	−642.207	−492.023	32.126
900	151.879	451.964	350.399	91.408	−637.539	−473.531	27.483
1000	151.879	467.966	361.369	106.596	−633.020	−455.552	23.796

PREVIOUS: June 1964 CURRENT: June 1968

0 to	311.4 K	crystal
above	311.4 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−28.556	−592.684	−592.684	INFINITE
100	94.098	120.922	349.954	−22.903	−593.178	−593.675	310.104
200	117.273	194.146	255.191	−12.209	−594.203	−593.819	155.090
298.15	131.503	243.622	243.622	0.	−617.977	−590.681	103.485
300	131.815	244.436	243.624	0.244	−618.060	−590.512	102.817
311.400	133.779	249.388	243.745	1.757	____ CRYSTAL <--> LIQUID ____		
311.400	151.879	290.772	243.745	14.644	TRANSITION		
400	151.879	328.800	258.549	28.101	−661.776	−573.053	74.833
500	151.879	362.691	276.114	43.289	−656.712	−551.461	57.611
600	151.879	390.382	292.921	58.476	−651.789	−530.876	46.217
700	151.879	413.794	308.559	73.664	−646.966	−511.106	38.139
800	151.879	434.075	323.009	88.852	−642.207	−492.023	32.126
900	151.879	451.964	336.363	104.040	−637.539	−473.531	27.483
1000	151.879	467.966	348.738	119.228	−633.020	−455.552	23.796

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = 398.60 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -520.3 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -550.2 \pm 5.0\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
229.5(1)	382 (3)
74 (2)	90.5(3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distance: Ti–Br = 2.31 Å
Bond Angle: Br–Ti–Br = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 6.73056 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiBr_4$ (g) is calculated from those of $TiBr_4$ (cr) and $TiBr_4$ (l) and the enthalpies of reaction for the processes (A) $TiBr_4(cr) = TiBr_4(g)$ and (B) $TiBr_4(l) = TiBr_4(g)$. 2nd and 3rd law analyses of the vapor pressure data for these processes yield the following results. The first four investigations employed the spoon gauge method, the last investigation being a manometric determination.

Source	Reaction	Points	T/K	2nd law	3rd law	$cal \cdot K^{-1} \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
Boni, 1966[1]	A	13	275–311	16.4 ± 0.2	16.19	−0.6 ± 0.5	−131.5
Funaki *et al.*, 1961[2]	B	14	385–493	12.2 ± 0.3	12.92	1.6 ± 0.3	−131.8
Seki, 1941[3]	A	12	286–306	15.4 ± 0.5	15.90	1.6 ± 1.6	−131.8
Hall *et al.*, 1958[4]	B	89*	341–499	13.2 ± 0.1	13.14	−0.1 ± 0.1	−131.5
Keavney & Smith, 1960[5]	A	14	287–310	16.1 ± 0.3	16.14	0.2 ± 0.8	−131.6

* Four points rejected due to failure of a statistical test.

The adopted value of $-131.5\ kcal \cdot mol^{-1}$ ($-550.196\ kJ \cdot mol^{-1}$) is that obtained from the data of Hall *et al.*,[4] whose 3rd law drift was adjusted to zero by changing the entropy of the crystal within its uncertainty.

Heat Capacity and Entropy

The interatomic distance was reported by Lister and Sutton.[6] The tetrahedral configuration is confirmed by spectroscopic studies.[7,8] The principal moments of inertia are: $I_A = I_B = I_C = 188.8066 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies have been reported by Delwaulle and Francois[7] and by Miller and Carlson.[8] These values are based primarily on the Raman and infrared spectra of $TiBr_4$(l), the value of υ_3 being the only frequency measured for $TiBr_4$(g).

The electronic spectra of $TiBr_4$ in solution have been measured by Dijkgraaf.[9] Di Sipio *et al.*[10] have reported the near ultraviolet spectra of $TiBr_4$(g). Both of these studies indicate that $TiBr_4$ has no low lying electronic levels which would contribute significantly to the entropy.

References

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[8]F. A. Miller and G. L. Carlson, Spectrochim. Acta **16**, 6 (1960).
[9]C. Dijkgraaf, Spectrochim. Acta **21**, 769 (1965).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−23.904	−520.252	−520.252	INFINITE
100	76.813	300.230	482.949	−18.272	−520.766	−539.194	281.646
200	94.011	359.619	407.640	−9.604	−523.818	−556.528	145.350
250	98.156	381.078	400.246	−4.792	−525.801	−564.484	117.943
298.15	100.711	398.601	398.601	0.	−550.196	−569.107	99.705
300	100.790	399.224	398.603	0.186	−550.336	−569.224	99.111
350	102.533	414.900	399.837	5.272	−611.838	−569.000	84.919
400	103.734	428.675	402.598	10.431	−611.665	−562.892	73.506
450	104.591	440.945	406.189	15.640	−611.496	−556.805	64.632
500	105.222	451.999	410.227	20.886	−611.333	−550.737	57.535
600	106.066	471.264	418.841	31.454	−611.030	−538.647	46.893
700	106.588	487.657	427.530	42.089	−610.760	−526.605	39.296
800	106.932	501.914	435.956	52.766	−610.513	−514.599	33.600
900	107.171	514.523	443.999	63.472	−610.326	−502.623	29.171
1000	107.343	525.824	451.626	74.198	−610.269	−490.660	25.629
1100	107.471	536.061	458.844	84.939	−610.410	−478.694	22.731
1200	107.568	545.417	465.674	95.691	−614.736	−466.586	20.310
1300	107.644	554.030	472.144	106.452	−614.557	−454.248	18.252
1400	107.705	562.009	478.281	117.219	−614.467	−441.921	16.488
1500	107.754	569.442	484.114	127.992	−614.482	−429.597	14.960
1600	107.794	576.398	489.667	138.770	−614.618	−417.267	13.622
1700	107.827	582.934	494.963	149.551	−614.891	−404.925	12.442
1800	107.855	589.098	500.023	160.335	−615.318	−392.563	11.392
1900	107.879	594.930	504.866	171.122	−615.917	−380.172	10.452
2000	107.899	600.464	509.508	181.911	−631.391	−367.291	9.593
2100	107.917	605.729	513.966	192.702	−633.132	−354.043	8.806
2200	107.932	610.749	518.252	203.494	−634.911	−340.712	8.090
2300	107.945	615.547	522.379	214.288	−636.732	−327.299	7.433
2400	107.957	620.142	526.357	225.083	−638.596	−313.805	6.830
2500	107.967	624.549	530.197	235.879	−640.504	−300.233	6.273
2600	107.976	628.784	533.908	246.676	−642.457	−286.584	5.758
2700	107.984	632.859	537.498	257.474	−644.453	−272.859	5.279
2800	107.991	636.786	540.974	268.273	−646.492	−259.059	4.833
2900	107.998	640.576	544.344	279.073	−648.570	−245.185	4.416
3000	108.004	644.237	547.613	289.873	−650.684	−231.240	4.026
3100	108.009	647.779	550.787	300.673	−652.831	−217.223	3.660
3200	108.014	651.208	553.872	311.475	−655.005	−203.136	3.316
3300	108.018	654.532	556.872	322.276	−657.201	−188.981	2.991
3400	108.022	657.756	559.792	333.078	−659.415	−174.760	2.685
3500	108.026	660.888	562.636	343.881	−661.641	−160.473	2.395
3600	108.029	663.931	565.408	354.683	−663.873	−146.122	2.120
3700	108.032	666.891	568.111	365.486	−1075.206	−123.921	1.749
3800	108.035	669.772	570.748	376.290	−1076.202	−98.198	1.350
3900	108.038	672.578	573.324	387.093	−1077.245	−72.447	0.970
4000	108.040	675.314	575.839	397.897	−1078.329	−46.669	0.609
4100	108.042	677.982	578.298	408.701	−1079.447	−20.864	0.266
4200	108.045	680.585	580.703	419.506	−1080.595	4.969	−0.062
4300	108.047	683.127	583.055	430.310	−1081.767	30.829	−0.375
4400	108.048	685.611	585.358	441.115	−1082.958	56.718	−0.673
4500	108.050	688.040	587.613	451.920	−1084.163	82.633	−0.959
4600	108.052	690.414	589.822	462.725	−1085.378	108.575	−1.233
4700	108.053	692.738	591.987	473.530	−1086.599	134.544	−1.495
4800	108.055	695.013	594.110	484.336	−1087.821	160.538	−1.747
4900	108.056	697.241	596.192	495.141	−1089.041	186.558	−1.989
5000	108.057	699.424	598.235	505.947	−1090.255	212.604	−2.221
5100	108.058	701.564	600.240	516.753	−1091.462	238.673	−2.445
5200	108.059	703.662	602.209	527.559	−1092.657	264.765	−2.660
5300	108.060	705.721	604.142	538.365	−1093.838	290.881	−2.867
5400	108.061	707.741	606.042	549.171	−1095.004	317.019	−3.067
5500	108.062	709.723	607.909	559.977	−1096.151	343.178	−3.259
5600	108.063	711.671	609.745	570.783	−1097.279	369.358	−3.445
5700	108.064	713.583	611.550	581.590	−1098.386	395.558	−3.625
5800	108.065	715.463	613.325	592.396	−1099.469	421.776	−3.799
5900	108.066	717.310	615.072	603.202	−1100.528	448.014	−3.966
6000	108.066	719.126	616.791	614.009	−1101.562	474.269	−4.129

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [224.7 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 723 \pm 1\ K$

$\Delta_f H°(0\ K) = [-734.3 \pm 8.4]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -760.7 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

Turnbull[1] measured the enthalpies of reaction for the dissolution of the zirconium tetrahalides in caustic and in water. The reported enthalpies of reaction and the corresponding reactions may be combined to yield the following:

$$ZrBr_4(cr) + 4NaCl(aq) = ZrCl_4(cr) + 4NaBr(aq),\ \Delta_r H°(298.15\ K) = -8.10 \pm 0.9\ kcal \cdot mol^{-1}$$

$$ZrBr_4(cr) + 4Cl^-(aq) = ZrCl_4(cr) + 4Br^-(aq),\ \Delta_r H°(298.15\ K) = -9.83 \pm 0.6\ kcal \cdot mol^{-1}$$

Using auxiliary data,[2,4] we calculate $\Delta_f H°(298.15\ K) = -182.67$ and $-181.02\ kcal \cdot mol^{-1}$ for $ZrBr_4$(cr) from these two reactions. We adopt a mean of these two values, $\Delta_f H°(298.15\ K) = -181.8\ kcal \cdot mol^{-1}$ ($-760.651\ kJ \cdot mol^{-1}$), and assign an uncertainty of $\pm 1.5\ kcal \cdot mol^{-1}$. This same value was suggested by NBS.[3]

Heat Capacity and Entropy

There are no heat capacity and enthalpy data reported in the literature for $ZrBr_4$(cr). The adopted heat capacity values are estimated so as to give reasonable trends in comparison with $ZrCl_4$ and ZrI_4 and to be consistent with the existing sublimation data.

The crystal data compilation of Donnay and Ondik[5] tabulated both $ZrCl_4$ and $ZrBr_4$ as cubic structures. Thus, the adopted heat capacity values are estimated so as to parallel those for $ZrCl_4$. The heat capacity values below 300 K are calculated by summing contributions due to hindered translations, librations, and internal vibrations of the crystal. The parameters used in the calculations are determined by a correlation with corresponding parameters for $ZrCl_4$[6] and a consideration of the sublimation data for $ZrBr_4$.[6] The high temperature heat capacities are obtained graphically.

Fusion Data

The melting point was observed by Rahlfs and Fischer[7] to be 723 ± 1 K and by Nisel'son[8] to be 723 ± 0.5 K.

Sublimation Data

The sublimation data is treated in the $ZrBr_4$(g) table.[6] The enthalpy of sublimation is adopted as $\Delta H°(298.15\ K) = 27.7 \pm 0.3\ kcal \cdot mol^{-1}$ ($115.897 \pm 1.3\ kJ \cdot mol^{-1}$). The sublimation temperture, T_{sub}, is calculated as that temperature for which $\Delta_r G° = 0$ for the process $ZrBr_4(cr) = ZrBr_4(g)$ at one bar. Since T_{sub} is less than T_{fus}, the liquid phase is thermodynamically unstable at a pressure of one atmosphere.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−28.162	−734.298	−734.298	INFINITE
100	93.625	103.324	328.883	−22.556	−735.164	−733.321	383.048
200	116.077	176.515	235.865	−11.870	−736.473	−730.998	190.917
298.15	124.805	224.689	224.689	0.	−760.651	−725.293	127.068
300	124.917	225.462	224.692	0.231	−760.747	−725.073	126.246
400	129.286	262.045	229.650	12.958	−819.539	−700.929	91.532
500	131.629	291.157	239.139	26.009	−816.496	−671.627	70.164
600	133.344	315.313	249.879	39.260	−813.375	−642.945	55.973
700	134.725	335.974	260.738	52.666	−810.213	−614.789	45.876
800	135.896	354.041	271.295	66.197	−807.037	−587.089	38.333
900	137.068	370.115	281.398	79.845	−803.864	−559.786	32.489
1000	138.239	384.617	291.007	93.610	−800.703	−532.835	27.832

PREVIOUS: March 1964 CURRENT: June 1975

$S°(298.15\ K) = 414.49 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -615.2 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -644.8 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
223 (1)
60 (2)
315 (3)
72 (3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Zr–Br = 2.44 ± 0.02 Å
Bond Angle: Br–Zr–Br = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 9.34800 \times 10^{-111}\ g^3·cm^6$

Enthaply of Formation

The enthaply of formation for $ZrBr_4$(g) is calculated from the enthaplies of formation and sublimation of $ZrBr_4$(cr) at 298.15 K. The adopted value for the enthaply of sublimation, $\Delta_{sub}H°(298.15\ K) = 27.7 \pm 0.3\ kcal·mol^{-1}$, is based on the mean of the 3rd law results from the following sublimation data.

In analyzing the vapor pressure data for the four sublimation studies,[1-4] corrections were made for non–ideality by means of the equation $\Delta G°/T = -R\ln p - Bp/T$. The Berthelot equation of state and the critical constants T_c = 805.15 K and P_c = 42.9 atm, as reported by Nisel'son and Sokolova,[5] are used to calculate B.

Source	Method	Data Points	T/K	$\Delta_{sub}H°(298.15\ K)$,kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Rahlfs and Fischer[1]	static	15	538–633	27.85 ± 0.24	27.78 ± 0.09	−0.1 ± 0.4	−154.02
Schlafer and Skoludek[2]	static	eqn	494–620	28.59	27.66	−1.7	−154.14
Berdonosova *et al.*[3]		17	489–606	28.87 ± 0.12	28.03 ± 0.12	−1.5 ± 0.2	−153.77
Normanton and Shelton[4]	effusion	eqn	400–500	26.32	27.30	2.2	−154.50

For the enthalpy of sublimation, we adopt the mean of the 3rd law results and assign an uncertainty of ±0.3 kcal·mol^{-1}. Combining the adopted $\Delta_{sub}H°(298.15\ K)$ value with the enthalpy of formation of $ZrBr_4$(cr), $\Delta_f H°(298.15\ K) = -181.8 \pm 1.5\ kcal·mol^{-1}$,[6] we calculate $\Delta_f H°(298.15\ K) = -154.1\ kcal·mol^{-1}$ (−644.754 kJ·mol^{-1}) for $ZrBr_4$(g) and assign an uncertainty of ±2.0 kcal·mol^{-1} (±8.4 kJ·mol^{-1}).

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark *et al.*,[7-9] who recorded the Raman spectra of $ZrBr_4$in the vapor phase (380–420°C). These studies by Clark *et al.*[7-9] indicated that $ZrBr_4$ is a tetrahedral monomer in the vapor phase. Shimanouchi, in his compilation of molecular vibrational frequencies,[10] also adopted the values of Clark *et al.*[7-9] for $ZrBr_4$(g). Rahlfs and Fischer,[1] through vapor density measurements, had earlier concluded that $ZrBr_4$ was monomeric in the vapor phase.

Berdonosov *et al.*[11] referenced an electron diffraction study by Cherkasov[12] which showed that, in the vapor phase, the Zr–Br internuclear distance was 2.44 ± 0.02 Å. We adopt this value. The principal moments of inertia are: $I_A = I_B = I_C = 210.6556 \times 10^{-39}\ g·cm^2$.

Much literature has been published on the inter–relationships between force constants and vibrational frequencies. Since the majority of these articles are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of $ZrBr_4$(g). One exception is that Clark *et al.*[7] calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is very similar to ours in the range *100–1000 K*; the difference in entropy being less than 0.02 cal·K^{-1}·mol^{-1} in this range.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−24.954	−615.192	−615.192	INFINITE
100	81.107	312.254	501.497	−18.924	−615.635	−634.686	331.526
200	97.300	374.463	423.743	−9.856	−618.562	−652.677	170.462
250	100.676	396.571	416.167	−4.899	−620.453	−660.995	138.107
298.15	102.669	414.487	414.487	0.	−644.754	−665.984	116.678
300	102.730	415.122	414.489	0.190	−644.891	−666.115	115.981
350	104.052	431.064	415.745	5.362	−706.291	−666.288	99.438
400	104.947	445.021	418.550	10.588	−706.012	−660.593	86.265
450	105.577	457.420	422.193	15.852	−705.736	−654.932	76.022
500	106.038	468.569	426.283	21.143	−705.465	−649.301	67.832
600	106.649	487.960	434.994	31.780	−704.959	−638.117	55.553
700	107.023	504.431	443.766	42.465	−704.517	−627.013	46.788
800	107.269	518.739	452.263	53.180	−704.156	−615.966	40.218
900	107.439	531.384	460.366	63.916	−703.896	−604.959	35.111
1000	107.561	542.710	468.044	74.667	−703.750	−593.976	31.026
1100	107.652	552.966	475.305	85.428	−703.727	−583.000	27.684
1200	107.721	562.336	482.173	96.196	−707.543	−571.800	24.890
1300	107.775	570.961	488.675	106.971	−707.238	−560.500	22.521
1400	107.818	578.949	494.842	117.751	−706.988	−549.223	20.492
1500	107.852	586.389	500.700	128.534	−706.806	−537.961	18.733
1600	107.881	593.351	506.275	139.321	−706.704	−526.708	17.195
1700	107.904	599.892	511.592	150.110	−706.698	−515.459	15.838
1800	107.924	606.060	516.670	160.902	−706.800	−504.208	14.632
1900	107.941	611.896	521.530	171.695	−707.025	−492.947	13.552
2000	107.955	617.433	526.188	182.490	−707.388	−481.671	12.580
2100	107.967	622.700	530.659	193.286	−707.903	−470.373	11.700
2200	107.978	627.723	534.958	204.083	−729.907	−458.301	10.881
2300	107.987	632.523	539.096	214.882	−731.183	−445.927	10.127
2400	107.995	637.119	543.085	225.681	−732.503	−433.496	9.435
2500	108.003	641.528	546.936	236.481	−733.868	−421.009	8.797
2600	108.009	645.764	550.656	247.281	−735.278	−408.468	8.206
2700	108.015	649.840	554.254	258.082	−736.732	−395.870	7.659
2800	108.020	653.769	557.739	268.884	−738.228	−383.219	7.149
2900	108.024	657.559	561.116	279.686	−739.763	−370.513	6.674
3000	108.028	661.221	564.392	290.489	−741.335	−357.754	6.229
3100	108.032	664.764	567.573	301.292	−742.939	−344.941	5.812
3200	108.036	668.194	570.664	312.095	−744.571	−332.077	5.421
3300	108.039	671.518	573.670	322.899	−746.226	−319.160	5.052
3400	108.041	674.743	576.596	333.703	−747.898	−306.194	4.704
3500	108.044	677.875	579.445	344.507	−749.582	−293.179	4.375
3600	108.046	680.919	582.221	355.312	−751.273	−280.114	4.064
3700	108.049	683.880	584.929	366.117	−752.966	−267.003	3.769
3800	108.051	686.761	587.571	376.922	−754.655	−253.847	3.489
3900	108.052	689.568	590.151	387.727	−756.336	−240.646	3.223
4000	108.054	692.303	592.670	398.532	−758.003	−227.401	2.970
4100	108.056	694.972	595.133	409.338	−759.653	−214.116	2.728
4200	108.057	697.575	597.541	420.143	−761.281	−200.791	2.497
4300	108.059	700.118	599.897	430.949	−762.884	−187.426	2.277
4400	108.060	702.602	602.203	441.755	−764.459	−174.025	2.066
4500	108.061	705.031	604.462	452.561	−766.002	−160.589	1.864
4600	108.062	707.406	606.674	463.367	−767.512	−147.119	1.671
4700	108.063	709.730	608.842	474.173	−768.985	−133.616	1.485
4800	108.064	712.005	610.967	484.980	−1331.356	−108.465	1.180
4900	108.065	714.233	613.052	495.786	−1332.403	−82.977	0.885
5000	108.066	716.416	615.098	506.593	−1333.426	−57.468	0.600
5100	108.067	718.556	617.106	517.399	−1334.423	−31.938	0.327
5200	108.068	720.655	619.077	528.206	−1335.391	−6.391	0.064
5300	108.068	722.713	621.013	539.013	−1336.329	19.177	−0.189
5400	108.069	724.733	622.915	549.820	−1337.234	44.761	−0.433
5500	108.070	726.716	624.784	560.627	−1338.107	70.361	−0.668
5600	108.070	728.664	626.622	571.434	−1338.944	95.977	−0.895
5700	108.071	730.576	628.429	582.241	−1339.746	121.608	−1.114
5800	108.072	732.456	630.206	593.048	−1340.510	147.252	−1.326
5900	108.072	734.303	631.955	603.855	−1341.237	172.909	−1.531
6000	108.073	736.120	633.676	614.662	−1341.926	198.579	−1.729

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K)$ = [258.78 ± 6.3] $J·K^{-1}·mol^{-1}$
T_{fus} = 527 ± 3 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −556.05 ± 12.6 $kJ·mol^{-1}$
$\Delta_{fus} H°$ = 24.016 ± 6.3 $kJ·mol^{-1}$

Enthalpy of Formation

The adopted value for the enthalpy of formation of $NbBr_5$(cr), $\Delta_f H°(298.15\ K) = -132.9 \pm 3.0$ $kcal·mol^{-1}$ (-556.054 ± 12.6 $kJ·mol^{-1}$) is based on the study of the direct bromination of Nb(cr) by Gross *et al.*[1]

Shchukarev *et al.*[2] studied the hydrolysis of $NbBr_5$(cr). Using the experimental results reported by Shchukarev *et al.*[2] and auxiliary data,[4,5] we calculate, $\Delta_f H°(298.15\ K) = -135.5 \pm 1.2$ $kcal·mol^{-1}$. Schafer and Heine[3] also determined the enthaply of formation of $NbBr_5$(cr) via calorimetric measurements of the heats of solution of Nb(cr) and $NbBr_5$(cr) in hydrofluoric acid. Using their data and auxiliary results,[4,5] we calculate $\Delta_f H°(298.15\ K) = -131.86 \pm 1.0$ $kcal·mol^{-1}$. These two solution results[2,3] are in reasonable agreement with the adopted value. The direct bromination[1] is thought to be the more reliable.

Heat Capacity and Entropy

The heat capacity and entropy are estimated in comparison with $NbCl_5$(cr).[4] As there is no low temperature heat capacity data reported in the literature, the entropy at 298.15 K is calculated from the equation $\Delta_{sub}S°(298.15\ K) = S°(g, 298.15\ K) - S°(cr, 298.15\ K)$; $S°(g, 298.15\ K)$ = 107.35 $cal·K^{-1}·mol^{-1}$ as given in the $NbBr_5$(g) table[4] and $\Delta_{sub}S°(298.15\ K)$ = 45.5 $cal·K^{-1}·mol^{-1}$ as suggested by comparison with $NbCl_5$ and $TaCl_5$.[4]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, is the difference between the $\Delta_f H°(298.15\ K)$ values for $NbBr_5$(g) and $NbBr_5$(cr). Two sublimation studies are summarized in the $NbBr_5$(g) table.[4]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	147.904	258.780	258.780	0.	−556.054	−508.887	89.155
300	147.904	259.695	258.783	0.274	−556.176	−508.593	88.554
400	147.904	302.245	264.585	15.064	−630.093	−477.367	62.338
500	147.904	335.249	275.540	29.854	−627.096	−439.535	45.918
527.000	147.904	343.027	278.800	33.848	--- CRYSTAL <--> LIQUID ---		
600	147.904	362.215	287.807	44.645	−624.217	−402.295	35.023
700	147.904	385.014	300.107	59.435	−621.429	−365.530	27.276
800	147.904	404.764	311.982	74.226	−618.717	−329.159	21.492

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = [274.005]\ J·K^{-1}·mol^{-1}$
$T_{fus}H° = 527 \pm 3\ K$

$\Delta_fH°(298.15\ K) = [-545.074]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 24.016 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(298.15)$ is calculated from that of $NbBr_5$(cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(527\ K)$–H(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be identical with that of $NbCl_5$(l)[3] including the assumed glass transition at 350 K. The entropy at 298.15 K is calcualted in a manner analogous to that used for $\Delta_fH°(298.15\ K)$.

Fusion Data

The adopted melting point, $T_{fus} = 527 \pm 3$ K (254°C), is based on the studies by *Nisel'son et al.*[1] and *Berdonosov et al.*[2] The melting point was determined by Nisel'son *et al.*[1] from cooling curves, $T_{fus} = 255$°C. Berdonosov *et al.*[2] determined the melting point by three methods: $T_{fus} = 252.0 \pm 1.5$ based on an analysis of their vapor pressure data, $T_{fus} = 255 \pm 2$ based on visual observation, and $T_{fus} = 254 \pm 1$ based on cooling curves.

The heat of melting is chosen to be $\Delta_{fus}H° = 5.74 \pm 1.5\ kcal·mol^{-1}$ ($24.016 \pm 6.3\ kJ·mol^{-1}$). This value is consistent with the vaporization data and the thermodynamic functions we have adopted. The entropy of melting, $\Delta_{fus}S° = 10.89\ cal·K^{-1}·mol^{-1}$ is somewhat lower than anticipated, based on the expected similarity with $NbCl_5$ and $TaCl_5$ as far as condensed phase dimerization is concerned.[3]

Vaporization Data

T_{vap}, the normal boiling point, is calculated as that temperature for which the Gibbs energy approaches zero for the process $NbBr_5(l) = NbBr_5(g)$. $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_fH°$ values for $NbBr_5$(g) and $NbBr_5$(l) at T_{vap}. Two vaporization studies are summarized in the $NbBr_5$(g) table.

References

[1]L. A. Nisel'son and J. D. Sokolova, Russ. J. Inorg. Chem. **9**, 1117 (1964).
[2]S. S. Berdonosov, A. V. Lapitskii, and E. K. Bakov, Russ. J. Inorg. Chem. **10**, 173 (1965).
[3]JANAF Thermochemical Tables: $NbCl_5$(l), 12–31–74.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
250							
298.15	147.904	274.005	274.005	0.	−545.074	−502.446	88.026
300	147.904	274.920	274.008	0.274	−545.196	−502.181	87.438
350	147.904	297.720	275.809	7.669	−620.672	−490.908	73.264
350.000	147.904	297.720	275.809	7.669	GLASS <--> LIQUID		
350.000	228.280	297.720	275.809	7.669	TRANSITION		
400	224.848	327.984	280.486	18.999	−615.178	−472.748	61.735
500	216.564	377.299	295.131	41.084	−604.887	−438.351	45.794
527.000	215.228	388.599	299.634	46.884	--- CRYSTAL <--> LIQUID ---		
600	206.397	415.912	312.167	62.247	−595.635	−405.932	35.339
700	194.430	446.854	329.276	82.304	−587.580	−374.969	27.981
800	180.611	471.921	345.594	101.061	−580.902	−345.069	22.531
900	166.218	492.368	360.805	118.407	−575.705	−315.918	18.335

PREVIOUS: CURRENT: December 1974

298.15	to	527 K	crystal
above		527 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	147.904	258.780	258.780	0.	−556.054	−508.887	89.155
300	147.904	259.695	258.783	0.274	−556.176	−508.593	88.554
400	147.904	302.245	264.585	15.064	−630.093	−477.367	62.338
500	147.904	335.249	275.540	29.854	−627.096	−439.535	45.918
527.000	147.904	343.027	278.800	33.848	CRYSTAL <--> LIQUID		
527.000	215.228	388.599	278.800	57.864	TRANSITION		
600	206.397	415.912	293.867	73.227	−595.635	−405.932	35.339
700	194.430	446.854	313.591	93.284	−587.580	−374.969	27.981
800	180.611	471.921	331.870	112.041	−580.902	−345.069	22.531
900	166.218	492.368	348.605	129.387	−575.705	−315.918	18.335

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 449.26 \pm 3.1\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -406.5 \pm 12.6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -443.6 \pm 12.6\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
234.0 (1)	[375.6](2)
178.0 (1)	119.0 (2)
[288.9](1)	67.0 (2)
[106.2](1)	101.0 (2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point group: D_{3h}
Bond Distance: Nb–Br = 2.45 ± 0.02 Å
Bond Angles: Br*–Nb–Br* = 120°; Br*–Nb–Br** = 90°; Br**–Nb–Br** = 180°
(* – *equatorial* ** – *axial*)
Product of the Moments of Inertia: $I_A I_B I_C = 1.85664 \times 10^{-110}\ g^3\cdot cm^6$

Enthalpy of Formation

The vapor pressures over $NbBr_5$(cr, l) have been measured by Alexander and Fairbrother[1] and Berdonosov *et al.*[2] A 2nd and 3rd law analysis of their data is given below. The enthalpy of formation for $NbBr_5$(g) is derived from the sublimation data of Berdonosov *et al.*[2] Our 3rd law analysis of their data gives $\Delta_{sub}H°(298.15\ K) = 26.88\ kcal\cdot mol^{-1}$ which leads to the adopted value, $\Delta_f H°(298.15\ K) = -106.02\ kcal\cdot mol^{-1}$ ($-443.588\ kJ\cdot mol^{-1}$) for $NbBr_5$(g). The sublimation data of Alexander and Fairbrother[1] is not acceptable as it leads to a large entropy drift, $-45 \pm 6\ cal\cdot K^{-1}\cdot mol^{-1}$.

The enthalpy of melting is chosen as 5.74 $kcal\cdot mol^{-1}$ so as to give reasonable entropy drifts for the vaporization data.

Source	Reaction[a]	Method	Data Points	T/K	$\Delta_r H°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$
Alexander and Fairbrother[1]	A	static	4	480–517	50.82 ± 2.94	27.77 ± 1.57	−45 ± 6
Berdonosov *et al.*[2]	A	static	12[b]	478–524	27.28 ± 0.16	26.88 ± 0.04	−0.8 ± 0.3
Alexander and Fairbrother[1]	B	static	26	528–635	24.07 ± 0.13	24.26 ± 0.06	+0.3 ± 0.2
Berdonosov *et al.*[2]	B	static	14	529–606	24.80 ± 0.27	24.23 ± 0.09	−1.0 ± 0.5

[a]Reaction: (A) $NbBr_5(l) = NbBr_5(g)$, (B) $NbBr_5(cr) = NbBr_5(g)$
[b]One point rejected due to a statistical test.

Heat Capacity and Entropy

Monomeric $NbBr_5$(g) was shown by Spiridonov and Romanov,[4,5] using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Nb–Br bond lengths being equal within expeirmental uncertainty, Nb–Br = 2.45 ± 0.02 Å. Skinner and Sutton[3] earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with their experimental results. We adopt the results of Spiridonov and Romanov.[4,5] The principal moments of inertia are: $I_A = 238.9340 \times 10^{-39}$, $I_B = I_C = 278.7563 \times 10^{-39}\ g\cdot cm^2$. A normal coordinate treatment of $NbBr_5$(g) in the Urey–Bradley force fields was performed by So[7] using the reported vibrational frequencies of Beattie and Ozin.[6] This work by So[7] was intended to check the correctness of the reported fundamental frequencies and predict those unobserved frequencies (ν_3, ν_4, ν_5). Beattie and Ozin[6] had recorded the gas phase Raman spectra of niobium and tantalum chloride and bromide. We adopt the results of So[7] which support the work of Beattie and Ozin.[6]

References

[1]K. A. Alexander and F. Fairbrother, J. Chem. Soc. (London) **1949**, S223 (1949).
[2]S. S. Berdonosov, A. V. Lapitskii, and E. K. Bakov, Russ. J. Inorg. Chem. **10**, 173 (1965).
[3]H. Skinner and L. Sutton, Trans. Faraday Soc. **36**, 668 (1940).
[4]V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. **21**, 109 (1966).
[5]V. P. Spiridonov and G. V. Romanov, Vestn. Mosk. Univ., Khim. **24**, 65 (1969).
[6]I. R. Beattie and G. A. Ozin, J. Chem. Soc. (London) **A1969**, 1691.
[7]S. P. So, J. Mol. Struct. **16**, 311 (1973).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−29.426	−406.500	−406.500	INFINITE
100	95.964	325.261	555.381	−23.012	−407.850	−425.658	222.341
200	118.641	400.321	460.586	−12.053	−411.242	−442.220	115.496
250	123.151	427.323	451.317	−5.998	−413.411	−449.724	93.965
298.15	125.806	449.259	449.259	0.	−443.588	−453.212	79.401
300	125.886	450.037	449.261	0.233	−443.750	−453.271	78.922
350	127.648	469.585	450.801	6.574	−520.280	−450.669	67.259
400	128.840	486.712	454.242	12.988	−519.703	−440.764	57.558
450	129.681	501.939	458.711	19.452	−519.118	−430.932	50.021
500	130.295	515.635	463.730	25.953	−518.532	−421.165	43.999
600	131.109	539.469	474.425	39.026	−517.370	−401.801	34.980
700	131.610	559.720	485.200	52.164	−516.234	−382.629	28.552
800	131.938	577.317	495.639	65.343	−515.135	−363.618	23.742
900	132.165	592.871	505.595	78.548	−514.078	−344.743	20.008
1000	132.328	606.805	515.032	91.773	−513.067	−325.983	17.028
1100	132.449	619.423	523.957	105.012	−512.107	−307.321	14.593
1200	132.541	630.952	532.400	118.262	−511.197	−288.745	12.569
1300	132.613	641.564	540.394	131.520	−510.339	−270.242	10.858
1400	132.670	651.394	547.976	144.784	−509.536	−251.804	9.395
1500	132.717	660.548	555.179	158.054	−508.796	−233.421	8.128
1600	132.754	669.115	562.035	171.327	−508.128	−215.084	7.022
1700	132.786	677.164	568.573	184.604	−507.544	−196.787	6.047
1800	132.812	684.755	574.819	197.884	−507.055	−178.522	5.181
1900	132.835	691.936	580.796	211.167	−506.671	−160.281	4.406
2000	132.854	698.750	586.525	224.451	−506.404	−142.058	3.710
2100	132.870	705.233	592.024	237.737	−506.262	−123.844	3.080
2200	132.884	711.414	597.312	251.025	−506.257	−105.635	2.508
2300	132.897	717.321	602.402	264.314	−506.399	−87.422	1.985
2400	132.908	722.978	607.309	277.604	−506.702	−69.200	1.506
2500	132.917	728.403	612.045	290.896	−507.181	−50.961	1.065
2600	132.926	733.617	616.621	304.188	−507.862	−32.700	0.657
2700	132.933	738.633	621.048	317.481	−508.781	−14.408	0.279
2800	132.940	743.468	625.334	330.774	−536.348	4.407	−0.082
2900	132.946	748.133	629.489	344.069	−536.593	23.725	−0.427
3000	132.952	752.640	633.519	357.364	−536.884	43.051	−0.750
3100	132.957	757.000	637.432	370.659	−537.215	62.387	−1.051
3200	132.961	761.221	641.235	383.955	−537.580	81.735	−1.334
3300	132.965	765.313	644.933	397.251	−537.974	101.095	−1.600
3400	132.969	769.282	648.533	410.548	−538.389	120.467	−1.851
3500	132.973	773.137	652.038	423.845	−538.820	139.851	−2.087
3600	132.976	776.883	655.454	437.143	−539.260	159.248	−2.311
3700	132.979	780.526	658.785	450.440	−539.701	178.657	−2.522
3800	132.981	784.072	662.036	463.738	−540.138	198.077	−2.723
3900	132.984	787.527	665.210	477.037	−540.564	217.510	−2.913
4000	132.986	790.894	668.310	490.335	−540.973	236.953	−3.094
4100	132.988	794.177	671.340	503.634	−541.361	256.406	−3.267
4200	132.990	797.382	674.303	516.933	−541.722	275.868	−3.431
4300	132.992	800.511	677.202	530.232	−542.051	295.338	−3.588
4400	132.994	803.569	680.039	543.531	−542.344	314.816	−3.737
4500	132.996	806.558	682.818	556.831	−542.599	334.300	−3.880
4600	132.997	809.481	685.539	570.130	−542.811	353.789	−4.017
4700	132.998	812.341	688.207	583.430	−542.977	373.282	−4.149
4800	133.000	815.141	690.822	596.730	−543.096	392.779	−4.274
4900	133.001	817.884	693.388	610.030	−543.166	412.277	−4.395
5000	133.002	820.571	695.904	623.330	−543.184	431.776	−4.511
5100	133.003	823.204	698.375	636.631	−543.149	451.275	−4.622
5200	133.004	825.787	700.800	649.931	−1233.733	480.082	−4.822
5300	133.005	828.321	703.183	663.231	−1233.923	513.042	−5.056
5400	133.006	830.807	705.523	676.532	−1234.031	546.001	−5.282
5500	133.007	833.247	707.823	689.833	−1234.158	578.966	−5.499
5600	133.008	835.644	710.084	703.133	−1234.259	611.932	−5.708
5700	133.009	837.998	712.308	716.434	−1234.333	644.901	−5.910
5800	133.009	840.311	714.495	729.735	−1234.381	677.870	−6.105
5900	133.010	842.585	716.647	743.036	−1234.405	710.840	−6.293
6000	133.011	844.821	718.764	756.337	−1234.405	743.810	−6.475

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [272 \pm 21]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 559 \pm 10\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -311.7 \pm 13\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.154\ kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev and Kokovin[1] have measured calorimetrically the enthalpy of reaction $\Delta_r H°(298.15\ K) = -187.475 \pm 0.9\ kcal·mol^{-1}$ for $WBr_5(cr) + 1/2Br_2(l) + 8NaOH(77.4H_2O) \rightarrow Na_2WO_4(cr) + 6NaBr(cr) + 4H_2O(l)$. This leads to $\Delta_f H°(WBr_5, cr, 298.15\ K) = -74.5 \pm 3\ kcal·mol^{-1} (-311.708 \pm 13\ kJ·mol^{-1})$, using $\Delta_f H°(NaOH·77.4H_2O, 298.15\ K) = -112.348\ kcal·mol^{-1}$,[2] $\Delta_f H°(NaWO_4, cr, 298.15\ K) = -369.2\ kcal·mol^{-1}$,[3] $\Delta_f H°(NaBr, cr, 298.15\ K) = -86.38\ kcal·mol^{-1}$ [3] and $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal·mol^{-1}$.[4]

Heat Capacity and Entropy

$C_p°(300\ K) = 6.2\ cal·K^{-1}·g\text{–}atom^{-1}$ and $C_p°(559\ K) = 7.25\ cal·K^{-1}·g\text{–}atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[5] Between 300 K and 559 K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S°(298.15\ K) = 65\ cal·K^{-1}·mol^{-1}$ ($271.960\ J·K^{-1}·mol^{-1}$), is estimated from that of $WCl_5(cr)$[3] and the entropy difference between bromides and chlorides. The latter is estimated to be $13\ cal·K^{-1}·mol^{-1}$ based on an extrapolation to pentavalent compounds of the entropy values of bromides and chlorides given by Latimer.[7] Both WBr_5 and WCl_5 are paramagnetic with an effective moment of about 1.1 Bohr magnetons as indicated by Figgis and Lewis.[8]

Fusion Data

Shchukarev *et al.*[6] have found the melting point, 559 K, by the thermographic method and 568 K by the tensimetric method. The value of 559 K is adopted in the tabulation.

The heat of melting is calculated from the difference between the enthalpies of sublimation and vaporization at the melting point. The enthalpies are both calculated from a 2nd law analysis of the vapor pressure data reported by Shchukarev *et al.*,[6] who gave the uncorrected enthalpy of fusion, $5\ kcal·mol^{-1}$. This value, when corrected for $\Delta C_p°$ of vaporization and sublimation, is in good agreement with the value adopted in the tabulation.

References

[1] S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
[2] The value $\Delta_f H°(NaOH·77.4H_2O, 298.15\ K) = -112.348\ kcal·mol^{-1}$ is calculated from $\Delta_f H°(NaOH·\infty H_2O, 298.15\ K) = -112.448\ kcal·mol^{-1}$ and $\phi_L = 100\ cal\ mol^{-1}$ for $NaOH(\infty H_2O) \rightarrow NaOH(77.4H_2O)$. The former is obtained from JANAF NaOH(cr) table (March 31, 1966) and the latter is obtained from V. B. Parker, U. S. Nat. Bur. Stand. NSRDS–NBS 2, (1965).
[3] JANAF Thermochemcial Tables: Na2WO4(cr), 6–30–67; NaBr(cr), 9–30–64; WCl_5(cr), 12–31–66.
[4] U. S. Nat. Bur. Stand. Tech. Note 270–1, 124 pp. (1965).
[5] O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[6] S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).
[7] W. M. Latimer, J. Amer. Chem. Soc. **73**, 1480 (1951).
[8] B. N. Figgis and J. L. Lewis, "Progress in Inorg. Chem.," Vol. 6, p. 121, Interscience Publishers, New York, (1964).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	155.461	271.960	271.960	0.	−311.708	−269.605	47.234
300	155.645	272.922	271.963	0.288	−311.815	−269.343	46.897
400	165.686	319.074	278.188	16.354	−384.412	−239.991	31.340
500	175.728	357.110	290.273	33.419	−379.091	−204.484	21.362
559.000	182.004	377.052	298.393	43.971	−−− CRYSTAL <−−> LIQUID −−−		
600	185.770	390.077	304.218	51.516	−372.851	−170.133	14.811
700	195.811	419.468	318.618	70.595	−365.719	−136.898	10.215
800	205.853	446.270	332.923	90.678	−357.662	−104.748	6.839
900	215.894	471.096	346.912	111.765	−348.673	−73.664	4.275
1000	225.936	494.362	360.506	133.857	−338.750	−43.631	2.279

PREVIOUS: December 1962 CURRENT: June 1967

$S°(298.15\ K) = [293.341]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 559 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-298.059]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 17.154\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(WBr_5, l, 298.15\ K)$ is calculated from that of WBr_5(cr) by adding the $\Delta_{fus}H°$ and the difference in enthalpy, $H°(559\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be a constant, 7.25 $cal·K^{-1}·g$-atom.

$S°(298.15\ K)$ is calcualted in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the Gibbs energy of reaction $WBr_5(l) \rightarrow WBr_5(g)$ approaches zero. The difference between the enthalpies of formation for liquid and gas at the normal boiling point is $\Delta_{vap}H°$.

Shchukarev *et al.*[1] derived the boiling point 665 K and the enthalpy of vaporization 14.5 ± 0.5 $kcal·mol^{-1}$ from vapor pressure data. Our 2nd law values, corrected for $\Delta C_p°$, are T_{vap} = 666 K and $\Delta_{vap}H° = 13.8\ kcal·mol^{-1}$. The adopted values are significantly different because the 2nd law value of $\Delta_{vap}S$ is not adopted in the table.

Reference

[1] S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	182.004	293.341	293.341	0.	−298.059	−262.330	45.959
300	182.004	294.467	293.344	0.337	−298.117	−262.108	45.637
400	182.004	346.826	300.483	18.537	−368.580	−235.260	30.722
500	182.004	387.439	313.964	36.738	−362.123	−202.680	21.174
600	182.004	420.622	329.059	54.938	−355.779	−171.389	14.921
700	182.004	448.678	344.195	73.138	−349.526	−141.153	10.533
800	182.004	472.982	358.808	91.339	−343.351	−111.808	7.300
900	182.004	494.419	372.708	109.539	−337.250	−83.232	4.831
1000	182.004	513.595	385.855	127.740	−331.218	−55.332	2.890

PREVIOUS: December 1962 CURRENT: June 1967

298.15	to	559 K	crystal
above		559 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
298.15	155.461	271.960	271.960	0.	−311.708	−269.605	47.234
300	155.645	272.922	271.963	0.288	−311.815	−269.343	46.897
400	165.686	319.074	278.188	16.354	−384.412	−239.991	31.340
500	175.728	357.110	290.273	33.419	−379.091	−204.484	21.362
559.000	182.004	377.052	298.393	43.971	____ CRYSTAL <--> LIQUID ____		
559.000	182.004	407.740	298.393	61.125	TRANSITION		
600	182.004	420.622	306.310	68.587	−355.779	−171.389	14.921
700	182.004	448.678	324.696	86.788	−349.526	−141.153	10.533
800	182.004	472.982	341.747	104.988	−343.351	−111.808	7.300
900	182.004	494.419	357.543	123.188	−337.250	−83.232	4.831
1000	182.004	513.595	372.206	141.389	−331.218	−55.332	2.890

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K)$ = [461.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -162.9 \pm 21\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -199.2 \pm 21\ kJ·mol^{-1}$

Eletronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[300](1)	[240](2)
[250](1)	[100](2)
[235](1)	[70](2)
[90](1)	[110](2)

Ground State Quantum Weight: [2] σ = [6]
Point Group: [D_{3h}]
Bond Distance: W–Br = [2.40] Å
Bond Angles: Br*–W–Br* = [120°]; Br*–W–Br** = [90°]
Br**–W–Br** = [180°]
*Equatorial **Axial
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.6458] × 10^{-110} $g^3·cm^6$

Enthalpy of Formation

Shchukarev *et al.*[5] measured the vapor pressure of WBr_5(cr, l) using a null manometer. Their results are given as below. The adopted enthalpy of formation is −47.6 $kcal·mol^{-1}$ (−199.158 $kJ·mol^{-1}$).

Reaction	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
WBr_5(l) → WBr_5(g)	13	573.3–657.5	18.37	24.11	9.4 ± 0.1	−47.13
WBr_5(cr) → WBr_5(g)	6	443.5–496.5	21.61	26.46	9.4 ± 0.4	−48.04

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $MoCl_5$ determined by electron diffraction.[1] The bond distance is estimated to be the same as that in WBr_6(g). The principal moments of inertia are: $I_A = 229.2811 \times 10^{-39}$ and $I_B = I_C = 267.4946 \times 10^{-39}$ g·cm^2.

All vibrational frequencies are estimated from those of WCl_5(g),[2] using the average value of $\nu(WBr_5)/\nu(WCl_5) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX_6^{2-}, SnX_6^{2-} and PtX_6^{2-} summarized by Siebert[3] and Nakamoto.[4]

The electronic levels and quantum weights are estimated to be the same as those in WCl_5(g).[2]

References

[1]R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. **34**, 1358 (1938).
[2]JANAF Thermochemical Table: WCl_5(g), 12–31–66.
[3]H. Siebert, "Anwendungen der Schwingunsspektroskopie in der Anorganischen Chemie," Springer–Verlag, Berlin, (1966).
[4]K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, (1963).
[5]S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−30.021	−162.933	−162.933	INFINITE
100	98.777	334.646	569.460	−23.481	−164.028	−183.070	95.626
200	121.036	411.719	472.895	−12.235	−167.043	−201.022	52.501
250	124.972	439.192	463.494	−6.076	−169.080	−209.292	43.729
298.15	127.212	461.411	461.411	0.	−199.158	−213.540	37.411
300	127.279	462.198	461.413	0.235	−199.318	−213.629	37.196
350	128.733	481.935	462.969	6.638	−275.765	−211.832	31.614
400	129.704	499.193	466.441	13.101	−275.116	−202.743	26.476
450	130.382	514.511	470.947	19.604	−274.468	−193.735	22.488
500	130.873	528.275	476.003	26.136	−273.824	−184.799	19.306
600	131.522	552.199	486.768	39.258	−272.558	−167.114	14.549
700	131.918	572.505	497.602	52.432	−271.332	−149.637	11.166
800	132.180	590.138	508.091	65.638	−270.152	−132.334	8.640
900	132.368	605.718	518.090	78.866	−269.023	−115.175	6.685
1000	132.517	619.673	527.562	92.110	−267.947	−98.139	5.126
1100	132.650	632.309	536.520	105.368	−266.926	−81.208	3.856
1200	132.781	643.857	544.990	118.640	−265.959	−64.367	2.802
1300	132.921	654.490	553.010	131.925	−265.045	−47.605	1.913
1400	133.073	664.346	560.614	145.225	−264.185	−30.912	1.153
1500	133.242	673.533	567.840	158.540	−263.379	−14.278	0.497
1600	133.426	682.138	574.717	171.873	−262.629	2.304	−0.075
1700	133.624	690.233	581.276	185.226	−261.936	18.841	−0.579
1800	133.835	697.877	587.544	198.599	−261.302	35.338	−1.025
1900	134.055	705.118	593.543	211.993	−260.733	51.803	−1.424
2000	134.281	712.000	599.295	225.410	−260.231	68.239	−1.782
2100	134.511	718.557	604.820	238.849	−259.801	84.652	−2.106
2200	134.743	724.820	610.133	252.312	−259.447	101.045	−2.399
2300	134.974	730.815	615.251	265.798	−259.173	117.425	−2.667
2400	135.202	736.564	620.186	279.307	−258.982	133.795	−2.912
2500	135.425	742.088	624.953	292.838	−258.875	150.158	−3.137
2600	135.643	747.404	629.561	306.392	−258.849	166.518	−3.345
2700	135.854	752.527	634.021	319.966	−258.933	182.880	−3.538
2800	136.057	757.471	638.342	333.562	−259.158	199.246	−3.717
2900	136.252	762.249	642.533	347.178	−259.561	215.625	−3.884
3000	136.438	766.871	646.601	360.812	−260.166	232.020	−4.040
3100	136.614	771.348	650.553	374.465	−261.013	248.439	−4.186
3200	136.781	775.688	654.396	388.135	−262.127	264.890	−4.324
3300	136.939	779.899	658.136	401.821	−263.529	281.381	−4.454
3400	137.087	783.990	661.777	415.522	−265.249	297.918	−4.577
3500	137.225	787.966	665.326	429.238	−267.344	314.511	−4.694
3600	137.353	791.833	668.787	442.967	−269.906	331.171	−4.805
3700	137.473	795.598	672.163	456.708	−307.794	348.100	−4.914
3800	137.583	799.266	675.460	470.461	−307.985	365.829	−5.029
3900	137.683	802.841	678.681	484.224	−308.156	383.563	−5.137
4000	137.775	806.328	681.828	497.997	−308.300	401.301	−5.240
4100	137.859	809.731	684.907	511.779	−308.414	419.043	−5.339
4200	137.934	813.054	687.918	525.569	−308.493	436.786	−5.432
4300	138.002	816.300	690.866	539.366	−308.533	454.532	−5.521
4400	138.061	819.474	693.753	553.169	−308.532	472.278	−5.607
4500	138.114	822.577	696.582	566.978	−308.487	490.023	−5.688
4600	138.159	825.613	699.354	580.791	−308.394	507.767	−5.766
4700	138.198	828.585	702.072	594.609	−308.251	525.508	−5.840
4800	138.230	831.495	704.738	608.431	−308.058	543.246	−5.912
4900	138.257	834.345	707.354	622.255	−307.812	560.979	−5.980
5000	138.277	837.138	709.922	636.082	−307.513	578.706	−6.046
5100	138.293	839.877	712.443	649.910	−307.159	596.428	−6.109
5200	138.303	842.562	714.920	663.740	−306.751	614.140	−6.169
5300	138.308	845.197	717.353	677.571	−306.288	631.846	−6.227
5400	138.309	847.782	719.745	691.402	−305.770	649.542	−6.283
5500	138.306	850.320	722.096	705.233	−305.198	667.228	−6.337
5600	138.299	852.812	724.408	719.063	−304.571	684.902	−6.389
5700	138.288	855.260	726.682	732.892	−303.891	702.566	−6.438
5800	138.274	857.665	728.920	746.720	−303.158	720.216	−6.486
5900	138.256	860.028	731.122	760.547	−302.373	737.854	−6.532
6000	138.236	862.352	733.290	774.371	−301.537	755.478	−6.577

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = [313.8 \pm 21]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 582\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -343.088\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

Shchukarev and Kokovin[1] have measured calorimetrically the enthalpy of reaction $\Delta_r H°(298.15\ K) = -180.0 \pm 0.8\ kcal \cdot mol^{-1}$ for $WBr_6(cr) + 8NaOH(77.4H_2O) \rightarrow Na_2WO_4(cr) + 6NaBr(cr) + 4H_2O(l)$. This leads to $\Delta_f H°(WBr_6, cr, 298.15\ K) = -82.0 \pm 3\ kcal \cdot mol^{-1}$ ($-343.088 \pm 13\ kJ \cdot mol^{-1}$), using $\Delta_f H°(NaOH \cdot 77.4H_2O, 298.15\ K) = -112.348\ kcal \cdot mol^{-1}$,[2] $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -369.2\ kcal \cdot mol^{-1}$,[3] $\Delta_f H°(NaBr, cr, 298.15\ K) = -86.38\ kcal \cdot mol^{-1}$[3] and $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$.[4]

Heat Capacity and Entropy

$C_p°(300\ K) = 6.2\ cal \cdot K^{-1}\ g\text{-}atom^{-1}$ and $C_p°(582\ K) = 7.25\ cal \cdot K^{-1}\ g\text{-}atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[5] Between 300 and 582 K, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S°(WBr_6, cr, 298.15\ K) = 75\ cal \cdot K^{-1} \cdot mol^{-1}$ ($313.800\ J \cdot K^{-1} \cdot mol^{-1}$), is estimated by assuming $S°(WBr_6, 298.15\ K) = S°(WCl_6, 298.15\ K) + 6[S°(Br^-, 298.15\ K) - S°(Cl^-, 298.15\ K)]$. The value, $S°(WCl_6, cr, 298.15\ K) = 57\ cal \cdot K^{-1} \cdot mol^{-1}$, is obtained from $WCl_6(cr, \alpha)$[3]; and the value, $S°(Br^-, 298.15\ K) - S°(Cl^-, 298.15\ K) = 3\ cal \cdot K^{-1} \cdot mol^{-1}$, is obtained from the average entropy values for Br^- and Cl^- ions given by Latimer[6] and Kelley.[7]

Fusion Data

Shchukarev *et al.*[8] have found the melting point, 582 K, under 50 atm pressure of Br_2(g) by the thermographic method. The heat of fusion is unknown.

References

1S. A. Shchukarev and G. A. Kokovin, Zh. Neorg. Khim. **9**, 1309 (1964).
[2]This value, $\Delta_f H°(NaOH \cdot 77.4H_2O, 298.15\ K) = -112.348\ kcal \cdot mol^{-1}$ is calculated from $\Delta_f H°(NaOH \cdot \infty H_2O, 298.15\ K) = 112.448\ kcal \cdot mol^{-1}$ and $\phi_L = 100\ kcal \cdot mol^{-1}$ for $NaOH(\infty H_2O) \rightarrow NaOH(77.4H_2O)$. The former is obtained from JANAF NaOH(cr) table (March 31, 1966) and the latter is obtained from V. B. Parker, U. S. Nat. Bur. Stand. NSRDS–NBS 2, (1965).
[3]JANAF Thermochemical Tables: Na_2WO_4(cr), 6–30–67; NaBr(cr), 6–30–64; WCl_6(cr, α), 12–31–66.
[4]U. S. Nat. Bur. Stand. Tech. Note 270–1, 124 pp. (1965).
[5]O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[6]W. M. Latimer, J. Amer. Chem. Soc. **73**, 1480 (1951).
[7]K. K. Kelley, personal communication, (June, 1960).
[8]S. A. Shchukarev, G. I. Novikov and G. A. Kokovin, Zh. Neorg. Khim. **4**, 2185 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	181.385	313.800	313.800	0.	−343.088	−290.769	50.942
300	181.586	314.923	313.803	0.336	−343.217	−290.444	50.571
400	192.464	368.651	321.056	19.038	−430.418	−254.610	33.249
500	203.342	412.767	335.110	38.829	−424.217	−211.356	22.080
600	214.221	450.802	351.291	59.707	−417.055	−169.440	14.751
700	225.099	484.642	367.966	81.673	−408.905	−128.801	9.611
800	235.978	515.410	384.501	104.727	−399.754	−89.399	5.837
900	246.856	543.832	400.645	128.868	−389.593	−51.204	2.972
1000	257.734	570.404	416.306	154.098	−378.419	−14.195	0.741

PREVIOUS: December 1962 CURRENT: June 1967

$S°(298.15\ K) = [482.7 \pm 42]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-199.8 \pm 42]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-243.1 \pm 42]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[250](1)	[110](3)
[200](2)	[130](3)
[250](3)	[70](3)

Ground State Quantum Weight: [1] σ = [24]
Point Group: [O_h]
Bond Distance: W–Br = [2.40] Å
Bond Angle: Br–W–Br = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.85707 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(WBr_6, g, 298.15\ K) = -58.1\ kcal \cdot mol^{-1}$ ($-243.090\ kJ \cdot mol^{-1}$) is calculated from that of the crystal plus the estimated enthalpy of sublimation $\Delta_{sub} H°(298.15\ K) = 23.9\ kcal \cdot mol^{-1}$ for $WBr_6(cr) \rightarrow WBr_6(g)$. The value of $\Delta_{sub} H°(298.15\ K)$ is assumed to be the same as that for $WCl_6(cr) \rightarrow WCl_6(g)$. Refer to the WCl_6 table (December 31, 1966) for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be an octahedron similar to those of WF_6(g) and WCl_6(g) as determined by electron diffraction. The bond distance is estimated to be 2.40 Å by assuming $r_{W-Br} = r_{W-Cl} + (r_{Na-Br} - r_{Na-Cl})$. The bond distances, W–Cl, Na–Br and Na–Cl, are given in JANAF WCl(g), NaBr(g) and NaCl(g) tables, as 2.26 Å, 2.50 Å, and 2.36 Å respectively. The principal moments of inertia are: $I_A = I_B = I_C = 305.7081 \times 10^{-39}\ g \cdot cm^2$.

All vibrational frequencies are estimated from those of WCl_6(g)[1], using the average value of $\upsilon(WBr_6)/\upsilon(WCl_6) = 0.62$ for modes which are independent of the central atom and 0.68 for modes involving the central atom. These average values of 0.62 and 0.68 are obtained from the ratios of corresponding vibrational frequencies of ReX_6^-, SnX_6^- and PtX_6^- summarized by Siebert,[2] and Nakamoto.[3]

References

[1]J. C. Evans and G. Y–S Lo, The Dow Chemical Company, personal communication, (June 6, 1967), have obtained the six fundamental vibrational frequencies of 408, 312, 367, 165, 206 and 97 cm^{-1} for WCl_6(g) by infrared spectrometry.
[2]H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie," Springer–Verlag, Berlin, (1966).
[3]K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−35.204	−199.793	−199.793	INFINITE
100	116.477	331.931	611.326	−27.940	−201.561	−217.638	113.683
200	144.174	423.537	496.369	−14.566	−204.899	−232.499	60.722
250	148.782	456.254	485.179	−7.231	−207.167	−239.149	49.968
298.15	151.369	482.699	482.699	0.	−243.090	−241.129	42.245
300	151.446	483.636	482.702	0.280	−243.275	−241.116	41.982
350	153.112	507.116	484.553	7.897	−334.833	−235.752	35.184
400	154.218	527.638	488.683	15.582	−333.877	−221.663	28.946
450	154.988	545.849	494.042	23.313	−332.922	−207.694	24.108
500	155.544	562.209	500.055	31.077	−331.971	−193.830	20.249
600	156.277	590.639	512.853	46.672	−330.092	−166.379	14.485
700	156.723	614.765	525.732	62.323	−328.257	−139.240	10.390
800	157.014	635.713	538.199	78.011	−326.472	−112.360	7.336
900	157.214	654.219	550.082	93.723	−324.741	−85.700	4.974
1000	157.358	670.791	561.339	109.452	−323.068	−59.230	3.094
1100	157.464	685.794	571.981	125.193	−321.455	−32.925	1.563
1200	157.545	699.498	582.045	140.944	−319.904	−6.764	0.294
1300	157.608	712.111	591.571	156.702	−318.418	19.270	−0.774
1400	157.659	723.793	600.604	172.465	−316.999	45.192	−1.686
1500	157.699	734.672	609.183	188.233	−315.651	71.016	−2.473
1600	157.732	744.851	617.348	204.005	−314.376	96.752	−3.159
1700	157.760	754.414	625.132	219.779	−313.181	122.410	−3.761
1800	157.783	763.432	632.567	235.557	−312.071	148.001	−4.295
1900	157.802	771.963	639.681	251.336	−311.050	173.532	−4.771
2000	157.819	780.058	646.500	267.117	−310.127	199.012	−5.198
2100	157.834	787.758	653.044	282.900	−309.306	224.448	−5.583
2200	157.846	795.101	659.336	298.684	−308.593	249.848	−5.932
2300	157.857	802.118	665.392	314.469	−307.992	275.218	−6.250
2400	157.866	808.836	671.230	330.255	−307.507	300.564	−6.542
2500	157.875	815.281	676.864	346.042	−307.140	325.893	−6.809
2600	157.882	821.473	682.308	361.830	−306.887	351.208	−7.056
2700	157.889	827.432	687.573	377.618	−306.774	376.517	−7.284
2800	157.895	833.174	692.671	393.408	−306.833	401.824	−7.496
2900	157.900	838.715	697.612	409.197	−307.101	427.138	−7.694
3000	157.905	844.068	702.405	424.988	−307.598	452.464	−7.878
3100	157.909	849.246	707.059	440.778	−308.363	477.811	−8.051
3200	157.913	854.259	711.581	456.570	−309.418	503.188	−8.214
3300	157.917	859.119	715.979	472.361	−310.784	528.602	−8.367
3400	157.920	863.833	720.258	488.153	−312.486	554.063	−8.512
3500	157.923	868.411	724.426	503.945	−314.581	579.578	−8.650
3600	157.926	872.860	728.488	519.738	−317.157	605.162	−8.781
3700	157.929	877.187	732.449	535.530	−355.072	631.014	−8.908
3800	157.931	881.398	736.313	551.323	−355.301	657.668	−9.040
3900	157.933	885.501	740.086	567.116	−355.517	684.327	−9.166
4000	157.935	889.499	743.772	582.910	−355.713	710.993	−9.285
4100	157.937	893.399	747.374	598.703	−355.883	737.663	−9.398
4200	157.939	897.205	750.896	614.497	−356.020	764.336	−9.506
4300	157.940	900.921	754.342	630.291	−356.120	791.013	−9.609
4400	157.942	904.552	757.715	646.085	−356.177	817.691	−9.707
4500	157.943	908.102	761.017	661.880	−356.187	844.370	−9.801
4600	157.945	911.573	764.253	677.674	−356.146	871.049	−9.891
4700	157.946	914.970	767.423	693.468	−356.051	897.726	−9.977
4800	157.947	918.295	770.532	709.263	−355.899	924.401	−10.060
4900	157.948	921.552	773.581	725.058	−355.687	951.071	−10.139
5000	157.949	924.743	776.573	740.853	−355.414	977.738	−10.214
5100	157.950	927.871	779.509	756.648	−355.078	1004.398	−10.287
5200	157.951	930.938	782.391	772.443	−354.678	1031.050	−10.357
5300	157.952	933.947	785.223	788.238	−354.212	1057.695	−10.424
5400	157.953	936.899	788.004	804.033	−353.682	1084.330	−10.489
5500	157.953	939.797	790.738	819.828	−353.085	1110.954	−10.551
5600	157.954	942.643	793.425	835.624	−352.423	1137.567	−10.611
5700	157.955	945.439	796.067	851.419	−351.695	1164.168	−10.668
5800	157.955	948.186	798.667	867.215	−350.903	1190.754	−10.724
5900	157.956	950.886	801.224	883.010	−350.046	1217.327	−10.777
6000	157.957	953.541	803.740	898.806	−349.125	1243.885	−10.829

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

Continued from page 460

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$S°(298.15\ K) = 34.966 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -138.061 \pm 2.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -138.909 \pm 2.5\ kJ \cdot mol^{-1}$

Enthalpy of Formation

There are five oxygen bomb calorimetry studies on NbC reported in the literature[1-5] and one CO(g) equilibrium study.[6] The adopted $\Delta_f H°(298.15\ K)$ value is derived from the calorimetric study of Huber *et al.*[3] These authors studied the combustion of eight NbC_x samples where x covers the range 0.686 to 0.984. For each composition six to eight combustions were performed. Huber *et al.*[3] reported that the combustions varied from 98.78 to 100% of completion. Corrections of the order 0.51% or less were made to the enthalpy of combustion value to account for impurities in seven of the eight samples. The correction was 3.33% for the $x = 0.984$ sample. The calculated heats of formation were fitted to a quadratic equation by the least squares method by Huber *et al.*[3] Each value was weighted inversely proportional to the square of its uncertainty. Using the quadratic equation for $\Delta_f H°(298.15\ K)$ and correcting for the JANAF value of $\Delta_f H°(Nb_2O_5, cr, 298.15\ K)$,[7] we interpolate to $x = 0.98$, calculate and adopt $\Delta_f H°(298.15\ K) = -33.20 \pm 0.6\ kcal \cdot mol^{-1}$. Due to the large error in the data points, a linear equation can be chosen to fit the data without making a statistically significant difference.[3]

Huber *et al.*[3] and Storms[8] have reanalyzed much of the calorimetric and equilibrium data[1-6] for NbC_x ($x = 0.686$ to 0.984). A graphical comparison of the results (i.e., $\Delta_f H°(298.15\ K)$ values vs. x) indicated that the quadratic equation suggested by Huber *et al.*[3] is a satisfactory representation of the various $\Delta_f H°(298.15\ K)$ results for NbC_x. The shortcomings of the various studies have been discussed by Huber *et al.*[3] and Storms.[8] For comparison, the oxygen combustion study by Mah and Boyle[1] leads to $\Delta_f H°(298.15\ K) = -31.14 \pm 0.8\ kcal \cdot mol^{-1}$ for $NbC_{0.9445}$.

Heat Capacity and Entropy

There have been three low temperature heat capacity studies for NbC_x: Pankratz *et al.*[13] using a $NbC_{0.996}$ sample (52–296 K), Toth *et al.*[19] using five NbC_x samples where $x = 0.77$, 0.83, 0.86, 0.91, and 0.96 (1.5–18 K), and Sandernaw and Storms[14] using three NbC_x samples where $x = 0.702$, 0.825, and 0.980 (7.5–320 K). In addition there are numerous high temperature heat capacity and enthalpy studies on various NbC_x samples.[9-13, 15-18] The adopted heat capacity values are those suggested by Turchanin *et al.*[20] Their $C_p°$ values were represented by a five term equation for the range 0–3000 K and is a compromise of the reported data mentioned, all adjusted to the composition $NbC_{0.98}$.

Phase Data

NbC has a face centered cubic structure of the NaCl type.[8] The NbC phase exists, following the phase diagram of Storms,[8] from roughly $NbC_{0.70}$ to near $NbC_{0.99}$. At the NbC–C eutectic temperature of 3573 ± 50 K, the phase limit is $NbC_{0.97}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0.98	0.98						
0	0.	0.	INFINITE	−5.422	−138.061	−138.061	INFINITE
100	14.426	7.983	56.725	−4.874	−138.352	−137.801	71.980
200	27.476	22.238	35.932	−2.739	−138.635	−137.103	35.808
298.15	36.233	34.966	34.966	0.	−138.909	−136.785	23.964
300	36.380	35.190	34.966	0.067	−138.903	−136.772	23.814
400	41.882	46.463	36.466	3.999	−138.481	−136.120	17.776
500	45.145	56.179	39.461	8.359	−137.986	−135.587	14.165
600	47.363	64.616	42.966	12.990	−137.514	−135.153	11.766
700	48.911	72.038	46.600	17.806	−137.091	−134.793	10.058
800	50.124	78.651	50.200	22.760	−136.718	−134.491	8.781
900	51.087	84.611	53.698	27.822	−136.389	−134.233	7.791
1000	51.923	90.038	57.065	32.973	−136.097	−134.009	7.000
1100	52.635	95.021	60.292	38.202	−135.839	−133.813	6.354
1200	53.304	99.630	63.380	43.499	−135.609	−133.640	5.817
1300	53.932	103.921	66.336	48.861	−135.398	−133.484	5.363
1400	54.504	107.939	69.165	54.283	−135.207	−133.344	4.975
1500	55.061	111.718	71.878	59.761	−135.038	−133.217	4.639
1600	55.605	115.289	74.480	65.295	−134.894	−133.101	4.345
1700	56.134	118.676	76.981	70.882	−134.781	−132.992	4.086
1800	56.651	121.900	79.388	76.521	−134.705	−132.889	3.856
1900	57.153	124.976	81.707	82.211	−134.671	−132.790	3.651
2000	57.656	127.920	83.944	87.952	−134.683	−132.691	3.466
2100	58.158	130.746	86.106	93.743	−134.745	−132.590	3.298
2200	58.660	133.463	88.197	99.583	−134.863	−132.484	3.146
2300	59.162	136.081	90.223	105.475	−135.042	−132.373	3.006
2400	59.664	138.610	92.187	111.416	−135.293	−132.251	2.878
2500	60.166	141.056	94.093	117.407	−135.630	−132.118	2.760
2600	60.668	143.425	95.945	123.449	−136.076	−131.969	2.651
2700	61.170	145.724	97.746	129.541	−136.669	−131.801	2.550
2800	61.672	147.958	99.500	135.683	−163.822	−131.122	2.446
2900	62.174	150.131	101.208	141.875	−163.565	−129.959	2.341
3000	62.676	152.247	102.874	148.118	−163.272	−128.805	2.243

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 5.74\ 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is zero by definition for the adopted standard reference state of Achesson spectroscopic graphite, artificial graphite of spectroscopic grade which is graphitized near 2600°C in an Acheson–type elesctric furnace. This standard state was adopted by CODATA[1] in order to be more consistent with the samples used in determing $\Delta_f H°(298.15)$ of CO_2(g). CODATA[1] cites references which show the effects of various graphite samples on $\Delta_f H°(CO_2)$. Their assigned uncertainty[1] of ±0.031 kcal·mol^{-1} for $\Delta_f H°(CO_2)$ is a rough measure of the deviations of various high purity graphites from our standard state. Larger deviations occur in carbon samples which are impure or less completely graphitized or which have much disorder or high surface area. Gross deviations (up to several kcal·mol) have been found for other carbons; e.g., many "glassy" carbons appear to be more stable than graphite at elevated temperatures due to large $\Delta_f S$ values[2] which compensate for positive values of $\Delta_f H$.

Heat Capacity and Entropy

$S°(298.15)$ and $H°(298.15\ K)–H°(0\ K)$ are the values selected by CODATA[1] based on $C_p°$ (13–301 K) of CS–grade Acheson graphite measured by DeSorbo and Tyler.[3] DeSorbo's later study[3] gave minor corrections to $C_p°$ and more information on his sample. Due to differences in $C_p°$ of various graphites, we increase the uncertainty of $S°(298.15)$ from ±0.029[1] to ±0.05 cal·K^{-1}·mol^{-1}. The entropy extrapolation below 13 K was given[3] as 0.0041 cal·K^{-1}·mol^{-1}. Properties tabulated below 298.15 K are from our smoothing of the data.[3] $C_p°$ above 298.15 K is based on enthalpy data of McDonald[4] and West and Ishihara[5] and on $C_p°$ data of Cezairliyan *et al.*[6,7] Deviations of the enthalpy data from our table are −0.3 to +0.6%, (omitting 341 and 1037 K)[4] and 0.0 to −0.6%.[5] Deviations of the $C_p°$ equations[6,7] from our table are much less than the estimated uncertainties of 3%[6] and 3 to 5%.[7] The selected studies[4–7] show reasonable agreement in their regions of overlap even though they involve different grades of graphite. Together, they yield mutually consistent data extending up to 3800 K.

Discrepancies in other $C_p°$ data are of concern since no single type of graphite has been accurately measured over the whole temperature range. At all temperatures the many studies show unusually large differences, some of which are due to deviations of the graphite samples from our chosen standard state. For example, the $C_p°$ of natural (Ceylon) graphite[3] was found to be approximately 9% lower from 200 to 300 K, yielding values of $S°(298.15)$ and $H°(298.15\ K)–H°(0\ K)$ which are lower by 0.08 cal·K^{-1}·mol^{-1} and 21 cal·mol^{-1}, respectively. Lutkov *et al.*[8] reported similar differences in $C_p°$ among two graphites and one pyrolytic carbon. Discrepancies are even larger below 30 K[9,10] and above 3000 K.[6,10–15] vaporization and melting. New studies of various graphites by laser flash[16] and differential scanning calorimetry[17] tend to confirm our $C_p°$ at 350–950 K, where the largest deviations (−3%) are roughly equal to the experimental error. More controversial are $C_p°$[12] and enthalpy[13] studies which gave $C_p°$ curves that rise very rapidly near 3500 K. Recent pulse–heating data,[7] however, gave a slowly rising $C_p°$ which is linear up to 3800 K. Four $C_p°$ studies[6,7,12,14] and an enthalpy study[15] agree satisfactorily below 3500 K, so the discrepancy must be due to temperature–dependent differences in experimental methods or graphite samples. This is a region where some graphites degrade rapidly with emission of particles, leading to possible bias in $C_p°$ data. Moreover, Whittaker has proposed[18] that graphite is metastable in this region and slowly transforms to carbynes. If e this is the case, then very rapid measurements[7] should yield $C_p°$ data which are different and more appropriate to graphite. Th rapidly rising enthalpy data[13] could be explained by Whittaker's proposal or by differences in the various graphite samples.[13]

Sublimation Data

See the tables for C(g), C_2(g), C_3(g), C_4(g), etc. The most abundant species is C_3. Recent analyses gave sublimation temperature values (corresponding to 1 atm total pressure of all carbon species) of 3895–4020 K[19] from carbon arc data, ≤4070 K[20] from mass–loss data at 0.1–11 atm, and approximately 3915 K[21] from extrapolation of mass–spectrometric data at low pressure. Earlier values for this controversial point (see below) were summarized by Palmer.[22]

Fusion Data and Phase Data

Controversy surrounds the solid–liquid–vapor triple point which recent studies place either at approximately 4000 K and approximately 1 atm (carbyne form)[18] or at 4130 ± 30 K and 120 ± 10 atm (pyrolytic graphite).[23] We doubt the latter triple point because the temperature is displaced by 400 to 800 kelvins from the sublimation curves (and ref. cited therein).[19–22] The nature of the observed phenomenon[22–24] has been questioned[18] as well as the measurement of temperature.[18,19,24] Also controversial is Whittaker's proposal[18] that several carbyne forms are more stable than graphite above 2600 K. Evidence includes X–ray data which were interpreted[18] to indicate slow forward transitions, graphite → carbynes, but rapid reverse transitions. These transitions might explain discrepancies observed in various $C_p°$ curves but alternative explanations are possible. We retain graphite as the reference state at all temperatures; this arbitrary choice avoids the need to switch phases at the proposed transition point, sublimation point or melting point, all of which are subject to change.

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[4]R. A. McDonald, J. Chem. Eng. Data **10**, 243 (1965); H (341–1723 K) of SPK–grade graphite.

Continued on page 700

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°–H°(T_r)]/T$	$H°–H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−1.051	0.	0.	0.
100	1.674	0.952	10.867	−0.991	0.	0.	0.
200	5.006	3.082	6.407	−0.665	0.	0.	0.
250	6.816	4.394	5.871	−0.369	0.	0.	0.
298.15	8.517	5.740	5.740	0.	0.	0.	0.
300	8.581	5.793	5.741	0.016	0.	0.	0.
350	10.241	7.242	5.851	0.487	0.	0.	0.
400	11.817	8.713	6.117	1.039	0.	0.	0.
450	13.289	10.191	6.487	1.667	0.	0.	0.
500	14.623	11.662	6.932	2.365	0.	0.	0.
600	16.844	14.533	7.961	3.943	0.	0.	0.
700	18.537	17.263	9.097	5.716	0.	0.	0.
800	19.827	19.826	10.279	7.637	0.	0.	0.
900	20.824	22.221	11.475	9.672	0.	0.	0.
1000	21.610	24.457	12.662	11.795	0.	0.	0.
1100	22.244	26.548	13.831	13.989	0.	0.	0.
1200	22.766	28.506	14.973	16.240	0.	0.	0.
1300	23.204	30.346	16.085	18.539	0.	0.	0.
1400	23.578	32.080	17.167	20.879	0.	0.	0.
1500	23.904	33.718	18.216	23.253	0.	0.	0.
1600	24.191	35.270	19.234	25.658	0.	0.	0.
1700	24.448	36.744	20.221	28.090	0.	0.	0.
1800	24.681	38.149	21.178	30.547	0.	0.	0.
1900	24.895	39.489	22.107	33.026	0.	0.	0.
2000	25.094	40.771	23.008	35.525	0.	0.	0.
2100	25.278	42.000	23.883	38.044	0.	0.	0.
2200	25.453	43.180	24.734	40.581	0.	0.	0.
2300	25.618	44.315	25.561	43.134	0.	0.	0.
2400	25.775	45.408	26.365	45.704	0.	0.	0.
2500	25.926	46.464	27.148	48.289	0.	0.	0.
2600	26.071	47.483	27.911	50.889	0.	0.	0.
2700	26.212	48.470	28.654	53.503	0.	0.	0.
2800	26.348	49.426	29.379	56.131	0.	0.	0.
2900	26.481	50.353	30.086	58.773	0.	0.	0.
3000	26.611	51.253	30.777	61.427	0.	0.	0.
3100	26.738	52.127	31.451	64.095	0.	0.	0.
3200	26.863	52.978	32.111	66.775	0.	0.	0.
3300	26.986	53.807	32.756	69.467	0.	0.	0.
3400	27.106	54.614	33.387	72.172	0.	0.	0.
3500	27.225	55.401	34.005	74.889	0.	0.	0.
3600	27.342	56.170	34.610	77.617	0.	0.	0.
3700	27.459	56.921	35.203	80.357	0.	0.	0.
3800	27.574	57.655	35.784	83.109	0.	0.	0.
3900	27.688	58.372	36.354	85.872	0.	0.	0.
4000	27.801	59.075	36.913	88.646	0.	0.	0.
4100	27.913	59.763	37.462	91.432	0.	0.	0.
4200	28.024	60.437	38.001	94.229	0.	0.	0.
4300	28.134	61.097	38.531	97.037	0.	0.	0.
4400	28.245	61.745	39.051	99.856	0.	0.	0.
4500	28.354	62.381	39.562	102.685	0.	0.	0.
4600	28.462	63.006	40.065	105.526	0.	0.	0.
4700	28.570	63.619	40.560	108.378	0.	0.	0.
4800	28.678	64.222	41.047	111.240	0.	0.	0.
4900	28.785	64.814	41.526	114.114	0.	0.	0.
5000	28.893	65.397	41.997	116.997	0.	0.	0.
5100	28.999	65.970	42.462	119.892	0.	0.	0.
5200	29.106	66.534	42.919	122.797	0.	0.	0.
5300	29.211	67.089	43.370	125.713	0.	0.	0.
5400	29.317	67.636	43.814	128.640	0.	0.	0.
5500	29.422	68.175	44.252	131.577	0.	0.	0.
5600	29.528	68.706	44.684	134.524	0.	0.	0.
5700	29.632	69.230	45.110	137.482	0.	0.	0.
5800	29.737	69.746	45.531	140.451	0.	0.	0.
5900	29.842	70.255	45.945	143.429	0.	0.	0.
6000	29.946	70.758	46.355	146.419	0.	0.	0.

PREVIOUS: March 1978 (1 atm) CURRENT: March 1983 (1 bar)

IP(C, g) = 90820.42 ± 0.1 cm^{-1}
$S°$(298.15 K) = 158.100 ± 0.86 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 711.19 ± 0.46 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 716.67 ± 0.46 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0.00	1
16.40	3
43.40	5
10192.63	5
21648.01	1
33735.20	5

Enthalpy of Formation

$\Delta_f H°$(298.15 K) = 171.29 ± 0.11 $kcal·mol^{-1}$ is the value selected by CODATA[1] based on $D°_0$(CO) = 89595 ± 30 cm^{-1} (256.165 ± 0.086 $kcal·mol^{-1}$) from Douglas and Moller.[2] The conversion factor used by CODATA[1] corresponds to the negligibly different value of 256.163 $kcal·mol^{-1}$; this yields the adopted $\Delta_f H°$ when combined with $\Delta_f H°$(CO, 0 K) = −27.201 ± 0.024 $kcal·mol^{-1}$.[1,3] According to Krupenie[4] it is most likely that the atomic dissociation products are in their ground states as assumed in the adopted $D°_0$(CO).

The enthalpy of sublimation, $\Delta_{sub}H° = \Delta_f H°$, is confirmed by Knudsen–effusion mass–spectrometric data of Wachi and Gilmartin[5] for graphite. They obtained absolute pressures from calibrations using gold and cobalt; pressures from the latter were higher by 8.74%. Our 3rd law analyses yield $\Delta_{sub}H°$(298.15 K) = 171.22 ± 0.61 and 170.78 ± 0.61 $kcal·mol^{-1}$ from gold and cobalt, respectively. 2nd law values are $\Delta_{sub}H°$(298.15 K) = 172.5 ± 3.3 $kcal·mol^{-1}$ and $\Delta_{sub}S°$(2nd law)–$\Delta_{sub}S°$(3rd law) = 0.5 ± 1.2 (gold) and 0.7 ± 1.2 (cobalt) $cal·K^{-1}·mol^{-1}$). The data consisted of 14 points in the range 2509–2753 K. None of the other studies of C(g) over pure graphite included calibrations for conversion of ion intensities to absolute pressures.

Heat Capacity and Entropy

The atomic energy levels are from Moore.[6] $S°$(298.15 K) and $H°(0\ K)–H°(298.15\ K)$ are the same as the values selected by CODATA.[1] Observed and predicted levels above 60333 cm^{-1} are omitted since they do not change the thermodynamic functions at 6000 K. At 14000 K the BETHE–FILL cut–off method would yield a Gibbs energy function ~0.1 $cal·K^{-1}·mol^{-1}$ larger than either the present cut–off method (TEMPER).[7]

Reference

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[4]P. H. Krupenie, U. S. Natl. Bur. Stand., NSRDS–NBS 5, (1966).
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[6]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS 3, Section 3, (1970).
[7]J. R. Downey, The Dow Chemical Co., Rept. AFOSR–TR–78–0960, Contract No F44620–75–C–0048, (March 9, 1978).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.536	711.185	711.185	INFINITE
100	21.271	135.180	176.684	−4.150	713.511	700.088	−365.689
200	20.904	149.768	160.007	−2.048	715.287	685.950	−179.152
250	20.861	154.427	158.443	−1.004	716.035	678.527	−141.770
298.15	20.838	158.100	158.100	0.	716.670	671.244	−117.599
300	20.838	158.228	158.100	0.039	716.693	670.962	−116.825
350	20.824	161.439	158.354	1.080	717.263	663.294	−98.991
400	20.815	164.219	158.917	2.121	717.752	655.550	−85.606
450	20.809	166.671	159.645	3.162	718.165	647.749	−75.189
500	20.804	168.863	160.459	4.202	718.507	639.906	−66.851
600	20.799	172.655	162.185	6.282	719.009	624.135	−54.336
700	20.795	175.861	163.916	8.362	719.315	608.296	−45.392
800	20.793	178.638	165.587	10.441	719.474	592.424	−38.681
900	20.792	181.087	167.175	12.520	719.519	576.539	−33.461
1000	20.791	183.278	168.678	14.600	719.475	560.654	−29.286
1100	20.791	185.259	170.097	16.679	719.360	544.777	−25.869
1200	20.793	187.068	171.437	18.758	719.188	528.913	−23.023
1300	20.796	188.733	172.704	20.837	718.968	513.066	−20.615
1400	20.803	190.274	173.905	22.917	718.709	497.237	−18.552
1500	20.814	191.710	175.044	24.998	718.415	481.427	−16.765
1600	20.829	193.053	176.128	27.080	718.092	465.639	−15.202
1700	20.850	194.317	177.162	29.164	717.744	449.871	−13.823
1800	20.878	195.509	178.148	31.250	717.373	434.124	−12.598
1900	20.912	196.639	179.092	33.340	716.984	418.399	−11.503
2000	20.952	197.713	179.996	35.433	716.577	402.694	−10.517
2100	20.999	198.736	180.864	37.530	716.156	387.010	−9.626
2200	21.052	199.714	181.699	39.633	715.722	371.347	−8.817
2300	21.110	200.651	182.503	41.741	715.277	355.703	−8.078
2400	21.174	201.551	183.278	43.855	714.821	340.079	−7.402
2500	21.241	202.417	184.026	45.976	714.357	324.474	−6.780
2600	21.313	203.251	184.750	48.103	713.884	308.888	−6.206
2700	21.387	204.057	185.450	50.238	713.405	293.321	−5.675
2800	21.464	204.836	186.129	52.381	712.920	277.771	−5.182
2900	21.542	205.591	186.787	54.531	712.429	262.239	−4.723
3000	21.621	206.322	187.426	56.689	711.932	246.723	−4.296
3100	21.701	207.032	188.047	58.856	711.431	231.224	−3.896
3200	21.780	207.723	188.651	61.030	710.925	215.742	−3.522
3300	21.859	208.394	189.239	63.212	710.414	200.275	−3.170
3400	21.936	209.048	189.812	65.401	709.899	184.824	−2.839
3500	22.012	209.685	190.371	67.599	709.380	169.389	−2.528
3600	22.087	210.306	190.916	69.804	708.857	153.968	−2.234
3700	22.159	210.912	191.448	72.016	708.329	138.561	−1.956
3800	22.230	211.504	191.968	74.235	707.797	123.169	−1.693
3900	22.298	212.082	192.477	76.462	707.260	107.791	−1.444
4000	22.363	212.648	192.974	78.695	706.719	92.427	−1.207
4100	22.426	213.201	193.461	80.934	706.173	77.077	−0.982
4200	22.487	213.742	193.937	83.180	705.621	61.740	−0.768
4300	22.544	214.272	194.404	85.432	705.065	46.416	−0.564
4400	22.600	214.791	194.861	87.689	704.503	31.105	−0.369
4500	22.652	215.299	195.310	89.951	703.936	15.807	−0.183
4600	22.702	215.797	195.750	92.219	703.363	0.521	−0.006
4700	22.750	216.286	196.182	94.492	702.784	−14.752	0.164
4800	22.795	216.766	196.605	96.769	702.199	−30.012	0.327
4900	22.838	217.236	197.022	99.051	701.607	−45.261	0.482
5000	22.878	217.698	197.431	101.337	701.009	−60.497	0.632
5100	22.917	218.151	197.832	103.626	700.404	−75.721	0.776
5200	22.953	218.597	198.227	105.920	699.793	−90.933	0.913
5300	22.987	219.034	198.616	108.217	699.174	−106.133	1.046
5400	23.020	219.464	198.998	110.517	698.548	−121.322	1.174
5500	23.051	219.887	199.374	112.821	697.914	−136.499	1.296
5600	23.080	220.302	199.744	115.127	697.273	−151.664	1.415
5700	23.107	220.711	200.108	117.437	696.625	−166.818	1.529
5800	23.133	221.113	200.467	119.749	695.968	−181.961	1.639
5900	23.157	221.509	200.820	122.063	695.304	−197.092	1.745
6000	23.181	221.898	201.168	124.380	694.631	−212.211	1.847

PREVIOUS: March 1978 (1 atm) CURRENT: March 1983 (1 bar)

IP(C^+, g) = 196664.7 ± 0.5 cm^{-1}
$S°$(298.15 K) = 154.662 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1797.639 ± 0.46 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1809.435] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{1/2}$	0.0	2
$^2P_{3/2}$	63.42	4
$^4P_{1/2}$	43003.3	2
$^4P_{3/2}$	43025.3	4
$^4P_{5/2}$	43053.6	6

Enthalpy of Formation

$\Delta_f H°(C^+, g, 0 K)$ is calculated from $\Delta_f H°(C, g, 0 K)$[1] using the spectroscopic value of IP(C) = 90820.42 ± 0.1 cm^{-1} (1086.454 ± 0.001 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(C^+, g, 298.15 K)$ is calculated from $\Delta_f H°(C, g, 0 K)$ by using IP(C) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for C(g), C^+(g), and e^-(ref). $\Delta_f H°(C \rightarrow C^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2] is incomplete because many theoritically predicted levels that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is 74930.1 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: C (g), 3–31–83; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.649	1797.639		
100	22.496	131.192	173.519	−4.233			
200	21.213	146.246	156.586	−2.068			
250	21.056	150.961	155.008	−1.012			
298.15	20.974	154.662	154.662	0.	1809.435	1758.779	−308.131
300	20.971	154.792	154.662	0.039	1809.496	1758.464	−306.176
350	20.921	158.020	154.918	1.086	1811.112	1749.830	−261.148
400	20.889	160.812	155.484	2.131	1812.644	1740.970	−227.347
450	20.867	163.271	156.215	3.175	1814.099	1731.923	−201.036
500	20.851	165.468	157.032	4.218	1815.483	1722.717	−179.971
600	20.831	169.268	158.765	6.302	1818.067	1703.917	−148.339
700	20.819	172.478	160.500	8.384	1820.455	1684.701	−125.714
800	20.811	175.257	162.175	10.466	1822.695	1665.154	−108.723
900	20.806	177.708	163.768	12.547	1824.819	1645.332	−95.493
1000	20.802	179.900	165.273	14.627	1826.855	1625.279	−84.896
1100	20.799	181.883	166.694	16.707	1828.820	1605.026	−76.216
1200	20.797	183.692	168.037	18.787	1830.727	1584.597	−68.976
1300	20.795	185.357	169.306	20.866	1832.586	1564.010	−62.843
1400	20.794	186.898	170.508	22.946	1834.405	1543.282	−57.581
1500	20.793	188.333	171.649	25.025	1836.188	1522.425	−53.016
1600	20.792	189.675	172.734	27.105	1837.941	1501.450	−49.017
1700	20.791	190.935	173.768	29.184	1839.667	1480.366	−45.486
1800	20.791	192.123	174.755	31.263	1841.368	1459.182	−42.344
1900	20.790	193.247	175.699	33.342	1843.047	1437.903	−39.531
2000	20.790	194.314	176.603	35.421	1844.705	1416.537	−36.996
2100	20.790	195.328	177.471	37.500	1846.344	1395.088	−34.701
2200	20.789	196.295	178.305	39.579	1847.964	1373.562	−32.613
2300	20.789	197.219	179.107	41.658	1849.568	1351.962	−30.704
2400	20.789	198.104	179.881	43.737	1851.156	1330.293	−28.953
2500	20.789	198.953	180.627	45.815	1852.729	1308.558	−27.341
2600	20.788	199.768	181.347	47.894	1854.286	1286.761	−25.851
2700	20.788	200.553	182.044	49.973	1855.829	1264.903	−24.471
2800	20.788	201.309	182.719	52.052	1857.359	1242.989	−23.188
2900	20.788	202.038	183.372	54.131	1858.875	1221.021	−21.993
3000	20.788	202.743	184.006	56.209	1860.377	1199.000	−20.876
3100	20.788	203.425	184.622	58.288	1861.867	1176.929	−19.831
3200	20.788	204.085	185.220	60.367	1863.345	1154.811	−18.850
3300	20.787	204.724	185.801	62.446	1864.809	1132.647	−17.928
3400	20.787	205.345	186.367	64.525	1866.262	1110.438	−17.060
3500	20.787	205.947	186.918	66.603	1867.703	1088.187	−16.240
3600	20.787	206.533	187.455	68.682	1869.132	1065.895	−15.466
3700	20.787	207.103	187.978	70.761	1870.549	1043.563	−14.732
3800	20.787	207.657	188.489	72.839	1871.955	1021.193	−14.037
3900	20.788	208.197	188.987	74.918	1873.349	998.787	−13.377
4000	20.788	208.723	189.474	76.997	1874.732	976.344	−12.750
4100	20.788	209.236	189.950	79.076	1876.104	953.868	−12.152
4200	20.788	209.737	190.415	81.155	1877.464	931.358	−11.583
4300	20.789	210.227	190.870	83.233	1878.814	908.815	−11.040
4400	20.789	210.705	191.315	85.312	1880.153	886.242	−10.521
4500	20.790	211.172	191.751	87.391	1881.480	863.638	−10.025
4600	20.791	211.629	192.179	89.470	1882.797	841.005	−9.550
4700	20.792	212.076	192.597	91.550	1884.103	818.343	−9.095
4800	20.794	212.514	193.008	93.629	1885.399	795.653	−8.658
4900	20.795	212.942	193.410	95.708	1886.683	772.937	−8.240
5000	20.797	213.362	193.805	97.788	1887.958	750.195	−7.837
5100	20.800	213.774	194.192	99.868	1889.222	727.427	−7.450
5200	20.803	214.178	194.573	101.948	1890.475	704.634	−7.078
5300	20.806	214.575	194.947	104.028	1891.718	681.818	−6.720
5400	20.810	214.964	195.314	106.109	1892.951	658.978	−6.374
5500	20.814	215.345	195.674	108.190	1894.174	636.115	−6.041
5600	20.819	215.720	196.029	110.272	1895.387	613.230	−5.720
5700	20.824	216.089	196.378	112.354	1896.590	590.324	−5.410
5800	20.831	216.451	196.721	114.437	1897.782	567.397	−5.110
5900	20.838	216.807	197.058	116.520	1898.965	544.449	−4.820
6000	20.845	217.158	197.390	118.604	1900.139	521.481	−4.540

PREVIOUS: March 1978 (1 atm) CURRENT: March 1983 (1 bar)

EA(C, g) = 1.2629 ± 0.0003 eV
$S°$(298.15 K) = 151.384 ± 0.003 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 589.33 ± 2 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [588.284] kJ·mol^{-1}

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4S_3$	0	4
^2D	9920	10

Enthalpy of Formation

$\Delta_f H°(C^-, g, 0 K)$ is calculated from $\Delta_f H°(C, g, 0 K)$[1] using the adopted electron affinity of EA(C) = 1.2629 + 0.0003 eV (121.850 ± 0.029 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $C^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(C^-, g, 298.15 K)$ is obtained from $\Delta_f H°(C, g, 0 K)$ by using EA(C) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for $C^-(g)$, C(g), and e^-(ref). $\Delta_r H°(C^- \rightarrow C + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°$(298.15 K) should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

Electronic energy levels are from the laser photodetachment study of Feldmann.[3] He found that the $C^-(^2D)$ state has a binding energy of 0.033 ± 0.001 eV (266 ± 8 cm^{-1}) relative to ground state $C(^3P_0)$. The electronic energy of 9920 cm^{-1} is the difference in binding energy between ground and excited states. Spin–orbit splitting of the ^2D state was not resolved[3] but has been estimated[2,4] to be 3 cm^{-1}. We neglect this splitting because its effect is negligible. $C^-(^2D)$ binding energies obtained by other mehtods[4,7] are in satisfactory agreement.

Note that we include the excited state even though its binding energy is only 266 cm^{-1}. If this state were omitted, the Gibbs energy function (J·K^{-1}·mol^{-1}) would change by −0.004 (1700 K), −0.176 (3000 K) and −1.732 (6000 K).

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[1]JANAF Thermochemical Tables: C(g), 3–31–83; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
0	0.	0. INFINITE	−6.197	589.335		
100	20.786	128.676 169.864	−4.119			
200	20.786	143.084 153.285	−2.040			
250	20.786	147.722 151.726	−1.001			
298.15	20.786	151.384 151.384	0.	588.284	551.115	−96.553
300	20.786	151.512 151.384	0.038	588.268	550.885	−95.918
350	20.786	154.716 151.637	1.078	587.797	544.690	−81.291
400	20.786	157.492 152.199	2.117	587.245	538.569	−70.330
450	20.786	159.940 152.926	3.156	586.617	532.521	−61.813
500	20.786	162.130 153.739	4.196	585.919	526.547	−55.008
600	20.786	165.920 155.463	6.274	584.340	514.817	−44.819
700	20.786	169.124 157.191	8.353	582.568	503.368	−37.562
800	20.786	171.900 158.860	10.431	580.647	492.183	−32.136
900	20.787	174.348 160.448	12.510	578.612	481.247	−27.931
1000	20.789	176.538 161.949	14.589	576.489	470.541	−24.579
1100	20.794	178.520 163.367	16.668	574.296	460.052	−21.846
1200	20.806	180.330 164.706	18.748	572.046	449.765	−19.578
1300	20.829	181.996 165.973	20.830	569.750	439.668	−17.666
1400	20.867	183.541 167.173	22.914	567.416	429.749	−16.034
1500	20.925	184.982 168.313	25.004	565.053	419.998	−14.626
1600	21.007	186.335 169.398	27.100	562.665	410.405	−13.398
1700	21.117	187.612 170.432	29.206	560.261	400.963	−12.320
1800	21.256	188.822 171.420	31.324	557.844	391.662	−11.366
1900	21.425	189.976 172.367	33.458	555.420	382.496	−10.516
2000	21.625	191.080 173.275	35.610	552.994	373.457	−9.754
2100	21.853	192.141 174.148	37.784	550.570	364.540	−9.067
2200	22.108	193.163 174.989	39.982	548.153	355.738	−8.446
2300	22.385	194.152 175.801	42.206	545.745	347.046	−7.882
2400	22.683	195.111 176.586	44.459	543.350	338.458	−7.366
2500	22.996	196.043 177.346	46.743	540.970	329.970	−6.894
2600	23.320	196.951 178.082	49.059	538.608	321.577	−6.461
2700	23.653	197.837 178.798	51.408	536.263	313.274	−6.061
2800	23.989	198.704 179.493	53.790	533.939	305.058	−5.691
2900	24.325	199.551 180.170	56.205	531.634	296.924	−5.348
3000	24.658	200.382 180.830	58.655	529.350	288.870	−5.030
3100	24.984	201.195 181.474	61.137	527.086	280.891	−4.733
3200	25.301	201.994 182.103	63.651	524.842	272.985	−4.456
3300	25.607	202.777 182.717	66.197	522.616	265.149	−4.197
3400	25.899	203.546 183.319	68.772	520.409	257.380	−3.954
3500	26.176	204.301 183.908	71.376	518.217	249.676	−3.726
3600	26.437	205.042 184.484	74.007	516.041	242.034	−3.512
3700	26.680	205.769 185.050	76.663	513.879	234.453	−3.310
3800	26.905	206.484 185.604	79.342	511.728	226.929	−3.119
3900	27.112	207.186 186.149	82.043	509.587	219.463	−2.939
4000	27.300	207.874 186.683	84.764	507.455	212.051	−2.769
4100	27.469	208.551 187.209	87.502	505.329	204.692	−2.608
4200	27.621	209.214 187.725	90.257	503.208	197.385	−2.455
4300	27.754	209.866 188.232	93.026	501.091	190.128	−2.310
4400	27.870	210.505 188.731	95.807	498.974	182.921	−2.172
4500	27.969	211.133 189.222	98.599	496.858	175.762	−2.040
4600	28.052	211.748 189.705	101.401	494.740	168.650	−1.915
4700	28.120	212.352 190.180	104.209	492.618	161.584	−1.796
4800	28.173	212.945 190.648	107.024	490.492	154.563	−1.682
4900	28.212	213.526 191.109	109.843	488.359	147.587	−1.573
5000	28.239	214.097 191.563	112.666	486.220	140.654	−1.469
5100	28.253	214.656 192.011	115.491	484.071	133.764	−1.370
5200	28.256	215.205 192.452	118.316	481.913	126.916	−1.275
5300	28.249	215.743 192.886	121.142	479.744	120.110	−1.184
5400	28.232	216.271 193.314	123.966	477.563	113.345	−1.096
5500	28.207	216.789 193.736	126.788	475.369	106.620	−1.013
5600	28.173	217.297 194.152	129.607	473.162	99.935	−0.932
5700	28.132	217.795 194.563	132.422	470.941	93.290	−0.855
5800	28.084	218.284 194.968	135.233	468.705	86.684	−0.781
5900	28.030	218.763 195.367	138.039	466.453	80.117	−0.709
6000	27.971	219.234 195.761	140.839	464.185	73.588	−0.641

PREVIOUS: March 1978 (1 atm) CURRENT: March 1983 (1 bar)

$S°(298.15\ K) = [223.4 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [686.2 \pm 10]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [689.5 \pm 10]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4

$\omega_e = [760]\ cm^{-1}$ $\omega_e x_e = [5.0]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.650]\ cm^{-1}$ $\alpha_e = [0.006]\ cm^{-1}$ $r_e = [1.77]$ Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was calculated from $D_0^\circ = 83.0\ kcal \cdot mol^{-1}$, estimated by Gordon.[1] The spectrum originally attributed to AlC(g)[2] was later shown to be due to $Al_2(g)$.[3,4]

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] The recent review by Huber and Herzberg[5] did not indicate any experimental data available for the vibrational–rotational constants for AlC(g).

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[5]K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," Van Nostrand Reinhold Company, New York, (1979).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.928	686.185	686.185	INFINITE
100	29.131	190.573	250.776	−6.020	688.550	670.287	−350.122
200	30.241	210.997	226.335	−3.067	689.375	651.620	−170.186
250	31.276	217.855	223.975	−1.530	689.503	642.164	−134.173
298.15	32.256	223.449	223.449	0.	689.523	633.044	−110.907
300	32.292	223.649	223.450	0.060	689.522	632.693	−110.162
350	33.178	228.695	223.846	1.697	689.454	623.226	−93.011
400	33.913	233.175	224.738	3.375	689.307	613.774	−80.151
450	34.513	237.205	225.903	5.086	689.086	604.345	−70.151
500	35.001	240.868	227.219	6.824	688.797	594.944	−62.153
600	35.729	247.318	230.046	10.363	688.022	576.242	−50.166
700	36.233	252.866	232.919	13.963	687.001	557.689	−41.615
800	36.598	257.729	235.722	17.605	685.742	539.299	−35.213
900	36.872	262.056	238.412	21.279	684.240	521.082	−30.243
1000	37.087	265.952	240.975	24.978	671.900	503.805	−26.316
1100	37.260	269.496	243.409	28.695	670.249	487.075	−23.129
1200	37.405	272.744	245.720	32.429	668.556	470.497	−20.480
1300	37.528	275.743	247.916	36.176	666.829	454.062	−18.244
1400	37.636	278.528	250.004	39.934	665.072	437.761	−16.333
1500	37.733	281.128	251.993	43.703	663.291	421.586	−14.681
1600	37.820	283.566	253.891	47.480	661.489	405.531	−13.239
1700	37.900	285.862	255.705	51.266	659.668	389.589	−11.971
1800	37.975	288.030	257.441	55.060	657.830	373.755	−10.846
1900	38.045	290.085	259.106	58.861	655.977	358.024	−9.843
2000	38.112	292.038	260.704	62.669	654.110	342.391	−8.942
2100	38.176	293.899	262.241	66.484	652.231	326.851	−8.130
2200	38.237	295.677	263.720	70.304	650.340	311.401	−7.394
2300	38.296	297.378	265.147	74.131	648.438	296.037	−6.723
2400	38.354	299.009	266.524	77.963	646.526	280.756	−6.110
2500	38.410	300.576	267.855	81.802	644.604	265.555	−5.548
2600	38.465	302.083	269.143	85.645	642.672	250.431	−5.031
2700	38.519	303.536	270.390	89.495	640.732	235.382	−4.554
2800	38.571	304.938	271.599	93.349	344.883	221.372	−4.130
2900	38.623	306.292	272.772	97.209	344.021	216.976	−3.908
3000	38.675	307.602	273.911	101.074	343.152	212.610	−3.702
3100	38.726	308.871	275.018	104.944	342.275	208.273	−3.509
3200	38.776	310.102	276.096	108.819	341.390	203.965	−3.329
3300	38.826	311.296	277.144	112.699	340.497	199.684	−3.161
3400	38.875	312.455	278.166	116.584	339.596	195.431	−3.002
3500	38.924	313.583	279.162	120.474	338.688	191.204	−2.854
3600	38.973	314.680	280.133	124.369	337.771	187.003	−2.713
3700	39.021	315.749	281.081	128.269	336.847	182.827	−2.581
3800	39.069	316.790	282.008	132.173	335.915	178.677	−2.456
3900	39.117	317.805	282.912	136.082	334.974	174.552	−2.338
4000	39.165	318.796	283.797	139.997	334.024	170.450	−2.226
4100	39.213	319.764	284.663	143.915	333.066	166.373	−2.120
4200	39.260	320.710	285.510	147.839	332.098	162.319	−2.019
4300	39.307	321.634	286.339	151.767	331.120	158.288	−1.923
4400	39.354	322.538	287.152	155.700	330.132	154.280	−1.832
4500	39.401	323.423	287.948	159.638	329.135	150.295	−1.745
4600	39.448	324.290	288.729	163.581	328.125	146.331	−1.662
4700	39.495	325.138	289.494	167.528	327.104	142.390	−1.582
4800	39.541	325.970	290.245	171.480	326.069	138.471	−1.507
4900	39.588	326.786	290.983	175.436	325.022	134.574	−1.435
5000	39.634	327.586	291.707	179.397	323.959	130.698	−1.365
5100	39.680	328.372	292.418	183.363	322.882	126.843	−1.299
5200	39.727	329.143	293.117	187.333	321.788	123.010	−1.236
5300	39.773	329.900	293.804	191.308	320.677	119.198	−1.175
5400	39.819	330.644	294.479	195.288	319.549	115.407	−1.116
5500	39.865	331.375	295.144	199.272	318.401	111.637	−1.060
5600	39.911	332.094	295.797	203.261	317.233	107.888	−1.006
5700	39.957	332.800	296.440	207.254	316.043	104.160	−0.955
5800	40.003	333.496	297.073	211.252	314.834	100.453	−0.905
5900	40.049	334.180	297.696	215.255	313.599	96.768	−0.857
6000	40.095	334.853	298.310	219.262	312.362	93.101	−0.811

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = [208.56]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 822.0 \pm 41\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 828.4 \pm 41\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^4\Sigma^-$	0	4

$\omega_e = [1350]\ cm^{-1}$ $\omega_e x_e = [12.0]\ cm^{-1}$ $\sigma = 1$
$B_e = [1.555]\ cm^{-1}$ $\alpha_e = [0.018]\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation at 298.15 K was calculated from $\Delta_f H°(0\ K) = 105 \pm 10\ kcal·mol^{-1}$ for the reaction BC(g) = B(g) + C(g) reported by Verhaegen *et al.*[1,2]

Heat Capacity and Entropy

All spectroscopic constants were obtained from Gordon.[3] Theoretical calculations by Kruba[4] predict a $^4\Sigma^-$ ground state. The recent review by Huber and Herzberg[5] did not indicate any experimental data available on the vibrational–rotational constants for BC(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.700	821.997	821.997	INFINITE
100	29.109	176.645	234.607	−5.796	824.817	807.279	−421.679
200	29.172	196.831	211.250	−2.884	827.070	788.804	−206.015
250	29.358	203.357	209.042	−1.421	827.866	779.141	−162.793
298.15	29.700	208.555	208.555	0.	828.432	769.702	−134.849
300	29.716	208.739	208.556	0.055	828.450	769.338	−133.954
350	30.212	213.355	208.919	1.553	828.850	759.452	−113.342
400	30.788	217.427	209.733	3.077	829.087	749.520	−97.877
450	31.388	221.088	210.795	4.632	829.186	739.567	−85.847
500	31.975	224.425	211.993	6.216	829.168	729.609	−76.222
600	33.032	230.351	214.571	9.468	828.861	709.720	−61.787
700	33.898	235.510	217.202	12.816	828.281	689.906	−51.481
800	34.589	240.084	219.782	16.242	827.503	670.190	−43.759
900	35.138	244.191	222.270	19.729	826.574	650.580	−37.759
1000	35.578	247.917	224.651	23.266	825.525	631.080	−32.964
1100	35.934	251.325	226.923	26.842	824.378	611.691	−29.047
1200	36.227	254.464	229.089	30.450	823.146	592.409	−25.787
1300	36.471	257.374	231.154	34.086	821.841	573.234	−23.033
1400	36.677	260.085	233.125	37.743	820.469	554.161	−20.676
1500	36.854	262.621	235.008	41.420	819.037	535.189	−18.637
1600	37.007	265.005	236.809	45.113	817.549	516.314	−16.856
1700	37.142	267.252	238.534	48.821	816.008	497.533	−15.287
1800	37.262	269.379	240.189	52.541	814.417	478.845	−13.896
1900	37.369	271.396	241.779	56.273	812.778	460.247	−12.653
2000	37.466	273.316	243.308	60.015	811.093	441.736	−11.537
2100	37.555	275.146	244.781	63.766	809.363	423.310	−10.529
2200	37.637	276.895	246.201	67.526	807.589	404.968	−9.615
2300	37.713	278.570	247.573	71.293	805.772	386.708	−8.782
2400	37.784	280.176	248.898	75.068	753.654	369.596	−8.044
2500	37.851	281.720	250.180	78.850	751.676	353.634	−7.389
2600	37.914	283.206	251.422	82.638	749.689	337.752	−6.786
2700	37.974	284.638	252.626	86.432	747.694	321.946	−6.228
2800	38.032	286.020	253.794	90.233	745.692	306.214	−5.712
2900	38.087	287.355	254.928	94.039	743.681	290.554	−5.233
3000	38.140	288.647	256.031	97.850	741.663	274.963	−4.788
3100	38.191	289.899	257.103	101.667	739.637	259.440	−4.372
3200	38.241	291.112	258.147	105.488	737.603	243.982	−3.983
3300	38.289	292.290	259.164	109.315	735.562	228.588	−3.618
3400	38.336	293.433	260.155	113.146	733.514	213.256	−3.276
3500	38.382	294.545	261.122	116.982	731.458	197.984	−2.955
3600	38.427	295.627	262.066	120.822	729.395	182.771	−2.652
3700	38.471	296.681	262.987	124.667	727.325	167.616	−2.366
3800	38.514	297.707	263.887	128.516	725.248	152.516	−2.096
3900	38.557	298.708	264.767	132.370	723.163	137.471	−1.841
4000	38.598	299.685	265.628	136.228	721.072	122.480	−1.599
4100	38.640	300.639	266.470	140.090	718.973	107.542	−1.370
4200	38.681	301.570	267.295	143.956	237.018	99.678	−1.240
4300	38.721	302.481	268.103	147.826	235.992	96.420	−1.171
4400	38.761	303.371	268.894	151.700	234.958	93.186	−1.106
4500	38.800	304.243	269.670	155.578	233.914	89.976	−1.044
4600	38.839	305.096	270.431	159.460	232.861	86.789	−0.986
4700	38.878	305.932	271.177	163.346	231.799	83.625	−0.929
4800	38.916	306.751	271.910	167.235	230.727	80.484	−0.876
4900	38.954	307.554	272.629	171.129	229.645	77.365	−0.825
5000	38.992	308.341	273.336	175.026	228.552	74.268	−0.776
5100	39.030	309.113	274.030	178.927	227.449	71.193	−0.729
5200	39.067	309.872	274.712	182.832	226.335	68.140	−0.684
5300	39.104	310.616	275.382	186.741	225.209	65.109	−0.642
5400	39.141	311.347	276.041	190.653	224.072	62.099	−0.601
5500	39.178	312.066	276.690	194.569	222.923	59.110	−0.561
5600	39.215	312.772	277.328	198.489	221.761	56.142	−0.524
5700	39.251	313.467	277.956	202.412	220.587	53.195	−0.487
5800	39.287	314.150	278.574	206.339	219.400	50.268	−0.453
5900	39.324	314.822	279.183	210.269	218.199	47.363	−0.419
6000	39.360	315.483	279.782	214.204	216.985	44.477	−0.387

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 27.175 \pm 0.13\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2743 \pm 20\ K$

$\Delta_f H°(0\ K) = -62.40 \pm 6.28\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -62.68 \pm 6.28\ kJ·mol^{-1}$
$\Delta_{fus} H° = [104.6 \pm 10]\ kJ·mol^{-1}$

Enthalpy of Formation

Using a high temperature solution calorimetric technique, Hong and Kleppa[1] measured $\Delta_f H°(B_4C, cr, 1320\ K) = -15.98 \pm 0.84$ kcal·mol^{-1}. We adopt this value and correct to 298.15 K using tabulated enthalpy data[2] to obtain $\Delta_f H°(B_4C, cr, 298.15\ K) = -14.98 \pm 1.5$ kcal·mol^{-1} which is a correction to that reported by Hong and Kleppa.[1] The uncertainty limit is that recommended by Hong and Kleppa.

Two additional experimental determinations of $\Delta_f H°(B_4C, cr, 298.15\ K)$ have been made. Smith *et al.*[3] measured a value of $\Delta_r H°(298.15\ K) = -683.2 \pm 2.2$ kcal·mol^{-1} for the reaction $B_4C(cr) + 4\ O_2(g) \rightarrow 2\ B_2O_3(am) + CO_2(g)$. Due to the amorphous nature of the B_2O_3 product, a value of $\Delta_f H°(298.15\ K)$ derived from this reaction may be unreliable. Domalski and Armstrong[4] determined $\Delta_f H°(298.15\ K) = -17.1 \pm 2.7$ kcal·mol^{-1} based on careful fluorine bomb calorimetry of the non- stoichiometric compound $B_{4.222}C(cr)$. The data were corrected to the stoichiometric $B_4C(cr)$ assuming the presence of excess free elemental boron. Note that the Hong and Kleppa[1] result lies within the stated uncertainty limits of the Domalski and Armstrong value.[4] In a review of similar data, Gurvich *et al.*[5] adopted a value for $\Delta_f H°(298.15\ K)$ of -14.82 ± 1.43 kcal·mol^{-1}.

Heat Capacity and Entropy

The low temperature heat capacities, 54–294 K, were taken from Kelley.[6] Above 298 K at least four enthalpy determinations have been made. The enthalpy data of King[7] in the range 298 to 1726 K were used to determine the equation: $C_p°/cal·K^{-1}·mol^{-1} = 22.99 + 5.40 \times 10^{-3}T - 10.72 \times 10^5 T^{-2}$. Similar measurements of Ancey–Moret and Deniel[8] lead to the equation $C_p°/cal·K^{-1}·mol^{-1} = 23.077 + 5.24 \times 10^{-3}T - 10.75 \times 10^5 T^{-2}$. Enthalpy measurements of Mathieu *et al.*[9] in the range 661–1014 K also support the latter two studies. We adopt the high temperature equation of King which joins smoothly at 298 K with the low temperature data of Kelley. The $S°(298.15\ K)$ is calculated based on the low temperature heat capacities of Kelley using $S°(53.1\ K) = 0.047\ cal·K^{-1}·mol^{-1}$. The heat capacities adopted by Gurvich *et al.*[5] are in essential agreement with those adopted here up to 1500 K but are larger in the high temperature range (T>1500 K). This is due to the adoption (by Gurvich *et al.*) of the heat capacity results of Sheindlin *et al.*[10] which can be represented by the equation $C_p°/cal·K^{-1}·mol^{-1} = 22.65 + 5.27 \times 10^{-3}T - 12.82 \times 10^5 T^{-2} + 6.45 \times 10^{13} T^{-2} \exp(-33 \times 10^3/T)$. Note the additional exponential term which causes the high temperature disparity. Due to the relatively high impurity content of the material used (5.6 mole%) and also the thermodynamic propensity and endothermicity of the reaction by $B_4C(cr) = 4\ B(cr) + C(cr)$ at temperatures greater than 1500 K, we are in doubt as to the exponential behavior of $C_p°$ as reported in the Sheindlin study.

Fusion Data

Of the several reported values of the fusion temperature, T_{fus}/K, [2623,[11,13] 2723,[12] 2713 ± 20,[10] 2633,[14] 2743 ± 20],[15] we adopt the value of Dolloff.[15] The value for $\Delta_{fus} H°$ is estimated. Note that $B_4C(cr)$ decomposes at moderate temperatures to form B(cr, g) + C(cr).[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.635	−62.404	−62.404	INFINITE
100	5.071	1.634	56.731	−5.510	−62.435	−62.380	32.584
200	27.426	11.311	31.236	−3.985	−62.568	−62.279	16.266
298.15	53.764	27.175	27.175	0.	−62.676	−62.109	10.881
300	54.266	27.509	27.176	0.100	−62.676	−62.106	10.814
400	76.358	46.353	29.595	6.703	−62.546	−61.931	8.087
500	89.789	64.925	34.822	15.051	−62.448	−61.791	6.455
600	98.366	82.103	41.293	24.486	−62.517	−61.657	5.368
700	103.680	97.682	48.254	34.599	−62.796	−61.494	4.589
800	107.654	111.793	55.329	45.171	−63.277	−61.277	4.001
900	110.989	124.666	62.328	56.104	−63.906	−60.991	3.540
1000	114.299	136.533	69.163	67.370	−64.611	−60.630	3.167
1100	117.336	147.571	75.795	78.954	−65.341	−60.196	2.858
1200	120.190	157.904	82.211	90.831	−66.071	−59.696	2.599
1300	122.909	167.632	88.411	102.987	−66.781	−59.136	2.376
1400	125.533	176.837	94.402	115.410	−67.456	−58.522	2.183
1500	128.089	185.585	100.191	128.091	−68.086	−57.862	2.015
1600	130.587	193.932	105.791	141.025	−68.663	−57.161	1.866
1700	133.047	201.923	111.213	154.207	−69.178	−56.426	1.734
1800	135.474	209.596	116.467	167.633	−69.626	−55.663	1.615
1900	137.875	216.986	121.564	181.301	−70.004	−54.877	1.509
2000	140.256	224.118	126.514	195.208	−70.307	−54.072	1.412
2100	142.620	231.019	131.327	209.352	−70.532	−53.255	1.325
2200	144.971	237.708	136.012	223.731	−70.677	−52.428	1.245
2300	147.306	244.203	140.575	238.345	−70.739	−51.597	1.172
2400	149.637	250.522	145.025	253.193	−271.756	−46.490	1.012
2500	151.955	256.677	149.369	268.272	−271.961	−37.099	0.775
2600	154.268	262.682	153.612	283.583	−271.950	−27.704	0.557
2700	156.578	268.548	157.760	299.126	−271.722	−18.313	0.354
2743.000	157.569	271.030	159.517	305.880	--- CRYSTAL <--> LIQUID ---		
2800	158.887	274.284	161.820	314.899	−271.276	−8.935	0.167
2900	161.197	279.900	165.795	330.903	−270.614	0.423	−0.008
3000	163.507	285.403	169.691	347.138	−269.733	9.755	−0.170
3100	165.816	290.802	173.511	363.604	−268.635	19.054	−0.321
3200	168.126	296.103	177.259	380.301	−267.318	28.313	−0.462

PREVIOUS: December 1965 CURRENT: June 1983

$S°(298.15\ K)$ = [69.426] $J·K^{-1}·mol^{-1}$
T_{fus} = 2743 ± 20 K

$\Delta_f H°(298.15\ K)$ = [51.885] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [104.6 ± 10] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(B_4C, l, 298.15\ K)$ is calculated from $\Delta_f H°(B_4C, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2743\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1750 K. The heat capacity below 1750 K is assumed to be that of the crystal. Above 1750 K the heat capacity is assumed constant and estimated as 135.98 $J·K^{-1}·mol^{-1}$ or 27.196 $J·K^{-1}$ $g·atom^{-1}$ (6.5 $cal·K^{-1}$ $g·atom^{-1}$).

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	53.764	69.426	69.426	0.	51.885	39.855	−6.982
300	54.266	69.760	69.427	0.100	51.885	39.780	−6.926
400	76.358	88.604	71.846	6.703	52.016	35.730	−4.666
500	89.789	107.176	77.074	15.051	52.113	31.645	−3.306
600	98.366	124.354	83.544	24.486	52.045	27.554	−2.399
700	103.680	139.933	90.506	34.599	51.765	23.491	−1.753
800	107.654	154.045	97.580	45.171	51.285	19.483	−1.272
900	110.989	166.917	104.580	56.104	50.656	15.544	−0.902
1000	114.299	178.785	111.414	67.370	49.950	11.681	−0.610
1100	117.336	189.822	118.046	78.954	49.220	7.889	−0.375
1200	120.190	200.155	124.463	90.831	48.491	4.164	−0.181
1300	122.909	209.884	130.663	102.987	47.781	0.499	−0.020
1400	125.533	219.089	136.653	115.410	47.105	−3.113	0.116
1500	128.089	227.837	142.443	128.091	46.475	−6.677	0.233
1600	130.587	236.184	148.043	141.025	45.899	−10.202	0.333
1700	133.047	244.174	153.464	154.207	45.384	−13.692	0.421
1750.000	134.265	248.049	156.112	160.890	GLASS <--> LIQUID		
1750.000	135.980	248.049	156.112	160.890	TRANSITION		
1800	135.980	251.879	158.719	167.689	44.991	−17.155	0.498
1900	135.980	259.231	163.817	181.287	44.544	−20.596	0.566
2000	135.980	266.206	168.764	194.885	43.932	−24.009	0.627
2100	135.980	272.841	173.563	208.483	43.161	−27.388	0.681
2200	135.980	279.167	178.221	222.081	42.235	−30.726	0.730
2300	135.980	285.211	182.742	235.679	41.156	−34.019	0.773
2400	135.980	290.998	187.133	249.277	−161.109	−32.987	0.718
2500	135.980	296.549	191.399	262.875	−162.796	−27.614	0.577
2600	135.980	301.883	195.547	276.473	−164.498	−22.173	0.445
2700	135.980	307.014	199.581	290.071	−166.215	−16.666	0.322
2743.000	135.980	309.163	201.282	295.918	--- CRYSTAL <--> LIQUID ---		
2800	135.980	311.960	203.507	303.669	−167.945	−11.096	0.207
2900	135.980	316.731	207.329	317.267	−169.688	−5.463	0.098
3000	135.980	321.341	211.053	330.865	−171.445	0.230	−0.004
3100	135.980	325.800	214.683	344.463	−173.214	5.981	−0.101
3200	135.980	330.117	218.223	358.061	−174.996	11.790	−0.192
3300	135.980	334.302	221.678	371.659	−176.791	17.655	−0.279
3400	135.980	338.361	225.050	385.257	−178.597	23.574	−0.362
3500	135.980	342.303	228.344	398.855	−180.416	29.547	−0.441
3600	135.980	346.133	231.563	412.453	−182.246	35.572	−0.516
3700	135.980	349.859	234.710	426.051	−184.088	41.648	−0.588
3800	135.980	353.486	237.788	439.649	−185.942	47.773	−0.657
3900	135.980	357.018	240.801	453.247	−187.807	53.948	−0.723
4000	135.980	360.460	243.749	466.845	−189.684	60.171	−0.786
4100	135.980	363.818	246.637	480.443	−191.571	66.440	−0.846
4200	135.980	367.095	249.466	494.041	−2112.868	100.853	−1.254
4300	135.980	370.295	252.239	507.639	−2110.429	153.532	−1.865
4400	135.980	373.421	254.958	521.237	−2108.008	206.154	−2.447
4500	135.980	376.477	257.624	534.835	−2105.607	258.721	−3.003

PREVIOUS: December 1965 CURRENT: June 1983

0 to 2743 K crystal
above 4500 K liquid

Refer to the individual tables for the details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.635	−62.404	−62.404	INFINITE
100	5.071	1.634	56.731	−5.510	−62.435	−62.380	32.584
200	27.426	11.311	31.236	−3.985	−62.568	−62.279	16.266
298.15	53.764	27.175	27.175	0.	−62.676	−62.109	10.881
300	54.266	27.509	27.176	0.100	−62.676	−62.106	10.814
400	76.358	46.353	29.595	6.703	−62.546	−61.931	8.087
500	89.789	64.925	34.822	15.051	−62.448	−61.791	6.455
600	98.366	82.103	41.293	24.486	−62.517	−61.657	5.368
700	103.680	97.682	48.254	34.599	−62.796	−61.494	4.589
800	107.654	111.793	55.329	45.171	−63.277	−61.277	4.001
900	110.989	124.666	62.328	56.104	−63.906	−60.991	3.540
1000	114.299	136.533	69.163	67.370	−64.611	−60.630	3.167
1100	117.336	147.571	75.795	78.954	−65.341	−60.196	2.858
1200	120.190	157.904	82.211	90.831	−66.071	−59.696	2.599
1300	122.909	167.632	88.411	102.987	−66.781	−59.136	2.376
1400	125.533	176.837	94.402	115.410	−67.456	−58.522	2.183
1500	128.089	185.585	100.191	128.091	−68.086	−57.862	2.015
1600	130.587	193.932	105.791	141.025	−68.663	−57.161	1.866
1700	133.047	201.923	111.213	154.207	−69.178	−56.426	1.734
1800	135.474	209.596	116.467	167.633	−69.626	−55.663	1.615
1900	137.875	216.986	121.564	181.301	−70.004	−54.877	1.509
2000	140.256	224.118	126.514	195.208	−70.307	−54.072	1.412
2100	142.620	231.019	131.327	209.352	−70.532	−53.255	1.325
2200	144.971	237.708	136.012	223.731	−70.677	−52.428	1.245
2300	147.306	244.203	140.575	238.345	−70.739	−51.597	1.172
2400	149.637	250.522	145.025	253.193	−271.756	−46.490	1.012
2500	151.955	256.677	149.369	268.272	−271.961	−37.099	0.775
2600	154.268	262.682	153.612	283.583	−271.950	−27.704	0.557
2700	156.578	268.548	157.760	299.126	−271.722	−18.313	0.354
2743.000	157.569	271.030	159.517	305.880	____ CRYSTAL <--> LIQUID ____		
2743.000	135.980	309.163	159.517	410.480	TRANSITION		
2800	135.980	311.960	162.592	418.231	−167.945	−11.096	0.207
2900	135.980	316.731	167.825	431.829	−169.688	−5.463	0.098
3000	135.980	321.341	172.866	445.427	−171.445	0.230	−0.004
3100	135.980	325.800	177.728	459.025	−173.214	5.981	−0.101
3200	135.980	330.117	182.423	472.623	−174.996	11.790	−0.192
3300	135.980	334.302	186.962	486.221	−176.791	17.655	−0.279
3400	135.980	338.361	191.356	499.819	−178.597	23.574	−0.362
3500	135.980	342.303	195.612	513.417	−180.416	29.547	−0.441
3600	135.980	346.133	199.741	527.015	−182.246	35.572	−0.516
3700	135.980	349.859	203.748	540.613	−184.088	41.648	−0.588
3800	135.980	353.486	207.641	554.211	−185.942	47.773	−0.657
3900	135.980	357.018	211.426	567.809	−187.807	53.948	−0.723
4000	135.980	360.460	215.109	581.407	−189.684	60.171	−0.786
4100	135.980	363.818	218.695	595.005	−191.571	66.440	−0.846
4200	135.980	367.095	222.189	608.603	−2112.868	100.853	−1.254
4300	135.980	370.295	225.597	622.201	−2110.429	153.532	−1.865
4400	135.980	373.421	228.921	635.799	−2108.008	206.154	−2.447
4500	135.980	376.477	232.166	649.397	−2105.607	258.721	−3.003

PREVIOUS: CURRENT: June 1983

$S°(298.15\ K) = [16.3 \pm 4.2]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [2400]\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -90.79 \pm 10.5\ kJ·mol^{-1}$
$\Delta_{fus} H° = [75.312]\ kJ·mol^{-1}$

Enthalpy of Formation

The selected $\Delta_f H°(298.15\ K)$ was calculated by the 3rd law method using vapor pressures reported by Pollock.[1] Pressures for the reaction $Be_2C(cr) \rightarrow 2Be(g) + C(graphite)$ were measured by Pollock in the temperature range 1430–1669 K by Knudsen technique. Vapor pressure data for this decomposition reaction have also been reported by Baboin,[2] Quirk[3] and Muratov and Novoselova.[4] The calculated $\Delta_f H°(298.15\ K)$ values are summarized as follows:

Calc. Method	Number of Presentation	T/K	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	Source
3rd law	14	1430–1669	89.117	−21.7	Pollock[1]
2nd law	14	1430–1669	90.8	−25.1	Least squares fit of Pollock's v.p. to the equation: log P (atm) = 6.946–19,593/T
3rd law	6	1673–1953	71.411	+13.7	Muratov and Novoselova[4]
3rd law	8	1900–2600	81.278	− 6.1	Quirk[3]
3rd law	8	1600–2300	96.266	−36.0	Baboin[2]

Schick *et al.*[5] have listed the measured vapor pressures. The vapor pressures reported by Baboin[2] used in the 3rd law calculation were those listed by Schick *et al.*[5]

Heat Capacity and Entropy

The heat capacity values, from 298.15 to 1200 K, were derived from; the mean $C_p°$ data measured by Neely *et al.*[6] Neely *et al.* estimated an overall error of 15% in their mean heat capacity data. The powdered Be_2C material which was used analyzed 80 to 74% Be_2C. The impurities were mainly oxide and nitride of Be. No corrections were made for the effect of these impurities.

From 1200–2400 K the $C_p°$ was extrapolated so as to approach the value, 22 cal·K^{-1}·mol^{-1} calculated from Krikorian.[7] The $S°(298.15\ K) = 3.9$ cal·K^{-1}·mol^{-1}, was estimated by Krikorian.[7]

Fusion Data

Schick *et al.*,[5] have summarized the available melting data i.e.: Oishi and Hamona[8] have reported decomposition upon heating as low as 1873 K. Brewer *et al.*[9] and Gaev[10] reported melting or dissociation between 2373 and 2423 K.

The melting point is assumed to be 2400 K as estimated by Douglas and Victor[11] and Schick *et al.*[5] From the estimated melting point, 2400 K, and an estimated 2.5 cal·K^{-1}·g·atom^{-1} for the entropy of melting, the heat of melting was calculated.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	43.250	16.318	16.318	0.	−90.793	−88.317	15.473
300	43.329	16.585	16.318	0.080	−90.789	−88.302	15.375
400	47.614	29.689	18.076	4.645	−90.931	−87.468	11.422
500	49.752	40.543	21.516	9.513	−91.595	−86.535	9.040
600	51.890	49.706	25.469	14.542	−92.678	−85.426	7.437
700	60.434	58.401	29.552	20.194	−93.582	−84.139	6.279
800	64.706	66.750	33.686	26.451	−94.240	−82.744	5.403
900	68.977	74.617	37.801	33.135	−94.775	−81.273	4.717
1000	73.249	82.106	41.860	40.246	−95.153	−79.751	4.166
1100	77.525	89.288	45.847	47.785	−95.351	−78.200	3.713
1200	81.797	96.224	49.758	55.760	−95.343	−76.639	3.336
1300	85.011	102.905	53.591	64.108	−95.184	−75.087	3.017
1400	87.278	109.292	57.343	72.728	−94.968	−73.549	2.744
1500	88.881	115.371	61.011	81.540	−94.772	−72.026	2.508
1600	90.023	121.145	64.590	90.488	−123.720	−69.463	2.268
1700	90.843	126.629	68.080	99.534	−122.903	−66.096	2.031
1800	91.349	131.837	71.478	108.645	−122.087	−62.778	1.822
1900	91.621	136.784	74.786	117.795	−121.299	−59.505	1.636
2000	91.722	141.486	78.005	126.963	−120.556	−56.272	1.470
2100	91.797	145.963	81.135	136.139	−119.867	−53.075	1.320
2200	91.885	150.235	84.180	145.323	−119.231	−49.910	1.185
2300	91.964	154.322	87.141	154.515	−118.646	−46.772	1.062
2400	92.048	158.237	90.023	163.716	−118.113	−43.659	0.950
2400.000	92.048	158.237	90.023	163.716	--- CRYSTAL <---> LIQUID ---		
2500	92.153	161.997	92.827	172.926	−117.628	−40.567	0.848
2600	92.253	165.613	95.557	182.146	−117.191	−37.493	0.753
2700	92.350	169.097	98.217	191.376	−116.802	−34.435	0.666
2800	92.443	172.457	100.809	200.616	−698.373	−18.946	0.353
2900	92.534	175.703	103.335	209.865	−695.951	5.276	−0.095
3000	92.621	178.841	105.800	219.122	−693.543	29.416	−0.512
3100	92.705	181.879	108.206	228.389	−691.152	53.475	−0.901
3200	92.786	184.824	110.554	237.663	−688.781	77.457	−1.264
3300	92.864	187.680	112.848	246.946	−686.432	101.366	−1.604
3400	92.939	190.454	115.090	256.236	−684.110	125.203	−1.924
3500	93.010	193.149	117.282	265.534	−681.817	148.973	−2.223

PREVIOUS: March 1962 CURRENT: June 1963

$S°(298.15\ K) = [47.467]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [2400]\ K$

$\Delta_f H°(298.15\ K) = [15.893]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [75.312]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(2400\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed constant and equal to the heat capacity of solid Be_2C at the estimated melting point. $S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The U. S. Nat. Bur. Stand.,[1] states that Be_2C seems to decompose easily only at temperatures above its reported melting point. For this reason they extended their Be_2C table into the liquid region. For detailed fusion data see the crystal table.

Reference

[1] U. S. Nat. Bur. Stand. Report 6645, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	43.250	47.467	47.467	0.	−15.893	−22.704	3.978
300	43.329	47.735	47.468	0.080	−15.889	−22.747	3.961
400	47.614	60.838	49.225	4.645	−16.031	−25.027	3.268
500	49.752	71.692	52.665	9.513	−16.694	−27.209	2.843
600	51.890	80.855	56.618	14.542	−17.778	−29.215	2.543
700	60.434	89.550	60.702	20.194	−18.682	−31.043	2.316
800	64.706	97.899	64.835	26.451	−19.340	−32.763	2.139
900	68.977	105.767	68.950	33.135	−19.875	−34.407	1.997
1000	73.249	113.255	73.009	40.246	−20.253	−36.000	1.880
1100	77.525	120.437	76.996	47.785	−20.450	−37.564	1.784
1200	81.797	127.374	80.907	55.760	−20.443	−39.118	1.703
1300	85.011	134.054	84.740	64.108	−20.284	−40.680	1.635
1400	87.278	140.441	88.492	72.728	−20.068	−42.257	1.577
1500	88.881	146.520	92.160	81.540	−19.872	−43.849	1.527
1600	90.023	152.295	95.739	90.489	−48.819	−44.401	1.450
1600.000	90.023	152.295	95.739	90.489	GLASS <--> LIQUID		
1600.000	92.048	152.295	95.739	90.489	TRANSITION		
1700	92.048	157.876	99.232	99.694	−47.843	−44.155	1.357
1800	92.048	163.137	102.638	108.899	−46.934	−43.965	1.276
1900	92.048	168.114	105.954	118.104	−46.090	−43.823	1.205
2000	92.048	172.835	109.181	127.308	−45.310	−43.724	1.142
2100	92.048	177.326	112.320	136.513	−44.592	−43.663	1.086
2200	92.048	181.608	115.373	145.718	−43.936	−43.634	1.036
2300	92.048	185.700	118.342	154.923	−43.339	−43.634	0.991
2400	92.048	189.617	121.231	164.128	−42.801	−43.659	0.950
2400.000	92.048	189.617	121.231	164.128	--- CRYSTAL <--> LIQUID ---		
2500	92.048	193.375	124.042	173.332	−42.321	−43.705	0.913
2600	92.048	196.985	126.779	182.537	−41.900	−43.769	0.879
2700	92.048	200.459	129.444	191.742	−41.535	−43.848	0.848
2800	92.048	203.807	132.040	200.947	−623.142	−31.494	0.588
2900	92.048	207.037	134.571	210.152	−620.764	−10.406	0.187
3000	92.048	210.157	137.039	219.356	−618.409	10.601	−0.185
3100	92.048	213.176	139.446	228.561	−616.080	31.529	−0.531
3200	92.048	216.098	141.796	237.766	−613.778	52.383	−0.855
3300	92.048	218.930	144.091	246.971	−611.507	73.166	−1.158
3400	92.048	221.678	146.333	256.176	−609.270	93.880	−1.442
3500	92.048	224.347	148.524	265.380	−607.070	114.528	−1.709

PREVIOUS: March 1962 CURRENT: June 1963

0	*to*	2400 K	*crystal*
above		2400 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	43.250	16.318	16.318	0.	−90.793	−88.317	15.473
300	43.329	16.585	16.318	0.080	−90.789	−88.302	15.375
400	47.614	29.689	18.076	4.645	−90.931	−87.468	11.422
500	49.752	40.543	21.516	9.513	−91.595	−86.535	9.040
600	51.890	49.706	25.469	14.542	−92.678	−85.426	7.437
700	60.434	58.401	29.552	20.194	−93.582	−84.139	6.279
800	64.706	66.750	33.686	26.451	−94.240	−82.744	5.403
900	68.977	74.617	37.801	33.135	−94.775	−81.273	4.717
1000	73.249	82.106	41.860	40.246	−95.153	−79.751	4.166
1100	77.525	89.288	45.847	47.785	−95.351	−78.200	3.713
1200	81.797	96.224	49.758	55.760	−95.343	−76.639	3.336
1300	85.011	102.905	53.591	64.108	−95.184	−75.087	3.017
1400	87.278	109.292	57.343	72.728	−94.968	−73.549	2.744
1500	88.881	115.371	61.011	81.540	−94.772	−72.026	2.508
1600	90.023	121.145	64.590	90.488	−123.720	−69.463	2.268
1700	90.843	126.629	68.080	99.534	−122.903	−66.096	2.031
1800	91.349	131.837	71.478	108.645	−122.087	−62.778	1.822
1900	91.621	136.784	74.786	117.795	−121.299	−59.505	1.636
2000	91.722	141.486	78.005	126.963	−120.556	−56.272	1.470
2100	91.797	145.963	81.135	136.139	−119.867	−53.075	1.320
2200	91.885	150.235	84.180	145.323	−119.231	−49.910	1.185
2300	91.964	154.322	87.141	154.515	−118.646	−46.772	1.062
2400	92.048	158.237	90.023	163.716	−118.113	−43.659	0.950
2400.000	92.048	158.237	90.023	163.716	CRYSTAL <--> LIQUID TRANSITION		
2400.000	92.048	189.617	90.023	239.028			
2500	92.048	193.375	94.082	248.233	−42.321	−43.705	0.913
2600	92.048	196.985	97.971	257.437	−41.900	−43.769	0.879
2700	92.048	200.459	101.703	266.642	−41.535	−43.848	0.848
2800	92.048	203.807	105.290	275.847	−623.142	−31.494	0.588
2900	92.048	207.037	108.743	285.052	−620.764	−10.406	0.187
3000	92.048	210.157	112.072	294.257	−618.409	10.601	−0.185
3100	92.048	213.176	115.285	303.461	−616.080	31.529	−0.531
3200	92.048	216.098	118.390	312.666	−613.778	52.383	−0.855
3300	92.048	218.930	121.394	321.871	−611.507	73.166	−1.158
3400	92.048	221.678	124.303	331.076	−609.270	93.880	−1.442
3500	92.048	224.347	127.124	340.281	−607.070	114.528	−1.709

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = [233.45]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 514.3 \pm 63\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 510.4 \pm 63\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X_2\ ^2\Pi_{1/2}$	0	2
$X_1\ ^2\Pi_{3/3}$	465	2
$A_1\ ^2\Delta_{3/2}$	33163	2
$A_2\ ^2\Delta_{5/2}$	33218	2
	[40000]	[2]

$\omega_e = [736]\ cm^{-1}$ $\omega_e x_e = [4.0]\ cm^{-1}$ $\sigma = 1$
$B_e = 0.4890\ cm^{-1}$ $\alpha_e = [0.0036]\ cm^{-1}$ $r_e = 1.8170$ Å

Enthalpy of Formation

Dixon and Kroto[1] have observed predissociation of CBr(g) which indicates that the dissociation energy $D_0°$ is less than 94.7 kcal·mol^{-1}. They evaluated the kinetic data of Simons and Yarwood,[2] obtaining a value of $D_0° = 97 \pm 5$ kcal·mol^{-1}, based on the enthalpy of formation of bromoform and the dissociation energy of HBr, and concluded that the true value of $D_0°$ is very close to the upper limit of 94.7 kcal·mol^{-1}. Comparisons of C–X bond energies of CX_4 and CX compounds, however, indicate that this value is too high to be consistent with other carbon halides. Therefore the value of $D_0°$ adopted is 75 ± 15 kcal·mol^{-1}. The corresponding $\Delta_f H°$(CBr, g, 298.15 K) is 122 ± 15 kcal·mol^{-1} (510.448 ± 63 kJ·mol^{-1}).

Heat Capacity and Entropy

The rotational structure of the near UV spectra of CBr(g) has been investigated by Dixon and Kroto[1] in the 3000 Å region. They assigned the above doublet electronic levels to the ground ($^2\Pi$) and first excited ($^2\Delta$) states and reported a value of $B_0 = 0.4872 \pm 0.0003\ cm^{-1}$ for the ground state. An additional electronic level ($^2\Sigma$) is expected to be close to the first excited state by analogy with CF(g) and CCl(g).

The fundamental vibrational frequency ω_e is estimated from Guggenheimer's relation for single bonded molecules.[3] The anharmonic vibrational term $\omega_e x_e$ is estimated by assuming $\omega_e x_e = \omega_e^2/(4D_0 + 2\omega_e)$. The value of α_e is calculated from the Morse potential function. The rotational constant B_e is calculated from $B_e = B_0 + \alpha_e/2$. The bond distance is calculated from B_e.

References

[1] R. N. Dixon and H. W. Kroto, Trans. Faraday Soc. **59**, 1484 (1963).
[2] J. P. Simons and A. J. Yarwood, Trans. Faraday Soc. **57**, 2167 (1961).
[3] K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.482	514.272	514.272	INFINITE
100	29.596	197.941	263.600	−6.566	515.732	498.725	−260.507
200	33.413	219.553	236.680	−3.425	516.095	481.543	−125.766
250	35.011	227.191	234.040	−1.712	516.105	472.901	−98.807
298.15	36.041	233.452	233.452	0.	510.448	465.246	−81.509
300	36.072	233.675	233.453	0.067	510.429	464.965	−80.958
350	36.733	239.290	233.895	1.888	495.454	458.199	−68.382
400	37.139	244.223	234.884	3.736	495.835	452.850	−59.136
450	37.388	248.613	236.170	5.599	496.150	447.457	−51.939
500	37.544	252.561	237.615	7.473	496.400	442.033	−46.179
600	37.708	259.423	240.695	11.237	496.726	431.125	−37.533
700	37.785	265.242	243.796	15.012	496.859	420.179	−31.354
800	37.829	270.291	246.800	18.793	496.842	409.224	−26.720
900	37.861	274.748	249.662	22.577	496.711	398.279	−23.115
1000	37.889	278.739	252.374	26.365	496.488	387.353	−20.233
1100	37.916	282.351	254.937	30.155	496.193	376.453	−17.876
1200	37.944	285.651	257.361	33.948	495.839	365.583	−15.913
1300	37.973	288.690	259.656	37.744	495.435	354.745	−14.254
1400	38.002	291.505	261.831	41.543	494.989	343.939	−12.833
1500	38.033	294.128	263.898	45.344	494.507	333.166	−11.602
1600	38.065	296.583	265.865	49.149	493.993	322.426	−10.526
1700	38.097	298.892	267.741	52.957	493.448	311.720	−9.578
1800	38.130	301.070	269.532	56.769	492.876	301.047	−8.736
1900	38.163	303.133	271.247	60.583	492.277	290.406	−7.984
2000	38.197	305.091	272.891	64.401	491.653	279.797	−7.308
2100	38.232	306.956	274.469	68.223	491.004	269.220	−6.696
2200	38.267	308.735	275.986	72.048	490.330	258.674	−6.142
2300	38.302	310.437	277.447	75.876	489.632	248.160	−5.636
2400	38.337	312.068	278.856	79.708	488.910	237.677	−5.173
2500	38.373	313.633	280.216	83.544	488.166	227.224	−4.748
2600	38.408	315.139	281.530	87.383	487.398	216.801	−4.356
2700	38.444	316.589	282.802	91.225	486.609	206.409	−3.993
2800	38.480	317.988	284.034	95.071	485.799	196.046	−3.657
2900	38.517	319.339	285.228	98.921	484.969	185.712	−3.345
3000	38.553	320.646	286.387	102.775	484.120	175.407	−3.054
3100	38.590	321.910	287.513	106.632	483.254	165.131	−2.782
3200	38.626	323.136	288.607	110.493	482.372	154.883	−2.528
3300	38.663	324.325	289.671	114.357	481.475	144.663	−2.290
3400	38.700	325.480	290.708	118.225	480.566	134.470	−2.066
3500	38.737	326.602	291.717	122.097	479.645	124.304	−1.855
3600	38.775	327.694	292.702	125.973	478.714	114.165	−1.656
3700	38.813	328.757	293.662	129.852	477.775	104.051	−1.469
3800	38.851	329.793	294.599	133.735	476.829	93.963	−1.292
3900	38.889	330.802	295.514	137.622	475.878	83.900	−1.124
4000	38.928	331.787	296.409	141.513	474.922	73.862	−0.965
4100	38.968	332.749	297.284	145.408	473.963	63.847	−0.813
4200	39.008	333.689	298.139	149.307	473.003	53.856	−0.670
4300	39.048	334.607	298.977	153.210	472.041	43.887	−0.533
4400	39.089	335.505	299.797	157.117	471.080	33.941	−0.403
4500	39.131	336.384	300.600	161.028	470.120	24.017	−0.279
4600	39.174	337.244	301.387	164.943	469.161	14.115	−0.160
4700	39.217	338.087	302.159	168.862	468.205	4.233	−0.047
4800	39.261	338.914	302.916	172.786	467.252	−5.629	0.061
4900	39.306	339.724	303.659	176.715	466.303	−15.471	0.165
5000	39.353	340.518	304.389	180.647	465.358	−25.293	0.264
5100	39.400	341.298	305.105	184.585	464.417	−35.097	0.359
5200	39.448	342.063	305.808	188.528	463.481	−44.882	0.451
5300	39.498	342.815	306.499	192.475	462.551	−54.650	0.539
5400	39.549	343.554	307.179	196.427	461.625	−64.399	0.623
5500	39.601	344.280	307.847	200.385	460.705	−74.132	0.704
5600	39.654	344.994	308.504	204.347	459.791	−83.848	0.782
5700	39.709	345.697	309.150	208.315	458.883	−93.548	0.857
5800	39.765	346.388	309.786	212.289	457.980	−103.232	0.930
5900	39.822	347.068	310.412	216.268	457.083	−112.900	1.000
6000	39.881	347.738	311.029	220.254	456.193	−122.554	1.067

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = 297.83 \pm 0.50\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -636.9 \pm 2.9\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -648.9 \pm 2.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1086 (1)	1206 (2)
761 (1)	549 (2)
348 (1)	300 (2)

Ground State Quantum Weight: 1 $\sigma = 4$

Point Group: C_{3v}

Bond Distances: C–F = 1.328 Å; C–Br = 1.909 Å

Bond Angles: F–C–F = 108.6 ± 1°; F–C–Br = 110.33°

Product of the Moments of Inertia: $I_A I_B I_C = 2.340709 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the enthalpies of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given by Syverud.[1] Coomber and Whittle[2-4] have determined equilibrium data for $CClF_3(g) + BrCl(g) = CBrF_3(g) + Cl_2(g)$ and for $CF_3X(g) + Br_2(g) = CF_3Br(g) + BrX(g)$ where X = H, Cl, and CF. Equilibrium data for $CF_3I(g) + BrI(g) = CBrF_3(g) + I_2(g)$ were obtained by Lord *et al.*[5] These data link $CBrF_3$ with C_2F_6, CHF_3, $CClF_3$ and CF_3I.

Heat Capacity and Entropy

The molecular structure has been derived from electron–diffraction studies by Sharbaugh *et al.*,[6] Bowen,[7] and Anderson[8] and from microwave data by Sheridan and Gordy.[9] The adoped parameters are an average of those reported by.[8,9] Infrared spectra of the gas were observed by several investigators[10-12] and Raman spectra of the liquid were obtained by Edgell and May.[12] The vibrational assignments of McGee *et al.*[11] and Edgell and May[12] are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. The value for ν_6 is taken as 300 cm^{-1} which is between the values of 305 and 297 ± 3 cm^{-1} derived from Raman spectra and IR (combination and overtone) spectra, respectively.

The thermodynamic functions of this table are essentially the same as those calculated by McGee *et al.*[11] Uncertainty in the entropy is estimated to vary from 0.12 to 0.5 cal/(K·mol^{-1}) over the range from 300 to 1000 K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for $CClF_3(g)$ and $CF_4(g)$. The principal moments of inertia are: $I_A = 14.6768 \times 10^{-39}$ and $I_B = I_C = 39.9354 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.468	−636.863	−636.863	INFINITE
100	39.323	240.114	350.236	−11.012	−639.224	−634.892	331.634
200	56.420	272.770	303.778	−6.202	−641.584	−629.584	164.431
250	63.460	286.136	298.936	−3.200	−642.540	−626.472	130.894
298.15	69.330	297.827	297.827	0.	−648.938	−622.641	109.084
300	69.540	298.256	297.828	0.128	−648.983	−622.478	108.383
350	74.784	309.380	298.695	3.740	−664.551	−617.201	92.112
400	79.273	319.667	300.681	7.594	−664.608	−610.432	79.714
450	83.084	329.230	303.329	11.656	−664.596	−603.660	70.071
500	86.305	338.156	306.370	15.893	−664.531	−596.892	62.357
600	91.313	354.359	313.046	24.788	−664.284	−583.385	50.788
700	94.902	368.720	319.994	34.108	−663.933	−569.929	42.529
800	97.514	381.572	326.902	43.736	−663.517	−556.527	36.338
900	99.454	393.175	333.631	53.589	−663.062	−543.181	31.525
1000	100.923	403.733	340.122	63.611	−662.585	−529.886	27.678
1100	102.058	413.407	346.350	73.762	−662.099	−516.640	24.533
1200	102.949	422.327	352.315	84.014	−661.613	−503.437	21.914
1300	103.660	430.596	358.022	94.346	−661.134	−490.276	19.700
1400	104.236	438.300	363.485	104.742	−660.669	−477.150	17.803
1500	104.708	445.508	368.715	115.190	−660.220	−464.058	16.160
1600	105.100	452.279	373.728	125.681	−659.792	−450.994	14.723
1700	105.428	458.661	378.539	136.208	−659.386	−437.957	13.457
1800	105.705	464.695	383.159	146.765	−659.002	−424.943	12.332
1900	105.942	470.417	387.602	157.348	−658.640	−411.950	11.325
2000	106.145	475.856	391.880	167.952	−658.300	−398.974	10.420
2100	106.321	481.039	396.003	178.576	−657.978	−386.017	9.602
2200	106.475	485.989	399.982	189.216	−657.670	−373.073	8.858
2300	106.609	490.725	403.825	199.870	−657.375	−360.143	8.179
2400	106.727	495.265	407.541	210.537	−657.086	−347.227	7.557
2500	106.832	499.624	411.138	221.215	−656.800	−334.322	6.985
2600	106.925	503.816	414.622	231.903	−656.512	−321.428	6.458
2700	107.008	507.853	418.001	242.600	−656.217	−308.546	5.969
2800	107.083	511.746	421.280	253.304	−655.910	−295.675	5.516
2900	107.150	515.504	424.464	264.016	−655.587	−282.815	5.094
3000	107.211	519.138	427.560	274.734	−655.243	−269.966	4.701
3100	107.266	522.654	430.571	285.458	−654.874	−257.130	4.333
3200	107.316	526.061	433.502	296.187	−654.477	−244.306	3.988
3300	107.361	529.364	436.357	306.921	−654.048	−231.494	3.664
3400	107.403	532.569	439.140	317.659	−653.584	−218.697	3.360
3500	107.441	535.683	441.854	328.401	−653.082	−205.913	3.073
3600	107.476	538.711	444.503	339.147	−652.540	−193.144	2.802
3700	107.508	541.656	447.089	349.896	−651.956	−180.391	2.547
3800	107.538	544.523	449.616	360.649	−651.329	−167.655	2.305
3900	107.566	547.317	452.085	371.404	−650.657	−154.935	2.075
4000	107.591	550.041	454.500	382.162	−649.939	−142.233	1.857
4100	107.615	552.698	456.863	392.922	−649.175	−129.550	1.650
4200	107.637	555.291	459.176	403.685	−648.363	−116.886	1.454
4300	107.658	557.824	461.440	414.450	−647.505	−104.242	1.266
4400	107.677	560.299	463.659	425.216	−646.599	−91.618	1.088
4500	107.695	562.719	465.834	435.985	−645.647	−79.015	0.917
4600	107.712	565.087	467.966	446.755	−644.648	−66.435	0.754
4700	107.727	567.403	470.057	457.527	−643.603	−53.876	0.599
4800	107.742	569.671	472.109	468.301	−642.512	−41.340	0.450
4900	107.756	571.893	474.122	479.076	−641.377	−28.827	0.307
5000	107.769	574.070	476.100	489.852	−640.198	−16.338	0.171
5100	107.781	576.204	478.042	500.630	−638.976	−3.873	0.040
5200	107.793	578.297	479.950	511.408	−637.713	8.568	−0.086
5300	107.804	580.351	481.825	522.188	−636.408	20.984	−0.207
5400	107.814	582.366	483.668	532.969	−635.064	33.375	−0.323
5500	107.824	584.344	485.481	543.751	−633.681	45.741	−0.434
5600	107.833	586.287	487.263	554.534	−632.261	58.082	−0.542
5700	107.842	588.196	489.017	565.318	−630.804	70.396	−0.645
5800	107.851	590.072	490.744	576.102	−629.313	82.684	−0.745
5900	107.859	591.915	492.443	586.888	−627.787	94.948	−0.841
6000	107.866	593.728	494.116	597.674	−626.229	107.184	−0.933

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 248.363 \pm 0.040\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 192.75 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 186.19 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
575 (1)
342.5 (2)
2200 (1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: C–Br = 1.789 Å; C–N = 1.158 Å
Bond Angle: Br–C–N = 180°
Rotational Constants: $B_0 = 0.137172\ cm^{-1}$; $D_0 = 2.929 \times 10^{-8}\ cm^{-1}$

Spectroscopic constants used in calculating corrections to rigid-rotator-harmonic oscillator approximation (cm^{-1}).

$\alpha_1 = 5.17 \times 10^{-4}$ $x_{11} = [-3.0]$ $x_{12} = [-4.0]$
$\alpha_2 = -3.84 \times 10^{-4}$ $x_{22} = -0.86$ $x_{23} = -6.19$
$\alpha_3 = 6.77 \times 10^{-4}$ $x_{33} = [-5.0]$ $x_{13} = [-3.0]$
$g_{22} = 1.14$

Enthalpy of Formation

The enthalpy of formation is calculated from $\Delta_f H°$(BrCN, cr, 298.15 K) = 33.58 kcal·mol^{-1}[11] and $\Delta_{sub} H°$ (298.15 K) = 10.92 ± 0.1 kcal·mol^{-1}. This latter is obtained from an anlysis of the vapor pressure data of Lord and Woof[2] and Baxter *et al.*[3]

The enthalpy of formation of the crystal is calculated from $\Delta_r H°(298.15\ K) = -56.0$ kcal·mol^{-1} obtained by Lord and Woolf[2] for the reaction

$$BrCN(cr) + 2NaOH(56\ H_2O) = NaCNO(2800\ H_2O) + NaBr(2800\ H_2O) + H_2O(l).$$

The auxiliary data used were $\Delta_f H°$(NaOH·56H_2O, 298.15 K) = −112.26 kcal·mol^{-1},[1,4] $\Delta_f H$(NaCNO·2800H_2O, 298.15 K) = −92.25 kcal·mol^{-1},[1,4] and $\Delta_f H°$(NaBr·2800H_2O, 298.15 K) = −70.54 kcal·mol^{-1}.[1,4] The uncertainty in the final value reflects the uncertainty in $\Delta_f H$(NaCNO·2800H_2O) which was determined by Lord and Woolf[2] to be −93.6 kcal·mol^{-1} in excess NaOH·56H_2O.

Heat Capacity and Entropy

Gordon[5] used the constants given above to calculate the adopted table, using the method of Pennington and Kobe[6] for anharmonicity, vibration rotation interaction, and centrifugal stretching corrections.

The bond lengths and angle were reported by Tyler and Sheridan.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.075	192.754	192.754	INFINITE
100	32.213	205.109	286.153	−8.104	192.817	183.084	−95.633
200	41.714	230.527	252.430	−4.381	192.308	173.560	−45.329
298.15	47.124	248.363	248.363	0.	186.188	165.104	−28.926
300	47.196	248.655	248.364	0.087	186.163	164.974	−28.724
400	50.137	262.658	250.253	4.962	171.316	160.993	−21.023
500	52.095	274.064	253.910	10.077	171.789	158.355	−16.543
600	53.664	283.704	258.092	15.367	172.149	155.632	−13.549
700	55.020	292.080	262.362	20.802	172.421	152.857	−11.406
800	56.204	299.506	266.550	26.365	172.631	150.047	−9.797
900	57.237	306.187	270.589	32.038	172.800	147.214	−8.544
1000	58.137	312.265	274.457	37.808	172.939	144.363	−7.541
1100	58.915	317.843	278.151	43.661	173.059	141.500	−6.719
1200	59.597	322.999	281.676	49.587	173.163	138.626	−6.034
1300	60.191	327.793	285.042	55.577	173.257	135.744	−5.454
1400	60.714	332.273	288.257	61.623	173.342	132.856	−4.957
1500	61.174	336.478	291.333	67.718	173.418	129.961	−4.526
1600	61.588	340.440	294.280	73.856	173.488	127.062	−4.148
1700	61.961	344.185	297.106	80.034	173.550	124.158	−3.815
1800	62.300	347.736	299.821	86.247	173.605	121.251	−3.519
1900	62.614	351.113	302.433	92.493	173.653	118.341	−3.253
2000	62.898	354.332	304.948	98.769	173.692	115.429	−3.015
2100	63.162	357.407	307.373	105.072	173.722	112.515	−2.799
2200	63.409	360.351	309.715	111.401	173.742	109.600	−2.602
2300	63.643	363.175	311.978	117.753	173.752	106.684	−2.423
2400	63.860	365.888	314.168	124.129	173.751	103.768	−2.258
2500	64.070	368.500	316.290	130.525	173.739	100.852	−2.107
2600	64.270	371.016	318.346	136.942	173.716	97.937	−1.968
2700	64.459	373.446	320.342	143.379	173.683	95.023	−1.838
2800	64.643	375.793	322.281	149.834	173.640	92.110	−1.718
2900	64.819	378.065	324.166	156.307	173.587	89.200	−1.607
3000	64.990	380.265	325.999	162.797	173.525	86.291	−1.502
3100	65.157	382.399	327.784	169.305	173.456	83.384	−1.405
3200	65.321	384.470	329.524	175.829	173.381	80.480	−1.314
3300	65.480	386.482	331.219	182.369	173.300	77.578	−1.228
3400	65.634	388.440	332.873	188.925	173.216	74.678	−1.147
3500	65.785	390.344	334.488	195.496	173.130	71.781	−1.071
3600	65.931	392.200	336.066	202.081	173.042	68.887	−1.000
3700	66.078	394.008	337.608	208.682	172.954	65.995	−0.932
3800	66.224	395.772	339.115	215.297	172.868	63.105	−0.867
3900	66.362	397.494	340.590	221.926	172.785	60.218	−0.807
4000	66.505	399.176	342.034	228.570	172.705	57.333	−0.749
4100	66.643	400.820	343.448	235.227	172.630	54.449	−0.694
4200	66.781	402.428	344.833	241.898	172.562	51.568	−0.641
4300	66.915	404.001	346.191	248.583	172.500	48.688	−0.591
4400	67.049	405.540	347.522	255.281	172.446	45.809	−0.544
4500	67.182	407.049	348.828	261.993	172.400	42.931	−0.498
4600	67.312	408.527	350.110	268.718	172.363	40.055	−0.455
4700	67.442	409.976	351.368	275.455	172.336	37.179	−0.413
4800	67.572	411.397	352.604	282.206	172.319	34.303	−0.373
4900	67.701	412.792	353.818	288.970	172.312	31.428	−0.335
5000	67.831	414.161	355.011	295.746	172.315	28.553	−0.298
5100	67.957	415.505	356.184	302.536	172.330	25.678	−0.263
5200	68.086	416.826	357.338	309.338	172.356	22.802	−0.229
5300	68.212	418.124	358.473	316.153	172.393	19.925	−0.196
5400	68.337	419.400	359.589	322.980	172.441	17.048	−0.165
5500	68.463	420.655	360.688	329.820	172.500	14.170	−0.135
5600	68.584	421.890	361.770	336.673	172.571	11.291	−0.105
5700	68.710	423.105	362.835	343.537	172.652	8.410	−0.077
5800	68.835	424.301	363.885	350.414	172.745	5.528	−0.050
5900	68.956	425.479	364.919	357.304	172.848	2.644	−0.023
6000	69.078	426.639	365.938	364.206	172.961	−0.242	0.002

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 358.095\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [79.890]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [50.208]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
267.2(1)	670.7(3)
122.5(2)	182.5(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: C–Br = 1.942 Å
Bond Angle: Br–C–Br = 109° 28'
Product of the Moments of Inertia: $I_A I_B I_C = 2.376154 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated and reported by Rossini *et al.*[1]

Heat Capacity and Entropy

The molecular constants, bond distance, and bond angle were determined by electron diffraction by Finbak *et al.*[2, 3] The constants reported by Finbak *et al.*[3] in 1943 were selected. These constants are listed in "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society (London), 1958. The principal moments of inertia calculated from these constants are: $I_A = I_B = I_C = 133.4417 \times 10^{-39}\ g·cm^2$.

The vibrational frequencies used were assigned by Meister *et al.*[4] They measured the infrared and Raman spectrum, considered the previous literature, calculated force constants and made most probable value assignments for the frequencies. A more recent paper by Moszynska and Mathieu[5] made assignments from Raman and infrared spectra which agreed with all of Meister *et al.*'s[4] assignments except for ν_2 which they found was 126 cm^{-1} rather than 122 cm^{-1}.

References

[1]U. S. Nat. Bur. Stand. Circ. 500, (1952).
[2]C. Finbak, O. Hassel and B. Ottar, Arch. Math. Naturv. B44, No. 13 (1941).
[3]C. Finbak, O. Hassel and O. Olaussen, Tidsskr. Kjemi Bergv. **3**, 13 (1943).
[4]A. O. Meister, S. E. Rosser, and F. F. Cleveland, J. Chem. Phys. **18**, 346 (1950).
[5]B. Moszynska and J. P. Mathieu, Compt. Rend **256**, 2820 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.388	79.890	79.890	INFINITE
100	63.538	273.277	432.002	−15.873	78.759	62.296	−32.540
200	81.403	323.603	366.156	−8.511	75.992	46.857	−12.238
250	87.009	342.397	359.574	−4.294	74.282	39.763	−8.308
298.15	91.180	358.095	358.095	0.	50.208	35.914	−6.292
300	91.319	358.659	358.096	0.169	50.081	35.826	−6.238
350	94.594	372.993	359.221	4.820	−11.039	36.793	−5.491
400	97.081	385.795	361.757	9.615	−10.455	43.587	−5.692
450	98.987	397.344	365.080	14.519	−9.863	50.306	−5.839
500	100.464	407.853	368.840	19.507	−9.274	56.960	−5.951
600	102.548	426.368	376.926	29.665	−8.132	70.099	−6.103
700	103.902	442.285	385.153	39.992	−7.055	83.051	−6.197
800	104.823	456.223	393.184	50.431	−6.042	95.854	−6.259
900	105.475	468.609	400.889	60.948	−5.088	108.533	−6.299
1000	105.951	479.748	408.227	71.520	−4.187	121.108	−6.326
1100	106.310	489.864	415.196	82.134	−3.333	133.596	−6.344
1200	106.586	499.126	421.810	92.780	−2.523	146.008	−6.356
1300	106.802	507.666	428.090	103.449	−1.753	158.354	−6.363
1400	106.976	515.588	434.060	114.139	−1.022	170.642	−6.367
1500	107.116	522.973	439.744	124.844	−0.329	182.880	−6.368
1600	107.232	529.890	445.165	135.561	0.325	195.072	−6.368
1700	107.328	536.394	450.342	146.289	0.939	207.225	−6.367
1800	107.409	542.531	455.295	157.026	1.511	219.343	−6.365
1900	107.478	548.341	460.040	167.771	2.039	231.430	−6.362
2000	107.537	553.855	464.594	178.522	2.519	243.491	−6.359
2100	107.588	559.103	468.971	189.278	2.949	255.528	−6.356
2200	107.632	564.109	473.182	200.039	3.325	267.547	−6.352
2300	107.670	568.894	477.240	210.804	3.646	279.549	−6.349
2400	107.704	573.477	481.155	221.573	3.910	291.540	−6.345
2500	107.734	577.875	484.937	232.345	4.116	303.520	−6.342
2600	107.760	582.101	488.593	243.119	4.265	315.492	−6.338
2700	107.784	586.168	492.132	253.897	4.357	327.461	−6.335
2800	107.805	590.088	495.561	264.676	4.395	339.427	−6.332
2900	107.824	593.872	498.886	275.458	4.381	351.392	−6.329
3000	107.841	597.527	502.114	286.241	4.319	363.359	−6.327
3100	107.857	601.064	505.249	297.026	4.213	375.329	−6.324
3200	107.871	604.488	508.297	307.812	4.068	387.302	−6.322
3300	107.884	607.808	511.262	318.600	3.889	399.281	−6.320
3400	107.896	611.029	514.150	329.389	3.681	411.266	−6.318
3500	107.906	614.156	516.962	340.179	3.450	423.257	−6.317
3600	107.916	617.196	519.705	350.970	3.202	435.255	−6.315
3700	107.925	620.153	522.380	361.762	2.940	447.260	−6.314
3800	107.934	623.032	524.991	372.555	2.671	459.272	−6.313
3900	107.941	625.835	527.541	383.349	2.400	471.291	−6.312
4000	107.949	628.568	530.032	394.143	2.132	483.318	−6.311
4100	107.955	631.234	532.468	404.939	1.870	495.351	−6.311
4200	107.962	633.835	534.851	415.735	1.619	507.390	−6.310
4300	107.967	636.376	537.183	426.531	1.383	519.435	−6.310
4400	107.973	638.858	539.465	437.328	1.164	531.485	−6.310
4500	107.978	641.285	541.701	448.126	0.966	543.540	−6.309
4600	107.982	643.658	543.892	458.924	0.792	555.599	−6.309
4700	107.987	645.980	546.039	469.722	0.644	567.662	−6.309
4800	107.991	648.254	548.145	480.521	0.523	579.728	−6.309
4900	107.995	650.480	550.211	491.320	0.431	591.795	−6.309
5000	107.998	652.662	552.238	502.120	0.370	603.865	−6.309
5100	108.002	654.801	554.228	512.920	0.340	615.935	−6.308
5200	108.005	656.898	556.183	523.720	0.343	628.005	−6.308
5300	108.008	658.956	558.103	534.521	0.379	640.076	−6.308
5400	108.011	660.974	559.989	545.322	0.448	652.145	−6.308
5500	108.014	662.956	561.843	556.123	0.551	664.213	−6.308
5600	108.016	664.903	563.666	566.925	0.687	676.278	−6.308
5700	108.019	666.815	565.459	577.726	0.857	688.341	−6.308
5800	108.021	668.693	567.223	588.528	1.059	700.399	−6.308
5900	108.023	670.540	568.958	599.331	1.295	712.455	−6.308
6000	108.026	672.355	570.667	610.133	1.562	724.506	−6.307

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = 224.52 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 498.3 \pm 20\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 502.1 \pm 20\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	134.92	2
$[^4\Sigma]$	[20000]	[4]
$A^2\Delta$	36004	4

$\omega_e = 876.4\ cm^{-1}$ $\omega_e x_e = 6.15\ cm^{-1}$ $\sigma = 1$
$B_e = 0.69666\ cm^{-1}$ $\alpha_e = [0.0066]\ cm^{-1}$ $r_e = 1.642$ Å

Enthalpy of Formation

The data of Miller and Palmer[1] provide a value of $D_0°$(CCl) = 80 ± 5 kcal·mol^{-1}, which appears to be reasonably substantiated. They studied the chemiluminescence from flames of $CHCl_3$ and CCl_4 burning in potassium vapor. These flames exhibit C_2 Swan band radiation with major departures from vibrational and rotational equilibrium. The spectra are interpreted as due to the reaction C + CCl → C_2 + Cl where the carbon atom is either ^{3}D ground state or ^{1}D first excited state. The separation between the ground and first excited state of the carbon atom is matched closely by the difference in preferential population of the excited C_2 levels. The assumption is made that all the exothermicity of the reaction is retained as vibrational excitation of the C_2, thus the populated levels are measures of the heat of reaction. In this manner we obtain a heat of reaction of 67 ± 2.5 kcal·mol^{-1} for the reaction C + CCl → C_2 + Cl which, using JANAF auxiliary data, gives $\Delta_f H°$(CCl, g) = 124 ± 2.5 kcal·mol^{-1}; however, this represents the initial state of the CCl which in the flame is presumed to have about 4 kcal·mol^{-1} of vibrational energy at roughly 2000 K. Thus, we obtain $\Delta_f H°$(CCl, g) = 120 ± 5 kcal·mol^{-1} (502.080 ± 20 kJ·mol^{-1}) which is adopted.

The enthalpy of formation can also be estimated from the dissociation energy calculated from the linear Birge–Sponer extrapolation of the ground state vibrational constants. This yields $D_0°$ = 89 kcal·mol^{-1} or $\Delta_f H°$(298.15 K) = 111 kcal·mol^{-1}. There are several indications that this dissociation energy is probably a maximum value, for example, Hildenbrand[5] has applied an ionic–covalent correction to the linear extrapolation which gives $D_0°$ = 72 kcal·mol^{-1}. We would expect this enthalpy of formation to be a minimum value. A real minimum for the dissociation energy can be obtained from the knowledge that the first vibrational level of the $^2\Delta$ state is occupied and so the dissociation energy of this state must be greater than 850 cm^{-1}. This yields a minimum dissociation energy of the ground state of 76 kcal·mol^{-1}, assuming the dissociation products are C($^1\Delta$) and Cl(^{2}P), and $\Delta_f H°$(CCl, g, 298.15 K) = 124 kcal·mol^{-1} which is the maximum value of the heat of formation.

Heat Capacity and Entropy

The rotational and electronic constants are those of Verma and Mulliken.[2] The vibrational constants are those derived by Ovcharenko *et al.*[3] from the data of Gordon and King.[4] The anharmonicities listed by Verma and Mulliken are not used, since these are based only on the 0,0 and 0,1 transitions. The $^4\Sigma$ level is estimated by analogy with CF(g). The value for α_e was obtained from the other constants assuming a Morse potential function.

References

[1]W. J. Miller and H. B. Palmer, J. Chem. Phys. **40**, 3701 (1964).
[2]R. D. Verma and R. S. Mulliken, J. Mol. Spectrosc. **6**, 419 (1961).
[3]I. E. Ovcharenko, Yu. Ya. Kuzyakov, and V. M. Tatievskii, Opt. Spectrosc. (Eng. Transl.) **19**, 294 (1965).
[4]R. D. Gordon and G. W. King, Can. J. Phys. **39**, 252 (1961).
[5]D. L. Hildenbrand, Douglas Advanced Research Laboratories, Huntington Beach, Calif., private communication, (December 30, 1969).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.395	498.327	498.327	INFINITE
100	32.553	189.824	252.667	−6.284	499.922	490.485	−256.203
200	31.329	211.872	227.428	−3.111	501.249	480.488	−125.491
250	31.663	218.890	225.043	−1.538	501.717	475.241	−99.296
298.15	32.254	224.516	224.516	0.	502.080	470.108	−82.361
300	32.279	224.715	224.516	0.060	502.092	469.909	−81.818
350	32.956	229.742	224.912	1.691	502.393	464.521	−69.326
400	33.594	234.185	225.799	3.355	502.630	459.093	−59.951
450	34.156	238.175	226.956	5.049	502.807	453.640	−52.657
500	34.637	241.799	228.262	6.769	502.932	448.170	−46.820
600	35.391	248.185	231.064	10.272	503.041	437.205	−38.062
700	35.934	253.684	233.912	13.840	503.000	426.233	−31.806
800	36.335	258.509	236.691	17.455	502.843	415.276	−27.115
900	36.639	262.807	239.359	21.104	502.598	404.344	−23.468
1000	36.877	266.680	241.900	24.780	502.283	393.443	−20.551
1100	37.068	270.204	244.316	28.478	501.911	382.577	−18.167
1200	37.226	273.437	246.610	32.193	501.494	371.747	−16.182
1300	37.360	276.422	248.789	35.922	501.038	360.953	−14.503
1400	37.476	279.195	250.863	39.664	500.550	350.195	−13.066
1500	37.577	281.784	252.839	43.417	500.033	339.473	−11.822
1600	37.668	284.212	254.725	47.179	499.490	328.787	−10.734
1700	37.751	286.498	256.528	50.950	498.925	318.135	−9.775
1800	37.827	288.658	258.253	54.729	498.338	307.517	−8.924
1900	37.898	290.705	259.908	58.515	497.732	296.932	−8.163
2000	37.965	292.651	261.497	62.309	497.107	286.380	−7.479
2100	38.029	294.505	263.025	66.108	496.464	275.859	−6.862
2200	38.090	296.275	264.496	69.914	495.803	265.370	−6.301
2300	38.149	297.970	265.915	73.726	495.124	254.911	−5.789
2400	38.207	299.595	267.285	77.544	494.428	244.481	−5.321
2500	38.264	301.155	268.608	81.367	493.714	234.082	−4.891
2600	38.321	302.657	269.889	85.197	492.982	223.711	−4.494
2700	38.378	304.105	271.130	89.032	492.233	213.368	−4.128
2800	38.436	305.501	272.333	92.872	491.466	203.054	−3.788
2900	38.494	306.851	273.500	96.719	490.682	192.767	−3.472
3000	38.555	308.157	274.633	100.571	489.881	182.508	−3.178
3100	38.616	309.422	275.735	104.430	489.063	172.276	−2.903
3200	38.680	310.649	276.807	108.295	488.230	162.070	−2.646
3300	38.746	311.841	277.851	112.166	487.382	151.891	−2.404
3400	38.814	312.998	278.868	116.044	486.520	141.737	−2.178
3500	38.885	314.124	279.859	119.929	485.646	131.609	−1.964
3600	38.959	315.221	280.826	123.821	484.760	121.506	−1.763
3700	39.035	316.289	281.770	127.721	483.865	111.428	−1.573
3800	39.114	317.331	282.692	131.628	482.961	101.374	−1.393
3900	39.196	318.348	283.594	135.543	482.051	91.344	−1.223
4000	39.281	319.342	284.475	139.467	481.135	81.338	−1.062
4100	39.369	320.313	285.337	143.400	480.217	71.355	−0.909
4200	39.459	321.263	286.181	147.341	479.296	61.393	−0.764
4300	39.553	322.192	287.008	151.292	478.376	51.454	−0.625
4400	39.649	323.103	287.818	155.252	477.458	41.536	−0.493
4500	39.748	323.995	288.612	159.222	476.543	31.639	−0.367
4600	39.849	324.870	289.391	163.201	475.632	21.763	−0.247
4700	39.953	325.728	290.155	167.192	474.728	11.906	−0.132
4800	40.059	326.570	290.905	171.192	473.831	2.068	−0.023
4900	40.167	327.397	291.641	175.203	472.943	−7.751	0.083
5000	40.277	328.210	292.364	179.226	472.065	−17.553	0.183
5100	40.390	329.008	293.075	183.259	471.197	−27.336	0.280
5200	40.503	329.794	293.774	187.304	470.342	−37.103	0.373
5300	40.619	330.566	294.461	191.360	469.500	−46.854	0.462
5400	40.736	331.327	295.136	195.427	468.671	−56.588	0.547
5500	40.854	332.075	295.801	199.507	467.857	−66.308	0.630
5600	40.974	332.812	296.456	203.598	467.057	−76.012	0.709
5700	41.095	333.539	297.100	207.702	466.273	−85.703	0.785
5800	41.216	334.254	297.734	211.817	465.505	−95.380	0.859
5900	41.338	334.960	298.359	215.945	464.753	−105.044	0.930
6000	41.462	335.656	298.975	220.085	464.018	−114.696	0.999

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K)$ = [277.012] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = [−424.3 ± 33] $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−426.8 ± 33] $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
776(1)	1095(1)
1868(1)	415(1)
501(1)	667(1)

Ground State Quantum Weight: 1 σ = 1
Point Group: C_s
Product of the Moments of Inertia: $I_A I_B I_C = 2.7911 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpies of formation of $COCl_2$ and COF_2 have been averaged to obtain that of COCIF.

Heat Capacity and Entropy

The molecular constants are from Lovell *et al.*[1] The principle moments of inertia are: $I_A = 7.480 \times 10^{-39}$, $I_B = 16.008 \times 10^{-39}$, and $I_C = 23.31 \times 10^{-39}\ g \cdot cm^2$.

References

[1]R. J. Lovell, C. V. Stephenson and E. A. Jones, J. Chem. Phys. **22**, 1953 (1954).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.904	−424.276	−424.276	INFINITE
100	34.405	231.656	317.256	−8.560	−425.354	−421.790	220.320
200	43.300	257.957	281.526	−4.714	−426.273	−417.838	109.128
250	48.207	268.154	277.852	−2.424	−426.569	−415.693	86.854
298.15	52.396	277.012	277.012	0.	−426.768	−413.579	72.457
300	52.545	277.337	277.013	0.097	−426.774	−413.497	71.996
350	56.256	285.723	277.667	2.820	−426.915	−411.272	61.379
400	59.407	293.446	279.163	5.713	−427.011	−409.031	53.414
450	62.091	300.602	281.152	8.753	−427.080	−406.779	47.218
500	64.390	307.266	283.434	11.916	−427.133	−404.520	42.260
600	68.086	319.349	288.434	18.549	−427.211	−399.990	34.822
700	70.879	330.064	293.631	25.503	−427.268	−395.448	29.509
800	73.020	339.674	298.796	32.703	−427.313	−390.899	25.523
900	74.684	348.375	303.829	40.091	−427.349	−386.345	22.423
1000	75.993	356.314	308.686	47.628	−427.380	−381.788	19.943
1100	77.036	363.608	313.352	55.281	−427.410	−377.227	17.913
1200	77.876	370.348	317.825	63.028	−427.442	−372.664	16.222
1300	78.561	376.610	322.109	70.851	−427.481	−368.097	14.790
1400	79.124	382.453	326.213	78.736	−427.528	−363.528	13.563
1500	79.593	387.928	330.146	86.673	−427.587	−358.954	12.500
1600	79.987	393.078	333.920	94.653	−427.660	−354.377	11.569
1700	80.320	397.938	337.544	102.668	−427.750	−349.794	10.748
1800	80.605	402.537	341.028	110.715	−427.856	−345.205	10.018
1900	80.849	406.902	344.382	118.788	−427.982	−340.610	9.364
2000	81.060	411.054	347.612	126.884	−428.126	−336.008	8.776
2100	81.244	415.014	350.728	134.999	−428.290	−331.398	8.243
2200	81.405	418.797	353.737	143.132	−428.473	−326.780	7.759
2300	81.546	422.419	356.645	151.279	−428.675	−322.153	7.316
2400	81.672	425.892	359.458	159.440	−428.897	−317.517	6.911
2500	81.783	429.228	362.183	167.613	−429.136	−312.871	6.537
2600	81.882	432.438	364.824	175.797	−429.393	−308.216	6.192
2700	81.971	435.530	367.385	183.989	−429.666	−303.550	5.873
2800	82.051	438.512	369.873	192.191	−429.955	−298.874	5.576
2900	82.123	441.393	372.290	200.399	−430.259	−294.187	5.299
3000	82.188	444.178	374.640	208.615	−430.576	−289.489	5.040
3100	82.247	446.874	376.927	216.837	−430.905	−284.781	4.799
3200	82.301	449.486	379.153	225.064	−431.245	−280.062	4.572
3300	82.350	452.019	381.323	233.297	−431.596	−275.332	4.358
3400	82.395	454.478	383.439	241.534	−431.954	−270.592	4.157
3500	82.437	456.867	385.503	249.776	−432.320	−265.841	3.967
3600	82.475	459.190	387.518	258.021	−432.691	−261.079	3.788
3700	82.510	461.451	389.485	266.271	−433.066	−256.307	3.618
3800	82.542	463.651	391.408	274.523	−433.444	−251.524	3.457
3900	82.572	465.796	393.288	282.779	−433.823	−246.731	3.305
4000	82.600	467.887	395.127	291.038	−434.203	−241.930	3.159
4100	82.626	469.927	396.927	299.299	−434.581	−237.118	3.021
4200	82.650	471.918	398.689	307.563	−434.956	−232.297	2.889
4300	82.672	473.863	400.415	315.829	−435.329	−227.468	2.763
4400	82.693	475.764	402.105	324.097	−435.696	−222.630	2.643
4500	82.713	477.623	403.763	332.368	−436.058	−217.783	2.528
4600	82.731	479.441	405.389	340.640	−436.414	−212.929	2.418
4700	82.748	481.220	406.983	348.914	−436.763	−208.067	2.312
4800	82.765	482.962	408.548	357.189	−437.104	−203.197	2.211
4900	82.780	484.669	410.084	365.467	−437.438	−198.320	2.114
5000	82.794	486.342	411.593	373.745	−437.763	−193.437	2.021
5100	82.808	487.981	413.074	382.025	−438.080	−188.547	1.931
5200	82.820	489.589	414.530	390.307	−438.388	−183.652	1.845
5300	82.832	491.167	415.962	398.589	−438.688	−178.750	1.762
5400	82.844	492.715	417.369	406.873	−438.979	−173.843	1.682
5500	82.854	494.236	418.752	415.158	−439.262	−168.931	1.604
5600	82.865	495.729	420.114	423.444	−439.538	−164.012	1.530
5700	82.874	497.195	421.453	431.731	−439.807	−159.090	1.458
5800	82.883	498.637	422.772	440.019	−440.068	−154.163	1.388
5900	82.892	500.054	424.069	448.308	−440.324	−149.232	1.321
6000	82.900	501.447	425.347	456.597	−440.575	−144.296	1.256

PREVIOUS: June1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 285.35 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -702.84 \pm 3.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -707.93 \pm 3.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1106(1)	1217(2)
782(1)	560(2)
474(1)	350(2)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Bond Distances: C–F = 1.328 Å; C–Cl = 1.751 Å

Bond Angles: F–C–F = 108.6 ± 0.5°; F–C–Cl = 110.33°

Product of the Moments of Inertia: $I_A I_B I_C = 9.444771 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given by Syverud.[1] Coomber and Whittle[2] have determined equilibrium data for $CClF_3(g) + BrX(g) = CBrF_3(g) + ClX(g)$ where X = Cl and Br. Lord *et al.*[3] studied the analogous equilibria $CF_3I(g) + ClI(g) = CClF_3(g) + I_2(g)$. These data link $CClF_3$ with $CBrF_3$ and CF_3I.

Other data which were omitted from the adjustment include those of Baibuz,[4,5] Mears and Stahl,[6] Kolesov *et al.*,[7] Kirkbride and Davidson,[8] and von Wartenberg and Schiefer.[9] Baibuz[4,5] derived $\Delta_f H° = -166.2 \pm 2.2\ kcal·mol^{-1}$ by applying the method of explosion in a spherical bomb to mixtures of H_2, O_2 and $CClF_3$. By comparison with similar data for CF_4 and CCl_4, we estimate the bias in Baibuz' value to be about +2 $kcal·mol^{-1}$. Mears and Stahl[6] gave a preliminary report of values of $\Delta_f H$ at 300°C for reactions involving HF, HCl and CCl_nF_{4-n}(n = 1, 2, 3, 4). We derive $\Delta_f H° = -172$ and $-173\ kcal·mol^{-1}$ from two different combinations of reactions; however, no detailed account of the data has been published. The other authors[7-9] measured $\Delta_f H$ for reaction of $CClF_3$ with an alkali metal (Na or K) to form amorphous carbon and mixtures of the fluoride and chloride. Discrepancies of many $kcal·mol^{-1}$ exist in these studies, presumably due to inadequate characterization of the thermochemical reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron–diffraction studies by Bowen[10] and Bartell and Brockway.[11] Results from Bartell and Brockway are adopted. These parameters are consistent with the microwave data of Coles and Hughes.[12] The principal moments of inertia are: $I_A = 14.6768 \times 10^{-39}$ and $I_B = I_C = 25.3677 \times 10^{-39}\ g·cm^2$. Vibrational assignments are based on the work of Claassen[13] and the gas–phase Raman spectra observed by Holzer and Moser.[14]

The largest uncertainty in $C_p°$ and $S°$ probably results from the neglect of anharmonicity. Barho[15] and Albright *et al.*[16] have given estimates for the anharmonic contributions. These vary from 0.1 to 0.3 $cal·K^{-1}·mol^{-1}$ in both $C_p°$ and $S°$ over the range from 300 to 1000 K, respectively. Somewhat larger contributions are possible based on the anharmonic functions calculated by McBride *et al.*[17] for CF_4(g). We estimate the overall uncertainty in the entropy of this JANAF table to be 0.1 $cal·K^{-1}·mol^{-1}$ at 300 K and 0.4 $cal·K^{-1}·mol^{-1}$ at 1000 K. $C_p°$ is consistent with $C_v°$ measured at 300 K by the wire–ribbon method.[18]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−13.782	−702.836	−702.836	INFINITE
100	36.815	231.109	335.022	−10.391	−705.321	−693.331	362.159
200	53.051	261.466	291.051	−5.917	−707.086	−680.571	177.747
250	60.573	274.131	286.420	−3.072	−707.600	−673.878	140.799
298.15	66.887	285.353	285.353	0.	−707.933	−667.351	116.917
300	67.112	285.767	285.354	0.124	−707.943	−667.099	116.152
350	72.738	296.546	286.192	3.624	−708.157	−660.274	98.540
400	77.534	306.581	288.121	7.384	−708.270	−653.424	85.328
450	81.595	315.954	290.699	11.365	−708.305	−646.566	75.051
500	85.019	324.733	293.668	15.533	−708.282	−639.707	66.830
600	90.333	340.731	300.206	24.315	−708.103	−626.006	54.499
700	94.135	354.958	307.030	33.549	−707.806	−612.345	45.694
800	96.901	367.718	313.833	43.108	−707.432	−598.733	39.093
900	98.953	379.255	320.471	52.906	−707.010	−585.170	33.962
1000	100.508	389.765	326.883	62.882	−706.560	−571.657	29.860
1100	101.709	399.403	333.044	72.996	−706.096	−558.189	26.506
1200	102.652	408.295	338.949	83.215	−705.627	−544.763	23.713
1300	103.404	416.542	344.604	93.520	−705.162	−531.377	21.351
1400	104.014	424.229	350.020	103.891	−704.706	−518.026	19.328
1500	104.513	431.422	355.210	114.319	−704.265	−504.707	17.575
1600	104.927	438.181	360.187	124.791	−703.840	−491.417	16.043
1700	105.274	444.553	364.964	135.302	−703.434	−478.153	14.692
1800	105.568	450.579	369.554	145.844	−703.047	−464.913	13.491
1900	105.818	456.294	373.970	156.414	−702.678	−451.694	12.418
2000	106.033	461.727	378.224	167.007	−702.325	−438.493	11.452
2100	106.219	466.905	382.324	177.620	−701.985	−425.310	10.579
2200	106.381	471.850	386.282	188.250	−701.656	−412.143	9.786
2300	106.523	476.582	390.106	198.895	−701.334	−398.990	9.061
2400	106.648	481.118	393.804	209.554	−701.014	−385.851	8.398
2500	106.759	485.474	397.384	220.224	−700.693	−372.726	7.788
2600	106.858	489.663	400.854	230.905	−700.367	−359.614	7.225
2700	106.946	493.698	404.218	241.596	−700.030	−346.514	6.704
2800	107.025	497.589	407.484	252.294	−699.680	−333.428	6.220
2900	107.096	501.346	410.656	263.000	−699.313	−320.353	5.770
3000	107.160	504.977	413.740	273.713	−698.926	−307.293	5.350
3100	107.218	508.492	416.740	284.432	−698.515	−294.245	4.958
3200	107.271	511.897	419.661	295.156	−698.078	−281.211	4.590
3300	107.319	515.199	422.506	305.886	−697.611	−268.191	4.245
3400	107.363	518.403	425.280	316.620	−697.113	−255.186	3.920
3500	107.404	521.516	427.985	327.359	−696.582	−242.195	3.615
3600	107.441	524.542	430.625	338.101	−696.015	−229.220	3.326
3700	107.475	527.486	433.203	348.847	−695.411	−216.262	3.053
3800	107.507	530.353	435.722	359.596	−694.769	−203.321	2.795
3900	107.536	533.146	438.185	370.348	−694.088	−190.397	2.550
4000	107.563	535.869	440.593	381.103	−693.365	−177.491	2.318
4100	107.588	538.525	442.949	391.860	−692.601	−164.603	2.097
4200	107.611	541.118	445.256	402.620	−691.795	−151.735	1.887
4300	107.633	543.650	447.515	413.382	−690.946	−138.887	1.687
4400	107.653	546.125	449.728	424.147	−690.053	−126.058	1.496
4500	107.672	548.544	451.897	434.913	−689.117	−113.250	1.315
4600	107.690	550.911	454.024	445.681	−688.136	−100.464	1.141
4700	107.707	553.227	456.110	456.451	−687.112	−87.700	0.975
4800	107.722	555.495	458.157	467.222	−686.045	−74.957	0.816
4900	107.737	557.716	460.166	477.995	−684.933	−62.238	0.663
5000	107.751	559.893	462.139	488.770	−683.778	−49.541	0.518
5100	107.764	562.027	464.077	499.546	−682.580	−36.868	0.378
5200	107.776	564.120	465.981	510.323	−681.340	−24.219	0.243
5300	107.788	566.173	467.852	521.101	−680.058	−11.594	0.114
5400	107.799	568.188	469.691	531.880	−678.734	1.006	−0.010
5500	107.809	570.166	471.500	542.660	−677.369	13.581	−0.129
5600	107.819	572.108	473.280	553.442	−675.964	26.131	−0.244
5700	107.828	574.017	475.030	564.224	−674.520	38.655	−0.354
5800	107.837	575.892	476.753	575.007	−673.037	51.154	−0.461
5900	107.845	577.736	478.449	585.792	−671.516	63.628	−0.563
6000	107.853	579.548	480.119	596.576	−669.959	76.074	−0.662

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 236.334\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -137.24\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -137.95\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
714.52 (1)
378.3 (2)
2215.5 (1)

Ground State Quantum Weight: 1 σ=1
Point Group: $C_{\infty v}$
Bond Distances: Cl–C = 1.631 Å; C–N = 1.162 Å
Bond Angle: Cl–C–N = 180°
Rotational Constants: $B_o = 0.19817\ cm^{-1}$; $D_o = 5.503 \times 10^{-8}\ cm^{-1}$

Spectroscopic constants used in calculating corrections to rigid rotator–harmonic oscillator approximation (cm^{-1}):

$\alpha_1 = 8.25 - 10^{-4}$ $x_{11} = [-4]$ $x_{12} = [-6.8]$ $g_{22} = 0.95$
$\alpha_2 = -5.46 - 10^{-4}$ $x_{22} = -0.65$ $x_{23} = -7.236$
$\alpha_3 = 1.06 - 10^{-3}$ $x_{33} = [-7]$ $x_{13} = -2.8$

Enthalpy of Formation

The enthalpy of formation was taken from U.S. NBS Tech. Note 270–1.[1]

Heat Capacity and Entropy

Gordon[2] has used the constants listed above to calculate $C_p°$ from 298.15 to 6000 K using the method of Pennington and Kobe[3] which takes anharmonicity, vibration–rotation interaction, and centrifugal stretching into account. The constants B_o and D_o were taken from Burrus and Gordy,[4] ω_1, x_1, x_3, x_{22}, x_{23}, x_{13}, and g_{22} were obtained by Lafferty *et al.*,[5] α_2 has been taken from Townes *et al.*,[6] and x_{11}, x_{33} and x_{12} were estimated by Gordon.[2] The bond distances and bond angle were taken from Lafferty *et al.*[5]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.686	137.237	137.237	INFINITE
100	31.246	195.017	272.421	−7.740	137.216	135.250	−70.648
200	39.643	219.305	240.225	−4.184	137.472	133.222	−34.794
298.15	45.271	236.334	236.334	0.	137.946	131.015	−22.953
300	45.346	236.614	236.335	0.084	137.956	130.972	−22.804
400	48.718	250.147	238.157	4.796	138.452	128.567	−16.789
500	51.024	261.275	241.701	9.787	138.861	126.046	−13.168
600	52.831	270.742	245.771	14.982	139.170	123.453	−10.748
700	54.354	279.003	249.941	20.343	139.401	120.814	−9.015
800	55.656	286.348	254.041	25.845	139.578	118.146	−7.714
900	56.781	292.970	258.005	31.469	139.718	115.459	−6.701
1000	57.748	299.003	261.807	37.196	139.834	112.757	−5.890
1100	58.504	304.543	265.444	43.009	139.929	110.044	−5.226
1200	59.204	309.664	268.918	48.895	140.009	107.324	−4.672
1300	59.847	314.429	272.238	54.848	140.079	104.597	−4.203
1400	60.432	318.886	275.412	60.862	140.147	101.865	−3.801
1500	60.961	323.073	278.452	66.932	140.213	99.129	−3.452
1600	61.365	327.021	281.365	73.049	140.275	96.388	−3.147
1700	61.745	330.752	284.161	79.205	140.331	93.643	−2.877
1800	62.103	334.292	286.849	85.397	140.384	90.895	−2.638
1900	62.437	337.659	289.435	91.624	140.433	88.144	−2.423
2000	62.747	340.869	291.927	97.884	140.480	85.391	−2.230
2100	63.010	343.937	294.331	104.172	140.523	82.636	−2.055
2200	63.262	346.874	296.653	110.485	140.560	79.878	−1.897
2300	63.503	349.692	298.899	116.824	140.591	77.119	−1.751
2400	63.733	352.399	301.072	123.186	140.616	74.359	−1.618
2500	63.952	355.005	303.177	129.570	140.635	71.598	−1.496
2600	64.150	357.518	305.219	135.975	140.646	68.836	−1.383
2700	64.342	359.942	307.201	142.400	140.648	66.074	−1.278
2800	64.529	362.286	309.127	148.844	140.642	63.312	−1.181
2900	64.710	364.553	310.999	155.306	140.628	60.551	−1.091
3000	64.885	366.750	312.821	161.785	140.604	57.790	−1.006
3100	65.050	368.880	314.596	168.282	140.572	55.030	−0.927
3200	65.212	370.948	316.324	174.795	140.530	52.271	−0.853
3300	65.371	372.957	318.010	181.325	140.481	49.514	−0.784
3400	65.527	374.911	319.655	187.870	140.424	46.758	−0.718
3500	65.680	376.813	321.261	194.430	140.360	44.004	−0.657
3600	65.828	378.665	322.830	201.005	140.290	41.252	−0.599
3700	65.973	380.471	324.364	207.595	140.215	38.502	−0.544
3800	66.117	382.232	325.864	214.200	140.137	35.754	−0.491
3900	66.259	383.951	327.331	220.819	140.055	33.008	−0.442
4000	66.400	385.631	328.768	227.452	139.973	30.264	−0.395
4100	66.536	387.272	330.175	234.099	139.890	27.523	−0.351
4200	66.670	388.877	331.553	240.759	139.808	24.783	−0.308
4300	66.804	390.447	332.905	247.433	139.729	22.045	−0.268
4400	66.937	391.984	334.230	254.120	139.653	19.309	−0.229
4500	67.070	393.490	335.530	260.820	139.582	16.575	−0.192
4600	67.201	394.966	336.806	267.534	139.518	13.842	−0.157
4700	67.331	396.412	338.059	274.260	139.460	11.111	−0.123
4800	67.461	397.831	339.290	281.000	139.411	8.380	−0.091
4900	67.590	399.224	340.499	287.752	139.372	5.651	−0.060
5000	67.718	400.590	341.687	294.518	139.342	2.922	−0.031
5100	67.845	401.933	342.855	301.296	139.323	0.194	−0.002
5200	67.972	403.251	344.004	308.087	139.316	−2.534	0.025
5300	68.097	404.547	345.134	314.890	139.321	−5.262	0.052
5400	68.222	405.821	346.246	321.706	139.339	−7.990	0.077
5500	68.346	407.074	347.341	328.535	139.370	−10.718	0.102
5600	68.469	408.307	348.418	335.375	139.415	−13.448	0.125
5700	68.591	409.520	349.480	342.228	139.474	−16.178	0.148
5800	68.712	410.714	350.525	349.093	139.547	−18.909	0.170
5900	68.833	411.889	351.555	355.971	139.634	−21.642	0.192
6000	68.952	413.047	352.571	362.860	139.735	−24.376	0.212

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = [265.965]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-64.3 \pm 42]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-62.8 \pm 42]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
570 (1)
281 (1)
1880 (1)

Ground State Quantum Weight: 2 $\sigma = 1$

Point Group: C_s

Bond Distances: C–Cl = [1.75] Å; C–O = [1.17] Å

Bond Angle: Cl–C–O = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.276664 \times 10^{-115}]\ g^3·cm^6$

Enthaply of Formation

The enthalpy change ($\Delta_f H°$) for the reaction $COCl_2(g) = CO(g) + 2Cl(g)$ is calculated to be 82 kcal·mol^{-1}, which is the sum of two bond energies, i.e. D(Cl–COCl) + D(Cl–CO). By comparison with values, $D(H_3C–COCH_3)/D(H_3C–CO) = 72/18 = 4.0$ for CH_3COCH_3 (g) and $D(H_3C–COCl)/D(Cl–CO) = 4.3$ for CH_3COCl(g), the ratio of D(Cl–COCl)/D(Cl–CO) is estimated to be 4.0 for $COCl_2$(g). Hence the enthalpy change for the reaction $COCl_2(g) = COCl(g) + Cl(g)$ is calculated as $82 \times (4/5) = 65.6$ kcal·mol^{-1}. Using the $\Delta_f H°$ value obtained, the enthalpy of formation for COCl(g) is derived to be -15 ± 10 kcal·mol^{-1}.

Heat Capacity and Entropy

The vibrational frequencies were reported by Jacox and Milligan.[1] The bond distances and angle were estimated by Jacox and Milligan.[1] Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The principal moments of inertia are: $I_A = 0.7159 \times 10^{-39}$, $I_B = 13.0005 \times 10^{-39}$, and $I_C = 13.7165 \times 10^{-39}$ g·cm^2.

References

[1]M. E. Jacox and D. E. Milligan, J. Chem. Phys. **43**, 866 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.551	−64.327	−64.327	INFINITE
100	35.882	221.891	303.521	−8.163	−63.908	−67.886	35.460
200	41.634	248.636	269.991	−4.271	−63.317	−72.083	18.826
250	43.627	258.152	266.699	−2.137	−63.016	−74.309	15.526
298.15	45.072	265.965	265.965	0.	−62.760	−76.508	13.404
300	45.120	266.244	265.966	0.083	−62.751	−76.593	13.336
350	46.289	273.290	266.520	2.370	−62.533	−78.918	11.778
400	47.265	279.537	267.764	4.709	−62.369	−81.271	10.613
450	48.125	285.154	269.389	7.094	−62.258	−83.641	9.709
500	48.908	290.266	271.225	9.520	−62.199	−86.020	8.987
600	50.301	299.309	275.171	14.483	−62.211	−90.786	7.904
700	51.487	307.155	279.192	19.574	−62.356	−95.539	7.129
800	52.484	314.097	283.130	24.774	−62.595	−100.264	6.547
900	53.312	320.328	286.923	30.065	−62.901	−104.955	6.091
1000	53.996	325.981	290.550	35.431	−63.257	−109.609	5.725
1100	54.560	331.155	294.010	40.860	−63.652	−114.225	5.424
1200	55.028	335.923	297.306	46.340	−64.079	−118.804	5.171
1300	55.417	340.344	300.449	51.863	−64.533	−123.346	4.956
1400	55.743	344.463	303.447	57.421	−65.011	−127.852	4.770
1500	56.018	348.318	306.312	63.010	−65.513	−132.324	4.608
1600	56.251	351.941	309.051	68.624	−66.038	−136.761	4.465
1700	56.450	355.357	311.676	74.259	−66.585	−141.164	4.337
1800	56.621	358.589	314.193	79.913	−67.155	−145.535	4.223
1900	56.769	361.654	316.611	85.582	−67.748	−149.874	4.120
2000	56.898	364.570	318.937	91.266	−68.364	−154.180	4.027
2100	57.010	367.348	321.176	96.961	−69.004	−158.455	3.941
2200	57.109	370.003	323.336	102.667	−69.669	−162.699	3.863
2300	57.196	372.543	325.420	108.383	−70.359	−166.913	3.791
2400	57.274	374.979	327.435	114.106	−71.076	−171.096	3.724
2500	57.343	377.319	329.384	119.837	−71.820	−175.248	3.662
2600	57.405	379.569	331.271	125.575	−72.592	−179.370	3.604
2700	57.460	381.737	333.100	131.318	−73.391	−183.461	3.549
2800	57.510	383.827	334.875	137.066	−74.219	−187.523	3.498
2900	57.555	385.846	336.598	142.820	−75.075	−191.555	3.450
3000	57.596	387.798	338.272	148.577	−75.960	−195.556	3.405
3100	57.633	389.687	339.900	154.339	−76.872	−199.527	3.362
3200	57.667	391.517	341.485	160.104	−77.812	−203.469	3.321
3300	57.698	393.292	343.028	165.872	−78.779	−207.381	3.283
3400	57.726	395.015	344.532	171.643	−79.772	−211.263	3.246
3500	57.752	396.689	345.998	177.417	−80.789	−215.116	3.210
3600	57.776	398.316	347.429	183.193	−81.830	−218.939	3.177
3700	57.798	399.900	348.826	188.972	−82.893	−222.734	3.144
3800	57.818	401.441	350.190	194.753	−83.978	−226.498	3.113
3900	57.837	402.943	351.524	200.536	−85.082	−230.234	3.084
4000	57.855	404.408	352.828	206.320	−86.204	−233.942	3.055
4100	57.871	405.837	354.103	212.107	−87.343	−237.621	3.027
4200	57.887	407.231	355.352	217.895	−88.497	−241.273	3.001
4300	57.901	408.594	356.574	223.684	−89.666	−244.896	2.975
4400	57.914	409.925	357.772	229.475	−90.846	−248.493	2.950
4500	57.926	411.227	358.945	235.267	−92.038	−252.063	2.926
4600	57.938	412.500	360.095	241.060	−93.241	−255.606	2.902
4700	57.949	413.746	361.224	246.854	−94.452	−259.122	2.880
4800	57.959	414.966	362.331	252.650	−95.672	−262.613	2.858
4900	57.969	416.161	363.417	258.446	−96.899	−266.078	2.836
5000	57.978	417.333	364.484	264.244	−98.132	−269.518	2.816
5100	57.986	418.481	365.531	270.042	−99.372	−272.933	2.795
5200	57.994	419.607	366.560	275.841	−100.616	−276.325	2.776
5300	58.002	420.712	367.572	281.641	−101.867	−279.691	2.757
5400	58.009	421.796	368.566	287.441	−103.122	−283.035	2.738
5500	58.016	422.860	369.543	293.242	−104.381	−286.355	2.720
5600	58.023	423.906	370.505	299.044	−105.646	−289.652	2.702
5700	58.029	424.933	371.451	304.847	−106.915	−292.927	2.684
5800	58.035	425.942	372.382	310.650	−108.189	−296.179	2.667
5900	58.040	426.934	373.298	316.454	−109.469	−299.410	2.651
6000	58.045	427.910	374.200	322.258	−110.754	−302.618	2.635

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [265.346]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 237.3 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 238.5 \pm 21\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	1
[4000]	[3]
[17500]	[1]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
721 (1)
[350] (1)
748 (1)

Point Group: C_{2v}
Bond Distance: C–Cl = [1.76] Å
Bond Angle: Cl–C–Cl = [100 ± 10]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.101940 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

Shapiro and Lossing[1] have measured mass-spectrometrically the appearance potentials 12.2 and 14.7 eV for the processes $CHCl_3(g) + e^- \rightarrow CCl_2^+(g) + HCl(g) + 2e^-$ and $C_2Cl_4(g) + e^- \rightarrow CCl_2^+(g) + CCl_2(g) + 2e^-$, respectively. The difference in these two processes gives $\Delta_f H° = 2.5$ eV (57.65 kcal·mol^{-1}), for the reaction $C_2Cl_4(g) + HCl(g) \rightarrow CCl_2(g) + CHCl_3(g)$ which leads to $\Delta_f H°(CCl_2, g, 298.15\ K) = 57.32$ kcal·mol^{-1}, using $\Delta_f H°(298.15\ K) = -2.97$, -22.063 and -24.7 kcal·mol^{-1} for $C_2Cl_4(g)$, HCl(g) and $CHCl_3(g)$, respectively. Since the authors claimed that the experimental error was probably 5 kcal·mol^{-1}, the value 57 ± 5 kcal·mol^{-1} (238.488 ± 21 kJ·mol^{-1}), is adopted for the enthalpy of formation.

Heat Capacity and Entropy

Milligan and Jacox[2] have found two stretching fundamentals (721 and 748 cm^{-1}) for the CCl_2 radical in the infrared and ultraviolet spectra by matrix-isolation, and proposed a bent molecular structure (the valence angle = 100 ± 10°) with a ground singlet state which was based on the analogy with the electronic absorption spectrum of CF_2. L. Andrews[3] has confirmed all these observations in his infrared spectrometric studies of dichlorocarbene in solid argon, and made vibrational assignment to the fundamentals and also eliminated the possibility of a linear molecular structure for CCl_2. The bending frequency (350 cm^{-1}) is estimated by the valence force method,[4] using the same ratio of bending over stretching force constants from $CF_2(g)$.[5] The bond distance is estimated to be the same as that of $CCl_4(g)$ measured by Bartell *et al.*[6] The principal moments of inertia are $I_A = 2.1829 \times 10^{-39}$, $I_B = 21.4029 \times 10^{-39}$, and $I_C = 23.5858 \times 10^{-39}$ g·cm^2.

The triplet low lying electronic level of 4000 cm^{-1} is estimated by analogy with that of $CF_2(g)$. The other level of 17,5000 cm^{-1} is also estimated based on a weak band appearing between 4400 and 5600 Å in the spectra of CCl_2 observed by Milligan and Jacox.[2]

References

[1] J. S. Shapiro and F. P. Lossing, J. Phys. Chem. **72**, 1552 (1968).
[2] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 703 (1967).
[3] L. Andrews, J. Chem. Phys. **48**, 979 (1968).
[4] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, (1945).
[5] JANAF Thermochemical Tables: $CF_2(g)$, 9–30–66.
[6] L. S. Bartell, L. O. Brockway and R. H. Schwendeman, J. Chem. Phys. **23**, 1854 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.388	237.332	237.332	INFINITE
100	34.695	222.225	302.564	−8.034	237.714	234.488	−122.484
200	40.669	248.013	269.408	−4.279	238.105	231.112	−60.360
250	43.720	257.422	266.094	−2.168	238.302	229.341	−47.918
298.15	46.249	265.346	265.346	0.	238.488	227.598	−39.874
300	46.337	265.632	265.347	0.086	238.495	227.530	−39.617
350	48.459	272.941	265.919	2.458	238.677	225.688	−33.682
400	50.142	279.526	267.215	4.924	238.841	223.821	−29.228
450	51.476	285.511	268.921	7.466	238.978	221.935	−25.762
500	52.546	290.992	270.858	10.067	239.086	220.035	−22.987
600	54.180	300.725	275.045	15.408	239.216	216.211	−18.823
700	55.475	309.176	279.330	20.892	239.256	212.373	−15.847
800	56.676	316.663	283.538	26.500	239.243	208.533	−13.616
900	57.888	323.408	287.599	32.228	239.216	204.696	−11.880
1000	59.129	329.571	291.492	38.079	239.207	200.861	−10.492
1100	60.369	335.265	295.216	44.054	239.238	197.025	−9.356
1200	61.560	340.569	298.777	50.151	239.322	193.184	−8.409
1300	62.656	345.541	302.185	56.362	239.462	189.334	−7.608
1400	63.622	350.220	305.451	62.677	239.656	185.471	−6.920
1500	64.437	354.638	308.584	69.082	239.895	181.593	−6.324
1600	65.093	358.819	311.594	75.559	240.168	177.697	−5.801
1700	65.593	362.781	314.490	82.095	240.463	173.784	−5.340
1800	65.948	366.541	317.278	88.673	240.767	169.853	−4.929
1900	66.173	370.113	319.965	95.280	241.068	165.905	−4.561
2000	66.286	373.510	322.558	101.904	241.354	161.941	−4.229
2100	66.306	376.745	325.062	108.534	241.618	157.964	−3.929
2200	66.250	379.829	327.482	115.163	241.849	153.975	−3.656
2300	66.134	382.771	329.823	121.782	242.040	149.976	−3.406
2400	65.971	385.583	332.088	128.388	242.187	145.970	−3.177
2500	65.776	388.272	334.282	134.976	242.285	141.959	−2.966
2600	65.556	390.848	336.408	141.542	242.330	137.945	−2.771
2700	65.321	393.317	338.470	148.086	242.320	133.930	−2.591
2800	65.078	395.688	340.472	154.606	242.253	129.917	−2.424
2900	64.831	397.968	342.415	161.102	242.129	125.907	−2.268
3000	64.585	400.161	344.304	167.572	241.947	121.902	−2.123
3100	64.343	402.275	346.140	174.019	241.709	117.904	−1.987
3200	64.107	404.314	347.926	180.441	241.415	113.915	−1.859
3300	63.879	406.283	349.665	186.840	241.068	109.936	−1.740
3400	63.660	408.187	351.359	193.217	240.670	105.968	−1.628
3500	63.451	410.030	353.009	199.573	240.223	102.013	−1.522
3600	63.253	411.814	354.618	205.908	239.731	98.071	−1.423
3700	63.064	413.545	356.187	212.224	239.197	94.143	−1.329
3800	62.886	415.224	357.719	218.521	238.624	90.230	−1.240
3900	62.718	416.855	359.214	224.801	238.015	86.333	−1.156
4000	62.560	418.441	360.675	231.065	237.375	82.452	−1.077
4100	62.411	419.984	362.103	237.314	236.707	78.587	−1.001
4200	62.272	421.486	363.499	243.548	236.015	74.739	−0.930
4300	62.141	422.950	364.865	249.768	235.302	70.907	−0.861
4400	62.018	424.377	366.201	255.976	234.572	67.092	−0.796
4500	61.903	425.770	367.509	262.172	233.827	63.294	−0.735
4600	61.795	427.129	368.791	268.357	233.072	59.513	−0.676
4700	61.694	428.457	370.046	274.531	232.309	55.748	−0.620
4800	61.599	429.755	371.277	280.696	231.542	52.000	−0.566
4900	61.510	431.024	372.483	286.851	230.771	48.267	−0.515
5000	61.427	432.266	373.666	292.998	230.001	44.550	−0.465
5100	61.348	433.482	374.827	299.137	229.234	40.849	−0.418
5200	61.275	434.672	375.967	305.268	228.470	37.162	−0.373
5300	61.206	435.839	377.085	311.392	227.713	33.491	−0.330
5400	61.141	436.982	378.184	317.509	226.964	29.833	−0.289
5500	61.080	438.103	379.263	323.620	226.224	26.190	−0.249
5600	61.022	439.203	380.324	329.725	225.495	22.559	−0.210
5700	60.968	440.283	381.366	335.825	224.778	18.942	−0.174
5800	60.916	441.343	382.391	341.919	224.073	15.337	−0.138
5900	60.868	442.384	383.399	348.008	223.382	11.744	−0.104
6000	60.822	443.406	384.391	354.093	222.705	8.162	−0.071

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 300.897 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -487.4 \pm 8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -491.6 \pm 8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1099 (1)	457.5(1)	436(1)
261.5(1)	322 (1)	1162(1)
667.2(1)	922 (1)	446(1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: C–Cl = 1.77 ± 0.02 Å; C–F = 1.33 ± 0.02 Å

Bond Angles: F–C–F = 109.5 ± 3°; Cl–C–Cl = 108.5 ± 2°

F–C–F plane perpendicular to Cl–C–Cl plane

Product of the Moments of Inertia: $I_A I_B I_C = 2.537004 \times 10^{113}\ g^3\ cm^6$

Enthalpy of Formation

Mears and Stahl[1] investigated several heats of reaction involving CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, HF and HCl. Using JANAF values for all compounds except CF_2Cl_2 and $CFCl_3$ we obtain the following observations:

1. $\Delta_f H°(CCl_3F, g, 298.15\ K) = -70.12 \pm 1.1\ kcal \cdot mol^{-1}$
2. $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -116.53 \pm 1.5\ kcal \cdot mol^{-1}$
3. $\Delta_f H°(CCl_2F_2, g, 298.15\ K) - \Delta_f H°(CCl_3F, g, 298.15\ K) = -49.39 \pm 1.0\ kcal \cdot mol^{-1}$
4. $\Delta_f H°(CCl_2F_2, g, 298.15\ K) - 2\ \Delta_f H°(CCl_3F, g, 298.15\ K) = 20.34 \pm 1.0\ kcal \cdot mol^{-1}$
5. $\Delta_f H°(CCl_3F, g, 298.15\ K) - 2\ \Delta_f H°(CCl_2F_2, g, 298.15\ K) = 165.47 \pm 1.0\ kcal \cdot mol^{-1}$

The sum of the squares of the deviations is smallest when $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -117.5\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_3F, g, 298.15\ K) = -69\ kcal \cdot mol^{-1}$, and all the values are within their uncertainty ranges.

Peterson and Pitzer[8] obtained an approximate equilibrium constant for the reaction $2\ CClF_3(g) + CCl_4(g) = 3\ CCl_2F_2(g)$ of $\log K_{400} = -3.0$. This on 3rd law reaction gives $\Delta_r H°(298.15\ K) = 7.64\ kcal \cdot mol^{-1}$ and with $\Delta_f H°(CClF_3, g, 298.15\ K) = -169.2\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_4, g, 298.15\ K) = -22.94\ kcal \cdot mol^{-1}$ this yields $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -117.9\ kcal \cdot mol^{-1}$.

Kirkbride and Davidson[2] investigated the reaction of potassium with the chlorofluoromethanes and obtained $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -115.1 \pm 2\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_3F, g, 298.15\ K) = -72.9 \pm 4\ kcal \cdot mol^{-1}$ after correction with JANAF auxiliary data. Wartenberg and Schiefer[3] investigated the same reaction and we obtain, after correction with JANAF auxiliary data, $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -112.7\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_3F, g, 298.15\ K) = -63.1\ kcal \cdot mol^{-1}$. Kolesov *et al.*[4] have reported analogous data for the reaction with sodium which, after correction with JANAF auxiliary data, yields $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -114.4 \pm 3.5\ kcal \cdot mol^{-1}$.

We adopt the values calculated above from Mears and Stahl,[1] since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF_4 to CCl_4. With the adopted heats of formation, the successive replacement of F by Cl changes the atomization heats by 43.8, 41.6, 38.5, and 36.0 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Claassen[5] chose the frequencies given above from his own gas-phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict.[6] Masi[9] has measured the gas phase heat capacities at 243, 273, 318 and 363 K, within this range our adopted heat capacities are from 0.3 to 0.7% high. The entropies agree to within 0.05% and further adjustment to obtain better fits was not considered necessary. The molecular structure was determined from the microwave measurements of Long *et al.*[7] The principal moments of inertia are: $I_A = 21.0747 \times 10^{-39}$, $I_B = 31.7398 \times 10^{-39}$, and $I_C = 37.9277 \times 10^{-39}\ g\ cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.866	−487.429	−487.429	INFINITE
100	39.629	241.343	355.353	−11.401	−489.843	−477.944	249.652
200	58.584	274.768	307.109	−6.468	−491.203	−465.417	121.554
250	66.235	288.688	302.056	−3.342	−491.494	−458.933	95.889
298.15	72.404	300.897	300.897	0.	−491.620	−452.648	79.302
300	72.620	301.346	300.899	0.134	−491.622	−452.406	78.771
350	77.938	312.952	301.803	3.902	−491.633	−445.868	66.542
400	82.349	323.657	303.875	7.913	−491.556	−439.335	57.371
450	85.998	333.574	306.630	12.124	−491.416	−432.815	50.240
500	89.016	342.796	309.791	16.502	−491.230	−426.314	44.537
600	93.597	359.456	316.711	25.647	−490.769	−413.372	35.987
700	96.801	374.138	323.887	35.176	−490.236	−400.514	29.887
800	99.095	387.222	331.001	44.977	−489.666	−387.735	25.316
900	100.779	398.996	337.913	54.975	−489.077	−375.029	21.766
1000	102.044	409.683	344.564	65.119	−488.483	−362.389	18.929
1100	103.015	419.456	350.935	75.374	−487.891	−349.808	16.611
1200	103.773	428.453	357.025	85.715	−487.310	−337.281	14.681
1300	104.377	436.784	362.843	96.123	−486.741	−324.801	13.051
1400	104.864	444.538	368.405	106.586	−486.191	−312.365	11.654
1500	105.262	451.787	373.725	117.093	−485.659	−299.968	10.446
1600	105.592	458.591	378.819	127.636	−485.150	−287.605	9.389
1700	105.867	465.001	383.701	138.210	−484.663	−275.274	8.458
1800	106.100	471.059	388.388	148.808	−484.198	−262.970	7.631
1900	106.298	476.801	392.891	159.428	−483.756	−250.692	6.892
2000	106.469	482.258	397.224	170.067	−483.335	−238.436	6.227
2100	106.616	487.456	401.398	180.721	−482.935	−226.202	5.626
2200	106.744	492.419	405.424	191.390	−482.554	−213.985	5.081
2300	106.856	497.166	409.310	202.070	−482.190	−201.785	4.583
2400	106.955	501.716	413.066	212.760	−481.841	−189.602	4.127
2500	107.042	506.084	416.700	223.460	−481.505	−177.432	3.707
2600	107.120	510.284	420.219	234.169	−481.181	−165.275	3.320
2700	107.190	514.328	423.630	244.884	−480.866	−153.131	2.962
2800	107.252	518.228	426.940	255.606	−480.559	−140.998	2.630
2900	107.308	521.992	430.153	266.334	−480.256	−128.877	2.321
3000	107.358	525.631	433.275	277.068	−479.957	−116.765	2.033
3100	107.404	529.152	436.311	287.806	−479.658	−104.664	1.764
3200	107.446	532.563	439.266	298.548	−479.357	−92.572	1.511
3300	107.484	535.869	442.144	309.295	−479.053	−80.490	1.274
3400	107.518	539.079	444.948	320.045	−478.742	−68.417	1.051
3500	107.550	542.196	447.682	330.798	−478.422	−56.353	0.841
3600	107.579	545.226	450.350	341.555	−478.092	−44.298	0.643
3700	107.606	548.174	452.954	352.314	−477.747	−32.253	0.455
3800	107.631	551.044	455.498	363.076	−477.386	−20.218	0.278
3900	107.654	553.840	457.984	373.840	−477.007	−8.192	0.110
4000	107.675	556.566	460.414	384.607	−476.607	3.824	−0.050
4100	107.695	559.225	462.792	395.375	−476.183	15.830	−0.202
4200	107.713	561.820	465.119	406.146	−475.733	27.825	−0.346
4300	107.731	564.355	467.397	416.918	−475.256	39.808	−0.484
4400	107.746	566.832	469.629	427.692	−474.749	51.781	−0.615
4500	107.761	569.253	471.816	438.467	−474.211	63.742	−0.740
4600	107.775	571.622	473.960	449.244	−473.639	75.690	−0.859
4700	107.788	573.940	476.063	460.022	−473.032	87.625	−0.974
4800	107.801	576.210	478.126	470.802	−472.389	99.547	−1.083
4900	107.812	578.432	480.150	481.582	−471.709	111.456	−1.188
5000	107.823	580.611	482.138	492.364	−470.990	123.350	−1.289
5100	107.833	582.746	484.090	503.147	−470.232	135.229	−1.385
5200	107.843	584.840	486.007	513.931	−469.434	147.093	−1.478
5300	107.852	586.894	487.891	524.716	−468.595	158.942	−1.566
5400	107.861	588.910	489.743	535.501	−467.715	170.774	−1.652
5500	107.869	590.890	491.564	546.288	−466.794	182.589	−1.734
5600	107.877	592.833	493.356	557.075	−465.831	194.388	−1.813
5700	107.884	594.743	495.118	567.863	−464.827	206.168	−1.889
5800	107.891	596.619	496.851	578.652	−463.782	217.931	−1.963
5900	107.897	598.463	498.558	589.441	−462.695	229.676	−2.033
6000	107.904	600.277	500.238	600.231	−461.568	241.400	−2.102

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 283.796\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -218.371 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -220.08 \pm 3.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[570] (1)
1827 (1)
285 (1)
849 (1)
440 (1)
[585] (1)

Ground State Quantum Weight: 1
Point Group: C_{2v} $\sigma = 2$
Bond Distances: C–O = 1.166 ± 0.002 Å; Cl–O = 2.589 ± 0.001 Å;
Cl–Cl = 2.884 ± 0.001 Å; C–Cl = 1.746 ± 0.004 Å
Bond Angle: Cl–C–Cl = 111.3 ± 0.1°
Product of the Moments of Inertia: $I_A I_B I_C = 9.138289 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

Thomsen[1] reports the enthaply of alkaline hydrolysis of $COCl_2$, from which $\Delta_f H°(298.15\ K)$ is calculated to be -54.4 ± 0.3 kcal·mol^{-1}. From the enthalpy of combustion of $COCl_2$ in O_2 and H_2, reported by Thomsen,[2] $\Delta_f H°(298.15\ K)$ is calculated to be -51.73 ± 0.43 kcal·mol^{-1}. Bodenstein and Plaut,[3] Christiansen,[4] and Bodenstein and Dunant[5] report 10 values of K_p from 647 to 876 K for the reaction $CO + Cl_2 = COCl_2$. These yield -25.91 ± 0.04 kcal for $\Delta_f H°(298.15\ K)$ for $COCl_2$ is -52.33 ± 0.62 kcal·mol^{-1}. The average of the 3 foregoing values of $\Delta_f H°(298.15\ K)$ weighted for the uncertainties, is adopted here. Values calculated from the degree of dissociation of $COCl_2$ from 374 to 778 K, reported by Atkinson *et al.*,[6] range from -47.06 to -53.11 kcal·mol^{-1} and are ignored.

Heat Capacity and Entropy

The vibrational frequencies were assigned by Catalano and Pitzer,[7] on the basis of their own infra-red spectra and other data. The molecular dimensions listed above were deduced from microwave spectra by Robinson,[8] and are confirmed by electron-diffraction values compiled by Allen and Sutton.[9] The moments of inertia are weighted for the isotopes and were calculated from Robinson's dimensions by Giauque and Ott.[10] Giauque and Ott[10] determined $S°(298.15\ K)$ experimentally to be 67.81 cal·K^{-1}·mol^{-1}, with which the value calculated here agrees, i.e. 67.816 cal·K^{-1}·mol^{-1}. The principal moments of inertia are: $I_A = 10.6393 \times 10^{-39}$, $I_B = 24.4666 \times 10^{-39}$, and $I_C = 35.1059 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.867	−218.372	−218.372	INFINITE
100	36.537	233.747	328.453	−9.471	−219.399	−215.113	112.363
200	48.362	262.618	288.800	−5.236	−219.985	−210.551	54.990
250	53.603	273.992	284.724	−2.683	−220.075	−208.180	43.497
298.15	57.695	283.796	283.796	0.	−220.078	−205.887	36.071
300	57.835	284.153	283.797	0.107	−220.077	−205.799	35.833
350	61.211	293.332	284.514	3.086	−220.026	−203.423	30.359
400	63.938	301.689	286.147	6.217	−219.945	−201.056	26.255
450	66.184	309.354	288.305	9.472	−219.853	−198.701	23.065
500	68.068	316.427	290.768	12.830	−219.760	−196.356	20.513
600	71.048	329.115	296.127	19.793	−219.587	−191.691	16.688
700	73.282	340.242	301.650	27.014	−219.438	−187.054	13.958
800	74.993	350.144	307.105	34.432	−219.309	−182.437	11.912
900	76.324	359.057	312.390	42.000	−219.198	−177.835	10.321
1000	77.373	367.155	317.468	49.687	−219.102	−173.244	9.049
1100	78.210	374.570	322.327	57.468	−219.020	−168.662	8.009
1200	78.886	381.406	326.969	65.324	−218.952	−164.087	7.143
1300	79.437	387.742	331.403	73.241	−218.898	−159.517	6.409
1400	79.891	393.646	335.641	81.208	−218.859	−154.951	5.781
1500	80.270	399.172	339.694	89.217	−218.836	−150.387	5.237
1600	80.588	404.363	343.575	97.260	−218.831	−145.824	4.761
1700	80.857	409.256	347.296	105.332	−218.845	−141.261	4.340
1800	81.086	413.885	350.868	113.430	−218.880	−136.697	3.967
1900	81.284	418.274	354.301	121.549	−218.937	−132.130	3.632
2000	81.455	422.448	357.605	129.686	−219.018	−127.559	3.331
2100	81.604	426.426	360.788	137.839	−219.125	−122.983	3.059
2200	81.734	430.225	363.859	146.006	−219.259	−118.402	2.811
2300	81.849	433.861	366.824	154.185	−219.423	−113.814	2.585
2400	81.950	437.347	369.690	162.375	−219.618	−109.218	2.377
2500	82.040	440.694	372.464	170.575	−219.846	−104.614	2.186
2600	82.120	443.913	375.150	178.783	−220.108	−99.999	2.009
2700	82.192	447.014	377.755	186.999	−220.405	−95.374	1.845
2800	82.257	450.004	380.282	195.221	−220.738	−90.737	1.693
2900	82.316	452.892	382.737	203.450	−221.108	−86.088	1.551
3000	82.368	455.683	385.122	211.684	−221.515	−81.425	1.418
3100	82.416	458.385	387.442	219.923	−221.958	−76.748	1.293
3200	82.460	461.002	389.700	228.167	−222.437	−72.057	1.176
3300	82.500	463.540	391.899	236.415	−222.951	−67.350	1.066
3400	82.537	466.004	394.043	244.667	−223.498	−62.626	0.962
3500	82.570	468.397	396.133	252.922	−224.076	−57.887	0.864
3600	82.601	470.723	398.173	261.181	−224.685	−53.130	0.771
3700	82.629	472.987	400.164	269.443	−225.320	−48.356	0.683
3800	82.656	475.191	402.110	277.707	−225.981	−43.564	0.599
3900	82.680	477.338	404.011	285.974	−226.664	−38.754	0.519
4000	82.703	479.432	405.871	294.243	−227.366	−33.927	0.443
4100	82.724	481.474	407.690	302.514	−228.085	−29.083	0.371
4200	82.743	483.468	409.471	310.787	−228.819	−24.220	0.301
4300	82.761	485.415	411.214	319.063	−229.564	−19.340	0.235
4400	82.778	487.318	412.922	327.340	−230.318	−14.442	0.171
4500	82.794	489.178	414.596	335.618	−231.079	−9.528	0.111
4600	82.809	490.998	416.237	343.898	−231.844	−4.596	0.052
4700	82.823	492.779	417.847	352.180	−232.611	0.352	−0.004
4800	82.836	494.523	419.426	360.463	−233.378	5.317	−0.058
4900	82.848	496.231	420.976	368.747	−234.143	10.299	−0.110
5000	82.860	497.905	422.498	377.033	−234.905	15.295	−0.160
5100	82.871	499.546	423.993	385.319	−235.662	20.306	−0.208
5200	82.881	501.155	425.462	393.607	−236.413	25.332	−0.254
5300	82.891	502.734	426.905	401.895	−237.157	30.373	−0.299
5400	82.900	504.284	428.323	410.185	−237.893	35.428	−0.343
5500	82.909	505.805	429.718	418.476	−238.620	40.496	−0.385
5600	82.917	507.299	431.090	426.767	−239.339	45.577	−0.425
5700	82.925	508.766	432.440	435.059	−240.048	50.671	−0.464
5800	82.932	510.209	433.769	443.352	−240.748	55.778	−0.502
5900	82.939	511.626	435.076	451.645	−241.438	60.896	−0.539
6000	82.946	513.020	436.364	459.940	−242.119	66.026	−0.575

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 296.83 \pm 6.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 80.1 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 79.5 \pm 8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[450] (1)
[460] (1)
898 (2)
[240] (2)

Ground State Quantum Weight: 2 $\sigma = 6$

Point Group: D_{3h}

Bond Distance: C–Cl = [1.74]Å

Bond Angle: Cl–C–Cl = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.822311 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

Benson[1] has reanalysed the kinetic data of Sullivan and Davidson[2] for the reaction $Br_2(g) + CHCl_3(g) = HBr(g) + CBrCl_3(g)$ and has obtained from it the enthalpy of the initial step, $Br(g) + CHCl_3(g) \rightarrow CCl_3(g) + HBr(g)$, as 8.2 ± 1 kcal·mol^{-1}. Substituting this value and $\Delta_f H°(Br, g, 298.15\ K) = 26.74\ kcal·mol^{-1}$, $\Delta_f H°(CHCl_3, g, 298.15\ K) = -24.66\ kcal·mol^{-1}$ and $\Delta_f H°(HBr, g, 298.15\ K) = -8.71\ kcal·mol^{-1}$, we obtain $\Delta_f H°(CCl_3, g, 298.15\ K) = 19 \pm 2\ kcal·mol^{-1}$ (79.496 ± 8 kJ·mol^{-1}), which is adopted here.

Heat Capacity and Entropy

Walsh[3] has predicted that CCl_3 is non–planar on the basis of his orbital correlation diagram. Andrews[4] indicates that his matrix infrared observations of the symmetric and antisymmetric stretches are consistent with a non–planar C_{3v} structure and a near tetrahedral angle. The antisymmetric stretch has been confirmed by Current and Burdett.[5] They rationalize the absence of the symmetric stretch and claim support of the C_{3v} structure. Rogers *et al.*[6] have made a thorough search for the symmetric stretch and did not find it in the region where is was reported by Andrews.[4] Thus, they conclude that since only the antisymmetric stretch has been confirmed, the possibility of a planar D_{3h} molecule cannot be excluded. Maget *et al.*[7] have observed the NMR spectrum of trapped CCl_3 and find it consistent with a planar molecule. The absence of the symmetric stretch strongly implies a planar configuration, and we adopt such a configuration until more definitive proof of the non–planarity can be obtained. The remaining vibrational frequencies are estimated by comparison with those of BCl_3. The bond length was estimated as 1.74 Å by Andrews[4] from a correlation with related molecules. The principal moments of inertia are: $I_A = I_B = 26.7361 \times 10^{-39}$ and $I_C = 53.4723 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.194	80.125	80.125	INFINITE
100	40.983	240.296	346.941	−10.665	79.226	83.643	−43.691
200	54.687	273.207	302.392	−5.837	79.171	88.135	−23.018
250	59.708	285.968	297.860	−2.973	79.311	90.361	−18.880
298.15	63.649	296.833	296.833	0.	79.496	92.473	−16.201
300	63.784	297.228	296.835	0.118	79.504	92.554	−16.115
350	67.068	307.316	297.624	3.392	79.729	94.711	−14.135
400	69.696	316.450	299.415	6.814	79.972	96.835	−12.645
450	71.799	324.785	301.778	10.353	80.219	98.928	−11.483
500	73.488	332.440	304.466	13.987	80.462	100.994	−10.551
600	75.965	346.073	310.293	21.468	80.916	105.057	−9.146
700	77.636	357.916	316.269	29.153	81.321	109.048	−8.137
800	78.803	368.364	322.141	36.978	81.676	112.984	−7.377
900	79.643	377.697	327.805	44.903	81.985	116.878	−6.783
1000	80.266	386.122	333.222	52.900	82.254	120.741	−6.307
1100	80.739	393.795	338.385	60.951	82.486	124.578	−5.916
1200	81.106	400.837	343.300	69.044	82.685	128.395	−5.589
1300	81.396	407.341	347.979	77.170	82.853	132.197	−5.312
1400	81.629	413.381	352.438	85.321	82.993	135.988	−5.074
1500	81.818	419.020	356.690	93.494	83.105	139.769	−4.867
1600	81.975	424.306	360.753	101.684	83.190	143.544	−4.686
1700	82.105	429.279	364.639	109.888	83.249	147.314	−4.526
1800	82.215	433.975	368.362	118.104	83.282	151.081	−4.384
1900	82.309	438.423	371.933	126.331	83.288	154.847	−4.257
2000	82.389	442.647	375.364	134.566	83.268	158.614	−4.143
2100	82.458	446.669	378.665	142.808	83.219	162.383	−4.039
2200	82.518	450.506	381.844	151.057	83.140	166.154	−3.945
2300	82.571	454.175	384.909	159.311	83.030	169.930	−3.859
2400	82.617	457.690	387.869	167.571	82.886	173.711	−3.781
2500	82.658	461.064	390.730	175.835	82.708	177.499	−3.709
2600	82.694	464.306	393.498	184.102	82.492	181.295	−3.642
2700	82.726	467.428	396.179	192.373	82.239	185.100	−3.581
2800	82.756	470.437	398.777	200.647	81.947	188.914	−3.524
2900	82.782	473.342	401.299	208.924	81.615	192.740	−3.472
3000	82.805	476.148	403.747	217.204	81.243	196.578	−3.423
3100	82.827	478.864	406.127	225.485	80.831	200.430	−3.377
3200	82.846	481.494	408.441	233.769	80.381	204.294	−3.335
3300	82.864	484.043	410.694	242.054	79.893	208.175	−3.295
3400	82.880	486.517	412.887	250.342	79.370	212.069	−3.258
3500	82.895	488.920	415.026	258.630	78.814	215.980	−3.223
3600	82.908	491.255	417.111	266.921	78.228	219.908	−3.191
3700	82.921	493.527	419.146	275.212	77.614	223.852	−3.160
3800	82.932	495.739	421.132	283.505	76.976	227.812	−3.131
3900	82.943	497.893	423.073	291.798	76.319	231.790	−3.104
4000	82.953	499.993	424.970	300.093	75.645	235.785	−3.079
4100	82.962	502.042	426.825	308.389	74.959	239.797	−3.055
4200	82.971	504.041	428.640	316.686	74.265	243.826	−3.032
4300	82.979	505.993	430.416	324.983	73.566	247.872	−3.011
4400	82.986	507.901	432.155	333.281	72.866	251.933	−2.991
4500	82.993	509.766	433.859	341.580	72.170	256.011	−2.972
4600	82.999	511.590	435.529	349.880	71.480	260.104	−2.954
4700	83.005	513.375	437.167	358.180	70.800	264.212	−2.936
4800	83.011	515.123	438.773	366.481	70.133	268.334	−2.920
4900	83.016	516.835	440.348	374.782	69.483	272.470	−2.905
5000	83.022	518.512	441.895	383.084	68.852	276.619	−2.890
5100	83.026	520.156	443.413	391.387	68.242	280.780	−2.876
5200	83.031	521.768	444.905	399.689	67.656	284.953	−2.862
5300	83.035	523.350	446.370	407.993	67.095	289.138	−2.850
5400	83.039	524.902	447.810	416.296	66.562	293.332	−2.837
5500	83.043	526.426	449.226	424.601	66.059	297.537	−2.826
5600	83.046	527.922	450.617	432.905	65.586	301.749	−2.815
5700	83.050	529.392	451.987	441.210	65.144	305.970	−2.804
5800	83.053	530.836	453.334	449.515	64.736	310.199	−2.794
5900	83.056	532.256	454.659	457.820	64.360	314.435	−2.784
6000	83.059	533.652	455.964	466.126	64.019	318.676	−2.774

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 309.735 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -285.52 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -288.70 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
349.5(1)	241(2)
535.3(1)	398(2)
1085 (1)	847(2)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Bond Distances: C–Cl = 1.76 Å; C–F = 1.33 Å

Bond Angles: Cl–C–Cl = 109°40'; F–C–Cl = 109°28'

Product of the Moments of Inertia: $I_A I_B I_C = 5.736023 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

Mears and Stahl[1] investigated several enthalpiess of reaction involving CF_4, CF_3Cl, CF_2Cl_2, $CFCl_3$, CCl_4, HF and HCl. Using JANAF values for all compounds except CF_2Cl_2 and $CFCl_3$, we obtain the following observations:

1. $\Delta_f H°(CCl_3F, g, 298.15\ K) = -70.12 \pm 1.1\ kcal \cdot mol^{-1}$
2. $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -116.53 \pm 1.5\ kcal \cdot mol^{-1}$
3. $\Delta_f H°(CCl_2F_2, g, 298.15\ K) - \Delta_f H°(CCl_3F, g, 298.15\ K) = -49.39 \pm 1.0\ kcal \cdot mol^{-1}$
4. $\Delta_f H°(CCl_2F_2, g, 298.15\ K) - 2\Delta_f H°(CCl_3F, g, 298.15\ K) = 20.34 \pm 1.0\ kcal \cdot mol^{-1}$
5. $\Delta_f H°(CCl_3F, g, 298.15\ K) - 2\Delta_f H°(CCl_2F_2, g, 298.15\ K) = 165.47 \pm 1.0\ kcal \cdot mol^{-1}$

The sum of the squares of the deviations is smallest when $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -117.5\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_3F, g, 298.15\ K) = -69\ kcal \cdot mol^{-1}$, and all the values are within their uncertainty ranges.

Petersen and Pitzer[9] obtained an approximate equilibrium constant for the reaction $CClF_3(g) + 2CCl_4(g) = 3CCl_3F(g)$ of $\log K_{400} = -4.5$. This on third law reduction gives $\Delta_f H°(298.15\ K) = 10.56\ kcal \cdot mol^{-1}$ and with $\Delta_f H°(CClF_3, g, 298.15\ K) = -169.2\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_4, g, 298.15\ K) = -22.94\ kcal \cdot mol^{-1}$ this yields $\Delta H°(CCl_3F, g, 298.15K) = -68.2\ kcal \cdot mol^{-1}$. Kirkbride and Davidson[2] investigated the reaction of potassium with the chlorofluoromethanes and obtained $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -115.1 \pm 2\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_3F, g, 298.15\ K) = -72.9 \pm 4\ kcal \cdot mol^{-1}$ after correction with JANAF auxiliary data. Wartenberg and Schiefer[3] investigated the same reaction and we obtain, after correction with JANAF auxiliary data, $\Delta_f H°(CCl_2F_2, g, 298.15\ K) = -112.7\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_3F, g, 298.15\ K) = -63.1\ kcal \cdot mol^{-1}$. Baibuz[4] has reported $\Delta_f H°(CCl_3F, g, 298.15\ K) = -66.4 \pm 2.1$ from heat of explosion measurements. A correlation of his other results would indicate that this value is not negative enough, possibly by as much as 3 $kcal \cdot mol^{-1}$.

We adopt the values calculated above from Mears and Stahl,[1] since they have a high degree of internal consistency and also lead to a realistic progression in the heats of atomization in going from CF_4 to CCl_4. With the adopted enthalpies of formation, the successive replacement of F by Cl changes the atomization enthalpies by 43.8, 41.6, 38.5 and 36.0 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Claassen[5] chose the frequencies given above from his own gas phase Raman measurements and the infrared values of earlier investigators. The values are in good agreement with the assignment of Plyler and Benedict,[6] and the matrix studies of King.[7] The molecular structure was *determined from the microwave measurements of Long et al.*[8] The principal moments of inertia are: $I_A = I_B = 34.3029 \times 10^{-39}$ and $I_C = 48.7471 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.060	−285.522	−285.522	INFINITE
100	43.323	244.360	369.234	−12.487	−287.829	−275.301	143.802
200	64.411	281.288	316.474	−7.037	−288.727	−262.314	68.509
250	72.066	296.515	310.988	−3.618	−288.783	−255.700	53.426
298.15	78.018	309.735	309.735	0.	−288.696	−249.335	43.682
300	78.223	310.219	309.737	0.145	−288.691	−249.090	43.371
350	83.173	322.662	310.708	4.184	−288.494	−242.505	36.192
400	87.149	334.038	312.924	8.446	−288.227	−235.952	30.812
450	90.347	344.494	315.859	12.886	−287.912	−229.437	26.632
500	92.930	354.151	319.211	17.470	−287.569	−222.957	23.292
600	96.749	371.455	326.511	26.967	−286.835	−210.103	18.291
700	99.350	386.577	334.034	36.780	−286.079	−197.374	14.728
800	101.178	399.969	341.455	46.811	−285.322	−184.754	12.063
900	102.502	411.967	348.635	56.999	−284.577	−172.228	9.996
1000	103.488	422.820	355.520	67.300	−283.848	−159.784	8.346
1100	104.238	432.720	362.094	77.688	−283.139	−147.412	7.000
1200	104.822	441.816	368.364	88.143	−282.452	−135.104	5.881
1300	105.284	450.225	374.342	98.649	−281.788	−122.852	4.936
1400	105.655	458.042	380.044	109.196	−281.148	−110.650	4.128
1500	105.959	465.342	385.490	119.778	−280.533	−98.493	3.430
1600	106.209	472.189	390.697	130.386	−279.943	−86.377	2.820
1700	106.418	478.634	395.682	141.018	−279.379	−74.296	2.283
1800	106.594	484.722	400.461	151.669	−278.842	−62.248	1.806
1900	106.744	490.489	405.049	162.336	−278.330	−50.229	1.381
2000	106.872	495.968	409.459	173.017	−277.845	−38.237	0.999
2100	106.983	501.185	413.704	183.710	−277.387	−26.268	0.653
2200	107.080	506.164	417.794	194.413	−276.957	−14.320	0.340
2300	107.164	510.926	421.741	205.125	−276.553	−2.391	0.054
2400	107.239	515.488	425.552	215.846	−276.178	9.521	−0.207
2500	107.304	519.867	429.238	226.573	−275.830	21.418	−0.448
2600	107.363	524.077	432.805	237.306	−275.510	33.302	−0.669
2700	107.415	528.130	436.261	248.045	−275.219	45.174	−0.874
2800	107.462	532.037	439.612	258.789	−274.955	57.035	−1.064
2900	107.504	535.809	442.865	269.537	−274.719	68.888	−1.241
3000	107.542	539.454	446.024	280.290	−274.508	80.732	−1.406
3100	107.576	542.981	449.095	291.045	−274.323	92.571	−1.560
3200	107.607	546.397	452.083	301.805	−274.161	104.403	−1.704
3300	107.636	549.708	454.991	312.567	−274.020	116.231	−1.840
3400	107.662	552.922	457.824	323.332	−273.897	128.055	−1.967
3500	107.685	556.043	460.586	334.099	−273.791	139.875	−2.088
3600	107.707	559.077	463.280	344.869	−273.697	151.693	−2.201
3700	107.728	562.029	465.909	355.640	−273.613	163.509	−2.308
3800	107.746	564.902	468.477	366.414	−273.534	175.321	−2.410
3900	107.763	567.701	470.985	377.190	−273.458	187.132	−2.506
4000	107.779	570.429	473.437	387.967	−273.381	198.942	−2.598
4100	107.794	573.091	475.836	398.745	−273.298	210.749	−2.685
4200	107.808	575.688	478.182	409.526	−273.206	222.554	−2.768
4300	107.821	578.225	480.480	420.307	−273.102	234.356	−2.847
4400	107.832	580.704	482.729	431.090	−272.982	246.156	−2.922
4500	107.844	583.128	484.934	441.873	−272.842	257.953	−2.994
4600	107.854	585.498	487.094	452.658	−272.679	269.747	−3.063
4700	107.864	587.818	489.213	463.444	−272.490	281.537	−3.129
4800	107.873	590.089	491.291	474.231	−272.273	293.322	−3.192
4900	107.882	592.313	493.330	485.019	−272.024	305.103	−3.252
5000	107.890	594.493	495.331	495.807	−271.742	316.878	−3.310
5100	107.897	596.629	497.297	506.597	−271.424	328.648	−3.366
5200	107.905	598.724	499.227	517.387	−271.068	340.410	−3.419
5300	107.911	600.780	501.124	528.178	−270.674	352.166	−3.471
5400	107.918	602.797	502.988	538.969	−270.238	363.913	−3.520
5500	107.924	604.777	504.821	549.761	−269.761	375.653	−3.568
5600	107.930	606.722	506.623	560.554	−269.241	387.383	−3.613
5700	107.935	608.632	508.396	571.347	−268.678	399.103	−3.657
5800	107.940	610.510	510.140	582.141	−268.070	410.814	−3.700
5900	107.945	612.355	511.857	592.935	−267.418	422.513	−3.741
6000	107.950	614.169	513.547	603.730	−266.721	434.200	−3.780

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 309.809 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -93.81 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -95.98 \pm 2.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
458 (1)
218 (2)
776 (3)
314 (3)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: T_d

Bond Distance: C–Cl = 1.760 Å

Bond Angle: Cl–C–Cl = 109.47°

Product of the Moments of Inertia: $I_A I_B I_C = 1.150034 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

Hu and Sinke[1] have measured the enthalpy of combustion of CCl_4(l) in the rotating platinum bomb calorimeter, using As_2O_3 solution as the reducing agent. They reported $\Delta_c H°(298.15\ K) = -86.02\ kcal \cdot mol^{-1}$ for $CCl_4(l) + 2H_2O(l) \rightarrow CO_2(g) + 4HCl$ (600 H_2O, aq) which leads to $\Delta_f H°(CCl_4, l, 298.15\ K) = -30.69\ kcal \cdot mol^{-1}$, using $\Delta_f H°(298.15\ K) = -94.051$, − 39.823 and − 68.315 $kcal \cdot mol^{-1}$ for CO_2(g), HCl(600 H_2O, aq) and H_2O(l), respectively.[2] The standard deviation of five combustion runs was ± 0.074 $kcal \cdot mol^{-1}$. Employing the enthalpy of vaporization of CCl_4(l) at 298.15 K as 7.75 $kcal \cdot mol^{-1}$,[3] we obtain $\Delta_f H°(CCl_4, g, 298.15K) = -22.94\ kcal \cdot mol^{-1}$ which is adopted in the tabulation.

Smith *et al.*,[5] based on the combustion data of Eftring,[4] re–evaluated the enthalpy of combustion of carbon tetrachloride at 18.7°C as $\Delta_c E°/M = -567.5\ cal \cdot g^{-1}$ for $CCl_4(l) + 2\ H_2O(l) \rightarrow CO_2(g) + 4HCl(600H_2O, aq)$. This value needs to be further corrected for a change in the heat of oxidation of As_2O_3[6] and calculated to 25°C to give $\Delta_c E°(298.15\ K) = -88.105\ kcal \cdot mol^{-1}$. $\Delta_c H°(298.15\ K) = -87.513\ kcal \cdot mol^{-1}$, $\Delta_f H°(CCl_4, l, 298.15\ K) = -29.20\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CCl_4, g, 298.15\ K) = -21.45\ kcal \cdot mol^{-1}$.

Neugebauer[7] has measured the enthalpy of reaction of CCl_4 with Mg in presence of hydrogen in the stationary bomb calorimeter and then derived the enthalpy of formation, $\Delta_f H°(CCl_4, l, 298.15\ K) = -32.3 \pm 2\ kcal \cdot mol^{-1}$ which yields $\Delta_f H°(CCl_4, g, 298.15\ K) = -24.55 \pm 2\ kcal \cdot mol^{-1}$. Baibuz,[8] using an explosion technique, obtained $\Delta_f H°(CCl_4, g, 298.15\ K) = -24.6 \pm 1.9\ kcal \cdot mol^{-1}$. Bodenstein and Gunther[9] have measured calorimetrically $\Delta_f H°(293\ K) = -62.57 \pm 0.35\ kcal \cdot mol^{-1}$ for $CCl_4(g) + 2H_2(g) \rightarrow C(cr) + 4HCl(g)$. They calibrated their calorimeter by means of the reaction $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ for which they took $\Delta_f H°(293\ K) = -44\ kcal \cdot mol^{-1}$. Their data have been re–evaluated to give $\Delta_f H°(CCl_4, g, 298.15\ K) = -25.68\ kcal \cdot mol^{-1}$, but no correction is applied for the enthalpy of formation of carbon which was not the reference state "graphite" formed in the reaction. Domalski and Armstrong[10] reviewed several cases of active carbon formed in similar reactions and quoted a enthalpy of formation of carbon from +1.9 to +3.95 $kcal \cdot mol^{-1}$. If this correction is applied to the data of Bodenstein, their enthalpy of formation of CCl_4(g) should be 2 to 4 $kcal \cdot mol^{-1}$ less negative than $-25.68\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Bartell *et al.*[11] have measured the bond distance as 1.760 ± 0.004 Å by the electron diffrction measurement. The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection[12] in which they are essentially the same as those frequencies determined from Raman and infrared spectra by Classen.[13] The principal moments of inertia are $I_A = I_B = I_C = 48.6299 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.238	−93.806	−93.806	INFINITE
100	47.244	238.738	374.168	−13.543	−95.995	−81.972	42.818
200	69.995	279.142	317.054	−7.582	−96.436	−67.662	17.672
250	77.656	295.619	311.152	−3.883	−96.270	−60.485	12.638
298.15	83.401	309.809	309.809	0.	−95.981	−53.617	9.393
300	83.594	310.326	309.811	0.154	−95.968	−53.354	9.290
350	88.174	323.571	310.846	4.454	−95.577	−46.282	6.907
400	91.707	335.586	313.200	8.954	−95.131	−39.270	5.128
450	94.451	346.553	316.305	13.611	−94.654	−32.315	3.751
500	96.602	356.620	319.840	18.390	−94.165	−25.415	2.655
600	99.676	374.525	327.500	28.215	−93.182	−11.757	1.024
700	101.698	390.052	335.352	38.290	−92.223	1.737	−0.130
800	103.086	403.728	343.061	48.534	−91.300	15.096	−0.986
900	104.074	415.930	350.492	58.894	−90.415	28.342	−1.645
1000	104.800	426.935	357.595	69.340	−89.566	41.492	−2.167
1100	105.348	436.950	364.361	79.848	−88.751	54.558	−2.591
1200	105.771	446.135	370.798	90.405	−87.969	67.551	−2.940
1300	106.103	454.615	376.923	100.999	−87.219	80.481	−3.234
1400	106.370	462.488	382.757	111.624	−86.498	93.353	−3.483
1500	106.586	469.835	388.320	122.272	−85.806	106.175	−3.697
1600	106.765	476.720	393.632	132.940	−85.142	118.952	−3.883
1700	106.913	483.197	398.712	143.624	−84.508	131.689	−4.046
1800	107.038	489.311	403.577	154.321	−83.902	144.389	−4.190
1900	107.144	495.101	408.243	165.031	−83.326	157.055	−4.318
2000	107.235	500.600	412.725	175.750	−82.781	169.693	−4.432
2100	107.313	505.834	417.035	186.477	−82.270	182.304	−4.535
2200	107.381	510.827	421.186	197.212	−81.793	194.891	−4.627
2300	107.441	515.602	425.188	207.953	−81.354	207.458	−4.712
2400	107.493	520.176	429.051	218.700	−80.954	220.006	−4.788
2500	107.539	524.565	432.784	229.452	−80.597	232.539	−4.859
2600	107.580	528.783	436.396	240.208	−80.285	245.058	−4.923
2700	107.617	532.844	439.893	250.968	−80.019	257.566	−4.983
2800	107.650	536.759	443.283	261.731	−79.802	270.065	−5.038
2900	107.679	540.537	446.572	272.497	−79.633	282.557	−5.089
3000	107.706	544.188	449.765	283.267	−79.514	295.044	−5.137
3100	107.730	547.720	452.869	294.038	−79.444	307.528	−5.182
3200	107.752	551.140	455.886	304.813	−79.422	320.010	−5.224
3300	107.772	554.456	458.823	315.589	−79.446	332.493	−5.263
3400	107.790	557.674	461.684	326.367	−79.513	344.977	−5.300
3500	107.807	560.799	464.471	337.147	−79.621	357.464	−5.335
3600	107.822	563.836	467.189	347.928	−79.766	369.954	−5.368
3700	107.836	566.790	469.841	358.711	−79.943	382.448	−5.399
3800	107.849	569.666	472.431	369.495	−80.148	394.948	−5.429
3900	107.861	572.468	474.960	380.281	−80.377	407.453	−5.457
4000	107.872	575.199	477.432	391.067	−80.623	419.965	−5.484
4100	107.883	577.863	479.849	401.855	−80.883	432.483	−5.510
4200	107.892	580.462	482.214	412.644	−81.150	445.007	−5.534
4300	107.901	583.001	484.528	423.434	−81.419	457.538	−5.558
4400	107.909	585.482	486.795	434.224	−81.686	470.075	−5.581
4500	107.917	587.907	489.015	445.015	−81.946	482.618	−5.602
4600	107.925	590.279	491.191	455.808	−82.193	495.167	−5.623
4700	107.931	592.600	493.324	466.600	−82.423	507.720	−5.643
4800	107.938	594.873	495.416	477.394	−82.632	520.279	−5.662
4900	107.944	597.098	497.468	488.188	−82.815	532.842	−5.680
5000	107.949	599.279	499.483	498.983	−82.971	545.407	−5.698
5100	107.955	601.417	501.460	509.778	−83.094	557.977	−5.715
5200	107.960	603.513	503.403	520.574	−83.181	570.547	−5.731
5300	107.965	605.570	505.311	531.370	−83.231	583.119	−5.747
5400	107.969	607.588	507.187	542.166	−83.241	595.692	−5.762
5500	107.973	609.569	509.030	552.964	−83.209	608.265	−5.777
5600	107.977	611.515	510.843	563.761	−83.132	620.837	−5.791
5700	107.981	613.426	512.626	574.559	−83.010	633.406	−5.805
5800	107.985	615.304	514.380	585.357	−82.841	645.974	−5.818
5900	107.988	617.150	516.106	596.156	−82.624	658.538	−5.830
6000	107.992	618.965	517.806	606.955	−82.358	671.097	−5.842

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 90.002 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 746\ K$

$\Delta_f H°(0\ K) = 93.32 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 94.98 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 12 \pm 4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Taylor *et al.*[1] determined by solution calorimetry the enthalpy of reaction, $\Delta_r H°(298.15\ K) = -13.437 \pm 100\ cal \cdot K^{-1} \cdot mol^{-1}$ for NaCN(cr) + 0.5 Cu_2O(cr) + 0.5 H_2O(l) → CuCN(cr) + NaOH(128.5 H_2O). This leads to $\Delta_f H°$(CuCN, cr, 298.15 K) = 22.70 ± 0.5 kcal·mol^{-1} using the following auxiliary data: $\Delta_f H°$(NaCN, cr, 298.15 K) = −21.68 ± 0.3 kcal·mol^{-1},[2] $\Delta_f H°$(Cu_2O, cr, 298.15 K) = −40.7 ± 0.5 kcal·mol^{-1},[3] $\Delta_f H°$(H_2O, l, 298.15 K) = −68.315 kcal·mol^{-1} [4] and $\Delta_f H°$(NaOH·128.5 H_2O, aq, 298.15 K) = −112.321 kcal·mol^{-1}.[2,4]

Heat Capacity and Entropy

The heat capacity of CuCN(cr) has been measured adiabatically over the temperature range from 8 to 402 K by Taylor *et al.*[1] The smooth $C_p°$ values are adopted in the tabulation. The value of $S°(298.15\ K)$ is calculated from the $C_p°$ data and is based on an extrapolation of $S°(8\ K) = 0.104\ cal \cdot K^{-1} \cdot mol^{-1}$. They also found an anomaly in the heat capacity at 300 K which is considered as a second order phase transition. Heat capacities above 402 K are estimated by extrapolation of the measured $C_p°$ data.

Fusion Data

The melting point 746 K was determined by Truthe.[5] The heat of melting is calculated from the phase diagram studies of KCN–CuCN and NaCN–CuCN reported by Truthe.[5]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.052	93.317	93.317	INFINITE
100	35.238	36.869	137.842	−10.097	93.093	98.495	−51.449
200	52.484	67.308	95.337	−5.606	93.790	103.689	−27.081
298.15	61.024	90.002	90.002	0.	94.977	108.306	−18.975
300	62.195	90.383	90.003	0.114	95.003	108.389	−18.872
400	66.735	108.930	92.500	6.572	96.486	112.628	−14.708
500	70.249	124.212	97.358	13.427	97.978	116.491	−12.170
600	73.136	137.282	102.949	20.600	99.462	120.054	−10.452
700	75.689	148.753	108.689	28.045	100.938	123.370	−9.206
800	78.032	159.016	114.350	35.733	102.427	126.473	−8.258
900	80.249	168.337	119.838	43.649	103.943	129.388	−7.509
1000	82.341	176.900	125.122	51.778	105.495	132.132	−6.902

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = 213.03 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 251.6 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 255.2 \pm 8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_r$	0	2
	77.11	2
[$^4\Sigma$]	[25000]	[4]
	42705	2
	49452	2

$\omega_e = 1308.1\ cm^{-1}$ $\omega_e x_e = 11.10\ cm^{-1}$ $\sigma = 1$

$B_e = 1.4172\ cm^{-1}$ $\alpha_e = 0.0184\ cm^{-1}$ $r_e = 1.2667$ Å

Enthalpy of Formation

Faber *et al.*[1] have studied the weight change of graphite in CF_4 at high temperatures. Our reanalysis of their data use the equilibrium constants for CF_4, CF_3 and CF_2 from the JANAF Tables;[2] the only other C–F species considered is assumed to be CF. This treatment yields negative values for the CF pressure except at the highest temperature, where 3rd law analysis of the equilibrium constant yields $\Delta_f H°$(CF, g, 298.15 K) = 59.4 kcal·mol^{-1}. Farber *et al.*[1] also investigated mass–spectrometrically the vapor species present at equilibrium and followed the intensities of CF^+ and F^+. From a 2nd law treatment of the intensities they report $\Delta_f H°$(CF, g, 2300 K) = 62.0 kcal·mol^{-1}, or $\Delta_f H°$(CF, g, 298.15 K) = 64 kcal·mol^{-1}.

Porter *et al.*[3] have investigated the A–X band system under high dispersion. From an analytical extrapolation of the 10 observed levels they reported a dissociation energy of 126.9 ± 2.9 kcal·mol^{-1}, which yields $\Delta_f H°$(CF, g, 298.15 K) = 61.9 ± 2.9 kcal·mol^{-1}.

The predissociation limit of CF(g) has been reported by Thrush and Zwolenik[4] as <132 kcal·mol^{-1}; Kuzyakov and Tatievsky[5] determined the same quantity as <133 kcal·mol^{-1}. These results yield $\Delta_f H°$(CF, g, 298.15 K) > 56 kcal·mol^{-1}. Thrush and Zwolenik[4] also report a predissociation limit for the reaction $CF_2 \rightarrow CF + F$ which is <120 kcal·mol^{-1}. This value has now been shown to be erroneous (see the CF_2(g) table for details).

Modica[6] has studied the equilibrium $CF_2 \rightarrow CF + F$ in a shock tube in the range 2680 to 3400 K. Since functions for CF_2, CF and F are well established, the data were analyzed using 2nd and 3rd law treatments. The 2nd law analysis gives $\Delta_r H°(298.15\ K) = 107.2 \pm 7.6$ kcal·mol^{-1}, in agreement with with value reported by Modica. The 3rd law analysis yields $\Delta_r H°(298.15\ K) = 134.9 \pm 7.2$ kcal·mol^{-1} and a drift of 9.7 ± 2.5 cal·K^{-1}·mol^{-1}. The excessive drift indicates that the reported equilibrium constants do not represent the stated reaction.

Andrews and Barrow[7] report a dissociation energy of 114 kcal·mol^{-1} from an extrapolation of four B state levels. This extrapolation is considered unreliable by Porter *et al.*[3] since this state is formed from an avoided crossing and is likely to be perturbed.

The adopted value of $\Delta_f H°$(CF, g, 298.15 K) is 61 ± 2 kcal·mol^{-1} (255.224 ± 8 kJ·mol^{-1}), which is within the uncertainties and ranges of the acceptable investigations.

Heat Capacity and Entropy

The vibrational and rotational constants are from Porter *et al.*;[3] the higher electronic levels are those reported by Andrews and Barrow,[7] except that the B state is now considered to be $^2\Sigma$. The estimated level at 25000 cm^{-1} is proposed in order to explain the low bond dissociation energy of C_2F_2, by analogy with the reasoning used by Simons[8] for C_2F_4. This level would be a $^4\Sigma$ level and could correlate with the ground state atoms.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.082	251.605	251.605	INFINITE
100	31.017	180.140	239.625	−5.948	253.226	243.826	−127.361
200	29.778	201.126	215.766	−2.928	254.455	233.912	−61.092
250	29.792	207.766	213.526	−1.440	254.896	228.723	−47.789
298.15	30.060	213.033	213.033	0.	255.224	223.650	−39.183
300	30.074	213.219	213.034	0.056	255.235	223.455	−38.907
350	30.537	217.888	213.402	1.570	255.484	218.137	−32.555
400	31.094	222.002	214.224	3.111	255.658	212.789	−27.787
450	31.681	225.698	215.297	4.680	255.765	207.423	−24.077
500	32.253	229.066	216.508	6.279	255.816	202.049	−21.108
600	33.280	235.040	219.111	9.557	255.779	191.296	−16.654
700	34.116	240.235	221.766	12.928	255.602	180.561	−13.474
800	34.780	244.836	224.368	16.374	255.322	169.859	−11.091
900	35.305	248.964	226.875	19.880	254.966	159.197	−9.240
1000	35.725	252.706	229.274	23.432	254.550	148.577	−7.761
1100	36.064	256.127	231.562	27.022	254.086	138.002	−6.553
1200	36.343	259.278	233.742	30.643	253.583	127.471	−5.549
1300	36.576	262.196	235.820	34.289	253.046	116.983	−4.700
1400	36.773	264.914	237.802	37.957	252.479	106.538	−3.975
1500	36.942	267.457	239.695	41.643	251.885	96.134	−3.348
1600	37.088	269.846	241.506	45.344	251.267	85.771	−2.800
1700	37.218	272.098	243.240	49.060	250.628	75.447	−2.318
1800	37.333	274.229	244.903	52.787	249.969	65.161	−1.891
1900	37.436	276.250	246.500	56.526	249.292	54.913	−1.510
2000	37.530	278.173	248.036	60.274	248.601	44.700	−1.167
2100	37.617	280.006	249.515	64.032	247.896	34.522	−0.859
2200	37.697	281.758	250.941	67.797	247.180	24.378	−0.579
2300	37.771	283.435	252.318	71.571	246.456	14.267	−0.324
2400	37.841	285.044	253.648	75.352	245.725	4.187	−0.091
2500	37.907	286.591	254.935	79.139	244.990	−5.861	0.122
2600	37.970	288.079	256.181	82.933	244.253	−15.881	0.319
2700	38.030	289.513	257.389	86.733	243.516	−25.872	0.501
2800	38.089	290.897	258.561	90.539	242.780	−35.836	0.669
2900	38.145	292.234	259.700	94.351	242.047	−45.774	0.824
3000	38.200	293.528	260.806	98.168	241.319	−55.686	0.970
3100	38.254	294.782	261.882	101.991	240.597	−65.574	1.105
3200	38.307	295.997	262.929	105.819	239.882	−75.439	1.231
3300	38.360	297.177	263.949	109.652	239.175	−85.282	1.350
3400	38.413	298.323	264.943	113.491	238.477	−95.104	1.461
3500	38.466	299.437	265.913	117.335	237.789	−104.905	1.566
3600	38.519	300.521	266.859	121.184	237.110	−114.686	1.664
3700	38.572	301.578	267.783	125.038	236.442	−124.449	1.757
3800	38.627	302.607	268.686	128.898	235.785	−134.195	1.845
3900	38.682	303.611	269.569	132.764	235.139	−143.922	1.928
4000	38.738	304.591	270.432	136.635	234.505	−153.634	2.006
4100	38.796	305.548	271.277	140.511	233.882	−163.330	2.081
4200	38.855	306.484	272.104	144.394	233.270	−173.010	2.152
4300	38.915	307.399	272.915	148.282	232.670	−182.676	2.219
4400	38.977	308.294	273.709	152.177	232.081	−192.329	2.283
4500	39.040	309.171	274.487	156.078	231.504	−201.968	2.344
4600	39.105	310.030	275.250	159.985	230.938	−211.594	2.403
4700	39.172	310.871	275.999	163.899	230.383	−221.209	2.458
4800	39.241	311.697	276.734	167.820	229.839	−230.811	2.512
4900	39.311	312.507	277.456	171.747	229.306	−240.403	2.563
5000	39.383	313.301	278.165	175.682	228.784	−249.983	2.612
5100	39.457	314.082	278.862	179.624	228.272	−259.553	2.658
5200	39.532	314.849	279.546	183.573	227.771	−269.114	2.703
5300	39.610	315.603	280.220	187.530	227.279	−278.664	2.746
5400	39.689	316.344	280.882	191.495	226.798	−288.206	2.788
5500	39.769	317.073	281.533	195.468	226.327	−297.739	2.828
5600	39.851	317.790	282.174	199.449	225.865	−307.263	2.866
5700	39.935	318.496	282.805	203.438	225.413	−316.779	2.903
5800	40.021	319.192	283.427	207.436	224.970	−326.288	2.939
5900	40.107	319.876	284.039	211.443	224.536	−335.788	2.973
6000	40.196	320.551	284.642	215.458	224.111	−345.282	3.006

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 201.51 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1140.0 \pm 5.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 1149.4 \pm 5.0\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma$	0	1
$[a^3\Pi]$	[35000]	[6]

ω_e = [1380] cm^{-1} $\omega_e x_e$ = [11.6] cm^{-1} σ = 1
B_e = [1.4361] cm^{-1} α_e = [0.0193] cm^{-1} r_e = [1.263] Å

Enthalpy of Formation

There have been no direct determinations of the ionization potential but Johns and Barrow[1] have calculated a value by assuming the $B^2\Sigma^+$ state of CF to be the first of a Rydberg series. They report IP = 8.91 eV (205.464 $kcal·mol^{-1}$) which yields $\Delta_f H°(CF^+, g, 0\ K) = 265.6 \pm 10\ kcal·mol^{-1}$. An identical value has been calculated by Carroll and Grennan[7] who assumed the $A^2\Sigma^+$ state of CF to be the start of a Rydberg series and estimated the termination by comparison with the same series in N_2, CO and NO.

Diebler and Liston[2] have measured the photoionization onset of the process $FCN + h\nu \rightarrow CF^+ + N + e^-$ ($\Delta H°(0\ K) = 377.03\ kcal·mol^{-1}$). Using JANAF auxiliary data,[3] we obtain $\Delta_f H°(CF^+, g, 0\ K) = 273.0 \pm 4\ kcal·mol^{-1}$.

Walter *et al.*[4] have observed the photoionization onset of the process $C_2F_4 + h\nu \rightarrow CF^+ + CF_3 + e^-$ ($\Delta H°(0\ K) = 317.306 \pm 0.23\ kcal·mol^{-1}$. The JANAF values[3] for C_2F_4 and CF_3 are consistent since they are both derived from the same simultaneous solution, they yield $\Delta_f H°(CF^+, g, 0\ K) = 272.464 \pm 1.2\ kcal·mol^{-1}$(1139.989 $\pm$ 5.0 $kJ·mol^{-1}$), which is adopted. This corresponds to an ionization potential of 212.328 $kcal·mol^{-1}$ (9.21 eV).

Heat Capacity and Entropy

Spectra reported in the literature, Verma,[5] were later shown to belong to BF by Verma.[6] We estimated the molecular constants by comparison with CF(g) and BF(g).[3] The $^3\Pi$ electronic level was estimated by comparison with AlCl(g).[3] The enthalpy between 0 and 298.15 K is 2.072 $kcal·mol^{-1}$.

References

[1] J. W. C. Johns and R. F. Barrow, Proc. Phys. Soc. (London) **71A**, 476 (1958).
[2] V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).
[3] JANAF Thermochemical Tables: FCN(g), 6–30–69; N(g), 3–31–61; C_2F_4(g), 6–30–69; CF_3(g), 6–30–69; CF(g), 6–30–70; BF(g), 12–31–64;AlCl(g), 6–30–70.
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[6] R. D. Verma, Can. J. Phys. **40**, 1852 (1962).
[7] P. K. Carroll and T. P. Grennan, J. Phys. At. Mol. Phys. **3B**, 865 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.697	1139.985		
100	29.108	169.611	227.538	−5.793			
200	29.161	189.794	204.197	−2.881			
250	29.327	196.316	201.993	−1.419			
298.15	*29.641*	*201.507*	*201.507*	*0.*	*1149.416*	*1115.024*	*−195.348*
300	29.656	201.690	201.507	0.055	1149.464	1114.811	−194.106
350	30.125	206.295	201.870	1.549	1150.732	1108.934	−165.499
400	30.680	210.353	202.681	3.069	1151.925	1102.880	−144.021
450	31.266	214.001	203.740	4.617	1153.051	1096.682	−127.299
500	31.845	217.325	204.935	6.195	1154.120	1090.360	−113.909
600	32.900	223.227	207.504	9.434	1156.123	1077.418	−93.798
700	33.775	228.367	210.125	12.769	1157.988	1064.151	−79.408
800	34.477	232.924	212.695	16.183	1159.754	1050.624	−68.599
900	35.038	237.019	215.174	19.660	1161.448	1036.881	−60.179
1000	35.488	240.734	217.547	23.187	1163.086	1022.952	−53.434
1100	35.854	244.134	219.812	26.755	1164.678	1008.861	−47.907
1200	36.155	247.267	221.971	30.356	1166.234	994.627	−43.295
1300	36.405	250.172	224.030	33.984	1167.757	980.264	−39.388
1400	36.617	252.877	225.995	37.635	1169.252	965.785	−36.034
1500	36.798	255.410	227.873	41.306	1170.722	951.201	−33.124
1600	36.955	257.790	229.669	44.994	1172.169	936.519	−30.574
1700	37.093	260.035	231.390	48.697	1173.595	921.747	−28.322
1800	37.215	262.158	233.041	52.412	1175.003	906.891	−26.317
1900	37.325	264.174	234.627	56.139	1176.394	891.958	−24.522
2000	37.424	266.091	236.152	59.877	1177.770	876.952	−22.904
2100	37.514	267.919	237.622	63.624	1179.133	861.878	−21.438
2200	37.598	269.666	239.039	67.380	1180.486	846.739	−20.104
2300	37.675	271.339	240.407	71.143	1181.831	831.538	−18.885
2400	37.747	272.944	241.730	74.914	1183.169	816.279	−17.766
2500	37.814	274.486	243.009	78.693	1184.503	800.965	−16.735
2600	37.878	275.971	244.249	82.477	1185.836	785.597	−15.783
2700	37.939	277.401	245.450	86.268	1187.168	770.178	−14.900
2800	37.996	278.782	246.616	90.065	1188.501	754.710	−14.079
2900	38.052	280.116	247.748	93.867	1189.838	739.193	−13.314
3000	38.105	281.407	248.849	97.675	1191.179	723.631	−12.600
3100	38.157	282.658	249.919	101.488	1192.526	708.024	−11.930
3200	38.207	283.870	250.962	105.306	1193.880	692.373	−11.302
3300	38.256	285.046	251.977	109.130	1195.241	676.680	−10.711
3400	38.304	286.189	252.966	112.958	1196.611	660.946	−10.154
3500	38.352	287.300	253.931	116.790	1197.990	645.171	−9.629
3600	38.399	288.381	254.873	120.628	1199.379	629.356	−9.132
3700	38.446	289.434	255.793	124.470	1200.777	613.503	−8.661
3800	38.493	290.460	256.692	128.317	1202.186	597.612	−8.215
3900	38.540	291.460	257.571	132.169	1203.605	581.684	−7.791
4000	38.588	292.437	258.430	136.025	1205.034	565.719	−7.388
4100	38.637	293.390	259.271	139.886	1206.474	549.718	−7.003
4200	38.687	294.322	260.095	143.753	1207.925	533.682	−6.637
4300	38.738	295.233	260.901	147.624	1209.386	517.611	−6.288
4400	38.791	296.124	261.692	151.500	1210.858	501.507	−5.954
4500	38.846	296.996	262.467	155.382	1212.340	485.369	−5.634
4600	38.904	297.851	263.227	159.270	1213.833	469.197	−5.328
4700	38.964	298.688	263.972	163.163	1215.336	452.993	−5.034
4800	39.027	299.509	264.704	167.063	1216.849	436.757	−4.753
4900	39.094	300.314	265.423	170.969	1218.374	420.490	−4.482
5000	39.163	301.105	266.128	174.881	1219.908	404.191	−4.223
5100	39.237	301.881	266.822	178.801	1221.453	387.861	−3.973
5200	39.315	302.644	267.503	182.729	1223.008	371.501	−3.732
5300	39.396	303.393	268.174	186.665	1224.574	355.111	−3.500
5400	39.483	304.131	268.833	190.608	1226.150	338.691	−3.276
5500	39.574	304.856	269.481	194.561	1227.738	322.242	−3.060
5600	39.669	305.570	270.119	198.523	1229.336	305.764	−2.852
5700	39.770	306.273	270.747	202.495	1230.945	289.257	−2.651
5800	39.876	306.965	271.366	206.478	1232.565	272.722	−2.456
5900	39.988	307.648	271.975	210.471	1234.196	256.160	−2.268
6000	40.105	308.321	272.575	214.475	1235.839	239.569	−2.086

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 225.40 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 35.51 \pm 16.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 35.98 \pm 16.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1077 (1)
[420] (2)
2290 (1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: $C_{\infty v}$

Bond Distances: C–F = 1.262 Å; C–N = 1.159 Å

Bond Angle: F–C–N = 180°

Rotational Constant: $B_0 = 0.353106\ cm^{-1}$

Enthalpy of Formation

Davis and Okabe[1] have determined the dissociation energy of FCN to F(g) and CN(g) by measuring the threshold energies of incident photon radiation to produce $B^2\Sigma^+$ CN which is monitored by its fluorescence. The dissociation energy determined by this technique is ≤111 $kcal \cdot mol^{-1}$ with an uncertainty of about 1 kcal in the determination of the limit.

Dibeler and Liston[2] have reported a dissociation energy of ≤115.6 $kcal \cdot mol^{-1}$ from the threshold of the CN^+ ion as determined by photoionization.

We adopt a median value of 113.1 ± 2.5 $kcal \cdot mol^{-1}$ which leads to $\Delta_f H°$(FCN, g, 298.15 K) = 8.6 ± 4 $kcal \cdot mol^{-1}$ (35.982 ± 16.7 $kJ \cdot mol^{-1}$) with auxiliary JANAF values for F(g) and CN(g).

Heat Capacity and Entropy

The molecular structure and bond lengths and angle were determined using microwave spectroscopy by Tyler and Sheridan.[3] The vibrational frequencies were reported by Aynsley *et al.*[4] from the infrared spectrum, except for the bending frequency which is estimated from the values for ClCN, BrCN and ICN, by comparison of bending force constants. The reasonable limits for this value as calculated from generous limits on the bending force constant are 405–450 cm^{-1}.

References

[1]D. D. Davis and H. Okabe, J. Chem. Phys. **49**, 5526 (1968).

[2]V. H. Dibeler and S. K. Liston, J. Chem. Phys. **47**, 4548 (1967).

[3]J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).

[4]E. E. Aynsley, R. E. Dodd, and R. Little, Proc. Chem. Soc. (London) **1959**, 265.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.272	35.509	35.509	INFINITE
100	30.550	186.140	259.533	−7.339	35.477	33.468	−17.482
200	37.491	209.468	229.132	−3.933	35.638	31.424	−8.207
250	40.199	218.136	226.088	−1.988	35.808	30.352	−6.342
298.15	42.312	225.403	225.403	0.	35.982	29.285	−5.131
300	42.385	225.665	225.404	0.078	35.989	29.243	−5.092
350	44.203	232.339	225.927	2.244	36.161	28.105	−4.194
400	45.750	238.345	227.110	4.494	36.314	26.944	−3.518
450	47.097	243.814	228.667	6.816	36.441	25.764	−2.991
500	48.291	248.839	230.436	9.201	36.542	24.573	−2.567
600	50.339	257.830	234.270	14.136	36.670	22.165	−1.930
700	52.041	265.722	238.211	19.258	36.721	19.743	−1.473
800	53.470	272.767	242.098	24.535	36.719	17.317	−1.131
900	54.669	279.136	245.865	29.944	36.677	14.894	−0.864
1000	55.674	284.950	249.487	35.463	36.608	12.477	−0.652
1100	56.518	290.297	252.957	41.073	36.516	10.068	−0.478
1200	57.227	295.246	256.278	46.762	36.406	7.668	−0.334
1300	57.826	299.851	259.454	52.515	36.279	5.279	−0.212
1400	58.333	304.155	262.495	58.324	36.136	2.899	−0.108
1500	58.765	308.195	265.408	64.179	35.977	0.531	−0.018
1600	59.135	311.999	268.203	70.075	35.804	−1.827	0.060
1700	59.453	315.594	270.886	76.005	35.616	−4.173	0.128
1800	59.729	319.000	273.465	81.964	35.415	−6.508	0.189
1900	59.969	322.236	275.947	87.949	35.200	−8.831	0.243
2000	60.178	325.318	278.339	93.957	34.973	−11.143	0.291
2100	60.362	328.258	280.647	99.984	34.736	−13.443	0.334
2200	60.524	331.070	282.876	106.028	34.489	−15.731	0.374
2300	60.668	333.764	285.030	112.088	34.234	−18.008	0.409
2400	60.796	336.349	287.115	118.162	33.974	−20.274	0.441
2500	60.910	338.833	289.134	124.247	33.708	−22.529	0.471
2600	61.013	341.224	291.092	130.343	33.440	−24.773	0.498
2700	61.105	343.528	292.992	136.449	33.171	−27.007	0.522
2800	61.188	345.752	294.836	142.564	32.902	−29.231	0.545
2900	61.264	347.901	296.629	148.687	32.634	−31.445	0.566
3000	61.332	349.979	298.373	154.816	32.369	−33.650	0.586
3100	61.394	351.991	300.071	160.953	32.107	−35.847	0.604
3200	61.451	353.941	301.724	167.095	31.850	−38.035	0.621
3300	61.503	355.833	303.335	173.243	31.598	−40.215	0.637
3400	61.551	357.669	304.906	179.395	31.352	−42.387	0.651
3500	61.595	359.454	306.439	185.553	31.112	−44.552	0.665
3600	61.635	361.190	307.936	191.714	30.878	−46.711	0.678
3700	61.672	362.879	309.398	197.880	30.652	−48.863	0.690
3800	61.707	364.524	310.827	204.049	30.432	−51.009	0.701
3900	61.739	366.128	312.225	210.221	30.218	−53.149	0.712
4000	61.769	367.691	313.592	216.396	30.012	−55.284	0.722
4100	61.796	369.217	314.930	222.575	29.812	−57.414	0.731
4200	61.822	370.706	316.241	228.756	29.618	−59.539	0.740
4300	61.846	372.161	317.524	234.939	29.430	−61.660	0.749
4400	61.869	373.583	318.782	241.125	29.248	−63.776	0.757
4500	61.890	374.974	320.015	247.313	29.072	−65.888	0.765
4600	61.909	376.334	321.225	253.503	28.901	−67.997	0.772
4700	61.928	377.666	322.412	259.695	28.735	−70.101	0.779
4800	61.945	378.970	323.577	265.888	28.572	−72.203	0.786
4900	61.962	380.247	324.720	272.084	28.414	−74.300	0.792
5000	61.977	381.499	325.843	278.281	28.259	−76.395	0.798
5100	61.992	382.727	326.947	284.479	28.108	−78.487	0.804
5200	62.005	383.931	328.031	290.679	27.959	−80.575	0.809
5300	62.018	385.112	329.097	296.880	27.812	−82.661	0.815
5400	62.031	386.271	330.145	303.083	27.667	−84.744	0.820
5500	62.042	387.410	331.176	309.286	27.523	−86.824	0.825
5600	62.053	388.528	332.190	315.491	27.380	−88.902	0.829
5700	62.064	389.626	333.188	321.697	27.238	−90.978	0.834
5800	62.074	390.706	334.170	327.904	27.095	−93.050	0.838
5900	62.083	391.767	335.138	334.112	26.952	−95.120	0.842
6000	62.092	392.810	336.090	340.320	26.808	−97.188	0.846

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K)$ = [248.48] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−172.1 ± 63] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−171.5 ± 63] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1018(1)
626(1)
1855(1)

Ground State Quantum Weight: 2 σ = 1
Point Group: C_s
Bond Distances: C–F = [1.34] Å; C–O = [1.18] Å
Bond Angle: F–C–O = [135]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [2.199751− 10^{-116}] $g^3·cm^6$

Enthalpy of Formation

The enthalpy change $\Delta_f H°$ for the reaction $COF_2(g) = CO + 2F(g)$ was calculated as 160.5 $kcal·mol^{-1}$. By analogy with $\Delta_{at}H°$(Cl–COCl, 0 K), $\Delta_{at}H°$(Cl–CO, 0 K), the value of $\Delta_{at}H°$(F–COF, 0 K), $\Delta_{at}H°$(F–CO, 0 K) was taken to be 4. Based on $\Delta_f H° = 160.5–(4/5) = 128.4$ $kcal·mol^{-1}$ for the reaction $COF_2(g) = COF(g) + F(g)$, the enthalpy of formation of COF(g) was derived as −41 ± 15 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies were reported by Milligan *et al.*[1] The bond distances and bond angle were estimated by comparison with those for HFCO(g). Due to the presence of one unpaired electron on C atom, the ground state quantum weight is calculated to be 2. The principal moments of inertia are: $I_A = 0.3399 \times 10^{-39}$, $I_B = 7.8768 \times 10^{-39}$, and $I_C = 8.2167 \times 10^{-39}$ $g·cm^2$.

References

[1]D. E. Milligan, M. E. Jacox, M. A. Bass, J. J. Comeford and D. E. Mann, J. Chem. Phys. **42**, 3187 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
T/K	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.393	−172.132	−172.132	INFINITE
100	33.341	210.080	280.740	−7.066	−171.770	−175.499	91.671
200	35.464	233.679	251.926	−3.649	−171.600	−179.306	46.830
250	37.207	241.777	249.110	−1.833	−171.560	−181.237	37.867
298.15	38.930	248.479	248.479	0.	−171.544	−183.103	32.079
300	38.995	248.720	248.479	0.072	−171.544	−183.175	31.894
350	40.702	254.860	248.960	2.065	−171.555	−185.113	27.627
400	42.284	260.400	250.050	4.140	−171.594	−187.048	24.426
450	43.733	265.465	251.485	6.291	−171.663	−188.975	21.936
500	45.051	270.142	253.120	8.511	−171.762	−190.894	19.943
600	47.318	278.564	256.674	13.134	−172.034	−194.696	16.950
700	49.151	286.001	260.343	17.960	−172.383	−198.447	14.808
800	50.621	292.663	263.974	22.952	−172.786	−202.143	13.199
900	51.799	298.696	267.502	28.075	−173.227	−205.787	11.944
1000	52.747	304.205	270.901	33.304	−173.697	−209.380	10.937
1100	53.514	309.269	274.162	38.618	−174.191	−212.924	10.111
1200	54.140	313.953	277.285	44.002	−174.706	−216.423	9.421
1300	54.655	318.308	280.275	49.443	−175.241	−219.877	8.835
1400	55.082	322.374	283.138	54.930	−175.795	−223.290	8.331
1500	55.440	326.187	285.883	60.457	−176.368	−226.663	7.893
1600	55.741	329.775	288.515	66.016	−176.962	−229.997	7.509
1700	55.997	333.162	291.042	71.603	−177.575	−233.293	7.168
1800	56.216	336.369	293.472	77.214	−178.209	−236.552	6.865
1900	56.405	339.414	295.811	82.846	−178.862	−239.776	6.592
2000	56.569	342.311	298.064	88.495	−179.535	−242.964	6.346
2100	56.711	345.075	300.237	94.159	−180.226	−246.119	6.122
2200	56.836	347.716	302.336	99.836	−180.934	−249.240	5.918
2300	56.947	350.245	304.364	105.526	−181.657	−252.329	5.731
2400	57.044	352.671	306.327	111.225	−182.396	−255.386	5.558
2500	57.131	355.001	308.228	116.934	−183.147	−258.412	5.399
2600	57.209	357.243	310.070	122.651	−183.909	−261.407	5.252
2700	57.278	359.404	311.857	128.375	−184.680	−264.373	5.115
2800	57.341	361.488	313.593	134.106	−185.460	−267.310	4.987
2900	57.397	363.501	315.279	139.843	−186.246	−270.220	4.867
3000	57.448	365.448	316.919	145.586	−187.038	−273.102	4.755
3100	57.495	367.332	318.515	151.333	−187.833	−275.958	4.650
3200	57.537	369.158	320.070	157.084	−188.631	−278.788	4.551
3300	57.576	370.930	321.584	162.840	−189.432	−281.593	4.457
3400	57.611	372.649	323.061	168.599	−190.233	−284.374	4.369
3500	57.643	374.319	324.502	174.362	−191.035	−287.131	4.285
3600	57.673	375.944	325.908	180.128	−191.836	−289.865	4.206
3700	57.701	377.524	327.282	185.897	−192.637	−292.577	4.130
3800	57.726	379.063	328.624	191.668	−193.436	−295.267	4.059
3900	57.750	380.563	329.937	197.442	−194.235	−297.936	3.990
4000	57.772	382.026	331.221	203.218	−195.032	−300.586	3.925
4100	57.792	383.452	332.478	208.996	−195.828	−303.215	3.863
4200	57.811	384.845	333.708	214.776	−196.623	−305.824	3.803
4300	57.829	386.206	334.913	220.558	−197.416	−308.415	3.746
4400	57.845	387.535	336.094	226.342	−198.209	−310.987	3.692
4500	57.861	388.835	337.252	232.127	−199.001	−313.541	3.639
4600	57.875	390.107	338.387	237.914	−199.792	−316.078	3.589
4700	57.889	391.352	339.501	243.702	−200.584	−318.597	3.541
4800	57.901	392.571	340.594	249.492	−201.377	−321.100	3.494
4900	57.913	393.765	341.667	255.283	−202.170	−323.586	3.449
5000	57.925	394.935	342.720	261.075	−202.966	−326.056	3.406
5100	57.935	396.082	343.755	266.868	−203.764	−328.509	3.365
5200	57.945	397.207	344.773	272.662	−204.565	−330.948	3.324
5300	57.955	398.311	345.772	278.457	−205.370	−333.370	3.286
5400	57.964	399.395	346.755	284.253	−206.179	−335.778	3.248
5500	57.972	400.458	347.722	290.049	−206.993	−338.171	3.212
5600	57.980	401.503	348.673	295.847	−207.814	−340.548	3.176
5700	57.988	402.529	349.609	301.645	−208.642	−342.911	3.142
5800	57.995	403.538	350.530	307.445	−209.477	−345.259	3.109
5900	58.002	404.529	351.437	313.244	−210.321	−347.594	3.077
6000	58.008	405.504	352.330	319.045	−211.175	−349.913	3.046

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = 240.833 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -182.48 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -182.00 \pm 6.3\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X^1A_1	0	1
a^3B_1	[16000]	3
A^1B_1	37226	1

Vibrational Frequencies and Degeneracies		
ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
1222 (1)	665 (1)	1110 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: C–F = 1.300 Å
Bond Angle: F–C–F = 104.9°
Product of the Moments of Inertia: $I_A I_B I_C = 4.88015 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

Thrush and Zwolenik[1] reported a predissociation limit for $CF_2 \rightarrow CF + F$; however, Marsigny *et al.*[2] have since observed in emission the assumed predissociated level, and others above it, which invalidates the reported limit.

Walter *et al.*[3] have obtained the photoionization threshold at 0 K for onset of the reaction $C_2F_4 + e^- \rightarrow CF_2^+ + CF_2 + 2\bar{e}$, as 14.63 ± 0.04 eV (337.37 kcal·mol^{-1}). The ionization potential of CF_2 has been reported as 11.7 eV,[4] 11.8 ± 0.3 eV[5] and 11.86 ± 0.1 eV.[6] Since these values were obtained by electron impact methods, there may be excess energy involved. Thus, adopting the lowest value as 11.7 ± 0.2 eV, we obtain $\Delta_f H°(CF_2, g, 298.15\ K) = -44.4 \pm 2.5$ kcal·mol^{-1}.[7] All previous electron impact methods are considered superseded by this photoionization result.

Modica and LaGraff[8] determined equilibrium constants for the reaction (A) $C_2F_4 \rightarrow 2CF_2$ by use of a shock tube to achieve high temperatures and ultra violet absorption to detect the CF_2 concentration. Carlson[9] has studied the same reaction using a similar technique, and also Zmbov *et al.*[5] have investigated this equilibrium in a mass spectrometer. A 2nd and 3rd law analysis of all three sets of data is given below along with our recalculated equilibrium data of Farber *et al.*[10] for the reaction (B) $C + 2F \rightarrow CF_2$ from weight loss experiments in the system $C + CF_4$.

Kinetic methods were used by Edwards and Small[11] to study the equilibrium (C) $CHF_2Cl(g) \rightleftarrows CF_2(g) + HCl(g)$. They analysed their data by assuming that the only other equilibrium occurring was $2CF_2(g) \rightleftarrows C_2F_4(g)$, and fit their kinetic data by trial and error. In this manner they obtained activation energies of the forward and back reaction (C) of 55.79 ± 0.49 and 6.21 ± 3.0 kcal·mol^{-1}, thus $\Delta E_a = 49.6 \pm 3.0$ and $\Delta H(900\ K) = 51.4 \pm 3$ kcal·mol^{-1}, which yields $\Delta_f H(CF_2, 298.15\ K) = -42 \pm 4$ kcal·mol^{-1}.[7] They also obtained the activation energy of reaction (A) as 70.36 ± 1.3 kcal·mol^{-1}. Dalby[12] has reported the activation energy of the reverse of (A) as 1.2 ± 0.2 kcal·mol^{-1}, thus, $\Delta E_a = 69.2 \pm 1.3$ and $\Delta H(900\ K) = 71.0 \pm 1.3$ kcal·mol^{-1}, which yields $\Delta_f H(CF_2, 298.15\ K) = -42.6 \pm 1.0$ kcal·mol^{-1}.[7] Gozzo and Patrick[13] also investigated the kinetics of reaction C and obtained activation energies of 51.4 ± 2.5 and 14.4 ± 5 kcal·mol^{-1}, the latter value being corrected for the activation energy of CF_2 recombination.[12] Thus, we obtain $\Delta E_a = 37 \pm 7$ and $\Delta H(1000\ K) = 39 \pm 7$ kcal·mol^{-1}, which yields $\Delta_f H°(CF_2, 298.15\ K) = -54 \pm 9$ kcal·mol^{-1}.[7]

Modica and LaGraff[14] investigated the kinetics of CHF_3 decomposition by a mass spectrometer coupled to a shock tube. They investigated the pressure dependence of the rate and concluded that at the hgh pressure limit $E_o = 58.4 \pm 2.2$ kcal·mol^{-1}. Taking this value as $\Delta H°(0\ K)$ for the reaction (D) $CHF_3(g) \rightarrow CF_2(g) + HF(g)$, we obtain $\Delta_f H°(CF_2, 298.15\ K) = -41.3 \pm 2.5$ kcal·mol^{-1}.[7] However, any activation energy of the reverse reaction (D) will make this value more negative. Since values of the reverse activation energy of analogous reaction (C) range from 6.2 to 14.4 kcal·mol^{-1}, it appears likely that reverse reaction (D) will have a significant activation energy; thus, $\Delta_f H(CF_2, 298.15\ K) < -41.3 \pm 2.5$ kcal·mol^{-1}. Tschiukow-Roux[15] has investigated the same reaction in a shock tube, but was unable to obtain sufficient variation of rate with pressure to calculate the high pressure limit.

Reference and Reaction		Points	T/R	$\Delta_f H(298.15\ K)$ kcal·mol^{-1} 2nd law	3rd law	Drift eV	**$\Delta_f H(CF_2, g, 298.15\ K)$ kcal·mol^{-1}
[8]	A	20*	1165-1620	70.89 ± 2.7	66.68 ± 2.28	−2.4 ± 2.1	−45.4 ± 2.0
[9]	A	35*	1240–1742	67.92 ± 0.7	68.40 ± 0.72	0.3 ± 0.5	−44.5 ± 0.7
[5]	A	11	1127–1244	77.3 ± 2.1	75.13 ± 0.5	−1.8 ± 1.8	−41.15 ± 1.5
[10]	B	8	2023–2474	−73.8 ± 1.4	−80.04 ± 1.0	−2.8 ± 0.6	−42.3 ± 1.0

*Points ommitted due to failure of a statistical test **Calculated from the 3rd law heat of reaction.

A median value of $\Delta_f H(CF_2, g, 298.15\ K)$ covering the area of maximum probability is adopted as -43.5 ± 1.5 kcal·mol^{-1}.

Continued on page 700

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.354	−182.482	−182.482	INFINITE
100	33.311	202.633	272.908	−7.028	−182.122	−185.253	96.766
200	35.154	226.123	244.265	−3.628	−181.979	−188.456	49.220
250	36.964	234.154	241.463	−1.827	−181.975	−190.077	39.714
298.15	38.948	240.833	240.833	0.	−182.004	−191.635	33.574
300	39.026	241.074	240.834	0.072	−182.006	−191.695	33.377
350	41.119	247.248	241.316	2.076	−182.061	−193.306	28.849
400	43.097	252.869	242.414	4.182	−182.138	−194.907	25.452
450	44.887	258.051	243.867	6.383	−182.232	−196.498	22.809
500	46.465	262.864	245.529	8.667	−182.345	−198.077	20.693
600	49.020	271.573	249.160	13.448	−182.616	−201.199	17.516
700	50.913	279.279	252.923	18.449	−182.939	−204.271	15.243
800	52.319	286.173	256.656	23.614	−183.305	−207.294	13.535
900	53.376	292.400	260.287	28.901	−183.706	−210.269	12.204
1000	54.184	298.067	263.786	34.281	−184.139	−213.197	11.136
1100	54.812	303.262	267.142	39.732	−184.602	−216.081	10.261
1200	55.308	308.053	270.354	45.239	−185.092	−218.921	9.529
1300	55.705	312.497	273.427	50.791	−185.609	−221.719	8.909
1400	56.028	316.637	276.367	56.378	−186.152	−224.477	8.375
1500	56.293	320.512	279.182	61.994	−186.721	−227.195	7.912
1600	56.515	324.152	281.880	67.635	−187.314	−229.874	7.505
1700	56.702	327.584	284.469	73.296	−187.930	−232.515	7.144
1800	56.864	330.830	286.955	78.975	−188.568	−235.119	6.823
1900	57.006	333.908	289.346	84.668	−189.225	−237.688	6.534
2000	57.134	336.836	291.648	90.375	−189.899	−240.221	6.274
2100	57.252	339.626	293.867	96.095	−190.585	−242.721	6.037
2200	57.365	342.292	296.008	101.825	−191.280	−245.187	5.821
2300	57.475	344.844	298.076	107.567	−191.980	−247.621	5.624
2400	57.586	347.293	300.076	113.321	−192.680	−250.026	5.442
2500	57.700	349.646	302.012	119.085	−193.376	−252.401	5.274
2600	57.820	351.911	303.888	124.861	−194.062	−254.748	5.118
2700	57.947	354.096	305.707	130.649	−194.734	−257.069	4.973
2800	58.083	356.206	307.473	136.451	−195.388	−259.366	4.839
2900	58.229	358.246	309.189	142.266	−196.020	−261.640	4.713
3000	58.384	360.223	310.858	148.097	−196.625	−263.892	4.595
3100	58.551	362.140	312.481	153.943	−197.201	−266.125	4.484
3200	58.728	364.002	314.062	159.807	−197.743	−268.339	4.380
3300	58.916	365.812	315.603	165.689	−198.249	−270.538	4.282
3400	59.115	367.574	317.106	171.591	−198.716	−272.721	4.190
3500	59.323	369.290	318.572	177.513	−199.143	−274.891	4.103
3600	59.541	370.964	320.004	183.456	−199.527	−277.050	4.020
3700	59.768	372.599	321.404	189.421	−199.866	−279.199	3.942
3800	60.002	374.196	322.772	195.410	−200.160	−281.339	3.867
3900	60.242	375.758	324.111	201.422	−200.407	−283.472	3.797
4000	60.488	377.286	325.421	207.458	−200.607	−285.599	3.730
4100	60.739	378.783	326.705	213.520	−200.760	−287.722	3.666
4200	60.993	380.249	327.962	219.606	−200.865	−289.841	3.605
4300	61.250	381.687	329.195	225.718	−200.922	−291.959	3.547
4400	61.508	383.098	330.404	231.856	−200.932	−294.076	3.491
4500	61.766	384.484	331.590	238.020	−200.895	−296.193	3.438
4600	62.024	385.844	332.755	244.209	−200.811	−298.312	3.387
4700	62.280	387.181	333.899	250.425	−200.682	−300.433	3.339
4800	62.533	388.495	335.023	256.665	−200.508	−302.557	3.292
4900	62.783	389.786	336.127	262.931	−200.290	−304.685	3.248
5000	63.029	391.057	337.213	269.222	−200.029	−306.818	3.205
5100	63.270	392.308	338.281	275.537	−199.727	−308.957	3.164
5200	63.506	393.539	339.332	281.875	−199.385	−311.102	3.125
5300	63.735	394.751	340.366	288.238	−199.003	−313.254	3.087
5400	63.958	395.944	341.384	294.622	−198.584	−315.413	3.051
5500	64.174	397.120	342.387	301.029	−198.129	−317.581	3.016
5600	64.383	398.278	343.375	307.457	−197.639	−319.757	2.983
5700	64.584	399.419	344.348	313.905	−197.116	−321.943	2.950
5800	64.776	400.544	345.307	320.373	−196.561	−324.138	2.919
5900	64.961	401.653	346.253	326.860	−195.976	−326.342	2.889
6000	65.137	402.746	347.185	333.365	−195.361	−328.557	2.860

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = [246.77 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 935.12 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 941.79 \pm 12.6\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	2
$^2B_1$	[15000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1100] (1)
[650] (1)
[1400] (1)

Point Group: C_{2v}
Bond Distance: C–F = [1.32] Å
Bond Angle: F–C–F = [116 ± 10°]
Product of the Moments of inertia: $I_A I_B I_C = [5.07002 \times 10^{-116}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The ionization potential has been reported as 11.7 eV,[1] 11.8 eV,[2, 3] and 11.86 eV[4] from electron impact measurements. Since there may be excess energy involved we prefer the lowest value, 11.7 ± 0.2 eV. This leads to $\Delta_f H°(CF^+, g, 0\ K) = 226.2 \pm 6\ kcal \cdot mol^{-1}$ using the JANAF $\Delta_f H°(CF_2, g, 0\ K) = -43.61 \pm 1.5\ kcal \cdot mol^{-1}$.[5]

A more precise value is available from the photoionization measurements of Walter *et al.*,[6] who measured the photoionization threshold the process for:

$$C_2F_4 + h\nu \rightarrow CF_2^+ + CF_2 + e^- \qquad \Delta H°(0\ K) = 337.4 \pm 0.9\ kcal \cdot mol^{-1}$$

Employing JANAF auxiliary enthalpies[5] we obtain $\Delta_f H°(CF_2^+, g, 0\ K) = 223.5 \pm 3.0\ kcal \cdot mol^{-1}$ which is adopted.

Heat Capacity and Entropy

The configuration of CF_2^+ is predicted to be bent by Walsh,[7] since it has 17 electrons, thus, its ground state is $^2A_1$, a low lying electronic state is predicted by analogy with NO_2.[8] We estimate the angle to be 116 ± 10°, which is larger than CF_2 at 105°, this is expected from the Walsh correlations,[7] but smaller than isoelectronic CO_2^- at 127° and NO_2 at 134°. The vibrational frequencies were estimated by comparison with those for CF_2, CO_2^- and COF[7] as 1100 ± 150 cm^{-1}, 650 ± 50 cm^{-1} and 1400 ± 200 cm^{-1}.

The principal moments of interia are: $I_A = 0.7415 \times 10^{-39}$, $I_B = 7.9066 \times 10^{-39}$, and $I_C = 8.6481 \times 10^{-39}\ g \cdot cm^2$.

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[5] JANAF Thermochemical Tables: CF_2(g), 6–30–70; C_2F_4(g), 6–30–69; $CO2^-$(g), 12–31–66; COF(g), 12–31–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.354	935.118		
100	33.321	208.556	278.829	−7.027			
200	35.209	232.075	250.193	−3.624			
250	36.922	240.111	247.397	−1.822			
298.15	38.754	246.769	246.769	0.	941.793	924.137	−161.905
300	38.826	247.009	246.770	0.072	941.830	924.028	−160.888
350	40.758	253.140	247.250	2.062	942.799	920.984	−137.449
400	42.608	258.704	248.339	4.146	943.741	917.803	−119.853
450	44.312	263.823	249.779	6.320	944.658	914.505	−106.153
500	45.841	268.572	251.423	8.574	945.555	911.106	−95.183
600	48.379	277.165	255.013	13.291	947.299	904.052	−78.705
700	50.311	284.774	258.731	18.230	948.992	896.710	−66.913
800	51.776	291.592	262.420	23.338	950.648	889.127	−58.054
900	52.895	297.758	266.010	28.574	952.274	881.339	−51.152
1000	53.761	303.378	269.470	33.908	953.874	873.372	−45.620
1100	54.440	308.535	272.790	39.320	955.450	865.245	−41.087
1200	54.980	313.296	275.970	44.792	957.003	856.976	−37.303
1300	55.415	317.715	279.013	50.312	958.534	848.578	−34.096
1400	55.770	321.835	281.926	55.872	960.043	840.063	−31.343
1500	56.063	325.693	284.717	61.464	961.528	831.441	−28.953
1600	56.308	329.319	287.392	67.083	962.992	822.721	−26.859
1700	56.515	332.739	289.960	72.724	964.435	813.910	−25.008
1800	56.692	335.974	292.427	78.385	965.857	805.014	−23.361
1900	56.846	339.044	294.801	84.062	967.262	796.040	−21.885
2000	56.982	341.963	297.086	89.754	968.652	786.993	−20.554
2100	57.103	344.746	299.290	95.458	970.029	777.876	−19.349
2200	57.214	347.405	301.417	101.174	971.397	768.693	−18.251
2300	57.317	349.951	303.472	106.901	972.761	759.449	−17.248
2400	57.414	352.392	305.460	112.637	974.123	750.145	−16.326
2500	57.507	354.738	307.385	118.383	975.488	740.785	−15.478
2600	57.598	356.995	309.250	124.138	976.859	731.370	−14.693
2700	57.688	359.171	311.059	129.903	978.242	721.902	−13.966
2800	57.778	361.270	312.815	135.676	979.638	712.382	−13.290
2900	57.869	363.299	314.521	141.458	981.052	702.813	−12.659
3000	57.961	365.263	316.180	147.250	982.486	693.194	−12.070
3100	58.054	367.165	317.794	153.051	983.943	683.526	−11.517
3200	58.150	369.010	319.366	158.861	985.426	673.812	−10.999
3300	58.247	370.800	320.897	164.681	986.936	664.051	−10.511
3400	58.346	372.541	322.391	170.510	988.476	654.243	−10.051
3500	58.446	374.233	323.848	176.350	990.045	644.390	−9.617
3600	58.549	375.881	325.270	182.200	991.647	634.492	−9.206
3700	58.653	377.487	326.660	188.060	993.281	624.549	−8.817
3800	58.758	379.053	328.018	193.930	994.948	614.560	−8.448
3900	58.864	380.580	329.346	199.811	996.648	604.528	−8.097
4000	58.970	382.072	330.646	205.703	998.381	594.452	−7.763
4100	59.077	383.529	331.918	211.605	1000.148	584.332	−7.444
4200	59.184	384.954	333.164	217.518	1001.949	574.168	−7.141
4300	59.291	386.348	334.385	223.442	1003.782	563.961	−6.851
4400	59.397	387.712	335.581	229.377	1005.647	553.711	−6.573
4500	59.503	389.048	336.755	235.322	1007.544	543.419	−6.308
4600	59.607	390.357	337.906	241.277	1009.472	533.084	−6.053
4700	59.710	391.640	339.035	247.243	1011.431	522.707	−5.809
4800	59.812	392.898	340.144	253.219	1013.419	512.287	−5.575
4900	59.912	394.133	341.234	259.205	1015.436	501.826	−5.350
5000	60.010	395.344	342.304	265.201	1017.481	491.324	−5.133
5100	60.105	396.533	343.356	271.207	1019.552	480.780	−4.924
5200	60.199	397.702	344.389	277.223	1021.650	470.196	−4.723
5300	60.290	398.849	345.406	283.247	1023.772	459.570	−4.529
5400	60.378	399.977	346.406	289.280	1025.918	448.905	−4.342
5500	60.464	401.086	347.391	295.323	1028.088	438.199	−4.162
5600	60.547	402.176	348.359	301.373	1030.279	427.455	−3.987
5700	60.628	403.248	349.313	307.432	1032.491	416.670	−3.818
5800	60.705	404.303	350.252	313.499	1034.723	405.846	−3.655
5900	60.780	405.342	351.177	319.573	1036.975	394.985	−3.497
6000	60.851	406.364	352.088	325.655	1039.244	384.084	−3.344

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 258.887 \pm 0.08\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -635.8 \pm 1.71\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -638.9 \pm 1.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
965 (1)	1249 (1)
1928 (1)	584 (1)
626 (1)	774 (1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: C–F = 1.312 Å; C–O = 1.174 Å

Bond Angles: F–C–F = 108°; F–C–O = 126° 1'

Product of the Moments of Inertia: $I_A I_B I_C = 7.225667 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

Ruff and Li[1] measured equilibrium constants for the reaction

$$2COF_2(g) \rightleftarrows CO\ (_2g) + CF\ (_4g)$$

in the temperature range 573–1273 K. These equilibrium data were recently analyzed by Stull *et al.*[2] Their 3rd law analysis of the data clearly indicates that the three low temperature points are in error and should not be used in calculating $\Delta_f H(298.15\ K)$. They reported $\Delta_f H(298.15\ K) = -12 \pm 3\ kcal·mol^{-1}$ based upon an average of the five high temperature points. Combining this result with the enthalpy of formation of carbon dioxide and carbon tetrafluoride,[3] we derive,

$$\Delta_f H°(COF_2, g, 298.15\ K) = -152.5 \pm 3.3\ kcal·mol^{-1}.$$

Wartenberg and Riteris[4] measured the enthalpy of hydrolysis of CF_2O. They reported $\Delta_r H = -26.7 \pm 0.2\ kcal·mol^{-1}$ for the reaction

$$COF_2(g) + H_2O(l) \rightarrow CO_2(g) + 2HF·300\ H_2O.$$

Combining this result with enthaply of formation data for carbon dioxide and HF($\Delta_f H°(HF·300\ H_2O, 298.15\ K) = -76.84\ kcal·mol^{-1}$),[5] we derive

$$\Delta_f H°(COF_2, g, 298.15\ K) = -152.7 \pm 0.4\ kcal·mol^{-1}.$$

Armstrong *et al.*[6] measured the enthalpies of combustion of CH_4 in O_2–F_2 mixtures and found $\Delta_f H°(COF_2, g, 298.15\ K) = -154.8\ kcal·mol^{-1}$. The value calculated from Wartenberg's data[4] is adopted here.

Heat Capacity nd Entropy

The vibrational frequencies are from the infrared studies of Hopper *et al.*[7] and are in good agreement with the results of Lovell *et al.*[8] and Nielsen *et al.*[9] The molecular constants are from the microwave studies of Laurie *et al.*[10] and are in reasonable agreement with the electron–diffraction work of Brown and Livingston.[11] The principal moments of inertia are: $I_A = 7.1086 \times 10^{-39}$, $I_B = 7.1359 \times 10^{-39}$, and $I_C = 14.2445 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.119	−635.798	−635.798	INFINITE
100	33.489	217.322	295.224	−7.790	−636.888	−632.823	330.553
200	38.897	241.797	262.939	−4.228	−638.038	−628.302	164.096
250	43.168	250.931	259.642	−2.178	−638.514	−625.811	130.756
298.15	47.255	258.887	258.887	0.	−638.897	−623.329	109.205
300	47.407	259.180	258.888	0.088	−638.910	−623.232	108.514
350	51.305	266.786	259.480	2.557	−639.239	−620.592	92.618
400	54.778	273.868	260.841	5.211	−639.514	−617.909	80.691
450	57.831	280.500	262.661	8.028	−639.751	−615.194	71.410
500	60.502	286.735	264.759	10.988	−639.959	−612.454	63.983
600	64.875	298.170	269.393	17.266	−640.312	−606.918	52.837
700	68.225	308.434	274.250	23.929	−640.602	−601.329	44.872
800	70.811	317.720	279.112	30.886	−640.843	−595.701	38.895
900	72.827	326.181	283.879	38.072	−641.049	−590.046	34.245
1000	74.417	333.940	288.503	45.437	−641.228	−584.369	30.524
1100	75.686	341.094	292.963	52.945	−641.388	−578.676	27.479
1200	76.709	347.725	297.253	60.566	−641.538	−572.968	24.941
1300	77.544	353.899	301.376	68.280	−641.684	−567.247	22.792
1400	78.231	359.672	305.336	76.070	−641.831	−561.516	20.950
1500	78.804	365.089	309.141	83.923	−641.984	−555.774	19.354
1600	79.284	370.191	312.799	91.828	−642.147	−550.021	17.956
1700	79.691	375.010	316.318	99.777	−642.321	−544.258	16.723
1800	80.038	379.575	319.706	107.764	−642.508	−538.485	15.626
1900	80.337	383.911	322.973	115.783	−642.710	−532.700	14.645
2000	80.595	388.038	326.123	123.830	−642.925	−526.905	13.761
2100	80.820	391.976	329.166	131.901	−643.152	−521.098	12.962
2200	81.016	395.741	332.107	139.993	−643.390	−515.280	12.234
2300	81.189	399.346	334.953	148.103	−643.637	−509.452	11.570
2400	81.342	402.804	337.709	156.230	−643.890	−503.612	10.961
2500	81.478	406.128	340.379	164.371	−644.146	−497.762	10.400
2600	81.600	409.326	342.970	172.525	−644.402	−491.902	9.882
2700	81.708	412.408	345.485	180.691	−644.656	−486.031	9.403
2800	81.806	415.381	347.929	188.867	−644.904	−480.152	8.957
2900	81.894	418.253	350.304	197.052	−645.145	−474.264	8.542
3000	81.974	421.031	352.616	205.245	−645.376	−468.367	8.155
3100	82.046	423.720	354.866	213.446	−645.595	−462.463	7.792
3200	82.112	426.326	357.059	221.654	−645.800	−456.553	7.452
3300	82.173	428.854	359.196	229.869	−645.989	−450.636	7.133
3400	82.228	431.308	361.281	238.089	−646.162	−444.713	6.832
3500	82.278	433.692	363.316	246.314	−646.317	−438.786	6.549
3600	82.325	436.010	365.304	254.544	−646.453	−432.854	6.281
3700	82.368	438.267	367.245	262.779	−646.570	−426.920	6.027
3800	82.408	440.464	369.143	271.018	−646.668	−420.982	5.787
3900	82.444	442.605	371.000	279.260	−646.746	−415.041	5.559
4000	82.478	444.693	372.816	287.506	−646.804	−409.099	5.342
4100	82.510	446.730	374.594	295.756	−646.843	−403.156	5.136
4200	82.539	448.718	376.335	304.008	−646.863	−397.212	4.940
4300	82.567	450.661	378.041	312.264	−646.864	−391.268	4.753
4400	82.592	452.559	379.713	320.522	−646.846	−385.325	4.574
4500	82.616	454.415	381.353	328.782	−646.811	−379.381	4.404
4600	82.639	456.232	382.961	337.045	−646.760	−373.439	4.241
4700	82.660	458.009	384.539	345.310	−646.692	−367.498	4.084
4800	82.680	459.750	386.088	353.577	−646.609	−361.558	3.935
4900	82.698	461.455	387.608	361.846	−646.512	−355.621	3.791
5000	82.716	463.125	389.102	370.116	−646.402	−349.685	3.653
5100	82.732	464.764	390.570	378.389	−646.279	−343.752	3.521
5200	82.748	466.370	392.012	386.663	−646.146	−337.821	3.393
5300	82.762	467.947	393.430	394.938	−646.003	−331.893	3.271
5400	82.776	469.494	394.824	403.215	−645.851	−325.968	3.153
5500	82.789	471.013	396.196	411.493	−645.691	−320.047	3.040
5600	82.802	472.505	397.545	419.773	−645.525	−314.126	2.930
5700	82.814	473.970	398.873	428.054	−645.354	−308.211	2.824
5800	82.825	475.411	400.180	436.336	−645.179	−302.297	2.722
5900	82.836	476.827	401.467	444.619	−645.001	−296.387	2.624
6000	82.846	478.219	402.735	452.903	−644.822	−290.480	2.529

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 265.082 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -467.52 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -470.28 \pm 4.2\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1090 (1)	1259 (2)
701 (1)	[500] (2)

Ground State Quantum Weight: 2 $\sigma = 3$
Point Group: C_{3v}
Bond Distance: C–F = [1.33] Å
Bond Angle: F–C–F = [112]°
Product of the Moments of Inertia: $I_A I_B I_C = [9.610547 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the enthalpies of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given by Syverud.[1] Kinetic data provide the most consistent paths to $\Delta_f H°$ of CF_3(g). Forward and reverse activation energies for the reactions $CHF_3(g) + X(g) \rightarrow CF_3(g) + HX(g)$ have been reported for X = Cl by Coomber and Whittle,[2] for X + Br by Amphlett and Whittle,[3] and for X = I by Goy *et al.*[4] Increases of about 0.3 $kcal \cdot mol^{-1}$ in the reverse activation energies for X = Cl and Br were proposed by Arthur and Gray[5] on the basis of additional data. Combining these values and reducing to 298.15 K, we get $\Delta_r H° = 2.93 \pm 0.7$ (X = Cl), 18.89 ± 0.7 (X = Br), and 35.5 ± 3 $kcal \cdot mol^{-1}$ (X = I). Coomber and Whittle[2] reviewed data for the analogous reactions with X = CH_3 and CD_3; these yield $\Delta_r H° = 0.6 \pm 2$ $kcal \cdot mol^{-1}$ at 298.15 K for X = CH_3. Activation energies have also been reported[6] for $CF_3I(g) + I(g) \rightarrow CF_3I(g) + I_2(g)$ from which we derive the average value $\Delta_r H° = 17.1 \pm 2$ $kcal \cdot mol^{-1}$. The data of Tschuikow–Roux[7] for $C_2F_6(g) \rightarrow 2CF_3(g)$, recalculated as suggested by Coomber and Whittle[8] but with JANAF functions, yield $\Delta_r H° = 97.6 \pm 6$ $kcal \cdot mol^{-1}$. Differences between the calculated and observed values of $\Delta_r H°$ are all less than half of the uncertainties assigned to the observed values.

The thorough discussion of photoionization data by Noutary[9] emphasized that CF_3^+ is formed with large amounts of excess energy both during ionization of CF_3 and during fragmentation of other fluorides. The amount of excess energy varies with the parent molecule. This may also be involved in electron–impact studies and could account for some of the discrepancies in bond– dissociation energies derived from appearance potentials and ionization potentials. Such data have been summarized by Coomber and Whittle.[10] Ionization data were omitted from the simultaneous adjustment due to uncertainty in the amounts of excess energy.

Also omitted was the mass–spectrometric study of $3C_2F_4(g) \rightarrow 4CF_3(g) + 2C(graphite)$ by Ehlert[11] which gave $\Delta_r H° = -102 \pm 3$ $kcal \cdot mol^{-1}$. The discrepancy of 10 $kcal \cdot mol^{-1}$ suggests that the data may not represent equilibrium for the above reaction. This reaction was one of many which resulted from heating MnF_3 in an effusion cell made of graphite.

Heat Capacity and Entropy

The bond length is assumed to be 1.33 Å by comparison with the molecules CF_3X, and the bond angle is estimated from molecular–orbital calculations of Morokuma *et al.*[12] and Beveridge *et al.*[13] The nonplanar structure is consistent with electron–spin–resonance spectra[14] of CF_3 in krypton and xenon matrices, with infrared spectra of CF_3 in various matrices[15] and in the gaseous phase,[16] and with photoionization spectra.[17] The principal moments of inertia are: $I_A = I_B = 7.9146 \times 10^{-39}$ and $I_C = 15.3421 \times 10^{-39}$ $g \cdot cm^2$. The observed vibrational fundamentals of Carlson and Pimentel[16] are confirmed by the matrix spectra of Milligan *et al.*[15] The latter estimated ν_4 to be in the range of 500 to 600 cm^{-1}. We choose the lower value by comparison with CF_3H, SiF_3H and SiF_3.[18]

The uncertainty in ν_4 corresponds to an uncertainty in the entropy of 0.4 $cal \cdot K^{-1} \cdot mol^{-1}$ at 300 K and 0.7 $cal \cdot K^{-1} \cdot mol^{-1}$ at 1000 K. Coomber and Whittle[2] and Amphlett and Whittle[19] used kinetic data to derive entropies of 63.2 $cal \cdot K^{-1} \cdot mol^{-1}$ at 350 K and 71.5 $cal \cdot K^{-1} \cdot mol^{-1}$ at 600 K. The calculated entropies from this table are higher by 2.0 and 1.7 $cal \cdot K^{-1} \cdot mol^{-1}$, respectively. These differences are only slightly larger than our estimate of the uncertainty in the kinetic results. We estimate the overall uncertainty in the calculated entropies as 1.0 $cal \cdot K^{-1} \cdot mol^{-1}$ at 298.15 K and 1.6 $cal \cdot K^{-1} \cdot mol^{-1}$ at 1000 K.

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Continued on page 700

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.525	−467.518	−467.518	INFINITE
100	33.941	221.531	303.427	−8.190	−468.603	−465.105	242.946
200	41.234	246.999	269.364	−4.473	−469.606	−461.194	120.452
250	45.682	256.679	265.879	−2.300	−469.982	−459.046	95.912
298.15	49.804	265.082	265.082	0.	−470.282	−456.912	80.049
300	49.957	265.390	265.082	0.092	−470.292	−456.829	79.541
350	53.911	273.393	265.705	2.691	−470.548	−454.564	67.840
400	57.467	280.828	267.136	5.477	−470.759	−452.266	59.060
450	60.598	287.782	269.048	8.430	−470.935	−449.943	52.228
500	63.315	294.311	271.251	11.530	−471.081	−447.602	46.761
600	67.663	306.259	276.110	18.090	−471.310	−442.884	38.556
700	70.862	316.942	281.193	25.024	−471.476	−438.132	32.694
800	73.232	326.567	286.274	32.235	−471.601	−433.360	28.296
900	75.013	335.300	291.243	39.651	−471.700	−428.574	24.874
1000	76.373	343.277	296.054	47.223	−471.786	−423.778	22.136
1100	77.431	350.608	300.684	54.915	−471.867	−418.973	19.895
1200	78.265	357.382	305.131	62.702	−471.951	−414.160	18.028
1300	78.934	363.674	309.395	70.563	−472.043	−409.341	16.448
1400	79.477	369.544	313.484	78.484	−472.147	−404.514	15.093
1500	79.923	375.043	317.407	86.455	−472.266	−399.679	13.918
1600	80.294	380.214	321.172	94.467	−472.403	−394.836	12.890
1700	80.605	385.091	324.790	102.512	−472.558	−389.983	11.983
1800	80.869	389.706	328.269	110.586	−472.730	−385.121	11.176
1900	81.094	394.085	331.619	118.685	−472.918	−380.249	10.454
2000	81.287	398.249	334.847	126.804	−473.120	−375.366	9.804
2100	81.455	402.219	337.962	134.941	−473.332	−370.473	9.215
2200	81.601	406.012	340.969	143.094	−473.550	−365.570	8.680
2300	81.729	409.642	343.877	151.261	−473.769	−360.657	8.191
2400	81.842	413.123	346.690	159.439	−473.985	−355.734	7.742
2500	81.942	416.466	349.415	167.629	−474.193	−350.803	7.330
2600	82.031	419.682	352.056	175.827	−474.388	−345.863	6.948
2700	82.110	422.779	354.618	184.034	−474.564	−340.917	6.595
2800	82.182	425.766	357.106	192.249	−474.719	−335.964	6.267
2900	82.246	428.651	359.524	200.470	−474.848	−331.006	5.962
3000	82.304	431.441	361.875	208.698	−474.947	−326.044	5.677
3100	82.356	434.140	364.163	216.931	−475.013	−321.080	5.410
3200	82.404	436.756	366.390	225.169	−475.044	−316.113	5.160
3300	82.448	439.292	368.561	233.412	−475.037	−311.147	4.925
3400	82.488	441.754	370.678	241.659	−474.992	−306.181	4.704
3500	82.524	444.146	372.743	249.909	−474.905	−301.217	4.495
3600	82.558	446.471	374.759	258.163	−474.777	−296.256	4.299
3700	82.589	448.733	376.728	266.421	−474.607	−291.299	4.112
3800	82.618	450.936	378.652	274.681	−474.394	−286.348	3.936
3900	82.644	453.083	380.533	282.944	−474.139	−281.403	3.769
4000	82.668	455.175	382.373	291.210	−473.841	−276.464	3.610
4100	82.691	457.217	384.174	299.478	−473.501	−271.534	3.459
4200	82.712	459.210	385.937	307.748	−473.120	−266.612	3.316
4300	82.732	461.156	387.663	316.020	−472.698	−261.701	3.179
4400	82.750	463.059	389.355	324.294	−472.236	−256.799	3.049
4500	82.768	464.918	391.014	332.570	−471.734	−251.908	2.924
4600	82.784	466.738	392.640	340.848	−471.195	−247.029	2.805
4700	82.799	468.518	394.236	349.127	−470.619	−242.162	2.691
4800	82.813	470.262	395.802	357.408	−470.007	−237.307	2.582
4900	82.826	471.969	397.339	365.690	−469.360	−232.466	2.478
5000	82.839	473.643	398.848	373.973	−468.680	−227.639	2.378
5100	82.851	475.283	400.331	382.257	−467.968	−222.825	2.282
5200	82.862	476.892	401.788	390.543	−467.224	−218.025	2.190
5300	82.872	478.471	403.220	398.830	−466.451	−213.240	2.102
5400	82.882	480.020	404.628	407.117	−465.648	−208.470	2.017
5500	82.892	481.541	406.012	415.406	−464.818	−203.716	1.935
5600	82.900	483.034	407.374	423.696	−463.962	−198.975	1.856
5700	82.909	484.502	408.715	431.986	−463.080	−194.252	1.780
5800	82.917	485.944	410.034	440.277	−462.174	−189.544	1.707
5900	82.924	487.361	411.332	448.569	−461.245	−184.850	1.637
6000	82.932	488.755	412.611	456.862	−460.294	−180.174	1.569

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 254.53 \pm 1.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 417.55 \pm 11.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 421.01 \pm 11.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[888] (1)
830 (1)
[1404] (2)
[480] (2)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: D_{3h}

Bond Distance: C–F = [1.33] Å

Bond Angle: F–C–F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.173095 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The ionization potential of CF_3 has been carefully measured by Lifshitz and Chupka.[1] They used a photoionization technique on CF_3 radicals prepared by heating CF_3CH_2ONO. Because of the low ionization cross-section near the threshold it is very difficult to determine the value exactly. The authors conclude that it is improbable that the ionization potential differs from 9.25 eV by as much as 0.2 eV. They choose to accept a value of 9.25 ± 0.04 eV (213.3 ± 0.9 kcal·mol^{-1}) based on their interpretation of the regular structure near the threshold. In a later paper, Walter *et al.*[9] use photodissociative ionization of CF_3I, CF_3Br and CF_3Cl to obtain an indirect ionization potential for CF_3 of 9.11 eV. We adopt a median value of 9.17 ± 0.08 eV (211.5 ± 1.8 kcal·mol^{-1}), which with $\Delta_f H°(CF_3, g, 0\ K) = -111.7 \pm 1.0$ kcal·mol^{-1} [2] gives $\Delta_f H°(CF_3^+, g, 0\ K) = 99.8 \pm 2.8$ kcal·mol^{-1}.

The above value supercedes all earlier values for the ionization potential of CF_3 which generally were obtained by electron impact methods, which do not have the energy resolution available in the photoionization technique. For further details of the older values see references.[3–7]

Heat Capacity and Entropy

The correlation rules proposed by Walsh[8] for AB_3 molecules indicate that molecules with less than 25 valence electrons are planar in their ground states. Since BF_3 is isoelectronic with CF_3^+, we estimate the vibrational frequencies by transferring the valence force field constants from BF_3 to CF_3^+. This gives 888, 674, 1404 and 480 cm^{-1}; however, Lifshitz and Chupka[1] conclude that the 674 cm^{-1} frequency is in fact at 830 cm^{-1}. This value is obtained from the spacings in the fine structure of the photoionization curve near threshold. They believe that the out-of-plane motion is most likely to be excited by the transition from pyramidal CF_3 to planar CF_3^+, thus, they ascribe the 830 cm^{-1} spacing to this motion. We adopt this one frequency in place of the calculated value. The bond lengths are assumed equal to those in CF_3. The principal moments of inertia are: $I_A = I_B = 8.3708 \times 10^{-39}$, and $I_C = 16.7416 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.543	417.554		
100	34.065	210.860	292.920	−8.206			
200	41.352	236.450	258.810	−4.472			
250	45.673	246.144	255.327	−2.296			
298.15	49.645	254.532	254.532	0.	421.007	431.267	−75.556
300	49.792	254.839	254.533	0.092	421.034	431.331	−75.101
350	53.582	262.804	255.153	2.678	421.805	432.987	−64.620
400	56.993	270.186	256.576	5.444	422.613	434.529	−56.744
450	60.013	277.077	258.475	8.371	423.450	435.969	−50.606
500	62.659	283.540	260.662	11.439	424.312	437.314	−45.686
600	66.955	295.363	265.479	17.930	426.093	439.748	−38.283
700	70.176	305.937	270.517	24.794	427.935	441.879	−32.973
800	72.600	315.474	275.551	31.939	429.823	443.742	−28.973
900	74.445	324.136	280.475	39.295	431.742	445.367	−25.848
1000	75.869	332.057	285.243	46.814	433.682	446.777	−23.337
1100	76.983	339.342	289.835	54.458	435.631	447.992	−21.273
1200	77.869	346.080	294.244	62.203	437.584	449.030	−19.546
1300	78.582	352.342	298.475	70.026	439.534	449.904	−18.077
1400	79.163	358.188	302.534	77.915	441.475	450.629	−16.813
1500	79.642	363.666	306.429	85.856	443.404	451.216	−15.713
1600	80.041	368.819	310.169	93.840	445.320	451.674	−14.746
1700	80.377	373.682	313.763	101.862	447.219	452.013	−13.889
1800	80.662	378.285	317.221	109.914	449.104	452.240	−13.124
1900	80.906	382.652	320.551	117.993	450.974	452.363	−12.436
2000	81.116	386.808	323.761	126.094	452.833	452.389	−11.815
2100	81.298	390.770	326.858	134.215	454.683	452.321	−11.251
2200	81.457	394.556	329.850	142.353	456.529	452.165	−10.736
2300	81.596	398.180	332.742	150.506	458.374	451.925	−10.264
2400	81.719	401.655	335.542	158.672	460.224	451.605	−9.829
2500	81.828	404.993	338.254	166.849	462.083	451.208	−9.427
2600	81.925	408.205	340.883	175.037	463.956	450.736	−9.055
2700	82.012	411.298	343.434	183.234	465.848	450.192	−8.709
2800	82.090	414.282	345.911	191.439	467.762	449.577	−8.387
2900	82.160	417.164	348.319	199.651	469.704	448.893	−8.085
3000	82.223	419.950	350.660	207.871	471.675	448.142	−7.803
3100	82.281	422.647	352.939	216.096	473.679	447.325	−7.537
3200	82.333	425.261	355.158	224.327	475.720	446.442	−7.287
3300	82.381	427.795	357.321	232.562	477.798	445.495	−7.052
3400	82.424	430.255	359.430	240.803	479.916	444.485	−6.829
3500	82.464	432.645	361.488	249.047	482.074	443.411	−6.618
3600	82.501	434.968	363.497	257.295	484.275	442.276	−6.417
3700	82.535	437.229	365.460	265.547	486.519	441.078	−6.227
3800	82.566	439.431	367.377	273.802	488.805	439.819	−6.046
3900	82.595	441.576	369.253	282.060	491.134	438.500	−5.873
4000	82.622	443.667	371.087	290.321	493.505	437.121	−5.708
4100	82.647	445.708	372.882	298.585	495.919	435.681	−5.551
4200	82.670	447.700	374.640	306.851	498.375	434.182	−5.400
4300	82.692	449.645	376.362	315.119	500.872	432.624	−5.255
4400	82.712	451.546	378.049	323.389	503.408	431.008	−5.117
4500	82.731	453.405	379.703	331.661	505.984	429.334	−4.984
4600	82.748	455.224	381.325	339.935	508.598	427.601	−4.856
4700	82.765	457.004	382.916	348.211	511.250	425.812	−4.732
4800	82.780	458.746	384.478	356.488	513.937	423.966	−4.614
4900	82.795	460.453	386.011	364.767	516.659	422.064	−4.499
5000	82.809	462.126	387.517	373.047	519.415	420.105	−4.389
5100	82.822	463.766	388.996	381.328	522.203	418.091	−4.282
5200	82.834	465.374	390.449	389.611	525.022	416.023	−4.179
5300	82.846	466.952	391.878	397.895	527.872	413.899	−4.079
5400	82.856	468.501	393.282	406.180	530.750	411.722	−3.983
5500	82.867	470.021	394.664	414.466	533.656	409.491	−3.889
5600	82.876	471.515	396.023	422.754	536.589	407.207	−3.798
5700	82.886	472.982	397.360	431.042	539.547	404.870	−3.710
5800	82.895	474.423	398.677	439.331	542.529	402.481	−3.625
5900	82.903	475.840	399.972	447.621	545.535	400.041	−3.542
6000	82.911	477.234	401.249	455.911	548.562	397.549	−3.461

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 307.629 \pm 0.63\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -583.23 \pm 3.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -589.11 \pm 3.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1074 (1)	1185 (2)
742 (1)	539 (2)
284 (1)	260 (2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: C–F = 1.332 Å; C–I = 2.130 Å
Bond Angles: F–C–F = 108.3° ± 1°; F–C–I = 110.62°
Product of the Moments of Inertia: $I_A I_B I_C = 4.410587 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the enthalpies of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given by Syverud.[1] Lord *et al.*[2,3] report equilibrium data for the reactions $CF_3X(g) + I_2(g) = CF_3I(g) + XI(g)$ where X = H, Cl, and Br. In addition to these prime links, there is a weak link to CF_3 through kinetic studies of $CF_3I(g) + I(g) \rightarrow CF_3(g) + I_2(g)$. Data for this reaction[3,12] yield the average value $\Delta_f H° = 17.1 \pm 2\ kcal·mol^{-1}$ at 298.15 K.

Heat Capacity and Entropy

The molecular structure has been derived from electron-diffraction studies by Bowen,[4] Anderson,[5] and Wong and Schomaker.[6] Differences among the data are small. The results of Anderson are adopted since they are intermediate between the others. Microwave data[7] are consistent with the adopted parameters. Infrared spectra of the gas were observed by several investigators[8–10] and Raman spectra of the liquid were obtained by Edgell and May.[10] The vibrational assignments of[9,10] are in close agreement. These assignments are adopted but preference is given to frequencies observed for the gas. In particular, ν_6 is taken as 260 cm^{-1} (from overtone and combination bands of the gas) rather than 265 cm^{-1} (from the Raman spectra of the liquid). The approximate values of ν_2, ν_3 and ν_6 have been confirmed by analysis[11] of absorption spectra in the UV.

The thermodynamic functions of this table are essentially the same as those calculated by McGee *et al.*[9] Uncertainty in the entropy is estimated to vary from 0.15 to 0.6 $cal·K^{-1}·mol^{-1}$ over the range from 300 to 1000 K. Uncertainty in ν_6 and neglect of anharmonicity are the major sources of error. Discussions of the magnitude of anharmonic effects appear on the tables for $CClF_3$(g) and CF_4(g). The principal moments of inertia are: $I_A = 14.7097 \times 10^{-39}$ and $I_B = I_C = 54.7578 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.008	−583.227	−583.227	INFINITE
100	41.917	247.280	361.949	−11.467	−585.632	−581.659	303.828
200	58.726	281.794	313.747	−6.391	−587.742	−576.793	150.643
250	65.362	295.629	308.766	−3.284	−588.499	−573.965	119.923
298.15	70.940	307.629	307.629	0.	−589.107	−571.109	100.056
300	71.139	308.068	307.630	0.131	−589.129	−570.997	99.419
350	76.154	319.420	308.515	3.817	−589.704	−567.930	84.759
400	80.462	329.878	310.541	7.735	−598.196	−564.510	73.717
450	84.124	339.573	313.234	11.852	−599.224	−560.237	65.031
500	87.220	348.601	316.325	16.138	−620.266	−553.952	57.871
600	92.033	364.953	323.096	25.114	−619.956	−540.717	47.074
700	95.478	379.413	330.129	34.499	−619.555	−527.541	39.366
800	97.982	392.335	337.111	44.179	−619.100	−514.427	33.589
900	99.840	403.988	343.905	54.074	−618.615	−501.372	29.099
1000	101.246	414.583	350.451	64.132	−618.117	−488.371	25.510
1100	102.331	424.286	356.729	74.313	−617.617	−475.421	22.576
1200	103.184	433.228	362.736	84.590	−617.126	−462.516	20.133
1300	103.863	441.515	368.481	94.944	−616.653	−449.651	18.067
1400	104.413	449.233	373.977	105.359	−616.208	−436.822	16.298
1500	104.864	456.452	379.237	115.823	−615.797	−424.023	14.766
1600	105.238	463.233	384.277	126.329	−615.428	−411.250	13.426
1700	105.551	469.622	389.111	136.869	−615.106	−398.499	12.244
1800	105.816	475.663	393.753	147.438	−614.834	−385.766	11.195
1900	106.042	481.390	398.216	158.031	−614.613	−373.046	10.256
2000	106.236	486.835	402.512	168.645	−614.440	−360.336	9.411
2100	106.403	492.022	406.652	179.277	−614.311	−347.635	8.647
2200	106.550	496.975	410.646	189.925	−614.220	−334.938	7.952
2300	106.678	501.715	414.503	200.586	−614.157	−322.245	7.318
2400	106.791	506.257	418.232	211.260	−614.113	−309.554	6.737
2500	106.890	510.619	421.841	221.944	−614.078	−296.865	6.203
2600	106.979	514.813	425.337	232.638	−614.041	−284.177	5.709
2700	107.059	518.852	428.726	243.339	−613.991	−271.491	5.252
2800	107.130	522.747	432.015	254.049	−613.919	−258.807	4.828
2900	107.194	526.507	435.209	264.765	−613.815	−246.126	4.433
3000	107.252	530.142	438.313	275.488	−613.671	−233.450	4.065
3100	107.304	533.660	441.332	286.215	−613.479	−220.779	3.720
3200	107.352	537.067	444.271	296.948	−613.233	−208.115	3.397
3300	107.395	540.371	447.133	307.686	−612.929	−195.459	3.094
3400	107.435	543.578	449.923	318.427	−612.561	−182.814	2.809
3500	107.471	546.693	452.643	329.172	−612.126	−170.181	2.540
3600	107.505	549.721	455.298	339.921	−611.622	−157.560	2.286
3700	107.536	552.667	457.890	350.673	−611.047	−144.955	2.046
3800	107.564	555.535	460.422	361.428	−610.400	−132.367	1.820
3900	107.590	558.329	462.897	372.186	−609.681	−119.796	1.604
4000	107.615	561.054	465.317	382.946	−608.890	−107.245	1.400
4100	107.637	563.711	467.685	393.709	−608.028	−94.715	1.207
4200	107.658	566.305	470.002	404.474	−607.094	−82.206	1.022
4300	107.678	568.839	472.271	415.241	−606.091	−69.721	0.847
4400	107.696	571.314	474.494	426.009	−605.021	−57.259	0.680
4500	107.713	573.735	476.673	436.780	−603.883	−44.822	0.520
4600	107.729	576.102	478.808	447.552	−602.681	−32.412	0.368
4700	107.744	578.419	480.903	458.326	−601.417	−20.028	0.223
4800	107.758	580.688	482.959	469.101	−600.091	−7.672	0.083
4900	107.772	582.910	484.976	479.877	−598.707	4.656	−0.050
5000	107.784	585.087	486.956	490.655	−597.265	16.955	−0.177
5100	107.796	587.222	488.901	501.434	−595.770	29.224	−0.299
5200	107.807	589.315	490.812	512.214	−594.221	41.465	−0.417
5300	107.817	591.369	492.690	522.995	−592.622	53.674	−0.529
5400	107.827	593.384	494.537	533.778	−590.974	65.853	−0.637
5500	107.837	595.363	496.352	544.561	−589.279	78.000	−0.741
5600	107.845	597.306	498.137	555.345	−587.540	90.118	−0.841
5700	107.854	599.215	499.894	566.130	−585.757	102.202	−0.937
5800	107.862	601.091	501.623	576.916	−583.934	114.255	−1.029
5900	107.869	602.935	503.324	587.702	−582.071	126.278	−1.118
6000	107.876	604.748	504.999	598.489	−580.170	138.268	−1.204

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 261.419 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -927.23 \pm 1.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -933.20 \pm 1.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
908.5 (1)	1283.0 (3)
435.0 (2)	631.5 (3)

Ground State Quantum Weight: 1 σ = 12
Point Group: T_d
Bond Distance: C–F = 1.320 Å
Bond Angle: F–C–F = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 3.149690 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the enthaplies of formation of HF(g), HF(50 H_2O) and five closely related fluorides. Adjustment of 23 selected observations relating the 7 variables gives the following enthalpies of formation in $kcal \cdot mol^{-1}$ at 298.15 K: HF(g), −65.14 ± 0.2; HF(50 H_2O), −76.78 ± 0.1; NaF(cr), −137.52 ± 0.2; BF_3(g), −271.42 ± 0.4; CF_4(g), −223.04 ± 0.3; NF_3(g), −31.43 ± 0.3; and C_2F_4(polymer), −198.2 ± 0.7. The ± values are estimates of the overall uncertainty including systematic error. Further details of the simultaneous adjustment are given by Syverud.[1]

The selected value is essentially the same as that obtained by Greenberg and Hubbard[2] in their thorough calorimetric study of the combustion in fluorine of natural and synthetic graphite. Their results is confirmed by the data of Domalski and Armstrong[3] for combustion of graphite–Teflon mixtures. Reliable data[1] also link CF_4(g) with HF(n H_2O), NF_3(g) and C_2F_4(polymer). Armstrong[4,3] critically reviewed the more uncertain data which were omitted from the adjustment.

Heat Capacity and Entropy

The fundamental vibrations are those observed in the gas-phase Raman spectra by Monostori and Weber[5] and the gas-phase infrared spectra by Maki *et al.*[6] and Chalmers and McKean.[7] The frequencies are essentially the same as those selected by Shimanouchi[8] who also lists earlier spectral studies. Electron–diffraction studies of the gas were reported by Thornton[9] and Hoffman and Livingston.[10] The adopted bond length is the average of these two results which differ by only 0.006 Å. The principal moments of inertia are: $I_A = I_B = I_C = 14.6585 \times 10^{-39}\ g \cdot cm^2$.

The most significant uncertainty in the calculated thermodynamic functtions is due to neglect of anharmonic contributions. Estimates for these contributions were given by Barho[11] and Albright *et al.*,[12] and functions calculated with anharmonic terms were given by McBride *et al.*[13] Differences between McBride and this JANAF table vary from 0.1 to 0.75 $cal \cdot K^{-1} \cdot mol^{-1}$ in $C_p°$ and 0.05 to 0.49 $cal \cdot K^{-1} \cdot mol^{-1}$ in $S°$ over the range from 300 to 1000 K. Measurements[14] of C_v(303–473 K) suggest that anharmonic contributions are significant, but the data are not sufficiently accurate to test the calculations of McBride *et al.*[13] Heat capacity data[15] for the condensed phases were reviewed by Kelley and King[16] who derived $S°(298.15\ K) = 62.8 \pm 0.5\ cal \cdot K^{-1} \cdot mol^{-1}$ for CF_4(g).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.731	−927.229	−927.229	INFINITE
100	34.745	212.363	306.188	−9.383	−929.755	−916.822	478.899
200	47.370	239.882	266.577	−5.339	−931.896	−902.995	235.838
250	54.623	251.239	262.389	−2.788	−932.645	−895.679	187.142
298.15	61.054	261.419	261.419	0.	−933.199	−888.507	155.663
300	61.288	261.798	261.420	0.113	−933.218	−888.229	154.654
350	67.217	271.700	262.189	3.329	−933.651	−880.695	131.437
400	72.400	281.022	263.966	6.822	−933.970	−873.107	114.016
450	76.875	289.815	266.354	10.557	−934.198	−865.485	100.463
500	80.712	298.118	269.120	14.499	−934.351	−857.841	89.618
600	86.781	313.399	275.249	22.890	−934.485	−842.523	73.348
700	91.209	327.127	281.697	31.801	−934.451	−827.197	61.726
800	94.476	339.530	288.164	41.093	−934.298	−811.884	53.011
900	96.927	350.806	294.507	50.669	−934.065	−796.596	46.233
1000	98.797	361.119	300.660	60.459	−933.778	−781.337	40.813
1100	100.249	370.607	306.593	70.415	−933.456	−766.108	36.379
1200	101.394	379.380	312.298	80.499	−933.115	−750.909	32.686
1300	102.312	387.534	317.776	90.686	−932.766	−735.739	29.562
1400	103.057	395.144	323.033	100.956	−932.417	−720.597	26.886
1500	103.669	402.276	328.081	111.293	−932.075	−705.479	24.567
1600	104.178	408.983	332.930	121.686	−931.744	−690.383	22.539
1700	104.605	415.312	337.591	132.126	−931.428	−675.308	20.750
1800	104.966	421.302	342.077	142.605	−931.125	−660.251	19.160
1900	105.275	426.986	346.398	153.117	−930.835	−645.210	17.738
2000	105.540	432.392	350.563	163.658	−930.556	−630.184	16.459
2100	105.770	437.547	354.584	174.224	−930.283	−615.173	15.302
2200	105.970	442.473	358.467	184.811	−930.011	−600.174	14.250
2300	106.146	447.187	362.223	195.417	−929.735	−585.187	13.290
2400	106.301	451.708	365.858	206.040	−929.449	−570.213	12.410
2500	106.438	456.050	369.379	216.677	−929.146	−555.251	11.601
2600	106.560	460.227	372.794	227.327	−928.821	−540.302	10.855
2700	106.669	464.251	376.107	237.988	−928.466	−525.365	10.164
2800	106.767	468.132	379.325	248.660	−928.077	−510.442	9.522
2900	106.855	471.880	382.452	259.342	−927.649	−495.534	8.926
3000	106.935	475.504	385.494	270.031	−927.177	−480.642	8.369
3100	107.007	479.012	388.454	280.728	−926.656	−465.766	7.848
3200	107.073	482.410	391.337	291.432	−926.084	−450.907	7.360
3300	107.132	485.706	394.147	302.143	−925.458	−436.068	6.902
3400	107.187	488.905	396.888	312.859	−924.775	−421.248	6.472
3500	107.237	492.013	399.561	323.580	−924.034	−406.449	6.066
3600	107.283	495.034	402.171	334.306	−923.233	−391.671	5.683
3700	107.326	497.974	404.721	345.036	−922.372	−376.918	5.321
3800	107.365	500.837	407.213	355.771	−921.450	−362.188	4.979
3900	107.401	503.626	409.650	366.509	−920.468	−347.483	4.654
4000	107.435	506.346	412.033	377.251	−919.425	−332.804	4.346
4100	107.466	508.999	414.366	387.996	−918.322	−318.153	4.053
4200	107.495	511.589	416.650	398.744	−917.160	−303.528	3.775
4300	107.522	514.119	418.887	409.495	−915.940	−288.932	3.510
4400	107.547	516.591	421.080	420.249	−914.663	−274.365	3.257
4500	107.571	519.008	423.229	431.005	−913.330	−259.827	3.016
4600	107.593	521.373	425.337	441.763	−911.943	−245.321	2.786
4700	107.614	523.687	427.405	452.523	−910.503	−230.844	2.566
4800	107.633	525.953	429.435	463.285	−909.011	−216.399	2.355
4900	107.651	528.172	431.427	474.050	−907.470	−201.986	2.153
5000	107.669	530.347	433.384	484.816	−905.880	−187.604	1.960
5100	107.685	532.480	435.306	495.583	−904.243	−173.255	1.774
5200	107.700	534.571	437.195	506.353	−902.562	−158.937	1.597
5300	107.714	536.622	439.052	517.123	−900.837	−144.653	1.426
5400	107.728	538.636	440.877	527.895	−899.069	−130.403	1.261
5500	107.741	540.613	442.673	538.669	−897.262	−116.185	1.103
5600	107.753	542.554	444.439	549.444	−895.416	−102.000	0.951
5700	107.765	544.461	446.177	560.219	−893.532	−87.849	0.805
5800	107.776	546.336	447.888	570.997	−891.613	−73.731	0.664
5900	107.786	548.178	449.572	581.775	−889.659	−59.645	0.528
6000	107.796	549.990	451.231	592.554	−887.672	−45.595	0.397

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 322.53 \pm 2.9\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -756.4 \pm 13\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -764.8 \pm 13\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1294.4 (1)	679.0 (1)	1223.2 (1)
1262.5 (1)	584.1 (1)	607.5 (1)
947.3 (1)	433.7 (1)	250.0 (1)
882.1 (1)	227.5 (1)	internal rotation

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: C–F = [1.33] Å; F–O = [1.42] Å; C–O = [1.43] Å
Bond Angles: C–O–F = [103.2]°; F–C–F = [109.5]°
Product of the Moments of Inertia: $I_A I_B I_C = 1.151629 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

Porter and Cady[1] measured equilibrium constants for the reaction $CF_3OF(g) = COF_2(g) + F_2(g)$ in the temperature range 630–750 K. Equilibrium constants were also determined with excess fluorine added to the system. 2nd and 3rd law analyses of these data yield the following enthalpy of reaction:

	$\Delta_r H°(298.15\ K)$, $kcal \cdot mol^{-1}$		Drift
	2nd law	3rd law	$cal \cdot K^{-1} \cdot mol^{-1}$
Set 1	27.65 ± 0.2	30.10	3.6 ± 0.3
Set added fluorine	25.11 ± 0.3	30.09	7.2 ± 0.5

The 3rd law analyses indicate significant trends within each set of equilibrium data. If the entire error is assigned to the Gibbs energy functions, then the drifts in the 3rd law analysis imply that the Gibbs energy functions for CF_3OF should be increased by 3.6 or 7.2 $cal \cdot K^{-1} \cdot mol^{-1}$. However, the real error in these Gibbs energy functions is probably no larger than 1 $cal \cdot K^{-1} \cdot mol^{-1}$ in the temperature range of the experimental data. Apparently, the equilibrium reaction investigated by Porter and Cady[1] was affected by side reactions possibly involving perfluorodimethyl peroxide. However, since the only other approach to the enthalpy of formation of CF_3OF involves bond energies, we adopt the 3rd law value, $\Delta_r H° = 30.1\ kcal \cdot mol^{-1}$, and derive $\Delta_f H°(CF_3OF, g, 298.15\ K) = -182.8 \pm 3\ kcal \cdot mol^{-1}$ with $\Delta_f H°(COF_2, g, 298.15\ K) = -152.7 \pm 0.4\ kcal \cdot mol^{-1}$.[2]

Czarnowski *et al.*[3] recently determined the O–F bond energy in CF_3OF from kinetic studies on the thermal decomposition of CF_3OF in the presence of SO_3. They reported the value $D°_0(O–F) = 43.5 \pm 0.5\ kcal \cdot mol^{-1}$. Combining this result with the following data,

$\Delta_f H°(C, g, 298.15\ K) = 170.89 \pm kcal \cdot mol^{-1}$ [4]
$\Delta_f H°(F, g, 298.15\ K) = 18.86 \pm 0.40\ kcal \cdot mol^{-1}$ [5]
$\Delta_f H°(O, g, 298.15\ K) = 59.559 \pm 0.03\ kcal \cdot mol^{-1}$ [6]
$D°_0(C–F) = 117.4\ kcal \cdot mol^{-1}$ (from $\Delta_f H°(CF_4, g, 298.15\ K) = -223.04 \pm 0.3\ kcal \cdot mol^{-1}$ [7]
$D°_0(C–O) = 84\ kcal \cdot mol^{-1}$ [8]

we derive $\Delta_f H°(CF_3OF, g, 298.15\ K) = -173.8\ kcal \cdot mol^{-1}$.

The value determined from Porter and Cady's equilibrium data[1] is adopted here.

Heat Capacity and Entropy

The vibrational frequencies are from the intrared and Raman studies of Wilt and Jones[9] and are in reasonable agreement with nine of the twelve expected fundamentals observed by Lagemann *et al.*[10] Bond lengths and angles are estimated quantities chosen by Wilt and Jones.[9] The principal moments of inertia are: $I_A = 14.8190 \times 10^{-39}$, $I_B = 27.8485 \times 10^{-39}$, and $I_C = 27.9057 \times 10^{-39}\ g\ cm^2$. The contributions of hindered internal rotation to the thermodynamic properties of CF_3OF are from the tables of Pitzer and Gwinn.[11] The reduced moment of inertia, I_r, and the potential barrier, V_o, are from the work of Wilt and Jones[9] and are:

$I_r = 2.939 \times 10^{-39}\ g \cdot cm^{-1}$ $V_o = 1130\ kcal \cdot mol^{-1}$ ($\nu_{12} = 56\ cm^{-1}$)

Continued on page 700

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$		$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.644	−756.437	−756.437	INFINITE
100	50.170	253.856	383.560	−12.970	−762.089	−744.640	388.960
200	65.831	293.567	329.248	−7.136	−763.895	−726.383	189.712
298.15	79.354	322.533	322.533	0.	−764.835	−707.781	124.000
300	79.617	323.024	322.534	0.147	−764.847	−707.427	123.174
400	91.023	347.556	325.802	8.702	−765.239	−688.216	89.872
500	99.876	368.861	332.329	18.266	−765.263	−668.951	69.885
600	106.462	387.683	340.017	28.599	−765.034	−649.707	56.562
700	111.056	404.453	348.047	39.484	−764.652	−630.514	47.050
800	114.533	419.520	356.055	50.772	−764.174	−611.383	39.919
900	117.089	433.163	363.877	62.358	−763.633	−592.316	34.377
1000	119.039	445.604	371.437	74.167	−763.058	−573.312	29.947
1100	120.625	457.028	378.706	86.154	−762.459	−554.366	26.325
1200	121.779	467.574	385.678	98.275	−761.855	−535.475	23.309
1300	122.779	477.362	392.358	110.505	−761.254	−516.634	20.759
1400	123.591	486.492	398.760	122.825	−760.662	−497.840	18.575
1500	124.256	495.042	404.897	135.218	−760.085	−479.087	16.683
1600	124.805	503.080	410.784	147.672	−759.527	−460.372	15.030
1700	125.206	510.658	416.439	160.173	−758.995	−441.691	13.572
1800	125.599	517.826	421.874	172.714	−758.488	−423.041	12.276
1900	125.934	524.626	427.105	185.291	−758.004	−404.419	11.118
2000	126.219	531.093	432.144	197.899	−757.539	−385.821	10.077
2100	126.470	537.257	437.003	210.533	−757.090	−367.246	9.135
2200	126.687	543.146	441.695	223.192	−756.651	−348.692	8.279
2300	126.876	548.782	446.229	235.870	−756.218	−330.158	7.498
2400	127.043	554.185	450.616	248.566	−755.785	−311.644	6.783
2500	127.189	559.374	454.863	261.278	−755.345	−293.147	6.125
2600	127.261	564.364	458.979	274.001	−754.895	−274.668	5.518
2700	127.340	569.168	462.972	286.730	−754.431	−256.206	4.957
2800	127.445	573.801	466.848	299.470	−753.943	−237.762	4.436
2900	127.541	578.275	470.614	312.219	−753.425	−219.336	3.951
3000	127.629	582.601	474.275	324.978	−752.873	−200.929	3.498
3100	127.705	586.787	477.837	337.744	−752.280	−182.540	3.076
3200	127.775	590.842	481.305	350.518	−751.645	−164.172	2.680
3300	127.841	594.775	484.685	363.299	−750.964	−145.823	2.308
3400	127.901	598.593	487.979	376.086	−750.234	−127.497	1.959
3500	127.955	602.301	491.193	388.879	−749.453	−109.192	1.630
3600	128.005	605.906	494.329	401.677	−748.620	−90.910	1.319
3700	128.051	609.414	497.392	414.480	−747.734	−72.653	1.026
3800	128.093	612.830	500.386	427.287	−746.794	−54.420	0.748
3900	128.132	616.157	503.312	440.099	−745.799	−36.212	0.485
4000	128.168	619.402	506.173	452.914	−744.751	−18.031	0.235
4100	128.201	622.567	508.974	465.732	−743.649	0.123	−0.002
4200	128.231	625.657	511.715	478.554	−742.494	18.251	−0.227
4300	128.261	628.674	514.400	491.378	−741.287	36.349	−0.442
4400	128.289	631.623	517.031	504.206	−740.029	54.419	−0.646
4500	128.315	634.507	519.610	517.036	−738.721	72.461	−0.841
4600	128.340	637.327	522.138	529.869	−737.364	90.471	−1.027
4700	128.363	640.088	524.619	542.704	−735.961	108.453	−1.205
4800	128.384	642.790	527.053	555.541	−734.511	126.404	−1.376
4900	128.403	645.438	529.442	568.381	−733.019	144.325	−1.539
5000	128.420	648.032	531.788	581.222	−731.484	162.214	−1.695
5100	128.437	650.575	534.092	594.065	−729.909	180.073	−1.844
5200	128.454	653.069	536.356	606.909	−728.297	197.900	−1.988
5300	128.470	655.516	538.581	619.755	−726.647	215.696	−2.126
5400	128.485	657.918	540.769	632.603	−724.964	233.460	−2.258
5500	128.499	660.276	542.921	645.452	−723.248	251.192	−2.386
5600	128.512	662.591	545.037	658.303	−721.501	268.894	−2.508
5700	128.522	664.866	547.119	671.155	−719.727	286.563	−2.626
5800	128.533	667.101	549.169	684.007	−717.925	304.202	−2.740
5900	128.545	669.298	551.186	696.861	−716.099	321.810	−2.849
6000	128.558	671.459	553.173	709.716	−714.250	339.385	−2.955

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = [379.97 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1700.4 \pm 63]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1717.1 \pm 63]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1168(1)	Free Rotation	591(2)
883(1)	627(1)	558(2)
755(1)	319(1)	425(2)
692(1)	501(1)	290(2)
612(1)	1256(2)	220(2)
325(1)	903(2)	

Ground State Quantum Weight: 1 σ (overall) = 12

Point Group: C_{4v}

Bond Distances: C–F = [1.32] Å; S–F = [1.56] Å; C–S = 1.92 Å

Bond Angles: S–C–F = [109.5°]; F*–S–F* = 90°
F*–S–C = [90°]; F**–S–C = 180°
(* – equatorial ** – axial)

Product of Moments of Inertia: $I_A I_B I_C = [2.659738 \times 10^{-112}]\ g^3 \cdot cm^6$

Reduced Moment of Inertia: $I_{red} = [9.9216 \times 10^{-39}]\ g \cdot cm^2$

Enthalpy of Formation

We adopt $D_0°(CF_3–SF_5) = 80 \pm 10\ kcal \cdot mol^{-1}$ from which $\Delta_f H°$ is calculated to be $-406.4 \pm 15\ kcal \cdot mol^{-1}$ at 0 K by combining $D_0°$ with $\Delta_f H°(CF_3, g) = -111.7 \pm 1.0\ kcal \cdot mol^{-1}$ and $\Delta_f H°(SF_5, g, 0\ K) = -214.7 \pm 3.6\ kcal \cdot mol^{-1}$.[1] We estimate that the $D_0°$(C–S) in CF_3SF_5 of the C–C, S–S, and C–S bond lengths and the corresponding stretching frequencies for C_2F_6, S_2F_{10}, and CF_3SF_5 indicates that $D_0°$(C–S) should be intermediate between those for C–C and S–S. We calculate the heat of atomization ($\Delta_a H°$) and $\Delta_f H°$ value at 298.15 K as 788.6 ± 19 $kcal \cdot mol^{-1}$ and $-410.385 \pm 15\ kcal \cdot mol^{-1}$, respectively.

Heat Capacity and Entropy

The microwave spectrum of CSF_8 observed by Kisliuk and Silvey[2] shows that the molecule is a symmetric rotor comprised of CF_3 and SF_5 groups joined by a C–S bond. The infrared,[3,4] and Raman[4] spectra obey the selection rules predicted for the point group C_{4v}. We estimate all structural data except for the C–S bond length by analogy with the CF_3 structure in C_2F_6 and the SF_5 structure in S_2F_{10}.[1] We select a value for the C–S bond length which when combined with the estimated data reproduces the experimentally determined amount of inertia ($I_A = I_B = 7.656 \times 10^{-38}\ g \cdot cm^2$)[2] within the experimental error. The principal moment of inertia about the symmetry axis is $I_C = 45.3692 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies are rounded values taken from the gas phase infrared and liquid phase Raman study of Griffiths.[4] The infrared data are supported by results obtained in an earlier study.[3] Griffiths[4] assigned the Raman band at 262 cm^{-1} to the b_1 SF_2 out–of–plane deformation mode (ν_9) by analogy with his assignment for $ClSF_5$ ($\nu_6 = 271\ cm^{-1}$). More recent information[1] on $ClSF_5$ indicates that the 271 cm^{-1} Raman band is the low–frequency SF_5 rocking fundamental π_{11}. By analogy with this new assignment for $ClSF_5$, we assign the infrared band observed at 290 cm^{-1} by Griffiths[4] to the SF_5 rocking fundamental (π_{16}). The Raman band at 319 cm^{-1} is believed to be π_9 since it is close to the values (332 cm^{-1} and 317 cm^{-1}) predicted for the analogous deformation mode (π_6) in $ClSF_5$[1] by force field calculations. We assume that the internal rotation about the C–S bond is unrestricted based on spectroscopic evidence[3,4] which indicates that the barrier is very small. Kisliuk and Silvey[2] have derived a potential barrier of 219 cm^{-1} (0.63 $kcal \cdot mol^{-1}$) from satellite lines observed in their microwave spectrum; however, these lines are probably due to the CF_3 rocking mode (π_{17}) rather than the torsional vibration (π_7), as indicated by Eggers *et al.*[3] The overall symmetry number is calculated as the product of the external (λ) and internal (x) symmetry numbers with x assumed equal to 12.

References

[1]JANAF Thermochemical Tables: CF_3(g) and C_2F_6(g), 6–30–69; SF_5(g), S_2F_{10}(g), and ClSF5(g),12–31–77.

[2]P. Kisliuk and G. A. Silvey, J. Chem. Phys. **20**, 517 (1952).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	4.157	0.	INFINITE	−24.084	−1700.372	−1700.372	INFINITE
100	55.764	278.734	477.625	−19.889	−1708.555	−1666.933	870.716
200	102.475	331.780	391.607	−11.965	−1714.316	−1622.806	423.833
250	122.790	356.890	382.170	−6.320	−1715.995	−1599.720	334.243
298.15	139.222	379.967	379.967	0.	−1717.051	−1577.222	276.323
300	139.794	380.830	379.969	0.258	−1717.082	−1576.354	274.468
350	153.755	403.463	381.725	7.609	−1717.724	−1552.844	231.749
400	165.138	424.764	385.787	15.591	−1720.246	−1529.177	199.690
450	174.415	444.768	391.241	24.087	−1720.972	−1505.256	174.726
500	181.997	463.550	397.543	33.004	−1721.551	−1481.253	154.745
600	193.374	497.804	411.456	51.808	−1721.803	−1433.155	124.767
700	201.250	528.240	426.007	71.563	−1721.375	−1385.073	103.355
800	206.857	555.499	440.520	91.983	−1720.525	−1337.084	87.303
900	210.958	580.112	454.685	112.884	−1772.531	−1288.138	74.762
1000	214.031	602.505	468.364	134.141	−1770.014	−1234.451	64.481
1100	216.384	623.020	481.505	155.667	−1767.433	−1181.020	56.082
1200	218.223	641.930	494.096	177.401	−1764.821	−1127.824	49.093
1300	219.683	659.457	506.150	199.299	−1762.201	−1074.847	43.188
1400	220.861	675.781	517.690	221.328	−1759.592	−1022.072	38.134
1500	221.824	691.053	528.744	243.464	−1757.006	−969.483	33.760
1600	222.621	705.396	539.341	265.687	−1754.451	−917.064	29.939
1700	223.287	718.913	549.510	287.984	−1751.931	−864.805	26.572
1800	223.850	731.692	559.280	310.341	−1749.446	−812.693	23.584
1900	224.329	743.808	568.676	332.751	−1746.992	−760.718	20.914
2000	224.740	755.325	577.723	355.205	−1744.564	−708.872	18.514
2100	225.095	766.299	586.443	377.697	−1742.151	−657.147	16.346
2200	225.405	776.778	594.859	400.222	−1739.742	−605.537	14.377
2300	225.676	786.803	602.988	422.777	−1737.327	−554.035	12.583
2400	225.914	796.413	610.848	445.356	−1734.891	−502.640	10.940
2500	226.125	805.640	618.457	467.958	−1732.421	−451.347	9.430
2600	226.313	814.512	625.828	490.581	−1729.903	−400.154	8.039
2700	226.480	823.057	632.975	513.220	−1727.325	−349.058	6.753
2800	226.630	831.296	639.912	535.876	−1724.676	−298.059	5.560
2900	226.765	839.251	646.649	558.546	−1721.944	−247.156	4.452
3000	226.888	846.941	653.198	581.229	−1719.119	−196.350	3.419
3100	226.998	854.382	659.569	603.923	−1716.194	−145.640	2.454
3200	227.099	861.591	665.770	626.628	−1713.161	−95.024	1.551
3300	227.190	868.581	671.810	649.342	−1710.014	−44.506	0.704
3400	227.274	875.364	677.698	672.066	−1706.748	5.915	−0.091
3500	227.351	881.953	683.440	694.797	−1703.361	56.239	−0.839
3600	227.421	888.359	689.044	717.536	−1699.849	106.465	−1.545
3700	227.486	894.591	694.515	740.281	−1696.212	156.590	−2.211
3800	227.546	900.658	699.860	763.033	−1692.447	206.615	−2.840
3900	227.601	906.570	705.085	785.790	−1688.555	256.540	−3.436
4000	227.652	912.333	710.195	808.553	−1684.538	306.364	−4.001
4100	227.700	917.955	715.194	831.320	−1680.395	356.085	−4.537
4200	227.744	923.442	720.087	854.093	−1676.130	405.704	−5.046
4300	227.786	928.802	724.879	876.869	−1671.743	455.219	−5.530
4400	227.824	934.039	729.573	899.650	−1667.238	504.632	−5.991
4500	227.860	939.159	734.174	922.434	−1662.617	553.942	−6.430
4600	227.894	944.168	738.685	945.222	−1657.883	603.146	−6.849
4700	227.925	949.069	743.109	968.013	−1653.040	652.247	−7.249
4800	227.955	953.868	747.450	990.807	−1648.090	701.244	−7.631
4900	227.983	958.569	751.711	1013.603	−1643.036	750.136	−7.997
5000	228.009	963.175	755.894	1036.403	−1637.883	798.924	−8.346
5100	228.034	967.690	760.003	1059.205	−1632.632	847.608	−8.681
5200	228.057	972.118	764.040	1082.010	−1627.289	896.189	−9.002
5300	228.079	976.463	768.007	1104.816	−1621.856	944.666	−9.310
5400	228.099	980.726	771.907	1127.625	−1616.336	993.039	−9.606
5500	228.119	984.912	775.741	1150.436	−1610.733	1041.308	−9.890
5600	228.138	989.022	779.513	1173.249	−1605.049	1089.477	−10.162
5700	228.155	993.060	783.225	1196.064	−1599.288	1137.541	−10.424
5800	228.172	997.028	786.877	1218.880	−1593.453	1185.504	−10.677
5900	228.188	1000.929	790.472	1241.698	−1587.547	1233.369	−10.919
6000	228.203	1004.764	794.011	1264.518	−1581.573	1281.129	−11.153

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 183.04 \pm 0.04\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 590.683 \pm 17.5\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 594.128 \pm 17.5\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_r$	0	2
	17.9	2
$^4\Sigma^-$	[4500]	[4]
	23150	4
	25949	2
	31821	2

$\omega_e = 2861.39\ cm^{-1}$ $\omega_e x_e = 64.29\ cm^{-1}$ $\sigma = 1$
$B_e = 14.455\ cm^{-1}$ $\alpha_e = 0.5339\ cm^{-1}$ $r_e = 1.1198$ Å

Enthalpy of Formation

Herzberg[1] reanalyzed the rotational predissociation reported by Shidei[2] and concluded that $D_0^\circ = 80.0\ kcal\cdot mol^{-1}$ (3.47 eV). This yields $\Delta_f H°(CH, g, 298.15\ K) = 142.0\ kcal\cdot mol^{-1}$(594.128 ± 17.5 $kJ\cdot mol^{-1}$), and is the adopted value.

Brewer and Kester[3] have confirmed the value as 142 ± 5 $kcal\cdot mol^{-1}$, from an equilibrium study of the temperature variation of the intensity of the $^2\Delta \rightarrow {}^2\Pi$ emission band.

Linevsky[4] determined the concentration of CH radicals in equilibrium with 1 atm. of hydrogen gas, by application of a high resolution spectro–photographic technique to three electronic transitions in absorption. A third law analysis, using the present functions, of 27 determinations in the temperature range 3065–3155 K yielded $\Delta_f H°(CH, g, 298.15\ K) = 142.01 \pm 1.28\ kcal\cdot mol^{-1}$ with a negligible drift. This value is in excellent agreement with the spectroscopic predissociation value.

Heat Capacity and Entropy

The vibrational and rotational constants and electronic levels are from Herzberg[1] with the exception of the estimated $^4\Sigma$ level. All the constants have been adjusted to the normal isotopic abundances for both carbon and hydrogen. The $^4\Sigma$ level is estimated from the ab initio calculations of Hurley[5] which include electron correlation effects. Earlier LCAO calculations had predicted the $^4\Sigma^-$ level to be the ground state, but Higuchi[6] used LCAO–SCF calculations and obtained the $^4\Sigma$ level at 800 cm^{-1}. Krauss and Wehner,[7] using essentially the same technique as Hurley,[5] obtained $^4\Sigma$ at 3000 cm^{-1}.

References

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[2]T. Shidei, Japan J. Phys. **11**, 23 (1936).
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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.730	590.683	590.683	INFINITE
100	29.261	151.151	208.978	−5.783	592.071	582.087	−304.051
200	29.171	171.393	185.708	−2.863	593.317	571.596	−149.286
250	29.167	177.902	183.520	−1.404	593.782	566.110	−118.282
298.15	29.171	183.040	183.040	0.	594.128	560.747	−98.241
300	29.171	183.220	183.040	0.054	594.139	560.540	−97.599
350	29.187	187.718	183.395	1.513	594.403	554.918	−82.817
400	29.223	191.617	184.185	2.973	594.583	549.264	−71.727
450	29.291	195.063	185.206	4.436	594.687	543.592	−63.099
500	29.400	198.154	186.349	5.903	594.725	537.913	−56.195
600	29.757	203.543	188.778	8.859	594.638	526.555	−45.841
700	30.292	208.168	191.225	11.860	594.397	515.226	−38.447
800	30.967	212.256	193.603	14.922	594.062	503.937	−32.904
900	31.739	215.947	195.884	18.057	593.675	492.695	−28.595
1000	32.565	219.334	198.062	21.272	593.265	481.496	−25.151
1100	33.411	222.477	200.140	24.570	592.850	470.340	−22.335
1200	34.250	225.420	202.126	27.954	592.443	459.220	−19.989
1300	35.062	228.194	204.025	31.420	592.050	448.135	−18.006
1400	35.831	230.821	205.846	34.965	591.673	437.078	−16.308
1500	36.548	233.318	207.595	38.584	591.314	426.049	−14.836
1600	37.208	235.698	209.278	42.272	590.972	415.042	−13.550
1700	37.808	237.972	210.899	46.024	590.644	404.057	−12.415
1800	38.348	240.149	212.464	49.832	590.329	393.090	−11.407
1900	38.830	242.235	213.977	53.691	590.023	382.141	−10.506
2000	39.257	244.238	215.440	57.596	589.723	371.207	−9.695
2100	39.632	246.163	216.857	61.541	589.426	360.289	−8.962
2200	39.961	248.014	218.232	65.521	589.130	349.385	−8.295
2300	40.247	249.797	219.566	69.532	588.832	338.494	−7.687
2400	40.495	251.515	220.861	73.569	588.529	327.616	−7.130
2500	40.709	253.173	222.121	77.630	588.219	316.751	−6.618
2600	40.893	254.773	223.346	81.710	587.901	305.898	−6.146
2700	41.051	256.319	224.539	85.807	587.572	295.058	−5.708
2800	41.187	257.815	225.701	89.919	587.231	284.231	−5.302
2900	41.303	259.262	226.833	94.044	586.878	273.415	−4.925
3000	41.402	260.664	227.938	98.179	586.510	262.613	−4.572
3100	41.488	262.023	229.015	102.324	586.127	251.822	−4.243
3200	41.562	263.341	230.067	106.477	585.729	241.044	−3.935
3300	41.627	264.621	231.095	110.636	585.314	230.280	−3.645
3400	41.683	265.865	232.100	114.802	584.883	219.527	−3.373
3500	41.734	267.074	233.082	118.973	584.435	208.788	−3.116
3600	41.780	268.250	234.042	123.148	583.970	198.062	−2.874
3700	41.822	269.396	234.982	127.328	583.487	187.349	−2.645
3800	41.861	270.511	235.903	131.513	582.988	176.649	−2.428
3900	41.899	271.599	236.804	135.701	582.471	165.963	−2.223
4000	41.936	272.661	237.687	139.892	581.937	155.290	−2.028
4100	41.973	273.696	238.553	144.088	581.386	144.630	−1.843
4200	42.010	274.708	239.402	148.287	580.819	133.985	−1.666
4300	42.048	275.697	240.235	152.490	580.235	123.352	−1.498
4400	42.087	276.664	241.052	156.696	579.635	112.734	−1.338
4500	42.127	277.611	241.854	160.907	579.020	102.130	−1.185
4600	42.170	278.537	242.641	165.122	578.388	91.539	−1.039
4700	42.214	279.444	243.414	169.341	577.742	80.962	−0.900
4800	42.260	280.334	244.174	173.565	577.082	70.400	−0.766
4900	42.309	281.206	244.921	177.793	576.407	59.850	−0.638
5000	42.359	282.061	245.655	182.027	575.719	49.316	−0.515
5100	42.412	282.900	246.378	186.265	575.018	38.794	−0.397
5200	42.468	283.724	247.088	190.509	574.304	28.287	−0.284
5300	42.525	284.534	247.787	194.759	573.579	17.794	−0.175
5400	42.585	285.329	248.475	199.014	572.842	7.314	−0.071
5500	42.647	286.111	249.152	203.276	572.095	−3.152	0.030
5600	42.711	286.880	249.819	207.544	571.337	−13.604	0.127
5700	42.777	287.637	250.476	211.818	570.571	−24.043	0.220
5800	42.846	288.381	251.123	216.099	569.795	−34.468	0.310
5900	42.916	289.114	251.760	220.387	569.012	−44.879	0.397
6000	42.987	289.836	252.389	224.683	568.221	−55.278	0.481

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = 171.67 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1617.20 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 1626.74 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
$^1\Pi$	23596.94	2

$\omega_e = 2885.7\ cm^{-1}$ $\omega_e x_e = [73]\ cm^{-1}$ $\sigma = 1$

$B_e = 14.1776\ cm^{-1}$ $\alpha_e = 0.4917\ cm^{-1}$ $r_e = 1.3909$ Å

Enthalpy of Formation

Douglas and Herzberg[1] first observed the spectrum of CH^+ and concluded that $D_0°(CH^+) = 3.61 \pm 0.22$ eV from a short extrapolation of the A state vibrational separations, this leads to IP = 11.13 ± 0.22 eV. Later Douglas and Morton[2] showed that the basis for this extrapolation was incorrect and the value was thus invalidated. Herzberg and Johns[3] then reported a value of IP(CH) = 10.64 eV (245.36 $kcal \cdot mol^{-1}$) which was obtained from the limit of the Rydberg states of CH (see also Herzberg).[4] This value in conjuntion with the JANAF value for $\Delta_f H°$(CH, g, 0 K) = 141.178 $kcal \cdot mol^{-1}$ leads to $\Delta_f H°(CH^+, g, 0\ K) = 386.5 \pm 0.5\ kcal \cdot mol^{-1}$ (1617.116 ± 2.1 $kJ \cdot mol^{-1}$) and is adopted.

Heat Capacity and Entropy

The molecular constants are those reported by Douglas and Morton.[2] The value for ω_e is derived from the observed $\Delta G_{1/2}$ by adding $2\omega_e x_e$. The $\omega_e x_e$ value is that calculated by Moore *et al.*[5] from ab initio variational calculations of the $^1\Sigma$ and $^1\Pi$ states.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−8.628	1617.199		
100	29.124	139.844	197.578	−5.773			
200	29.135	160.035	174.337	−2.860			
250	29.143	166.537	172.151	−1.403			
298.15	29.153	171.671	171.671	.000	1626.739	1590.493	−278.648
300	29.154	171.851	171.671	.054	1626.789	1590.268	−276.890
350	29.173	176.346	172.026	1.512	1628.091	1584.077	−236.411
400	29.211	180.244	172.815	2.972	1629.310	1577.706	−206.027
450	29.279	183.688	173.836	4.434	1630.453	1571.186	−182.378
500	29.385	186.778	174.978	5.900	1631.529	1564.542	−163.447
600	29.723	192.163	177.406	8.854	1633.519	1550.955	−135.023
700	30.205	196.780	179.852	11.850	1635.351	1537.048	−114.696
800	30.778	200.850	182.227	14.898	1637.081	1522.885	−99.434
900	31.390	204.510	184.503	18.006	1638.746	1508.510	−87.552
1000	32.000	207.849	186.673	21.176	1640.369	1493.952	−78.036
1100	32.585	210.927	188.740	24.406	1641.964	1479.233	−70.243
1200	33.132	213.786	190.709	27.692	1643.538	1464.370	−63.742
1300	33.634	216.458	192.588	31.031	1645.096	1449.376	−58.237
1400	34.092	218.967	194.384	34.417	1646.640	1434.263	−53.513
1500	34.507	221.334	196.102	37.848	1648.170	1419.039	−49.415
1600	34.884	223.573	197.750	41.317	1649.688	1403.714	−45.827
1700	35.225	225.698	199.332	44.823	1651.194	1388.295	−42.657
1800	35.535	227.721	200.853	48.361	1652.687	1372.787	−39.837
1900	35.817	229.650	202.319	51.929	1654.168	1357.196	−37.312
2000	36.074	231.494	203.732	55.524	1655.637	1341.528	−35.037
2100	36.311	233.259	205.096	59.143	1657.093	1325.787	−32.977
2200	36.528	234.954	206.415	62.785	1658.538	1309.977	−31.103
2300	36.729	236.582	207.691	66.448	1659.970	1294.101	−29.390
2400	36.916	238.149	208.928	70.131	1661.391	1278.163	−27.818
2500	37.090	239.660	210.127	73.831	1662.800	1262.166	−26.372
2600	37.254	241.118	211.291	77.548	1664.197	1246.113	−25.035
2700	37.408	242.526	212.422	81.282	1665.583	1230.007	−23.796
2800	37.555	243.890	213.522	85.030	1666.957	1213.849	−22.645
2900	37.695	245.210	214.592	88.792	1668.319	1197.643	−21.572
3000	37.830	246.490	215.634	92.569	1669.671	1181.389	−20.570
3100	37.960	247.733	216.649	96.358	1671.012	1165.091	−19.632
3200	38.087	248.940	217.640	100.161	1672.342	1148.750	−18.751
3300	38.211	250.114	218.606	103.976	1673.661	1132.367	−17.924
3400	38.334	251.256	219.550	107.803	1674.970	1115.945	−17.144
3500	38.455	252.369	220.471	111.642	1676.269	1099.484	−16.409
3600	38.577	253.454	221.373	115.494	1677.559	1082.986	−15.714
3700	38.698	254.513	222.254	119.358	1678.839	1066.452	−15.056
3800	38.820	255.546	223.117	123.233	1680.109	1049.884	−14.432
3900	38.943	256.556	223.961	127.122	1681.371	1033.283	−13.839
4000	39.067	257.544	224.788	131.022	1682.625	1016.649	−13.276
4100	39.193	258.510	225.599	134.935	1683.870	999.985	−12.740
4200	39.322	259.456	226.394	138.861	1685.108	983.290	−12.229
4300	39.453	260.383	227.174	142.800	1686.339	966.565	−11.741
4400	39.586	261.291	227.939	146.751	1687.563	949.812	−11.276
4500	39.723	262.183	228.690	150.717	1688.780	933.031	−10.830
4600	39.862	263.057	229.428	154.696	1689.992	916.223	−10.404
4700	40.003	263.916	230.152	158.689	1691.199	899.389	−9.996
4800	40.148	264.760	230.865	162.697	1692.401	882.530	−9.604
4900	40.296	265.589	231.565	166.719	1693.598	865.645	−9.228
5000	40.446	266.405	232.253	170.756	1694.792	848.736	−8.867
5100	40.599	267.207	232.931	174.808	1695.983	831.803	−8.519
5200	40.755	267.997	233.598	178.876	1697.172	814.846	−8.185
5300	40.913	268.775	234.254	182.959	1698.359	797.867	−7.863
5400	41.074	269.541	234.900	187.059	1699.545	780.866	−7.553
5500	41.237	270.296	235.537	191.174	1700.730	763.842	−7.254
5600	41.402	271.041	236.165	195.306	1701.915	746.797	−6.966
5700	41.569	271.775	236.783	199.455	1703.101	729.731	−6.687
5800	41.738	272.499	237.392	203.620	1704.289	712.644	−6.418
5900	41.908	273.214	237.994	207.803	1705.478	695.536	−6.158
6000	42.080	273.920	238.586	212.002	1706.671	678.409	−5.906

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 234.91 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [334 \pm 42]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [335 \pm 42]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	1
[3000]	3
12288	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[2800] (1)
1201 (1)
815 (1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: C–H = 1.12 Å; C–Cl = 1.689 Å
Bond Angle: H–C–Cl = 103.4°
Product of the Moments of Inertia: $I_A I_B I_C = 3.9883 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation can be estimated as the average of those of the CH_2 and CCl_2 radicals, which gives $\Delta_f H°$(CHCl, g 298.15 K) = 74.5 ± 15 kcal·mol^{-1}. A better value for the enthalpy of formation can be obtained by considering the reactions CHCl → CH + Cl and CHCl → CCl + H. When $\Delta_f H°$(CCl, g, 298.15 K) = 74.5 kcal·mol^{-1} is substituted into the above equations it gives $D°_0$(C–Cl) = 96 kcal·mol^{-1} and $D°_0$(C–H) = 98 kcal·mol^{-1}. Although these values are not unreasonable, the $D°_0$(C–H) value appears to be too high compared to that in CFH. Thus, we adopt $\Delta_f H°$(CHCl, g, 298.15 K) = 80 kcal·mol^{-1} which gives $D°_0$(C–Cl) = 91 kcal·mol^{-1} and $D°_0$(C–H) = 92 kcal·mol^{-1}.

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis[1] from an analysis of the rotational structure of the visible absoorption bands. The estimated triplet state is based on the electronic levels of CCl_2 and CH_2 as given in these tables. The vibrational levels are from Jacox and Milligan[2] who investigated the infrared spectrum of matrix-isolated CHCl, and also estimated the missing frequency.

The principal moments of inertia are: $I_A = 0.1780 \times 10^{-39}$, $I_B = 4.6457 \times 10^{-39}$, and $I_C = 4.8237 \times 10^{-39}$ g·cm^2.

References

[1]A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 525 (1966).
[2]M. E. Jacox and D. E. Milligan, J. Chem. Phys. **47**, 1626 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.154	334.441	334.441	INFINITE
100	33.267	197.591	265.877	−6.829	334.751	329.574	−172.152
200	34.185	220.819	238.182	−3.473	334.915	324.305	−84.700
250	35.365	228.567	235.509	−1.735	334.849	321.659	−67.207
298.15	36.737	234.912	234.912	0.	334.720	319.129	−55.910
300	36.792	235.139	234.912	0.068	334.714	319.032	−55.548
350	38.276	240.922	235.366	1.945	334.536	316.432	−47.225
400	39.724	246.128	236.391	3.895	334.330	313.860	−40.986
450	41.113	250.888	237.741	5.916	334.105	311.315	−36.136
500	42.461	255.290	239.278	8.006	333.867	308.795	−32.260
600	45.130	263.267	242.625	12.385	333.388	303.826	−26.450
700	47.839	270.427	246.094	17.033	332.958	298.934	−22.307
800	50.542	276.992	249.551	21.953	332.631	294.097	−19.203
900	53.113	283.095	252.943	27.137	332.433	289.294	−16.790
1000	55.427	288.814	256.247	32.567	332.369	284.505	−14.861
1100	57.404	294.192	259.454	38.211	332.426	279.717	−13.283
1200	59.013	299.258	262.562	44.035	332.578	274.919	−11.967
1300	60.262	304.034	265.571	50.002	332.799	270.105	−10.853
1400	61.187	308.535	268.480	56.077	333.062	265.273	−9.897
1500	61.837	312.780	271.294	62.230	333.341	260.421	−9.069
1600	62.264	316.786	274.013	68.437	333.617	255.551	−8.343
1700	62.515	320.569	276.641	74.677	333.874	250.663	−7.702
1800	62.634	324.146	279.182	80.935	334.100	245.762	−7.132
1900	62.656	327.533	281.638	87.201	334.287	240.849	−6.621
2000	62.610	330.746	284.014	93.464	334.427	235.927	−6.162
2100	62.517	333.799	286.313	99.721	334.518	231.000	−5.746
2200	62.393	336.705	288.538	105.967	334.557	226.069	−5.368
2300	62.253	339.475	290.693	112.199	334.544	221.138	−5.022
2400	62.103	342.121	292.781	118.417	334.477	216.209	−4.706
2500	61.952	344.653	294.806	124.620	334.357	211.283	−4.415
2600	61.803	347.080	296.770	130.807	334.185	206.364	−4.146
2700	61.659	349.410	298.677	136.980	333.962	201.451	−3.897
2800	61.522	351.650	300.529	143.139	333.688	196.549	−3.667
2900	61.394	353.807	302.329	149.285	333.367	191.656	−3.452
3000	61.274	355.886	304.080	155.418	332.998	186.776	−3.252
3100	61.162	357.893	305.783	161.540	332.584	181.908	−3.065
3200	61.060	359.833	307.442	167.651	332.126	177.055	−2.890
3300	60.965	361.711	309.059	173.752	331.626	172.217	−2.726
3400	60.878	363.529	310.634	179.845	331.086	167.394	−2.572
3500	60.798	365.293	312.171	185.928	330.508	162.588	−2.426
3600	60.725	367.005	313.670	192.004	329.893	157.799	−2.290
3700	60.657	368.668	315.134	198.073	329.245	153.028	−2.160
3800	60.595	370.284	316.564	204.136	328.564	148.274	−2.038
3900	60.538	371.858	317.962	210.193	327.854	143.539	−1.922
4000	60.486	373.390	319.329	216.244	327.115	138.822	−1.813
4100	60.438	374.883	320.666	222.290	326.349	134.124	−1.709
4200	60.393	376.338	321.974	228.331	325.560	129.445	−1.610
4300	60.351	377.759	323.255	234.369	324.747	124.785	−1.516
4400	60.312	379.146	324.509	240.402	323.914	120.145	−1.426
4500	60.276	380.501	325.739	246.431	323.062	115.523	−1.341
4600	60.242	381.825	326.943	252.457	322.192	110.921	−1.260
4700	60.211	383.121	328.125	258.480	321.307	106.337	−1.182
4800	60.181	384.388	329.284	264.499	320.407	101.773	−1.108
4900	60.152	385.629	330.421	270.516	319.495	97.227	−1.036
5000	60.125	386.844	331.538	276.530	318.570	92.701	−0.968
5100	60.100	388.034	332.634	282.541	317.636	88.193	−0.903
5200	60.075	389.201	333.710	288.550	316.692	83.703	−0.841
5300	60.052	390.345	334.768	294.556	315.741	79.231	−0.781
5400	60.029	391.467	335.808	300.560	314.783	74.778	−0.723
5500	60.007	392.568	336.830	306.562	313.819	70.342	−0.668
5600	59.986	393.649	337.835	312.562	312.850	65.924	−0.615
5700	59.966	394.711	338.823	318.559	311.877	61.524	−0.564
5800	59.946	395.754	339.796	324.555	310.901	57.140	−0.515
5900	59.927	396.778	340.753	330.548	309.923	52.773	−0.467
6000	59.908	397.785	341.695	336.540	308.943	48.423	−0.422

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 280.97 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -475.3 \pm 13\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -481.6 \pm 13\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3024(1)	812(1)	1350(1)
1312(1)	598(1)	1108(1)
836(1)	417(1)	400(1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_s

Bond Distances: C–H = 1.09 Å; C–Cl = 1.74 Å; C–F = 1.35 Å

Bond Angles: H–C–Cl = 107°; Cl–C–F = 110.5°; F–C–F = 107°

Product of the Moments of Inertia: $I_A I_B I_C = 3.435053 - 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Edwards and Small[1] determined a single equilibrium constant at 600°C for the reaction $2CHClF_2(g) \rightarrow C_2F_4(g) + 2HCl(g)$. The value was was obtained by extrapolation to eliminate the effects of side reactions. The equilibrium constant was used with JANAF free energy functions[2] to obtain $\Delta_f H°(298.15\ K) = 28.75\ kcal \cdot mol^{-1}$, which yields $\Delta_f H°(CHClF_2, g, 298.15\ K) = -115.1\ kcal \cdot mol^{-1}$. An uncertainty of $\pm 3\ kcal \cdot mol^{-1}$ corresponds to an uncertainty of about ±500% in the equilibrium constant.

Heat Capacity and Entropy

The gas phase vibrational frequencies have been observed in the Raman by Holzer and Moser;[3] they do not see anything in the 1350 cm^{-1} region as reported in the liquid by Glockler and Edgell.[4] Plyler and Benedict[5] in their assignment replaced 831 cm^{-1} frequency by 1178 cm^{-1}. We essentially adopt Glockler and Edgell's assignment with updated gas phase values for the observed frequencies. The microwave spectrum gas been analyzed by McLay and Mann[6] and Beeson *et al.*,[7] who derive bond lengths and angles in excellent agreement with each other. The values given by Beeson *et al.* are adopted here.

Neilson and White[8] have measured the low temperature heat capacity and heat of vaporization and have reported an entropy in the gas phase at 232.5 K of 63.91 ± 0.28 $cal \cdot K^{-1} \cdot mol^{-1}$. This compares with 63.959 $cal \cdot K^{-1} \cdot mol^{-1}$ calculated from our adopted functions.

The principal moments of inertia are: $I_A = 8.2033 \times 10^{-39}$, $I_B = 17.4031 \times 10^{-39}$, and $I_C = 24.0612 \times 10^{-39}\ g \cdot cm^2$.

References

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[5] E. K. Plyler and W. S. Benedict, J. Res. Nat. Bur. Stand. **47**, 202 (1951).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.413	−475.292	−475.292	INFINITE
100	35.011	233.244	323.826	−9.058	−477.859	−469.564	245.275
200	45.732	260.548	285.833	−5.057	−479.979	−460.404	120.245
250	51.680	271.395	281.879	−2.621	−480.848	−455.407	95.152
298.15	57.126	280.968	280.968	0.	−481.578	−450.439	78.915
300	57.328	281.322	280.969	0.106	−481.604	−450.246	78.395
350	62.496	290.554	281.687	3.104	−482.250	−444.967	66.408
400	67.107	299.207	283.342	6.346	−482.794	−439.603	57.406
450	71.156	307.350	285.561	9.805	−483.249	−434.176	50.398
500	74.683	315.034	288.128	13.453	−483.626	−428.702	44.786
600	80.420	329.181	293.813	21.221	−484.191	−417.660	36.361
700	84.813	341.923	299.791	29.492	−484.549	−406.541	30.336
800	88.253	353.481	305.791	38.152	−484.745	−395.382	25.816
900	91.004	364.041	311.685	47.120	−484.814	−384.206	22.299
1000	93.244	373.749	317.412	56.336	−484.781	−373.029	19.485
1100	95.093	382.725	322.947	65.756	−484.670	−361.858	17.183
1200	96.636	391.067	328.280	75.345	−484.498	−350.701	15.266
1300	97.935	398.855	333.413	85.075	−484.282	−339.560	13.644
1400	99.038	406.154	338.351	94.925	−484.036	−328.436	12.254
1500	99.979	413.020	343.102	104.877	−483.768	−317.331	11.050
1600	100.788	419.499	347.676	114.917	−483.488	−306.245	9.998
1700	101.488	425.631	352.083	125.031	−483.202	−295.176	9.070
1800	102.096	431.450	356.332	135.211	−482.914	−284.123	8.245
1900	102.627	436.984	360.433	145.448	−482.628	−273.088	7.508
2000	103.093	442.260	364.393	155.734	−482.346	−262.066	6.844
2100	103.505	447.300	368.222	166.065	−482.068	−251.059	6.245
2200	103.869	452.124	371.927	176.434	−481.795	−240.065	5.700
2300	104.192	456.748	375.515	186.837	−481.526	−229.083	5.203
2400	104.481	461.189	378.993	197.271	−481.260	−218.113	4.747
2500	104.740	465.460	382.367	207.732	−480.996	−207.154	4.328
2600	104.972	469.572	385.642	218.218	−480.732	−196.206	3.942
2700	105.182	473.538	388.824	228.726	−480.467	−185.268	3.584
2800	105.372	477.367	391.919	239.254	−480.199	−174.339	3.252
2900	105.544	481.067	394.929	249.800	−479.926	−163.420	2.944
3000	105.700	484.648	397.861	260.362	−479.647	−152.511	2.655
3100	105.843	488.116	400.716	270.939	−479.361	−141.612	2.386
3200	105.974	491.479	403.500	281.530	−479.065	−130.721	2.134
3300	106.093	494.742	406.216	292.134	−478.758	−119.840	1.897
3400	106.203	497.910	408.867	302.749	−478.440	−108.968	1.674
3500	106.305	500.990	411.455	313.374	−478.108	−98.106	1.464
3600	106.398	503.986	413.984	324.009	−477.761	−87.254	1.266
3700	106.484	506.903	416.456	334.654	−477.399	−76.411	1.079
3800	106.564	509.744	418.874	345.306	−477.021	−65.579	0.901
3900	106.639	512.513	421.239	355.966	−476.624	−54.757	0.733
4000	106.708	515.213	423.555	366.634	−476.209	−43.945	0.574
4100	106.772	517.849	425.823	377.308	−475.775	−33.144	0.422
4200	106.832	520.423	428.045	387.988	−475.321	−22.353	0.278
4300	106.888	522.937	430.222	398.674	−474.846	−11.574	0.141
4400	106.940	525.395	432.358	409.365	−474.349	−0.806	0.010
4500	106.989	527.799	434.452	420.062	−473.831	9.951	−0.116
4600	107.035	530.151	436.507	430.763	−473.291	20.696	−0.235
4700	107.078	532.453	438.524	441.468	−472.727	31.428	−0.349
4800	107.119	534.708	440.504	452.178	−472.141	42.149	−0.459
4900	107.157	536.917	442.449	462.892	−471.531	52.857	−0.563
5000	107.193	539.082	444.361	473.610	−470.898	63.553	−0.664
5100	107.227	541.206	446.239	484.331	−470.241	74.235	−0.760
5200	107.259	543.288	448.085	495.055	−469.560	84.905	−0.853
5300	107.289	545.331	449.901	505.782	−468.855	95.561	−0.942
5400	107.318	547.337	451.687	516.513	−468.126	106.203	−1.027
5500	107.345	549.307	453.444	527.246	−467.373	116.832	−1.110
5600	107.371	551.241	455.173	537.982	−466.596	127.447	−1.189
5700	107.395	553.142	456.875	548.720	−465.796	138.048	−1.265
5800	107.418	555.010	458.551	559.461	−464.971	148.634	−1.339
5900	107.441	556.846	460.201	570.204	−464.123	159.207	−1.410
6000	107.462	558.652	461.827	580.949	−463.251	169.764	−1.478

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 293.260 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-277.7 \pm 13]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-283.3 \pm 13]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3023(1)	741(1)	1242(1)
1313(1)	455(1)	806(1)
1079(1)	270(1)	368(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: C–H = 1.09 Å; C–Cl = 1.75 Å; C–F = 1.367 Å
Bond Angles: Cl–C–Cl = 112°12'; F–C–Cl = 109°; H–C–Cl = 109°45'
Product of the Moments of Inertia: $I_A I_B I_C = 1.110094 \text{–} 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The change in enthalpy of atomization by successive replacement of F by Cl in the CF_4 to CCl_4 series follows a regular pattern (see CCl_2F_2 table). A similar pattern is to be expected in the CHF_3 to $CHCl_3$ series. The first replacement of the series is, in fact, 4 $kcal \cdot mol^{-1}$ higher than the mean versus 3.8 $kcal \cdot mol^{-1}$ higher in the CF_4–CCl_4 series. Thus, we have selected the atomization energy of the second and third replacements to continue this pattern. In this manner we have selected the atomization energy of $CHCl_2F$ as 367.4 $kcal \cdot mol^{-1}$ which corresponds to $\Delta_f H°(CHCl_2F, g, 298.15\ K) = -67.7\ kcal \cdot mol^{-1}$. With this adopted value, the successive replacement of F by Cl changes the enthalpy of atomization by 41.4, 37.3 and 33.0 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Holzer[1] has reported the gas phase Raman spectra which is in excellent agreement with the assignments of Plyler and Benedict.[2] The only discrepancy is in ν_7, which Plyler and Benedict assign at 1242 cm^{-1}, and Holzer[1] does not report a band in this region. Holzer does, however, report a band at 728 cm^{-1} which has not been reported in the earlier liquid studies. There is strong evidence from correlations with $CHCl_3$ and CHF_3 that two frequencies should occur between 1220 and 1376 cm^{-1}. On this basis we adopt the assignment of Plyler and Benedict for ν_7, while accepting the gas phase values of Holzer for the other frequencies. The extra band at 728 cm^{-1} is not used. It is probable that the bands at 741 and 728 cm^{-1} are due to the Fermi resonance of ν_4 with $2\nu_9$; the unperturbed level would lie at 735 cm^{-1}. The symmetry classes of ν_4 and $2\nu_9$ are identical and thus Fermi resonance is allowed.

McLay[3] has reported the molecular structure from his microwave investigations. The principle moments of inertia are: $I_A = 12.028 \times 10^{-39}$, $I_B = 25.7010 \times 10^{-39}$, and $I_C = 35.9855 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.293	−277.672	−277.672	INFINITE
100	37.673	241.161	339.849	−9.869	−280.172	−271.738	141.941
200	50.180	271.154	298.501	−5.469	−281.948	−262.564	68.575
250	55.897	282.973	294.236	−2.816	−282.659	−257.633	53.830
298.15	60.995	293.260	293.260	0.	−283.257	−252.758	44.282
300	61.182	293.638	293.261	0.113	−283.278	−252.569	43.976
350	65.973	303.436	294.024	3.294	−283.806	−247.407	36.924
400	70.228	312.529	295.776	6.701	−284.245	−242.177	31.625
450	73.950	321.021	298.114	10.308	−284.606	−236.896	27.498
500	77.184	328.983	300.807	14.088	−284.900	−231.578	24.193
600	82.432	343.542	306.740	22.081	−285.319	−220.871	19.229
700	86.446	356.563	312.944	30.534	−285.556	−210.108	15.678
800	89.594	368.320	319.143	39.342	−285.650	−199.322	13.014
900	92.119	379.024	325.211	48.432	−285.629	−188.532	10.942
1000	94.182	388.840	331.090	57.750	−285.517	−177.748	9.285
1100	95.891	397.899	336.757	67.256	−285.334	−166.980	7.929
1200	97.322	406.306	342.206	76.919	−285.097	−156.230	6.801
1300	98.530	414.145	347.442	86.713	−284.819	−145.502	5.846
1400	99.558	421.485	352.471	96.619	−284.512	−134.797	5.029
1500	100.438	428.385	357.305	106.620	−284.186	−124.115	4.322
1600	101.195	434.891	361.952	116.702	−283.848	−113.454	3.704
1700	101.851	441.047	366.426	126.856	−283.505	−102.815	3.159
1800	102.422	446.885	370.735	137.070	−283.162	−92.196	2.675
1900	102.922	452.436	374.890	147.338	−282.822	−81.596	2.243
2000	103.361	457.727	378.901	157.652	−282.490	−71.014	1.855
2100	103.748	462.779	382.775	168.008	−282.168	−60.448	1.504
2200	104.091	467.614	386.523	178.400	−281.857	−49.898	1.185
2300	104.397	472.248	390.150	188.825	−281.560	−39.361	0.894
2400	104.669	476.697	393.664	199.279	−281.277	−28.836	0.628
2500	104.914	480.974	397.071	209.758	−281.010	−18.324	0.383
2600	105.134	485.094	400.378	220.261	−280.759	−7.821	0.157
2700	105.332	489.065	403.590	230.784	−280.525	2.672	−0.052
2800	105.511	492.899	406.711	241.326	−280.308	13.157	−0.245
2900	105.674	496.605	409.747	251.886	−280.108	23.634	−0.426
3000	105.822	500.190	412.703	262.461	−279.925	34.105	−0.594
3100	105.958	503.662	415.581	273.050	−279.758	44.570	−0.751
3200	106.081	507.028	418.387	283.652	−279.606	55.029	−0.898
3300	106.195	510.294	421.122	294.266	−279.468	65.485	−1.037
3400	106.299	513.466	423.792	304.890	−279.343	75.936	−1.167
3500	106.395	516.548	426.398	315.525	−279.228	86.383	−1.289
3600	106.483	519.547	428.944	326.169	−279.123	96.828	−1.405
3700	106.565	522.465	431.433	336.822	−279.026	107.270	−1.514
3800	106.641	525.308	433.866	347.482	−278.933	117.709	−1.618
3900	106.711	528.079	436.246	358.150	−278.844	128.146	−1.716
4000	106.777	530.782	438.576	368.824	−278.755	138.580	−1.810
4100	106.838	533.419	440.857	379.505	−278.666	149.013	−1.898
4200	106.895	535.994	443.092	390.191	−278.572	159.443	−1.983
4300	106.948	538.510	445.282	400.884	−278.473	169.870	−2.064
4400	106.997	540.970	447.429	411.581	−278.366	180.296	−2.140
4500	107.044	543.375	449.534	422.283	−278.249	190.719	−2.214
4600	107.087	545.728	451.600	432.990	−278.120	201.139	−2.284
4700	107.128	548.031	453.627	443.700	−277.978	211.556	−2.351
4800	107.167	550.287	455.617	454.415	−277.819	221.970	−2.416
4900	107.203	552.497	457.572	465.134	−277.643	232.380	−2.477
5000	107.237	554.663	459.492	475.856	−277.449	242.787	−2.536
5100	107.269	556.787	461.379	486.581	−277.234	253.190	−2.593
5200	107.300	558.871	463.234	497.310	−276.998	263.588	−2.648
5300	107.329	560.915	465.058	508.041	−276.739	273.981	−2.700
5400	107.356	562.921	466.852	518.775	−276.457	284.370	−2.751
5500	107.382	564.891	468.616	529.512	−276.150	294.752	−2.799
5600	107.406	566.826	470.353	540.252	−275.818	305.130	−2.846
5700	107.430	568.728	472.062	550.993	−275.460	315.500	−2.891
5800	107.452	570.596	473.745	561.737	−275.075	325.865	−2.935
5900	107.473	572.433	475.402	572.484	−274.662	336.222	−2.977
6000	107.493	574.240	477.034	583.232	−274.222	346.572	−3.017

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 295.620 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -98.27 \pm 1.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -103.18 \pm 1.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3034(1)	1220
680(1)	774
363(1)	261

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: C–H = 1.100 Å; C–Cl = 1.758 Å
Bond Angles: Cl–C–Cl = 111°18'; H–C–Cl = 107°34'
Product of the Moments of Inertia: $I_A I_B I_C = 3.282103 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

Hu and Sinke[1] have measured the enthalpy of combustion of $CHCl_3$(l) in the rotating bomb calorimeter, using As_2O_3 solution as the reducing agent. The reported $\Delta_c H°(298.15\ K) = -113.10\ kcal \cdot mol^{-1}$ for $CHCl_3(l) + 0.5O_2(g) + H_2O(l) \rightarrow CO_2(g) + 3HCl(aq, 600H_2O)$ which leads to $\Delta_f H°(CHCl_3, l, 298.15\ K) = -32.10\ kcal \cdot mol^{-1}$, using $\Delta_f H°(298.15\ K) = -94.051, -39.823, -68.315\ kcal \cdot mol^{-1}$ for CO_2(g), HCl(aq, $600H_2O$) and H_2O(l), respectively.[2] The standard deviation of six combustion runs was 0.09 $kcal \cdot mol^{-1}$. Employing the heat of vaporization of chloroform at 298.15 K as 7.44 $kcal \cdot mol^{-1}$,[3] we obtain $\Delta_f H°(CHCl_3, g, 298.15\ K) = -24.66\ kcal \cdot mol^{-1}$ ($-103.177 \pm 1.3\ kJ \cdot mol^{-1}$) which is adopted in the tabulation.

Simth *et al.*,[4] based on the combustion data of Eftring,[5] re-evaluated the enthalpy of combustion of chloroform at 18.7°C as $\Delta_c E/M° = -947.7\ cal \cdot K^{-1} \cdot mol^{-1}$ for $CHCl_3(l) + 0.5O_2(g) + H_2O(l) \rightarrow CO_2(g) + 3HCl(aq, 600H_2O)$. This value needs to be further corrected for a change in the enthalpy of oxidation of As_2O_3[6] and calculated to 25°C to give $\Delta_c H°(298.15\ K) = -113.44\ kcal \cdot mol^{-1}$, $\Delta_f H°(CHCl_3, l, 298.15\ K) = -31.76\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CHCl_3, g, 298.15\ K) = -24.32\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection,[7] based on the infrared and Raman spectra measured by Nielson and Ward,[8] Madigan and Cleveland,[9] Gibian and McKinney,[10] and Stanevich and Yaroslaviskii.[11]

The bond distances and angles were obtained from the microwave spectra by Jen and Lide.[12] The principle moments of inertia are: $I_A = I_B = 25.7217 \times 10^{-39}$ and $I_C = 49.6081 \times 10^{-39}\ g \cdot cm^2$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.153	−98.275	−98.275	INFINITE
100	40.321	239.353	345.889	−10.654	−100.702	−91.155	47.614
200	54.302	271.795	301.259	−5.893	−102.171	−80.983	21.151
250	60.243	284.561	296.668	−3.027	−102.727	−75.620	15.800
298.15	65.383	295.620	295.620	0.	−103.177	−70.357	12.326
300	65.568	296.025	295.621	0.121	−103.193	−70.154	12.215
350	70.235	306.492	296.437	3.519	−103.569	−64.616	9.643
400	74.255	316.139	298.305	7.134	−103.861	−59.031	7.709
450	77.685	325.089	300.790	10.935	−104.083	−53.413	6.200
500	80.609	333.429	303.641	14.894	−104.246	−47.774	4.991
600	85.262	348.558	309.893	23.199	−104.432	−36.459	3.174
700	88.772	361.977	316.394	31.908	−104.472	−25.125	1.875
800	91.513	374.017	322.857	40.928	−104.399	−13.794	0.901
900	93.716	384.927	329.157	50.193	−104.236	−2.477	0.144
1000	95.524	394.898	335.240	59.658	−104.001	8.817	−0.461
1100	97.031	404.075	341.086	69.288	−103.710	20.085	−0.954
1200	98.299	412.574	346.693	79.056	−103.375	31.325	−1.364
1300	99.376	420.485	352.069	88.941	−103.007	42.535	−1.709
1400	100.296	427.884	357.223	98.926	−102.617	53.717	−2.004
1500	101.086	434.832	362.168	108.996	−102.212	64.869	−2.259
1600	101.770	441.378	366.916	119.140	−101.798	75.994	−2.481
1700	102.363	447.566	371.479	129.347	−101.383	87.094	−2.676
1800	102.881	453.432	375.871	139.610	−100.970	98.169	−2.849
1900	103.336	459.007	380.101	149.921	−100.565	109.221	−3.003
2000	103.735	464.318	384.180	160.275	−100.172	120.252	−3.141
2100	104.089	469.388	388.118	170.667	−99.794	131.264	−3.265
2200	104.402	474.237	391.923	181.092	−99.436	142.258	−3.378
2300	104.682	478.885	395.604	191.546	−99.102	153.236	−3.480
2400	104.932	483.345	399.167	202.027	−98.795	164.201	−3.574
2500	105.156	487.633	402.621	212.532	−98.518	175.153	−3.660
2600	105.358	491.762	405.970	223.058	−98.273	186.095	−3.739
2700	105.540	495.741	409.222	233.603	−98.065	197.029	−3.812
2800	105.705	499.583	412.381	244.165	−97.893	207.955	−3.879
2900	105.855	503.295	415.452	254.743	−97.761	218.875	−3.942
3000	105.991	506.886	418.440	265.336	−97.669	229.792	−4.001
3100	106.116	510.363	421.350	275.941	−97.616	240.706	−4.056
3200	106.230	513.734	424.184	286.559	−97.604	251.620	−4.107
3300	106.335	517.004	426.948	297.187	−97.630	262.534	−4.156
3400	106.431	520.180	429.643	307.825	−97.695	273.448	−4.201
3500	106.519	523.267	432.275	318.473	−97.794	284.366	−4.244
3600	106.601	526.269	434.844	329.129	−97.927	295.286	−4.284
3700	106.677	529.190	437.355	339.793	−98.091	306.211	−4.323
3800	106.747	532.036	439.809	350.464	−98.282	317.140	−4.359
3900	106.812	534.810	442.209	361.142	−98.497	328.075	−4.394
4000	106.872	537.515	444.558	371.826	−98.732	339.016	−4.427
4100	106.929	540.155	446.858	382.516	−98.984	349.963	−4.459
4200	106.981	542.732	449.110	393.212	−99.249	360.916	−4.489
4300	107.030	545.250	451.317	403.913	−99.524	371.876	−4.517
4400	107.076	547.711	453.480	414.618	−99.804	382.842	−4.545
4500	107.119	550.118	455.601	425.328	−100.086	393.814	−4.571
4600	107.160	552.473	457.681	436.042	−100.367	404.793	−4.597
4700	107.198	554.778	459.722	446.760	−100.643	415.777	−4.621
4800	107.233	557.035	461.726	457.481	−100.910	426.768	−4.644
4900	107.267	559.246	463.694	468.206	−101.167	437.764	−4.667
5000	107.299	561.414	465.627	478.935	−101.410	448.765	−4.688
5100	107.328	563.539	467.526	489.666	−101.636	459.771	−4.709
5200	107.357	565.623	469.392	500.400	−101.843	470.781	−4.729
5300	107.383	567.668	471.227	511.137	−102.029	481.795	−4.748
5400	107.409	569.676	473.032	521.877	−102.191	492.812	−4.767
5500	107.433	571.647	474.807	532.619	−102.329	503.832	−4.785
5600	107.455	573.583	476.554	543.363	−102.440	514.854	−4.802
5700	107.477	575.485	478.273	554.110	−102.523	525.878	−4.819
5800	107.497	577.354	479.965	564.859	−102.576	536.903	−4.835
5900	107.517	579.192	481.631	575.609	−102.598	547.929	−4.851
6000	107.535	580.999	483.272	586.362	−102.590	558.954	−4.866

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 223.35 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [125.2 \pm 29]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [125.5 \pm 29]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
υ_i, cm^{-1}	g_i
0	1
[10000]	3
17287	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
714.52(1)
378.3 (2)
2215.5 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: C–H = 1.121 Å; C–F = 1.314 Å
Bond Angle: H–C–F = 101.6°
Product of the Moments of Inertia: $I_A I_B I_C = 1.0217 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation can be estimated as the average of the CH_2 and CF_2 radicals, which gives $\Delta_f H°(CHF, g, 298.15\ K) = 25 \pm 20$ kcal·mol^{-1}. A better value for the enthalpy of formation can be obtained by considering bond energies CHF → CH + F → CF + H. When $\Delta_f H°(CHF, g, 298.15\ K) = 25$ kcal·mol^{-1} is substituted into the above equation it gives $D°_0(CF) = 136$ kcal·mol^{-1} and $D°_0(CH) = 86$ kcal·mol^{-1}. These are not unreasonable values but are probably close to the upper and lower limits respectively. A value of $\Delta_f H°(CHF, g, 298.15\ K) = 30$ kcal·mol^{-1} gives $D°_0(CF) = 131$ kcal·mol^{-1} and $D°_0(CH) = 81$ kcal·mol^{-1} which are more probable since both fall within the bonds of normal bond strengths. The strongest established C–F bond is 135 kcal·mol^{-1} in CF_3 and the weakest established C–H bond is 80 kcal·mol^{-1} in CH. We adopt $\Delta_f H°(CHF, g, 298.15\ K) = 30 \pm 7$ kcal·mol^{-1} (125.520 kJ·mol^{-1}).

Heat Capacity and Entropy

The structure and electronic levels of the molecule have been established by Merer and Travis[1] from an analysis of the rotational structure of the visible absorption basis. The estinated triplet state is based on the electronic levels of CF_2 and CH_2 as given in these tables. The vibrational levels are from Merer and Travis[1] and Jacox and Milligan,[2] the latter investigated the infrared spectrum of matrix-isolated HCF and also estimated the missing frequency.

The principal moments of inertia are: $I_A = 0.1795 \times 10^{-39}$, $I_B = 2.2980 \times 10^{-39}$, and $I_C = 2.4774 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.982	125.235	125.235	INFINITE
100	33.258	186.756	253.322	−6.657	125.548	120.522	−62.954
200	33.415	209.828	226.465	−3.327	125.739	115.396	−30.138
250	33.855	217.325	223.913	−1.647	125.675	112.816	−23.572
298.15	34.604	223.348	223.348	0.	125.520	110.352	−19.333
300	34.639	223.562	223.349	0.064	125.513	110.258	−19.198
350	35.681	228.978	223.774	1.821	125.280	107.733	−16.078
400	36.860	233.818	224.732	3.634	124.998	105.245	−13.744
450	38.079	238.230	225.990	5.508	124.679	102.795	−11.932
500	39.277	242.304	227.421	7.442	124.334	100.382	−10.487
600	41.503	249.666	230.528	11.483	123.596	95.660	−8.328
700	43.461	256.214	233.738	15.733	122.829	91.064	−6.795
800	45.165	262.132	236.923	20.167	122.060	86.579	−5.653
900	46.649	267.539	240.029	24.759	121.303	82.190	−4.770
1000	47.940	272.522	243.032	29.490	120.564	77.883	−4.068
1100	49.066	277.146	245.926	34.342	119.843	73.650	−3.497
1200	50.052	281.458	248.709	39.299	119.136	69.482	−3.024
1300	50.922	285.499	251.385	44.348	118.442	65.373	−2.627
1400	51.701	289.302	253.959	49.480	117.757	61.316	−2.288
1500	52.408	292.894	256.436	54.686	117.079	57.308	−1.996
1600	53.063	296.297	258.822	59.960	116.408	53.345	−1.742
1700	53.680	299.533	261.122	65.297	115.744	49.425	−1.519
1800	54.273	302.618	263.343	70.695	115.088	45.542	−1.322
1900	54.851	305.568	265.488	76.151	114.443	41.696	−1.146
2000	55.422	308.396	267.563	81.665	113.811	37.884	−0.989
2100	55.990	311.113	269.573	87.235	113.197	34.103	−0.848
2200	56.557	313.731	271.521	92.863	112.604	30.350	−0.721
2300	57.126	316.258	273.411	98.547	112.035	26.624	−0.605
2400	57.696	318.701	275.248	104.288	111.494	22.923	−0.499
2500	58.265	321.068	277.033	110.086	110.984	19.243	−0.402
2600	58.832	323.364	278.771	115.941	110.509	15.583	−0.313
2700	59.394	325.595	280.465	121.852	110.071	11.940	−0.231
2800	59.949	327.765	282.115	127.820	109.672	8.313	−0.155
2900	60.494	329.878	283.726	133.842	109.313	4.700	−0.085
3000	61.027	331.938	285.299	139.918	108.995	1.098	−0.019
3100	61.544	333.948	286.836	146.047	108.719	−2.494	0.042
3200	62.043	335.910	288.339	152.226	108.485	−6.078	0.099
3300	62.523	337.826	289.810	158.455	108.291	−9.655	0.153
3400	62.982	339.700	291.250	164.730	108.138	−13.227	0.203
3500	63.417	341.532	292.660	171.050	108.023	−16.794	0.251
3600	63.828	343.324	294.043	177.413	107.945	−20.359	0.295
3700	64.214	345.078	295.398	183.815	107.903	−23.923	0.338
3800	64.575	346.795	296.728	190.255	107.894	−27.486	0.378
3900	64.909	348.477	298.034	196.729	107.915	−31.048	0.416
4000	65.218	350.124	299.316	203.236	107.965	−34.612	0.452
4100	65.500	351.738	300.574	209.772	108.041	−38.177	0.486
4200	65.757	353.320	301.812	216.335	108.140	−41.745	0.519
4300	65.989	354.870	303.028	222.923	108.260	−45.315	0.550
4400	66.196	356.389	304.223	229.532	108.399	−48.888	0.580
4500	66.380	357.879	305.399	236.161	108.553	−52.464	0.609
4600	66.541	359.340	306.556	242.807	108.721	−56.044	0.636
4700	66.681	360.773	307.694	249.469	108.900	−59.628	0.663
4800	66.799	362.178	308.815	256.143	109.087	−63.216	0.688
4900	66.898	363.556	309.918	262.828	109.282	−66.807	0.712
5000	66.979	364.908	311.004	269.522	109.481	−70.403	0.735
5100	67.042	366.235	312.074	276.223	109.684	−74.003	0.758
5200	67.089	367.538	313.128	282.930	109.887	−77.606	0.780
5300	67.120	368.816	314.167	289.640	110.090	−81.214	0.800
5400	67.138	370.071	315.191	296.353	110.291	−84.825	0.821
5500	67.142	371.303	316.200	303.067	110.489	−88.441	0.840
5600	67.134	372.513	317.194	309.781	110.683	−92.059	0.859
5700	67.115	373.701	318.175	316.494	110.871	−95.681	0.877
5800	67.085	374.868	319.143	323.204	111.052	−99.307	0.894
5900	67.047	376.014	320.097	329.910	111.226	−102.935	0.911
6000	67.000	377.141	321.038	336.613	111.392	−106.566	0.928

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 246.520 \pm 0.8\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-372.964]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-376.560]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2981 (1)	1064.8(1)
1836.9(1)	662.5(1)
1342.5(1)	[1030] (1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_1

Bond Distances: C–F = 1.31 ± 0.02 Å; C–O = 1.183 ± 0.003 Å; C–H = 1.10 ± 0.02 Å

Bond Angles: F–C–O = 122.7 ± 0.05°; H–C–F = 108.3 ± 3°; H–C–O = 129 ± 3°

Product of the Moments of Inertia: $I_A I_B I_C = 4.96336 \times 10^{-116}\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$ for III was estimated to be the average of the $\Delta_f H$'s of I and II.

(I) $CH_2O(g) = CO(g) + 2\ H(g)$ 106 $kcal\cdot mol^{-1}$

(II) $CF_2O(g) = CO(g) + 2\ F(g)$ 162 $kcal\cdot mol^{-1}$

(III) $CHFO(g) = CO(g) + F(g) + H(g)$ [134] $kcal\cdot mol^{-1}$

The auxiliary $\Delta_f H°(298.15\ K)$ of $CH_2O = -28$, H = 52, F = 19, CO = −26, $CF_2O = -150\ kcal\cdot mol^{-1}$ was used. See the respective sheets for details. The estimated enthalpy of formation is consistent with the instability of CHFO(g) at room temperature.

Heat Capacities and Entropies

The molecular structural parameters were obtained by LeBlanc *et al.*[1] from combining the results of microwave measurements with those of electron diffraction determined by Jones *et al.*[2] Agreement within the assigned uncertainties was obtained by Stratton and Nielsen[3] on the basis of infrared measurements.

Five of the fundamentals were observed by Stratton and Nielsen[3] in agreement with those obtained by Morgan *et al.*[4] The estimated frequency was based upon the observed value of 857.4 cm^{-1} for the fundamental in the infrared spectrum of the deuterated compound and the application of the Teller–Redlich isotope rule. The principal moments of inertia are:

$$I_A = 0.9081 \times 10^{-39},\ I_B = 6.9527 \times 10^{-39},\ \text{and}\ I_C = 7.8608 \times 10^{-39}\ g\cdot cm^2.$$

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.443	−372.964	−372.964	INFINITE
100	33.314	207.960	279.124	−7.116	−374.103	−372.583	194.617
200	35.452	231.500	250.043	−3.709	−375.288	−370.617	96.795
250	37.759	239.647	247.170	−1.881	−375.934	−369.375	77.177
298.15	40.414	246.520	246.520	0.	−376.560	−368.054	64.482
300	40.521	246.771	246.521	0.075	−376.584	−368.002	64.075
350	43.451	253.236	247.025	2.174	−377.213	−366.521	54.700
400	46.351	259.229	248.180	4.419	−377.810	−364.952	47.658
450	49.110	264.849	249.723	6.807	−378.373	−363.311	42.172
500	51.678	270.158	251.504	9.327	−378.903	−361.609	37.777
600	56.197	279.992	255.446	14.728	−379.861	−358.058	31.172
700	59.958	288.946	259.601	20.541	−380.693	−354.356	26.442
800	63.083	297.163	263.790	26.698	−381.406	−350.544	22.888
900	65.689	304.748	267.925	33.141	−382.016	−346.649	20.119
1000	67.874	311.785	271.963	39.822	−382.535	−342.690	17.900
1100	69.714	318.343	275.885	46.704	−382.981	−338.684	16.083
1200	71.270	324.478	279.682	53.755	−383.367	−334.639	14.566
1300	72.594	330.236	283.351	60.950	−383.708	−330.564	13.282
1400	73.724	335.658	286.896	68.268	−384.014	−326.465	12.181
1500	74.694	340.779	290.319	75.690	−384.297	−322.344	11.225
1600	75.531	345.627	293.625	83.202	−384.563	−318.205	10.388
1700	76.256	350.228	296.821	90.792	−384.820	−314.050	9.650
1800	76.888	354.605	299.910	98.450	−385.074	−309.880	8.992
1900	77.441	358.777	302.900	106.167	−385.328	−305.696	8.404
2000	77.926	362.762	305.794	113.936	−385.585	−301.498	7.874
2100	78.355	366.575	308.598	121.751	−385.848	−297.287	7.395
2200	78.734	370.229	311.317	129.605	−386.118	−293.063	6.958
2300	79.072	373.736	313.955	137.496	−386.396	−288.827	6.559
2400	79.374	377.108	316.517	145.419	−386.682	−284.579	6.194
2500	79.644	380.354	319.006	153.370	−386.976	−280.319	5.857
2600	79.887	383.482	321.426	161.347	−387.277	−276.047	5.546
2700	80.106	386.501	323.781	169.346	−387.585	−271.763	5.258
2800	80.304	389.418	326.073	177.367	−387.900	−267.467	4.990
2900	80.484	392.239	328.306	185.407	−388.220	−263.161	4.740
3000	80.648	394.971	330.483	193.463	−388.546	−258.842	4.507
3100	80.797	397.618	332.606	201.536	−388.876	−254.513	4.289
3200	80.934	400.185	334.678	209.622	−389.211	−250.174	4.084
3300	81.059	402.678	336.701	217.722	−389.549	−245.824	3.891
3400	81.174	405.099	338.677	225.834	−389.890	−241.463	3.710
3500	81.280	407.454	340.609	233.957	−390.234	−237.093	3.538
3600	81.377	409.745	342.498	242.089	−390.580	−232.713	3.377
3700	81.468	411.976	344.345	250.232	−390.930	−228.323	3.223
3800	81.551	414.149	346.154	258.383	−391.282	−223.923	3.078
3900	81.629	416.269	347.925	266.542	−391.637	−219.514	2.940
4000	81.701	418.336	349.659	274.708	−391.995	−215.096	2.809
4100	81.768	420.355	351.359	282.882	−392.356	−210.669	2.684
4200	81.831	422.326	353.025	291.062	−392.721	−206.233	2.565
4300	81.889	424.252	354.659	299.248	−393.089	−201.789	2.451
4400	81.944	426.135	356.263	307.440	−393.461	−197.336	2.343
4500	81.995	427.977	357.836	315.637	−393.838	−192.875	2.239
4600	82.043	429.780	359.380	323.838	−394.219	−188.405	2.139
4700	82.088	431.545	360.897	332.045	−394.606	−183.926	2.044
4800	82.131	433.274	362.387	340.256	−394.999	−179.439	1.953
4900	82.171	434.968	363.851	348.471	−395.399	−174.944	1.865
5000	82.208	436.628	365.290	356.690	−395.805	−170.441	1.781
5100	82.244	438.256	366.705	364.913	−396.218	−165.929	1.699
5200	82.278	439.854	368.096	373.139	−396.639	−161.410	1.621
5300	82.309	441.421	369.465	381.368	−397.069	−156.882	1.546
5400	82.339	442.960	370.812	389.601	−397.508	−152.346	1.474
5500	82.368	444.471	372.137	397.836	−397.956	−147.803	1.404
5600	82.395	445.955	373.442	406.074	−398.413	−143.250	1.336
5700	82.420	447.414	374.727	414.315	−398.882	−138.690	1.271
5800	82.445	448.848	375.993	422.558	−399.361	−134.120	1.208
5900	82.468	450.257	377.240	430.804	−399.852	−129.544	1.147
6000	82.490	451.643	378.468	439.052	−400.355	−124.958	1.088

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 259.657 \pm 0.34\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-690.10 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -697.05 \pm 3.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3035(1)	1376(2)
1137(1)	1152(2)
700(1)	508(2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: C–F = 1.333 Å; C–H = 1.098 Å
Bond Angles: F–C–F = 108.6 ± 0.5°; F–C–H = 110.33°
Product of the Moments of Inertia: $I_A I_B I_C = 9.722739 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the enthalpies of formation of CF_3, CF_3X (X=H,Cl,Br,I,CF_3) and C_2F_4. Details of the input data and the adjustment are given in Syverud's study.[1] Trifluoromethane is linked to HF(aq, 21.5 H_2O) by calorimetric data, to $CBrF_3$(g) and CF_3I(g) by equilibrium data, and to CF_3(g) by kinetic data. Neugebauer and Margrave[2] reported calorimetric data for $CHF_3(g) + 0.5\ O_2(g) + H_2O(l) = CO_2(g) + 3HF(aq, 21.5\ H_2O)$, where CF_4 was also formed in a competing reaction. Recalculation of the original data with $\Delta_f H°(CF_4, g, 298.15\ K) = -223.0\ kcal·mol^{-1}$ yields the mean value $\Delta_f H°(298.15\ K) = -90.35 \pm 0.7\ kcal·mol^{-1}$, but the individual values of $\Delta_r H°$ show a disturbing trend with the amount of competing reaction. Possible causes for the trend include corrosion and error in the analysis of the reaction products. Calibration was done in the presence of HF in an attempt to eliminate the heat due to corrosion. Because of this unexplained trend, we increase the uncertainty to ± 1.0 $kcal·mol^{-1}$. Goy *et al.*[3] and Coomber and Whittle[4] determined equilibrium data for $CHF_3(g) + X_2(g) = CF_3X(g) + HX(g)$ where X = I and Br. Kinetic data pertinent to CHF_3 are noted on the table for CF_3(g).

Heat Capacity and Entropy

The molecular strcuture has been derived from electron–diffraction data by Thorton[5] and from microwave data by Ghosh *et al.*[6] The results are in close agreement with and average values are adopted. Vibrational frequencies are from the assignment of Long *et al.*[7] who reviewed the spectral data and gave force–constant calculations. Preferences have been given to the gas–phase spectra, particularly the Raman data of Claassesn and Nielsen.[8] Shimanouchi[9] assigned $\nu_2 = 1117$ rather than 1137 cm^{-1}, but he apparently did not consider previous gas–phase data.[8,10] The principal moments of inertia are: $I_A = I_B = 8.1086 \times 10^{-39}$ and $I_C = 14.7875 \times 10^{-39}\ g·cm^2$.

Valentine *et al.*[11] used low–temperature calorimetric data to derive the ideal gas entropy at the normal boiling point of 190.97 K. The experimental value of 57.18 $cal·K^{-1}·mol^{-1}$ is in good agreement with 57.216 $cal·K^{-1}·mol^{-1}$ obtained from this table. Schwing[12] measured $C_v°$ for CHF_3 vapor (25–100°C) and confirmed that the vibrational assignment is adequate. Uncertainty in the $C_p°$ and $S°$ increases at higher temperatures due to neglect of anharmonicity in the calculations. Discussions of anharmonic contributions are given on the tables for CF_4(g) and $CClF_3$(g). The error probably does not exceed 0.3 $cal·K^{-1}·mol^{-1}$in $S°$ at 1000 K. $C_p°$ is consistent with $C_v°$ measured at 300 K by the wire–ribbon method.[13]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.564	−690.096	−690.096	INFINITE
100	33.889	215.987	298.282	−8.230	−692.682	−683.593	357.072
200	41.227	241.391	264.002	−4.522	−695.041	−673.566	175.917
250	46.139	251.112	260.470	−2.339	−696.106	−668.072	139.586
298.15	51.040	259.657	259.657	0.	−697.054	−662.586	116.082
300	51.228	259.973	259.658	0.095	−697.089	−662.372	115.329
350	56.250	268.250	260.300	2.782	−697.980	−656.514	97.979
400	61.000	276.075	261.787	5.715	−698.773	−650.535	84.951
450	65.358	283.515	263.791	8.876	−699.472	−644.462	74.807
500	69.278	290.608	266.121	12.244	−700.081	−638.317	66.685
600	75.849	303.844	271.322	19.513	−701.065	−625.867	54.487
700	80.998	315.939	276.845	27.366	−701.781	−613.274	45.763
800	85.065	327.031	282.435	35.677	−702.282	−600.593	39.215
900	88.323	337.245	287.965	44.352	−702.610	−587.861	34.119
1000	90.969	346.692	293.371	53.321	−702.801	−575.100	30.040
1100	93.146	355.468	298.622	62.530	−702.885	−562.325	26.703
1200	94.954	363.652	303.704	71.938	−702.886	−549.546	23.921
1300	96.470	371.314	308.613	81.511	−702.826	−536.770	21.568
1400	97.751	378.512	313.352	91.224	−702.721	−524.000	19.551
1500	98.842	385.294	317.924	101.055	−702.584	−511.239	17.803
1600	99.777	391.704	322.337	110.987	−702.426	−498.488	16.274
1700	100.583	397.778	326.597	121.006	−702.253	−485.747	14.925
1800	101.282	403.547	330.713	131.100	−702.073	−473.016	13.727
1900	101.891	409.040	334.693	141.260	−701.887	−460.296	12.654
2000	102.425	414.280	338.542	151.476	−701.696	−447.585	11.690
2100	102.895	419.289	342.269	161.742	−701.502	−434.885	10.817
2200	103.310	424.085	345.879	172.053	−701.302	−422.193	10.024
2300	103.679	428.686	349.380	182.403	−701.093	−409.511	9.300
2400	104.008	433.106	352.777	192.788	−700.874	−396.838	8.637
2500	104.302	437.357	356.076	203.203	−700.640	−384.175	8.027
2600	104.567	441.453	359.282	213.647	−700.389	−371.521	7.464
2700	104.805	445.404	362.399	224.116	−700.116	−358.877	6.943
2800	105.020	449.220	365.432	234.607	−699.818	−346.244	6.459
2900	105.215	452.909	368.385	245.119	−699.493	−333.622	6.009
3000	105.393	456.479	371.262	255.650	−699.138	−321.012	5.589
3100	105.555	459.937	374.067	266.197	−698.750	−308.415	5.197
3200	105.703	463.291	376.803	276.760	−698.327	−295.830	4.829
3300	105.838	466.545	379.474	287.337	−697.868	−283.258	4.484
3400	105.962	469.707	382.081	297.928	−697.371	−270.702	4.159
3500	106.077	472.780	384.629	308.530	−696.835	−258.161	3.853
3600	106.183	475.770	387.119	319.143	−696.261	−245.635	3.564
3700	106.280	478.681	389.555	329.766	−695.647	−233.126	3.291
3800	106.371	481.516	391.938	340.398	−694.994	−220.634	3.033
3900	106.454	484.280	394.270	351.040	−694.302	−208.160	2.788
4000	106.532	486.976	396.554	361.689	−693.572	−195.704	2.556
4100	106.605	489.608	398.792	372.346	−692.803	−183.267	2.335
4200	106.673	492.178	400.985	383.010	−691.998	−170.848	2.125
4300	106.736	494.688	403.135	393.680	−691.156	−158.450	1.925
4400	106.795	497.143	405.244	404.357	−690.279	−146.072	1.734
4500	106.850	499.544	407.313	415.039	−689.368	−133.713	1.552
4600	106.902	501.893	409.343	425.727	−688.424	−121.376	1.378
4700	106.951	504.192	411.337	436.419	−687.448	−109.059	1.212
4800	106.996	506.444	413.295	447.117	−686.441	−96.763	1.053
4900	107.039	508.651	415.219	457.819	−685.405	−84.489	0.901
5000	107.080	510.814	417.109	468.525	−684.340	−72.236	0.755
5100	107.118	512.935	418.967	479.235	−683.247	−60.005	0.615
5200	107.154	515.015	420.794	489.948	−682.127	−47.795	0.480
5300	107.189	517.057	422.591	500.665	−680.983	−35.608	0.351
5400	107.221	519.060	424.359	511.386	−679.813	−23.442	0.227
5500	107.252	521.028	426.099	522.110	−678.620	−11.298	0.107
5600	107.281	522.961	427.812	532.836	−677.405	0.825	−0.008
5700	107.308	524.860	429.498	543.566	−676.167	12.924	−0.118
5800	107.334	526.726	431.158	554.298	−674.908	25.003	−0.225
5900	107.359	528.561	432.793	565.033	−673.629	37.060	−0.328
6000	107.383	530.366	434.404	575.770	−672.330	49.094	−0.427

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 201.828 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 135.53 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 135.14 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2096.3(1)
713.5(2)
3311.5(1)

Ground State Quantum Weights: 1 $\sigma = 1$

Point Group: $C_{\infty v}$

Bond Distances: C–H = 1.066 Å; C–N = 1.153 Å

Bond Angle: H–C–N = 180°

Rotational Constant: $B_0 = 1.484360\ cm^{-1}$

Spectroscopic constants used in calculating corrections to the rigid–rotator harmonic oscillator approximation (cm^{-1}):

$\alpha_1 = 10.10 \times 10^{-3}$	$-x_{11} = 7.07$	$-x_{12} = 2.53$	$g_{22} = 5.16$
$\alpha_2 = -3.61 \times 10^{-3}$	$-x_{22} = 2.65$	$-x_{23} = 19.01$	
$\alpha_3 = 10.42 \times 10^{-3}$	$-x_{33} = 52.49$	$-x_{13} = 10.44$	

Enthalpy of Formation

The value adopted is from NBS.[1] The data of Thomsen[2] who measured both C_2N_2 and HCN and Berthelot[3] were used in conjunction with the well established value for C_2N_2 to derive the adopted value.[4]

Badger[5] studied the equilibrium $NH_3(g) + C(cr) = HCN(g) + H_2(g)$ from both sides; we obtain a 3rd law $\Delta_f H°(298.15\ K) = 46 \pm 0.9$ $kcal \cdot mol^{-1}$ and a 2nd law $\Delta_f H°(298.15\ K) = 34.5 \pm 19\ kcal \cdot mol^{-1}$, the 3rd law drift is $14 \pm 24\ cal \cdot K^{-1} \cdot mol^{-1}$. The 3rd law value leads to $\Delta_f H°(HCN, g, 298.15\ K) = 35 \pm 1\ kcal \cdot mol^{-1}$.

Horiuchi *et al.*[6] studied the equilibrium $2\ CO(g) + NH_3(g) = HCN(g) + CO_2(g) + H_2(g)$. We obtain $\Delta_r H°(298.15\ K) = 1.1 \pm 0.5\ kcal \cdot mol^{-1}$ from a 3rd law analysis with a drift of $-2 \pm 3\ cal \cdot K^{-1} \cdot mol^{-1}$, and a 2nd law value of $2.9 \pm 2.6\ kcal \cdot mol^{-1}$. The 3rd law value leads to $\Delta_f H°(HCN, g, 298.15\ K) = 31.35 \pm 0.6\ kcal \cdot mol^{-1}$. The two sets of equilibrium data are self–consistent but disagree with each other and the direct combustions. We adopt an uncertainty of $2.0\ kcal \cdot mol^{-1}$ to draw attention to this unsatisfactory situation.

Heat Capacity and Entropy

McBride *et al.*[7] used the constants listed above to calculate the adopted table which includes first and second corrections for anharmonicity, vibration–rotation interaction and centrifugal stretching. The bond lengths and molecular constants are those listed by Rank *et al.*[8] A more extensive set of anharmonic constants has recently been determined by Nakagawa and Morino,[9] they are in generally good agreement with the values used.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.234	135.529	135.529	INFINITE
100	29.167	167.608	230.911	−6.330	135.422	131.784	−68.837
200	31.719	188.377	204.966	−3.318	135.306	128.187	−33.479
298.15	35.857	201.828	201.828	0.	135.143	124.725	−21.851
300	35.928	202.050	201.829	0.066	135.140	124.660	−21.705
400	39.229	212.863	203.281	3.833	134.972	121.192	−15.826
500	41.731	221.894	206.125	7.885	134.766	117.769	−12.303
600	43.806	229.690	209.417	12.164	134.511	114.393	−9.959
700	45.643	236.583	212.815	16.638	134.222	111.063	−8.288
800	47.317	242.788	216.180	21.287	133.919	107.775	−7.037
900	48.844	248.451	219.456	26.096	133.618	104.525	−6.066
1000	50.229	253.670	222.619	31.051	133.328	101.308	−5.292
1100	51.484	258.517	225.665	36.137	133.052	98.120	−4.659
1200	52.610	263.046	228.594	41.343	132.793	94.955	−4.133
1300	53.618	267.298	231.409	46.655	132.549	91.812	−3.689
1400	54.522	271.305	234.117	52.063	132.318	88.687	−3.309
1500	55.329	275.095	236.724	57.556	132.099	85.579	−2.980
1600	56.049	278.689	239.235	63.126	131.889	82.484	−2.693
1700	56.697	282.107	241.657	68.764	131.685	79.403	−2.440
1800	57.275	285.364	243.996	74.463	131.486	76.333	−2.215
1900	57.794	288.475	246.255	80.217	131.289	73.274	−2.014
2000	58.262	291.451	248.441	86.020	131.094	70.226	−1.834
2100	58.689	294.304	250.558	91.868	130.898	67.187	−1.671
2200	59.070	297.043	252.609	97.756	130.700	64.158	−1.523
2300	59.421	299.677	254.598	103.681	130.499	61.138	−1.388
2400	59.739	302.213	256.530	109.639	130.294	58.127	−1.265
2500	60.028	304.657	258.406	115.628	130.085	55.124	−1.152
2600	60.296	307.017	260.231	121.644	129.869	52.130	−1.047
2700	60.542	309.297	262.006	127.686	129.647	49.144	−0.951
2800	60.764	311.503	263.735	133.752	129.417	46.167	−0.861
2900	60.973	313.639	265.419	139.838	129.180	43.198	−0.778
3000	61.170	315.710	267.061	145.946	128.934	40.237	−0.701
3100	61.347	317.718	268.663	152.072	128.679	37.284	−0.628
3200	61.513	319.669	270.226	158.215	128.415	34.340	−0.561
3300	61.669	321.564	271.754	164.374	128.141	31.405	−0.497
3400	61.814	323.407	273.246	170.548	127.856	28.478	−0.438
3500	61.948	325.201	274.705	176.736	127.560	25.559	−0.381
3600	62.074	326.948	276.132	182.938	127.253	22.649	−0.329
3700	62.190	328.650	277.528	189.151	126.934	19.748	−0.279
3800	62.300	330.310	278.896	195.376	126.603	16.855	−0.232
3900	62.401	331.930	280.235	201.611	126.259	13.971	−0.187
4000	62.496	333.511	281.547	207.855	125.902	11.097	−0.145
4100	62.587	335.055	282.833	214.110	125.532	8.231	−0.105
4200	62.672	336.564	284.095	220.373	125.148	5.375	−0.067
4300	62.750	338.040	285.332	226.644	124.750	2.528	−0.031
4400	62.823	339.483	286.546	232.923	124.338	−0.310	0.004
4500	62.890	340.896	287.739	239.208	123.911	−3.138	0.036
4600	62.952	342.279	288.909	245.500	123.469	−5.957	0.068
4700	63.011	343.633	290.059	251.799	123.013	−8.765	0.097
4800	63.065	344.961	291.189	258.102	122.541	−11.564	0.126
4900	63.115	346.261	292.300	264.412	122.054	−14.353	0.153
5000	63.162	347.537	293.392	270.725	121.552	−17.131	0.179
5100	63.206	348.788	294.466	277.044	121.034	−19.900	0.204
5200	63.245	350.016	295.522	283.366	120.501	−22.658	0.228
5300	63.278	351.221	296.562	289.693	119.952	−25.406	0.250
5400	63.308	352.404	297.585	296.022	119.388	−28.143	0.272
5500	63.335	353.566	298.593	302.354	118.808	−30.870	0.293
5600	63.358	354.707	299.584	308.689	118.212	−33.586	0.313
5700	63.378	355.829	300.561	315.026	117.601	−36.292	0.333
5800	63.395	356.931	301.524	321.364	116.975	−38.986	0.351
5900	63.407	358.015	302.472	327.705	116.333	−41.670	0.369
6000	63.417	359.081	303.407	334.046	115.675	−44.342	0.386

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 238.228 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -98.7 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -101.7 \pm 8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3531(1)	659.8(1)
2274(1)	577.5(1)
1327(1)	777.1(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: H–N = 0.987 Å; N–C = 1.207 Å; C–O = 1.171 Å
Bong Angles: H–N–C = 128.1°; N–C–O = 180°
Product of the Moments of Inertia: $I_A I_B I_C = 5.3166 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

Okabe[1] has measured the onset of photodissociation for the process HNCO(g) → NH(c' Π) + CO(g) as 8.79 ± 0.03 eV (202.7 ± 0.7 kcal·mol^{-1}). Okabe and Lenzi[2] have also reported the onset of photodissociation for the process $NH_3(g) \rightarrow NH(c'\Pi) + H_2(g)$ as 9.35 ± 0.06 eV (215.6 ± 1.4 kcal·mol^{-1}). Elimination of the NH(c'Π) gives

$$NH_3(g) + CO(g) \rightarrow NHCO(g) + H_2(g) \quad \Delta_f H°(0\ K) = 12.9 \pm 2\ kcal \cdot mol^{-1}$$

which with JANAF auxiliary data[3] yields $\Delta_f H°$(HNCO, g, 0 K) = −23.6 ± 2 kcal·mol^{-1}, or $\Delta_f H°$(HNCO, g, 298.15 K) = −24.3 ± 2 kcal·mol^{-1}.

The heat of formation of ionized cyanic acid in aqueous solution is −34.9 kcal·mol^{-1}.[4] Since the ions from cyanic acid and isocyanic acid are identical in solution we can use this value for aqueous isocyanic acid. Assuming the heat of solution is −3 ± 3 kcal·mol^{-1}, a value covering the range of heats of solution of most organic liquids,[4] we obtain $\Delta_f H°$(HNCO, l, 298.15 K) = −32 ± 3 kcal·mol^{-1}. Using $\Delta_{vap}H° = 7.2$ kcal·mol^{-1} [5] we obtain $\Delta_f H°$(HNCO, g, 298.15 K) = −25 ± 3 kcal·mol^{-1}. If we assume that $\Delta_f H°$(HNCO, g, 298.15 K)–$\Delta_f H°$(HNCO, ionized aq, 298.15 K) = $\Delta_f H°$(HNCS, g, 298.15 K)–$\Delta_f H°$(HCNS, ionized aq, 298.15 K) then we obtain $\Delta_f H°$(HNCO, g, 298.15 K) = −23 kcal·mol^{-1} employing values from U.S. Nat. Bur. Stand. Tech. Note 270-3.[4] We adopt the value $\Delta_f H°$(HNCO, g, 298.15 K) = −24.3 ± 2 kcal·mol^{-1} (−101.671 ± 8 kJ·mol^{-1}).

Heat Capacity and Entropy

The vibrational frequency determinations have been summarized by Herzberg and Reid.[6] Ashby and Werner[7] have remeasured the three lower fundamentals under much higher resolution. They reverse the assignments of ν_5 and ν_6 of Herzberg and Reid. Dixon and Kirby[8] have discussed the corrections due to Coriolis interaction made by Ashby and Werner and conclude they are in the wrong direction. On this basis they reverse the ν_4 and ν_6 assignments of Herzberg and Reid.

The bond distances and angles are from the microwave measurements of Jones *et al.*[9] which give rotational constants in good agreement with the later microwave work of Kewley.[10] The principal moments are: $I_A = 0.0912 \times 10^{-39}$, $I_B = 7.5910 \times 10^{-39}$, and $I_C = 7.6822 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.961	−98.671	−98.671	INFINITE
100	33.470	197.325	273.654	−7.633	−99.805	−97.750	51.060
200	38.269	221.663	242.134	−4.094	−100.851	−95.279	24.884
250	41.813	230.583	238.952	−2.092	−101.299	−93.833	19.605
298.15	45.043	238.228	238.228	0.	−101.671	−92.360	16.181
300	45.160	238.507	238.229	0.083	−101.684	−92.302	16.071
350	48.133	245.697	238.790	2.417	−102.013	−90.712	13.538
400	50.729	252.297	240.071	4.890	−102.297	−89.077	11.632
450	53.001	258.407	241.773	7.485	−102.553	−87.409	10.146
500	55.007	264.097	243.724	10.186	−102.789	−85.714	8.954
600	58.410	274.437	247.999	15.863	−103.226	−82.257	7.161
700	61.228	283.659	252.446	21.849	−103.631	−78.730	5.875
800	63.627	291.995	256.877	28.094	−104.006	−75.147	4.907
900	65.704	299.612	261.208	34.563	−104.349	−71.519	4.151
1000	67.516	306.631	265.404	41.226	−104.662	−67.854	3.544
1100	69.104	313.142	269.452	48.059	−104.946	−64.159	3.047
1200	70.498	319.216	273.348	55.041	−105.204	−60.439	2.631
1300	71.724	324.908	277.098	62.153	−105.439	−56.699	2.278
1400	72.802	330.264	280.706	69.381	−105.657	−52.941	1.975
1500	73.752	335.320	284.180	76.709	−105.862	−49.169	1.712
1600	74.591	340.107	287.527	84.127	−106.057	−45.383	1.482
1700	75.333	344.652	290.755	91.624	−106.248	−41.585	1.278
1800	75.990	348.976	293.870	99.191	−106.437	−37.776	1.096
1900	76.575	353.101	296.880	106.820	−106.628	−33.956	0.934
2000	77.095	357.042	299.790	114.504	−106.824	−30.126	0.787
2100	77.560	360.815	302.607	122.237	−107.028	−26.287	0.654
2200	77.977	364.433	305.336	130.014	−107.241	−22.437	0.533
2300	78.351	367.908	307.981	137.831	−107.465	−18.577	0.422
2400	78.688	371.250	310.548	145.683	−107.702	−14.707	0.320
2500	78.992	374.468	313.041	153.568	−107.954	−10.828	0.226
2600	79.268	377.572	315.464	161.481	−108.220	−6.937	0.139
2700	79.518	380.568	317.820	169.420	−108.504	−3.036	0.059
2800	79.745	383.464	320.113	177.384	−108.804	0.875	−0.016
2900	79.953	386.266	322.346	185.369	−109.122	4.798	−0.086
3000	80.143	388.980	324.522	193.374	−109.459	8.732	−0.152
3100	80.316	391.611	326.644	201.397	−109.814	12.678	−0.214
3200	80.476	394.163	328.714	209.437	−110.189	16.635	−0.272
3300	80.623	396.642	330.735	217.492	−110.583	20.604	−0.326
3400	80.758	399.051	332.709	225.561	−110.997	24.585	−0.378
3500	80.883	401.393	334.638	233.643	−111.430	28.579	−0.427
3600	80.999	403.674	336.524	241.737	−111.884	32.586	−0.473
3700	81.106	405.894	338.369	249.842	−112.358	36.605	−0.517
3800	81.205	408.059	340.175	257.958	−112.852	40.638	−0.559
3900	81.298	410.169	341.943	266.083	−113.367	44.684	−0.598
4000	81.384	412.229	343.674	274.217	−113.903	48.744	−0.637
4100	81.464	414.239	345.371	282.360	−114.459	52.817	−0.673
4200	81.539	416.203	347.034	290.510	−115.037	56.904	−0.708
4300	81.610	418.123	348.665	298.667	−115.635	61.005	−0.741
4400	81.675	420.000	350.265	306.832	−116.255	65.119	−0.773
4500	81.737	421.836	351.835	315.002	−116.895	69.248	−0.804
4600	81.795	423.633	353.377	323.179	−117.558	73.392	−0.833
4700	81.850	425.393	354.890	331.361	−118.241	77.551	−0.862
4800	81.901	427.116	356.377	339.549	−118.947	81.724	−0.889
4900	81.949	428.806	357.838	347.741	−119.674	85.912	−0.916
5000	81.995	430.462	359.274	355.939	−120.424	90.116	−0.941
5100	82.038	432.086	360.686	364.140	−121.196	94.334	−0.966
5200	82.079	433.679	362.074	372.346	−121.990	98.567	−0.990
5300	82.117	435.243	363.440	380.556	−122.806	102.817	−1.013
5400	82.154	436.778	364.784	388.770	−123.646	107.082	−1.036
5500	82.188	438.286	366.107	396.987	−124.508	111.362	−1.058
5600	82.221	439.767	367.409	405.207	−125.393	115.659	−1.079
5700	82.252	441.223	368.691	413.431	−126.302	119.971	−1.099
5800	82.282	442.654	369.954	421.658	−127.234	124.300	−1.119
5900	82.310	444.060	371.198	429.887	−128.190	128.644	−1.139
6000	82.337	445.444	372.424	438.120	−129.170	133.006	−1.158

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 224.649 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 43.2 \pm 8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 43.5 \pm 8\ kJ \cdot mol^{-1}$

Electronic Levels and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	B_0, cm^{-1}	$I_A I_B I_C$ g^3·cm^6
X^2A'	0	2	2488 (1)	1083 (1)	1820 (1)	—	0.4655×10^{-117}
$\tilde{A}^2\Sigma^-$	9294	2	3316.2 (1)	802.3 (2)	1813.4(1)	1.333284	—
$\tilde{B}^2A'$	38691	2	[2488] (1)	[1083] (1)	[1820] (1)	—	1.0087×10^{-117}
$\tilde{C}^2A''$	41270	2	[2488] (1)	[1083] (1)	[1820] (1)	—	$[0.4655] \times 10^{-117}$

Point Group: C_s $\sigma = 1$

Bond Distance (X^2A'): C–H = 1.16 Å; C–O = 1.17 Å

Bond Angle (X^2A'): H–C–O = 123.8°

Enthalpy of Formation

The adopted $\Delta_f H°$(HCO, g, 298.15 K) = 10.4 ± 2 kcal·mol^{-1} is calculated from $\Delta_{at} H°$(OHC–CHO, g) = 71.5 ± 2 kcal·mol^{-1} and $\Delta_f H°$(glyoxal, g, 298.15 K) = −50.66 ± 0.2 kcal·mol^{-1}. The C–C bond dissociation energy in glyoxal was determined from chemiluminescent recombination of formyl radicals by Hartley.[1] The heat of formation of glyoxal was determined from flame combustion calorimetry by Fletcher and Pilcher.[2]

The other route to derive the enthalpy of formation of formyl radical was from $\Delta_{at} H°$(H–CHO) which has been studied by many investigators listed below. There are several conflicting values between 77 to 91 kcal·mol^{-1} for $\Delta_{at} H°$(H–CHO). Based on the adopted $\Delta_f H°$(HCO, g, 298.15 K) = 10.4 ± 2 kcal·mol^{-1}, we have derived $\Delta_{at} H°$(H–CHO) = 89.3 ± 2 kcal·mol^{-1} which is in essential agreement with the high values of $\Delta_{at} H°$(H–CHO). The low values were probably not reliable as pointed out by Calvert,[3] Walsh and Benson,[5] Haney and Franklin.[9]

Source	Method	$\Delta_{at} H°$(H–CHO) kcal·mol^{-1}	
Calvert[3]	Kinetic	91	
Klein and Schoen[4]	Kinetic	77	
Walsh and Benson[5]	Kinetic	87	±1
Brand and Reed[6]	Spectroscopic	<82.3	
Reed and Brand[7]	Electron Impact	75	±2.3
Shannon and Harrison[8]	Electron Impact	79	±3
Haney and Franklin[9]	Electron Impact	87	±3

Heat Capacity and Entropy

The thermodynamic functions were calculated by summing over the individual partition functions for the separate states. The observed molecular constants and electronic levels were taken from Herzberg and Ramsay[10–12] and Dixon.[13] The vibrational frequency (ν_1 = 2488 cm^{-1}) was observed using the matrix isolation infrared technique by Milligan and Jacox.[14] Using the same technique, Ewing *et al.*[15] found ν_2 = 1091 cm^{-1} and ν_3 = 1860 cm^{-1} which are in good agreement with the values adopted.[10] These small differences are probably due to matrix shifts. The bond lengths and angle were calculated from the normal coordinate analyses by Shirk and Pimentel.[16] These values are a better fit than those calculated by Johns *et al.*[12] who assumed a normal CH bond length of 1.08 Å.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.989	43.151	43.151	INFINITE
100	33.258	188.025	254.660	−6.664	43.465	38.459	−20.089
200	33.469	211.108	227.769	−3.332	43.667	33.352	−8.711
250	33.921	218.619	225.214	−1.649	43.628	30.776	−6.430
298.15	34.597	224.649	224.649	0.	43.514	28.309	−4.960
300	34.627	224.863	224.650	0.064	43.508	28.215	−4.913
350	35.518	230.266	225.074	1.817	43.327	25.680	−3.833
400	36.530	235.074	226.029	3.618	43.100	23.174	−3.026
450	37.614	239.438	227.280	5.471	42.837	20.698	−2.403
500	38.733	243.459	228.699	7.380	42.545	18.254	−1.907
600	40.965	250.719	231.777	11.365	41.908	13.455	−1.171
700	43.068	257.194	234.954	15.568	41.242	8.765	−0.654
800	44.962	263.071	238.106	19.972	40.580	4.171	−0.272
900	46.623	268.465	241.184	24.553	39.936	−0.341	0.020
1000	48.056	273.454	244.165	29.289	39.316	−4.783	0.250
1100	49.282	278.093	247.041	34.157	38.717	−9.164	0.435
1200	50.329	282.427	249.811	39.139	38.134	−13.491	0.587
1300	51.224	286.492	252.478	44.218	37.562	−17.770	0.714
1400	51.991	290.317	255.045	49.380	36.995	−22.004	0.821
1500	52.651	293.927	257.518	54.613	36.429	−26.199	0.912
1600	53.223	297.343	259.901	59.907	35.859	−30.356	0.991
1700	53.722	300.585	262.200	65.255	35.282	−34.477	1.059
1800	54.161	303.669	264.419	70.650	34.695	−38.563	1.119
1900	54.549	306.608	266.563	76.085	34.096	−42.617	1.172
2000	54.896	309.415	268.636	81.558	33.483	−46.638	1.218
2100	55.206	312.101	270.642	87.063	32.854	−50.629	1.259
2200	55.488	314.675	272.585	92.598	32.209	−54.589	1.296
2300	55.744	317.148	274.469	98.160	31.546	−58.520	1.329
2400	55.978	319.525	276.298	103.746	30.866	−62.422	1.359
2500	56.195	321.815	278.073	109.355	30.167	−66.294	1.385
2600	56.395	324.023	279.798	114.985	29.450	−70.139	1.409
2700	56.581	326.155	281.475	120.634	28.713	−73.955	1.431
2800	56.755	328.215	283.108	126.300	27.959	−77.744	1.450
2900	56.918	330.210	284.698	131.984	27.185	−81.505	1.468
3000	57.071	332.142	286.248	137.684	26.393	−85.240	1.484
3100	57.216	334.016	287.758	143.398	25.582	−88.947	1.499
3200	57.353	335.835	289.233	149.127	24.753	−92.629	1.512
3300	57.483	337.601	290.672	154.868	23.905	−96.284	1.524
3400	57.606	339.319	292.077	160.623	23.039	−99.913	1.535
3500	57.723	340.991	293.451	166.389	22.154	−103.517	1.545
3600	57.835	342.619	294.794	172.167	21.252	−107.094	1.554
3700	57.942	344.205	296.108	177.956	20.331	−110.647	1.562
3800	58.044	345.751	297.395	183.756	19.393	−114.174	1.569
3900	58.141	347.260	298.654	189.565	18.436	−117.676	1.576
4000	58.235	348.733	299.888	195.384	17.462	−121.154	1.582
4100	58.324	350.172	301.096	201.212	16.469	−124.607	1.588
4200	58.410	351.579	302.282	207.048	15.459	−128.036	1.592
4300	58.493	352.954	303.444	212.894	14.430	−131.440	1.597
4400	58.573	354.300	304.585	218.747	13.384	−134.821	1.601
4500	58.650	355.617	305.704	224.608	12.320	−138.178	1.604
4600	58.724	356.907	306.803	230.477	11.238	−141.510	1.607
4700	58.796	358.171	307.883	236.353	10.137	−144.819	1.609
4800	58.866	359.409	308.944	242.236	9.018	−148.104	1.612
4900	58.933	360.624	309.986	248.126	7.881	−151.365	1.614
5000	58.999	361.815	311.011	254.022	6.726	−154.603	1.615
5100	59.063	362.984	312.018	259.926	5.552	−157.818	1.616
5200	59.126	364.132	313.009	265.835	4.360	−161.010	1.617
5300	59.187	365.258	313.985	271.751	3.149	−164.179	1.618
5400	59.248	366.365	314.945	277.673	1.919	−167.325	1.619
5500	59.307	367.453	315.889	283.600	0.671	−170.448	1.619
5600	59.365	368.522	316.820	289.534	−0.596	−173.547	1.619
5700	59.423	369.573	317.736	295.473	−1.882	−176.624	1.619
5800	59.480	370.607	318.639	301.418	−3.188	−179.678	1.618
5900	59.536	371.625	319.528	307.369	−4.512	−182.711	1.618
6000	59.593	372.626	320.405	313.326	−5.855	−185.719	1.617

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [203.417 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 827.2 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 833.0 \pm 8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[3223](1)
[707](2)
[2088](1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $[C_{\infty v}]$
Bond Distances: C–H = [1.07] Å; C–O = [1.17] Å
Bond Angles: H–C–O = [180]°
Rotational Constant: $B_0 = [1.367073]\ cm^{-1}$

Enthalpy of Formation

Using the photoionization technique, Matthews and Warneck[1] measured the appearance potentials of $HCO^+(g)$ from formaldehyde, formic acid and acetaldehyde as 11.95, 12.79 and 11.79 eV, respectively, whose average yields $\Delta_f H°(CHCO^+, g, 0\ K) = 197.7 \pm 1.5\ kcal \cdot mol^{-1}$, based on the following $\Delta_f H°(0\ K)$ data (in units of $kcal \cdot mol^{-1}$): 51.63 for H(g), 9.35 for OH(g), 35.62 for $CH_3(g)$, −26.78 for $H_2CO(g)$,[2] −88.74 for $HCOOH(g)$[3] and −37.14 for CH_3CHO.[4] The appearance potentials obtained from photoionization are several tenths to 1 eV lower than the recent electron impact data.[5-9] The appearance potentials determined by the electron impact method tend to be high because the fundamental nature of the process does not lead to a sharp onset in contrast to the step–function behavior of photoionization onset.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear based on two reasons: (1) the molecule $HCO^+(g)$ is isoelectronic with HCN(g) which is linear; (2) Walsh[10] predicted that "HAB" molecules with 10 or less valence electrons will be linear in their ground state. $HCO^+(g)$ has 10 valence electrons.

The bond distances HC and CO were estimated to be the same as those in HCN and HCO molecules, respectively. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants which were obtained from HCN(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.249	827.215		
100	29.166	169.137	232.573	−6.344			
200	31.793	189.930	206.575	−3.329			
250	33.980	197.259	203.998	−1.685			
298.15	35.963	203.417	203.417	0.	833.034	817.906	−143.294
300	36.035	203.639	203.417	0.067	833.070	817.812	−142.394
350	37.811	209.331	203.863	1.914	834.023	815.193	−121.661
400	39.328	214.482	204.873	3.843	834.964	812.439	−106.094
450	40.645	219.192	206.206	5.843	835.886	809.568	−93.972
500	41.819	223.536	207.725	7.905	836.787	806.595	−84.264
600	43.892	231.348	211.025	12.194	838.531	800.392	−69.680
700	45.727	238.254	214.431	16.676	840.223	793.901	−59.242
800	47.389	244.471	217.804	21.333	841.893	787.169	−51.397
900	48.895	250.141	221.087	26.149	843.563	780.229	−45.283
1000	50.251	255.364	224.256	31.107	845.244	773.102	−40.383
1100	51.463	260.211	227.307	36.194	846.942	765.805	−36.365
1200	52.541	264.736	230.240	41.395	848.657	758.354	−33.010
1300	53.496	268.980	233.058	46.698	850.387	750.759	−30.166
1400	54.339	272.976	235.768	52.091	852.130	743.029	−27.723
1500	55.084	276.751	238.376	57.563	853.881	735.175	−25.601
1600	55.741	280.327	240.887	63.105	855.638	727.204	−23.741
1700	56.322	283.725	243.308	68.708	857.395	719.124	−22.096
1800	56.837	286.959	245.644	74.367	859.151	710.939	−20.631
1900	57.293	290.044	247.900	80.074	860.901	702.657	−19.317
2000	57.700	292.993	250.082	85.824	862.644	694.284	−18.133
2100	58.062	295.818	252.193	91.612	864.377	685.823	−17.059
2200	58.386	298.526	254.238	97.435	866.098	677.280	−16.081
2300	58.677	301.128	256.220	103.288	867.806	668.659	−15.186
2400	58.939	303.631	258.144	109.169	869.499	659.964	−14.364
2500	59.175	306.042	260.012	115.075	871.175	651.199	−13.606
2600	59.388	308.367	261.827	121.004	872.835	642.367	−12.905
2700	59.581	310.612	263.593	126.952	874.478	633.472	−12.255
2800	59.757	312.782	265.311	132.919	876.102	624.516	−11.650
2900	59.917	314.882	266.984	138.903	877.707	615.502	−11.086
3000	60.063	316.916	268.615	144.902	879.293	606.434	−10.559
3100	60.197	318.887	270.205	150.915	880.859	597.313	−10.065
3200	60.320	320.800	271.756	156.941	882.406	588.141	−9.600
3300	60.433	322.658	273.271	162.979	883.933	578.921	−9.164
3400	60.537	324.464	274.750	169.028	885.439	569.656	−8.752
3500	60.633	326.220	276.196	175.086	886.925	560.347	−8.363
3600	60.722	327.930	277.609	181.154	888.391	550.995	−7.995
3700	60.804	329.594	278.992	187.230	889.837	541.603	−7.646
3800	60.880	331.217	280.345	193.314	891.262	532.172	−7.315
3900	60.951	332.799	281.670	199.406	892.666	522.705	−7.001
4000	61.017	334.343	282.967	205.504	894.050	513.200	−6.702
4100	61.078	335.851	284.239	211.609	895.413	503.662	−6.417
4200	61.136	337.323	285.485	217.720	896.755	494.091	−6.145
4300	61.190	338.762	286.707	223.836	898.077	484.488	−5.885
4400	61.240	340.170	287.907	229.958	899.377	474.855	−5.637
4500	61.287	341.546	289.083	236.084	900.657	465.192	−5.400
4600	61.331	342.894	290.239	242.215	901.915	455.501	−5.172
4700	61.373	344.213	291.373	248.350	903.152	445.783	−4.954
4800	61.412	345.506	292.487	254.490	904.368	436.039	−4.745
4900	61.449	346.773	293.582	260.633	905.563	426.270	−4.544
5000	61.484	348.014	294.659	266.779	906.736	416.476	−4.351
5100	61.517	349.232	295.717	272.929	907.888	406.660	−4.165
5200	61.548	350.427	296.757	279.083	909.018	396.820	−3.986
5300	61.577	351.600	297.781	285.239	910.127	386.960	−3.814
5400	61.605	352.751	298.788	291.398	911.213	377.079	−3.648
5500	61.632	353.882	299.780	297.560	912.277	367.177	−3.487
5600	61.657	354.992	300.756	303.724	913.319	357.257	−3.332
5700	61.680	356.084	301.717	309.891	914.339	347.318	−3.183
5800	61.703	357.157	302.664	316.060	915.337	337.362	−3.038
5900	61.724	358.212	303.596	322.232	916.312	327.388	−2.898
6000	61.745	359.249	304.515	328.405	917.264	317.398	−2.763

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 215.06 \pm 0.04\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [151.2 \pm 63]\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [149.9 \pm 63]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$a^3\Sigma^+$	24440	3
$b^3\Sigma^+$	30430	6
$c^3\Sigma^-$	31024	3
A^1A-	34746	1
$B^1\pi$	35927	2
$d^3\pi$	35976	6
C^1A-	40248	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
3216.9(1)
674.7(2)
1278.4(1)

Spectroscopic constants used in calculating corrections to rigid rotator–harmonic oscillator approximation (cm^{-1}):

$\alpha_1 = 3.4 \times 10^{-3}$ $-x_{11} = [3.7]$ $-x_{12} = [1.9]$
$\alpha_2 = -3.4 \times 10^{-4}$ $-x_{22} = [2.4]$ $-x_{23} = [18.0]$
$\alpha_3 = 3.1 \times 10^{-3}$ $-x_{33} = [51.0]$ $-x_{13} = [8.0]$

Point Group: $C\infty_v$ $\sigma = 1$
Bond Distances: C–H = 1.0667 Å; C–P = 1.5421 Å
Bond Angle: H–C–P = 180°
Rotational Constant: $B_o = 0.667545\ cm^{-1}$

Enthalpy of Formation

The bonding in HCP and HCN is very similar, as evidenced by the bond lengths and vibrational frequencies. We assume that the C–H bond strength is thus the same in these two molecules. For the reactions HCN → H + CN we derive $\Delta_f H° = 128\ kcal\cdot mol^{-1}$ from $\Delta_f H°$(HCN, 2981.5 K) = 32.3, $\Delta_f H°$(H, 298.15 K) = 52.1 and $\Delta_f H°$(C, 2981.5 K) = 104 $kcal\cdot mol^{-1}$. Applying this to the reaction HCP → H + CP, we obtain $\Delta_f H°$(HCP, g, 2981.5 K) = 40 ± 15 $kcal\cdot mol^{-1}$, from $\Delta_f H°$(CP, 2981.5 K) = 111.7 $kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration was first obtained by Gier,[1] and later the bond lengths were determined by Tyler[2] using microwave spectroscopy. The vibrational frequencies and electronic levels were obtained from an analysis of the ultraviolet spectrum by Johns *et al.*[3] Since the first excited state is above 24000 cm^{-1} and the first nonlinear state at 34000 cm^{-1}, there is negligible error introduced by assuming ground state molecular constants for all excited states. The anharmonic constants were estimated from those of Hcn by Gordon[4] and the adopted table includes these corrections and the electronic contributions.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.353	151.192	151.192	INFINITE
100	29.196	180.303	244.749	−6.445	151.654	140.524	−73.402
200	32.275	201.236	218.271	−3.407	150.755	129.490	−33.819
298.15	37.166	215.062	215.062	0.	149.900	119.219	−20.887
300	37.254	215.293	215.063	0.069	149.882	119.029	−20.725
400	41.430	226.606	216.577	4.011	148.097	109.082	−14.245
500	44.593	236.205	219.567	8.319	146.984	99.458	−10.390
600	47.011	244.556	223.051	12.903	145.893	90.055	−7.840
700	48.936	251.951	226.661	17.703	144.819	80.834	−6.032
800	50.551	258.594	230.245	22.679	143.765	71.766	−4.686
900	51.944	264.630	233.735	27.806	142.737	62.828	−3.646
1000	53.166	270.167	237.105	33.062	141.736	54.003	−2.821
1100	54.254	275.287	240.346	38.434	140.762	45.277	−2.150
1200	55.225	280.050	243.459	43.909	76.242	37.717	−1.642
1300	56.095	284.505	246.447	49.476	76.091	34.513	−1.387
1400	56.869	288.691	249.316	55.125	75.956	31.319	−1.169
1500	57.568	292.639	252.074	60.847	75.833	28.136	−0.980
1600	58.195	296.374	254.727	66.636	75.721	24.959	−0.815
1700	58.764	299.920	257.282	72.484	75.617	21.790	−0.670
1800	59.279	303.293	259.745	78.387	75.519	18.627	−0.541
1900	59.743	306.511	262.123	84.338	75.426	15.468	−0.425
2000	60.170	309.586	264.419	90.334	75.337	12.315	−0.322
2100	60.563	312.532	266.641	96.371	75.249	9.166	−0.228
2200	60.923	315.358	268.791	102.445	75.162	6.021	−0.143
2300	61.254	318.073	270.876	108.554	75.074	2.881	−0.065
2400	61.568	320.687	272.897	114.696	74.986	−0.256	0.006
2500	61.852	323.206	274.859	120.867	74.896	−3.389	0.071
2600	62.128	325.637	276.766	127.066	74.804	−6.519	0.131
2700	62.383	327.987	278.619	133.292	74.709	−9.645	0.187
2800	62.626	330.260	280.423	139.542	74.611	−12.768	0.238
2900	62.856	332.462	282.180	145.816	74.510	−15.887	0.286
3000	63.078	334.596	283.892	152.113	74.405	−19.002	0.331
3100	63.300	336.668	285.561	158.432	74.296	−22.114	0.373
3200	63.509	338.681	287.190	164.773	74.184	−25.222	0.412
3300	63.718	340.639	288.780	171.134	74.068	−28.326	0.448
3400	63.923	342.544	290.333	177.516	73.949	−31.428	0.483
3500	64.132	344.400	291.852	183.919	73.827	−34.525	0.515
3600	64.337	346.209	293.337	190.342	73.703	−37.619	0.546
3700	64.551	347.975	294.790	196.787	73.577	−40.710	0.575
3800	64.772	349.700	296.212	203.253	73.450	−43.797	0.602
3900	64.990	351.385	297.605	209.741	73.322	−46.881	0.628
4000	65.220	353.033	298.970	216.251	73.195	−49.961	0.652
4100	65.471	354.647	300.309	222.786	73.070	−53.038	0.676
4200	65.714	356.227	301.621	229.345	72.948	−56.113	0.698
4300	65.977	357.777	302.909	235.929	72.830	−59.184	0.719
4400	66.258	359.297	304.174	242.541	72.718	−62.253	0.739
4500	66.547	360.789	305.415	249.181	72.613	−65.319	0.758
4600	66.852	362.255	306.635	255.851	72.518	−68.384	0.777
4700	67.178	363.696	307.834	262.552	72.433	−71.446	0.794
4800	67.513	365.114	309.012	269.287	72.361	−74.506	0.811
4900	67.873	366.509	310.172	276.056	72.304	−77.565	0.827
5000	68.249	367.884	311.312	282.862	72.265	−80.623	0.842
5100	68.647	369.240	312.435	289.706	72.244	−83.681	0.857
5200	69.065	370.577	313.540	296.592	72.245	−86.738	0.871
5300	69.496	371.896	314.629	303.520	72.270	−89.796	0.885
5400	69.948	373.200	315.701	310.492	72.321	−92.854	0.898
5500	70.425	374.487	316.758	317.510	72.401	−95.914	0.911
5600	70.919	375.761	317.801	324.577	72.511	−98.975	0.923
5700	71.433	377.021	318.829	331.695	72.655	−102.038	0.935
5800	71.965	378.268	319.843	338.865	72.834	−105.104	0.947
5900	72.521	379.502	320.843	346.089	73.052	−108.174	0.958
6000	73.090	380.726	321.831	353.369	73.311	−111.248	0.969

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 193.93 \pm 0.5\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) \approx 385.92 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) \approx 386.39 \pm 4.2\ kJ·mol^{-1}$

Electronic Levels, Quantum Weights and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ν, cm^{-1}	C–H Distance, Å	H–C–H Angle, °	$I_A I_B I_C$ $g^3·cm^6$
X $^3B_1$	0	3	[2954](1) [1056(1) [3123](1)	1.029	136	4.506×10^{-120}
a $^1A_1$	[2600]	1	[3026](1) [1398](1) [3074](1)	1.11	102.4	13.53×10^{-120}
b $^1B_1$	7100 + [2600]	1	[2931](1) [761](1) [3110](1)	1.05	140	4.373×10^{-120}
c $^1A_1$	27700 + [2600]	1	[2954](1) [1056](1) [3123](1)	[1.029]	[136]	4.506×10^{-120}

Point Group = C_{2v}

Enthalpy of Formation

The electron impact data of Langer *et al.*[1] was reanalyzed by Prophet[2] to give $\Delta_f H°(CH_2, g, 298.15\ K) = 95 \pm 5\ kcal·mol^{-1}$. Dibeler and Liston[3] reported the photoionization threshold for the process $CH_3CN \rightarrow CH_2^+ + HCN$ as 14.94 eV (344.55 $kcal·mol^{-1}$). Using auxiliary data from[4] and,[5] we obtain $\Delta_f H°(CH_2, g, 0\ K) = 95\ kcal·mol^{-1}$, which is a maximum value as the process is likely to occur with excess energy. $\Delta_f H°(CH_2, g, 0\ K)$ values of 95.5 $kcal·mol^{-1}$ (a maximum) and $86.8 \pm 6.0\ kcal·mol^{-1}$ have been obtained by Chupka *et al.*[6] from the appearance threshold of CH_2^+ from C_2H_4(g) by photoionization,[6] and from chemical equilibria measured in a mass spectrometer,[7] respectively. Chupka[8] and Dibeler *et al.*[9] have determined the photoionization threshold for the production of CH_2^+ from CH_4. If the latter value is corrected for rotational energy effects as suggested by Chupka,[8] then both studies yield $\Delta_f H°(CH_2, g, 0\ K) = 94.6\ kcal·mol^{-1}$. Chupka[8] indicates that this is a maximum value since the process of H_2 elimation is likely to occur with excess energy in the products at the threshold.

Chupka and Lifshitz[10] have obtained the photoionization threshold for CH_2^+ from CH_3 as 15.09 ± 0.03 eV. Combining this with the spectroscopic IP,[4] they report $\Delta_{at}H°(CH_2–H) = 4.694 \pm 0.033$ eV ($108.25 \pm 0.77\ kcal·mol^{-1}$). Using $\Delta_f H°(CH_3, g, 0\ K) = 35.64\ kcal·mol^{-1}$ and $\Delta_f H°(H, g, 0\ K) = 51.63\ kcal·mol^{-1}$ from these tables yields $\Delta_f H°(CH_2, g, 0\ K) = 92.24 \pm 1.0\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Bernheim *et al.*,[11] in examining the EPR spectra of CH_2 which was produced by the photolysis of diazirine and trapped in xenon at 4 K, concluded that the ground state of CH_2 is a triplet state and it is bent. In similar followup work, they deduced a bond angle of 137.7 ± 0.6 for CD_2 from a measurement of the isotropic component of the ^{13}C hyperfine interaction. Wasserman *et al.*,[12] observing the EPR spectra on photolysis of diazomethane and diazirine at 4K, concluded that CH_2 has a triplet ground state with a probable bond angle of 136 ± 8. Waserman *et al.*[13] also reported that their investigation of the EPR spectra of CD_2 and CHD supported their earlier conclusions.[12] In these latter two works,[12, 13] the bond angle was determined from the zero-field parameter. In more recent work by Wasserman *et al.*,[14] the ^{13}C hyperfine structure was observed in the EPR spectrum of ground state $^{13}CD_2$ at 4 K. The authors conclude that ground state CH_2, by analogy, has an angle of 137–143°.

Herzberg and Johns[15] state that the electronic spectra of CH_2 and its isotopic derivatives is not only compatible with a linear ground state but it is also consistent with a bond angle of 136° if an ad hoc assumption of a heterogeneous predissociation of the excited state is made. Recent theoretical calculations indicate a bent ground state.[16, 17] We adopt the triplet ground state, X $^3B_1$, as bent with an angle of $136 \pm 5°$ on the basis of the previously mentioned experimental work and weighted by the remarks of Herzberg and Johns.[15] The bond length is 1.029 Å as reported by Herzberg.[4] The bond lengths and angles for the a $^1A_1$ and b $^1B_1$ states are also from Herzberg and Johns.[18]

The singlet electronic levels are firmly established.[19] The unobserved singlet–triplet separation is likely to be less then 8000 cm^{-1}, as suggested by Herzberg.[19] Many theoretical arguments yield energy separations within 10% of this value.[16, 17, 20] Goldberg and Riter[24] estimate a value of $2600 \pm 2000\ cm^{-1}$ by calculations which allow for correlation energy effects in different states, all assumed to be linear, however. Foner and Hudson[21] suggest a "small" separation due to the absence of resolved structure in the CH_2 ionization curve. Carr *et al.*[22] via ketone photolysis deduced an energy gap of roughly 350–700 cm^{-1}. Halberstadt and McNesby[23] suggest 880 cm^{-1} based on ketone photolysis in the presence of methane and propane. The value chosen for the singlet–triplet energy separation is $2600 \pm 2000\ cm^{-1}$. This value is intermediate between the experimental and theoretical suggestions.

The vibrational frequencies for the three lower lying states were calculated via the valence force field method using the force constants calculated by O'Neil *et al.*[17] The geometry and vibrational levels for the c $^1A_1$ state were estimated. The uncertainty in the entropy mainly reflects the uncertain position of the low lying electronic levels.

References

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Continued on page 700

Enthalpy Reference Temperature = $T_r \approx 298.15$ K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.994	385.917	385.917	INFINITE
100	33.258	157.288	223.967	−6.668	386.184	380.623	−198.817
200	33.499	180.376	197.055	−3.336	386.496	374.920	−97.919
298.15	34.600	193.931	193.931	0.	386.392	369.245	−64.690
300	34.627	194.146	193.932	0.064	386.387	369.139	−64.273
400	36.142	204.313	195.308	3.602	385.996	363.443	−47.461
500	37.663	212.541	197.957	7.292	385.437	357.866	−37.386
600	39.206	219.544	200.985	11.135	384.773	352.413	−30.680
700	40.808	225.707	204.085	15.135	384.063	347.076	−25.899
800	42.442	231.263	207.140	19.298	383.351	341.841	−22.320
900	44.048	236.355	210.107	23.623	382.667	336.693	−19.541
1000	45.571	241.075	212.971	28.105	382.022	331.620	−17.322
1100	46.976	245.486	215.728	32.733	381.418	326.609	−15.509
1200	48.247	249.629	218.382	37.495	380.850	321.652	−14.001
1300	49.379	253.536	220.938	42.378	380.313	316.741	−12.727
1400	50.381	257.233	223.399	47.367	379.799	311.870	−11.636
1500	51.264	260.740	225.773	52.450	379.299	307.036	−10.692
1600	52.040	264.073	228.063	57.616	378.809	302.234	−9.867
1700	52.724	267.249	230.276	62.855	378.323	297.463	−9.140
1800	53.327	270.280	232.415	68.158	377.835	292.721	−8.495
1900	53.861	273.178	234.484	73.518	377.343	288.005	−7.918
2000	54.336	275.953	236.489	78.928	376.844	283.316	−7.399
2100	54.760	278.615	238.432	84.384	376.335	278.652	−6.931
2200	55.142	281.171	240.317	89.879	375.815	274.013	−6.506
2300	55.485	283.630	242.147	95.411	375.282	269.398	−6.118
2400	55.797	285.998	243.925	100.975	374.736	264.806	−5.763
2500	56.080	288.282	245.654	106.569	374.174	260.237	−5.437
2600	56.338	290.486	247.336	112.190	373.598	255.690	−5.137
2700	56.575	292.617	248.974	117.836	373.005	251.167	−4.859
2800	56.792	294.678	250.570	123.505	372.396	246.665	−4.602
2900	56.993	296.675	252.125	129.194	371.770	242.186	−4.362
3000	57.177	298.610	253.643	134.903	371.127	237.728	−4.139
3100	57.348	300.488	255.124	140.629	370.466	233.292	−3.931
3200	57.506	302.311	256.570	146.372	369.787	228.878	−3.736
3300	57.652	304.083	257.983	152.130	369.089	224.486	−3.553
3400	57.787	305.806	259.364	157.902	368.372	220.115	−3.382
3500	57.913	307.483	260.715	163.687	367.636	215.765	−3.220
3600	58.030	309.116	262.037	169.484	366.880	211.436	−3.068
3700	58.139	310.708	263.331	175.293	366.103	207.129	−2.924
3800	58.240	312.259	264.598	181.112	365.307	202.843	−2.788
3900	58.334	313.773	265.840	186.940	364.489	198.578	−2.660
4000	58.421	315.251	267.057	192.778	363.650	194.335	−2.538
4100	58.502	316.695	268.250	198.624	362.790	190.113	−2.422
4200	58.577	318.106	269.420	204.478	361.908	185.912	−2.312
4300	58.647	319.485	270.569	210.339	361.003	181.732	−2.208
4400	58.713	320.834	271.696	216.207	360.077	177.573	−2.108
4500	58.773	322.154	272.802	222.082	359.129	173.436	−2.013
4600	58.830	323.446	273.889	227.962	358.158	169.320	−1.923
4700	58.882	324.712	274.957	233.848	357.164	165.226	−1.836
4800	58.931	325.952	276.007	239.738	356.149	161.153	−1.754
4900	58.976	327.168	277.039	245.634	355.111	157.101	−1.675
5000	59.018	328.360	278.053	251.533	354.052	153.071	−1.599
5100	59.058	329.529	279.051	257.437	352.971	149.062	−1.527
5200	59.094	330.676	280.033	263.345	351.868	145.074	−1.457
5300	59.128	331.802	280.999	269.256	350.745	141.108	−1.391
5400	59.160	332.908	281.950	275.170	349.602	137.164	−1.327
5500	59.189	333.993	282.886	281.088	348.438	133.240	−1.265
5600	59.217	335.060	283.809	287.008	347.256	129.338	−1.206
5700	59.242	336.108	284.717	292.931	346.054	125.457	−1.150
5800	59.266	337.139	285.612	298.857	344.835	121.598	−1.095
5900	59.288	338.152	286.494	304.784	343.599	117.759	−1.043
6000	59.309	339.149	287.363	310.714	342.347	113.942	−0.992

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 264.421 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-254.649 \pm 13]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-261.918\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2993 (1)	1068 (1)	3048 (1)
1470 (1)	760 (1)	1236 (1)
1351 (1)	385 (1)	1004 (1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_S

Bond Distances: C–H = 1.078 ± 0.005 Å; C–Cl = 1.759 Å; C–F = 1.378 Å

Bond Angles: H–C–H = 111°54'; F–C–Cl = 110°; H–C–Cl = 109°06'

Product of the Moments of Inertia: $I_A I_B I_C = 4.818560 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

The change in enthalpy of atomization by successive replacement of F by Cl, in the CF_4 CCl_4 series and CHF_3 to $CHCl_3$ series, follows a regular pattern (see CCl_2F_2 and $CHCl_2F$ tables). We make the assumption that this same regular variation occurs also in the CH_2F_2 to CH_2Cl_2 series. Thus, the difference between the atomization energies of HC_2F_2 andf CH_2Cl_2 is divided into two unequal parts which fall into the patter n established in the CF_4 and CHF_2 sequences. We adopt an enthalpy of atomization of 385.5 kcal which corresponds to a $\Delta_f H°(CH_2ClF, g, 298.15\ K) = -62.6\ kcal \cdot mol^{-1}$. The changes in kcal, in the enthalpy of atomization by successive replacement of F by Cl are tabulated, below for all three series.

CF_4		
43.8		
CF_3Cl	CHF_3	
41.6	41.4	
CF_2Cl_2	CHF_2Cl	CH_2F_2
38.5	37.3	35.0
$CFCl_3$	$CHFCl_2$	CH_2FCl
36.0	33.0	29.7
CCl_4	$CHCl_3$	CH_2Cl_2

Heat Capacity and Entropy

Plyler and Benedict[1] assigned the vibrational frequencies from the infrared and Raman data for the liquid. The molecular structure was obtained from the microwave measurements of Muller.[2] The principal moments of inertia are: $I_A = 2.0097 \times 10^{-39}$, $I_B = 14.7640 \times 10^{-39}$, and $I_C = 16.2396 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.251	−254.649	−254.649	INFINITE
100	34.287	222.046	301.119	−7.907	−257.273	−251.341	131.287
200	39.571	247.291	268.467	−4.235	−259.604	−244.502	63.857
250	43.143	256.493	265.173	−2.170	−260.791	−240.589	50.268
298.15	47.037	264.421	264.421	0.	−261.918	−236.595	41.451
300	47.192	264.712	264.422	0.087	−261.961	−236.438	41.168
350	51.421	272.304	265.012	2.552	−263.069	−232.096	34.638
400	55.568	279.443	266.374	5.228	−264.093	−227.600	29.722
450	59.472	286.216	268.205	8.105	−265.026	−222.981	25.883
500	63.064	292.671	270.331	11.170	−265.869	−218.264	22.802
600	69.292	304.738	275.075	17.798	−267.301	−208.603	18.160
700	74.417	315.817	280.115	24.991	−268.430	−198.726	14.829
800	78.676	326.041	285.225	32.652	−269.297	−188.707	12.321
900	82.258	335.520	290.293	40.704	−269.942	−178.592	10.365
1000	85.296	344.348	295.262	49.086	−270.401	−168.416	8.797
1100	87.887	352.603	300.104	57.748	−270.706	−158.201	7.512
1200	90.108	360.347	304.805	66.651	−270.887	−147.965	6.441
1300	92.019	367.637	309.361	75.760	−270.968	−137.717	5.534
1400	93.668	374.518	313.771	85.046	−270.972	−127.467	4.756
1500	95.097	381.031	318.040	94.486	−270.915	−117.218	4.082
1600	96.340	387.209	322.172	104.059	−270.812	−106.975	3.492
1700	97.425	393.083	326.172	113.749	−270.675	−96.739	2.972
1800	98.376	398.679	330.046	123.540	−270.514	−86.512	2.511
1900	99.212	404.021	333.799	133.420	−270.335	−76.295	2.097
2000	99.950	409.129	337.439	143.379	−270.145	−66.087	1.726
2100	100.604	414.021	340.970	153.407	−269.948	−55.889	1.390
2200	101.186	418.715	344.398	163.497	−269.749	−45.700	1.085
2300	101.705	423.225	347.728	173.642	−269.549	−35.521	0.807
2400	102.170	427.563	350.965	183.837	−269.352	−25.350	0.552
2500	102.587	431.743	354.113	194.075	−269.159	−15.187	0.317
2600	102.964	435.774	357.176	204.353	−268.971	−5.032	0.101
2700	103.304	439.666	360.160	214.666	−268.789	5.116	−0.099
2800	103.612	443.429	363.067	225.012	−268.614	15.258	−0.285
2900	103.892	447.069	365.901	235.388	−268.445	25.393	−0.457
3000	104.147	450.596	368.666	245.790	−268.285	35.523	−0.619
3100	104.381	454.015	371.364	256.216	−268.131	45.647	−0.769
3200	104.594	457.332	373.999	266.665	−267.985	55.766	−0.910
3300	104.790	460.554	376.573	277.135	−267.847	65.882	−1.043
3400	104.970	463.685	379.090	287.623	−267.715	75.992	−1.167
3500	105.136	466.730	381.550	298.128	−267.590	86.100	−1.285
3600	105.290	469.694	383.958	308.650	−267.470	96.203	−1.396
3700	105.432	472.581	386.314	319.186	−267.356	106.304	−1.501
3800	105.563	475.394	388.622	329.736	−267.247	116.401	−1.600
3900	105.686	478.138	390.882	340.298	−267.142	126.496	−1.694
4000	105.799	480.815	393.097	350.873	−267.040	136.588	−1.784
4100	105.905	483.429	395.268	361.458	−266.941	146.677	−1.869
4200	106.004	485.982	397.398	372.053	−266.843	156.765	−1.950
4300	106.096	488.477	399.487	382.658	−266.747	166.849	−2.027
4400	106.183	490.918	401.537	393.272	−266.652	176.932	−2.100
4500	106.263	493.305	403.550	403.895	−266.556	187.012	−2.171
4600	106.339	495.641	405.527	414.525	−266.459	197.090	−2.238
4700	106.411	497.929	407.469	425.162	−266.360	207.166	−2.302
4800	106.478	500.170	409.377	435.807	−266.259	217.241	−2.364
4900	106.541	502.366	411.252	446.458	−266.154	227.312	−2.423
5000	106.601	504.519	413.096	457.115	−266.046	237.382	−2.480
5100	106.657	506.631	414.909	467.778	−265.933	247.449	−2.534
5200	106.710	508.702	416.693	478.446	−265.814	257.514	−2.587
5300	106.760	510.735	418.448	489.120	−265.690	267.577	−2.637
5400	106.808	512.731	420.176	499.798	−265.560	277.638	−2.686
5500	106.853	514.692	421.877	510.481	−265.422	287.695	−2.732
5600	106.896	516.617	423.551	521.169	−265.276	297.751	−2.777
5700	106.936	518.510	425.201	531.860	−265.121	307.804	−2.821
5800	106.975	520.370	426.826	542.556	−264.958	317.854	−2.863
5900	107.011	522.199	428.427	553.255	−264.784	327.900	−2.903
6000	107.046	523.998	430.005	563.958	−264.600	337.944	−2.942

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 270.293 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -88.663 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -95.521 \pm 1.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2999 (1)	282 (1)	898 (1)
1467 (1)	1153 (1)	1268 (1)
717 (1)	3040 (1)	758 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: C–H = 1.068 Å; C–Cl = 1.7724 Å
Bond Angles: H–C–H = 112°; Cl–C–Cl = 111.8°
Product of the Moments of Inertia: $I_A I_B I_C = 1.869359 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Hu and Sinke[1] have measured the enthalpy of combustion of CH_2Cl_2(l) in the rotating bomb calorimeter, using As_2O_3 solution as the reducing agent. They reported $\Delta_c H°(298.15\ K) = -144.00\ kcal \cdot mol^{-1}$ for $CH_2Cl_2(l) + CO_2(g) + 2\ HCl(aq, 600\ H_2O)$ which leads $\Delta_f H°(CH_2Cl_2,(l), 298.15\ K) = -29.70\ kcal \cdot mol^{-1}$, using $\Delta_f H°(298.15\ K) = -94.051$ and $-39.823\ kcal \cdot mol^{-1}$ for CO_2(g) and HCl(aq, 600 H_2O), respectively.[2] The standard deviation of five combustion runs was 0.12 $kcal \cdot mol^{-1}$. Employing the heat of vaporization of CH_2Cl_2(l) at 298.15 K as 6.87 $kcal \cdot mol^{-1}$,[3] we obtain $\Delta_f H°(CH_2Cl_2, g, 298.15\ K) = -22.83\ kcal \cdot mol^{-1}$ ($-95.521 \pm 1.3\ kJ \cdot mol^{-1}$ which is adopted in the tabulation.

Smith *et al.*,[4] based on the combustion data of Eftring,[5] re-evaluated the enthalpy of combustion of dichloromethane at 18.7°C as $\Delta E°/M = -1701.4\ cal \cdot g^{-1}$ for $CH_2Cl_2(l) + O_2(g) + CO_2(g) + 2\ HCl(aq, 600\ H_2O)$. This value needs to be further corrected for a change in the enthalpy of oxidation of As_2O_3,[6] and calculated to 25°C to give $\Delta_c E°(298.15\ K) = \Delta_c H°(298.15\ K) = -144.89\ kcal \cdot mol^{-1}$, $\Delta_f H°(CH_2Cl_2, l, 298.15\ K) = -28.80\ kcal \cdot mol^{-1}$ and $\Delta_f H°(CH_2Cl_2, g, 298.15\ K) = -21.93\ kcal \cdot mol^{-1}$.

Lacher *et al.*[7] have measured the enthalpy of hydrogenation of dichloromethane to methane and hydrogen chloride at 250°C as $-40.07\ kcal \cdot mol^{-1}$. Correction to 298.15 K gives $\Delta_f H°(CH_2Cl_2, g\ 298.15\ K) = -23.05\ kcal \cdot mol^{-1}$ which is in good agreement with the value adopted.

Heat Capacity and Entropy

The bond distances and angles have been determined from the microwave spectra by Meyers and Gwinn.[8] The principal moments of inertia are: $I_A = 2.6307 \times 10^{-39}$, $I_B = 25.6246 \times 10^{-39}$, and $I_C = 27.7305 \times 10^{-39}\ g \cdot cm^2$.

The assigned fundamental vibrational frequencies are obtained from Shimanouchi's selection,[9] based on infrared and Raman spectra by Shimanouchi and Syzuki,[10] Welsh *et al.*,[12] and Palma *et al.*[11]

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.842	−88.663	−88.663	INFINITE
100	35.760	225.132	309.694	−8.456	−91.248	−84.693	44.239
200	42.366	251.822	274.664	−4.568	−93.419	−77.291	20.186
250	46.584	261.721	271.107	−2.347	−94.507	−73.133	15.280
298.15	50.896	270.293	270.293	0.	−95.521	−68.924	12.075
300	51.062	270.609	270.294	0.094	−95.558	−68.759	11.972
350	55.459	278.813	270.932	2.758	−96.533	−64.214	9.583
400	59.570	286.490	272.402	5.635	−97.416	−59.536	7.775
450	63.309	293.726	274.373	8.709	−98.207	−54.752	6.355
500	66.667	300.574	276.654	11.960	−98.912	−49.885	5.211
600	72.367	313.251	281.715	18.922	−100.090	−39.964	3.479
700	76.997	324.766	287.055	26.398	−100.996	−29.868	2.229
800	80.838	335.306	292.437	34.295	−101.672	−19.658	1.284
900	84.079	345.020	297.747	42.545	−102.151	−9.376	0.544
1000	86.842	354.025	302.930	51.095	−102.465	0.951	−0.050
1100	89.211	362.416	307.961	59.901	−102.643	11.302	−0.537
1200	91.252	370.268	312.829	68.926	−102.708	21.664	−0.943
1300	93.014	377.643	317.534	78.142	−102.685	32.028	−1.287
1400	94.542	384.593	322.078	87.521	−102.591	42.387	−1.581
1500	95.869	391.163	326.467	97.043	−102.442	52.738	−1.836
1600	97.026	397.388	330.707	106.690	−102.252	63.077	−2.059
1700	98.039	403.301	334.804	116.444	−102.032	73.404	−2.255
1800	98.927	408.930	338.767	126.293	−101.791	83.717	−2.429
1900	99.710	414.300	342.603	136.226	−101.537	94.016	−2.585
2000	100.403	419.433	346.317	146.232	−101.278	104.301	−2.724
2100	101.017	424.347	349.916	156.304	−101.019	114.574	−2.850
2200	101.564	429.059	353.407	166.433	−100.765	124.834	−2.964
2300	102.052	433.584	356.796	176.615	−100.523	135.083	−3.068
2400	102.490	437.937	360.086	186.842	−100.295	145.322	−3.163
2500	102.883	442.129	363.285	197.111	−100.086	155.552	−3.250
2600	103.238	446.171	366.395	207.417	−99.899	165.773	−3.330
2700	103.559	450.074	369.423	217.757	−99.738	175.988	−3.405
2800	103.849	453.845	372.371	228.128	−99.603	186.198	−3.474
2900	104.114	457.494	375.244	238.526	−99.499	196.403	−3.538
3000	104.355	461.028	378.044	248.950	−99.425	206.605	−3.597
3100	104.575	464.453	380.777	259.397	−99.383	216.806	−3.653
3200	104.777	467.777	383.444	269.864	−99.373	227.005	−3.705
3300	104.962	471.004	386.049	280.352	−99.395	237.205	−3.755
3400	105.133	474.140	388.594	290.856	−99.450	247.405	−3.801
3500	105.290	477.189	391.082	301.378	−99.536	257.608	−3.845
3600	105.435	480.158	393.515	311.914	−99.651	267.814	−3.886
3700	105.570	483.048	395.896	322.464	−99.796	278.023	−3.925
3800	105.694	485.865	398.226	333.028	−99.967	288.237	−3.962
3900	105.810	488.612	400.509	343.603	−100.164	298.455	−3.997
4000	105.917	491.293	402.745	354.189	−100.383	308.679	−4.031
4100	106.018	493.909	404.937	364.786	−100.624	318.908	−4.063
4200	106.111	496.465	407.086	375.393	−100.883	329.144	−4.094
4300	106.199	498.963	409.194	386.008	−101.159	339.386	−4.123
4400	106.280	501.405	411.262	396.632	−101.448	349.634	−4.151
4500	106.357	503.795	413.292	407.264	−101.750	359.889	−4.177
4600	106.429	506.133	415.284	417.903	−102.061	370.152	−4.203
4700	106.497	508.423	417.242	428.550	−102.379	380.420	−4.228
4800	106.560	510.665	419.165	439.203	−102.702	390.697	−4.252
4900	106.620	512.863	421.055	449.862	−103.028	400.979	−4.274
5000	106.677	515.018	422.913	460.527	−103.355	411.268	−4.296
5100	106.730	517.131	424.739	471.197	−103.682	421.564	−4.318
5200	106.780	519.204	426.536	481.872	−104.005	431.866	−4.338
5300	106.828	521.238	428.304	492.553	−104.325	442.174	−4.358
5400	106.873	523.236	430.043	503.238	−104.637	452.488	−4.377
5500	106.916	525.197	431.756	513.927	−104.943	462.808	−4.395
5600	106.956	527.124	433.441	524.621	−105.239	473.134	−4.413
5700	106.995	529.017	435.102	535.319	−105.524	483.464	−4.430
5800	107.031	530.878	436.737	546.020	−105.798	493.800	−4.447
5900	107.066	532.708	438.348	556.725	−106.058	504.140	−4.463
6000	107.099	534.508	439.936	567.433	−106.304	514.484	−4.479

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 246.698 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -443.005 \pm 1.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -450.659 \pm 1.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2949 (1)	530 (1)	1176 (1)
1508 (1)	1262 (1)	1435 (1)
1116 (1)	3013 (1)	1090 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: C–F = 1.358 ± 0.001 Å; C–H = 1.092 ± 0.003 Å
Bond Angles: F–C–F = 108° 17' ± 6'; H–C–H = 111° 52' ± 25'
Product of the Moments of Inertia: $I_A I_B I_C = 1.22816 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

Neugebauer and Margrave[1] measured the enthalpy of combustion of CH_2F_2. Their result for the combustion reaction

$$CH_2F_2(g) + O_2(g) \rightarrow CO_2(g) + 2HF·21.5\ H_2O$$

was $\Delta_f H(298.15\ K) = -139.84 \pm 0.22\ kcal·mol^{-1}$. Using $\Delta_f H°(HF·21.5\ H_2O, 298.15\ K) = -76.75 \pm 0.1\ kcal·mol^{-1}$,[2] obtained with dilution data compiled by Parker,[3] we derive, $\Delta_f H°(CH_2F_2, g, 298.15\ K) = -107.7 \pm 0.4\ kcal·mol^{-1}$ ($-450.659 \pm 1.7\ kJ·mol^{-1}$) from Neugebauer and Margrave's data.

Heat Capacity and Entropy

The vibrational frequencies are average values from the infrared studies of Stewart and Nielsen[4] and Plyler and Benedict.[5] Pricipal moments of inertia are calculated from the rotational constants reported by Lide[6] with the result $I_A = 1.7088 \times 10^{-39}$, $I_B = 7.9171 \times 10^{-39}$, and $I_C = 9.0781 \times 10^{-39}\ g·cm^2$. The molecular structure data are from the microwave studies of Lide[6] and are in excellent agreement with electron-diffraction studies of Brockway, Thornton, and Bartell whose results are reported in the Annual review of Physical Chemistry.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.690	−443.005	−443.005	INFINITE
100	33.494	206.992	280.603	−7.361	−445.642	−439.137	229.381
200	36.678	230.995	250.396	−3.880	−448.111	−431.680	112.743
250	39.472	239.465	247.384	−1.980	−449.405	−427.424	89.305
298.15	42.859	246.698	246.698	0.	−450.659	−423.076	74.121
300	43.000	246.964	246.699	0.079	−450.706	−422.905	73.634
350	46.984	253.888	247.237	2.328	−451.967	−418.171	62.409
400	51.113	260.431	248.481	4.780	−453.153	−413.261	53.966
450	55.154	266.686	250.158	7.438	−454.252	−408.208	47.384
500	58.973	272.697	252.114	10.292	−455.257	−403.037	42.105
600	65.767	284.068	256.503	16.539	−456.991	−392.424	34.164
700	71.458	294.646	261.206	23.408	−458.383	−381.549	28.472
800	76.212	304.508	266.009	30.799	−459.476	−370.494	24.191
900	80.205	313.722	270.804	38.625	−460.313	−359.319	20.854
1000	83.577	322.352	275.532	46.819	−460.936	−348.062	18.181
1100	86.438	330.455	280.161	55.324	−461.384	−336.752	15.991
1200	88.876	338.083	284.673	64.093	−461.691	−325.407	14.165
1300	90.962	345.282	289.061	73.087	−461.885	−314.042	12.618
1400	92.754	352.090	293.322	82.275	−461.991	−302.665	11.293
1500	94.301	358.543	297.457	91.630	−462.030	−291.282	10.143
1600	95.641	364.673	301.468	101.129	−462.016	−279.900	9.138
1700	96.807	370.507	305.359	110.752	−461.963	−268.519	8.251
1800	97.825	376.070	309.134	120.485	−461.881	−257.142	7.462
1900	98.719	381.384	312.798	130.313	−461.776	−245.770	6.757
2000	99.507	386.468	316.355	140.225	−461.655	−234.404	6.122
2100	100.203	391.340	319.811	150.212	−461.520	−223.045	5.548
2200	100.822	396.016	323.169	160.263	−461.373	−211.693	5.026
2300	101.373	400.510	326.435	170.374	−461.215	−200.347	4.550
2400	101.866	404.835	329.612	180.536	−461.047	−189.009	4.114
2500	102.308	409.003	332.704	190.745	−460.868	−177.677	3.712
2600	102.706	413.023	335.717	200.996	−460.677	−166.353	3.342
2700	103.065	416.906	338.652	211.285	−460.473	−155.037	2.999
2800	103.391	420.660	341.514	221.608	−460.255	−143.729	2.681
2900	103.686	424.294	344.307	231.962	−460.022	−132.428	2.385
3000	103.955	427.813	347.032	242.344	−459.773	−121.136	2.109
3100	104.201	431.226	349.693	252.752	−459.507	−109.853	1.851
3200	104.426	434.538	352.293	263.184	−459.223	−98.578	1.609
3300	104.632	437.754	354.834	273.637	−458.922	−87.312	1.382
3400	104.822	440.881	357.319	284.110	−458.602	−76.056	1.168
3500	104.997	443.922	359.750	294.601	−458.264	−64.810	0.967
3600	105.158	446.882	362.130	305.109	−457.908	−53.573	0.777
3700	105.307	449.765	364.459	315.632	−457.534	−42.347	0.598
3800	105.445	452.576	366.741	326.170	−457.143	−31.131	0.428
3900	105.573	455.316	368.978	336.721	−456.735	−19.925	0.267
4000	105.693	457.991	371.170	347.284	−456.310	−8.730	0.114
4100	105.804	460.602	373.319	357.859	−455.870	2.454	−0.031
4200	105.907	463.153	375.428	368.445	−455.415	13.627	−0.169
4300	106.004	465.646	377.497	379.040	−454.947	24.789	−0.301
4400	106.095	468.084	379.528	389.645	−454.465	35.940	−0.427
4500	106.180	470.469	381.523	400.259	−453.970	47.080	−0.546
4600	106.259	472.804	383.482	410.881	−453.465	58.209	−0.661
4700	106.334	475.090	385.407	421.511	−452.948	69.327	−0.770
4800	106.404	477.329	387.299	432.148	−452.421	80.434	−0.875
4900	106.471	479.524	389.158	442.791	−451.885	91.529	−0.976
5000	106.533	481.676	390.987	453.442	−451.340	102.614	−1.072
5100	106.592	483.786	392.786	464.098	−450.787	113.687	−1.164
5200	106.647	485.856	394.556	474.760	−450.226	124.750	−1.253
5300	106.700	487.888	396.298	485.427	−449.658	135.802	−1.338
5400	106.750	489.883	398.013	496.100	−449.083	146.843	−1.420
5500	106.797	491.842	399.701	506.777	−448.501	157.873	−1.499
5600	106.842	493.767	401.364	517.459	−447.912	168.893	−1.575
5700	106.884	495.658	403.001	528.145	−447.317	179.902	−1.649
5800	106.925	497.518	404.615	538.836	−446.716	190.901	−1.719
5900	106.963	499.346	406.205	549.530	−446.108	201.889	−1.787
6000	106.999	501.144	407.772	560.228	−445.494	212.866	−1.853

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 218.950 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta H_f°(0\ K) = -112.057 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -115.897 \pm 6.3\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2766.4 (1)	2843.4(1)
1746.07(1)	1247.4(1)
1500.6 (1)	1163.5(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: C–H = 1.12 ± 0.01 Å; C–O = 1.21 ± 0.01 Å
Bond Angle: H–C–H = 118 ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 1.6597 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

Delepine and Badoche[1] measured the enthalpy of combustion of a formaldehyde polymer. Their value is revised to $\Delta_f H°(298.15\ K) = -25.0$ kcal·mol^{-1} based on the following thermochemical cycle:

I	$C(cr) + 1/2O_2(g) + H_2(g) = \frac{1}{n}(CH_2O)_n(cr)$	−42.3 kcal·mol^{-1}
II	$[1/n](CH_2O)_n(cr) + H_2O = CH_2O(aq)$	2.4
III	$CH_2O(g) = CH_2O(aq)$	14.9

Equation I and II are based upon data listed by Delepine and Badoche.[1] For reaction III, Delepine and Badoche obtained 15 kcal·mol^{-1}. Whereas, Walker[2] obtained 14.8 kcal·mol^{-1}. A value of −27.7 kcal·mol^{-1} is obtained from the combustion experiments of Wartenberg and Lerner–Steinberg.[3] Corrections of −0.6 and 0.1 kcal·mol^{-1} were applied to obtain a enthalpy of reaction at constant pressure and at 298.15 K.

Equilibrium constant determinations of reaction (IV) by Newton and Dodge[4] lead to a $\Delta_f H°(298.15\ K) \approx -29.0$ kcal·mol^{-1}.

IV $H_2(g) + CO(g) = H_2CO(g)$

The value obtained from the measurements of Wartenberg and Lerner–Steinberg[3] is believed to be the most reliable.

Heat Capacity and Entropy

Frequencies were measured by Blau and Nielson[5] in the I. R. Microwave determinations of Lawrence and Strandberg,[6] and those of Erlandson[7] are in essential agreement. The principal moments of inertia are: $I_A = 0.3085 \times 10^{-39}$, $I_B = 2.1701 \times 10^{-39}$, and $I_C = 2.4786 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.021	−112.057	−112.057	INFINITE
100	33.258	182.208	249.156	−6.695	−113.243	−112.630	58.832
200	33.502	205.292	222.109	−3.363	−114.387	−111.598	29.146
250	34.194	212.831	219.525	−1.673	−115.118	−110.819	23.154
298.15	35.402	218.950	218.950	0.	−115.897	−109.921	19.258
300	35.458	219.169	218.951	0.066	−115.928	−109.884	19.132
350	37.203	224.761	219.388	1.880	−116.771	−108.810	16.239
400	39.264	229.861	220.383	3.791	−117.616	−107.615	14.053
450	41.489	234.613	221.703	5.810	−118.445	−106.314	12.341
500	43.766	239.102	223.220	7.941	−119.245	−104.923	10.961
600	48.216	247.478	226.575	12.542	−120.731	−101.917	8.873
700	52.319	255.224	230.121	17.572	−122.039	−98.675	7.363
800	55.983	262.455	233.716	22.991	−123.162	−95.259	6.220
900	59.199	269.239	237.290	28.754	−124.111	−91.712	5.323
1000	61.995	275.624	240.807	34.817	−124.906	−88.068	4.600
1100	64.411	281.649	244.249	41.140	−125.570	−84.351	4.005
1200	66.494	287.345	247.605	47.688	−126.127	−80.578	3.507
1300	68.290	292.740	250.871	54.429	−126.596	−76.763	3.084
1400	69.840	297.859	254.046	61.338	−126.998	−72.914	2.720
1500	71.182	302.724	257.131	68.390	−127.349	−69.039	2.404
1600	72.346	307.356	260.126	75.568	−127.661	−65.141	2.127
1700	73.360	311.773	263.035	82.855	−127.946	−61.225	1.881
1800	74.246	315.992	265.861	90.236	−128.213	−57.292	1.663
1900	75.023	320.028	268.606	97.700	−128.470	−53.345	1.467
2000	75.709	323.894	271.275	105.237	−128.724	−49.385	1.290
2100	76.314	327.602	273.869	112.839	−128.979	−45.411	1.130
2200	76.852	331.165	276.393	120.498	−129.240	−41.426	0.984
2300	77.331	334.592	278.850	128.208	−129.510	−37.428	0.850
2400	77.759	337.893	281.241	135.963	−129.792	−33.419	0.727
2500	78.143	341.075	283.572	143.758	−130.090	−29.397	0.614
2600	78.489	344.146	285.843	151.590	−130.404	−25.363	0.510
2700	78.801	347.115	288.057	159.455	−130.736	−21.317	0.412
2800	79.083	349.986	290.218	167.349	−131.088	−17.258	0.322
2900	79.339	352.765	292.327	175.270	−131.461	−13.186	0.238
3000	79.573	355.459	294.387	183.216	−131.855	−9.101	0.158
3100	79.786	358.072	296.399	191.184	−132.272	−5.002	0.084
3200	79.981	360.608	298.366	199.173	−132.713	−0.890	0.015
3300	80.159	363.072	300.290	207.180	−133.177	3.236	−0.051
3400	80.323	365.467	302.172	215.204	−133.666	7.377	−0.113
3500	80.475	367.798	304.014	223.244	−134.179	11.533	−0.172
3600	80.614	370.067	305.817	231.299	−134.717	15.704	−0.228
3700	80.743	372.277	307.584	239.367	−135.281	19.890	−0.281
3800	80.863	374.432	309.315	247.447	−135.871	24.092	−0.331
3900	80.974	376.534	311.011	255.539	−136.486	28.310	−0.379
4000	81.077	378.586	312.675	263.641	−137.128	32.543	−0.425
4100	81.173	380.589	314.307	271.754	−137.796	36.793	−0.469
4200	81.263	382.546	315.909	279.876	−138.491	41.060	−0.511
4300	81.346	384.459	317.481	288.006	−139.213	45.343	−0.551
4400	81.425	386.330	319.024	296.145	−139.962	49.643	−0.589
4500	81.498	388.161	320.541	304.291	−140.738	53.961	−0.626
4600	81.567	389.953	322.030	312.444	−141.540	58.296	−0.662
4700	81.631	391.708	323.494	320.604	−142.371	62.650	−0.696
4800	81.692	393.427	324.933	328.771	−143.228	67.021	−0.729
4900	81.749	395.112	326.348	336.943	−144.113	71.410	−0.761
5000	81.803	396.764	327.740	345.120	−145.025	75.818	−0.792
5100	81.854	398.384	329.109	353.303	−145.964	80.244	−0.822
5200	81.902	399.974	330.457	361.491	−146.930	84.689	−0.851
5300	81.948	401.535	331.783	369.683	−147.924	89.153	−0.879
5400	81.991	403.067	333.089	377.880	−148.944	93.636	−0.906
5500	82.031	404.572	334.375	386.082	−149.991	98.137	−0.932
5600	82.070	406.050	335.642	394.287	−151.064	102.659	−0.958
5700	82.107	407.503	336.890	402.495	−152.164	107.199	−0.982
5800	82.141	408.932	338.120	410.708	−153.290	111.759	−1.007
5900	82.175	410.336	339.332	418.924	−154.442	116.338	−1.030
6000	82.206	411.717	340.527	427.143	−155.619	120.938	−1.053

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar)

$S°(298.15\ K) = 194.171 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 149.031 \pm 0.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 145.687 \pm 0.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
46205	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[3002] (1)
580 (1)
[3184] (2)
1383 (2)

Point Group: D_{3h} $\sigma = 6$
Bond Distance: C–H = 1.079 Å
Bond Angle: H–C–H = 120°
Product of the Moments of Inertia: $I_A I_B I_C = 4.99 \times 10^{-119}\ g^3 \cdot cm^6$

Enthalpy of Formation

Chupka[1] measured the photoionization spectrum of methane and from the onset of CH_3^+ production has reported $\Delta_{at}H°(CH_3–H) = 103.244 \pm 0.12\ kcal \cdot mol^{-1}$. The value was corrected for the thermal rotation energy of the fragment ions and is the value adopted here.

Dibeler *et al.*[2] had earlier reported $\Delta_{at}H°(CH_3–H) = 101.7 \pm 0.5\ kcal \cdot mol^{-1}$ but they did not apply the rotational energy correction, which bring them closer to Chupka.

The photoionization values are in good agreement with earlier electron impact determiantions as summarized by Stevenson[3] who gives $\Delta_{at}H°(CH_3–H) = 101.9 \pm 1\ kcal \cdot mol^{-1}$. Kinetic determinations have been recently reviewed by Kerr[4] and yield $\Delta_{at}H°(CH_3–H) = 102.5 \pm 1\ kcal \cdot mol^{-1}$ again in excellent agreement.

Heat Capacity and Entropy

The structure, bond length, angles and electronic levels are those reported by Herzberg.[5] A set of vibrational frequencies have been reported by Andrews and Pimentel[6] in an argon matrix, of which only two were observed. Milligan and Jacox[7] observed $\nu_2 = 611\ cm^{-1}$ in an argon matrix and disagreed with Andrews and Pimentel who reported 730 cm^{-1}. Later, Tan and Pimentel[8] agreed that the earlier values were for a methyl radical interacting with an alkali halide molecule. This would affect the ν_2 mode strongest, thus, we adopt the remaining in plane frequencies which appear to be of the correct magnitudes. The ν_2 mode is taken fro mthe analysis of Herzberg[5] since this represents the gas phase molcule and is in resonable agreement with the matrix value of Milligan and Jacox.[7] The uncertainity in the entropy reflects the uncertainties in the vibrational frequencies.

The principal moments of inertia are: $I_A = I_B = 0.2923 \times 10^{-39}$, and $I_C = 0.5846 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.407	149.031	149.031	INFINITE
100	33.395	155.665	226.465	−7.080	147.800	147.438	−77.014
200	35.638	179.380	197.609	−3.646	146.868	147.432	−38.505
250	37.162	187.495	194.799	−1.826	146.297	147.637	−30.847
298.15	38.693	194.170	194.170	0.	145.687	147.950	−25.920
300	38.753	194.410	194.171	0.072	145.663	147.964	−25.763
350	40.392	200.506	194.649	2.050	144.997	148.400	−22.147
400	42.041	206.008	195.730	4.111	144.320	148.932	−19.449
450	43.668	211.054	197.156	6.254	143.644	149.549	−17.359
500	45.252	215.737	198.783	8.477	142.976	150.241	−15.696
600	48.288	224.258	202.333	13.155	141.682	151.817	−13.217
700	51.174	231.921	206.021	18.130	140.477	153.602	−11.462
800	53.926	238.935	209.703	23.386	139.383	155.554	−10.157
900	56.527	245.438	213.316	28.910	138.411	157.635	−9.149
1000	58.954	251.521	216.836	34.686	137.557	159.817	−8.348
1100	61.187	257.247	220.252	40.694	136.814	162.080	−7.697
1200	63.217	262.659	223.562	46.916	136.167	164.406	−7.156
1300	65.048	267.793	226.769	53.331	135.602	166.783	−6.701
1400	66.690	272.675	229.875	59.919	135.105	169.201	−6.313
1500	68.156	277.327	232.885	66.663	134.662	171.652	−5.977
1600	69.463	281.768	235.802	73.545	134.262	174.131	−5.685
1700	70.628	286.015	238.632	80.551	133.896	176.634	−5.427
1800	71.667	290.082	241.378	87.667	133.554	179.158	−5.199
1900	72.594	293.982	244.045	94.881	133.230	181.701	−4.995
2000	73.422	297.727	246.636	102.182	132.917	184.260	−4.812
2100	74.165	301.327	249.155	109.562	132.610	186.835	−4.647
2200	74.831	304.793	251.606	117.013	132.305	189.424	−4.497
2300	75.430	308.133	253.991	124.526	131.999	192.027	−4.361
2400	75.971	311.355	256.315	132.097	131.688	194.644	−4.236
2500	76.459	314.466	258.579	139.719	131.369	197.273	−4.122
2600	76.902	317.474	260.787	147.387	131.041	199.916	−4.016
2700	77.304	320.384	262.940	155.098	130.701	202.571	−3.919
2800	77.670	323.202	265.042	162.847	130.348	205.239	−3.829
2900	78.003	325.933	267.095	170.630	129.980	207.921	−3.745
3000	78.309	328.583	269.101	178.446	129.595	210.615	−3.667
3100	78.588	331.155	271.061	186.291	129.193	213.322	−3.594
3200	78.845	333.655	272.979	194.163	128.772	216.042	−3.527
3300	79.082	336.084	274.854	202.060	128.331	218.777	−3.463
3400	79.300	338.449	276.690	209.979	127.869	221.524	−3.403
3500	79.501	340.750	278.488	217.919	127.385	224.286	−3.347
3600	79.687	342.992	280.248	225.879	126.879	227.061	−3.295
3700	79.860	345.178	281.974	233.856	126.349	229.852	−3.245
3800	80.020	347.310	283.665	241.850	125.796	232.656	−3.198
3900	80.169	349.391	285.324	249.860	125.217	235.476	−3.154
4000	80.308	351.422	286.951	257.884	124.613	238.311	−3.112
4100	80.438	353.407	288.548	265.921	123.984	241.161	−3.072
4200	80.559	355.346	290.115	273.971	123.328	244.027	−3.035
4300	80.672	357.243	291.654	282.033	122.645	246.909	−2.999
4400	80.778	359.099	293.166	290.105	121.936	249.807	−2.966
4500	80.878	360.916	294.652	298.188	121.199	252.721	−2.934
4600	80.972	362.694	296.112	306.281	120.436	255.652	−2.903
4700	81.060	364.437	297.547	314.382	119.645	258.600	−2.874
4800	81.143	366.144	298.958	322.492	118.827	261.565	−2.846
4900	81.221	367.818	300.347	330.611	117.982	264.547	−2.820
5000	81.295	369.460	301.712	338.737	117.111	267.548	−2.795
5100	81.365	371.070	303.057	346.870	116.214	270.565	−2.771
5200	81.432	372.651	304.380	355.009	115.292	273.601	−2.748
5300	81.495	374.203	305.683	363.156	114.345	276.654	−2.727
5400	81.554	375.726	306.966	371.308	113.373	279.726	−2.706
5500	81.611	377.223	308.230	379.467	112.379	282.815	−2.686
5600	81.666	378.694	309.475	387.630	111.362	285.923	−2.667
5700	81.718	380.140	310.702	395.800	110.324	289.050	−2.649
5800	81.767	381.562	311.911	403.974	109.266	292.195	−2.631
5900	81.815	382.960	313.104	412.153	108.188	295.357	−2.615
6000	81.860	384.336	314.280	420.337	107.094	298.539	−2.599

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 234.367 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -75.753 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -83.680 \pm 2.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2968 (1)	3054 (2)
1355 (1)	1455 (2)
732 (1)	1017 (2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: C–H = 1.0959 Å; C–Cl = 1.7812 Å
Bond Angles: H–C–H = 108°; H–C–Cl = 110°55'
Product of the Moments of Inertia: $I_A I_B I_C = 2.14799 \times 10^{-116}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation has been determined by hydrogenation of methyl chloride to give methane and hydrogen chloride by Lacher *et al.*,[1] and by Lacher *et al.*.[2] They reported an average enthalpy of hydrogenation at 248°C to be $-19{,}655 \pm 45\ cal \cdot K^{-1} \cdot mol^{-1}$. Using this value, together with JANAF data[5] for $H_2(g)$. $CH_4(g)$, HCl(g), the enthalpy of formation of methyl chloride is calculated to be $\Delta_f H°(298.15\ K) = -20.69\ kcal \cdot mol^{-1}$. Fowell *et al.*,[3] using a similar hydrogenation technique almost ten years later, report a value $\Delta_f H°(CH_3Cl, g, 298.15\ K) = -20.741\ kcal \cdot mol^{-1}$.

Fletcher and Pilcher[4] derived the enthalpy of formation by measuring the enthalpy of combustion of methyl chloride by flame calorimetry. They reported a value $\Delta_f H°(CH_3Cl, g, 298.15\ K) = -19.59 \pm 0.16\ kcal \cdot mol^{-1}$ where the error, according to the authors, is twice the standard deviation of the mean including the uncertainty in calibration, measurement, determination of ignition energy, and values of auxiliary data used.

In support of their results, Fletcher and Pilcher[4] have compared the enthalpies of formation of $C_2H_5Cl(g)$ and $i\text{–}C_3H_7Cl(g)$ as determined by equilibrium studies (2nd and 3rd law) with their work via flame calorimetry. The agreement is excellent (<0.2 $kcal \cdot mol^{-1}$ difference) but in both cases results for hydrogenation studies are at least 1 $kcal \cdot mol^{-1}$ less negative. In the case of $CH_3Cl(g)$ no equilibrium results are currently available and the results of $\Delta_f H°(298.15\ K)$ from hydrogenation studies are approximately 1 $kcal \cdot mol^{-1}$ more negative than the results from flame calorimetry.

The value chosen as the enthalpy of formation is $\Delta_f H°(CH_3Cl, g, 298.15\ K) = -20.0 \pm 0.5\ kcal \cdot mol^{-1}$. This value is close to the median value and is arbitrarily chosen as it is uncertain whether the flame calorimetry or hydrogenation studies are the more accurate. Slightly more weight was given to the flame calorimetry work due to favorable comparisons with equilibrium studfies in related compounds. An error of $\pm 0.5\ kcal \cdot mol^{-1}$ is chosen so as to encompass the current $\Delta_f H°(298.15\ K)$ experimental values even though the actual experimental error is considerably less.

Heat Capacity and Entropy

The vibrational frequencies are essentially typical values which were taken from the experimental work of Plyler and Benedict,[6] Reichman and Overend,[7] Morino and Nakamura,[8] Jones *et al.*,[9] Fletcher,[10] and King *et al.*.[11] The value of ω_1 as given by Plyler and Benedict[6] appears too low and was not included. Costain[12] has calculated the bond distances and angles based on a isotopic substitution method. From this latter data, the moments of inertia are calculated to be: $I_A = 0.5263 \times 10^{-39}$ and $I_B = I_C = 6.3887 \times 10^{-39}\ g \cdot cm^2$.

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[5] JANAF Thermochemical Tables: $H_2(g)$, 3–31–61; $CH_4(g)$, 3–31–61; HCl(g), 9–30–64.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.415	−75.753	−75.753	INFINITE
100	33.284	195.966	266.858	−7.089	−78.441	−73.383	38.331
200	35.151	219.389	237.889	−3.700	−80.938	−67.379	17.598
250	37.631	227.482	235.019	−1.884	−82.322	−63.831	13.337
298.15	40.731	234.367	234.367	0.	−83.680	−60.146	10.537
300	40.859	234.619	234.368	0.075	−83.732	−60.000	10.447
350	44.466	241.186	234.878	2.208	−85.103	−55.936	8.348
400	48.155	247.365	236.056	4.523	−86.401	−51.679	6.749
450	51.745	253.245	237.642	7.022	−87.609	−47.266	5.486
500	55.145	258.875	239.486	9.695	−88.725	−42.722	4.463
600	61.284	269.485	243.613	15.523	−90.685	−33.332	2.902
700	66.605	279.341	248.021	21.924	−92.300	−23.640	1.764
800	71.239	288.545	252.518	28.822	−93.602	−13.740	0.897
900	75.294	297.175	257.005	36.153	−94.627	−3.692	0.214
1000	78.845	305.296	261.432	43.864	−95.414	6.456	−0.337
1100	81.952	312.960	265.771	51.907	−95.998	16.672	−0.792
1200	84.669	320.209	270.009	60.241	−96.413	26.935	−1.172
1300	87.043	327.082	274.137	68.829	−96.691	37.226	−1.496
1400	89.119	333.611	278.154	77.640	−96.857	47.534	−1.774
1500	90.936	339.823	282.060	86.644	−96.935	57.851	−2.015
1600	92.529	345.743	285.856	95.819	−96.941	68.170	−2.226
1700	93.929	351.396	289.547	105.144	−96.894	78.488	−2.412
1800	95.162	356.800	293.134	114.599	−96.804	88.803	−2.577
1900	96.253	361.975	296.622	124.171	−96.684	99.111	−2.725
2000	97.219	366.937	300.015	133.846	−96.543	109.412	−2.858
2100	98.079	371.702	303.316	143.612	−96.388	119.706	−2.978
2200	98.845	376.283	306.529	153.459	−96.227	129.993	−3.086
2300	99.531	380.692	309.658	163.378	−96.064	140.272	−3.186
2400	100.147	384.941	312.707	173.362	−95.906	150.544	−3.277
2500	100.701	389.041	315.679	183.405	−95.755	160.810	−3.360
2600	101.201	393.000	318.577	193.501	−95.617	171.069	−3.437
2700	101.654	396.828	321.405	203.644	−95.495	181.324	−3.508
2800	102.065	400.533	324.165	213.830	−95.390	191.575	−3.574
2900	102.439	404.121	326.860	224.056	−95.306	201.822	−3.635
3000	102.780	407.600	329.494	234.317	−95.244	212.067	−3.692
3100	103.092	410.975	332.068	244.611	−95.206	222.309	−3.746
3200	103.378	414.253	334.586	254.934	−95.194	232.551	−3.796
3300	103.640	417.438	337.048	265.286	−95.207	242.794	−3.843
3400	103.882	420.535	339.458	275.662	−95.247	253.037	−3.887
3500	104.105	423.550	341.818	286.061	−95.314	263.281	−3.929
3600	104.311	426.486	344.129	296.482	−95.408	273.528	−3.969
3700	104.502	429.346	346.394	306.923	−95.530	283.778	−4.006
3800	104.678	432.135	348.614	317.382	−95.678	294.032	−4.042
3900	104.843	434.857	350.790	327.858	−95.852	304.289	−4.075
4000	104.996	437.513	352.925	338.350	−96.053	314.552	−4.108
4100	105.138	440.107	355.020	348.857	−96.278	324.820	−4.138
4200	105.271	442.643	357.076	359.378	−96.529	335.094	−4.167
4300	105.395	445.121	359.095	369.911	−96.802	345.373	−4.195
4400	105.512	447.545	361.078	380.456	−97.098	355.660	−4.222
4500	105.621	449.918	363.026	391.013	−97.416	365.953	−4.248
4600	105.723	452.240	364.940	401.580	−97.755	376.254	−4.272
4700	105.819	454.515	366.822	412.158	−98.113	386.562	−4.296
4800	105.910	456.744	368.672	422.744	−98.489	396.879	−4.319
4900	105.995	458.929	370.492	433.339	−98.883	407.203	−4.341
5000	106.076	461.071	372.282	443.943	−99.293	417.536	−4.362
5100	106.151	463.172	374.044	454.554	−99.717	427.876	−4.382
5200	106.223	465.234	375.778	465.173	−100.156	438.225	−4.402
5300	106.291	467.258	377.485	475.799	−100.606	448.583	−4.421
5400	106.355	469.246	379.166	486.431	−101.068	458.950	−4.439
5500	106.416	471.198	380.821	497.070	−101.539	469.324	−4.457
5600	106.474	473.116	382.452	507.714	−102.018	479.708	−4.475
5700	106.529	475.001	384.060	518.364	−102.505	490.101	−4.491
5800	106.581	476.854	385.643	529.020	−102.997	500.502	−4.508
5900	106.630	478.676	387.205	539.680	−103.493	510.910	−4.523
6000	106.677	480.469	388.744	550.346	−103.992	521.328	−4.539

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

Trichloromethylsilane ($Si(CH_3)Cl_3$) IDEAL GAS $M_r = 149.47932$

$S°(298.15\ K) = 351.147\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) =$ Unknown

$\Delta_f H°(298.15\ K) = [-528.858]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Source unknown.

Heat Capacity and Entropy

$C_p°$ values are taken from Janz *et al.*[1]

Reference

[1]G. J. Janz, Y. Mikawa, and F. Behnke, Silanes Vibrational Spectra, Molecular Parameters, and Thermodynamic Properties, Rensselaer Polytechnic Institute, Troy, N. Y., (1960).

Trichloromethylsilane ($SiCH_3Cl_3$) $C_1H_3Cl_3Si_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	102.382	351.147	351.147	.000	−528.858	−468.020	81.995
300	102.634	351.781	351.149	.190	−528.895	−467.642	81.424
400	114.725	383.033	355.328	11.082	−530.711	−446.939	58.364
500	123.888	409.653	363.596	23.029	−532.110	−425.826	44.486
600	131.127	432.901	373.250	35.791	−533.144	−404.466	35.212
700	137.026	453.570	383.275	49.206	−533.864	−382.959	28.577
800	141.963	472.197	393.245	63.161	−534.317	−361.368	23.595
900	146.231	489.170	402.974	77.576	−534.541	−339.733	19.718
1000	149.871	504.769	412.384	92.385	−534.577	−318.084	16.615
1100	153.051	519.206	421.447	107.535	−534.460	−296.440	14.077
1200	155.770	532.643	430.160	122.979	−534.227	−274.811	11.962
1300	158.155	545.207	438.532	138.678	−533.906	−253.206	10.174
1400	160.205	557.004	446.577	154.598	−533.527	−231.627	8.642
1500	162.004	568.120	454.313	170.711	−533.112	−210.077	7.316

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

Trichloromethylsilane ($SiCH_3Cl_3$) $C_1H_3Cl_3Si_1(g)$

$S°(298.15\ K) = 222.843\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -226.3 \pm 33\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -234.3 \pm 29\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2965 (1)	3006 (2)
1464 (1)	1467 (2)
1049 (1)	1182 (2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: C–F = 1.391 ± 0.005 Å; C–H = 1.095 ± 0.010 Å
Bond Angle: H–C–H = 109.5° ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 5.8630 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

Appearance potentials for CH_3^+ from CH_4 and CH_3F reported by Lossing *et al.*[1] the enthalpies of dissociation of hydrogen (104.20 $kcal·mol^{-1}$) and fluorine (37.72 $kcal·mol^{-1}$), and the enthalpy of formation of methane ($-17.90\ kcal·mol^{-1}$) were used to calculate the enthalpy of formation of gaseous CH_3F. These authors measured an appearance potential for CH_3^+ from CH_3F of 14.6 ± 0.6 eV, which would give an uncertainty of about $\pm 15\ kcal·mol^{-1}$ in the enthalpy of formation of methyl fluoride. However, a correlation of the enthalpy of formation from the atoms of the methyl fluorides and methyl chlorides indicates that the uncertainty can be reduced to $\pm 7\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Fundamental vibrational frequencies were taken from the summary reported by Smith and Mills.[2] Moments of inertia from the microwave results of Gilliam *et al.*[3] are: $I_A = 0.5354 \times 10^{-39}$, $I_B = I_C = 3.3093 \times 10^{-39}\ g·cm^2$. Bond parameters are the values of Brockway *et al.*[4] from electron diffraction results. These values are in close agreement with the microwave parameters reported by Gilliam *et al.*[3]

References

[1]F. P. Lossing, K. V. Ingold, and I. H. S. Henderson, J. Chem. Phys. **22**, 1489 (1954).
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[3]O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. **75**, 1014 (1949).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.135	−226.275	−226.275	INFINITE
100	33.258	185.647	253.738	−6.809	−228.961	−223.802	116.902
200	33.825	208.776	226.124	−3.470	−231.453	−217.703	56.858
250	35.227	216.456	223.446	−1.748	−232.872	−214.103	44.734
298.15	37.500	222.843	222.843	0.	−234.304	−210.359	36.854
300	37.603	223.075	222.843	0.069	−234.359	−210.210	36.601
350	40.695	229.097	223.312	2.025	−235.843	−206.068	30.754
400	44.167	234.755	224.392	4.145	−237.275	−201.716	26.341
450	47.751	240.164	225.846	6.443	−238.629	−197.188	22.889
500	51.280	245.378	227.540	8.919	−239.894	−192.515	20.112
600	57.871	255.322	231.350	14.383	−242.139	−182.822	15.916
700	63.705	264.690	235.450	20.468	−244.010	−172.783	12.893
800	68.812	273.538	239.663	27.100	−245.533	−162.500	10.610
900	73.269	281.906	243.896	34.209	−246.747	−152.045	8.824
1000	77.150	289.831	248.097	41.734	−247.695	−141.470	7.390
1100	80.526	297.347	252.236	49.622	−248.420	−130.810	6.212
1200	83.459	304.482	256.295	57.825	−248.959	−120.093	5.228
1300	86.009	311.265	260.265	66.301	−249.347	−109.338	4.393
1400	88.227	317.723	264.140	75.016	−249.614	−98.557	3.677
1500	90.161	323.877	267.919	83.937	−249.784	−87.761	3.056
1600	91.851	329.751	271.601	93.040	−249.878	−76.956	2.512
1700	93.332	335.365	275.188	102.300	−249.912	−66.147	2.032
1800	94.633	340.737	278.682	111.700	−249.900	−55.338	1.606
1900	95.780	345.885	282.084	121.222	−249.852	−44.530	1.224
2000	96.795	350.824	285.399	130.852	−249.777	−33.725	0.881
2100	97.696	355.569	288.628	140.577	−249.682	−22.925	0.570
2200	98.499	360.133	291.775	150.388	−249.571	−12.130	0.288
2300	99.216	364.527	294.843	160.274	−249.449	−1.339	0.030
2400	99.858	368.764	297.835	170.228	−249.318	9.445	−0.206
2500	100.436	372.852	300.755	180.243	−249.180	20.224	−0.423
2600	100.957	376.802	303.604	190.314	−249.038	30.998	−0.623
2700	101.429	380.621	306.386	200.433	−248.892	41.765	−0.808
2800	101.856	384.317	309.104	210.598	−248.743	52.528	−0.980
2900	102.245	387.899	311.760	220.803	−248.593	63.285	−1.140
3000	102.599	391.371	314.356	231.046	−248.441	74.037	−1.289
3100	102.923	394.741	316.895	241.322	−248.290	84.783	−1.429
3200	103.220	398.013	319.379	251.630	−248.138	95.525	−1.559
3300	103.492	401.193	321.810	261.965	−247.988	106.262	−1.682
3400	103.743	404.287	324.191	272.327	−247.839	116.995	−1.797
3500	103.974	407.297	326.522	282.713	−247.693	127.723	−1.906
3600	104.187	410.229	328.807	293.122	−247.550	138.447	−2.009
3700	104.385	413.087	331.046	303.550	−247.410	149.168	−2.106
3800	104.568	415.873	333.242	313.998	−247.276	159.884	−2.198
3900	104.738	418.591	335.396	324.463	−247.147	170.597	−2.285
4000	104.896	421.245	337.509	334.945	−247.024	181.307	−2.368
4100	105.044	423.837	339.583	345.442	−246.908	192.014	−2.446
4200	105.181	426.370	341.619	355.954	−246.800	202.718	−2.521
4300	105.310	428.847	343.619	366.478	−246.700	213.420	−2.593
4400	105.430	431.269	345.584	377.015	−246.609	224.119	−2.661
4500	105.543	433.640	347.514	387.564	−246.528	234.816	−2.726
4600	105.649	435.961	349.412	398.124	−246.457	245.512	−2.788
4700	105.748	438.234	351.278	408.694	−246.397	256.206	−2.847
4800	105.842	440.461	353.113	419.273	−246.348	266.900	−2.904
4900	105.930	442.644	354.918	429.862	−246.309	277.592	−2.959
5000	106.013	444.785	356.694	440.459	−246.282	288.284	−3.012
5100	106.091	446.885	358.442	451.064	−246.266	298.974	−3.062
5200	106.165	448.946	360.162	461.677	−246.261	309.666	−3.111
5300	106.235	450.969	361.857	472.297	−246.267	320.357	−3.157
5400	106.302	452.956	363.525	482.924	−246.283	331.048	−3.202
5500	106.364	454.907	365.169	493.557	−246.310	341.739	−3.246
5600	106.424	456.824	366.789	504.197	−246.347	352.431	−3.287
5700	106.481	458.708	368.385	514.842	−246.392	363.124	−3.328
5800	106.534	460.560	369.958	525.493	−246.446	373.818	−3.367
5900	106.585	462.382	371.509	536.149	−246.508	384.512	−3.404
6000	106.634	464.174	373.039	546.810	−246.576	395.208	−3.441

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = 314.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = [-1232.71]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Source unknown.

Heat Capacity and Entropy

Data from Janz *et al.*[1]

Reference

[1]G. J. Janz, Y. Mikawa, and F. Behnke, "Silanes. Vibrational Spectra, Molecular Parameters, and Thermodynamic Properties," Rensselaer Polytechnic Institute, Troy, N. Y., (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
250							
298.15	90.876	314.202	314.202	.000	−1232.711	−1169.932	204.967
300	91.169	314.765	314.204	.168	−1232.762	−1169.542	203.635
400	105.269	342.993	317.957	10.014	−1235.248	−1148.078	149.924
500	116.483	367.732	325.489	21.122	−1237.178	−1126.052	117.638
600	125.311	389.777	334.400	33.226	−1238.632	−1103.683	96.084
700	132.382	409.640	343.753	46.121	−1239.692	−1081.103	80.673
800	138.239	427.710	353.135	59.660	−1240.426	−1058.393	69.106
900	143.135	444.282	362.355	73.735	−1240.891	−1035.609	60.105
1000	147.277	459.582	371.322	88.260	−1241.140	−1012.785	52.902
1100	150.875	473.793	379.999	103.173	−1241.216	−989.944	47.009
1200	153.888	487.052	388.374	118.414	−1241.161	−967.103	42.097
1300	156.523	499.476	396.448	133.937	−1241.012	−944.270	37.941
1400	158.825	511.161	404.228	149.706	−1240.797	−921.451	34.380
1500	160.917	522.192	411.728	165.695	−1240.535	−898.650	31.294

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = 186.251 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -66.911 \pm 0.34\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -74.873 \pm 0.34\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2916.5 (1)
1534.0 (2)
3018.7 (3)
1306 (3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: C–H = 1.091 ± 0.002 Å
Bond Angle: H–C–H = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 1.499 \times 10^{-118}\ g^3 \cdot cm^6$.

Enthalpy of Formation

Rossini[1] measured the enthalpy of combustion of methane gas. His value at 298.15 K was corrected to the presently accepted molecular weight of water. The enthalpy of formation was calculated using −68.3174 and −94.0540 kcal·mol^{-1} for the enthalpy of formation of H_2O(l) and CO_2(g), respectively.

Heat Capacity and Entropy

Stevenson and Ibers,[2] calculated the bond distance from an analysis of available spectroscopic data. Vibrational frequencies listed by Jones and McDowell,[3] are consistent with their results of a force constant calculation. The principal moments of inertia are: $I_A = I_B = I_C = 0.5313 \times 10^{-39}\ g \cdot cm^2$.

References

[1]F. D. Rossini, J. Res. Nat. Bur. Stand. **6**, 37 (1931).
[2]D. P. Stevenson and J. A. Ibers, J. Chem. Phys. **33**, 100 (1960).
[3]L. H. Jones and R. S. McDowell, J. Mol. Spectrosc. **3**, 632 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.024	−66.911	−66.911	INFINITE
100	33.258	149.500	216.485	−6.698	−69.644	−64.353	33.615
200	33.473	172.577	189.418	−3.368	−72.027	−58.161	15.190
250	34.216	180.113	186.829	−1.679	−73.426	−54.536	11.395
298.15	35.639	186.251	186.251	0.	−74.873	−50.768	8.894
300	35.708	186.472	186.252	0.066	−74.929	−50.618	8.813
350	37.874	192.131	186.694	1.903	−76.461	−46.445	6.932
400	40.500	197.356	187.704	3.861	−77.969	−42.054	5.492
450	43.374	202.291	189.053	5.957	−79.422	−37.476	4.350
500	46.342	207.014	190.614	8.200	−80.802	−32.741	3.420
600	52.227	215.987	194.103	13.130	−83.308	−22.887	1.993
700	57.794	224.461	197.840	18.635	−85.452	−12.643	0.943
800	62.932	232.518	201.675	24.675	−87.238	−2.115	0.138
900	67.601	240.205	205.532	31.205	−88.692	8.616	−0.500
1000	71.795	247.549	209.370	38.179	−89.849	19.492	−1.018
1100	75.529	254.570	213.162	45.549	−90.750	30.472	−1.447
1200	78.833	261.287	216.895	53.270	−91.437	41.524	−1.807
1300	81.744	267.714	220.558	61.302	−91.945	52.626	−2.115
1400	84.305	273.868	224.148	69.608	−92.308	63.761	−2.379
1500	86.556	279.763	227.660	78.153	−92.553	74.918	−2.609
1600	88.537	285.413	231.095	86.910	−92.703	86.088	−2.810
1700	90.283	290.834	234.450	95.853	−92.780	97.265	−2.989
1800	91.824	296.039	237.728	104.960	−92.797	108.445	−3.147
1900	93.188	301.041	240.930	114.212	−92.770	119.624	−3.289
2000	94.399	305.853	244.057	123.592	−92.709	130.802	−3.416
2100	95.477	310.485	247.110	133.087	−92.624	141.975	−3.531
2200	96.439	314.949	250.093	142.684	−92.521	153.144	−3.636
2300	97.301	319.255	253.007	152.371	−92.409	164.308	−3.732
2400	98.075	323.413	255.854	162.141	−92.291	175.467	−3.819
2500	98.772	327.431	258.638	171.984	−92.174	186.622	−3.899
2600	99.401	331.317	261.359	181.893	−92.060	197.771	−3.973
2700	99.971	335.080	264.020	191.862	−91.954	208.916	−4.042
2800	100.489	338.725	266.623	201.885	−91.857	220.058	−4.105
2900	100.960	342.260	269.171	211.958	−91.773	231.196	−4.164
3000	101.389	345.690	271.664	222.076	−91.705	242.332	−4.219
3100	101.782	349.021	274.106	232.235	−91.653	253.465	−4.271
3200	102.143	352.258	276.498	242.431	−91.621	264.598	−4.319
3300	102.474	355.406	278.842	252.662	−91.609	275.730	−4.364
3400	102.778	358.470	281.139	262.925	−91.619	286.861	−4.407
3500	103.060	361.453	283.391	273.217	−91.654	297.993	−4.447
3600	103.319	364.360	285.600	283.536	−91.713	309.127	−4.485
3700	103.560	367.194	287.767	293.881	−91.798	320.262	−4.521
3800	103.783	369.959	289.894	304.248	−91.911	331.401	−4.555
3900	103.990	372.658	291.982	314.637	−92.051	342.542	−4.588
4000	104.183	375.293	294.032	325.045	−92.222	353.687	−4.619
4100	104.363	377.868	296.045	335.473	−92.422	364.838	−4.648
4200	104.531	380.385	298.023	345.918	−92.652	375.993	−4.676
4300	104.688	382.846	299.967	356.379	−92.914	387.155	−4.703
4400	104.834	385.255	301.879	366.855	−93.208	398.322	−4.729
4500	104.972	387.612	303.758	377.345	−93.533	409.497	−4.753
4600	105.101	389.921	305.606	387.849	−93.891	420.679	−4.777
4700	105.223	392.182	307.424	398.365	−94.281	431.869	−4.800
4800	105.337	394.399	309.213	408.893	−94.702	443.069	−4.822
4900	105.445	396.572	310.973	419.432	−95.156	454.277	−4.843
5000	105.546	398.703	312.707	429.982	−95.641	465.495	−4.863
5100	105.642	400.794	314.414	440.541	−96.157	476.722	−4.883
5200	105.733	402.847	316.095	451.110	−96.703	487.961	−4.902
5300	105.818	404.861	317.750	461.688	−97.278	499.210	−4.920
5400	105.899	406.840	319.382	472.274	−97.882	510.470	−4.938
5500	105.976	408.784	320.990	482.867	−98.513	521.741	−4.955
5600	106.049	410.694	322.575	493.469	−99.170	533.025	−4.972
5700	106.118	412.572	324.137	504.077	−99.852	544.320	−4.988
5800	106.184	414.418	325.678	514.692	−100.557	555.628	−5.004
5900	106.247	416.234	327.197	525.314	−101.284	566.946	−5.019
6000	106.306	418.020	328.696	535.942	−102.032	578.279	−5.034

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar)

Cyanogen Iodide (ICN) — IDEAL GAS — M_r = 152.9222

$S°(298.15\ K) = 257.34 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 226.5 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 225.9 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
485.8 (1)
304.5 (2)
2188 (1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: $C_{\infty v}$

Bond Distances: C–I = 1.994 Å; C–N = 1.159 Å

Bond Angle: I–C–N = 180°

Rotational Constant: $B_0 = 0.107604\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from $\Delta_f H°$(ICN, cr, 298.15 K) = 39.71 kcal·mol^{-1} [1] and $\Delta_{sub} H°(298.15\ K) = 14.29 \pm 0.15$ kcal·mol^{-1}. This latter value is obtained from a 2nd and 3rd law analysis of the vapor pressure data of Yost and Stone[2] and Ketelaar and Kruyer,[3] which are in good agreement after dropping the lowest point in the first set and the lowest 3 points in the second set.

The enthalpy of formation of the crystal is calculated from $\Delta_f H°(298.15\ K) = -46.3 \pm 0.08$ kcal·mol^{-1} obtained by Lord and Woolf[4] for the reaction ICN(cr) + 2 NaOH(56 H_2O) = NaCNO(2800 H_2O) + NaI(2800 H_2O) + H_2O(l). The auxiliary data used were $\Delta_f H°$(NaOH·56 H_2O, 298.15 K) = −112.26 kcal·mol^{-1};[1,5] $\Delta_f H°$(NaCNO·2800 H_2O, 298.15 K) = −92.25 kcal·mol^{-1} [1,5] and $\Delta_f H°$(NaI·2800·H_2O, 298.15 K) = −70.54 kcal·mol^{-1}.[1,5] The uncertainty in the final value reflects the uncertainty in $\Delta_f H°$(NaCNO·2800 H_2O, 298.15 K) which was determined by Lord and Woolf to be −93.6 kcal·mol^{-1} in excess NaOH·56 H_2O.

Heat Capacity and Entropy

The molecular structure, bond distances and angle were determined using microwave spectroscopy by Tyler and Sheridan.[6] The infrared spectrum of the gas has been reported by Hemple and Nixon[7] using a 10m folded path cell. The fundamentals have been confirmed by the Raman data of West and Farnsworth[8] on a solution in methanol; and by the infrared data of Freitag and Nixon[9] on solid ICN.

References:

[1]U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[2]D. M. Yost and W. E. Stone, J. Amer. Chem. Soc. **55**, 1889 (1933).
[3]J. A. A. Ketelaar and S. Kruyer, Rec. Trav. Chem. **62**, 550 (1943).
[4]G. Lord and A. A. Woolf, J. Chem. Soc. (London), 2546 (1954).
[5]V. B. Parker, U. S. Nat. Bur. Stand. NSRDS–NBS 2, (1965).
[6]J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).
[7]S. Hemple and E. R. Nixon, J. Chem. Phys. **47**, 4273 and **48**, 5288 (1968).
[8]W. West and M. Farnsworth, J. Chem. Phys. **1**, 402 (1933).
[9]W. O. Freitag and E. R. Nixon, J. Chem. Phys. **24**, 109 (1956).

Cyanogen Iodide (CNI) — $C_1I_1N_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.470	226.451	226.451	INFINITE
100	33.571	212.187	296.813	−8.463	226.423	216.340	−113.004
200	43.694	238.890	261.644	−4.551	226.087	206.419	−53.911
250	46.561	248.970	258.128	−2.289	226.011	201.512	−42.104
298.15	48.420	257.340	257.340	0.	225.936	196.800	−34.478
300	48.479	257.640	257.341	0.090	225.932	196.619	−34.234
350	49.827	265.220	257.937	2.549	225.787	191.743	−28.616
400	50.845	271.942	259.275	5.067	217.609	187.166	−24.441
450	51.676	277.980	261.024	7.631	216.795	183.409	−21.290
500	52.398	283.463	262.998	10.233	195.880	181.645	−18.976
600	53.662	293.131	267.235	15.537	196.238	178.762	−15.563
700	54.769	301.488	271.545	20.960	196.483	175.828	−13.120
800	55.742	308.866	275.758	26.487	196.644	172.866	−11.287
900	56.587	315.482	279.811	32.104	196.744	169.887	−9.860
1000	57.312	321.482	283.682	37.800	196.796	166.899	−8.718
1100	57.930	326.975	287.372	43.563	196.808	163.909	−7.783
1200	58.456	332.038	290.886	49.383	196.786	160.919	−7.005
1300	58.903	336.735	294.234	55.252	196.731	157.932	−6.346
1400	59.284	341.115	297.428	61.161	196.641	154.950	−5.781
1500	59.610	345.217	300.479	67.107	196.514	151.977	−5.292
1600	59.890	349.073	303.397	73.082	196.346	149.013	−4.865
1700	60.132	352.711	306.192	79.083	196.135	146.061	−4.488
1800	60.342	356.154	308.872	85.107	195.877	143.122	−4.153
1900	60.525	359.422	311.448	91.151	195.572	140.200	−3.854
2000	60.684	362.530	313.925	97.211	195.218	137.294	−3.586
2100	60.825	365.495	316.310	103.287	194.819	134.408	−3.343
2200	60.949	368.327	318.611	109.376	194.376	131.541	−3.123
2300	61.059	371.039	320.832	115.476	193.894	128.696	−2.923
2400	61.157	373.640	322.978	121.587	193.377	125.872	−2.740
2500	61.245	376.138	325.055	127.708	192.832	123.070	−2.571
2600	61.323	378.542	327.066	133.836	192.264	120.291	−2.417
2700	61.394	380.858	329.016	139.972	191.680	117.534	−2.274
2800	61.458	383.091	330.908	146.115	191.084	114.799	−2.142
2900	61.516	385.249	332.744	152.263	190.483	112.085	−2.019
3000	61.568	387.335	334.530	158.418	189.881	109.392	−1.905
3100	61.616	389.355	336.266	164.577	189.283	106.719	−1.798
3200	61.660	391.312	337.956	170.741	188.692	104.065	−1.699
3300	61.700	393.210	339.601	176.909	188.112	101.429	−1.605
3400	61.736	395.053	341.205	183.081	187.545	98.811	−1.518
3500	61.770	396.843	342.769	189.256	186.992	96.209	−1.436
3600	61.801	398.583	344.296	195.435	186.456	93.623	−1.358
3700	61.830	400.277	345.786	201.616	185.938	91.051	−1.285
3800	61.857	401.926	347.242	207.801	185.438	88.494	−1.216
3900	61.881	403.533	348.665	213.987	184.956	85.949	−1.151
4000	61.904	405.100	350.056	220.177	184.493	83.416	−1.089
4100	61.925	406.629	351.417	226.368	184.049	80.895	−1.031
4200	61.945	408.122	352.750	232.562	183.622	78.384	−0.975
4300	61.964	409.579	354.054	238.757	183.213	75.883	−0.922
4400	61.981	411.004	355.333	244.954	182.822	73.391	−0.871
4500	61.997	412.397	356.585	251.153	182.446	70.909	−0.823
4600	62.012	413.760	357.813	257.354	182.087	68.434	−0.777
4700	62.027	415.094	359.018	263.556	181.741	65.967	−0.733
4800	62.040	416.400	360.200	269.759	181.410	63.508	−0.691
4900	62.053	417.679	361.360	275.964	181.092	61.055	−0.651
5000	62.065	418.933	362.499	282.170	180.785	58.608	−0.612
5100	62.076	420.162	363.618	288.377	180.490	56.167	−0.575
5200	62.086	421.368	364.717	294.585	180.205	53.732	−0.540
5300	62.096	422.550	365.797	300.794	179.930	51.303	−0.506
5400	62.106	423.711	366.858	307.004	179.663	48.878	−0.473
5500	62.115	424.851	367.902	313.215	179.404	46.459	−0.441
5600	62.123	425.970	368.929	319.427	179.152	44.044	−0.411
5700	62.131	427.070	369.940	325.640	178.906	41.633	−0.382
5800	62.139	428.150	370.934	331.853	178.666	39.227	−0.353
5900	62.146	429.213	371.913	338.068	178.430	36.825	−0.326
6000	62.153	430.257	372.877	344.283	178.197	34.427	−0.300

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

Cyanogen Iodide (CNI) $C_1I_1N_1(g)$

$S°(298.15\ K) = 127.780 \pm 1.05\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 168.3 \pm 0.1\ K$
$T_{fus} = 895 \pm 2\ K$

$\Delta_f H°(0\ K) = -118.34 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -113.47 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.167\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 14.644\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy change, $\Delta_r H°(298.15\ K) = 2.80 \pm 0.10\ kcal \cdot mol^{-1}$, for the reaction KCN(cr) → KCN(aq, ∞) was reported by Parker.[1] Incorporating these data with the enthalpy of formation for K^+(aq, ∞) and CN^-(aq, ∞), reported by Wagman *et al.*,[2] the value of $\Delta_f H°$(KCN, cr, 298.15 K) was evaluated to be $-27.12 \pm 0.2\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacity for KCN(cr) has been measured with a heat conduction method by Messer and Ziegler,[3] 101.6–345.8 K, and adiabatically by Suga *et al.*,[4] 14.23–308.5 K. The data of Suga[4] were adopted after correction for curvature. The anomaleous region between 50–105 K has been treated as second order by inclusion of the enthalpy in the heat capacity. The $C_p°$ values above 310 K were estimated by graphical extrapolation. The value of $S°(298.15\ K)$ was evaluated based on $S°(15\ K) = 0.193\ cal \cdot K^{-1} \cdot mol^{-1}$. This extrapolated value appears more reasonable than the value, $S°(15\ K) = 0.307\ cal \cdot K^{-1} \cdot mol^{-1}$ reported by Suga *et al.*[4]

Transition Data

T_{trs} was taken from Suga *et al.*[4] $\Delta_{trs} H°$ was calculated as the difference between the total enthalpy change, $H°(173.80\ K) - H°(159.02\ K) = 0.533\ kcal \cdot mol^{-1}$ obtained from $C_p°$ values measured by Messer and Ziegler,[3] and the enthalpy change, $0.254\ kcal \cdot mol^{-1}$, calculated from the arbitrarily smoothed $C_p°$ curve. Suga *et al.*[4] reported $\Delta_{trs} H° = 0.339\ kcal \cdot mol^{-1}$; however, their $C_p°$ data do not adequately define the total enthalpy change through the transition region. The values of T_{trs} and $\Delta_{trs} H°$ reported by Messer and Ziegler[3] were 168.3 ± 0.4 K and $0.30\ kcal \cdot mol^{-1}$, respectively. The lower transition, $T_{trs} = 82.9 \pm 0.2$ K and $\Delta_f H° = 0.095 \pm 0.001\ kcal \cdot mol^{-1}$ reported by Suga *et al.*[4] was treatment as second order by inclusion of the enthalpy in the heat capacity.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The difference between $\Delta_f H°(298.15\ K)$ for $(KCN)_2$(g) and 2 KCN(cr) is $\Delta_{sub} H°$(cr → dimer, 298.15 K) and for KCN(g) and KCN(cr) is $\Delta_{sub} H°$(cr → monomer, 298.15 K).

References

[1] V. B. Parker, NSRDS–NBS 2, (1965).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–1, (1965).
[3] C. E. Messer and W. T. Ziegler, J. Amer. Chem. Soc. **63**, 2703 (1941).
[4] H. Suga, T. Matsuo and S. Seki, Bull. Chem. Soc. Japan **38**, 1115 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.343	−118.345	−118.345	INFINITE
100	55.483	49.213	191.980	−14.277	−118.522	−111.797	58.397
168.300	76.283	82.687	141.073	−9.826	I <--> II		
168.300	67.280	89.623	141.073	−8.659	TRANSITION		
200	66.828	101.196	133.862	−6.533	−115.154	−106.080	27.705
298.15	66.391	127.780	127.780	0.	−113.470	−102.011	17.872
300	66.383	128.191	127.781	0.123	−113.445	−101.940	17.749
400	66.316	147.269	130.383	6.755	−114.772	−97.829	12.775
500	66.354	162.072	135.295	13.388	−114.043	−93.681	9.787
600	66.392	174.173	140.797	20.025	−113.515	−89.662	7.806
700	66.431	184.410	146.315	26.667	−113.164	−85.716	6.396
800	66.471	193.283	151.644	33.312	−112.972	−81.810	5.342
895.000	66.509	200.744	156.467	39.628	----- I <--> LIQUID -----		
900	66.511	201.115	156.714	39.961	−112.928	−77.919	4.522
1000	66.551	208.124	161.510	46.614	−113.031	−74.025	3.867
1100	66.590	214.469	166.041	53.271	−192.235	−65.504	3.111
1200	66.629	220.265	170.322	59.932	−191.578	−54.012	2.351
1300	66.669	225.600	174.371	66.597	−190.988	−42.573	1.711
1400	66.708	230.542	178.209	73.266	−190.455	−31.177	1.163
1500	66.747	235.146	181.853	79.938	−189.970	−19.817	0.690
1600	66.787	239.455	185.320	86.615	−189.529	−8.488	0.277
1700	66.826	243.505	188.625	93.296	−189.125	2.815	−0.086
1800	66.865	247.325	191.781	99.980	−188.757	14.094	−0.409
1900	66.905	250.942	194.800	106.669	−188.422	25.355	−0.697
2000	66.944	254.375	197.694	113.361	−188.117	36.598	−0.956

PREVIOUS: June 1962 CURRENT: March 1966

$S°(298.15\ K) = [134.321]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-104.148]\ kJ·mol^{-1}$

$T_{fus} = 895 \pm 2\ K$ $\Delta_{fus}H° = 14.644\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(895\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Heat capacity is estimated and assumed constant in the temperature range 298.15–3000 K. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature was reported by Truthe.[1] The value of $\Delta_{fus}H°$ was taken from Kelly[2] on phase diagrams of the systems KCN–AgCN, KCN–$Cu_2(CN)_2$, KCN–KCl, KCN–NaCN, and KCN–$Zn(CN)_2$ reported by Truthe.[1]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the reaction KCN(l) = KCN(g) becomes zero. The difference between $\Delta_f H°$ for KCN(g) and KCN(l) at T_{vap} is $\Delta_{vap}H°$.

References

[1]W. Truthe, Z. Anorg. Chem. **76**, 129 (1912).
[2]K. K. Kelley, U. S. Bur. Mines Bull. 393, (1936).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	75.312	134.321	134.321	0.	−104.148	−94.638	16.580
300	75.312	134.787	134.323	0.139	−104.106	−94.580	16.468
400	75.312	156.453	137.277	7.671	−104.534	−91.264	11.918
500	75.312	173.258	142.855	15.202	−102.907	−88.139	9.208
600	75.312	186.989	149.101	22.733	−101.485	−85.322	7.428
700	75.312	198.599	155.364	30.264	−100.244	−82.729	6.173
800	75.312	208.655	161.411	37.795	−99.166	−80.302	5.243
895.000	75.312	217.106	166.883	44.950	----- I <--> LIQUID -----		
900	75.312	217.526	167.163	45.327	−98.240	−78.001	4.527
1000	75.312	225.461	172.603	52.858	−97.465	−75.795	3.959
1100	75.312	232.639	177.740	60.389	−175.795	−69.050	3.279
1200	75.312	239.192	182.592	67.920	−174.268	−59.414	2.586
1300	75.312	245.220	187.180	75.451	−172.811	−49.902	2.005
1400	75.312	250.801	191.528	82.983	−171.416	−40.500	1.511
1500	75.312	255.997	195.655	90.514	−170.073	−31.197	1.086
1600	75.312	260.858	199.580	98.045	−168.777	−21.981	0.718
1700	75.312	265.423	203.320	105.576	−167.523	−12.844	0.395
1800	75.312	269.728	206.891	113.107	−166.308	−3.781	0.110
1900	75.312	273.800	210.306	120.639	−165.130	5.216	−0.143
2000	75.312	277.663	213.578	128.170	−163.986	14.152	−0.370
2100	75.312	281.337	216.718	135.701	−162.878	23.031	−0.573
2200	75.312	284.841	219.735	143.232	−161.804	31.859	−0.756
2300	75.312	288.189	222.639	150.763	−160.764	40.638	−0.923
2400	75.312	291.394	225.438	158.295	−159.761	49.373	−1.075
2500	75.312	294.468	228.138	165.826	−158.794	58.067	−1.213
2600	75.312	297.422	230.746	173.357	−157.867	66.723	−1.340
2700	75.312	300.264	233.269	180.888	−156.980	75.344	−1.458
2800	75.312	303.003	235.711	188.419	−156.136	83.933	−1.566
2900	75.312	305.646	238.077	195.951	−155.338	92.493	−1.666
3000	75.312	308.199	240.372	203.482	−154.588	101.026	−1.759

PREVIOUS: June 1962 CURRENT: March 1966

0	to	168.3 K	crystal, I
168.3	to	895 K	crystal, II
above		895 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−17.343	−118.345	−118.345	INFINITE
100	55.483	49.213	191.980	−14.277	−118.522	−111.797	58.397
168.300	76.283	82.687	141.073	−9.826	I <--> II		
168.300	67.280	89.623	141.073	−8.659	TRANSITION		
200	66.828	101.196	133.862	−6.533	−115.154	−106.080	27.705
298.15	66.391	127.780	127.780	0.	−113.470	−102.011	17.872
300	66.383	128.191	127.781	0.123	−113.445	−101.940	17.749
400	66.316	147.269	130.383	6.755	−114.772	−97.829	12.775
500	66.354	162.072	135.295	13.388	−114.043	−93.681	9.787
600	66.392	174.173	140.797	20.025	−113.515	−89.662	7.806
700	66.431	184.410	146.315	26.667	−113.164	−85.716	6.396
800	66.471	193.283	151.644	33.312	−112.972	−81.810	5.342
895.000	66.509	200.744	156.467	39.628	I <--> LIQUID		
895.000	75.312	217.106	156.467	54.272	TRANSITION		
900	75.312	217.526	156.805	54.649	−98.240	−78.001	4.527
1000	75.312	225.461	163.281	62.180	−97.465	−75.795	3.959
1100	75.312	232.639	169.265	69.711	−175.795	−69.050	3.279
1200	75.312	239.192	174.823	77.242	−174.268	−59.414	2.586
1300	75.312	245.220	180.009	84.774	−172.811	−49.902	2.005
1400	75.312	250.801	184.869	92.305	−171.416	−40.500	1.511
1500	75.312	255.997	189.440	99.836	−170.073	−31.197	1.086
1600	75.312	260.858	193.753	107.367	−168.777	−21.981	0.718
1700	75.312	265.423	197.836	114.898	−167.523	−12.844	0.395
1800	75.312	269.728	201.712	122.430	−166.308	−3.781	0.110
1900	75.312	273.800	205.400	129.961	−165.130	5.216	−0.143
2000	75.312	277.663	208.917	137.492	−163.986	14.152	−0.370
2100	75.312	281.337	212.279	145.023	−162.878	23.031	−0.573
2200	75.312	284.841	215.498	152.554	−161.804	31.859	−0.756
2300	75.312	288.189	218.586	160.086	−160.764	40.638	−0.923
2400	75.312	291.394	221.554	167.617	−159.761	49.373	−1.075
2500	75.312	294.468	224.409	175.148	−158.794	58.067	−1.213
2600	75.312	297.422	227.161	182.679	−157.867	66.723	−1.340
2700	75.312	300.264	229.816	190.210	−156.980	75.344	−1.458
2800	75.312	303.003	232.381	197.742	−156.136	83.933	−1.566
2900	75.312	305.646	234.862	205.273	−155.338	92.493	−1.666
3000	75.312	308.199	237.265	212.804	−154.588	101.026	−1.759

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = [253.15]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [80 \pm 21]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [79 \pm 21]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[370] (1)
207 (2)
2158 (1)

Ground State Quantum Weight: 1 σ = 1
Point Group: $C_{\infty v}$
Bond Distances: C–N = 1.16 ± 0.01 Å; K–C = [2.294] Å
Bond Angle: K–C–C = 180°
Rotational Constant: B_o = [0.118914] cm^{-1}

Enthalpy of Formation

The vapor pressure of KCN(g) at 870°C was estimated to be 1–10 mm Hg by Villars.[1] Assuming the vapor pressure at this temperature to be 1 mm Hg, the enthalpy of vaporization, $\Delta_{vap}H°(298.15\ K)$, for KCN(l) was evaluated as 44 $kcal·mol^{-1}$. Based on $\Delta_f H°(298.15\ K) = -24.89\ kcal·mol^{-1}$ for KCN(l), the value of $\Delta_f H°$(KCN, g, 298.15 K) is calculated to be 19 ± 5 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular structure of KCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C–N bond distance was determined by Elliott and Hastings[2] by use of neutron diffraction measurements. The K–C bond distance was taken from Leroi,[3] which was estimated. The vibrational frequencies, ν_2 and ν_3, were obtained from Leroi and Klemperer.[4] The value of ν_1 was calculated by valence force method described by Herzberg[5] using appropriate force constants.

References

[1]D. S. Villars, J. Am. Chem. Soc. **53**, 405 (1931).
[2]N. Elliott and J. Hastings, Acta Cryst. **14**, 1018 (1961).
[3]G. E. Leroi, Ph. D. Dissertation, Harvard University, (1961).
[4]G. E. Leroi and W. Klemperer, J. Chem. Phys. **35**, 774 (1961).
[5]G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, (1945).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.456	79.509	79.509	INFINITE
100	38.592	203.295	295.884	−9.259	79.462	70.779	−36.971
200	47.724	233.411	257.718	−4.861	79.484	62.115	−16.223
250	49.674	244.289	253.978	−2.422	79.525	57.767	−12.070
298.15	50.857	253.146	253.146	0.	79.496	53.578	−9.387
300	50.894	253.461	253.147	0.094	79.493	53.417	−9.301
350	51.734	261.373	253.770	2.661	76.969	49.177	−7.339
400	52.384	268.325	255.164	5.264	76.703	45.225	−5.906
450	52.944	274.528	256.977	7.898	76.412	41.307	−4.795
500	53.465	280.133	259.017	10.558	76.093	37.424	−3.910
600	54.456	289.969	263.378	15.955	75.380	29.755	−2.590
700	55.391	298.435	267.795	21.447	74.583	22.213	−1.658
800	56.246	305.888	272.100	27.030	73.713	14.790	−0.966
900	57.006	312.558	276.231	32.694	72.771	7.481	−0.434
1000	57.666	318.599	280.171	38.428	71.749	0.280	−0.015
1100	58.234	324.122	283.919	44.224	−8.316	−2.203	0.105
1200	58.719	329.211	287.484	50.072	−8.472	−1.641	0.071
1300	59.133	333.927	290.877	55.965	−8.654	−1.065	0.043
1400	59.487	338.323	294.111	61.896	−8.858	−0.473	0.018
1500	59.790	342.438	297.197	67.861	−9.082	0.133	−0.005
1600	60.051	346.305	300.147	73.853	−9.325	0.756	−0.025
1700	60.277	349.952	302.970	79.870	−9.585	1.393	−0.043
1800	60.472	353.403	305.677	85.907	−9.864	2.047	−0.059
1900	60.643	356.678	308.276	91.963	−10.161	2.717	−0.075
2000	60.792	359.792	310.774	98.035	−10.477	3.403	−0.089
2100	60.923	362.761	313.180	104.121	−10.814	4.105	−0.102
2200	61.039	365.598	315.499	110.219	−11.173	4.824	−0.115
2300	61.142	368.314	317.736	116.329	−11.555	5.559	−0.126
2400	61.234	370.918	319.898	122.448	−11.964	6.312	−0.137
2500	61.316	373.420	321.989	128.575	−12.401	7.083	−0.148
2600	61.389	375.826	324.014	134.710	−12.870	7.871	−0.158
2700	61.456	378.144	325.976	140.853	−13.372	8.678	−0.168
2800	61.515	380.380	327.880	147.001	−13.911	9.505	−0.177
2900	61.569	382.540	329.727	153.156	−14.489	10.351	−0.186
3000	61.619	384.628	331.523	159.315	−15.111	11.218	−0.195
3100	61.663	386.649	333.269	165.479	−15.779	12.106	−0.204
3200	61.704	388.607	334.967	171.648	−16.498	13.017	−0.212
3300	61.742	390.507	336.622	177.820	−17.261	13.951	−0.221
3400	61.776	392.350	338.234	183.996	−18.088	14.909	−0.229
3500	61.808	394.142	339.806	190.175	−18.972	15.892	−0.237
3600	61.837	395.883	341.339	196.357	−19.924	16.901	−0.245
3700	61.864	397.578	342.837	202.542	−20.946	17.938	−0.253
3800	61.888	399.228	344.299	208.730	−22.041	19.003	−0.261
3900	61.912	400.836	345.728	214.920	−23.215	20.099	−0.269
4000	61.933	402.404	347.126	221.112	−24.465	21.224	−0.277
4100	61.953	403.933	348.492	227.307	−25.804	22.383	−0.285
4200	61.971	405.426	349.830	233.503	−27.239	23.575	−0.293
4300	61.989	406.885	351.140	239.701	−28.772	24.803	−0.301
4400	62.005	408.310	352.423	245.900	−30.129	26.040	−0.309
4500	62.020	409.704	353.681	252.102	−31.800	27.336	−0.317
4600	62.034	411.067	354.914	258.304	−33.571	28.669	−0.326
4700	62.048	412.401	356.123	264.509	−35.422	30.040	−0.334
4800	62.060	413.708	357.309	270.714	−37.267	31.440	−0.342
4900	62.072	414.987	358.473	276.921	−39.319	32.892	−0.351
5000	62.083	416.241	359.616	283.128	−41.475	34.387	−0.359
5100	62.094	417.471	360.738	289.337	−43.736	35.927	−0.368
5200	62.104	418.677	361.841	295.547	−46.103	37.512	−0.377
5300	62.113	419.860	362.924	301.758	−48.577	39.143	−0.386
5400	62.122	421.021	363.990	307.970	−51.157	40.822	−0.395
5500	62.130	422.161	365.037	314.182	−53.843	42.550	−0.404
5600	62.138	423.280	366.067	320.396	−56.633	44.328	−0.413
5700	62.146	424.380	367.080	326.610	−59.183	46.109	−0.423
5800	62.153	425.461	368.078	332.825	−62.136	47.981	−0.432
5900	62.160	426.524	369.059	339.040	−65.186	49.906	−0.442
6000	62.166	427.569	370.026	345.257	−68.329	51.883	−0.452

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 155.519 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1174 \pm 1\ K$

$\Delta_f H°(0\ K) = -1144.61 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1150.18 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 27.614 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was obtained from the enthalpy of solution $\Delta_{sol}H° = -7.6 \pm 0.5$ kcal·mol^{-1} and the enthalpies of formation for K^+(aq) and $CO_3^{=}$(aq), −60.32 and −161.84 kcal·mol^{-1}, respectively. The standard enthalpy solution, $\Delta_{sol}H° = -7.6 \pm 0.5$ kcal·mol^{-1}, was calculated by extrapolation to infinite dilution of the calorimetric data of Benjamin,[1] using the methods suggested by Rupert *et al.*[2] The equilibrium constant for the hydrolysis $CO_3^{=}(aq, \infty) + H_2O(l) \rightarrow HCO_3^-(aq, \infty) + OH^-(\infty H_2O)$ was taken as $K = 2.1 \times 10^{-4}$ based on the selected values of Wagman *et al.*[3] The resulting extrapolations were not so consistent as those of Rupert *et al.*[2] for Na_2CO_3. The ionic enthalpies of formation were taken from Wagman *et al.*[3] This procedure was adopted even though it may involve an inconsistency between the extrapolations for $\Delta_{sol}H°$ and $CO_3^{=}(\infty H_2O)$. The alternative evaluation of $\Delta_f H°(298.15\ K)$ for $K_2CO_3(\sim 1900\ H_2O)$ from the enthalpies of mixing given by Muller[4] and Berthelot[5] may be subject to significant error if dissolved CO_2 was not excluded from the solutions. Presumably, this path was used by Wagman[6] in the selection of $\Delta_f H°(298.15\ K) = -274.3$ kcal·mol^{-1}. This value is 0.6 kcal·mol^{-1} less negative than the value adopted here.

Heat Capacity and Entropy

The low temperature heat capacity, 14.0–315 K was measured by Oetting.[7] Janz *et al.*[8] measured the heat content by drop calorimetry in the temperature range 630–1250 K, and gave enthalpy and heat capacity equations based on their measurements. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity above 298.15 K. The values from the low and high temperature sources join smoothly at 298.15 K. The heat capacity was graphically extrapolated above the melting point. The entropy at 14.0 K was calculated from the extrapolated low temperature $C_p°$ data, using the cubic law. The value of $S°(14\ K) = 0.109\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was obtained from Reisman[9] and $\Delta_{fus}H°$ was taken from Janz.[8]

References

[1] L. Benjamin, J. Chem. Eng. Data **7**, 239–40 (1962).
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[6] D. D. Wagman, U. S. Nat. Bur. Stand. Report 8628, (1965).
[7] F. L. Oetting, unpublished data, Thermal Research Laboratory, Dow Chemical Company, Midland, Michigan, (1963).
[8] G. I. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963).
[9] A. Reisman, J. Amer. Chem. Soc. **80**, 3558 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.673	−1144.614	−1144.614	INFINITE
100	72.383	53.095	246.061	−19.297	−1149.119	−1121.217	585.664
200	99.140	113.018	165.506	−10.498	−1150.202	−1092.747	285.396
298.15	114.437	155.519	155.519	0.	−1150.182	−1064.528	186.501
300	114.699	156.228	155.521	0.212	−1150.176	−1063.997	185.258
400	128.135	191.103	160.186	12.367	−1154.457	−1034.430	135.083
500	140.049	221.005	169.426	25.790	−1153.165	−1004.553	104.945
600	150.666	247.493	180.270	40.334	−1151.017	−975.020	84.883
700	160.483	271.462	191.611	55.896	−1148.102	−945.907	70.584
800	170.043	293.516	202.989	72.422	−1144.456	−917.262	59.891
900	179.515	314.092	214.202	89.901	−1140.085	−889.118	51.603
1000	188.949	333.495	225.170	108.325	−1135.003	−861.499	45.000
1100	198.321	351.944	235.863	127.688	−1287.134	−825.202	39.186
1174.000	205.259	365.079	243.596	142.621	− − − CRYSTAL <− −> LIQUID − − −		
1200	207.695	369.602	246.277	147.989	−1278.565	−783.580	34.108
1300	217.066	386.596	256.421	169.227	−1269.158	−742.707	29.842
1400	226.438	403.026	266.309	191.403	−1258.901	−702.590	26.214
1500	235.810	418.968	275.958	214.515	−1247.784	−663.237	23.096
1600	245.182	434.486	285.383	238.565	−1235.802	−624.653	20.393
1700	254.555	449.631	294.601	263.552	−1222.949	−586.845	18.032
1800	263.927	464.446	303.626	289.476	−1209.226	−549.819	15.955
1900	273.299	478.967	312.474	316.337	−1194.631	−513.579	14.119
2000	282.671	493.224	321.156	344.135	−1179.164	−478.131	12.487

PREVIOUS: December 1961 CURRENT: March 1966

$S°(298.15\ K) = [170.373]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1174 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1130.609]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 27.614 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1174\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 800 K. The heat capacity below 800 K is obtained from the heat capacity of the crystal. Above 800 K the heat capacity is adopted as 50.0 $cal·K^{-1}·mol^{-1}$, based on the enthalpy measurements in the range 1169–1250 K reported by Janz *et al.*[1] The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Reference

[1]G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	114.437	170.373	170.373	0.	−1130.609	−1049.385	183.848
300	114.699	171.082	170.375	0.212	−1130.604	−1048.881	182.626
400	128.135	205.957	175.039	12.367	−1134.885	−1020.799	133.303
500	140.049	235.859	184.280	25.790	−1133.593	−992.408	103.676
600	150.666	262.347	195.124	40.334	−1131.445	−964.360	83.955
700	160.483	286.316	206.465	55.896	−1128.530	−936.732	69.900
800	183.110	308.360	217.832	72.422	−1124.884	−909.565	59.388
800.000	183.110	308.360	217.832	72.422	GLASS <--> LIQUID		
800.000	209.200	308.360	217.832	72.422	TRANSITION		
900	209.200	333.000	229.286	93.342	−1117.071	−883.121	51.255
1000	209.200	355.041	240.779	114.262	−1109.493	−857.535	44.793
1100	209.200	374.980	252.087	135.182	−1260.068	−823.476	39.104
1174.000	209.200	388.601	260.267	150.663	--- CRYSTAL <--> LIQUID ---		
1200	209.200	393.183	263.098	156.102	−1250.880	−784.193	34.135
1300	209.200	409.928	273.757	177.022	−1241.791	−745.671	29.961
1400	209.200	425.431	284.044	197.942	−1232.789	−707.846	26.410
1500	209.200	439.865	293.957	218.862	−1223.865	−670.663	23.355
1600	209.200	453.366	303.502	239.782	−1215.012	−634.072	20.700
1700	209.200	466.049	312.695	260.702	−1206.226	−598.032	18.375
1800	209.200	478.006	321.550	281.622	−1197.507	−562.508	16.324
1900	209.200	489.317	330.084	302.542	−1188.853	−527.467	14.501
2000	209.200	500.048	338.317	323.462	−1180.265	−492.879	12.873
2100	209.200	510.255	346.263	344.382	−1171.745	−458.720	11.410
2200	209.200	519.987	353.940	365.302	−1163.295	−424.964	10.090
2300	209.200	529.286	361.363	386.222	−1154.918	−391.592	8.893
2400	209.200	538.189	368.547	407.142	−1146.618	−358.582	7.804
2500	209.200	546.729	375.504	428.062	−1138.398	−325.917	6.810

PREVIOUS: December 1961 CURRENT: March 1966

0	to	1174 K	crystal
above		1174 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.673	−1144.614	−1144.614	INFINITE
100	72.383	53.095	246.061	−19.297	−1149.119	−1121.217	585.664
200	99.140	113.018	165.506	−10.498	−1150.202	−1092.747	285.396
298.15	114.437	155.519	155.519	0.	−1150.182	−1064.528	186.501
300	114.699	156.228	155.521	0.212	−1150.176	−1063.997	185.258
400	128.135	191.103	160.186	12.367	−1154.457	−1034.430	135.083
500	140.049	221.005	169.426	25.790	−1153.165	−1004.553	104.945
600	150.666	247.493	180.270	40.334	−1151.017	−975.020	84.883
700	160.483	271.462	191.611	55.896	−1148.102	−945.907	70.584
800	170.043	293.516	202.989	72.422	−1144.456	−917.262	59.891
900	179.515	314.092	214.202	89.901	−1140.085	−889.118	51.603
1000	188.949	333.495	225.170	108.325	−1135.003	−861.499	45.000
1100	198.321	351.944	235.863	127.688	−1287.134	−825.202	39.186
1174.000	205.259	365.079	243.596	142.621	CRYSTAL <--> LIQUID TRANSITION		
1174.000	209.200	388.601	243.596	170.235			
1200	209.200	393.183	246.788	175.675	−1250.880	−784.193	34.135
1300	209.200	409.928	258.701	196.595	−1241.791	−745.671	29.961
1400	209.200	425.431	270.064	217.515	−1232.789	−707.846	26.410
1500	209.200	439.865	280.908	238.435	−1223.865	−670.663	23.355
1600	209.200	453.366	291.270	259.355	−1215.012	−634.072	20.700
1700	209.200	466.049	301.181	280.275	−1206.226	−598.032	18.375
1800	209.200	478.006	310.676	301.195	−1197.507	−562.508	16.324
1900	209.200	489.317	319.783	322.115	−1188.853	−527.467	14.501
2000	209.200	500.048	328.530	343.035	−1180.265	−492.879	12.873
2100	209.200	510.255	336.943	363.955	−1171.745	−458.720	11.410
2200	209.200	519.987	345.044	384.875	−1163.295	−424.964	10.090
2300	209.200	529.286	352.854	405.795	−1154.918	−391.592	8.893
2400	209.200	538.189	360.392	426.715	−1146.618	−358.582	7.804
2500	209.200	546.729	367.676	447.635	−1138.398	−325.917	6.810

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 90.171 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1} = 623\ K$
$T_{trs2} = 683 \pm 3\ K$
$T_{fus} = 993 \pm 1\ K$

$\Delta_f H°(0\ K) = -1207.891 \pm 0.17\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1216.038 \pm 0.17\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = [0.561]\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = [2.238]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 44.769 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was derived from the enthalpy change of the following reactions:

	$\Delta_f H°(298.15K)$ kcal·mol^{-1}	References
$2\ Li^+(aq, \infty) + CO_3^{=}(aq, \infty) = Li_2CO_3(cr)$	4.20	1
$2\ Li(cr) + 2\ H_2O(l) = 2\ Li^+(aq, \infty) + 2\ OH^-(aq, \infty) + H_2(g)$	−106.310	2, 3, 4, 5

Summation of these two reactions gives

$2\ Li(cr) + 2\ H_2O(l) + CO_3^{=}(aq, \infty) = Li_2CO_3(cr) + 2\ OH^-(aq, \infty) + H_2(g) = -102.110$

Using $\Delta_f H°$ [6] of $H_2O(l)$, $CO_3^{=}(aq, \infty)$ and $OH^-(aq, \infty)$ yields $\Delta_f H°$ (Li_2CO_3, cr, 298.15 K) = −290.64 kcal·mol^{-1}.

Heat Capacity and Entropy

The low temperature heat capacity, 16.68–300.20 K, was measured by Brown and Latimer.[1] Janz *et al.*[7] measured the heat content by drop calorimetry in the temperature range 560–1150 K and gave enthalpy and heat capacity equations based on their measurement. The above information was used in a Shomate analysis in order to smooth the enthalpy and calculate heat capacity. The values from the low and high temperature sources join smoothly at 298 K. The heat capacity was graphically extrapolated above the melting point. The entropy at 16.68 K was calculated from the extrapolated low temperature $C_p°$ data, using the cubic law. The value of $S°(16.68\ K) = 0.053\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

T_{trs} were taken from Reisman.[8] The enthalpies of transition were estimated from the relative areas of the transitions and the heat of fusion of the differential analysis curve reported by Reisman.[8]

Fusion Data

T_{fus} was obtained from Reisman[8] and $\Delta_{fus} H°$ was taken from Janz *et al.*[7]

References

[1] O. L. I. Brown and W. M. Latimer, J. Amer. Chem. Soc. **58**, 2228 (1936).
[2] JANAF Thermochemical tables: LiOH(cr), 3–31–66.
[3] S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. **80**, 4782 (1958); S. R. Gunn, "Note Concerning an Electrical Heater Error in the Rocking–Bomb Solution Calorimeters," UCRL–7992, (October 1964).
[4] C. B. Messer, L. G. Fasolino and C. E. Thalmayer, J. Amer. Chem. Soc. **77**, 4524 (1955).
[5] V. B. Parker, NSRDS–NBS 2, (1965).
[6] U. S. Nat. Bur. Stand. Tech. Note 270–1, (1965).
[7] G. I. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963).
[8] A. Reisman, J. Amer. Chem. Soc. **80**, 3558 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.174	−1207.891	−1207.891	INFINITE
100	34.811	20.048	158.357	−13.831	−1211.955	−1186.400	619.712
200	72.425	56.513	98.271	−8.352	−1214.852	−1159.562	302.847
298.15	96.232	90.171	90.171	0.	−1216.038	−1132.120	198.343
300	96.567	90.767	90.172	0.178	−1216.048	−1131.600	197.029
400	112.173	120.752	94.156	10.638	−1216.269	−1103.403	144.090
500	128.951	147.525	102.190	22.668	−1222.020	−1074.589	112.262
600	149.369	172.780	111.863	36.550	−1220.421	−1045.224	90.995
623.150	154.643	178.533	114.233	40.069	I <-- -> II		
623.150	154.638	179.433	114.233	40.630	TRANSITION		
683.150	170.212	194.286	120.612	50.331	II <-- -> III		
683.150	138.782	197.563	120.612	52.569	TRANSITION		
700	140.875	200.969	122.505	54.925	−1214.552	−1016.396	75.844
800	158.992	220.962	133.565	69.917	−1212.279	−988.225	64.524
900	177.025	240.727	144.376	86.716	−1208.404	−960.434	55.742
993.150	194.096	258.989	154.270	104.001	----- III <-- -> LIQUID -----		
1000	194.723	260.350	154.993	105.357	−1202.852	−933.163	48.743
1100	205.936	279.471	165.446	125.428	−1196.001	−906.517	43.047
1200	212.673	297.699	175.714	146.382	−1188.373	−880.533	38.329
1300	216.564	314.883	185.765	167.853	−1180.320	−855.204	34.363
1400	219.325	331.040	195.571	189.656	−1172.009	−830.506	30.987
1500	221.083	346.233	205.114	211.678	−1163.538	−806.408	28.082
1600	222.589	360.553	214.386	233.868	−1154.954	−782.878	25.558
1700	223.426	374.072	223.385	256.168	−1436.778	−745.536	22.908
1800	224.262	386.867	232.115	278.553	−1426.584	−705.169	20.463
1900	225.099	399.014	240.582	301.021	−1416.368	−665.369	18.292
2000	225.936	410.582	248.795	323.572	−1406.127	−626.107	16.352

PREVIOUS: CURRENT: March 1966

Lithium Carbonate (Li_2CO_3) LIQUID M_r = 73.8912

$S°(298.15\ K)$ = [130.567] $J·K^{-1}·mol^{-1}$
T_{fus} = 993.15 ± 1 K

$\Delta_f H°(298.15\ K)$ = [−1175.083] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 44.769 ± 0.4 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(993.15\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 683.15 K. The heat capacity below 683.15 K is obtained from the heat capacity of the crystal. Above 683.15 K the heat capacity is adopted as 44.32 $cal·deg^{-1}·mol^{-1}$, based on the enthalpy measurements in the range 996–1150 K reported by Janz *et al.*[1] The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Reference

[1]G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	96.232	130.567	130.567	0.	−1175.083	−1103.210	193.278
300	96.567	131.163	130.569	0.178	−1175.094	−1102.764	192.008
400	112.173	161.148	134.553	10.638	−1175.314	−1078.607	140.852
500	128.951	187.921	142.586	22.668	−1181.066	−1053.833	110.093
600	149.369	213.176	152.259	36.550	−1179.467	−1028.507	89.540
623.150	154.643	218.930	154.629	40.069	I <--> II		
623.150	154.638	219.829	154.629	40.630	TRANSITION		
683.150	170.212	234.683	161.008	50.331	II <--> III		
683.150	185.435	234.683	161.008	50.331	TRANSITION		
700	185.435	239.201	162.836	53.455	−1175.067	−1003.674	74.895
800	185.435	263.962	173.964	71.999	−1169.242	−979.589	63.961
900	185.435	285.803	185.201	90.542	−1163.624	−956.222	55.498
993.150	185 .435	304.066	195.507	107.816	----- III <--> LIQUID -----		
1000	185.435	305.341	196.255	109.086	−1158.169	−933.471	48.760
1100	185.435	323.015	206.988	127.629	−1152.845	−911.260	43.272
1200	185.435	339.150	217.339	146.173	−1147.628	−889.528	38.720
1300	185.435	353.992	227.288	164.716	−1142.503	−868.229	34.886
1400	185.435	367.735	236.835	183.260	−1137.451	−847.320	31.614
1500	185.435	380.528	245.993	201.803	−1132.459	−826.772	28.791
1600	185.435	392.496	254.779	220.347	−1127.520	−806.554	26.331
1700	185.435	403.738	263.214	238.890	−1413.101	−772.291	23.730
1800	185.435	414.337	271.318	257.434	−1406.749	−734.781	21.323
1900	185.435	424.363	279.112	275.977	−1400.457	−697.621	19.179
2000	185.435	433.875	286.614	294.521	−1394.224	−660.791	17.258

PREVIOUS: CURRENT: March 1966

0	to	623 K	crystal, I
623	to	683 K	crystal, II
683	to	993 K	crystal, III
above		993 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−15.174	−1207.891	−1207.891	INFINITE
100	34.811	20.048	158.357	−13.831	−1211.955	−1186.400	619.712
200	72.425	56.513	98.271	−8.352	−1214.852	−1159.562	302.847
298.15	96.232	90.171	90.171	0.	−1216.038	−1132.120	198.343
300	96.567	90.767	90.172	0.178	−1216.048	−1131.600	197.029
400	112.173	120.752	94.156	10.638	−1216.269	−1103.403	144.090
500	128.951	147.525	102.190	22.668	−1222.020	−1074.589	112.262
600	149.369	172.780	111.863	36.550	−1220.421	−1045.224	90.995
623.150	154.643	178.533	114.233	40.069	I <--> II		
623.150	154.638	179.433	114.233	40.630	TRANSITION		
683.150	170.212	194.286	120.612	50.331	II <--> III		
683.150	138.782	197.563	120.612	52.569	TRANSITION		
700	140.875	200.969	122.505	54.925	−1214.552	−1016.396	75.844
800	158.992	220.962	133.565	69.917	−1212.279	−988.225	64.524
900	177.025	240.727	144.376	86.716	−1208.404	−960.434	55.742
993.150	194.096	258.989	154.270	104.001	III <--> LIQUID		
993.150	185.435	304.066	154.270	148.770	TRANSITION		
1000	185.435	305.341	155.301	150.040	−1158.169	−933.471	48.760
1100	185.435	323.015	169.757	168.584	−1152.845	−911.260	43.272
1200	185.435	339.150	183.210	187.127	−1147.628	−889.528	38.720
1300	185.435	353.992	195.784	205.671	−1142.503	−868.229	34.886
1400	185.435	367.735	207.582	224.214	−1137.451	−847.321	31.614
1500	185.435	380.528	218.690	242.758	−1132.459	−826.772	28.791
1600	185.435	392.496	229.183	261.301	−1127.520	−806.554	26.331
1700	185.435	403.738	239.124	279.845	−1413.101	−772.291	23.730
1800	185.435	414.337	248.566	298.388	−1406.749	−734.781	21.323
1900	185.435	424.363	257.557	316.932	−1400.457	−697.621	19.179
2000	185.435	433.875	266.137	335.475	−1394.224	−660.791	17.258

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 65.854\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1104.3 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1111.7 \pm 8\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -265.7 \pm 2\ kcal·mol^{-1}$ ($-1111.689 \pm 8\ kJ·mol^{-1}$) is the average value derived from the dissociation pressures of $MgCO_3$(cr) in the temperature range 671–782 K measured by Marc and Simek[1] and from the $\Delta_r H°(923\ K) = 25.9 \pm 0.6\ kcal·mol^{-1}$ determined by Thomasson and Cunningham[2] using a high temperature differential calorimeter. The decomposition of $MgCO_3$ has been studied in a bomb calorimeter by Roth;[3] this yields $\Delta_r H°(293\ K) = 23.8\ kcal·mol^{-1}$ when corrected to constant pressure. The value is derived from the small difference between two large heats of combustion, so the uncertainty is probably large. Roth also reported $\Delta_r H°(363\ K) = 26.15\ kcal·mol^{-1}$ from calorimetric data on the heat of solution in HCl. Berthelot[4] measured the heat of solution of $MgSO_4$(aq) with K_2CO_3(aq). Analyzing his data we find $\Delta_f H°(298.15\ K) = -268.6\ kcal·mol^{-1}$.

Discrepancies are apparent in the wide range of the calorimetric results and in the 3rd law drift of the equilibrium data. Possible sources for the drift include lack of true equilibrium (e.g., excess surface energy for MgO) and uncertainty in the high temperature entropy of $MgCO_3$ (refer to entropy write-up). Non-standard state behavior of the crystal phases may also be a problem in the calorimetric studies. The data of Thomasson and Cunningham,[2] based on a high temperature differential thermal analysis technique, are probably the most reliable of the calorimetric values; however, there are uncertainties in the absolute energy calibration. The first result of Roth[3] may be dismissed as too discrepant and the remaining two calorimetric values are within $\pm 3\ kcal·mol^{-1}$ of the selected enthalpy of formation.

Source	Method	Reaction	T/K	$\Delta_r H°(298.15\ K)$ kcal·mol		Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
[1]	*Kp*	$MgCO_3(cr) = MgO(cr) + CO_2(g)$	671–782	–	28.3	4.8 ± 0.9	−266.04
[2]	Calorimetric	$MgCO_3(cr) = MgO(cr) + CO_2(g)$	923	25.9	27.7		−265.45
[3]	Calorimetric	$MgCO_3(cr) = MgO(cr) + CO_2(g)$	293	23.8	23.8		−260.35
[3]	Calorimetric	$MgCO_3(cr) = MgO(cr) + CO_2(g)$	363	26.15	26.10		−263.95
[4]	Calorimetric	$K_2CO_3(\sim.5m) + MgSO_4(\sim.5m) = MgCO_3(cr) + K_2SO_4(\sim.5m)$	288	1.05	1.35		−268.6

Heat Capacity and Entropy

Low temperature heat capacities (56.3–291.6 K) were measured by Anderson.[5] The high temperature heat capacities are derived by a Shomate analysis of smoothed enthalpies reported by Kelley.[6] Kelley obtained the smoothed values from unpublished high temperature (400–743 K) enthalpy measurements by Shomate.[7] The data were joined smoothly at 298.15 K and extrapolated graphically above 743 K. The entropy was obtained from the heat capacities using $S°(56.2) = 0.57\ cal·K^{-1}·mol^{-1}$.

Because of the drift in the decomposition pressure data, it is pertinent to assess the uncertainty in the functions. The greatest potential source for error is in the values above room temperature where the increment of entropy is about 20 $cal·K^{-1}·mol^{-1}$ between 298.15 and 700 K. Unfortunately, no evaluation of the unpublished enthalpies is possible, but an increase of 10% in the entropy increment would reduce the drift to a tolerable level.

Decomposition Data

T_{dcm} is calculated as the temperature at which $\Delta_r G°$ equals zero for $MgCO_3(cr) = MgO(cr) + CO_2(g)$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−11.689	−1104.304	−1104.304	INFINITE
100	24.683	10.780	119.865	−10.909	−1108.582	−1082.618	565.502
200	57.572	39.145	72.274	−6.626	−1110.999	−1055.538	275.678
298.15	76.210	65.854	65.854	0.	−1111.689	−1028.124	180.123
300	76.501	66.327	65.856	0.141	−1111.691	−1027.606	178.922
400	89.855	90.253	69.028	8.490	−1111.377	−999.603	130.535
500	100.061	111.423	75.430	17.996	−1110.452	−971.756	101.519
600	109.035	130.486	83.043	28.466	−1109.068	−944.140	82.195
700	116.232	147.849	91.080	39.739	−1107.322	−916.786	68.411
800	122.256	163.771	99.185	51.669	−1105.306	−889.702	58.092
900	127.612	178.491	107.189	64.172	−1103.064	−862.883	50.080
1000	131.796	192.163	115.011	77.152	−1109.256	−835.612	43.648

PREVIOUS: December 1960 CURRENT: December 1966

$S°(298.15\ K) = 202.64 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 436.8 \pm 10\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 435.1 \pm 10\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	58960	2
9118	4	59683	4
25798	2	60939	4
53955	4	64782	4

$\omega_e = 2068.61\ cm^{-1}$ $\omega_e x_e = 13.114\ cm^{-1}$ $\sigma = 1$

$B_e = 1.8989\ cm^{-1}$ $\alpha_e = 0.0172\ cm^{-1}$ $r_e = 1.175$ Å

Enthalpy of Formation

The enthalpy of formation of CN has been the subject of considerable uncertainty for many years. Berkowitz[1] has reviewed the earlier work and he concludes that $\Delta_f H°(CN, g, 0\ K) = 109\ kcal \cdot mol^{-1}$. Since this review a considerable body of work has emerged which supports a value near 100 $kcal \cdot mol^{-1}$.

Tsang *et al.*[2] obtained $\Delta_f H°(CN, g, 298.15\ K) = 100 \pm 4\ kcal \cdot mol^{-1}$ from shock tube studies of the decomposition of cyanogen.

Dibeler and Liston[3,4] have studied a series of cyanogen compounds and obtained their enthaplies of dissociation from photoionization threshold measurements. The values below are obtained from the halogen ion threshold measurements, except for HCN which is from the CN^+ threshold measurements. The value below is calculated using the IP from CNCl measurements.[3]

Davis and Okabe[5] employed a direct photodissociation technique to obtain dissociation energies for many of the same molecules. The method determines the disappearance threshold for fluorescence due to decay of excited CN $B^2\Sigma^+ - X^2\Sigma^+$. This corresponds to the energy needed to just break the bond and form excited cyanogen in the $B^2\Sigma^+$ state, whose energy above ground is well known.

Setser and Steadman[6] used metastable excited argon atoms with a maximum electronic energy of 270 $kcal \cdot mol^{-1}$ to break the bonds in HCN and $(CN)_2$. From the emission spectra of the excited $B^2\Sigma^+$ CN they were able to calculate the highest populated vibrational level and thus a maximum limit to the dissociation energy.

Berkowitz *et al.*[7] have recently examined the photoionization spectrum of HCN using the H^+ ion threshold. They also determined the threshold for the CN^+ ion which agrees exactly with that of Diebeler and Liston[4] when the latter is corrected for rotational energy contributions (0.7 $kcal \cdot mol^{-1}$). Berkowitz *et al.*[7] suggest that the HCN limit of Setser and Steadman[6] should be <105 due to neglect of the significant vibrational population of the first harmonic of the bending mode. However, if the same allowance is made for the C_2N_2 data the limit is only ≤104 and this presumes significant occupation of the third harmonic of the bending mode of C_2N_2.

It is apparent from the data that considerable scatter still exists and several sources of error are probable. HCN and the cyanogen halides all have significant uncertainties in their enthalpy of formation, and the effects of rotational and vibrational contributions at 300 K are uncertain, but could be eliminated by using refrigerated gases. We choose to adopt a median value within the range of almost all determinations of $\Delta_f H°(CN, g, 0\ K) = 103.2 \pm 2.5\ kcal \cdot mol^{-1}$.

	$\Delta_r H°(CNX \rightarrow CN + X, 0\ K)$, $kcal \cdot mol^{-1}$					$\Delta_f H°(CN, g, 0\ K)$, $kcal \cdot mol^{-1}$				
Reference	[2]	[3,4]	[5]	[6]	[7]	[2]	[3,4]	[5]	[6]	[7]
Cl		99.23 ± 0.5	99.86 ± 1.2				103.5 ± 2.0	104.1 ± 2.5		
Br		84.72 ± 0.5	86.94 ± 1.2				102.6 ± 2.0	104.8 ± 2.5		
I		72.95 ± 0.5	71.72 ± 1.0				101.4 ± 2.0	100.2 ± 2.5		
H		119.99 ± 0.5	119.92 ± 1.2	≤124	124.57 ± 0.3		100.7 ± 2.5	100.7 ± 3.0	≤103	105.3 ± 2.5
CN	125 ± 8		129.61 ± 1.2	≤133		100 ± 4		101.5 ± 0.8	≤103	

Heat Capacity and Entropy

The therodynamic functions are taken from Johnston *et al.*[8] calculated based on the direct summation of the energy levels. All the electronic levels and molecular constants listed above are from Carroll.[9] Johnston *et al.* used only the first two excited electronic states but the contribution of the higher levels is negligible.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.000	0.000	INFINITE	−8.672	431.850	431.850	INFINITE
100	29.104	170.835	228.528	−5.769	433.242	424.244	−221.603
200	29.108	191.009	205.304	−2.859	434.371	414.784	−108.330
298.15	29.154	202.638	202.638	0.000	435.136	404.995	−70.953
300	29.157	202.819	202.639	.054	435.147	404.808	−70.483
400	29.408	211.235	203.785	2.980	435.592	394.619	−51.532
500	29.936	217.849	205.959	5.945	435.760	384.352	−40.153
600	30.650	223.368	208.413	8.973	435.719	374.071	−32.566
700	31.423	228.151	210.898	12.077	435.528	363.810	−27.148
800	32.171	232.396	213.325	15.257	435.233	353.583	−23.087
900	32.852	236.226	215.660	18.509	434.862	343.399	−19.930
1000	33.456	239.719	217.894	21.825	434.435	333.258	−17.408
1100	33.987	242.933	220.026	25.198	433.965	323.163	−15.346
1200	34.457	245.911	222.060	28.620	433.462	313.112	−13.629
1300	34.882	248.686	224.003	32.088	432.933	303.105	−12.179
1400	35.277	251.285	225.860	35.596	432.385	293.138	−10.937
1500	35.656	253.732	227.637	39.143	431.823	283.211	−9.862
1600	36.031	256.046	229.341	42.727	431.253	273.323	−8.923
1700	36.408	258.241	230.977	46.349	430.680	263.469	−8.095
1800	36.795	260.333	232.550	50.009	430.109	253.650	−7.361
1900	37.194	262.333	234.066	53.708	429.544	243.862	−6.704
2000	37.608	264.251	235.527	57.448	428.990	234.104	−6.114
2100	38.033	266.097	236.939	61.230	428.451	224.373	−5.581
2200	38.474	267.876	238.305	65.055	427.930	214.667	−5.097
2300	38.921	269.596	239.629	68.925	427.429	204.985	−4.655
2400	39.374	271.262	240.912	72.840	426.952	195.324	−4.251
2500	39.829	272.879	242.159	76.800	426.499	185.682	−3.880
2600	40.282	274.450	243.371	80.806	426.071	176.058	−3.537
2700	40.730	275.978	244.550	84.856	425.670	166.449	−3.220
2800	41.169	277.467	245.699	88.951	425.295	156.856	−2.926
2900	41.596	278.920	246.820	93.090	424.945	147.275	−2.653
3000	42.008	280.337	247.913	97.270	424.621	137.705	−2.398
3100	42.403	281.721	248.982	101.491	424.321	128.147	−2.159
3200	42.779	283.073	250.026	105.750	424.044	118.597	−1.936
3300	43.135	284.395	251.048	110.046	423.788	109.056	−1.726
3400	43.470	285.688	252.048	114.376	423.552	99.522	−1.529
3500	43.783	286.952	253.027	118.739	423.333	89.995	−1.343
3600	44.073	288.190	253.986	123.132	423.130	80.474	−1.168
3700	44.341	289.401	254.927	127.553	422.941	70.958	−1.002
3800	44.586	290.587	255.850	131.999	422.764	61.448	−.845
3900	44.810	291.748	256.756	136.469	422.597	51.942	−.696
4000	45.013	292.885	257.645	140.961	422.437	42.440	−.554
4100	45.196	293.999	258.518	145.471	422.284	32.942	−.420
4200	45.359	295.090	259.376	149.999	422.134	23.447	−.292
4300	45.504	296.159	260.219	154.542	421.987	13.956	−.170
4400	45.631	297.207	261.048	159.099	421.841	4.469	−.053
4500	45.742	298.233	261.863	163.668	421.694	−5.015	.058
4600	45.838	299.240	262.664	168.247	421.544	−14.496	.165
4700	45.920	300.226	263.453	172.835	421.391	−23.973	.266
4800	45.988	301.194	264.229	177.431	421.233	−33.447	.364
4900	46.044	302.143	264.993	182.032	421.068	−42.918	.458
5000	46.090	303.073	265.746	186.639	420.896	−52.386	.547
5100	46.126	303.986	266.486	191.250	420.716	−61.849	.633
5200	46.153	304.882	267.216	195.864	420.527	−71.310	.716
5300	46.171	305.762	267.935	200.480	420.327	−80.766	.796
5400	46.183	306.625	268.644	205.098	420.117	−90.219	.873
5500	46.187	307.472	269.342	209.717	419.896	−99.667	.947
5600	46.186	308.305	270.030	214.335	419.662	−109.112	1.018
5700	46.175	309.122	270.709	218.953	419.415	−118.552	1.086
5800	46.166	309.925	271.378	223.571	419.155	−127.988	1.153
5900	46.145	310.714	272.038	228.186	418.881	−137.419	1.217
6000	46.129	311.489	272.689	232.800	418.593	−146.846	1.278

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 213.44 \pm 6.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1793.26 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 1802.76 \pm 12.6\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[6]
[1500]	[1]
[6000]	[2]
[8000]	[3]
[15000]	[2]

$\omega_e = [1580]\ cm^{-1}$ $\omega_e x_e = [12.5]\ cm^{-1}$ $\sigma = 1$

$B_e = [1.566]\ cm^{-1}$ $\alpha_e = [0.017]\ cm^{-1}$ $r_e = [1.29]$ Å

Enthalpy of Formation

Dibeler and Liston[1] have measured the photoionization thresholds for the processes:

$ClCN + h\nu \rightarrow Cl^+ + CN + e^-$ $\Delta_r H°(0\ K) = 399.44 \pm 0.5\ kcal·mol^{-1}$

$ClCN + h\nu \rightarrow Cl + CN^+ + e^-$ $\Delta_r H°(0\ K) = 426.65 \pm 0.5\ kcal·mol^{-1}$

By subtraction we obtain

$Cl + CN^+ \rightarrow Cl^+ + CN$ $\Delta_r H°(0\ K) = -27.21 \pm 0.7\ kcal·mol^{-1}$

Using JANAF vlaues for Cl, Cl^+ and CN we obtain $\Delta H°(CN^+, 0\ K) = 430.6 \pm 3.0\ kcal·mol^{-1}$ and IP(CN) = $327.42 \pm 0.7\ kcal·mol^{-1}$. Berkowitz *et al.*[2] have measured the photoionization thresholds for the processes:

$HCN + h\nu \rightarrow H^+ + CN + e^-$ $\Delta_r H°(0\ K) = 438.18 \pm 0.3\ kcal·mol^{-1}$

$HCN + h\nu \rightarrow H + CN^+$ $\Delta_r H°(0\ K) = 448.09 \pm 0.3\ kcal·mol^{-1}$

By subtraction we obtain

$H + CN^+ \rightarrow H^+ + CN$ $\Delta_r H°(0\ K) = -9.91 \pm 0.4\ kcal·mol^{-1}$

Using JANAF values for H, H^+ and CN we obtain $\Delta_f H°(CN^+, 0\ K) = 426.7 \pm 3.0\ kcal·mol^{-1}$, and IP(CN) = $323.51 \pm 0.4\ kcal·mol^{-1}$. We adopt a median value for $\Delta_f H°(CN^+, 0\ K) = 428.6 \pm 3.0\ kcal·mol^{-1}$ and $325.4 \pm 2\ kcal·mol^{-1}$ for IP(CN).

Heat Capacity and Entropy

The molecule has eight valence electrons and thus we expect that its molecular constants should fall between those for C_2 and BN. The ground electronic state is either $^1\Sigma$ or $^3\Pi$ and the two levels are likely to be very close. As a consequence the thermodynamic functions are dominated by the $^3\Pi$ contribution and so we choose this to be the ground state. The other levels are estimated based on the values of Fougere and Nesbet[3] for C_2 and of Verhaegen *et al.*[4] for BN. The vibrational constants and bond length are estimated between those for the $^3\Pi$ states of BN and C_2. The rotational constants B_e is obtained from the estimated bond length and α_e is calculated from the other constants assuming a Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.685	1793.264		
100	29.106	181.588	239.398	−5.781			
200	29.130	201.766	216.115	−2.870			
250	29.221	208.274	213.920	−1.411			
298.15	29.431	213.437	213.437	0.	1802.760	1763.145	−308.896
300	29.442	213.619	213.437	0.054	1802.810	1762.899	−306.948
350	29.809	218.183	213.797	1.535	1804.131	1756.142	−262.090
400	30.294	222.194	214.601	3.037	1805.390	1749.199	−228.422
450	30.852	225.794	215.648	4.566	1806.597	1742.102	−202.218
500	31.440	229.075	216.829	6.123	1807.758	1734.874	−181.241
600	32.585	234.910	219.368	9.325	1809.969	1720.087	−149.747
700	33.585	240.010	221.960	12.635	1812.063	1704.940	−127.224
800	34.412	244.551	224.505	16.036	1814.068	1689.498	−110.313
900	35.083	248.644	226.964	19.512	1815.999	1673.811	−97.145
1000	35.630	252.370	229.321	23.049	1817.871	1657.911	−86.600
1100	36.083	255.788	231.574	26.635	1819.694	1641.826	−77.964
1200	36.469	258.944	233.725	30.263	1821.475	1625.578	−70.760
1300	36.807	261.877	235.779	33.927	1823.221	1609.182	−64.658
1400	37.112	264.616	237.742	37.624	1824.940	1592.653	−59.423
1500	37.394	267.186	239.620	41.349	1826.635	1576.001	−54.881
1600	37.659	269.608	241.419	45.102	1828.312	1559.238	−50.904
1700	37.912	271.899	243.146	48.881	1829.975	1542.370	−47.391
1800	38.155	274.073	244.804	52.684	1831.626	1525.404	−44.266
1900	38.389	276.142	246.399	56.511	1833.267	1508.347	−41.467
2000	38.615	278.117	247.936	60.362	1834.903	1491.203	−38.946
2100	38.832	280.006	249.419	64.234	1836.532	1473.978	−36.663
2200	39.042	281.818	250.850	68.128	1838.158	1456.676	−34.586
2300	39.242	283.557	252.235	72.042	1839.781	1439.299	−32.688
2400	39.435	285.232	253.575	75.976	1841.401	1421.852	−30.946
2500	39.618	286.845	254.874	79.929	1843.019	1404.338	−29.342
2600	39.792	288.402	256.134	83.899	1844.635	1386.759	−27.860
2700	39.957	289.907	257.357	87.887	1846.249	1369.118	−26.487
2800	40.113	291.363	258.545	91.890	1847.861	1351.416	−25.211
2900	40.261	292.774	259.702	95.909	1849.471	1333.658	−24.022
3000	40.400	294.141	260.827	99.942	1851.078	1315.844	−22.911
3100	40.530	295.468	261.923	103.989	1852.683	1297.976	−21.871
3200	40.652	296.756	262.991	108.048	1854.284	1280.057	−20.895
3300	40.766	298.009	264.034	112.119	1855.882	1262.088	−19.977
3400	40.873	299.228	265.051	116.201	1857.476	1244.070	−19.113
3500	40.972	300.414	266.045	120.293	1859.065	1226.005	−18.297
3600	41.065	301.570	267.015	124.395	1860.650	1207.896	−17.526
3700	41.151	302.696	267.965	128.506	1862.230	1189.742	−16.796
3800	41.231	303.794	268.893	132.625	1863.804	1171.545	−16.104
3900	41.305	304.866	269.802	136.752	1865.372	1153.307	−15.447
4000	41.373	305.913	270.691	140.886	1866.933	1135.030	−14.822
4100	41.436	306.935	271.563	145.026	1868.488	1116.713	−14.227
4200	41.495	307.935	272.417	149.173	1870.036	1098.358	−13.660
4300	41.548	308.912	273.255	153.325	1871.576	1079.966	−13.119
4400	41.598	309.867	274.076	157.483	1873.109	1061.539	−12.602
4500	41.643	310.803	274.882	161.645	1874.634	1043.077	−12.108
4600	41.685	311.718	275.673	165.811	1876.150	1024.581	−11.634
4700	41.724	312.615	276.449	169.982	1877.658	1006.053	−11.181
4800	41.759	313.494	277.212	174.156	1879.157	987.492	−10.746
4900	41.791	314.355	277.961	178.333	1880.647	968.900	−10.329
5000	41.820	315.200	278.697	182.514	1882.128	950.278	−9.927
5100	41.846	316.028	279.421	186.697	1883.599	931.627	−9.542
5200	41.871	316.841	280.133	190.883	1885.060	912.946	−9.171
5300	41.893	317.639	280.833	195.071	1886.511	894.238	−8.813
5400	41.913	318.422	281.522	199.261	1887.952	875.502	−8.469
5500	41.931	319.192	282.200	203.454	1889.382	856.740	−8.137
5600	41.947	319.947	282.867	207.647	1890.803	837.952	−7.816
5700	41.962	320.690	283.524	211.843	1892.212	819.138	−7.507
5800	41.975	321.420	284.171	216.040	1893.610	800.300	−7.207
5900	41.987	322.137	284.809	220.238	1894.997	781.438	−6.918
6000	41.997	322.843	285.437	224.437	1896.373	762.553	−6.639

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 195.98 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 63.6 \pm 13\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 60.7 \pm 13\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^1\Sigma^+$]	0	[1]
	[67000]	[2]

$\omega_e = [2250]\ cm^{-1}$ $\omega_e x_e = [13.8]\ cm^{-1}$ $\sigma = 1$

$B_e = [2.116]\ cm^{-1}$ $\alpha_e = [0.0177]\ cm^{-1}$ $r_e = [1.11]$ Å

Enthalpy of Formation

Berkowitz *et al.*[1] reported 88 ± 0.5 kcal·mol^{-1} for the electron affinity of CN from the photoionization thresholds of the reactions HCN → $N^+ + CN^-$ and HCN → $H^+ + CN + e^-$.

Other values have been reported by Page,[2] who reinterpreted his earlier data,[3] to yield 73 ± 1 kcal·mol^{-1}; Bakulina and Ionov[4] in conjunction with the data of Branscomb and Smith[5] reported 78 ± 5 kcal·mol^{-1} and Inoue[6] who obtained 83 ± 7 kcal·mol^{-1}.

We adopt the value given by Berkowitz *et al.*[1] as being the most well defined in terms of both the precision of measurements and the reactions being studied. This leads to $\Delta_f H°(CN^-, g, 0\ K) = 15.2 \pm 3$ kcal·mol^{-1} or $\Delta_f H°(CN^-, g, 298.15\ K) = 14.5 \pm 3$ kcal·mol^{-1}.

Heat Capacity and Entropy

The electronic structure and molecular constants are estimated by analogy with the isoelectronic species CO and N_2. The uncertainties in the constants are generally small since N_2 and CO are quite similar, thus the entropy has an uncertainty of only 0.5 cal·K^{-1}·mol^{-1}.

References

[1] J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys. **50**, 1497 (1969).
[2] F. M. Page, J. Chem. Phys. **49**, 2466 (1968).
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[4] I. N. Bakulina and N. I. Ionov, Russ. J. Phys. Chem. **33**, 286 (1959).
[5] L. M. Branscomb and S. J. Smith, J. Chem. Phys. **25**, 598 (1956).
[6] M. Inoue, J. Chim. Phys. **63**, 1061 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.670	63.581		
100	29.105	164.176	221.860	−5.768			
200	29.109	184.351	198.640	−2.858			
250	29.114	190.847	196.456	−1.402			
298.15	29.133	195.976	195.976	0.	60.668	38.768	−6.792
300	29.135	196.156	195.977	0.054	60.641	38.632	−6.726
350	29.190	200.651	196.332	1.512	59.860	35.025	−5.227
400	29.297	204.555	197.121	2.974	59.001	31.535	−4.118
450	29.466	208.015	198.143	4.443	58.069	28.157	−3.268
500	29.695	211.131	199.288	5.921	57.073	24.886	−2.600
600	30.291	216.595	201.730	8.919	54.923	18.647	−1.623
700	30.986	221.316	204.198	11.983	52.613	12.782	−0.954
800	31.693	225.500	206.604	15.117	50.193	7.256	−0.474
900	32.362	229.272	208.917	18.320	47.695	2.038	−0.118
1000	32.969	232.714	211.127	21.587	45.140	−2.898	0.151
1100	33.506	235.882	213.235	24.912	42.544	−7.576	0.360
1200	33.976	238.818	215.246	28.286	39.914	−12.017	0.523
1300	34.385	241.554	217.166	31.705	37.258	−16.237	0.652
1400	34.741	244.116	219.000	35.161	34.580	−20.252	0.756
1500	35.050	246.523	220.756	38.651	31.882	−24.074	0.838
1600	35.321	248.794	222.438	42.170	29.168	−27.716	0.905
1700	35.557	250.943	224.052	45.714	26.439	−31.188	0.958
1800	35.766	252.981	225.603	49.281	23.695	−34.499	1.001
1900	35.950	254.920	227.095	52.867	20.939	−37.657	1.035
2000	36.114	256.768	228.533	56.470	18.170	−40.669	1.062
2100	36.260	258.534	229.920	60.089	15.389	−43.542	1.083
2200	36.391	260.224	231.259	63.722	12.596	−46.283	1.099
2300	36.510	261.844	232.554	67.367	9.793	−48.897	1.110
2400	36.617	263.400	233.807	71.023	6.978	−51.388	1.118
2500	36.714	264.897	235.021	74.690	4.153	−53.762	1.123
2600	36.804	266.339	236.198	78.366	1.317	−56.023	1.126
2700	36.885	267.729	237.340	82.050	−1.529	−58.174	1.125
2800	36.961	269.072	238.450	85.743	−4.386	−60.220	1.123
2900	37.030	270.370	239.528	89.442	−7.252	−62.164	1.120
3000	37.095	271.627	240.577	93.149	−10.129	−64.008	1.114
3100	37.155	272.844	241.599	96.861	−13.016	−65.757	1.108
3200	37.212	274.025	242.593	100.579	−15.912	−67.412	1.100
3300	37.265	275.170	243.563	104.303	−18.819	−68.976	1.092
3400	37.314	276.284	244.509	108.032	−21.735	−70.452	1.082
3500	37.361	277.366	245.433	111.766	−24.661	−71.843	1.072
3600	37.406	278.419	246.335	115.504	−27.597	−73.149	1.061
3700	37.448	279.445	247.216	119.247	−30.543	−74.374	1.050
3800	37.488	280.444	248.077	122.994	−33.499	−75.519	1.038
3900	37.526	281.418	248.919	126.745	−36.464	−76.586	1.026
4000	37.563	282.369	249.744	130.499	−39.439	−77.577	1.013
4100	37.598	283.297	250.551	134.257	−42.424	−78.493	1.000
4200	37.632	284.203	251.341	138.019	−45.418	−79.337	0.987
4300	37.664	285.089	252.116	141.784	−48.422	−80.109	0.973
4400	37.696	285.955	252.875	145.552	−51.436	−80.811	0.959
4500	37.726	286.803	253.620	149.323	−54.460	−81.445	0.945
4600	37.755	287.632	254.350	153.097	−57.493	−82.011	0.931
4700	37.783	288.444	255.067	156.874	−60.536	−82.511	0.917
4800	37.811	289.240	255.771	160.653	−63.588	−82.947	0.903
4900	37.838	290.020	256.462	164.436	−66.650	−83.318	0.888
5000	37.864	290.785	257.141	168.221	−69.723	−83.627	0.874
5100	37.889	291.535	257.808	172.009	−72.805	−83.875	0.859
5200	37.914	292.271	258.463	175.799	−75.897	−84.062	0.844
5300	37.939	292.993	259.108	179.591	−78.998	−84.189	0.830
5400	37.962	293.703	259.742	183.386	−82.110	−84.258	0.815
5500	37.986	294.399	260.366	187.184	−85.231	−84.269	0.800
5600	38.009	295.084	260.980	190.984	−88.362	−84.223	0.786
5700	38.031	295.757	261.584	194.786	−91.504	−84.121	0.771
5800	38.053	296.419	262.179	198.590	−94.655	−83.964	0.756
5900	38.075	297.069	262.765	202.396	−97.817	−83.753	0.741
6000	38.096	297.709	263.342	206.205	−100.989	−83.488	0.727

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [118.47 \pm 2.1]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 835\ K$

$\Delta_f H°(0\ K) = -98.3 \pm 1.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -90.7 \pm 1.3\ kJ·mol^{-1}$
$\Delta_{fus} H° = [8.786]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy change for the reaction NaCN(cr) → NaCN(aq, ∞) was reported to be 0.29 ± 0.20 kcal·mol^{-1} by Parker.[1] Incorporating this data with the heats of formation for Na^+(aq, ∞), −57.39, and CN^-(aq, ∞), 36.0 kcal·mol^{-1}, reported by Wagman *et al.*,[2] the value of $\Delta_f H°$(298.15 K) for NaCN(cr) was derived and adopted.

Lord and Woolf[3] determined the value, $\Delta_f H°$(NaCN, cr, 298.15 K) = −21.4 kcal·mol^{-1}, by solution calorimetry. This value is in agreement with the adopted one.

Heat Capacity and Entropy

The low temperature heat capacities, 101.6–345.8 K, were reported by Messer and Ziegler.[4] The $C_p°$ values above 345.8 K were estimated by graphical extrapolation. $S°$(298.15 K) was derived from low temperature heat capacities, based on $S°$(100 K) = 8.4 cal·deg^{-1}·mol^{-1} which was estimated by comparison with the $S°$(298.15 K) values for NaCl, KCl, and KCN crystals.

Transition Data

The transition temperatures, T_{trs} and T_{trs}, were determined by Messer and Ziegler.[4] The corresponding enthalpies of transition were reported to be 0.15 and 0.70 kcal·mol^{-1}, respectively. However, these quantities were incorporated with $C_p°$ values used to evaluate $H°(0\ K) - H°(298.15\ K)$. Therefore $\Delta_{trs} H°$ values are not listed.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The difference between $\Delta_f H°$(298.15 K) for $(NaCN)_2$(g) and 2 NaCN(cr) is $\Delta_{sub} H°$(cr → dimer, 298.15 K); for NaCN(g) and NaCN(cr) is $\Delta_{sub} H°$(cr→ monomer, 298.15 K).

References

[1]V. B. Parker, NSRDS–NBS 2, (1965).
[2]U. S. Nat. Bur. Stand. Tech. Note 270–1, (1965).
[3]G. Lord and A. A. Woolf, J. Chem. Soc. 2546 (1954).
[4]C. E. Messer and W. T. Ziegler, J. Amer. Chem. Soc. **63**, 2703 (1941).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.422	−98.299	−98.299	INFINITE
100	47.363	35.146	200.082	−16.494	−98.220	−91.268	47.673
172.100	93.722	69.586	138.127	−11.796	I <--> II		
172.100	93.724	69.588	138.127	−11.796	TRANSITION		
200	67.877	80.075	129.338	−9.853	−95.817	−85.077	22.220
288.500	1548.088	111.062	118.520	−2.152	II <--> III		
288.500	1548.129	111.063	118.520	−2.151	TRANSITION		
298.15	68.681	118.467	118.467	0.	−90.709	−80.413	14.088
300	68.575	118.892	118.469	0.127	−90.677	−80.349	13.990
400	68.659	138.659	121.165	6.998	−91.909	−76.931	10.046
500	68.752	153.990	126.254	13.868	−90.937	−73.303	7.658
600	68.848	166.534	131.953	20.748	−90.143	−69.854	6.081
700	68.945	177.154	137.671	27.638	−89.499	−66.526	4.964
800	69.046	186.367	143.195	34.537	−88.985	−63.280	4.132
835.000	69.082	189.324	145.067	36.955	----- III <--> LIQUID -----		
900	69.145	194.505	148.453	41.447	−88.585	−60.092	3.488
1000	69.245	201.795	153.429	48.367	−88.296	−56.943	2.974
1100	69.354	208.400	158.131	55.297	−88.117	−53.817	2.556
1200	69.462	214.439	162.575	62.237	−184.812	−48.263	2.101
1300	69.570	220.004	166.781	69.189	−183.935	−36.920	1.483
1400	69.676	225.163	170.769	76.151	−183.108	−25.642	0.957
1500	69.781	229.974	174.558	83.124	−182.322	−14.422	0.502
1600	69.885	234.481	178.164	90.107	−181.572	−3.254	0.106
1700	69.988	238.721	181.602	97.101	−180.852	7.869	−0.242
1800	70.090	242.724	184.888	104.105	−180.158	18.950	−0.550
1900	70.191	246.516	188.032	111.119	−179.488	29.993	−0.825
2000	70.291	250.119	191.047	118.143	−178.837	41.002	−1.071

PREVIOUS: December 1960 CURRENT: March 1966

$S°(298.15\ K) = [125.507]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 835\ K$

$\Delta_f H°(298.15\ K) = [-84.398]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [8.7]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) was obtained from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(835\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for NaCN(cr), KCN(cr) and KCN(l). A glass transition temperature is assumed at 600 K. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature was reported by Truthe.[1] $\Delta_{fus} H°$ is estimated such that the derived third law value for $\Delta_{vap} H°$(NaCN, l) agrees with the 2nd law value. Refer to the ideal gas table for details.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the reaction NaCN(l) = NaCN(g) becomes zero. The difference between $\Delta_f H°$ for NaCN(g) and NACN(l) at T_{vap} is $\Delta_{vap} H°$.

Reference

[1]W. Truthe, Z. Anorg. Chem. **76**, 129 (1912).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	68.680	125.507	125.507	0.	−84.398	−76.201	13.350
300	68.575	125.931	125.508	0.127	−84.366	−76.150	13.259
400	68.659	145.699	128.205	6.998	−85.598	−73.436	9.590
500	68.749	161.029	133.293	13.868	−84.626	−70.512	7.366
600	68.848	173.572	138.993	20.748	−83.832	−67.767	5.900
600.000	68.848	173.573	138.993	20.748	GLASS <--> LIQUID TRANSITION		
600.000	79.496	173.573	138.993	20.748			
700	79.496	185.827	144.830	28.698	−82.128	−65.226	4.867
800	79.496	196.443	150.633	36.647	−80.563	−62.920	4.108
835.000	79.496	199.847	152.625	39.430	----- III <--> LIQUID -----		
900	79.496	205.806	156.254	44.597	−79.124	−60.802	3.529
1000	79.496	214.182	161.635	52.547	−77.805	−58.838	3.073
1100	79.496	221.758	166.762	60.496	−76.606	−57.000	2.707
1200	79.496	228.675	171.637	68.446	−172.292	−52.827	2.299
1300	79.496	235.039	176.273	76.395	−170.417	−42.948	1.726
1400	79.496	240.930	180.683	84.345	−168.603	−33.211	1.239
1500	79.496	246.414	184.885	92.295	−166.841	−23.601	0.822
1600	79.496	251.545	188.892	100.244	−165.124	−14.108	0.461
1700	79.496	256.364	192.721	108.194	−163.448	−4.722	0.145
1800	79.496	260.908	196.384	116.143	−161.809	4.568	−0.133
1900	79.496	265.206	199.894	124.093	−160.203	13.767	−0.378
2000	79.496	269.284	203.263	132.043	−158.627	22.883	−0.598
2100	79.496	273.163	206.500	139.992	−157.079	31.920	−0.794
2200	79.496	276.861	209.615	147.942	−155.559	40.884	−0.971
2300	79.496	280.395	212.616	155.891	−154.064	49.780	−1.131
2400	79.496	283.778	215.511	163.841	−152.593	58.611	−1.276
2500	79.496	287.023	218.307	171.791	−151.148	67.381	−1.408
2600	79.496	290.141	221.010	179.740	−149.726	76.094	−1.529
2700	79.496	293.141	223.626	187.690	−148.329	84.753	−1.640
2800	79.496	296.032	226.161	195.639	−146.956	93.360	−1.742
2900	79.496	298.822	228.619	203.589	−145.608	101.919	−1.836
3000	79.496	301.517	231.004	211.539	−144.287	110.432	−1.923

PREVIOUS: December 1960 CURRENT: March 1966

0	to	835 K	crystal
above		835 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.422	−98.299	−98.299	INFINITE
100	47.363	35.146	200.082	−16.494	−98.220	−91.268	47.673
172.100	93.722	69.586	138.127	−11.796	I <--> II		
172.100	93.724	69.588	138.127	−11.796	TRANSITION		
200	67.877	80.075	129.338	−9.853	−95.817	−85.077	22.220
288.500	1548.088	111.062	118.520	−2.152	II <--> III		
288.500	1548.129	111.063	118.520	−2.151	TRANSITION		
298.15	68.681	118.467	118.467	0.	−90.709	−80.413	14.088
300	68.575	118.892	118.469	0.127	−90.677	−80.349	13.990
400	68.659	138.659	121.165	6.998	−91.909	−76.931	10.046
500	68.752	153.990	126.254	13.868	−90.937	−73.303	7.658
600	68.848	166.534	131.953	20.748	−90.143	−69.854	6.081
700	68.945	177.154	137.671	27.638	−89.499	−66.526	4.964
800	69.046	186.367	143.195	34.537	−88.985	−63.280	4.132
835.000	69.082	189.324	145.067	36.955	III <--> LIQUID		
835.000	79.496	199.847	145.067	45.741	TRANSITION		
900	79.496	205.806	149.241	50.908	−79.124	−60.802	3.529
1000	79.496	214.182	155.324	58.858	−77.805	−58.838	3.073
1100	79.496	221.758	161.024	66.807	−76.606	−57.000	2.707
1200	79.496	228.675	166.378	74.757	−172.292	−52.826	2.299
1300	79.496	235.039	171.418	82.707	−170.417	−42.947	1.726
1400	79.496	240.930	176.175	90.656	−168.603	−33.210	1.239
1500	79.496	246.414	180.677	98.606	−166.840	−23.601	0.822
1600	79.496	251.545	184.948	106.555	−165.124	−14.108	0.461
1700	79.496	256.364	189.009	114.505	−163.448	−4.721	0.145
1800	79.496	260.908	192.878	122.455	−161.809	4.568	−0.133
1900	79.496	265.206	196.573	130.404	−160.202	13.767	−0.378
2000	79.496	269.284	200.107	138.354	−158.627	22.883	−0.598
2100	79.496	273.163	203.494	146.303	−157.079	31.920	−0.794
2200	79.496	276.861	206.746	154.253	−155.559	40.884	−0.971
2300	79.496	280.395	209.872	162.203	−154.064	49.780	−1.131
2400	79.496	283.778	212.881	170.152	−152.593	58.611	−1.276
2500	79.496	287.023	215.782	178.102	−151.147	67.381	−1.408
2600	79.496	290.141	218.583	186.051	−149.726	76.094	−1.529
2700	79.496	293.141	221.289	194.001	−148.328	84.753	−1.640
2800	79.496	296.032	223.907	201.951	−146.956	93.361	−1.742
2900	79.496	298.822	226.442	209.900	−145.608	101.919	−1.836
3000	79.496	301.517	228.900	217.850	−144.287	110.432	−1.923

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = [243.37]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 93.97 \pm 2.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 94.27 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[400] (1)
239 (2)
2176 (1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: Na–C = [1.992] Å; C–N = [1.16] Å
Bond Angle: Na–C–N = [180]°
Rotational Constant: B_o = [0.182724] cm^{-1}

Enthalpy of Formation

The vapor pressures of NaCN(l) at temperatures 805–1353 K were measured by Ingold.[1] According to the investigation reported by Porter,[2] the vapor consists of NaCN and $(NaCN)_2$. Based on his data the dimer/monomer ratios at temperatures 805–1353°C(1078.2–1626.2 K) were calculated to be 0.29–0.09. Hence the respective partial pressures for NaCN(g) and $(NaCN)_2$(g) were derived. By the 2nd and 3rd law methods, the values of $\Delta_{vap}H°$(l → monomer, 298.15 K) were evaluated to be 43.43 and 42.69 $kcal·mol^{-1}$, respectively. The enthalpy of formation for NaCN(g) is calculated from $\Delta_f H°$(NaCN, cr, 298.15 K) and the 3rd law value for $\Delta_{vap}H°$.

Heat Capacity and Entropy

The molecular structure of NaCN(g) has not been determined. It was assumed to be linear by comparison with that for HCN(g). The C–N bond distance was assumed to be the same as that in KCN(g) and the Na–C bond distance was taken from Leroi,[3] which was calculated. The vibrational frequencies, ν_2 and ν_3, were measured by Leroi and Klemperer[4] from infrared absorption spectra. The value of ν_1 was calculated by valence force method described by Herzberg,[5] using appropriate force constants.

References

[1]C. K. Ingold, J. Chem. Soc. **123**, 885 (1923).
[2]R. F. Porter, J. Chem. Phys. **35**, 318 (1961).
[3]G. E. Leroi, Ph. D. Dissertation, Harvard University, 1960.
[4]G. E. Leroi and W. Klemperer, J. Chem. Phys. **35**, 774 (1961).
[5]G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand, Inc., New York, (1945).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.125	93.973	93.973	INFINITE
100	36.717	195.016	285.125	−9.011	94.237	85.203	−44.505
200	46.524	224.002	247.863	−4.772	94.238	76.192	−19.899
250	48.786	234.647	244.186	−2.385	94.278	71.676	−14.976
298.15	50.178	243.367	243.367	0.	94.266	67.323	−11.795
300	50.222	243.678	243.368	0.093	94.263	67.155	−11.693
350	51.210	251.498	243.983	2.630	94.148	62.645	−9.349
400	51.962	258.387	245.362	5.210	91.278	58.365	−7.622
450	52.595	264.544	247.157	7.824	90.968	54.269	−6.299
500	53.168	270.116	249.179	10.469	90.638	50.209	−5.245
600	54.227	279.904	253.506	15.839	89.923	42.189	−3.673
700	55.203	288.338	257.893	21.311	89.149	34.294	−2.559
800	56.088	295.768	262.172	26.877	88.329	26.513	−1.731
900	56.870	302.420	266.281	32.525	87.468	18.837	−1.093
1000	57.548	308.448	270.201	38.247	86.559	11.259	−0.588
1100	58.130	313.961	273.932	44.032	85.593	3.776	−0.179
1200	58.627	319.041	277.483	49.870	−12.205	−1.177	0.051
1300	59.051	323.751	280.863	55.755	−12.395	−0.251	0.010
1400	59.414	328.141	284.085	61.678	−12.606	0.691	−0.026
1500	59.725	332.251	287.160	67.636	−12.836	1.649	−0.057
1600	59.992	336.114	290.100	73.622	−13.083	2.622	−0.086
1700	60.223	339.758	292.915	79.633	−13.346	3.612	−0.111
1800	60.424	343.206	295.614	85.666	−13.623	4.617	−0.134
1900	60.598	346.478	298.206	91.717	−13.915	5.639	−0.155
2000	60.752	349.590	300.698	97.784	−14.221	6.676	−0.174
2100	60.886	352.558	303.097	103.867	−14.542	7.728	−0.192
2200	61.005	355.393	305.410	109.961	−14.876	8.797	−0.209
2300	61.111	358.107	307.643	116.067	−15.224	9.880	−0.224
2400	61.205	360.710	309.800	122.183	−15.588	10.980	−0.239
2500	61.289	363.210	311.887	128.308	−15.967	12.094	−0.253
2600	61.364	365.615	313.907	134.440	−16.362	13.225	−0.266
2700	61.432	367.933	315.866	140.580	−16.774	14.370	−0.278
2800	61.493	370.168	317.765	146.727	−17.205	15.532	−0.290
2900	61.549	372.327	319.610	152.879	−17.655	16.709	−0.301
3000	61.599	374.414	321.402	159.036	−18.126	17.902	−0.312
3100	61.645	376.435	323.145	165.199	−18.619	19.110	−0.322
3200	61.687	378.393	324.841	171.365	−19.135	20.336	−0.332
3300	61.725	380.291	326.493	177.536	−19.676	21.577	−0.342
3400	61.761	382.135	328.102	183.710	−20.245	22.836	−0.351
3500	61.793	383.925	329.672	189.888	−20.842	24.112	−0.360
3600	61.823	385.667	331.203	196.069	−21.470	25.405	−0.369
3700	61.851	387.361	332.698	202.252	−22.131	26.716	−0.377
3800	61.876	389.011	334.158	208.439	−22.827	28.045	−0.386
3900	61.900	390.618	335.585	214.628	−23.559	29.394	−0.394
4000	61.922	392.186	336.981	220.819	−24.332	30.761	−0.402
4100	61.942	393.715	338.346	227.012	−25.147	32.149	−0.410
4200	61.961	395.208	339.682	233.207	−26.004	33.556	−0.417
4300	61.979	396.666	340.991	239.404	−26.910	34.985	−0.425
4400	61.996	398.091	342.272	245.603	−27.824	36.432	−0.432
4500	62.011	399.484	343.528	251.803	−28.811	37.902	−0.440
4600	62.026	400.848	344.759	258.005	−29.858	39.396	−0.447
4700	62.040	402.182	345.967	264.208	−30.961	40.914	−0.455
4800	62.052	403.488	347.152	270.413	−32.121	42.455	−0.462
4900	62.065	404.767	348.315	276.619	−33.343	44.021	−0.469
5000	62.076	406.021	349.456	282.826	−34.620	45.612	−0.477
5100	62.087	407.251	350.578	289.034	−35.970	47.230	−0.484
5200	62.097	408.457	351.679	295.243	−37.388	48.875	−0.491
5300	62.106	409.639	352.762	301.453	−38.878	50.548	−0.498
5400	62.116	410.800	353.826	307.664	−40.441	52.250	−0.505
5500	62.124	411.940	354.872	313.876	−42.081	53.982	−0.513
5600	62.132	413.060	355.901	320.089	−43.800	55.744	−0.520
5700	62.140	414.160	356.913	326.303	−45.601	57.537	−0.527
5800	62.147	415.240	357.910	332.517	−47.485	59.363	−0.535
5900	62.154	416.303	358.891	338.732	−49.455	61.222	−0.542
6000	62.161	417.347	359.856	344.948	−51.355	63.097	−0.549

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 232.2 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 159.0 \pm 10.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 159.4 \pm 10.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	95.6	2
$A^2\Sigma^+$	22802	2
$B^2\Pi$	31811	4

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1922 (1)
536 (2)
1275 (1)

Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distances: N–C = [1.23] Å; C–O = [1.18] Å
Bond Angle: N–C–O = 108°
Rotational Constant: $B_0 = 0.388394\ cm^{-1}$

Enthalpy of Formation

Okabe[1] has measured the onset of photodissociation for the process HNCO(g) → H(g) + NCO($A^2\Sigma$) as 7.73 ± 0.01 eV (178.25 ± 0.25 kcal·mol^{-1}). This result in combination with JANAF auxiliary data[2] results in $\Delta_f H°$(NCO, g, 0 K) = 38 ± 2.5 kcal·mol^{-1}.

Dixon[3] has discussed the diffusencess in the $^2\Pi$–$^2\Pi$ bands of NCO above 33700 cm^{-1} and concludes this is due to either predissociation or unresolved groups of lines due to a perturbing state. Assuming the dissociation is to N(^{2}D) + CO($^1\Sigma$) yields $D_0°$(N–CO) ≤ 41 kcal·mol^{-1}, or $\Delta_f H°$(NCO, 0 K) ≥ 44 kcal·mol^{-1}; assuming the products CN($^2\Sigma$) + O(^{3}P) then $D_0°$(NC–O) ≤ 97 kcal·mol^{-1}, or $\Delta_f H°$(NCO, 0 K) ≥ 65 kcal·mol^{-1}. Milligan and Jacox[4] confirm the diffuseness and observe increased amounts of CO. Thus, they prefer the first dissociation mechanism which favors $\Delta_f H°$(NCO, 0 K) ≥ 44 kcal·mol^{-1}. An upper limit to the enthalpy formation can be obtained from HNCO(g)[2] by assuming a maximum $D_0°$(H–NCO) ≤ 122 kcal·mol^{-1}, equal to $D_0°$(H–CN), which yields $\Delta_f H°$(NCO, 0 K) ≤ 45 kcal·mol^{-1}. Another estimate may be obtained by making the reasonable assumption that the sum of the atomization energies of NCN + NNO equal those of NNN + NCO, where the central atoms are simply interchanged. Using respective atomization values[2] of 282, 264 and 242 kcal·mol^{-1} yields 304 kcal·mol^{-1} for NCO, or $\Delta_f H°$(NCO, 0 K) = 38 kcal·mol^{-1}. It appears that the diffuseness in the spectrum is not due to predissociation, since all the estimates and measurements fall below the vlaues calculated on that basis. We adopt $\Delta_f H°$(NCO, g, 0 K) = 38 ± 2.5 kcal·mol^{-1}.

Heat Capacity and Entropy

The electronic levels, structure, and ν_2 are from Dixon.[3] The ν_1 and ν_3 vibrational frequencies are from the matrix isolation data of Milligan and Jacox.[4] The individual bond lengths are those selected by Milligan and Jacox[4] to fit the overall length determined by Dixon.[3]

References

[1]H. Okabe, J. Chem. Phys. **53**, 3507 (1970).
[2]JANAF Thermochemical Tables: HNCO(g), 12–31–70; HCN(g), 12–31–69; NCN(g), 12–31–70; NNO(g), 12–31–64; NNN(g), 12–31–70; CN(g), 6–30–69; H(g), 9–30–65.
[3]R. N. Dixon, Phil. Trans. Roy. Soc. (London) **252A**, 165 (1960) and Can. J. Phys. **38**, 10 (1960).
[4]D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 5157 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.196	158.943	158.943	INFINITE
100	32.077	194.218	264.724	−7.051	159.125	156.454	−81.723
200	35.509	217.193	235.771	−3.716	159.222	153.747	−40.155
250	37.940	225.381	232.896	−1.879	159.307	152.369	−31.836
298.15	40.053	232.248	232.248	0.	159.410	151.024	−26.459
300	40.130	232.496	232.249	0.074	159.415	150.972	−26.286
350	42.089	238.832	232.744	2.131	159.533	149.555	−22.320
400	43.865	244.570	233.869	4.280	159.654	148.121	−19.343
450	45.485	249.831	235.355	6.514	159.768	146.673	−17.025
500	46.967	254.701	237.049	8.826	159.874	145.212	−15.170
600	49.543	263.500	240.740	13.656	160.054	142.262	−12.385
700	51.652	271.301	244.559	18.719	160.196	139.285	−10.394
800	53.361	278.314	248.347	23.973	160.305	136.290	−8.899
900	54.740	284.681	252.036	29.381	160.387	133.283	−7.736
1000	55.855	290.508	255.596	34.912	160.445	130.268	−6.805
1100	56.761	295.876	259.017	40.545	160.480	127.249	−6.043
1200	57.503	300.848	262.298	46.259	160.495	124.227	−5.407
1300	58.114	305.475	265.444	52.041	160.489	121.205	−4.870
1400	58.622	309.801	268.459	57.878	160.463	118.184	−4.409
1500	59.048	313.861	271.352	63.763	160.418	115.165	−4.010
1600	59.408	317.683	274.130	69.686	160.353	112.150	−3.661
1700	59.713	321.294	276.799	75.642	160.269	109.140	−3.353
1800	59.975	324.715	279.367	81.627	160.165	106.135	−3.080
1900	60.201	327.964	281.840	87.636	160.040	103.137	−2.835
2000	60.397	331.057	284.224	93.666	159.895	100.146	−2.616
2100	60.568	334.008	286.525	99.715	159.730	97.162	−2.417
2200	60.718	336.829	288.748	105.779	159.544	94.187	−2.236
2300	60.851	339.531	290.897	111.858	159.337	91.221	−2.072
2400	60.968	342.123	292.978	117.949	159.109	88.264	−1.921
2500	61.073	344.614	294.994	124.051	158.860	85.317	−1.783
2600	61.167	347.012	296.949	130.163	158.591	82.381	−1.655
2700	61.251	349.322	298.846	136.284	158.301	79.455	−1.537
2800	61.328	351.551	300.689	142.413	157.992	76.541	−1.428
2900	61.398	353.704	302.480	148.550	157.661	73.637	−1.326
3000	61.462	355.787	304.222	154.693	157.312	70.746	−1.232
3100	61.521	357.803	305.918	160.842	156.942	67.866	−1.144
3200	61.576	359.757	307.570	166.997	156.554	64.999	−1.061
3300	61.627	361.652	309.181	173.157	156.147	62.144	−0.984
3400	61.676	363.493	310.751	179.322	155.721	59.302	−0.911
3500	61.722	365.281	312.284	185.492	155.278	56.472	−0.843
3600	61.766	367.021	313.780	191.666	154.817	53.656	−0.779
3700	61.808	368.714	315.242	197.845	154.338	50.852	−0.718
3800	61.850	370.363	316.671	204.028	153.843	48.062	−0.661
3900	61.891	371.970	318.068	210.215	153.332	45.285	−0.607
4000	61.931	373.537	319.436	216.406	152.804	42.521	−0.555
4100	61.971	375.067	320.774	222.601	152.261	39.771	−0.507
4200	62.011	376.561	322.084	228.800	151.702	37.034	−0.461
4300	62.052	378.020	323.368	235.003	151.128	34.311	−0.417
4400	62.092	379.447	324.627	241.211	150.539	31.601	−0.375
4500	62.134	380.843	325.861	247.422	149.936	28.904	−0.336
4600	62.176	382.209	327.071	253.637	149.317	26.221	−0.298
4700	62.219	383.547	328.258	259.857	148.685	23.552	−0.262
4800	62.263	384.857	329.424	266.081	148.038	20.896	−0.227
4900	62.308	386.142	330.568	272.310	147.376	18.255	−0.195
5000	62.355	387.401	331.692	278.543	146.700	15.626	−0.163
5100	62.402	388.636	332.797	284.781	146.010	13.012	−0.133
5200	62.451	389.848	333.882	291.023	145.305	10.411	−0.105
5300	62.501	391.038	334.950	297.271	144.585	7.824	−0.077
5400	62.552	392.207	335.999	303.524	143.851	5.250	−0.051
5500	62.605	393.355	337.031	309.782	143.101	2.690	−0.026
5600	62.659	394.484	338.047	316.045	142.337	0.144	−0.001
5700	62.714	395.593	339.047	322.313	141.556	−2.388	0.022
5800	62.771	396.685	340.032	328.588	140.759	−4.906	0.044
5900	62.829	397.758	341.001	334.868	139.946	−7.412	0.066
6000	62.888	398.815	341.956	341.154	139.116	−9.902	0.086

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 231.716\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 584 \pm 126\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 585 \pm 126\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1241 (1)
393 (2)
2847 (1)

Ground State Quantum Weight: [3]
Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distances: C–N = [1.15] Å; N-N = [1.25] Å
Bond Angle: C–N–N = 180°
Rotational Constant: B_0 = [0.450392] cm^{-1}

Enthalpy of Formation

The enthalpy of formation is calculated from the estimated enthalpy of reaction $\Delta_r H°(0\ K) = 255 \pm 30\ kcal·mol^{-1}$ for CNN(g) → C(g) + 2 N(g). Since CNN radical can dissociate to give C + N_2 or CN + N, the molecule must have more energy than either CN or N_2. It is assumed *that the extra bond will be quite weak, for this we estimate* 30 ± 30 kcal·mol^{-1} *which gives* $\Delta_f H°(0\ K) = 255 \pm 30\ kcal·mol^{-1}$ (583.856 ± 126 $kJ·mol^{-1}$) for the first path and $\Delta_f H° = 204 \pm 30\ kcal·mol^{-1}$ for the second. We adopt the former value.

Heat Capacity and Entropy

Milligan and Jacox[1] have measured three fundamental vibrational frequencies for CNN radical (g) in the infrared and ultraviolet spectra by matrix-isolation, and proposed a linear molecular configuration with a $^3\Sigma$ ground state which has been confirmed by Wasserman *et al.*[2] in the electron paramagnetic resonance observations. Also Milligan and Jacox[1] suggested a C ≡ N = N bond structure, based on the agreement between the C–N and N–N stretching force constants (calculated from observed vibrational frequencies in the CNN radical) and the typical C ≡ N and N = N stretching force constants. In addition, they estimated the bond distances r(C–N) = 1.15 Å and r(N–N) = 1.25 Å from the proposed structure.

References

[1]D. E. Milligan, M. E. Jacox, J. Chem. Phys. **44**, 3149 (1966).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.372	583.854	583.854	INFINITE
100	30.975	191.895	266.206	−7.431	583.833	580.720	−303.337
200	38.075	215.660	235.463	−3.961	584.066	577.548	−150.840
250	40.478	224.427	232.403	−1.994	584.282	575.894	−120.326
298.15	42.281	231.716	231.716	0.	584.505	574.258	−100.608
300	42.343	231.978	231.717	0.078	584.513	574.195	−99.976
350	43.883	238.624	232.238	2.235	584.742	572.457	−85.435
400	45.200	244.572	233.415	4.463	584.958	570.687	−74.524
450	46.353	249.964	234.959	6.752	585.154	568.891	−66.035
500	47.377	254.902	236.709	9.096	585.325	567.075	−59.242
600	49.142	263.700	240.493	13.925	585.592	563.398	−49.048
700	50.642	271.391	244.369	18.916	585.768	559.684	−41.764
800	51.950	278.241	248.182	24.047	585.868	555.950	−36.300
900	53.100	284.427	251.871	29.300	585.911	552.207	−32.049
1000	54.111	290.075	255.413	34.662	585.909	548.462	−28.649
1100	54.997	295.275	258.804	40.118	585.874	544.718	−25.867
1200	55.772	300.095	262.046	45.658	585.814	540.979	−23.548
1300	56.449	304.586	265.148	51.270	585.733	537.246	−21.587
1400	57.040	308.791	268.117	56.945	585.634	533.520	−19.906
1500	57.556	312.745	270.961	62.675	585.522	529.802	−18.449
1600	58.007	316.474	273.691	68.454	585.397	526.091	−17.175
1700	58.404	320.003	276.312	74.275	585.260	522.388	−16.051
1800	58.752	323.351	278.833	80.133	585.113	518.694	−15.052
1900	59.060	326.536	281.261	86.024	584.954	515.009	−14.159
2000	59.332	329.573	283.601	91.944	584.786	511.332	−13.355
2100	59.573	332.473	285.860	97.889	584.608	507.663	−12.627
2200	59.788	335.250	288.042	103.857	584.420	504.004	−11.967
2300	59.981	337.912	290.153	109.846	584.222	500.353	−11.363
2400	60.153	340.468	292.196	115.853	584.014	496.711	−10.811
2500	60.308	342.927	294.177	121.876	583.795	493.078	−10.302
2600	60.448	345.295	296.097	127.914	583.567	489.453	−9.833
2700	60.574	347.579	297.962	133.965	583.328	485.838	−9.399
2800	60.689	349.784	299.774	140.028	583.079	482.232	−8.996
2900	60.793	351.915	301.535	146.102	582.819	478.635	−8.621
3000	60.888	353.978	303.249	152.187	582.550	475.047	−8.271
3100	60.975	355.976	304.918	158.280	582.269	471.468	−7.944
3200	61.054	357.913	306.544	164.381	581.978	467.898	−7.638
3300	61.127	359.793	308.129	170.490	581.676	464.338	−7.350
3400	61.195	361.619	309.676	176.607	581.363	460.787	−7.079
3500	61.257	363.394	311.185	182.729	581.039	457.245	−6.824
3600	61.314	365.120	312.660	188.858	580.704	453.713	−6.583
3700	61.367	366.801	314.100	194.992	580.359	450.190	−6.356
3800	61.416	368.438	315.509	201.131	580.002	446.677	−6.140
3900	61.461	370.034	316.886	207.275	579.634	443.173	−5.936
4000	61.504	371.590	318.235	213.423	579.255	439.679	−5.742
4100	61.543	373.110	319.555	219.576	578.865	436.194	−5.557
4200	61.580	374.593	320.847	225.732	578.463	432.719	−5.382
4300	61.614	376.043	322.114	231.891	578.050	429.254	−5.214
4400	61.647	377.459	323.356	238.055	577.626	425.799	−5.055
4500	61.677	378.845	324.574	244.221	577.190	422.353	−4.903
4600	61.705	380.201	325.768	250.390	576.743	418.917	−4.757
4700	61.732	381.528	326.941	256.562	576.284	415.491	−4.618
4800	61.757	382.828	328.092	262.736	575.813	412.075	−4.484
4900	61.780	384.102	329.222	268.913	575.331	408.668	−4.356
5000	61.803	385.350	330.332	275.092	574.837	405.272	−4.234
5100	61.824	386.574	331.423	281.274	574.331	401.886	−4.116
5200	61.844	387.775	332.495	287.457	573.812	398.510	−4.003
5300	61.862	388.953	333.549	293.642	573.282	395.143	−3.894
5400	61.880	390.110	334.586	299.829	572.740	391.787	−3.790
5500	61.897	391.245	335.606	306.018	572.186	388.442	−3.689
5600	61.913	392.361	336.609	312.209	571.619	385.106	−3.592
5700	61.928	393.457	337.597	318.401	571.039	381.780	−3.499
5800	61.942	394.534	338.569	324.594	570.447	378.465	−3.408
5900	61.956	395.593	339.527	330.789	569.842	375.160	−3.321
6000	61.969	396.634	340.470	336.985	569.223	371.866	−3.237

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 226.21 \pm 0.42\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 472 \pm 21\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 473 \pm 21\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^3\Sigma_g^-$	0	3
$A^3\Pi_u$	30384	6
$a^1\ \Delta$	[38000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1197 (1)
423 (2)
1475 (1)

Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distance: C–N = 1.232 Å
Bond Angle: N–C–N = 180°
Rotational Constant: $B_O = 0.396469\ cm^{-1}$

Enthalpy of Formation

Okabe and Mele[1] have measured the photodissociation onset of the process

$$CNN_3(g) \rightarrow NCN(g) + N_2(A^3\Sigma) \qquad \Delta_f H°(0\ K) = 149.3 \pm 2.5\ kcal\cdot mol^{-1}$$

Using $\Delta_f H°(N_2, A^3\Sigma, 298.15\ K) = 143.5\ kcal\cdot mol^{-1}$ [2] and $\Delta_f H°(CNN_3, g, 298.15\ K) = 107 \pm 3\ kcal\cdot mol^{-1}$,[3] we obtain $\Delta_f H°(NCN, g, 298.15\ K) = 113 \pm 5\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The X and A electronic levels, ground state structure, and rotational constants are from Herzberg and Travis,[4] the $a^1\Delta$ level is estimated from the work of Schoen.[5] The vibrational frequencies have been observed in the matrix-isolated species by Milligan and Jacox.[6,7] Wasserman *et al.*[8] have confirmed the ground state is linear and triplet by electron paramagnetic resonance.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.244	472.269	472.269	INFINITE
100	30.508	187.072	260.196	−7.312	472.239	469.608	−245.298
200	37.333	210.338	229.916	−3.916	472.399	466.945	−121.953
250	40.004	218.965	226.885	−1.980	472.583	465.561	−97.274
298.15	42.192	226.203	226.203	0.	472.792	464.189	−81.324
300	42.271	226.464	226.203	0.078	472.800	464.136	−80.813
350	44.309	233.135	226.726	2.243	473.038	462.673	−69.050
400	46.171	239.175	227.910	4.506	473.288	461.176	−60.223
450	47.866	244.713	229.474	6.858	473.546	459.646	−53.354
500	49.391	249.837	231.257	9.290	473.806	458.088	−47.856
600	51.948	259.078	235.141	14.362	474.317	454.896	−39.602
700	53.928	267.241	239.155	19.660	474.799	451.621	−33.700
800	55.451	274.546	243.130	25.133	475.241	448.279	−29.270
900	56.627	281.148	246.993	30.739	475.636	444.884	−25.820
1000	57.545	287.163	250.714	36.449	475.984	441.448	−23.059
1100	58.270	292.683	254.282	42.242	476.285	437.980	−20.798
1200	58.849	297.779	257.697	48.099	476.542	434.486	−18.913
1300	59.317	302.509	260.964	54.008	476.758	430.972	−17.317
1400	59.700	306.919	264.091	59.959	476.936	427.443	−15.948
1500	60.017	311.049	267.086	65.945	477.080	423.903	−14.762
1600	60.282	314.931	269.956	71.961	477.191	420.354	−13.723
1700	60.505	318.593	272.710	78.000	477.273	416.799	−12.807
1800	60.695	322.057	275.356	84.061	477.328	413.240	−11.992
1900	60.857	325.343	277.901	90.138	477.356	409.678	−11.263
2000	60.997	328.468	280.352	96.231	477.361	406.116	−10.607
2100	61.119	331.447	282.715	102.337	477.344	402.554	−10.013
2200	61.225	334.293	284.995	108.455	477.304	398.994	−9.473
2300	61.318	337.016	287.198	114.582	477.245	395.435	−8.981
2400	61.400	339.628	289.329	120.718	477.166	391.880	−8.529
2500	61.473	342.136	291.391	126.862	477.068	388.329	−8.114
2600	61.538	344.548	293.390	133.012	476.952	384.781	−7.730
2700	61.597	346.872	295.328	139.169	476.819	381.239	−7.376
2800	61.649	349.113	297.209	145.331	476.669	377.701	−7.046
2900	61.697	351.277	299.036	151.499	476.503	374.170	−6.740
3000	61.740	353.369	300.812	157.671	476.321	370.644	−6.453
3100	61.779	355.394	302.541	163.847	476.123	367.125	−6.186
3200	61.816	357.356	304.223	170.026	475.910	363.612	−5.935
3300	61.849	359.259	305.862	176.210	475.682	360.106	−5.700
3400	61.881	361.106	307.460	182.396	475.439	356.607	−5.479
3500	61.910	362.900	309.019	188.586	475.183	353.116	−5.270
3600	61.938	364.645	310.540	194.778	474.912	349.632	−5.073
3700	61.966	366.342	312.025	200.973	474.628	346.156	−4.887
3800	61.992	367.995	313.476	207.171	474.329	342.688	−4.711
3900	62.018	369.606	314.895	213.372	474.018	339.228	−4.543
4000	62.043	371.176	316.282	219.575	473.694	335.776	−4.385
4100	62.069	372.708	317.640	225.780	473.357	332.332	−4.234
4200	62.095	374.204	318.969	231.989	473.007	328.896	−4.090
4300	62.122	375.666	320.271	238.199	472.645	325.469	−3.954
4400	62.150	377.094	321.546	244.413	472.272	322.051	−3.823
4500	62.179	378.491	322.796	250.629	471.886	318.641	−3.699
4600	62.209	379.858	324.022	256.849	471.489	315.240	−3.580
4700	62.241	381.196	325.224	263.071	471.081	311.848	−3.466
4800	62.274	382.507	326.404	269.297	470.662	308.464	−3.357
4900	62.309	383.792	327.562	275.526	470.231	305.090	−3.252
5000	62.347	385.051	328.699	281.759	469.791	301.724	−3.152
5100	62.386	386.286	329.816	287.996	469.340	298.367	−3.056
5200	62.428	387.498	330.914	294.236	468.879	295.019	−2.964
5300	62.472	388.687	331.993	300.481	468.408	291.680	−2.875
5400	62.519	389.855	333.053	306.731	467.929	288.350	−2.789
5500	62.568	391.003	334.097	312.985	467.440	285.029	−2.707
5600	62.620	392.131	335.123	319.244	466.942	281.717	−2.628
5700	62.674	393.240	336.133	325.509	466.435	278.414	−2.551
5800	62.732	394.330	337.127	331.779	465.919	275.119	−2.478
5900	62.792	395.403	338.105	338.056	465.395	271.834	−2.407
6000	62.854	396.459	339.069	344.338	464.863	268.558	−2.338

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 138.797 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 723.15\ K$
$T_{fus} = 1123.15\ K$

$\Delta_f H°(0\ K) = -1124.610 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1130.768 \pm kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.690\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 29.665\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was obtained from the enthalpy of solution $\Delta_{sol}H = -6.36\ kcal \cdot mol^{-1}$ and the enthalpies of formation for $Na^+(aq, \infty)$ and $CO_3^{2-}(aq, \infty)$, -57.39 and $-161.84\ kcal \cdot mol^{-1}$, respectively. The enthalpy of solution was taken from Rupert *et al.*[1] The ionic enthalpies of formation were taken from Wagman *et al.*[2]

A value of $\Delta_f H°(298.15\ K) = -270.9\ kcal \cdot mol^{-1}$ has been selected by Wagman.[3]

Heat Capacity and Entropy

The low temperature heat capacities, 54.6–292.1 K, were measured by Anderson.[4] In the temperature range 473.15–873.15 K, Popov and Galchenko[5] measured the heat capacities (by heat conduction calorimetry) and observed two transformations, one at about 623 K and the other at about 750 K. Popov and Ginzburg[6] measured enthalpies in the temperature range 480–1350 K and tabulated their data only in the range 476–872 K. Ginzburg[7] has given heat capacity equations based on the data from[5, 6] and has tabulated thermodynamic functions in the range 500–1500 K. There appear to be inconsistencies among the data, equations and functions. Rolin and Recapet[8] also measured the enthalpy in the temperature range 645–1322 K. Janz *et al.*[9] have given an enthalpy equation based on their heat content measured data in the range 707–1127 K. May[10] has tabulated smoothed measured enthalpy values in the range 400–1500 K. All the above information was used in a Shomate analysis in order to smooth the enthalpies and calculate heat capacities. The values from the low and high temperature sources join smoothly at 298 K. The heat capacity was graphically extrapolated above the melting point.

The entropy was calculated at 54.60 using the Debye and Einstein function $D(138/T) + 2E(266/T) + 2D(737/T)$ given by Anderson.[4] The value of $S°(54.6\ K) = 3.943\ cal \cdot deg^{-1} \cdot mole^{-1}$.

Transition Data

T_{trs} was taken from Ginzburg[7] and $\Delta_{trs}H°$ was obtained from the above reported enthalpy measurements by means of Shomate function analysis. The heat of transition at 593.15 K has been incorporated in the heat capacity.

Fusion Data

T_{fus} was taken from Ginzburg[7] and $\Delta_{fus}H°$ was obtained from the above reported enthalpy measurements by means of Shomate function analysis.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.812	−1124.610	−1124.610	INFINITE
100	61.241	43.237	225.158	−18.192	−1129.086	−1102.556	575.916
200	94.140	97.766	148.470	−10.141	−1130.640	−1075.252	280.827
298.15	111.003	138.797	138.797	0.	−1130.768	−1048.009	183.607
300	111.253	139.484	138.799	0.206	−1130.764	−1047.496	182.385
400	125.102	173.307	143.317	11.996	−1135.696	−1019.370	133.116
500	142.214	203.007	152.332	25.337	−1134.473	−990.400	103.466
600	163.302	230.759	163.106	40.592	−1131.568	−961.826	83.734
700	187.569	257.722	174.702	58.115	−1126.604	−933.897	69.688
723.150	193.385	263.919	177.459	62.524	I <--> II		
723.150	143.762	264.873	177.459	63.214	TRANSITION		
800	153.344	279.866	186.580	74.628	−1122.835	−906.701	59.202
900	166.230	298.668	197.996	90.605	−1119.776	−879.857	51.066
1000	179.201	316.851	208.977	107.874	−1115.597	−853.412	44.578
1100	192.046	334.537	219.591	126.441	−1110.305	−827.441	39.292
1123.150	195.101	338.569	222.002	130.922	----- II <--> LIQUID -----		
1200	200.748	351.719	229.891	146.194	−1297.547	−797.118	34.698
1300	206.188	368.015	239.895	166.556	−1289.016	−755.759	30.367
1400	209.744	383.430	249.602	187.359	−1280.130	−715.071	26.680
1500	212.547	398.000	259.014	208.478	−1271.004	−675.027	23.507
1600	214.765	411.789	268.136	229.845	−1261.701	−635.598	20.750
1700	216.899	424.875	276.974	251.431	−1252.242	−596.755	18.336
1800	218.656	437.323	285.539	273.210	−1242.651	−558.473	16.206
1900	220.204	449.186	293.843	295.153	−1232.955	−520.727	14.316
2000	221.752	460.521	301.895	317.251	−1223.161	−483.495	12.628

PREVIOUS: December 1960 CURRENT: March 1966

$S°(298.15\ K)$ = [156.423] $J·K^{-1}·mol^{-1}$
T_{fus} = 1123.15 K

$\Delta_f H°(298.15\ K)$ = [−1108.515] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 29.665 $kJ·mol^{-1}$

Enthalpy of Formation

The $\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference enthalpy, $H°(1123.15\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 723.15 K. The heat capacity below 723.15 K is obtained from the heat capacity of the crystal. Above 723.15 K the heat capacity is adopted as 45.30 $cal·K^{-1}·mol^{-1}$, based on the enthalpy measurements in the range 1127–1210 K reported by Janz *et al.*[1] The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Reference

[1]G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc. **59**, 841 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	111.002	156.423	156.423	0.	−1108.515	−1031.011	180.629
300	111.253	157.110	156.425	0.206	−1108.511	−1030.531	179.431
400	125.102	190.934	160.944	11.996	−1113.443	−1004.168	131.131
500	142.214	220.614	169.957	25.329	−1112.228	−976.960	102.062
600	163.302	248.359	180.729	40.578	−1109.329	−950.147	82.718
700	187.569	275.336	192.322	58.110	−1104.356	−923.979	68.948
723.150	193.387	281.533	195.079	62.519	I <--> II		
723.150	189.535	281.533	195.079	62.519	TRANSITION		
800	189.535	300.675	204.319	77.085	−1098.125	−898.639	58.675
900	189.535	322.999	216.289	96.039	−1092.089	−874.068	50.730
1000	189.535	342.969	227.976	114.992	−1086.226	−850.159	44.408
1100	189.535	361.033	239.264	133.946	−1080.547	−826.828	39.263
1123.150	189.535	364.981	241.815	138.333	----- II <--> LIQUID -----		
1200	189.535	377.525	250.109	152.899	−1268.589	−799.127	34.785
1300	189.535	392.696	260.501	171.853	−1261.466	−760.294	30.549
1400	189.535	406.742	270.452	190.806	−1254.430	−722.007	26.938
1500	189.535	419.818	279.979	209.760	−1247.470	−684.221	23.827
1600	189.535	432.051	289.105	228.713	−1240.579	−646.896	21.119
1700	189.535	443.541	297.855	247.667	−1233.753	−610.000	18.743
1800	189.535	454.375	306.252	266.620	−1226.988	−573.504	16.643
1900	189.535	464.622	314.320	285.574	−1220.282	−537.383	14.774
2000	189.535	474.344	322.081	304.527	−1213.632	−501.613	13.101
2100	189.535	483.592	329.553	323.481	−1207.037	−466.174	11.595
2200	189.535	492.409	336.757	342.434	−1200.497	−431.048	10.234
2300	189.535	500.834	343.709	361.388	−1194.012	−396.219	8.998
2400	189.535	508.901	350.425	380.341	−1187.582	−361.671	7.872
2500	189.535	516.638	356.920	399.295	−1181.206	−327.389	6.840

PREVIOUS: December 1960 CURRENT: March 1966

0	to	723.15 K	crystal, I
723.15	to	1123.15 K	crystal, II
above		1123.15 K	liquid

Refer to the individual tables for details

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.812	−1124.610	−1124.610	INFINITE
100	61.241	43.237	225.158	−18.192	−1129.086	−1102.556	575.916
200	94.140	97.766	148.470	−10.141	−1130.640	−1075.252	280.827
298.15	111.003	138.797	138.797	0.	−1130.768	−1048.009	183.607
300	111.253	139.484	138.799	0.206	−1130.764	−1047.496	182.385
400	125.102	173.307	143.317	11.996	−1135.696	−1019.370	133.116
500	142.214	203.007	152.332	25.337	−1134.473	−990.400	103.466
600	163.302	230.759	163.106	40.592	−1131.568	−961.826	83.734
700	187.569	257.722	174.702	58.115	−1126.604	−933.897	69.688
723.150	193.387	263.919	177.459	62.524	I <--> II		
723.150	143.761	264.873	177.459	63.214	TRANSITION		
800	153.344	279.866	186.580	74.628	−1122.835	−906.701	59.202
900	166.230	298.668	197.996	90.605	−1119.776	−879.857	51.066
1000	179.201	316.851	208.977	107.874	−1115.597	−853.412	44.578
1100	192.046	334.537	219.591	126.441	−1110.305	−827.441	39.292
1123.150	195.101	338.569	222.002	130.922	II <--> LIQUID		
1123.150	189.535	364.981	222.002	160.586	TRANSITION		
1200	189.535	377.525	231.565	175.152	−1268.589	−799.127	34.785
1300	189.535	392.696	243.384	194.106	−1261.466	−760.294	30.549
1400	189.535	406.742	254.557	213.059	−1254.430	−722.007	26.938
1500	189.535	419.818	265.143	232.013	−1247.470	−684.221	23.827
1600	189.535	432.051	275.197	250.966	−1240.579	−646.896	21.119
1700	189.535	443.541	284.765	269.920	−1233.753	−610.000	18.743
1800	189.535	454.375	293.890	288.873	−1226.988	−573.504	16.643
1900	189.535	464.622	302.608	307.827	−1220.282	−537.383	14.774
2000	189.535	474.344	310.954	326.780	−1213.632	−501.613	13.101
2100	189.535	483.592	318.957	345.734	−1207.037	−466.174	11.595
2200	189.535	492.409	326.642	364.687	−1200.497	−431.048	10.234
2300	189.535	500.834	334.034	383.641	−1194.012	−396.219	8.998
2400	189.535	508.901	341.153	402.594	−1187.582	−361.671	7.872
2500	189.535	516.638	348.019	421.548	−1181.206	−327.389	6.840

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 197.65 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -113.81 \pm 0.17\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -110.53 \pm 0.17\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 2169.52\ cm^{-1}$ $\omega_e x_e = 13.453\ cm^{-1}$ $\sigma = 1$

$B_e = 1.9302\ cm^{-1}$ $\alpha_e = 0.01746\ cm^{-1}$ $r_e = 1.1281$ Å

Enthalpy of Formation

The enthalpy change $\Delta_r H°(298.15\ K)$ for the reaction: $CO(g) + 1/2\ O_2(g) = CO_2(g)$ was reported to be $-67.636 \pm 0.029\ kcal \cdot mol^{-1}$, based on molecular weight of $CO_2 = 44.010$, by Rossini.[1] It was recalculated to be $-67.638 \pm 0.03\ kcal \cdot mol^{-1}$, using molecular weight of $CO_2 = 44.011$, for internal consistency. From the value of $\Delta_r H°(298.15\ K)$, the enthalpy of formation $\Delta_f H°(298.15\ K)$ for CO(g) was derived to be $-26.417 \pm 0.04\ kcal \cdot mol^{-1}$, which yields $D_0°(CO) = 11.09$ eV.

The $D_0°(CO)$ value has been proposed to be 6.92 to 11.11 eV in the past few decades in order to explain data collected from spectroscopic, flame, shock-wave, detonation, and electron–impact studies. Recent evaluations by Brewer and Searcy,[2] Fineman and Petrocelli,[3] and Giese and Maier[4] favored the value 11.11 eV, reported by Gaydon.[5]

The enthaply of combustion of CO(g) was also determined by Awbery and Griffiths,[6] Fenning and Cotton,[7] and Roth and Banse.[8]

Heat Capacity and Entropy

The functions adopted here were obtained from Belzer *et al.*,[9] assuming the thermodynamic functions for the naturally occurring isotopic mixture to be the same as those for $C^{12}O^{16}$(g). The spectroscopic constants employed for calculation were reported by Herzberg.[10] The tabulated functions include the second order corrections to the rigid–rotator and harmonic–oscillator molecular model for vibrational anharmonicity, rotational stretching and rotational–vibrational interaction.

The spectroscopic constants listed above are for the naturally occurring isotopic composition given by Strominger et al.[11]

Thermodynamic properties for CO from 70 to 300 K, with pressures to 300 atmospheres were reported by Hust *et al.*[12] Calculations of the vapor pressure and enthalpies of vaporization and sublimation of CO and CO_2 below one atmosphere were reported by Mullins *et al.*[13]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.000	0.000	INFINITE	−8.671	−113.805	−113.805	INFINITE
100	29.104	165.850	223.539	−5.769	−112.415	−120.239	62.807
200	29.108	186.025	200.317	−2.858	−111.286	−128.526	33.568
298.15	29.142	197.653	197.653	0.000	−110.527	−137.163	24.030
300	29.142	197.833	197.653	0.054	−110.516	−137.328	23.911
400	29.342	206.238	198.798	2.976	−110.102	−146.338	19.110
500	29.794	212.831	200.968	5.931	−110.003	−155.414	16.236
600	30.443	218.319	203.415	8.942	−110.150	−164.486	14.320
700	31.171	223.066	205.890	12.023	−110.469	−173.518	12.948
800	31.899	227.277	208.305	15.177	−110.905	−182.497	11.916
900	32.577	231.074	210.628	18.401	−111.418	−191.416	11.109
1000	33.183	234.538	212.848	21.690	−111.983	−200.275	10.461
1100	33.710	237.726	214.967	25.035	−112.586	−209.075	9.928
1200	34.175	240.679	216.988	28.430	−113.217	−217.819	9.481
1300	34.572	243.431	218.917	31.868	−113.870	−226.509	9.101
1400	34.920	246.006	220.761	35.343	−114.541	−235.149	8.774
1500	35.217	248.426	222.526	38.850	−115.229	−243.740	8.488
1600	35.480	250.707	224.216	42.385	−115.933	−252.284	8.236
1700	35.710	252.865	225.839	45.945	−116.651	−260.784	8.013
1800	35.911	254.912	227.398	49.526	−117.384	−269.242	7.813
1900	36.091	256.859	228.897	53.126	−118.133	−277.658	7.633
2000	36.250	258.714	230.342	56.744	−118.896	−286.034	7.470
2100	36.392	260.486	231.736	60.376	−119.675	−294.372	7.322
2200	36.518	262.182	233.081	64.021	−120.470	−302.672	7.186
2300	36.635	263.808	234.382	67.679	−121.282	−310.936	7.062
2400	36.740	265.369	235.641	71.348	−122.109	−319.165	6.946
2500	36.836	266.871	236.860	75.027	−122.953	−327.358	6.840
2600	36.924	268.318	238.043	78.715	−123.813	−335.517	6.741
2700	37.003	269.713	239.190	82.411	−124.689	−343.643	6.648
2800	37.083	271.060	240.304	86.116	−125.582	−351.736	6.562
2900	37.150	272.362	241.387	89.827	−126.490	−359.797	6.481
3000	37.217	273.623	242.441	93.546	−127.415	−367.826	6.404
3100	37.279	274.844	243.467	97.271	−128.356	−375.824	6.333
3200	37.338	276.029	244.466	101.001	−129.312	−383.792	6.265
3300	37.392	277.178	245.440	104.738	−130.283	−391.730	6.201
3400	37.443	278.295	246.390	108.480	−131.270	−399.638	6.140
3500	37.493	279.382	247.317	112.227	−132.271	−407.517	6.082
3600	37.543	280.438	248.222	115.978	−133.288	−415.366	6.027
3700	37.589	281.468	249.107	119.735	−134.318	−423.188	5.974
3800	37.631	282.471	249.972	123.496	−135.363	−430.981	5.924
3900	37.673	283.449	250.818	127.261	−136.422	−438.746	5.876
4000	37.715	284.403	251.645	131.031	−137.495	−446.485	5.830
4100	37.756	285.335	252.456	134.804	−138.581	−454.196	5.787
4200	37.794	286.245	253.250	138.582	−139.681	−461.881	5.744
4300	37.832	287.135	254.027	142.363	−140.794	−469.539	5.704
4400	37.869	288.005	254.790	146.148	−141.921	−477.171	5.665
4500	37.903	288.856	255.537	149.937	−143.062	−484.778	5.627
4600	37.941	289.690	256.271	153.729	−144.215	−492.359	5.591
4700	37.974	290.506	256.990	157.525	−145.383	−499.915	5.556
4800	38.007	291.306	257.697	161.324	−146.563	−507.446	5.522
4900	38.041	292.090	258.391	165.126	−147.758	−514.951	5.489
5000	38.074	292.859	259.073	168.932	−148.967	−522.433	5.458
5100	38.104	293.613	259.743	172.741	−150.190	−529.890	5.427
5200	38.137	294.354	260.401	176.553	−151.427	−537.323	5.397
5300	38.171	295.080	261.049	180.368	−152.679	−544.732	5.369
5400	38.200	295.794	261.685	184.187	−153.946	−552.118	5.341
5500	38.233	296.495	262.312	188.008	−155.228	−559.480	5.313
5600	38.263	297.184	262.929	191.833	−156.527	−566.818	5.287
5700	38.296	297.862	263.535	195.661	−157.841	−574.133	5.261
5800	38.325	298.528	264.133	199.492	−159.172	−581.424	5.236
5900	38.355	299.184	264.722	203.326	−160.521	−588.694	5.212
6000	38.388	299.829	265.301	207.163	−161.887	−595.939	5.188

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 231.581\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -138.531 \pm 1.05\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -138.407 \pm 1.05\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
859(1)
524(2)
2064(1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: $C_{\infty v}$

Rotational Constant: $B_{000} = 0.20287\ cm^{-1}$

Spectroscopic constants used in calculating corrections to rigid rotator–harmonic oscillator approximation (cm^{-1}):

$\alpha_1 = 0.0006044$ $x_{11} = -4.0$ $x_{12} = -6.8$ $A_{000} = 0$ $g_{22} = 3.2$

$\alpha_2 = 0.0003539$ $x_{22} = -0.4$ $x_{23} = -11.5$ $C_{000} = 0$

$\alpha_3 = 0.001838$ $x_{33} = -7.0$ $x_{13} = -4.5$ $D_{000} = 4.37 \times 10^{-8}$

Enthalpy of Formation

Terres and Wesemann,[1] report equilibrium constants from 623 to 873 K for the reaction $CO_2(g) + H_2S(g) \rightarrow COS(g) + H_2O(g)$. These yield $\Delta_f H°(700\ K) = 8.19 \pm 0.23\ kcal·mol^{-1}$, whence $\Delta_f H°(298.15\ K)$ for COS is $-33.08 \pm 0.25\ kcal·mol^{-1}$. The same authors report equilibrium constants for the reaction $COS(g) + H_2S(g) \rightarrow CS_2(g) + H_2O(g)$, but regard these as less reliable than the others. The resulting value of $-26.39\ kcal·mol^{-1}$ for $\Delta_f H°(298.15\ K)$ of COS has been disregarded.

Heat Capacity

Gordon[2] has used the constants listed above to calculate $C_p°$ from 298.15 to 6000 K by the method of Pennington and Kobe,[3] which takes anharmonicity, vibration–rotation interaction, and centrifugal stretching into account. The constants have been taken from.[4–8] The thermodynamic functions below 298.15 K have been calculated for the rigidly rotating harmonic oscillator.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−9.929	−138.531	−138.531	INFINITE
100	29.610	194.193	264.316	−7.012	−137.816	−147.223	76.901
200	35.472	216.276	235.229	−3.791	−138.018	−156.581	40.895
298.15	41.497	231.581	231.581	0.	−138.407	−165.601	29.013
300	41.589	231.838	231.582	0.077	−138.415	−165.770	28.863
400	45.852	244.415	233.268	4.459	−141.138	−174.727	22.817
500	48.903	254.988	236.582	9.203	−143.179	−182.902	19.108
600	51.250	264.118	240.428	14.214	−144.910	−190.679	16.600
700	53.137	272.164	244.398	19.436	−146.435	−198.184	14.789
800	54.677	279.363	248.327	24.829	−147.842	−205.480	13.416
900	55.940	285.878	252.143	30.362	−202.304	−211.523	12.276
1000	56.990	291.828	255.818	36.010	−202.366	−212.544	11.102
1100	57.861	297.302	259.344	41.754	−202.442	−213.559	10.141
1200	58.597	302.369	262.721	47.577	−202.531	−214.565	9.340
1300	59.216	307.084	265.954	53.469	−202.633	−215.564	8.661
1400	59.748	311.492	269.051	59.418	−202.748	−216.555	8.080
1500	60.208	315.631	272.020	65.416	−202.878	−217.536	7.575
1600	60.605	319.529	274.869	71.457	−203.024	−218.509	7.134
1700	60.957	323.214	277.605	77.535	−203.187	−219.472	6.744
1800	61.266	326.707	280.237	83.647	−203.366	−220.425	6.397
1900	61.547	330.027	282.771	89.788	−203.563	−221.367	6.086
2000	61.798	333.191	285.213	95.955	−203.778	−222.299	5.806
2100	62.024	336.211	287.570	102.146	−204.011	−223.219	5.552
2200	62.233	339.102	289.847	108.359	−204.261	−224.128	5.321
2300	62.423	341.872	292.050	114.592	−204.529	−225.025	5.110
2400	62.601	344.533	294.181	120.843	−204.815	−225.910	4.917
2500	62.764	347.092	296.247	127.112	−205.118	−226.783	4.738
2600	62.919	349.556	298.250	133.396	−205.437	−227.643	4.573
2700	63.065	351.934	300.195	139.695	−205.773	−228.491	4.420
2800	63.203	354.230	302.084	146.009	−206.124	−229.326	4.278
2900	63.333	356.450	303.920	152.336	−206.491	−230.148	4.145
3000	63.459	358.599	305.707	158.675	−206.873	−230.958	4.021
3100	63.576	360.682	307.447	165.027	−207.270	−231.754	3.905
3200	63.691	362.702	309.143	171.390	−207.681	−232.537	3.796
3300	63.802	364.664	310.795	177.765	−208.107	−233.308	3.693
3400	63.910	366.570	312.408	184.151	−208.546	−234.064	3.596
3500	64.015	368.424	313.982	190.547	−208.998	−234.809	3.504
3600	64.114	370.229	315.520	196.954	−209.464	−235.539	3.418
3700	64.211	371.987	317.022	203.370	−209.944	−236.257	3.335
3800	64.306	373.701	318.491	209.796	−210.436	−236.962	3.257
3900	64.400	375.372	319.928	216.231	−210.942	−237.653	3.183
4000	64.492	377.004	321.335	222.676	−211.462	−238.331	3.112
4100	64.582	378.597	322.712	229.129	−211.994	−238.997	3.045
4200	64.670	380.155	324.061	235.592	−212.540	−239.649	2.980
4300	64.757	381.677	325.384	242.063	−213.100	−240.287	2.919
4400	64.843	383.167	326.680	248.543	−213.673	−240.913	2.860
4500	64.927	384.625	327.952	255.032	−214.261	−241.526	2.804
4600	65.009	386.053	329.199	261.529	−214.863	−242.125	2.749
4700	65.090	387.452	330.424	268.034	−215.479	−242.711	2.697
4800	65.170	388.823	331.626	274.547	−216.111	−243.284	2.647
4900	65.250	390.168	332.807	281.068	−216.759	−243.843	2.599
5000	65.329	391.487	333.968	287.597	−217.422	−244.389	2.553
5100	65.407	392.781	335.108	294.133	−218.101	−244.922	2.509
5200	65.484	394.052	336.230	300.678	−218.797	−245.441	2.465
5300	65.561	395.300	337.332	307.230	−219.511	−245.946	2.424
5400	65.638	396.527	338.417	313.790	−220.242	−246.439	2.384
5500	65.714	397.732	339.485	320.358	−220.991	−246.917	2.345
5600	65.789	398.916	340.536	326.933	−221.759	−247.381	2.307
5700	65.864	400.082	341.570	333.516	−222.546	−247.832	2.271
5800	65.939	401.228	342.589	340.106	−223.353	−248.268	2.236
5900	66.013	402.355	343.592	346.704	−224.180	−248.692	2.202
6000	66.086	403.466	344.581	353.308	−225.028	−249.099	2.169

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar)

$S°(298.15\ K) = 213.795 \pm 0.12\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -393.151 \pm 0.05\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -393.522 \pm 0.05\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1384.86 (1)
667.30 (2)
2349.30 (1)

Ground State Quantum Weight: 1
Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distances: C–O = 1.16 Å
Bond Angle: O–C–O = 180°
Rotational Constant: $B_O = 0.391514\ cm^{-1}$

Enthalpy of Formation

The enthalpy change of the reaction C(c, graphite) + O_2(g) = CO_2(g) has been measured by Dewey and Harper.[1] Jessup,[2] and Prosen and Rossini.[3] Based on these data, the enthalpy of formation for CO_2(g) was reported to be -94.0518 ± 0.0108 kcal·mol^{-1}, using molecular weight of CO_2 = 44.010, by Prosen *et al.*[4] This value was recalculated to be -94.054 ± 0.011 kcal·mol^{-1}, based on molecular weight of CO_2 = 44.011, for internal consistency.

Heat Capacity and Entropy

The functions adopted here were obtained from Woolley,[5] who calculated the thermodynamic functions by means of a direct summation for the naturally occurring isotopic composition. The spectroscopic constants used are essentially those selected by Wentnik.[6] Slightly different sets of spectroscopic constants were obtained by Courtoy[7] and Stull *et al.*[8] The high–resolution infrared spectrum of O^{18} – enriched CO_2 was examined in the region 5400–1620 cm^{-1}, using an Ebert grating Spectrometer with spectral slit widths ranging from 0.4 to 0.2 cm^{-1} by Berney.[9]

The molecular structure was reported by Herzberg.[10] The rotational constant, B_o, was obtained from Woolley.[5] The value of bond distance, r_e, was calculated from B_e which was derived from B_o, using $B_e - B_o = 0.0011\ cm^{-1}$ given in Herzberg.[10] Heat capacities of CO_2(g) at high pressures were reported by Vukalovich *et al.*,[11] Krueger,[12] and Vukalovich and Gureev.[13]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.364	−393.151	−393.151	INFINITE
100	29.208	179.009	243.568	−6.456	−393.208	−393.683	205.639
200	32.359	199.975	217.046	−3.414	−393.404	−394.085	102.924
298.15	37.129	213.795	213.795	0.	−393.522	−394.389	69.095
300	37.221	214.025	213.795	0.069	−393.523	−394.394	68.670
400	41.325	225.314	215.307	4.003	−393.583	−394.675	51.539
500	44.627	234.901	218.290	8.305	−393.666	−394.939	41.259
600	47.321	243.283	221.772	12.907	−393.803	−395.182	34.404
700	49.564	250.750	225.388	17.754	−393.983	−395.398	29.505
800	51.434	257.494	228.986	22.806	−394.188	−395.586	25.829
900	52.999	263.645	232.500	28.030	−394.405	−395.748	22.969
1000	54.308	269.299	235.901	33.397	−394.623	−395.886	20.679
1100	55.409	274.528	239.178	38.884	−394.838	−396.001	18.805
1200	56.342	279.390	242.329	44.473	−395.050	−396.098	17.242
1300	57.137	283.932	245.356	50.148	−395.257	−396.177	15.919
1400	57.802	288.191	248.265	55.896	−395.462	−396.240	14.784
1500	58.379	292.199	251.062	61.705	−395.668	−396.288	13.800
1600	58.886	295.983	253.753	67.569	−395.876	−396.323	12.939
1700	59.317	299.566	256.343	73.480	−396.090	−396.344	12.178
1800	59.701	302.968	258.840	79.431	−396.311	−396.353	11.502
1900	60.049	306.205	261.248	85.419	−396.542	−396.349	10.896
2000	60.350	309.293	263.574	91.439	−396.784	−396.333	10.351
2100	60.622	312.244	265.822	97.488	−397.039	−396.304	9.858
2200	60.865	315.070	267.996	103.562	−397.309	−396.262	9.408
2300	61.086	317.781	270.102	109.660	−397.596	−396.209	8.998
2400	61.287	320.385	272.144	115.779	−397.900	−396.142	8.622
2500	61.471	322.890	274.124	121.917	−398.222	−396.062	8.275
2600	61.647	325.305	276.046	128.073	−398.562	−395.969	7.955
2700	61.802	327.634	277.914	134.246	−398.921	−395.862	7.658
2800	61.952	329.885	279.730	140.433	−399.299	−395.742	7.383
2900	62.095	332.061	281.497	146.636	−399.695	−395.609	7.126
3000	62.229	334.169	283.218	152.852	−400.111	−395.461	6.886
3100	62.347	336.211	284.895	159.081	−400.545	−395.298	6.661
3200	62.462	338.192	286.529	165.321	−400.998	−395.122	6.450
3300	62.573	340.116	288.124	171.573	−401.470	−394.932	6.251
3400	62.681	341.986	289.681	177.836	−401.960	−394.726	6.064
3500	62.785	343.804	291.202	184.109	−402.467	−394.506	5.888
3600	62.884	345.574	292.687	190.393	−402.991	−394.271	5.721
3700	62.980	347.299	294.140	196.686	−403.532	−394.022	5.563
3800	63.074	348.979	295.561	202.989	−404.089	−393.756	5.413
3900	63.166	350.619	296.952	209.301	−404.662	−393.477	5.270
4000	63.254	352.219	298.314	215.622	−405.251	−393.183	5.134
4100	63.341	353.782	299.648	221.951	−405.856	−392.874	5.005
4200	63.426	355.310	300.955	228.290	−406.475	−392.550	4.882
4300	63.509	356.803	302.236	234.637	−407.110	−392.210	4.764
4400	63.588	358.264	303.493	240.991	−407.760	−391.857	4.652
4500	63.667	359.694	304.726	247.354	−408.426	−391.488	4.544
4600	63.745	361.094	305.937	253.725	−409.106	−391.105	4.441
4700	63.823	362.466	307.125	260.103	−409.802	−390.706	4.342
4800	63.893	363.810	308.292	266.489	−410.514	−390.292	4.247
4900	63.968	365.128	309.438	272.882	−411.242	−389.862	4.156
5000	64.046	366.422	310.565	279.283	−411.986	−389.419	4.068
5100	64.128	367.691	311.673	285.691	−412.746	−388.959	3.984
5200	64.220	368.937	312.762	292.109	−413.522	−388.486	3.902
5300	64.312	370.161	313.833	298.535	−414.314	−387.996	3.824
5400	64.404	371.364	314.888	304.971	−415.123	−387.493	3.748
5500	64.496	372.547	315.925	311.416	−415.949	−386.974	3.675
5600	64.588	373.709	316.947	317.870	−416.794	−386.439	3.605
5700	64.680	374.853	317.953	324.334	−417.658	−385.890	3.536
5800	64.772	375.979	318.944	330.806	−418.541	−385.324	3.470
5900	64.865	377.087	319.920	337.288	−419.445	−384.745	3.406
6000	64.957	378.178	320.882	343.779	−420.372	−384.148	3.344

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) \approx [240.65]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) \approx [-435.6 \pm 113]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) \approx [-441.4 \pm 113]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1400] (1)
[800] (1)
1671 (1)

Ground State Quantum Weight: [2] $\sigma = 2$

Point Group: [C_{2v}]

Bond Distances: C–O = [1.25] Å

Bond Angle: O–C–O = 127° ± 8°

Product of the Moments of Inertia: $I_A I_B I_C = [2.13011 \times 10^{-116}]$

Enthalpy of Formation

$\Delta_f H°(CO_2^-, g, 298.15\ K) = -105.5 \pm 27$ kcal·mol^{-1} is estimated from $\Delta_f H°(298.15\ K) = 88.6 \pm 10$ kcal·mol^{-1} for $HCO_2^-(g) \rightarrow H(g) + CO_2^-(g)$, using the $\Delta_f H°(HCO_2^-, g, 298.15\ K) = 142 \pm 17$ kcal·mol^{-1} and $\Delta_f H°(H, g, 298.15\ K) = 52.1$ kcal·mol^{-1}. The value of $\Delta_f H°(298.15\ K)$ is assumed to be the same as that for $HCOOH(g) \rightarrow H(G) + COOH(g)$. The values of $\Delta_f H°$(HCOOH, g, 298.15 K) and $\Delta_f H°$(H, g, 298.15 K), −90.5 and 52.1 kcal·mol^{-1}, respectively, are from NBS,[1] and the value of $\Delta_f H°$(COOH, g, 298.15 K) = −54 ± 3 kcal·mol^{-1} is from Benson.[2] The value of $\Delta_f H°(HCO_2^-, g, 298.15\ K)$ is estimated from an approximate lattice energy calculation for sodium formate. The derived electron affinity of CO_2(g) is 11.5 kcal·mol^{-1} (0.5 eV) with an estimated uncertainty range of 0–40 kcal·mol^{-1}.

Heat Capacity and Entropy

The correlations of Walsh[3] predict a bent molecular structure of CO_2^- based on its 17 valence electrons. Hartman and Hisatsune[4] measured the asymmetric C–O stretching frequency and derived the bond angle of 127 ± 8° from the infrared spectrum of matrix isolated CO_2^-. They also estimated the bond distance C–O and the symmetric stretching and the bending vibrational frequencies by the valence force method. These molecular constants are adopted in the tabulation. The principal moments of inertia are: $I_A = 0.4511 \times 10^{-39}$, $I_B = 6.6497 \times 10^{-39}$, and $I_C = 7.1008 \times 10^{-39}$ g·cm^2.

Ovenall and Whiffen[5] have derived a bond angle of 134° which is in good agreement with the value selected. This result was obtained from electron spin resonance for the CO_2^- radical trapped in sodium formate.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.147	−435.628		
100	33.269	203.352	271.567	−6.822			
200	34.178	226.586	243.909	−3.465			
250	35.280	234.325	241.243	−1.730			
298.15	36.593	240.648	240.648	0.	−441.412	−444.030	77.792
300	36.647	240.875	240.649	0.068	−441.453	−444.047	77.315
350	38.163	246.636	241.100	1.938	−442.570	−444.391	66.322
400	39.737	251.835	242.122	3.885	−443.708	−444.573	58.055
450	41.295	256.606	243.470	5.911	−444.867	−444.612	51.609
500	42.785	261.034	245.008	8.013	−446.044	−444.521	46.439
600	45.454	269.078	248.363	12.429	−448.445	−443.992	38.653
700	47.653	276.256	251.844	17.088	−450.891	−443.057	33.061
800	49.420	282.739	255.307	21.945	−453.371	−441.769	28.845
900	50.828	288.644	258.688	26.960	−455.874	−440.168	25.547
1000	51.952	294.060	261.958	32.101	−458.397	−438.288	22.894
1100	52.854	299.055	265.106	37.343	−460.937	−436.154	20.711
1200	53.586	303.686	268.131	42.667	−463.492	−433.789	18.882
1300	54.183	308.000	271.034	48.056	−466.063	−431.209	17.326
1400	54.677	312.034	273.820	53.500	−468.651	−428.431	15.985
1500	55.088	315.821	276.495	58.989	−471.257	−425.468	14.816
1600	55.433	319.387	279.065	64.515	−473.881	−422.330	13.788
1700	55.725	322.757	281.537	70.073	−476.525	−419.027	12.875
1800	55.974	325.949	283.917	75.659	−479.191	−415.568	12.059
1900	56.188	328.981	286.209	81.267	−481.880	−411.960	11.326
2000	56.374	331.868	288.421	86.895	−484.592	−408.210	10.661
2100	56.535	334.623	290.556	92.541	−487.329	−404.324	10.057
2200	56.676	337.256	292.619	98.202	−490.092	−400.306	9.504
2300	56.800	339.778	294.615	103.876	−492.881	−396.163	8.997
2400	56.910	342.198	296.548	109.561	−495.697	−391.898	8.529
2500	57.008	344.523	298.420	115.257	−498.539	−387.514	8.097
2600	57.095	346.761	300.237	120.962	−501.409	−383.017	7.695
2700	57.173	348.917	302.000	126.676	−504.305	−378.408	7.321
2800	57.243	350.998	303.713	132.397	−507.229	−373.691	6.971
2900	57.306	353.008	305.378	138.124	−510.179	−368.871	6.644
3000	57.363	354.951	306.999	143.858	−513.156	−363.947	6.337
3100	57.415	356.833	308.576	149.597	−516.159	−358.924	6.048
3200	57.462	358.657	310.113	155.341	−519.187	−353.804	5.775
3300	57.505	360.426	311.611	161.089	−522.241	−348.589	5.518
3400	57.545	362.143	313.072	166.842	−525.319	−343.280	5.274
3500	57.581	363.811	314.498	172.598	−528.422	−337.881	5.043
3600	57.615	365.434	315.890	178.358	−531.548	−332.393	4.823
3700	57.645	367.013	317.251	184.121	−534.698	−326.818	4.614
3800	57.674	368.551	318.581	189.887	−537.871	−321.156	4.415
3900	57.700	370.049	319.881	195.655	−541.066	−315.411	4.224
4000	57.724	371.510	321.154	201.427	−544.283	−309.585	4.043
4100	57.747	372.936	322.399	207.200	−547.523	−303.677	3.869
4200	57.768	374.328	323.619	212.976	−550.783	−297.691	3.702
4300	57.788	375.687	324.814	218.754	−554.066	−291.625	3.543
4400	57.806	377.016	325.986	224.533	−557.370	−285.485	3.389
4500	57.823	378.315	327.134	230.315	−560.695	−279.268	3.242
4600	57.839	379.586	328.261	236.098	−564.041	−272.978	3.100
4700	57.854	380.830	329.366	241.883	−567.409	−266.614	2.963
4800	57.869	382.049	330.451	247.669	−570.799	−260.178	2.831
4900	57.882	383.242	331.516	253.456	−574.211	−253.671	2.704
5000	57.894	384.411	332.562	259.245	−577.646	−247.094	2.581
5100	57.906	385.558	333.590	265.035	−581.103	−240.449	2.463
5200	57.917	386.683	334.601	270.826	−584.584	−233.736	2.348
5300	57.928	387.786	335.594	276.619	−588.089	−226.955	2.237
5400	57.938	388.869	336.570	282.412	−591.620	−220.109	2.129
5500	57.947	389.932	337.531	288.206	−595.175	−213.197	2.025
5600	57.956	390.976	338.476	294.001	−598.757	−206.218	1.924
5700	57.965	392.002	339.406	299.797	−602.367	−199.177	1.825
5800	57.973	393.010	340.322	305.594	−606.005	−192.071	1.730
5900	57.980	394.001	341.223	311.392	−609.672	−184.905	1.637
6000	57.987	394.976	342.111	317.190	−613.369	−177.673	1.547

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 216.26 \pm 0.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) \approx 447.6 \pm 9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) \approx 449.9 \pm 9\ kJ \cdot mol^{-1}$

Electronic States and Molecular Constants

State	T_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	D_e, cm^{-1}	r_e, Å
$X\ ^2\Sigma^+$	0	1239.67	6.86	0.7986	0.00597	[1.33]	1.5622
$A\ ^2\Pi_i$	7053.2	1061.99	6.035	0.7135	0.0058	[1.3]	1.653
$B\ ^2\Sigma^+$	29100.4	836.32	5.917	0.6829	0.00628	[1.82]	1.6894

Enthalpy of Formation

We adopt the value which Huber and Herzberg[1] recommended, $D_0°$(CP, g) = 5.28 eV (509.4 $kJ \cdot mol^{-1}$), based on the mass-spectrometric studies of Gingerich,[2] Smoes *et al.*,[3] and Kordis and Gingerich.[4] Smoes *et al.*[3] studied the equilibrium between graphite and mono- and di-atomic phosphorus vapor when gadolinium phosphide was heated in a graphite Knudsen cell in the absence of excess graphite powder (2120–2500 K). Kordis and Gingerich[4] studied the effusate from a graphite-lined tantalum Knudsen cell containing a mixture of graphite(-excess)-TiP-Rh.

Heat Capacity and Entropy

The molecular constants for the three electronic states are taken from Huber and Herzberg[1] based on their review in 1976 of the data of Barwald *et al.*,[5] Thakur and Singh,[6] Chaudhry and Upadhya,[7] and Wentink and Spindler.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.715	447.589	447.589	INFINITE
100	29.105	184.299	242.380	−5.808	449.549	432.983	−226.167
200	29.207	204.487	218.963	−2.895	449.872	416.016	−108.652
250	29.473	211.029	216.745	−1.429	449.951	407.540	−85.151
298.15	29.910	216.255	216.255	0.	449.893	399.375	−69.969
300	29.930	216.440	216.256	0.055	449.888	399.062	−69.483
350	30.515	221.097	216.622	1.566	448.992	390.674	−58.305
400	31.154	225.213	217.444	3.108	448.666	382.365	−49.932
450	31.789	228.919	218.516	4.681	448.295	374.099	−43.424
500	32.388	232.300	219.728	6.286	447.885	365.877	−38.223
600	33.423	238.300	222.336	9.578	446.967	349.559	−30.432
700	34.239	243.516	224.997	12.963	445.946	333.404	−24.879
800	34.872	248.131	227.606	16.420	444.849	317.401	−20.724
900	35.364	252.268	230.120	19.933	443.695	301.538	−17.501
1000	35.752	256.015	232.526	23.489	442.496	285.807	−14.929
1100	36.061	259.438	234.819	27.081	441.261	270.198	−12.831
1200	36.312	262.586	237.003	30.700	376.424	255.781	−11.134
1300	36.519	265.501	239.085	34.342	375.909	245.748	−9.874
1400	36.692	268.214	241.070	38.002	375.367	235.756	−8.796
1500	36.838	270.751	242.965	41.679	374.803	225.803	−7.863
1600	36.964	273.132	244.777	45.369	374.218	215.888	−7.048
1700	37.074	275.377	246.511	49.071	373.614	206.011	−6.330
1800	37.170	277.499	248.174	52.784	372.994	196.170	−5.693
1900	37.256	279.511	249.771	56.505	372.357	186.364	−5.123
2000	37.333	281.424	251.306	60.235	371.706	176.592	−4.612
2100	37.403	283.247	252.784	63.972	371.041	166.852	−4.150
2200	37.466	284.988	254.209	67.715	370.362	157.145	−3.731
2300	37.525	286.655	255.583	71.465	369.671	147.468	−3.349
2400	37.579	288.253	256.912	75.220	368.967	137.822	−3.000
2500	37.630	289.788	258.196	78.980	368.252	128.206	−2.679
2600	37.678	291.265	259.440	82.746	367.525	118.619	−2.383
2700	37.723	292.688	260.645	86.516	366.786	109.059	−2.110
2800	37.765	294.061	261.814	90.290	366.037	99.528	−1.857
2900	37.806	295.387	262.949	94.069	365.277	90.023	−1.621
3000	37.845	296.669	264.052	97.851	364.506	80.544	−1.402
3100	37.882	297.911	265.124	101.638	363.725	71.092	−1.198
3200	37.918	299.114	266.168	105.428	362.933	61.665	−1.007
3300	37.953	300.281	267.184	109.221	362.131	52.262	−0.827
3400	37.987	301.415	268.174	113.018	361.319	42.885	−0.659
3500	38.019	302.516	269.140	116.819	360.497	33.531	−0.500
3600	38.051	303.588	270.082	120.622	359.666	24.201	−0.351
3700	38.082	304.631	271.001	124.429	358.824	14.894	−0.210
3800	38.113	305.647	271.900	128.239	357.973	5.610	−0.077
3900	38.143	306.637	272.778	132.052	357.112	−3.652	0.049
4000	38.172	307.603	273.636	135.867	356.241	−12.891	0.168
4100	38.201	308.546	274.476	139.686	355.360	−22.109	0.282
4200	38.229	309.467	275.299	143.507	354.471	−31.304	0.389
4300	38.257	310.367	276.104	147.332	353.571	−40.479	0.492
4400	38.285	311.247	276.892	151.159	352.662	−49.632	0.589
4500	38.312	312.107	277.665	154.989	351.744	−58.765	0.682
4600	38.339	312.950	278.423	158.821	350.816	−67.877	0.771
4700	38.366	313.775	279.167	162.657	349.879	−76.969	0.855
4800	38.392	314.583	279.896	166.495	348.933	−86.041	0.936
4900	38.418	315.375	280.612	170.335	347.977	−95.093	1.014
5000	38.444	316.151	281.315	174.178	347.012	−104.126	1.088
5100	38.470	316.912	282.006	178.024	346.038	−113.139	1.159
5200	38.496	317.660	282.684	181.872	345.054	−122.133	1.227
5300	38.521	318.393	283.351	185.723	344.061	−131.108	1.292
5400	38.546	319.114	284.007	189.576	343.059	−140.064	1.355
5500	38.571	319.821	284.652	193.432	342.048	−149.001	1.415
5600	38.596	320.516	285.286	197.291	341.028	−157.920	1.473
5700	38.621	321.200	285.910	201.151	339.998	−166.821	1.529
5800	38.645	321.872	286.524	205.015	338.959	−175.703	1.582
5900	38.670	322.532	287.129	208.881	337.911	−184.568	1.634
6000	38.694	323.182	287.724	212.749	336.854	−193.414	1.684

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 210.55 \pm 0.04\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 277.1 \pm 25\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 280.3 \pm 25\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
a^3	27509	2
	27590	2
	27607	2
$a(^3\pi)$	38613.9	6
$A^1\pi$	38797.6	2
$a'^3\Sigma^+$	38851.8	3
$c^3\Sigma^-$	39160.8	3
$(^1\Delta)$	39170	2
$(^1\Delta)$	39950	2

$\omega_e = 1285.08\ cm^{-1}$ $\omega_e x_e = 6.46\ cm^{-1}$ $\sigma = 1$
$B_e = 0.820046\ cm^{-1}$ $\alpha_e = 0.005922\ cm^{-1}$ $r_e = 1.5349$ Å

Enthalpy of Formation

Several values have been proposed for the enthalpy of formation or the dissociation energy of CS(g).[1-17] Many of these have been summarized by Hubin–Franksin *et al.*[16] although distinction was not made between $\Delta_f H°(0\ K)$ and $\Delta_f H°(298.15\ K)$. The values proposed or derivable for $\Delta_f H°(298.15\ K)$ vary from <32 kcal·mol^{-1} (electron impact of COS) to 77 ± 4 kcal·mol^{-1}(photodissociation of COS).[15] We give more weight to the equilibrium measurements — $\Delta_f H(298.15\ K) = 69$ kcal·mol^{-1} derived from,[3] 58 ± 5 and 60 ± 6 kcal·mol^{-1},[5] 55 ± 1 kcal·mol^{-1},[7] and 70 ± 2 kcal·mol^{-1} [11] (lack of data prohibits a complete re-analysis of these values) — and adopt $\Delta_f H°$(CS, g, 298.15 K) = 67 ± 6 kcal·mol^{-1} (280.328 ± 25 kJ·mol^{-1}). This leads to $\Delta_f H°(0\ K) = 66.2 \pm 6$ kcal·mol^{-1} and to $D_0° = 169.1 \pm 6$ kcal·mol^{-1} for the process CS(g) = C(g) + S(g), using JANAF values for the heats of formation of C(g) and S(g).[18]

Heat Capacity and Entropy

The molecular constants and electronic levels are those compiled by Rosen[19] except that the value of $\omega_e x_e = 8.46\ cm^{-1}$ given by Rosen[19] and by Suchard[20] appears to be a transcription error for the original $\omega_e x_e = 6.46\ cm^{-1}$ by Lagerqvist *et al.*[4]

The microwave spectra of carbon monosulfide have been critically reviewed by Lovas and Krupenie.[21] Their derived rotational constants are in agreement with those adopted.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.708	277.083	277.083	INFINITE
100	29.105	178.626	236.638	−5.801	279.240	262.725	−137.234
200	29.184	198.810	213.254	−2.889	280.184	245.766	−64.188
250	29.409	205.343	211.042	−1.425	280.333	237.141	−49.548
298.15	29.798	210.554	210.554	0.	280.328	228.820	−40.088
300	29.816	210.738	210.555	0.055	280.325	228.501	−39.786
350	30.358	215.374	210.920	1.559	280.192	219.872	−32.814
400	30.965	219.467	211.737	3.092	277.742	211.358	−27.601
450	31.583	223.150	212.804	4.656	276.753	203.110	−23.576
500	32.174	226.509	214.009	6.250	275.646	194.988	−20.370
600	33.214	232.470	216.601	9.521	273.754	179.039	−15.587
700	34.046	237.655	219.247	12.886	271.999	163.393	−12.193
800	34.698	242.245	221.840	16.324	270.305	147.994	−9.663
900	35.208	246.363	224.340	19.820	215.510	133.886	−7.771
1000	35.612	250.094	226.732	23.362	215.073	124.839	−6.521
1100	35.934	253.504	229.013	26.940	214.585	115.839	−5.501
1200	36.197	256.642	231.186	30.547	214.054	106.886	−4.653
1300	36.412	259.548	233.257	34.178	213.483	97.978	−3.937
1400	36.593	262.253	235.233	37.828	212.876	89.115	−3.325
1500	36.745	264.783	237.120	41.496	212.235	80.297	−2.796
1600	36.876	267.159	238.924	45.177	211.563	71.523	−2.335
1700	36.989	269.398	240.651	48.870	210.862	62.792	−1.929
1800	37.088	271.515	242.307	52.574	210.133	54.103	−1.570
1900	37.176	273.523	243.898	56.287	209.378	45.455	−1.250
2000	37.255	275.432	245.427	60.009	208.598	36.848	−0.962
2100	37.326	277.251	246.900	63.738	207.796	28.280	−0.703
2200	37.391	278.989	248.319	67.474	206.973	19.751	−0.469
2300	37.450	280.653	249.689	71.216	206.129	11.259	−0.256
2400	37.505	282.248	251.013	74.964	205.267	2.805	−0.061
2500	37.557	283.780	252.293	78.717	204.386	−5.613	0.117
2600	37.605	285.254	253.532	82.475	203.489	−13.995	0.281
2700	37.651	286.674	254.734	86.238	202.575	−22.342	0.432
2800	37.696	288.044	255.899	90.005	201.647	−30.656	0.572
2900	37.740	289.367	257.031	93.777	200.704	−38.936	0.701
3000	37.783	290.648	258.130	97.553	199.746	−47.183	0.822
3100	37.827	291.887	259.199	101.334	198.776	−55.398	0.933
3200	37.871	293.089	260.239	105.119	197.793	−63.581	1.038
3300	37.917	294.255	261.253	108.908	196.798	−71.734	1.135
3400	37.966	295.388	262.240	112.702	195.791	−79.856	1.227
3500	38.017	296.489	263.203	116.501	194.774	−87.949	1.313
3600	38.072	297.561	264.142	120.306	193.745	−96.012	1.393
3700	38.132	298.605	265.060	124.116	192.707	−104.046	1.469
3800	38.198	299.622	265.956	127.932	191.659	−112.053	1.540
3900	38.269	300.615	266.832	131.756	190.602	−120.031	1.608
4000	38.348	301.585	267.689	135.586	189.537	−127.983	1.671
4100	38.435	302.533	268.527	139.426	188.464	−135.908	1.731
4200	38.530	303.461	269.348	143.274	187.384	−143.806	1.788
4300	38.636	304.368	270.152	147.132	186.298	−151.679	1.843
4400	38.752	305.258	270.940	151.001	185.206	−159.526	1.894
4500	38.879	306.130	271.712	154.883	184.111	−167.348	1.943
4600	39.018	306.986	272.469	158.777	183.012	−175.147	1.989
4700	39.171	307.827	273.213	162.687	181.911	−182.921	2.033
4800	39.337	308.653	273.943	166.612	180.809	−190.671	2.075
4900	39.517	309.466	274.659	170.555	179.707	−198.399	2.115
5000	39.712	310.267	275.363	174.516	178.607	−206.105	2.153
5100	39.922	311.055	276.056	178.497	177.509	−213.788	2.190
5200	40.148	311.832	276.736	182.501	176.416	−221.450	2.224
5300	40.391	312.599	277.406	186.528	175.329	−229.091	2.258
5400	40.651	313.357	278.064	190.580	174.249	−236.711	2.290
5500	40.927	314.105	278.713	194.658	173.178	−244.312	2.320
5600	41.221	314.845	279.351	198.766	172.118	−251.893	2.350
5700	41.532	315.578	279.981	202.903	171.070	−259.455	2.378
5800	41.861	316.303	280.601	207.073	170.036	−266.999	2.405
5900	42.207	317.021	281.212	211.276	169.018	−274.525	2.430
6000	42.571	317.734	281.815	215.515	168.018	−282.035	2.455

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 237.977 \pm 0.08\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 116.131 \pm 0.84\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 116.943 \pm 0.84\ kJ·mol^{-1}$

Vibrational Frequencies, Degeneracies, and Anharmonicity and Rotational Constants			
ν, cm^{-1}	x_{ij} cm^{-1}	x_{ij} cm^{-1}	α_i,cm^{-1}
657.98 (1)	$x_{11} = -0.83$	$x_{12} = -1.75$	$\alpha_1 = 0.0002144$
395.93 (2)	$x_{22} = 0.82$	$x_{23} = -6.49$	$\alpha_2 = 0.0007130$
1535.35 (1)	$x_{33} = -6.54$	$x_{13} = -7.59$	$\alpha_3 = 0.0002148$

Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distance: C–S = 1.553 Å
Bond Angle: S–C–S = 180°
$B_e = 0.109277\ cm^{-1}$; $g_{22} = -0.74\ cm^{-1}$
$D_o = 1.05 \times 10^{-8}\ cm^{-1}$

Enthalpy of Formation

Good *et al.*[1] have determined $\Delta_f H°(CS_2, l, 298.15\ K) = 21.37 \pm 0.17$ kcal·mol^{-1} by rotating bomb combustion calorimetry. They combined this with an unpublished measurement of $\Delta_{vap}H°(298.15\ K) = 6.61 \pm 0.02$ kcal·mol^{-1} to obtain $\Delta_f H°(CS_2, g, 298.15\ K) = 27.98 \pm 0.19$ kcal·mol^{-1}. We adopt $\Delta_{vap}H°(298.15\ K) = 6.578 \pm 0.003$ kcal·mol^{-1} determined by Weddington *et al.*[2] by vapor flow calorimetry and obtain the adopted $\Delta_f H°(CS_2, g, 298.15\ K) = 27.95 \pm 0.20$ kcal·mol^{-1}.

The resulting $\Delta_f H°(CS_2, g, 0\ K) = 27.75 \pm 0.20$ kcal·mol^{-1} leads to $\Delta_a H°(0\ K) = 273.33 \pm 0.66$ kcal·mol^{-1} for the process $CS_2(g) = C(g) + 2\ S(g)$. Auxiliary data are from the JANAF Tables.[12]

Heat Capacity and Entropy

The fundamental ground state vibrational frequencies are those from a re-analysis of infra-red and Raman spectra by Guenther and Stoicheff, referenced by Kleman[3] as a private communication. Several sets of anharmonicity constants and/or rotational constants have been published.[2,4-9] Some are corrected for Fermi resonance to some degree in some manner,[6,7,9] others are not.[2,4] We adopt the x_{ij}, x_{ij}, α_i, and g_{22} terms determined from the least-square estimates of the force constants in the general quartic force field by Giguere *et al.*[9] The rotational constants B_e and D_o are from McBride and Gordon.[7] The bond distance, r_e, is a rounded average of 1.5529 ± 0.0005 Å[4] and 1.5523 ± 0.0005 Å[5] and is consistent with the adopted B_e. The bond angle of 180° is from Cross and Brockway.[10]

Waddington *et al.*[2] have measured $C_p°$ of carbon disulfide gas in the 325.65–502.25 K range. At 325.65 K, the value calculated by Waddington *et al.*,[2] where Fermi resonance was not considered explicitly, is approximately 0.03% lower than the observed value; at 300 K, the present table is higher than the table calculated by Waddington *et al.*[2] by about 0.3%. At 502.25 K, the present table is approximately 0.6% higher (0.074 cal·K^{-1}·mol^{-1}) than the measured value of 12.484 cal·K^{-1}·mol^{-1}. The value calculated by Waddington *et al.*[2] is 0.2% higher (0.025 cal·K^{-1}·mol^{-1}) than the observed value. At 6000 K, the value of $C_p°$ in the present table is approximately 1.1% higher (0.17 cal·K^{-1}·mol^{-1}) than the value calculated with the anharmonicity constants used by Waddington *et al.*[2]

The tabulated functions have been generated by the NASA–Lewis computer program.[11] We adopted these functions directly for 0 to 298.15 K and reproduce the functions at higher temperatures by integration of $C_p°$.

The allowed error of ±0.02 cal·K^{-1}·mol^{-1} for $S°$(298.15 K) includes the values calculated using other anharmonicity correction constants.[2,6,7]

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[12]JANAF Thermochemical Tables: C(g), 3-31-61; S(g), 6-30-71.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.687	116.131	116.131	INFINITE
100	30.995	196.787	274.228	−7.744	117.634	100.555	−52.525
200	39.648	220.929	241.981	−4.210	117.558	83.443	−21.793
298.15	45.664	237.977	237.977	0.	116.943	66.816	−11.706
300	45.751	238.260	237.978	0.085	116.927	66.505	−11.580
400	49.677	251.995	239.824	4.868	111.494	50.016	−6.531
500	52.494	263.398	243.431	9.984	107.427	35.091	−3.666
600	54.616	273.165	247.592	15.344	104.039	20.954	−1.824
700	56.242	281.711	251.868	20.890	101.119	7.342	−0.548
800	57.503	289.307	256.082	26.580	98.466	−5.871	0.383
900	58.493	296.140	260.160	32.382	−10.281	−16.601	0.963
1000	59.283	302.345	264.073	38.272	−10.226	−17.306	0.904
1100	59.923	308.026	267.814	44.233	−10.201	−18.016	0.855
1200	60.450	313.263	271.386	50.253	−10.207	−18.726	0.815
1300	60.891	318.120	274.796	56.320	−10.243	−19.435	0.781
1400	61.266	322.646	278.054	62.429	−10.311	−20.139	0.751
1500	61.588	326.884	281.170	68.572	−10.409	−20.838	0.726
1600	61.869	330.868	284.153	74.745	−10.537	−21.530	0.703
1700	62.118	334.627	287.012	80.944	−10.695	−22.212	0.682
1800	62.340	338.184	289.757	87.167	−10.882	−22.884	0.664
1900	62.539	341.560	292.396	93.412	−11.095	−23.545	0.647
2000	62.722	344.772	294.935	99.675	−11.335	−24.194	0.632
2100	62.889	347.837	297.382	105.955	−11.598	−24.831	0.618
2200	63.045	350.766	299.742	112.252	−11.882	−25.455	0.604
2300	63.189	353.571	302.022	118.564	−12.188	−26.065	0.592
2400	63.325	356.264	304.226	124.890	−12.514	−26.661	0.580
2500	63.453	358.851	306.360	131.229	−12.857	−27.244	0.569
2600	63.575	361.342	308.427	137.580	−13.217	−27.812	0.559
2700	63.691	363.744	310.432	143.943	−13.592	−28.366	0.549
2800	63.802	366.062	312.377	150.318	−13.981	−28.906	0.539
2900	63.909	368.303	314.267	156.704	−14.384	−29.432	0.530
3000	64.012	370.471	316.105	163.100	−14.800	−29.944	0.521
3100	64.111	372.572	317.893	169.506	−15.228	−30.442	0.513
3200	64.208	374.609	319.633	175.922	−15.668	−30.926	0.505
3300	64.303	376.586	321.329	182.348	−16.118	−31.396	0.497
3400	64.394	378.507	322.983	188.782	−16.580	−31.852	0.489
3500	64.484	380.375	324.596	195.226	−17.054	−32.294	0.482
3600	64.572	382.193	326.171	201.679	−17.538	−32.723	0.475
3700	64.658	383.963	327.709	208.141	−18.034	−33.138	0.468
3800	64.742	385.689	329.212	214.611	−18.541	−33.539	0.461
3900	64.825	387.371	330.682	221.089	−19.060	−33.927	0.454
4000	64.907	389.014	332.120	227.576	−19.591	−34.302	0.448
4100	64.988	390.617	333.527	234.070	−20.135	−34.663	0.442
4200	65.067	392.184	334.905	240.573	−20.692	−35.010	0.435
4300	65.145	393.716	336.255	247.084	−21.261	−35.344	0.429
4400	65.223	395.215	337.578	253.602	−21.845	−35.665	0.423
4500	65.299	396.682	338.875	260.128	−22.443	−35.973	0.418
4600	65.375	398.118	340.148	266.662	−23.056	−36.267	0.412
4700	65.450	399.524	341.396	273.203	−23.684	−36.547	0.406
4800	65.524	400.903	342.621	279.752	−24.327	−36.814	0.401
4900	65.598	402.255	343.825	286.308	−24.987	−37.067	0.395
5000	65.671	403.581	345.007	292.871	−25.663	−37.307	0.390
5100	65.743	404.882	346.168	299.442	−26.355	−37.533	0.384
5200	65.815	406.159	347.309	306.020	−27.065	−37.745	0.379
5300	65.886	407.414	348.432	312.605	−27.793	−37.944	0.374
5400	65.957	408.646	349.535	319.197	−28.538	−38.128	0.369
5500	66.027	409.857	350.621	325.796	−29.301	−38.299	0.364
5600	66.097	411.047	351.690	332.403	−30.082	−38.455	0.359
5700	66.166	412.218	352.741	339.016	−30.882	−38.598	0.354
5800	66.235	413.369	353.777	345.636	−31.700	−38.726	0.349
5900	66.303	414.502	354.796	352.263	−32.536	−38.840	0.344
6000	66.372	415.617	355.801	358.896	−33.392	−38.940	0.339

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 16.485 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -70.530 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -71.546 \pm 6.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from $\Delta_f H°(298.15\ K) = -591.9\ kcal \cdot mol^{-1}$ for $SIC(\alpha) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$ based on the tentative value of $\Delta_f H°(298.15\ K) = -223 \pm 1\ kcal \cdot mol^{-1}$ for $CF_4(g)$. Greenberg *et al.*[1] determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey *et al.*[2] obtained by oxygen bomb calorimetry yield a $\Delta_f H°$ which is over 2 $kcal \cdot mol^{-1}$ more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained mass spectrometrically by Drowart *et al.*[3] are in close agreement with the selected $\Delta_f H°$, but Knudsen weight loss data of Grieveson and Alcock[4] and solubility–activity data of Kirkwood and Chipman[5] yield values less negative by 2 and 3 $kcal \cdot mol^{-1}$, respectively. The results are summarized below.

The data of Drowart *et al.*[3] show a significant drift while those of Grieveson and Alcock[4] do not, but the latter should be corrected for $C_2Si(g)$ and $CSi_2(g)$ which are present in amounts of about 4 and 3%, respectively, at 2000 K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin *et al.*[6] and Ghoshtagore[7] yield apparent pressures which are smaller by factors of 1/30 to 1/10000.

Source	Method	Reaction	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	F_2 Calorimetry	A	298	–	−591.9		–	−17.1
2	O_2Calorimetry	B	303	–	−292.0		–	−19.6
3	Mass Spec.	C	2149–2316	7	136.9 ± 0.7	124.61	−5.6 ± 0.3	−16.9(−17.6)*
4	Knudsen Wt. Loss	C	1785–2004	10	122.9 ± 0.7	122.66	−0.2 ± 0.4	−15.0
5	Soly. in Pb	D	1693	1	–	25.66	–	−14.1

A) $SiC(\alpha) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$

B) $SiC(\alpha) + 2O_2(g) \rightarrow SiO_2$(low–quartz) $+ CO_2(g)$

C) $SiC(\alpha) \rightarrow C$(graph) $+ Si(g)$

D) $SiC(\alpha) \rightarrow C$(graph) $+ Si(l)$

*Value in parentheses is based on authors' data for $Si(l) \rightarrow Si(g)$ rather than JANAF value.

Heat Capacity and Entropy

Low temperature heat capacities are from data (54–296 K) of Humphrey *et al.*[2] and are in good agreement with earlier data (54–295 K) of Kelley.[8] The entropy is obtained from $C_p°$ using $S°(50\ K) = 0.038\ cal \cdot K^{-1} \cdot mol^{-1}$. $C_p°$ above room temperature is based on enthalpy data of Humphrey *et al.*[2] [389–1789 K], Walker *et al.*[9] [373–1073 K] and Magnus[10] [372–1172 K]. Maximum deviations of the data from the selected values are 1.4, 2 and −1.7%, respectively; these occur in the range 370–621 K. Kirillin *et al.*[11] obtained enthalpy data (1114–2843 K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.73% iron impurity, these data deviate by −1 ± 1.5% from the selected values. Enthalpies (793–1790 K) of Fieldhouse and Hedge[12] are high by 1–8% while those of Maksimenko and Polubelova[13] were not available for analysis.

Transition Data

SiC(α), also called hexagonal II or 6H, is one of the more common of many hexagonal forms which arise from various possible stacking sequences of the hexagonal SiC layers.[14] The properties of these phases are so similar that they have not been adequately differentiated thermodynamically. It has frequently been assumed that cubic SiC(β) transforms to alpha at about 2300 K, but this seems unlikely since both phases have been prepared over temperature ranges of 1700–3000 K.[14] Heat of formation and equilibrium data indicate that alpha is less stable up to 2000 K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data

The decomposition temperature, $T_{dcm} = \sim 3245$ K, is calculated as the value at which the total pressure reaches one atm for vapor consisting of C_2Si(44.3 mol %), Si(32.0%), CSi_2(21.2%), Si_2(1.9%), CSi(0.27%), and Si_3(0.25%). The tables predict decomposition to graphite and pure liquid silicon at about 3280 K; however, Scace and Slack[15] observed peritectic decomposition to graphite and solution containing 19 atom % of carbon at 3103 ± 40 K. In contrast, Dolloff[16] reported the peritectic at 2813 ± 40 K and 27% carbon. Badami[17] has shown that decomposition in vacuum at lower temperatures (2400 K) leads to graphite.

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Continued on page 700

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−3.252	−70.530	−70.530	INFINITE
100	4.197	1.414	32.865	−3.145	−70.748	−70.411	36.779
200	16.246	7.954	18.613	−2.132	−71.240	−69.881	18.251
298.15	26.761	16.485	16.485	0.	−71.546	−69.139	12.113
300	26.932	16.651	16.485	0.050	−71.550	−69.124	12.036
400	34.100	25.466	17.639	3.131	−71.613	−68.301	8.919
500	38.610	33.593	20.030	6.781	−71.567	−67.477	7.049
600	41.723	40.922	22.912	10.806	−71.496	−66.666	5.804
700	44.007	47.534	25.965	15.098	−71.425	−65.866	4.915
800	45.769	53.530	29.042	19.590	−71.363	−65.076	4.249
900	47.170	59.004	32.071	24.239	−71.310	−64.294	3.732
1000	48.321	64.035	35.019	29.016	−71.268	−63.517	3.318
1100	49.283	68.687	37.871	33.897	−71.236	−62.743	2.979
1200	50.108	73.011	40.622	38.868	−71.216	−61.972	2.698
1300	50.823	77.051	43.270	43.915	−71.208	−61.202	2.459
1400	51.451	80.841	45.820	49.029	−71.216	−60.432	2.255
1500	52.011	84.410	48.275	54.203	−71.241	−59.661	2.078
1600	52.518	87.783	50.640	59.430	−71.285	−58.888	1.922
1700	52.974	90.981	52.919	64.704	−121.527	−57.665	1.772
1800	53.396	94.021	55.119	70.023	−121.385	−53.912	1.564
1900	53.781	96.918	57.243	75.382	−121.224	−50.168	1.379
2000	54.141	99.686	59.297	80.779	−121.047	−46.432	1.213
2100	54.476	102.336	61.284	86.210	−120.854	−42.706	1.062
2200	54.785	104.877	63.208	91.673	−120.647	−38.990	0.926
2300	55.082	107.319	65.073	97.166	−120.427	−35.283	0.801
2400	55.363	109.669	66.882	102.689	−120.194	−31.586	0.687
2500	55.630	111.935	68.640	108.238	−119.949	−27.899	0.583
2600	55.881	114.122	70.347	113.814	−119.693	−24.222	0.487
2700	56.124	116.235	72.008	119.414	−119.426	−20.555	0.398
2800	56.358	118.281	73.624	125.039	−119.149	−16.898	0.315
2900	56.580	120.262	75.198	130.686	−118.864	−13.251	0.239
3000	56.798	122.184	76.732	136.355	−118.569	−9.615	0.167
3100	57.007	124.050	78.229	142.045	−118.266	−5.988	0.101
3200	57.208	125.863	79.689	147.756	−117.955	−2.371	0.039
3300	57.404	127.626	81.115	153.486	−117.636	1.236	−0.020
3400	57.593	129.343	82.509	159.236	−117.310	4.833	−0.074
3500	57.781	131.015	83.871	165.005	−116.978	8.421	−0.126
3600	57.961	132.645	85.203	170.792	−500.790	22.460	−0.326
3700	58.137	134.236	86.507	176.597	−500.031	36.984	−0.522
3800	58.312	135.789	87.783	182.420	−499.268	51.488	−0.708
3900	58.480	137.305	89.034	188.259	−498.500	65.971	−0.884
4000	58.647	138.788	90.259	194.116	−497.728	80.435	−1.050

PREVIOUS: December 1962 CURRENT: March 1967

$S°(298.15\ K) = 16.610 \pm 0.13\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -72.221 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -73.220 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from $\Delta_r H°(298.15\ K) = -591.5\ kcal·mol^{-1}$ for $SiC(\beta) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$, based on the tentative value of $\Delta_f H°(CF_4, g, 298.15\ K) = -223 \pm 1\ kcal·mol^{-1}$. Greenberg *et al.*[1] determined the enthalpy of reaction by fluorine bomb calorimetry. Data of Humphrey *et al.*[2] obtained by oxygen bomb calorimetry yield a $\Delta_f H°$ which is over 3 $kcal·mol^{-1}$ more negative; however, this difference is probably within the uncertainties due to use of large amounts of Ti as a kindling agent and to corrections for incomplete combustion. Decomposition pressure data obtained with the Knudsen weight loss method by Davis *et al.*[3] are in good agreement with the selected $\Delta_f H°$, but similar data of Grieveson and Alcock[4] and solubility–activity data of Rein and Chipman[5] and d'Entremont and Chipman[6] yield values less negative by 1.6 to 2.5 $kcal·mol^{-1}$. The results ar summarized below. Other equilibrium data[5] relating SiC and SiO_2 are not included, pending the revision of tables for SiO_2.

The data of Davis *et al.* show a serious drift, while those of Grieveson *et al.* do not; but the latter should be corrrected for $C_2Si(g)$ and $CSi_2(g)$ which are present in amounts of about 4 and 3%, respectively, at 2000 K. Silicon carbide may have a small vaporization coefficient, since rates of free evaporation reported by Voronin *et al.*[7] and Ghoshtagore[8] yield apparent pressures which are smaller by factors of 1/30 to 1/10000.

Source	Method	Reaction	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	F_2 Calorimetry	A	298	–	−591.5		–	−17.5
2	O_2 Calorimetry	B	303	–	−290.9		–	−20.6
3	Knudsen Wt. Loss	C	2117–2171	8	167 ± 28	126.10	−19 ± 13	−18.4(−17.6)*
4	Knudson Wt. Loss	C	1808–1973	6	123.3 ± 0.3	122.65	−04 ± 0.2	−15.0
5	Soly. in C–Fe	D	1823–1873	2	32.0	27.43	−2.5	−15.9
6	Soly. in Ag	D	1693	1	–	27.31	–	−15.7

A) $SiC(\beta) + 4F_2(g) \rightarrow SiF_4(g) + CF_4(g)$
B) $SiC(\beta) + 2O_2(g) \rightarrow SiO_2$(low quartz) $+ CO_2(g)$
C) $SiC(\beta) \rightarrow C$(graph) $+ Si(g)$
D) $SiC(\beta) \rightarrow C$(graph) $+ Si(l)$

*Value in parentheses is based on author's data for $Si(l) \rightarrow Si(g)$ rather than JANAF value.

Heat Capacity and Entropy

Low temperature heat capacities are from data (54–296 K) of Humphrey *et al.*[2] The entropy is obtained from $C_p°$ using $S°(50\ K) = 0.041$ cal·K^{-1}·mol^{-1}. $C_p°$ above room temperature is based on Humphrey's enthalpy data (389–1693 K), which show a maximum deviation of ±1.2% from the selected functions. Humphrey's sample contained about 1% of α–SiC and about 0.6% of other impurities. Kirillin *et al.*[9] obtained enthalpy data (1114–2843 K) for SiC mixed with 12% free carbon. When corrected for free carbon but not for 0.73% iron impurity, these data deviate by −1 ± 2% from the selected values.

Transition Data

SiC(β), also called cubic or 3C, has a structure of the diamond or zinc blend type.[10] The cubic phase differs from the many hexagonal forms only in the order of the stacking sequence of the hexagonal SiC layers. It has frequently been assumed that β transforms into α at about 2300 K, but this seems unlikely, since both phases have been prepared over temperature ranges of 1700–3000 K.[10] Heat of formation and equilibrium data indicate that β is more stable up to 2000 K. The adopted functions suggest that this is the case at all temperatures; however, the stability difference is small.

Decomposition Data

The decomposition temperature, T_{dcm} = ~3259 K, is calculated as the value at which the total pressure reaches one atm for vapor consisting of C_2Si(45.4 mol %), Si(32.1%), CSi_2(20.1%), Si_2(1.8%), CSi(0.28%) and Si_3(0.23%). The tables predict decomposition to graphite and pure liquid silicon at about 3337 K; however, Scace and Slack[11] observed peritectic decomposition to graphite and solution containing 19 atom % of carbon at 3103 ± 40 K. In contrast, Dolloff[12] reported the peritectic at 2813 ± 40 K and 27% carbon.

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Continued on page 701

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−3.270	−72.221	−72.221	INFINITE
100	4.263	1.460	33.062	−3.160	−72.437	−72.104	37.664
200	16.301	8.033	18.740	−2.141	−72.923	−71.580	18.695
298.15	26.840	16.610	16.610	0.	−73.220	−70.850	12.413
300	27.008	16.777	16.611	0.050	−73.223	−70.835	12.333
400	34.100	25.598	17.765	3.133	−73.284	−70.025	9.144
500	38.639	33.727	20.158	6.784	−73.237	−69.215	7.231
600	41.790	41.066	23.042	10.814	−73.161	−68.417	5.956
700	44.108	47.690	26.098	15.115	−73.082	−67.633	5.047
800	45.878	53.700	29.178	19.618	−73.009	−66.859	4.365
900	47.283	59.188	32.212	24.278	−72.945	−66.094	3.836
1000	48.421	64.231	35.165	29.065	−72.892	−65.336	3.413
1100	49.363	68.891	38.022	33.956	−72.851	−64.583	3.067
1200	50.158	73.221	40.777	38.932	−72.824	−63.832	2.779
1300	50.840	77.263	43.430	43.983	−72.813	−63.084	2.535
1400	51.430	81.053	45.984	49.097	−72.821	−62.335	2.326
1500	51.944	84.619	48.442	54.266	−72.851	−61.585	2.145
1600	52.400	87.986	50.809	59.484	−72.904	−60.832	1.986
1700	52.806	91.176	53.090	64.745	−123.160	−59.629	1.832
1800	53.170	94.204	55.291	70.044	−123.038	−55.895	1.622
1900	53.497	97.088	57.416	75.377	−122.903	−52.169	1.434
2000	53.798	99.840	59.469	80.742	−122.757	−48.450	1.265
2100	54.070	102.471	61.454	86.136	−122.601	−44.738	1.113
2200	54.321	104.992	63.376	91.556	−122.438	−41.034	0.974
2300	54.555	107.412	65.239	97.000	−122.267	−37.338	0.848
2400	54.769	109.739	67.045	102.466	−122.090	−33.649	0.732
2500	54.965	111.979	68.797	107.953	−121.908	−29.967	0.626
2600	55.153	114.138	70.500	113.459	−121.722	−26.294	0.528
2700	55.329	116.223	72.155	118.983	−121.531	−22.627	0.438
2800	55.492	118.238	73.765	124.524	−121.338	−18.967	0.354
2900	55.643	120.188	75.332	130.081	−121.142	−15.315	0.276
3000	55.789	122.077	76.859	135.653	−120.944	−11.669	0.203
3100	55.928	123.908	78.348	141.239	−120.746	−8.030	0.135
3200	56.057	125.686	79.799	146.838	−120.546	−4.397	0.072
3300	56.183	127.413	81.216	152.450	−120.346	−0.770	0.012
3400	56.300	129.092	82.600	158.074	−120.146	2.850	−0.044
3500	56.413	130.726	83.951	163.710	−119.946	6.465	−0.096
3600	56.522	132.316	85.273	169.357	−503.899	20.535	−0.298
3700	56.626	133.866	86.565	175.014	−503.288	35.094	−0.495
3800	56.722	135.378	87.830	180.681	−502.679	49.637	−0.682
3900	56.819	136.853	89.068	186.359	−502.074	64.163	−0.859
4000	56.911	138.292	90.281	192.045	−501.472	78.675	−1.027

PREVIOUS: CURRENT: March 1967

$S°(298.15\ K) = [213.04]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 714.7 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 719.6 \pm 33\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma]$	0	[1]
	[1000]	[6]
	[5000]	[3]
	[8000]	[2]
	[14000]	[2]
	[18000]	[1]

$\omega_e = [1226]\ cm^{-1}$ $\omega_e x_e = [5]\ cm^{-1}$ $\alpha = 1$
$B_e = [0.6933]\ cm^{-1}$ $\alpha_e = [0.006]\ cm^{-1}$ $r_e = [1.7]$ Å

Enthalpy of Formation

Drowart *et al.* have used the Knudsen effusion–mass spectrometric technique to determine the vapor equilibrium over the systems SiC–graphite[1] and boron–silicon–graphite.[2] 3rd law analysis of the partial pressures of Si and SiC yields the results summarized below. The adopted value, $\Delta_f H°(298.15\ K) = 172 \pm 8$ is the mean of the two results and the uncertainty reflects the possible effect of an error of up to 4 $cal·K^{-1}·mol^{-1}$ in the functions. The corresponding dissociation energy is $D_0° = 106.5 \pm 8\ kcal·mol^{-1}$.

Source	Method	Reaction*	T/K	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15)$ kcal·mol⁻¹
1	Mass Spec.	A	2181–2316	3	27.1 ± 4	65.94	17 ± 2	173.6
2	Mass Spec.	A	2249–2344	3	48.7 ± 4	62.67	6 ± 2	170.4

*Reaction: (A) C(graphite) + Si(g) = SiC(g)

Heat Capacity and Entropy

The ground state is assumed to be $^1\Sigma$, as suggested by Weltner and McLeod.[3] By analogy with C_2, there should be a low-lying $^3\Pi$ excited state; this would dominate the thermodynamic functions at temperatures above 2000 K if the level lies below 5000 cm^{-1}. The $^3\Pi$ level is assumed to lie at 1000 cm^{-1}, intermediate between the value[4] observed for C_2 and that estimated for Si_2 (see JANAF table). Additional excited states, $^3\Sigma$, $^1\Pi$, $^1\Delta$ and $^1\Sigma$, are estimated by comparison with those observed or predicted[5] for C_2. The estimates for the electronic levels are relatively uncertain and probably yield an upper limit for the entropy at temperatures where SiC(g) is significant. A probable lower limit for the electronic contribution may be obtained by increasing the $^3\Pi$ level to 7000 cm^{-1} and omitting the other excited states. This would reduce the entropy by 3.5 and 2.0 $cal·K^{-1}·mol^{-1}$ at 2000 and 4000 K.

The vibrational frequency is that estimated by Weltner and McLeod[3] from a valence bond calculation using $k = 7.44 \times 10^5$ dyn/cm obtained from C_2Si. The constants $\omega_e x_e$, α_e, and r_e are estimated by interpolation between those[4,6] for the $^3\Pi_u$ states of Si_2 and C_2. Use of constants based on the $^3\Pi$ state is consistent with the assumption that this state dominates the electronic partition function at high temperatures. B_e is calculated from r_e.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹·mol⁻¹)	$S°$ (J·K⁻¹·mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹·mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−9.266	714.651	714.651	INFINITE
100	29.111	178.849	242.437	−6.359	717.232	699.826	−365.552
200	31.133	199.342	216.303	−3.392	718.694	681.775	−178.061
250	34.526	206.629	213.654	−1.756	719.184	672.487	−140.508
298.15	38.417	213.044	213.044	0.	719.648	663.452	−116.234
300	38.562	213.282	213.044	0.071	719.666	663.103	−115.456
350	42.006	219.498	213.527	2.090	720.179	653.636	−97.550
400	44.241	225.267	214.639	4.251	720.702	644.093	−84.110
450	45.276	230.548	216.118	6.494	721.192	634.487	−73.649
500	45.426	235.333	217.804	8.764	721.610	624.830	−65.276
600	44.395	243.540	221.433	13.264	722.156	605.416	−52.706
700	42.946	250.274	225.087	17.631	722.302	585.943	−43.724
800	41.723	255.925	228.598	21.861	722.103	566.473	−36.987
900	40.839	260.785	231.911	25.987	721.631	547.045	−31.750
1000	40.250	265.055	235.016	30.039	720.950	527.681	−27.563
1100	39.884	268.872	237.923	34.044	720.105	508.394	−24.142
1200	39.677	272.333	240.649	38.021	719.132	489.190	−21.294
1300	39.581	275.504	243.210	41.983	718.055	470.071	−18.888
1400	39.561	278.437	245.622	45.940	716.889	451.038	−16.828
1500	39.591	281.167	247.902	49.897	715.648	432.092	−15.047
1600	39.654	283.724	250.062	53.859	714.339	413.231	−13.491
1700	39.737	286.130	252.113	57.828	662.791	394.900	−12.134
1800	39.831	288.404	254.067	61.807	661.593	379.176	−11.003
1900	39.931	290.560	255.931	65.795	660.383	363.519	−9.994
2000	40.031	292.611	257.715	69.793	659.162	347.926	−9.087
2100	40.129	294.567	259.423	73.801	657.931	332.395	−8.268
2200	40.224	296.436	261.063	77.819	656.693	316.922	−7.525
2300	40.314	298.226	262.641	81.846	655.447	301.506	−6.847
2400	40.398	299.943	264.159	85.881	654.193	286.144	−6.228
2500	40.477	301.594	265.624	89.925	652.932	270.834	−5.659
2600	40.550	303.183	267.038	93.976	651.664	255.575	−5.135
2700	40.618	304.714	268.405	98.035	650.389	240.366	−4.650
2800	40.680	306.193	269.729	102.100	649.106	225.203	−4.201
2900	40.738	307.621	271.011	106.171	647.816	210.086	−3.784
3000	40.791	309.003	272.254	110.247	646.518	195.014	−3.396
3100	40.839	310.342	273.461	114.329	645.212	179.986	−3.033
3200	40.884	311.639	274.634	118.415	643.899	164.999	−2.693
3300	40.925	312.898	275.775	122.505	642.577	150.054	−2.375
3400	40.963	314.120	276.885	126.600	641.248	135.149	−2.076
3500	40.998	315.308	277.966	130.698	639.910	120.283	−1.795
3600	41.030	316.463	279.019	134.799	254.411	115.917	−1.682
3700	41.060	317.588	280.046	138.904	253.470	112.082	−1.582
3800	41.087	318.683	281.049	143.011	252.518	108.274	−1.488
3900	41.112	319.751	282.027	147.121	251.557	104.490	−1.399
4000	41.135	320.792	282.984	151.234	250.585	100.732	−1.315
4100	41.157	321.808	283.918	155.348	249.603	96.998	−1.236
4200	41.176	322.800	284.832	159.465	248.612	93.288	−1.160
4300	41.194	323.769	285.727	163.583	247.611	89.601	−1.088
4400	41.211	324.716	286.602	167.704	246.601	85.938	−1.020
4500	41.227	325.643	287.459	171.826	245.582	82.298	−0.955
4600	41.241	326.549	288.299	175.949	244.554	78.681	−0.893
4700	41.254	327.436	289.123	180.074	243.516	75.086	−0.834
4800	41.266	328.305	289.930	184.200	242.470	71.514	−0.778
4900	41.277	329.156	290.722	188.327	241.414	67.963	−0.724
5000	41.287	329.990	291.499	192.455	240.349	64.434	−0.673
5100	41.296	330.807	292.261	196.584	239.274	60.926	−0.624
5200	41.305	331.609	293.010	200.714	238.190	57.440	−0.577
5300	41.312	332.396	293.746	204.845	237.097	53.974	−0.532
5400	41.319	333.168	294.469	208.977	235.993	50.529	−0.489
5500	41.326	333.927	295.180	213.109	234.881	47.105	−0.447
5600	41.331	334.671	295.878	217.242	233.757	43.701	−0.408
5700	41.337	335.403	296.565	221.375	232.623	40.317	−0.369
5800	41.341	336.122	297.241	225.509	231.478	36.954	−0.333
5900	41.346	336.829	297.906	229.643	230.323	33.610	−0.298
6000	41.350	337.524	298.561	233.778	229.156	30.285	−0.264

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K)$ = [242.286] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 531.7 \pm 25\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 535.6 \pm 25\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[1]
[12000]	[6]
[19000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[670](1)
[275](2)
[1600](1)

Ground State Quantum Weight: 1 σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: C–Si = [1.75] Å
Bond Angle: C–Si–Si = [180]°
Rotational Constant: B_O = [0.097996] cm^{-1}

Enthalpy of Formation

The selected value is an average based on the equilibrium data summarized below. Drowart *et al.*[1] have used the Knudsen effusion–mass spectrometric technique to determine the vapor species over the SiC–graphite,[1] SiC–silicon[2] and boron–carbon–silicon[3] systems. 3rd law analysis of the aprtial pressures of CSi_2 and Si yields the concordant values 127.4, 127.9 and 128.6 $kcal·mol^{-1}$. Two of the drifts are rather large, but they are opposite in sign so that no consistent entropy difference is apparent between the data and the tabulated functions. The drifts may be related to the low condensation coefficient for CSi_2 suggested by Drowart and DeMaria.[2] Rates of free evaporation reported by Voronin *et al.*[4] yield apparent pressures which are lower by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of $\Delta_f H°(298.15\ K)$ = 128 ± 6 $kcal·mol^{-1}$ (535.552 ± 25 $kJ·mol^{-1}$) includes allowance for an error in the entropy of up to 3 $cal·K^{-1}·mol^{-1}$.

Source	Method	Reaction*	T/K	Data Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
[1]	Mass Spec.	A	2149–2316	7	−104 ± 7	−88.0	7.4 ± 3.0	127.4
[2]	Mass Spec.	B	1825–2160	7	141 ± 3	134.4	−3.4 ± 1.7	127.9
[3]	Mass Spec.	A	2083–2344	6	−68 ± 25	−86.8	−9 ± 12	128.6

*Reactions: A) C(graph) + 2 Si(g) = CSi_2(g) B) SiC(α) + Si(l) = CSi_2(g)

Heat Capacity and Entropy

Weltner and McLeod[5] observed a band system in absorption at 5300 Å in matrix isolation and assigned this tentatively to the transition $^1\Pi_u$ X Σ^1_g of CSi_2. This assignment is adopted, although the evidence is not at all conclusive. A $^3\Pi_u$ excited state is assumed to lie at 12000 cm^{-1}, presumably arising from the same molecular orbital configuration as the $^1\Pi_u$ state. A linear, symmetric structure is assumed, as suggested by Weltner. The bond distance is estimated by comparison with Si_2, C_2 and C_3. Vibrational frequencies are estimated from a valence bond calculation using $k_1 = 7.46 \times 10^5$ and $k\delta/l^2 = 0.11 \times 10^5$dyn/cm. The stretching force constant is taken from C_2Si,[5] while the bending force constant is from C_2Si and the $^1\Pi_u$excited state of C_3.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-\{G°-H°(T_r)\}/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−11.389	531.650	531.650	INFINITE
100	34.326	197.543	281.045	−8.350	534.097	515.204	−269.115
200	42.817	224.254	246.492	−4.448	535.316	495.747	−129.476
250	45.453	234.105	243.056	−2.238	535.530	485.825	−101.508
298.15	47.424	242.286	242.286	0.	535.552	476.248	−83.437
300	47.491	242.580	242.287	0.088	535.550	475.880	−82.858
350	49.147	250.029	242.871	2.505	535.427	465.943	−69.538
400	50.550	256.685	244.189	4.998	535.195	456.032	−59.552
450	51.770	262.711	245.918	7.557	534.877	446.155	−51.788
500	52.843	268.222	247.877	10.173	534.487	436.317	−45.582
600	54.631	278.022	252.104	15.550	533.534	416.769	−36.283
700	56.029	286.553	256.429	21.086	532.401	397.395	−29.654
800	57.122	294.108	260.676	26.746	531.122	378.195	−24.694
900	57.979	300.888	264.774	32.503	529.720	359.162	−20.845
1000	58.657	307.033	268.697	38.336	528.208	340.291	−17.775
1100	59.199	312.650	272.441	44.230	526.597	321.576	−15.270
1200	59.640	317.821	276.010	50.172	524.891	303.013	−13.190
1300	60.004	322.609	279.413	56.155	523.093	284.595	−11.435
1400	60.315	327.068	282.659	62.171	521.205	266.319	−9.936
1500	60.592	331.239	285.761	68.217	519.228	248.182	−8.642
1600	60.849	335.157	288.727	74.289	517.163	230.179	−7.515
1700	61.102	338.854	291.568	80.387	414.659	213.201	−6.551
1800	61.363	342.354	294.293	86.510	412.886	201.402	−5.845
1900	61.643	345.679	296.910	92.660	411.118	189.701	−5.215
2000	61.949	348.848	299.429	98.839	409.358	178.093	−4.651
2100	62.289	351.879	301.855	105.051	407.612	166.573	−4.143
2200	62.667	354.785	304.195	111.298	405.884	155.136	−3.683
2300	63.086	357.580	306.456	117.586	404.178	143.776	−3.265
2400	63.546	360.274	308.642	123.917	402.501	132.490	−2.884
2500	64.047	362.879	310.760	130.296	400.856	121.274	−2.534
2600	64.587	365.401	312.813	136.728	399.248	110.123	−2.212
2700	65.162	367.849	314.807	143.215	397.682	99.032	−1.916
2800	65.767	370.230	316.744	149.761	396.161	87.999	−1.642
2900	66.399	372.549	318.628	156.369	394.688	77.020	−1.387
3000	67.050	374.811	320.463	163.042	393.267	66.090	−1.151
3100	67.716	377.020	322.252	169.780	391.898	55.207	−0.930
3200	68.389	379.180	323.998	176.585	390.584	44.367	−0.724
3300	69.065	381.295	325.702	183.458	389.325	33.567	−0.531
3400	69.737	383.367	327.368	190.398	388.122	22.805	−0.350
3500	70.398	385.398	328.997	197.405	386.973	12.077	−0.180
3600	71.045	387.390	330.591	204.477	−382.426	22.303	−0.324
3700	71.672	389.346	332.153	211.613	−382.641	33.548	−0.474
3800	72.275	391.265	333.683	218.811	−382.810	44.799	−0.616
3900	72.849	393.150	335.184	226.067	−382.934	56.054	−0.751
4000	73.393	395.001	336.656	233.379	−383.016	67.311	−0.879
4100	73.902	396.820	338.102	240.744	−383.058	78.570	−1.001
4200	74.376	398.606	339.521	248.159	−383.062	89.829	−1.117
4300	74.812	400.362	340.915	255.618	−383.033	101.088	−1.228
4400	75.209	402.086	342.286	263.120	−382.973	112.346	−1.334
4500	75.568	403.780	343.634	270.659	−382.886	123.602	−1.435
4600	75.888	405.445	344.960	278.232	−382.776	134.856	−1.531
4700	76.169	407.080	346.264	285.835	−382.645	146.108	−1.624
4800	76.411	408.686	347.548	293.464	−382.499	157.356	−1.712
4900	76.617	410.264	348.812	301.116	−382.340	168.602	−1.797
5000	76.787	411.814	350.056	308.787	−382.172	179.844	−1.879
5100	76.923	413.336	351.282	316.472	−381.999	191.082	−1.957
5200	77.025	414.830	352.490	324.170	−381.824	202.318	−2.032
5300	77.097	416.298	353.680	331.876	−381.651	213.550	−2.105
5400	77.139	417.740	354.853	339.588	−381.483	224.778	−2.174
5500	77.153	419.155	356.009	347.303	−381.321	236.004	−2.241
5600	77.142	420.545	357.149	355.018	−381.171	247.226	−2.306
5700	77.108	421.911	358.274	362.731	−381.035	258.446	−2.368
5800	77.051	423.251	359.382	370.439	−380.916	269.664	−2.429
5900	76.974	424.568	360.476	378.140	−380.816	280.880	−2.487
6000	76.880	425.861	361.555	385.833	−380.736	292.095	−2.543

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 42.373 \pm 0.84\ J·K^{-1}·mol^{-1}$
$T_{fus} = 4273 \pm 200\ K$

$\Delta_f H°(0\ K) = -143.9 \pm 3.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -144.1 \pm 3.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = [104.6 \pm 20.9]\ kJ·mol^{-1}$

Enthalpy of Formation

There are eight oxygen bomb calorimetric studies on TaC reported in the literature[1-8] and one CO(g) equilibrium study.[9] The adopted $\Delta_f H°(298.15\ K)$ value is derived from the calorimetric study of Huber *et al.*[6] These authors studied the combustion of ten TaC_x samples where x covers the range 0.724 to 0.998. For each composition seven or eight combustions were performed. Huber *et al.*[6] reported that the combustions varied from 94.83% to 100% completion but were usually greater than 99%. Corrections of the order 0.4% or less were made to the heat of combustion value to account for impurities. The calculated heats of formation for the ten compositions were fitted to both a quadratic and linear equation by the least squares method by Huber *et al.*[6] Each value was weighted inversely proportional to the square of its uncertainty. Using the linear equation for $\Delta_f H°(298.15\ K)$ and correcting for the JANAF value of $\Delta_f H°(Ta_2O_5, cr, 298.15\ K)$,[10] we extrapolate to $x = 1.0$, calculate, and adopt $\Delta_f H°(298.15\ K) = -34.44 \pm 0.9\ kcal·mol^{-1}$ for TaC. The quadratic equation leads to a value of $-33.94 \pm 1.2\ kcal·mol^{-1}$ which is consistent with our adopted value.

Huber *et al.*[6] and Storms[11] have reanalyzed the calorimetric and equilibrium data[1-9] for TaC_x ($x = 0.724$ to 0.998). A graphical comparison of the results (i.e., $\Delta_f H°(298.15\ K)$ values vs. x) indicated that the linear or quadratic equation suggested by Huber *et al.*[6] is a satisfactory representation of all the $\Delta_f H°(298.15\ K)$ results for TaC_x. The shortcomings of the various studies have been discussed by Huber *et al.*[6] and Storms.[11] For comparison, the oxygen combustion study by Mah[8] led to a reported value of $\Delta_f H°(298.15\ K) = -35.4 \pm 0.5\ kcal·mol^{-1}$ for $TaC_{0.996}$ based on six combustions.

Heat Capacity and Entropy

Kelley[12] measured the heat capacity of TaC in the region 54–294 K (32 points). The reported data refer to stoichiometric TaC with corrections for 0.03% free carbon having been made by Kelley.[12,13] The sample contained less than 0.02% impurities other than free carbon. Using the Debye function suggested by Kelley,[12] we calculate and adopt $S°(50\ K) = 0.831\ cal·K^{-1}·mol^{-1}$ and $H°(50;0) = 30.10\ kcal·mol^{-1}$.

Of the numerous enthalpy and heat capacity studies on TaC,[14-24] the adopted $C_p°$ values for $T > 298$ K are derived primarily from the studies of Pankratz *et al.*,[21] Chang,[23] Levinson,[17] and Bolgar *et al.*[22] The heat capacity data for $200 \leq T \leq 298$ K are used to derive enthalpy values which in turn are used to constrain the high temperature enthalpy data. A polynomial curve fitting technique is used for the Pankratz *et al.*[21] and Levinson[17] data, with the above mentioned constraints, to obtain a smooth joining of the results near 298 K and to provide an equation suitable for extrapolation to T_{fus}. Pankratz *et al.*[21] determined the enthalpy of $TaC_{1.008}$ in the region 405–1700 K (14 data points) while Levinson[17] studied $TaC_{1.007}$ in the range 1289–2778 K (15 data points). Both sets of data are corrected to the stoichiometric composition (TaC) assuming excess free carbon. These corrections are roughly 20 $kcal·mol^{-1}$ at 1000 K and 90 $kcal·mol^{-1}$ at 2500 K.[10] Chang[23] determined the enthalpy of a reported stoichiometric TaC sample for 324–985 K (11 data points). Bolgar *et al.*[22] reported an equation for $C_p°$ values as a function of T and x for the 1200–2400 K range. This equation was based on a study of four TaC_x compositions. We use this equation to extrapolate to the TaC composition.

The adopted tabulation yields enthalpy values for $T < 1200$ K which are very similar to those suggested by Pankratz *et al.*,[21] the difference being no more than $\pm 20\ kcal·mol^{-1}$. Above 1200 K, the data of Pankratz *et al.*[21] lies low approaching roughly 1% in the 1700–1800 K region. The Chang data[23] lies below the tabulated enthalpy values for $T < 600$ K. The average deviation is 0.94% with the maximum of −2.5% occurring at 324.4 K. The Levinson data[17] has an average deviation of 0.5% with considerable scatter. The $C_p°$ values of Bolgar *et al.*[24] has considerable scatter and deviates from our tabulated values by an average deviation of 6%.

Phase Data

Refer to the liquid table for details.

Fusion Data

Refer to the liquid table for details.

References

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[3]G. L. Humphrey, J. Amer. Chem. Soc. **76**, 978 (1954).
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[10]JANAF Thermochemical Tables: Ta_2O_5(cr), 12–31–72; C(ref. st.), 3–31–61.
[11]E. K. Storms, "The Refractory Carbides," Academic Press, New York, (1967).

Continued on page 701

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.514	−143.879	−143.879	INFINITE
100	18.619	12.880	69.673	−5.679	−144.099	−143.677	75.049
200	29.192	29.187	45.519	−3.266	−144.264	−143.168	37.392
298.15	36.790	42.373	42.373	0.	−144.097	−142.654	24.992
300	36.903	42.601	42.374	0.068	−144.091	−142.645	24.837
400	41.664	53.915	43.884	4.012	−143.729	−142.215	18.571
500	44.530	63.537	46.877	8.330	−143.347	−141.882	14.822
600	46.447	71.833	50.361	12.883	−143.033	−141.620	12.329
700	47.890	79.104	53.959	17.602	−142.791	−141.404	10.552
800	49.074	85.578	57.514	22.451	−142.596	−141.220	9.221
900	50.116	91.419	60.962	27.411	−142.426	−141.058	8.187
1000	51.066	96.749	64.278	32.471	−142.270	−140.914	7.361
1100	51.928	101.656	67.456	37.621	−142.124	−140.786	6.685
1200	52.779	106.211	70.498	42.856	−141.987	−140.670	6.123
1300	53.616	110.469	73.411	48.176	−141.850	−140.566	5.648
1400	54.441	114.473	76.202	53.579	−141.697	−140.473	5.241
1500	55.254	118.257	78.881	59.064	−141.513	−140.392	4.889
1600	56.035	121.848	81.455	64.628	−141.291	−140.324	4.581
1700	56.813	125.268	83.932	70.271	−141.035	−140.271	4.310
1800	57.588	128.537	86.320	75.991	−140.761	−140.234	4.069
1900	58.360	131.672	88.625	81.788	−140.482	−140.213	3.855
2000	59.128	134.685	90.853	87.663	−140.200	−140.206	3.662
2100	59.890	137.588	93.010	93.614	−139.913	−140.213	3.488
2200	60.650	140.392	95.100	99.641	−139.621	−140.234	3.330
2300	61.409	143.104	97.129	105.744	−139.325	−140.269	3.186
2400	62.167	145.734	99.100	111.922	−139.030	−140.316	3.054
2500	62.923	148.287	101.016	118.177	−138.741	−140.376	2.933
2600	63.676	150.770	102.882	124.507	−138.467	−140.446	2.822
2700	64.429	153.187	104.701	130.912	−138.218	−140.527	2.719
2800	65.181	155.544	106.475	137.393	−138.006	−140.617	2.623
2900	65.933	157.844	108.207	143.948	−137.845	−140.713	2.535
3000	66.685	160.092	109.899	150.579	−137.753	−140.814	2.452
3100	67.436	162.291	111.554	157.285	−137.746	−140.916	2.374
3200	68.187	164.444	113.173	164.066	−137.846	−141.017	2.302
3300	68.938	166.553	114.759	170.923	−174.531	−140.642	2.226
3400	69.688	168.622	116.312	177.854	−174.488	−139.616	2.145
3500	70.438	170.653	117.836	184.860	−174.382	−138.592	2.068
3600	71.187	172.648	119.331	191.941	−174.213	−137.571	1.996
3700	71.935	174.609	120.799	199.098	−173.981	−136.557	1.928
3800	72.683	176.537	122.240	206.328	−173.686	−135.549	1.863
3900	73.431	178.435	123.657	213.634	−173.328	−134.550	1.802
4000	74.178	180.303	125.050	221.015	−172.905	−133.561	1.744
4100	74.925	182.144	126.420	228.470	−172.420	−132.583	1.689
4200	75.671	183.959	127.768	236.000	−171.871	−131.618	1.637
4273.000	76.216	185.267	128.739	241.544	--- CRYSTAL <--> LIQUID ---		
4300	76.418	185.748	129.096	243.604	−171.259	−130.667	1.587
4400	77.167	187.513	130.403	251.283	−170.582	−129.730	1.540
4500	77.914	189.256	131.692	259.037	−169.842	−128.810	1.495
4600	78.662	190.976	132.962	266.866	−169.038	−127.907	1.452
4700	79.408	192.676	134.215	274.770	−168.170	−127.022	1.412

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [68.279]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 4273 \pm 200\ K$

$\Delta_f H°(298.15\ K) = [-33.955]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [104.6 \pm 20.9]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of TaC(l) at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(4273\ K) - H°(298.15\ K)$, between TaC(cr) and TaC(l).

Heat Capacity and Entropy

The heat capacity for TaC(l) is assumed to be 16.0 $cal·K^{-1}·mol^{-1}$ for the entire liquid phase. A glass transition is assumed at 2800 K, below which the heat capacity values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Phase Data

TaC has a cubic structure of the NaCl type[1] and has a wide homogeneity range. From the phase diagram for the Ta–C system given by Storms,[1] the temperature dependent homogeneity range extends from $x = 0.58$ at 3603 ± 100 K to $x = 0.998$ or possibly $x = 1.00$. The phase boundary at a eutectic temperature of 3673 ± 50 K is $TaC_{0.98}$. A discussion of the phase diagram for TaC_x ($x = 0.00$ to 1.6) is given by Storms.[1]

Fusion Data

The phase diagram given by Storms[1] indicated a eutectic melting at 3673 ± 50 K. A congruent melting point was estimated by Storms[1] at roughly 4273 K for $TaC_{0.88}$. As an approximation due to the uncertainties in this area of the phase diagram, we adopt $T_{fus} = 4273 \pm 200$ K and assign this melting point to TaC. We assume a heat of melting $\Delta_{fus}H° = 25.0 \pm 5.0\ kcal·mol^{-1}$ ($\Delta_{fus}S° = 5.85\ cal·K^{-1}·mol^{-1}$).

Decomposition Data

Using JANAF auxiliary data,[2] we calculate $T_{dcm} = \sim 5580$ K, as that temperature at which $\Delta_f G°$ is zero for the reaction TaC(l) = Ta(l) + C(g).

References

[1]E. K. Storms, "The Refractory Carbides," Academic Press, New York, (1967).
[2]JANAF Thermochemical Tables: Ta(l), 12–31–72; C(g), 3–31–61.

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	36.790	68.279	68.279	0.	−33.955	−40.236	7.049
300	36.903	68.507	68.279	0.068	−33.950	−40.275	7.013
400	41.664	79.820	69.790	4.012	−33.587	−42.436	5.542
500	44.530	89.443	72.783	8.330	−33.205	−44.693	4.669
600	46.447	97.738	76.267	12.883	−32.891	−47.021	4.094
700	47.890	105.010	79.865	17.602	−32.649	−49.396	3.686
800	49.074	111.484	83.420	22.451	−32.454	−51.802	3.382
900	50.116	117.325	86.868	27.411	−32.285	−54.231	3.148
1000	51.066	122.654	90.184	32.471	−32.128	−56.678	2.961
1100	51.928	127.562	93.362	37.621	−31.982	−59.140	2.808
1200	52.779	132.117	96.404	42.856	−31.846	−61.615	2.682
1300	53.616	136.375	99.316	48.176	−31.708	−64.102	2.576
1400	54.441	140.378	102.108	53.579	−31.555	−66.599	2.485
1500	55.254	144.162	104.786	59.064	−31.371	−69.109	2.407
1600	56.035	147.753	107.361	64.628	−31.149	−71.631	2.339
1700	56.813	151.174	109.838	70.271	−30.894	−74.169	2.279
1800	57.588	154.443	112.226	75.991	−30.620	−76.723	2.226
1900	58.360	157.577	114.531	81.788	−30.340	−79.292	2.180
2000	59.128	160.590	116.759	87.663	−30.058	−81.875	2.138
2100	59.890	163.494	118.916	93.614	−29.771	−84.473	2.101
2200	60.651	166.297	121.006	99.641	−29.479	−87.085	2.068
2300	61.410	169.010	123.035	105.744	−29.183	−89.710	2.037
2400	62.167	171.640	125.005	111.923	−28.888	−92.348	2.010
2500	62.923	174.193	126.922	118.177	−28.599	−94.998	1.985
2600	63.678	176.675	128.788	124.507	−28.325	−97.659	1.962
2700	64.431	179.093	130.607	130.913	−28.075	−100.331	1.941
2800	65.183	181.449	132.380	137.393	−27.863	−103.011	1.922
2800.000	65.183	181.449	132.380	137.393	GLASS <-> LIQUID TRANSITION		
2800.000	66.944	181.449	132.380	137.393			
2900	66.944	183.799	134.113	144.088	−27.564	−105.701	1.904
3000	66.944	186.068	135.807	150.782	−27.408	−108.398	1.887
3100	66.944	188.263	137.464	157.476	−27.413	−111.098	1.872
3200	66.944	190.389	139.085	164.171	−27.600	−113.795	1.858
3300	66.944	192.449	140.671	170.865	−64.446	−116.013	1.836
3400	66.944	194.447	142.224	177.560	−64.641	−117.572	1.806
3500	66.944	196.388	143.744	184.254	−64.847	−119.126	1.778
3600	66.944	198.273	145.232	190.948	−65.065	−120.674	1.751
3700	66.944	200.108	146.691	197.643	−65.294	−122.215	1.725
3800	66.944	201.893	148.120	204.337	−65.536	−123.751	1.701
3900	66.944	203.632	149.521	211.032	−65.788	−125.279	1.678
4000	66.944	205.327	150.895	217.726	−66.052	−126.801	1.656
4100	66.944	206.980	152.243	224.420	−66.328	−128.317	1.635
4200	66.944	208.593	153.566	231.115	−66.614	−129.825	1.615
4273.000	66.944	209.746	154.516	236.002	--- CRYSTAL <--> LIQUID ---		
4300	66.944	210.168	154.864	237.809	−66.912	−131.327	1.595
4400	66.944	211.707	156.138	244.504	−67.220	−132.821	1.577
4500	66.944	213.212	157.390	251.198	−67.540	−134.309	1.559
4600	66.944	214.683	158.619	257.892	−67.870	−135.789	1.542
4700	66.944	216.123	159.828	264.587	−68.211	−137.262	1.525
4800	66.944	217.532	161.015	271.281	−68.563	−138.727	1.510
4900	66.944	218.912	162.183	277.976	−68.926	−140.185	1.494
5000	66.944	220.265	163.331	284.670	−69.300	−141.636	1.480
5100	66.944	221.591	164.460	291.364	−69.684	−143.078	1.465
5200	66.944	222.890	165.571	298.059	−70.079	−144.514	1.452
5300	66.944	224.166	166.665	304.753	−70.484	−145.941	1.438
5400	66.944	225.417	167.741	311.448	−70.900	−147.361	1.425
5500	66.944	226.645	168.801	318.142	−71.327	−148.773	1.413
5600	66.944	227.852	169.845	324.836	−71.764	−150.177	1.401
5700	66.944	229.036	170.873	331.531	−72.211	−151.574	1.389
5800	66.944	230.201	171.886	338.225	−811.424	−150.161	1.352
5900	66.944	231.345	172.884	344.920	−812.106	−138.754	1.228
6000	66.944	232.470	173.868	351.614	−812.842	−127.335	1.109

PREVIOUS: CURRENT: December 1973

0	to	4273 K	crystal
above		4273 K	liquid

Refer to the individual tables for details

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.514	−143.879	−143.879	INFINITE
100	18.619	12.880	69.673	−5.679	−144.099	−143.677	75.049
200	29.192	29.187	45.519	−3.266	−144.264	−143.168	37.392
298.15	36.790	42.373	42.373	0.	−144.097	−142.654	24.992
300	36.903	42.601	42.374	0.068	−144.091	−142.645	24.837
400	41.664	53.915	43.884	4.012	−143.729	−142.215	18.571
500	44.530	63.537	46.877	8.330	−143.347	−141.882	14.822
600	46.447	71.833	50.361	12.883	−143.033	−141.620	12.329
700	47.890	79.104	53.959	17.602	−142.791	−141.404	10.552
800	49.074	85.578	57.514	22.451	−142.596	−141.220	9.221
900	50.116	91.419	60.962	27.411	−142.426	−141.058	8.187
1000	51.066	96.749	64.278	32.471	−142.270	−140.914	7.361
1100	51.928	101.656	67.456	37.621	−142.124	−140.786	6.685
1200	52.779	106.211	70.498	42.856	−141.987	−140.670	6.123
1300	53.616	110.469	73.411	48.176	−141.850	−140.566	5.648
1400	54.441	114.473	76.202	53.579	−141.697	−140.473	5.241
1500	55.254	118.257	78.881	59.064	−141.513	−140.392	4.889
1600	56.035	121.848	81.455	64.628	−141.291	−140.324	4.581
1700	56.813	125.268	83.932	70.271	−141.035	−140.271	4.310
1800	57.588	128.537	86.320	75.991	−140.761	−140.234	4.069
1900	58.360	131.672	88.625	81.788	−140.482	−140.213	3.855
2000	59.128	134.685	90.853	87.663	−140.200	−140.206	3.662
2100	59.890	137.588	93.010	93.614	−139.913	−140.213	3.488
2200	60.650	140.392	95.100	99.641	−139.621	−140.234	3.330
2300	61.409	143.104	97.129	105.744	−139.325	−140.269	3.186
2400	62.167	145.734	99.100	111.922	−139.030	−140.316	3.054
2500	62.923	148.287	101.016	118.177	−138.741	−140.376	2.933
2600	63.676	150.770	102.882	124.507	−138.467	−140.446	2.822
2700	64.429	153.187	104.701	130.912	−138.218	−140.527	2.719
2800	65.181	155.544	106.475	137.393	−138.006	−140.617	2.623
2900	65.933	157.844	108.207	143.948	−137.845	−140.713	2.535
3000	66.685	160.092	109.899	150.579	−137.753	−140.814	2.452
3100	67.436	162.291	111.554	157.285	−137.746	−140.916	2.374
3200	68.187	164.444	113.173	164.066	−137.846	−141.017	2.302
3300	68.938	166.553	114.759	170.923	−174.531	−140.642	2.226
3400	69.688	168.622	116.312	177.854	−174.488	−139.616	2.145
3500	70.438	170.653	117.836	184.860	−174.382	−138.592	2.068
3600	71.187	172.648	119.331	191.941	−174.213	−137.571	1.996
3700	71.935	174.609	120.799	199.098	−173.981	−136.557	1.928
3800	72.683	176.537	122.240	206.328	−173.686	−135.549	1.863
3900	73.431	178.435	123.657	213.634	−173.328	−134.550	1.802
4000	74.178	180.303	125.050	221.015	−172.905	−133.561	1.744
4100	74.925	182.144	126.420	228.470	−172.420	−132.583	1.689
4200	75.671	183.959	127.768	236.000	−171.871	−131.618	1.637
4273.000	76.216	185.267	128.739	241.544	CRYSTAL <--> LIQUID		
4273.000	66.944	209.746	128.739	346.144	TRANSITION		
4300	66.944	210.168	129.249	347.951	−66.912	−131.327	1.595
4400	66.944	211.707	131.106	354.645	−67.220	−132.821	1.577
4500	66.944	213.212	132.914	361.340	−67.540	−134.309	1.559
4600	66.944	214.683	134.676	368.034	−67.870	−135.789	1.542
4700	66.944	216.123	136.393	374.729	−68.211	−137.262	1.525
4800	66.944	217.532	138.069	381.423	−68.563	−138.727	1.510
4900	66.944	218.912	139.705	388.117	−68.926	−140.185	1.494
5000	66.944	220.265	141.302	394.812	−69.300	−141.636	1.480
5100	66.944	221.591	142.864	401.506	−69.684	−143.078	1.465
5200	66.944	222.890	144.390	408.201	−70.079	−144.514	1.452
5300	66.944	224.166	145.884	414.895	−70.484	−145.941	1.438
5400	66.944	225.417	147.345	421.589	−70.900	−147.361	1.425
5500	66.944	226.645	148.775	428.284	−71.327	−148.773	1.413
5600	66.944	227.852	150.177	434.978	−71.764	−150.177	1.401
5700	66.944	229.036	151.550	441.673	−72.211	−151.574	1.389
5800	66.944	230.201	152.896	448.367	−811.424	−150.161	1.352
5900	66.944	231.345	154.216	455.061	−812.106	−138.754	1.228
6000	66.944	232.470	155.511	461.756	−812.842	−127.335	1.109

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 24.229 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 3290 \pm 15\ K$

$\Delta_f H°(0\ K) = -182.8 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -184.1 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [71.128]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -44.0\ kcal \cdot mol^{-1}$ ($-184.096\ kJ \cdot mol^{-1}$) is derived from $\Delta_r H°(298.15\ K) = -275.72\ kcal \cdot mol^{-1}$ for reaction (a) determined by Humphrey[1] who burned TiC(cr) in an oxygen bomb calorimeter. The author reported that the combustion product TiO_2 was >95% rutile and <5% anatase, the heat of formation is calculated assuming the above distribution. The uncertainty adopted is due mainly to the uncertainty in TiO_2(rutile).

Using atomic absorbtion spectroscopy Vidale[2] determined that the pressure (log $P_{Ti} = -7.269$) of Ti(g) at 1666 K was equal to the pressure of TiC(cr) at 2220 K. Using this data for reaction (b) we obtain a $\Delta_f H°(298.15\ K) = -43.02\ kcal \cdot mol^{-1}$. Lowell and Williams[3] measured the $\Delta_f H°(2028\ K) = -43.3 \pm 4\ kcal \cdot mol^{-1}$ of TiC(cr) directly using a high temperature calorimeter, which reduces to $\Delta_f H°(298.15\ K) = -37.7 \pm 4\ kcal \cdot mol^{-1}$.

Fujishiro and Gokcen[4] determined the equilibrium pressure of Ti(g) in reaction (d) in the temperature range 2383–2593 K. 3rd law analysis of the data yields a $\Delta_f H°(298.15\ K) = -31.6\ kcal \cdot mol^{-1}$. Brantley and Beckman[5] measured equilibirum pressures of CO for reaction (e) in the temperature range 1278–1428 K. 3rd law analysis of the data yields a $\Delta_f H°(298.15\ K) = -61.9\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Low temperature heat capacities (55–295 K) have been taken from Kelley.[6] Naylor[7] measured heat contents from 360 to 1738 K and Levinson[8] from 1274 to 2799 K. High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 2799 K the heat capacity is graphically extrapolated. The entropy is based on $S°(50;0) = 0.065\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

Source	Method	Reaction	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	Calorimetry	(a) $TiC(cr)+2O_2(g) \rightarrow CO_2(g)+TiO_2$(rutile)	298	−275.72			−44.00
2	Equilibrium	(b) $TiC(cr) \rightarrow Ti(g)+C(cr)$			156.02		−43.02
3	Calorimetry	(c) $Ti(cr)+C(cr) \rightarrow TiC(cr)$		−37.7 ± 4			−37.7
4	Equilibrium	(d) $TiC(cr) \rightarrow C(graph)+Ti(g)$	2383–2593	169.5 ± 10.3	144.6	−10.0 ± 4.1	−31.60
5	Equilibrium	(e) TiO_2(rutile)$+3C(graph) \rightarrow TiC(cr)+2CO(g)$	1278–1428	48.07 ± 1.83	111.07	46.7 ± 1.36	−61.90

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−4.607	−182.822	−182.822	INFINITE
100	7.335	2.602	46.702	−4.410	−183.245	−182.584	95.372
200	23.293	12.780	27.026	−2.849	−183.928	−181.622	47.435
298.15	33.807	24.229	24.229	0.	−184.096	−180.438	31.612
300	33.936	24.439	24.230	0.063	−184.096	−180.415	31.413
400	40.685	35.180	25.648	3.813	−183.982	−179.200	23.401
500	45.166	44.777	28.533	8.122	−183.740	−178.031	18.599
600	47.647	53.248	31.962	12.772	−183.494	−176.913	15.402
700	49.032	60.703	35.546	17.610	−183.316	−175.831	13.121
800	49.903	67.310	39.112	22.558	−183.214	−174.770	11.411
900	50.572	73.227	42.579	27.583	−183.215	−173.715	10.082
1000	51.179	78.586	45.916	32.670	−183.372	−172.653	9.018
1100	51.794	83.493	49.112	37.818	−183.732	−171.566	8.147
1200	52.446	88.027	52.169	43.030	−188.267	−170.317	7.414
1300	53.145	92.252	55.091	48.309	−188.267	−168.821	6.783
1400	53.894	96.218	57.889	53.661	−188.314	−167.324	6.243
1500	54.689	99.963	60.570	59.090	−188.410	−165.821	5.774
1600	55.530	103.519	63.144	64.600	−188.559	−164.311	5.364
1700	56.404	106.912	65.620	70.197	−188.767	−162.789	5.002
1800	57.317	110.161	68.005	75.882	−189.042	−161.254	4.679
1900	58.254	113.285	70.306	81.661	−189.390	−159.701	4.390
2000	59.220	116.298	72.531	87.534	−204.508	−157.674	4.118
2100	60.208	119.211	74.685	93.506	−205.780	−155.301	3.863
2200	61.216	122.035	76.773	99.577	−206.969	−152.869	3.630
2300	62.241	124.779	78.801	105.749	−208.073	−150.384	3.415
2400	63.283	127.450	80.773	112.025	−209.091	−147.854	3.218
2500	64.337	130.054	82.692	118.406	−210.019	−145.283	3.036
2600	65.400	132.598	84.563	124.893	−210.856	−142.677	2.866
2700	66.480	135.087	86.388	131.487	−211.600	−140.040	2.709
2800	67.563	137.524	88.171	138.189	−212.249	−137.378	2.563
2900	68.659	139.914	89.914	145.000	−212.803	−134.694	2.426
3000	69.760	142.260	91.620	151.921	−213.261	−131.992	2.298
3100	70.869	144.566	93.291	158.952	−213.621	−129.277	2.178
3200	71.982	146.833	94.929	166.095	−213.882	−126.552	2.066
3290.000	72.987	148.844	96.376	172.618	--- CRYSTAL <---> LIQUID ---		
3300	73.101	149.066	96.536	173.349	−214.044	−123.820	1.960
3400	74.224	151.264	98.113	180.715	−214.106	−121.085	1.860
3500	75.353	153.432	99.663	188.194	−214.068	−118.349	1.766
3600	76.485	155.571	101.186	195.786	−213.928	−115.616	1.678
3700	77.621	157.682	102.684	203.491	−622.785	−105.100	1.484
3800	78.760	159.767	104.159	211.310	−621.207	−91.129	1.253
3900	79.902	161.828	105.612	219.243	−619.582	−77.201	1.034
4000	81.048	163.865	107.042	227.291	−617.908	−63.315	0.827

PREVIOUS: December 1964 CURRENT: June 1968

$S°(298.15\ K) = [47.401]\ J·K^{-1}·mol^{-1}$

$T_{fus} = 3290 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-108.334]\ kJ·mol^{-1}$

$\Delta_{fus} H° = [71.128]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(3290\ K) - H°(198.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200 K below which the heat capacity is obtained from that of the crystal; above 2200 K it is assumed constant and estimated as 15 $cal·K^{-1}·mol^{-1}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted T_{fus} is taken from the phase diagram of the system Ti–C, at the composition 50% Ti and 50% C, reported by Rudy and Harmon.[1] Earlier reports by Friederich and Sittig[2] and Agte and Moers[3] gave a T_{fus} of 3430 ± 100 K and 3410 ± 90 K, respectively. $\Delta_{fus} H°$ is derived from an estimated $\Delta_{fus} S° = 2.5\ cal·K^{-1}\ g·atom^{-1}$, as suggested by Kubaschewski *et al.*[3]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	33.807	47.401	47.401	0.	−108.334	−111.585	19.549
300	33.936	47.610	47.401	0.063	−108.334	−111.605	19.432
400	40.685	58.352	48.820	3.813	−108.221	−112.707	14.718
500	45.166	67.949	51.705	8.122	−107.978	−113.855	11.894
600	47.647	76.420	55.133	12.772	−107.732	−115.054	10.016
700	49.032	83.875	58.718	17.610	−107.555	−116.290	8.678
800	49.903	90.481	62.283	22.558	−107.452	−117.545	7.675
900	50.572	96.398	65.751	27.583	−107.454	−118.808	6.895
1000	51.179	101.758	69.088	32.670	−107.610	−120.063	6.271
1100	51.794	106.664	72.284	37.818	−107.971	−121.293	5.760
1200	52.446	111.199	75.340	43.030	−112.505	−122.361	5.326
1300	53.145	115.424	78.263	48.309	−112.506	−123.183	4.950
1400	53.894	119.389	81.060	53.661	−112.552	−124.002	4.627
1500	54.689	123.135	83.742	59.090	−112.648	−124.817	4.347
1600	55.530	126.691	86.316	64.600	−112.797	−125.624	4.101
1700	56.404	130.083	88.791	70.197	−113.006	−126.420	3.884
1800	57.317	133.333	91.176	75.882	−113.280	−127.201	3.691
1900	58.254	136.457	93.478	81.661	−113.629	−127.965	3.518
2000	59.220	139.470	95.702	87.534	−128.747	−128.256	3.350
2100	60.208	142.383	97.856	93.506	−130.018	−128.199	3.189
2200	61.216	145.207	99.945	99.577	−131.207	−128.085	3.041
2200.000	61.216	145.207	99.945	99.577	GLASS <--> LIQUID		
2200.000	62.760	145.207	99.945	99.577	TRANSITION		
2300	62.760	147.997	101.974	105.853	−132.209	−127.920	2.905
2400	62.760	150.668	103.947	112.129	−133.226	−127.712	2.780
2500	62.760	153.230	105.868	118.405	−134.259	−127.461	2.663
2600	62.760	155.691	107.737	124.681	−135.307	−127.169	2.555
2700	62.760	158.060	109.557	130.957	−136.369	−126.835	2.454
2800	62.760	160.342	111.330	137.233	−137.444	−126.463	2.359
2900	62.760	162.544	113.059	143.509	−138.534	−126.051	2.270
3000	62.760	164.672	114.744	149.785	−139.636	−125.602	2.187
3100	62.760	166.730	116.388	156.061	−140.751	−125.116	2.108
3200	62.760	168.723	117.992	162.337	−141.879	−124.594	2.034
3290.000	62.760	170.463	119.404	167.985	--- CRYSTAL <--> LIQUID ---		
3300	62.760	170.654	119.559	168.613	−143.019	−124.036	1.963
3400	62.760	172.527	121.089	174.889	−144.171	−123.443	1.896
3500	62.760	174.347	122.585	181.165	−145.336	−122.817	1.833
3600	62.760	176.115	124.048	187.441	−146.512	−122.157	1.772
3700	62.760	177.834	125.478	193.717	−556.798	−113.676	1.605
3800	62.760	179.508	126.878	199.993	−556.763	−101.700	1.398
3900	62.760	181.138	128.249	206.269	−556.795	−89.724	1.202
4000	62.760	182.727	129.591	212.545	−556.892	−77.747	1.015
4100	62.760	184.277	130.906	218.821	−557.053	−65.767	0.838
4200	62.760	185.789	132.195	225.097	−557.277	−53.781	0.669
4300	62.760	187.266	133.458	231.373	−557.560	−41.790	0.508
4400	62.760	188.709	134.698	237.649	−557.902	−29.792	0.354
4500	62.760	190.119	135.914	243.925	−558.301	−17.785	0.206

PREVIOUS: December 1964 CURRENT: June 1968

0 to 3290 K crystal
above 3290 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.607	−182.822	−182.822	INFINITE
100	7.335	2.602	46.702	−4.410	−183.245	−182.584	95.372
200	14.924	12.780	27.026	−2.849	−183.928	−181.622	47.435
298.15	33.807	24.229	24.229	0.	−184.096	−180.438	31.612
300	33.936	24.439	24.230	0.063	−184.096	−180.415	31.413
400	40.685	35.180	25.648	3.813	−183.982	−179.200	23.401
500	45.166	44.777	28.533	8.122	−183.740	−178.031	18.599
600	47.647	53.248	31.962	12.772	−183.494	−176.913	15.402
700	49.032	60.703	35.546	17.610	−183.316	−175.831	13.121
800	49.903	67.310	39.112	22.558	−183.214	−174.770	11.411
900	50.572	73.227	42.579	27.583	−183.215	−173.715	10.082
1000	51.179	78.586	45.916	32.670	−183.372	−172.653	9.018
1100	51.794	83.493	49.112	37.818	−183.732	−171.566	8.147
1200	52.446	88.027	52.169	43.030	−188.267	−170.317	7.414
1300	53.145	92.252	55.091	48.309	−188.267	−168.821	6.783
1400	53.894	96.218	57.889	53.661	−188.314	−167.324	6.243
1500	54.689	99.963	60.570	59.090	−188.410	−165.821	5.774
1600	55.530	103.519	63.144	64.600	−188.559	−164.311	5.364
1700	56.404	106.912	65.620	70.197	−188.767	−162.789	5.002
1800	57.317	110.161	68.005	75.882	−189.042	−161.254	4.679
1900	58.254	113.285	70.306	81.661	−189.390	−159.701	4.390
2000	59.220	116.298	72.531	87.534	−204.508	−157.674	4.118
2100	60.208	119.211	74.685	93.506	−205.780	−155.301	3.863
2200	61.216	122.035	76.773	99.577	−206.969	−152.869	3.630
2300	62.241	124.779	78.801	105.749	−208.073	−150.384	3.415
2400	63.283	127.450	80.773	112.025	−209.091	−147.854	3.218
2500	64.337	130.054	82.692	118.406	−210.019	−145.283	3.036
2600	65.400	132.598	84.563	124.893	−210.856	−142.677	2.866
2700	66.480	135.087	86.388	131.487	−211.600	−140.040	2.709
2800	67.563	137.524	88.171	138.189	−212.249	−137.378	2.563
2900	68.659	139.914	89.914	145.000	−212.803	−134.694	2.426
3000	69.760	142.260	91.620	151.921	−213.261	−131.992	2.298
3100	70.869	144.566	93.291	158.952	−213.621	−129.277	2.178
3200	71.982	146.833	94.929	166.095	−213.882	−126.552	2.066
3290.000	72.987	148.844	96.376	172.618	CRYSTAL <--> LIQUID TRANSITION		
3290.000	62.760	170.463	96.376	243.746			
3300	62.760	170.654	96.601	244.374	−143.019	−124.036	1.963
3400	62.760	172.527	98.807	250.650	−144.171	−123.443	1.896
3500	62.760	174.347	100.939	256.926	−145.336	−122.817	1.833
3600	62.760	176.115	103.003	263.202	−146.512	−122.157	1.772
3700	62.760	177.834	105.002	269.478	−556.798	−113.676	1.605
3800	62.760	179.508	106.941	275.754	−556.763	−101.700	1.398
3900	62.760	181.138	108.823	282.030	−556.795	−89.724	1.202
4000	62.760	182.727	110.650	288.306	−556.892	−77.747	1.015
4100	62.760	184.277	112.427	294.582	−557.053	−65.767	0.838
4200	62.760	185.789	114.156	300.858	−557.277	−53.781	0.669
4300	62.760	187.266	115.839	307.134	−557.560	−41.790	0.508
4400	62.760	188.709	117.479	313.410	−557.902	−29.792	0.354
4500	62.760	190.119	119.078	319.686	−558.301	−17.785	0.206

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = 33.321\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3805 \pm 125\ K$

$\Delta_f H°(0\ K) = -196.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -196.6 \pm 13\ kJ·mol^{-1}$
$\Delta_{fus} H° = [79.496]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = -47.16 \pm 1.5\ kcal·mol^{-1}$ was calculated from the standard Gibbs energy of formation of $-38.9 \pm 1.5\ kcal·mol^{-1}$ at 2675 K reported by Pollock.[1] Using spectrophotometric data reported by Vidale,[2] we calculated $\Delta_f H°(298.15\ K) = -46.9 \pm 1\ kcal·mol^{-1}$. These values were averaged with $\Delta_f H°(298.15\ K) = 47.0 \pm 0.6\ kcal·mol^{-1}$ reported by Mah.[3] The equilibria data reported by Prescott[4] and Kutsev *et al.*[5] were considered but not used.

Heat Capacity and Entropy

Enthalpy data over the range 470.8 to 1174.4 K were taken from a preliminary report by Mezaki *et al.*[6] These data were smoothed by means of the Shomate plot into low temperature data reported by Westrum and Feick.[7] High temperature data reported by Neel *et al.*[8] and McDonald *et al.*[9] were then used to obtain the heat capacity above 1174 K.

Fusion Data

Melting points were measured by Agte and Alterthum[10] and Fredrich and Sittig.[11] The value of 3805 ± 125 K by Agte and Alterthum was chosen. Frederich and Sittig[11] obtained a measurement of 3300 K but estimated 3500 K because of the clouding formation of ZrO_2. Worrell[12] quoted a value of 3480°C taken from Storms.[13] The enthalpy of melting is derived from an estimated $\Delta_{fus}S° = 2.5\ cal·K^{-1}\ g·atom^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.862	−195.961	−195.961	INFINITE
100	12.782	5.832	60.224	−5.439	−196.485	−195.567	102.154
200	28.706	19.970	36.518	−3.310	−196.875	−194.442	50.783
298.15	37.899	33.321	33.321	0.	−196.648	−193.282	33.862
300	37.656	33.555	33.322	0.070	−196.641	−193.262	33.650
400	43.593	45.309	34.885	4.170	−196.123	−192.208	25.100
500	47.133	55.452	38.009	8.721	−195.523	−191.299	19.985
600	49.380	64.257	41.666	13.554	−194.959	−190.508	16.585
700	50.965	72.009	45.459	18.585	−194.468	−189.806	14.164
800	52.070	78.890	49.216	23.740	−194.084	−189.168	12.351
900	52.836	85.070	52.862	28.987	−193.819	−188.570	10.944
1000	53.388	90.662	56.367	34.296	−193.689	−187.995	9.820
1100	54.229	95.794	59.721	39.680	−193.670	−187.428	8.900
1200	54.580	100.528	62.927	45.121	−197.482	−186.635	8.124
1300	54.932	104.910	65.990	50.596	−197.174	−185.744	7.463
1400	55.283	108.994	68.917	56.107	−196.914	−184.875	6.898
1500	55.635	112.820	71.718	61.653	−196.706	−184.023	6.408
1600	55.986	116.422	74.401	67.234	−196.556	−183.182	5.980
1700	56.338	119.827	76.974	72.850	−196.473	−182.349	5.603
1800	56.689	123.057	79.445	78.502	−196.464	−181.519	5.268
1900	57.040	126.131	81.822	84.188	−196.538	−180.687	4.967
2000	57.392	129.066	84.111	89.910	−196.702	−179.849	4.697
2100	57.743	131.875	86.319	95.667	−196.968	−179.001	4.452
2200	58.095	134.569	88.451	101.458	−218.665	−177.391	4.212
2300	58.446	137.159	90.513	107.285	−219.576	−175.494	3.986
2400	58.798	139.654	92.509	113.148	−220.468	−173.559	3.777
2500	59.149	142.061	94.443	119.045	−221.339	−171.586	3.585
2600	59.501	144.388	96.320	124.978	−222.191	−169.579	3.407
2700	59.852	146.640	98.142	130.945	−223.021	−167.540	3.241
2800	60.204	148.823	99.913	136.948	−223.830	−165.470	3.087
2900	60.555	150.942	101.637	142.986	−224.618	−163.372	2.943
3000	60.906	153.001	103.315	149.059	−225.384	−161.247	2.808
3100	61.258	155.004	104.950	155.167	−226.127	−159.097	2.681
3200	61.609	156.954	106.545	161.311	−226.848	−156.923	2.562
3300	61.961	158.855	108.101	167.489	−227.546	−154.727	2.449
3400	62.312	160.710	109.621	173.703	−228.220	−152.510	2.343
3500	62.664	162.522	111.107	179.952	−228.872	−150.274	2.243
3600	63.015	164.292	112.560	186.235	−229.501	−148.019	2.148
3700	63.367	166.023	113.981	192.555	−230.106	−145.747	2.058
3800	63.718	167.718	115.373	198.909	−230.687	−143.459	1.972
3805.000	63.736	167.802	115.442	199.227	--- CRYSTAL <--> LIQUID ---		
3900	64.070	169.377	116.737	205.298	−231.245	−141.157	1.891
4000	64.421	171.004	118.073	211.723	−231.779	−138.840	1.813
4100	64.772	172.599	119.384	218.182	−232.289	−136.510	1.739
4200	65.124	174.164	120.669	224.677	−232.775	−134.168	1.669
4300	65.475	175.701	121.931	231.207	−233.237	−131.815	1.601
4400	65.827	177.210	123.171	237.772	−233.674	−129.451	1.537
4500	66.178	178.693	124.388	244.373	−234.088	−127.078	1.475
4600	66.530	180.151	125.584	251.008	−234.477	−124.695	1.416
4700	66.881	181.586	126.761	257.679	−234.843	−122.305	1.359
4800	67.233	182.998	127.918	264.384	−796.120	−108.289	1.178
4900	67.584	184.388	129.056	271.125	−796.088	−93.960	1.002
5000	67.936	185.757	130.176	277.901	−796.049	−79.631	0.832

PREVIOUS: June 1964 CURRENT: December 1964

$S°(298.15\ K)$ = [53.577] $J·K^{-1}·mol^{-1}$
T_{fus} = 3805 ± 125 K

$\Delta_f H°(298.15\ K)$ = [−118.877] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [79.496] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(ZrC, l, 298.15 K) is calculated from $\Delta_f H°$(ZrC, cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(3805\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$(l) at and below 2500 K is assumed to be equal to that of ZrC(cr). Above 2500 K the heat capacity is estimated to be constant. $S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	37.899	53.577	53.577	0.	−118.877	−121.550	21.295
300	38.030	53.811	53.577	0.070	−118.869	−121.567	21.167
400	43.593	65.581	55.144	4.175	−118.347	−122.541	16.002
500	47.133	75.723	58.270	8.727	−117.746	−123.658	12.918
600	49.380	84.529	61.930	13.560	−117.183	−124.895	10.873
700	50.965	92.281	65.723	18.590	−116.692	−126.220	9.419
800	52.070	99.162	69.481	23.745	−116.308	−127.609	8.332
900	52.836	105.341	73.128	28.992	−116.043	−129.039	7.489
1000	53.388	110.934	76.633	34.301	−115.913	−130.491	6.816
1100	54.229	116.066	79.988	39.686	−115.893	−131.950	6.266
1200	54.580	120.799	83.194	45.126	−119.706	−133.185	5.797
1300	54.932	125.182	86.258	50.602	−119.398	−134.321	5.397
1400	55.283	129.266	89.186	56.112	−119.138	−135.479	5.055
1500	55.635	133.092	91.986	61.658	−118.929	−136.654	4.759
1600	55.986	136.694	94.669	67.239	−118.780	−137.841	4.500
1700	56.338	140.098	97.242	72.855	−118.697	−139.035	4.272
1800	56.689	143.329	99.714	78.507	−118.688	−140.232	4.069
1900	57.040	146.403	102.091	84.193	−118.761	−141.427	3.888
2000	57.392	149.338	104.380	89.915	−118.926	−142.617	3.725
2100	57.743	152.146	106.588	95.672	−119.191	−143.795	3.577
2200	58.095	154.841	108.721	101.464	−140.889	−144.213	3.424
2300	58.446	157.431	110.783	107.291	−141.800	−144.343	3.278
2400	58.798	159.926	112.779	113.153	−142.691	−144.435	3.144
2500	59.149	162.333	114.713	119.050	−143.563	−144.489	3.019
2500.000	*59.149*	*162.333*	*114.713*	*119.051*	*GLASS <--> LIQUID*		
2500.000	62.760	162.333	114.713	119.051	TRANSITION		
2600	62.760	164.795	116.592	125.327	−144.071	−144.516	2.903
2700	62.760	167.163	118.422	131.603	−144.593	−144.524	2.796
2800	62.760	169.446	120.203	137.879	−145.129	−144.511	2.696
2900	62.760	171.648	121.940	144.155	−145.678	−144.480	2.602
3000	62.760	173.776	123.632	150.431	−146.241	−144.429	2.515
3100	62.760	175.834	125.283	156.707	−146.816	−144.359	2.432
3200	62.760	177.826	126.894	162.983	−147.405	−144.270	2.355
3300	62.760	179.757	128.467	169.259	−148.005	−144.163	2.282
3400	62.760	181.631	130.003	175.535	−148.618	−144.037	2.213
3500	62.760	183.450	131.504	181.811	−149.242	−143.894	2.147
3600	62.760	185.218	132.972	188.087	−149.878	−143.732	2.085
3700	62.760	186.938	134.407	194.363	−150.527	−143.552	2.027
3800	62.760	188.612	135.812	200.639	−151.186	−143.355	1.971
3805.000	62.760	188.694	135.881	200.952	--- CRYSTAL <--> LIQUID ---		
3900	62.760	190.242	137.187	206.915	−151.857	−143.140	1.917
4000	62.760	191.831	138.533	213.191	−152.540	−142.908	1.866
4100	62.760	193.380	139.852	219.467	−153.233	−142.659	1.817
4200	62.760	194.893	141.145	225.743	−153.938	−142.392	1.771
4300	62.760	196.370	142.412	232.019	−154.654	−142.109	1.726
4400	62.760	197.812	143.654	238.295	−155.381	−141.809	1.683
4500	62.760	199.223	144.874	244.571	−156.119	−141.492	1.642
4600	62.760	200.602	146.070	250.847	−156.868	−141.159	1.603
4700	62.760	201.952	147.245	257.123	−157.627	−140.809	1.565
4800	62.760	203.273	148.398	263.399	−719.334	−128.826	1.402
4900	62.760	204.567	149.532	269.675	−719.767	−116.519	1.242
5000	62.760	205.835	150.645	275.951	−720.228	−104.203	1.089
5100	62.760	207.078	151.739	282.227	−720.715	−91.878	0.941
5200	62.760	208.297	152.815	288.503	−721.227	−79.543	0.799
5300	62.760	209.492	153.874	294.779	−721.762	−67.198	0.662
5400	62.760	210.665	154.914	301.055	−722.320	−54.842	0.530
5500	62.760	211.817	155.939	307.331	−722.899	−42.476	0.403
5600	62.760	212.948	156.946	313.607	−723.497	−30.100	0.281
5700	62.760	214.058	157.939	319.883	−724.113	−17.712	0.162
5800	62.760	215.150	158.916	326.159	−724.746	−5.314	0.048
5900	62.760	216.223	159.878	332.435	−725.396	7.096	−0.063
6000	62.760	217.278	160.826	338.711	−726.059	19.517	−0.170

PREVIOUS: June 1964 CURRENT: December 1964

Zirconium Carbide (ZrC) **CRYSTAL–LIQUID**

0	to	3805 K	crystal
above		3805 K	liquid

Refer to the indivicual tables for details.

M_r = 103.231 Zirconium Carbide (ZrC) **C_1Zr_1(cr,l)**

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.862	−195.961	−195.961	INFINITE
100	12.782	5.832	60.224	−5.439	−196.485	−195.567	102.154
200	28.706	19.970	36.518	−3.310	−196.875	−194.442	50.783
298.15	37.899	33.321	33.321	0.	−196.648	−193.282	33.862
300	37.656	33.555	33.322	0.070	−196.641	−193.262	33.650
400	43.593	45.309	34.885	4.170	−196.123	−192.208	25.100
500	47.133	55.452	38.009	8.721	−195.523	−191.299	19.985
600	49.380	64.257	41.666	13.554	−194.959	−190.508	16.585
700	50.965	72.009	45.459	18.585	−194.468	−189.806	14.164
800	52.070	78.890	49.216	23.740	−194.084	−189.168	12.351
900	52.836	85.070	52.862	28.987	−193.819	−188.570	10.944
1000	53.388	90.662	56.367	34.296	−193.689	−187.995	9.820
1100	54.229	95.794	59.721	39.680	−193.670	−187.428	8.900
1200	54.580	100.528	62.927	45.121	−197.482	−186.635	8.124
1300	54.932	104.910	65.990	50.596	−197.174	−185.744	7.463
1400	55.283	108.994	68.917	56.107	−196.914	−184.875	6.898
1500	55.635	112.820	71.718	61.653	−196.706	−184.023	6.408
1600	55.986	116.422	74.401	67.234	−196.556	−183.182	5.980
1700	56.338	119.827	76.974	72.850	−196.473	−182.349	5.603
1800	56.689	123.057	79.445	78.502	−196.464	−181.519	5.268
1900	57.040	126.131	81.822	84.188	−196.538	−180.687	4.967
2000	57.392	129.066	84.111	89.910	−196.702	−179.849	4.697
2100	57.743	131.875	86.319	95.667	−196.968	−179.001	4.452
2200	58.095	134.569	88.451	101.458	−218.665	−177.391	4.212
2300	58.446	137.159	90.513	107.285	−219.576	−175.494	3.986
2400	58.798	139.654	92.509	113.148	−220.468	−173.559	3.777
2500	59.149	142.061	94.443	119.045	−221.339	−171.586	3.585
2600	59.501	144.388	96.320	124.978	−222.191	−169.579	3.407
2700	59.852	146.640	98.142	130.945	−223.021	−167.540	3.241
2800	60.204	148.823	99.913	136.948	−223.830	−165.470	3.087
2900	60.555	150.942	101.637	142.986	−224.618	−163.372	2.943
3000	60.906	153.001	103.315	149.059	−225.384	−161.247	2.808
3100	61.258	155.004	104.950	155.167	−226.127	−159.097	2.681
3200	61.609	156.954	106.545	161.311	−226.848	−156.923	2.562
3300	61.961	158.855	108.101	167.489	−227.546	−154.727	2.449
3400	62.312	160.710	109.621	173.703	−228.220	−152.510	2.343
3500	62.664	162.522	111.107	179.952	−228.872	−150.274	2.243
3600	63.015	164.292	112.560	186.235	−229.501	−148.019	2.148
3700	63.367	166.023	113.981	192.555	−230.106	−145.747	2.058
3800	63.718	167.718	115.373	198.909	−230.687	−143.459	1.972
3805.000	63.736	167.802	115.442	199.227	CRYSTAL <--> LIQUID		
3805.000	62.760	188.694	115.442	278.723	TRANSITION		
3900	62.760	190.242	117.245	284.686	−151.857	−143.140	1.917
4000	62.760	191.831	119.090	290.962	−152.540	−142.908	1.866
4100	62.760	193.380	120.883	297.238	−153.233	−142.659	1.817
4200	62.760	194.893	122.628	303.514	−153.938	−142.392	1.771
4300	62.760	196.370	124.325	309.790	−154.654	−142.109	1.726
4400	62.760	197.812	125.979	316.066	−155.381	−141.809	1.683
4500	62.760	199.223	127.591	322.342	−156.119	−141.492	1.642
4600	62.760	200.602	129.164	328.618	−156.868	−141.159	1.603
4700	62.760	201.952	130.698	334.894	−157.627	−140.809	1.565
4800	62.760	203.273	132.196	341.170	−719.334	−128.826	1.402
4900	62.760	204.567	133.660	347.446	−719.767	−116.519	1.242
5000	62.760	205.835	135.091	353.722	−720.228	−104.203	1.089
5100	62.760	207.078	136.490	359.998	−720.715	−91.878	0.941
5200	62.760	208.297	137.859	366.274	−721.227	−79.543	0.799
5300	62.760	209.492	139.200	372.550	−721.762	−67.198	0.662
5400	62.760	210.665	140.512	378.826	−722.320	−54.842	0.530
5500	62.760	211.817	141.798	385.102	−722.899	−42.476	0.403
5600	62.760	212.948	143.059	391.378	−723.497	−30.100	0.281
5700	62.760	214.058	144.295	397.654	−724.113	−17.712	0.162
5800	62.760	215.150	145.507	403.930	−724.746	−5.314	0.048
5900	62.760	216.223	146.696	410.206	−725.396	7.096	−0.063
6000	62.760	217.278	147.864	416.482	−726.059	19.517	−0.170

PREVIOUS: CURRENT: December 1964

$S°(298.15\ K) = 199.38 \pm 0.04\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 829.3 \pm 3.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 837.7 \pm 3.8\ kJ\cdot mol^{-1}$

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
			Electronic Levels and Molecular Constants (σ = 2)				
$x\,^1\Sigma_g^+$	0	1	1.2425	1.81984	0.01765	1854.71	13.34
$X'^3\Pi_u$	610	6	1.3119	1.63246	0.01661	1641.35	11.67
$A'^3\Sigma_g^-$	6243.5	3	1.3693	1.49852	0.01634	1470.45	11.19
$b\,^1\Pi_u$	8268.33	2	1.3184	1.61634	0.01686	1608.35	12.078
$A''^3\Sigma_u^+$	13365	3	1.23	1.87	[0.018]	1961.6	13.65
$^1\Sigma_g^+$	[18570]	1	[1.38]	[1.475]	[0.013]	[1510]	[10.0]
$A\,^3\Pi_g$	19916	6	1.266	1.7527	0.01608	1788.2	16.44
$^5\Pi_g$	[22260]	10	[1.46]	[1.324]	[0.012]	[1400]	[9.9]
$^5\Sigma_g^+$	[30320]	5	[1.35]	[1.557]	[0.015]	[1550]	[11.7]
$c\,^1\Pi_g$	34262	2	1.2552	1.7334	0.018	1809.1	15.81
$^3\Delta_u$	[34530]	6	[1.51]	[1.23]	[0.013]	[1160]	[9.2]
$^1\Sigma_u^-$	[34760]	1	[1.90]	[0.778]	[0.005]	[1025]	[5.8]
$^3\phi_g$	[38020]	6	[1.53]	[1.20]	[0.011]	[1290]	[9.0]
$B\,^3\Pi_g$	40690	6	1.535	1.1922	0.0242	1106.56	39.26
$^3\Delta_u$	[40780]	6	[1.51]	[1.23]	[0.011]	[1380]	[9.2]
$^3\Pi_g$	[42370]	6	[1.49]	[1.265]	[0.012	[1340]	[9.5]
$^1\phi_g$	[42860]	2	[1.51]	[1.232]	[0.011]	[1360]	[9.2]
$d\,^1\Sigma_u^+$	43240	1	1.2378	1.8334	0.0204	1829.57	13.97
$^3\Sigma_u^+$	[43360]	3	[1.44]	[1.355]	[0.011]	[1660]	[10.21]

Enthalpy of Formation

Messerle and Krauss[1] have reported the dissociation energy as 49300 ± 300 cm^{-1} from the variation of the rotational structure cut-off with vibrational level in the $c\,^1\Pi_g$ state. This state dissociates into $C(^3P) + C^3(P)$, due to an avoided crossing,[2] these dissociation products are those of the ground state. The uncertainty in the determination is generous and thus we adopt D_0° = 140.95 ± 0.9 kcal or $\Delta_f H°(C_2, g, 0\ K)$ = 198.2 ± 0.9 $kcal\cdot mol^{-1}$, using $\Delta_f H°(C, g, 0\ K)$ = 169.576 $kcal\cdot mol^{-1}$.[3]

Brewer *et al.*[4] have reviewed several other earlier determinations which confirm $\Delta_f H°(0\ K)$ = 195 ± 5 $kcal\cdot mol^{-1}$. The extensive mass spectrometric data of Drowart *et al.*[5] yield a 3rd law $\Delta_f H°(0\ K)$ = 199.2 ± 1.4 $kcal\cdot mol^{-1}$ in excellent agreement with the adopted value.

Heat Capacity and Entropy

The observed molecular constants and electronic levels were taken from Ballik and Ramsay.[2] The estimated parameters are from the correlation calculations of Fougere and Nesbet[6] and Clementi,[7] the electronic levels are T_o values. Not all predicted states were included since the contribution of levels above 40000 cm^{-1} is neligible. The functions were calculated from the partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$, the values for Q_r^i and Q_v^i were calculated with first order anharmonic corrections. The functions are similar to those reported by Altman[8] and Clementi[7] but include several additional states.

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[1]G. Messerle and L. Krauss, Z. Naturforsch. **22A**, 2023 (1967), **22A** 1744 (1967) and **22A**, 2015 (1967).
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[4]L. Brewer, W. T. Hicks, and O. H Krikorian, J. Chem. Phys. **36**, 182 (1962).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.578	829.262	829.262	INFINITE
100	29.765	158.761	235.431	−7.667	832.053	816.367	−426.427
200	40.456	182.316	203.335	−4.204	834.863	799.633	−208.843
250	43.379	191.730	200.097	−2.092	836.384	790.649	−165.197
298.15	43.145	199.382	199.382	0.	837.737	781.714	−136.953
300	43.100	199.649	199.383	0.080	837.785	781.367	−136.048
350	41.443	206.176	199.902	2.196	838.960	771.867	−115.195
400	39.650	211.590	201.035	4.222	839.882	762.217	−99.535
450	38.191	216.172	202.469	6.166	840.570	752.465	−87.344
500	37.141	220.138	204.042	8.048	841.055	742.648	−77.584
600	36.000	226.793	207.299	11.696	841.547	722.911	−62.935
700	35.622	232.307	210.488	15.273	841.578	703.131	−52.468
800	35.603	237.060	213.520	18.833	841.295	683.369	−44.619
900	35.746	241.261	216.373	22.399	840.793	663.656	−38.518
1000	35.963	245.038	219.054	25.984	840.132	644.008	−33.640
1100	36.212	248.477	221.575	29.593	839.353	624.433	−29.652
1200	36.479	251.639	223.950	33.227	838.484	604.932	−26.332
1300	36.756	254.570	226.194	36.889	837.548	585.507	−23.526
1400	37.038	257.304	228.320	40.579	836.559	566.156	−21.124
1500	37.324	259.869	230.338	44.297	835.528	546.878	−19.044
1600	37.610	262.287	232.260	48.043	834.465	527.669	−17.227
1700	37.896	264.576	234.094	51.819	833.375	508.527	−15.625
1800	38.179	266.750	235.849	55.622	832.266	489.450	−14.203
1900	38.457	268.822	237.530	59.454	831.140	470.436	−12.933
2000	38.729	270.801	239.145	63.314	830.000	451.481	−11.791
2100	38.994	272.697	240.697	67.200	828.849	432.583	−10.760
2200	39.251	274.517	242.194	71.112	827.688	413.741	−9.823
2300	39.500	276.268	243.637	75.050	826.518	394.951	−8.970
2400	39.740	277.954	245.032	79.012	825.341	376.212	−8.188
2500	39.972	279.581	246.382	82.997	824.156	357.523	−7.470
2600	40.197	281.153	247.689	87.006	822.965	338.881	−6.808
2700	40.414	282.674	248.957	91.037	821.767	320.285	−6.196
2800	40.624	284.148	250.188	95.088	820.563	301.734	−5.629
2900	40.827	285.577	251.383	99.161	819.353	283.226	−5.101
3000	41.026	286.964	252.546	103.254	818.136	264.759	−4.610
3100	41.219	288.313	253.678	107.366	816.914	246.333	−4.151
3200	41.409	289.624	254.781	111.498	815.685	227.947	−3.721
3300	41.595	290.901	255.857	115.648	814.450	209.599	−3.318
3400	41.778	292.146	256.906	119.816	813.210	191.289	−2.939
3500	41.960	293.360	257.930	124.003	811.963	173.016	−2.582
3600	42.140	294.544	258.931	128.208	810.712	154.778	−2.246
3700	42.318	295.701	259.909	132.431	809.454	136.574	−1.928
3800	42.496	296.832	260.866	136.672	808.192	118.405	−1.628
3900	42.674	297.938	261.802	140.931	806.924	100.270	−1.343
4000	42.852	299.021	262.719	145.207	805.652	82.166	−1.073
4100	43.030	300.081	263.618	149.501	804.375	64.095	−0.817
4200	43.209	301.120	264.498	153.813	803.093	46.055	−0.573
4300	43.388	302.139	265.362	158.143	801.807	28.046	−0.341
4400	43.568	303.139	266.209	162.490	800.517	10.066	−0.119
4500	43.749	304.120	267.041	166.856	799.223	−7.884	0.092
4600	43.932	305.083	267.857	171.240	797.925	−25.806	0.293
4700	44.115	306.030	268.659	175.643	796.624	−43.699	0.486
4800	44.299	306.961	269.448	180.063	795.320	−61.564	0.670
4900	44.485	307.876	270.222	184.503	794.013	−79.402	0.846
5000	44.671	308.777	270.985	188.960	792.703	−97.214	1.016
5100	44.859	309.663	271.734	193.437	791.390	−114.999	1.178
5200	45.047	310.536	272.472	197.932	790.075	−132.759	1.334
5300	45.237	311.396	273.198	202.446	788.757	−150.493	1.483
5400	45.427	312.243	273.914	206.980	787.438	−168.202	1.627
5500	45.619	313.079	274.618	211.532	786.116	−185.887	1.765
5600	45.811	313.902	275.312	216.103	784.792	−203.548	1.899
5700	46.004	314.715	275.997	220.694	783.467	−221.185	2.027
5800	46.197	315.517	276.671	225.304	782.140	−238.799	2.151
5900	46.391	316.308	277.336	229.933	780.812	−256.390	2.270
6000	46.586	317.089	277.992	234.582	779.482	−273.959	2.385

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 196.60 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 443 \pm 84\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 444 \pm 84\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
[9000]	[4]
18484	[2]

$\omega_e = 1781.04\ cm^{-1}$ $\omega_e x_e = 11.585\ cm^{-1}$ $\sigma = 2$
$B_e = 1.74685\ cm^{-1}$ $\alpha_e = 0.0167\ cm^{-1}$ $r_e = 1.2682$ Å

Enthalpy of Formation

The electron affinity of C_2 has been obtained by Honig[1] as 4 ± 0.8 eV from the difference in enthalpies of sublimation of neutral C_2 and C_2^- and the work function of graphite. Thus, we have the reaction

$$C_2(g) + e^- \rightarrow C_2^-(g) \quad \Delta H(0\ K) = -92.2 \pm 20\ kcal \cdot mol^{-1}.$$

Using $\Delta_f H°(C_2, g, 0\ K) = 198.2\ kcal \cdot mol^{-1}$,[2] we obtain $\Delta_f H°(C_2^-, g, 0\ K) = 106 \pm 20\ kcal \cdot mol^{-1}$, which is adopted.

A value for the enthalpy of formation may be obtained from a linear Birge–Sponer extrapolation of the ground state vibrational levels, which gives 195.8 kcal for the reaction.

$$C_2^-(g) \rightarrow C(g) + C^-(g).$$

With auxiliary data[2] this yields $\Delta_f H°(C_2^-, g, 0\ K) = 114.5\ kcal \cdot mol^{-1}$, in good agreement with the adopted value.

Heat Capacity and Entropy

The molecular constants and electronic levels are from Herzberg and Lagerqvist.[3] The values are not definitely ascribed to C_2^- by Herzberg and Lagerqvist, but there is a good deal of evidence to support this assignment. Recently Milligan and Jacox[4] have shown that matrix isolated bands previously attributed to $C_2(g)$ are enhanced in the presence of a photoelectron source. The matrix spectra correspond to the gas system reported by Harzberg and Lagerqvist[3] and leave little doubt that the species is C_2^-.

The estimated electronic level is assumed to be a $^2\Pi$ state and is obtained from the isoelectronic CN(g).[2]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.676	443.127		
100	29.106	164.780	222.507	−5.773			
200	29.115	184.957	199.266	−2.862			
250	29.148	191.457	197.078	−1.405			
298.15	29.241	196.597	196.597	0.	443.504	394.566	−69.126
300	29.246	196.778	196.598	0.054	443.488	394.263	−68.647
350	29.438	201.300	196.955	1.521	442.974	386.097	−57.622
400	29.726	205.248	197.750	2.999	442.309	378.015	−49.364
450	30.092	208.770	198.782	4.495	441.509	370.025	−42.951
500	30.511	211.962	199.943	6.010	440.588	362.131	−37.832
600	31.407	217.604	202.428	9.105	438.448	346.635	−30.177
700	32.272	222.511	204.954	12.290	436.008	331.522	−24.738
800	33.042	226.872	207.426	15.556	433.354	316.774	−20.683
900	33.703	230.803	209.809	18.895	430.545	302.369	−17.549
1000	34.263	234.383	212.090	22.294	427.619	288.283	−15.058
1100	34.741	237.672	214.268	25.744	424.604	274.495	−13.035
1200	35.154	240.713	216.347	29.240	421.518	260.985	−11.360
1300	35.522	243.541	218.331	32.774	418.375	247.734	−9.954
1400	35.861	246.186	220.227	36.343	415.187	234.727	−8.758
1500	36.185	248.672	222.041	39.945	411.962	221.950	−7.729
1600	36.503	251.017	223.780	43.580	408.707	209.388	−6.836
1700	36.824	253.240	225.448	47.246	405.431	197.031	−6.054
1800	37.152	255.354	227.051	50.945	402.137	184.867	−5.365
1900	37.490	257.372	228.594	54.677	398.833	172.886	−4.753
2000	37.840	259.303	230.082	58.443	395.522	161.080	−4.207
2100	38.199	261.158	231.518	62.245	392.208	149.440	−3.717
2200	38.568	262.944	232.906	66.083	388.894	137.957	−3.276
2300	38.943	264.666	234.249	69.959	385.584	126.625	−2.876
2400	39.323	266.332	235.552	73.872	382.279	115.437	−2.512
2500	39.704	267.945	236.815	77.823	378.982	104.386	−2.181
2600	40.083	269.509	238.043	81.813	375.692	93.467	−1.878
2700	40.459	271.029	239.237	85.840	372.413	82.675	−1.599
2800	40.828	272.507	240.399	89.904	369.142	72.003	−1.343
2900	41.189	273.946	241.531	94.005	365.882	61.449	−1.107
3000	41.539	275.349	242.635	98.142	362.630	51.007	−0.888
3100	41.876	276.716	243.712	102.313	359.388	40.673	−0.685
3200	42.200	278.051	244.764	106.517	356.153	30.443	−0.497
3300	42.510	279.354	245.793	110.752	352.925	20.315	−0.322
3400	42.803	280.628	246.799	115.018	349.703	10.284	−0.158
3500	43.081	281.872	247.783	119.312	346.486	0.348	−0.005
3600	43.342	283.090	248.747	123.634	343.272	−9.496	0.138
3700	43.587	284.281	249.691	127.980	340.059	−19.251	0.272
3800	43.815	285.446	250.617	132.351	336.848	−28.919	0.398
3900	44.027	286.587	251.525	136.743	333.635	−38.503	0.516
4000	44.223	287.704	252.415	141.155	330.420	−48.004	0.627
4100	44.403	288.798	253.289	145.587	327.202	−57.425	0.732
4200	44.567	289.870	254.148	150.036	323.978	−66.767	0.830
4300	44.717	290.921	254.991	154.500	320.748	−76.032	0.924
4400	44.853	291.951	255.819	158.979	317.510	−85.222	1.012
4500	44.976	292.960	256.633	163.470	314.263	−94.339	1.095
4600	45.085	293.950	257.434	167.973	311.006	−103.383	1.174
4700	45.182	294.920	258.221	172.487	307.738	−112.356	1.249
4800	45.268	295.873	258.996	177.009	304.457	−121.260	1.320
4900	45.343	296.807	259.758	181.540	301.163	−130.095	1.387
5000	45.407	297.723	260.508	186.077	297.854	−138.862	1.451
5100	45.462	298.623	261.246	190.621	294.529	−147.564	1.511
5200	45.507	299.506	261.974	195.169	291.189	−156.200	1.569
5300	45.545	300.374	262.690	199.722	287.831	−164.771	1.624
5400	45.574	301.225	263.396	204.278	284.456	−173.279	1.676
5500	45.596	302.062	264.091	208.837	281.062	−181.725	1.726
5600	45.611	302.883	264.777	213.397	277.649	−190.108	1.773
5700	45.620	303.691	265.452	217.959	274.216	−198.431	1.818
5800	45.624	304.484	266.118	222.521	270.762	−206.693	1.861
5900	45.622	305.264	266.775	227.083	267.288	−214.895	1.903
6000	45.615	306.031	267.423	231.645	263.793	−223.038	1.942

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K)$ = [218.643] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = [558.678] $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [564.840] $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1580](1)
[423](2)
[1947](1)

Ground State Quantum Weight: 1 σ = 1
Point Group: $[C_{\infty v}]$
Bond Distances: Be–C = [1.407] Å; C ≡ C = [1.2] Å
Bond Angle: Be–C–C = [180]°
Rotational Constant: B_0 = [0.481016] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was estimated as a lower positive limit by U. S. Nat. Bur. Stand.[1]

Heat Capacity and Entropy

The vibrational frequencies, bond angle, and configuration were estimated by Chupka *et al.*[2] Bond distances were calculated assuming the C–C bond distance was the same as in acetylene.

References

[1]G. T. Armstrong and L. A. Krieger, U. S. Nat. Bur. Stand. Report 6645, Chapter A2, (1960).
[2]Chupka, Berkowitz, Giese, and Inghram, J. Phys. Chem. **62**, 611 (1958)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.196	558.678	558.678	INFINITE
100	30.508	179.700	252.347	−7.265	561.451	543.722	−284.011
200	37.212	202.950	222.304	−3.871	563.615	525.092	−137.140
250	39.569	211.521	219.313	−1.948	564.354	515.371	−107.681
298.15	41.282	218.643	218.643	0.	564.840	505.889	−88.630
300	41.341	218.898	218.643	0.076	564.854	505.523	−88.019
350	42.814	225.384	219.152	2.181	565.139	495.610	−73.966
400	44.152	231.189	220.300	4.356	565.246	485.668	−63.422
450	45.426	236.464	221.808	6.595	565.202	475.722	−55.220
500	46.651	241.314	223.519	8.897	565.032	465.787	−48.660
600	48.933	250.025	227.227	13.679	564.390	445.993	−38.827
700	50.936	257.722	231.044	18.675	563.449	426.331	−31.813
800	52.634	264.638	234.818	23.856	562.291	406.819	−26.563
900	54.048	270.921	238.486	29.192	560.965	387.464	−22.488
1000	55.215	276.678	242.021	34.657	559.501	368.263	−19.236
1100	56.179	281.988	245.416	40.228	557.914	349.215	−16.583
1200	56.976	286.911	248.672	45.887	556.212	330.317	−14.378
1300	57.639	291.498	251.792	51.619	554.401	311.565	−12.519
1400	58.194	295.791	254.783	57.411	552.481	292.956	−10.930
1500	58.661	299.822	257.652	63.255	550.455	274.489	−9.559
1600	59.057	303.621	260.408	69.141	533.786	256.686	−8.380
1700	59.395	307.212	263.056	75.064	531.947	239.423	−7.357
1800	59.685	310.615	265.605	81.019	530.068	222.270	−6.450
1900	59.936	313.849	268.060	87.000	528.151	205.222	−5.642
2000	60.155	316.929	270.427	93.005	526.194	188.276	−4.917
2100	60.345	319.869	272.712	99.030	524.197	171.429	−4.264
2200	60.513	322.680	274.919	105.073	522.161	154.678	−3.673
2300	60.660	325.373	277.055	111.132	520.086	138.021	−3.135
2400	60.792	327.958	279.122	117.205	517.971	121.455	−2.643
2500	60.908	330.442	281.126	123.290	515.815	104.977	−2.193
2600	61.013	332.833	283.069	129.386	513.620	88.587	−1.780
2700	61.106	335.137	284.955	135.492	511.385	72.282	−1.398
2800	61.191	337.361	286.787	141.607	218.152	62.283	−1.162
2900	61.267	339.509	288.568	147.730	216.899	56.738	−1.022
3000	61.336	341.588	290.301	153.860	215.622	51.237	−0.892
3100	61.399	343.600	291.988	159.997	214.320	45.779	−0.771
3200	61.456	345.550	293.632	166.139	212.991	40.363	−0.659
3300	61.508	347.442	295.234	172.288	211.634	34.989	−0.554
3400	61.556	349.279	296.796	178.441	210.246	29.657	−0.456
3500	61.600	351.064	298.322	184.599	208.827	24.366	−0.364
3600	61.641	352.800	299.811	190.761	207.373	19.117	−0.277
3700	61.678	354.489	301.266	196.927	205.884	13.908	−0.196
3800	61.712	356.135	302.688	203.096	204.356	8.740	−0.120
3900	61.744	357.738	304.079	209.269	202.788	3.612	−0.048
4000	61.774	359.302	305.440	215.445	201.177	−1.475	0.019
4100	61.802	360.827	306.773	221.624	199.522	−6.520	0.083
4200	61.827	362.317	308.078	227.805	197.819	−11.525	0.143
4300	61.851	363.772	309.356	233.989	196.068	−16.489	0.200
4400	61.874	365.194	310.609	240.176	194.265	−21.412	0.254
4500	61.895	366.585	311.837	246.364	192.409	−26.292	0.305
4600	61.914	367.946	313.042	252.554	190.498	−31.132	0.354
4700	61.933	369.277	314.225	258.747	188.530	−35.928	0.399
4800	61.950	370.581	315.385	264.941	186.503	−40.683	0.443
4900	61.966	371.859	316.525	271.137	184.416	−45.394	0.484
5000	61.982	373.111	317.644	277.334	182.267	−50.063	0.523
5100	61.996	374.339	318.744	283.533	180.054	−54.687	0.560
5200	62.010	375.543	319.825	289.733	177.777	−59.268	0.595
5300	62.023	376.724	320.887	295.935	175.435	−63.804	0.629
5400	62.035	377.883	321.932	302.138	173.026	−68.296	0.661
5500	62.046	379.022	322.959	308.342	170.550	−72.742	0.691
5600	62.057	380.140	323.971	314.547	168.007	−77.143	0.720
5700	62.068	381.238	324.966	320.753	165.395	−81.498	0.747
5800	62.077	382.318	325.945	326.961	162.716	−85.806	0.773
5900	62.087	383.379	326.910	333.169	159.968	−90.067	0.797
6000	62.096	384.423	327.860	339.378	157.151	−94.281	0.821

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K)$ = [272.027 ± 13] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [206.3 ± 42] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [209.6 ± 42] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[410](1)
[2200](1)
[925](1)
[380](2)
[165](2)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distances: C–C = 1.195 Å; C–Cl = 1.64 Å
Bond Angle: Cl–C–C = 180°
Rotational Constant: $B_0 = 0.046368\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation of dichloroacetylene is calculated from the estimated $\Delta_f H°(298.15\ K) = -53 \pm 10$ $kcal·mol^{-1}$ for ClC ≡ CCl(g) + Cl_2(g) → Cl_2C = CCl_2(g), using $\Delta_f H°(C_2Cl_4, g, 298.15\ K) = -2.9$ kcal mol^{-1}.[1] The value of $\Delta_f H°(298.15\ K)$ is assumed to be the same as that for the reaction HC ≡ CH(g) + Cl_2(g) → CHCl = CHCl(g), using $\Delta_f H°$(CHCl = CHCl, g, 298.15 K) = 1.2 $kcal·mol^{-1}$.[2]

Heat Capacity and Entropy

The linear molecular structure and bond distances were determined from electron diffraction studies by Hassel and Viervoll.[3]

All five fundamental vibrational frequencies are calculated by the modified valence force method[4] from estimated force constants which are interpolated from those of C_2I_2,[5] CH ≡ CF,[6] CH ≡ CCl,[6] CH ≡ CBr,[6] and C_2D_2.[4]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0	0.	0. INFINITE	−14.565	206.336	206.336	INFINITE
100	42.627	212.575 324.555	−11.198	206.672	204.506	−106.823
200	57.837	247.336 277.809	−6.095	208.085	201.843	−52.716
250	62.360	260.755 273.089	−3.084	208.886	200.190	−41.827
298.15	65.573	272.027 272.027	0.	209.618	198.448	−34.767
300	65.680	272.433 272.028	0.121	209.645	198.378	−34.541
350	68.213	282.756 272.837	3.471	210.335	196.445	−29.318
400	70.218	292.000 274.665	6.934	210.942	194.418	−25.388
450	71.861	300.368 277.063	10.487	211.463	192.320	−22.324
500	73.250	308.013 279.782	14.116	211.900	190.169	−19.867
600	75.515	321.577 285.646	21.559	212.554	185.757	−16.172
700	77.312	333.358 291.639	29.203	212.981	181.255	−13.525
800	78.775	343.780 297.517	37.010	213.246	176.703	−11.538
900	79.977	353.130 303.186	44.950	213.396	172.125	−9.990
1000	80.970	361.610 308.611	52.999	213.462	167.535	−8.751
1100	81.794	369.367 313.787	61.138	213.464	162.942	−7.737
1200	82.480	376.514 318.720	69.353	213.414	158.351	−6.893
1300	83.055	383.139 323.424	77.630	213.322	153.765	−6.178
1400	83.539	389.312 327.912	85.961	213.191	149.189	−5.566
1500	83.950	395.090 332.200	94.336	213.026	144.623	−5.036
1600	84.300	400.520 336.302	102.749	212.829	140.069	−4.573
1700	84.600	405.640 340.232	111.194	212.602	135.528	−4.164
1800	84.859	410.483 344.001	119.667	212.344	131.002	−3.802
1900	85.084	415.077 347.622	128.165	212.056	126.490	−3.477
2000	85.280	419.447 351.105	136.683	211.738	121.995	−3.186
2100	85.452	423.612 354.459	145.220	211.389	117.516	−2.923
2200	85.604	427.590 357.694	153.773	211.008	113.055	−2.684
2300	85.738	431.399 360.816	162.340	210.594	108.611	−2.467
2400	85.857	435.050 363.834	170.920	210.146	104.187	−2.268
2500	85.964	438.557 366.753	179.511	209.662	99.782	−2.085
2600	86.059	441.931 369.580	188.112	209.142	95.397	−1.917
2700	86.144	445.180 372.320	196.723	208.583	91.033	−1.761
2800	86.222	448.315 374.978	205.341	207.987	86.689	−1.617
2900	86.291	451.341 377.560	213.967	207.351	82.368	−1.484
3000	86.355	454.268 380.068	222.599	206.677	78.070	−1.359
3100	86.412	457.100 382.508	231.238	205.963	73.795	−1.243
3200	86.465	459.845 384.882	239.881	205.211	69.543	−1.135
3300	86.513	462.506 387.194	248.530	204.421	65.316	−1.034
3400	86.557	465.090 389.447	257.184	203.595	61.113	−0.939
3500	86.598	467.599 391.644	265.842	202.734	56.935	−0.850
3600	86.635	470.039 393.788	274.503	201.840	52.782	−0.766
3700	86.670	472.413 395.881	283.169	200.915	48.654	−0.687
3800	86.702	474.725 397.926	291.837	199.961	44.551	−0.612
3900	86.731	476.978 399.924	300.509	198.981	40.474	−0.542
4000	86.759	479.174 401.878	309.183	197.978	36.423	−0.476
4100	86.784	481.317 403.790	317.861	196.953	32.396	−0.413
4200	86.808	483.408 405.660	326.540	195.909	28.395	−0.353
4300	86.830	485.451 407.492	335.222	194.850	24.420	−0.297
4400	86.851	487.447 409.287	343.906	193.776	20.468	−0.243
4500	86.870	489.399 411.046	352.592	192.692	16.542	−0.192
4600	86.888	491.309 412.770	361.280	191.599	12.639	−0.144
4700	86.906	493.178 414.461	369.970	190.500	8.761	−0.097
4800	86.922	495.008 416.120	378.661	189.397	4.906	−0.053
4900	86.937	496.800 417.748	387.354	188.291	1.074	−0.011
5000	86.951	498.557 419.347	396.048	187.185	−2.736	0.029
5100	86.964	500.279 420.917	404.744	186.079	−6.523	0.067
5200	86.977	501.967 422.459	413.441	184.977	−10.289	0.103
5300	86.989	503.624 423.975	422.140	183.878	−14.034	0.138
5400	87.000	505.250 425.465	430.839	182.785	−17.758	0.172
5500	87.011	506.847 426.930	439.540	181.698	−21.461	0.204
5600	87.021	508.415 428.372	448.241	180.617	−25.146	0.235
5700	87.031	509.955 429.789	456.944	179.545	−28.811	0.264
5800	87.040	511.469 431.185	465.647	178.481	−32.456	0.292
5900	87.048	512.957 432.558	474.352	177.427	−36.084	0.319
6000	87.057	514.420 433.910	483.057	176.381	−39.695	0.346

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 343.421\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -11.873 \pm 2.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -12.426 \pm 2.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	63557	[1]
[37700]	[1]	70097	[1]
[50350]	[1]	72410	[1]
[59000]	[1]		

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1571 (1)	1000 (1)	918 (1)
447 (1)	347 (1)	176 (1)
235 (1)	324 (1)	777 (1)
110 (1)	512 (1)	288 (1)

Point Group: D_{2h} $\sigma = 4$
Bond Distances: Cl–C = 1.724 Å; C–C = 1.327 Å
Bond Angle: Cl–C–Cl = 113.3°
Product of the Moments of Inertia: $I_A I_B I_C = 3.431926 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of combustion $\Delta E(Cl_2Cl_4, l, 293\ K)$ has been determined by the "Quartz Wool" method by Smith *et al.*[1] The free chlorine produced from combustion was reduced to hydrogen chloride by a quartz spiral moistened with a solution of arsenious acid in the combustion bomb. Based on the reported results, the enthalpy change at 298.15 K for the reaction $C_2Cl_4(l) + O_2(g) + 2H_2O(l) = 2CO_2(g) + 4HCl(aq, 600H_2O)$ is evaluated as $-198.40\ kcal·mol^{-1}$, using recent auxiliary data from[2] and Parker[3] and $C_p°$ for C_2Cl_4(l) from Kurbatov.[4] Employing $\Delta_f H°(298.15\ K) = -94.054$, -39.823 and $-68.315\ kcal·mol^{-1}$ for CO_2(g), HCl(aq, $600H_2O$) and H_2O(l), respectively, we calculate the enthalpy of formation for C_2Cl_4(l) as $-12.367\ kcal·mol^{-1}$. Incorporating this value with the value $\Delta_{vap}H°(298.15\ K) = 9.4\ kcal·mol^{-1}$ obtained from Eftring,[5] we derive $\Delta_f H°(298.15\ K) = -2.97 \pm 0.7\ kcal·mol^{-1}$ for C_2Cl_4(g).

Heat Capacity and Entropy

The molecular structure of C_2Cl_4(g) was investigated by the sector–visual method of electron diffraction by Ramachandra and Livingston.[6] The reported bond distances and angle are in agreement with those measured by Karle and Karle,[7] using the sector–microphotometer method, and Lipscomb.[8] The molecular structure has also been determined by Brockway *et al.*,[9] Laszlo,[10] and Dornte[11] by use of electron diffraction. The values reported by Ramachandra and Livingston,[6] are adopted.

The vibrational spectra of tetrachloroethylene have been studied by numerous investigators. The vibrational frequencies assigned by Mann *et al.*[12] are adopted here. These authors also reviewed the results of earlier investigations in detail.

The electronic levels and quantum weights are obtained from Herzberg.[13]

The principal moments of inertia are: $I_A = 48.8379 \times 10^{-39}$, $I_B = 62.8935 \times 10^{-39}$, and $I_C = 111.7314 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.911	−11.873	−11.873	INFINITE
100	56.855	260.362	417.923	−15.756	−13.662	−1.706	0.891
200	81.269	308.108	351.744	−8.727	−13.361	10.236	−2.673
250	89.301	327.140	344.961	−4.455	−12.918	16.086	−3.361
298.15	95.546	343.421	343.421	0.	−12.426	21.628	−3.789
300	95.762	344.013	343.423	0.177	−12.407	21.839	−3.802
350	101.048	359.185	344.609	5.101	−11.861	27.504	−4.105
400	105.411	372.972	347.306	10.266	−11.303	33.089	−4.321
450	109.036	385.603	350.869	15.630	−10.747	38.605	−4.481
500	112.065	397.253	354.933	21.160	−10.205	44.059	−4.603
600	116.755	418.123	363.766	32.614	−9.171	54.814	−4.772
700	120.131	436.388	372.863	44.468	−8.208	65.401	−4.880
800	122.611	452.600	381.836	56.611	−7.306	75.854	−4.953
900	124.471	467.154	390.521	68.969	−6.457	86.198	−5.003
1000	125.893	480.345	398.854	81.490	−5.655	96.449	−5.038
1100	126.999	492.398	406.818	94.137	−4.897	106.623	−5.063
1200	127.874	503.487	414.418	106.883	−4.177	116.729	−5.081
1300	128.576	513.751	421.669	119.706	−3.496	126.776	−5.094
1400	129.147	523.301	428.592	132.593	−2.852	136.773	−5.103
1500	129.616	532.228	435.206	145.532	−2.244	146.725	−5.109
1600	130.007	540.606	441.535	158.514	−1.672	156.637	−5.114
1700	130.336	548.498	447.597	171.532	−1.135	166.515	−5.116
1800	130.614	555.956	453.412	184.579	−0.636	176.362	−5.118
1900	130.852	563.024	458.996	197.653	−0.175	186.182	−5.119
2000	131.057	569.741	464.367	210.749	0.247	195.979	−5.118
2100	131.234	576.140	469.538	223.863	0.627	205.757	−5.118
2200	131.389	582.249	474.524	236.995	0.964	215.517	−5.117
2300	131.525	588.092	479.335	250.141	1.254	225.262	−5.116
2400	131.645	593.692	483.984	263.299	1.496	234.996	−5.115
2500	131.751	599.069	488.481	276.469	1.686	244.721	−5.113
2600	131.845	604.238	492.834	289.649	1.822	254.440	−5.112
2700	131.930	609.215	497.053	302.838	1.903	264.155	−5.110
2800	132.005	614.015	501.145	316.035	1.925	273.867	−5.109
2900	132.074	618.648	505.118	329.239	1.890	283.580	−5.108
3000	132.135	623.127	508.977	342.449	1.796	293.295	−5.107
3100	132.191	627.460	512.730	355.666	1.643	303.013	−5.106
3200	132.242	631.658	516.381	368.887	1.432	312.738	−5.105
3300	132.289	635.728	519.936	382.114	1.166	322.471	−5.104
3400	132.331	639.678	523.400	395.345	0.847	332.212	−5.104
3500	132.370	643.515	526.777	408.580	0.478	341.963	−5.104
3600	132.406	647.244	530.072	421.819	0.063	351.726	−5.103
3700	132.440	650.872	533.288	435.061	−0.395	361.500	−5.103
3800	132.470	654.405	536.429	448.307	−0.891	371.287	−5.104
3900	132.499	657.846	539.498	461.555	−1.419	381.088	−5.104
4000	132.525	661.201	542.499	474.807	−1.976	390.904	−5.105
4100	132.550	664.474	545.434	488.060	−2.555	400.733	−5.105
4200	132.574	667.668	548.307	501.317	−3.151	410.576	−5.106
4300	132.596	670.788	551.119	514.575	−3.760	420.434	−5.107
4400	132.617	673.836	553.874	527.836	−4.376	430.306	−5.108
4500	132.636	676.817	556.573	541.098	−4.994	440.192	−5.110
4600	132.655	679.732	559.219	554.363	−5.609	450.092	−5.111
4700	132.674	682.585	561.813	567.629	−6.217	460.005	−5.112
4800	132.691	685.379	564.358	580.898	−6.814	469.931	−5.114
4900	132.708	688.115	566.856	594.168	−7.395	479.870	−5.115
5000	132.725	690.796	569.308	607.439	−7.957	489.819	−5.117
5100	132.741	693.425	571.716	620.713	−8.496	499.780	−5.119
5200	132.758	696.002	574.082	633.987	−9.010	509.751	−5.121
5300	132.774	698.531	576.406	647.264	−9.496	519.732	−5.122
5400	132.790	701.013	578.691	660.542	−9.951	529.722	−5.124
5500	132.807	703.450	580.937	673.822	−10.372	539.720	−5.126
5600	132.823	705.843	583.146	687.104	−10.759	549.725	−5.128
5700	132.840	708.194	585.319	700.387	−11.110	559.737	−5.129
5800	132.857	710.505	587.458	713.672	−11.422	569.755	−5.131
5900	132.875	712.776	589.563	726.958	−11.696	579.777	−5.133
6000	132.893	715.009	591.635	740.247	−11.930	589.804	−5.135

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 397.880\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -135.83 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -134.22 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
976(1)	678(1)	223(1)
431(1)	377(1)	778(2)
164(1)	858(1)	267(2)
Internal Rotation	340(2)	139(2)

Point Group: D_{3d}
Bond Distances: Cl–C = 1.74 Å; C–C = 1.55 Å; $\sigma = 6$
Bond Angles: Cl–C–Cl = 110°; Cl–C–C = 109°
Product of the Moments of Inertia: $I_A I_B I_C = 9.144710 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

Smith *et al.*[1] determined the heat of combustion of C_2Cl_6(cr) to be $\Delta E(293\ K) = -718.7 \pm 2\ cal·g^{-1}$ (uncorrected) by use of the 'Quartz Wool' method. The free chlorine produced was reduced to HCl by employing the quartz spiral moistened iwth a solution of arsenious acid in the combustion bomb. Adopting the reported results and recent auxiliary data,[2,3,4] we evaluate the values $\Delta_c H°(298.15\ K) = -173.525$ and $\Delta_f H°(298.15\ K) = -48.58\ kcal·mol^{-1}$ for C_2Cl_6(cr). Kirkbride[5] measured the enthalpy changes as −32.0 and 4.7 $kcal·mol^{-1}$ for the following two reactions by solution calorimetry: $C_2Cl_4(l)+Cl_2(g) = C_2Cl_6(aq)$ and $C_2Cl_6(cr) = C_2Cl_6(aq)$. Hence we obtain $\Delta_f H°(298.15\ K) = -49.07\ kcal·mol^{-1}$ for C_2Cl_6(cr), using $\Delta_f H°(C_2Cl_4, l, 298.15\ K) = -12.37\ kcal·mol^{-1}$. This value is in reasonable agreement with the adopted value $-48.58\ kcal·mol^{-1}$.

Hexachloroethane (cr) has three modifications, namely triclinic, monoclinic and cubic, with transition temperatures of 318 and 345 K.[4] The sublimiation pressures over the different phases have been measured by Ivin,[8] Lee,[7] and Nitta.[26] Based oin these data, values for $\Delta_{sub}H°$(triclinic, 298.15 K) are derived by a modified second and third law method to be 16.5, 17.1 and 14.8 $kcal·mol^{-1}$, respectively. The analysis depends on the $C_p°$ and $\Delta_{trs}H°$ data determined by Seki and Momotani.[4] The order of magnitude of the two $\Delta_{trs}H°$ values is confirmed by McDonald, private communication, Thermal Research Laboratory, The Dow Chemical Company, Midland, Michigan. Pressures reported by Nelson[6] are systematically lower than the above data by about 10%; therefore, his data are not used. Third law analysis is not applicable to the pressure data due to lack of $S°$(triclinic, 298.15 K). Adopting $\Delta_{sub}H°(298.15\ K) = 16.5$ and $\Delta_f H°(298.15\ K) = -48.58\ kcal·mol^{-1}$ for C_2Cl_6 (triclinic), we obtain $\Delta_f H°(298.15\ K) = -32.08\ kcal·mol^{-1}$ for C_2Cl_6(g).

The equilibrium constant at 776 K for the reaction $C_2Cl_6(g) = C_2Cl_4(g) + Cl_2(g)$ was reported as 0.8 ± 0.1 (atm) by Puyo *et al.*[9] The corresponding enthalpy change at 298.15 K is evaluated to be 30.8 $kcal·mol^{-1}$ by the third law method, yielding $\Delta_f H°(C_2Cl_6, g, 298.15\ K) = -33.77\ kcal·mol^{-1}$ which is in fair agreement with the adopted one.

Heat Capacity and Entropy

The molecular structure of C_2Cl_6 has been studied previously by means of infrared and Raman spectroscopy,[10] X-ray,[11] and electron diffraction.[12–18] The molecule was found to be in the staggered position in the vapor and solid states. The bond distances and angles adopted here are those reported by Swick *et al.*[16]

Incomplete assignments of vibrational frequencies for C_2Cl_6(g) were reported by many investigators.[21–24] The adopted frequencies, except the torsional mode ν_4, are obtained from Carney *et al.*[19] The torsional mode is treated as a hindered internal rotation, and thermodynamic properties are calculated[25] from the barrier height of $V_0 = 12.8\ kcal·mol^{-1}$ which was evaluated by Karle[20] from electron diffraction data. The value of $S°(298.15\ K)$ is calculated based on $S°(400\ K) = 105.355\ cal·K^{-1}·mol^{-1}$ which is derived from the free rotor value $S°(400\ K) = 108.121\ cal·K^{-1}·mol^{-1}$ by subtraction of the entropy difference between a free rotor and hindered rotor at 400 K. Internal rotation contributions to $C_p°$ at temperatures below 350 K could not be calculated since they are beyond the range of the values above 350 K and the corresponding harmonic oscillator values ($\nu_4 = 67\ cm^{-1}$) below 150 K. This calculation presumes that the internal rotation approaches harmonic oscillation as $V/RT >> 1$.

The principal moments of inertia are: $I_A = 79.9217 \times 10^{-39}$, $I_B = 92.8302 \times 10^{-39}$, and $I_C = 123.2582 \times 10^{-39}\ g·cm^2$.

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Continued on page 701

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100	76.371	280.567	504.581	−22.401	−135.834	−106.999	55.890
200	115.964	346.938	409.925	−12.597	−135.796	−77.973	20.364
298.15	138.934	397.880	397.880	0.	−134.223	−49.894	8.741
300	139.267	398.741	397.883	0.257	−134.186	−49.371	8.596
400	153.457	440.913	403.536	14.951	−131.948	−21.427	2.798
500	162.260	476.174	414.636	30.769	−129.496	5.921	−0.619
600	167.954	506.295	427.464	47.298	−127.020	32.772	−2.853
700	171.799	532.488	440.638	64.295	−124.584	59.211	−4.418
800	174.531	555.615	453.593	81.618	−122.203	85.304	−5.570
900	176.536	576.293	466.098	99.175	−119.875	111.102	−6.448
1000	178.033	594.973	478.066	116.907	−117.600	136.644	−7.138
1100	179.128	611.994	489.479	134.766	−115.378	161.960	−7.691
1200	180.012	627.620	500.349	152.725	−113.208	187.076	−8.143
1300	180.651	642.055	510.701	170.760	−111.088	212.014	−8.519
1400	181.150	655.462	520.568	188.851	−109.022	236.790	−8.835
1500	181.478	667.971	529.983	206.983	−107.011	261.420	−9.103
1600	181.732	679.692	538.977	225.144	−105.059	285.919	−9.334
1700	181.832	690.713	547.582	243.322	−103.171	310.296	−9.534
1800	181.910	701.108	555.825	261.510	−101.350	334.565	−9.709
1900	181.968	710.945	563.733	279.704	−99.596	358.734	−9.862
2000	182.004	720.280	571.329	297.902	−97.908	382.813	−9.998
2100	181.922	729.158	578.635	316.099	−96.295	406.809	−10.119
2200	181.841	737.619	585.671	334.287	−94.762	430.730	−10.227
2300	181.761	745.701	592.454	352.467	−93.311	454.584	−10.324
2400	181.681	753.435	599.002	370.639	−91.945	478.375	−10.412
2500	181.602	760.850	605.328	388.803	−90.666	502.112	−10.491
2600	181.523	767.971	611.448	406.960	−89.475	525.800	−10.563
2700	181.445	774.820	617.372	425.108	−88.375	549.443	−10.630
2800	181.367	781.417	623.114	443.249	−87.367	573.047	−10.690
2900	181.290	787.780	628.683	461.381	−86.452	596.617	−10.746
3000	181.213	793.925	634.089	479.506	−85.630	620.157	−10.798
3100	181.128	799.865	639.342	497.624	−84.899	643.670	−10.846
3200	181.045	805.615	644.448	515.732	−84.258	667.162	−10.890
3300	180.965	811.185	649.417	533.833	−83.704	690.636	−10.932
3400	180.888	816.586	654.255	551.925	−83.232	714.093	−10.971
3500	180.813	821.828	658.968	570.010	−82.837	737.538	−11.007
3600	180.740	826.921	663.563	588.088	−82.513	760.972	−11.041
3700	180.671	831.872	668.045	606.158	−82.253	784.399	−11.074
3800	180.603	836.689	672.420	624.222	−82.049	807.818	−11.104
3900	180.539	841.380	676.693	642.279	−81.894	831.234	−11.133
4000	180.477	845.950	680.867	660.330	−81.781	854.646	−11.161
4100	180.423	850.405	684.948	678.375	−81.699	878.056	−11.187
4200	180.370	854.753	688.940	696.414	−81.642	901.464	−11.211
4300	180.319	858.996	692.845	714.449	−81.600	924.871	−11.235
4400	180.269	863.141	696.669	732.478	−81.566	948.277	−11.257
4500	180.221	867.192	700.413	750.503	−81.533	971.682	−11.279
4600	180.174	871.152	704.082	768.522	−81.492	995.087	−11.300
4700	180.128	875.026	707.678	786.538	−81.437	1018.489	−11.319
4800	180.084	878.818	711.204	804.548	−81.362	1041.891	−11.338
4900	180.041	882.531	714.663	822.554	−81.259	1065.292	−11.356
5000	180.000	886.168	718.057	840.556	−81.123	1088.688	−11.373
5100	179.960	889.732	721.388	858.554	−80.950	1112.084	−11.390
5200	179.922	893.226	724.659	876.548	−80.734	1135.474	−11.406
5300	179.885	896.653	727.872	894.539	−80.471	1158.860	−11.421
5400	179.849	900.015	731.029	912.525	−80.157	1182.241	−11.436
5500	179.815	903.315	734.131	930.509	−79.789	1205.616	−11.450
5600	179.782	906.555	737.182	948.488	−79.365	1228.983	−11.463
5700	179.751	909.736	740.181	966.465	−78.881	1252.342	−11.476
5800	179.721	912.862	743.131	984.439	−78.335	1275.693	−11.489
5900	179.692	915.934	746.034	1002.409	−77.726	1299.033	−11.501
6000	179.665	918.954	748.891	1020.377	−77.053	1322.361	−11.512

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 85.434 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -86.21 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -85.35 \pm 12.6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Mah[1] determined the enthalpy of combustion of Cr_3C_2(cr) using oxygen bomb calorimetry. She reported $\Delta_c H°(298.15\ K) = -574.5 \pm 0.4$ kcal·mol^{-1} based on the reaction $Cr_3C_2(cr) + 17/4O_2(g) = 3/2Cr_2O_3(cr) + 2CO_2(g)$. Using auxiliary JANAF data,[2] we calculate $\Delta_f H°(298.15\ K) = -20.4$ kcal·mol^{-1} for Cr_3C_2(cr). Mah[1] reported that of the six combustion runs four were complete combustions whereas the other two were 99.17% and 98.57% complete. Corrections were made by Mah[1] for incomplete combustion, formation of small amounts of CO(g), and impurities. These corrections amount to less than 1.95% of the $\Delta_c E°v_c$. There are many equilibrium studies involving Cr_3C_2(cr).[3-13] Our analysis of a portion of these studies is tabulated below:

Source	Reaction	T/K	Method	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[4]	A(14 pts.)**	1244–1382	CO equilibrium pressure	528.39	533.26	3.7 ± 3.4	−21.29
[8]	A(18 pts.)	1316–1366	CO equilibrium pressure	495.46	526.56	23.0 ± 6.4	−24.64
[10]	B(eqn)	880–1100	emf (CaF_2)	−9.34	−12.60	−3.3	−12.60
[11]	B(eqn)	1073–1303	emf ($ThO_2Y_2O_3$)	−12.70	−15.73	−2.5	−15.73
[12]	B(eqn)	885–1095	emf (CaF_2)	−15.42	−14.92	0.5	−14.92

Reactions: (A) $3Cr_2O_3(cr) + 13C(cr) = 2Cr_3C_2(cr) + 9CO(g)$. (B) $3Cr(cr) + 2C(cr) \approx Cr_3C_2(cr)$.
**1374 K point rejected due to statistical test.

The CO(g) equilibrium pressures measured by Heusler[3] in the range 1159–1369 K are higher than those of Kelley *et al.*[4] by a factor varying from 2.0 to 1.4 with increasing temperature. Three studies measured the chromium pressure in equilibrium with C(cr) and Cr_3C_2(cr).[5, 7, 9] Reported heats of formation for Cr_3C_2 from these studies are −23.1 kcal·mol^{-1},[5] −14.2 kcal·mol^{-1},[7] and −22 kcal·mol^{-1}.[9] Alekseev and Shvartsman[6] studied the decarburization of the chromium carbides. Mah[1] analyzed their data and reported $\Delta_f H°(298.15\ K) = -16.6$ kcal·mol^{-1} for Cr_3C_2(cr).

The $\Delta_f H°$ results are quite scattered with the emf results being roughly 5 kcal·mol^{-1} more positive than the combustion and pressure equilibrium studies. Possible explanations for these discrepancies are discussed by Kulkarni and Worrell.[16] We adopt $\Delta_f H°(298.15\ K) = -20.4 \pm 3.0$ kcal·mol^{-1} (−85.354 ± 12.6 kJ·mol^{-1}) for Cr_3C_2(cr) based on the combustion study by Mah.[1]

Heat Capacity and Entropy

The heat capacity of Cr_3C_2(cr) has been measured by Kelley *et al.*[4] [53–296 K, 29 pts.) and DeSorbo[14] (12–301 K, 65 pts.). As reported by DeSorbo,[14] the results of these two studies differ by no more than 0.1%. Using the Debye function $3D$ $(300/T)$ as suggested by DeSorbo,[14] we calculate and adopt $S°(12\ K) = 0.0297$ cal·K^{-1}·mol^{-1} and $H°(12;0) = 0.268$ kcal·mol^{-1}. The enthalpy has been measured by Kelley *et al.*[4] [481–1576 K, 17 pts.] and Oriani and Murphy[15] [297–1188 K, 11 pts.]. As stated by Oriani and Murphy,[15] their results are somewhat lower than those of Kelley *et al.*;[4] the maximum difference is 1.2% at 970 K. For $T > 298.15$ K, we base our adopted values on the enthalpy data of Kelley *et al.*[4] The enthalpy data is subjected to a curve fit procedure with the constraint that it join smoothly in the 298 K region with the enthalpy derived from the heat capacity data of Kelley *et al.*[4] The deviations between the tabulated and observed enthalpy average 0.26% with a maximum of 0.78% at the lowest observed temperature, 480.7 K.

Phase Data

Storms[17] has summarized the phase information for the Cr–Cr_3C_2 system and reported that Cr_3C_2 has an orthorhombic structure. The range of homogeneity is unknown.[17]

Decomposition Data

The tentative phase diagram for the Cr–Cr_3C_2 system proposed by Storms[17] indicated that Cr_3C_2 has an incongruent melting point at 2168 K.

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Continued on page 701

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−15.132	−86.211	−86.211	INFINITE
100	31.322	14.297	155.599	−14.130	−86.263	−86.216	45.035
200	74.718	50.620	93.807	−8.637	−86.175	−86.144	22.499
298.15	99.299	85.434	85.434	0.	−85.354	−86.277	15.115
300	99.663	86.049	85.436	0.184	−85.331	−86.283	15.023
400	115.478	117.037	89.553	10.994	−84.193	−86.719	11.324
500	125.549	143.964	97.805	23.079	−82.549	−87.540	9.145
600	131.486	167.406	107.496	35.946	−80.997	−88.687	7.721
700	135.658	187.997	117.555	49.309	−79.624	−90.079	6.722
800	139.101	206.340	127.528	63.050	−78.422	−91.657	5.985
900	142.260	222.907	137.220	77.118	−77.406	−93.374	5.419
1000	145.327	238.054	146.556	91.498	−76.621	−95.193	4.972
1100	148.377	252.048	155.518	106.183	−76.120	−97.077	4.610
1200	151.448	265.090	164.112	121.174	−75.926	−98.993	4.309
1300	154.553	277.335	172.355	136.474	−76.068	−100.912	4.055
1400	157.695	288.903	180.270	152.086	−76.569	−102.807	3.836
1500	160.871	299.891	187.882	168.014	−77.437	−104.653	3.644
1600	164.084	310.376	195.213	184.261	−78.678	−106.429	3.475
1700	167.322	320.420	202.284	200.831	−80.296	−108.115	3.322
1800	170.586	330.077	209.117	217.727	−82.294	−109.696	3.183
1900	173.870	339.388	215.730	234.949	−84.677	−111.155	3.056
2000	177.176	348.390	222.139	252.501	−87.445	−112.479	2.938
2100	180.489	357.115	228.360	270.385	−90.603	−113.655	2.827
2200	183.761	365.586	234.406	288.597	−152.162	−112.705	2.676
2300	187.075	373.828	240.289	307.139	−150.527	−110.947	2.520
2400	190.389	381.860	246.021	326.012	−148.592	−109.267	2.378
2500	193.702	389.699	251.612	345.217	−146.356	−107.673	2.250

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K)$ = [244.06 ± 63] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [19.4 ± 21] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [20.9 ± 21] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[1050](1)	[450](2)
[1900](1)	[300](2)
1149 (1)	

Ground State Quantum Weight: 1 σ = 2
Point Group: [$D_{\infty h}$]
Bond Distances: C–F = [1.28] Å; C–C = [1.20] Å
Bond Angle: F–C–C = [180]°
Rotational Constant: B_0 = [0.117932] cm^{-1}

Enthalpy of Formation

Farber *et al.*,[1] have obtained equilibrium-weight change data over the C–CF_4 system. Our reanalysis of these data assumes that the equilibrium constants for CF_4, CF_3 and CF_2 are those in the JANAF Tables, and that C_2F_2 was the only other C–F species present at equilibrium. This gives maximum possible concentrations of C_2F_2 and places a lower limit on the heat of formation. The $\Delta_f H°(C_2F_2, g, 298.15\ K)$ values so obtained range from +10 $kcal·mol^{-1}$ from data at 2023 K to −10 $kcal·mol^{-1}$ from data at 2373 K; we adopt a weighted mean of +5 ± 5 $kcal·mol^{-1}$ (20.920 ± 21 $kJ·mol^{-1}$). This value still predicts complete dimerization of CF at 1 atmosphere pressure below about 2200 K, but only CF would exist under experimental conditions such as the study by Farber.

Farber *et al.*[1] also investigated the mass spectrum of the vapor over the C–CF_4 system and did not detect any ion ascribable to C_2F_2. This is additional support for the value adopted.

The C–C bond dissociation energy in C_2F_2 is 113 $kcal·mol^{-1}$, using JANAF CF(g) table (December 31, 1967). This value is 115 $kcal·mol^{-1}$ weaker than the bond dissociation energy of acetylene. In order to explain such a large decrease, a crossing of the repulsive approach of two $^2\Pi$ CF molecules with an attractive approach of two $^4\Sigma$ CF molecules may be postulated. This follows the reasoning used by Simons[2] to explain the bond dissociation energy of C_2F_4.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that for C_2H_2(g). The C–F and C–C bond distances are estimated from those in HC = CF reported by Tyler and Sheridan.[3] The assymmetric stretching frequency, ν_3 = 1149 cm^{-1}, was observed by Heicklen and Knight.[4] The other vibrational frequencies were estimated by comparison with those for C_2H_2(g) and C_2HF(g) reported by Herzberg,[5] Hunt and Wilson,[6] and Brown and Tyler.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.403	19.444	19.444	INFINITE
100	34.428	194.599	288.398	−9.380	19.441	17.208	−8.989
200	48.351	223.037	249.016	−5.196	20.043	14.799	−3.865
250	53.162	234.364	244.977	−2.653	20.492	13.436	−2.807
298.15	56.935	244.060	244.060	0.	20.920	12.038	−2.109
300	57.068	244.412	244.061	0.105	20.936	11.983	−2.086
350	60.380	253.465	244.768	3.044	21.344	10.458	−1.561
400	63.249	261.719	246.379	6.136	21.702	8.878	−1.159
450	65.757	269.317	248.511	9.363	22.005	7.256	−0.842
500	67.957	276.361	250.948	12.707	22.253	5.604	−0.585
600	71.592	289.087	256.267	19.692	22.609	2.238	−0.195
700	74.412	300.344	261.775	26.998	22.818	−1.176	0.088
800	76.610	310.429	267.237	34.554	22.922	−4.612	0.301
900	78.336	319.556	272.552	42.304	22.949	−8.056	0.468
1000	79.704	327.883	277.674	50.209	22.917	−11.499	0.601
1100	80.799	335.533	282.591	58.236	22.837	−14.938	0.709
1200	81.685	342.603	287.302	66.362	22.714	−18.366	0.799
1300	82.410	349.171	291.811	74.568	22.553	−21.784	0.875
1400	83.007	355.301	296.130	82.839	22.355	−25.187	0.940
1500	83.506	361.045	300.268	91.166	22.122	−28.575	0.995
1600	83.924	366.448	304.237	99.538	21.855	−31.946	1.043
1700	84.279	371.547	308.048	107.949	21.556	−35.300	1.085
1800	84.582	376.373	311.711	116.392	21.227	−38.635	1.121
1900	84.843	380.953	315.236	124.864	20.868	−41.951	1.153
2000	85.069	385.311	318.631	133.360	20.484	−45.247	1.182
2100	85.265	389.466	321.906	141.876	20.077	−48.524	1.207
2200	85.437	393.437	325.068	150.412	19.649	−51.781	1.229
2300	85.588	397.238	328.124	158.963	19.205	−55.018	1.249
2400	85.722	400.884	331.080	167.529	18.748	−58.235	1.267
2500	85.841	404.386	333.943	176.107	18.282	−61.433	1.284
2600	85.948	407.754	336.717	184.697	17.809	−64.612	1.298
2700	86.043	411.000	339.409	193.296	17.334	−67.773	1.311
2800	86.128	414.131	342.022	201.905	16.859	−70.917	1.323
2900	86.205	417.154	344.561	210.522	16.387	−74.043	1.334
3000	86.275	420.078	347.030	219.146	15.920	−77.154	1.343
3100	86.339	422.908	349.432	227.776	15.462	−80.249	1.352
3200	86.397	425.650	351.771	236.413	15.012	−83.329	1.360
3300	86.449	428.310	354.050	245.056	14.574	−86.395	1.368
3400	86.498	430.891	356.273	253.703	14.148	−89.448	1.374
3500	86.542	433.399	358.440	262.355	13.735	−92.489	1.380
3600	86.583	435.838	360.557	271.011	13.336	−95.518	1.386
3700	86.620	438.210	362.624	279.671	12.951	−98.537	1.391
3800	86.655	440.521	364.643	288.335	12.581	−101.545	1.396
3900	86.687	442.772	366.618	297.002	12.226	−104.544	1.400
4000	86.717	444.967	368.549	305.673	11.885	−107.533	1.404
4100	86.745	447.109	370.439	314.346	11.558	−110.515	1.408
4200	86.771	449.200	372.290	323.022	11.246	−113.488	1.411
4300	86.795	451.242	374.102	331.700	10.947	−116.455	1.415
4400	86.817	453.237	375.878	340.381	10.661	−119.414	1.418
4500	86.838	455.189	377.619	349.063	10.387	−122.367	1.420
4600	86.858	457.097	379.326	357.748	10.125	−125.315	1.423
4700	86.876	458.966	381.001	366.435	9.875	−128.256	1.425
4800	86.894	460.795	382.644	375.123	9.634	−131.192	1.428
4900	86.910	462.587	384.257	383.814	9.403	−134.124	1.430
5000	86.925	464.343	385.842	392.505	9.181	−137.051	1.432
5100	86.940	466.064	387.398	401.199	8.967	−139.973	1.434
5200	86.954	467.752	388.927	409.893	8.760	−142.892	1.435
5300	86.966	469.409	390.430	418.589	8.559	−145.806	1.437
5400	86.979	471.035	391.907	427.287	8.364	−148.717	1.439
5500	86.990	472.631	393.361	435.985	8.174	−151.624	1.440
5600	87.001	474.198	394.790	444.685	7.989	−154.528	1.441
5700	87.011	475.738	396.197	453.385	7.806	−157.429	1.443
5800	87.021	477.252	397.581	462.087	7.626	−160.326	1.444
5900	87.031	478.739	398.944	470.789	7.448	−163.220	1.445
6000	87.039	480.202	400.287	479.493	7.271	−166.111	1.446

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = 298.533 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -491.61 \pm 2.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -495.39 \pm 2.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2271(1)	1215(2)
1228(1)	625(2)
801(1)	464(2)
521(1)	192(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: C–F = 1.335 Å; C–C = 1.461 Å; CN = 1.153 Å
Bond Angles: F–C–F = 107.5°; F–C–C = 111.38°
Product of the Moments of Inertia: $I_A I_B I_C = 1.186732 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the enthalpies of formation of CF_3, C_2F_4, and CF_3X(X = H, Cl, Br, I, CN). Details of the input data and adjustment are given by Syverud.[1] Input included a calorimetric link to NF_3(g) and CF_4(g) plus an equilibrium link to C_2F_6(g) and C_2N_2(g). The calorimetric study[2] gave $\Delta_f H° = -824.4 \pm 0.6$ kcal·mol^{-1} at 298.15 K for the reaction $3CF_3CN(g) + 5NF_3(g) \rightarrow 6CF_4(g) + 4N_2(g)$. Equilibrium data[3] in the range 865–925 K give $\Delta_f H°$(3rd law) = 10.59 and $\Delta_f H°$(2nd law) = 10.59 ± 0.20 kcal·mol^{-1} at 298.15 K for the reaction $C_2F_6(g) + C_2N_2(g) \rightarrow 2CF_3CN(g)$. The entropy difference, $\Delta_r S°$ (2nd law)–$\Delta_r S°$ (3rd law), is 0.0 ± 1.5 cal·K^{-1}·mol^{-1}. Deviations between the selected $\Delta_f H°$ and the two observations are 1.37 and 0.15 kcal·mol^{-1}, respectively, both considerably less than the overall uncertainties including those in auxiliary values of $\Delta_f H°$. Subsequent to the adjustment, Curnutt and Sinke[4] reported $\Delta_r H° = -197.6 \pm 0.9$ kcal·mol^{-1} from a calorimetric study of $CF_3CN(g) + 1.25\ O_2(g) + 1.5\ H_2O(l) \rightarrow 2\ CO_2(g) + 0.5\ N_2(g) + 3HF(aq, 120\ H_2O)$. Their result of $\Delta_f H° = -118.4 \pm 1.2$ kcal·mol^{-1} is confirmation of the selected value.

Heat Capacity and Entropy

The molecular structure has been derived from electron–diffraction data by Danford and Livingston[5] and from microwave data by Sheridan and Gordy[6] and Thomas *et al.*[7] These studies are in substantial agreement except for a difference of about 0.04 Å in the C–C bond distance. We adopt the results of Thomas *et al.*[7] since they are based on data for several isotopic species. Principal moments of inertia are: $I_A = 14.6267 \times 10^{-39}$ and $I_B = I_C = 28.4842 \times 10^{-39}\ g \cdot cm^2$. Vibrational frequencies are taken from the assignments of Edgell and Potter.[8] All values except ν_8 are from infrared spectra of the vapor phase. Raman spectra of the liquid provide $\nu_8$and confirm the infrared data. Similar assignments have been given by Janz and Wait[9] based on spectra of Wait and Janz.[10]

Pace and Bobka[11] used low temperature calorimetric data to derive the entropy of the ideal gas at the normal boiling point of 205.47 K. The experimental value of 65.01 ± 0.2 cal·K^{-1}·mol^{-1} is in good agreement with 65.03 cal·K^{-1}·mol^{-1} obtained from this table. The largest uncertainty in $C_p°$ and $S°$ probably arises from neglect of anharmonicity and rotational distortion. Uncertainty in the entropy is estimated to vary from 0.1 to 0.5 cal·K^{-1}·mol^{-1} over the range 300 to 1000 K. Discussions of the neglect of anharmonicity are given on the tables for $CClF_3$(g) and CF_4(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.897	−491.608	−491.608	INFINITE
100	43.761	234.503	356.929	−12.243	−493.884	−483.598	252.606
200	62.441	270.513	305.210	−6.939	−495.083	−472.759	123.472
250	71.031	285.389	299.782	−3.598	−495.314	−467.147	97.605
298.15	78.255	298.533	298.533	0.	−495.386	−461.713	80.890
300	78.513	299.017	298.534	0.145	−495.386	−461.505	80.355
350	84.951	311.616	299.514	4.236	−495.349	−455.859	68.033
400	90.470	323.330	301.768	8.625	−495.239	−450.225	58.793
450	95.200	334.266	304.778	13.270	−495.084	−444.607	51.609
500	99.263	344.512	308.244	18.134	−494.902	−439.008	45.863
600	105.795	363.216	315.878	28.402	−494.492	−427.867	37.249
700	110.730	379.912	323.855	39.240	−494.049	−416.797	31.102
800	114.522	394.956	331.818	50.510	−493.589	−405.793	26.496
900	117.482	408.623	339.604	62.116	−493.122	−394.846	22.916
1000	119.823	421.126	347.140	73.986	−492.653	−383.952	20.056
1100	121.700	432.638	354.396	86.066	−492.190	−373.104	17.717
1200	123.221	443.295	361.366	98.314	−491.737	−362.298	15.770
1300	124.468	453.208	368.054	110.701	−491.299	−351.529	14.125
1400	125.500	462.471	374.471	123.201	−490.881	−340.794	12.715
1500	126.362	471.160	380.630	135.795	−490.486	−330.087	11.495
1600	127.089	479.339	386.547	148.469	−490.115	−319.406	10.428
1700	127.706	487.063	392.234	161.209	−489.769	−308.748	9.487
1800	128.234	494.378	397.707	174.007	−489.449	−298.109	8.651
1900	128.690	501.324	402.980	186.854	−489.153	−287.487	7.904
2000	129.084	507.935	408.064	199.743	−488.879	−276.880	7.231
2100	129.428	514.241	412.971	212.669	−488.623	−266.287	6.624
2200	129.730	520.270	417.712	225.627	−488.382	−255.705	6.071
2300	129.996	526.042	422.297	238.614	−488.152	−245.134	5.567
2400	130.232	531.580	426.736	251.625	−487.927	−234.572	5.105
2500	130.441	536.901	431.037	264.659	−487.704	−224.021	4.681
2600	130.629	542.020	435.208	277.713	−487.477	−213.478	4.289
2700	130.797	546.954	439.256	290.784	−487.241	−202.944	3.926
2800	130.948	551.713	443.188	303.872	−486.993	−192.419	3.590
2900	131.084	556.311	447.010	316.973	−486.729	−181.903	3.276
3000	131.208	560.757	450.727	330.088	−486.445	−171.396	2.984
3100	131.320	565.061	454.347	343.214	−486.139	−160.900	2.711
3200	131.422	569.232	457.872	356.352	−485.807	−150.413	2.455
3300	131.516	573.277	461.308	369.499	−485.448	−139.938	2.215
3400	131.601	577.205	464.659	382.654	−485.060	−129.474	1.989
3500	131.680	581.021	467.930	395.819	−484.642	−119.021	1.776
3600	131.752	584.731	471.123	408.990	−484.192	−108.581	1.575
3700	131.819	588.342	474.242	422.169	−483.710	−98.154	1.386
3800	131.881	591.858	477.291	435.354	−483.197	−87.741	1.206
3900	131.938	595.285	480.273	448.545	−482.651	−77.340	1.036
4000	131.991	598.626	483.190	461.741	−482.073	−66.955	0.874
4100	132.040	601.885	486.046	474.943	−481.464	−56.585	0.721
4200	132.086	605.068	488.842	488.149	−480.824	−46.229	0.575
4300	132.128	608.176	491.581	501.360	−480.153	−35.890	0.436
4400	132.168	611.214	494.266	514.575	−479.454	−25.566	0.304
4500	132.206	614.185	496.898	527.793	−478.726	−15.259	0.177
4600	132.241	617.091	499.479	541.016	−477.970	−4.968	0.056
4700	132.274	619.936	502.012	554.241	−477.189	5.307	−0.059
4800	132.304	622.721	504.498	567.470	−476.382	15.564	−0.169
4900	132.333	625.449	506.938	580.702	−475.552	25.804	−0.275
5000	132.361	628.123	509.335	593.937	−474.699	36.027	−0.376
5100	132.386	630.744	511.690	607.174	−473.825	46.233	−0.474
5200	132.411	633.315	514.005	620.414	−472.930	56.422	−0.567
5300	132.434	635.837	516.280	633.656	−472.017	66.593	−0.656
5400	132.455	638.313	518.517	646.901	−471.086	76.747	−0.742
5500	132.476	640.744	520.717	660.147	−470.138	86.883	−0.825
5600	132.495	643.131	522.882	673.396	−469.175	97.002	−0.905
5700	132.514	645.476	525.012	686.646	−468.198	107.103	−0.981
5800	132.531	647.781	527.109	699.899	−467.208	117.187	−1.055
5900	132.548	650.047	529.173	713.153	−466.207	127.256	−1.127
6000	132.564	652.275	531.207	726.408	−465.195	137.305	−1.195

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 300.015 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -655.14 \pm 2.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -658.56 \pm 2.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1872(1)	1340(1)	1337(1)
778(1)	551(1)	218(1)
394(1)	406(1)	1186(1)
190(1)	508(1)	558(1)

Ground State Quantum Weight: 1 $\sigma = 4$

Point Group: D_{2h}

Bond Distances: C–F = 1.313 Å; C–C = 1.313 Å

Bond Angle: F–C–F = 114°

Product of the Moments of Inertia: $I_A I_B I_C = 1.588028 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in[1]. In this case, the selected $\Delta_f H°$ corresponds to the weighted average of three calorimetric studies[2,3] which may be reduced to the following:

Source	Reaction	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
2	$C_2F_4(g) \rightarrow CF_4(g) + C$(graphite)	-65.4 ± 0.5	-157.6 ± 0.6
2	$C_2F_4(g) + 2H_2(g) \rightarrow 4HF(50\ H_2O) + 2C$(graphite)	-150.9 ± 1.2	-156.2 ± 1.3
3	$C_2F_4(g) + 4Na(cr) \rightarrow 4NaF(cr) + 2C$(graphite)	-392.9 ± 1.3	-157.2 ± 1.4

Amorphous carbon was formed in all three calorimetric reactions and separate combustions were made to refer the observed product to the standard state of graphite. Other calorimetric studies[4,5,6] are omitted because of apparent uncertainties in the reductions to the standard-state reactions.

Heat Capacity and Entropy

The molecular structure has been derived from electron–diffraction data by Karle and Karle,[7] Broun and Livingston[8] and Young.[9] The resulting structures differ in minor respects, particularly in the exact location of the two carbons. Values from Karle[7] are adopted since they are intermediate between the others. Values from Young[9] and Broun and Livingston[8] correspond to changes of ±2.2% in the product of the moments of inertia. Principal moments of inertia for the adopted structure are: $I_A = 15.3019 \times 10^{-39}$, $I_B = 25.4600 \times 10^{-39}$ and $I_C = 40.7619 \times 10^{-39}\ g \cdot cm^2$. Vibrational fundamentals are those selected by Shimanouchi[10] from the data of Mann *et al.*,[11] Monfils and Duchesne[12] and Nielsen *et al.*[13]

Furukawa *et al.*[14] reported low–temperature calorimetric data from which the ideal gas entropy may be derived as 64.54 ± 0.09 $cal \cdot K^{-1} \cdot mol^{-1}$ at 197.53 K. The calculated entropy from this table is also 64.54 $cal \cdot K^{-1} \cdot mol^{-1}$. The range in values of $I_A I_B I_C$ corresponds to an entropy change of ±0.022 $cal \cdot K^{-1} \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.330	−655.140	−655.140	INFINITE
100	44.191	233.706	360.595	−12.689	−657.432	−646.538	337.717
200	65.202	270.959	306.921	−7.192	−658.446	−635.144	165.883
250	73.646	286.445	301.303	−3.715	−658.565	−629.302	131.485
298.15	80.458	300.015	300.015	0.	−658.562	−623.665	109.263
300	80.698	300.514	300.017	0.149	−658.560	−623.448	108.552
350	86.707	313.416	301.022	4.338	−658.491	−617.601	92.172
400	91.903	325.342	303.326	8.806	−658.387	−611.767	79.889
450	96.426	336.433	306.396	13.517	−658.267	−605.946	70.336
500	100.373	346.802	309.923	18.439	−658.138	−600.140	62.696
600	106.824	365.699	317.676	28.814	−657.867	−588.565	51.239
700	111.747	382.553	325.762	39.753	−657.577	−577.037	43.059
800	115.524	397.732	333.826	51.125	−657.266	−565.553	36.927
900	118.450	411.515	341.704	62.830	−656.939	−554.108	32.160
1000	120.743	424.118	349.324	74.794	−656.601	−542.700	28.348
1100	122.561	435.715	356.658	86.963	−656.259	−531.327	25.231
1200	124.020	446.444	363.699	99.294	−655.922	−519.984	22.634
1300	125.206	456.419	370.452	111.758	−655.595	−508.669	20.439
1400	126.179	465.735	376.929	124.328	−655.285	−497.380	18.557
1500	126.986	474.468	383.143	136.988	−654.995	−486.111	16.928
1600	127.662	482.686	389.110	149.721	−654.729	−474.860	15.503
1700	128.233	490.443	394.845	162.517	−654.489	−463.626	14.245
1800	128.720	497.787	400.362	175.365	−654.274	−452.405	13.128
1900	129.137	504.758	405.675	188.258	−654.082	−441.196	12.129
2000	129.498	511.391	410.796	201.191	−653.911	−429.995	11.230
2100	129.811	517.717	415.738	214.156	−653.757	−418.804	10.417
2200	130.085	523.762	420.512	227.152	−653.614	−407.619	9.678
2300	130.326	529.550	425.128	240.172	−653.477	−396.440	9.003
2400	130.539	535.102	429.595	253.216	−653.339	−385.268	8.385
2500	130.728	540.434	433.923	266.279	−653.195	−374.101	7.816
2600	130.896	545.565	438.119	279.361	−653.038	−362.940	7.292
2700	131.047	550.508	442.190	292.458	−652.862	−351.786	6.806
2800	131.182	555.276	446.144	305.570	−652.662	−340.639	6.355
2900	131.305	559.882	449.987	318.694	−652.432	−329.499	5.935
3000	131.415	564.335	453.725	331.830	−652.167	−318.368	5.543
3100	131.515	568.646	457.363	344.977	−651.865	−307.246	5.177
3200	131.607	572.823	460.906	358.133	−651.521	−296.135	4.834
3300	131.690	576.874	464.359	371.298	−651.132	−285.035	4.512
3400	131.766	580.806	467.727	384.471	−650.697	−273.947	4.209
3500	131.836	584.627	471.012	397.651	−650.214	−262.873	3.923
3600	131.901	588.342	474.220	410.838	−649.681	−251.813	3.654
3700	131.960	591.957	477.354	424.031	−649.097	−240.770	3.399
3800	132.015	595.476	480.416	437.230	−648.463	−229.743	3.158
3900	132.066	598.906	483.410	450.434	−647.778	−218.732	2.930
4000	132.113	602.250	486.340	463.643	−647.042	−207.740	2.713
4100	132.156	605.513	489.207	476.856	−646.257	−196.768	2.507
4200	132.197	608.698	492.014	490.074	−645.422	−185.814	2.311
4300	132.235	611.809	494.764	503.295	−644.539	−174.882	2.124
4400	132.270	614.850	497.459	516.521	−643.609	−163.970	1.947
4500	132.303	617.823	500.101	529.749	−642.633	−153.080	1.777
4600	132.334	620.731	502.692	542.981	−641.613	−142.212	1.615
4700	132.363	623.577	505.233	556.216	−640.550	−131.367	1.460
4800	132.391	626.364	507.728	569.454	−639.446	−120.545	1.312
4900	132.416	629.094	510.177	582.694	−638.301	−109.746	1.170
5000	132.440	631.770	512.582	595.937	−637.118	−98.971	1.034
5100	132.463	634.393	514.945	609.182	−635.899	−88.220	0.904
5200	132.484	636.965	517.267	622.430	−634.644	−77.493	0.778
5300	132.505	639.489	519.549	635.679	−633.356	−66.791	0.658
5400	132.524	641.966	521.793	648.930	−632.036	−56.114	0.543
5500	132.542	644.398	524.001	662.184	−630.686	−45.461	0.432
5600	132.559	646.786	526.172	675.439	−629.307	−34.833	0.325
5700	132.575	649.132	528.309	688.696	−627.900	−24.231	0.222
5800	132.591	651.438	530.412	701.954	−626.468	−13.652	0.123
5900	132.606	653.705	532.482	715.214	−625.011	−3.098	0.027
6000	132.620	655.934	534.521	728.475	−623.532	7.430	−0.065

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 332.185 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1335.6 \pm 5.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1343.9 \pm 5.0\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1228(1)	1117(1)	376(2)
807(1)	714(1)	1251(2)
348(1)	1243(2)	523(2)
Torsion	619(2)	220(2)

Ground State Quantum Weight: 1 $\sigma = 6$

Point Group: D_{3d}

Bond Distances: C–F = 1.32 Å; C–C = 1.56 Å

Bond Angle: C–C–F = 109.5 ± 1.5°

Product of the Moments of Inertia: $I_A I_B I_C = 6.005449 \times 10^{-113}\ g^3 \cdot cm^6$

Reduced Moment of Inertia: $I_{red} = 7.32 \times 10^{-39}\ g\ cm^2$

Barrier to Internal Rotation: $V = 3.96\ kcal \cdot mol^{-1}$

Enthalpy of Formation

The selected value is obtained from least squares, simultaneous adjustment of the heats of formation of CF_3, CF_3X (X = H, Cl, Br, I, CF_3) and C_2F_4. Details of the input data and the adjustment are given in.[1] Data pertinent to C_2F_6 are summarized below. Calorimetric data[2] for the reaction of C_2F_6 with potassium were omitted from the adjustment due to insufficient characterization of the products.

Source	Method	Reaction	$\Delta_f H°(298.15\ K)$ $kcal^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15K)$ $kcal^{-1} \cdot mol^{-1}$
[2]	Calorimetric	$3\ C_2F_6(g) + 2\ NF_3(g) \rightarrow 6\ CF_4(g) + N_2(g)$	−311.6 ± 3.0	−321.3 ± 1.2
[3]	Calorimetric	$3\ CF_3CN(g) + 5\ NF_3(g) \rightarrow 6\ CF_4(g) + 4\ N_2(g)$	−824.4 ± 0.6	—
[4]	Equilibrium	$2\ CF_3CN(g) \rightarrow C_2F_6(g) + C_2N_2(g)$	−10.59 ± 0.5	−322.2 ± 1.8
[5]	Equilibrium	$C_2F_6(g) + Br_2(g) \rightarrow 2\ CBrF_3(g)$	3.30 ± 0.7	−320.9 ± 1.6
[6,5]	Kinetic	$C_2F_6(g) \rightarrow 2\ CF_3(g)$	97.6 ± 6	−322.4 ± 6

Heat Capacity and Entropy

The adopted molecular structure was derived from electron–diffraction data by Swick and Karle.[8] The vibrational frequencies are from the assignment of Carney *et al.*,[9] who reviewed the extensive spectral data. Shimanouchi[10] has selected the same frequencies. Low–temperature calorimetric data were used by Pace and Aston[11] to derive a value for the entropy of the ideal gas of 69.88 ± 0.20 $cal \cdot K^{-1} \cdot mol^{-1}$ at 194.87 K. This value is used to fix the barrier to internal rotation at 3960 cal/mol. Thermodynamic functions are calculated from these parameters, using hindered internal rotation in place of a torsional vibration. Principal moments of inertia are: $I_A = 29.3165 \times 10^{-39}$, and $I_B = I_C = 45.2602 \times 10^{-39}\ g \cdot cm^2$.

An uncertainty of ±0.2 $cal \cdot K^{-1} \cdot mol^{-1}$ in the 3rd law entropy corresponds to a variation in the barrier to internal rotation of about ±700 $cal \cdot mol^{-1}$. This range easily includes the barrier of 4300 $cal \cdot mol^{-1}$ derived by Karle[12] from analysis of the electron–diffraction data.[8] Uncertainty in the entropy of this table should not exceed 0.5 $cal \cdot K^{-1} \cdot mol^{-1}$ at 1000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.255	−1335.579	−1335.579	INFINITE
100	53.137	248.355	409.522	−16.117	−1340.281	−1313.815	686.267
200	82.437	294.717	341.306	−9.318	−1342.922	−1286.241	335.932
298.15	106.407	332.185	332.185	0.	−1343.901	−1258.134	220.420
300	106.809	332.845	332.187	0.197	−1343.909	−1257.602	218.968
400	125.545	366.266	336.617	11.859	−1343.950	−1228.806	160.466
500	139.139	395.825	345.562	25.132	−1343.428	−1200.072	125.371
600	148.708	422.089	356.170	39.551	−1342.585	−1171.476	101.986
700	155.465	445.549	367.293	54.779	−1341.558	−1143.037	85.294
800	160.310	466.640	378.416	70.579	−1340.428	−1114.753	72.786
900	163.804	485.732	389.296	86.792	−1339.247	−1086.614	63.065
1000	166.486	503.134	399.823	103.311	−1338.044	−1058.608	55.296
1100	168.458	519.097	409.951	120.061	−1336.841	−1030.723	48.945
1200	170.088	533.827	419.668	136.991	−1335.652	−1002.946	43.657
1300	171.296	547.490	428.981	154.062	−1334.487	−975.268	39.187
1400	172.318	560.223	437.906	171.244	−1333.356	−947.679	35.358
1500	173.114	572.140	446.462	188.517	−1332.263	−920.169	32.043
1600	173.808	583.335	454.670	205.864	−1331.213	−892.731	29.145
1700	174.312	593.887	462.552	223.270	−1330.207	−865.356	26.589
1800	174.770	603.864	470.128	240.725	−1329.245	−838.040	24.319
1900	175.182	613.325	477.418	258.222	−1328.321	−810.777	22.290
2000	175.548	622.320	484.440	275.759	−1327.426	−783.560	20.465
2100	175.816	630.891	491.211	293.328	−1326.556	−756.389	18.814
2200	176.065	639.076	497.748	310.922	−1325.704	−729.258	17.315
2300	176.293	646.908	504.064	328.540	−1324.858	−702.166	15.947
2400	176.502	654.415	510.173	346.180	−1324.007	−675.110	14.693
2500	176.690	661.624	516.088	363.840	−1323.141	−648.091	13.541
2600	176.839	668.557	521.820	381.516	−1322.251	−621.106	12.478
2700	176.978	675.234	527.379	399.207	−1321.328	−594.156	11.495
2800	177.107	681.672	532.775	416.912	−1320.362	−567.242	10.582
2900	177.226	687.889	538.017	434.628	−1319.346	−540.362	9.733
3000	177.335	693.899	543.114	452.356	−1318.271	−513.519	8.941
3100	177.426	699.716	548.072	470.095	−1317.131	−486.713	8.201
3200	177.511	705.350	552.900	487.841	−1315.923	−459.944	7.508
3300	177.590	710.814	557.602	505.597	−1314.640	−433.214	6.857
3400	177.662	716.116	562.187	523.359	−1313.279	−406.525	6.245
3500	177.728	721.267	566.659	541.129	−1311.838	−379.876	5.669
3600	177.783	726.275	571.024	558.904	−1310.315	−353.270	5.126
3700	177.834	731.146	575.286	576.685	−1308.708	−326.707	4.612
3800	177.881	735.890	579.450	594.471	−1307.017	−300.190	4.126
3900	177.924	740.511	583.521	612.261	−1305.242	−273.717	3.666
4000	177.962	745.016	587.502	630.056	−1303.384	−247.291	3.229
4100	177.994	749.411	591.398	647.853	−1301.442	−220.913	2.814
4200	178.022	753.700	595.211	665.654	−1299.419	−194.582	2.420
4300	178.048	757.889	598.946	683.458	−1297.316	−168.302	2.044
4400	178.071	761.983	602.605	701.264	−1295.134	−142.071	1.687
4500	178.092	765.985	606.191	719.072	−1292.875	−115.889	1.345
4600	178.108	769.899	609.708	736.882	−1290.542	−89.760	1.019
4700	178.122	773.730	613.157	754.693	−1288.136	−63.682	0.708
4800	178.135	777.480	616.541	772.506	−1285.661	−37.655	0.410
4900	178.146	781.153	619.863	790.320	−1283.117	−11.682	0.125
5000	178.155	784.752	623.125	808.135	−1280.509	14.239	−0.149
5100	178.159	788.280	626.329	825.951	−1277.837	40.108	−0.411
5200	178.163	791.740	629.477	843.767	−1275.105	65.924	−0.662
5300	178.167	795.134	632.571	861.584	−1272.314	91.687	−0.904
5400	178.171	798.464	635.612	879.401	−1269.468	117.396	−1.136
5500	178.176	801.733	638.603	897.218	−1266.568	143.051	−1.359
5600	178.180	804.944	641.545	915.036	−1263.617	168.655	−1.573
5700	178.184	808.098	644.439	932.854	−1260.616	194.203	−1.780
5800	178.188	811.197	647.288	950.673	−1257.568	219.699	−1.979
5900	178.192	814.243	650.092	968.492	−1254.475	245.145	−2.170
6000	178.197	817.238	652.852	986.311	−1251.339	270.535	−2.355

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = [207.444 \pm 5.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [473.9 \pm 29]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [477.0 \pm 29]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[9000]	[4]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1920](1)
[640](2)
[3220](1)

Point Group: [$C_{\infty v}$] σ = 1
Bond Distances: C–C = [1.207] Å; C–H = [1.061] Å
Bond Angle: C–C–H = [180]°
Rotational Constant: B_0 = [1.474960] cm^{-1}

Enthalpy of Formation

The enthalpy of formation of C_2H(g) is not well established; however, we can place reliable upper and lower limits on the value.

Cottrell,[1] gives an upper limit for the C–H bond dissociation energy in acetylene, $\Delta_{at}H°$(HCC–H) <121 kcal·mol^{-1}. This was obtained from the fact that ultra violet light of 121 kcal·mol^{-1} energy causes acetylene to from diacetylene and hydrogen; assuming that this process occurs through the CCH radical, the light energy is equated with $\Delta_{at}H°$(HCC–H). This value of $\Delta_{at}H°$ (HCC–H) gives an upper limit for $\Delta_f H°$(CCH, g, 298.15 K) <123 kcal·mol^{-1}.

A lower limit for $\Delta_{at}H°$(HCC–H) is obtained from a consideration of the C–H bond dissociation energies in ethylene and ethane, $\Delta_{at}H°(C_2H_3–H)$ = 103 kcal·mol^{-1} and $\Delta_{at}H°(C_2H_5–H)$ = 98 kcal·mol^{-1}. The heats of formation of the C_2H_3 and C_2H_5 radicals and their parent compounds are taken from Benson.[2] The vibrational frequency of the C–H stretch increases steadily form ethane to ethylene and acetylene. Similarly we expect the bond strength to increase, and so $\Delta_{at}H°$(HCC–H) >103 kcal·mol^{-1}; this yields $\Delta_f H°$(CCH, g, 298.15 K) >105 kcal·mol^{-1}.

Coats and Anderson,[3] obtained several values for $\Delta_f H°$(CCH, g, 298.15 K) from mass–spectroscopic measurements; their values range from 110 kcal·mol^{-1} to 153 kcal·mol^{-1}, but they chose to adopt 112 ± 3 kcal·mol^{-1}.

Our adopted value of $\Delta_f H°$(CCH, g, 298.15 K), 114 ± 7 kcal·mol^{-1}, (476.976 ± 29 kJ·mol^{-1}), is 2 kcal·mol^{-1} smaller than that estimated by Tsang *et al.*[4]

Heat Capacity and Entropy

The molecule is assumed to be linear; the bond lengths are assumed to be the same as in acetylene and were taken from Sutton.[5]

The vibrational frequencies are those estimated by Plooster and Reed.[6] It should be noted that the values of the free energy function given by Plooster and Reed[6] are incorrect due to the neglect of the electronic contributions.

The electronic levels, $X^2\Sigma$ and $A^2\Pi$, were estimated by analogy with those of CN(g) which is isoelectronic; this assumption holds very well in the parent molecules HCCH and HCN.[7] The molecule $C_2H_2^+$, which is also isoelectronic with CCH, is predicted to have a $^2\Pi$ ground state by Herzberg.[7]

References

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[6]M. N. Plooster and T. B. Reed, J. Chem. Phys. **31**, 66 (1959).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.404	473.908	473.908	INFINITE
100	29.242	172.435	237.415	−6.498	475.195	463.178	−241.940
200	32.702	193.530	210.703	−3.435	476.258	450.726	−117.718
250	35.084	201.087	208.044	−1.739	476.664	444.295	−92.830
298.15	37.104	207.444	207.444	0.	476.976	438.031	−76.741
300	37.175	207.673	207.444	0.069	476.986	437.789	−76.226
350	38.922	213.539	207.904	1.972	477.224	431.236	−64.358
400	40.395	218.835	208.944	3.956	477.376	424.655	−55.454
450	41.675	223.669	210.316	6.009	477.441	418.060	−48.527
500	42.818	228.120	211.877	8.122	477.426	411.463	−42.985
600	44.837	236.109	215.265	12.507	477.190	398.288	−34.674
700	46.615	243.157	218.755	17.081	476.750	385.170	−28.742
800	48.212	249.487	222.208	21.824	476.174	372.125	−24.297
900	49.651	255.251	225.564	26.718	475.512	359.158	−20.845
1000	50.943	260.550	228.801	31.749	474.795	346.268	−18.087
1100	52.102	265.461	231.913	36.902	474.041	333.451	−15.834
1200	53.142	270.040	234.902	42.165	473.263	320.705	−13.960
1300	54.081	274.331	237.771	47.527	472.466	308.024	−12.377
1400	54.935	278.370	240.528	52.979	471.656	295.405	−11.022
1500	55.720	282.188	243.180	58.512	470.837	282.844	−9.849
1600	56.451	285.807	245.732	64.121	470.010	270.338	−8.826
1700	57.140	289.251	248.191	69.801	469.179	257.884	−7.924
1800	57.795	292.535	250.564	75.548	468.346	245.478	−7.124
1900	58.424	295.677	252.857	81.359	467.512	233.120	−6.409
2000	59.032	298.689	255.073	87.232	466.681	220.805	−5.767
2100	59.622	301.584	257.220	93.165	465.854	208.531	−5.187
2200	60.194	304.371	259.300	99.156	465.032	196.297	−4.661
2300	60.750	307.059	261.318	105.203	464.217	184.100	−4.181
2400	61.289	309.656	263.279	111.305	463.409	171.938	−3.742
2500	61.810	312.168	265.184	117.460	462.609	159.810	−3.339
2600	62.313	314.602	267.038	123.666	461.817	147.714	−2.968
2700	62.796	316.963	268.844	129.922	461.032	135.648	−2.624
2800	63.258	319.255	270.604	136.225	460.254	123.611	−2.306
2900	63.698	321.483	272.320	142.573	459.482	111.602	−2.010
3000	64.115	323.649	273.995	148.964	458.715	99.619	−1.735
3100	64.509	325.758	275.631	155.395	457.951	87.662	−1.477
3200	64.878	327.812	277.230	161.865	457.190	75.729	−1.236
3300	65.223	329.814	278.793	168.370	456.428	63.820	−1.010
3400	65.544	331.766	280.322	174.909	455.666	51.934	−0.798
3500	65.840	333.670	281.819	181.478	454.900	40.071	−0.598
3600	66.113	335.529	283.286	188.076	454.128	28.230	−0.410
3700	66.362	337.344	284.722	194.700	453.350	16.410	−0.232
3800	66.588	339.117	286.130	201.347	452.562	4.611	−0.063
3900	66.792	340.849	287.511	208.017	451.763	−7.166	0.096
4000	66.975	342.542	288.866	214.705	450.952	−18.924	0.247
4100	67.138	344.198	290.195	221.411	450.126	−30.660	0.391
4200	67.281	345.818	291.501	228.132	449.284	−42.376	0.527
4300	67.407	347.402	292.782	234.867	448.424	−54.073	0.657
4400	67.515	348.953	294.041	241.613	447.544	−65.748	0.781
4500	67.607	350.472	295.278	248.369	446.644	−77.404	0.898
4600	67.684	351.958	296.495	255.134	445.722	−89.040	1.011
4700	67.746	353.415	297.690	261.905	444.777	−100.655	1.119
4800	67.796	354.842	298.866	268.683	443.807	−112.249	1.222
4900	67.834	356.240	300.023	275.464	442.812	−123.824	1.320
5000	67.860	357.611	301.161	282.249	441.792	−135.377	1.414
5100	67.876	358.955	302.281	289.036	440.744	−146.910	1.505
5200	67.882	360.273	303.383	295.824	439.669	−158.422	1.591
5300	67.880	361.566	304.469	302.612	438.567	−169.914	1.675
5400	67.871	362.834	305.538	309.400	437.436	−181.384	1.755
5500	67.854	364.080	306.591	316.186	436.276	−192.833	1.831
5600	67.830	365.302	307.629	322.970	435.087	−204.261	1.905
5700	67.801	366.502	308.651	329.752	433.870	−215.667	1.976
5800	67.766	367.681	309.659	336.530	432.623	−227.051	2.045
5900	67.727	368.839	310.652	343.305	431.348	−238.414	2.111
6000	67.684	369.977	311.631	350.075	430.043	−249.755	2.174

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 241.996\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [212.9 \pm 42]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [213.8 \pm 42]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3340(1)	604(2)
2110(1)	326(2)
756(1)	

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: C–C = 1.204 Å; C–H = 1.055 Å; C–Cl = 1.637 Å
Bond Angles: Cl–C–C = 180°; C–C–H = 180°
Rotational Constant: $B_0 = 0.188645\ cm^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(298.15\ K) = 51.1\ kcal·mol^{-1}$ is calculated from the estimated $\Delta_f H°(298.15\ K) = -53 \pm 10\ kcal·mol^{-1}$ for HCC-Cl(g) + Cl_2(g) → CHCl=CCl_2(g), using $\Delta_f H°$(CHCl=CCl_2, g, 298.15 K) = −1.86 kcal·mol^{-1}.[1] The value of $\Delta_f H°(298.15\ K)$ is assumed to be the same as that for the reaction HCCH(g) + Cl (2g) → CHCl=CHCl(g), using $\Delta_f H°$(C_2H_2, g, 298.15 K) = 54.19 kcal·mol^{-1} [1] and $\Delta_f H°$(CHCl=CHCl, g, 298.15 K) = 1.2 kcal·mol^{-1}.[2]

Heat Capacity and Entropy

The linear molecular structure and bond distances were determined from the microwave spectrometrical studies by Tyler and Sheridan.[3] Their results are in good agreement with those of Westenberg *et al.*[4]

The vibrational frequencies were observed in the infrared spectra by Hunt and Wilson,[5] and Richardson and Goldstein.[6]

References

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[2]This is an average value of 0.9 and 1.47 kcal·mol^{-1} for cis– and trans– CHCl = CHCl(g), respectively which are obtained from NBS.[1]
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.787	212.941	212.941	INFINITE
100	32.752	195.662	283.695	−8.803	212.851	207.961	−108.628
200	45.079	222.136	246.697	−4.912	213.223	202.966	−53.009
250	50.310	232.778	242.869	−2.523	213.513	200.369	−41.865
298.15	54.319	241.996	241.996	0.	213.802	197.811	−34.656
300	54.455	242.332	241.997	0.101	213.813	197.712	−34.425
350	57.682	250.979	242.672	2.907	214.094	195.006	−29.103
400	60.227	258.854	244.210	5.857	214.337	192.261	−25.107
450	62.290	266.071	246.244	8.922	214.527	189.490	−21.995
500	64.017	272.725	248.564	12.081	214.660	186.701	−19.504
600	66.824	284.655	253.608	18.629	214.771	181.095	−15.766
700	69.104	295.133	258.807	25.428	214.720	175.485	−13.095
800	71.050	304.491	263.943	32.438	214.562	169.889	−11.093
900	72.751	312.959	268.926	39.630	214.337	164.318	−9.537
1000	74.248	320.704	273.722	46.982	214.072	158.775	−8.294
1100	75.570	327.844	278.322	54.474	213.782	153.259	−7.278
1200	76.735	334.470	282.728	62.091	213.476	147.770	−6.432
1300	77.762	340.654	286.948	69.817	213.157	142.308	−5.718
1400	78.667	346.450	290.994	77.639	212.828	136.870	−5.107
1500	79.466	351.905	294.874	85.546	212.487	131.456	−4.578
1600	80.170	357.057	298.601	93.529	212.134	126.065	−4.116
1700	80.793	361.936	302.185	101.578	211.767	120.697	−3.709
1800	81.345	366.570	305.634	109.685	211.386	115.351	−3.347
1900	81.835	370.982	308.958	117.845	210.987	110.027	−3.025
2000	82.271	375.191	312.165	126.050	210.570	104.724	−2.735
2100	82.660	379.214	315.263	134.297	210.133	99.442	−2.473
2200	83.009	383.068	318.258	142.581	209.673	94.182	−2.236
2300	83.322	386.765	321.157	150.898	209.191	88.943	−2.020
2400	83.603	390.317	323.965	159.244	208.683	83.725	−1.822
2500	83.857	393.735	326.688	167.618	208.148	78.530	−1.641
2600	84.087	397.029	329.330	176.015	207.586	73.356	−1.474
2700	84.295	400.206	331.897	184.434	206.995	68.205	−1.319
2800	84.485	403.275	334.392	192.874	206.374	63.075	−1.177
2900	84.658	406.243	336.818	201.331	205.722	57.969	−1.044
3000	84.816	409.116	339.181	209.805	205.039	52.886	−0.921
3100	84.960	411.899	341.482	218.293	204.324	47.826	−0.806
3200	85.093	414.598	343.725	226.796	203.578	42.789	−0.698
3300	85.215	417.219	345.912	235.312	202.800	37.777	−0.598
3400	85.327	419.764	348.047	243.839	201.990	32.788	−0.504
3500	85.431	422.239	350.132	252.377	201.150	27.823	−0.415
3600	85.527	424.647	352.168	260.925	200.279	22.884	−0.332
3700	85.616	426.992	354.159	269.482	199.379	17.968	−0.254
3800	85.698	429.276	356.106	278.048	198.450	13.078	−0.180
3900	85.775	431.503	358.011	286.621	197.493	8.212	−0.110
4000	85.846	433.676	359.875	295.202	196.510	3.371	−0.044
4100	85.913	435.796	361.701	303.790	195.500	−1.445	0.018
4200	85.975	437.868	363.490	312.385	194.467	−6.236	0.078
4300	86.033	439.891	365.244	320.985	193.410	−11.002	0.134
4400	86.088	441.870	366.963	329.591	192.331	−15.744	0.187
4500	86.139	443.805	368.649	338.203	191.230	−20.460	0.237
4600	86.187	445.699	370.303	346.819	190.110	−25.152	0.286
4700	86.232	447.553	371.927	355.440	188.972	−29.820	0.331
4800	86.275	449.369	373.522	364.065	187.815	−34.463	0.375
4900	86.315	451.148	375.088	372.695	186.642	−39.081	0.417
5000	86.352	452.892	376.627	381.328	185.454	−43.676	0.456
5100	86.388	454.603	378.139	389.965	184.251	−48.247	0.494
5200	86.422	456.280	379.625	398.606	183.034	−52.793	0.530
5300	86.454	457.927	381.087	407.249	181.804	−57.317	0.565
5400	86.484	459.543	382.525	415.896	180.562	−61.817	0.598
5500	86.512	461.130	383.940	424.546	179.309	−66.294	0.630
5600	86.540	462.689	385.332	433.199	178.046	−70.748	0.660
5700	86.565	464.221	386.703	441.854	176.772	−75.180	0.689
5800	86.590	465.727	388.053	450.512	175.490	−79.588	0.717
5900	86.613	467.207	389.382	459.172	174.199	−83.975	0.743
6000	86.635	468.663	390.691	467.834	172.900	−88.341	0.769

PREVIOUS: December1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 231.611 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [124.8 \pm 63]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [125.5 \pm 63]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
3360(1)
2250(1)
1060(1)
580(2)
367(2)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: C–F = 1.279 Å; C–C = 1.198 Å; C–H = 1.053 Å
Bond Angles: F–C–C = 180°; C–C–H = 180°
Rotational Constant: $B_0 = 0.323577\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation is estimated by assuming that the C–C bond strength is the average of those in C_2F_2(113 kcal·mol^{-1}) and C_2H_2(229 kcal·mol^{-1}). Combining the average value (171 kcal·mol^{-1}) with the enthalpies of formation of CF and CH from the JANAF Tables, yields $\Delta_f H°(C_2HF, g, 298.15\ K) = 30 \pm 15$ kcal·mol^{-1}.

Heat Capacity and Entropy

Hunt and Wilson[1] and Brown and Tyler,[2] have reported the infrared spectrum and have assigned the fundamental frequencies. The frequencies used in the present table are median values of the two sets and are generally within 5 cm^{-1} of each set.

The molecule has been shown to be linear by Tyler and Sheridan,[3] who reported the rotational constant B_0.

The electronic ground is assumed to be $^1\Sigma$ by analogy with C_2H_2.

References

[1]G. R. Hunt and M. K. Wilson, J. Chem. Phys. **34**, 1301 (1961).
[2]J. K. Brown and J. K. Tyler, Proc. Chem. Soc. (London) **1961**, 13.
[3]J. K. Tyler an J. Sheridan, Trans. Faraday Soc. **59**, 2661 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.452	124.816	124.816	INFINITE
100	31.761	186.882	271.833	−8.495	124.701	119.758	−62.555
200	43.530	212.465	236.141	−4.735	124.996	114.742	−29.968
250	48.488	222.731	232.452	−2.430	125.261	112.149	−23.432
298.15	52.321	231.611	231.611	0.	125.520	109.600	−19.201
300	52.452	231.935	231.612	0.097	125.530	109.501	−19.066
350	55.619	240.268	232.263	2.802	125.774	106.810	−15.941
400	58.190	247.868	233.746	5.649	125.974	104.087	−13.592
450	60.324	254.849	235.708	8.613	126.118	101.342	−11.763
500	62.143	261.301	237.949	11.676	126.203	98.584	−10.299
600	65.147	272.907	242.830	18.046	126.216	93.055	−8.101
700	67.611	283.140	247.872	24.688	126.067	87.538	−6.532
800	69.723	292.309	252.863	31.557	125.813	82.051	−5.357
900	71.570	300.630	257.715	38.624	125.496	76.599	−4.446
1000	73.196	308.257	262.393	45.864	125.143	71.185	−3.718
1100	74.630	315.302	266.887	53.256	124.769	65.807	−3.125
1200	75.894	321.851	271.198	60.784	124.382	60.464	−2.632
1300	77.007	327.971	275.332	68.430	123.985	55.153	−2.216
1400	77.987	333.714	279.299	76.181	123.579	49.874	−1.861
1500	78.850	339.125	283.109	84.024	123.164	44.623	−1.554
1600	79.612	344.238	286.771	91.948	122.738	39.401	−1.286
1700	80.285	349.085	290.295	99.943	122.300	34.206	−1.051
1800	80.882	353.692	293.690	108.002	121.848	29.037	−0.843
1900	81.411	358.079	296.965	116.117	121.383	23.893	−0.657
2000	81.882	362.267	300.126	124.282	120.903	18.775	−0.490
2100	82.302	366.273	303.181	132.492	120.409	13.680	−0.340
2200	82.678	370.110	306.137	140.741	119.901	8.610	−0.204
2300	83.015	373.793	308.999	149.026	119.379	3.563	−0.081
2400	83.319	377.332	311.773	157.343	118.845	−1.461	0.032
2500	83.593	380.739	314.464	165.689	118.298	−6.463	0.135
2600	83.840	384.023	317.076	174.061	117.740	−11.442	0.230
2700	84.065	387.191	319.615	182.456	117.172	−16.400	0.317
2800	84.269	390.252	322.083	190.873	116.594	−21.337	0.398
2900	84.455	393.213	324.485	199.309	116.008	−26.252	0.473
3000	84.625	396.079	326.824	207.764	115.413	−31.148	0.542
3100	84.781	398.856	329.103	216.234	114.812	−36.024	0.607
3200	84.924	401.550	331.325	224.719	114.203	−40.879	0.667
3300	85.055	404.165	333.493	233.218	113.587	−45.716	0.724
3400	85.176	406.706	335.609	241.730	112.965	−50.534	0.776
3500	85.288	409.177	337.676	250.253	112.337	−55.334	0.826
3600	85.391	411.581	339.696	258.787	111.703	−60.115	0.872
3700	85.487	413.922	341.670	267.331	111.062	−64.879	0.916
3800	85.576	416.203	343.602	275.885	110.415	−69.626	0.957
3900	85.659	418.427	345.492	284.446	109.760	−74.355	0.996
4000	85.735	420.597	347.343	293.016	109.099	−79.068	1.033
4100	85.807	422.715	349.155	301.593	108.430	−83.764	1.067
4200	85.874	424.783	350.931	310.177	107.754	−88.443	1.100
4300	85.937	426.805	352.673	318.768	107.069	−93.107	1.131
4400	85.995	428.781	354.380	327.365	106.376	−97.754	1.160
4500	86.051	430.714	356.055	335.967	105.673	−102.385	1.188
4600	86.102	432.606	357.698	344.575	104.962	−107.001	1.215
4700	86.151	434.458	359.312	353.187	104.240	−111.601	1.240
4800	86.196	436.273	360.897	361.805	103.509	−116.186	1.264
4900	86.240	438.050	362.453	370.426	102.767	−120.755	1.287
5000	86.280	439.793	363.982	379.052	102.015	−125.309	1.309
5100	86.319	441.502	365.486	387.682	101.251	−129.848	1.330
5200	86.355	443.178	366.964	396.316	100.476	−134.372	1.350
5300	86.389	444.824	368.417	404.953	99.690	−138.881	1.369
5400	86.422	446.439	369.847	413.594	98.892	−143.374	1.387
5500	86.452	448.025	371.254	422.238	98.083	−147.854	1.404
5600	86.482	449.583	372.639	430.884	97.262	−152.318	1.421
5700	86.509	451.114	374.003	439.534	96.429	−156.767	1.437
5800	86.536	452.619	375.345	448.186	95.584	−161.202	1.452
5900	86.561	454.098	376.667	456.841	94.727	−165.622	1.466
6000	86.585	455.553	377.970	465.498	93.858	−170.027	1.480

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = 200.958\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 235.755 \pm 0.79\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 226.731 \pm 0.79\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
3373.7(1)
1973.8(1)
3281.9(1)
611.6(2)
729.3(2)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Rotational Constant $B_0 = 1.17684 \pm 0.00016\ cm^{-1}$

Spectroscopic constants used in calculating corrections to rigid rotator–harmonic oscillator approximation (cm^{-1}):

$x_{11} = -24.08$	$x_{22} = -7.92$	$x_{34} = -9.06$	$D_0 = 2.19 \times 10^{-6}$
$x_{12} = -16.94$	$x_{23} = -1.38$	$x_{35} = -5.73$	$g_{44} = 1.1$
$x_{13} = -99.01$	$x_{24} = -6.15$	$x_{44} = 5.38$	$g_{55} = 2.49$
$x_{14} = -16.46$	$x_{25} = -0.85$	$x_{45} = -12.65$	
$x_{15} = -11.75$	$x_{33} = -25.69$	$x_{55} = -2.27$	

Values of α_i not available.

Enthalpy of Formation

Taken from Wagman *et al.*[1]

Heat Capacity and Entropy

Gordon[2] has used the constants listed above to calculate C_p^o from 298.15 K to 6000 K by the method of Pennington and Kobe.[3] The constants are from Bell and Nielsen[4] and Allen *et al.*[5] Heat capacities below 298.15 K have been calculated for a rigidly rotating harmonic oscillator.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.000	0.000	INFINITE	−10.012	227.288	227.288	INFINITE
100	29.347	163.294	234.338	−7.104	227.078	221.011	−115.444
200	35.585	185.097	204.720	−3.925	226.911	215.006	−56.154
298.15	44.095	200.958	200.958	0.000	226.731	209.200	−36.651
300	44.229	201.231	200.959	.082	226.728	209.092	−36.406
400	50.480	214.856	202.774	4.833	226.527	203.242	−26.541
500	54.869	226.610	206.393	10.108	226.227	197.452	−20.628
600	58.287	236.924	210.640	15.771	225.804	191.735	−16.692
700	61.149	246.127	215.064	21.745	225.294	186.097	−13.887
800	63.760	254.466	219.476	27.992	224.747	180.534	−11.788
900	66.111	262.113	223.794	34.487	224.198	175.041	−10.159
1000	68.275	269.192	227.984	41.208	223.669	169.607	−8.859
1100	70.245	275.793	232.034	48.136	223.170	164.226	−7.798
1200	72.053	281.984	235.941	55.252	222.705	158.888	−6.916
1300	73.693	287.817	239.709	62.540	222.275	153.588	−6.171
1400	75.178	293.334	243.344	69.985	221.877	148.319	−5.534
1500	76.530	298.567	246.853	77.572	221.506	143.078	−4.982
1600	77.747	303.546	250.242	85.286	221.160	137.861	−4.501
1700	78.847	308.293	253.518	93.117	220.833	132.665	−4.076
1800	79.852	312.829	256.688	101.053	220.521	127.487	−3.700
1900	80.760	317.171	259.758	109.084	220.222	122.327	−3.363
2000	81.605	321.335	262.733	117.203	219.931	117.182	−3.060
2100	82.362	325.335	265.620	125.401	219.647	112.052	−2.787
2200	83.065	329.183	268.422	133.673	219.367	106.935	−2.539
2300	83.712	332.890	271.145	142.012	219.088	101.830	−2.313
2400	84.312	336.465	273.793	150.414	218.809	96.738	−2.105
2500	84.858	339.918	276.369	158.873	218.527	91.658	−1.915
2600	85.370	343.256	278.878	167.384	218.242	86.589	−1.740
2700	85.846	346.487	281.322	175.945	217.950	81.530	−1.577
2800	86.295	349.618	283.706	184.553	217.652	76.483	−1.427
2900	86.713	352.653	286.031	193.203	217.346	71.447	−1.287
3000	87.111	355.600	288.301	201.895	217.030	66.421	−1.157
3100	87.474	358.462	290.519	210.624	216.705	61.406	−1.035
3200	87.825	361.245	292.686	219.389	216.368	56.402	−.921
3300	88.164	363.952	294.804	228.189	216.019	51.409	−.814
3400	88.491	366.589	296.877	237.022	215.658	46.426	−.713
3500	88.805	369.159	298.906	245.886	215.285	41.454	−.619
3600	89.101	371.665	300.892	254.782	214.899	36.493	−.529
3700	89.388	374.110	302.838	263.706	214.499	31.542	−.445
3800	89.666	376.498	304.745	272.659	214.084	26.603	−.366
3900	89.935	378.830	306.615	281.639	213.655	21.675	−.290
4000	90.194	381.110	308.449	290.646	213.210	16.758	−.219
4100	90.439	383.341	310.248	299.678	212.750	11.852	−.151
4200	90.678	385.523	312.015	308.733	212.273	6.958	−.087
4300	90.910	387.659	313.749	317.813	211.779	2.076	−.025
4400	91.137	389.752	315.453	326.915	211.268	−2.795	.033
4500	91.358	391.802	317.127	336.040	210.740	−7.655	.089
4600	91.563	393.813	318.772	345.186	210.194	−12.502	.142
4700	91.768	395.784	320.390	354.353	209.630	−17.337	.193
4800	91.970	397.718	321.981	363.540	209.049	−22.160	.241
4900	92.171	399.617	323.546	372.747	208.450	−26.971	.288
5000	92.370	401.481	325.086	381.974	207.833	−31.769	.332
5100	92.571	403.312	326.602	391.221	207.201	−36.555	.374
5200	92.768	405.111	328.094	400.488	206.553	−41.328	.415
5300	92.963	406.880	329.564	409.775	205.889	−46.089	.454
5400	93.153	408.620	331.012	419.080	205.211	−50.836	.492
5500	93.341	410.331	332.439	428.405	204.517	−55.572	.528
5600	93.525	412.014	333.845	437.748	203.810	−60.294	.562
5700	93.706	413.671	335.231	447.110	203.090	−65.004	.596
5800	93.883	415.302	336.597	456.489	202.356	−69.701	.628
5900	94.057	416.909	337.945	465.886	201.610	−74.386	.659
6000	94.228	418.491	339.274	475.301	200.853	−79.057	.688

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar

$S°(298.15\ K) = 219.330\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 60.986 \pm 0.29\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 52.467 \pm 0.29\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3026.4(1)	3102.5(1)	3105.5(1)
1622.9(1)	1222.0(1)	826.0(1)
1342.2(1)	949.3(1)	2988.7(1)
1023.0(1)	943.0(1)	1443.5(1)

Ground State and Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distances: H–C = 1.086 Å; C–C = 1.337 Å
Bond Angles: H–C–H = 117° 22'; H–C–C = 121° 19'
Product of the Moments of Inertia: $I_A I_B I_C = 5.4496 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of combustion of ethylene was measured by Rossini and Knowlton.[1] From the value, $\Delta_f H°(298.15\ K) = -337.28 \pm 0.07$ $kcal·mol^{-1}$ for the reaction $C_2H_4(g) + 3\ O_2(g) = 2\ CO_2(g) + 2\ H_2O(l)$, the enthalpy of formation, $\Delta_f H°(298.15\ K)$, for $C_2H_4(g)$ was derived to be 12.54 ± 0.07 $kcal·mol^{-1}$. The values of $\Delta_f H°(298.15\ K)$ for $CO_2(g)$ and $H_2O(l)$ used for calculation were obtained from Rossini *et al.*[2]

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from Allen and Plyler.[3] The vibrational frequencies were taken from Smith and Mills.[4] Eight of the twelve frequencies were reported by Arnett and Crawford;[5] Crawford *et al.*;[6] Stoicheff;[7] Feldman *et al.*;[8] and Allen and Plyler.[3] Herzberg[9] also reported the vibrational frequencies for ethylene as 3019.3 (1), 1623.3 (1), 1342.4 (1), 825.0 (1), 3272.3 (1), 1050 (1), 949.2 (1), 943 (1), 3105.5 (1), 995 (1), 298.5 (1) and 1443.5 (1) which are very close to the values adopted. The infrared and Raman spectra of ethylene before 1945 have been summarized by Herzberg.[9] The molecular structure of ethylene was also determined by Bartell and Bonham.[10] Their results, r(C–H) = 1.085 Å, r(C–C) = 1.334 Å principal moments of inertia are $I_A = 0.5763 \times 10^{-39}$, $I_B = 2.8004 \times 10^{-39}$, and $I_C = 3.3767 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.518	60.986	60.986	INFINITE
100	33.270	180.542	252.466	−7.192	58.194	60.476	−31.589
200	35.359	203.955	222.975	−3.804	55.542	63.749	−16.649
250	38.645	212.172	220.011	−1.960	54.002	65.976	−13.785
298.15	42.886	219.330	219.330	0.	52.467	68.421	−11.987
300	43.063	219.596	219.331	0.079	52.408	68.521	−11.930
350	48.013	226.602	219.873	2.355	50.844	71.330	−10.645
400	53.048	233.343	221.138	4.882	49.354	74.360	−9.710
450	57.907	239.874	222.858	7.657	47.951	77.571	−9.004
500	62.477	246.215	224.879	10.668	46.641	80.933	−8.455
600	70.663	258.348	229.456	17.335	44.294	88.017	−7.663
700	77.714	269.783	234.408	24.763	42.300	95.467	−7.124
800	83.840	280.570	239.511	32.847	40.637	103.180	−6.737
900	89.200	290.761	244.644	41.505	39.277	111.082	−6.447
1000	93.899	300.408	249.742	50.665	38.183	119.122	−6.222
1100	98.018	309.555	254.768	60.266	37.318	127.259	−6.043
1200	101.626	318.242	259.698	70.252	36.645	135.467	−5.897
1300	104.784	326.504	264.522	80.576	36.129	143.724	−5.775
1400	107.550	334.372	269.233	91.196	35.742	152.016	−5.672
1500	109.974	341.877	273.827	102.074	35.456	160.331	−5.583
1600	112.103	349.044	278.306	113.181	35.249	168.663	−5.506
1700	113.976	355.898	282.670	124.486	35.104	177.007	−5.439
1800	115.628	362.460	286.922	135.968	35.005	185.357	−5.379
1900	117.089	368.752	291.064	147.606	34.938	193.712	−5.326
2000	118.386	374.791	295.101	159.381	34.894	202.070	−5.278
2100	119.540	380.596	299.035	171.278	34.864	210.429	−5.234
2200	120.569	386.181	302.870	183.284	34.839	218.790	−5.195
2300	121.491	391.561	306.610	195.388	34.814	227.152	−5.159
2400	122.319	396.750	310.258	207.580	34.783	235.515	−5.126
2500	123.064	401.758	313.818	219.849	34.743	243.880	−5.096
2600	123.738	406.598	317.294	232.190	34.688	252.246	−5.068
2700	124.347	411.280	320.689	244.595	34.616	260.615	−5.042
2800	124.901	415.812	324.006	257.058	34.524	268.987	−5.018
2900	125.404	420.204	327.248	269.573	34.409	277.363	−4.996
3000	125.864	424.463	330.418	282.137	34.269	285.743	−4.975
3100	126.284	428.597	333.518	294.745	34.102	294.128	−4.956
3200	126.670	432.613	336.553	307.393	33.906	302.518	−4.938
3300	127.024	436.516	339.523	320.078	33.679	310.916	−4.921
3400	127.350	440.313	342.432	332.797	33.420	319.321	−4.906
3500	127.650	444.009	345.281	345.547	33.127	327.734	−4.891
3600	127.928	447.609	348.074	358.326	32.800	336.156	−4.877
3700	128.186	451.118	350.812	371.132	32.436	344.588	−4.865
3800	128.424	454.539	353.497	383.962	32.035	353.030	−4.853
3900	128.646	457.878	356.130	396.816	31.596	361.482	−4.842
4000	128.852	461.138	358.715	409.691	31.118	369.947	−4.831
4100	129.045	464.322	361.252	422.586	30.600	378.424	−4.821
4200	129.224	467.434	363.743	435.500	30.041	386.915	−4.812
4300	129.392	470.476	366.190	448.430	29.441	395.418	−4.803
4400	129.549	473.453	368.594	461.378	28.799	403.937	−4.795
4500	129.696	476.366	370.957	474.340	28.116	412.470	−4.788
4600	129.835	479.218	373.280	487.317	27.390	421.019	−4.781
4700	129.965	482.012	375.563	500.307	26.623	429.584	−4.774
4800	130.087	484.749	377.810	513.309	25.813	438.167	−4.768
4900	130.202	487.433	380.020	526.324	24.962	446.766	−4.763
5000	130.311	490.064	382.194	539.349	24.069	455.384	−4.757
5100	130.413	492.646	384.335	552.386	23.136	464.019	−4.753
5200	130.510	495.179	386.442	565.432	22.162	472.673	−4.748
5300	130.602	497.666	388.517	578.488	21.149	481.346	−4.744
5400	130.689	500.108	390.561	591.552	20.097	490.040	−4.740
5500	130.771	502.507	392.575	604.625	19.008	498.751	−4.737
5600	130.849	504.864	394.559	617.706	17.884	507.485	−4.734
5700	130.923	507.180	396.515	630.795	16.724	516.238	−4.731
5800	130.993	509.458	398.442	643.891	15.531	525.012	−4.728
5900	131.060	511.698	400.343	656.993	14.306	533.806	−4.726
6000	131.124	513.901	402.217	670.103	13.051	542.621	−4.724

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 243.012\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -40.119 \pm 0.63\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -52.635 \pm 0.63\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3005(1)	3063 (1)	1153(1)
1490(1)	[1345] (1)	892(1)
1266(1)	807 (1)	3079(1)
1120(1)	3019 (1)	1143(1)
877(1)	1470 (1)	821(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: C–H = 1.0802 Å; C–O = 1.4363 Å; C–C = 1.4728 Å
Bond Angles: H–C–H = 116° 51'; H_2–C–C = 158° 5'; H_2–C–O = 142° 45.6'
Product of the Moments of Inertia: $I_A I_B I_C = 7.42728 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of combustion of ethylene oxide (g) was determined by Pell and Pilcher[1] and Crog and Hunt[2] as -312.15 ± 0.14 and $-312.55 \pm 0.20\ kcal·mol^{-1}$, respectively. The corresponding value of $\Delta_f H°(C_2H_4O, g, 298.15\ K)$ was evaluated to be -12.58 ± 0.15 and $-12.19 \pm 0.22\ kcal·mol^{-1}$. The former value is adopted.

Heat Capacity and Entropy

The vibrational frequencies were taken from Lord and Nolin.[3] The infrared and Raman spectra of ethylene oxide have also been examined by Linnett[4] and Thompson and Cave.[5] The vibrational frequencies assigned were slightly different from the ones reported by Lord and Nolin.[3] As a result of analogies between ethylene oxide and ethylene imine, small changes of Lord and Nolin's assignment have been made by Potts.[6] The bond distances and angles were obtained from Cunningham *et al.*[7] The investigation of the structure of ethylene oxide by electron diffraction was reported by Ackermann and Mayer[8] and Igarashi.[9] The principal moments of inertia are: $I_A = 3.2793 \times 10^{-39}$, $I_B = 3.8059 \times 10^{-39}$, and $I_C = 5.9511 \times 10^{-39}\ g·cm^2$.

The calculated heat capacities (307.2–371.2 K) are in good agreement with the experimentally measured ones reported by Kistiakowsky and Rice.[10]

References

[1]A. S. Pell and G. Pilcher, Trans. Faraday Soc. **61**, 71 (1965).
[2]R. S. Crog and H. Hunt, J. Phys. Chem. **46**, 1162 (1942).
[3]R. C. Lord and B. Nolin, J. Chem. Phys. **24**, 656 (1956).
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[7]G. L. Cunningham, A. W. Boyd, and W. D. Gwinn, J. Chem. Phys. **17**, 211 (1949).
[8]P. C. Ackermann and J. E. Mayer, J. Chem. Phys. **4**, 377 (1936).
[9]M. Igarashi, Bull. Chem. Soc. Japan **26**, 330 (1953).
[10]B. Kistiakowsky and W. W. Rice, J. Chem. Phys. **8**, 618 (1940).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.863	−40.119	−40.119	INFINITE
100	33.285	202.794	278.161	−7.537	−44.363	−35.641	18.617
200	36.701	226.467	246.985	−4.104	−48.426	−25.373	6.627
250	41.673	235.154	243.764	−2.153	−50.588	−19.360	4.045
298.15	47.901	243.012	243.012	0.	−52.635	−13.159	2.305
300	48.157	243.309	243.013	0.089	−52.711	−12.914	2.249
350	55.277	251.264	243.625	2.674	−54.705	−6.121	0.914
400	62.396	259.112	245.071	5.616	−56.527	0.946	−0.124
450	69.157	266.856	247.063	8.907	−58.172	8.230	−0.955
500	75.408	274.471	249.424	12.524	−59.648	15.689	−1.639
600	86.312	289.214	254.837	20.627	−62.139	31.000	−2.699
700	95.366	303.220	260.757	29.724	−64.090	46.685	−3.484
800	102.969	316.465	266.901	39.652	−65.578	62.616	−4.088
900	109.430	328.976	273.110	50.280	−66.671	78.710	−4.568
1000	114.963	340.800	279.293	61.507	−67.429	94.907	−4.957
1100	119.723	351.986	285.398	73.247	−67.909	111.166	−5.279
1200	123.832	362.584	291.392	85.430	−68.160	127.458	−5.548
1300	127.388	372.639	297.259	97.995	−68.226	143.763	−5.776
1400	130.472	382.195	302.987	110.892	−68.143	160.068	−5.972
1500	133.156	391.291	308.573	124.076	−67.944	176.362	−6.141
1600	135.498	399.961	314.016	137.511	−67.655	192.640	−6.289
1700	137.549	408.238	319.317	151.166	−67.297	208.898	−6.419
1800	139.350	416.152	324.478	165.013	−66.890	225.133	−6.533
1900	140.938	423.730	329.504	179.029	−66.447	241.344	−6.635
2000	142.342	430.996	334.398	193.194	−65.982	257.532	−6.726
2100	143.589	437.971	339.165	207.492	−65.505	273.696	−6.808
2200	144.699	444.677	343.810	221.908	−65.025	289.838	−6.882
2300	145.691	451.131	348.337	236.428	−64.549	305.957	−6.948
2400	146.580	457.351	352.750	251.042	−64.083	322.056	−7.009
2500	147.379	463.351	357.055	265.741	−63.632	338.136	−7.065
2600	148.101	469.146	361.255	280.516	−63.201	354.198	−7.116
2700	148.753	474.748	365.356	295.359	−62.793	370.243	−7.163
2800	149.344	480.168	369.360	310.264	−62.411	386.275	−7.206
2900	149.882	485.419	373.272	325.226	−62.059	402.293	−7.246
3000	150.373	490.508	377.095	340.239	−61.738	418.300	−7.283
3100	150.821	495.446	380.834	355.299	−61.451	434.296	−7.318
3200	151.232	500.241	384.491	370.402	−61.199	450.283	−7.350
3300	151.609	504.901	388.069	385.544	−60.984	466.264	−7.380
3400	151.956	509.432	391.572	400.723	−60.807	482.239	−7.409
3500	152.275	513.842	395.003	415.934	−60.670	498.208	−7.435
3600	152.571	518.135	398.364	431.177	−60.574	514.175	−7.460
3700	152.844	522.320	401.658	446.448	−60.519	530.139	−7.484
3800	153.098	526.399	404.887	461.745	−60.508	546.103	−7.507
3900	153.333	530.379	408.054	477.067	−60.540	562.067	−7.528
4000	153.553	534.264	411.161	492.411	−60.616	578.032	−7.548
4100	153.757	538.058	414.210	507.777	−60.738	593.999	−7.568
4200	153.947	541.765	417.203	523.162	−60.906	609.971	−7.586
4300	154.125	545.390	420.142	538.566	−61.120	625.947	−7.604
4400	154.292	548.935	423.029	553.987	−61.381	641.927	−7.621
4500	154.448	552.404	425.866	569.424	−61.688	657.915	−7.637
4600	154.595	555.801	428.654	584.876	−62.043	673.909	−7.652
4700	154.732	559.127	431.394	600.343	−62.446	689.913	−7.668
4800	154.862	562.386	434.089	615.822	−62.896	705.926	−7.682
4900	154.984	565.580	436.740	631.315	−63.393	721.948	−7.696
5000	155.099	568.712	439.349	646.819	−63.938	737.981	−7.710
5100	155.207	571.785	441.915	662.334	−64.530	754.025	−7.723
5200	155.310	574.800	444.442	677.860	−65.168	770.081	−7.736
5300	155.407	577.759	446.930	693.396	−65.852	786.150	−7.748
5400	155.499	580.665	449.379	708.941	−66.582	802.233	−7.760
5500	155.586	583.519	451.792	724.496	−67.357	818.328	−7.772
5600	155.669	586.323	454.170	740.058	−68.175	834.439	−7.783
5700	155.747	589.079	456.512	755.629	−69.037	850.565	−7.795
5800	155.821	591.788	458.822	771.208	−69.942	866.707	−7.806
5900	155.892	594.453	461.098	786.793	−70.887	882.862	−7.816
6000	155.960	597.073	463.342	802.386	−71.873	899.036	−7.827

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = [373.129]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-8.2 \pm 42]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-8.4 \pm 42]\ kJ·mol^{-1}$

Vibratonal Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[240](1)	[220](1)	[2158](1)
[130](1)	[225](1)	[2158](1)
[205](1)	[207](1)	[2158](1)
[130](1)	[207](1)	[2158](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: [D_{2h}]
Bond Distances: K–C = [2.75] Å; C–N = [1.16] Å
Bond Angles: N–C–K = [140]°; C–K–C = [100]°; K–C–K = [80]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.948540 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°((KCN)_2, g, 298.15\ K)$ was calculated based on an estimated enthalpy of dissociation, 40 $kcal·mol^{-1}$ for the reaction $(KCN)_2(g) \rightarrow 2\ KCN(g)$, which was obtained by comparison with that for $(NaCN)_2(g)$.

Heat Capacity and Entropy

The molecular structure and bond angles were assumed to be the same as those for KCN(cr) reported by Bijvoet and Lely.[1] The C–N bond distance was assumed to be the same as that for KCN(g), and the K–C bond distance was assumed to be 10% longer than that in KCN(g). The vibrational frequencies were estimated by comparison with those for $K_2F_2(g)$. The last six frequencies were adopted from the bending and asymmetric stretching frequencies for KCN(g). The three principal moments of inertia are: $I_A = 40.5737 \times 10^{-39}$, $I_B = 67.3413 \times 10^{-39}$, and $I_C = 107.9149 \times 10^{-39}\ g·cm^2$.

Reference

[1] J. M. Bijvoet and J. A. Lely, Rec. Trav. Chim. **59**, 908 (1940).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−24.786	−8.217	−8.217	INFINITE
100	77.547	266.448	465.521	−19.907	−9.825	−13.178	6.883
200	103.437	330.321	383.046	−10.545	−9.215	−16.652	4.349
250	107.785	353.916	374.932	−5.254	−8.720	−18.570	3.880
298.15	110.262	373.129	373.129	0.	−8.368	−20.502	3.592
300	110.337	373.812	373.132	0.204	−8.359	−20.578	3.583
350	112.029	390.955	374.482	5.766	−12.978	−22.435	3.348
400	113.310	406.001	377.500	11.400	−13.082	−23.779	3.105
450	114.405	419.411	381.425	17.094	−13.238	−25.107	2.914
500	115.421	431.518	385.839	22.839	−13.451	−26.415	2.760
600	117.361	452.734	395.269	34.479	−14.030	−28.957	2.521
700	119.200	470.965	404.811	46.308	−14.781	−31.388	2.342
800	120.890	486.995	414.102	58.314	−15.680	−33.700	2.200
900	122.393	501.322	423.011	70.480	−16.725	−35.892	2.083
1000	123.702	514.287	431.500	82.786	−17.931	−37.958	1.983
1100	124.828	526.131	439.573	95.214	−177.226	−30.675	1.457
1200	125.791	537.035	447.246	107.747	−176.702	−17.376	0.756
1300	126.614	547.137	454.546	120.368	−176.230	−4.118	0.165
1400	127.317	556.547	461.500	133.065	−175.804	9.105	−0.340
1500	127.920	565.352	468.133	145.828	−175.417	22.299	−0.777
1600	128.439	573.624	474.470	158.647	−175.069	35.468	−1.158
1700	128.888	581.425	480.534	171.514	−174.757	48.617	−1.494
1800	129.277	588.803	486.346	184.422	−174.481	61.749	−1.792
1900	129.616	595.802	491.924	197.367	−174.241	74.866	−2.058
2000	129.913	602.458	497.286	210.344	−174.041	87.971	−2.298
2100	130.175	608.803	502.447	223.349	−173.881	101.068	−2.514
2200	130.405	614.864	507.420	236.378	−173.766	114.158	−2.710
2300	130.610	620.666	512.218	249.429	−173.699	127.244	−2.890
2400	130.793	626.228	516.854	262.499	−173.684	140.328	−3.054
2500	130.956	631.571	521.336	275.587	−173.726	153.412	−3.205
2600	131.102	636.710	525.675	288.690	−173.831	166.499	−3.345
2700	131.234	641.660	529.880	301.807	−174.002	179.592	−3.474
2800	131.353	646.435	533.958	314.936	−174.248	192.692	−3.595
2900	131.460	651.046	537.916	328.077	−174.573	205.803	−3.707
3000	131.558	655.505	541.762	341.228	−174.984	218.926	−3.812
3100	131.647	659.820	545.501	354.388	−175.488	232.064	−3.910
3200	131.729	664.001	549.139	367.557	−176.094	245.221	−4.003
3300	131.803	668.056	552.682	380.734	−176.789	258.396	−4.090
3400	131.871	671.991	556.133	393.917	−177.609	271.596	−4.173
3500	131.934	675.815	559.498	407.108	−178.547	284.820	−4.251
3600	131.992	679.532	562.781	420.304	−179.619	298.074	−4.325
3700	132.046	683.150	565.986	433.506	−180.830	311.360	−4.396
3800	132.095	686.672	569.116	446.713	−182.188	324.680	−4.463
3900	132.141	690.104	572.174	459.925	−183.704	338.038	−4.528
4000	132.184	693.450	575.164	473.141	−185.374	351.436	−4.589
4100	132.224	696.714	578.089	486.362	−187.220	364.878	−4.649
4200	132.261	699.901	580.952	499.586	−189.258	378.368	−4.706
4300	132.295	703.013	583.754	512.814	−191.491	391.909	−4.761
4400	132.327	706.055	586.499	526.045	−193.373	405.450	−4.813
4500	132.358	709.029	589.189	539.279	−195.885	419.087	−4.865
4600	132.386	711.939	591.826	552.516	−198.594	432.783	−4.914
4700	132.413	714.786	594.412	565.756	−201.465	446.535	−4.963
4800	132.438	717.574	596.949	578.999	−204.323	460.327	−5.009
4900	132.461	720.305	599.439	592.244	−207.595	474.208	−5.055
5000	132.483	722.981	601.883	605.491	−211.075	488.157	−5.100
5100	132.504	725.605	604.283	618.740	−214.766	502.178	−5.143
5200	132.524	728.178	606.641	631.992	−218.669	516.273	−5.186
5300	132.542	730.703	608.958	645.245	−222.784	530.446	−5.228
5400	132.560	733.180	611.236	658.500	−227.113	544.698	−5.269
5500	132.577	735.613	613.475	671.757	−231.652	559.032	−5.309
5600	132.593	738.002	615.678	685.016	−236.402	573.451	−5.349
5700	132.608	740.349	617.844	698.276	−240.670	587.861	−5.387
5800	132.622	742.655	619.976	711.537	−245.745	602.440	−5.426
5900	132.635	744.922	622.075	724.800	−251.012	617.109	−5.463
6000	132.648	747.152	624.141	738.064	−256.468	631.869	−5.501

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 58.6 \pm 4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -59.4 \pm 8\ kJ \cdot mol^{-1}$

Enthalpy of Formation
Data from the U. S. Nat. Bur. of Stand.[1]

Heat Capacity and Entropy
Data from the U. S. Nat. Bur. of Stand.[1]

Reference
[1]G. T. Fursukawa, M. L. Reilly *et al.*, U. S. Nat. Bur. Stand. Report 6928, Appendix B, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	71.546	58.576	58.576	0.000	−59.413	−56.111	9.830
300	71.965	59.020	58.577	.133	−59.403	−56.090	9.766
400	87.404	82.023	61.608	8.166	−58.616	−55.096	7.195
500	95.060	102.405	67.777	17.314	−63.987	−53.685	5.608
600	99.705	120.169	75.062	27.064	−63.360	−51.682	4.499
700	102.926	135.791	82.644	37.203	−62.618	−49.793	3.716
800	105.353	149.698	90.173	47.620	−61.835	−48.014	3.135
900	107.361	162.225	97.494	58.258	−61.048	−46.333	2.689
1000	109.077	173.628	104.546	69.082	−60.243	−44.741	2.337
1100	110.583	184.095	111.308	80.066	−59.409	−43.231	2.053
1200	112.006	193.779	117.782	91.196	−58.533	−41.799	1.819
1300	113.345	202.797	123.979	102.464	−57.608	−40.442	1.625
1400	114.600	211.243	129.914	113.862	−56.621	−39.158	1.461
1500	115.813	219.191	135.603	125.383	−55.564	−37.947	1.321
1600	116.985	226.703	141.064	137.022	−54.433	−36.809	1.202
1700	118.156	233.831	146.313	148.780	−343.695	−21.392	.657
1800	119.286	240.616	151.365	160.652	−340.897	−2.513	.073
1900	120.416	247.096	156.234	172.637	−338.033	16.208	−.446
2000	121.503	253.301	160.934	184.734	−335.103	34.777	−.908

PREVIOUS: CURRENT: December 1960

Magnesium Carbide (MgC_2) CRYSTAL $M_r = 48.327$

$S°(298.15\ K) \approx 54.4 \pm 8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) \approx$ Unknown

$\Delta_f H°(298.15\ K) = 87.9 \pm 21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Data from.[1]

Heat Capacity and Entropy

Data from Furukawa, *et al.*[1]

Reference

[1]G. T. Furukawa, M. L. Reilly *et al.*, U. S. Nat. Bur. Stand. Report 6928, Appendix B, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	56.233	54.392	54.392	0.000	87.864	84.811	−14.859
300	56.442	54.740	54.393	.104	87.891	84.792	−14.764
400	64.392	72.161	56.714	6.179	89.364	83.538	−10.909
500	68.408	86.989	61.326	12.832	90.697	81.921	−8.558
600	70.877	99.691	66.688	19.802	91.744	80.063	−6.970
700	72.634	110.753	72.210	26.981	92.505	78.052	−5.824
800	74.015	120.545	77.651	34.315	93.009	75.950	−4.959
900	75.145	129.329	82.914	41.774	93.280	73.799	−4.283
1000	76.149	137.300	87.960	49.340	84.744	72.342	−3.779
1100	77.027	144.599	92.782	56.999	84.584	71.109	−3.377
1200	77.864	151.337	97.384	64.744	84.396	69.892	−3.042
1300	78.701	157.603	101.778	72.573	84.196	68.692	−2.760
1400	79.454	163.463	105.977	80.480	−43.416	70.674	−2.637
1500	80.207	168.971	109.995	88.464	−42.260	78.783	−2.743
1600	80.919	174.170	113.845	96.520	−41.092	86.814	−2.834
1700	81.630	179.097	117.540	104.647	−39.908	94.772	−2.912
1800	82.341	183.783	121.091	112.846	−38.701	102.660	−2.979
1900	83.011	188.253	124.509	121.114	−37.470	110.480	−3.037
2000	83.722	192.529	127.804	129.450	−36.211	118.234	−3.088
2100	84.391	196.630	130.984	137.856	−34.922	125.925	−3.132
2200	85.061	200.571	134.058	146.329	−33.602	133.553	−3.171
2300	85.730	204.367	137.033	154.868	−32.249	141.121	−3.205
2400	86.400	208.030	139.916	163.475	−30.863	148.629	−3.235
2500	87.069	211.571	142.711	172.148	−29.442	156.079	−3.261

PREVIOUS: CURRENT: December 1960

$S°(298.15\ K)$ = [230 ± 8] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [552 ± 126] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [556 ± 126] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
26.41	2
30338.53	4
34802.33	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1200] (1)
321 (2)
[900] (1)

Point Group: $D_{\infty h}$ σ = 2
Bond Distance: C–N = 1.245 Å
Bond Angle: C–N–C = 180°
Rotational Constant: B_0 = 0.452740 cm^{-1}

Enthalpy of Formation

Merer and Travis[1] stated that the observed bond length in CNC(g) indicated double–bonded CN links. The value of the C = N dissociation energy is derived as 147 $kcal·mol^{-1}$ from the enthalpy of combustion of n–butyl–isobutylidine amine determined by Coates and Sutton.[2] However, due to possible extra binding energy from the unpaired electron, we assume here a slightly higher value of 160 $kcal·mol^{-1}$. This yields a $\Delta_f H°$(CNC, g, 298.15 K) = 133 $kcal·mol^{-1}$. It is also possible to calculate another value by assuming that the ratio of the enthalpy of atomization of Si_2N to that of C_2N(g) is equal to the ratio of the dissociation energies of SiN(g) and CN(g); by this method $\Delta_f H°$(CNC, g, 298.15 K) = 144 $kcal·mol^{-1}$.

Heat Capacity and Entropy

Merer and Travis[1] have observed the ultraviolet absorption sectrum of the CNC radical. They ave assigned the configuration, bond distance, and the electronic levels. In addition, they have derived ν_2; the remaining frequencies are estimated by comparison with the $^1\Pi$ state of C_3(g), which has been assigned by Weltner and McLeod.[3]

References

[1]A. J. Merer and D. N. Travis, Can. J. Phys. **44**, 353 (1956).
[2]G. E. Coates and L. E. Sutton, J. Chem. Soc. 1187 (1948).
[3]W. Weltner and D. J. McLeod, J. Chem. Phys. **40**, 1305 (1964); **45**, 3096 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.080	551.829	551.829	INFINITE
100	32.963	188.237	267.905	−7.967	553.372	542.729	−283.493
200	40.683	213.673	234.935	−4.252	554.978	531.475	−138.807
250	43.425	223.053	231.645	−2.148	555.764	525.507	−109.799
298.15	45.751	230.905	230.905	0.	556.472	519.615	−91.034
300	45.835	231.188	230.906	0.085	556.498	519.386	−90.433
350	47.975	238.418	231.472	2.431	557.174	513.147	−76.583
400	49.849	244.949	232.755	4.878	557.787	506.814	−66.183
450	51.465	250.916	234.446	7.412	558.332	500.409	−58.086
500	52.844	256.412	236.371	10.020	558.807	493.947	−51.602
600	55.010	266.249	240.550	15.419	559.557	480.901	−41.866
700	56.572	274.852	244.849	21.002	560.073	467.748	−34.904
800	57.713	282.485	249.086	26.719	560.394	454.534	−29.678
900	58.563	289.334	253.184	32.535	560.552	441.291	−25.612
1000	59.208	295.539	257.114	38.425	560.576	428.037	−22.358
1100	59.706	301.206	260.868	44.372	560.486	414.786	−19.697
1200	60.097	306.419	264.450	50.363	560.300	401.549	−17.479
1300	60.410	311.242	267.866	56.389	560.031	388.330	−15.603
1400	60.663	315.728	271.126	62.443	559.689	375.134	−13.996
1500	60.871	319.921	274.241	68.520	559.283	361.966	−12.605
1600	61.043	323.855	277.220	74.616	558.820	348.826	−11.388
1700	61.187	327.560	280.074	80.728	558.305	335.717	−10.315
1800	61.309	331.061	282.810	86.853	557.742	322.639	−9.363
1900	61.414	334.379	285.438	92.989	557.135	309.594	−8.511
2000	61.503	337.532	287.964	99.135	556.488	296.583	−7.746
2100	61.580	340.534	290.397	105.289	555.802	283.604	−7.054
2200	61.648	343.400	292.741	111.450	555.080	270.659	−6.426
2300	61.707	346.142	295.004	117.618	554.324	257.748	−5.854
2400	61.759	348.770	297.190	123.792	553.536	244.870	−5.329
2500	61.805	351.292	299.304	129.970	552.716	232.025	−4.848
2600	61.846	353.716	301.350	136.153	551.865	219.214	−4.404
2700	61.883	356.051	303.333	142.339	550.985	206.437	−3.994
2800	61.916	358.302	305.256	148.529	550.077	193.692	−3.613
2900	61.946	360.476	307.123	154.722	549.141	180.981	−3.260
3000	61.973	362.576	308.937	160.918	548.178	168.302	−2.930
3100	61.998	364.609	310.700	167.117	547.188	155.656	−2.623
3200	62.020	366.577	312.416	173.318	546.173	143.042	−2.335
3300	62.041	368.486	314.086	179.521	545.132	130.460	−2.065
3400	62.061	370.339	315.713	185.726	544.065	117.910	−1.811
3500	62.079	372.138	317.300	191.933	542.974	105.392	−1.573
3600	62.096	373.887	318.848	198.141	541.859	92.905	−1.348
3700	62.113	375.588	320.358	204.352	540.719	80.450	−1.136
3800	62.129	377.245	321.834	210.564	539.556	68.026	−0.935
3900	62.145	378.859	323.275	216.778	538.369	55.632	−0.745
4000	62.160	380.433	324.685	222.993	537.159	43.270	−0.565
4100	62.176	381.968	326.063	229.210	535.926	30.938	−0.394
4200	62.191	383.466	327.412	235.428	534.670	18.636	−0.232
4300	62.207	384.930	328.733	241.648	533.392	6.365	−0.077
4400	62.224	386.360	330.026	247.870	532.092	−5.877	0.070
4500	62.241	387.759	331.294	254.093	530.769	−18.088	0.210
4600	62.259	389.127	332.536	260.318	529.425	−30.271	0.344
4700	62.277	390.466	333.754	266.545	528.059	−42.423	0.471
4800	62.297	391.777	334.950	272.773	526.671	−54.546	0.594
4900	62.318	393.062	336.123	279.004	525.262	−66.641	0.710
5000	62.339	394.321	337.274	285.237	523.833	−78.706	0.822
5100	62.362	395.556	338.405	291.472	522.382	−90.742	0.929
5200	62.387	396.767	339.515	297.709	520.911	−102.750	1.032
5300	62.412	397.956	340.607	303.949	519.419	−114.729	1.131
5400	62.439	399.123	341.680	310.192	517.907	−126.680	1.225
5500	62.468	400.269	342.735	316.437	516.376	−138.603	1.316
5600	62.498	401.395	343.772	322.686	514.824	−150.498	1.404
5700	62.530	402.501	344.793	328.937	513.253	−162.364	1.488
5800	62.563	403.589	345.797	335.192	511.662	−174.204	1.569
5900	62.598	404.659	346.786	341.450	510.051	−186.015	1.647
6000	62.634	405.711	347.759	347.711	508.421	−197.799	1.722

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 241.565\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 307.219 \pm 1.80\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 309.072 \pm 1.80\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2328.5 (1)
850.6 (1)
2149 (1)
507.2 (2)
240 (2)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distances: C–N = 1.157 Å; C–C = 1.380 Å
Bond Angle: N–C–C–N = 180°
Rotational Constant: $B_0 = 0.157545 \pm 0.00015\ cm^{-1}$

Enthalpy of Formation

Knowlton and Prosen[1] reported $\Delta_f H°(298.15\ K) = -261.94 \pm 0.43\ kcal·mol^{-1}$ for the reaction $C_2N_2(g) + 2O_2(g) \rightarrow CO_2(g) + N_2(g)$. When corrected for a change in the atomic weight of carbon, this becomes $\Delta_f H°(298.15\ K) = -261.95 \pm 0.43$ kcal, whence $\Delta_f H°(298.15\ K)$ for $C_2N_2(g)$ is found to be $73.87 \pm 0.43\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Langseth and Moller[2] determined the vibrational frequencies by Raman spectroscopy. Moller and Stoicheff[3] determined B_0 by Raman spectroscopy and calculated the bond lengths listed above. These agree with lengths found from electron–diffraction measurements by Langseth and Moller[2] (C–N distance = 1.15 Å, C–C distance = 1.38 Å) and Pauling *et al.*[4] (C–N distance = 1.16 ± 0.02 Å, C–C distance = 1.37 ± 0.02 Å). From measurements reported by Ruehrwein and Giauque,[5] $S°(298.15\ K)$ is calculated by the 3rd law to be 57.63 $cal·K^{-1}·mol^{-1}$, in satisfactory agreement with the value calculated here.

References

[1]J. W. Knowlton and E. J. Prosen, J. Res. Nat. Bur. Stand. **46**, 489 (1951).
[2]A. Langseth and C. K. Moller, Acta Chem. Scand. **4**, 725 (1950).
[3]C. K. Moller and B. P. Stoicheff, Can. J. Phys. **32**, 625 (1954).
[4]L. Pauling, H. D. Springall, and K. J. Palmer, J. Amer. Chem. Soc. **61**, 927 (1939).
[5]R. A. Ruehrwein and W. F. Giauque, J. Amer. Chem. Soc. **61**, 2940 (1939).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.626	307.219	307.219	INFINITE
100	36.399	191.121	286.323	−9.520	307.303	304.362	−158.982
200	48.910	220.447	246.531	−5.217	308.042	301.183	−78.661
250	53.388	231.863	242.482	−2.655	308.558	299.409	−62.558
298.15	56.746	241.565	241.565	0.	309.072	297.601	−52.138
300	56.859	241.917	241.566	0.105	309.092	297.529	−51.804
350	59.585	250.894	242.269	3.019	309.606	295.561	−44.110
400	61.799	259.000	243.862	6.055	310.079	293.522	−38.330
450	63.677	266.390	245.961	9.193	310.495	291.427	−33.828
500	65.332	273.186	248.348	12.419	310.850	289.288	−30.222
600	68.218	285.360	253.526	19.101	311.392	284.922	−24.805
700	70.704	296.067	258.853	26.050	311.752	280.479	−20.930
800	72.861	305.652	264.114	33.230	311.982	275.995	−18.021
900	74.717	314.344	269.220	40.612	312.117	271.487	−15.757
1000	76.302	322.301	274.136	48.165	312.184	266.969	−13.945
1100	77.650	329.638	278.852	55.864	312.199	262.446	−12.463
1200	78.795	336.445	283.371	63.688	312.171	257.924	−11.227
1300	79.769	342.791	287.701	71.618	312.109	253.406	−10.182
1400	80.598	348.734	291.850	79.637	312.015	248.894	−9.286
1500	81.308	354.320	295.831	87.733	311.895	244.389	−8.510
1600	81.918	359.587	299.652	95.895	311.748	239.893	−7.832
1700	82.445	364.569	303.326	104.114	311.577	235.407	−7.233
1800	82.901	369.295	306.861	112.382	311.382	230.932	−6.701
1900	83.299	373.788	310.266	120.692	311.165	226.469	−6.226
2000	83.648	378.070	313.550	129.040	310.925	222.017	−5.798
2100	83.954	382.159	316.720	137.421	310.663	217.578	−5.412
2200	84.225	386.071	319.784	145.830	310.379	213.152	−5.061
2300	84.465	389.820	322.748	154.265	310.073	208.740	−4.741
2400	84.679	393.419	325.619	162.722	309.746	204.341	−4.447
2500	84.870	396.880	328.400	171.199	309.397	199.956	−4.178
2600	85.041	400.212	331.099	179.695	309.026	195.586	−3.929
2700	85.195	403.425	333.718	188.207	308.634	191.230	−3.700
2800	85.335	406.525	336.263	196.734	308.220	186.889	−3.486
2900	85.461	409.522	338.738	205.274	307.785	182.563	−3.288
3000	85.576	412.421	341.146	213.826	307.328	178.253	−3.104
3100	85.680	415.229	343.491	222.388	306.850	173.958	−2.931
3200	85.775	417.951	345.776	230.961	306.350	169.680	−2.770
3300	85.863	420.592	348.003	239.543	305.828	165.417	−2.618
3400	85.943	423.156	350.176	248.134	305.285	161.170	−2.476
3500	86.016	425.649	352.297	256.732	304.720	156.939	−2.342
3600	86.084	428.073	354.368	265.337	304.134	152.725	−2.216
3700	86.147	430.432	356.392	273.948	303.526	148.528	−2.097
3800	86.205	432.730	358.371	282.566	302.896	144.347	−1.984
3900	86.259	434.970	360.306	291.189	302.244	140.183	−1.878
4000	86.309	437.155	362.200	299.818	301.571	136.036	−1.776
4100	86.356	439.287	364.055	308.451	300.876	131.906	−1.681
4200	86.399	441.368	365.871	317.089	300.159	127.794	−1.589
4300	86.439	443.402	367.650	325.731	299.420	123.699	−1.503
4400	86.477	445.389	369.395	334.376	298.659	119.621	−1.420
4500	86.513	447.333	371.105	343.026	297.877	115.561	−1.341
4600	86.546	449.235	372.783	351.679	297.073	111.518	−1.266
4700	86.577	451.096	374.429	360.335	296.247	107.493	−1.195
4800	86.606	452.919	376.046	368.994	295.398	103.486	−1.126
4900	86.634	454.705	377.633	377.656	294.528	99.497	−1.061
5000	86.660	456.456	379.192	386.321	293.635	95.525	−0.998
5100	86.684	458.172	380.724	394.988	292.720	91.572	−0.938
5200	86.707	459.856	382.229	403.658	291.783	87.637	−0.880
5300	86.729	461.508	383.710	412.329	290.824	83.720	−0.825
5400	86.750	463.129	385.165	421.003	289.842	79.822	−0.772
5500	86.769	464.721	386.597	429.679	288.837	75.942	−0.721
5600	86.788	466.285	388.006	438.357	287.811	72.080	−0.672
5700	86.805	467.821	389.393	447.037	286.761	68.237	−0.625
5800	86.822	469.331	390.759	455.718	285.688	64.413	−0.580
5900	86.838	470.815	392.103	464.401	284.592	60.607	−0.537
6000	86.853	472.275	393.427	473.086	283.472	56.820	−0.495

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar)

$S°$(298.15 K) = [347.102] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = [−8.3 ± 13] kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [−8.8 ± 13] kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[295](1)	[250](1)	[239](1)
[175](1)	[290](1)	[239](1)
[250](1)	[239](1)	[2176](1)
[170](1)	[239](1)	[2176](1)

Ground State Quantum Weight: 1 σ = [4]
Point Group: [D_{2h}]
Bond Distances: N–C = [1.16] Å; C–Na = [2.19] Å
Bond Angles: C–Na–C = [105]°; Na–C–Na = [75]°; N–C–Na = [142.5]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [4.483815 × 10^{-113}] g^3·cm^6

Enthalpy of Formation

The mass spectra of vapors from samples of NaCN have been observed by Porter[1] at temperatures around 1000 K. The results indicate that the compound evaporates as NaCN(g) and $Na_2(CN)_2$(g). A comparison of relative ion currents produced by electron bombardment of NaCN vapors effusing from single–and double–oven–type Knudsen cells, yielded information on the partial pressures of monomer and dimer. Based on the partial pressures for NaCN(g) and $(NaCN)_2$(g) reported at temperatures, 903–1049 K, the vapor pressures of $(NaCN)_2$(g) over NaCN(l), 1078.2–1626.2 K, were calculated from the total vapor pressure measurements reported by Ingold.[2] By the 2nd and 3rd law methods, the values of $\Delta_{vap}H°$(298.15 K) (*l* → *dimer*) were evaluated to be 38.89 and 38.21 kcal·mol^{-1}, respectively. Using the 3rd law value, the enthalpy of formation for $(NaCN)_2$(g) was evaluated.

Heat Capacity and Entropy

The molecular structure, bond distances and C–Na–C bond angle were estimated by Porter.[1] The vibrational frequencies were estimated by comparison with those for NaCl(g). The last six frequencies were the bending and asymmetric stretching frequencies for NaCN(g). The principal moments of inertia are: I_A = 13.5707 × 10^{-39}, I_B = 51.0944 × 10^{-39}, and I_C = 64.6652 × 10^{-39} g·cm^2.

References

[1]R. F. Porter, J. Chem. Phys. **35**, 318 (1961).
[2]C. K. Ingold, J. Chem. Soc. **123**, 885 (1923).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−23.178	−8.299	−8.299	INFINITE
100	67.677	247.172	435.395	−18.822	−9.644	−13.427	7.013
200	98.488	305.757	356.722	−10.193	−9.489	−17.132	4.474
250	104.306	328.419	348.858	−5.110	−9.102	−19.087	3.988
298.15	107.686	347.102	347.102	0.	−8.786	−21.041	3.686
300	107.789	347.768	347.104	0.199	−8.777	−21.117	3.677
350	110.089	364.568	348.426	5.650	−8.631	−23.189	3.461
400	111.781	379.383	351.387	11.198	−13.984	−24.854	3.246
450	113.163	392.631	355.247	16.823	−14.207	−26.200	3.041
500	114.386	404.618	359.594	22.512	−14.466	−27.519	2.875
600	116.596	425.672	368.900	34.063	−15.087	−30.073	2.618
700	118.601	443.798	378.335	45.824	−15.818	−32.514	2.426
800	120.401	459.755	387.535	57.776	−16.636	−34.844	2.275
900	121.985	474.030	396.366	69.897	−17.535	−37.067	2.151
1000	123.355	486.955	404.789	82.166	−18.527	−39.185	2.047
1100	124.529	498.769	412.803	94.562	−19.633	−41.199	1.956
1200	125.531	509.648	420.426	107.066	−214.401	−38.226	1.664
1300	126.385	519.731	427.682	119.663	−213.953	−23.563	0.947
1400	127.115	529.124	434.596	132.339	−213.547	−8.933	0.333
1500	127.740	537.916	441.194	145.083	−213.178	5.669	−0.197
1600	128.278	546.178	447.500	157.884	−212.842	20.248	−0.661
1700	128.743	553.969	453.536	170.736	−212.538	34.807	−1.069
1800	129.146	561.339	459.322	183.631	−212.264	49.348	−1.432
1900	129.497	568.332	464.877	196.563	−212.018	63.875	−1.756
2000	129.805	574.982	470.218	209.529	−211.801	78.390	−2.047
2100	130.075	581.322	475.358	222.523	−211.611	92.895	−2.311
2200	130.314	587.379	480.314	235.543	−211.449	107.391	−2.550
2300	130.526	593.176	485.096	248.585	−211.316	121.881	−2.768
2400	130.715	598.735	489.716	261.647	−211.212	136.366	−2.968
2500	130.884	604.075	494.184	274.727	−211.139	150.846	−3.152
2600	131.035	609.211	498.510	287.823	−211.099	165.325	−3.321
2700	131.171	614.159	502.702	300.934	−211.093	179.803	−3.478
2800	131.294	618.932	506.768	314.057	−211.124	194.281	−3.624
2900	131.406	623.541	510.716	327.192	−211.193	208.760	−3.760
3000	131.507	627.998	514.552	340.338	−211.303	223.243	−3.887
3100	131.599	632.311	518.281	353.493	−211.458	237.731	−4.006
3200	131.683	636.491	521.910	366.658	−211.660	252.224	−4.117
3300	131.761	640.544	525.444	379.830	−211.912	266.724	−4.222
3400	131.831	644.478	528.887	393.010	−212.218	281.232	−4.321
3500	131.896	648.301	532.245	406.196	−212.581	295.751	−4.414
3600	131.956	652.017	535.521	419.389	−213.006	310.280	−4.502
3700	132.012	655.634	538.718	432.587	−213.497	324.823	−4.586
3800	132.063	659.155	541.841	445.791	−214.057	339.379	−4.665
3900	132.111	662.586	544.894	459.000	−214.692	353.951	−4.741
4000	132.155	665.931	547.878	472.213	−215.406	368.541	−4.813
4100	132.196	669.195	550.797	485.430	−216.204	383.149	−4.881
4200	132.234	672.381	553.654	498.652	−217.087	397.778	−4.947
4300	132.270	675.493	556.452	511.877	−218.069	412.429	−5.010
4400	132.303	678.534	559.192	525.106	−219.066	427.097	−5.070
4500	132.334	681.508	561.877	538.338	−220.208	441.794	−5.128
4600	132.364	684.417	564.510	551.573	−221.471	456.519	−5.184
4700	132.391	687.264	567.091	564.810	−222.845	471.272	−5.238
4800	132.417	690.051	569.624	578.051	−224.335	486.056	−5.289
4900	132.441	692.782	572.110	591.294	−225.947	500.872	−5.339
5000	132.464	695.458	574.550	604.539	−227.670	515.722	−5.388
5100	132.486	698.081	576.946	617.786	−229.538	530.608	−5.435
5200	132.506	700.654	579.301	631.036	−231.543	545.532	−5.480
5300	132.526	703.178	581.614	644.288	−233.691	560.496	−5.524
5400	132.544	705.655	583.888	657.541	−235.987	575.502	−5.567
5500	132.561	708.088	586.125	670.796	−238.436	590.552	−5.609
5600	132.577	710.476	588.324	684.053	−241.043	605.647	−5.649
5700	132.593	712.823	590.488	697.312	−243.813	620.791	−5.689
5800	132.608	715.129	592.617	710.572	−246.750	635.985	−5.728
5900	132.622	717.396	594.712	723.833	−249.859	651.231	−5.766
6000	132.635	719.625	596.776	737.096	−252.828	666.495	−5.802

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 233.07\ J·K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K) = 282.6 \pm 63\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 286.6 \pm 63\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	3
[4050]	[2]
[6450]	[1]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1074 (1)
381 (2)
1978 (1)

Point Group: $C_{\infty h}$ $\sigma = 1$
Bond Distance: C–C = [1.160] Å
Bond Angle: C–C–O = 180°
Rotational Constant: B_0 = [0.408483] cm^{-1}

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°(C_2O, g, 298.15\ K) = 68.5\ kcal·mol^{-1}$, was calculated from the enthalpy of reaction $\Delta_r H°(298.15\ K) = 65.5\ kcal·mol^{-1}$ for $C_3O_2(g) = C_2O(g) + CO(g)$ using all JANAF functions (dated Sept. 30, 1965). The value of $\Delta_r H°$ was obtained from the 3rd law calculation of the equilibrium constant ($K_p = 3.3 \times 10^{-6}$ atm at 1060 K) which was determined in the studies of decomposition rate of $C_3O_2(g)$ by Palmer and Cross.[1]

Jacox *et al.*[2] observed the photodissociation of C_2O near 5000 Å which corresponds to a minimum of 57 $kcal·mol^{-1}$ for $C_2O(g) \rightarrow C(g) + CO(g)$. This yields $\Delta_f H°(C_2O, g, 298.15\ K) \leq 87\ kcal·mol^{-1}$ which was not adopted because the irradiation was not monochromatic and thus possibly contained all wavelengths below 5000 Å.

Heat Capacity and Entropy

Jacox *et al.*[2] have observed three vibrational fundamentals in the infrared spectrum by matrix isolation, and suggested a linear structure with $^3\Sigma$ ground state for the CCO radical (g). They also estimated the bond distances C–C = 1.160 Å and C–O = 1.279 Å based on the structural analogy between the carbon suboxide and the CCO radical. Bayes[3] has predicted that the ^1Z and $^1\Sigma$ states lie respectively 0.5 and 0.8 eV above the ground state. These two elctronic states have been included in the tabulation.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.473	282.575	282.575	INFINITE
100	31.198	192.768	268.031	−7.526	283.950	273.529	−142.877
200	38.530	216.773	236.873	−4.020	285.348	262.574	−68.577
250	41.079	225.656	233.764	−2.027	286.020	256.802	−53.656
298.15	43.064	233.066	233.066	0.	286.604	251.121	−43.995
300	43.133	233.333	233.067	0.080	286.625	250.900	−43.686
350	44.880	240.116	233.599	2.281	287.146	244.904	−36.550
400	46.416	246.211	234.801	4.564	287.578	238.839	−31.189
450	47.795	251.759	236.381	6.920	287.919	232.725	−27.014
500	49.044	256.861	238.178	9.342	288.173	226.578	−23.670
600	51.227	266.001	242.071	14.358	288.454	214.228	−18.650
700	53.064	274.040	246.075	19.576	288.498	201.851	−15.062
800	54.626	281.230	250.028	24.962	288.374	189.479	−12.372
900	55.971	287.744	253.862	30.494	288.133	177.131	−10.280
1000	57.142	293.703	257.553	36.150	287.813	164.814	−8.609
1100	58.173	299.199	261.092	41.917	287.438	152.532	−7.243
1200	59.086	304.300	264.483	47.781	287.025	140.286	−6.106
1300	59.896	309.062	267.731	53.731	286.585	128.075	−5.146
1400	60.617	313.528	270.844	59.757	286.125	115.899	−4.324
1500	61.258	317.732	273.831	65.852	285.650	103.756	−3.613
1600	61.825	321.704	276.700	72.006	285.161	91.646	−2.992
1700	62.325	325.468	279.459	78.214	284.659	79.567	−2.445
1800	62.764	329.043	282.115	84.469	284.143	67.517	−1.959
1900	63.148	332.447	284.676	90.765	283.611	55.497	−1.526
2000	63.481	335.695	287.146	97.097	283.063	43.505	−1.136
2100	63.769	338.799	289.532	103.460	282.495	31.541	−0.785
2200	64.016	341.771	291.840	109.850	281.908	19.605	−0.465
2300	64.226	344.622	294.073	116.262	281.298	7.695	−0.175
2400	64.402	347.359	296.237	122.694	280.663	−4.187	0.091
2500	64.550	349.991	298.335	129.142	280.004	−16.043	0.335
2600	64.671	352.525	300.370	135.603	279.317	−27.871	0.560
2700	64.769	354.968	302.348	142.075	278.602	−39.672	0.768
2800	64.847	357.325	304.269	148.556	277.858	−51.447	0.960
2900	64.907	359.602	306.138	155.044	277.084	−63.194	1.138
3000	64.952	361.803	307.957	161.537	276.280	−74.914	1.304
3100	64.983	363.933	309.729	168.034	275.444	−86.607	1.459
3200	65.002	365.997	311.455	174.533	274.576	−98.273	1.604
3300	65.012	367.997	313.138	181.034	273.676	−109.910	1.740
3400	65.012	369.938	314.780	187.535	272.745	−121.520	1.867
3500	65.005	371.822	316.383	194.036	271.780	−133.102	1.986
3600	64.991	373.653	317.949	200.536	270.784	−144.656	2.099
3700	64.972	375.434	319.479	207.034	269.755	−156.182	2.205
3800	64.948	377.166	320.974	213.530	268.693	−167.680	2.305
3900	64.921	378.853	322.437	220.024	267.600	−179.149	2.399
4000	64.890	380.496	323.868	226.514	266.474	−190.590	2.489
4100	64.856	382.098	325.268	233.002	265.315	−202.002	2.574
4200	64.821	383.661	326.640	239.486	264.125	−213.386	2.654
4300	64.784	385.185	327.984	245.966	262.902	−224.741	2.730
4400	64.745	386.674	329.301	252.442	261.648	−236.067	2.802
4500	64.705	388.129	330.592	258.915	260.362	−247.364	2.871
4600	64.665	389.551	331.859	265.383	259.043	−258.633	2.937
4700	64.624	390.941	333.101	271.848	257.693	−269.872	2.999
4800	64.583	392.301	334.320	278.308	256.311	−281.082	3.059
4900	64.542	393.632	335.517	284.764	254.897	−292.263	3.116
5000	64.500	394.936	336.692	291.216	253.451	−303.415	3.170
5100	64.459	396.213	337.847	297.664	251.973	−314.537	3.222
5200	64.418	397.464	338.981	304.108	250.462	−325.631	3.271
5300	64.378	398.690	340.097	310.548	248.919	−336.695	3.318
5400	64.338	399.893	341.193	316.984	247.342	−347.730	3.364
5500	64.299	401.074	342.271	323.416	245.733	−358.735	3.407
5600	64.260	402.232	343.331	329.844	244.090	−369.710	3.449
5700	64.222	403.369	344.375	336.268	242.414	−380.656	3.488
5800	64.184	404.486	345.401	342.688	240.703	−391.572	3.526
5900	64.147	405.582	346.412	349.105	238.959	−402.459	3.563
6000	64.111	406.660	347.407	355.517	237.179	−413.315	3.598

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = 236.731\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 609.3 \pm 29\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 615.0 \pm 29\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	1
[13000]	[6]
20085	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
853 (1)
300 (2)
1742 (1)

Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distances: C–C = [128] Å; C–Si = [1.75] Å
Bond Angle: C–C–Si = 180°
Rotational Constant: B_o = [0.201171] cm^{-1}

Enthalpy of Formation

The selected value is an average based on the equilibrium data summarized below. Drowart and co–workers have used the Knudsen effusion–mass spectrometric technique to determine the vapor equilibria over the systems SiC–graphite,[1] SiC–silison[2] and boron–carbon–silicon.[3] 3rd law analysis of the partial pressures of C_2Si and Si lead to the concordant values 146.7, 149.0 and 146.0 $kcal·mol^{-1}$. Although the drifts all suggest that the entropy of C_2Si may be about 3.5 less than tabulated, this is of doubtful significance because the uncertainty bands are so large. The low condensation coefficient suggested by Drowart[2] may also be involved. Rates of free evaporation reported by Voronin[4] lead to apparent pressures which are smaller by a factor of 1/30, thus confirming the existence of a low evaporation coefficient. The adopted value of $\Delta_f H°(298.15\ K) = 147 \pm 7\ kcal·mol^{-1}$ includes allowance for the unlikely possibility that the entropy may be in error by up to 3.5 $cal·K^{-1}·mol^{-1}$.

Source	Method	Reaction*	T/K	Dat Points	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Drowart	Mass Spec.	A	2149–2316	7	31 ± 9	38.98	3.5 ± 4.1	146.7
Drowart	Mass Spec.	B	1935–2160	4	188 ± 10	194.8	3.3 ± 4.9	149.0
Verhaegen	Mass Spec.	A	2166–2344	5	30 ± 16	38.31	3.9 ± 7.2	146.0

*Reactions: (A) 2 C(graph) + Si(g) = C_2Si(g) (B) 2 SiC(α) = Si(l) + C_2Si(g)

Heat Capacity and Entropy

The known molecular constants are from the assignments of Weltner and McLeod.[5] These authors observed the infrared spectrum, emission spectrum and visible absorption spectrum of C_2Si in matrix isolation. The matrix data allowed more certain assignment of the A–X band system of the gas as observed by Kleman[6] and McKellar.[7] Weltner concluded that this system probably involves transitions between a $^1\Sigma^+$ ground state and a $^1\Pi$ excited state. The two stretching frequencies were observed in the matrix infrared spectrum, whereas the bending mode, 300 cm^{-1}, was derived solely from the analysis of the A–X band system. The analysis presumed a linear unsymmetrical structure for the molecule.

A $^3\pi$ excited state is assumed to lie 7000 cm^{-1} below the $^1\pi$ state, which presumably arises from the same molecular orbital configuration. The effect of the estimated level is to increase the entropy by about 0.2 and 1.8 $cal·K^{-1}·mol^{-1}$ at 3000 and 6000 K. Bond distances are estimated by comparison with those in Si_2, C_2 and C_3.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}mol^{-1}	$S°$ J·K^{-1}mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−11.055	609.313	609.313	INFINITE
100	33.354	193.558	274.049	−8.049	611.934	593.151	−309.831
200	41.224	219.393	240.775	−4.276	613.875	573.562	−149.799
250	43.686	228.867	237.472	−2.151	614.559	563.400	−117.716
298.15	*45.611*	*236.731*	*236.731*	*0.*	*615.048*	*553.501*	*−96.971*
300	45.678	237.014	236.732	0.084	615.064	553.119	−96.307
350	47.364	244.185	237.295	2.412	615.414	542.765	−81.003
400	48.832	250.607	238.564	4.817	615.630	532.370	−69.520
450	50.132	256.435	240.231	7.292	615.724	521.956	−60.587
500	51.292	261.779	242.122	9.828	615.709	511.537	−53.440
600	53.260	271.311	246.212	15.059	615.408	490.725	−42.721
700	54.831	279.643	250.405	20.467	614.822	469.988	−35.071
800	56.080	287.050	254.531	26.015	614.019	449.350	−29.340
900	57.074	293.715	258.521	31.674	613.047	428.823	−24.888
1000	57.869	299.771	262.348	37.423	611.939	408.412	−21.333
1100	58.510	305.317	266.006	43.243	610.715	388.118	−18.430
1200	59.031	310.431	269.497	49.121	609.392	367.939	−16.016
1300	59.462	315.174	272.831	55.046	607.979	347.875	−13.978
1400	59.823	319.594	276.015	61.011	606.482	327.922	−12.235
1500	60.133	323.732	279.060	67.009	604.907	308.080	−10.728
1600	60.409	327.622	281.974	73.036	603.258	288.345	−9.413
1700	60.662	331.292	284.769	79.090	551.363	269.162	−8.270
1800	60.907	334.766	287.451	85.169	549.808	252.606	−7.330
1900	61.153	338.066	290.028	91.272	548.234	236.138	−6.492
2000	61.410	341.209	292.509	97.400	546.643	219.753	−5.739
2100	61.685	344.212	294.901	103.554	545.041	203.448	−5.060
2200	61.985	347.088	297.208	109.737	543.431	187.219	−4.445
2300	62.314	349.851	299.437	115.952	541.819	171.064	−3.885
2400	62.676	352.511	301.593	122.201	540.209	154.979	−3.373
2500	63.073	355.077	303.682	128.488	538.607	138.960	−2.903
2600	63.504	357.559	305.706	134.817	537.016	123.006	−2.471
2700	63.971	359.964	307.672	141.191	535.441	107.112	−2.072
2800	64.471	362.300	309.581	147.612	533.887	91.277	−1.703
2900	65.001	364.571	311.438	154.086	532.358	75.496	−1.360
3000	65.558	366.784	313.246	160.613	530.857	59.768	−1.041
3100	66.140	368.943	315.008	167.198	529.387	44.090	−0.743
3200	66.740	371.053	316.727	173.842	527.951	28.458	−0.465
3300	67.355	373.116	318.405	180.547	526.551	12.870	−0.204
3400	67.980	375.136	320.044	187.313	525.189	−2.675	0.041
3500	68.609	377.115	321.646	194.143	523.866	−18.181	0.271
3600	69.239	379.057	323.214	201.035	138.430	−23.189	0.336
3700	69.864	380.963	324.749	207.990	137.600	−27.667	0.391
3800	70.480	382.834	326.253	215.008	136.806	−32.123	0.442
3900	71.083	384.673	327.727	222.086	136.050	−36.559	0.490
4000	71.669	386.480	329.174	229.224	135.329	−40.975	0.535
4100	72.234	388.256	330.593	236.419	134.642	−45.374	0.578
4200	72.775	390.004	331.987	243.670	133.988	−49.757	0.619
4300	73.290	391.722	333.356	250.973	133.365	−54.124	0.657
4400	73.776	393.413	334.702	258.327	132.769	−58.478	0.694
4500	74.232	395.076	336.025	265.727	132.199	−62.818	0.729
4600	74.656	396.712	337.327	273.172	131.651	−67.145	0.762
4700	75.047	398.322	338.607	280.657	131.122	−71.461	0.794
4800	75.404	399.905	339.868	288.180	130.610	−75.766	0.825
4900	75.728	401.464	341.109	295.737	130.111	−80.060	0.853
5000	76.018	402.997	342.332	303.325	129.621	−84.345	0.881
5100	76.274	404.504	343.536	310.939	129.138	−88.619	0.908
5200	76.498	405.988	344.723	318.578	128.657	−92.884	0.933
5300	76.689	407.447	345.892	326.238	128.177	−97.140	0.957
5400	76.850	408.882	347.046	333.915	127.692	−101.387	0.981
5500	76.980	410.293	348.183	341.607	127.202	−105.625	1.003
5600	77.082	411.681	349.304	349.310	126.702	−109.853	1.025
5700	77.156	413.046	350.411	357.022	126.188	−114.073	1.045
5800	77.204	414.389	351.502	364.740	125.659	−118.283	1.065
5900	77.228	415.709	352.579	372.462	125.112	−122.485	1.084
6000	77.229	417.007	353.642	380.185	124.544	−126.677	1.103

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 237.2 \pm 13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 811 \pm 17\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 820 \pm 17\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1225 (1)
63.5 (2)
2040 (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distances: C–C = 1.277 Å
Bond Angle: C–C–C = 180°
Rotational Constant: $B_0 = 0.430334\ cm^{-1}$

Enthalpy of Formation

Drowart *et al.*[1] have measured mass spectrometrically the ion intensity ratio C_3^+/C^+ as a function of temperature from 1800 to 2700 K. We derive from a 2nd law analysis of their data $\Delta_f H°(2200\ K) = 185.2 \pm 3.3$ kcal·mol^{-1}, and $S°(2200\ K) = 74.9 \pm 2.8$ cal·K^{-1}·mol^{-1} by calculation of the absolute pressure from the vapor pressure of monatomic carbon and a relative ionization cross-section ratio of 2.3. The entropy uncertainty includes 1.3 cal·K^{-1}·mol^{-1} for uncertainty in the absolute pressure. Several earlier mass-spectrometric determinations[2-4] are in reasonable agreement. The absolute magnitude of the pressure is also confirmed by the work of Thorn and Winslow[5] who measured the total pressure of all species over graphite as 1.2 to 4.8×10^{-7} atm at 2400 K. Subtracting the JANAF values for C and C_2 we obtain $C_3 = 5.4 \times 10^{-8}$ to 2.2×10^{-7} atm, which compares with Drowart's value of 3.3×10^{-8} to 1.3×10^{-7} atm. The 2nd law enthalpy of formation is reported[5] to be $\Delta_f H°(2400\ K) = 184.4$ kcal·mol^{-1} but the range is only 80 K. It does, however, confirm the magnitude of the mass-spectrometric values for both enthalpy and entropy. We have adopted a enthalpy of formation within the uncertainty limits of Dowart's measurements which with the adopted functions yields pressures in the 2000–3000 K range consistent with the measurements. We were not able to generate functions which agree exactly with the 2nd law entropies, since even direct summation over only the observed levels of the bending frequency gives an entropy which is already too large.

Heat Capacity and Entropy

The stretching frequencies are from Merer,[6] Weltner *et al.*[7] and Weltner and McLeod.[8] The bending frequency and its harmonics are from Gausset *et al.*[9] and Merer.[6] The rotational constant and bond distance are from Gausset *et al.*[9]

As indicated briefly above, the calculated entropy of C_3 gas is higher than the experimental value even when a summation is performed only over the observed first six levels of the bending frequency. Treatment of the vibration as a harmonic oscillator or as a anharmonic oscillator gives values considerably higher. Strauss and Thiele[10] have also calculated functions based on a quartic potential function whlich still yields values several units higher than the experiments. In order to reduce the entropy to the approximate range of the measurements we have made the assumption that the potential function is of an unusual form above the sixth vibrational level. We assume that the large amplitude of the bending vibration causes a drastic change in the function, possibly due to the increasing repulsion between end carbons, as the amplitude increases. Thus, we assume a very steeply rising potential above the sixth vibrational level. We have chosen to represent this part of the potential by a harmonic oscillator of 650 cm^{-1}. The choice of 650 cm^{-1} is arbitrary, but is not unreasonable for a bending vibration, and yields functions which approximate the experimental data.

In order to explain the observed spectrum of C_3O_2, a molecule with a bending frequency of 63 cm^{-1}, Smith and Barrett[11] have proposed that potential maxima occur in the bending potential away from linearity. Thus, the adoption of an unusual potential function for C_3 bending may be justifiable. We do not claim that our functions are necessarily correct but only that they include all known facts and satisfy the experimental equilibrium observations. Further investigation of the carbon vapor pressure and of the higher vibrational levels of C_3 is desirable.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.761	811.456	811.456	INFINITE
100	42.459	193.021	272.308	−7.929	815.110	796.093	−415.836
200	39.861	221.795	240.748	−3.791	818.268	775.758	−202.607
298.15	37.740	237.246	237.246	0.	820.064	754.464	−132.179
300	37.719	237.479	237.247	0.070	820.086	754.057	−131.293
400	37.497	248.274	238.720	3.821	820.770	731.916	−95.578
500	38.380	256.727	241.504	7.612	820.580	709.709	−74.143
600	39.706	263.841	244.649	11.515	819.749	687.604	−59.861
700	41.125	270.069	247.844	15.557	818.472	665.676	−49.673
800	42.480	275.650	250.977	19.738	816.891	643.953	−42.046
900	43.714	280.726	254.005	24.049	815.098	622.441	−36.126
1000	44.815	285.390	256.913	28.477	813.156	601.138	−31.400
1100	45.786	289.708	259.701	33.008	811.105	580.035	−27.544
1200	46.647	293.729	262.371	37.630	808.974	559.122	−24.338
1300	47.413	297.494	264.929	42.334	806.781	538.389	−21.633
1400	48.095	301.033	267.383	47.110	804.538	517.828	−19.320
1500	48.710	304.372	269.739	51.951	802.255	497.428	−17.322
1600	49.267	307.534	272.003	56.850	799.940	477.181	−15.578
1700	49.773	310.536	274.182	61.802	797.595	457.081	−14.044
1800	50.233	313.394	276.282	66.803	795.226	437.119	−12.685
1900	50.660	316.122	278.307	71.848	792.834	417.289	−11.472
2000	51.053	318.731	280.264	76.934	790.421	397.586	−10.384
2100	51.417	321.230	282.155	82.057	787.989	378.004	−9.402
2200	51.760	323.630	283.986	87.216	785.538	358.538	−8.513
2300	52.081	325.938	285.761	92.408	783.069	339.184	−7.703
2400	52.384	328.161	287.481	97.632	780.584	319.938	−6.963
2500	52.667	330.305	289.152	102.885	778.081	300.796	−6.285
2600	52.936	332.376	290.775	108.165	775.562	281.754	−5.661
2700	53.189	334.379	292.353	113.471	773.025	262.809	−5.084
2800	53.430	336.318	293.888	118.802	770.472	243.959	−4.551
2900	53.659	338.197	295.384	124.157	767.902	225.200	−4.056
3000	53.877	340.019	296.842	129.534	765.315	206.531	−3.596
3100	54.084	341.789	298.263	134.932	762.711	187.947	−3.167
3200	54.283	343.510	299.650	140.350	760.089	169.448	−2.766
3300	54.476	345.183	301.005	145.788	757.450	151.031	−2.391
3400	54.660	346.812	302.328	151.245	754.793	132.695	−2.039
3500	54.834	348.399	303.622	156.720	752.118	114.437	−1.708
3600	55.003	349.946	304.887	162.212	749.425	96.256	−1.397
3700	55.164	351.455	306.126	167.720	746.713	78.149	−1.103
3800	55.321	352.929	307.338	173.244	743.982	60.116	−0.826
3900	55.472	354.368	308.526	178.784	741.233	42.156	−0.565
4000	55.618	355.774	309.689	184.339	738.464	24.266	−0.317
4100	55.757	357.149	310.830	189.907	735.676	6.445	−0.082
4200	55.893	358.494	311.949	195.490	732.868	−11.307	0.141
4300	56.024	359.811	313.047	201.086	730.040	−28.992	0.352
4400	56.151	361.100	314.124	206.695	727.192	−46.611	0.553
4500	56.275	362.364	315.182	212.316	724.324	−64.165	0.745
4600	56.392	363.602	316.222	217.949	721.434	−81.655	0.927
4700	56.506	364.816	317.243	223.594	718.524	−99.082	1.101
4800	56.618	366.007	318.246	229.250	715.593	−116.447	1.267
4900	56.726	367.175	319.233	234.918	712.641	−133.751	1.426
5000	56.831	368.322	320.203	240.596	709.667	−150.994	1.577
5100	56.932	369.449	321.158	246.284	706.672	−168.178	1.722
5200	57.031	370.555	322.097	251.982	703.654	−185.302	1.861
5300	57.127	371.642	323.022	257.690	700.614	−202.368	1.994
5400	57.221	372.711	323.932	263.407	697.552	−219.377	2.122
5500	57.312	373.762	324.828	269.134	694.468	−236.329	2.244
5600	57.402	374.795	325.712	274.870	691.361	−253.225	2.362
5700	57.488	375.812	326.582	280.614	688.232	−270.064	2.475
5800	57.573	376.813	327.439	286.367	685.080	−286.849	2.583
5900	57.655	377.798	328.284	292.129	681.904	−303.579	2.688
6000	57.735	378.767	329.118	297.898	678.706	−320.256	2.788

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 88.969 \pm 1.26\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [2500]\ K$

$\Delta_f H°(0\ K) = -210.84 \pm 6.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -215.69 \pm 6.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

The $\Delta_f H°(298.15\ K) = -51.55 \pm 1.6\ kcal \cdot mol^{-1}$ is the average value of $\Delta_f H°(298.15\ K) = -49.7 \pm 1.2\ kcal \cdot mol^{-1}$ by King and Armstrong[1] and that of $\Delta_f H°(298.15\ K) = -53.4 \pm 2.0\ kcal \cdot mol^{-1}$ by Mah.[2] Both measured the enthalpy of reaction $Al_4C_3(cr) + 6O_2(g) \rightarrow 2Al_2O_3(cr, \alpha) + 3CO_2(g)$ and used their $\Delta_r H°(298.15\ K)$ and the $\Delta_f H°(298.15\ K)$ of $Al_2O_3(cr)$ and $CO_2(g)$ to calculate the $\Delta_f H°(298.15\ K)$ of $Al_4C_3(cr)$. The $\Delta_r H°(298.15\ K)$ measured by King and Armstrong was $-1033.3 \pm 1.1\ kcal \cdot mol^{-1}$, the $\Delta_r H°(298.15\ K)$ measured by Mah[2] was $-1029.6 \pm 1.9\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The low temperature heat capacities, 18–390 K, were measured by Saba and Furukawa.[3] The high temperature heat capacities, 273–1173 K, were measured by Victor *et al.*[4] These two sets of heat capacity data were joined smoothly and extrapolated to 2000 K by Saba and Furukawa.[3] The values of $C_p°$ above 2000 K were estimated by extrapolation graphically. $S°(298.15\ K)$ was reported by Saba and Furukawa,[3] using $S°(\text{extrap. } 20\ K) = 0.013\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was estimated by Ruff and Jellinek.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.468	−210.843	−210.843	INFINITE
100	29.702	11.749	167.728	−15.598	−212.086	−210.181	109.787
200	82.098	49.200	98.655	−9.891	−214.566	−207.241	54.126
298.15	116.784	88.969	88.969	0.	−215.685	−203.356	35.627
300	117.298	89.693	88.971	0.217	−215.695	−203.279	35.394
400	138.507	126.645	93.865	13.112	−215.901	−199.095	25.999
500	150.892	158.981	103.729	27.626	−215.898	−194.894	20.360
600	159.201	187.262	115.345	43.150	−216.050	−190.683	16.600
700	165.180	212.270	127.440	59.381	−216.527	−186.423	13.911
800	169.707	234.633	139.466	76.134	−217.461	−182.065	11.888
900	173.264	254.834	151.181	93.288	−218.975	−177.557	10.305
1000	176.142	273.243	162.480	110.762	−263.532	−169.804	8.870
1100	178.527	290.146	173.328	128.499	−265.077	−160.356	7.615
1200	180.540	305.768	183.722	146.455	−266.575	−150.769	6.563
1300	182.268	320.288	193.675	164.597	−268.030	−141.059	5.668
1400	183.770	333.852	203.209	182.900	−269.446	−131.239	4.897
1500	185.096	346.577	212.347	201.345	−270.825	−121.318	4.225
1600	186.276	358.561	221.114	219.914	−272.171	−111.307	3.634
1700	187.334	369.886	229.536	238.596	−273.486	−101.213	3.110
1800	188.297	380.621	237.634	257.378	−274.774	−91.042	2.642
1900	189.171	390.826	245.430	276.252	−276.037	−80.800	2.221
2000	189.979	400.550	252.945	295.210	−277.278	−70.492	1.841
2100	190.631	409.835	260.196	314.241	−278.504	−60.123	1.495
2200	191.251	418.718	267.202	333.335	−279.719	−49.695	1.180
2300	191.836	427.232	273.976	352.490	−280.926	−39.212	0.891
2400	192.389	435.408	280.533	371.701	−282.124	−28.677	0.624
2500	192.907	443.273	286.886	390.966	−283.314	−18.093	0.378
2600	193.393	450.848	293.047	410.282	−284.499	−7.460	0.150
2700	193.845	458.155	299.028	429.644	−285.679	3.217	−0.062
2800	194.263	465.213	304.838	449.050	−1462.462	17.810	−0.332
2900	194.648	472.037	310.486	468.495	−1459.259	70.620	−1.272
3000	194.999	478.641	315.982	487.978	−1456.059	123.320	−2.147

PREVIOUS: June 1963 CURRENT: September 1965

$S°(298.15\ K) = 200.983 \pm 1.26\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -163.51 \pm 16.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -160.67 \pm 16.7\ kJ·mol^{-1}$

Enthalpy of Formation

Mah[1] determined the heat of combustion of Cr_7C_3(cr) using oxygen bomb calorimetry. She reported $\Delta_c H°(298.15\ K) = -1193.0 \pm 0.9$ kcal·mol^{-1} based on the reaction $Cr_7C_3(cr) + 33/4O_2(g) = 7/2\ Cr_2O_3(cr) + 3CO_2(g)$. Using JANAF auxiliary data,[2] we calculate $\Delta_f H°(298.15\ K) = -38.4$ kcal·mol^{-1} for Cr_7C_3(cr). Mah[1] reported that the six combustion runs gave 99.90 to 99.84% completion of combustion. Corrections for incomplete combustion, formation of small amounts of CO(g), and impurities were made by Mah.[1] These corrections amount to no more than 1.04% of the $\Delta_c E$ value.

The pressures of CO(g) in equilibrium with a Cr_2O_3–Cr_7C_3–$Cr_{23}C_6$ mixture have been measured by Kelley *et al.*[3] and Kulkarni and Worrell.[4] Kelley *et al.*[3] also examined the Cr_2O_3–Cr_3C_2–Cr_7C_3 system. Kulkarni and Worrell[4] measured the CO pressure using a torsion effusion technique while Kelley *et al.*[3] measured the pressure manometrically. The results of our analyses are tabulated in the following table. In all cases we have assumed unit activity for the condensed species.

Source	T/K	Data Points	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[3]	1307–1497	9	A	994.44	970.74	-16.9 ± 4.3	−41.53
[4]	1111–1250	11[b]	B	220.48	218.99	-1.3 ± 0.6	−35.18
[3]	1505–1723	15[c]	B	211.34	220.89	5.8 ± 2.0	−35.81

[a]Reactions: (A) $5Cr_2O_3(cr) + 27Cr_3C_2(cr) = 13Cr_7C_3(cr) + 15CO(g)$ (B) $Cr_2O_3(cr) + 3Cr_7C_3(cr) = Cr_{23}C_6(cr) + 3CO(g)$.
[b]1234.6, 1250.0 K points deleted due to statistical test; effective range is now 1111–1220 K.
[c]1524 K point deleted due to statistical test.

We adopt $\Delta_f H°(298.15\ K) = -38.4 \pm 4.0$ kcal·mol^{-1} for Cr_7C_3(cr) based on the combustion data of Mah.[1] The equilibrium studies by Kulkarni and Worrell[4] and Kelley *et al.*[3] are in reasonable agreement with the adopted value. Equilibrium studies involving Cr_7C_3(cr) by Hancock and Pidgeon,[5] Alekseev and Shvartsman,[6] and Bolgar *et al.*[7] are not considered.[2]

Heat Capacity and Entropy

The heat capacity (54–295 K, 29 pts.) and enthalpy (480–1580 K, 15 pts.) have been measured by Kelley *et al.*[3] Using the Debye function suggested,[3] we calculate $S°(50\ K) = 1.679$ cal·K^{-1}·mol^{-1} and $H°(50;0) = 62.66$ cal·K^{-1}·mol^{-1}. The adopted heat capacity curve is based solely on the above mentioned study with the constraint that the heat capacity values derived from the enthalpy data join smoothly with the low temperature heat capacity values near 298.15 K. The observed $C_p°$ values deviate from the adopted values within ±0.2% for $T < 298.15$ K. The enthalpy data agrees within ±0.35% with the tabulated values except for the 1263.4 K data (1.66% or ~1.0 kcal·mol^{-1} too low) and the two points at 1545.1 and 1578.1 K which were not included in the polynomial curve fit.[3] The polynomial is used to extrapolate $C_p°$ values above 1500 K.

Phase Data

Storms[8] has summarized much of the phase data for the chromium carbides and reported a hexagonal structure for Cr_7C_3. The homogeneity range for Cr_7C_3 is not known.[8]

Decomposition Data

The tentative phase diagram for the Cr–Cr_3C_2 system as proposed by Storms[8] indicated an incongruent melting at 2053 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−34.397	−163.508	−163.508	INFINITE
100	80.414	39.481	355.684	−31.620	−163.089	−163.752	85.535
200	167.414	125.392	218.991	−18.720	−162.255	−164.668	43.007
298.15	209.748	200.983	200.983	0.	−160.666	−166.161	29.111
300	210.372	202.282	200.987	0.389	−160.628	−166.195	28.937
400	236.714	266.701	209.591	22.844	−159.033	−168.182	21.962
500	252.873	321.361	226.622	47.369	−156.663	−170.748	17.838
600	263.504	368.438	246.427	73.206	−154.596	−173.765	15.128
700	271.956	409.702	266.865	99.986	−152.839	−177.103	13.216
800	279.608	446.519	287.061	127.566	−151.313	−180.676	11.797
900	287.006	479.880	306.660	155.897	−150.046	−184.425	10.704
1000	294.369	510.499	325.534	184.966	−149.159	−188.297	9.836
1100	301.779	538.903	343.655	214.773	−148.794	−192.233	9.128
1200	309.269	565.481	361.045	245.324	−149.015	−196.177	8.539
1300	316.842	590.535	377.743	276.629	−149.909	−200.076	8.039
1400	324.494	614.295	393.798	308.695	−151.542	−203.879	7.607
1500	332.214	636.945	409.259	341.530	−153.940	−207.538	7.227
1600	339.992	658.634	424.171	375.140	−157.128	−211.012	6.889
1700	347.824	679.481	438.580	409.531	−161.123	−214.261	6.583
1800	355.703	699.585	452.525	444.707	−165.938	−217.252	6.304
1900	363.619	719.028	466.043	480.672	−171.585	−219.953	6.047
2000	371.568	737.882	479.166	517.431	−178.075	−222.334	5.807
2100	379.552	756.204	491.924	554.987	−185.417	−224.370	5.581
2200	387.543	774.045	504.344	593.342	−328.970	−221.450	5.258
2300	395.530	791.448	516.450	632.496	−325.008	−216.649	4.920
2400	403.526	808.451	528.264	672.449	−320.295	−212.036	4.615
2500	411.517	825.085	539.805	713.201	−314.828	−207.635	4.338

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 100.41 \pm 13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = 79.5 \pm 33\ kJ \cdot mol^{-1}$

Enthalpy of Formation
Data from Furukawa *et al.*[1]

Heat Capacity and Entropy
Data from Furukawa *et al.*[1]

References
[1]G. T. Furukawa, M. L. Reilly *et al.*, U. S. Nat. Bur. Stand. Report 6928, Appendix B, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	93.763	100.416	100.416	0.	79.496	74.173	−12.995
300	94.140	100.997	100.418	0.174	79.530	74.140	−12.909
400	107.361	130.046	104.288	10.303	81.481	72.052	−9.409
500	114.056	154.770	111.979	21.395	83.260	69.481	−7.259
600	118.198	175.949	120.919	33.018	84.614	66.591	−5.797
700	121.127	194.398	130.127	44.990	85.523	63.509	−4.739
800	123.386	210.724	139.200	57.219	86.012	60.326	−3.939
900	125.269	225.368	147.975	69.653	86.106	57.106	−3.314
1000	126.943	238.654	156.389	82.265	68.636	55.320	−2.890
1100	128.449	250.825	164.428	95.036	67.964	54.021	−2.565
1200	129.830	262.061	172.102	107.950	67.262	52.784	−2.298
1300	131.168	272.506	179.428	121.001	66.554	51.606	−2.074
1400	132.424	282.272	186.429	134.180	−188.965	56.817	−2.120
1500	133.679	291.452	193.128	147.486	−186.940	74.303	−2.587
1600	134.892	300.118	199.547	160.915	−184.884	91.652	−2.992
1700	136.064	308.331	205.706	174.463	−182.790	108.871	−3.345
1800	137.235	316.142	211.626	188.128	−180.652	125.967	−3.655
1900	138.365	323.592	217.325	201.907	−178.466	142.942	−3.930
2000	139.536	330.719	222.817	215.803	−176.227	159.800	−4.174
2100	140.666	337.554	228.119	229.813	−173.931	176.545	−4.391
2200	141.754	344.123	233.244	243.934	−171.579	193.180	−4.587
2300	142.884	350.449	238.203	258.166	−169.167	209.706	−4.763
2400	144.013	356.554	243.008	272.511	−166.692	226.126	−4.921
2500	145.101	362.455	247.669	286.967	−164.155	242.441	−5.066

PREVIOUS: CURRENT: December 1960

$S°(298.15\ K) = 276.07 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -96.819 \pm 1.84\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -93.638 \pm 1.84\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2200(1)	2258(1)	550(2)
830(1)	1573(1)	63(2)
	577(2)	

Ground State Quantum Weight: I $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distances: C–C = 1.28 Å; C–O = 1.16 Å
Bond Angles: C–C–C = 180°; O–C–C = 180°
Rotational Constant: $B_0 = 0.073337\ cm^{-1}$

Enthalpy of Formation

Kybett *et al.*[1] have determined the enthalpy of combustion of the liquid form under its own pressure using the sample from the heat capacity determinations.[2]

The average of four determinations gave $\Delta_f H°(l, 298.15\ K) = -28.03 \pm 0.24\ kcal \cdot mol^{-1}$; the authors report −29.03 due to an arithmetic error. The sample was 99.98 mol % pure. McDougall and Kilpatrick[2] measured $\Delta_{vap} H°(230\ K) = 6.421 \pm 0.012\ kcal \cdot mol^{-}$ from which we calculate $\Delta_{vap} H°(298.15\ K) = 5.65 \pm 0.2\ kcal \cdot mol^{-1}$. Thus the enthalpy of formation of the gas is found to be $22.38 \pm 0.44\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

There has been considerable controversy as to the configuration of this molecule and the assignment of its vibrational frequencies. However, the evidence seems fairly conclusive for the linearity of the molecule from the work of Lafferty *et al.*[3] and Miller and Fateley.[4] The rotational constant adopted here is that found by Lafferty *et al.*[3] and the vibrational frequencies are those reported by Miller and Fateley,[4] except for ν_7 which is taken from Miller *et al.*[5] and Borgers.[7] The low frequency Π_u mode is confirmed by the work of McDougall and Kilpatrick,[2] who measured the low temperature entropy of C_3O_2(cr) and (l) and also the enthalpy of vaporization. From a comparison of the entropy calculated statistically and that measured, they conclude $\nu_7 = 63.2\ cm^{-1}$. The values adopted are confirmed by 3rd law analysis of the vapor pressure data of McDougall *et al.*[5] which indicates a enthalpy of vaporization in fair agreement with their calorimetric value. The drift in the 3rd law analysis indicates that the entropy of the solid is too low or that of the gas is too high by 1 $cal \cdot K^{-1} \cdot mol^{-1}$. Alternatively as systematic error in the pressure measurements could have caused this deviation.

The bond distances are taken from the electron diffraction experiments of Livingston and Rao[6] and are in good accord with the adopted rotational constant.

References

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[2]L. A. McDougall and J. E. Kilpatrick, J. Chem. Phys. **42**, 2311 (1965).
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[5]F. A. Miller, D. H. Lemmon and R. E. Witkowski, Spectrochim. Acta **21**, 1709–16 (1965).
[6]R. L. Livingston and C. N. R. Rao, J. Amer. Chem. Soc. **81**, 285 (1959).
[7]T. R. Borgers, Ph.D. Thesis, University of California, Berkeley, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.018	−96.819	−96.819	INFINITE
100	45.309	217.230	328.013	−11.078	−95.963	−100.070	52.271
200	56.055	251.539	281.870	−6.066	−94.842	−104.603	27.320
250	62.055	264.706	277.147	−3.110	−94.230	−107.114	22.380
298.15	66.989	276.071	276.071	0.	−93.638	−109.649	19.210
300	67.161	276.486	276.072	0.124	−93.616	−109.749	19.109
350	71.401	287.167	276.906	3.591	−93.038	−112.484	16.787
400	74.976	296.941	278.808	7.253	−92.526	−115.298	15.056
450	78.069	305.955	281.330	11.081	−92.100	−118.171	13.717
500	80.806	314.324	284.216	15.054	−91.764	−121.087	12.650
600	85.504	329.486	290.524	23.377	−91.335	−126.996	11.056
700	89.406	342.969	297.071	32.129	−91.157	−132.957	9.921
800	92.664	355.126	303.580	41.237	−91.148	−138.931	9.071
900	95.380	366.202	309.932	50.643	−91.251	−144.898	8.410
1000	97.642	376.372	316.075	60.298	−91.428	−150.850	7.880
1100	99.527	385.770	321.989	70.159	−91.657	−156.781	7.445
1200	101.103	394.499	327.672	80.193	−91.926	−162.690	7.082
1300	102.426	402.646	333.129	90.371	−92.228	−168.575	6.773
1400	103.542	410.278	338.370	100.671	−92.560	−174.436	6.508
1500	104.490	417.455	343.406	111.074	−92.921	−180.272	6.278
1600	105.298	424.225	348.247	121.565	−93.313	−186.083	6.075
1700	105.993	430.630	352.907	132.130	−93.736	−191.868	5.895
1800	106.592	436.706	357.395	142.760	−94.192	−197.628	5.735
1900	107.112	442.483	361.722	153.446	−94.683	−203.361	5.591
2000	107.566	447.989	365.899	164.180	−95.209	−209.067	5.460
2100	107.964	453.247	369.934	174.957	−95.774	−214.746	5.342
2200	108.314	458.278	373.837	185.771	−96.378	−220.397	5.233
2300	108.625	463.100	377.613	196.619	−97.022	−226.020	5.133
2400	108.900	467.729	381.272	207.495	−97.708	−231.615	5.041
2500	109.146	472.179	384.820	218.398	−98.435	−237.179	4.956
2600	109.367	476.465	388.263	229.324	−99.205	−242.714	4.876
2700	109.565	480.596	391.607	240.270	−100.018	−248.218	4.802
2800	109.744	484.584	394.857	251.236	−100.875	−253.691	4.733
2900	109.905	488.438	398.018	262.218	−101.774	−259.134	4.668
3000	110.052	492.166	401.094	273.216	−102.717	−264.544	4.606
3100	110.185	495.777	404.090	284.228	−103.703	−269.921	4.548
3200	110.307	499.277	407.011	295.253	−104.733	−275.268	4.493
3300	110.419	502.673	409.858	306.290	−105.805	−280.581	4.441
3400	110.521	505.971	412.637	317.337	−106.919	−285.860	4.392
3500	110.615	509.176	415.349	328.393	−108.076	−291.106	4.345
3600	110.701	512.294	417.999	339.459	−109.274	−296.319	4.299
3700	110.781	515.328	420.589	350.533	−110.514	−301.498	4.256
3800	110.855	518.283	423.121	361.615	−111.796	−306.642	4.215
3900	110.924	521.163	425.598	372.704	−113.118	−311.752	4.175
4000	110.987	523.973	428.023	383.800	−114.481	−316.828	4.137
4100	111.046	526.714	430.396	394.902	−115.885	−321.870	4.101
4200	111.102	529.391	432.722	406.009	−117.329	−326.876	4.065
4300	111.153	532.005	435.000	417.122	−118.814	−331.848	4.031
4400	111.201	534.561	437.234	428.240	−120.339	−336.785	3.998
4500	111.246	537.061	439.425	439.362	−121.905	−341.687	3.966
4600	111.288	539.506	441.574	450.489	−123.511	−346.554	3.935
4700	111.328	541.900	443.683	461.620	−125.157	−351.384	3.905
4800	111.365	544.244	445.754	472.754	−126.845	−356.180	3.876
4900	111.400	546.541	447.788	483.892	−128.574	−360.939	3.848
5000	111.433	548.792	449.785	495.034	−130.345	−365.663	3.820
5100	111.464	550.999	451.748	506.179	−132.158	−370.351	3.793
5200	111.493	553.164	453.678	517.327	−134.015	−375.005	3.767
5300	111.521	555.288	455.575	528.477	−135.914	−379.620	3.741
5400	111.547	557.372	457.441	539.631	−137.859	−384.201	3.716
5500	111.572	559.419	459.276	550.787	−139.848	−388.745	3.692
5600	111.595	561.430	461.083	561.945	−141.883	−393.251	3.668
5700	111.618	563.405	462.861	573.106	−143.966	−397.722	3.645
5800	111.639	565.347	464.611	584.269	−146.096	−402.155	3.622
5900	111.659	567.255	466.334	595.434	−148.275	−406.552	3.599
6000	111.678	569.132	468.032	606.600	−150.504	−410.911	3.577

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 228.3 \pm 16.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 964 \pm 33\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 971 \pm 33\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[2150] (1)
[950] (1)
[1700] (1)
[550] (2)
[550] (2)

Ground State Configuration: [$^1\Sigma$] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distances: C–C = [1.28] Å
Bond Angle: C–C–C = [180°]
Rotational Constant: B_0 = [0.171328] cm^{-1}

Enthalpy of Formation

The enthalpy of formation is obtained from the mass-spectrometric results of Drowart *et al.*[1] who obtained $\Delta_f H°(2400\ K) = 226 \pm 7$ $kcal \cdot mol^{-1}$. This was obtained from a 2nd law analysis of the ion intensity ratio C_3^+/C^+ over a temperature range of 2200–2700 K. the absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross–section ratio of 4.96, yields a 2nd law entropy at 2400 K of 90.5 ± 3 $cal \cdot K^{-1} \cdot mol^{-1}$. The uncertainty in the ionization cross–section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of $\pm 4.5\ cal \cdot K^{-1} \cdot mol^{-1}$. The enthalpy of formation at temperatures other than 2400 K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C_4 are all estimated. We have chosen a set of functions which is consistent with the mass– spectrometric observations of Drowart *et al.*[1] The thermodynamic functions of C_4 were first estimated by Pitzer and Clementi[2] but the basis for this estimate has completely changed. Originally they were calculated by analogy with C_3, C_3O_2 and CO_2, but the discovery of very low bending frequencies in C_3 and C_3O_2 complicated the picture by raising the calculated entropies significantly. Sandborn[3] has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C_4 and C_5. These vibrational frequencies yield high entropies outside the limits of the 2nd law determination. Since these frequencies are estimates based on a basically triatomic correlation we have chosen to adopt two bending frequencies of 550 cm^{-1} rather than the 200 cm^{-1} and 440 cm^{-1} estimated by Sandborn. In addition we have assumed that the ground state arising from a π^2 term is Σ^1 and not Σ^3 as assumed by Pitzer and Clementi. The basis for both these changes is to make the functions conform to the only available measured data. Use of the present table will yield values for the vapor pressure of C_4 in excellent agreement with the measurements in the 2000–3000 K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn[3] and the bond length is estimated from C_3.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.791	964.101	964.101	INFINITE
100	29.865	187.031	265.752	−7.872	966.782	948.459	−495.424
200	39.876	210.373	232.603	−4.446	968.902	929.293	−242.706
250	45.537	219.893	229.123	−2.308	969.858	919.279	−192.073
298.15	50.176	228.322	228.322	0.	970.688	909.460	−159.334
300	50.338	228.633	228.323	0.093	970.718	909.080	−158.285
350	54.319	236.701	228.951	2.712	971.454	898.747	−134.131
400	57.657	244.179	230.393	5.514	972.048	888.318	−116.002
450	60.512	251.139	232.316	8.470	972.491	877.823	−101.895
500	62.998	257.646	234.527	11.559	972.786	867.287	−90.605
600	67.134	269.512	239.389	18.074	972.988	846.161	−73.665
700	70.424	280.117	244.463	24.958	972.781	825.034	−61.565
800	73.067	289.700	249.528	32.137	972.276	803.959	−52.493
900	75.201	298.434	254.484	39.554	971.555	782.961	−45.442
1000	76.933	306.450	259.285	47.164	970.672	762.052	−39.806
1100	78.348	313.851	263.914	54.930	969.663	741.238	−35.198
1200	79.511	320.719	268.365	62.825	968.553	720.520	−31.363
1300	80.475	327.123	272.641	70.826	967.358	699.899	−28.122
1400	81.279	333.117	276.749	78.915	966.088	679.372	−25.348
1500	81.955	338.748	280.697	87.078	964.753	658.939	−22.946
1600	82.528	344.056	284.492	95.303	963.358	638.596	−20.848
1700	83.017	349.075	288.145	103.580	961.907	618.343	−18.999
1800	83.437	353.832	291.663	111.904	960.404	598.176	−17.359
1900	83.800	358.353	295.055	120.266	958.850	578.095	−15.893
2000	84.115	362.660	298.329	128.662	957.248	558.096	−14.576
2100	84.390	366.770	301.491	137.088	955.599	538.179	−13.386
2200	84.632	370.702	304.548	145.539	953.904	518.341	−12.307
2300	84.846	374.469	307.507	154.013	952.164	498.582	−11.323
2400	85.035	378.084	310.373	162.507	950.379	478.899	−10.423
2500	85.204	381.559	313.151	171.019	948.551	459.291	−9.596
2600	85.355	384.903	315.847	179.548	946.679	439.758	−8.835
2700	85.490	388.127	318.464	188.090	944.765	420.297	−8.131
2800	85.612	391.239	321.008	196.645	942.808	400.908	−7.479
2900	85.722	394.245	323.482	205.212	940.809	381.590	−6.873
3000	85.822	397.153	325.890	213.789	938.768	362.341	−6.309
3100	85.913	399.968	328.234	222.376	936.684	343.161	−5.782
3200	85.996	402.697	330.519	230.971	934.560	324.049	−5.290
3300	86.071	405.345	332.746	239.575	932.393	305.004	−4.828
3400	86.140	407.915	334.919	248.186	930.186	286.025	−4.394
3500	86.204	410.413	337.041	256.803	927.937	267.112	−3.986
3600	86.263	412.842	339.113	265.426	925.646	248.263	−3.602
3700	86.317	415.207	341.138	274.055	923.315	229.479	−3.240
3800	86.367	417.509	343.117	282.689	920.943	210.758	−2.897
3900	86.413	419.753	345.054	291.328	918.530	192.101	−2.573
4000	86.456	421.942	346.949	299.972	916.075	173.505	−2.266
4100	86.496	424.077	348.804	308.620	913.580	154.972	−1.974
4200	86.533	426.162	350.621	317.271	911.044	136.500	−1.698
4300	86.568	428.198	352.402	325.926	908.468	118.089	−1.434
4400	86.600	430.189	354.147	334.584	905.850	99.738	−1.184
4500	86.631	432.135	355.858	343.246	903.192	81.447	−0.945
4600	86.659	434.040	357.537	351.911	900.493	63.216	−0.718
4700	86.686	435.904	359.185	360.578	897.754	45.044	−0.501
4800	86.711	437.729	360.802	369.248	894.974	26.930	−0.293
4900	86.734	439.517	362.391	377.920	892.154	8.875	−0.095
5000	86.756	441.270	363.951	386.594	889.293	−9.122	0.095
5100	86.777	442.988	365.484	395.271	886.391	−27.062	0.277
5200	86.797	444.673	366.990	403.950	883.449	−44.944	0.451
5300	86.816	446.327	368.472	412.630	880.466	−62.769	0.619
5400	86.833	447.950	369.929	421.313	877.443	−80.538	0.779
5500	86.850	449.543	371.362	429.997	874.379	−98.250	0.933
5600	86.866	451.108	372.772	438.683	871.275	−115.906	1.081
5700	86.881	452.646	374.160	447.370	868.130	−133.507	1.223
5800	86.895	454.157	375.526	456.059	864.945	−151.052	1.360
5900	86.908	455.642	376.871	464.749	861.719	−168.541	1.492
6000	86.921	457.103	378.196	473.441	858.453	−185.976	1.619

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 361.189\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = [-286.604]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Source unknown.

Heat Capacity and Entropy

$C_p^°$ taken from Janz *et al.*[1]

Reference

[1]G. J. Janz, Y. Mikawa, and F. Behnke, Rensseler Polytechnic Institute, personal communication, (March 16, 1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	138.574	361.189	361.189	0.	−286.604	−148.063	25.940
300	139.076	362.047	361.191	0.257	−286.768	−147.202	25.630
400	167.695	406.038	366.996	15.617	−295.056	−99.399	12.980
500	193.761	446.324	378.886	33.719	−302.074	−49.646	5.186
600	216.271	483.685	393.276	54.245	−307.811	1.399	−0.122
700	235.852	518.525	408.708	76.871	−312.352	53.310	−3.978
800	253.006	551.160	424.497	101.331	−315.801	105.794	−6.908
900	268.153	581.853	440.292	127.405	−318.275	158.652	−9.208
1000	281.416	610.807	455.910	154.897	−319.909	211.739	−11.060
1100	293.047	638.185	471.247	183.632	−320.839	264.954	−12.582
1200	303.256	664.131	486.249	213.457	−321.187	318.227	−13.852
1300	312.210	688.765	500.888	244.241	−321.064	371.510	−14.927
1400	319.992	712.196	515.152	275.862	−320.568	424.768	−15.848
1500	326.352	734.499	529.037	308.192	−319.809	477.981	−16.645

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°$(298.15 K) = 290.11 ± 0.8 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 528.60 ± 0.8 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 533.46 ± 0.8 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2290(1)	2241(1)	263(2)
2119(1)	1154(1)	472(2)
692(1)	504(2)	107(2]

Ground State Quantum Weight: 1 σ = 2
Point Group: $D_{\infty h}$
Bond Distances: CN = 1.14 Å; C–C = 1.37 Å; C–C = 1.19 Å
Rotational Constant: B_0 = 0.045397 cm^{-1}

Enthalpy of Formation

Armstrong and Marantz,[1] measured the enthalpy of combustion of the liquid for which they obtain a $\Delta_f H°$(298.15 K) of 120.6 kcal·mol^{-1} using 94.05 kcal·mol^{-1} for $\Delta_f H°(CO_2, g, 298.15 K)$. They calculate the $\Delta_f H°(C_4N_2, g, 298.15 K)$ with a $\Delta_{vap}H$ taken from Saggiomo.[2]

Heat Capacity and Entropy

Bond lengths determined by Miller and Hannan[3] from X-ray diffraction measurements on the solid. The vibrational frequencies were observed in the infrared and Raman by Miller *et al.*[4]

References

[1]G. T. Armstrong and S. Marantz, J. Phys. Chem. **64**, 1776 (1960).
[2]A. J. Saggiomo, J. Org. Chem. **22**, 1171 (1957).
[3]F. A. Miller and R. B. Hannan Jr., J. Chem. Phys. **21**, 110 (1953).
[4]F. A. Miller, R. B. Hannan Jr., and L. R. Cousins, J. Chem. Phys. **23**, 2127 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.734	528.600	528.600	INFINITE
100	49.991	216.793	356.363	−13.957	529.237	523.919	−273.667
200	71.983	258.541	297.572	−7.806	531.171	517.925	−135.268
250	79.961	275.500	291.495	−3.999	532.341	514.480	−107.495
298.15	85.888	290.112	290.112	0.	533.460	510.937	−89.514
300	86.088	290.644	290.114	0.159	533.502	510.797	−88.938
350	90.899	304.290	291.181	4.588	534.590	506.926	−75.655
400	94.823	316.692	293.606	9.234	535.569	502.906	−65.673
450	98.158	328.058	296.811	14.061	536.417	498.770	−57.896
500	101.091	338.554	300.467	19.043	537.132	494.548	−51.665
600	106.147	357.446	308.425	29.413	538.205	485.923	−42.303
700	110.417	374.138	316.643	40.247	538.905	477.150	−35.605
800	114.050	389.126	324.782	51.475	539.340	468.295	−30.577
900	117.130	402.742	332.699	63.038	539.588	459.398	−26.663
1000	119.730	415.222	340.336	74.885	539.703	450.481	−23.531
1100	121.921	426.739	347.674	86.971	539.716	441.557	−20.968
1200	123.768	437.429	354.714	99.258	539.649	432.636	−18.832
1300	125.329	447.399	361.464	111.715	539.516	423.724	−17.025
1400	126.654	456.737	367.940	124.316	539.325	414.823	−15.477
1500	127.784	465.514	374.155	137.039	539.082	405.938	−14.136
1600	128.751	473.793	380.126	149.867	538.791	397.071	−12.963
1700	129.584	481.624	385.868	162.785	538.455	388.224	−11.929
1800	130.305	489.052	391.396	175.780	538.075	379.398	−11.010
1900	130.933	496.114	396.723	188.843	537.651	370.594	−10.188
2000	131.481	502.844	401.862	201.964	537.186	361.813	−9.450
2100	131.963	509.271	406.825	215.137	536.679	353.057	−8.782
2200	132.388	515.420	411.623	228.355	536.130	344.325	−8.175
2300	132.764	521.314	416.265	241.613	535.541	335.620	−7.622
2400	133.099	526.971	420.760	254.906	534.910	326.941	−7.116
2500	133.398	532.411	425.118	268.231	534.239	318.290	−6.650
2600	133.667	537.648	429.346	281.585	533.526	309.666	−6.221
2700	133.908	542.697	433.451	294.964	532.772	301.070	−5.825
2800	134.126	547.571	437.441	308.366	531.978	292.503	−5.457
2900	134.323	552.281	441.320	321.788	531.142	283.964	−5.115
3000	134.502	556.838	445.095	335.230	530.265	275.456	−4.796
3100	134.665	561.251	448.771	348.688	529.348	266.977	−4.499
3200	134.813	565.529	452.353	362.162	528.389	258.529	−4.220
3300	134.950	569.679	455.846	375.650	527.388	250.111	−3.959
3400	135.075	573.710	459.254	389.152	526.347	241.724	−3.714
3500	135.189	577.627	462.580	402.665	525.264	233.369	−3.483
3600	135.295	581.437	465.829	416.189	524.140	225.045	−3.265
3700	135.393	585.145	469.004	429.724	522.975	216.752	−3.060
3800	135.484	588.757	472.108	443.268	521.768	208.492	−2.866
3900	135.567	592.278	475.144	456.820	520.519	200.264	−2.682
4000	135.645	595.711	478.116	470.381	519.230	192.069	−2.508
4100	135.718	599.061	481.025	483.949	517.898	183.906	−2.343
4200	135.785	602.333	483.874	497.524	516.525	175.777	−2.186
4300	135.848	605.528	486.667	511.106	515.110	167.680	−2.037
4400	135.907	608.652	489.404	524.694	513.654	159.617	−1.895
4500	135.962	611.707	492.088	538.287	512.155	151.588	−1.760
4600	136.014	614.696	494.721	551.886	510.615	143.592	−1.631
4700	136.062	617.621	497.305	565.490	509.034	135.630	−1.507
4800	136.108	620.487	499.841	579.098	507.410	127.703	−1.390
4900	136.151	623.293	502.332	592.711	505.744	119.809	−1.277
5000	136.191	626.044	504.779	606.328	504.036	111.950	−1.170
5100	136.229	628.742	507.183	619.949	502.285	104.126	−1.066
5200	136.265	631.387	509.546	633.574	500.493	96.336	−0.968
5300	136.299	633.983	511.870	647.202	498.658	88.581	−0.873
5400	136.331	636.531	514.155	660.834	496.781	80.862	−0.782
5500	136.361	639.033	516.403	674.468	494.861	73.177	−0.695
5600	136.390	641.490	518.614	688.106	492.899	65.528	−0.611
5700	136.418	643.905	520.791	701.746	490.894	57.914	−0.531
5800	136.444	646.278	522.935	715.389	488.846	50.335	−0.453
5900	136.468	648.610	525.045	729.035	486.754	42.793	−0.379
6000	136.492	650.904	527.124	742.683	484.619	35.286	−0.307

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar)

$S°(298.15\ K) = [319.56 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 253.86 \pm 0.1\ K$

$\Delta_f H°(298.15\ K) = -631.78 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 13.832 \pm 0.021\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is a weighted average based on enthalpy of combustion data of Smagina and Ormont[1] and Fischer *et al.*[2] The results of Smagina and Ormont[1] have been recalculated along the lines indicated by Sykes,[3] using recent values of $\Delta_f H°$(NiO, cr)[4] and other auxiliary data.[5] Their corrected value of $\Delta_f H°(Ni(CO)_4, l, 298.15\ K)$ is $-150.3 \pm 3.0\ kcal \cdot mol^{-1}$ (average of 3 determinations using Pt fuse). Fischer *et al.*[2] made two sets of determinations yielding the following values of $\Delta_f H°(Ni(CO)_4, l, 298.15\ K)$; $-150.3 \pm 0.5\ kcal \cdot mol^{-1}$ (average of 5 determinations using benzoic acid fuse) and $-152.3 \pm 0.5\ kcal \cdot mol^{-1}$ (average of 4 determinations using Pt fuse). Fischer *et al.*[2] mention that the difference in their two sets of values may be due to hydration effects but a more likely explanation is higher uncertainties in the percentage combustion, as suggested by Sykes.[3] Therefore, we adopt an uncertainty of $\pm 2.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

We adopt the smooth values of $C_p°$ (90–270 K) reported by Spice *et al.*[6] Values above 270 K are based on a linear extrapolation of liquid $C_p°$ values from 255–270 K. The $C_p°$ data reported by Duncan and Murray[7] were calculated from gas phase $C_p°$ data via a poorly defined procedure and show large deviations from the adopted $C_p°$.

The value of $S°(298.15\ K)$ is difficult to assess because of the lack of $C_p°$ data below 90 K. The adopted value of $S°(298.15\ K)$ is chosen so as to get the best agreement between second and third law analysis of the consistent vapor pressure data of Suginuma and Satozaki,[8] Walsh,[9] and Baev.[10] This treatment results in a value of $S°(cr, 90\ K) = 23.95\ cal \cdot K^{-1} \cdot mol^{-1}$. Spice *et al.*[6] had estimated a value of $S°(cr, 90\ K) = 20.6\ cal \cdot K^{-1} \cdot mol^{-1}$ based on comparisons (at 90 and 120 K) with a "standard" heat capacity curve.

Fusion Data

The adopted values of T_{fus} and $\Delta_{fus} H°$ are those reported by Spice *et al.*[6] The value of $\Delta_{fus} H°$ is the mean of three calorimetrically determined values. Walsh[9] reported a value of T_{fus} approximately 2 K higher than the adopted value and also reported that T_{fus} is very sensitive to purity of the $Ni(CO)_4$. However, we find the purity determinations of Spice *et al.*[6] more than compelling than those of Walsh.[9]

Vaporization Data

The normal boiling point at 1 atm, $T_{vap} = 315.4 \pm 0.2$ K, is based on the vapor pressure measurements of Suginuma and Satozaki,[8] Walsh[9] and Baev;[10] fugacity corrections have not been made. See $Ni(CO)_4$(g) table[5] for analysis of $\Delta_{vap} H°$.

References

[1]E. I. Smagina and B. F. Ormont, J. Gen. Chem. (USSR) **25**, 207 (1955).
[2]A. K. Fischer, F. A. Cotton, and G. Wilkinson, J. Amer. Chem. Soc. **79**, 2044 (1957).
[3]K. W. Sykes, J. Chem. Soc., 2053 (1958).
[4]A. D. Mah and L. B. Pankratz, U. S. Bur. Mines Bull. 668, (1976).
[5]JANAF Thermochemical Tables: CO_2(g), 9–30–65; $Ni(CO)_4$(g), 3–31–78.
[6]J. E. Spice, L. A. K. Staveley and G. A. Harrow, J. Chem. Soc., 100 (1955).
[7]A. B. F. Duncan and J. W. Murray, J. Chem. Phys. **2**, 636 (1934).
[8]B. Suginuma and K. Satozaki, Bull. Inst. Phys. Chem. Research (Tokyo) **21**, 432 (1942).
[9]K. A. Walsh, U. S. Atomic Energy Commission Report LA–1649, (1953).
[10]A. K. Baev, Obshch. Prikl. Khim. **2**, 146 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100	98.031	145.316	484.659	−33.934	−645.917	−624.661	326.289
170.000	138.490	207.499	358.113	−25.604	GLASS <--> LIQUID		
170.000	196.230	207.499	358.113	−25.604	TRANSITION		
200	197.903	239.525	337.985	−19.692	−640.692	−604.698	157.931
298.15	203.342	319.560	319.560	0.	−631.784	−588.980	103.187
300	203.426	320.818	319.564	0.376	−631.628	−588.715	102.504
400	208.949	380.097	327.609	20.995	−623.770	−575.626	75.169
500	214.472	427.315	342.983	42.166	−616.991	−564.395	58.962
600	219.995	466.906	360.424	63.889	−611.178	−554.437	48.268
700	225.518	501.234	378.141	86.165	−605.825	−545.398	40.698

PREVIOUS: CURRENT: March 1978

$S°(298.15\ K) = 415.51 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -605.71 \pm 10.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -601.58 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Degeneracies, and Anharmonicities		
ν, cm^{-1}	ν, cm^{-1}	x_{ij}, cm^{-1}
2132.4(1)	458.9(3)	$x_{11} = -2.6$
370.8(1)	423.1(3)	$x_{15} = -11.0$
380 (2)	79 (3)	$x_{55} = -5.0$
62 (2)	300 (3)	$g_{55} = -4.5$
2057.8(3)		All others = 0

Ground State Quantum Weight: 1 $\sigma = 12$

Point Group: T_d

Bond Distances: Ni–C = 1.82 ± 0.03 Å; C–O = 1.15 ± 0.02 Å

Bond Angles: C–Ni–C = 109.4712°; Ni–C–O = 180°

Product of the Moments of Inertia: $I_A I_B I_C = 5.14154 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

The value of $\Delta_f H°$(g, 298.15 K) is obtained from $\Delta_f H°$(l, 298.15 K)[1] by addition of the enthalpy of vaporization, $\Delta_{vap} H°(298.15\ K) = 7.22 \pm 1.5\ kcal \cdot mol^{-1}$. The adopted value of the enthalpy of vaporization is selected from our 3rd law analysis of the vaporization data given below and is based primarily on the data of Suginuma and Satozaki,[2] Baev[3] and Walsh.[4] The uncertainty has been increased above that indicated in the table below to account for uncertainties in the free energy functions of the liquid and gas. Fugacity corrections have not been applied but they are expected to be within the stated uncertainty. The enthalpy of vaporization at the boiling point, $\Delta_{vap} H°$, is the difference between $\Delta_f H°$(g) and $\Delta_f H°$(l) at the boiling point.

Data for the equilibrium Ni(cr) + 4CO(g) = $Ni(CO)_4$(g) have been reviewed by Kipnis.[7] The data show considerable scatter and this has been attributed to differences in chemical potential of nickel (sheet or powder) used in the reaction.[7,8] Values of $\Delta_f H°$(298.15 K) derived from these studies are less negative than the adopted value by several $kcal \cdot mol^{-1}$ and are less reliable due to uncertainty in the chemical potential of nickel.

Source	Data Points	T/K	$\Delta_{vap} H°$(298.15 K), $kcal \cdot mol^{-1}$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°$(298.15 K) $kcal \cdot mol^{-1}$
2	20	273–298	7.209 ± 0.024	7.217 ± 0.005	0.026 ± 0.084	143.78 ± 2.5
2	18	273–307	7.285 ± 0.015	7.224 ± 0.005	−0.208 ± 0.052	143.78 ± 2.5
3	33*	285–312	7.146 ± 0.013	7.216 ± 0.006	0.231 ± 0.043	143.78 ± 2.5
4	5	273–308	7.233 ± 0.031	7.222 ± 0.005	−0.037 ± 0.105	143.78 ± 2.5
5	9	253–316	6.933 ± 0.025	7.209 ± 0.043	0.961 ± 0.086	143.79 ± 2.5
6	8	275–313	7.284 ± 0.075	7.264 ± 0.016	−0.068 ± 0.255	143.74 ± 2.5

*Point at 281.94 K rejected by statistical test.

Heat Capacity and Entropy

The adopted vibrational data, including anharmonicity, are from Jones *et al.*[9] The largest uncertainty in these assignments is in the frequency of the MCO bending vibration, ν_3. Jones *et al.*[9] chose 380 cm^{-1} based on a study of the spectra of substituted carbonyls by Bigorgne and Bouquet.[10] Ross *et al.*[11] summarized values of $S°(298.15\ K)$ (96.2 to 99.8 $cal \cdot K^{-1} \cdot mol^{-1}$) obtained from various frequency assignments; most of this variation is due to alternate assignments for ν_3. The adopted molecular structure data are from the electron diffraction study of Brockway and Cross[12] which conclusively indicates a tetrahedral structure. Moment of inertia calculations based on the adopted bond distances and angles yield $I_A = I_B = I_C = 8.01120 \times 10^{-38}\ g \cdot cm^2$.

The thermodynamic functions, including the effects of available vibrational anharmonicities, are calculated using the computer program of McDowell.[13] Compared to a harmonic oscillator calculation using the same data the present results are identical at 298.15 K, while at 6000 K the entropy is 0.333 $cal \cdot K^{-1} \cdot mol^{-1}$ higher.

References

[1]JANAF Thermochemical Tables: $Ni(CO)_4$(l), 3–31–78.

[2]B. Suginuma and K. Satozaki, Bull. Inst. Phys. Chem. Research (Tokyo) **21**, 432 (1942).

[3]A. K. Baev, Obshch Prikl. Khim. **2**, 146 (1970).

[4]K. A. Walsh, U. S. Atomic Energy Commission Report LA–1649, (1953).

Continued on page 701

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−30.495	−605.714	−605.714	INFINITE
100	84.479	286.831	532.198	−24.537	−606.311	−599.206	312.993
200	127.972	359.892	428.595	−13.741	−604.533	−592.611	154.774
298.15	149.289	415.507	415.507	0.	−601.576	−587.378	102.906
300	149.557	416.431	415.510	0.276	−601.519	−587.290	102.256
400	160.377	461.081	421.524	15.823	−598.734	−582.983	76.130
500	167.490	497.670	433.204	32.233	−596.716	−579.297	60.519
600	173.167	528.724	446.600	49.274	−595.585	−575.934	50.140
700	178.000	555.790	460.306	66.839	−594.943	−572.706	42.736
800	182.138	579.836	473.772	84.851	−594.376	−569.571	37.189
900	185.652	601.497	486.781	103.245	−594.059	−566.492	32.878
1000	188.623	621.216	499.253	121.963	−593.948	−563.436	29.431
1100	191.125	639.314	511.174	140.954	−594.007	−560.383	26.610
1200	193.238	656.037	522.558	160.175	−594.219	−557.319	24.259
1300	195.025	671.577	533.431	179.590	−594.575	−554.230	22.269
1400	196.543	686.087	543.822	199.171	−595.076	−551.109	20.562
1500	197.836	699.692	553.765	218.891	−595.721	−547.947	19.081
1600	198.949	712.496	563.289	238.731	−596.514	−544.737	17.784
1700	199.902	724.587	572.425	258.675	−597.462	−541.473	16.637
1800	200.748	736.037	581.199	278.708	−615.719	−537.434	15.596
1900	201.472	746.911	589.637	298.820	−616.893	−533.053	14.655
2000	202.121	757.262	597.762	319.000	−618.127	−528.608	13.806
2100	202.683	767.137	605.594	339.241	−619.424	−524.101	13.036
2200	203.192	776.578	613.153	359.535	−620.783	−519.529	12.335
2300	203.641	785.620	620.456	379.877	−622.208	−514.895	11.694
2400	204.049	794.296	627.520	400.262	−623.699	−510.199	11.104
2500	204.412	802.633	634.359	420.685	−625.257	−505.437	10.561
2600	204.744	810.657	640.986	441.143	−626.882	−500.613	10.057
2700	205.042	818.390	647.415	461.633	−628.575	−495.724	9.590
2800	205.317	825.852	653.655	482.151	−630.336	−490.771	9.155
2900	205.566	833.061	659.718	502.695	−632.164	−485.756	8.749
3000	205.798	840.034	665.613	523.264	−634.059	−480.674	8.369
3100	206.013	846.785	671.349	543.854	−636.021	−475.528	8.013
3200	206.213	853.329	676.934	564.466	−1014.883	−465.132	7.592
3300	206.396	859.678	682.376	585.096	−1015.322	−447.946	7.090
3400	206.568	865.842	687.682	605.745	−1015.825	−430.744	6.618
3500	206.730	871.832	692.858	626.409	−1016.390	−413.529	6.172
3600	206.882	877.658	697.911	647.090	−1017.019	−396.295	5.750
3700	207.024	883.328	702.846	667.786	−1017.711	−379.044	5.351
3800	207.158	888.851	707.668	688.495	−1018.466	−361.771	4.973
3900	207.284	894.234	712.383	709.217	−1019.284	−344.479	4.614
4000	207.405	899.483	716.995	729.951	−1020.166	−327.166	4.272
4100	207.521	904.606	721.509	750.698	−1021.112	−309.829	3.947
4200	207.631	909.608	725.928	771.455	−1022.122	−292.469	3.637
4300	207.736	914.495	730.257	792.224	−1023.197	−275.083	3.342
4400	207.836	919.272	734.499	813.002	−1024.338	−257.673	3.059
4500	207.932	923.944	738.657	833.791	−1025.546	−240.236	2.789
4600	208.024	928.515	742.735	854.589	−1026.822	−222.772	2.530
4700	208.113	932.989	746.735	875.395	−1028.167	−205.277	2.281
4800	208.200	937.372	750.661	896.211	−1029.583	−187.754	2.043
4900	208.285	941.666	754.516	917.035	−1031.071	−170.199	1.814
5000	208.367	945.874	758.301	937.868	−1032.634	−152.615	1.594
5100	208.446	950.001	762.019	958.709	−1034.273	−134.997	1.383
5200	208.522	954.050	765.673	979.557	−1035.991	−117.350	1.179
5300	208.596	958.022	769.265	1000.413	−1037.789	−99.665	0.982
5400	208.669	961.922	772.797	1021.276	−1039.673	−81.948	0.793
5500	208.738	965.752	776.271	1042.147	−1041.642	−64.195	0.610
5600	208.807	969.514	779.688	1063.024	−1043.702	−46.404	0.433
5700	208.874	973.210	783.051	1083.908	−1045.855	−28.577	0.262
5800	208.941	976.843	786.361	1104.799	−1048.103	−10.709	0.096
5900	209.006	980.416	789.620	1125.696	−1050.452	7.194	−0.064
6000	209.070	983.929	792.829	1146.600	−1052.904	25.143	−0.219

PREVIOUS: March 1978 (1 atm) CURRENT: March 1978 (1 bar)

$S°(298.15\ K) = 242.0 \pm 16.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 972 \pm 25\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 979 \pm 25\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[1920] (1)	[550] (2)
[770] (1)	[550] (2)
[2210] (1)	[550] (2)
[1430] (1)	

Ground State Configuration: [$^1\Sigma$] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: C–C = [1.28] Å
Bond Angle: C–C–C = [180°]
Rotational Constant: B_O = [0.085664] cm^{-1}

Enthalpy of Formation

The enthalpy of formation is obtained from the mass-spectrometric results of Drowart *et al.*[1] who obtained $\Delta_f H°(2400\ K) = 230 \pm 5$ $kcal \cdot mol^{-1}$. This was obtained from a 2nd law analysis of the ion intensity ration C_3^+/C^+ over a temperature range of 2200–2700 K. The absolute pressure, obtained from a knowledge of the monatomic carbon vapor pressure and an estimated ionization cross-section ratio of 6.3, yields a 2nd law entropy at 2400 K of 103.7 ± 2 $cal \cdot K^{-1} \cdot mol^{-1}$. The uncertainty in the ionization cross-section ratio is probably no more than a factor of two which gives an overall entropy uncertainty of ± 3.5 $cal \cdot K^{-1} \cdot mol^{-1}$. The enthalpy of formation at temperatures other than 2400 K depend on the functions adopted, for a discussion of these see below.

Heat Capacity and Entropy

The molecular properties of C_5 are all estimated. We have chosen a set of functions which is consistent with the mass-spectrometric observations of Drowart *et al.*[1] The thermodynamic functions of C_5 were first estimated by Pitzer and Clementi[2] but the basis for this estimate has completely changed. Originally they were calculated by analogy with C_3, C_3O_2 and CO_2, but the discovery of very low bending frequencies in C_3 and C_3O_2 complicated the picture by raising the calculated entropies significantly. Sandborn[3] has correlated the bending force constants in several related triatomics and has estimated the vibrational frequencies in C_4 and C_5. These vibrational frequencies yield high entropies outside the limits of the 2nd law determination. Since these frequencies are estimates, based on a basically triatomic correlation we have chosen to adopt three doubly degenerate bending frequencies of 550 cm^{-1} in place of the 130 cm^{-1}, 330 cm^{-1} and 520 cm^{-1} frequencies estimated by Sandborn.[3] The basis for this change is to make the functions conform to the only available measured data. Use of the present tables will yield values for the vapor pressure of C_4 is excellent agreement with the measurements in the 2000–3000 K range. Outside this range they provide only a general indication of the variation since they may not correspond to the real situation.

The stretching frequencies are from Sandborn[3] and the bond length is estimated equal to that in C_3.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.914	972.398	972.398	INFINITE
100	30.260	195.633	285.525	−8.989	975.024	955.937	−499.330
200	45.669	220.670	247.105	−5.287	977.094	936.042	−244.469
250	54.253	231.807	242.941	−2.784	978.119	925.660	−193.406
298.15	61.135	241.972	241.972	0.	979.056	915.470	−160.387
300	61.372	242.350	241.973	0.113	979.090	915.075	−159.329
350	67.147	252.260	242.742	3.331	979.954	904.336	−134.965
400	71.899	261.546	244.519	6.811	980.674	893.482	−116.677
450	75.903	270.252	246.899	10.509	981.231	882.548	−102.444
500	79.347	278.432	249.648	14.392	981.622	871.561	−91.051
600	85.013	293.421	255.718	22.622	981.961	849.508	−73.956
700	89.478	306.874	262.081	31.355	981.829	827.437	−61.744
800	93.049	319.064	268.454	40.488	981.357	805.410	−52.588
900	95.926	330.195	274.705	49.942	980.638	783.458	−45.471
1000	98.259	340.427	280.772	59.655	979.736	761.595	−39.782
1100	100.164	349.885	286.631	69.579	978.691	739.831	−35.132
1200	101.731	358.670	292.273	79.676	977.532	718.167	−31.261
1300	103.029	366.865	297.699	89.916	976.277	696.603	−27.990
1400	104.113	374.541	302.916	100.275	974.938	675.140	−25.190
1500	105.025	381.756	307.934	110.733	973.524	653.774	−22.766
1600	105.798	388.560	312.763	121.276	972.041	632.506	−20.649
1700	106.457	394.994	317.412	131.889	970.494	611.332	−18.784
1800	107.023	401.096	321.893	142.564	968.885	590.251	−17.129
1900	107.513	406.895	326.216	153.291	967.218	569.261	−15.650
2000	107.938	412.421	330.389	164.064	965.493	548.360	−14.322
2100	108.310	417.697	334.422	174.877	963.713	527.547	−13.122
2200	108.637	422.743	338.323	185.725	961.877	506.820	−12.033
2300	108.925	427.579	342.099	196.603	959.988	486.177	−11.041
2400	109.181	432.220	345.758	207.509	958.045	465.618	−10.134
2500	109.409	436.682	349.306	218.439	956.049	445.142	−9.301
2600	109.613	440.977	352.750	229.390	954.001	424.745	−8.533
2700	109.796	445.117	356.095	240.360	951.900	404.429	−7.824
2800	109.960	449.113	359.346	251.348	949.748	384.192	−7.167
2900	110.109	452.974	362.508	262.352	947.544	364.032	−6.557
3000	110.244	456.710	365.586	273.370	945.289	343.949	−5.989
3100	110.367	460.327	368.584	284.400	942.982	323.942	−5.458
3200	110.479	463.832	371.506	295.443	940.624	304.011	−4.962
3300	110.581	467.234	374.356	306.496	938.215	284.154	−4.498
3400	110.675	470.536	377.137	317.559	935.755	264.371	−4.062
3500	110.761	473.746	379.851	328.631	933.244	244.660	−3.651
3600	110.840	476.867	382.503	339.711	930.682	225.023	−3.265
3700	110.913	479.905	385.094	350.798	928.069	205.457	−2.901
3800	110.981	482.864	387.629	361.893	925.406	185.962	−2.556
3900	111.043	485.747	390.108	372.994	922.692	166.539	−2.231
4000	111.101	488.559	392.534	384.101	919.927	147.185	−1.922
4100	111.155	491.303	394.910	395.214	917.111	127.901	−1.629
4200	111.206	493.983	397.237	406.332	914.245	108.687	−1.352
4300	111.252	496.600	399.517	417.455	911.328	89.541	−1.088
4400	111.296	499.158	401.753	428.583	908.361	70.464	−0.837
4500	111.337	501.660	403.945	439.714	905.343	51.455	−0.597
4600	111.376	504.107	406.096	450.850	902.275	32.513	−0.369
4700	111.412	506.503	408.207	461.990	899.156	13.639	−0.152
4800	111.446	508.849	410.279	473.132	895.987	−5.168	0.056
4900	111.477	511.147	412.315	484.279	892.767	−23.909	0.255
5000	111.507	513.399	414.314	495.428	889.496	−42.584	0.445
5100	111.536	515.608	416.278	506.580	886.176	−61.192	0.627
5200	111.562	517.774	418.209	517.735	882.804	−79.735	0.801
5300	111.587	519.899	420.108	528.892	879.383	−98.213	0.968
5400	111.611	521.985	421.976	540.052	875.910	−116.626	1.128
5500	111.634	524.033	423.813	551.215	872.388	−134.974	1.282
5600	111.655	526.045	425.620	562.379	868.815	−153.257	1.430
5700	111.676	528.021	427.399	573.546	865.191	−171.477	1.571
5800	111.695	529.964	429.151	584.714	861.517	−189.632	1.708
5900	111.713	531.873	430.876	595.885	857.793	−207.723	1.839
6000	111.730	533.751	432.575	607.057	854.018	−225.751	1.965

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 337.08 \pm 4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 253.1 \pm 0.1\ K$

$\Delta_f H°(298.15\ K) = -766.09 \pm 7.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 13.226 \pm 0.013\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is based on the enthalpy of combustion measurements of Cotton *et al.*[1] The average energy of combustion reported by these authors is -386.86 ± 1.7 kcal·mol^{-1} which yields a value of $\Delta_c H°(298.15\ K) = -385.82 \pm 1.7$ kcal·mol^{-1}. Using auxiliary JANAF data[2] we calculate the adopted value of $\Delta_f H°(298.15\ K) = -183.1 \pm 1.7$ kcal·mol^{-1}. Earlier combustion work by Roth[3] and Mittasch[4] appears less reliable due to incomplete characterization of products.

Heat Capacity and Entropy

The adopted heat capacity is derived by merging the $C_p°$ data of Leadbetter and Spice[5] (22–287 K) with $C_p°$ data derived from the enthalpy measurements of Welty *et al.*[6] (302–387 K). Leadbetter and Spice report a small anomaly in $C_p°$(cr) near 230 K which they attribute to the presence of a small amount of impurity; therefore we have smoothed through this anomaly. The heat capacity[5] and enthalpy data[6] of the liquid merge smoothly and yield a constant $C_p° = 55.876\ cal \cdot K^{-1} \cdot mol^{-1}$ from the melting point to 387 K. We assume $C_p°$ remains constant at this value above this temperature.

The adopted value of $S°(298.15\ K)$ is obtained by the appropriate integration of $C_p°$ data assuming $S°(25\ K) = 3.49 \pm 1.0\ cal \cdot K^{-1} \cdot mol^{-1}$. $S°(25\ K)$ is obtained by using a single Debye function with 18 degrees of freedom and $\theta_D = 155$ K as suggested by Leadbetter and Spice.[5] The uncertainty in this procedure is rather large since a single Debye function fits the observed $C_p°$ data quite poorly.

Fusion Data

The adopted values of T_{fus} and $\Delta_{fus}H°$ are those reported by Leadbetter and Spice.[5] The value of T_{fus} agrees well with that listed by Brynestad.[7] For $\Delta_{fus}H°$ the only other value is $\Delta_{fus}H° = 3250 \pm 40\ cal \cdot K^{-1} \cdot mol^{-1}$ reported by Mittasch.[4] This is much less precise than the adopted value which is an average of two determinations.

Vaporization Data

The adopted boiling point, $T_{vap}(1\ atm) = \sim 377$ K, is based on the vapor pressure data of Trautz and Badstubner[8] and Baev;[9] fugacity corrections have not been made. See the enthalpy of formation section of the $Fe(CO)_5$(g) table[2] for details of the selected value of $\Delta_{vap}H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−52.934	−787.554	−787.554	INFINITE
100	105.240	113.401	580.650	−46.725	−789.327	−756.258	395.029
200	164.163	204.889	370.766	−33.175	−786.457	−724.021	189.095
253.100	191.020	246.527	340.393	−23.758	CRYSTAL <--> LIQUID		
253.100	233.785	298.781	340.393	−10.532	TRANSITION		
298.15	233.785	337.078	337.078	0.	−766.090	−696.975	122.107
300	233.785	338.524	337.083	0.432	−765.919	−696.547	121.280
400	233.785	405.780	346.253	23.811	−757.710	−674.716	88.109
500	233.785	457.948	363.569	47.190	−751.465	−654.729	68.399
600	233.785	500.572	382.958	70.568	−746.962	−635.831	55.354
700	233.785	536.610	402.401	93.947	−743.911	−617.569	46.084

PREVIOUS: CURRENT: March 1978

$\Delta_f H°(0\ K) = -729.52 \pm 7.1$ kJ·mol^{-1}

$S°(298.15\ K) = 439.3 \pm 12.6$ J·K^{-1}·mol^{-1} $\Delta_f H°(298.15\ K) = -727.85 \pm 7.1$ kJ·mol^{-1}

Vibrational Frequencies, Degeneracies, and Anharmonicities				
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	x_{ij}, cm^{-1}	x_{ij}, cm^{-1}
2120.7 (1)	618.8 (1)	474.3 (2)	$x_{1,1} = -2.2$	$x_{1,6} = -11.9$
2041.7 (1)	429.0 (1)	104.9 (2)	$x_{2,10} = -6.9$	$x_{1,10} = -7.2$
442.8 (1)	100 (1)	74.3 (2)	$x_{6,6} = -7.7$	$x_{2,6} = -14.1$
413.4 (1)	2013.3 (2)	488 (2)	$x_{10,10} = -5.6$	$x_{2,2} = x_{6,10} = -2.0$
383 (1)	645.0 (2)	375 (2)	$x_{1,2} = -9.3$	all others = 0
2034.0 (1)	542.5 (2)	97.3 (2)		

Point Group: D_{3h} $\sigma = 6$

Bond Distances: Fe–C_{eq} = 1.833 ± 0.004 Å; Fe–C_{ax} = 1.806 ± 0.005 Å; C–O = 1.145 ± 0.003 Å

Bond Angles: Fe–C–O = 180°; C_{ax}–Fe–C_{ax} = 180°; C_{eq}–Fe–C_{eq} = 120°; C_{ax}–Fe–C_{eq} = 90°

Product of the Moments of Inertia: $I_A I_B I_C = 9.94833 \times 10^{-112}$ g^3·cm^6

Enthalpy of Formation

The adopted value of $\Delta_f H°$(g, 298.15 K) is obtained from $\Delta_f H°$(l, 298.15 K)[1] by addition of the enthalpy of vaporization, $\Delta_{vap}H°(298.15\ K) = 9.14 \pm 1.2$ kcal·mol^{-1}. The adopted value of the enthalpy of vaporization is selected from our 3rd law analysis of the vaporization data below and is based primarily on the data of Trautz and Badstubner[2] and Baev.[3] The uncertainty has been increased above that indicated in the table below to account for uncertainties in the free functions of the liquid and gas. Fugacity corrections have not been made but they are expected to be well within the stated uncertainty. The enthalpy of vaporization at the boiling point, $\Delta_{vap}H°$, is calculated from the difference between $\Delta_f H°$(g) and $\Delta_f H°$(l) at the boiling point.

Source	Data Points	T/K	$\Delta_{vap}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal^{-1}·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[2]	69	320–377	9.727 ± 0.004	9.138 ± 0.49	−1.688 ± 0.011	173.96 ± 1.7
[3]	28	266–353	9.215 ± 0.041	9.141 ± 0.036	−0.224 ± 0.125	173.96 ± 1.7
[4]	16	293–306	9.754 ± 0.095	9.219 ± 0.017	−1.780 ± 0.317	173.88 ± 1.7
[5]	12	254–306	9.207 ± 0.106	9.241 ± 0.042	0.121 ± 0.381	173.86 ± 1.7
[6]	13	258–293	9.505 ± 0.014	9.247 ± 0.025	−0.936 ± 0.052	173.85 ± 1.7
[7]	7	266–351	7.195 ± 0.550	8.977 ± 0.440	5.915 ± 1.816	174.12 ± 1.8

Heat Capacity and Entropy

The selected vibrational data, including anharmonicity, are from Jones *et al.*[8] The largest uncertainty in these assignments is for ν_9; Jones estimates it to lie at 100 ± 15 cm^{-1}. The uncertainty in this assignment coupled with unknown anharmonicities for the low frequency vibrational modes lead to rather large uncertainties in the thermal functions. Following the arguments of Jones we estimate an uncertainty at ±3.0 cal·K^{-1}·mol^{-1} in $S°$(298.15 K).

The adopted molecular structure data are from the electron diffraction data of Beagley *et al.*[9] which clearly indicate that the Fe–C axial bond is shorter than the Fe–C equatorial bond. Moment of inertia calculations based on the adopted bond distances and angles yield $I_A = 9.078946 \times 10^{-38}$ g·cm^2 and $I_B = I_C = 1.046785 \times 10^{-37}$ g·cm^2. The electron diffraction study of Almenningen *et al.*[10] is in excellent agreement with the adopted data although a slightly smaller difference between the axial and equatorial Fe–C bond lengths is indicated. This would lead to an insignificant difference in $S°$(298.15 K).

The thermodynamic functions, including the effects of available vibrational anharmonicities, are calculated using the computer program of McDowell.[11] Compared to a harmonic oscillator calculation using the same data the present results are identical at 298.15 K, while at 6000 K the entropy is 0.407 cal·K^{-1}·mol^{-1} higher.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−33.145	−729.524	−729.524	INFINITE
100	90.843	299.071	568.282	−26.921	−731.282	−716.779	374.407
200	139.336	377.190	454.024	−15.367	−730.407	−702.431	183.456
298.15	170.703	439.286	439.286	0.	−727.849	−689.207	120.746
300	171.134	440.344	439.290	0.316	−727.794	−688.968	119.960
400	189.027	492.243	446.244	18.399	−724.880	−676.471	88.338
500	200.830	535.762	459.914	37.924	−722.489	−664.660	69.437
600	209.820	573.204	475.747	58.474	−720.815	−653.263	56.872
700	217.105	606.113	492.067	79.832	−719.784	−642.094	47.914
800	223.115	635.508	508.193	101.852	−719.325	−631.034	41.202
900	228.088	662.084	523.839	124.420	−719.472	−619.996	35.984
1000	232.209	686.335	538.894	147.442	−720.469	−608.900	31.806
1100	235.633	708.633	553.325	170.839	−722.455	−597.633	28.379
1200	238.490	729.261	567.137	194.549	−723.964	−586.239	25.518
1300	240.887	748.448	580.355	218.521	−723.888	−574.766	23.094
1400	242.910	766.375	593.009	242.713	−723.955	−563.293	21.017
1500	244.628	783.194	605.133	267.092	−724.162	−551.811	19.216
1600	246.097	799.030	616.761	291.630	−724.511	−540.311	17.639
1700	247.362	813.989	627.927	316.305	−725.955	−528.765	16.247
1800	248.458	828.159	638.661	341.097	−726.933	−517.139	15.007
1900	249.413	841.619	648.992	365.991	−742.160	−504.751	13.877
2000	250.250	854.434	658.946	390.975	−743.682	−492.217	12.855
2100	250.989	866.662	668.548	416.038	−745.279	−479.605	11.930
2200	251.644	878.353	677.821	441.170	−746.953	−466.913	11.086
2300	252.227	889.552	686.785	466.364	−748.706	−454.146	10.314
2400	252.751	900.298	695.459	491.614	−750.540	−441.301	9.605
2500	253.222	910.626	703.861	516.913	−752.456	−428.377	8.950
2600	253.647	920.566	712.005	542.256	−754.454	−415.374	8.345
2700	254.032	930.146	719.908	567.640	−756.537	−402.293	7.783
2800	254.387	939.391	727.583	593.062	−758.702	−389.133	7.259
2900	254.708	948.323	735.041	618.517	−760.951	−375.896	6.771
3000	255.006	956.963	742.296	644.003	−763.284	−362.578	6.313
3100	255.279	965.329	749.356	669.517	−765.698	−349.180	5.884
3200	255.534	973.438	756.233	695.058	−1116.495	−328.282	5.359
3300	255.768	981.305	762.934	720.623	−1117.171	−303.641	4.806
3400	255.988	988.944	769.470	746.211	−1117.960	−278.976	4.286
3500	256.193	996.367	775.847	771.820	−1118.861	−254.288	3.795
3600	256.386	1003.587	782.073	797.449	−1119.874	−229.571	3.331
3700	256.566	1010.614	788.156	823.097	−1120.999	−204.827	2.892
3800	256.737	1017.459	794.100	848.762	−1122.235	−180.047	2.475
3900	256.898	1024.130	799.913	874.444	−1123.583	−155.234	2.079
4000	257.051	1030.636	805.600	900.141	−1125.043	−130.388	1.703
4100	257.196	1036.985	811.167	925.854	−1126.615	−105.502	1.344
4200	257.335	1043.184	816.617	951.580	−1128.299	−80.577	1.002
4300	257.466	1049.241	821.957	977.320	−1130.098	−55.609	0.676
4400	257.593	1055.161	827.190	1003.073	−1132.010	−30.601	0.363
4500	257.714	1060.952	832.321	1028.839	−1134.038	−5.547	0.064
4600	257.831	1066.617	837.353	1054.616	−1136.182	19.553	−0.222
4700	257.942	1072.163	842.290	1080.405	−1138.445	44.703	−0.497
4800	258.050	1077.595	847.136	1106.204	−1140.828	69.902	−0.761
4900	258.155	1082.917	851.894	1132.015	−1143.332	95.152	−1.014
5000	258.256	1088.133	856.566	1157.835	−1145.961	120.454	−1.258
5100	258.353	1093.249	861.157	1183.666	−1148.717	145.811	−1.493
5200	258.449	1098.266	865.669	1209.506	−1151.602	171.219	−1.720
5300	258.541	1103.190	870.104	1235.355	−1154.619	196.688	−1.938
5400	258.631	1108.024	874.465	1261.214	−1157.773	222.213	−2.149
5500	258.719	1112.770	878.755	1287.081	−1161.066	247.797	−2.353
5600	258.804	1117.433	882.976	1312.958	−1164.504	273.445	−2.551
5700	258.888	1122.014	887.129	1338.842	−1168.089	299.153	−2.741
5800	258.970	1126.517	891.218	1364.735	−1171.827	324.929	−2.926
5900	259.050	1130.945	895.244	1390.636	−1175.723	350.764	−3.105
6000	259.129	1135.299	899.209	1416.545	−1179.782	376.673	−3.279

PREVIOUS: March 1978 (1 atm) CURRENT: March 1978 (1 bar)

$S°(298.15\ K) = 612.044 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -333.57 \pm 41.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -328.44 \pm 41.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Mah[1] determined the enthalpy of combustion of $Cr_{23}C_6$(cr) using oxygen bomb calorimetry. Using auxiliary JANAF data[2] and the value $\Delta_c H°(303.15\ K) = -3604.2 \pm 1.5$ kcal·mol^{-1} reported by Mah[1] for the combustion of $Cr_{23}C_6$, we calculate $\Delta_f H°(298.15\ K) = -78.5$ kcal·mol^{-1} for $Cr_{23}C_6$(cr). The combustion equation is $Cr_{23}C_6(cr) + 93/4\ O_2(g) = 23/2\ Cr_2O_3(cr) + 6\ CO_2(g)$. The factor (23/2) makes the $\Delta_f H$ value for $Cr_{23}C_6$ extremely sensitive to the corresponding value for Cr_2O_3(cr). Of the nine combustion runs, Mah[1] reported complete combustion in three runs and 99.40 to 99.85% completion in the remaining six. Corrections for incomplete combustion, formation of small amounts of CO(g) and impurities were made by Mah.[1] These corrections amount to no more than 0.7% of the $\Delta_c E°$ value.

The pressures of CO(g) in equilibrium with a $Cr_{23}C_6$–Cr_2O_3–Cr mixture have been measured by Kelley *et al.*[3] and Kulkarni and Worrell.[4] Our analysis of their data is tabulated below. Kulkarni and Worrell[4] measured the CO pressure using a torsion effusion technique while Kelley *et al.*[3] measured the pressure manometrically. In all cases unit activity is assumed for the condensed species.

Source	T/K	Comments[a]	Reaction[c]	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
4	1170–1307	1/4 mm	A(15 pts.)	466.37	462.43	−3.2 ± 2.5	−78.53
4	1158–1286	1/3 mm	A(8 pts.)	450.14	462.31	9.9 ± 7.2	−78.41
4	1156–1283	1/2 mm	A(9 pts.)	451.46	467.72	13.3 ± 3.3	−83.82
3	1571–1772		A(18 pts.)[b]	459.47	467.19	4.6 ± 4.0	−83.29

[a]effusion orifice diameter
[b]1725, 1775 K points rejected due to statistical test.
[c]Reaction: (A)$Cr_{23}C_6$ (cr) + 2 Cr_2O_3(cr) = 27Cr(cr)

We adopt $\Delta_f H°(298.15\ K) = -78.5 \pm 10.0$ kcal·mol^{-1} for $Cr_{23}C_6$(cr) based on the combustion data of Mah,[1] with excellent support in the equilibrium studies by Kulkarni and Worrell[4] for orifice diameters of 1/4 and 1/3 mm. Kulkarni and Worrell[4] concluded that equilibrium was not obtained in the cell with the 1/2 mm orifice in order to provide an explanation for the low pressures observed. Equilibrium studies involving $Cr_{23}C_6$(cr) by Hancock and Pidgeon,[5] Alekseev and Shvartsman,[6] and Bolgar *et al.*[7] are not considered.[2]

Heat Capacity and Entropy

The heat capacity (55–295 K, 29 pts.) and enthalpy (467–1697 K, 26 pts.) have been measured by Kelley *et al.*[3] When the research was performed, Kelley *et al.*[3] considered the sample to be Cr_4C. All the data are corrected to the composition $Cr_{23}C_6$, assuming that the sample actually contained excess Cr. The contribution of the assumed free Cr was subtracted from the reported heat capacity and enthalpy values using JANAF data for Cr.[2] These corrections amount to 0.6 cal·K^{-1}·mol^{-1} at 55 K and 5.0 cal·K^{-1}·mol^{-1} at 295 K for the heat capacity data and are in a range of 1.00–1.85 kcal·mol^{-1} for the enthalpy data. We adopt $S°(50\ K) = 4.861$ cal·K^{-1}·mol^{-1} and $H°(50;0) = 181.6$ cal·mol^{-1}. The enthalpy data are fit to a six term polynomial with a constraint to join smoothly in the 298.15 K region with the enthalpy derived from the heat capacity data. There is considerable scatter in the enthalpy data. Deviations of the observed data from the tabulated data are within ±0.6% except for the 486.5 K data point which is approximately 1% (500 cal·mol^{-1}) too high. The enthalpy polynomial is used to extrapolate the results to 2000 K.

Phase Data

Storms[8] has summarized the phase information in the Cr–C system and reported that $Cr_{23}C_6$ has a complex face-centered-cubic structure. The range of homogeneity for $Cr_{23}C_6$ is unknown.[8]

Decomposition Data

The tentative phase diagram of the Cr–Cr_3C_2 system proposed by Storms[8] indicated that $Cr_{23}C_6$ has an incongruent melting point at 1793 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−104.755	−333.575	−333.575	INFINITE
100	250.316	117.835	1081.808	−96.397	−332.734	−334.089	174.510
200	509.447	383.581	666.329	−56.550	−331.274	−335.894	87.726
298.15	628.152	612.044	612.044	0.	−328.444	−338.693	59.338
300	629.692	615.935	612.056	1.164	−328.373	−338.757	58.983
400	704.376	808.005	637.736	68.108	−326.027	−342.211	44.688
500	753.538	970.840	688.496	141.172	−320.639	−346.880	36.238
600	785.751	1111.290	747.532	218.255	−315.571	−352.615	30.698
700	808.114	1234.112	808.454	297.960	−311.244	−359.142	26.799
800	829.072	1343.386	868.614	379.818	−307.585	−366.242	23.913
900	850.247	1442.252	926.944	463.778	−304.702	−373.756	21.692
1000	872.142	1532.961	983.070	549.890	−302.997	−381.534	19.929
1100	894.857	1617.144	1036.931	638.234	−302.930	−389.406	18.491
1200	918.329	1696.008	1088.602	728.888	−304.701	−397.203	17.290
1300	942.471	1770.464	1138.215	821.923	−308.594	−404.770	16.264
1400	967.178	1841.209	1185.923	917.402	−314.817	−411.950	15.370
1500	992.361	1908.794	1231.877	1015.375	−323.452	−418.601	14.577
1600	1017.946	1973.655	1276.225	1115.888	−334.571	−424.596	13.862
1700	1043.862	2036.143	1319.099	1218.976	−348.224	−429.817	13.207
1800	1070.058	2096.549	1360.622	1324.670	−364.452	−434.162	12.599
1900	1096.488	2155.112	1400.903	1432.996	−383.294	−437.533	12.029
2000	1123.115	2212.030	1440.043	1543.974	−404.778	−439.843	11.488

PREVIOUS: CURRENT: December 1973

Continued from page 550

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Continued from page 582

Heat Capacity and Entropy

The structure of CF_2 has been reported by Powell and Lide[16] from microwave measurements and has been confirmed by Mathews[17] from the fine structure of the 2500 Å absorption band. Mathews also reported ν_2, and Herr and Pimentel[18] reported ν_3, both from gas phase studies. Milligan *et al.*[19] have observed all three vibrations in matrix–isolated CF_2 as 1222, 668 and 1102 cm^{-1}. The electronic levels are from Mathews[17] with the triplet level estimated by Simons[20] to explain the low C = C bond energy of 70 kcal in C_2F_4.

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REFERENCE STATE

0	to	716	K crystal, alpha
716	to	1115	K crystal, beta
1115	to	1773.658	K liquid
above		1773.658	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−5.736	0.	0.	0.
100	19.504	15.967	63.525	−4.756	0.	0.	0.
200	24.542	31.489	43.924	−2.487	0.	0.	0.
298.15	25.929	41.588	41.588	0.	0.	0.	0.
300	25.946	41.749	41.589	0.048	0.	0.	0.
400	26.868	49.322	42.615	2.683	0.	0.	0.
500	28.487	55.487	44.590	5.448	0.	0.	0.
600	30.382	60.846	46.861	8.391	0.	0.	0.
700	32.406	65.680	49.210	11.529	0.	0.	0.
716.000	32.737	66.416	49.586	12.051	ALPHA <--> BETA TRANSITION		
716.000	31.503	67.715	49.586	12.981			
800	33.818	71.335	51.681	15.723	0.	0.	0.
900	36.713	75.484	54.097	19.249	0.	0.	0.
1000	39.706	79.507	56.437	23.069	0.	0.	0.
1100	42.763	83.434	58.714	27.192	0.	0.	0.
1115.000	43.226	84.017	59.050	27.837	BETA <--> LIQUID TRANSITION		
1115.000	35.000	91.676	59.050	36.377			
1200	35.000	94.247	61.453	39.352	0.	0.	0.
1300	35.000	97.049	64.085	42.852	0.	0.	0.
1400	35.000	99.642	66.533	46.352	0.	0.	0.
1500	35.000	102.057	68.822	49.852	0.	0.	0.
1600	35.000	104.316	70.971	53.352	0.	0.	0.
1700	35.000	106.438	72.995	56.852	0.	0.	0.
1773.658	35.000	107.922	74.415	59.430	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1773.658	20.837	191.956	74.415	208.477			
1800	20.845	192.263	76.138	209.026	0.	0.	0.
1900	20.888	193.391	82.279	211.112	0.	0.	0.
2000	20.953	194.464	87.862	213.204	0.	0.	0.
2100	21.046	195.489	92.963	215.304	0.	0.	0.
2200	21.173	196.470	97.646	217.415	0.	0.	0.
2300	21.343	197.415	101.963	219.540	0.	0.	0.
2400	21.561	198.328	105.959	221.685	0.	0.	0.
2500	21.836	199.214	109.672	223.854	0.	0.	0.
2600	22.173	200.076	113.132	226.054	0.	0.	0.
2700	22.578	200.921	116.368	228.291	0.	0.	0.
2800	23.057	201.750	119.403	230.572	0.	0.	0.
2900	23.614	202.569	122.257	232.905	0.	0.	0.
3000	24.251	203.380	124.947	235.298	0.	0.	0.
3100	24.970	204.186	127.490	237.758	0.	0.	0.
3200	25.772	204.992	129.900	240.295	0.	0.	0.
3300	26.655	205.798	132.187	242.915	0.	0.	0.
3400	27.618	206.608	134.364	245.628	0.	0.	0.
3500	28.657	207.423	136.440	248.441	0.	0.	0.
3600	29.767	208.246	138.423	251.362	0.	0.	0.
3700	30.944	209.077	140.321	254.397	0.	0.	0.
3800	32.180	209.919	142.142	257.553	0.	0.	0.
3900	33.469	210.771	143.891	260.835	0.	0.	0.
4000	34.801	211.635	145.573	264.248	0.	0.	0.
4100	36.169	212.511	147.195	267.796	0.	0.	0.
4200	37.564	213.400	148.761	271.482	0.	0.	0.
4300	38.977	214.300	150.275	275.309	0.	0.	0.
4400	40.389	215.212	151.740	279.275	0.	0.	0.
4500	41.755	216.131	153.161	283.367	0.	0.	0.
4600	43.135	217.063	154.540	287.607	0.	0.	0.
4700	44.507	218.005	155.880	291.990	0.	0.	0.
4800	45.851	218.956	157.184	296.508	0.	0.	0.
4900	47.160	219.915	158.454	301.159	0.	0.	0.
5000	48.426	220.881	159.693	305.938	0.	0.	0.
5200	50.805	222.827	162.084	315.861	0.	0.	0.
5400	52.964	224.785	164.370	326.242	0.	0.	0.
5600	54.857	226.745	166.562	337.021	0.	0.	0.
5800	56.500	228.699	168.671	348.161	0.	0.	0.
6000	57.878	230.639	170.705	359.603	0.	0.	0.

PREVIOUS: December 1968 (1 atm) CURRENT: September 1983 (1 bar)

Pearson Notation: cF4
$S°(298.15\ K) = 41.588\ J·K^{-1}·mol^{-1}$
$T_{trs}\ (\alpha \rightarrow \beta) = 716 \pm 3\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0.930 \pm 0.08\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The thermal functions given here are those recommended by CODATA.[1] The low temperature heat capacity of α–CA(cr) has been measured many times: Griffil *et al*. (1.8–4.2 K),[2] Agarwal and Betterton (1.1–4.2 K),[3] Roberts (1.5–20 K),[4] Clusius and Vaughen (10–200 K),[5] Gunther (22–62 K),[6] and Eastman and Rodebush (67–293 K).[7] The adopted heat capacity values are derived assuming that the heat capacity curve should lie below and be similar to the shape of the α–Sr(cr) curve, but remain higher than the Mg curve. The experimental data would imply a crossing of the curves below 300 K which does not appear reasonable. The adopted curve is in reasonable agreement with Griffil *et al*.,[2] Roberts,[4] and Clusius and Vaughen.[5]

The high temperature heat capacities for the α and β phasis are estimates based on the experimental enthalpy studies in Zalensinskii and Zulinski,[8] Jauch,[9] and Eastman *et al*.[10] with the two constraints that the values mesh smoothly with the low temperature results and show a similarity with the Mg and Sr results.

Transition Data

Refer to Ca(β, cr) tables for details.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.736	0.	0.	0.
100	19.504	15.967	63.525	−4.756	0.	0.	0.
200	24.542	31.489	43.924	−2.487	0.	0.	0.
250	25.411	37.065	42.012	−1.237	0.	0.	0.
298.15	25.929	41.588	41.588	0.	0.	0.	0.
300	25.946	41.749	41.589	0.048	0.	0.	0.
350	26.320	45.774	41.906	1.354	0.	0.	0.
400	26.868	49.322	42.615	2.683	0.	0.	0.
450	27.643	52.531	43.541	4.045	0.	0.	0.
500	28.487	55.487	44.590	5.448	0.	0.	0.
600	30.382	60.846	46.861	8.391	0.	0.	0.
700	32.406	65.680	49.210	11.529	0.	0.	0.
716.000	32.737	66.416	49.586	12.051	---- ALPHA <--> BETA ----		
800	34.613	70.150	51.551	14.879	−0.844	0.104	−0.007
900	36.819	74.354	53.853	18.451	−0.798	0.219	−0.013
1000	39.026	78.348	56.105	22.243	−0.826	0.333	−0.017
1100	41.232	82.171	58.302	26.256	−0.936	0.453	−0.022

PREVIOUS: December 1968 CURRENT: September 1983

Pearson Notation: cI4
$S°(298.15\ K)$ = [43.070] $J·K^{-1}·mol^{-1}$
T_{trs} ($\alpha \rightarrow \beta$) = 716 ± 3 K
$T_{fus}(\beta \rightarrow I)$ = 1115 ± 2 K

$\Delta_f H(298.15\ K)$ = [1.056] $kJ·mol^{-1}$
$\Delta_{trs}H°$ = 0.930 ± $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 8.540 ± 0.10 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Ca(β, cr) is calculated from that of the Ca(α, cr) by adding the enthalpy of transition and the difference in enthalpy, $H°(716\ K)–H°(298.15\ K)$, between Ca(α, cr) and Ca(β, cr).

Heat Capacity and Entropy

The high temperatures heat capacities for the α and β phases are estimates based on the experimental enthalpy studies in Zalinsinski andAulinski.[1] Jauch,[2] and Eastman *et al.*[3] with the two constraints that the values mesh smoothly with the low temperature results and show a similarity with the Mg and Sr results.

Transition and Fusion Data

According to Pearson,[4] calcium exists in two crystalline modifications. The low temperature phase (α) has a face – centered – cubic (cF4) structure, as does α–Sr(cr). The high temperature phase (β) has a body – centered – cubic (cI2) structure, as does β–Sr(cr). In comparison, magnesium has a hexagonal – close – packed structure. The β–Ca(cr) region of stability is 716 ± 3 K to 1115 ± 2 K.[5]

The enthalpies of transition and fusion are the values determined by Chiotti *et al.*[6] using an adiabatic calorimeter.

Sublimation Data

Refer to the ideal gas table for details.

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[2]R. Jauch, Diplomarbeit, Techn. Hochochule, Stuttgart, (1946).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	25.951	43.070	43.070	0.	1.056	0.614	−0.108
300	25.971	43.231	43.071	0.048	1.056	0.611	−0.106
350	26.345	47.260	43.388	1.355	1.057	0.537	−0.080
400	26.894	50.812	44.098	2.685	1.058	0.463	−0.060
450	27.708	54.026	45.025	4.051	1.061	0.388	−0.045
500	28.514	56.988	46.075	5.456	1.064	0.313	−0.033
600	30.099	62.336	48.349	8.392	1.057	0.163	−0.014
700	31.062	67.008	50.688	11.424	0.951	0.021	−0.002
716.000	31.503	67.715	51.061	11.925	---- ALPHA <--> BETA ----		
800	33.818	71.335	53.001	14.668	0.	0.	0.
900	36.713	75.484	55.270	18.193	0.	0.	0.
1000	39.706	79.507	57.493	22.014	0.	0.	0.
1100	42.763	83.434	59.674	26.137	0.	0.	0.
1115.000	43.226	84.017	59.997	26.782	---- BETA <--> LIQUID ----		
1200	45.850	87.287	61.815	30.567	−7.729	0.622	−0.027
1300	48.949	91.080	63.920	35.307	−6.489	1.270	−0.051
1400	52.048	94.818	65.994	40.354	−4.943	1.811	−0.068
1500	55.566	98.527	68.039	45.731	−3.066	2.230	−0.078

PREVIOUS: December 1968 CURRENT: September 1983

$S°(298.15\ K) = [45.510]\ J·K^{-1}·mol^{-1}$
$T_{fus}(\beta \rightarrow l) = 1115 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [7.788]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 8.540 \pm 0.10\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the liquid is calculated from that of Ca(β, cr) by adding the enthalpy of fusion and the difference in enthalpy, $H°(1115\ K)–H°(298.15\ K)$, between Ca(β, cr) and the liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is chosen to be a value intermediate between the adopted values for Mg(l) and Sr(l).

Fusion Data

Refer to the β–Ca(cr) table for details.

Vaporization Data

T_{vap} (1 bar) is calculated as the temperature at which $\Delta_f G° = 0$ for the process Ca(l) = Ca(g). $\Delta_{vap}H°$ is calculated as the difference in the enthalpies of formation between the ideal gas and liquid at T_{vap}.

Refer to the ideal gas table for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	35.000	45.510	45.510	0.	7.788	6.618	−1.159
300	35.000	45.727	45.511	0.065	7.804	6.611	−1.151
350	35.000	51.122	45.937	1.815	8.248	6.377	−0.952
400	35.000	55.796	46.884	3.565	8.670	6.080	−0.794
450	35.000	59.918	48.107	5.315	9.057	5.733	−0.665
500	35.000	63.606	49.476	7.065	9.404	5.345	−0.558
600	35.000	69.987	52.379	10.565	9.962	4.477	−0.390
700	35.000	75.382	55.290	14.065	10.323	3.532	−0.264
800	35.000	80.056	58.100	17.565	9.629	2.652	−0.173
900	35.000	84.178	60.773	21.065	9.603	1.779	−0.103
1000	35.000	87.866	63.301	24.565	9.283	0.924	−0.048
1100	35.000	91.202	65.688	28.065	8.660	0.116	−0.005
1115.000	35.000	91.676	66.035	28.590	---- BETA <--> LIQUID ----		
1200	35.000	94.247	67.943	31.565	0.	0.	0.
1300	35.000	97.049	70.076	35.065	0.	0.	0.
1400	35.000	99.642	72.096	38.565	0.	0.	0.
1500	35.000	102.057	74.014	42.065	0.	0.	0.
1600	35.000	104.316	75.838	45.565	0.	0.	0.
1700	35.000	106.438	77.576	49.065	0.	0.	0.
1773.658	35.000	107.922	78.806	51.643	----- FUGACITY = 1 bar -----		
1800	35.000	108.438	79.236	52.565	−148.674	2.211	−0.064
1900	35.000	110.331	80.823	56.065	−147.260	10.555	−0.290
2000	35.000	112.126	82.344	59.565	−145.852	18.824	−0.492
2100	35.000	113.834	83.803	63.065	−144.452	27.024	−0.672
2200	35.000	115.462	85.205	66.565	−143.062	35.157	−0.835
2300	35.000	117.018	86.555	70.065	−141.688	43.227	−0.982
2400	35.000	118.507	87.855	73.565	−140.333	51.237	−1.115
2500	35.000	119.936	89.110	77.065	−139.002	59.192	−1.237

PREVIOUS: December 1968 CURRENT: September 1983

0	to	716	K alpha
716	to	1115	K beta
above		1115	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−5.736	0.	0.	0.
100	19.504	15.967	63.525	−4.756	0.	0.	0.
200	24.542	31.489	43.924	−2.487	0.	0.	0.
250	25.411	37.065	42.012	−1.237	0.	0.	0.
298.15	25.929	41.588	41.588	0.	0.	0.	0.
300	25.946	41.749	41.589	0.048	0.	0.	0.
350	26.320	45.774	41.906	1.354	0.	0.	0.
400	26.868	49.322	42.615	2.683	0.	0.	0.
450	27.643	52.531	43.541	4.045	0.	0.	0.
500	28.487	55.487	44.590	5.448	0.	0.	0.
600	30.382	60.846	46.861	8.391	0.	0.	0.
700	32.406	65.680	49.210	11.529	0.	0.	0.
716.000	32.737	66.416	49.586	12.051	ALPHA <--> BETA TRANSITION		
716.000	31.503	67.715	49.586	12.981			
800	33.818	71.335	51.681	15.723	0.	0.	0.
900	36.713	75.484	54.097	19.249	0.	0.	0.
1000	39.706	79.507	56.437	23.069	0.	0.	0.
1100	42.763	83.434	58.714	27.192	0.	0.	0.
1115.000	43.226	84.017	59.050	27.837	BETA <--> LIQUID TRANSITION		
1115.000	35.000	91.676	59.050	36.377			
1200	35.000	94.247	61.453	39.352	0.	0.	0.
1300	35.000	97.049	64.085	42.852	0.	0.	0.
1400	35.000	99.642	66.533	46.352	0.	0.	0.
1500	35.000	102.057	68.822	49.852	0.	0.	0.
1600	35.000	104.316	70.971	53.352	0.	0.	0.
1700	35.000	106.438	72.995	56.852	0.	0.	0.
1773.658	35.000	107.922	74.415	59.430	FUGACITY = 1 bar		
1800	35.000	108.438	74.909	60.352	−148.674	2.211	−0.064
1900	35.000	110.331	76.724	63.852	−147.260	10.555	−0.290
2000	35.000	112.126	78.450	67.352	−145.852	18.824	−0.492
2100	35.000	113.834	80.094	70.852	−144.452	27.024	−0.672
2200	35.000	115.462	81.665	74.352	−143.062	35.157	−0.835
2300	35.000	117.018	83.169	77.852	−141.688	43.227	−0.982
2400	35.000	118.507	84.610	81.352	−140.332	51.237	−1.115
2500	35.000	119.936	85.995	84.852	−139.002	59.192	−1.237

PREVIOUS: CURRENT: September 1983

IP (Ca, g) = 49305.96 ± 0.08 cm^{-1}
$S°$(298.15 K) = 154.886 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 177.3 ± 0.8 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 177.8 ± 0.8 $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.00	1
$^3P_0$	15157.901	1
$^3P_1$	15210.063	3
$^3P_2$	15315.943	5

Enthalpy of Formation

The adopted enthalpy of formation value for Ca(g), $\Delta_f H°$(298.15 K) = 177.8 ± 0.8 $kJ·mol^{-1}$, is that recommended by CODATA.[1] This value was calculated, according to CODATA, from the vapor pressure measurements by Bogoslovskii *et al.* (773–1023 K),[2] Smith (844–965 K),[3] Bohdansky and Schins (1313–2060 K),[4] Schins *et al.* (1558–2115 K,[5]. The study by DeMaria and Piacente (1126–1300 K),[6] and others cited in Hultgren *et al.*[7] were also considered.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Sugar and Corliss,[8] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels (for $n < 80$) and cutting off the summation in the partition function[9] has no effect on the thermodynamic functions to 4000 K. This is a result of the high energy of all levels other than the ground state and the levels listed above; the next excited state is approximately 20335 cm^{-1} above the ground state. Although we list only a few levels, all levels listed by Sugar and Corliss[8] and the estimated levels (for $n < 80$) are considered in the calculation. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of additional excited states and use of different fill and cutoff procedures.[9]

The thermal functions at 298.15 K differ from the CODATA recommendations[1] for two reasons. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas CODATA recommendations are based on 1 atm. Second, small changes, −0.002 $J·K^{-1}·mol^{-1}$, arise due to the use of slightly different values for the fundamental constants.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	177.339	177.339	INFINITE
100	20.786	132.179	173.366	−4.119	178.437	166.816	−87.136
200	20.786	146.586	156.787	−2.040	178.247	155.227	−40.541
250	20.786	151.225	155.228	−1.001	178.036	149.496	−31.236
298.15	20.786	154.886	154.886	0.	177.800	144.020	−25.232
300	20.786	155.014	154.886	0.038	177.790	143.811	−25.040
350	20.786	158.219	155.139	1.078	177.524	138.168	−20.620
400	20.786	160.994	155.701	2.117	177.234	132.565	−17.311
450	20.786	163.442	156.428	3.156	176.911	127.001	−14.742
500	20.786	165.632	157.241	4.196	176.547	121.474	−12.690
600	20.786	169.422	158.965	6.274	175.684	110.538	−9.623
700	20.786	172.626	160.694	8.353	174.623	99.761	−7.444
800	20.786	175.402	162.363	10.431	172.508	89.255	−5.828
900	20.786	177.850	163.950	12.510	171.061	78.932	−4.581
1000	20.786	180.040	165.452	14.589	169.319	68.786	−3.593
1100	20.786	182.021	166.869	16.667	167.275	58.829	−2.794
1200	20.786	183.830	168.208	18.746	157.193	49.694	−2.163
1300	20.787	185.494	169.475	20.825	155.772	40.793	−1.639
1400	20.789	187.034	170.675	22.903	154.351	32.002	−1.194
1500	20.793	188.469	171.814	24.982	152.930	23.313	−0.812
1600	20.802	189.811	172.897	27.062	151.510	14.718	−0.480
1700	20.818	191.072	173.929	29.143	150.091	6.212	−0.191
1773.658	20.837	191.956	174.660	30.677	----- FUGACITY = 1 bar -----		
1800	20.845	192.263	174.915	31.226	0.	0.	0.
1900	20.888	193.391	175.858	33.313	0.	0.	0.
2000	20.953	194.464	176.762	35.405	0.	0.	0.
2100	21.046	195.489	177.629	37.504	0.	0.	0.
2200	21.173	196.470	178.464	39.615	0.	0.	0.
2300	21.343	197.415	179.267	41.740	0.	0.	0.
2400	21.561	198.328	180.043	43.885	0.	0.	0.
2500	21.836	199.214	180.792	46.054	0.	0.	0.
2600	22.173	200.076	181.517	48.254	0.	0.	0.
2700	22.578	200.921	182.220	50.491	0.	0.	0.
2800	23.057	201.750	182.903	52.773	0.	0.	0.
2900	23.614	202.569	183.567	55.105	0.	0.	0.
3000	24.251	203.380	184.214	57.498	0.	0.	0.
3100	24.970	204.186	184.845	59.958	0.	0.	0.
3200	25.772	204.992	185.462	62.495	0.	0.	0.
3300	26.655	205.798	186.066	65.115	0.	0.	0.
3400	27.618	206.608	186.658	67.828	0.	0.	0.
3500	28.657	207.423	187.240	70.641	0.	0.	0.
3600	29.767	208.246	187.812	73.562	0.	0.	0.
3700	30.944	209.077	188.375	76.597	0.	0.	0.
3800	32.180	209.919	188.931	79.753	0.	0.	0.
3900	33.469	210.771	189.480	83.035	0.	0.	0.
4000	34.801	211.635	190.023	86.448	0.	0.	0.
4100	36.169	212.511	190.561	89.996	0.	0.	0.
4200	37.564	213.400	191.094	93.682	0.	0.	0.
4300	38.977	214.300	191.623	97.509	0.	0.	0.
4400	40.389	215.212	192.149	101.475	0.	0.	0.
4500	41.755	216.131	192.672	105.568	0.	0.	0.
4600	43.135	217.063	193.192	109.808	0.	0.	0.
4700	44.507	218.005	193.710	114.190	0.	0.	0.
4800	45.851	218.956	194.226	118.708	0.	0.	0.
4900	47.160	219.915	194.740	123.359	0.	0.	0.
5000	48.426	220.881	195.253	128.138	0.	0.	0.
5100	49.646	221.852	195.765	133.042	0.	0.	0.
5200	50.805	222.827	196.276	138.061	0.	0.	0.
5300	51.914	223.805	196.786	143.198	0.	0.	0.
5400	52.964	224.785	197.296	148.442	0.	0.	0.
5500	53.952	225.766	197.805	153.789	0.	0.	0.
5600	54.857	226.745	198.312	159.221	0.	0.	0.
5700	55.712	227.723	198.820	164.750	0.	0.	0.
5800	56.500	228.699	199.327	170.361	0.	0.	0.
5900	57.222	229.671	199.833	176.047	0.	0.	0.
6000	57.878	230.639	200.338	181.803	0.	0.	0.

PREVIOUS: December 1968 (1 atm) CURRENT: September 1983 (1 bar)

$IP(Ca^+, g) = 95751.87 \pm 0.03\ cm^{-1}$
$S°(298.15\ K) = 160.649 \pm 0.02\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 767.17 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [773.828]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.0	2
$^2D_{3/2}$	13650.1	4
$^2D_{5/2}$	13710.8	6
$^2P_{1/2}$	25191.5	2
$^2P_{3/2}$	25414.40	4

Enthalpy of Formation

$\Delta_f H°(Ca^+, g, 0\ K)$ is calculated from $\Delta_f H°(Ca, g, 0\ K)$[1] using the spectroscopic value of IP(Ca) = 49305.96 ± 0.08 cm^{-1}(589.830 ± 0.001 $kJ \cdot mol^{-1}$) from Sugar and Corliss.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ca^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Ca, g, 0\ K)$ by using IP(Ca) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for Ca(g), $Ca^+(g)$, and e^-(ref). $\Delta_r H°(Ca \rightarrow Ca^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Sugar and Corliss,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is approximately 52167 cm^{-1} above the ground state. Since inclusion of these higher excited states has little effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.197	767.169		
100	20.786	137.942	179.129	−4.119			
200	20.786	152.349	162.550	−2.040			
250	20.786	156.988	160.991	−1.001			
298.15	20.786	160.649	160.649	0.	773.828	732.075	−128.257
300	20.786	160.777	160.649	0.038	773.857	731.816	−127.420
350	20.786	163.981	160.902	1.078	774.629	724.748	−108.163
400	20.786	166.757	161.464	2.117	775.379	717.570	−93.705
450	20.786	169.205	162.191	3.156	776.095	710.301	−82.450
500	20.786	171.395	163.004	4.196	776.771	702.954	−73.437
600	20.786	175.185	164.728	6.274	777.986	688.073	−59.902
700	20.786	178.389	166.457	8.353	779.004	673.004	−50.220
800	20.786	181.165	168.126	10.431	778.967	657.908	−42.957
900	20.786	183.613	169.713	12.510	779.599	642.734	−37.303
1000	20.786	185.803	171.214	14.589	779.936	627.506	−32.778
1100	20.786	187.784	172.632	16.667	779.970	612.259	−29.074
1200	20.787	189.593	173.971	18.746	771.967	597.645	−26.015
1300	20.789	191.257	175.238	20.825	772.625	583.091	−23.429
1400	20.792	192.798	176.438	22.904	773.282	568.487	−21.211
1500	20.800	194.232	177.577	24.983	773.940	553.836	−19.286
1600	20.814	195.575	178.660	27.064	774.600	539.141	−17.601
1700	20.838	196.838	179.693	29.147	775.261	524.405	−16.113
1800	20.874	198.030	180.679	31.232	627.251	511.840	−14.853
1900	20.927	199.160	181.622	33.322	629.333	505.372	−13.894
2000	20.999	200.235	182.526	35.418	631.416	498.793	−13.027
2100	21.095	201.262	183.394	37.523	633.500	492.111	−12.241
2200	21.218	202.246	184.228	39.638	635.583	485.329	−11.523
2300	21.369	203.192	185.032	41.767	637.665	478.453	−10.866
2400	21.550	204.105	185.808	43.913	639.745	471.486	−10.262
2500	21.764	204.989	186.558	46.078	641.819	464.433	−9.704
2600	22.009	205.847	187.283	48.267	643.886	457.297	−9.187
2700	22.286	206.683	187.986	50.481	645.943	450.081	−8.707
2800	22.594	207.499	188.669	52.725	647.984	442.789	−8.260
2900	22.931	208.298	189.332	55.001	650.005	435.425	−7.843
3000	23.296	209.081	189.977	57.312	652.003	427.992	−7.452
3100	23.686	209.851	190.606	59.661	653.970	420.492	−7.085
3200	24.098	210.610	191.219	62.050	655.901	412.930	−6.740
3300	24.529	211.358	191.818	64.481	657.790	405.308	−6.415
3400	24.977	212.097	192.404	66.956	659.631	397.629	−6.109
3500	25.438	212.827	192.977	69.477	661.417	389.897	−5.819
3600	25.908	213.551	193.538	72.044	663.142	382.115	−5.544
3700	26.385	214.267	194.089	74.659	664.800	374.285	−5.284
3800	26.865	214.977	194.629	77.321	666.386	366.412	−5.037
3900	27.345	215.681	195.160	80.031	667.893	358.498	−4.802
4000	27.822	216.379	195.682	82.790	669.317	350.547	−4.578
4100	28.294	217.072	196.195	85.596	670.653	342.561	−4.364
4200	28.757	217.759	196.700	88.448	671.898	334.543	−4.161
4300	29.210	218.441	197.198	91.347	673.048	326.497	−3.966
4400	29.651	219.118	197.689	94.290	674.104	318.425	−3.780
4500	30.077	219.789	198.172	97.276	675.077	310.330	−3.602
4600	30.487	220.455	198.649	100.305	675.943	302.214	−3.432
4700	30.880	221.115	199.120	103.373	676.708	294.081	−3.268
4800	31.254	221.769	199.585	106.480	677.376	285.933	−3.112
4900	31.608	222.417	200.045	109.623	677.946	277.772	−2.961
5000	31.942	223.059	200.499	112.801	678.424	269.600	−2.816
5100	32.255	223.694	200.947	116.011	678.808	261.419	−2.677
5200	32.546	224.324	201.391	119.251	679.108	253.232	−2.544
5300	32.817	224.946	201.829	122.520	679.318	245.040	−2.415
5400	33.066	225.562	202.263	125.814	679.447	236.845	−2.291
5500	33.293	226.171	202.692	129.132	679.497	228.648	−2.172
5600	33.500	226.773	203.117	132.472	679.483	220.450	−2.056
5700	33.685	227.367	203.537	135.831	679.392	212.253	−1.945
5800	33.851	227.954	203.953	139.208	679.237	204.059	−1.838
5900	33.997	228.534	204.365	142.601	679.021	195.868	−1.734
6000	34.124	229.107	204.772	146.007	678.751	187.681	−1.634

PREVIOUS: December 1970 (1 atm) CURRENT: September 1983 (1 bar)

$S°(298.15\ K) = 241.56 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -103.9 \pm 13\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -104.6 \pm 13\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	16093.3	2
	16162.8	2
$B^2\Sigma$	16850.6	2
$C^2\Pi$	26498.9	2
	26574.7	2
$D[^2\Sigma]$	31107.8	2
$E[^2\Sigma]$	34266.4	2
$F^2\Pi$	35675	2
	35700	2
$G^2\Delta$	36705	2
	36710	2

$\omega_e = 369.8\ cm^{-1}$ $\omega_e x_e = 1.31\ cm^{-1}$ $\sigma = 1$

$B_e = 0.1516\ cm^{-1}$ $\alpha_e = [0.0007]\ cm^{-1}$ $r_e = 2.439$ Å

Enthalpy of Formation

Potter[1] investigated mass spectrometrically the gaseous equilibria among Ca, CaCl, and $CaCl_2$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the equilibrium constants $K = I(CaCl^+)^2/I(Ca^+)I(CaCl_{2+})$ which we calculate from the reported ion intensities for the reaction $Ca(g) + CaCl_2(g) \rightarrow 2\ CaCl(g)$ in the temperature range 1252–1557 K, we obtain $\Delta_r H°(298.15\ K) = 15.81$ $kcal \cdot mol^{-1}$ by the 3rd law method. The 3rd law drift is $-2.8 \pm 3.5\ cal \cdot K^{-1} \cdot mol^{-1}$. The enthalpy of formation is derived as $\Delta_f H°(CaCl, g, 298.15\ K) = -27.0\ kcal \cdot mol^{-1}$.

Zmbov[7] determined by mass spectrometry the enthalpy of the above reaction as $24.4 \pm 1.3\ kcal \cdot mol^{-1}$ with a drift of 12.5 ± 9.4 $cal \cdot K^{-1} \cdot mol^{-1}$. This yields the enthalpy of formation, $\Delta_f H°(CaCl, g, 298.15\ K) = -22.7\ kcal \cdot mol^{-1}$.

Hildenbrand[2] also determined the equilibrium constants for the reaction (a) $Ca(g) + CaCl_2(g) \rightarrow 2\ CaCl(g)$ and the reaction (b) $Ca(g) + AlCl(g) \rightarrow CaCl(g) + Al(g)$ by mass spectrometry in the temperature range 1219–1353 K. 3rd law analysis of the reported equilibrium constants gives $\Delta_r H°(298.15\ K) = 21.08\ kcal \cdot mol^{-1}$ and drift $= -1.4 \pm 1.8\ cal \cdot K^{-1} \cdot mol^{-1}$ for reaction (a); and $\Delta_r H°(298.15\ K) = 24.20$ $kcal \cdot mol^{-1}$ and drift $= 0.5 \pm 1.3\ cal \cdot K^{-1} \cdot mol^{-1}$ for reaction (b). From 3rd law $\Delta_r H°(298.15\ K)$ of (a) and (b), we derived $\Delta_f H°(CaCl, g, 298.15\ K) = -24.4$ and $-23.3\ kcal \cdot mol^{-1}$, respectively, using all JANAF functions. Hildenbrand has also derived a corrected $D°_0(Ca–Cl) = 95.0\ kcal \cdot mol^{-1}$ from a linear Birge–Sponer extrapolation of the ground state vibrational levels with correction for its ionicity. This corrected $D°_0(Ca–Cl)$ yields the enthalpy of formation, $\Delta_f H°(CaCl, g, 298.15\ K) = -23.9\ kcal \cdot mol^{-1}$.

Ryabova and Gurvich[3] reported $D°_0(Ca–Cl) = 102 \pm 6\ kcal \cdot mol^{-1}$ from flame spectra studies. This leads to $\Delta_f H°(CaCl, g, 298.15\ K) = -30.9\ kcal \cdot mol^{-1}$.

Hildenbrand[6] determined the dissociation energy of $CaCl_2(g)$ by electron impact as $\Delta_{at} H°(CaCl–Cl) = 5.04 \pm 0.02\ kcal \cdot mol^{-1}$ which, combined with JANAF $\Delta_f H°(298.15\ K)$ of $CaCl_2(g)$ and Cl(g), gives $\Delta_f H°(CaCl, g, 298.15\ K) = -23.1\ kcal \cdot mol^{-1}$.

A weighted average, $\Delta_f H°(CaCl, g, 298.15\ K) = -25 \pm 3\ kcal \cdot mol^{-1}$ ($-104.6 \pm 13\ kJ \cdot mol^{-1}$) is adopted in the tabulation.

Heat Capacity and Entropy

The vibrational constants (ω_e and $\omega_e x_e$), electronic levels and ground state configuration were taken from Herzberg.[4] Morgan and Barrow[5] made rotational analysis of the $C^2\Pi–X^2\Sigma$ system and reported $B_0 = 0.1516\ cm^{-1}$ and $r_e = 2.439$ Å for the ground state. The value of α_e is calculated from the Morse potential function. The F and G states were reported by Schutte.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.589	−103.862	−103.862	INFINITE
100	30.307	205.406	271.974	−6.657	−103.367	−112.860	58.952
200	33.959	227.636	244.777	−3.428	−103.925	−122.158	31.905
250	35.001	235.334	242.143	−1.702	−104.259	−126.679	26.468
298.15	35.665	241.559	241.559	0.	−104.600	−130.966	22.945
300	35.685	241.780	241.560	0.066	−104.613	−131.129	22.832
350	36.151	247.318	241.996	1.863	−104.982	−135.520	20.225
400	36.481	252.168	242.971	3.679	−105.370	−139.856	18.263
450	36.724	256.480	244.237	5.509	−105.791	−144.142	16.732
500	36.910	260.359	245.658	7.350	−106.250	−148.379	15.501
600	37.174	267.114	248.688	11.055	−107.303	−156.709	13.643
700	37.356	272.858	251.741	14.783	−108.551	−164.847	12.301
800	37.493	277.856	254.699	18.525	−110.852	−172.689	11.275
900	37.602	282.278	257.523	22.280	−112.483	−180.324	10.466
1000	37.693	286.245	260.200	26.045	−114.407	−187.761	9.808
1100	37.773	289.841	262.734	29.818	−116.632	−194.992	9.259
1200	37.846	293.131	265.132	33.599	−126.891	−201.384	8.766
1300	37.913	296.163	267.404	37.387	−128.489	−207.526	8.339
1400	37.976	298.975	269.560	41.182	−130.086	−213.546	7.968
1500	38.037	301.597	271.609	44.983	−131.681	−219.452	7.642
1600	38.095	304.054	273.561	48.789	−133.274	−225.252	7.354
1700	38.154	306.365	275.423	52.602	−134.866	−230.951	7.096
1800	38.213	308.548	277.203	56.420	−285.130	−234.347	6.801
1900	38.273	310.616	278.908	60.244	−285.306	−231.521	6.365
2000	38.336	312.580	280.543	64.075	−285.486	−228.685	5.973
2100	38.404	314.452	282.113	67.912	−285.673	−225.841	5.617
2200	38.477	316.241	283.624	71.756	−285.870	−222.987	5.294
2300	38.558	317.953	285.080	75.607	−286.081	−220.124	4.999
2400	38.646	319.596	286.484	79.467	−286.310	−217.251	4.728
2500	38.745	321.175	287.840	83.337	−286.562	−214.369	4.479
2600	38.854	322.697	289.152	87.217	−286.843	−211.476	4.249
2700	38.975	324.165	290.422	91.108	−287.159	−208.571	4.035
2800	39.110	325.585	291.652	95.012	−287.515	−205.654	3.837
2900	39.257	326.960	292.846	98.930	−287.919	−202.723	3.651
3000	39.418	328.294	294.006	102.864	−288.377	−199.778	3.478
3100	39.594	329.589	295.133	106.815	−288.895	−196.816	3.316
3200	39.784	330.849	296.229	110.783	−289.481	−193.837	3.164
3300	39.988	332.076	297.297	114.772	−290.140	−190.838	3.021
3400	40.207	333.273	298.338	118.782	−290.878	−187.818	2.885
3500	40.439	334.442	299.353	122.814	−291.702	−184.775	2.758
3600	40.685	335.585	300.343	126.870	−292.616	−181.707	2.637
3700	40.944	336.703	301.311	130.951	−293.625	−178.613	2.522
3800	41.215	337.799	302.257	135.059	−294.732	−175.490	2.412
3900	41.498	338.873	303.182	139.195	−295.941	−172.336	2.308
4000	41.792	339.927	304.087	143.359	−297.255	−169.150	2.209
4100	42.096	340.963	304.974	147.553	−298.674	−165.930	2.114
4200	42.409	341.981	305.843	151.779	−300.200	−162.674	2.023
4300	42.731	342.983	306.695	156.035	−301.833	−159.381	1.936
4400	43.060	343.969	307.531	160.325	−303.568	−156.048	1.853
4500	43.396	344.940	308.352	164.648	−305.394	−152.676	1.772
4600	43.738	345.898	309.158	169.004	−307.326	−149.262	1.695
4700	44.086	346.842	309.949	173.396	−309.360	−145.804	1.620
4800	44.438	347.774	310.728	177.822	−311.487	−142.302	1.549
4900	44.793	348.694	311.493	182.283	−313.703	−138.754	1.479
5000	45.151	349.602	312.246	186.780	−316.001	−135.161	1.412
5100	45.511	350.500	312.988	191.314	−318.378	−131.520	1.347
5200	45.873	351.387	313.717	195.883	−320.823	−127.833	1.284
5300	46.235	352.264	314.436	200.488	−323.336	−124.098	1.223
5400	46.597	353.132	315.145	205.130	−325.909	−120.315	1.164
5500	46.958	353.990	315.844	209.807	−328.535	−116.483	1.106
5600	47.317	354.840	316.532	214.521	−331.196	−112.605	1.050
5700	47.675	355.680	317.212	219.271	−333.905	−108.677	0.996
5800	48.029	356.513	317.882	224.056	−336.646	−104.702	0.943
5900	48.381	357.337	318.544	228.877	−339.413	−100.679	0.891
6000	48.729	358.153	319.197	233.732	−342.199	−96.610	0.841

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 104.6 \pm 4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1045\ K$

$\Delta_f H°(0\ K) = -796.3 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -795.8 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 28.543 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Parker[1] has selected the standard enthalpy of formation at 298.15 K as −190.2 kcal·mol^{-1} (−795.797 kJ·mol^{-1}) which is adopted in the tabulation. The enthalpy of formation was derived from two independent paths. The first path involves $\Delta_f H°(Ca^{++}, aq, \infty, 298.15\ K) = -129.74$ kcal·mol^{-1},[1] $\Delta_f H°(Cl^-, aq, \infty, 298.15\ K) = -39.952$ kcal·mol^{-1} [2] and the enthaply of solution of $CaCl_2$(cr) in water.[3-7] The second path involves the enthalpies of reaction of Ca(cr), CaO(cr) and $CaCl_2$(cr) in aqueous HCl solution.[4,8-20]

Heat Capacity and Entropy

Kelley and Moore[21] measured the low temperature heat capacities in the temperature range from 52.6 to 295.1 K and made an extrapolation to 0 K which yielded an entropy of 4.59 ± 0.4 cal·K^{-1}·mol^{-1} at 50.12 K. We have adopted the measured heat capacities, but made our own extrapolation to 0 K by comparison with the measured heat capacities of $BaCl_2$(cr)[22] and $SrCl_2$(cr)[23] from 6 to 50 K. The extrapolation gives $S°(50\ K) = 2.45 \pm 1$ cal·K^{-1}·mol^{-1}, which is used in the table. Moore[24] measured high temperature enthalpy data from 403.7 to 1667 K by drop calorimetry. The low temperature heat capacities and the heat capacities from the high temperature enthalpy data are smoothly joined at 298.15 K. The deviations of the observed enthalpies from the adopted values are about 2% near 400–500 K and only a few tenths percent at higher temperatures. Dworkin and Bredig[25] determined drop–calorimetrically $H°(1045\ K) - H°(298.15\ K) = 14.3$ kcal·mol^{-1}, which is in very good agreement with the adopted value of 14.2 kcal·mol^{-1}.

Fusion Data

The adopted melting point 1045 K was determined by Tokareva.[26] Dworkin and Bredig[25] determined the enthalpy of fusion $\Delta_{fus} H°(1045\ K) = 6.78 \pm 0.1$ kcal·mol^{-1} by drop calorimetry. Chiotti *et al.*[27] also measured the enthalpy of fusion $\Delta_{fus} H°(1055\ K) = 6.79 \pm 0.2$ kcal·mol^{-1} in an adiabatic calorimeter. The adopted enthalpy of fusion, 6.822 kcal·mol^{-1} (28.543 kJ·mol^{-1}), is calculated from the difference between the observed relative enthalpy of the liquid and the adopted value for the crystal at the melting point.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $CaCl_2$(cr) and $CaCl_2$(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.391	−796.270	−796.270	INFINITE
100	48.812	35.596	164.875	−12.928	−797.700	−780.762	407.828
200	67.357	76.550	111.119	−6.914	−796.992	−764.012	199.539
298.15	72.856	104.602	104.602	0.	−795.797	−748.073	131.059
300	72.927	105.053	104.603	0.135	−795.773	−747.777	130.200
400	75.647	126.448	107.502	7.578	−794.434	−731.979	95.587
500	77.153	143.502	113.054	15.224	−793.125	−716.519	74.854
600	78.199	157.663	119.342	22.992	−791.931	−701.312	61.055
700	79.370	169.801	125.704	30.868	−790.866	−686.294	51.212
800	80.919	180.495	131.897	38.878	−790.750	−671.318	43.833
900	83.094	190.145	137.841	47.074	−789.800	−656.447	38.099
1000	85.772	199.033	143.521	55.512	−788.919	−641.678	33.518
1045.000	87.090	202.837	145.994	59.401	--- CRYSTAL <--> LIQUID ---		
1100	88.701	207.345	148.950	64.236	−788.069	−626.995	29.774
1200	91.630	215.189	154.146	73.252	−794.974	−611.767	26.630
1300	94.558	222.639	159.130	82.561	−792.937	−596.580	23.971
1400	97.487	229.754	163.922	92.164	−790.616	−581.561	21.698
1500	100.416	236.579	168.540	102.059	−788.012	−566.717	19.735
1600	103.345	243.154	172.999	112.247	−785.124	−552.057	18.023
1700	106.274	249.507	177.314	122.728	−781.951	−537.586	16.518
1800	109.202	255.664	181.497	133.502	−927.169	−521.099	15.122
1900	112.131	261.647	185.558	144.568	−922.016	−498.679	13.710
2000	115.060	267.473	189.509	155.928	−916.586	−476.537	12.446

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = [123.868]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1045\ K$

$\Delta_f H°(298.15\ K) = [-774.094]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 28.543 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding the enthalpy of melting and the difference in enthalpy, $H°(1045\ K)-H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

The constant heat capacity above the assumed glass transition at 700 K is derived from high temperature enthalpy data in a drop calorimeter from the melting point up to 1667 K by Moore.[1] Below the glass transition point, the heat capacity is assumed to be the same as that of the crystal. Dworkin and Bredig[2] reported $C_p°(l) = 23.6\ cal·K^{-1}·mol^{-1}$ from enthalpy measurements in a short temperature range by drop calorimetry.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point, T_{vap}, is calculated as the temperature at which $\Delta_r G = 0$ for $CaCl_2(l) \rightarrow CaCl_2(g)$ at one bar. The enthalpy of vaporization is the difference in $\Delta_f H°$ at T_{vap} between liquid and gas.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	72.856	123.868	123.868	0.	−774.094	−732.115	128.264
300	72.927	124.319	123.869	0.135	−774.070	−731.855	127.427
400	75.647	145.714	126.768	7.578	−772.732	−717.983	93.759
500	77.153	162.768	132.320	15.224	−771.423	−704.449	73.593
600	78.199	176.929	138.608	22.992	−770.229	−691.169	60.172
700	79.370	189.067	144.970	30.868	−769.164	−678.078	50.599
700.000	79.370	189.067	144.970	30.868	GLASS <--> LIQUID		
700.000	102.533	189.067	144.970	30.868	TRANSITION		
800	102.533	202.759	151.357	41.121	−766.804	−665.184	43.432
900	102.533	214.835	157.752	51.375	−763.797	−652.665	37.880
1000	102.533	225.638	164.010	61.628	−761.101	−640.465	33.454
1045.000	102.533	230.151	166.762	66.242	--- CRYSTAL <--> LIQUID ---		
1100	102.533	235.411	170.064	71.881	−758.720	−628.519	29.846
1200	102.533	244.332	175.887	82.135	−764.389	−616.153	26.820
1300	102.533	252.539	181.472	92.388	−761.408	−603.921	24.266
1400	102.533	260.138	186.822	102.641	−758.436	−591.918	22.085
1500	102.533	267.212	191.949	112.895	−755.474	−580.128	20.202
1600	102.533	273.829	196.862	123.148	−752.520	−568.534	18.561
1700	102.533	280.045	201.574	133.401	−749.576	−557.126	17.118
1800	102.533	285.906	206.098	143.655	−895.314	−543.679	15.777
1900	102.533	291.449	210.445	153.908	−890.974	−524.262	14.413
2000	102.533	296.709	214.628	164.161	−886.650	−505.073	13.191
2100	102.533	301.711	218.657	174.415	−882.345	−486.100	12.091
2200	102.533	306.481	222.541	184.668	−878.063	−467.332	11.096
2300	102.533	311.039	226.291	194.921	−873.809	−448.758	10.192
2400	102.533	315.403	229.913	205.174	−869.590	−430.368	9.367
2500	102.533	319.588	233.417	215.428	−865.410	−412.153	8.611
2600	102.533	323.610	236.809	225.681	−861.279	−394.104	7.918
2700	102.533	327.479	240.096	235.934	−857.203	−376.214	7.278
2800	102.533	331.208	243.284	246.188	−853.189	−358.473	6.687
2900	102.533	334.806	246.378	256.441	−849.247	−340.874	6.140
3000	102.533	338.282	249.384	266.694	−845.384	−323.410	5.631

PREVIOUS: CURRENT: June 1970

0	to 1045	K	crystal
above	1045	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.391	−796.270	−796.270	INFINITE
100	48.812	35.596	164.875	−12.928	−797.700	−780.762	407.828
200	67.357	76.550	111.119	−6.914	−796.992	−764.012	199.539
298.15	72.856	104.602	104.602	0.	−795.797	−748.073	131.059
300	72.927	105.053	104.603	0.135	−795.773	−747.777	130.200
400	75.647	126.448	107.502	7.578	−794.434	−731.979	95.587
500	77.153	143.502	113.054	15.224	−793.125	−716.519	74.854
600	78.199	157.663	119.342	22.992	−791.931	−701.312	61.055
700	79.370	169.801	125.704	30.868	−790.866	−686.294	51.212
800	80.919	180.495	131.897	38.878	−790.750	−671.318	43.833
900	83.094	190.145	137.841	47.074	−789.800	−656.447	38.099
1000	85.772	199.033	143.521	55.512	−788.919	−641.678	33.518
1045.000	87.090	202.837	145.994	59.401	CRYSTAL <--> LIQUID		
1045.000	102.533	230.151	145.994	87.944	TRANSITION		
1100	102.533	235.411	150.335	93.584	−758.720	−628.519	29.846
1200	102.533	244.332	157.801	103.837	−764.389	−616.153	26.820
1300	102.533	252.539	164.777	114.090	−761.408	−603.921	24.266
1400	102.533	260.138	171.321	124.344	−758.436	−591.918	22.085
1500	102.533	267.212	177.480	134.597	−755.474	−580.128	20.202
1600	102.533	273.829	183.298	144.850	−752.520	−568.534	18.561
1700	102.533	280.045	188.808	155.104	−749.576	−557.126	17.118
1800	102.533	285.906	194.041	165.357	−895.314	−543.679	15.777
1900	102.533	291.449	199.023	175.610	−890.974	−524.262	14.413
2000	102.533	296.709	203.777	185.864	−886.650	−505.073	13.191
2100	102.533	301.711	208.322	196.117	−882.345	−486.100	12.091
2200	102.533	306.481	212.677	206.370	−878.063	−467.332	11.096
2300	102.533	311.039	216.855	216.623	−873.809	−448.758	10.192
2400	102.533	315.403	220.871	226.877	−869.590	−430.368	9.367
2500	102.533	319.588	224.736	237.130	−865.410	−412.153	8.611
2600	102.533	323.610	228.462	247.383	−861.279	−394.104	7.918
2700	102.533	327.479	232.058	257.637	−857.202	−376.214	7.278
2800	102.533	331.208	235.533	267.890	−853.189	−358.473	6.687
2900	102.533	334.806	238.895	278.143	−849.247	−340.874	6.140
3000	102.533	338.282	242.150	288.397	−845.384	−323.410	5.631

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = 290.3 \pm 8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -471.7 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -471.5 \pm 4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[217](1)
64 (2)
402 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Ca–Cl – 2.51 Å
Bond Angle: Cl–Ca–Cl = 180°
Rotational Constant: $B_0 = 0.037737\ cm^{-1}$

Enthalpy of Formation

2nd and 3rd law analyses of vapor pressure data are given below. The selected 3rd law enthalpy of vaporization is taken from Novikov's measurement[1] as $\Delta_{vap}H°(298.15\ K) = 72.30\ kcal \cdot mol^{-1}$ which is combined with $\Delta_f H°(298.15\ K)$ of the liquid to give $\Delta_f H°(CaCl_2, g, 298.15\ K) = -112.7 \pm 1\ kcal \cdot mol^{-1}$ ($-471.5 \pm 4\ kJ \cdot mol^{-1}$).

3rd law analyses indicate zero dirft for Novikov's data, positive and negative drifts for Hildenbrand's [2] and Bautista's[3] data, respectively. Their enthalpies are in good agreement within ±1 kcal. Wartenberg[4] reported there was no boiling at 1819 K at 62 mm Hg pressure, and his value, $\Delta_{vap}H°(298.15\ K) = 71.1 \pm 0.7\ kcal \cdot mol^{-1}$, serves as a guide for the minimum enthalpy of vaporization.

Source	Method	T/K	Data Points	$\Delta_{vap}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Bautista and Margrave[3]	Langmuir	952–993	7	75.25 (80.34)*	73.39 (78.57)*	−1.7 ± 6.9
Hildenbrand and Potter[2]	Torsion Effusion 0.0096 cm^2 Orifice	1142–1228	12	64.99	71.24	5.3 ± 0.4
Hildenbrand and Potter[2]	Torsion Effusion 0.015 cm^2 Orifice	1111–1281	17	68.71	71.24	2.0 ± 0.2
Hildenbrand and Potter[2]	Torsion Effusion Combined	1111–1281	29	68.91	71.24	2.4 ± 0.3
Dewing[5]	Knudsen Effusion	1069–1225	4	59.37	71.03	10.2 ± 1.6
Wartenberg and Bosse[4]	Boiling Point	1819	1	—	>71.10	—
Novikov and Gavryuchenkov[1]	Boiling Point	1591–1701	5	72.25	72.30	0.0 ± 1.2
Lukashenko and Reutova[10]	Langmuir	973–1023	6	78.0	69.01	−9.0
	Knudsen Effusion	1073–1273	6	61.8	69.78	+8.0

*Value in parentheses is the enthalpy of sublimation.

Heat Capacity and Entropy

The linear structure and vibrational frequencies were determined by White and co–workers[6] in the matrix–infrared– spectrometric studies. The linear structure is consistent with experimental error with the electric–quadrupole–deflection studies,[7] and electron–diffraction data.[8] Hayes[9] has qualitatively rationalized the linear structure through molecular orbital theory. The bond length was measured by Akishin and Spiridonov.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−15.118	−471.738	−471.738	INFINITE
100	49.371	230.265	340.874	−11.061	−471.573	−474.102	247.646
200	56.575	267.082	295.620	−5.708	−471.526	−476.652	124.489
250	58.277	279.904	291.236	−2.833	−471.520	−477.934	99.859
298.15	*59.325*	290.265	290.265	0.	−471.537	−479.169	83.948
300	59.357	290.632	290.266	0.110	−471.538	−479.216	83.439
350	60.073	299.839	290.991	3.097	−471.576	−480.493	71.710
400	60.566	307.895	292.611	6.113	−471.639	−481.763	62.912
450	60.919	315.050	294.714	9.151	−471.740	−483.023	56.068
500	61.178	321.482	297.075	12.204	−471.885	−484.269	50.591
600	61.525	332.670	302.102	18.340	−472.323	−486.708	42.372
700	61.740	342.171	307.165	24.504	−472.970	−489.057	36.494
800	61.882	350.425	312.068	30.686	−474.682	−491.195	32.072
900	61.980	357.720	316.743	36.879	−475.734	−493.199	28.625
1000	62.051	364.254	321.173	43.081	−477.090	−495.070	25.860
1100	62.104	370.171	325.363	49.289	−478.755	−496.790	23.591
1200	62.144	375.577	329.325	55.502	−488.464	−497.722	21.665
1300	62.175	380.552	333.077	61.718	−489.521	−498.451	20.028
1400	62.200	385.161	336.635	67.936	−490.584	−499.098	18.622
1500	62.221	389.453	340.014	74.158	−491.653	−499.669	17.400
1600	62.237	393.469	343.231	80.380	−492.730	−500.168	16.329
1700	62.251	397.242	346.298	86.605	−493.814	−500.600	15.382
1800	62.262	400.801	349.228	92.831	−643.580	−498.756	14.474
1900	62.272	404.168	352.032	99.057	−643.267	−490.719	13.491
2000	62.281	407.362	354.719	105.285	−642.969	−482.698	12.607
2100	62.288	410.401	357.299	111.513	−642.688	−474.692	11.807
2200	62.294	413.299	359.779	117.742	−642.431	−466.698	11.081
2300	62.299	416.068	362.167	123.972	−642.201	−458.715	10.418
2400	62.304	418.719	364.468	130.202	−642.004	−450.742	9.810
2500	62.308	421.263	366.690	136.433	−641.847	−442.776	9.251
2600	62.312	423.707	368.836	142.664	−641.738	−434.816	8.736
2700	62.315	426.058	370.912	148.895	−641.684	−426.858	8.258
2800	62.318	428.325	372.922	155.127	−641.692	−418.902	7.815
2900	62.321	430.512	374.871	161.359	−641.771	−410.944	7.402
3000	62.324	432.624	376.761	167.591	−641.929	−402.982	7.017
3100	62.326	434.668	378.596	173.824	−642.175	−395.013	6.656
3200	62.328	436.647	380.379	180.056	−642.514	−387.035	6.318
3300	62.330	438.565	382.113	186.289	−642.956	−379.045	6.000
3400	62.331	440.426	383.801	192.522	−643.506	−371.039	5.700
3500	62.333	442.232	385.445	198.756	−644.172	−363.016	5.418
3600	62.334	443.988	387.047	204.989	−644.958	−354.972	5.151
3700	62.335	445.696	388.609	211.222	−645.869	−346.905	4.897
3800	62.337	447.359	390.133	217.456	−646.910	−338.811	4.657
3900	62.338	448.978	391.622	223.690	−648.084	−330.688	4.429
4000	62.339	450.556	393.075	229.923	−649.393	−322.534	4.212
4100	62.340	452.095	394.496	236.157	−650.838	−314.344	4.005
4200	62.340	453.598	395.885	242.391	−652.420	−306.119	3.807
4300	62.341	455.065	397.245	248.625	−654.138	−297.853	3.618
4400	62.342	456.498	398.575	254.860	−655.989	−289.547	3.437
4500	62.343	457.899	399.878	261.094	−657.958	−281.198	3.264
4600	62.343	459.269	401.154	267.328	−660.063	−272.802	3.098
4700	62.344	460.610	402.405	273.563	−662.296	−264.360	2.938
4800	62.345	461.922	403.631	279.797	−664.650	−255.868	2.784
4900	62.345	463.208	404.834	286.031	−667.119	−247.327	2.637
5000	62.346	464.467	406.014	292.266	−669.696	−238.734	2.494
5100	62.346	465.702	407.173	298.501	−672.377	−230.088	2.357
5200	62.347	466.913	408.310	304.735	−675.151	−221.389	2.224
5300	62.347	468.100	409.427	310.970	−678.018	−212.636	2.096
5400	62.347	469.266	410.524	317.205	−680.968	−203.827	1.972
5500	62.348	470.410	411.603	323.439	−683.993	−194.963	1.852
5600	62.348	471.533	412.663	329.674	−687.077	−186.045	1.735
5700	62.348	472.637	413.705	335.909	−690.230	−177.070	1.623
5800	62.349	473.721	414.731	342.144	−693.437	−168.040	1.513
5900	62.349	474.787	415.740	348.379	−696.690	−158.953	1.407
6000	62.349	475.835	416.732	354.614	−699.982	−149.812	1.304

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 229.65 \pm 0.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -271 \pm 8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -272 \pm 8\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A^2\Pi$	16482	2
	16557	2
$B^2\Sigma$	18844	2
$C^2\Pi$	30256	2
	30285	2
$D^2\Sigma$	30772	2
$E^2\Sigma$	34135	2
$F^2\Pi$	37548	4

$\omega_e = 587.1\ cm^{-1}$ $\omega_e x_e = 2.74\ cm^{-1}$ $\sigma = 1$
$B_e = 0.3225\ cm^{-1}$ $\alpha_e = [0.0020]\ cm^{-1}$ $r_e = 2.01$ Å

Enthalpy of Formation

Hastie and Margrave[1] have recently reviewed the dissociation energy of CaF and conclude that it is 127.5 ± 2.5 kcal·mol^{-1}. The analysis below considers basically the same data except that all values are JANAF.

Hildenbrand and Murad[2] in a mass spectrometric determination of the equilibria among BF, BF_3, Ca, CaF and CaF_2 reported equilibrium constants for the reaction

(A) $Ca(g) + CaF_2(g) \rightarrow 2CaF(g)$.

Blue *et al.*[3] have also examined several equilibria mass-spectrometrically and report equilibrium constants for reaction

(B) $Ca(g) + CaF_2(cr) \rightarrow 2CaF(g)$ and reaction

(C) $Ca(g) + AlF(g) \rightarrow Al(g) + CaF(g)$.

Ryabova and Gurvich [4] give a enthalpy of dissociation from flame studies for the reaction

(D) $CaF(g) \rightarrow Ca(g) + F(g)$.

The remaining reactions considered by Hastie and Margrave[1] were not included since they involved subtracting reactions not performed simultaneously, or involve species such as SiF_2 whose enthalpy of formation is dependent on that of CaF and CaF_2.

Source	T/K	Reaction	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Hildenbrand[2]	1583–1734	A	15	11.5 ± 6.8	14.70 ± 1.27	2.2 ± 4.1	−65.5 ± 1.8
Blue[3]	1271–1351	B	9	146.9 ± 8.0	121.08 ± 1.65	−19.4 ± 6.2	−64.5 ± 1.7
Blue[3]	1271–1351	C	10*	34.6 ± 3.5	32.87 ± 0.47	−1.4 ± 2.7	−65.7 ± 3.2
Ryobova[4]		D		135 ± 7			−73.3 ± 7
Hildenbrand[5]	1423–1443	A	2		32.97		−65.6 ± 3.2

*1 point rejected due to failure of a statistical test

The auxiliary enthalpies of formation used were, in kcal·mol^{-1}, AlF(g) = −63.4, Al(g) = 78, $CaF_2(g)$ = −187.5, $CaF_2(cr)$ = −293.0 and Ca(g) = 42.85.

We adopt a median value of $\Delta_f H°(CaF, g, 298.15\ K) = -65 \pm 2$ kcal·mol^{-1} (−271.960 ± 8 kJ·mol^{-1}) which corresponds to an enthalpy of dissociation of 126.7 ± 2 kcal·mol^{-1}.

Heat Capacity and Entropy

Herzberg[6] gives the vibrational constants and electronic levels. Harvey[7] has reported a value for B_0 which corresponds to a bond length of 2.02 Å. The Morse potential function was used to calculate α_e.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.130	−270.942	−270.942	INFINITE
100	29.245	195.821	258.018	−6.220	−270.465	−279.932	146.221
200	31.424	216.653	232.661	−3.201	−271.180	−289.148	75.518
250	32.678	223.804	230.196	−1.598	−271.578	−293.593	61.343
298.15	33.661	229.647	229.647	0.	−271.960	−297.799	52.173
300	33.695	229.855	229.648	0.062	−271.975	−297.959	51.879
350	34.477	235.111	230.061	1.767	−272.370	−302.259	45.110
400	35.075	239.756	230.988	3.507	−272.775	−306.501	40.025
450	35.534	243.914	232.197	5.273	−273.205	−310.692	36.064
500	35.893	247.678	233.560	7.059	−273.671	−314.832	32.890
600	36.409	254.271	236.478	10.676	−274.733	−322.968	28.117
700	36.755	259.911	239.432	14.335	−275.989	−330.910	24.693
800	37.002	264.836	242.307	18.023	−278.299	−338.555	22.105
900	37.188	269.205	245.057	21.733	−279.942	−345.991	20.081
1000	37.335	273.131	247.672	25.460	−281.881	−353.229	18.451
1100	37.454	276.695	250.151	29.199	−284.124	−360.258	17.107
1200	37.556	279.959	252.500	32.950	−294.406	−366.446	15.951
1300	37.644	282.968	254.730	36.710	−296.031	−372.384	14.963
1400	37.722	285.761	256.848	40.478	−297.658	−378.196	14.111
1500	37.793	288.366	258.863	44.254	−299.287	−383.892	13.368
1600	37.860	290.807	260.784	48.037	−300.919	−389.479	12.715
1700	37.922	293.104	262.619	51.826	−302.552	−394.964	12.136
1800	37.983	295.274	264.373	55.621	−452.861	−398.142	11.554
1900	38.043	297.329	266.054	59.423	−453.082	−395.096	10.862
2000	38.103	299.282	267.667	63.230	−453.307	−392.038	10.239
2100	38.165	301.142	269.217	67.043	−453.537	−388.969	9.675
2200	38.230	302.919	270.709	70.863	−453.772	−385.889	9.162
2300	38.300	304.620	272.147	74.689	−454.016	−382.798	8.694
2400	38.375	306.252	273.534	78.523	−454.268	−379.697	8.264
2500	38.457	307.820	274.874	82.364	−454.533	−376.584	7.868
2600	38.548	309.330	276.170	86.215	−454.814	−373.460	7.503
2700	38.647	310.787	277.426	90.074	−455.115	−370.326	7.164
2800	38.757	312.194	278.642	93.944	−455.440	−367.180	6.850
2900	38.877	313.556	279.823	97.826	−455.794	−364.021	6.557
3000	39.009	314.876	280.970	101.720	−456.183	−360.850	6.283
3100	39.153	316.158	282.084	105.628	−456.612	−357.666	6.027
3200	39.309	317.403	283.168	109.551	−457.089	−354.466	5.786
3300	39.476	318.615	284.224	113.490	−457.618	−351.251	5.560
3400	39.657	319.797	285.253	117.447	−458.207	−348.019	5.347
3500	39.849	320.949	286.257	121.422	−458.860	−344.769	5.145
3600	40.053	322.074	287.236	125.417	−459.585	−341.499	4.955
3700	40.269	323.175	288.193	129.433	−460.387	−338.208	4.775
3800	40.496	324.251	289.127	133.471	−461.269	−334.895	4.603
3900	40.734	325.306	290.042	137.533	−462.238	−331.556	4.441
4000	40.982	326.341	290.936	141.619	−463.297	−328.192	4.286
4100	41.239	327.356	291.812	145.730	−464.448	−324.801	4.138
4200	41.506	328.353	292.670	149.867	−465.695	−321.380	3.997
4300	41.781	329.333	293.512	154.031	−467.038	−317.928	3.862
4400	42.063	330.296	294.337	158.223	−468.476	−314.444	3.733
4500	42.352	331.245	295.146	162.444	−469.996	−310.927	3.609
4600	42.648	332.179	295.941	166.694	−471.619	−307.375	3.490
4700	42.949	333.099	296.722	170.974	−473.338	−303.786	3.376
4800	43.254	334.007	297.489	175.284	−475.149	−300.160	3.266
4900	43.564	334.902	298.244	179.625	−477.046	−296.495	3.161
5000	43.878	335.785	298.986	183.997	−479.026	−292.790	3.059
5100	44.194	336.657	299.716	188.400	−481.086	−289.045	2.960
5200	44.512	337.518	300.435	192.835	−483.215	−285.259	2.865
5300	44.831	338.369	301.142	197.303	−485.417	−281.432	2.774
5400	45.152	339.210	301.840	201.802	−487.682	−277.562	2.685
5500	45.473	340.042	302.527	206.333	−490.004	−273.649	2.599
5600	45.793	340.864	303.204	210.896	−492.368	−269.695	2.516
5700	46.112	341.677	303.872	215.492	−494.785	−265.698	2.435
5800	46.430	342.482	304.531	220.119	−497.242	−261.657	2.356
5900	46.747	343.278	305.181	224.778	−499.731	−257.574	2.280
6000	47.060	344.067	305.822	229.468	−502.247	−253.448	2.206

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 68.572 \pm 0.33\ J·K^{-1}·mol^{-1}$
$T_{trs} = 1424 \pm 20\ K\ (\alpha–\beta)$
$T_{fus} = 1691 \pm 5\ K$

$\Delta_f H°(0\ K) = -1223.0 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1225.9 \pm 6.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 4.770 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 29.706 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

Torgeson and Sahama[1] measured the enthalpy of solution of CaO in aqueous 20.1% HF as -54.96 ± 0.02 kcal·mol^{-1}. Using $\Delta_f H°$(CaO, cr, 298.15 K) = -151.79 kcal·mol^{-1},[2] $\Delta_f H°(H_2O, l, 298.15\ K) = -68.317$ kcal·mol^{-1}[3] and $\Delta_f H°$(HF4.4H_2O, 298.15 K) = -76.60 kcal·mol^{-1}, we obtain $\Delta_f H°(CaF_2, cr, 298.15\ K) = -291.6 \pm 0.6$ kcal·mol^{-1}.

Smyshlyaev and Edeleva[5] report the solubility product of CaF_2 as $2.7 \pm 0.27 \times 10^{-11}$ in dilute HCl, which yields $\Delta G°(298.15\ K) = 14.42$ kcal·mol^{-1} for the reaction $CaF_2(cr) \rightarrow Ca^{++}(aq, \infty) + 2F^-(aq, \infty)$. Using $\Delta_f G°(Ca^{++}, aq, \infty, 298.15\ K) = -132.30$ kcal·mol^{-1}[2] and $\Delta_f G°(F^-, aq, \infty, 298.15\ K) = -66.95$ kcal·mol^{-1} [4] we obtain $\Delta_f G°(CaF_2, cr, 298.15\ K) = -280.64 \pm 0.6$ kcal·mol^{-1}, which, using the adopted functions, yields $\Delta_f H°(CaF_2, cr, 298.15\ K) = -293.1 \pm 0.6$ kcal·mol^{-1}.

Vecher and Vecher[17] have measured the emf of a high temperature solid state cell and report $\Delta_r G°(1200) = -17.6 \pm 0.2$ kcal·mol^{-1} for the reaction $CaO(cr) + MgF_2(cr) \rightarrow CaF_2(cr) + MgO(cr)$. This reduces to $\Delta_f H°(298.15\ K) = -17.6$ kcal·mol^{-1}, using JANAF values for MgO and MgF_2 and CaO from reference 2, yields $\Delta_f H°(CaF_2, cr, 298.15\ K) = -294.4 \pm 1.3$ kcal·mol^{-1}.

Kohlrauch[18] reported the solubility of CaF_2 and fluorspar, which yield solubility products of 3.6×10^{-11} and 2.8×10^{-11} From these we obtain, as above, $\Delta_f H°(CaF_2, cr, 298.15\ K) = -292.9$ and -293.1 kcal·mol^{-1}.

Guntz[19] made measurements on the neutralization of $Ca(OH)_2$(aq) and HF(aq) which yield $\Delta_f H°(CaF_2, cr, 298.15\ K) = -293.1$ kcal·mol^{-1}, according to Parker.[2]

A median value of $\Delta_f H°(CaF_2, cr, 298.15\ K) = -293 \pm 1.5$ kcal·mol^{-1} (-1225.912 ± 6.3 kJ·mol^{-1}) is adopted.

Heat Capacity and Entropy

Huffman and Norwood[6] have measured the low temperature heat capacity in the range 3.6 to 30 K, Eucken and Schwers[7] in the range 17 to 86 K and Todd[8] from 54 to 296.5 K. We have fitted a smooth polynomial curve through the data of references 6 and 8 and this yields $S°(298.15\ K) = 16.38 \pm 0.08$ cal·K^{-1}·mol^{-1} based on $S°(3.6\ K) = 0.0002$ cal·K^{-1}·mol^{-1}. The values of reference 7 deviate considerably at the lowest temperatures but are in reasonable agreement at higher temperatures.

The high temperature enthalpy of calcium fluoride has been reported by Naylor[9] to 1789 K, Krestnikov and Karetnikov[10] to 1273 K, and Lyashenko[11] to 1490 K. All the data are in approximate agreement and the more extensive results of Naylor on a very pure sample are adopted. The heat capacities, below 1424 K, were derived from a polynomial fit of the enthalpy data of the form $H = aT^2 + bT + c + d/T + e/T^2$.

Transition Data

The temperature of transition is that reported by Naylor,[9] the large uncertainty has been assigned since at 1424 K the enthalpies indicate complete conversion to β–CaF_2, and the next lower point is at 1402 K. Evidence in support of a transition in this region comes from Lyashenko[11] whose plot indicates a break between 1273 and 1413 K. In addition, $SrCl_2$ which has the fluorite structure has a transition near the melting point. The enthalpy of transition is that reported by Naylor.[9]

Fusion Data

McCreary[12] reports the melting point of a 99.1% pure sample as 1687 ± 5 K. Porter and Brown[13] report 1675 ± 5 K as the melting point of 99.8% pure CaF_2 and Rogers *et al.*[14] obtained 1684 K as the melting point. The adopted melting point, 1691 ± 5 K, for a sample of natural fluorite of high purity, was reported by Naylor.[9] The enthalpy of melting, 7100 kcal·mol^{-1} (29.706 kJ m$_{\mu}$uccirclol^{-1}), is that measured by Naylor.[9] Three determinations from high temperature phase diagrams give 7250 ± 350 cal·mol^{-1},[15] 5500 cal·mol^{-1},[16] and 9800 cal·mol^{-1}.[14]

Sublimation Data

Refer to the ideal gas table for details.

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[1]D. R. Torgeson and T. G. Sahama, J. Amer. Chem. Soc. **70**, 2156 (1948).
[2]V. B. Parker, Nat. Bur. Stand., personal communication, (January 1969).
[3]U. S. Nat. Bur. Stand. Tech. Note 270–3, 264 pp. (1968).
[4]Consistent with the JANAF HF(g) value.
[5]S. I. Smyshlaev and N. P. Edeleva, Izv. Vysshykh Uchebn. Zavedenii, Khim. i Khim. Tekhol. **5**, 871 (1962).
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[7]A. Eucken and F. Schwers, Ber. Deut. Physik. Ges. **15**, 578 (1913).
[8]S. S. Todd, J. Amer. Chem. Soc. **71**, 4115 (1949).
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[10]A. N. Krestnikov and G. A. Karetnikov, Legkie Metal. **3**, 29 (1934) and **4**, 16 (1935).
[11]V. S. Lyashenko, Metallurg. **10**, 85 (1935).

Continued on page 736

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.655	−1223.006	−1223.006	INFINITE
100	28.619	13.347	120.374	−10.703	−1225.941	−1208.642	631.330
200	56.769	43.555	74.450	−6.179	−1226.615	−1190.898	311.031
298.15	68.588	68.572	68.572	0.	−1225.912	−1173.496	205.592
300	68.772	68.997	68.574	0.127	−1225.891	−1173.171	204.267
400	73.864	89.630	71.353	7.311	−1224.561	−1155.791	150.931
500	76.220	106.375	76.736	14.819	−1223.184	−1138.759	118.965
600	78.517	120.471	82.880	22.554	−1221.865	−1121.999	97.679
700	81.090	132.764	89.146	30.532	−1220.577	−1105.456	82.490
800	83.918	143.774	95.298	38.781	−1220.132	−1088.995	71.104
900	86.952	153.832	101.251	47.323	−1218.769	−1072.684	62.257
1000	90.128	163.157	106.981	56.177	−1217.427	−1056.525	55.187
1100	93.412	171.901	112.489	65.353	−1216.093	−1040.499	49.409
1200	96.780	180.172	117.788	74.862	−1222.490	−1023.973	44.572
1300	100.207	188.054	122.892	84.711	−1219.910	−1007.532	40.483
1400	103.680	195.607	127.818	94.905	−1217.007	−991.302	36.986
1424.000	104.520	197.376	128.975	97.403	ALPHA <--> BETA		
1424.000	122 .884	200.726	128.975	102.173	TRANSITION		
1500	123.679	207.136	132.774	111.542	−1207.680	−975.581	33.973
1600	124.725	215.151	137.675	123.963	−1202.588	−960.273	31.350
1691.000	125.677	222.077	142.032	135.356	---- BETA <--> LIQUID		----
1700	125.771	222.744	142.457	136.487	−1197.409	−945.287	29.045
1800	126.817	229.962	147.120	149.117	−1340.813	−928.397	26.941
1900	127.863	236.847	151.663	161.851	−1334.037	−905.669	24.899
2000	128.909	243.432	156.088	174.689	−1327.172	−883.301	23.069
2100	129.955	249.747	160.398	187.633	−1320.215	−861.278	21.423
2200	131.001	255.817	164.598	200.680	−1313.168	−839.589	19.934
2300	132.047	261.663	168.692	213.833	−1306.029	−818.222	18.582
2400	133.093	267.305	172.684	227.090	−1298.800	−797.167	17.350
2500	134.139	272.759	176.579	240.451	−1291.482	−776.416	16.222
2600	135.185	278.041	180.380	253.918	−1284.078	−755.959	15.187
2700	136.231	283.162	184.092	267.488	−1276.591	−735.789	14.235

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K)$ = [92.573] $J·K^{-1}·mol^{-1}$
T_{fus} = 1691 ± 5 K

$\Delta_fH°(298.15\ K)$ = [−1186.067] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 29.706 ± 0.4 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(CaF_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and difference in enthalpy, $H°(1691\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived from the enthalpy measurements of Naylor.[1] The heat capacity is constant in the real liquid range but at 1000 K a glass transition is assumed below which it follows that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization data

The boiling point, T_{vap}, is calculated as the temperature at which the fugacity of $CaF_2(g)$ is one bar for the process $CaF_2(l) = CaF_2(g)$. The enthalpy of vaporization is the difference in $\Delta_fH°$ at T_{vap} between the liquid and gas.

Reference

[1]B. F. Naylor, J. Amer. Chem. Soc. **67**, 150 (1945).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	68.588	92.573	92.573	0.	−1186.067	−1140.806	199.864
300	68.772	92.998	92.574	0.127	−1186.045	−1140.525	198.583
400	73.864	113.631	95.353	7.311	−1184.716	−1125.546	146.981
500	76.220	130.375	100.736	14.819	−1183.338	−1110.914	116.056
600	78.517	144.471	106.881	22.554	−1182.019	−1096.553	95.463
700	81.090	156.764	113.147	30.532	−1180.732	−1082.411	80.771
800	83.918	167.775	119.298	38.781	−1180.286	−1068.349	69.756
900	86.952	177.833	125.251	47.323	−1178.924	−1054.439	61.198
1000	90.128	187.157	130.981	56.176	−1177.581	−1040.680	54.360
1000.000	90.128	187.157	130.981	56.176	GLASS <--> LIQUID		
1000.000	99.914	187.157	130.981	56.176	TRANSITION		
1100	99.914	196.680	136.528	66.168	−1175.433	−1027.096	48.773
1200	99.914	205.374	141.908	76.159	−1181.347	−1013.072	44.098
1300	99.914	213.371	147.101	86.150	−1178.625	−999.159	40.147
1400	99.914	220.775	152.103	96.142	−1175.924	−985.456	36.768
1500	99.914	227.669	156.913	106.133	−1173.243	−971.944	33.846
1600	99.914	234.117	161.539	116.125	−1170.581	−958.611	31.295
1691.000	99.914	239.644	165.595	125.217	---- BETA <--> LIQUID		----
1700	99.914	240.174	165.988	126.116	−1167.935	−945.444	29.050
1800	99.914	245.885	170.270	136.107	−1313.977	−930.222	26.994
1900	99.914	251.287	174.393	146.099	−1309.944	−909.012	24.990
2000	99.914	256.412	178.367	156.090	−1305.925	−888.014	23.193
2100	99.914	261.287	182.201	166.082	−1301.921	−867.217	21.571
2200	99.914	265.935	185.902	176.073	−1297.929	−846.611	20.101
2300	99.914	270.376	189.479	186.064	−1293.952	−826.185	18.763
2400	99.914	274.629	192.939	196.056	−1289.988	−805.933	17.541
2500	99.914	278.707	196.289	206.047	−1286.041	−785.845	16.419
2600	99.914	282.626	199.534	216.038	−1282.112	−765.915	15.387
2700	99.914	286.397	202.682	226.030	−1278.204	−746.135	14.435
2800	99.914	290.031	205.737	236.021	−1274.321	−726.500	13.553
2900	99.914	293.537	208.705	246.013	−1270.468	−707.003	12.735
3000	99.914	296.924	211.589	256.004	−1266.651	−687.639	11.973
3100	99.914	300.200	214.395	265.995	−1262.874	−668.401	11.262
3200	99.914	303.372	217.126	275.987	−1259.145	−649.284	10.598
3300	99.914	306.447	219.787	285.978	−1255.470	−630.282	9.977
3400	99.914	309.429	222.380	295.970	−1251.856	−611.392	9.393
3500	99.914	312.326	224.908	305.961	−1248.310	−592.606	8.844
3600	99.914	315.140	227.376	315.952	−1244.837	−573.921	8.327
3700	99.914	317.878	229.785	325.944	−1241.446	−555.331	7.840
3800	99.914	320.542	232.138	335.935	−1238.141	−536.833	7.379
3900	99.914	323.138	234.439	345.927	−1234.928	−518.419	6.943
4000	99.914	325.667	236.688	355.918	−1231.812	−500.087	6.530

PREVIOUS: CURRENT: December 1968

0	to 1424	K	crystal, alpha
1424	to 1691	K	crystal, beta
above	1691	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.655	−1223.006	−1223.006	INFINITE
100	28.619	13.347	120.374	−10.703	−1225.941	−1208.642	631.330
200	56.769	43.555	74.450	−6.179	−1226.615	−1190.898	311.031
298.15	68.588	68.572	68.572	0.	−1225.912	−1173.496	205.592
300	68.772	68.997	68.574	0.127	−1225.891	−1173.171	204.267
400	73.864	89.630	71.353	7.311	−1224.561	−1155.791	150.931
500	76.220	106.375	76.736	14.819	−1223.184	−1138.759	118.965
600	78.517	120.471	82.880	22.554	−1221.865	−1121.999	97.679
700	81.090	132.764	89.146	30.532	−1220.577	−1105.456	82.490
800	83.918	143.774	95.298	38.781	−1220.132	−1088.995	71.104
900	86.952	153.832	101.251	47.323	−1218.769	−1072.684	62.257
1000	90.128	163.157	106.981	56.177	−1217.427	−1056.525	55.187
1100	93.412	171.901	112.489	65.353	−1216.093	−1040.499	49.409
1200	96.780	180.172	117.788	74.862	−1222.490	−1023.973	44.572
1300	100.207	188.054	122.892	84.711	−1219.910	−1007.532	40.483
1400	103.680	195.607	127.818	94.905	−1217.007	−991.302	36.986
1424.000	104.520	197.376	128.975	97.403	ALPHA <--> BETA		
1424.000	122.884	200.726	128.975	102.173	TRANSITION		
1500	123.679	207.136	132.774	111.542	−1207.680	−975.581	33.973
1600	124.725	215.151	137.675	123.963	−1202.588	−960.273	31.350
1691.000	125.677	222.077	142.032	135.356	BETA <--> LIQUID		
1691.000	99.914	239.644	142.032	165.062	TRANSITION		
1700	99.914	240.174	142.550	165.961	−1167.935	−945.444	29.050
1800	99.914	245.885	148.134	175.953	−1313.977	−930.222	26.994
1900	99.914	251.287	153.422	185.944	−1309.944	−909.012	24.990
2000	99.914	256.412	158.444	195.936	−1305.925	−888.014	23.193
2100	99.914	261.287	163.227	205.927	−1301.921	−867.217	21.571
2200	99.914	265.935	167.790	215.918	−1297.929	−846.611	20.101
2300	99.914	270.376	172.155	225.910	−1293.952	−826.185	18.763
2400	99.914	274.629	176.337	235.901	−1289.988	−805.933	17.541
2500	99.914	278.707	180.350	245.893	−1286.041	−785.845	16.419
2600	99.914	282.626	184.209	255.884	−1282.112	−765.915	15.387
2700	99.914	286.397	187.925	265.875	−1278.204	−746.135	14.435
2800	99.914	290.031	191.507	275.867	−1274.321	−726.500	13.553
2900	99.914	293.537	194.965	285.858	−1270.468	−707.003	12.735
3000	99.914	296.924	198.307	295.850	−1266.651	−687.639	11.973
3100	99.914	300.200	201.542	305.841	−1262.874	−668.401	11.262
3200	99.914	303.372	204.675	315.832	−1259.145	−649.284	10.598
3300	99.914	306.447	207.712	325.824	−1255.470	−630.282	9.977
3400	99.914	309.429	210.660	335.815	−1251.856	−611.392	9.393
3500	99.914	312.326	213.524	345.807	−1248.310	−592.606	8.844
3600	99.914	315.140	216.308	355.798	−1244.837	−573.921	8.327
3700	99.914	317.878	219.016	365.789	−1241.446	−555.331	7.840
3800	99.914	320.542	221.653	375.781	−1238.141	−536.833	7.379
3900	99.914	323.138	224.222	385.772	−1234.928	−518.419	6.943
4000	99.914	325.667	226.726	395.763	−1231.812	−500.087	6.530

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = 273.80 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -782.6 \pm 8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -784.5 \pm 8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
484 (1)
163 (1)
554 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Ca–F = 2.1 Å
Bond Angle: F–Ca–F = 135 ± 7°
Product of the Moments of Inertia: $I_A I_B I_C = 1.283897 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is obtained from that of the crystal by adding $\Delta_{sub}H°(298.15\ K)$. The vapor pressure data of five authors are analyzed by 2nd and 3rd law methods to give $\Delta_{sub}H°(298.15\ K)$ as listed below. Note that the drifts are small and both positive and negative confirming the correctness of the functions used.

Reference	T/K	Data Points	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Freeman[1]	1463–1668	9	106.2 ± 3.7	105.66 ± 0.9	−0.2 ± 2.3
Blue *et al.*[2]	1246–1498	6	99.6 ± 2.5	106.00 ± 1.0	4.1 ± 2.0
Schulz and Searcy[3]	1421–1689	34	102.4 ± 0.3	104.00 ± 0.2	1.0 ± 0.2
Pottie[4]	1823	1	106.4		
Ruff and LeBoucher[5]	2086–2208	7	106.7 ± 4.8	105.22 ± 0.5	−0.7 ± 2.2
Blue *et al.*[2]*	1242–1669	19	104.7 ± 0.5		

*This set was not analyzed by the 3rd law since the absolute pressures were adjusted by the authors to match their weight loss values.

A median value of 105.5 ± 0.5 kcal·mol^{-1} (441.412 ± 2.1 kJ·mol^{-1}) is adopted for the enthalpy of sublimation which yields $\Delta_f H°(CaF_2, g, 298.15\ K) = -187.5 \pm 2$ kcal·mol^{-1} (-784.5 ± 8 kJ·mol^{-1}).

Heat Capacity and Entropy

The bond length was measured by Aksihin and Spiridonov,[6] but the diffraction patterns were interpreted as indicating a linear molecule. The vibrational frequencies and bond angle are those reported by Calder[7] using matrix isolation spectroscopy and isotopically enriched materials.

The principal moments of inertia are: $I_A = 2.0918 \times 10^{-39}$, $I_B = 23.7505 \times 10^{-39}$, and $I_C = 25.8423 \times 10^{-39}\ g·cm^2$.

References

[1] R. D. Freeman, Tech. Doc. Rept. ASD TDR 63–754, Part II, Oklahoma State University, (1965).
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[3] D. A. Schulz and A. W. Searcy, J. Phys. Chem. **67**, 103 (1963).
[4] R. W. Pottie, quoted by Freeman.[1]
[5] O. Ruff and L. LeBoucher, Z. Anorg. Chem. **219**, 376 (1934).
[6] P. A. Akishin and V. P. Spiridonov, Kristallografiya, **2**, 475 (1957).
[7] G. V. Calder, Nat. Bur. Stand. Rept. 9389, 253 pp. (July 1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.658	−782.596	−782.596	INFINITE
100	39.182	224.769	315.945	−9.118	−782.944	−786.787	410.975
200	46.529	254.242	278.356	−4.823	−783.847	−790.267	206.397
250	49.301	264.937	274.632	−2.424	−784.200	−791.830	165.444
298.15	51.267	273.798	273.798	0.	−784.500	−793.272	138.978
300	51.331	274.115	273.799	0.095	−784.511	−793.326	138.130
350	52.798	282.144	274.430	2.700	−784.801	−794.772	118.613
400	53.870	289.268	275.848	5.368	−785.092	−796.177	103.970
450	54.666	295.661	277.700	8.082	−785.407	−797.544	92.577
500	55.269	301.454	279.791	10.832	−785.760	−798.874	83.458
600	56.100	311.610	284.271	16.403	−786.604	−801.421	69.770
700	56.627	320.300	288.812	22.042	−787.656	−803.811	59.981
800	56.981	327.886	293.233	27.723	−789.778	−805.930	52.622
900	57.228	334.613	297.464	33.434	−791.246	−807.864	46.887
1000	57.408	340.652	301.486	39.167	−793.024	−809.618	42.290
1100	57.543	346.131	305.299	44.914	−795.119	−811.179	38.520
1200	57.646	351.142	308.914	50.674	−805.266	−811.912	35.342
1300	57.727	355.759	312.342	56.443	−806.766	−812.405	32.643
1400	57.791	360.040	315.598	62.219	−808.281	−812.782	30.325
1500	57.843	364.029	318.695	68.001	−809.809	−813.051	28.313
1600	57.886	367.763	321.646	73.787	−811.352	−813.216	26.549
1700	57.922	371.274	324.463	79.578	−812.907	−813.285	24.989
1800	57.952	374.585	327.157	85.371	−963.146	−811.051	23.536
1900	57.977	377.719	329.736	91.168	−963.308	−802.598	22.065
2000	57.999	380.694	332.211	96.967	−963.482	−794.134	20.741
2100	58.017	383.524	334.587	102.768	−963.668	−785.663	19.542
2200	58.034	386.223	336.873	108.570	−963.866	−777.182	18.453
2300	58.048	388.803	339.076	114.374	−964.075	−768.691	17.458
2400	58.060	391.274	341.199	120.180	−964.298	−760.192	16.545
2500	58.071	393.645	343.250	125.986	−964.536	−751.682	15.706
2600	58.081	395.922	345.232	131.794	−964.790	−743.163	14.930
2700	58.090	398.115	347.151	137.602	−965.065	−734.634	14.212
2800	58.097	400.227	349.009	143.412	−965.364	−726.094	13.545
2900	58.104	402.266	350.810	149.222	−965.693	−717.543	12.924
3000	58.111	404.236	352.559	155.032	−966.056	−708.980	12.344
3100	58.116	406.142	354.256	160.844	−966.459	−700.404	11.802
3200	58.122	407.987	355.907	166.656	−966.910	−691.815	11.293
3300	58.126	409.775	357.512	172.468	−967.414	−683.210	10.814
3400	58.131	411.511	359.075	178.281	−967.978	−674.590	10.364
3500	58.135	413.196	360.597	184.094	−968.610	−665.952	9.939
3600	58.138	414.833	362.081	189.908	−969.315	−657.295	9.537
3700	58.142	416.426	363.529	195.722	−970.101	−648.617	9.157
3800	58.145	417.977	364.941	201.536	−970.973	−639.917	8.796
3900	58.147	419.487	366.321	207.351	−971.937	−631.192	8.454
4000	58.150	420.960	367.668	213.166	−972.998	−622.442	8.128
4100	58.153	422.396	368.986	218.981	−974.159	−613.664	7.818
4200	58.155	423.797	370.274	224.796	−975.425	−604.856	7.522
4300	58.157	425.165	371.535	230.612	−976.797	−596.017	7.240
4400	58.159	426.502	372.769	236.428	−978.276	−587.145	6.970
4500	58.161	427.809	373.977	242.243	−979.849	−578.239	6.712
4600	58.162	429.088	375.162	248.060	−981.538	−569.297	6.465
4700	58.164	430.339	376.322	253.876	−983.338	−560.315	6.227
4800	58.166	431.563	377.461	259.692	−985.244	−551.295	5.999
4900	58.167	432.762	378.577	265.509	−987.253	−542.234	5.780
5000	58.168	433.938	379.672	271.326	−989.361	−533.131	5.570
5100	58.170	435.090	380.748	277.143	−991.567	−523.984	5.367
5200	58.171	436.219	381.804	282.960	−993.860	−514.794	5.171
5300	58.172	437.327	382.841	288.777	−996.244	−505.558	4.983
5400	58.173	438.414	383.860	294.594	−998.711	−496.277	4.801
5500	58.174	439.482	384.862	300.412	−1001.254	−486.950	4.625
5600	58.175	440.530	385.846	306.229	−1003.860	−477.576	4.455
5700	58.176	441.560	386.815	312.046	−1006.538	−468.155	4.290
5800	58.177	442.572	387.767	317.864	−1009.276	−458.686	4.131
5900	58.177	443.566	388.705	323.682	−1012.068	−449.169	3.977
6000	58.178	444.544	389.627	329.500	−1014.907	−439.604	3.827

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [235.47 \pm 8]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -190.0 \pm 21\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -193.9 \pm 21\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[16050]	[2]
[16610]	[2]
[18050]	[2]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[587](1)
[466](2)
[3650](1)

Point Group: [$C_{\infty v}$] σ = 1
Bond Distances: Ca–O = [2.03] Å; O–H = [0.96] Å
Bond Angle: Ca–O–H = [180]°
Rotational Constant: B_0 = [0.318811] cm^{-1}

Enthalpy of Formation

The adopted $\Delta_f H°$(CaOH, g, 0 K) = −45.41 ± 5 kcal·mol^{-1}(−190.0 ± 21 kJ·mol^{-1}) is based on an assessment of $D_0°$ values derived from flame spectra of CaOH, SrOH, and BaOH. Cotton and Jenkins[1] found both the monohydroxides and dihydroxides of the alkaline earths to be present in significant amounts in fuel-rich hydrogen–oxygen–nitrogen flames. They determined equilibrium constants for the reactions M(g) + H_2O(g) = MOH(g) + H(g) and M(g) + 2 H_2O(g) = M$(OH)_2$(g) + 2 H(g) and derived $D_0°$ values. In earlier work, Ryabova and Gurvich[2] had considered CaOH to be the dominant compound, and Sugden and Schofield[3] had interpreted Ca$(OH)_2$ as dominant. Cotton and Jenkins[1] have recalculated the work of these last two investigations, considering both CaOH and Ca$(OH)_2$ to be present. Ryabova *et al.*[4] and Kalff and Alkemade[5] have made additional measurements.

	$D_0°$, kcal·mol^{-1} CaOH(g)=Ca(g)+OH(g)		
Reference	As Published	As Recalculated by Cotton and Jenkins[1]	As Corrected for Current JANAF Auxiliary Data[6]
Ryabova and Gurvich[2]	100 ± 8	99	
Sugden and Schofield[3]		102	
Cotton and Jenkins[1]	104 ± 5		105.5
Ryabova *et al.*[4]	94 ± 3		97.5[a]
Kalff and Alkemade[5]	102.4		

[a]An approximate correction of +3.5 kcal·mol^{-1} is made, 2 kcal·mol^{-1} assumed from the Cotton and Jekins' type calculation for the presence of both CaOH and Ca$(OH)_2$ and 1.5 kcal·mol^{-1} indicated by the recalculation of Cotton and Jenkins' work[1] using auxiliary data from the current JANAF Tables.[6]

The data analyses for BaOH(g) and Ba$(OH)_2$(g) indicate that flame-spectral data tend to give high dissociation energies. For Ca$(OH)_2$(g), the lowest value of $D_0°$(HO–Ca–OH) was adopted.[6] Similarly, $D_0°$(Ca–OH) = 97.5 kcal·mol^{-1} is adopted.

The ratio of the dissociation energies of the alkaline earth monohalides to those of the corresponding dihalides range from 0.40 to 0.51 with the ratio for the calcium fluorides being 0.47.[6] The similarity between the halides and hydroxides has been established.[7–10] The ratio of the adopted values for the dissociation energies of CaOH(g) and Ca$(OH)_2$(g) is 0.47 where $D_0°$ of the dihydroxide is defined by the reaction Ca$(OH)_2$ = Ca(g) + 2(OH)(g) and is 205.6 kcal·mol^{-1}.

Heat Capacity and Entropy

The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has been recognized.[7,10] The molecular configuration is assumed to be linear in accordance with the prediction of Walsh[11] and the evidence that gaseous alkali metal hydroxides are linear.[12,14] The ground state is assumed to be $^2\Sigma^+$ by analogy with CaF and CaCl [6]. The electronic levels are estimated from the band spectra observed by James and Sugden,[15] Gaydon,[16] Zhitkevich *et al.*[17] and van der Hurk *et al.*,[18] and the comparison with CaF and CaCl.[6]

The Ca–O bond distance is estimated to be slightly larger, 0.02 Å, than the Ca–F distance[6] after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[6]

The Ca–O stretching frequency, 587 cm^{-1}, is estimated to be the same as the CaF stretching frequency.[6,10] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 466 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[10,14]

The entropy in the present table is lower by 0.20 cal·K^{-1}·mol^{-1} at 298.15 K and 0.25 cal·K^{-1}·mol^{-1} at 1000 K than that proposed by Jackson;[10] the data relevant to the calculations are nearly the same.

Continued on page 736

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.429	−189.995	−189.995	INFINITE
100	30.146	195.611	270.666	−7.506	−191.004	−195.266	101.997
200	38.363	218.867	239.376	−4.102	−192.671	−198.857	51.936
250	42.001	227.836	236.191	−2.089	−193.335	−200.324	41.855
298.15	44.625	235.470	235.470	0.	−193.877	−201.620	35.323
300	44.711	235.746	235.471	0.083	−193.897	−201.668	35.113
350	46.687	242.795	236.023	2.370	−194.378	−202.924	30.285
400	48.139	249.129	237.272	4.743	−194.810	−204.115	26.655
450	49.226	254.864	238.913	7.178	−195.226	−205.253	23.825
500	50.062	260.096	240.774	9.661	−195.648	−206.345	21.557
600	51.270	269.337	244.785	14.732	−196.564	−208.400	18.143
700	52.148	277.309	248.875	19.904	−197.626	−210.291	15.692
800	52.879	284.321	252.876	25.156	−199.713	−211.914	13.837
900	53.544	290.589	256.724	30.478	−201.107	−213.359	12.383
1000	54.171	296.263	260.399	35.864	−202.774	−214.633	11.211
1100	54.769	301.454	263.898	41.311	−204.724	−215.727	10.244
1200	55.336	306.244	267.230	46.817	−214.692	−216.008	9.403
1300	55.868	310.695	270.404	52.377	−215.983	−216.065	8.682
1400	56.364	314.853	273.432	57.989	−217.260	−216.024	8.060
1500	56.823	318.758	276.325	63.649	−218.525	−215.891	7.518
1600	57.244	322.439	279.093	69.353	−219.781	−215.675	7.041
1700	57.631	325.921	281.747	75.097	−221.029	−215.380	6.618
1800	57.985	329.225	284.293	80.878	−370.947	−212.801	6.175
1900	58.311	332.369	286.741	86.693	−370.774	−204.020	5.609
2000	58.610	335.368	289.098	92.539	−370.606	−195.247	5.099
2100	58.888	338.234	291.370	98.414	−370.446	−186.483	4.639
2200	59.147	340.980	293.563	104.316	−370.299	−177.727	4.220
2300	59.390	343.614	295.683	110.243	−370.168	−168.976	3.838
2400	59.622	346.147	297.733	116.194	−370.059	−160.232	3.487
2500	59.845	348.585	299.719	122.167	−369.978	−151.490	3.165
2600	60.062	350.937	301.644	128.162	−369.929	−142.752	2.868
2700	60.276	353.208	303.512	134.179	−369.920	−134.015	2.593
2800	60.488	355.404	305.326	140.218	−369.956	−125.277	2.337
2900	60.701	357.530	307.090	146.277	−370.045	−116.537	2.099
3000	60.915	359.591	308.805	152.358	−370.194	−107.793	1.877
3100	61.132	361.592	310.476	158.460	−370.410	−99.043	1.669
3200	61.354	363.537	312.104	164.584	−370.700	−90.285	1.474
3300	61.580	365.428	313.691	170.731	−371.071	−81.516	1.290
3400	61.812	367.270	315.240	176.901	−371.531	−72.735	1.117
3500	62.049	369.065	316.753	183.094	−372.085	−63.939	0.954
3600	62.291	370.816	318.230	189.310	−372.741	−55.126	0.800
3700	62.538	372.526	319.675	195.552	−373.504	−46.294	0.654
3800	62.790	374.197	321.087	201.818	−374.380	−37.438	0.515
3900	63.047	375.832	322.470	208.110	−375.373	−28.558	0.382
4000	63.307	377.431	323.824	214.428	−376.487	−19.652	0.257
4100	63.571	378.998	325.151	220.772	−377.726	−10.716	0.137
4200	63.837	380.533	326.451	227.142	−379.092	−1.748	0.022
4300	64.105	382.038	327.727	233.539	−380.588	7.254	−0.088
4400	64.375	383.515	328.978	239.963	−382.210	16.291	−0.193
4500	64.644	384.965	330.206	246.414	−383.947	25.366	−0.294
4600	64.913	386.388	331.412	252.892	−385.820	34.482	−0.392
4700	65.181	387.787	332.597	259.397	−387.822	43.641	−0.485
4800	65.446	389.162	333.761	265.928	−389.948	52.843	−0.575
4900	65.709	390.515	334.905	272.486	−392.195	62.091	−0.662
5000	65.969	391.845	336.031	279.070	−394.558	71.386	−0.746
5100	66.224	393.154	337.138	285.679	−397.035	80.729	−0.827
5200	66.475	394.442	338.228	292.314	−399.616	90.121	−0.905
5300	66.720	395.710	339.300	298.974	−402.303	99.565	−0.981
5400	66.960	396.960	340.356	305.658	−405.089	109.060	−1.055
5500	67.193	398.191	341.397	312.366	−407.966	118.608	−1.126
5600	67.419	399.403	342.422	319.097	−410.921	128.208	−1.196
5700	67.639	400.599	343.432	325.850	−413.965	137.862	−1.263
5800	67.851	401.777	344.428	332.624	−417.083	147.571	−1.329
5900	68.055	402.938	345.410	339.419	−420.270	157.332	−1.393
6000	68.251	404.084	346.378	346.235	−423.521	167.150	−1.455

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [229.90 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 366.733 \pm 63\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [369.084 \pm 63]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[580](1)
[460](2)
[3650](1)

Ground State Quantum Weight = [1] $\sigma = 1$
Point Group: $[C_{\infty v}]$
Bond Distances: Ca–O = [2.03] Å; O–H = [0.96] Å
Bond Angle: Ca–O–H = [180°]
Rotational Constant: B_0 = [0.318830] cm^{-1}

Enthalpy of Formation

The ionization potential of CaOH(g) was deduced by Kelly and Padley[1] to be 5.9 ± 0.1 eV. These authors quantitatively examined the total positive ion concentrations produced from Ca aqueous salt additives in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data,[2] we recalculate the ionization potential to be 5.79 eV.

Jensen[3] determined the enthalpy of reaction $\Delta_r H°(0\ K) = 35 \pm 10$ kcal·mol^{-1} for $Ca(g) + OH(g) = CaOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for $XXCaOH^+$; the value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data,[2] we derive an ionization potential of 5.75 eV, which is in good agreement with the value derived from the data of Kelly and Padley.[1]

We adopt an ionization potential of 5.77 eV (133.06 kcal·mol^{-1}) which is average of the above two studies.[1,3] This leads to $\Delta_f H°(0\ K) = 87.651$ kcal·mol^{-1} and $\Delta_f H°(298.15\ K) = 88.213$ kcal·mol^{-1} (369.08 kJ·mol^{-1}) for $CaOH^+(g)$. We assign an uncertainty of ±15 kcal·mol^{-1}.

For comparison, the appearance potential of CaF(g) has been reported as 5.8 ± 0.3 eV,[4] 5.5 ± 0.3 eV[4] and 6.0 ± 0.5 eV.[5] These values are all very similar to the ionization potential adopted here for CaOH(g). In addition, the ionization potential for Ca(g) is 6.11 eV.[2]

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[2,6–8] In addition, Walsh[9] had predicted that triatomic molecules (containing hydrogen) with ten or less valence electrons ($CaOH^+$ has eight valence electrons) will be linear in their ground state. The molecule $CaOH^+$ is isoelectronic with KOH.

The bond dissociation energy for $CaOH^+$ (D_0° = 105.4 kcal mol^{-1})[2] for the process $CaOH^+(g) = Ca^+(g) + OH(g)$ is fairly close to that for CaOH (D_0° = 97.5 kcal·mol^{-1}).[2] This suggests a similar bonding in these two molecules. Thus, bond distances are assumed to be the same as those adopted for CaOH(g).[2] The ground state quantum weight is assumed to be the same as that of KOH(g).[2]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.466	366.733		
100	30.213	189.861	265.270	−7.541			
200	38.571	213.223	233.828	−4.121			
250	42.199	222.238	230.629	−2.098			
298.15	44.799	229.905	229.905	0.	369.084	356.746	−62.501
300	44.884	230.182	229.906	0.083	369.104	356.670	−62.102
350	46.834	237.255	230.460	2.378	369.670	354.554	−52.914
400	48.263	243.607	231.713	4.758	370.284	352.353	−46.013
450	49.331	249.356	233.359	7.199	370.913	350.073	−40.635
500	50.151	254.598	235.225	9.687	371.535	347.724	−36.327
600	51.336	263.854	239.245	14.765	372.705	342.850	−29.848
700	52.198	271.835	243.344	19.943	373.727	337.791	−25.206
800	52.919	278.853	247.353	25.200	373.724	332.702	−21.723
900	53.576	285.124	251.207	30.525	374.412	327.530	−19.009
1000	54.198	290.801	254.887	35.914	374.826	322.296	−16.835
1100	54.791	295.995	258.392	41.364	374.957	317.034	−15.055
1200	55.355	300.787	261.727	46.871	367.070	312.396	−13.598
1300	55.884	305.239	264.905	52.433	367.859	307.807	−12.368
1400	56.378	309.398	267.936	58.047	368.662	303.158	−11.311
1500	56.834	313.304	270.832	63.708	369.477	298.451	−10.393
1600	57.253	316.985	273.603	69.412	370.301	293.689	−9.588
1700	57.637	320.468	276.258	75.157	371.132	288.875	−8.876
1800	57.987	323.772	278.807	80.939	223.294	286.223	−8.306
1900	58.305	326.916	281.257	86.753	225.544	289.658	−7.963
2000	58.595	329.914	283.615	92.599	227.790	292.974	−7.652
2100	58.859	332.780	285.889	98.472	230.026	296.178	−7.367
2200	59.099	335.524	288.083	104.370	232.249	299.277	−7.106
2300	59.318	338.156	290.203	110.291	234.452	302.274	−6.865
2400	59.518	340.684	292.254	116.233	236.631	305.175	−6.642
2500	59.700	343.118	294.240	122.194	238.779	307.987	−6.435
2600	59.866	345.463	296.166	128.172	240.889	310.714	−6.242
2700	60.018	347.725	298.033	134.166	242.954	313.360	−6.062
2800	60.158	349.910	299.847	140.175	244.967	315.931	−5.894
2900	60.286	352.023	301.610	146.198	246.919	318.430	−5.736
3000	60.404	354.069	303.325	152.232	248.803	320.864	−5.587
3100	60.512	356.052	304.994	158.278	250.609	323.236	−5.446
3200	60.613	357.974	306.620	164.334	252.330	325.551	−5.314
3300	60.705	359.841	308.204	170.400	253.956	327.814	−5.189
3400	60.791	361.654	309.750	176.475	255.481	330.029	−5.070
3500	60.871	363.418	311.258	182.558	256.895	332.201	−4.958
3600	60.944	365.134	312.731	188.649	258.192	334.334	−4.851
3700	61.013	366.804	314.170	194.747	259.364	336.432	−4.750
3800	61.077	368.432	315.577	200.852	260.405	338.501	−4.653
3900	61.136	370.020	316.952	206.962	261.310	340.544	−4.561
4000	61.192	371.568	318.299	213.079	262.073	342.566	−4.473
4100	61.244	373.080	319.616	219.201	262.690	344.570	−4.390
4200	61.293	374.556	320.907	225.327	263.159	346.561	−4.310
4300	61.339	375.999	322.171	231.459	263.477	348.543	−4.234
4400	61.381	377.410	323.411	237.595	263.645	350.519	−4.161
4500	61.422	378.790	324.626	243.735	263.676	352.491	−4.092
4600	61.460	380.140	325.818	249.879	263.548	354.465	−4.025
4700	61.495	381.462	326.988	256.027	263.267	356.445	−3.961
4800	61.529	382.757	328.137	262.178	262.840	358.432	−3.901
4900	61.561	384.026	329.264	268.333	262.268	360.429	−3.842
5000	61.591	385.270	330.372	274.490	261.557	362.440	−3.786
5100	61.619	386.490	331.461	280.651	260.710	364.465	−3.733
5200	61.646	387.687	332.530	286.814	259.736	366.508	−3.682
5300	61.671	388.861	333.582	292.980	258.633	368.572	−3.633
5400	61.695	390.014	334.617	299.148	257.410	370.658	−3.585
5500	61.718	391.147	335.634	305.319	256.074	372.767	−3.540
5600	61.740	392.259	336.635	311.492	254.640	374.901	−3.497
5700	61.761	393.352	337.621	317.667	253.098	377.062	−3.455
5800	61.780	394.426	338.591	323.844	251.460	379.251	−3.416
5900	61.799	395.482	339.546	330.023	249.735	381.468	−3.377
6000	61.817	396.521	340.487	336.204	247.929	383.717	−3.341

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = 83.387 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -977.36 \pm 1.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -986.09 \pm 1.3\ kJ·mol^{-1}$

Enthalpy of Formation

Taylor and Wells[1] measured enthalpies of solution of $Ca(OH)_2$(cr) and CaO(cr) in dilute HCl and obtained $\Delta_r H°(298.15\ K) = -15.58 \pm 0.1$ kcal·mol^{-1} for CaO(cr) + H_2O(l) = $Ca(OH)_2$(cr) which leads to $\Delta_f H°(Ca(OH)_2, cr, 298.15\ K) = -235.68 \pm 0.3$ kcal·mol^{-1} using $\Delta_f H°$(CaO, cr, 298.15 K) = -151.79 ± 0.21 kcal·mol^{-1} [2] and $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315$ kcal·mol^{-1}.[3] This value, -235.68 ± 0.3 kcal·mol^{-1} (-986.09 kJ·mol^{-1}) is adopted in the tabulation. They also measured directly the enthalpy of hydration of CaO to $Ca(OH)_2$ and found $\Delta_r H°(298.15\ K) = -15.43 \pm 0.1$ kcal·mol^{-1} which leads to $\Delta_f H°(Ca(OH)_2, cr, 298.15\ K) = -235.53$ kcal·mol^{-1}. Both measurements are in very good agreement. Literature $\Delta_r H°$ data[4-8] determined by these two methods were within the limit of -15.40 ± 0.3 kcal·mol^{-1} which is in good agreement with the value adopted.

JANAF analyses of dissociation pressure data[9-11] for $Ca(OH)_2$(cr) → CaO(cr) + H_2O(g) are listed below. The data of Halstead and Moore[9] and of Tamaru and Shiomi[10] are in good agreement, but the pressures reported by Johnston[11] are too low due to failure to reach equilibrium. The enthalpy of formation derived from 3rd law $\Delta_r H$ of Halstead and Moore[9] or Tamaru and Shiomi[10] is in good agreement with the value adopted. However, the decomposition of $Ca(OH)_2$ may yield non-standard state CaO in the final product which was shown in a similar decomposition of $Mg(OH)_2$. See $Mg(OH)_2$ table[2] for details.

$Ca(OH)_2(cr) = CaO(cr) + H_2O(g)$

Source	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
Halstead and Moore[9]	Static	635–776.5	14	25.52	25.75 ± 0.15	0.2 ± 0.4	−235.34
Tamaru and Shiomi[10]	Static	694–776.5	8	26.48	25.90 ± 0.07	−0.8 ± 0.3	−235.49
Johnston[11]	Static	663–804	7	26.92	26.76 ± 0.24	−0.5 ± 1.0	−236.35

Heat Capacity and Entropy

The low temperature heat capacities up to 300 K are taken from the adiabatic calorimeter measurements (19–330 K) of Hatton *et al.*[12] Above 300 K, the heat capacities are based on the heat conduction calorimeter measurements (310–670 K) of Kobayashi[13] joined smoothly at 300 K with the low temperature heat capacities[12] and on a graphical comparison of the C_p vs T curve adopted for $Mg(OH)_2$(cr).[2] The entropy, $S°(298.15\ K) = 19.93 \pm 0.1$ cal·K^{-1}·mol^{-1} (83.387 ± 0.4 J·K^{-1}·mol^{-1}), is derived from the adjuccirclopted low temperature heat capacities, based on a T^3 extrapolation to obtain $S° = 0.070$ cal·K^{-1}·mol^{-1} at 20 K.[12]

Decomposition Data

T_{dcm} is calculated as the temperature at which $\Delta_r G° = 0$ for the reaction $Ca(OH)_2$(cr) = CaO(cr) + H_2O(g). Auxiliary data are from the JANAF Tables.[2]

Under a pressure of 1000 bars, Wyllie and Tuttle[14] found that $Ca(OH)_2$ melts congruently at 1108 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−14.160	−977.358	−977.358	INFINITE
100	32.539	17.226	147.109	−12.988	−983.071	−955.793	499.255
200	68.576	52.183	90.862	−7.736	−985.692	−927.251	242.173
298.15	87.487	83.387	83.387	0.	−986.085	−898.421	157.400
300	87.780	83.929	83.389	0.162	−986.079	−897.877	156.334
400	98.408	110.820	86.983	9.535	−985.218	−868.582	113.425
500	103.931	133.431	94.075	19.678	−983.822	−839.579	87.710
600	107.445	152.696	102.280	30.249	−982.281	−810.874	70.593
700	110.709	169.508	110.708	41.160	−980.702	−782.431	58.386
800	113.512	184.479	119.010	52.375	−979.971	−754.111	49.238
900	116.022	197.998	127.048	63.855	−978.396	−725.974	42.134
1000	117.989	210.328	134.768	75.560	−976.978	−698.005	36.460

PREVIOUS: December 1971 CURRENT: December 1975

$S°(298.15\ K)$ = [285.6 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -603.17 \pm 37.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -610.76 \pm 37.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[484](1)
[163](1)
[554](1)
[3650](2)
[466](4)

Ground State Quantum Weight = [1] σ = 2
Point Group: [C_{2v}]
Bond Distances: Ca–O = [2.12] Å; O–H = [0.96] Å
Bond Angles: O–Ca–O = [135°]; Ca–O–H = [180°]
Product of the Moments of Inertia: $I_A I_B I_C$ = [1261.6507 × 10^{-117}] $g^3·cm^6$

Enthalpy of Formation

Dissociation energies, $D_0°$, for the reaction $Ca(OH)_2(g) = Ca(g) + 2\ OH(g)$ have been derived from flame–spectral measurements.[1-3] Ryabova and Gurvich[1] believed the dominant reaction to be $Ca(g) + H_2O(g) = CaOH(g) + H(g)$, but they also considered the possibility that $Ca(g) + 2\ H_2O(g) = Ca(OH)_2(g) + 2\ H(g)$ was the dominant reaction and derived $D_0° = 200 \pm 20$ kcal·mol^{-1}. Sugden and Schofield[2] considered the dihydroxide to be the dominant product and derived $D_0° = 217 \pm 12$ kcal·mol^{-1}. Cotton and Jenkins[3] found both CaOH and $Ca(OH)_2$ to be present in significant amounts in fuel–rich hydrogen–oxygen–nitrogen flames and derived $D_0° = 203.8 \pm 5$ kcal·mol^{-1}. Cotton and Jenkins[3] recalculated the work of Ryabova and Gurvich[1] and Sugden and Schofield[2] considering both CaOH and $Ca(OH)_2$ to be present and obtained the recalculated $D_0°$ values of *199* and *201* kcal·mol^{-1}, respectively.

A 3rd law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins[3] using current JANAF auxiliary data[4] leads to $D_0° = 210.4$ kcal·mol^{-1} which is 6.6 kcal·mol^{-1} higher than the 203.8 kcal·mol^{-1} derived by Cotton and Jenkins.[3] Applying this difference to the data of Ryabova and Gurvich[1] and Sugden and Schofield[2] as recalculated by Cotton and Jenkins[3] gives $D_0° = 205.6$ and 207.6 kcal·mol^{-1}, respectively.

For $Ba(OH)_2(g)$,[4] the corrected dissociation energy of Ryabova and Gurvich,[4] $D_0° = 208.8$ kcal·mol^{-1}, is in better agreement with the "adopted" value of 209.6 kcal·mol^{-1}, based on good Knudsen–cell mass–spectrometric measurements, than are the corrected dissociation energies of Sugden and Schofield or Cotton and Jenkins.[4] We adopt $D_0° = 205.6$ kcal·mol^{-1} for the dissociation of $Ca(OH)_2$ from which is calculated $\Delta_f H°(0\ K) = -144.16 \pm 9$ kcal·mol^{-1} (-603.165 ± 37.7 kJ·mol^{-1}).

The enthalpy of dissociaton listed by Jackson[8] leads to $\Delta_f H°(Ca(OH)_2, g, 298.15\ K) = -142.65$ kcal·mol^{-1}. Another recent compilation[9] lists $\Delta_f H°(298.15\ K) = -130$ kcal·mol^{-1}.

Heat Capacity and Entropy

The analogy between gaseous mono– and dihydroxides and gaseous mono– and dihalides, particularly the mono– and difluorides, has been recognized.[5-8] The O–Ca–O bond angle is assumed to be the same as the F–Ca–F bond angle;[4] the Ca–O–H bond angle is considered to be linear as in CaOH.[4] The Ca–O bond distance is estimated to be slightly larger, 0.02 Å, than the Ca–F bond distance in CaF_2[4] after noting the close similarity in the bond distance of alkali metal fluorides and hydroxides. The O–H bond distance is taken to be the same as in water.[4]

The vibrational frequencies are estimated to be the same as in CaF_2[4] (O–Ca–O symmetrical and asymmetrical stretch, and bend) and as in CaOH,[4] (O–H stretch and Ca–O–H bend). The principal moments of inertia are $I_A = 2.1629 \times 10^{-39}$, $I_B = 23.0947 \times 10^{-39}$, and $I_C = 25.2576 \times 10^{-39}$ g·cm.

Jackson[8] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K) = 68.530$ cal·K^{-1}·mol^{-1}(1 atm). We assign an uncertainty of ±2.0 cal·K^{-1}·mol^{-1} to the adopted entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−15.288	−603.165	−603.165	INFINITE
100	41.018	224.358	341.567	−11.721	−606.482	−599.918	313.365
200	60.577	258.745	291.969	−6.645	−609.279	−592.151	154.654
250	68.164	273.122	286.787	−3.416	−610.155	−587.762	122.806
298.15	73.450	285.605	285.605	0.	−610.764	−583.390	102.208
300	73.620	286.060	285.606	0.136	−610.783	−583.221	101.548
350	77.512	297.717	286.518	3.920	−611.231	−578.589	86.350
400	80.329	308.261	288.588	7.869	−611.562	−573.903	74.944
450	82.418	317.849	291.315	11.941	−611.831	−569.179	66.069
500	84.012	326.619	294.413	16.103	−612.075	−564.426	58.965
600	86.304	342.152	301.108	24.626	−612.583	−554.850	48.304
700	87.972	355.587	307.953	33.343	−613.197	−545.181	40.682
800	89.371	367.427	314.662	42.212	−614.812	−535.310	34.952
900	90.655	378.028	321.124	51.214	−615.716	−525.321	30.489
1000	91.876	387.643	327.302	60.341	−616.875	−515.217	26.912
1100	93.045	396.455	333.194	69.587	−618.300	−504.984	23.980
1200	94.158	404.599	338.809	78.948	−627.726	−493.988	21.503
1300	95.206	412.178	344.165	88.417	−628.461	−482.813	19.400
1400	96.185	419.270	349.279	97.987	−629.168	−471.583	17.595
1500	97.090	425.937	354.169	107.651	−629.853	−460.303	16.029
1600	97.922	432.230	358.853	117.403	−630.521	−448.978	14.658
1700	98.684	438.190	363.346	127.233	−631.175	−437.611	13.446
1800	99.380	443.850	367.663	137.137	−780.494	−423.996	12.304
1900	100.014	449.241	371.816	147.107	−779.723	−404.211	11.113
2000	100.591	454.386	375.817	157.138	−778.957	−384.467	10.041
2100	101.116	459.306	379.676	167.224	−778.201	−364.761	9.073
2200	101.594	464.022	383.403	177.360	−777.463	−345.090	8.193
2300	102.030	468.547	387.008	187.541	−776.749	−325.454	7.391
2400	102.427	472.898	390.496	197.764	−776.065	−305.847	6.657
2500	102.789	477.087	393.877	208.025	−775.418	−286.268	5.981
2600	103.120	481.125	397.155	218.321	−774.816	−266.714	5.358
2700	103.424	485.022	400.338	228.649	−774.267	−247.182	4.782
2800	103.702	488.789	403.430	239.005	−773.779	−227.669	4.247
2900	103.957	492.432	406.436	249.388	−773.360	−208.174	3.750
3000	104.192	495.961	409.362	259.796	−773.020	−188.690	3.285
3100	104.408	499.381	412.211	270.226	−772.765	−169.217	2.851
3200	104.608	502.699	414.987	280.677	−772.606	−149.751	2.444
3300	104.793	505.921	417.694	291.147	−772.551	−130.288	2.062
3400	104.963	509.052	420.335	301.635	−772.608	−110.824	1.703
3500	105.122	512.096	422.914	312.139	−772.786	−91.358	1.363
3600	105.269	515.060	425.432	322.659	−773.091	−71.885	1.043
3700	105.406	517.946	427.894	333.193	−773.531	−52.402	0.740
3800	105.533	520.759	430.301	343.740	−774.112	−32.903	0.452
3900	105.652	523.502	432.656	354.299	−774.840	−13.388	0.179
4000	105.763	526.178	434.960	364.870	−775.721	6.146	−0.080
4100	105.866	528.791	437.217	375.451	−776.757	25.706	−0.327
4200	105.964	531.343	439.428	386.043	−777.952	45.292	−0.563
4300	106.055	533.837	441.595	396.644	−779.309	64.910	−0.788
4400	106.140	536.277	443.719	407.254	−780.826	84.559	−1.004
4500	106.220	538.663	445.802	417.872	−782.492	104.244	−1.210
4600	106.296	540.998	447.847	428.498	−784.327	123.968	−1.408
4700	106.367	543.285	449.853	439.131	−786.326	143.735	−1.597
4800	106.434	545.525	451.823	449.771	−788.482	163.547	−1.780
4900	106.497	547.720	453.758	460.417	−790.794	183.405	−1.955
5000	106.557	549.873	455.658	471.070	−793.256	203.311	−2.124
5100	106.614	551.983	457.527	481.729	−795.867	223.268	−2.287
5200	106.667	554.054	459.363	492.393	−798.615	243.277	−2.444
5300	106.718	556.086	461.169	503.062	−801.504	263.341	−2.595
5400	106.766	558.081	462.945	513.736	−804.524	283.460	−2.742
5500	106.811	560.041	464.693	524.415	−807.669	303.636	−2.884
5600	106.855	561.966	466.413	535.098	−810.925	323.871	−3.021
5700	106.896	563.858	468.106	545.786	−814.302	344.165	−3.154
5800	106.935	565.717	469.773	556.478	−817.785	364.520	−3.283
5900	106.972	567.545	471.414	567.173	−821.368	384.933	−3.408
6000	107.008	569.344	473.032	577.872	−825.045	405.411	−3.529

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = 261.31 \pm 0.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2.72 \pm 84\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -5.04 \pm 84\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X[^2\Sigma^+]$	0	2
$A[^2\Pi]$	15585.1	2
	15645.9	2
$B[^2\Sigma^+]$	15711.2	2
$C[^2\Pi]$	23314.0	2
	23741.9	2
$D[^2\Sigma^+]$	31062.0	2
		2

$\omega_e = 238.3\ cm^{-1}$ $\omega_e x_e = 0.61\ cm^{-1}$ $\sigma = 1$

$B_e = [0.0667]\ cm^{-1}$ $\alpha_e = [0.00023]\ cm^{-1}$ $r_e = [2.88]$ Å

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -0.65 \pm 20\ kcal \cdot mol^{-1}$ is calculated from the $D_0° = 3 \pm 1$ eV($69 \pm 23\ kcal \cdot mol^{-1}$) selected by Gaydon.[1] A linear Birge–Sponer extrapolation of ω_e and $\omega_e x_e$ data[2] with a correction for the ionic character of the molecule as described by Hildenbrand[3] gave $D_0° = 66.5\ kcal \cdot mol^{-1}$. Other $D_0°$ values are $63.9\ kcal \cdot mol^{-1}$ [4] as a lower bound from a consideration of ionic bonding forces and $64\ kcal \cdot mol^{-1}$ [5] derived as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. Of the four ratios, $D_0°(CaI)/\Delta_{at}H°(CaI_2)$, $D_0°(CaI) = 69\ kcal \cdot mol^{-1}$ gives 0.445 which is closest to 0.46 found for a series of mono- and difluorides[6] and for other alkaline earth halide systems.[8] $\Delta_f H°(298.15\ K) = -1.21 \pm 20\ kcal \cdot mol^{-1}$ is calculated from the adopted $\Delta_f H°(0\ K) = -0.65 \pm 20\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen.[2] The value of $r_e = 2.88$ Å is assumed the same as the bond distance in CaI_2.[7] B_e is calculated from the adopted r_e. α_e is calculuted assuming a Morse potential function.

The electronic levels and their probable designation are those given by Rosen.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.010	−2.719	−2.719	INFINITE
100	32.513	223.091	293.124	−7.003	−2.218	−19.881	10.385
200	35.706	246.842	264.634	−3.558	−3.508	−37.083	9.685
250	36.301	254.880	261.907	−1.757	−4.271	−45.390	9.484
298.15	36.646	261.306	261.306	0.	−5.045	−53.240	9.327
300	36.656	261.532	261.306	0.068	−5.075	−53.538	9.322
350	36.886	267.201	261.753	1.907	−5.948	−61.548	9.186
400	37.044	272.138	262.750	3.755	−14.842	−69.156	9.031
450	37.159	276.508	264.040	5.610	−16.366	−75.854	8.805
500	37.247	280.428	265.486	7.471	−37.990	−80.481	8.408
600	37.373	287.230	268.560	11.202	−39.078	−88.880	7.738
700	37.461	292.998	271.650	14.944	−40.359	−97.081	7.244
800	37.529	298.005	274.638	18.694	−42.692	−104.982	6.855
900	37.586	302.429	277.485	22.449	−44.357	−112.671	6.539
1000	37.635	306.392	280.181	26.211	−46.318	−120.159	6.276
1100	37.679	309.981	282.729	29.976	−48.583	−127.436	6.051
1200	37.720	313.261	285.139	33.746	−58.889	−133.871	5.827
1300	37.758	316.282	287.420	37.520	−60.543	−140.052	5.627
1400	37.795	319.081	289.583	41.298	−62.209	−146.106	5.451
1500	37.832	321.690	291.637	45.079	−63.891	−152.040	5.294
1600	37.868	324.133	293.593	48.864	−65.595	−157.861	5.154
1700	37.906	326.430	295.457	52.653	−67.324	−163.575	5.026
1800	37.946	328.597	297.239	56.445	−217.755	−166.975	4.845
1900	37.989	330.650	298.944	60.242	−218.130	−164.144	4.513
2000	38.037	332.600	300.578	64.043	−218.541	−161.292	4.213
2100	38.092	334.457	302.148	67.850	−218.988	−158.419	3.940
2200	38.155	336.231	303.657	71.662	−219.472	−155.523	3.693
2300	38.227	337.928	305.110	75.481	−219.991	−152.605	3.466
2400	38.310	339.557	306.512	79.308	−220.544	−149.663	3.257
2500	38.406	341.123	307.865	83.143	−221.130	−146.698	3.065
2600	38.516	342.631	309.173	86.989	−221.747	−143.709	2.887
2700	38.640	344.087	310.440	90.847	−222.395	−140.695	2.722
2800	38.779	345.495	311.667	94.718	−223.073	−137.657	2.568
2900	38.935	346.858	312.857	98.603	−223.783	−134.594	2.424
3000	39.107	348.181	314.012	102.505	−224.525	−131.506	2.290
3100	39.295	349.466	315.135	106.425	−225.302	−128.392	2.163
3200	39.499	350.717	316.228	110.365	−226.117	−125.253	2.045
3300	39.720	351.936	317.292	114.326	−226.973	−122.088	1.932
3400	39.955	353.125	318.328	118.309	−227.875	−118.897	1.827
3500	40.206	354.287	319.339	122.317	−228.827	−115.678	1.726
3600	40.471	355.423	320.325	126.351	−229.832	−112.431	1.631
3700	40.749	356.536	321.289	130.412	−230.896	−109.155	1.541
3800	41.039	357.626	322.231	134.501	−232.024	−105.850	1.455
3900	41.341	358.696	323.152	138.620	−233.218	−102.514	1.373
4000	41.652	359.747	324.054	142.770	−234.483	−99.147	1.295
4100	41.972	360.779	324.937	146.951	−235.822	−95.747	1.220
4200	42.299	361.794	325.803	151.164	−237.237	−92.313	1.148
4300	42.633	362.794	326.652	155.411	−238.731	−88.845	1.079
4400	42.971	363.778	327.484	159.691	−240.303	−85.342	1.013
4500	43.314	364.747	328.301	164.005	−241.940	−81.803	0.950
4600	43.659	365.703	329.104	168.354	−243.663	−78.226	0.888
4700	44.005	366.645	329.893	172.737	−245.468	−74.610	0.829
4800	44.351	367.576	330.668	177.155	−247.349	−70.955	0.772
4900	44.697	368.494	331.431	181.607	−249.304	−67.260	0.717
5000	45.040	369.400	332.181	186.094	−251.330	−63.524	0.664
5100	45.381	370.295	332.920	190.615	−253.424	−59.747	0.612
5200	45.717	371.180	333.647	195.170	−255.578	−55.929	0.562
5300	46.049	372.054	334.364	199.759	−257.795	−52.069	0.513
5400	46.375	372.918	335.069	204.380	−260.067	−48.166	0.466
5500	46.694	373.771	335.765	209.033	−262.390	−44.221	0.420
5600	47.006	374.616	336.452	213.718	−264.748	−40.233	0.375
5700	47.310	375.450	337.129	218.434	−267.155	−36.203	0.332
5800	47.606	376.276	337.796	223.180	−269.598	−32.130	0.289
5900	47.894	377.092	338.456	227.955	−272.070	−28.014	0.248
6000	48.171	377.899	339.106	232.759	−274.567	−23.857	0.208

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 145.29 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1052 \pm 2\ K$

$\Delta_f H°(0\ K) = -535.8 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -536.8 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 41.84 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Ehrlich, Peik and Koch[1] derived $\Delta_f H°(CaI_2, cr, 298.15\ K) = -128.1 \pm 0.4\ kcal \cdot mol^{-1}$ from enthalpy of solution measurements of Ca(cr) and CaI_2(cr) in 0.1 N HI. An auxiliary HI enthalpy of solution value, $-13.22\ kcal \cdot mol^{-1}$, calculated from data in referenece[2] was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA value of $\Delta_f H°(I^-, aq, std.\ state, 298.15\ K) = -13.60\ kcal \cdot mol^{-1}$ [3] in the $\Delta_f H°$(HI, aq solution, 298.15 K) table, so that the above derived enthalpy of formation of CaI_2(cr) will be approximately $-128.6\ kcal \cdot mol^{-1}$.

Combining $\Delta_f H°(Ca^{+2}, aq, std.\ state, 298.15\ K) = -129.74\ kcal \cdot mol^{-1}$, selected by Parker[4,5] with the CODATA value for I^-(aq, std. state)[3] gives $\Delta_f H°(CaI_2, aq, std.\ state, 298.15\ K) = -156.94\ kcal \cdot mol^{-1}$. Further combination with the enthalpy of solution, $-28.62\ kcal \cdot mol^{-1}$ [5,6] gives $\Delta_f H°(CaI_2, cr, 298.15\ K) = -128.32\ kcal \cdot mol^{-1}$. This enthalpy of solution value was based on several sets of data, one of which was that of Ehrlich, *et al.*[1,6] We adopt $-128.3 \pm 0.5\ kcal \cdot mol^{-1}$ ($-536.807\ kJ \cdot mol^{-1}$) because of the correlation of $\Delta_f H°(Ca^{+2}, aq, std.\ state, 298.15\ K)$ with the evaluation of data for several calcium compounds.[4]

Heat Capacity and Entropy

Paukov, Khriplovich, and Korotkikh[7] have measured $C_p°$ (13.10–309.18 K). Our T^3 extrapolation is in agreement with their vıuccirclalues of $S°(13\ K) = 0.516\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(13\ K) - H°(0\ K) = 4.99\ cal \cdot K^{-1} \cdot mol^{-1}$. The low temperature heat capacity joins smoothly with a linear extrapolation from $C_p° = 18.31\ cal \cdot K^{-1} \cdot mol^{-1}$ at 270 K to $C_p° = 22.0\ cal \cdot K^{-1} \cdot mol^{-1}$ at the adopted $T_{fus} = 1052$ K. The linearly extrapolated heat capacity at 300 K is only 0.3% higher than the Paukov *et al.*[7] value and $S°(298.15\ K) = 34.72\ cal \cdot K^{-1} \cdot mol^{-1}$ is in agreement with Paukov *et al.*[7] Dworkin and Bredig[8] determined the heat capacity of the crystal to be $23.2\ cal \cdot K^{-1} \cdot mol^{-1}$ (±5%) near the melting point. By using the lower limit, $C_p° = 22.0\ cal \cdot K^{-1} \cdot mol^{-1}$ of Dworkin and Bredig's value,[8] $H°(1052\ K) - H°(298.15\ K)$ is bıuccirclrought down to 15.24 $kcal \cdot mol^{-1}$, about 0.7% higher than Dworkin and Bredig's drop calorimeter measurement of 15.1 (±0.2%) $kcal \cdot mol^{-1}$.[8]

Fusion Data

Dworkin and Bredig[8] measured $\Delta_{fus} H° = 10.00\ kcal \cdot mol^{-1}$ (±2%) at $T_{fus} = 1052$ K ($S°_{fus} = 9.5\ cal \cdot K^{-1} \cdot mol^{-1}$) by drop calorimetry. Emons and Loeffelholz[9] determined $\Delta_{fus} H° = 6.65\ kcal \cdot mol^{-1}$ (±5%) and $T_{fus} = 1053$ K ($\Delta_{fus} S° = 6.3\ cal \cdot K^{-1} \cdot mol^{-1}$) by high temperature cryoscopy. The two pair of investigators are in much better agreement with other salts.[9] An entropy of melting criteria for choosing one of these values *is not conclusive because the entropies of melting of* CdI_2, $CdCl_2$, and $CdBr_2$*which* have similar layer crystal structure range from 7.5 to 9.5 $cal \cdot K^{-1} \cdot mol^{-1}$.[10] Hutchison[11] found $T_{fus} = 1018$ K, noting that only approximate melting points were obtained.

Because drop calorimetry is a more direct measure of the enthalpy of melting, we adopt $\Delta_{fus} H° = 10.00 \pm 0.20\ kcal \cdot mol^{-1}$ at $T_{fus} = 1052 \pm 2$ K.

Although unconfirmed by direct experimental evidence, the discrepancy in enthalpy of melting and the adjustments required in joining low temperature and high temperature heat capacities might be explained by the existence of a solid state transition in CaI_2 similar to the transitions in $BaCl_2$, $SrBr_2$, or $SrCl_2$.[8]

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference between the enthalpies of formation at 298.15 K of the ideal gas and crystal states.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.965	−535.838	−535.838	INFINITE
100	61.840	67.860	210.957	−14.310	−536.213	−535.303	279.614
200	73.304	115.131	152.260	−7.426	−536.530	−534.267	139.536
298.15	77.157	145.287	145.287	0.	−536.807	−533.097	93.396
300	77.195	145.764	145.288	0.143	−536.813	−533.074	92.816
400	79.161	168.244	148.340	7.962	−553.267	−531.211	69.369
500	81.170	186.124	154.168	15.978	−596.213	−521.572	54.488
600	83.136	201.097	160.775	24.194	−594.694	−506.786	44.120
700	85.103	214.060	167.481	32.605	−593.188	−492.254	36.732
800	87.069	225.553	174.035	41.214	−592.553	−477.833	31.199
900	89.036	235.921	180.344	50.019	−591.064	−463.583	26.906
1000	91.002	245.403	186.383	59.021	−589.684	−449.494	23.479
1052.000	92.048	250.043	189.416	63.780	−−− CRYSTAL <−−> LIQUID −−−		
1100	93.000	254.171	192.152	68.221	−588.422	−435.537	20.682
1200	94.977	262.348	197.664	77.620	−595.016	−421.067	18.329
1300	96.943	270.028	202.938	87.216	−592.776	−406.661	16.340
1400	98.910	277.284	207.992	97.009	−590.370	−392.433	14.642
1500	100.876	284.175	212.843	106.998	−587.808	−378.384	13.176

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [178.942]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-500.170]\ kJ·mol^{-1}$

$T_{fus} = 1052 \pm 2\ K$ $\Delta_{fus}H° = 41.84 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(CaI_2, l, 298.15\ K)$ is calculated from the sum of the enthalpy of formation of the crystal, the enthalpy of melting, and the difference in enthalpy, $H°(1052\ K)-H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, 24.7 $cal·K^{-1}·mol^{-1}$, was derived by Dworkin and Bredig[1] from drop calorimetric measurements. This value is adopted and is assumed constant from 700 K to 2500 K. A glass transition is assumed at 700 K below which the heat capacity is that of the crystal.

$S°(CaI_2, l, 298.15\ K)$ is calculated from the crystal entropy in a manner similar to that used for the enthalpy of formation calculation.

Vaporization Data

The temperature at which $\Delta_r G° = 0$ for the reaction $CaI_2(l) = CaI_2(g)$ at one bar is T_{vap}. Peterson and Hutchison[2] have extrapolated Knudsen effusion cell measurements in the 1076–1294 K range to obtain a normal boiling point of 1831 K (at 1 atm).

$\Delta_{vap}H°$ is the calculated difference between the enthalpies of formation of the ideal gas and the liquid at T_{vap}. Refer to the ideal gas table for details.

References

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[2]D. T. Peterson and J. F. Hutchison, J. Chem. Eng. Data **15**, 320 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.157	178.942	178.942	0.	−500.170	−506.494	88.736
300	77.195	179.419	178.943	0.143	−500.176	−506.534	88.195
400	79.161	201.899	181.995	7.962	−516.630	−508.036	66.343
500	81.170	219.779	187.823	15.978	−559.576	−501.762	52.419
600	83.136	234.752	194.430	24.194	−558.057	−490.342	42.688
700	85.103	247.715	201.136	32.605	−556.551	−479.176	35.757
700.000	85.103	247.715	201.136	32.605	GLASS <--> LIQUID		
700.000	103.345	247.715	201.136	32.605	TRANSITION		
800	103.345	261.515	207.840	42.940	−554.190	−468.240	30.573
900	103.345	273.687	214.494	53.274	−551.171	−457.680	26.563
1000	103.345	284.576	220.967	63.609	−548.459	−447.441	23.372
1052.000	103.345	289.815	224.242	68.983	--- CRYSTAL <--> LIQUID ---		
1100	103.345	294.426	227.204	73.943	−546.063	−437.458	20.773
1200	103.345	303.418	233.186	84.278	−551.721	−427.056	18.589
1300	103.345	311.690	238.911	94.612	−548.742	−416.788	16.747
1400	103.345	319.349	244.387	104.947	−545.795	−406.749	15.176
1500	103.345	326.479	249.624	115.281	−542.888	−396.919	13.822
1600	103.345	333.148	254.638	125.616	−540.030	−387.281	12.643
1700	103.345	339.414	259.443	135.950	−537.232	−377.820	11.609
1800	103.345	345.321	264.051	146.285	−683.172	−366.311	10.630
1900	103.345	350.908	268.477	156.619	−679.094	−348.819	9.590
2000	103.345	356.209	272.732	166.954	−675.092	−331.540	8.659
2100	103.345	361.251	276.828	177.288	−671.165	−314.459	7.822
2200	103.345	366.059	280.776	187.623	−667.312	−297.564	7.065
2300	103.345	370.653	284.584	197.957	−663.528	−280.842	6.378
2400	103.345	375.051	288.263	208.292	−659.808	−264.284	5.752
2500	103.345	379.270	291.819	218.626	−656.147	−247.879	5.179

PREVIOUS: CURRENT: June 1974

0 to 1052 K crystal
above 1052 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−17.965	−535.838	−535.838	INFINITE
100	61.840	67.860	210.957	−14.310	−536.213	−535.303	279.614
200	73.304	115.131	152.260	−7.426	−536.530	−534.267	139.536
298.15	77.157	145.287	145.287	0.	−536.807	−533.097	93.396
300	77.195	145.764	145.288	0.143	−536.813	−533.074	92.816
400	79.161	168.244	148.340	7.962	−553.267	−531.211	69.369
500	81.170	186.124	154.168	15.978	−596.213	−521.572	54.488
600	83.136	201.097	160.775	24.194	−594.694	−506.786	44.120
700	85.103	214.060	167.481	32.605	−593.188	−492.254	36.732
800	87.069	225.553	174.035	41.214	−592.553	−477.833	31.199
900	89.036	235.921	180.344	50.019	−591.064	−463.583	26.906
1000	91.002	245.403	186.383	59.021	−589.684	−449.494	23.479
1052.000	92.048	250.043	189.416	63.780	CRYSTAL <--> LIQUID TRANSITION		
1052.000	103.345	289.815	189.416	105.620			
1100	103.345	294.426	193.898	110.580	−546.063	−437.458	20.773
1200	103.345	303.418	202.655	120.915	−551.721	−427.056	18.589
1300	103.345	311.690	210.729	131.249	−548.742	−416.788	16.747
1400	103.345	319.349	218.217	141.584	−545.795	−406.749	15.176
1500	103.345	326.479	225.200	151.918	−542.888	−396.919	13.822
1600	103.345	333.148	231.740	162.253	−540.030	−387.281	12.643
1700	103.345	339.414	237.892	172.587	−537.232	−377.820	11.609
1800	103.345	345.321	243.697	182.922	−683.172	−366.311	10.630
1900	103.345	350.908	249.194	193.256	−679.094	−348.819	9.590
2000	103.345	356.209	254.414	203.591	−675.092	−331.540	8.659
2100	103.345	361.251	259.382	213.925	−671.165	−314.459	7.822
2200	103.345	366.059	264.123	224.260	−667.312	−297.564	7.065
2300	103.345	370.653	268.655	234.594	−663.528	−280.842	6.378
2400	103.345	375.051	272.997	244.929	−659.808	−264.284	5.752
2500	103.345	379.270	277.164	255.263	−656.147	−247.879	5.179

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [327.57 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -255.2 \pm 17\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -258.2 \pm 17\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[117](1)
[45](2)
[316](1)

Ground State Quantum Weight = [1] $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Ca–I = 2.88 ± 0.03 Å
Bond Angle: I–Ca–I = [180]°
Rotational Constant: $B_0 = 0.008008\ cm^{-1}$

Enthalpy of Formation

Peterson and Hutchison[1] used a weight loss Knudsen effusion technique to observe vapor pressures of the liquid at 18 temperatures ranging from 1076 K to 1294 K. Our 2nd and 3rd law analyses of these data, after rejection of one point due to failure of a statistical test, yield $\Delta_{vap}H°(298.15\ K)$ (2nd law) = 60.83 ± 2.04 $kcal·mol^{-1}$ and $\Delta_{vap}H°(298.15\ K)$ (3rd law) = 57.84 ± 0.98 $kcal·mol^{-1}$ with a drift of −2.6 ± 1.7 $cal·K^{-1}·mol^{-1}$. We adopt $\Delta_{vap}H°(298.15\ K)$ = 57.8 ± 3 $kcal·mol^{-1}$ and combine that with the adopted enthalpy of formation of the liquid to obtain $\Delta_f H°(CaI_2, g, 298.15\ K) = -61.7 \pm 4\ kcal·mol^{-1}$(−258.153 ± 17 $kJ·mol^{-1}$).

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from Akishin *et al.*[3] who also judged that the bond angle was 180° ± 10–20°. We have assumed a linear structure.

To estimate the vibrational frequencies, the stretching force constants for gaseous CaF, CaF_2, CaCl, and $CaCl_2$ are calculated from the vibrational frequencies[4] using a valence force model. The trend in the ratio of k(monohalide)/k_1(dihalide) indicates that $k(CaI)/k_1(CaI_2) = 1$ is a reasonable approximation, an approximation which has been used by Brewer *et al.*[5] The stretching force constant for CaI(g) is calculated from the ground state vibrational frequency given by Rosen.[6] The bending force constant is assumed to be 0.01 times the stretching force constant.[5] The adopted vibrational frequencies are calculated from the estimated force constants. Other estimates for υ_1, υ_2, and υ_3, are 121, 77, 327[7] and 118, 45, 321.[5]

We assign an uncertainty of ±2 $cal·K^{-1}·mol^{-1}$ to the entropy to allow for error in bond angle and vibrational frequency estimates.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−16.011	−255.230	−255.230	INFINITE
100	53.623	264.518	380.113	−11.559	−254.808	−273.564	142.895
200	58.924	303.667	333.072	−5.881	−256.331	−291.775	76.204
250	60.001	316.942	328.564	−2.905	−257.233	−300.533	62.793
298.15	60.636	327.569	327.569	0.	−258.153	−308.790	54.099
300	60.655	327.944	327.570	0.112	−258.189	−309.104	53.820
350	61.076	337.327	328.310	3.156	−259.263	−317.508	47.385
400	61.360	345.503	329.959	6.217	−276.357	−325.205	42.467
450	61.561	352.742	332.096	9.291	−278.680	−331.171	38.441
500	61.707	359.236	334.491	12.373	−321.164	−333.079	34.796
600	61.901	370.505	339.582	18.554	−321.679	−335.416	29.201
700	62.020	380.057	344.699	24.750	−322.389	−337.653	25.196
800	62.098	388.344	349.648	30.957	−324.156	−339.669	22.178
900	62.152	395.661	354.362	37.169	−325.259	−341.545	19.823
1000	62.191	402.212	358.825	43.386	−326.664	−343.282	17.931
1100	62.220	408.141	363.043	49.607	−328.382	−344.863	16.376
1200	62.242	413.556	367.030	55.830	−338.151	−345.652	15.046
1300	62.259	418.538	370.803	62.055	−339.282	−346.231	13.912
1400	62.272	423.153	374.380	68.282	−340.443	−346.722	12.936
1500	62.283	427.449	377.776	74.510	−341.642	−347.129	12.088
1600	62.292	431.469	381.008	80.738	−342.890	−347.454	11.343
1700	62.300	435.246	384.088	86.968	−344.197	−347.700	10.684
1800	62.306	438.807	387.030	93.198	−494.241	−345.656	10.031
1900	62.311	442.176	389.845	99.429	−494.267	−337.401	9.276
2000	62.316	445.372	392.542	105.661	−494.367	−329.143	8.596
2100	62.320	448.413	395.131	111.892	−494.543	−320.877	7.981
2200	62.323	451.312	397.619	118.125	−494.792	−312.602	7.422
2300	62.326	454.083	400.014	124.357	−495.111	−304.314	6.911
2400	62.329	456.735	402.323	130.590	−495.493	−296.010	6.442
2500	62.331	459.280	404.550	136.823	−495.933	−287.690	6.011
2600	62.333	461.724	406.703	143.056	−496.426	−279.350	5.612
2700	62.335	464.077	408.784	149.289	−496.966	−270.991	5.243
2800	62.337	466.344	410.800	155.523	−497.550	−262.611	4.899
2900	62.338	468.531	412.753	161.757	−498.174	−254.209	4.579
3000	62.339	470.645	414.648	167.991	−498.836	−245.786	4.280
3100	62.341	472.689	416.487	174.225	−499.535	−237.339	3.999
3200	62.342	474.668	418.275	180.459	−500.274	−228.870	3.736
3300	62.343	476.586	420.013	186.693	−501.054	−220.376	3.488
3400	62.343	478.448	421.704	192.927	−501.877	−211.859	3.255
3500	62.344	480.255	423.351	199.162	−502.748	−203.316	3.034
3600	62.345	482.011	424.957	205.396	−503.672	−194.748	2.826
3700	62.346	483.719	426.522	211.631	−504.653	−186.153	2.628
3800	62.346	485.382	428.049	217.865	−505.695	−177.531	2.440
3900	62.347	487.001	429.540	224.100	−506.805	−168.881	2.262
4000	62.348	488.580	430.996	230.335	−507.986	−160.202	2.092
4100	62.348	490.119	432.420	236.569	−509.243	−151.492	1.930
4200	62.349	491.622	433.811	242.804	−510.580	−142.750	1.775
4300	62.349	493.089	435.173	249.039	−512.000	−133.976	1.627
4400	62.349	494.522	436.506	255.274	−513.502	−125.168	1.486
4500	62.350	495.924	437.810	261.509	−515.076	−116.325	1.350
4600	62.350	497.294	439.089	267.744	−516.745	−107.446	1.220
4700	62.350	498.635	440.341	273.979	−518.504	−98.530	1.095
4800	62.351	499.948	441.570	280.214	−520.349	−89.574	0.975
4900	62.351	501.233	442.774	286.449	−522.279	−80.580	0.859
5000	62.351	502.493	443.956	292.684	−524.290	−71.546	0.747
5100	62.352	503.728	445.116	298.919	−526.381	−62.470	0.640
5200	62.352	504.938	446.255	305.155	−528.544	−53.353	0.536
5300	62.352	506.126	447.373	311.390	−530.783	−44.194	0.436
5400	62.352	507.291	448.472	317.625	−533.090	−34.991	0.338
5500	62.352	508.436	449.552	323.860	−535.461	−25.746	0.245
5600	62.353	509.559	450.613	330.096	−537.881	−16.457	0.154
5700	62.353	510.663	451.657	336.331	−540.362	−7.124	0.065
5800	62.353	511.747	452.684	342.566	−542.892	2.253	−0.020
5900	62.353	512.813	453.694	348.801	−545.465	11.674	−0.103
6000	62.353	513.861	454.688	355.037	−548.075	21.139	−0.184

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 38.212 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 3200 \pm 50\ K$

$\Delta_f H°(0\ K) = -631.76 \pm 0.88\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -635.09 \pm 0.88\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [79.5]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Huber and Holley[1] determined the enthalpy of combustion of calcium metal in a bomb calorimeter and derived the enthalpy of formation of calcium oxide (cr) as $-151.9\ kcal \cdot mol^{-1}$ which is adopted in the tabulation. The adopted value is in good agreement with the value, $-151.9\ kcal \cdot mol^{-1}$ [2] derived from solution calorimetry.

Heat Capacity and Entropy

Gmelin[3] measured low temperature C_p data from 4 to 300 K in an adiabatic calorimeter. We use his smoothed C_p values to derive $S°(298.15\ K) = 9.133 \pm 0.03\ cal \cdot K^{-1} \cdot mol^{-1}$ based on $S° = 0.0001\ cal \cdot K^{-1} \cdot mol^{-1}$ at 4 K. Lander[4] determined high temperature enthalpy data from 563.6 to 1176.4 K by drop calorimetry. The low temperature C_p and high temperature enthalpy data are smoothly joined at 298.15 K by a polynomial curve fitting method. The deviations of the observed enthalpies from the adopted values are about 0.2–1%, except the enthalpy value at 753 K (2.0%). Heat capacities above 1200 K are extrapolated from the adopted C_p functions. The extrapolated C_p at the melting point (2887 K), 14.8 $J \cdot K \cdot mol^{-1}$, is in reasonable agreement with the value $2 \times 7.25\ cal \cdot K^{-1}$ g-atom^{-1} suggested by Kubaschewski.[5]

Combination of the earlier low temperature C_p measurements of Nernst and Schwers (28–90 K)[6] and Parks and Kelley (87–293 K)[7] yields $S°(298.15\ K) = 9.5 \pm 0.2\ cal \cdot K^{-1} \cdot mol^{-1}$, based on $S°(298.15\ K) = 0.04\ cal \cdot K^{-1} \cdot mol^{-1}$.[8] These C_p measurements are less accurate than those of Gmelin,[3] and are not adopted in the tabulation.

Fischer and Ertmer[9] determined high temperature enthalpy data by drop calorimetry in the temperature range from 0° to 1716°C. The accuracy was claimed to be approximately ±4%. We have not adopted their enthalpy data in the tabulation since the heat capacities which we derive from their data are always less than those of MgO[10] when the temperature is above 1000 K. The deviations between their enthalpy data and the adopted values are approximately 1.8% at 693 K, 3.3% at 1283 K and 5.3% at 1989 K.

Fusion Data

Schneider[11] adjusted earlier melting points[12–15] to IPTS–48, yielding values ranging from 2565° to 2630°C. Recent studies by Foex,[16, 17] using solar energy to melt the center of a rotating crucible of oxide, gave values higher by about 300°C. Apparently the earlier values were depressed by formation of tungstates with the tungsten supports of the sample. Unfortunately, Foex reported three values: 2910°C (1968),[16] 2950°C(1968),[16] and 2900°C(1969).[17] We adopt an intermediate value of 2927°C = 3200 K and arbitrarily assign an uncertainty of 50 K.

The enthalpy of melting is assumed to be 19 $kcal \cdot mol^{-1}$ which is calculated from the estimated $\Delta_{fus} S° = 6\ cal \cdot K^{-1} \cdot mol^{-1}$ at the melting point. The latter is estimated to be the same as that of MgO.[10]

References

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.749	−631.760	−631.760	INFINITE
100	14.715	6.222	69.166	−6.294	−633.739	−624.099	325.996
200	33.677	23.041	41.825	−3.757	−634.925	−613.887	160.331
298.15	42.120	38.212	38.212	0.	−635.089	−603.501	105.731
300	42.242	38.473	38.213	0.078	−635.086	−603.305	105.045
400	46.626	51.300	39.932	4.547	−634.738	−592.755	77.406
500	48.982	61.980	43.305	9.338	−634.242	−582.316	60.834
600	50.480	71.052	47.193	14.315	−633.787	−571.975	49.795
700	51.555	78.917	51.175	19.419	−633.449	−561.701	41.915
800	52.400	85.858	55.085	24.618	−634.112	−551.362	36.000
900	53.112	92.072	58.856	29.894	−634.064	−541.024	31.400
1000	53.735	97.700	62.463	35.237	−634.273	−530.677	27.720
1100	54.300	102.849	65.904	40.639	−634.749	−520.297	24.707
1200	54.831	107.596	69.183	46.096	−643.226	−509.239	22.167
1300	55.329	112.005	72.309	51.604	−643.009	−498.082	20.013
1400	55.810	116.123	75.293	57.161	−642.759	−486.943	18.168
1500	56.275	119.989	78.146	62.766	−642.475	−475.823	16.570
1600	56.727	123.636	80.876	68.416	−642.159	−464.723	15.172
1700	57.174	127.088	83.494	74.111	−641.810	−453.644	13.939
1800	57.609	130.369	86.007	79.850	−790.102	−440.375	12.779
1900	58.045	133.495	88.425	85.633	−788.275	−420.996	11.574
2000	58.471	136.483	90.754	91.459	−786.423	−401.713	10.492
2100	58.894	139.346	93.000	97.327	−784.547	−382.523	9.515
2200	59.317	142.096	95.170	103.238	−782.651	−363.423	8.629
2300	59.735	144.742	97.268	109.190	−780.739	−344.411	7.822
2400	60.149	147.293	99.299	115.184	−778.816	−325.481	7.084
2500	60.563	149.757	101.269	121.220	−776.887	−306.632	6.407
2600	60.978	152.140	103.180	127.297	−774.958	−287.860	5.783
2700	61.388	154.449	105.036	133.415	−773.036	−269.161	5.207
2800	61.798	156.689	106.841	139.575	−771.126	−250.534	4.674
2900	62.208	158.865	108.597	145.775	−769.238	−231.976	4.178
3000	62.618	160.981	110.308	152.016	−767.378	−213.481	3.717
3100	63.024	163.040	111.976	158.298	−765.554	−195.048	3.287
3200	63.434	165.048	113.604	164.621	−763.774	−176.673	2.884
3200.000	63.434	165.048	113.604	164.621	--- CRYSTAL <--> LIQUID ---		
3300	63.839	167.006	115.192	170.985	−762.047	−158.353	2.507
3400	64.245	168.918	116.744	177.389	−760.379	−140.084	2.152
3500	64.651	170.786	118.262	183.834	−758.779	−121.864	1.819
3600	65.057	172.613	119.746	190.319	−757.254	−103.688	1.504

PREVIOUS: June 1971 CURRENT: June 1973

$S°(298.15\ K) = [62.321]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-557.335]\ kJ·mol^{-1}$

$T_{fus} = 3200 \pm 50\ K$ $\Delta_{fus}H° = [79.5]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H$ and the difference in enthalpy, $H°(3200\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2100 K. Heat capacities of the liquid below 2100 K are assumed to be the same as those of the crystal. Above 2100 K the heat capacity is assumed to be constant at 7.50 $cal·K^{-1}$ $g–atom^{-1}$.

The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition

CaO does not vaporize simply to CaO(g); extensive dissociation of CaO(g) to Ca(g) was found mass–spectrometrically.[1]

Reference

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	42.120	62.321	62.321	0.	−557.335	−532.935	93.368
300	42.242	62.582	62.322	0.078	−557.332	−532.783	92.766
400	46.626	75.409	64.041	4.547	−556.984	−524.644	68.511
500	48.982	86.089	67.413	9.338	−556.488	−516.616	53.971
600	50.480	95.160	71.301	14.315	−556.033	−508.686	44.285
700	51.555	103.026	75.284	19.419	−555.695	−500.823	37.372
800	52.400	109.966	79.194	24.618	−556.358	−492.895	32.183
900	53.112	116.180	82.964	29.894	−556.310	−484.968	28.147
1000	53.735	121.809	86.572	35.237	−556.519	−477.032	24.918
1100	54.300	126.957	90.012	40.639	−556.995	−469.062	22.274
1200	54.831	131.705	93.291	46.096	−565.472	−460.415	20.041
1300	55.329	136.114	96.418	51.604	−565.255	−451.669	18.148
1400	55.810	140.232	99.402	57.161	−565.005	−442.941	16.526
1500	56.275	144.098	102.254	62.766	−564.721	−434.232	15.121
1600	56.727	147.744	104.984	68.416	−564.405	−425.543	13.893
1700	57.174	151.197	107.602	74.111	−564.056	−416.874	12.809
1800	57.609	154.477	110.116	79.850	−712.348	−406.017	11.782
1900	58.045	157.604	112.534	85.633	−710.521	−389.048	10.696
2000	58.471	160.592	114.862	91.459	−708.669	−372.176	9.720
2100	58.894	163.455	117.109	97.327	−706.793	−355.397	8.840
2100.000	58.894	163.455	117.109	97.327	GLASS <--> LIQUID		
2100.000	62.760	163.455	117.109	97.327	TRANSITION		
2200	62.760	166.374	119.282	103.603	−704.531	−338.717	8.042
2300	62.760	169.164	121.391	109.879	−702.296	−322.140	7.316
2400	62.760	171.835	123.437	116.155	−700.092	−305.659	6.652
2500	62.760	174.397	125.425	122.431	−697.922	−289.269	6.044
2600	62.760	176.859	127.356	128.707	−695.794	−272.965	5.484
2700	62.760	179.227	129.234	134.983	−693.714	−256.741	4.967
2800	62.760	181.510	131.060	141.259	−691.688	−240.594	4.488
2900	62.760	183.712	132.838	147.535	−689.724	−224.519	4.044
3000	62.760	185.840	134.569	153.811	−687.829	−208.510	3.630
3100	62.760	187.898	136.257	160.087	−686.011	−192.562	3.245
3200	62.760	189.890	137.902	166.363	−684.278	−176.673	2.884
3200.000	62.760	189.890	137.902	166.363	--- CRYSTAL <--> LIQUID ---		
3300	62.760	191.821	139.507	172.639	−682.638	−160.836	2.546
3400	62.760	193.695	141.073	178.915	−681.099	−145.047	2.228
3500	62.760	195.514	142.603	185.191	−679.668	−129.302	1.930
3600	62.760	197.282	144.097	191.467	−678.352	−113.596	1.648
3700	62.760	199.002	145.558	197.743	−677.158	−97.925	1.382
3800	62.760	200.676	146.986	204.019	−676.092	−82.285	1.131
3900	62.760	202.306	148.384	210.295	−675.160	−66.670	0.893
4000	62.760	203.895	149.752	216.571	−674.364	−51.079	0.667
4100	62.760	205.444	151.091	222.847	−673.711	−35.505	0.452
4200	62.760	206.957	152.404	229.123	−673.202	−19.946	0.248
4300	62.760	208.434	153.690	235.399	−672.840	−4.396	0.053
4400	62.760	209.876	154.950	241.675	−672.622	11.146	−0.132
4500	62.760	211.287	156.187	247.951	−672.538	26.683	−0.310

PREVIOUS: June 1971 CURRENT: June 1973

0	to 3200	K	crystal
above	3200	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.749	−631.760	−631.760	INFINITE
100	14.715	6.222	69.166	−6.294	−633.739	−624.099	325.996
200	33.677	23.041	41.825	−3.757	−634.925	−613.887	160.331
298.15	42.120	38.212	38.212	0.	−635.089	−603.501	105.731
300	42.242	38.473	38.213	0.078	−635.086	−603.305	105.045
400	46.626	51.300	39.932	4.547	−634.738	−592.755	77.406
500	48.982	61.980	43.305	9.338	−634.242	−582.316	60.834
600	50.480	71.052	47.193	14.315	−633.787	−571.975	49.795
700	51.555	78.917	51.175	19.419	−633.449	−561.701	41.915
800	52.400	85.858	55.085	24.618	−634.112	−551.362	36.000
900	53.112	92.072	58.856	29.894	−634.064	−541.024	31.400
1000	53.735	97.700	62.463	35.237	−634.273	−530.677	27.720
1100	54.300	102.849	65.904	40.639	−634.749	−520.297	24.707
1200	54.831	107.596	69.183	46.096	−643.226	−509.239	22.167
1300	55.329	112.005	72.309	51.604	−643.009	−498.082	20.013
1400	55.810	116.123	75.293	57.161	−642.759	−486.943	18.168
1500	56.275	119.989	78.146	62.766	−642.475	−475.823	16.570
1600	56.727	123.636	80.876	68.416	−642.159	−464.723	15.172
1700	57.174	127.088	83.494	74.111	−641.810	−453.644	13.939
1800	57.609	130.369	86.007	79.850	−790.102	−440.375	12.779
1900	58.045	133.495	88.425	85.633	−788.275	−420.996	11.574
2000	58.471	136.483	90.754	91.459	−786.423	−401.713	10.492
2100	58.894	139.346	93.000	97.327	−784.547	−382.523	9.515
2200	59.317	142.096	95.170	103.238	−782.651	−363.423	8.629
2300	59.735	144.742	97.268	109.190	−780.739	−344.411	7.822
2400	60.149	147.293	99.299	115.184	−778.816	−325.481	7.084
2500	60.563	149.757	101.269	121.220	−776.887	−306.632	6.407
2600	60.978	152.140	103.180	127.297	−774.958	−287.860	5.783
2700	61.388	154.449	105.036	133.415	−773.036	−269.161	5.207
2800	61.798	156.689	106.841	139.575	−771.126	−250.534	4.674
2900	62.208	158.865	108.597	145.775	−769.238	−231.976	4.178
3000	62.618	160.981	110.308	152.016	−767.378	−213.481	3.717
3100	63.024	163.040	111.976	158.298	−765.554	−195.048	3.287
3200	63.434	165.048	113.604	164.621	−763.774	−176.673	2.884
3200.000	63.434	165.048	113.604	164.621	CRYSTAL <--> LIQUID TRANSITION		
3200.000	62.760	189.890	113.604	244.117			
3300	62.760	191.821	115.945	250.393	−682.638	−160.836	2.546
3400	62.760	193.695	118.204	256.669	−681.099	−145.047	2.228
3500	62.760	195.514	120.387	262.945	−679.668	−129.302	1.930
3600	62.760	197.282	122.499	269.221	−678.352	−113.596	1.648
3700	62.760	199.002	124.543	275.497	−677.158	−97.925	1.382
3800	62.760	200.676	126.525	281.773	−676.092	−82.285	1.131
3900	62.760	202.306	128.447	288.049	−675.160	−66.670	0.893
4000	62.760	203.895	130.313	294.325	−674.364	−51.079	0.667
4100	62.760	205.444	132.127	300.601	−673.711	−35.505	0.452
4200	62.760	206.957	133.891	306.877	−673.202	−19.946	0.248
4300	62.760	208.434	135.607	313.153	−672.840	−4.396	0.053
4400	62.760	209.876	137.279	319.429	−672.622	11.146	−0.132
4500	62.760	211.287	138.908	325.705	−672.538	26.684	−0.310

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = 219.717 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 45.1 \pm 21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 43.9 \pm 21\ kJ·mol^{-1}$

		Electronic and Molecular Constants (σ = 1)						
Source	State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
1-3	$X^1\Sigma^+$	0.0	1	1.822	0.44452	0.00338	733.4	5.28
1	$a^3\Pi$	8225.	6	2.097	0.3353	0.0015	556.2	3.30
1	$A''^1\Pi$	8612.	2	2.092	0.3372	0.0021	545.7	2.54
1,4,5	$^3\Sigma^+$	[10000]	3	[1.906]	[0.4059]	[0.0014]	[719]	[2.1]
1-3	$A^1\Sigma^+$	11549.	1	1.906	0.40592	0.00137	718.9	2.11
5	$^3\Sigma^+$	[21000]	3	[2.00]	[0.369]	[0.003]	[560]	[4.]
5	$^3\Delta$	[21000]	6	[2.00]	[0.369]	[0.003]	[560]	[4.]
5	$^1\Delta$	[23000]	2	[2.00]	[0.369]	[0.003]	[560]	[4.]
5	$^3\Sigma^-$	[23000]	3	[2.00]	[0.369]	[0.003]	[560]	[4.]
5	$^1\Sigma^-$	[23000]	1	[2.00]	[0.369]	[0.003]	[560]	[4.]
6	$C^1\Sigma^+$	28772.	1	1.989	0.3731	0.0032	560.9	4.0
5	$^3\Pi$	[24000]	6	[1.95]	[0.3882]	[0.0055]	[581]	[3.3]
7	$B^1\Pi$	25913.	2	1.950	0.3882	0.0055	581.0	[3.3]

Enthalpy of Formation

We adopt $D_0° = 91 \pm 5$ and $\Delta_f H°(298.15\ K) = 10.5 \pm 5\ kcal·mol^{-1}$ based on mass-spectrometric data[8,9] for four reactions analyzed below. We give "<" or ">" for $\Delta H°$ and $D_0°$ values which may be biased due to our auxiliary data. JANAF differences in $\Delta_f H°(298.15\ K)$ for WO_3–WO_2 and MoO_3–MoO_2[5] may be biased by up to −3.5 and + 4.1 $kcal·mol^{-1}$, respectively, leading to bias of the opposite sign in $D_0°$ values derived from reactions B and C. Adjustments for this possible bias would improve the agreement in $D_0°$ but leave the mean value almost unchanged. Kalff[10] used spectrometry of CO–N_2O flames to derive $D_0° = 86.5 \pm 4.6\ kcal·mol^{-1}$. This value becomes −89.5 $kcal·mol^{-1}$ when adjusted to be consistent with JANAF Gibbs energy functions. Our adopted $D_0° = 91 \pm 5$ is similar to that of Rosen[6] and is comparable with other selected values,[8,11] considering the difference in CaO functions.

The controversy over $D_0°$ of alkaline earth oxides has been reviewed in detail.[8,11-13] Uncertainty in the electronic partition function of CaO due to triplet states now is much reduced.[1] Schofields's criticism[12] of flame studies is supported by new evidence for importance of hydroxides;[10,14,15] thus, we dismiss higher flame values for $D_0°$.[12] Valid criticism[8] also causes us to dismiss higher $D_0°$ values derived from vaporization data. A linear Birge–Sponer extrapolation yields a very low estimate for $D_0°$, just as it does for the alkali halides,[13] unless $X^1\Sigma$ fails to dissociate to an excited state atom as predicted.[17,1]

Source	Method	Reaction[a]	T/K	Data Points	δS $cal·K^{-1}mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	kcal·mol $\Delta_f H°(298.15\ K)$	$D_0°$
8	Knudsen mass spec.	A	2168–2410	4	−2.3 ± 9.7	24 ± 22	29.4 ± 3	12.7	88.8
	Knudsen mass spec.	B	2328–2334	2	67	209	51.9 ± 3	>6.5	<95.0
	Knudsen mass spec.	C	2393–2410	3	12 ± 83	85 ± 100	55.8 ± 3	≤15.5	<85.9
9	Knudsen mass spec.	D	2180–2386	3	1 ± 31	31 ± 72	27.9 ± 6	5.6	95.8[b]

[a]Reactions: A) Ca(g) + O_2(g) = CaO(g) + O(g); C) Ca(g) + MoO_3(g) = CaO(g) + MoO_2(g);
B) Ca(g) + WO_3(g) = CaO(g) + WO_2(g); D) Ca(g) + SO(g) = CaO(g) + S(g).

[b]Ion intensities and $D_0°$ reported [9] at 2180 K are discrepant by −8 $kcal·mol^{-1}$; we use ion intensities.

Heat Capacity and Entropy

Electronic levels (T_o) and vibrational–rotational constants of the observed states are from (1, 2, 3, 6, 7). The long–sought $a^3\Pi$ and $A''^1\Pi$ states of CaO, SrO and BaO were characterized by Field[1] using a new method for assignment of perturbations. This study resolved the long–standing controversy over low–lying electronic levels and confirmed that $X^1\Sigma^+$ is the ground state. We estimate the other potentially low–lying state ($^3\Sigma^+$) at 10000 cm^{-1} by assuming that it lies 1500 ± 1200 cm^{-1} [1,4] below the isoconfigurational order of MgO.[5] Rotational analysis of a band near 5470 Å was attributed[16] to CaO, but we question this assignment. Our thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \Sigma_i Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

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[5]JANAF Thermochemical Tables: CaO(g), MgO(g), BeO(g) 12–31–74; SrO(g), BaO(g) 6–30–74; WO_2(g), WO_3(g) 9–30–66; MoO_2(g), MoO_3(g) 6–30–68.

Continued on page 736

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.953	45.057	45.057	INFINITE
100	29.136	186.730	247.175	−6.044	45.533	37.122	−19.390
200	30.381	207.194	222.620	−3.085	44.768	28.975	−7.568
298.15	32.455	219.717	219.717	0.	43.932	21.405	−3.750
300	32.491	219.918	219.717	0.060	43.917	21.266	−3.703
400	34.089	229.499	221.013	3.394	43.131	13.835	−1.807
500	35.139	237.226	223.508	6.859	42.301	6.604	−0.690
600	35.833	243.699	226.348	10.410	41.330	−0.447	0.039
700	36.313	249.260	229.233	14.019	40.172	−7.321	0.546
800	36.663	254.133	232.047	17.669	37.960	−13.911	0.908
900	36.947	258.468	234.747	21.349	36.412	−20.305	1.178
1000	37.218	262.375	237.317	25.058	34.569	−26.510	1.385
1100	37.532	265.936	239.760	28.794	32.428	−32.517	1.544
1200	37.947	269.219	242.079	32.567	22.266	−37.694	1.641
1300	38.518	272.278	244.286	36.389	20.797	−42.630	1.713
1400	39.291	275.159	246.389	40.278	19.378	−47.456	1.771
1500	40.298	277.903	248.399	44.255	18.035	−52.182	1.817
1600	41.551	280.542	250.326	48.345	16.792	−56.822	1.855
1700	43.046	283.105	252.179	52.573	15.674	−61.388	1.886
1800	44.755	285.613	253.967	56.962	−133.969	−63.682	1.848
1900	46.639	288.082	255.698	61.530	−133.357	−59.793	1.644
2000	48.642	290.525	257.378	66.293	−132.567	−55.941	1.461
2100	50.703	292.948	259.015	71.260	−131.592	−52.133	1.297
2200	52.757	295.354	260.612	76.434	−130.433	−48.375	1.149
2300	54.742	297.744	262.174	81.810	−129.098	−44.674	1.015
2400	56.603	300.113	263.706	87.378	−127.601	−41.036	0.893
2500	58.293	302.459	265.209	93.125	−125.962	−37.462	0.783
2600	59.778	304.775	266.686	99.030	−124.204	−33.956	0.682
2700	61.036	307.055	268.139	105.072	−122.357	−30.520	0.590
2800	62.057	309.294	269.569	111.229	−120.451	−27.153	0.507
2900	62.844	311.486	270.977	117.476	−118.515	−23.856	0.430
3000	63.404	313.627	272.363	123.790	−116.582	−20.624	0.359
3100	63.755	315.712	273.728	130.150	−114.681	−17.457	0.294
3200	63.918	317.739	275.072	136.535	−112.839	−14.350	0.234
3300	63.917	319.706	276.395	142.928	−111.082	−11.300	0.179
3400	63.776	321.613	277.697	149.314	−109.433	−8.301	0.128
3500	63.520	323.458	278.978	155.679	−107.913	−5.350	0.080
3600	63.172	325.243	280.239	162.015	−106.538	−2.439	0.035
3700	62.754	326.968	281.478	168.311	−105.323	0.435	−0.006
3800	62.283	328.635	282.698	174.564	−104.281	3.280	−0.045
3900	61.777	330.247	283.896	180.767	−103.420	6.099	−0.082
4000	61.250	331.804	285.075	186.918	−102.750	8.898	−0.116
4100	60.713	333.310	286.233	193.017	−102.274	11.683	−0.149
4200	60.175	334.767	287.371	199.061	−101.997	14.458	−0.180
4300	59.644	336.176	288.490	205.052	−101.920	17.230	−0.209
4400	59.125	337.542	289.589	210.990	−102.040	20.001	−0.237
4500	58.624	338.865	290.670	216.877	−102.344	22.777	−0.264
4600	58.142	340.148	291.731	222.715	−102.851	25.562	−0.290
4700	57.683	341.393	292.775	228.507	−103.554	28.361	−0.315
4800	57.246	342.603	293.800	234.253	−104.443	31.177	−0.339
4900	56.834	343.779	294.808	239.957	−105.514	34.014	−0.363
5000	56.446	344.923	295.799	245.620	−106.760	36.873	−0.385
5100	56.081	346.037	296.773	251.246	−108.175	39.760	−0.407
5200	55.739	347.123	297.731	256.837	−109.748	42.675	−0.429
5300	55.418	348.182	298.673	262.395	−111.478	45.623	−0.450
5400	55.119	349.215	299.600	267.922	−113.355	48.604	−0.470
5500	54.840	350.224	300.511	273.419	−115.371	51.621	−0.490
5600	54.580	351.209	301.408	278.890	−117.507	54.676	−0.510
5700	54.337	352.173	302.290	284.336	−119.775	57.771	−0.529
5800	54.110	353.116	303.158	289.758	−122.158	60.907	−0.549
5900	53.899	354.040	304.013	295.159	−124.648	64.083	−0.567
6000	53.702	354.944	304.854	300.539	−127.237	67.304	−0.586

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 56.6 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [2798]\ K$

$\Delta_f H°(0\ K) = -472.1 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -473.2 \pm 2.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Sabatier,[1] Mourlot,[2] and von Wartenberg,[3] all measured the enthalpy of solution of CaS in hydrochloric acid solution. Sabatier determined $\Delta_r H°(238.8) = -26.3 \pm 1.0$ kcal·mol^{-1} while Mourlot determined $\Delta_r H°(291) = -26.7 \pm 1.0$ kcal·mol^{-1} for CaS(cr) + 2HCl(100 H_2O, aq) → $CaCl_2$(100 H_2O, aq) + H_2S(aq). We derive $\Delta_f H°$(CaS, cr, 298.15 K) = −112.7 ± 2.0 kcal·mol^{-1} and $\Delta_f H°$(CaS, cr, 298.15 K) = −112.3 ± 2.0 kcal·mol^{-1} respectively, based on the following auxiliary data: $\Delta_f H°$(HCl·100 H_2O, aq, 298.15 K) = −39.657 kcal·mol^{-1},[4] $\Delta_f H°$(H_2S, aq, 298.15 K) = −9.5 kcal·mol^{-1},[4] and $\Delta_f H°$($CaCl_2$100 H_2O, aq, 298.15 K) = −208.849 kcal·mol^{-1}.[5] Von Wartenberg measured $\Delta_r H(293.15) = -20.6 \pm 0.4$ kcal·mol^{-1} for CaS(cr) + 2HCl(30 H_2O, aq) → $CaCl_2$(30 H_2O, aq) + H_2S(g). We derive $\Delta_f H°$(CaS, cr, 298.15 K) = −113.9 ± 0.6 kcal·mol^{-1} based on the following auxiliary data: $\Delta_f H°$(HCl·30 H_2O, aq, 298.15 K) = −39.357 kcal·mol^{-1},[4] $\Delta_f H°$(H_2S, g, 298.15 K) = −4.90 kcal·mol^{-1},[4, 18] and $\Delta_f H°$($CaCl_2$·30 H_2O, aq, 298.15 K) = −208.33 kcal·mol^{-1}.[5]

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K^{-1}mol^{-1}	$\Delta_r H$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[6]	Vap. Press.	A	1400–1700	Equation	−3.94	112.3	118.39 ± 1.0	−88.9 ± 30
[7]	Equilibrium	B	1019–1704	15	1.06 ± 0.1	15.6 ± 0.1	14.14 ± 0.5	−113.01 ± 0.8
[8]	Equilibrium	B	1031–1698	12	1.01 ± 0.2	15.4 ± 0.3	14.02 ± 0.5	−112.89 ± 0.8
[9]	Equilibrium	B	1173–1373	Equation	0.18	14.3	14.04 ± 1.0	−112.91 ± 1.0
[9]	Equilibrium	C	926–1026	Equation	0.03	−23.02	−23.06 ± 1.0	−113.31 ± 2.0
[10]	Equilibrium	D	1124–1348	6	5.5 ± 0.6	−51.2 ± 0.8	−58.0 ± 1.0	−111.98 ± 2.0
[11]	Equilibrium	D	1173–1393	10	7.3 ± 3.2	−76.3 ± 4.2	−66.8 ± 1.6	−103.2 ± 4
[11]	Equilibrium	E	1173–1393	10	−0.95 ± 5	254.06 ± 6.5	255.2 ± 1.9	−117.9 ± 4
[12]	Equilibrium	C	1400–1650	7	−2.8 ± 0.3	17.3 ± 0.5	22.3 ± 0.5	−114.04 ± 0.6
[13]	Mass Spec.	F	1709	1			212.5 ± 10	−103.4 ± 10
[14]	Mass Spec.	G	1849–2155	7	−11.8 ± 2.0	−1.4 ± 4.0	22.0 ± 2.0	−116.3 ± 8

[a]Reactions:
A) CaS(c) = CaS(g)
B) CaS(c) + H_2O(g) = CaO(c) + H_2S(g)
C) CaS(c) + 0.5O_2(g) = CaO(c) + 0.5S_2(g)
D) CaS(c) + 2SO_2(g) = $CaSO_4$(c) + S_2(g)
E) CaS(c) + 3$CaSO_4$(c) = 4CaO(c) + 4SO_2(g)
F) CaS(c) + CaS(c) = Ca(g) + S(g)
G) CaS(c) + 3S(g) = Ca(g) + 2S_2(g)

The calculated 3rd-law $\Delta_r H°(298.15\ K)$ may have an uncertainty of 0.5 kcal·mol^{-1} since the JANAF Gibbs energy functions are partially based on the estimated $C_p°$ data (above 300 K). The results of the majority of the equilibrium studies,[7–12] are in very good agreement with the enthalpy of solution[1–5] studies within combined experimental errors. The mass spectrometric studies[13, 14] are not as reliable in condensed phase equilibrium as they are in gas phase equilibrium.[18] A weighted average, $\Delta_f H°$(CaS, cr, 298.15 K) = −113.1 ± 0.7 kcal·mol^{-1} is adopted in the tabulation.

Heat Capacity and Entropy

Anderson[15] measured the low temperature heat capacities of CaS(cr) from 58.1 – 294.9 K in an isothermal calorimeter. We have smoothed his $C_p°$ data by a polynomial curve fitting technique and obtain $S°(298.15\ K) = 13.5 \pm 0.3$ cal·K^{-1}·mol^{-1} based on $S°$ (60 K) = 1.192 cal·K^{-1}·mol^{-1}. The value of $S°(60\ K)$ is calculated from the combination of Debye and Einstein functions ($\theta_D = 284$ and $\theta_E = 369$). The $C_p°$ values above 300 K are estimated by graphical extrapolation combined with a variant of method B of Kubaschewski *et al.*[16]

Fusion Data

The melting point of CaS(cr) is given as 2525°C.[17]

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Continued on page 736

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.999	−472.061	−472.061	INFINITE
100	25.945	14.477	94.617	−8.014	−472.746	−471.345	246.206
200	42.204	38.610	60.808	−4.440	−473.083	−469.779	122.694
298.15	47.442	56.601	56.601	0.	−473.210	−468.129	82.014
300	47.447	56.895	56.602	0.088	−473.213	−468.098	81.503
400	49.204	70.796	58.486	4.924	−475.608	−466.281	60.890
500	50.501	81.919	62.096	9.911	−477.314	−463.765	48.449
600	51.547	91.223	66.196	15.016	−478.737	−460.916	40.126
700	52.342	99.230	70.357	20.211	−480.027	−457.844	34.165
800	53.011	106.265	74.415	25.480	−482.164	−454.483	29.675
900	53.555	112.540	78.308	30.808	−536.618	−449.864	26.109
1000	54.099	118.211	82.020	36.192	−536.911	−440.212	22.994
1100	54.586	123.391	85.548	41.626	−537.471	−430.517	20.444
1200	55.020	128.159	88.903	47.107	−546.037	−420.137	18.288
1300	55.391	132.578	92.095	52.628	−545.919	−409.650	16.460
1400	55.731	136.695	95.135	58.184	−545.780	−399.173	14.893
1500	55.987	140.549	98.036	63.769	−545.629	−388.706	13.536
1600	56.317	144.172	100.807	69.384	−545.462	−378.250	12.349
1700	56.761	147.600	103.460	75.038	−545.271	−367.805	11.301
1800	57.195	150.857	106.003	80.736	−693.723	−355.161	10.306
1900	57.629	153.961	108.446	86.477	−692.057	−336.397	9.248
2000	58.032	156.927	110.797	92.261	−690.367	−317.722	8.298
2100	58.382	159.767	113.062	98.081	−688.659	−299.131	7.440
2200	58.743	162.491	115.247	103.938	−686.936	−280.623	6.663
2300	59.115	165.111	117.358	109.830	−685.201	−262.193	5.955
2400	59.496	167.634	119.401	115.761	−683.456	−243.839	5.307
2500	59.899	170.071	121.379	121.731	−681.704	−225.557	4.713
2600	60.291	172.428	123.298	127.740	−679.950	−207.346	4.166
2700	60.668	174.711	125.160	133.788	−678.201	−189.202	3.660
2800	61.045	176.924	126.969	139.874	−676.464	−171.123	3.192
2900	61.421	179.073	128.729	145.997	−674.747	−153.105	2.758
3000	61.798	181.161	130.442	152.158	−673.058	−135.147	2.353

PREVIOUS: December 1971 CURRENT: September 1977

$S°(298.15\ K) = 232.589 \pm 0.42\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -124.39 \pm 8.4\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -123.60 \pm 8.4\ kJ\cdot mol^{-1}$

Source	State	Electronic and Molecular Constants (σ = 1) ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
[3]	$X^1\Sigma^+$	0.0	1	2.3178	0.17667	0.000837	462.23	1.76
[4]	$^3\Pi$	[6800.]	6	[2.63]	[0.137]	[0.0006]	[330]	[1.5]
[4]	$^1\Pi$	[7200.]	2	[2.63]	[0.137]	[0.0006]	[330]	[1.5]
[3,4]	$^3\Sigma^+$	[14000.]	3	[2.3864]	[0.16666]	[0.000605]	[409.04]	[0.818]
[3]	$A^1\Sigma^+$	15194.44	1	2.3864	0.16666	0.000605	409.04	0.818

Enthalpy of Formation

The adopted value for the enthalpy of formation, $\Delta_f H°(CaS, g, 298.15\ K) = 29.54 \pm 2\ kcal\cdot mol^{-1}$, is based on the Knudsen mass spectrometric studies analyzed below. The two independent studies are in very good agreement and we have adopted the average value. Our value is intermediate between $\Delta_f H°(298.15\ K) = 32\ kcal\cdot mol^{-1}$ obtained by NBS[5] and $\Delta_f H°(298.15\ K) = 27.9 \pm 5\ kcal\cdot mol^{-1}$ obtained by Mills[6] in a recent critical compilation. Using auxiliary JANAF data[4] and a recommended value for $D_0°(S_2, g) = 100.69 \pm 01\ kcal\cdot mol^{-1}$,[1,4] we calculate $D_0°(CaS, g) = 78.7 \pm 2\ kcal\cdot mol^{-1}$.

Source	Method	Reaction[a]	T/K	Data Points	δS $cal\cdot K^{-1}mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ $kcal\cdot mol^{-1}$	$D_0°$
[1]	Mass Spec	A	2058–2319	9	2.83 ± 3.5	28.32 ± 7.5	22.32 ± 7.5	29.72 ± 1.7	78.6 ± 2
[2]	Mass Spec	A	1709–1962	2	0.22	22.37	21.97 ± 2	29.37 ± 2	78.9 ± 2

[a]Reaction: A) Ca(g) + S_2(g) = CaS(g) + (g)

Heat Capacity and Entropy

Electronic levels (T_∞) and vibrational–rotational constants for the observed states are from the optical study of Blues and Barrow.[3] Other low–lying electronic states and their vibrational–rotational constants are estimated in isoconfigurational groups by analogy with CaO[4] and from trends observed in the known states of the other alkaline–earth oxides and sulfides.[4] Uncertainty in the energy and constants for the estimated states may contribute as much as 2–3 $cal\cdot K^{-1}\cdot mol^{-1}$ to $S°$ at 3000 K. The molecular constants have been corrected to the natural isotopic abundances. The thermodynamic functions are calculated using first order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t\Sigma_i Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

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[4]JANAF Thermochemical Tables: Ca(g), 12–31–68; S(g), 6–30–71; S_2(g), 12–31–65; BaO(g), SrO(g), 6–30–74; BeO(g), MgO(g), CaO(g), 12–31–74; BeS(g), MgS(g), SrS(g), BaS(g), 9–30–77.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.358	124.385	124.385	INFINITE
100	29.604	197.623	262.034	−6.441	125.632	108.719	−56.789
200	32.744	219.086	235.716	−3.326	124.837	92.045	−24.040
298.15	34.803	232.589	232.589	0.	123.595	76.206	−13.351
300	34.830	232.804	232.590	0.064	123.570	75.912	−13.217
400	35.897	242.987	233.971	3.606	119.880	60.331	−7.878
500	36.487	251.066	236.610	7.228	116.808	45.785	−4.783
600	36.850	257.753	239.592	10.896	113.949	31.852	−2.773
700	37.106	263.454	242.604	14.595	111.162	18.389	−1.372
800	37.336	268.423	245.527	18.317	107.479	5.432	−0.355
900	37.624	272.837	248.321	22.064	51.444	−6.070	0.352
1000	38.061	276.822	250.975	25.847	49.550	−12.362	0.646
1100	38.732	280.478	253.493	29.684	47.393	−18.450	0.876
1200	39.703	283.888	255.885	33.603	37.265	−23.710	1.032
1300	41.007	287.115	258.164	37.636	35.895	−28.734	1.155
1400	42.641	290.212	260.344	41.815	34.657	−33.659	1.256
1500	44.564	293.218	262.435	46.174	33.581	−38.500	1.341
1600	46.705	296.161	264.452	50.736	32.695	−43.275	1.413
1700	48.971	299.060	266.402	55.519	32.015	−48.001	1.475
1800	51.260	301.924	268.296	60.530	−117.123	−50.483	1.465
1900	53.474	304.756	270.141	65.768	−115.961	−46.811	1.287
2000	55.523	307.552	271.942	71.220	−114.603	−43.206	1.128
2100	57.336	310.306	273.703	76.865	−113.070	−39.673	0.987
2200	58.863	313.009	275.429	82.677	−111.390	−36.217	0.860
2300	60.079	315.654	277.120	88.627	−109.598	−32.840	0.746
2400	60.977	318.231	278.780	94.683	−107.728	−29.542	0.643
2500	61.569	320.733	280.408	100.812	−105.816	−26.324	0.550
2600	61.878	323.155	282.006	106.987	−103.897	−23.182	0.466
2700	61.936	325.492	283.573	113.180	−102.004	−20.114	0.389
2800	61.781	327.742	285.111	119.367	−100.165	−17.115	0.319
2900	61.449	329.905	286.619	125.530	−98.409	−14.180	0.255
3000	60.977	331.980	288.096	131.652	−96.758	−11.304	0.197
3100	60.399	333.971	289.544	137.722	−95.232	−8.481	0.143
3200	59.743	335.878	290.963	143.729	−93.848	−5.705	0.093
3300	59.036	337.706	292.352	149.669	−92.622	−2.970	0.047
3400	58.298	339.457	293.711	155.536	−91.564	−0.269	0.004
3500	57.547	341.136	295.043	161.328	−90.685	2.403	−0.036
3600	56.796	342.747	296.345	167.045	−89.993	5.052	−0.073
3700	56.057	344.293	297.621	172.687	−89.494	7.685	−0.108
3800	55.336	345.778	298.868	178.257	−89.193	10.307	−0.142
3900	54.639	347.207	300.090	183.755	−89.094	12.923	−0.173
4000	53.972	348.581	301.285	189.186	−89.198	15.540	−0.203
4100	53.335	349.906	302.455	194.551	−89.508	18.162	−0.231
4200	52.730	351.184	303.600	199.854	−90.023	20.794	−0.259
4300	52.159	352.418	304.721	205.098	−90.742	23.441	−0.285
4400	51.620	353.611	305.819	210.287	−91.660	26.106	−0.310
4500	51.114	354.765	306.894	215.423	−92.763	28.794	−0.334
4600	50.639	355.884	307.946	220.511	−94.069	31.508	−0.358
4700	50.194	356.968	308.978	225.552	−95.568	34.254	−0.381
4800	49.778	358.020	309.989	230.550	−97.253	37.034	−0.403
4900	49.390	359.042	310.979	235.509	−99.117	39.851	−0.425
5000	49.027	360.037	311.951	240.429	−101.153	42.707	−0.446
5100	48.689	361.004	312.903	245.315	−103.356	45.606	−0.467
5200	48.374	361.946	313.837	250.168	−105.714	48.549	−0.488
5300	48.080	362.865	314.754	254.990	−108.226	51.539	−0.508
5400	47.806	363.761	315.653	259.784	−110.882	54.578	−0.528
5500	47.552	364.636	316.536	264.552	−113.673	57.668	−0.548
5600	47.315	365.491	317.402	269.295	−116.582	60.809	−0.567
5700	47.095	366.326	318.253	274.016	−119.617	64.003	−0.587
5800	46.890	367.143	319.089	278.715	−122.764	67.252	−0.606
5900	46.699	367.943	319.910	283.394	−126.014	70.556	−0.625
6000	46.522	368.727	320.718	288.055	−129.358	73.915	−0.643

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

D_0° = 12.740 ± 0.010 kJ·mol^{-1} (natural abundance)
S°(298.15 K) = 257.18 ± 0.5 J·K^{-1}·mol^{-1}

$\Delta_f H$(0 K) = 341.92 ± 0.80 kJ·mol^{-1}
$\Delta_f H$(298.15 K) = 341.64 ± 0.8 kJ·mol^{-1}

State	T_e	D_0°	Spectroscopic Constants for $^{40}Ca_2$ in cm^{-1} ω_e	$\omega_e x_e$	B_e	$10^3 \cdot \alpha_e$	$10^6 \cdot D_e$	r_e, Å
$^1\Sigma_g^+$	0	1063.1	65.046	1.0815[a]	0.46086	0.6966[c]	0.090731[e]	3.807
$^1\Sigma_u^+$	18964	22912	136.61	0.71797[b]	0.058178	0.2970[d]	0.043361[f]	4.277

[a] + 3.1093 × 10^{-3} (v + 1/2)^3 + 7.0080 × 10^{-6} (v + 1/2)^4 − 2.4380 × 10^{-8} (v + 1/2)^5
[b] − 2.8198 × 10^{-3} (v + 1/2)^3 − 1.4773 × 10^{-6} (v + 1/2)^4 + 1.692 × 10^{-6} (v + 1/2)^5 − 5.545 × 10^{-9} (v + 1/2)^6
[c] − 1.619 × 10^{-5} (v + 1/2)^2 + 1.60 × 10^{-6} (v + 1/2)^3
[d] − 3.202 × 10^{-6} (v + 1/2)^2 − 6.58 × 10^{-8} (v + 1/2)^3
[e] + 1.330336 × 10^{-9} (v + 1/2) + 7.192454 × 10^{-10} (v + 1/2)^2
[f] + 3.283167 × 10^{-10} (v + 1/2) + 4.881575 × 10^{-4} (v + 1/2)^2

Enthalpy of Formation

The ground state dissociation energy for $^{40}Ca_2$ was determined by Vidal (1) to be D_e = 1095.4 ± 0.5 cm^{-1} which gives D_0° = 1063.1 cm^{-1} using the spectroscopic data above. The adopted value for natural abundance Ca_2 was obtained from the $^{40}Ca_2$ value by correcting for the presence of the minor isotopic species.[14] Using this value and the recommended value for $\Delta_f H^\circ$(Ca, g, 0 K) = 177.33 kJ·mol^{-1} as deduced from CODATA,[2] we calculate the adopted value of $\Delta_f H^\circ$(Ca_2, g, 0 K) = 341.92 kJ·mol^{-1}. Note that Brewer and Winn[3] calculated a value of D_0° (Ca_2, natural abundance) = 12.47 ± 1.7 kJ·mol^{-1} based on some earlier spectroscopic work of Balfour and Whitlock.[4] Gurvich[9] adopted a value of $\Delta_f H^\circ$(0 K) = 342.266 ± 2.6 kJ·mol^{-1} which is also based on the earlier study of.[4]

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique, analogous to the alkali dimers.[13] Included in the calculation are the ground state ($^1\Sigma_g^+$) and the $^1\Sigma_u^+$ excited state at T_e = 18964 cm^{-1}. Spectroscopic constants for both states are taken from a detailed experimental investigation by Vidal[1] and are considered to be the most accurate. Presumably, other excited states, lower in energy than the $^1\Sigma_u^+$ state, exist as in the case of Mg_2(g),[5] however no known experimental or theoretical constants have been published. The effect in the heat capacity of these missing states would probably be to cause the second C_p maximum to occur at lower temperatures, similiar to Mg_2(g).[5] As with other diatomics possessing relatively shallow ground states, Ca_2(g) is another example where the traditional integration methods of calculating thermal functions fail.

The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[6] who proposed a simpler form of Wooley's method.[7] For the ground state only, we included the so-called quasibound rotational levels above the dissociation limit[8] with J_{lim} = 209 and v_{max} = 34 as determined by Gurvich.[9] Instead of performing separate calculations on all 21 isotopic species (made up of all possible dimeric combinations of the six isotopes), we adjust the spectroscopic constants of $^{40}Ca_2$ to a hypothetical natural abundance molecule using a standard reduced mass scaling routine.[10] Thermal functions calculated in this manner should be trivially different from the exact procedure of performing the calculation on each isotope and combining the results according to the natural abundances of each species. The adopted value of S°(298.15 K) is 0.39 J·K^{-1}·mol^{-1} smaller than that calculated by.[9] It should also be noted that the minor controversy in the literature over the correct assignment of the ground state[11] has apparently been satisfactorily resolved with the currently used data.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.189	341.920	341.920	INFINITE
100	38.200	214.556	291.717	−7.716	343.432	325.170	−169.851
200	39.844	241.757	260.663	−3.781	342.830	307.074	−80.199
250	38.647	250.545	257.797	−1.813	342.297	298.193	−62.304
298.15	36.577	257.183	257.183	0.	341.637	289.757	−50.764
300	36.490	257.409	257.184	0.068	341.608	289.435	−50.395
350	34.120	262.855	257.619	1.833	340.761	280.804	−41.908
400	31.951	267.266	258.558	3.483	339.754	272.305	−35.559
450	30.117	270.920	259.735	5.033	338.579	263.943	−30.638
500	28.619	274.013	261.012	6.500	337.240	255.721	−26.715
600	26.434	279.023	263.615	9.245	334.100	239.702	−20.868
700	25.000	282.983	266.109	11.812	330.390	224.254	−16.734
800	24.030	286.254	268.428	14.260	324.450	209.584	−13.684
900	23.352	289.043	270.567	16.628	319.766	195.500	−11.347
1000	22.862	291.476	272.539	18.937	314.435	181.972	−9.505
1100	22.498	293.637	274.361	21.204	308.456	169.010	−8.026
1200	22.221	295.583	276.050	23.439	286.371	157.865	−6.872
1300	22.005	297.352	277.621	25.650	281.582	147.350	−5.921
1400	21.835	298.977	279.089	27.842	276.774	137.205	−5.119
1500	21.697	300.478	280.466	30.018	271.950	127.404	−4.437
1600	21.585	301.875	281.761	32.182	267.114	117.926	−3.850
1700	21.492	303.180	282.983	34.336	262.268	108.750	−3.341
1800	21.415	304.407	284.139	36.481	−39.934	104.281	−3.026
1900	21.350	305.563	285.237	38.619	−41.969	112.348	−3.089
2000	21.295	306.656	286.281	40.752	−44.021	120.523	−3.148
2100	21.248	307.694	287.276	42.879	−46.093	128.801	−3.204
2200	21.209	308.682	288.227	45.002	−48.191	137.179	−3.257
2300	21.177	309.624	289.137	47.121	−50.323	145.652	−3.308
2400	21.150	310.525	290.009	49.237	−52.496	154.219	−3.356
2500	21.130	311.388	290.847	51.351	−54.721	162.878	−3.403
2600	21.115	312.216	291.653	53.463	−57.009	171.627	−3.448
2700	21.106	313.013	292.430	55.574	−59.371	180.465	−3.491
2800	21.103	313.780	293.178	57.685	−61.823	189.392	−3.533
2900	21.105	314.521	293.902	59.795	−64.379	198.409	−3.574
3000	21.115	315.236	294.601	61.906	−67.053	207.516	−3.613
3100	21.131	315.929	295.278	64.018	−69.861	216.714	−3.652
3200	21.154	316.600	295.934	66.132	−72.820	226.006	−3.689
3300	21.184	317.252	296.570	68.249	−75.944	235.392	−3.726
3400	21.222	317.884	297.188	70.369	−79.250	244.875	−3.762
3500	21.267	318.500	297.788	72.494	−82.752	254.459	−3.798
3600	21.320	319.100	298.371	74.623	−86.464	264.146	−3.833
3700	21.380	319.685	298.940	76.758	−90.399	273.938	−3.867
3800	21.449	320.256	299.493	78.899	−94.569	283.841	−3.902
3900	21.525	320.814	300.033	81.048	−98.985	293.856	−3.936
4000	21.609	321.360	300.559	83.205	−103.654	303.987	−3.970
4100	21.700	321.895	301.073	85.370	−108.585	314.239	−4.003
4200	21.799	322.419	301.575	87.545	−113.783	324.614	−4.037
4300	21.904	322.933	302.066	89.730	−119.252	335.116	−4.071
4400	22.017	323.438	302.546	91.926	−124.987	345.748	−4.105
4500	22.135	323.934	303.016	94.133	−130.965	356.512	−4.138
4600	22.260	324.422	303.476	96.353	−137.225	367.412	−4.172
4700	22.391	324.902	303.926	98.586	−143.757	378.453	−4.206
4800	22.527	325.375	304.368	100.831	−150.548	389.635	−4.240
4900	22.667	325.841	304.802	103.091	−157.590	400.961	−4.274
5000	22.812	326.300	305.227	105.365	−164.874	412.434	−4.309
5100	22.961	326.753	305.645	107.654	−172.393	424.054	−4.343
5200	23.113	327.201	306.055	109.957	−180.128	435.823	−4.378
5300	23.269	327.642	306.458	112.277	−188.082	447.744	−4.413
5400	23.427	328.079	306.855	114.611	−196.236	459.817	−4.448
5500	23.586	328.510	307.244	116.962	−204.578	472.043	−4.483
5600	23.748	328.937	307.628	119.329	−213.076	484.420	−4.518
5700	23.910	329.358	308.005	121.712	−221.751	496.952	−4.554
5800	24.073	329.776	308.377	124.111	−230.574	509.637	−4.590
5900	24.237	330.189	308.743	126.526	−239.532	522.476	−4.626
6000	24.400	330.597	309.104	128.958	−248.611	535.468	−4.662

PREVIOUS: December 1974 (1 atm) CURRENT: September 1983 (1 bar)

Continued from page 716

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IP(Cl, g) = 104591.0 ± 0.3 cm^{-1}
$S°(298.15\ K)$ = 165.189 ± 0.004 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 119.621 ± 0.006 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 121.302 ± 0.008 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P°_{3/2}$	0.0	4
$^2P°_{1/2}$	882.36	2

Enthalpy of Formation

The adopted value for the enthalpy of formation of Cl(g) is calculated from the dissociation energy of gaseous chlorine, $D°_0$ (natural abundance) = 19999.10 ± 1.0 cm^{-1} (239.242 ± 0.012 $kJ·mol^{-1}$). This value was calculated from the dissociation energy of $^{35}Cl_2(g)$, $D°_0$ = 19997.28 ± 0.10 cm^{-1}, obtained from the extensive spectroscopic measurements of Douglas and Hoy.[1] CODATA[2] used a slightly different value ($D°_0$ = 19997.25 ± 0.3 cm^{-1} for $^{35}Cl_2$), as obtained by LeRoy and Bernstein[3] from the measurements of Douglas *et al.*,[4] Brewer and Winn,[5] Huber and Herzberg,[6] and Gurvich *et al.*[7] have adopted one or the other of these two cited values. Wagman *et al.*[16] adopted a dissociation energy which is 63 cm^{-1} greater than our adopted value. Detailed discussions on the spectroscopic information are given by LeRoy,[8] Coxon[9] and Douglas and Hoy.[1]

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weight is taken from Moore.[10, 11] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 71954 cm^{-1}. Our calculations indicate that any reasonable method of filling in the missing levels and cutting off the summation in the partition function[12] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels. Therefore, we list only the ground state and the first excited state. Extension to higher temperatures may require consideration of the higher excited states and utilization of different fill and cutoff procedures.

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations[2] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the monatomic halogens arise due to the use of slightly different values for R; this tables uses R = 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[13] Gurvich *et al.*,[7] and Wagman *et al.*[16] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[14] and the 1973 values,[15] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.272	119.621	119.621	INFINITE
100	20.788	142.175	184.104	−4.193	120.244	115.476	−60.319
200	21.079	156.636	167.161	−2.105	120.813	110.482	−28.855
250	21.450	161.378	165.547	−1.042	121.066	107.869	−22.538
298.15	21.838	165.189	165.189	0.	121.302	105.306	−18.449
300	21.852	165.325	165.190	0.040	121.311	105.207	−18.318
350	22.202	168.720	165.457	1.142	121.553	102.504	−15.298
400	22.467	171.703	166.055	2.259	121.795	99.766	−13.028
450	22.644	174.361	166.833	3.387	122.035	96.998	−11.259
500	22.744	176.752	167.708	4.522	122.272	94.203	−9.841
600	22.781	180.905	169.571	6.800	122.734	88.546	−7.709
700	22.692	184.411	171.448	9.074	123.172	82.813	−6.180
800	22.549	187.432	173.261	11.337	123.585	77.019	−5.029
900	22.389	190.079	174.986	13.584	123.972	71.174	−4.131
1000	22.233	192.430	176.615	15.815	124.334	65.288	−3.410
1100	22.089	194.542	178.150	18.031	124.675	59.367	−2.819
1200	21.959	196.458	179.597	20.233	124.997	53.416	−2.325
1300	21.843	198.211	180.963	22.423	125.300	47.438	−1.906
1400	21.742	199.826	182.253	24.602	125.589	41.438	−1.546
1500	21.652	201.323	183.475	26.772	125.863	35.417	−1.233
1600	21.573	202.718	184.635	28.933	126.124	29.379	−0.959
1700	21.504	204.024	185.737	31.087	126.374	23.325	−0.717
1800	21.443	205.251	186.788	33.234	126.612	17.256	−0.501
1900	21.389	206.409	187.790	35.375	126.840	11.175	−0.307
2000	21.341	207.505	188.749	37.512	127.058	5.081	−0.133
2100	21.298	208.545	189.667	39.644	127.265	−1.023	0.025
2200	21.260	209.535	190.548	41.772	127.463	−7.136	0.169
2300	21.226	210.479	191.394	43.896	127.650	−13.259	0.301
2400	21.195	211.382	192.208	46.017	127.827	−19.389	0.422
2500	21.167	212.246	192.992	48.135	127.992	−25.526	0.533
2600	21.142	213.076	193.749	50.250	128.147	−31.670	0.636
2700	21.119	213.874	194.480	52.364	128.290	−37.820	0.732
2800	21.099	214.641	195.186	54.474	128.421	−43.974	0.820
2900	21.080	215.381	195.870	56.583	128.541	−50.133	0.903
3000	21.063	216.096	196.532	58.690	128.649	−56.297	0.980
3100	21.047	216.786	197.174	60.796	128.746	−62.463	1.052
3200	21.032	217.454	197.798	62.900	128.832	−68.633	1.120
3300	21.019	218.101	198.403	65.002	128.908	−74.804	1.184
3400	21.007	218.728	198.992	67.104	128.974	−80.979	1.244
3500	20.995	219.337	199.564	69.204	129.031	−87.155	1.301
3600	20.985	219.928	200.122	71.303	129.081	−93.332	1.354
3700	20.975	220.503	200.665	73.401	129.124	−99.511	1.405
3800	20.966	221.062	201.195	75.498	129.161	−105.691	1.453
3900	20.958	221.607	201.711	77.594	129.195	−111.871	1.498
4000	20.950	222.137	202.215	79.690	129.226	−118.053	1.542
4100	20.943	222.655	202.707	81.784	129.255	−124.235	1.583
4200	20.936	223.159	203.188	83.878	129.284	−130.418	1.622
4300	20.929	223.652	203.658	85.971	129.314	−136.602	1.659
4400	20.923	224.133	204.118	88.064	129.347	−142.786	1.695
4500	20.918	224.603	204.568	90.156	129.384	−148.972	1.729
4600	20.912	225.063	205.009	92.247	129.426	−155.158	1.762
4700	20.907	225.512	205.440	94.338	129.474	−161.345	1.793
4800	20.903	225.952	205.863	96.429	129.530	−167.533	1.823
4900	20.898	226.383	206.278	98.519	129.594	−173.723	1.852
5000	20.894	226.806	206.684	100.609	129.667	−179.914	1.880
5100	20.890	227.219	207.082	102.698	129.750	−186.106	1.906
5200	20.886	227.625	207.474	104.787	129.844	−192.300	1.932
5300	20.883	228.023	207.858	106.875	129.950	−198.496	1.956
5400	20.879	228.413	208.235	108.963	130.068	−204.694	1.980
5500	20.876	228.796	208.605	111.051	130.199	−210.895	2.003
5600	20.873	229.172	208.969	113.138	130.343	−217.098	2.025
5700	20.870	229.542	209.327	115.226	130.501	−223.304	2.046
5800	20.867	229.905	209.678	117.312	130.673	−229.512	2.067
5900	20.865	230.261	210.024	119.399	130.859	−235.724	2.087
6000	20.862	230.612	210.364	121.485	131.059	−241.939	2.106

PREVIOUS: June 1972 (1 atm) CURRENT: June 1982 (1 bar)

Chlorine, Ion (Cl^+) **IDEAL GAS** $M_r = 35.45245$ **Chlorine, Ion (Cl_2^+)** **Cl_2^+(g)**

$IP(Cl^+, g) = 192070 \pm 10\ cm^{-1}$
$S°(298.15\ K) = 167.556 \pm 0.005\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1370.807 \pm 0.01\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1378.801]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	696.1	3
$^3P_0$	996.4	1
$^1D_2$	11653.5	5
$^1S_0$	27877.8	1

Enthalpy of Formation

$\Delta_f H°(Cl^+, g, 0\ K)$ is calculated from $\Delta_f H°(Cl, g, 0\ K)$[1] using the spectroscopic value of IP(Cl) = 104591.0 ± 0.3 cm^{-1}(1251.187 ± 0.004 $kJ \cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization potential and appearance potential data.

$\Delta_f H°(Cl^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Cl, g, 0\ K)$ by using IP(Cl) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Cl(g), Cl^+(g), and e^-(ref). $\Delta_r H°(Cl \rightarrow Cl^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by $-6.197\ kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the lowest four excited states; the next lowest level is approximately 93366 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and four excited states, with the energy of these states taken from recent study by Moore.[2] The reported uncertainty is $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass, the fundamental constants, and the position of the four lowest excited states. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.386	1370.807		
100	20.809	144.033	187.107	−4.307			
200	21.681	158.648	169.618	−2.194			
250	22.383	163.562	167.931	−1.092			
298.15	22.958	167.556	167.556	0.	1378.801	1355.845	−237.538
300	22.977	167.698	167.556	0.042	1378.850	1355.702	−236.049
350	23.388	171.273	167.838	1.202	1380.190	1351.738	−201.736
400	23.621	174.413	168.467	2.378	1381.530	1347.582	−175.976
450	23.713	177.202	169.286	3.562	1382.865	1343.258	−155.921
500	23.706	179.700	170.205	4.748	1384.192	1338.787	−139.862
600	23.519	184.008	172.158	7.111	1386.817	1329.458	−115.740
700	23.239	187.613	174.115	9.449	1389.398	1319.694	−98.477
800	22.949	190.697	176.000	11.758	1391.936	1309.562	−85.506
900	22.681	193.385	177.785	14.039	1394.436	1299.115	−75.399
1000	22.446	195.762	179.467	16.295	1396.902	1288.391	−67.299
1100	22.244	197.891	181.046	18.530	1399.340	1277.422	−60.660
1200	22.073	199.819	182.532	20.745	1401.753	1266.232	−55.118
1300	21.928	201.580	183.930	22.945	1404.146	1254.841	−50.420
1400	21.806	203.201	185.250	25.132	1406.520	1243.267	−46.387
1500	21.704	204.702	186.497	27.307	1408.878	1231.523	−42.885
1600	21.620	206.100	187.679	29.473	1411.223	1219.623	−39.817
1700	21.552	207.408	188.801	31.631	1413.556	1207.577	−37.104
1800	21.498	208.639	189.870	33.784	1415.878	1195.393	−34.689
1900	21.458	209.800	190.888	35.932	1418.191	1183.081	−32.525
2000	21.430	210.900	191.862	38.076	1420.495	1170.647	−30.574
2100	21.414	211.945	192.793	40.218	1422.792	1158.098	−28.806
2200	21.409	212.941	193.687	42.359	1425.081	1145.440	−27.196
2300	21.413	213.893	194.545	44.500	1427.363	1132.678	−25.724
2400	21.426	214.804	195.370	46.642	1429.639	1119.817	−24.372
2500	21.447	215.679	196.165	48.786	1431.909	1106.861	−23.127
2600	21.475	216.521	196.932	50.932	1434.173	1093.814	−21.975
2700	21.510	217.332	197.672	53.081	1436.431	1080.681	−20.907
2800	21.551	218.115	198.389	55.234	1438.683	1067.464	−19.914
2900	21.596	218.872	199.082	57.391	1440.930	1054.166	−18.988
3000	21.645	219.605	199.754	59.553	1443.171	1040.791	−18.122
3100	21.698	220.316	200.406	61.720	1445.409	1027.342	−17.311
3200	21.753	221.005	201.039	63.893	1447.642	1013.820	−16.549
3300	21.811	221.676	201.654	66.071	1449.872	1000.229	−15.832
3400	21.869	222.327	202.252	68.255	1452.099	986.569	−15.157
3500	21.929	222.962	202.835	70.445	1454.325	972.845	−14.519
3600	21.989	223.581	203.403	72.641	1456.550	959.057	−13.916
3700	22.049	224.184	203.956	74.843	1458.775	945.207	−13.344
3800	22.109	224.773	204.497	77.051	1461.002	931.297	−12.802
3900	22.168	225.348	205.024	79.265	1463.232	917.328	−12.286
4000	22.227	225.910	205.539	81.484	1465.466	903.303	−11.796
4100	22.284	226.460	206.043	83.710	1467.705	889.221	−11.329
4200	22.339	226.997	206.535	85.941	1469.950	875.084	−10.883
4300	22.393	227.524	207.017	88.178	1472.202	860.894	−10.458
4400	22.445	228.039	207.489	90.420	1474.463	846.652	−10.051
4500	22.496	228.544	207.951	92.667	1476.733	832.358	−9.662
4600	22.544	229.039	208.404	94.919	1479.014	818.013	−9.289
4700	22.591	229.524	208.849	97.175	1481.307	803.619	−8.931
4800	22.635	230.000	209.284	99.437	1483.612	789.175	−8.588
4900	22.677	230.467	209.712	101.702	1485.930	774.684	−8.258
5000	22.717	230.926	210.132	103.972	1488.262	760.145	−7.941
5100	22.755	231.376	210.544	106.246	1490.608	745.560	−7.636
5200	22.791	231.818	210.949	108.523	1492.970	730.928	−7.342
5300	22.825	232.253	211.347	110.804	1495.346	716.250	−7.059
5400	22.857	232.680	211.738	113.088	1497.739	701.528	−6.786
5500	22.887	233.100	212.122	115.375	1500.148	686.761	−6.522
5600	22.915	233.512	212.501	117.665	1502.573	671.951	−6.268
5700	22.941	233.918	212.873	119.958	1505.015	657.096	−6.022
5800	22.965	234.317	213.239	122.254	1507.474	642.199	−5.784
5900	22.987	234.710	213.600	124.551	1509.950	627.260	−5.553
6000	23.008	235.097	213.955	126.851	1512.442	612.277	−5.330

PREVIOUS: June 1965 (1 atm) CURRENT: June 1982 (1 bar)

EA(Cl, g) = 3.617 ± 0.003 eV
$S°$(298.15 K) = 153.356 ± 0.005 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −229.36 ± 0.4 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [−233.954] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(Cl^-, g, 0 K)$ is calculated from $\Delta_f H°$(Cl, g, 0 K)[1] using the adopted electron affinity of EA(Cl) = 3.617 ± 0.003 eV (348.985 ± 0.289 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[10] is based on laser optogalvanic spectroscopic and plasma emission studies.[5,6] Additional information on Cl^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H°(Cl^-, g, 298.15 K)$ is obtained from $\Delta_f H°$(Cl, g, 0 K) by using EA(Cl) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Cl^-(g), Cl(g), and e^-(ref). $\Delta_r H(Cl^- \rightarrow Cl + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Cl^-(g) is given by Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

The entropy at all temperatures (0–6000 K) agrees within 0.001 J·K^{-1}·mol^{-1} with the values of Gurvich *et al.*[8] except for one minor difference. The entropy differs by 0.1094 J·K^{-1}·mol^{-1} because this table uses a standard-state pressure of 1 bar, whereas the tabulation of Gurvich *et al.*[8] is based on 1 atm. The estimated uncertainty is due to uncertainties in the relative ionic mass and the fundamental constants which are based on the 1981 scale[9] and the 1973 values,[7] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	−229.364		
100	20.786	130.649	171.836	−4.119			
200	20.786	145.057	155.257	−2.040			
250	20.786	149.695	153.698	−1.001			
298.15	20.786	153.356	153.356	0.	−233.954	−240.167	42.076
300	20.786	153.485	153.356	0.038	−233.986	−240.205	41.823
350	20.786	156.689	153.610	1.078	−234.845	−241.174	35.993
400	20.786	159.464	154.172	2.117	−235.721	−242.019	31.604
450	20.786	161.913	154.899	3.156	−236.609	−242.753	28.178
500	20.786	164.103	155.711	4.196	−237.506	−243.388	25.427
600	20.786	167.892	157.435	6.274	−239.322	−244.394	21.276
700	20.786	171.097	159.164	8.353	−241.158	−245.094	18.289
800	20.786	173.872	160.833	10.431	−243.008	−245.530	16.031
900	20.786	176.320	162.420	12.510	−244.868	−245.734	14.262
1000	20.786	178.510	163.922	14.589	−246.736	−245.730	12.836
1100	20.786	180.492	165.340	16.667	−248.612	−245.539	11.660
1200	20.786	182.300	166.679	18.746	−250.492	−245.177	10.672
1300	20.786	183.964	167.945	20.824	−252.379	−244.657	9.830
1400	20.786	185.504	169.145	22.903	−254.270	−243.992	9.103
1500	20.786	186.938	170.284	24.982	−256.165	−243.192	8.469
1600	20.786	188.280	171.367	27.060	−258.065	−242.265	7.909
1700	20.786	189.540	172.400	29.139	−259.969	−241.220	7.412
1800	20.786	190.728	173.385	31.217	−261.878	−240.062	6.966
1900	20.786	191.852	174.328	33.296	−263.792	−238.797	6.565
2000	20.786	192.918	175.231	35.375	−265.710	−237.432	6.201
2100	20.786	193.932	176.097	37.453	−267.635	−235.971	5.869
2200	20.786	194.899	176.930	39.532	−269.565	−234.418	5.566
2300	20.786	195.823	177.732	41.610	−271.502	−232.777	5.287
2400	20.786	196.708	178.504	43.689	−273.446	−231.052	5.029
2500	20.786	197.557	179.249	45.768	−275.399	−229.245	4.790
2600	20.786	198.372	179.969	47.846	−277.360	−227.360	4.568
2700	20.786	199.156	180.666	49.925	−279.330	−225.400	4.361
2800	20.786	199.912	181.339	52.004	−281.309	−223.366	4.167
2900	20.786	200.642	181.993	54.082	−283.298	−221.262	3.985
3000	20.786	201.346	182.626	56.161	−285.297	−219.089	3.815
3100	20.786	202.028	183.241	58.239	−287.306	−216.849	3.654
3200	20.786	202.688	183.838	60.318	−289.324	−214.544	3.502
3300	20.786	203.327	184.419	62.397	−291.351	−212.176	3.358
3400	20.786	203.948	184.985	64.475	−293.386	−209.746	3.222
3500	20.786	204.550	185.535	66.554	−295.429	−207.256	3.093
3600	20.786	205.136	186.071	68.632	−297.478	−204.708	2.970
3700	20.786	205.706	186.594	70.711	−299.533	−202.103	2.853
3800	20.786	206.260	187.105	72.790	−301.593	−199.442	2.742
3900	20.786	206.800	187.603	74.868	−303.655	−196.727	2.635
4000	20.786	207.326	188.089	76.947	−305.720	−193.959	2.533
4100	20.786	207.839	188.565	79.025	−307.785	−191.139	2.435
4200	20.786	208.340	189.030	81.104	−309.850	−188.269	2.341
4300	20.786	208.829	189.485	83.183	−311.913	−185.350	2.252
4400	20.786	209.307	189.930	85.261	−313.973	−182.383	2.165
4500	20.786	209.774	190.365	87.340	−316.028	−179.369	2.082
4600	20.786	210.231	190.792	89.418	−318.077	−176.309	2.002
4700	20.786	210.678	191.211	91.497	−320.120	−173.206	1.925
4800	20.786	211.116	191.621	93.576	−322.155	−170.058	1.851
4900	20.786	211.544	192.023	95.654	−324.181	−166.868	1.779
5000	20.786	211.964	192.418	97.733	−326.198	−163.638	1.710
5100	20.786	212.376	192.805	99.811	−328.204	−160.366	1.642
5200	20.786	212.780	193.185	101.890	−330.198	−157.056	1.578
5300	20.786	213.175	193.559	103.969	−332.181	−153.707	1.515
5400	20.786	213.564	193.926	106.047	−334.151	−150.322	1.454
5500	20.786	213.945	194.286	108.126	−336.108	−146.899	1.395
5600	20.786	214.320	194.641	110.204	−338.051	−143.441	1.338
5700	20.786	214.688	194.989	112.283	−339.981	−139.949	1.282
5800	20.786	215.049	195.332	114.362	−341.896	−136.423	1.229
5900	20.786	215.405	195.669	116.440	−343.796	−132.864	1.176
6000	20.786	215.754	196.001	118.519	−345.682	−129.273	1.125

PREVIOUS: June 1965 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 245.68 \pm 6.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 192.8 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 192.9 \pm 12.6\ kJ·mol^{-1}$

	Electronic Levels and Quantum Weights							
State	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
$^3\Sigma$	0	[3]	19868.1	[3]	21335.1	[3]	22182.5	[3]
	[11000]	[3]	19945.8	[3]	21640.4	[3]	22402.7	[3]
	17484.1	[3]	20969.1	[3]	22014.8	[3]	22966.2	[3]
	19826.3	[3]	21263.9	[3]	22072.3	[3]	[25000]	[3]

$\omega_e = 421.2\ cm^{-1}$ $\omega_e x_e = 0.74\ cm^{-1}$ $B_e = [0.17434]\ cm^{-1}$ $\alpha_e = [0.000459]\ cm^{-1}$ $r_e = [2.09]$ Å $\sigma = 1$

Enthalpy of Formation

Kulkarni and Dadape[1] have studied the reaction of $CoCl_2(g)$ with Co(cr) by a transpiration method. They used highly purified argon as the carrier gas and condensed the gaseous products on a mullite cold finger. Chemical and x-ray analyses of the condensate showed the presence of metallic cobalt. The transport of the Co metal was ascribed to the disproportionation of CoCl(g) according to the reaction $2\ CoCl(g) = Co(cr) + CoCl_2(g)$. Partial pressures for CoCl(g) and $CoCl_2(g)$ were reported for the temperature range 1395–1673 K. No consideration was given to possible dimerization of the dichloride. JANAF data[2] for $CoCl_2(g)$ and $Co_2Cl_4(g)$ are used to correct their $CoCl_2$ pressures for dimerization. The corrected pressures are 0.5% less than those of Kulkarni and Dadape[1] at 1395 K, and only 0.1% less at 1673 K. Hildenbrand[3] has also studied the disproportionation reaction of CoCl(g) by mass spectrometry. The monochloride was produced in the effusion cell[4] by vaporizing AgCl in the presence of metallic cobalt. The Ag^+ and $AgCl^+$ signals were also measured and used to derive equilibrium data for the process $Ag(g) + CoCl(g) = AgCl(g) + Co(g)$.

Source	Reaction	Point	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_{at} H°(298.15\ K)$ kcal·mol^{-1}
Kulkarni and Dadape[1]	A	9	1395–1673	83.3	79.65 ± 1.8	−2.4 ± 3.5	28.6 ± 2.0	101.9
Hildenbrand[3]	B	7	1461–1605	20.0	14.19 ± 0.53	−3.8 ± 1.5	46.6 ± 1.5	83.9
Hildenbrand[3]	C	7	1461–1605	6.21	9.87 ± 0.35	2.4 ± 1.1	45.6 ± 1.5[a]	84.9

Reactions: (A) $CoCl_2(g) + Co(cr) = 2\ CoCl(g)$ (B) $CoCl_2(g) + Co(g) = 2\ CoCl(g)$ (C) $Ag(g) + CoCl(g) = AgCl(g) + Co(g)$

[a] $\Delta_f H°(298.15\ K)$(3rd law) combined with $D_0°(AgCl, g, 298.15\ K) = 75.0 \pm 0.5$ kcal·mol^{-1}.[4]

The two sets of measurements of Hildenbrand[3] lead to consistent values for $\Delta_f H°$, while the results of Kulkarni and Dadape[1] suggest a value roughly 20 kcal·mol^{-1} lower. In the same paper, Kulkarni and Dadape[1] reported vapor pressures for $CoCl_2(l)$ which were also determined by their flow technique. These vapor pressures have been shown to be incompatible with JANAF data (see $CoCl_2(g)$ table). Furthermore, their value for the bond dissociation energy ($D_0°(298.15\ K) = 101.9$ kcal·mol^{-1}) of CoCl appears to be too high by comparison with similar data for other transition metal monochlorides. Values[5] of $D_0°$ for the monochlorides of Cr, Mn, Ni, and Cu show a random variation of from 83.0 to 88.6 kcal·mol^{-1}, suggesting a value for CoCl near 85 kcal·mol^{-1}. The results of Hildenbrand[3] are in agreement with these predictions. It is further noted that Hildenbrand[4] has used a similar technique to study the monochlorides of Ca, Sr, and Ba. The results of these studies are quite consistent with JANAF heat of formation data.[2] Thus, it appears that the method used by Hildenbrand[3, 4] is reliable, and we adopt an average value, $\Delta_f H°(298.15\ K) = 46.1$ kcal·mol^{-1}), of his two results. The uncertainty is estimated to be ±3.0 kcal·mol^{-1}. The adopted values for the ground state vibrational constants are judged to be of insufficient accuracy to warrant a Birge–Sponer calculation for $D_0°$(Co–Cl).

Heat Capacity and Entropy

The bond length is estimated as somewhat less than that for $CoCl_2$.[2] B_e is calculated from the value for r_e. The value for α_e is obtained from the other constants assuming a Morse potential function.

Several band systems have been observed in the electronic spectrum[6–9] of CoCl. Vibrational constants for the upper and lower states of the various systems have been summarized by Rosen.[5] However, since it is not certain which of the observed electronic transitions involve the ground state, no assignments were made. Also, confusion exists as to whether some of the systems belong to triplet–triplet transitions,[7–9] an electronic triplet,[8] or whether they are all separate systems.[9] We adopt the vibrational constants for the ground state suggested by Herzberg.[10] Comparison of these values with those listed by Rosen[5] for the lower states of other systems for CoCl indicate that the adopted ω_e value may be uncertain by as much as ±5 cm^{-1}. Krishnamurty[8] has shown that the ground state electronic configuration for CoCl is either $^5\Sigma$ or $^3\Sigma$. We prefer a triplet ground state, since the electronic configuration for Co^{+1} is ^3F.[11] Other transition metal monochlorides[5] and the corresponding unipositive metal ions[11] have the same ground state multiplicities. If the ground state is a quintet, then the value of $S°(298.15\ K)$ is increased by 1 cal·K^{-1}·mol^{-1}. The adopted electronic levels in the range 17,000–23,000 cm^{-1} are taken from the compilation of Rosen.[5] Each level is assumed to be a separate system and is assigned a quantum weight of 3. Two triplet levels are also included at 11,000 and 25,000 cm^{-1}, since Rao and Rao[9] are believed to have observed two components of a triplet–triplet transition near 14,000 cm^{-1}. By analogy with similar data for other transition metal monochlorides,[5] the lower triplet level is not expected to lie below 10,000 cm^{-1}. The adopted upper levels and assumed quantum weights contribute 0.31 cal·K^{-1}·mol^{-1} to the entropy of CoCl at 4000 K.

Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.447	192.797	192.797	INFINITE
100	29.838	210.257	275.505	−6.525	193.742	182.934	−95.555
200	33.228	232.008	248.842	−3.367	193.471	172.183	−44.970
250	34.377	239.554	246.253	−1.675	193.198	166.892	−34.870
298.15	35.139	245.679	245.679	0.	192.882	161.853	−28.356
300	35.163	245.896	245.679	0.065	192.870	161.661	−28.148
350	35.708	251.360	246.110	1.838	192.520	156.487	−23.354
400	36.097	256.155	247.072	3.633	192.135	151.365	−19.766
450	36.383	260.424	248.323	5.446	191.711	146.293	−16.981
500	36.599	264.269	249.728	7.270	191.249	141.271	−14.759
600	36.899	270.970	252.726	10.946	190.215	131.371	−11.437
700	37.097	276.674	255.750	14.647	189.043	121.654	−9.078
800	37.237	281.637	258.682	18.364	187.310	112.177	−7.324
900	37.342	286.030	261.482	22.093	185.835	102.872	−5.971
1000	37.426	289.969	264.137	25.832	184.133	93.743	−4.897
1100	37.495	293.539	266.650	29.578	182.168	84.796	−4.027
1200	37.556	296.804	269.029	33.330	179.904	76.042	−3.310
1300	37.611	299.812	271.283	37.089	177.193	67.493	−2.712
1400	37.664	302.602	273.421	40.853	173.908	59.175	−2.208
1500	37.718	305.202	275.454	44.622	171.635	51.061	−1.778
1600	37.775	307.638	277.390	48.396	169.616	43.090	−1.407
1700	37.837	309.930	279.238	52.177	167.697	35.241	−1.083
1800	37.906	312.094	281.003	55.964	149.513	27.798	−0.807
1900	37.984	314.146	282.694	59.758	147.344	21.095	−0.580
2000	38.073	316.097	284.316	63.561	145.178	14.507	−0.379
2100	38.175	317.957	285.874	67.373	143.016	8.026	−0.200
2200	38.289	319.735	287.373	71.196	140.858	1.649	−0.039
2300	38.419	321.440	288.817	75.032	138.706	−4.631	0.105
2400	38.566	323.078	290.211	78.881	136.561	−10.817	0.235
2500	38.730	324.656	291.557	82.745	134.423	−16.914	0.353
2600	38.914	326.178	292.860	86.627	132.294	−22.925	0.461
2700	39.119	327.651	294.121	90.529	130.175	−28.855	0.558
2800	39.346	329.077	295.344	94.452	128.069	−34.706	0.647
2900	39.596	330.462	296.532	98.399	125.977	−40.483	0.729
3000	39.872	331.809	297.685	102.372	123.901	−46.187	0.804
3100	40.174	333.121	298.807	106.374	121.844	−51.823	0.873
3200	40.503	334.402	299.900	110.408	−255.004	−55.620	0.908
3300	40.859	335.654	300.964	114.476	−255.587	−49.380	0.782
3400	41.244	336.879	302.003	118.580	−256.142	−43.123	0.662
3500	41.656	338.081	303.016	122.725	−256.669	−36.850	0.550
3600	42.097	339.260	304.007	126.913	−257.164	−30.562	0.443
3700	42.565	340.420	304.975	131.146	−257.625	−24.261	0.343
3800	43.060	341.562	305.923	135.427	−258.048	−17.948	0.247
3900	43.580	342.687	306.851	139.758	−258.433	−11.625	0.156
4000	44.124	343.797	307.761	144.143	−258.775	−5.292	0.069
4100	44.690	344.893	308.653	148.584	−259.073	1.049	−0.013
4200	45.275	345.977	309.529	153.082	−259.326	7.397	−0.092
4300	45.878	347.050	310.389	157.639	−259.530	13.750	−0.167
4400	46.496	348.111	311.235	162.258	−259.684	20.107	−0.239
4500	47.127	349.163	312.066	166.939	−259.787	26.467	−0.307
4600	47.766	350.206	312.884	171.684	−259.838	32.829	−0.373
4700	48.412	351.240	313.689	176.493	−259.835	39.191	−0.436
4800	49.061	352.266	314.482	181.366	−259.780	45.553	−0.496
4900	49.711	353.285	315.263	186.305	−259.671	51.913	−0.553
5000	50.357	354.295	316.034	191.308	−259.509	58.270	−0.609
5100	50.998	355.299	316.794	196.376	−259.294	64.624	−0.662
5200	51.630	356.295	317.544	201.508	−259.028	70.973	−0.713
5300	52.250	357.285	318.284	206.702	−258.712	77.316	−0.762
5400	52.856	358.267	319.016	211.957	−258.347	83.653	−0.809
5500	53.446	359.242	319.738	217.272	−257.937	89.982	−0.855
5600	54.017	360.211	320.452	222.646	−257.482	96.304	−0.898
5700	54.566	361.172	321.158	228.075	−256.987	102.617	−0.940
5800	55.093	362.125	321.856	233.558	−256.453	108.922	−0.981
5900	55.595	363.071	322.547	239.093	−255.839	115.213	−1.020
6000	56.071	364.010	323.230	244.676	−255.226	121.497	−1.058

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 101.182 \pm 0.021\ J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 743\ K$
$T_{fus} = 918\ K$

$\Delta_f H°(0\ K) = -442.98 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -442.83 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{trs} H° = 3.77\ kJ·mol^{-1}$
$\Delta_{fus} H° = 15.9\ kJ·mol^{-1}$

Enthalpy of Formation

The heat of solution ($\Delta_{sln}H°$) of CsCl(cr) in water has been measured by Forcrand,[1,2] Haigh,[3] Samoilov,[4,6] and Rodnikova.[5] Based on their results, Parker[7] derived the corresponding $\Delta_{sln}H°$(aq, ∞, 298.15) values as 4.30, 4.32, 4.08, 4.25, 4.18 and 4.18 kcal·mol^{-1}. Borob'ev *et al.*[8] determined the same quantity and reported $\Delta_{sln}H°$(298.15 K) (CsCl, aq, ∞, H_2O) = 4.20 ± 0.04 kcal·mol^{-1}. Using this value, 4.20 kcal·mol^{-1}, and $\Delta_f H°$(298.15 K) = −61.69[9] and −39.952 kcal·mol^{-1} [10] for Cs^+(aq, ∞) and Cl^-(aq, ∞, 298.15), respectively, we evaluate $\Delta_f H°$(CsCl, cr, 298.15 K) = −105.84 ± 0.2 kcal·mol^{-1}, which is adopted.

Heat Capacity and Entropy

Taylor *et al.*[11] measured the low temperature heat capacities, 7.19–299.38 K, with an adiabatic calorimeter; the sample purity was >99.95%. Employing these data we derive the value $S°(298.15\ K) = 24.183\ cal·K^{-1}·mol^{-1}$ based on $S°(7.19\ K) = 0.031\ cal·K^{-1}·mol^{-1}$.

The high temperature enthalpies, 385.2–904.9 K, were measured by Kaylor,[21,12,13] using a Bunsen ice calorimeter and a CsCl sample of 99.8% purity. The heat capacities derived from the reported enthalpy data at temperatures 385.2–740.5 K appear too low (less than the adopted $C_p°$'s systematically by 0.9 cal·K^{-1}·mol^{-1} to join smoothly with the low temperature data at 298.15 K. The $C_p°$ values derived from the measured enthalpy data in the temperature range 760–920 K increase rapidly from 14.46 to 16.3 cal·K^{-1}·mol^{-1}. In order to rationalize this situation, we adopt the high temperature heat capacities, 298–743 K, for CsCl(α) obtained by linear extrapolation of the low temperature data. The $C_p°$ values for CsCl(B) are adjusted such that the rate of increase in heat capacities is linear and less rapid than the original one, and the total enthalpy remains essentially unchanged. The discrepancy between the high and low temperature $C_p°$ for CsCl(α) may be caused by the incomplete β → α phase conversion involved. In order to resolve this discrepancy, independent enthalpy measurements using a high purity sample with composition well characterized before and after each drop experiment seem necessary.

Transition Data

The temperature of transition (in K) has been reported by many investigators as 718,[14] 752,[15] 745,[16] 742,[21] 742.5,[12] 743,[20] and 733,[17] using different methods and samples of different purity. The value adopted is 743 K.

The heat of transition (in kcal·mol^{-1}) was reported to be 1.8,[14] 1.55,[18] 1.4,[19] 0.80,[21] 0.58,[12] 0.90,[13] and 1.1.[17] A median value 0.90 kcal·mol^{-1} is tentatively adopted.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ is calculated as the difference between $\Delta_f H°(298.15\ K)$ for CsCl(g) and CsCl(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	9.146	3.540	INFINITE	−12.452	−442.979	−442.979	INFINITE
100	44.091	47.798	145.996	−9.820	−443.952	−433.786	226.587
200	50.128	80.726	105.914	−5.038	−443.369	−423.827	110.692
298.15	52.442	101.182	101.182	0.	−442.835	−414.360	72.594
300	52.472	101.506	101.183	0.097	−442.829	−414.183	72.116
400	54.685	116.906	103.267	5.455	−444.485	−404.011	52.758
500	56.902	129.347	107.277	11.035	−443.823	−393.965	41.157
600	59.099	139.916	111.858	16.835	−442.946	−384.072	33.436
700	61.296	149.191	116.541	22.855	−441.858	−374.343	27.934
743.000	62.237	152.873	118.538	25.511	ALPHA <--> BETA		
743.000	63.388	157.941	118.538	29.276	TRANSITION		
800	63.680	162.637	121.515	32.898	−436.758	−365.075	23.837
900	64.174	170.166	126.510	39.290	−435.321	−356.200	20.673
918.000	64.266	171.438	127.379	40.446	---- BETA <--> LIQUID ----		
1000	64.685	176.954	131.221	45.733	−500.972	−343.789	17.958
1100	65.187	183.142	135.664	52.227	−498.433	−328.193	15.585
1200	65.689	188.836	139.860	58.771	−495.849	−312.830	13.617
1300	66.191	194.114	143.833	65.365	−493.220	−297.685	11.961
1400	66.693	199.037	147.602	72.009	−490.548	−282.744	10.549
1500	67.195	203.656	151.187	78.703	−487.831	−267.995	9.332
1600	67.697	208.008	154.604	85.447	−485.073	−253.429	8.274
1700	68.241	212.129	157.867	92.245	−482.272	−239.037	7.345
1800	68.743	216.044	160.991	99.094	−479.431	−224.811	6.524
1900	69.245	219.774	163.988	105.993	−476.556	−210.743	5.794
2000	69.747	223.338	166.867	112.943	−473.651	−196.828	5.141

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = [101.708]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 918\ K$

$\Delta_f H°(298.15\ K) = [-434.468]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 15.9 \pm 4.2\ kJ·mol^{-1}$

Enthaply of Formation

$\Delta_f H°$(CsCl, l, 298.15 K) is calculated from $\Delta_f H°$(CsCl, cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(918 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The enthalpies of CsCl(l) at temperatures 923.6–1168.0 K were measured with a Bunsen ice calorimeter by Kaylor *et al.*[1,2] Dworkin[3] derived the heat capacity of CsCl(l) as 18.5 $cal·K^{-1}·mol^{-1}$ from enthalpy data at temperatures 918–980 K. This value is adopted since it is in agreement with the enthalpy values reported by Kaylor *et al.*[1,2] The heat capacity at temperatures above 1168 and below 923.6 K is assumed to be 18.5 $cal·K^{-1}·mol^{-1}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature (in K) of CsCl(cr) has been determined by many investigators as 904 ± 3,[4] 919,[5] 912,[6] 911,[7] 918,[8] 916,[9] and 919.[13] The cause of the discrepancies is probably due to the difference in purity of the samples. The melting temperature adopted is 918 K.

The heat of melting (in $kcal·mol^{-1}$) was reported to be 4.84,[14] 4.97,[15] 4.58,[10] 4.96,[11] and 4.79,[2] which were obtained calorimetrically. Using a modification of Kelley's method of obtaining heat of melting from freezing point data on binary systems involving CsCl,[16] we derive the value of $\Delta_{fus}H°$ as 3.6–4.0 $kcal·mol^{-1}$, based on the following systems: CsCl–NaCl,[5] CsCl–CuCl,[6] CsCl–AgCl,[6] CsCl–LiCl[8] and CsCl–$Cs_3(PO_3)_3$.[12] The heat of melting for CsCl(cr) is tentatively adopted as 3.8 $kcal·mol^{-1}$. The $\Delta_{fus}H°$ values obtained calorimetrically are not used due to the uncertainties of the state of the sample before and after the enthalpy measurements.

Vaporization Data

T_{vap} = 1597.3 K is the temperature at which the calculated total pressures of CsCl(g) and Cs_2Cl_2(g) equal one atmosphere. The vapor composition at T_{vap} is derived as CsCl 80.4% and Cs_2Cl_2 19.6%. The boiling point of CsCl(l) has been determined by several investigators as 1562,[17] 1572[18] and 1576.[19] The heat required to vaporize one mole of liquid to the above vapor mixture at T_{vap} is $\Delta_{vap}H°$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	77.404	101.708	101.708	0.	−434.468	−406.150	71.156
300	77.404	102.187	101.710	0.143	−434.416	−405.975	70.686
400	77.404	124.455	104.746	7.884	−433.690	−396.236	51.743
500	77.404	141.727	110.479	15.624	−430.867	−387.199	40.450
600	77.404	155.840	116.899	23.364	−428.050	−378.731	32.971
700	77.404	167.771	123.336	31.105	−425.242	−370.733	27.664
800	77.404	178.107	129.551	38.845	−422.445	−363.137	23.710
900	77.404	187.224	135.462	46.586	−419.659	−355.891	20.655
918.000	77.404	188.757	136.492	47.979	---- BETA <--> LIQUID ----		
1000	77.404	195.379	141.053	54.326	−484.013	−345.255	18.034
1100	77.404	202.757	146.333	62.066	−480.226	−331.563	15.745
1200	77.404	209.492	151.320	69.807	−476.446	−318.215	13.852
1300	77.404	215.688	156.036	77.547	−472.671	−305.182	12.262
1400	77.404	221.424	160.504	85.288	−468.902	−292.439	10.911
1500	77.404	226.764	164.745	93.028	−465.140	−279.966	9.749
1600	77.404	231.760	168.779	100.768	−461.386	−267.744	8.741
1700	77.404	236.452	172.624	108.509	−457.641	−255.756	7.858
1800	77.404	240.877	176.294	116.249	−453.909	−243.988	7.080
1900	77.404	245.062	179.804	123.990	−450.193	−232.427	6.390
2000	77.404	249.032	183.167	131.730	−446.498	−221.062	5.774
2100	77.404	252.808	186.394	139.470	−442.827	−209.880	5.220
2200	77.404	256.409	189.495	147.211	−439.186	−198.873	4.722
2300	77.404	259.850	192.480	154.951	−435.581	−188.030	4.270
2400	77.404	263.144	195.356	162.692	−432.019	−177.344	3.860
2500	77.404	266.304	198.131	170.432	−428.504	−166.805	3.485
2600	77.404	269.340	200.812	178.172	−425.045	−156.405	3.142
2700	77.404	272.261	203.405	185.913	−421.648	−146.138	2.827
2800	77.404	275.076	205.914	193.653	−418.318	−135.995	2.537
2900	77.404	277.792	208.346	201.394	−415.065	−125.970	2.269
3000	77.404	280.416	210.705	209.134	−411.893	−116.055	2.021

PREVIOUS: CURRENT: June 1968

0	to	743	K crystal, alpha
743	to	918	K crystal, beta
above		918	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	9.146	3.540	INFINITE	−12.452	−442.979	−442.979	INFINITE
100	44.091	47.798	145.996	−9.820	−443.952	−433.786	226.587
200	50.128	80.726	105.914	−5.038	−443.369	−423.827	110.692
298.15	52.442	101.182	101.182	0.	−442.835	−414.360	72.594
300	52.472	101.506	101.183	0.097	−442.829	−414.183	72.116
400	54.685	116.906	103.267	5.455	−444.485	−404.011	52.758
500	56.902	129.347	107.277	11.035	−443.823	−393.965	41.157
600	59.099	139.916	111.858	16.835	−442.946	−384.072	33.436
700	61.296	149.191	116.541	22.855	−441.858	−374.343	27.934
743.000	62.237	152.873	118.538	25.511	ALPHA <--> BETA TRANSITION		
743.000	63.388	157.941	118.538	29.276			
800	63.680	162.637	121.515	32.898	−436.758	−365.075	23.837
900	64.174	170.166	126.510	39.290	−435.321	−356.200	20.673
918.000	64.266	171.438	127.379	40.446	BETA <--> LIQUID TRANSITION		
918.000	77.404	188.757	127.379	56.345			
1000	77.404	195.379	132.687	62.692	−484.013	−345.255	18.034
1100	77.404	202.757	138.727	70.433	−480.226	−331.563	15.745
1200	77.404	209.492	144.347	78.173	−476.446	−318.215	13.852
1300	77.404	215.688	149.600	85.914	−472.671	−305.182	12.262
1400	77.404	221.424	154.528	93.654	−468.902	−292.439	10.911
1500	77.404	226.764	159.168	101.394	−465.140	−279.966	9.749
1600	77.404	231.760	163.550	109.135	−461.386	−267.744	8.741
1700	77.404	236.452	167.702	116.875	−457.641	−255.756	7.858
1800	77.404	240.877	171.646	124.616	−453.909	−243.988	7.080
1900	77.404	245.062	175.400	132.356	−450.193	−232.427	6.390
2000	77.404	249.032	178.984	140.096	−446.498	−221.062	5.774
2100	77.404	252.808	182.410	147.837	−442.827	−209.880	5.220
2200	77.404	256.409	185.692	155.577	−439.186	−198.873	4.722
2300	77.404	259.850	188.842	163.318	−435.581	−188.030	4.270
2400	77.404	263.144	191.870	171.058	−432.019	−177.344	3.860
2500	77.404	266.304	194.785	178.798	−428.504	−166.805	3.485
2600	77.404	269.340	197.594	186.539	−425.045	−156.405	3.142
2700	77.404	272.261	200.306	194.279	−421.648	−146.138	2.827
2800	77.404	275.076	202.926	202.020	−418.318	−135.995	2.537
2900	77.404	277.792	205.461	209.760	−415.065	−125.970	2.269
3000	77.404	280.416	207.916	217.500	−411.893	−116.055	2.021

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = 256.070 \pm 0.021\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -237.98 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -240.16 \pm 4.2\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 213.08\ cm^{-1}$ $\omega_e x_e = 0.733\ cm^{-1}$ $\sigma = 1$

$B_e = 0.07134\ cm^{-1}$ $\alpha_e = 0.000332\ cm^{-1}$ $r_e = 2.906$ Å

Enthalpy of Formation

The total pressures of CsCl(g) and Cs_2Cl_2(g) over CsCl(cr) and CsCl(l) in the temperature range 605–1577 K have been determined by manometric, transpiration and Knudsen effusion methods by many investigators. Based on the reported results, the partial pressures of CsCl(g) and Cs_2Cl_2(g) are calculated using the derived Gibbs energy functions for CsCl(cr), CsCl(l), CsCl(g) and Cs_2Cl_2(g) and the enthalpies of sublimation and vaporization which are adjusted so that the sum of the calculated partial pressures of CsCl(g) and Cs_2Cl_2(g) approaches the measured total pressures, and the evaluated 2nd and 3rd law $\Delta_f H°$(298.15 K) values are in reasonable agreement. The results obtained are presented in the table below. The value of $\Delta_f H°$(CsCl, g, 298.15 K) adopted is -57.4 ± 1 kcal·mol^{-1}(-240.162 ± 4.2 kJ·mol^{-1}).

Gaydon[10] reported $D°_0$(Cs–Cl) = 4.6 ± 0.2 eV or 106.08 ± 4.61 kcal·mol^{-1}. Using this $D°_0$ value and $\Delta_f H°$(0 K) = 18.683 and 28.52 kcal·mol^{-1} for Cs(g) and Cl(g), we evaluate $\Delta_f H°(298.15\ K) = -59.4 \pm 4.6$ kcal·mol^{-1} for CsCl(g), which is in fair agreement with the adopted value.

Source	Reaction*	Method	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[1]	1	A	793–893	11	46.81 ± 0.35	49.92	3.7 ± 0.4	−55.92
[2]	1	A	690–891	28	47.80 ± 0.31	47.88	0.1 ± 0.4	−57.96
[3]	1	B	784–905	10	47.08 ± 0.26	49.17	2.5 ± 0.3	−56.67
[4]	1	A	605–851	16	45.26 ± 0.38	48.74	4.7 ± 0.5	−57.10
[5]	2	C	1335–1577	9	49.36 ± 0.50	46.27	−2.1 ± 0.3	−57.57
[6]	2	C	1259–1568	7	51.61 ± 1.08	46.17	−3.8 ± 0.8	−57.67
[7]	2	C	1098–1293	9	47.57 ± 0.08	46.52	−0.9 ± 0.1	−57.32
[8]	2	B	1133–1263	3	48.73 ± 2.09	47.00	−1.4 ± 1.7	−56.84
[9]	2	C	1165–1387	10	47.46 ± 0.08	46.36	−0.9 ± 0.1	−57.48
[10]	1	A	1174–1353	10	47.97 ± 0.15	46.54	−1.1 ± 0.1	−57.30

*1 CsCl(cr) = CsCl(g); 2 CsCl(l) = CsCl(g); A = Knudsen effusion; B = transpiration; and C = manometric.

Heat Capacity and Entropy

Clouser and Gordy[11] studied the pure rotational spectra of CsCl(g) in the 0.96–3 mm range of the microwave region with the molecular-beam spectrometer, and derived the values of B_e, α_e, ω_e, $\omega_e x_e$ and r_e, which are adopted and corrected to the average isotopic species.

The Cs–Cl bond distance was measured as 3.06 ± 0.03 Å by the electron diffraction method by Maxwell *et al.*,[12] which is not used. Similar values of B_e and α_e were reported by Honig *et al.*[13] and Rice and Klemperer,[14] determined from microwave and infrared spectra, respectively. Barrow and Caunt[15] gave $\omega_e = 240\ cm^{-1}$($CsCl^{35}$) which is singificantly different from the adopted value 214.22 cm^{-1} for $CsCl^{35}$ and the value $209 \pm 6\ cm^{-1}$ reported by Rice and Klemperer.[14]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C°_p$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.130	−237.985	−237.985	INFINITE
100	33.194	217.326	288.246	−7.092	−238.551	−245.338	128.151
200	36.120	241.467	259.429	−3.593	−239.251	−251.857	65.778
250	36.643	249.588	256.677	−1.772	−239.660	−254.963	53.272
298.15	36.952	256.070	256.070	0.	−240.162	−257.867	45.177
300	36.961	256.299	256.071	0.068	−240.184	−257.977	44.918
350	37.175	262.014	256.522	1.922	−242.885	−260.558	38.886
400	37.330	266.988	257.526	3.785	−243.482	−263.042	34.350
450	37.450	271.392	258.827	5.655	−244.071	−265.451	30.813
500	37.548	275.343	260.284	7.530	−244.655	−267.795	27.976
600	37.702	282.203	263.383	11.292	−245.815	−272.314	23.707
700	37.827	288.025	266.498	15.069	−246.971	−276.640	20.643
800	37.935	293.083	269.512	18.857	−248.126	−280.799	18.334
900	38.034	297.557	272.384	22.656	−249.282	−284.814	16.530
1000	38.126	301.569	275.105	26.464	−317.569	−285.000	14.887
1100	38.215	305.207	277.679	30.281	−317.706	−281.737	13.379
1200	38.301	308.536	280.114	34.107	−317.840	−278.461	12.121
1300	38.386	311.605	282.420	37.941	−317.971	−275.174	11.057
1400	38.468	314.453	284.607	41.784	−318.100	−271.877	10.144
1500	38.550	317.110	286.686	45.635	−318.227	−268.571	9.352
1600	38.631	319.600	288.667	49.494	−318.354	−265.257	8.660
1700	38.712	321.945	290.556	53.361	−318.483	−261.934	8.048
1800	38.792	324.160	292.362	57.236	−318.616	−258.604	7.504
1900	38.872	326.259	294.091	61.119	−318.757	−255.266	7.018
2000	38.951	328.255	295.750	65.010	−318.911	−251.921	6.579
2100	39.030	330.157	297.343	68.909	−319.081	−248.567	6.183
2200	39.109	331.975	298.876	72.816	−319.274	−245.205	5.822
2300	39.188	333.715	300.354	76.731	−319.495	−241.833	5.492
2400	39.266	335.384	301.779	80.654	−319.750	−238.452	5.190
2500	39.345	336.989	303.155	84.585	−320.045	−235.058	4.911
2600	39.423	338.534	304.486	88.523	−320.388	−231.652	4.654
2700	39.502	340.023	305.775	92.469	−320.785	−228.232	4.415
2800	39.580	341.461	307.024	96.423	−321.242	−224.796	4.194
2900	39.658	342.851	308.236	100.385	−321.766	−221.342	3.987
3000	39.736	344.197	309.412	104.355	−322.365	−217.869	3.793
3100	39.814	345.501	310.555	108.333	−323.045	−214.375	3.612
3200	39.892	346.767	311.667	112.318	−323.812	−210.858	3.442
3300	39.970	347.995	312.750	116.311	−324.632	−207.318	3.282
3400	40.048	349.190	313.804	120.312	−325.574	−203.749	3.130
3500	40.126	350.352	314.831	124.321	−326.616	−200.151	2.987
3600	40.204	351.483	315.834	128.337	−327.763	−196.522	2.851
3700	40.282	352.586	316.812	132.361	−329.004	−192.861	2.723
3800	40.360	353.661	317.768	136.394	−330.355	−189.164	2.600
3900	40.438	354.710	318.702	140.433	−331.805	−185.432	2.484
4000	40.516	355.735	319.615	144.481	−333.386	−181.659	2.372
4100	40.593	356.737	320.508	148.537	−335.082	−177.845	2.266
4200	40.671	357.716	321.382	152.600	−336.895	−173.988	2.164
4300	40.749	358.674	322.239	156.671	−338.825	−170.087	2.066
4400	40.827	359.611	323.077	160.750	−340.577	−166.173	1.973
4500	40.905	360.530	323.899	164.836	−342.127	−162.250	1.883
4600	40.982	361.430	324.706	168.931	−344.225	−158.230	1.797
4700	41.060	362.312	325.496	173.033	−346.410	−154.163	1.713
4800	41.138	363.177	326.272	177.143	−348.679	−150.049	1.633
4900	41.216	364.026	327.034	181.260	−351.028	−145.887	1.555
5000	41.293	364.860	327.782	185.386	−353.449	−141.676	1.480
5100	41.371	365.678	328.518	189.519	−355.939	−137.416	1.407
5200	41.449	366.482	329.240	193.660	−357.960	−133.184	1.338
5300	41.526	367.272	329.950	197.809	−360.500	−128.837	1.270
5400	41.604	368.049	330.648	201.965	−362.809	−124.485	1.204
5500	41.682	368.813	331.335	206.130	−365.246	−120.073	1.140
5600	41.760	369.565	332.011	210.302	−367.853	−115.592	1.078
5700	41.837	370.305	332.677	214.481	−370.484	−111.064	1.018
5800	41.915	371.033	333.332	218.669	−373.133	−106.489	0.959
5900	41.993	371.751	333.977	222.864	−375.792	−101.869	0.902
6000	42.070	372.457	334.612	227.068	−378.457	−97.204	0.846

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 87.03 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 703\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -138.07 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 10.230 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

There have been three calorimetric determinations of the enthalpy of formation. Thomsen[1] reported $-32.875\ kcal \cdot mol^{-1}$. Berthelot[2] reported $-35.6\ kcal \cdot mol^{-1}$ and Wartenberg and Werth[3] reported $-32.1 \pm 0.4\ kcal \cdot mol^{-1}$. In addition, values of the enthalpy of formation have been derived from several sets of equilibrium data. Noyes and Chow[4] from a study of cell potentials derived a $\Delta_r H° = 7.19\ kcal \cdot mol^{-1}$ for the reaction $Cu(cr) + HCl(\infty,aq) \rightarrow CuCl(cr) + 1/2\ H_2(g)$ which yields $\Delta_f H°(CuCl, 298.15\ K) = -32.76\ kcal \cdot mol^{-1}$. Several investigators have studied the reaction $2\ CuCl(cr) + H_2(g) \rightarrow 2\ Cu(cr) + 2\ HCl(g)$ and its reverse reaction. These include Bagdasarian[5] who reported equilibrium constants which result in 2nd and 3rd law heats of reaction of 24.3 and 23.2 $kcal \cdot mol^{-1}$; Kapustinsky[6] who obtained similarly 20.1 and 21.8 $kcal \cdot mol^{-1}$; Shchukarev and Oranskaya[7] who obtained 25.4 and 21.5 $kcal \cdot mol^{-1}$ for the 2nd and 3rd law heat of reaction. These yield values for $\Delta_f H°(CuCl, 298.15\ K)$ ranging from -32.1 to -34.8. Watanabe[8] from cell studies reports $\Delta_f H°(CuCl, 298.15\ K) = -34.6\ kcal \cdot mol^{-1}$. A value of $\Delta_f H°(298.15\ K)$ can also be obtained from $\Delta_f H°(CuCl_3, g)$ which is fixed independently and known with good precision. Using the 3rd law heat of sublimation of CuCl(cr) to trimer determined by Magee[9] [see trimer table], we obtain $\Delta_f H°(CuCl, cr, 298.15\ K) = -33.01 \pm 0.3\ kcal \cdot mol^{-1}$. A weighted average of $-33.0 \pm 0.4\ kcal \cdot mol^{-1}$ ($-138.072 \pm 1.7\ kJ \cdot mol^{-1}$) was adopted.

Heat Capacity and Entropy

The entropy of CuCl was obtained from the several pieces of equilibrium data reported above and the adopted $\Delta_f H°(298.15\ K)$. A weighted average of $20.8 \pm 1\ cal \cdot K^{-1} \cdot mol^{-1}$ was adopted for $S°(CuCl, cr, 298.15\ K)$. The enthalpy and heat capacity above 298.15 K have been reported by Krestovnikov and Karetnikov.[10] However, these values were not adopted since they do not give reasonable heat capacities, and other data by these workers are not in agreement with established values. Heat capacities equal to those of AgCl, as given by Kelley,[11] were adopted here above 298.15 K.

Fusion Data

The temperature and enthalpy of fusion were those selected by Kelley[12] from phase studies. The enthalpy of fusion was reported by Krestovnikov and Karetnikov[10] as $2.54\ kcal \cdot mol^{-1}$.

Sublimation Data

The enthalpy of sublimation was calculated from the adopted enthalpies of formation at 298.15 K for the reaction $x\,CuCl(cr) \rightarrow (CuCl)_x(g)$ where x = 1 or 3. See the individual ideal gas tables for details.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	48.534	87.027	87.027	0.	−138.072	−120.876	21.177
300	48.771	87.328	87.028	0.090	−138.059	−120.769	21.028
400	56.902	102.675	89.065	5.444	−136.933	−115.157	15.038
500	59.831	115.711	93.128	11.291	−135.437	−109.882	11.479
600	61.505	126.773	97.838	17.361	−133.803	−104.924	9.134
700	62.760	136.354	102.671	23.578	−132.097	−100.244	7.480
703.000	62.791	136.623	102.815	23.767	--- CRYSTAL <---> LIQUID ---		
800	63.680	144.795	107.419	29.901	−130.348	−95.813	6.256
900	64.388	152.337	111.999	36.305	−128.580	−91.602	5.316
1000	65.019	159.155	116.379	42.776	−126.812	−87.588	4.575
1100	65.531	165.376	120.554	49.304	−125.064	−83.751	3.977
1200	66.011	171.099	124.531	55.881	−123.363	−80.071	3.485
1300	66.459	176.400	128.320	62.505	−121.753	−76.529	3.075
1400	66.874	181.341	131.932	69.172	−133.393	−72.700	2.712
1500	67.258	185.968	135.382	75.879	−131.866	−68.418	2.383

PREVIOUS: CURRENT: March 1966

Copper Chloride (CuCl) LIQUID M_r = 98.999

$S°(298.15\ K)$ = [93.752] $J·K^{-1}·mol^{-1}$
T_{fus} = 703°K

$\Delta_f H°(298.15\ K)$ = [−131.178] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 10.230 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(CuCl, I,298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(703\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated to be constant at 8 $cal·K^{-1}·mol^{-1}$. The entropy was calculated in a manner analogous to that of the heat of formation.

Vaporization Data

The boiling point and heat of vaporization were calculated from the respective liquid, monomer and trimer gas tables. The boiling point, T_{vap} = 1485 K, was taken as the point where the total pressure reached 1 atm. At this point the partial pressures are 0.021 atm of monomer and 0.979 atm of trimer.

Copper Chloride (CuCl) $Cl_1Cu_1(l)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	66.944	93.752	93.752	0.	−131.178	−115.987	20.320
300	66.944	94.166	93.754	0.124	−131.131	−115.893	20.179
400	66.944	113.425	96.379	6.818	−128.665	−111.189	14.520
500	66.944	128.363	101.338	13.513	−126.322	−107.093	11.188
600	66.944	140.569	106.890	20.207	−124.064	−103.461	9.007
700	66.944	150.888	112.457	26.901	−121.879	−100.201	7.477
703.000	66.944	151.174	112.622	27.102	--- CRYSTAL <--> LIQUID ---		
800	66.944	159.827	117.832	33.596	−119.759	−97.249	6.350
900	66.944	167.712	122.945	40.290	−117.701	−94.560	5.488
1000	66.944	174.765	127.781	46.985	−115.709	−92.096	4.811
1100	66.944	181.146	132.347	53.679	−113.795	−89.828	4.266
1200	66.944	186.971	136.659	60.373	−111.976	−87.731	3.819
1300	66.944	192.329	140.738	67.068	−110.296	−85.779	3.447
1400	66.944	197.290	144.603	73.762	−121.908	−83.545	3.117
1500	66.944	201.909	148.271	80.457	−120.394	−80.857	2.816
1600	66.944	206.229	151.760	87.151	−118.884	−78.271	2.555
1700	66.944	210.288	155.084	93.845	−117.378	−75.779	2.328
1800	66.944	214.114	158.259	100.540	−115.877	−73.375	2.129
1900	66.944	217.734	161.294	107.234	−114.381	−71.055	1.953
2000	66.944	221.167	164.203	113.929	−112.889	−68.813	1.797
2100	66.944	224.433	166.994	120.623	−111.404	−66.646	1.658
2200	66.944	227.548	169.676	127.317	−109.924	−64.549	1.533
2300	66.944	230.524	172.257	134.012	−108.451	−62.519	1.420
2400	66.944	233.373	174.745	140.706	−106.986	−60.554	1.318
2500	66.944	236.105	177.145	147.401	−105.528	−58.649	1.225
2600	66.944	238.731	179.464	154.095	−104.079	−56.803	1.141
2700	66.944	241.257	181.706	160.789	−102.639	−55.012	1.064
2800	66.944	243.692	183.876	167.484	−101.209	−53.274	0.994
2900	66.944	246.041	185.980	174.178	−399.992	−45.591	0.821
3000	66.944	248.311	188.020	180.873	−397.786	−33.408	0.582

PREVIOUS: CURRENT: March 1966

Copper Chloride (CuCl) $Cl_1Cu_1(l)$

0	to	703	K	crystal
above		703	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
T/K	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	48.534	87.027	87.027	0.	−138.072	−120.876	21.177
300	48.771	87.328	87.028	0.090	−138.059	−120.769	21.028
400	56.902	102.675	89.065	5.444	−136.933	−115.157	15.038
500	59.831	115.711	93.128	11.291	−135.437	−109.882	11.479
600	61.505	126.773	97.838	17.361	−133.803	−104.924	9.134
700	62.760	136.354	102.671	23.578	−132.097	−100.244	7.480
703.000	62.791	136.623	102.815	23.767	____ CRYSTAL <--> LIQUID ____		
703.000	66.944	151.174	102.815	33.996	TRANSITION		
800	66.944	159.827	109.215	40.490	−119.759	−97.249	6.350
900	66.944	167.712	115.285	47.184	−117.701	−94.560	5.488
1000	66.944	174.765	120.886	53.879	−115.709	−92.096	4.811
1100	66.944	181.146	126.079	60.573	−113.795	−89.828	4.266
1200	66.944	186.971	130.914	67.268	−111.976	−87.731	3.819
1300	66.944	192.329	135.435	73.962	−110.296	−85.779	3.447
1400	66.944	197.290	139.678	80.656	−121.908	−83.545	3.117
1500	66.944	201.909	143.675	87.351	−120.394	−80.857	2.816
1600	66.944	206.229	147.451	94.045	−118.884	−78.271	2.555
1700	66.944	210.288	151.029	100.740	−117.378	−75.779	2.328
1800	66.944	214.114	154.428	107.434	−115.877	−73.375	2.129
1900	66.944	217.734	157.666	114.128	−114.381	−71.055	1.953
2000	66.944	221.167	160.756	120.823	−112.889	−68.813	1.797
2100	66.944	224.433	163.711	127.517	−111.404	−66.646	1.658
2200	66.944	227.548	166.542	134.212	−109.924	−64.549	1.533
2300	66.944	230.524	169.260	140.906	−108.451	−62.519	1.420
2400	66.944	233.373	171.872	147.600	−106.986	−60.554	1.318
2500	66.944	236.105	174.387	154.295	−105.528	−58.649	1.225
2600	66.944	238.731	176.812	160.989	−104.079	−56.803	1.141
2700	66.944	241.257	179.152	167.684	−102.639	−55.012	1.064
2800	66.944	243.692	181.414	174.378	−101.209	−53.274	0.994
2900	66.944	246.041	183.602	181.072	−399.992	−45.591	0.821
3000	66.944	248.311	185.722	187.767	−397.786	−33.408	0.582

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 237.207\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 91.21 \pm 1.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 91.09 \pm 1.7\ kJ·mol^{-1}$

Electronic Level and Multiplicity		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 414.9\ cm^{-1}$ $\omega_e x_e = 1.577\ cm^{-1}$ $\sigma = 1$

$B_e = 0.1761\ cm^{-1}$ $\alpha_e = 0.001\ cm^{-1}$ $r_e = 2.050$ Å

Enthalpy of Formation

The enthalpy of formation was obtained from the equilibrium data of Brewer and Lofgren.[1] They studied the reaction xCu(cr) + x HCl(g) → Cu_2Cl_2(g) + $x/2$ H_2(g) by measuring the amount of CuCl formed when various ratios of HCl:H_2 were passed over heated copper. Brewer and Lofgren analyzed the data by a least squares fitting technique and deduced partial pressures of monomer and trimer. The monomer pressures were subjected to 2nd and 3rd law analysis and gave $\Delta_f H°(298.15\ K) = 46.85 \pm 3.2$ and $43.83 \pm 0.4\ kcal·mol^{-1}$, respectively. The 3rd law value yields $\Delta_f H°(CuCl, g, 298.15\ K) = 21.77 \pm 0.4\ kcal·mol^{-1}$, which was adopted.

Heat Capacity and Entropy

The molecular constants were corrected for normal isotopic abundance of both copper and chlorine and were calculated from the values for $^{65}Cu^{35}Cl$ given by Asundi *et al.*[2] The rotational constants were in good agreement with those reported by Lagerqvist and Lazarova–Girsamov[3] for $Cu^{65}Cl^{35}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.471	91.212	91.212	INFINITE
100	29.899	201.663	267.142	−6.548	92.010	82.298	−42.988
200	33.356	223.487	240.381	−3.379	91.647	72.692	−18.985
250	34.503	231.061	237.784	−1.681	91.373	67.985	−14.205
298.15	35.261	237.207	237.207	0.	91.086	63.506	−11.126
300	35.285	237.425	237.208	0.065	91.074	63.335	−11.028
350	35.830	242.908	237.639	1.844	90.757	58.736	−8.766
400	36.220	247.719	238.605	3.646	90.426	54.184	−7.076
450	36.509	252.003	239.860	5.464	90.081	49.675	−5.766
500	36.730	255.861	241.270	7.295	89.724	45.204	−4.722
600	37.044	262.587	244.279	10.985	88.978	36.369	−3.166
700	37.257	268.315	247.314	14.701	88.184	27.663	−2.064
800	37.415	273.300	250.257	18.435	87.344	19.074	−1.245
900	37.538	277.715	253.067	22.183	86.455	10.594	−0.615
1000	37.641	281.675	255.733	25.942	85.512	2.215	−0.116
1100	37.729	285.267	258.258	29.710	84.500	−6.067	0.288
1200	37.807	288.553	260.647	33.487	83.401	−14.252	0.620
1300	37.879	291.582	262.912	37.272	82.171	−22.341	0.898
1400	37.945	294.392	265.061	41.063	67.656	−29.923	1.116
1500	38.008	297.012	267.105	44.860	66.274	−36.845	1.283
1600	38.068	299.467	269.052	48.664	64.893	−43.674	1.426
1700	38.126	301.777	270.909	52.474	63.514	−50.418	1.549
1800	38.182	303.957	272.685	56.289	62.136	−57.080	1.656
1900	38.236	306.023	274.386	60.110	60.759	−63.665	1.750
2000	38.290	307.986	276.017	63.937	59.382	−70.178	1.833
2100	38.342	309.855	277.585	67.768	58.005	−76.622	1.906
2200	38.394	311.640	279.092	71.605	56.627	−83.001	1.971
2300	38.445	313.348	280.545	75.447	55.247	−89.317	2.028
2400	38.496	314.985	281.946	79.294	53.866	−95.573	2.080
2500	38.546	316.558	283.299	83.146	52.481	−101.771	2.126
2600	38.595	318.070	284.608	87.003	51.093	−107.913	2.168
2700	38.645	319.528	285.874	90.865	49.700	−114.003	2.206
2800	38.694	320.934	287.101	94.732	48.303	−120.040	2.239
2900	38.743	322.293	288.292	98.604	−253.302	−120.032	2.162
3000	38.792	323.607	289.447	102.481	−253.914	−115.426	2.010
3100	38.840	324.880	290.570	106.362	−254.581	−110.799	1.867
3200	38.889	326.114	291.661	110.249	−255.304	−106.150	1.733
3300	38.937	327.311	292.723	114.140	−256.081	−101.476	1.606
3400	38.985	328.474	293.758	118.036	−256.913	−96.779	1.487
3500	39.033	329.605	294.766	121.937	−257.798	−92.057	1.374
3600	39.081	330.705	295.749	125.843	−258.734	−87.308	1.267
3700	39.129	331.777	296.708	129.753	−259.719	−82.533	1.165
3800	39.176	332.821	297.645	133.668	−260.750	−77.730	1.068
3900	39.224	333.839	298.560	137.588	−261.825	−72.900	0.976
4000	39.272	334.833	299.455	141.513	−262.939	−68.042	0.889
4100	39.319	335.803	300.329	145.443	−264.089	−63.155	0.805
4200	39.367	336.751	301.185	149.377	−265.272	−58.240	0.724
4300	39.414	337.678	302.023	153.316	−266.484	−53.296	0.647
4400	39.462	338.585	302.844	157.260	−267.721	−48.324	0.574
4500	39.509	339.472	303.648	161.209	−268.980	−43.324	0.503
4600	39.556	340.341	304.436	165.162	−270.256	−38.295	0.435
4700	39.604	341.192	305.209	169.120	−271.547	−33.239	0.369
4800	39.651	342.027	305.968	173.083	−272.850	−28.155	0.306
4900	39.698	342.845	306.712	177.050	−274.160	−23.043	0.246
5000	39.745	343.647	307.443	181.022	−275.476	−17.905	0.187
5100	39.793	344.435	308.160	184.999	−276.795	−12.740	0.130
5200	39.840	345.208	308.865	188.981	−278.114	−7.550	0.076
5300	39.887	345.967	309.558	192.967	−279.431	−2.334	0.023
5400	39.934	346.713	310.239	196.958	−280.744	2.906	−0.028
5500	39.981	347.446	310.909	200.954	−282.053	8.171	−0.078
5600	40.028	348.167	311.568	204.954	−283.354	13.460	−0.126
5700	40.075	348.876	312.216	208.959	−284.647	18.771	−0.172
5800	40.122	349.573	312.855	212.969	−285.932	24.106	−0.217
5900	40.169	350.260	313.483	216.984	−287.208	29.462	−0.261
6000	40.216	350.935	314.101	221.003	−288.473	34.840	−0.303

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 192.741\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -93.131 \pm 0.21\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -93.345 \pm 0.21\ kJ·mol^{-1}$

	Electronic States and Molecular Constants (σ = 1)						
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	2144.0	26.90	5.4444	0.1121	1.2746
$B^1\Pi$	75160	2	2199.0	[26.9]	5.1793	[0.1121]	
$V^1\Sigma^+$	76520	1	684.6	[26.9]	1.555	[0.1121]	2.43
$C^1\Pi$	77525	2	2114.1	[26.9]	4.9605	[0.1121]	

Enthalpy of Formation (Provisional–evaluation incomplete)

The enthalpy of formation was calculated from the selected value of $\Delta_f H°(298.15\ K)$ of HCl(g) given by JANAF,[1] the appropriate thermal functions (refer to H_2, D_2, DCl tables, and HCl[1]) and zero point energies. The zero point energies of $H_2(g)$ and $D_2(g)$ are taken from Herzberg and Monfile.[2] The zero point energies of HCl(g) and DCl(g), including the Dunham correction, were calculated from the molecular constants taken from Rosen.[3]

Heat Capacity and Entropy

The vibrational and rotational constants at the respective electronic levels were taken from Rosen[3] and were adjusted to Cl^{35} = 75.4% and Cl^{37} = 24.6%.

The National Bureau of Standards prepared this table[4] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[4] we recalculate the table in terms of 1973 fundamental constants,[5] 1975 atomic weights,[6] and current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (June 1971).
[2]G. Herzberg and A. Monfils, J. Mol. Spectrosc. **5**, 482 (1960).
[3]B. Rosen, "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, Oxford, (1970).
[4]S. Abramowitz *et al.*, U. S. Natl. Bur. Stand. Rept. 10904, 239, (1972).
[5]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
[6]IUPAC Commission on Atomic Weights, Pure and Applied Chem. **47**, 75 (1976); **37**, 589 (1974).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.661	−93.131	−93.131	INFINITE
100	29.113	160.924	218.642	−5.772	−93.073	−94.076	49.140
200	29.124	181.107	195.407	−2.860	−93.157	−95.051	24.825
250	29.136	187.606	193.221	−1.404	−93.240	−95.516	19.957
298.15	29.170	192.741	192.741	0.	−93.345	−95.945	16.809
300	29.172	192.921	192.741	0.054	−93.349	−95.961	16.708
350	29.256	197.424	193.097	1.514	−93.478	−96.387	14.385
400	29.406	201.339	193.887	2.981	−93.618	−96.793	12.640
450	29.627	204.815	194.912	4.456	−93.763	−97.181	11.280
500	29.911	207.951	196.062	5.944	−93.905	−97.553	10.191
600	30.610	213.464	198.515	8.969	−94.170	−98.257	8.554
700	31.383	218.240	200.999	12.069	−94.397	−98.920	7.381
800	32.142	222.481	203.424	15.245	−94.582	−99.553	6.500
900	32.843	226.308	205.757	18.495	−94.732	−100.164	5.813
1000	33.467	229.801	207.990	21.811	−94.851	−100.762	5.263
1100	34.015	233.017	210.121	25.186	−94.948	−101.348	4.813
1200	34.491	235.998	212.154	28.612	−95.027	−101.926	4.437
1300	34.905	238.775	214.096	32.082	−95.094	−102.498	4.118
1400	35.266	241.375	215.953	35.591	−95.152	−103.065	3.845
1500	35.580	243.820	217.730	39.134	−95.205	−103.629	3.609
1600	35.857	246.125	219.433	42.706	−95.254	−104.189	3.401
1700	36.101	248.306	221.068	46.304	−95.301	−104.746	3.218
1800	36.318	250.376	222.639	49.925	−95.347	−105.300	3.056
1900	36.512	252.345	224.152	53.567	−95.395	−105.852	2.910
2000	36.687	254.222	225.608	57.227	−95.445	−106.401	2.779
2100	36.845	256.016	227.014	60.904	−95.498	−106.947	2.660
2200	36.989	257.733	228.372	64.596	−95.556	−107.491	2.552
2300	37.121	259.380	229.684	68.301	−95.619	−108.032	2.453
2400	37.242	260.963	230.955	72.019	−95.689	−108.570	2.363
2500	37.355	262.486	232.186	75.749	−95.766	−109.105	2.280
2600	37.460	263.953	233.380	79.490	−95.852	−109.637	2.203
2700	37.558	265.368	234.538	83.241	−95.946	−110.166	2.131
2800	37.650	266.736	235.664	87.002	−96.050	−110.691	2.065
2900	37.736	268.059	236.758	90.771	−96.164	−111.211	2.003
3000	37.819	269.339	237.823	94.549	−96.289	−111.728	1.945
3100	37.897	270.581	238.860	98.334	−96.424	−112.241	1.891
3200	37.971	271.785	239.870	102.128	−96.569	−112.749	1.840
3300	38.043	272.955	240.855	105.929	−96.724	−113.252	1.793
3400	38.111	274.091	241.816	109.736	−96.889	−113.750	1.748
3500	38.177	275.197	242.754	113.551	−97.063	−114.244	1.705
3600	38.241	276.273	243.670	117.372	−97.245	−114.732	1.665
3700	38.302	277.322	244.565	121.199	−97.434	−115.215	1.627
3800	38.362	278.344	245.441	125.032	−97.630	−115.693	1.590
3900	38.420	279.341	246.298	128.871	−97.831	−116.166	1.556
4000	38.477	280.315	247.136	132.716	−98.036	−116.633	1.523
4100	38.532	281.266	247.957	136.567	−98.245	−117.096	1.492
4200	38.586	282.195	248.761	140.422	−98.454	−117.553	1.462
4300	38.638	283.103	249.549	144.284	−98.665	−118.005	1.433
4400	38.690	283.992	250.322	148.150	−98.874	−118.452	1.406
4500	38.741	284.862	251.080	152.022	−99.082	−118.895	1.380
4600	38.790	285.714	251.823	155.898	−99.286	−119.333	1.355
4700	38.839	286.549	252.553	159.780	−99.486	−119.767	1.331
4800	38.888	287.367	253.270	163.666	−99.681	−120.196	1.308
4900	38.935	288.170	253.974	167.557	−99.869	−120.622	1.286
5000	38.982	288.957	254.666	171.453	−100.049	−121.043	1.265
5100	39.028	289.729	255.346	175.353	−100.221	−121.462	1.244
5200	39.074	290.487	256.015	179.259	−100.383	−121.876	1.224
5300	39.119	291.232	256.672	183.168	−100.535	−122.288	1.205
5400	39.164	291.964	257.319	187.082	−100.675	−122.697	1.187
5500	39.208	292.683	257.955	191.001	−100.803	−123.104	1.169
5600	39.252	293.390	258.582	194.924	−100.918	−123.508	1.152
5700	39.296	294.085	259.198	198.851	−101.020	−123.911	1.136
5800	39.339	294.769	259.806	202.783	−101.107	−124.312	1.120
5900	39.382	295.441	260.404	206.719	−101.180	−124.711	1.104
6000	39.424	296.104	260.994	210.660	−101.236	−125.110	1.089

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 240.25 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -75.34 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -78.24 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A'$	0	1
$^3A''$	[22000]	3

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
2666(1)
911(1)
728(1)

Point Group: C_s $\sigma = 1$
Bond Distances: O–Cl = 1.689 ± 0.003 Å; O–D = 0.960 ± 0.004 Å
Bond Angle: D–O–Cl = 102.5 ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 9.0222 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$(DOCl, g, 298.15 K) is calculated from the JANAF selection[1] for $\Delta_f H°$(298.15 K) of HOCl(g), the JANAF thermal functions,[1] and the zero point energies of H_2(g), D_2(g), HOCl(g), and DOCl(g). The zero point energies of H_2(g) and D_2(g) are those given by Herzberg and Monfils.[2] The zero–point energies of HOCl(g) and DOCl(g) are estimated from vibrational frequencies as listed by JANAF[1] using the first–order relation, zero–point energy = $(\omega_1 + \omega_2 + \omega_3)/2$.

Heat Capacity and Entropy

The molecular constants B_0 and C_0 are from the microwave work of Mirri *et al.*[3] The constant A_0 is calculated from the molecular structure given by Mirri *et al.*[3] and is somewhat uncertain. The rotational constants $A_0 = 11.105\ cm^{-1}$, $B_0 = 0.474852\ cm^{-1}$, and $C_0 = 0.454208\ cm^{-1}$ have been adjusted for the natural isotopic abundance of Cl. The vibrational frequencies are from the infrared spectroscopic work of Ashby[4] and that of Schwager and Arkell[5] and have not been corrected for isotopic abundances.

References

[1]JANAF Thermochemical Tables: HOCl(g), 3–31–79.
[2]G. Herzberg and A. Monfils, J. Mol. Spectrosc. **5**, 482 (1960).
[3]A. M. Mirri, F. Scappini, and G. Cazzoli, J. Mol. Spectrosc. **38**, 218 (1971).
[4]R. A. Ashby, J. Mol. Spectrosc. **23**, 439 (1967); **40**, 639 (1971).
[5]I. Schwager and A. Arkell, J. Amer. Chem. Soc. **89**, 6006 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.319	−75.344	−75.344	INFINITE
100	33.286	202.209	272.143	−6.993	−76.301	−72.767	38.010
200	34.993	225.626	243.654	−3.606	−77.365	−68.814	17.972
250	36.758	233.619	240.871	−1.813	−77.840	−66.621	13.920
298.15	38.540	240.246	240.246	0.	−78.241	−64.422	11.287
300	38.607	240.485	240.247	0.071	−78.255	−64.337	11.202
350	40.306	246.566	240.724	2.045	−78.609	−61.988	9.251
400	41.785	252.048	241.802	4.098	−78.909	−59.593	7.782
450	43.057	257.045	243.222	6.220	−79.166	−57.162	6.635
500	44.157	261.639	244.837	8.401	−79.386	−54.705	5.715
600	45.987	269.858	248.339	12.912	−79.746	−49.734	4.330
700	47.488	277.063	251.938	17.588	−80.023	−44.709	3.336
800	48.767	283.490	255.487	22.402	−80.240	−39.649	2.589
900	49.872	289.299	258.927	27.335	−80.408	−34.564	2.006
1000	50.830	294.604	262.233	32.371	−80.538	−29.463	1.539
1100	51.659	299.489	265.401	37.497	−80.639	−24.350	1.156
1200	52.376	304.015	268.432	42.700	−80.716	−19.230	0.837
1300	52.997	308.233	271.334	47.969	−80.775	−14.103	0.567
1400	53.534	312.180	274.112	53.296	−80.822	−8.973	0.335
1500	54.000	315.890	276.774	58.673	−80.860	−3.840	0.134
1600	54.406	319.388	279.330	64.094	−80.894	1.296	−0.042
1700	54.760	322.698	281.784	69.553	−80.927	6.434	−0.198
1800	55.070	325.837	284.145	75.045	−80.961	11.574	−0.336
1900	55.342	328.821	286.419	80.566	−80.999	16.716	−0.460
2000	55.583	331.666	288.610	86.112	−81.044	21.860	−0.571
2100	55.796	334.384	290.726	91.681	−81.097	27.006	−0.672
2200	55.986	336.984	292.770	97.270	−81.162	32.156	−0.763
2300	56.156	339.476	294.747	102.878	−81.239	37.308	−0.847
2400	56.310	341.869	296.661	108.501	−81.330	42.464	−0.924
2500	56.449	344.171	298.515	114.139	−81.436	47.624	−0.995
2600	56.577	346.387	300.314	119.791	−81.559	52.789	−1.061
2700	56.696	348.525	302.060	125.454	−81.699	57.959	−1.121
2800	56.807	350.589	303.757	131.129	−81.857	63.135	−1.178
2900	56.912	352.584	305.406	136.815	−82.034	68.316	−1.230
3000	57.013	354.515	307.011	142.512	−82.228	73.503	−1.280
3100	57.111	356.386	308.574	148.218	−82.440	78.698	−1.326
3200	57.207	358.201	310.097	153.934	−82.670	83.899	−1.370
3300	57.303	359.963	311.581	159.659	−82.916	89.108	−1.410
3400	57.400	361.675	313.030	165.395	−83.177	94.325	−1.449
3500	57.499	363.340	314.443	171.139	−83.453	99.550	−1.486
3600	57.600	364.962	315.824	176.894	−83.740	104.783	−1.520
3700	57.704	366.541	317.174	182.660	−84.039	110.023	−1.553
3800	57.812	368.081	318.493	188.435	−84.346	115.273	−1.585
3900	57.924	369.585	319.784	194.222	−84.661	120.530	−1.614
4000	58.041	371.052	321.047	200.020	−84.981	125.795	−1.643
4100	58.162	372.487	322.285	205.830	−85.303	131.069	−1.670
4200	58.289	373.890	323.497	211.653	−85.627	136.350	−1.696
4300	58.421	375.263	324.685	217.488	−85.950	141.639	−1.721
4400	58.559	376.608	325.849	223.337	−86.270	146.935	−1.744
4500	58.701	377.926	326.992	229.200	−86.585	152.239	−1.767
4600	58.849	379.217	328.113	235.078	−86.893	157.549	−1.789
4700	59.002	380.485	329.214	240.970	−87.194	162.867	−1.810
4800	59.160	381.728	330.295	246.878	−87.484	168.190	−1.830
4900	59.322	382.950	331.358	252.802	−87.763	173.520	−1.850
5000	59.488	384.150	332.401	258.743	−88.029	178.855	−1.868
5100	59.659	385.330	333.428	264.700	−88.281	184.195	−1.887
5200	59.833	386.490	334.437	270.675	−88.518	189.540	−1.904
5300	60.011	387.631	335.430	276.667	−88.739	194.890	−1.921
5400	60.191	388.755	336.407	282.677	−88.942	200.243	−1.937
5500	60.375	389.861	337.369	288.705	−89.128	205.600	−1.953
5600	60.560	390.950	338.316	294.752	−89.295	210.960	−1.968
5700	60.747	392.024	339.249	300.817	−89.444	216.323	−1.982
5800	60.935	393.082	340.168	306.901	−89.572	221.689	−1.997
5900	61.124	394.125	341.074	313.004	−89.681	227.056	−2.010
6000	61.314	395.154	341.966	319.126	−89.771	232.425	−2.023

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$S°(298.15\ K) = 217.938\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -50.197 \pm 0.42\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -50.292 \pm 0.42\ kJ·mol^{-1}$

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
	Electronic States and Molecular Constants (σ = 1)						
$X\ ^1\Sigma^+$	0	1	784.49	6.201	0.51409	0.004329	1.6281
$A\ ^3\Pi_0$	18721	6	312.74	2.207	0.37026	0.01390	1.92

Enthalpy of Formation

The selected value, $\Delta_f H°(ClF, 298.15\ K) = -12.02 \pm 0.1$ kcal·mol^{-1}, is based on spectroscopic data. Three studies of the visible absorption bands of ClF, by Wahrahftig,[1] by Schmitz and Schumacher,[2] and by Stricker[3] agree in indicating a band convergence limit at 21,514 ± 10 cm^{-1}. Assignment of this limit to $Cl(^2P_{1/2}) + F(^2P_{3/2})$ is supported by the dissociative ionization threshold for ClF reported by Dibeler *et al.*[4] whose ion–pair threshold, when reassigned to a hot band, corroborates this choice. From this assignment it follows that $D_0°(ClF) = 58.98 \pm 0.02$ kcal·mol^{-1}.

Combining this value with $D_0°(F_2) = 36.7 \pm 0.2$ kcal·mol^{-1}, reported by Berkowitz *et al.*,[5] and with $D_0°(Cl_2) = 57.177 \pm 0.006$ kcal·mol^{-1}, given by Douglas *et al.*,[6] one obtains $\Delta_f H°(ClF, 0\ K) = -12.0 \pm 0.1$ kcal·mol^{-1} (-50.200 ± 0.42 kJ·mol^{-1}).

Calorimetric values for $\Delta_f H°(298.15\ K)$, which bracket the selected value, are as follows: −11.6 kcal·mol^{-1}, Wicke;[7] −11.7 kcal·mol^{-1}, Wicke and Friz;[8] −14.34 and −15.0 kcal·mol^{-1}, Schmitz and Schumacher;[9] and -14.4 ± 0.8 kcal·mol^{-1}, Nuttall and Armstrong.[10]

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels are taken from Rosen[11] and are adjusted to Cl^{35} = 75.4% and Cl^{37} = 24.6%. The value of α_e listed for the ground state by Rosen[11] has been divided by 10 to agree with the original data.[12] The National Bureau of Standards prepared this table[13] by critical analysis of data existing is 1972 but used the incorrect value[11] for α_e of the ground state. Using the correct molecular constants and $\Delta_f H°$ selected by NBS,[13] we recalculate the table in terms of 1973 fundamental constants,[14] 1975 atomic weights,[15] and current JANAF reference states for the elements. The thermodyanmic functions of this table may be biased at temperatures above about 3000 K due to neglect of rotational cut–off.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.908	−50.197	−50.197	INFINITE
100	29.124	185.156	245.153	−6.000	−50.198	−50.745	26.506
200	30.126	205.546	220.809	−3.052	−50.234	−51.282	13.393
298.15	32.082	217.938	217.938	0.	−50.292	−51.784	9.072
300	32.118	218.136	217.939	0.059	−50.293	−51.793	9.018
400	33.751	227.613	219.220	3.358	−50.339	−52.285	6.828
500	34.866	235.273	221.689	6.792	−50.373	−52.768	5.513
600	35.619	241.700	224.503	10.319	−50.399	−53.244	4.635
700	36.143	247.233	227.364	13.908	−50.421	−53.717	4.008
800	36.522	252.085	230.157	17.542	−50.442	−54.186	3.538
900	36.807	256.404	232.838	21.210	−50.462	−54.653	3.172
1000	37.030	260.294	235.392	24.902	−50.483	−55.117	2.879
1100	37.210	263.832	237.819	28.614	−50.506	−55.580	2.639
1200	37.360	267.076	240.124	32.343	−50.531	−56.040	2.439
1300	37.487	270.072	242.314	36.085	−50.559	−56.498	2.270
1400	37.598	272.854	244.397	39.840	−50.591	−56.953	2.125
1500	37.697	275.451	246.382	43.605	−50.627	−57.407	1.999
1600	37.788	277.887	248.275	47.379	−50.667	−57.857	1.889
1700	37.873	280.181	250.085	51.162	−50.711	−58.305	1.792
1800	37.956	282.348	251.818	54.953	−50.758	−58.751	1.705
1900	38.040	284.402	253.479	58.753	−50.808	−59.193	1.627
2000	38.131	286.356	255.075	62.562	−50.858	−59.633	1.557
2100	38.233	288.219	256.609	66.380	−50.908	−60.071	1.494
2200	38.354	290.000	258.087	70.209	−50.954	−60.506	1.437
2300	38.500	291.708	259.512	74.051	−50.993	−60.939	1.384
2400	38.682	293.350	260.888	77.910	−51.020	−61.371	1.336
2500	38.908	294.934	262.218	81.789	−51.031	−61.802	1.291
2600	39.189	296.465	263.506	85.694	−51.018	−62.233	1.250
2700	39.535	297.950	264.754	89.629	−50.976	−62.665	1.212
2800	39.959	299.395	265.966	93.603	−50.895	−63.100	1.177
2900	40.470	300.806	267.143	97.624	−50.767	−63.538	1.144
3000	41.079	302.188	268.288	101.701	−50.580	−63.981	1.114
3100	41.796	303.547	269.404	105.843	−50.323	−64.432	1.086
3200	42.629	304.886	270.491	110.064	−49.983	−64.892	1.059
3300	43.587	306.212	271.554	114.373	−49.548	−65.364	1.035
3400	44.674	307.529	272.593	118.785	−49.004	−65.852	1.012
3500	45.894	308.842	273.610	123.312	−48.335	−66.356	0.990
3600	47.251	310.153	274.606	127.969	−47.528	−66.882	0.970
3700	48.742	311.468	275.585	132.767	−46.567	−67.433	0.952
3800	50.365	312.789	276.547	137.721	−45.437	−68.012	0.935
3900	52.115	314.120	277.493	142.844	−44.125	−68.622	0.919
4000	53.983	315.462	278.425	148.148	−42.617	−69.269	0.905
4100	55.960	316.819	279.345	153.645	−40.900	−69.956	0.891
4200	58.032	318.193	280.254	159.343	−38.964	−70.688	0.879
4300	60.184	319.583	281.152	165.254	−36.797	−71.469	0.868
4400	62.399	320.992	282.042	171.382	−34.392	−72.302	0.858
4500	64.658	322.420	282.923	177.735	−31.743	−73.193	0.850
4600	66.941	323.866	283.797	184.315	−28.845	−74.146	0.842
4700	69.228	325.330	284.665	191.123	−25.697	−75.164	0.835
4800	71.496	326.811	285.528	198.160	−22.297	−76.252	0.830
4900	73.725	328.308	286.386	205.421	−18.649	−77.413	0.825
5000	75.895	329.820	287.239	212.903	−14.757	−78.652	0.822
5100	77.985	331.344	288.089	220.597	−10.628	−79.970	0.819
5200	79.978	332.877	288.936	228.497	−6.269	−81.372	0.817
5300	81.858	334.419	289.779	236.589	−1.691	−82.860	0.817
5400	83.612	335.965	290.620	244.864	3.094	−84.436	0.817
5500	85.226	337.515	291.459	253.307	8.073	−86.102	0.818
5600	86.694	339.064	292.295	261.904	13.232	−87.861	0.820
5700	88.007	340.610	293.129	270.641	18.555	−89.713	0.822
5800	89.163	342.151	293.961	279.500	24.027	−91.660	0.825
5900	90.160	343.684	294.791	288.468	29.633	−93.702	0.830
6000	90.999	345.206	295.618	297.527	35.355	−95.841	0.834

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Lithium Chlorofluoride (Li_2ClF) IDEAL GAS $M_r = 68.333403$

$S°(298.15\ K) = 267.931\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -749.128\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-753.957]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is from NBS.[1]

Heat Capacity and Entropy

Data is from Koppang *et. al.*[2]

References

[1]U.S. National Bureau of Standards Report No. 6297, "Preliminary Report on the Thermodynamic Properties of Lithium, Beryllium, Magnesium, Aluminum, and their Compounds with Oxygen, Hydrogen, Fluorine, and Chlorine (Revised)," (January 1959).

[2]R. R. Koppang, C. M. Sherwood, and G. S. Bahn, "Some Provisional Tables of Species Thermodynamic Properties" Marquardt Corp., Van Nuys, California., (October 1959).

Lithium Chloride Fluoride (Li_2ClF) $Cl_1F_1Li_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.422	−749.132	−749.132	INFINITE
100	35.723	215.376	315.709	−10.033	−749.642	−751.742	392.670
200	51.877	245.279	273.438	−5.632	−751.907	−752.971	196.656
298.15	62.839	268.040	268.040	0.	−753.957	−753.043	131.930
300	62.986	268.429	268.041	0.116	−753.992	−753.038	131.116
400	69.601	287.518	270.599	6.768	−755.887	−752.436	98.258
500	73.601	303.506	275.626	13.940	−764.049	−750.717	78.427
600	76.128	317.161	281.439	21.433	−766.074	−747.856	65.107
700	77.801	329.029	287.408	29.134	−767.836	−744.677	55.568
800	78.948	339.496	293.278	36.974	−769.442	−741.258	48.399
900	79.772	348.845	298.942	44.912	−770.974	−737.642	42.812
1000	80.383	357.282	304.361	52.921	−772.451	−733.859	38.333
1100	80.759	364.961	309.526	60.978	−773.891	−729.930	34.661
1200	81.096	372.003	314.443	69.071	−775.303	−725.871	31.596
1300	81.396	378.506	319.124	77.196	−776.694	−721.695	28.998
1400	81.657	384.548	323.584	85.349	−778.059	−717.413	26.767
1500	81.881	390.190	327.839	93.526	−779.398	−713.034	24.830
1600	82.014	395.478	331.903	101.721	−780.716	−708.567	23.132
1700	82.136	400.454	335.790	109.929	−1072.490	−689.665	21.191
1800	82.245	405.152	339.514	118.148	−1072.271	−667.153	19.360
1900	82.343	409.601	343.087	126.378	−1072.054	−644.652	17.723
2000	82.429	413.827	346.519	134.616	−1071.842	−622.163	16.249
2100	82.488	417.851	349.821	142.862	−1071.637	−599.684	14.916
2200	82.543	421.689	353.001	151.114	−1071.441	−577.215	13.705
2300	82.593	425.359	356.068	159.371	−1071.255	−554.754	12.599
2400	82.639	428.876	359.029	167.632	−1071.082	−532.301	11.585
2500	82.680	432.250	361.891	175.898	−1070.924	−509.855	10.653
2600	82.712	435.493	364.660	184.168	−1070.782	−487.415	9.792
2700	82.741	438.615	367.341	192.440	−1070.661	−464.980	8.996
2800	82.769	441.625	369.941	200.716	−1070.560	−442.550	8.256
2900	82.794	444.530	372.463	208.994	−1070.485	−420.122	7.567
3000	82.818	447.337	374.912	217.275	−1070.435	−397.697	6.925
3100	82.838	450.053	377.293	225.558	−1070.415	−375.273	6.323
3200	82.857	452.683	379.608	233.842	−1070.427	−352.849	5.760
3300	82.874	455.233	381.861	242.129	−1070.471	−330.424	5.230
3400	82.891	457.708	384.056	250.417	−1070.551	−307.997	4.732
3500	82.906	460.111	386.194	258.707	−1070.669	−285.567	4.262
3600	82.919	462.446	388.280	266.998	−1070.825	−263.133	3.818
3700	82.932	464.718	390.316	275.291	−1071.024	−240.695	3.398
3800	82.944	466.930	392.303	283.585	−1071.265	−218.251	3.000
3900	82.954	469.085	394.244	291.880	−1071.550	−195.799	2.622
4000	82.965	471.185	396.141	300.176	−1071.882	−173.340	2.264
4100	82.973	473.234	397.997	308.472	−1072.263	−150.872	1.922
4200	82.981	475.234	399.812	316.770	−1072.694	−128.394	1.597
4300	82.988	477.186	401.589	325.069	−1073.177	−105.905	1.286
4400	82.995	479.094	403.329	333.368	−1073.673	−83.407	0.990
4500	83.002	480.959	405.033	341.668	−1074.247	−60.895	0.707
4600	83.009	482.784	406.704	349.968	−1074.881	−38.369	0.436
4700	83.015	484.569	408.341	358.269	−1075.573	−15.829	0.176
4800	83.021	486.317	409.948	366.571	−1076.325	6.726	−0.073
4900	83.027	488.029	411.524	374.874	−1077.140	29.298	−0.312
5000	83.031	489.706	413.071	383.176	−1078.019	51.887	−0.542
5100	83.035	491.350	414.590	391.480	−1078.954	74.494	−0.763
5200	83.039	492.963	416.081	399.784	−1079.969	97.120	−0.976
5300	83.042	494.545	417.547	408.088	−1081.056	119.767	−1.180
5400	83.045	496.097	418.987	416.392	−1082.220	142.435	−1.378
5500	83.048	497.621	420.403	424.697	−1083.463	165.125	−1.568
5600	83.051	499.117	421.795	433.002	−1084.788	187.838	−1.752
5700	83.054	500.587	423.165	441.307	−1086.199	210.576	−1.930
5800	83.056	502.032	424.512	449.612	−1087.698	233.339	−2.101
5900	83.059	503.451	425.838	457.918	−1089.289	256.129	−2.268
6000	83.061	504.847	427.143	466.224	−1090.974	278.947	−2.428

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

Lithium Chloride Fluoride (Li_2ClF) $Cl_1F_1Li_2(g)$

$S°(298.15\ K) = [265.990]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-567.5 \pm 21]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-569.2 \pm 21]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[719](1)
[205](1)
[453](1)

Ground State Quantum Weight: [1] σ = [1]
Point Group: C_1
Bond Distances: Mg–Cl = [2.18] Å; Mg–F = [1.77] Å
Bond Angle: Cl–Mg–F = [170]°
Product of the Moments of Inertia: $I_A I_B I_C = [8.66593 \times 10^{-116}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is based on an estimated $\Delta_f H°(298.15\ K) = 0$ for the reaction $MgCl_2(g) + MgF_2(g) \rightarrow 2MgClF(g)$, using $\Delta_f H°(298.15\ K) = -95.85$ and -176.2 kcal·mol^{-1} for $MgCl_2(g)$ and $MgF_2(g)$, respectively.

Heat Capacity and Entropy

The bond angle is taken to be the value we have adopted for $MgCl_2(g)$. The Mg–Cl and Mg–F bond distances are assumed to be the same as those in $MgCl_2(g)$ and $MgF_2(g)$. The vibrational frequencies are the averages of those for $MgCl_2(g)$ and $MgF_2(g)$. The principal moments of inertia are: $I_A = 0.0766 \times 10^{-39}$, $I_B = 33.5997 \times 10^{-39}$ and $I_C = 33.6763 \times 10^{-39}$ g·cm^2.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.330	−567.533	−567.533	INFINITE
100	38.027	218.339	306.941	−8.860	−567.615	−570.529	298.014
200	45.162	246.994	270.419	−4.685	−568.430	−573.138	149.688
250	47.875	257.375	266.801	−2.356	−568.833	−574.269	119.987
298.15	49.911	265.990	265.990	.000	−569.204	−575.282	100.787
300	49.979	266.299	265.991	.092	−569.218	−575.319	100.172
350	51.581	274.129	266.605	2.633	−569.593	−576.306	86.009
400	52.798	281.100	267.989	5.244	−569.966	−577.240	75.380
450	53.732	287.375	269.801	7.908	−570.344	−578.127	67.107
500	54.455	293.075	271.847	10.614	−570.731	−578.971	60.485
600	55.478	303.101	276.244	16.114	−571.551	−580.543	50.541
700	56.142	311.706	280.710	21.698	−572.452	−581.971	43.427
800	56.595	319.234	285.064	27.336	−573.456	−583.264	38.083
900	56.915	325.920	289.239	33.012	−574.586	−584.424	33.919
1000	57.149	331.929	293.213	38.716	−584.451	−584.738	30.544
1100	57.326	337.384	296.984	44.440	−585.893	−584.696	27.765
1200	57.461	342.378	300.562	50.180	−587.338	−584.524	25.444
1300	57.568	346.982	303.958	55.931	−588.788	−584.231	23.475
1400	57.653	351.252	307.186	61.693	−717.653	−580.658	21.665
1500	57.723	355.232	310.257	67.461	−717.764	−570.869	19.879
1600	57.780	358.959	313.186	73.237	−717.881	−561.072	18.317
1700	57.827	362.463	315.983	79.017	−718.007	−551.268	16.938
1800	57.867	365.770	318.658	84.802	−718.139	−541.456	15.713
1900	57.901	368.899	321.220	90.590	−718.279	−531.637	14.616
2000	57.930	371.870	323.679	96.382	−718.426	−521.809	13.628
2100	57.955	374.697	326.042	102.176	−718.578	−511.975	12.735
2200	57.976	377.394	328.315	107.973	−718.736	−502.133	11.922
2300	57.995	379.971	330.506	113.771	−718.898	−492.284	11.180
2400	58.012	382.440	332.618	119.572	−719.065	−482.428	10.500
2500	58.027	384.808	334.659	125.374	−719.234	−472.564	9.874
2600	58.040	387.084	336.632	131.177	−719.407	−462.694	9.296
2700	58.051	389.275	338.541	136.981	−719.581	−452.817	8.760
2800	58.062	391.387	340.391	142.787	−719.758	−442.934	8.263
2900	58.071	393.424	342.185	148.594	−719.936	−433.044	7.800
3000	58.080	395.393	343.926	154.401	−720.117	−423.148	7.368
3100	58.087	397.298	345.617	160.210	−720.299	−413.246	6.963
3200	58.094	399.142	347.261	166.019	−720.484	−403.338	6.584
3300	58.101	400.930	348.860	171.829	−720.671	−393.424	6.227
3400	58.106	402.664	350.417	177.639	−720.861	−383.505	5.892
3500	58.112	404.349	351.934	183.450	−721.056	−373.580	5.575
3600	58.117	405.986	353.413	189.261	−721.254	−363.649	5.276
3700	58.121	407.578	354.856	195.073	−721.458	−353.713	4.994
3800	58.125	409.128	356.264	200.885	−721.669	−343.771	4.725
3900	58.129	410.638	357.639	206.698	−721.886	−333.824	4.471
4000	58.133	412.110	358.982	212.511	−722.112	−323.871	4.229
4100	58.136	413.545	360.295	218.325	−722.348	−313.912	3.999
4200	58.139	414.946	361.580	224.138	−722.594	−303.947	3.780
4300	58.142	416.314	362.837	229.952	−722.852	−293.976	3.571
4400	58.144	417.651	364.068	235.767	−723.123	−283.999	3.371
4500	58.147	418.958	365.273	241.581	−723.409	−274.016	3.181
4600	58.149	420.236	366.454	247.396	−723.710	−264.026	2.998
4700	58.151	421.486	367.612	253.211	−724.029	−254.029	2.823
4800	58.153	422.711	368.747	259.026	−724.366	−244.026	2.656
4900	58.155	423.910	369.860	264.842	−724.724	−234.015	2.495
5000	58.157	425.085	370.953	270.657	−725.103	−223.997	2.340
5100	58.159	426.236	372.026	276.473	−725.505	−213.971	2.192
5200	58.160	427.366	373.079	282.289	−725.932	−203.937	2.049
5300	58.162	428.474	374.114	288.105	−726.383	−193.894	1.911
5400	58.163	429.561	375.131	293.922	−726.863	−183.843	1.778
5500	58.165	430.628	376.130	299.738	−727.370	−173.782	1.650
5600	58.166	431.676	377.113	305.554	−727.908	−163.712	1.527
5700	58.167	432.706	378.079	311.371	−728.477	−153.632	1.408
5800	58.168	433.717	379.030	317.188	−729.079	−143.542	1.293
5900	58.169	434.712	379.965	323.005	−729.716	−133.441	1.181
6000	58.170	435.689	380.886	328.822	−730.387	−123.329	1.074

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 302.849 \pm 1.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-549.1 \pm 21]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-556.5 \pm 21]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1228(1)	510(1)	1467(1)
824(1)	423(1)	474(1)
629(1)	300(1)	308(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: S–O = [1.404] Å; S–F = [1.530] Å; S–Cl = [2.011] Å
Bond Angles: O–S–O = [123.5]° Cl–S–F = [98.06]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.40403 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$ is estimated as the mean of the $\Delta_f H°$ values[1] for SO_2F_2(g) and SO_2Cl_2(g). This corresponds to use of the mean bond energies, $D°_0$(S–F) = 74 and $D°_0$(S–Cl) = 36 kcal·mol^{-1}, from SO_2F_2 and SO_2Cl_2, respectively. The resulting values of $\Delta_f G°$ are consistent with those methods of preparation for which thermodynamic tests are possible. Insufficient data preclude tests for preparation of SO_2ClF from AgF_2, CoF_3, MnF_3 and SbF_3. In other cases the tests are not stringent, since the calculated values of $\Delta_r G°$ are large and negative for the observed reactions.

Heat Capacity and Entropy

The point group and symmetry number are consistent with analysis of the spectral data, but the detailed structure is estimated from known coordinates of SO_2Cl in SO_2Cl_2[1,2] and SF in SO_2F_2.[1,3] This estimate should be quite reliable since the SO_2 coordinates are almost identical in SO_2Cl_2 and SO_2F_2. The resulting structure has an O–S–Cl angle of 107.7°, an O–S–F angle of 108.4° and pricipal moments of inertia of $I_A = 16.4743 \times 10^{-39}$, $I_B = 29.0842 \times 10^{-39}$ and $I_C = 29.3031 \times 10^{-39}$ g·cm^2.

Vibrational frequencies are based on infrared spectra of the vapor[4] and confirmed by Raman spectra of the liquid.[5] Birchall and Gillespie[4] assigned δ(FSCl) to a weak Raman band at 195 cm^{-1}, but force–constant calculations based on SO_2Cl_2 and SO_2F_2 predict a value near 300 cm^{-1}.[6,7] It appears that the twist(FSCl) and δ(FSCl) are nearly accidentally degenerate, so we assign them arbitrarily to the Raman band at 308 cm^{-1} and the infrared band at 300 cm^{-1}. The adopted assignments are those of Toyuki and Shimizu[6] and Pfeiffer.[7] All adopted values lie between the analogous modes for SO_2Cl_2 and SO_2F_2·δ(FSCl) = 195 cm^{-1} is unlikely since it would lie below δ(ClSCl) = 209 cm^{-1} in SO_2Cl_2; also the intensity of such bending modes should be strong not weak.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.701	−549.075	−549.075	INFINITE
100	38.907	244.096	356.685	−11.259	−552.137	−539.994	282.064
200	57.944	276.982	308.997	−6.403	−554.817	−526.728	137.567
250	65.602	290.764	303.995	−3.308	−555.760	−519.591	108.563
298.15	71.592	302.849	302.849	0.	−556.472	−512.558	89.798
300	71.799	303.292	302.850	0.133	−556.496	−512.285	89.197
350	76.869	314.753	303.744	3.853	−557.072	−504.869	75.348
400	81.066	325.300	305.788	7.805	−559.737	−497.292	64.940
450	84.571	335.057	308.505	11.949	−560.757	−489.433	56.812
500	87.514	344.124	311.619	16.253	−561.744	−481.452	50.297
600	92.099	360.508	318.431	25.246	−563.048	−465.260	40.505
700	95.414	374.968	325.496	34.630	−563.877	−448.892	33.497
800	97.855	387.876	332.501	44.300	−564.410	−432.426	28.235
900	99.686	399.512	339.311	54.181	−617.878	−414.825	24.076
1000	101.086	410.091	345.868	64.223	−616.868	−392.318	20.493
1100	102.174	419.779	352.153	74.388	−615.818	−369.913	17.566
1200	103.034	428.707	358.165	84.650	−614.746	−347.605	15.131
1300	103.724	436.983	363.914	94.989	−613.663	−325.387	13.074
1400	104.284	444.690	369.412	105.391	−612.580	−303.253	11.315
1500	104.745	451.902	374.673	115.843	−611.503	−281.196	9.792
1600	105.129	458.674	379.714	126.337	−610.438	−259.210	8.462
1700	105.451	465.058	384.548	136.866	−609.390	−237.291	7.291
1800	105.724	471.093	389.190	147.426	−608.362	−215.433	6.252
1900	105.957	476.816	393.652	158.010	−607.356	−193.631	5.323
2000	106.157	482.256	397.948	168.616	−606.373	−171.881	4.489
2100	106.331	487.439	402.087	179.240	−605.414	−150.180	3.736
2200	106.483	492.390	406.080	189.881	−604.479	−128.524	3.052
2300	106.616	497.126	409.936	200.536	−603.568	−106.910	2.428
2400	106.733	501.666	413.664	211.204	−602.680	−85.336	1.857
2500	106.837	506.025	417.272	221.883	−601.815	−63.798	1.333
2600	106.929	510.217	420.767	232.571	−600.971	−42.294	0.850
2700	107.012	514.254	424.155	243.268	−600.146	−20.822	0.403
2800	107.086	518.147	427.443	253.973	−599.340	0.620	−0.012
2900	107.153	521.906	430.636	264.685	−598.551	22.033	−0.397
3000	107.213	525.540	433.739	275.403	−597.778	43.419	−0.756
3100	107.268	529.056	436.757	286.127	−597.019	64.780	−1.092
3200	107.317	532.463	439.695	296.857	−596.272	86.116	−1.406
3300	107.363	535.766	442.557	307.591	−595.536	107.429	−1.700
3400	107.404	538.972	445.345	318.329	−594.809	128.720	−1.978
3500	107.442	542.086	448.065	329.071	−594.089	149.990	−2.238
3600	107.477	545.113	450.719	339.817	−593.376	171.240	−2.485
3700	107.509	548.058	453.310	350.567	−592.666	192.469	−2.717
3800	107.539	550.925	455.841	361.319	−591.960	213.680	−2.937
3900	107.567	553.719	458.315	372.074	−591.255	234.872	−3.146
4000	107.592	556.443	460.735	382.832	−590.550	256.045	−3.344
4100	107.616	559.100	463.102	393.593	−589.844	277.201	−3.532
4200	107.638	561.693	465.418	404.355	−589.136	298.340	−3.710
4300	107.658	564.226	467.687	415.120	−588.425	319.463	−3.881
4400	107.677	566.702	469.909	425.887	−587.709	340.568	−4.043
4500	107.695	569.122	472.087	436.656	−586.989	361.656	−4.198
4600	107.712	571.489	474.222	447.426	−586.264	382.729	−4.346
4700	107.728	573.806	476.317	458.198	−585.533	403.786	−4.488
4800	107.742	576.074	478.371	468.972	−584.797	424.828	−4.623
4900	107.756	578.295	480.388	479.747	−584.054	445.855	−4.753
5000	107.769	580.473	482.368	490.523	−583.306	466.866	−4.877
5100	107.782	582.607	484.313	501.300	−582.552	487.862	−4.997
5200	107.793	584.700	486.223	512.079	−581.793	508.842	−5.111
5300	107.804	586.753	488.101	522.859	−581.030	529.810	−5.222
5400	107.814	588.768	489.946	533.640	−580.262	550.761	−5.328
5500	107.824	590.747	491.761	544.422	−579.492	571.698	−5.430
5600	107.834	592.690	493.546	555.205	−578.718	592.623	−5.528
5700	107.842	594.598	495.302	565.989	−577.944	613.532	−5.622
5800	107.851	596.474	497.030	576.773	−577.169	634.430	−5.714
5900	107.859	598.318	498.732	587.559	−576.395	655.311	−5.802
6000	107.866	600.131	500.406	598.345	−575.623	676.182	−5.887

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = 278.984 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -12.69 \pm 2.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -21.42 \pm 2.9\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1061(1)	1315(2)
715(1)	589(2)
549(1)	405(2)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Bond Distances: F–Cl = [1.63] Å; O–Cl = [1.46] Å

Bond Angles: F–Cl–O = [95° 10']; O–Cl–O = [119° 12']

Product of the Moments of Inertia: $I_A I_B I_C = [4.29248 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Neugebauer and Margrave[1] measured the enthalpy of reaction of perchloryl fluoride and hydrogen.

$$ClO_3F(g) + 4H_2(g) = HF(aq., 0.6M) + HCl(aq, 0.6M) + 3H_2O(l)$$

The necessary, additional thermal data for the calculation of the enthalpy of formation was obtained by them from NBS.[2] Dibeler *et al.*[3] obtain a value of -5.3 ± 4 kcal·mol^{-1} from the observed appearance potential of Cl^+.

Heat Capacity and Entropy

The assignment of Lide and Mann,[4] based upon the infrared spectra of the gas is supported by the Raman measurements of Powell and Lippincott.[5]

The value of the spectroscopic constant B was obtained by Madden and Benedict[6] from a high resolution infrared spectrograph. The Cl–F bond distance was estimated assuming a single covalent bond with no ionic character as evidenced by the low dipole moment obtained by Maryott and Kreidler.[7] Electron spin resonance results are explained by Brownstein,[8] on the basis of a low dipole moment. The Cl–O distance was estimated to be that found in the chlorate ion, Pauling.[9] The resulting values of the bond angles and I_C are consistent with the measured I_B and the assumed bond lengths. The principal moments of inertia are: $I_A = I_B = [15.9597 \times 10^{-39}]$ and $I_C = [16.8522 \times 10^{-39}]$ g·cm^2.

A calorimetric entropy of 60.17 cal·K^{-1}·mol^{-1} at 226.48 K was obtained by Koehler and Giauque[10] for the ideal gas. If the lattice doesn't discriminate between F and O atoms then at 0 K a residual entropy of 2.75 cal·K^{-1}·mol^{-1} exists and the third law entropy would be 62.92 cal·K^{-1}·mol^{-1}. This value may be compared with 62.64 obtained statistically. The difference 0.3 cal·K^{-1}·mol^{-1} is within the range found for other molecules and explained on the basis of some discrimination in the lattice, see Koehler and Giauque,[10] for references.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.299	−12.693	−12.693	INFINITE
100	35.404	227.211	326.596	−9.939	−16.599	4.645	−2.426
200	50.513	256.003	284.485	−5.696	−19.707	27.199	−7.104
250	58.338	268.132	280.018	−2.971	−20.729	39.051	−8.159
298.15	64.924	278.984	278.984	0.	−21.422	50.632	−8.871
300	65.158	279.387	278.986	0.120	−21.444	51.079	−8.894
350	70.991	289.881	279.801	3.528	−21.905	63.206	−9.433
400	75.945	299.693	281.681	7.205	−22.161	75.384	−9.844
450	80.137	308.887	284.199	11.110	−22.253	87.584	−10.167
500	83.677	317.519	287.104	15.208	−22.215	99.788	−10.425
600	89.199	333.291	293.513	23.867	−21.848	124.159	−10.809
700	93.178	347.356	300.219	32.996	−21.212	148.446	−11.077
800	96.092	359.998	306.915	42.467	−20.401	172.629	−11.272
900	98.267	371.448	313.459	52.190	−19.473	196.703	−11.416
1000	99.922	381.891	319.788	62.103	−18.466	220.669	−11.527
1100	101.204	391.477	325.875	72.162	−17.406	244.532	−11.612
1200	102.214	400.328	331.716	82.335	−16.310	268.297	−11.679
1300	103.022	408.543	337.313	92.598	−15.193	291.969	−11.731
1400	103.677	416.202	342.678	102.934	−14.063	315.554	−11.773
1500	104.215	423.374	347.821	113.330	−12.930	339.058	−11.807
1600	104.662	430.115	352.756	123.774	−11.801	362.488	−11.834
1700	105.036	436.471	357.495	134.260	−10.680	385.846	−11.856
1800	105.353	442.484	362.051	144.779	−9.573	409.139	−11.873
1900	105.624	448.188	366.436	155.329	−8.482	432.371	−11.887
2000	105.857	453.612	370.660	165.903	−7.411	455.546	−11.898
2100	106.058	458.781	374.734	176.499	−6.361	478.668	−11.906
2200	106.234	463.719	378.668	187.114	−5.333	501.741	−11.913
2300	106.388	468.445	382.469	197.745	−4.329	524.767	−11.918
2400	106.524	472.976	386.146	208.391	−3.349	547.749	−11.921
2500	106.644	477.327	389.707	219.049	−2.393	570.692	−11.924
2600	106.751	481.512	393.158	229.719	−1.459	593.597	−11.926
2700	106.846	485.542	396.506	240.399	−0.548	616.467	−11.926
2800	106.932	489.430	399.755	251.088	0.341	639.303	−11.926
2900	107.009	493.183	402.913	261.785	1.210	662.107	−11.926
3000	107.079	496.812	405.982	272.489	2.059	684.883	−11.925
3100	107.142	500.324	408.969	283.201	2.891	707.630	−11.923
3200	107.199	503.727	411.878	293.918	3.706	730.350	−11.922
3300	107.252	507.026	414.711	304.640	4.507	753.045	−11.920
3400	107.300	510.229	417.474	315.368	5.296	775.716	−11.917
3500	107.344	513.340	420.169	326.100	6.074	798.364	−11.915
3600	107.384	516.364	422.799	336.836	6.843	820.990	11.912
3700	107.421	519.307	425.368	347.577	7.604	843.594	−11.909
3800	107.455	522.172	427.878	358.321	8.361	866.180	−11.906
3900	107.487	524.964	430.331	369.068	9.114	888.745	−11.903
4000	107.516	527.686	432.731	379.818	9.865	911.289	−11.900
4100	107.544	530.341	435.080	390.571	10.615	933.815	−11.897
4200	107.569	532.933	437.379	401.327	11.367	956.323	−11.894
4300	107.593	535.464	439.631	412.085	12.121	978.814	−11.890
4400	107.615	537.938	441.837	422.845	12.879	1001.286	−11.887
4500	107.636	540.357	443.999	433.608	13.641	1023.740	−11.883
4600	107.655	542.723	446.120	444.372	14.408	1046.178	−11.880
4700	107.673	545.038	448.200	455.139	15.180	1068.600	−11.876
4800	107.690	547.305	450.241	465.907	15.959	1091.005	−11.873
4900	107.706	549.526	452.245	476.677	16.744	1113.395	−11.869
5000	107.721	551.702	454.212	487.448	17.534	1135.767	−11.865
5100	107.735	553.835	456.145	498.221	18.330	1158.124	−11.862
5200	107.748	555.927	458.044	508.995	19.132	1180.464	−11.858
5300	107.761	557.980	459.910	519.770	19.938	1202.791	−11.854
5400	107.773	559.994	461.745	530.547	20.747	1225.100	−11.850
5500	107.784	561.972	463.549	541.325	21.560	1247.395	−11.847
5600	107.795	563.914	465.324	552.104	22.373	1269.677	−11.843
5700	107.805	565.822	467.070	562.884	23.187	1291.942	−11.839
5800	107.815	567.697	468.789	573.665	23.999	1314.195	−11.836
5900	107.824	569.540	470.481	584.447	24.808	1336.431	−11.832
6000	107.832	571.352	472.148	595.230	25.612	1358.656	−11.828

PREVIOUS: March 1961 (1 atm) CURRENT: March 1961 (1 bar)

$S°(298.15\ K) = 301.689\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-961.8]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-970.7]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
274(1)	424(2)	948(2)
410(1)	618(1)	1358(1)
895(1)		

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: P–Cl = 2.01 ± 0.04 Å; P–F = 1.51 ± 0.03 Å; P–O = 1.55 ± 0.03 Å
Bond Angles: F–P–F = 103°; F–P–Cl = 103°
Product of the Moments of Inertia: $I_A I_B I_C = 1.90249 \times 10^{-113}\ g·cm^6$

Enthaply of Formation

The $\Delta_f H°(298.15\ K)$ of $POClF_2$ was estimated to be $-232\ kcal·mol^{-1}$ from the $\Delta_f H°(298.15\ K)$ of POF_3 by assuming bond energies of 120 kcal for $D°_0$(P–F) and 80 kcal for $D°_0$(P–Cl). The $D°_0$(P–F) and $D°_0$(P–Cl) values were taken from Neale and Williams[1] and Neale *et al.*[2]

Essentially the same $\Delta_f H°(298.15\ K)$ may be obtained by assuming a $\Delta_r H° = 0$ for the following reaction: $POCl_3(g) + POF_3(g) \rightarrow POCl_2F(g) + POF_2Cl(g)$.

Heat Capacity and Entropy

The molecular constants were determined by Brockway and Beach[3] and by Williams *et al.*[4] Brockway and Beach[3] used electron diffraction. Williams *et al.*[4] measured microwave spectra. Brockway and Beach[3] assumed that the F–P–F and F–P–Cl angles were equal in POF_2Cl and $POFCl_2$. An analysis of Brockway and Beach's data by Williams *et al.*[4] indicates that the angles in POF_2Cl, $POFCl_2$, $POCl_3$, and POF_3 should be 103 rather than the reported 106 ± 3. The principal moments of inertia are: $I_A = 18.7062 \times 10^{-39}$, $I_B = 31.3539 \times 10^{-39}$, and $I_C = 32.4373 \times 10^{39}\ g·cm^2$.

The Raman spectra and vibrational frequencies for POF_2Cl were reported by Delwaulle and Francois.[5] The frequencies were reassigned by Delwaulle and Francois.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.198	−961.769	−961.769	INFINITE
100	38.154	245.398	353.098	−10.770	−965.044	−952.662	497.620
200	55.039	277.016	307.567	−6.110	−968.551	−939.053	245.256
250	62.542	290.122	302.789	−3.167	−969.739	−931.537	194.634
298.15	68.838	301.689	301.689	0.	−970.688	−924.090	161.897
300	69.062	302.116	301.691	0.128	−970.721	−923.801	160.848
350	74.631	313.192	302.553	3.724	−972.247	−915.844	136.682
400	79.327	323.473	304.533	7.576	−972.964	−907.735	118.538
450	83.259	333.051	307.176	11.644	−973.527	−899.546	104.417
500	86.541	341.998	310.216	15.891	−973.963	−891.302	93.114
600	91.583	358.249	316.895	24.812	−974.544	−874.709	76.150
700	95.154	372.650	323.851	34.159	−974.844	−858.043	64.028
800	97.736	385.534	330.771	43.810	−974.953	−841.348	54.934
900	99.646	397.161	337.512	53.684	−974.929	−824.648	47.861
1000	101.088	407.738	344.014	63.724	−974.811	−807.955	42.203
1100	102.200	417.427	350.254	73.891	−974.626	−791.278	37.575
1200	103.073	426.358	356.228	84.156	−1037.967	−773.542	33.671
1300	103.768	434.637	361.945	94.499	−1036.928	−751.548	30.198
1400	104.331	442.348	367.416	104.905	−1035.873	−729.635	27.223
1500	104.792	449.563	372.655	115.362	−1034.810	−707.798	24.648
1600	105.174	456.338	377.675	125.861	−1033.744	−686.032	22.397
1700	105.495	462.725	382.492	136.395	−1032.679	−664.333	20.412
1800	105.765	468.762	387.119	146.958	−1031.618	−642.696	18.651
1900	105.996	474.487	391.568	157.547	−1030.564	−621.118	17.076
2000	106.194	479.929	395.851	168.157	−1029.516	−599.596	15.660
2100	106.366	485.115	399.979	178.785	−1028.476	−578.125	14.380
2200	106.516	490.066	403.962	189.429	−1027.441	−556.704	13.218
2300	106.646	494.804	407.810	200.087	−1026.411	−535.330	12.158
2400	106.762	499.345	411.530	210.758	−1025.383	−514.001	11.187
2500	106.864	503.706	415.130	221.439	−1024.357	−492.714	10.295
2600	106.955	507.899	418.618	232.130	−1023.330	−471.469	9.472
2700	107.036	511.937	422.000	242.830	−1022.300	−450.263	8.711
2800	107.108	515.831	425.282	253.537	−1021.264	−429.095	8.005
2900	107.174	519.591	428.469	264.251	−1020.221	−407.965	7.348
3000	107.233	523.225	431.568	274.972	−1019.168	−386.871	6.736
3100	107.287	526.742	434.581	285.698	−1018.103	−365.811	6.164
3200	107.335	530.149	437.515	296.429	−1017.024	−344.787	5.628
3300	107.380	533.453	440.372	307.165	−1015.930	−323.797	5.125
3400	107.420	536.659	443.157	317.905	−1014.817	−302.839	4.653
3500	107.458	539.773	445.874	328.649	−1013.685	−281.916	4.207
3600	107.492	542.801	448.524	339.396	−1012.532	−261.024	3.787
3700	107.523	545.746	451.112	350.147	−1011.357	−240.165	3.391
3800	107.552	548.614	453.640	360.901	−1010.157	−219.338	3.015
3900	107.579	551.408	456.112	371.657	−1008.931	−198.542	2.659
4000	107.604	554.132	458.528	382.416	−1007.679	−177.779	2.322
4100	107.627	556.790	460.893	393.178	−1006.398	−157.048	2.001
4200	107.649	559.384	463.207	403.942	−1005.089	−136.347	1.696
4300	107.669	561.917	465.473	414.708	−1003.750	−115.679	1.405
4400	107.688	564.392	467.693	425.476	−1002.381	−95.042	1.128
4500	107.705	566.812	469.869	436.245	−1000.980	−74.436	0.864
4600	107.721	569.180	472.002	447.017	−999.548	−53.863	0.612
4700	107.737	571.497	474.095	457.789	−998.084	−33.320	0.370
4800	107.751	573.765	476.148	468.564	−996.588	−12.808	0.139
4900	107.765	575.987	478.163	479.340	−995.060	7.672	−0.082
5000	107.777	578.164	480.141	490.117	−993.500	28.120	−0.294
5100	107.789	580.299	482.084	500.895	−991.909	48.536	−0.497
5200	107.801	582.392	483.993	511.675	−990.286	68.921	−0.692
5300	107.811	584.445	485.869	522.455	−988.632	89.275	−0.880
5400	107.821	586.461	487.713	533.237	−986.948	109.597	−1.060
5500	107.831	588.439	489.527	544.019	−985.234	129.887	−1.234
5600	107.840	590.382	491.310	554.803	−983.491	150.147	−1.401
5700	107.849	592.291	493.065	565.587	−981.720	170.374	−1.561
5800	107.857	594.167	494.792	576.373	−979.922	190.571	−1.716
5900	107.864	596.011	496.492	587.159	−978.098	210.736	−1.866
6000	107.872	597.824	498.166	597.946	−976.248	230.870	−2.010

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 281.600\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -154.69 \pm 2.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -158.87 \pm 2.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
752 (1)	703 (1)
528 (1)	434 (1)
326 (1)	364 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: $Cl–F_1 = Cl–F_3 = 1.698$ Å; $Cl–F_2 = 1.598$ Å
Bond Angles: $F_1–Cl–F_2 = F_2–Cl–F_3 = 87° 29'$; $F_3–Cl–F_1 = 185° 02'$
Product of Moments of Inertia: $I_A I_B I_C = 2.69336 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(298.15\ K) = -37.97\ kcal·mol^{-1}$ was calculated from $\Delta_r H°(298.15\ K) = 25.83\ kcal·mol^{-1}$ obtained by third law analysis of the equilibrium data of Schmitz and Schumacher[1] for the reaction $ClF_3(g) = ClF(g) + F_2(g)$. Similar values are obtained from the equilibrium data of Schafer and Wicke.[2] Calorimetric values scatter widely, as summarized below; these were given little weight.

Source	Method	Reaction	Observation $kcal·mol^{-1}$	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
1a	$K_p°$(523–623 K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta_r H°(298.15\ K) = 25.83$	0.8 ± 0.3	−37.97
2a	$K_p°$(733 K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta_r H°(298.15\ K) = 25.77$	—	−37.91
2b	$K_p°$(570–680 K)	$ClF_3(g) \rightarrow ClF(g) + F_2(g)$	$\Delta_r H°(298.15\ K) = 26.12$	6 ± 3	−38.26
1b	Calorimetric	$3\ NaCl + ClF_3 \rightarrow 3\ NaF + 2\ Cl_2$	$\Delta_r H°(291\ K) = -76.5$		−40.02
1c	Calorimetric	$NaCl + 0.5\ F_2 = NaF + 0.5\ Cl_2$	$\Delta_r H°(291\ K) = -39.5$		−42.0*
3	Calorimetric	$3\ NaCl + ClF_3 \rightarrow 3\ NaF + 2\ Cl_2$	$\Delta_r H°(298.15\ K) = -86.8$		−29.7
4	Calorimetric	$0.5\ F_2 + NaCl \rightarrow NaF + 0.5\ Cl_2$	$\Delta_r H°(293\ K) = -39.3$		−31.1**
5	Flow Reaction	$0.5\ Cl_2(g) + 1.5\ F_2(g) = ClF_3(g)$	$\Delta_r H°(473\ K) = -26.4$		−26.4
		* from combination of 1b and 1c	**from combination of 3 and 4		

Heat Capacity and Entropy

The structural constants were obtained from the microwave study of Smith.[6] The planar distorted "T" structure is similar to that derived from X-ray studies of the solid by Burbank and Bensey.[7] Fundamental frequencies are taken from the infrared and Raman spectra of Claassen *et al.*[8] These data confirm the "T" structure as opposed to the pyramidal structure used in earlier spectral analyses.

Claassen *et al.*[8] calculate thermodynamic functions virtually identical with the JANAF values. These authors also correct the third law entropy reported by Grisard *et al.*[9] from measurements of heat capacity (14–285 K) and vapor pressure (226–303 K). The entropy at the normal boiling point becomes $S°(284.91\ K) = 67.04\ kcal·mol^{-1}$ when a non-ideality correction consistent with the dimer–monomer vapor equilibrium is applied. The corresponding statistical entropy, $S°(284.91\ K) = 66.59\ kcal·mol^{-1}$, is consistent with the third law value within the probable error in the entropy of the liquid and the entrophy of vaporization. The principal moments of inertia are: $I_A = 6.1123 \times 10^{-39}$, $I_B = 18.1568 \times 10^{-39}$ and $I_C = 24.2691 \times 10^{-39}\ g·cm^2$.

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[8]H. H. Claassen, B. Weinstock and J. G. Malm, J. Chem. Phys. **28**, 285 (1958).
[9]J. W. Grisard, H. A. Bernhardt and G. D. Oliver, J. Amer. Chem. Soc. **73**, 5725 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−13.648	−154.687	−154.687	INFINITE
100	37.121	227.838	330.328	−10.249	−157.104	−144.882	75.679
200	52.643	258.307	287.119	−5.762	−158.530	−131.999	34.475
250	59.050	270.771	282.625	−2.964	−158.794	−125.331	26.187
298.15	63.845	281.600	281.600	0.	−158.866	−118.877	20.827
300	64.005	281.995	281.601	0.118	−158.867	−118.629	20.655
350	67.760	292.157	282.395	3.417	−158.811	−111.926	16.704
400	70.605	301.399	284.202	6.879	−158.669	−105.237	13.743
450	72.781	309.847	286.589	10.466	−158.471	−98.569	11.442
500	74.465	317.606	289.308	14.149	−158.234	−91.926	9.603
600	76.839	331.409	295.203	21.723	−157.686	−78.715	6.853
700	78.380	343.377	301.249	29.489	−157.083	−65.600	4.895
800	79.428	353.916	307.187	37.383	−156.453	−52.574	3.433
900	80.170	363.317	312.911	45.365	−155.813	−39.627	2.300
1000	80.713	371.793	318.382	53.410	−155.171	−26.752	1.397
1100	81.121	379.506	323.594	61.503	−154.533	−13.941	0.662
1200	81.435	386.578	328.552	69.631	−153.904	−1.188	0.052
1300	81.681	393.106	333.270	77.788	−153.288	11.513	−0.463
1400	81.879	399.167	337.763	85.966	−152.687	24.168	−0.902
1500	82.039	404.822	342.047	94.162	−152.102	36.780	−1.281
1600	82.171	410.121	346.138	102.373	−151.534	49.353	−1.611
1700	82.280	415.106	350.050	110.596	−150.984	61.892	−1.902
1800	82.372	419.812	353.796	118.828	−150.449	74.398	−2.159
1900	82.451	424.267	357.389	127.070	−149.930	86.875	−2.388
2000	82.517	428.498	360.839	135.318	−149.421	99.326	−2.594
2100	82.575	432.526	364.158	143.573	−148.922	111.751	−2.780
2200	82.625	436.368	367.353	151.833	−148.426	124.152	−2.948
2300	82.669	440.042	370.434	160.098	−147.931	136.531	−3.101
2400	82.708	443.561	373.409	168.367	−147.431	148.888	−3.240
2500	82.742	446.938	376.283	176.639	−146.923	161.224	−3.369
2600	82.772	450.184	379.063	184.915	−146.402	173.540	−3.486
2700	82.799	453.308	381.755	193.193	−145.863	185.835	−3.595
2800	82.823	456.320	384.365	201.474	−145.302	198.110	−3.696
2900	82.844	459.227	386.897	209.758	−144.717	210.365	−3.789
3000	82.864	462.036	389.355	218.043	−144.102	222.599	−3.876
3100	82.882	464.753	391.743	226.331	−143.455	234.811	−3.957
3200	82.898	467.385	394.066	234.620	−142.773	247.003	−4.032
3300	82.912	469.936	396.327	242.910	−142.053	259.172	−4.102
3400	82.926	472.411	398.528	251.202	−141.293	271.319	−4.168
3500	82.938	474.815	400.674	259.495	−140.490	283.443	−4.230
3600	82.949	477.152	402.766	267.790	−139.643	295.544	−4.288
3700	82.960	479.425	404.807	276.085	−138.750	307.620	−4.343
3800	82.969	481.637	406.800	284.381	−137.809	319.671	−4.394
3900	82.978	483.792	408.747	292.679	−136.819	331.698	−4.443
4000	82.986	485.893	410.649	300.977	−135.778	343.698	−4.488
4100	82.994	487.943	412.509	309.276	−134.687	355.671	−4.531
4200	83.001	489.943	414.329	317.576	−133.544	367.618	−4.572
4300	83.007	491.896	416.111	325.876	−132.349	379.536	−4.610
4400	83.014	493.804	417.855	334.177	−131.101	391.426	−4.647
4500	83.019	495.670	419.563	342.479	−129.799	403.287	−4.681
4600	83.025	497.495	421.238	350.781	−128.444	415.119	−4.714
4700	83.030	499.280	422.879	359.084	−127.035	426.920	−4.745
4800	83.034	501.028	424.489	367.387	−125.573	438.691	−4.774
4900	83.039	502.740	426.069	375.691	−124.058	450.431	−4.802
5000	83.043	504.418	427.619	383.995	−122.489	462.140	−4.828
5100	83.047	506.063	429.141	392.299	−120.868	473.816	−4.853
5200	83.051	507.675	430.636	400.604	−119.195	485.461	−4.877
5300	83.054	509.257	432.104	408.909	−117.469	497.072	−4.899
5400	83.057	510.810	433.548	417.215	−115.693	508.651	−4.920
5500	83.060	512.334	434.966	425.521	−113.866	520.196	−4.940
5600	83.063	513.830	436.361	433.827	−111.988	531.708	−4.960
5700	83.066	515.301	437.733	442.134	−110.062	543.184	−4.978
5800	83.069	516.745	439.083	450.440	−108.087	554.628	−4.995
5900	83.071	518.165	440.412	458.747	−106.065	566.037	−5.011
6000	83.074	519.562	441.719	467.055	−103.996	577.411	−5.027

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$\Delta_f H°(0\ K) = [-1314 \pm 63]\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [308.68 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-1318 \pm 63]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Quantum Weights ν, cm^{-1}
[870](1)
[550](1)
[275](1)
[900](2)
[400](2)
[200](2)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Product of the Moments of Inertia: $I_A I_B I_C = 29.869 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

All data taken from Henderson and Scheffee.[1]

Heat Capacity and Entropy

All data is taken from Henderson and Scheffee.[1] The principal moments of inertia are: $I_A = [19.9 \times 10^{-39}]$, $I_B = [33.9 \times 10^{-39}]$ and $I_C = [39.9 \times 10^{-39}]\ g \cdot cm^2$.

Reference

[1]C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria, Va., (January 1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.612	−1313.526	−1313.526	INFINITE
100	46.502	240.797	369.839	−12.904	−1315.901	−1304.592	681.449
200	66.344	279.593	315.556	−7.193	−1317.280	−1292.674	337.612
250	73.615	295.204	309.955	−3.688	−1317.689	−1286.473	268.794
298.15	79.372	308.679	308.679	0.	−1317.960	−1280.434	224.327
300	79.571	309.171	308.681	0.147	−1317.968	−1280.201	222.903
350	84.392	321.812	309.668	4.250	−1318.142	−1273.891	190.118
400	88.261	333.343	311.918	8.570	−1318.230	−1267.563	165.527
450	91.361	343.925	314.894	13.064	−1318.250	−1261.227	146.399
500	93.851	353.684	318.292	17.696	−1318.216	−1254.893	131.098
600	97.504	371.141	325.680	27.276	−1318.039	−1242.243	108.147
700	99.969	386.368	333.286	37.158	−1317.768	−1229.631	91.756
800	101.689	399.836	340.779	47.246	−1317.454	−1217.061	79.466
900	102.929	411.889	348.022	57.480	−1317.123	−1204.531	69.909
1000	103.847	422.783	354.962	67.821	−1316.796	−1192.039	62.266
1100	104.544	432.715	361.586	78.242	−1316.486	−1179.578	56.014
1200	105.085	441.836	367.899	88.724	−1316.202	−1167.145	50.804
1300	105.512	450.264	373.914	99.255	−1315.952	−1154.734	46.398
1400	105.855	458.097	379.651	109.824	−1315.742	−1142.341	42.621
1500	106.134	465.410	385.127	120.424	−1315.578	−1129.961	39.349
1600	106.365	472.267	390.361	131.049	−1315.461	−1117.590	36.486
1700	106.557	478.721	395.371	141.695	−1365.572	−1104.779	33.946
1800	106.719	484.817	400.172	152.359	−1365.326	−1089.445	31.615
1900	106.857	490.590	404.781	163.038	−1365.089	−1074.125	29.530
2000	106.975	496.074	409.209	173.730	−1364.857	−1058.817	27.653
2100	107.077	501.296	413.471	184.433	−1364.628	−1043.521	25.956
2200	107.165	506.280	417.577	195.145	−1364.401	−1028.235	24.413
2300	107.243	511.045	421.538	205.865	−1364.169	−1012.960	23.005
2400	107.311	515.611	425.364	216.593	−1363.930	−997.695	21.714
2500	107.371	519.993	429.062	227.327	−1363.680	−982.441	20.527
2600	107.424	524.205	432.641	238.067	−1363.414	−967.196	19.431
2700	107.472	528.260	436.107	248.812	−1363.129	−951.962	18.417
2800	107.515	532.169	439.469	259.561	−1362.820	−936.740	17.475
2900	107.553	535.943	442.731	270.315	−1362.483	−921.528	16.599
3000	107.588	539.590	445.899	281.072	−1362.117	−906.329	15.781
3100	107.620	543.118	448.978	291.832	−1361.716	−891.143	15.016
3200	107.648	546.535	451.974	302.596	−1361.279	−875.970	14.299
3300	107.674	549.848	454.890	313.362	−1360.803	−860.811	13.626
3400	107.698	553.063	457.730	324.131	−1360.286	−845.668	12.992
3500	107.720	556.185	460.499	334.902	−1359.725	−830.540	12.395
3600	107.740	559.220	463.199	345.675	−1743.271	−804.968	11.680
3700	107.758	562.172	465.834	356.449	−1742.203	−778.918	10.996
3800	107.775	565.046	468.408	367.226	−1741.089	−752.899	10.349
3900	107.791	567.846	470.922	378.005	−1739.927	−726.909	9.736
4000	107.806	570.575	473.379	388.784	−1738.715	−700.949	9.153
4100	107.819	573.237	475.782	399.566	−1737.452	−675.021	8.600
4200	107.832	575.836	478.134	410.348	−1736.138	−649.123	8.073
4300	107.843	578.373	480.435	421.132	−1734.770	−623.258	7.571
4400	107.854	580.852	482.689	431.917	−1733.349	−597.425	7.092
4500	107.865	583.276	484.898	442.703	−1731.874	−571.625	6.635
4600	107.874	585.647	487.062	453.490	−1730.345	−545.859	6.198
4700	107.883	587.967	489.185	464.278	−1728.762	−520.126	5.781
4800	107.891	590.239	491.266	475.066	−1727.125	−494.427	5.380
4900	107.899	592.463	493.309	485.856	−1725.434	−468.764	4.997
5000	107.907	594.643	495.314	496.646	−1723.688	−443.135	4.629
5100	107.914	596.780	497.283	507.437	−1721.890	−417.542	4.277
5200	107.920	598.876	499.216	518.229	−1720.038	−391.984	3.938
5300	107.927	600.931	501.116	529.021	−1718.134	−366.463	3.612
5400	107.932	602.949	502.983	539.814	−1716.179	−340.978	3.298
5500	107.938	604.929	504.819	550.608	−1714.172	−315.530	2.997
5600	107.943	606.874	506.624	561.402	−1712.116	−290.118	2.706
5700	107.948	608.785	508.400	572.196	−1710.010	−264.745	2.426
5800	107.953	610.662	510.147	582.992	−1707.858	−239.408	2.156
5900	107.958	612.508	511.866	593.787	−1705.658	−214.108	1.896
6000	107.962	614.322	513.559	604.583	−1703.412	−188.847	1.644

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = 310.739\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-229.8 \pm 63]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-238.5 \pm 63]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
712(1)	488(1)	732 (2)
541(1)	346(1)	[440](2)
486(1)	375(1)	302 (2)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: C_{4v}
Bond Distances: $(Cl–F)_{basal} = 1.72$ Å; $(Cl–F)_{axial} = 1.62$ Å
Bond Angle: F–Cl–F = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 2.47347 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The heat of formation was estimated by assuming that the ratio [(A·B·E(ClF)–A·B·E(ClF_3))/[A·B·E(ClF_3)–A·B·E(ClF_5)] was equal to [A·B·E(BrF)–A·B·E(BrF_3)]/[A·B·E(BrF_3)–A·B·E(BrF_5)], where A·B·E represents average bond energy. All values were taken from these tables. A·B·E(ClF_5) was thus calculated to be 36 kcal·mol^{-1} which leads to $\Delta_f H° = -57 \pm 15$ kcal·mol^{-1}.

Heat Capacity and Entropy

Begun *et al.*[1] have reported the infrared spectra of the gas and the Raman spectra of the liquid. Their assignments have been adopted here, including one frequency ν_8 obtained from a valence force-field treatment. The values are consistent with those of IF_5(g) and BrF_5(g). Smith[2] had previously reported three infrared bands. The structure of the molecule has not been determined but the spectra can only be interpreted assuming C_{4v} symmetry, this is in accord with IF_5 and BrF_5(g). Begun[1] assumed a square pyramidal structure with the chlorine in the base of the pyramid. There is some evidence that the chlorine may not lie in the basal plane but this would not appreciably affect the calculations. The structure adopted was that given by Begun *et al.*[1] The principal moments of inertia are $I_A = 37.3328 \times 10^{-39}$ and $I_B = I_C = 25.7400 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−17.930	−229.765	−229.765	INFINITE
100	42.206	236.844	381.117	−14.427	−234.986	−206.628	107.931
200	75.005	276.255	319.001	−8.549	−237.949	−176.878	46.196
250	87.822	294.433	312.290	−4.464	−238.430	−161.544	33.753
298.15	97.165	310.739	310.739	0.	−238.488	−146.725	25.706
300	97.474	311.341	310.741	0.180	−238.484	−146.156	25.448
350	104.652	326.933	311.956	5.242	−238.254	−130.783	19.518
400	110.018	341.275	314.737	10.615	−237.832	−115.457	15.077
450	114.082	354.478	318.429	16.222	−237.281	−100.192	11.630
500	117.206	366.667	322.651	22.008	−236.639	−84.993	8.879
600	121.580	388.453	331.847	33.964	−235.183	−54.798	4.771
700	124.400	407.422	341.318	46.273	−233.589	−24.858	1.855
800	126.310	424.165	350.648	58.814	−231.922	4.847	−0.317
900	127.658	439.125	359.663	71.516	−230.215	34.341	−1.993
1000	128.641	452.628	368.295	84.333	−228.491	63.644	−3.324
1100	129.380	464.925	376.529	97.236	−226.763	92.774	−4.405
1200	129.948	476.208	384.372	110.204	−225.041	121.747	−5.299
1300	130.394	486.628	391.842	123.222	−223.332	150.576	−6.050
1400	130.751	496.305	398.962	136.280	−221.642	179.275	−6.689
1500	131.040	505.336	405.756	149.370	−219.974	207.853	−7.238
1600	131.277	513.801	412.247	162.486	−218.329	236.321	−7.715
1700	131.475	521.766	418.457	175.624	−216.709	264.687	−8.133
1800	131.641	529.285	424.408	188.780	−215.111	292.959	−8.501
1900	131.782	536.407	430.117	201.951	−213.533	321.141	−8.829
2000	131.902	543.169	435.602	215.135	−211.970	349.242	−9.121
2100	132.006	549.607	440.878	228.331	−210.417	377.264	−9.384
2200	132.097	555.750	445.961	241.536	−208.865	405.212	−9.621
2300	132.176	561.624	450.863	254.750	−207.310	433.091	−9.836
2400	132.245	567.251	455.596	267.971	−205.741	460.900	−10.031
2500	132.306	572.651	460.171	281.199	−204.152	488.645	−10.210
2600	132.361	577.841	464.598	294.432	−202.535	516.325	−10.373
2700	132.409	582.837	468.885	307.671	−200.883	543.942	−10.523
2800	132.452	587.653	473.041	320.914	−199.188	571.497	−10.661
2900	132.491	592.302	477.074	334.161	−197.444	598.991	−10.789
3000	132.527	596.794	480.990	347.412	−195.645	626.424	−10.907
3100	132.558	601.140	484.796	360.666	−193.786	653.795	−11.016
3200	132.587	605.349	488.498	373.923	−191.862	681.106	−11.118
3300	132.614	609.430	492.101	387.184	−189.868	708.356	−11.212
3400	132.638	613.389	495.611	400.446	−187.802	735.544	−11.300
3500	132.660	617.234	499.031	413.711	−185.659	762.670	−11.382
3600	132.680	620.972	502.367	426.978	−183.437	789.735	−11.459
3700	132.699	624.607	505.622	440.247	−181.135	816.736	−11.530
3800	132.716	628.146	508.800	453.518	−178.751	843.673	−11.597
3900	132.732	631.594	511.904	466.790	−176.282	870.547	−11.660
4000	132.747	634.955	514.939	480.064	−173.728	897.357	−11.718
4100	132.760	638.233	517.906	493.339	−171.089	924.101	−11.773
4200	132.773	641.432	520.809	506.616	−168.364	950.781	−11.825
4300	132.785	644.556	523.651	519.894	−165.552	977.393	−11.873
4400	132.796	647.609	526.433	533.173	−162.655	1003.940	−11.918
4500	132.806	650.593	529.159	546.453	−159.671	1030.421	−11.961
4600	132.816	653.512	531.831	559.734	−156.603	1056.833	−12.001
4700	132.825	656.369	534.451	573.016	−153.449	1083.178	−12.038
4800	132.833	659.165	537.020	586.299	−150.211	1109.456	−12.073
4900	132.841	661.904	539.541	599.583	−146.891	1135.665	−12.106
5000	132.849	664.588	542.015	612.867	−143.488	1161.804	−12.137
5100	132.856	667.219	544.444	626.153	−140.004	1187.876	−12.166
5200	132.862	669.799	546.830	639.438	−136.441	1213.879	−12.194
5300	132.869	672.330	549.174	652.725	−132.799	1239.812	−12.219
5400	132.875	674.813	551.478	666.012	−129.080	1265.675	−12.243
5500	132.880	677.252	553.743	679.300	−125.285	1291.468	−12.265
5600	132.885	679.646	555.970	692.588	−121.417	1317.194	−12.286
5700	132.891	681.998	558.160	705.877	−117.475	1342.847	−12.306
5800	132.895	684.309	560.315	719.166	−113.462	1368.432	−12.324
5900	132.900	686.581	562.436	732.456	−109.380	1393.948	−12.341
6000	132.904	688.815	564.524	745.746	−105.229	1419.392	−12.357

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 319.931 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1026.3 \pm 10.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1038.9 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
855(1)	625 (1)	579(2)
707(1)	[332] (1)	441(2)
602(1)	505 (1)	287(2)
402(1)	909 (2)	

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group = C_{4v}

Bond Distances: S–F* = 1.566 ± 0.003 Å; S–F** = 1.588 ± 0.009 Å

S–Cl = 2.047 ± 0.003 Å

Bond Angles: Cl–S–F* = 90.7 ± 0.2°; F*–S–F* = 90°

(* – equatorial ** – axial)

Product of Moments of Inertia: $I_A I_B I_C = 6.65952 \times 10^{-113}\ g^3 \cdot cm^6$

Heat of Formation

Leach and Roberts[1] have reported calorimetric measurements on the heat of hydrolysis of liquid sulfur chloride pentafluoride in aqueous caustic. Re–evaluation of their data using more recent auxiliary heats of formation[2] for aqueous NaOH, Na_2SO_4, NaCl, and NaF leads to $\Delta_f H°(ClSF_4, l, 298.15\ K) = -252.9 \pm 2.0\ kcal \cdot mol^{-1}$. The adopted value for the gas is obtained from that for the liquid by addition of the heat of vaporization at 298.15 K. We estimate a value for $\Delta_{vap}H°(298.15\ K)$ equal to $4.6 \pm 0.5\ kcal \cdot mol^{-1}$ from $\Delta_{vap}H° = 5.19\ kcal \cdot mol^{-1}$ reported by Griffiths[3] from an analysis of vapor pressure data. We assume that the reported $\Delta_{vap}H°$ value refers to a boiling temperature of 251.85 K, and we estimate the $\Delta_p C°$ of vaporization as $-12\ cal \cdot K^{-1} \cdot mol^{-1}$. Earlier vapor pressure measurements[4] lead to a lower value (3.9 $kcal \cdot mol^{-1}$) for $\Delta_{vap}H°(298.15\ K)$; however, we believe the earlier vapor pressure data are less reliable than the measurements of Griffiths.[3]

Electron–impact studies by Harland and Thynne[5] on SF_6 and $ClSF_5$ have provided information on the appearance potentials (AP) for the formation of SF_5^+ and SF_5^- from these neutral molecules. Our analysis of their AP data[5] leads to $\Delta_f H°$ values which are more than 15 $kcal \cdot mol^{-1}$ different than the adopted result.

The heat of atomization, $\Delta_a H°(0\ K)$, and S–Cl bond dissociation energy are calculated to be $431.8 \pm 4.5\ kcal \cdot mol^{-1}$ and $59.6 \pm 6.0\ kcal \cdot mol^{-1}$, respectively. The latter value appears reasonable when compared with the mean values for the S–Cl bond strength in SCl_2(63.8 $kcal \cdot mol^{-1}$).

Heat Capacity and Entropy

The structural parameters are taken from a study by Marsden and Bartell[6] who established the C_{4v} structure of $ClSF_5$ by a simultaneous least–squares analysis of electron diffraction and microwave spectroscopic data. The microwave data were based on the measurements of Kewley *et al.*[7] We use r_g distances to calculate the principal moments of inertia of $I_A = 30.9468 \times 10^{-38}$ and $I_B = I_C = 46.3888 \times 10^{-38}\ g \cdot cm^2$.

The vibrational spectrum of $ClSF_5$ has been studied using various spectroscopic techniques.[3,8,9] The observed vibratonal frequencies show good agreement, but conflicting assignments have been reported. Griffiths[3] has argued that the fundamentals assigned as $\nu_6 = 396\ cm^{-1}$ and $\nu_{11} = 270\ cm^{-1}$ by Cross *et al.*[8] should be reversed. A recent Raman study[9] of ClSF ν_5 isolated in an argon matrix has identified the band at $396\ cm^{-1}$ as the Cl component of the S–Cl stretching frequency (ν_4). A comparison of the vibrational spectra of $ClSF_5$ and $ClSeF_5$[10] and results from two force field studies[6, 11] suggest that the low–frequency SF_5 bending mode (ν_{11}) should lie in the range 270–290 cm^{-1}. We adopt $\nu_{11} = 287\ cm^{-1}$ which was observed in the gas phase infrared spectra by Griffiths.[3] As suggested by others[10,11] we believe that the SF_2 out–of–plane deformation (ν_6) has not been resolved, and we use an estimated value ($332\ cm^{-1}$) calculated from a general valency–force field.[11] An independent force–field calculation[6] supports this value ($\nu_6 = 317\ cm^{-1}$). All other fundamentals are rounded values taken from the gas phase infrared and liquid phase Raman study of Griffiths.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.458	−1026.280	−1026.280	INFINITE
100	42.459	243.875	393.298	−14.942	−1032.178	−1003.270	524.055
200	77.049	283.704	328.677	−8.995	−1036.714	−972.405	253.966
250	92.376	302.598	321.585	−4.747	−1038.051	−956.161	199.779
298.15	104.342	319.931	319.931	0.	−1038.887	−940.307	164.738
300	104.749	320.577	319.933	0.193	−1038.912	−939.696	163.616
350	114.465	337.485	321.246	5.684	−1039.419	−923.115	137.767
400	122.040	353.285	324.274	11.604	−1041.881	−906.393	118.363
450	127.964	368.015	328.326	17.860	−1042.606	−889.421	103.241
500	132.635	381.749	332.989	24.380	−1043.234	−872.363	91.135
600	139.350	406.569	343.230	38.003	−1043.695	−838.132	72.966
700	143.792	428.406	353.870	52.175	−1043.585	−803.874	59.986
800	146.853	447.818	364.423	66.716	−1043.129	−769.658	50.254
900	149.039	465.248	374.674	81.516	−1095.580	−734.432	42.625
1000	150.648	481.038	384.534	96.505	−1093.542	−694.413	36.272
1100	151.864	495.456	393.972	111.633	−1091.459	−654.601	31.084
1200	152.804	508.712	402.989	126.868	−1089.357	−614.979	26.769
1300	153.545	520.973	411.599	142.187	−1087.250	−575.533	23.125
1400	154.138	532.375	419.823	157.573	−1085.150	−536.249	20.008
1500	154.621	543.026	427.685	173.011	−1083.066	−497.115	17.311
1600	155.019	553.018	435.210	188.494	−1081.004	−458.119	14.956
1700	155.350	562.427	442.419	204.013	−1078.965	−419.251	12.882
1800	155.628	571.314	449.335	219.562	−1076.951	−380.502	11.042
1900	155.865	579.735	455.979	235.137	−1074.958	−341.866	9.399
2000	156.068	587.735	462.368	250.734	−1072.984	−303.333	7.922
2100	156.243	595.354	468.521	266.350	−1071.023	−264.899	6.589
2200	156.395	602.626	474.453	281.982	−1069.067	−226.558	5.379
2300	156.528	609.581	480.178	297.628	−1067.111	−188.305	4.277
2400	156.645	616.246	485.709	313.287	−1065.145	−150.138	3.268
2500	156.748	622.642	491.060	328.957	−1063.163	−112.054	2.341
2600	156.840	628.792	496.240	344.636	−1061.156	−74.049	1.488
2700	156.922	634.713	501.259	360.324	−1059.116	−36.122	0.699
2800	156.995	640.421	506.128	376.020	−1057.036	1.729	−0.032
2900	157.061	645.931	510.854	391.723	−1054.910	39.505	−0.712
3000	157.120	651.257	515.446	407.432	−1052.732	77.206	−1.344
3100	157.174	656.410	519.911	423.147	−1050.496	114.833	−1.935
3200	157.223	661.401	524.255	438.867	−1048.196	152.388	−2.487
3300	157.268	666.239	528.484	454.591	−1045.830	189.870	−3.005
3400	157.308	670.935	532.605	470.320	−1043.393	227.279	−3.492
3500	157.346	675.495	536.623	486.053	−1040.883	264.616	−3.949
3600	157.380	679.928	540.542	501.789	−1038.297	301.880	−4.380
3700	157.412	684.241	544.368	517.529	−1035.633	339.070	−4.787
3800	157.441	688.439	548.104	533.272	−1032.889	376.187	−5.171
3900	157.468	692.529	551.755	549.017	−1030.064	413.232	−5.535
4000	157.492	696.516	555.325	564.765	−1027.158	450.203	−5.879
4100	157.516	700.405	558.816	580.515	−1024.170	487.100	−6.206
4200	157.537	704.201	562.233	596.268	−1021.100	523.924	−6.516
4300	157.557	707.908	565.578	612.023	−1017.948	560.672	−6.811
4400	157.576	711.531	568.854	627.780	−1014.715	597.347	−7.091
4500	157.593	715.072	572.064	643.538	−1011.400	633.948	−7.359
4600	157.610	718.536	575.210	659.298	−1008.005	670.474	−7.613
4700	157.625	721.926	578.296	675.060	−1004.530	706.925	−7.857
4800	157.639	725.245	581.323	690.823	−1000.977	743.302	−8.089
4900	157.653	728.495	584.294	706.588	−997.347	779.604	−8.311
5000	157.665	731.680	587.210	722.354	−993.640	815.830	−8.523
5100	157.677	734.803	590.073	738.121	−989.859	851.982	−8.726
5200	157.689	737.864	592.886	753.889	−986.005	888.060	−8.921
5300	157.699	740.868	595.650	769.658	−982.079	924.062	−9.107
5400	157.709	743.816	598.366	785.429	−978.082	959.990	−9.286
5500	157.719	746.710	601.037	801.200	−974.016	995.842	−9.458
5600	157.728	749.552	603.664	816.973	−969.883	1031.621	−9.623
5700	157.736	752.344	606.248	832.746	−965.685	1067.324	−9.781
5800	157.744	755.087	608.791	848.520	−961.422	1102.954	−9.933
5900	157.752	757.784	611.293	864.295	−957.097	1138.510	−10.080
6000	157.759	760.435	613.757	880.070	−952.710	1173.991	−10.221

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K)$ = [257.573] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 249.8 ± 84 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 251.0 ± 84 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6\Sigma$	0	6
	[200]	[8]
	[1000]	[8]
	[4000]	[8]

ω_e = 404.92 cm^{-1} $\omega_e x_e$ = 1.19 cm^{-1} σ = 1
B_e = [0.17795] cm^{-1} α_e = [0.00075] cm^{-1} r_e = [2.09]

Enthalpy of Formation

The dissociation energy of FeCl(g) was reported as 3 ± 2 $cal·K^{-1}·mol^{-1}$ (69 ± 46 $kcal·mol^{-1}$) by Gaydon.[1] The corresponding $\Delta_f H°$(FeCl, g, 298.15 K) was evaluated to be 56 ± 46 $kcal·mol^{-1}$. By comparing $D_0°$(Fe–O) = 101 $kcal·mol^{-1}$ in FeO(g) with the coordinate bond energies obtained in organic complexes and iron carbonyl halides of E(Fe–O) = 59.4 and E(Fe–Cl) = 37.3 $kcal·mol^{-1}$, reported by Jones *et al.*,[2] the $D_0°$(Fe–Cl) in FeCl(g) was estimated as 101 × (37.3/59.4) = 63.3 $kcal·mol^{-1}$, yielding $\Delta_f H°$(FeCl, g, 298.15 K) = 64 $kcal·mol^{-1}$. The adopted value of $\Delta_f H°(298.15\ K)$ for FeCl(g) is 60 ± 20 $kcal·mol^{-1}$ (251.040 ± 84 $kJ·mol^{-1}$).

Heat Capacity and Entropy

The ground state configuration, ω_e and $\omega_e x_e$ (corrected to the average isotopic species) were obtained from Herzberg.[3] The Fe–Cl bond distance was assumed to be the same as that in $FeCl_2$(g). Hence the values of B_e and α_e were calculated. The electronic levels and quantum weights were estimated by comparison with the electronic levels in Fe^+(g) reported by Moore,[4] using the reasoning suggested by Hougen *et al.*[5] The total 30 for the quantum weight was obtained from the ground multiplet of Fe^+ and was split arbitrarily. The entropy values may be in error by a few entropy units due to the uncertainties in the low lying electronic levels.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.377	249.760	249.760	INFINITE
100	34.442	217.748	290.602	−7.285	250.973	239.255	−124.974
200	36.906	242.585	261.028	−3.689	251.282	227.351	−59.378
250	37.603	250.896	258.199	−1.826	251.198	221.376	−46.254
298.15	38.223	257.573	257.573	0.	251.040	215.646	−37.780
300	38.245	257.810	257.574	0.071	251.033	215.426	−37.509
350	38.782	263.747	258.041	1.997	250.814	209.508	−31.267
400	39.189	268.954	259.087	3.947	250.546	203.625	−26.591
450	39.472	273.587	260.445	5.914	250.227	197.779	−22.958
500	39.654	277.756	261.971	7.892	249.853	191.971	−20.055
600	39.813	285.003	265.224	11.867	248.926	180.477	−15.712
700	39.833	291.143	268.499	15.850	247.747	169.159	−12.623
800	39.813	296.460	271.669	19.833	246.265	158.029	−10.318
900	39.801	301.149	274.690	23.813	244.357	147.109	−8.538
1000	39.810	305.343	277.549	27.794	241.722	136.435	−7.127
1100	39.840	309.138	280.251	31.776	238.187	126.091	−5.988
1200	39.885	312.606	282.805	35.762	235.202	116.013	−5.050
1300	39.939	315.801	285.222	39.753	233.863	106.135	−4.265
1400	39.997	318.763	287.513	43.750	232.442	96.362	−3.595
1500	40.052	321.524	289.689	47.753	230.938	86.694	−3.019
1600	40.104	324.111	291.761	51.760	229.352	77.129	−2.518
1700	40.150	326.544	293.736	55.773	226.732	67.685	−2.080
1800	40.189	328.840	295.623	59.790	224.644	58.389	−1.694
1900	40.222	331.014	297.429	63.811	208.373	49.913	−1.372
2000	40.248	333.077	299.160	67.834	205.875	41.638	−1.087
2100	40.269	335.042	300.822	71.860	203.374	33.488	−0.833
2200	40.284	336.915	302.421	75.888	200.869	25.457	−0.604
2300	40.295	338.706	303.960	79.917	198.359	17.539	−0.398
2400	40.303	340.421	305.444	83.947	195.842	9.732	−0.212
2500	40.307	342.067	306.876	87.977	193.318	2.029	−0.042
2600	40.309	343.648	308.260	92.008	190.785	−5.573	0.112
2700	40.310	345.169	309.599	96.039	188.244	−13.077	0.253
2800	40.309	346.635	310.896	100.070	185.693	−20.486	0.382
2900	40.307	348.049	312.152	104.101	183.132	−27.805	0.501
3000	40.304	349.416	313.372	108.131	180.561	−35.035	0.610
3100	40.302	350.737	314.556	112.162	177.981	−42.179	0.711
3200	40.299	352.017	315.707	116.192	−172.910	−41.815	0.683
3300	40.297	353.257	316.826	120.222	−173.609	−37.708	0.597
3400	40.295	354.460	317.915	124.251	−174.349	−33.579	0.516
3500	40.293	355.628	318.976	128.280	−175.130	−29.427	0.439
3600	40.292	356.763	320.010	132.310	−175.952	−25.253	0.366
3700	40.293	357.867	321.018	136.339	−176.815	−21.055	0.297
3800	40.293	358.941	322.002	140.368	−177.717	−16.833	0.231
3900	40.295	359.988	322.963	144.398	−178.659	−12.587	0.169
4000	40.298	361.008	323.901	148.427	−179.641	−8.316	0.109
4100	40.302	362.003	324.819	152.457	−180.661	−4.021	0.051
4200	40.306	362.975	325.716	156.488	−181.719	0.300	−0.004
4300	40.312	363.923	326.593	160.519	−182.816	4.647	−0.056
4400	40.319	364.850	327.452	164.550	−183.950	9.019	−0.107
4500	40.326	365.756	328.293	168.582	−185.121	13.418	−0.156
4600	40.335	366.642	329.117	172.616	−186.330	17.844	−0.203
4700	40.345	367.510	329.925	176.649	−187.575	22.295	−0.248
4800	40.355	368.360	330.717	180.684	−188.858	26.774	−0.291
4900	40.367	369.192	331.494	184.721	−190.177	31.280	−0.333
5000	40.379	370.007	332.256	188.758	−191.534	35.813	−0.374
5100	40.392	370.807	333.004	192.796	−192.929	40.374	−0.414
5200	40.406	371.592	333.738	196.836	−194.361	44.963	−0.452
5300	40.421	372.361	334.460	200.878	−195.833	49.579	−0.489
5400	40.436	373.117	335.169	204.920	−197.345	54.223	−0.525
5500	40.453	373.859	335.866	208.965	−198.897	58.896	−0.559
5600	40.470	374.588	336.551	213.011	−200.492	63.598	−0.593
5700	40.488	375.305	337.224	217.059	−202.132	68.328	−0.626
5800	40.506	376.009	337.887	221.109	−203.817	73.088	−0.658
5900	40.525	376.702	338.539	225.160	−205.550	77.877	−0.689
6000	40.545	377.383	339.181	229.214	−207.333	82.695	−0.720

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K) = 186.901\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -92.127 \pm 0.21\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -92.312 \pm 0.21\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 2889.59\ cm^{-1}$ $\omega_e x_e = 52.06\ cm^{-1}$ $\sigma = 1$

$B_e = 10.5884\ cm^{-1}$ $\alpha_e = 0.3037\ cm^{-1}$ $r_e = 1.2746$ Å

Enthalpy of Formation

The selected value, Rossini's flow calorimetric measurement[1] of the direct combination of the elements, is essentially the same as that in the revised version[2] of NBS Circular 500. JANAF analyses of the more recent measurements are summarized below, while the earlier measurements have been reviewed by Rossini.[1]

Experimenters	Date	Method	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$	References
Johnson, Ambrose	1963	Comparison of HCl, H_2SO_4 and SO_2 by solution calorimetry	−22.14 ± 0.12	2,3,4,5,6,7,8,9,10)
Lacher *et al.*	1949–52	Catalytic combination in flow calorimeter	−22.10 ± 0.12	11,12
Roth and Richter	1934	Direct combination in bomb calorimeter	−21.90 ± 0.05	13
von Wartenberg and Hanisch	1932	Direct combination in flow calorimeter	−21.90 ± 0.01	14
Rossini	1932	Direct combination in flow calorimeter	−22.063 ± 0.012	1
—	1922–63	$\Delta_f G°$ from e.m.f. and $\Delta_f S°$ from statistical mechanics	−22.02 ± 0.03	15,16,17,18,19,20
Lewis	1906	Equilibria for reaction $HCl(g) + 1/4O_2(g) = 1/2\ H_2O(g) + 1/2\ Cl2(g)$	−22.30 ± 0.44	21

The direct combination values of Roth and Richter[13] and von Wartenberg and Hanisch[14] are 0.7% less negative than that of Rossini;[1] however, all of the other methods favor the more negative value. The Roth and Richter value may be affected by errors in the measurement of the extent of reaction by HCl titration (9, 22), since a set of experiments based on determination of the amount of H_2 gave a value of −22.02 $kcal·mol^{-1}$.

Rossini's value is confirmed by a variety of independent methods. The solution calorimetry,[3] though it is related through a complex reaction scheme, is based on species which are now quite well known. Emf measurements[15–20] give $\Delta_f G°(298.15\ K) = -22.733$; assuming an uncertainty of 1.0 mv. in $E°$, this leads to $\Delta_f H°(29815K) = -22.02 \pm 0.03$ when combined with the statistical entropies. The equilibria of Lewis (625–692 K) give $\Delta_f H°(298.15\ K)^{21} = -2220 \pm 044$(2nd law) and -22.30 ± 0.04 (3rd law).

Enthalpy Capacity and Entropy

Spectroscopic constants for HCl^{35} and HCl^{37} were selected from the work of Plyler *et al.*[23] and Haeusler and Barchewitz.[24] The values were adjusted to 75.53% HCl^{35}.

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Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.640	−92.127	−92.127	INFINITE
100	29.116	155.087	212.797	−5.771	−92.214	−93.236	48.702
200	29.124	175.270	189.566	−2.859	−92.168	−94.284	24.625
250	29.130	181.770	187.381	−1.403	−92.219	−94.809	19.809
298.15	29.136	186.901	186.901	0.	−92.312	−95.300	16.696
300	29.137	187.081	186.902	0.054	−92.316	−95.318	16.596
350	29.149	191.574	187.256	1.511	−92.443	−95.809	14.299
400	29.175	195.467	188.045	2.969	−92.589	−96.280	12.573
450	29.223	198.906	189.064	4.429	−92.747	−96.732	11.228
500	29.304	201.989	190.205	5.892	−92.913	−97.166	10.151
600	29.575	207.353	192.629	8.835	−93.251	−97.985	8.530
700	29.985	211.942	195.068	11.811	−93.579	−98.747	7.369
800	30.494	215.978	197.434	14.835	−93.881	−99.465	6.494
900	31.055	219.602	199.699	17.912	−94.152	−100.146	5.812
1000	31.628	222.903	201.857	21.046	−94.388	−100.799	5.265
1100	32.186	225.944	203.910	24.237	−94.591	−101.430	4.817
1200	32.713	228.768	205.866	27.482	−94.766	−102.044	4.442
1300	33.203	231.406	207.730	30.779	−94.916	−102.644	4.124
1400	33.651	233.883	209.510	34.122	−95.046	−103.234	3.852
1500	34.060	236.219	211.214	37.508	−95.160	−103.815	3.615
1600	34.431	238.429	212.846	40.932	−95.261	−104.388	3.408
1700	34.767	240.527	214.413	44.393	−95.351	−104.956	3.225
1800	35.071	242.523	215.920	47.885	−95.435	−105.519	3.062
1900	35.348	244.426	217.371	51.406	−95.514	−106.077	2.916
2000	35.600	246.246	218.769	54.953	−95.590	−106.631	2.785
2100	35.830	247.989	220.119	58.525	−95.665	−107.181	2.666
2200	36.040	249.660	221.424	62.119	−95.742	−107.727	2.558
2300	36.233	251.267	222.687	65.732	−95.820	−108.270	2.459
2400	36.411	252.812	223.910	69.365	−95.903	−108.810	2.368
2500	36.575	254.302	225.097	73.014	−95.991	−109.346	2.285
2600	36.728	255.740	226.248	76.679	−96.086	−109.878	2.207
2700	36.870	257.129	227.366	80.359	−96.188	−110.407	2.136
2800	37.002	258.472	228.453	84.053	−96.298	−110.932	2.069
2900	37.127	259.772	229.511	87.760	−96.418	−111.452	2.007
3000	37.243	261.033	230.540	91.478	−96.547	−111.968	1.950
3100	37.354	262.256	231.544	95.208	−96.685	−112.480	1.895
3200	37.458	263.444	232.522	98.949	−96.834	−112.987	1.844
3300	37.557	264.598	233.477	102.699	−96.992	−113.490	1.796
3400	37.651	265.720	234.409	106.460	−97.159	−113.987	1.751
3500	37.740	266.813	235.319	110.229	−97.334	−114.480	1.709
3600	37.826	267.878	236.209	114.008	−97.518	−114.967	1.668
3700	37.908	268.915	237.079	117.795	−97.708	−115.449	1.630
3800	37.987	269.927	237.930	121.589	−97.905	−115.926	1.594
3900	38.063	270.915	238.763	125.392	−98.107	−116.397	1.559
4000	38.137	271.879	239.579	129.202	−98.313	−116.864	1.526
4100	38.208	272.822	240.378	133.019	−98.521	−117.325	1.495
4200	38.276	273.744	241.162	136.843	−98.731	−117.781	1.465
4300	38.343	274.645	241.930	140.674	−98.942	−118.232	1.436
4400	38.408	275.527	242.684	144.512	−99.152	−118.678	1.409
4500	38.471	276.391	243.423	148.356	−99.360	−119.120	1.383
4600	38.532	277.237	244.149	152.206	−99.564	−119.557	1.358
4700	38.592	278.067	244.862	156.062	−99.764	−119.989	1.334
4800	38.651	278.880	245.562	159.924	−99.959	−120.417	1.310
4900	38.708	279.677	246.250	163.792	−100.147	−120.842	1.288
5000	38.764	280.460	246.927	167.666	−100.328	−121.262	1.267
5100	38.819	281.228	247.592	171.545	−100.499	−121.679	1.246
5200	38.873	281.982	248.246	175.430	−100.662	−122.093	1.226
5300	38.927	282.723	248.889	179.320	−100.814	−122.503	1.207
5400	38.979	283.451	249.523	183.215	−100.954	−122.911	1.189
5500	39.030	284.167	250.146	187.116	−101.083	−123.317	1.171
5600	39.081	284.871	250.760	191.021	−101.198	−123.720	1.154
5700	39.131	285.563	251.364	194.932	−101.300	−124.121	1.137
5800	39.181	286.244	251.960	198.847	−101.387	−124.520	1.121
5900	39.230	286.914	252.547	202.768	−101.460	−124.919	1.106
6000	39.278	287.574	253.125	206.693	−101.517	−125.316	1.091

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

$S°(298.15\ K) = 236.504 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -71.5 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -74.5 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	ϵ_i
$^1A'$	0	1
$^3A''$	[22000]	3

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
3609.5(1)
1239.4(1)
725 (1)

Point Group: C_s σ = 1
Bond Distances: O–Cl = 1.689 ± 0.003 Å; O–H = 0.960 ± 0.005 Å
Bond Angle: H–O–Cl = 102.5 ± 0.5°
Product of the Moments of Inertia: $4.2740 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

Our adopted value of $\Delta_f H°$(HOCl, g, 298.15 K) is based on the ultraviolet photometric equilibrium measurements of Knauth *et al.*[1] who determined $K_{333} = 0.132 \pm 0.008$ for the reaction $Cl_2O(g) + H_2O(g) = 2\ HOCl(g)$. Combining this result with JANAF auxiliary data,[2] we obtain $\Delta_f H°(298.15\ K) = 2.66 \pm 0.10\ kcal \cdot mol^{-1}$. When this result is combined with $\Delta_f H°(H_2O, g, 298.15\ K) = -57.795 \pm 0.01\ kcal \cdot mol^{-1}$ [3] and $\Delta_f H°(Cl_2O, g, 298.15\ K) = 19.46 \pm 0.4\ kcal \cdot mol^{-1}$ from Alqasmi *et al.*,[4] we obtain $\Delta_f H°$(HOCl, g, 298.15 K) = −17.8 ± 0.5 kcal·mol^{-1}. This is in agreement with $\Delta_f H°$(HOCl, g, 298.15 K) = −18.0 kcal·mol^{-1} derived from similar equilibrium measurements of Molina and Molina.[5] Niki *et al.*[6] also measured the gas phase equilibrium constant for the same reaction using an infrared method and obtained K(295 K) = 0.068 ± 0.01, from which we derive $\Delta_r H°(298.15\ K) = 2.75 \pm 0.2\ kcal \cdot mol^{-1}$, and $\Delta_f H°$(HOCl, g, 298.15 K) = −17.8 ± 0.6 kcal·mol^{-1} using the same auxiliary data as above. Hirsch *et al.*[7] have calculated a value of $\Delta_f H°$(HOCl, g, 298.15 K) = −19.2 ± 4 kcal·mol^{-1} from ab initio results.

Connick and Chia[8] determined $\Delta_r H°(298.15\ K) = 5.06 \pm 0.13\ kcal \cdot mol^{-1}$ for the reaction $Cl_2(aq) + H_2O(l) = H^+(aq) + Cl^-(aq) + HOCl(aq)$. The auxiliary data[3] $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$, $\Delta_f H°(Cl^-, aq, 298.15\ K) = -39.933\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Cl_2, aq, 298.15\ K) = -5.6\ kcal \cdot mol^{-1}$ [9] give $\Delta_f H°$(HOCl, aq, 298.15 K) = −28.92 ± 0.2 kcal·mol^{-1}. Similarly, Morris[10] determined $\Delta_r G°(298.15\ K) = 10.282\ kcal \cdot mol^{-1}$ for the reaction $HOCl(aq) = H^+(aq) + OCl^-(aq)$. Using entropies from NBS Tech Note 270–3[9] we obtain $\Delta_r H°(298.15\ K) = 3.13 \pm 0.5\ kcal \cdot mol^{-1}$, which when combined with auxiliary data from NBS Tech Note 270–3,[9] leads to $\Delta_f H°$(HOCl, aq, 298.15 K) = −28.73 ± 0.5 kcal·mol^{-1}. Combining the former value of $\Delta_f H°$(HOCl, aq, 298.15 K) with our adopted value for $\Delta_f H°$(HOCl, g, 298.15 K), we obtain $\Delta_r H°(298.15\ K) = -11.8 \pm 0.6\ kcal \cdot mol^{-1}$ for the heat of solution at infinite dilution of HOCl(g).

Heat Capacity and Entropy

The molecular structure given above is taken from the microwave work of Mirri *et al.*[11] The rotational constants used to determine the moments of inertia are taken from the high resolution infrared spectrum of Wells *et al.*[12] for the ν_1 vibrational band and are in reasonable agreement with rotational constants calculated from the above structure (the product of the moments of inertia calculated is 2% lower than our adopted value of $I_A I_B I_C$). Rotational constants are adjusted for the natural isotopic abundance of Cl and are $A_0 = 20.463\ cm^{-1}$, $B_0 = 0.50214\ cm^{-1}$, and $C_0 = 0.48910\ cm^{-1}$. Vibrational frequencies are taken from Wells *et al.* (12 (ν_1)) and from Ashby (13 (ν_2, ν_3)) Values of are adjusted for the natural isotopic abundance of chlorine. The vibrations are expected to be anharmonic[11] but no anharmonicity constants are available. The lowest-lying excited state has been calculated to lie at 22,000 cm^{-1}.[14] Omission of this state reduces $C_p°$ by 0.02 cal·K^{-1}·mol^{-1} and $S°$ by 0.002 cal·K^{-1}·mol^{-1} at 3000 K.

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Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.224	−71.533	−71.533	INFINITE
100	33.284	198.866	267.844	−6.898	−72.615	−69.350	36.225
200	34.588	222.209	239.823	−3.523	−73.561	−65.717	17.164
250	35.898	230.063	237.110	−1.762	−74.037	−63.701	13.310
298.15	37.285	236.504	236.504	0.	−74.475	−61.670	10.804
300	37.339	236.735	236.505	0.069	−74.491	−61.591	10.724
350	38.759	242.599	236.965	1.972	−74.911	−59.407	8.866
400	40.077	247.862	238.004	3.943	−75.291	−57.165	7.465
450	41.260	252.652	239.369	5.977	−75.634	−54.879	6.370
500	42.307	257.054	240.920	8.067	−75.943	−52.556	5.490
600	44.045	264.928	244.281	12.388	−76.483	−47.826	4.164
700	45.437	271.825	247.733	16.864	−76.939	−43.013	3.210
800	46.604	277.971	251.136	21.468	−77.330	−38.139	2.490
900	47.625	283.520	254.431	26.180	−77.667	−33.219	1.928
1000	48.538	288.586	257.597	30.989	−77.960	−28.265	1.476
1100	49.366	293.252	260.629	35.885	−78.213	−23.283	1.106
1200	50.118	297.580	263.530	40.860	−78.433	−18.279	0.796
1300	50.800	301.619	266.306	45.907	−78.624	−13.258	0.533
1400	51.418	305.406	268.965	51.018	−78.792	−8.224	0.307
1500	51.977	308.973	271.514	56.188	−78.942	−3.178	0.111
1600	52.481	312.344	273.962	61.411	−79.078	1.878	−0.061
1700	52.936	315.540	276.314	66.683	−79.204	6.941	−0.213
1800	53.346	318.577	278.579	71.997	−79.323	12.012	−0.349
1900	53.716	321.471	280.761	77.351	−79.439	17.089	−0.470
2000	54.049	324.235	282.866	82.739	−79.556	22.173	−0.579
2100	54.351	326.880	284.899	88.159	−79.675	27.262	−0.678
2200	54.625	329.415	286.865	93.608	−79.800	32.357	−0.768
2300	54.874	331.848	288.769	99.084	−79.933	37.458	−0.851
2400	55.101	334.189	290.613	104.583	−80.075	42.565	−0.926
2500	55.310	336.442	292.401	110.103	−80.229	47.678	−0.996
2600	55.502	338.615	294.137	115.644	−80.397	52.798	−1.061
2700	55.679	340.714	295.823	121.203	−80.578	57.924	−1.121
2800	55.846	342.741	297.463	126.779	−80.775	63.058	−1.176
2900	56.002	344.704	299.058	132.372	−80.987	68.198	−1.228
3000	56.151	346.605	300.612	137.980	−81.216	73.346	−1.277
3100	56.294	348.449	302.125	143.602	−81.460	78.502	−1.323
3200	56.432	350.238	303.601	149.238	−81.719	83.666	−1.366
3300	56.567	351.977	305.041	154.888	−81.993	88.839	−1.406
3400	56.699	353.667	306.446	160.551	−82.281	94.020	−1.444
3500	56.832	355.313	307.819	166.228	−82.582	99.209	−1.481
3600	56.964	356.916	309.161	171.918	−82.894	104.408	−1.515
3700	57.098	358.478	310.472	177.621	−83.215	109.615	−1.547
3800	57.233	360.003	311.756	183.337	−83.544	114.831	−1.578
3900	57.371	361.491	313.012	189.068	−83.879	120.056	−1.608
4000	57.512	362.945	314.242	194.812	−84.219	125.289	−1.636
4100	57.656	364.367	315.448	200.570	−84.561	130.532	−1.663
4200	57.805	365.758	316.629	206.343	−84.903	135.782	−1.689
4300	57.957	367.120	317.788	212.131	−85.243	141.040	−1.713
4400	58.113	368.455	318.924	217.935	−85.580	146.306	−1.737
4500	58.273	369.762	320.039	223.754	−85.911	151.580	−1.759
4600	58.438	371.045	321.134	229.589	−86.236	156.861	−1.781
4700	58.607	372.303	322.209	235.442	−86.551	162.149	−1.802
4800	58.779	373.539	323.266	241.311	−86.856	167.444	−1.822
4900	58.956	374.753	324.304	247.198	−87.149	172.745	−1.841
5000	59.136	375.946	325.325	253.102	−87.429	178.052	−1.860
5100	59.319	377.119	326.329	259.025	−87.695	183.365	−1.878
5200	59.505	378.272	327.317	264.966	−87.945	188.682	−1.895
5300	59.695	379.408	328.289	270.926	−88.178	194.004	−1.912
5400	59.886	380.525	329.246	276.905	−88.394	199.330	−1.928
5500	60.079	381.626	330.189	282.903	−88.592	204.660	−1.944
5600	60.274	382.710	331.117	288.921	−88.771	209.994	−1.959
5700	60.471	383.779	332.032	294.958	−88.931	215.330	−1.973
5800	60.668	384.832	332.933	301.015	−89.071	220.670	−1.987
5900	60.866	385.871	333.821	307.092	−89.191	226.010	−2.001
6000	61.063	386.895	334.697	313.188	−89.291	231.354	−2.014

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$S°(298.15\ K) = 250.761 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-132.77 \pm 8]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-141.84 \pm 8]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2201(1)	2211(2)
945(1)	952(2)
551(1)	663(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.486 ± 0.008 Å; Si–Cl = 2.049 Å
Bond Angles: H–Si–H = 110.42° ± 0.5°; H–Si–Cl = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 1.60170 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated from values for $SiCl_4$, $SiHCl_3$ and SiH_4.[1] Data for $SiHCl_3$[1] suggest that $\Delta_f H°$ shows minor deviations from linearity in the chlorosilanes. We assume that $\Delta_f H°$ has a cubic variation with a constant third difference of −1.5 kcal·mol^{-1}. $\Delta_f H°$ values of the chloromethanes yield an almost constant third difference of about −2.5 kcal·mol^{-1}.[2,3,1] This approximation corresponds to Allen's bond additivity scheme involving near–neighbor interactions taken two and three at a time.[2] Our adopted $\Delta_f H°$ is 0.4 kcal·mol^{-1} more negative than that estimated by linear interpolation between $SiCl_4$ and SiH_4.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley *et al.*[4] for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structures obtained by various methods.[5] The principal moments of inertia are $I_A = 0.9972 \times 10^{-39}$ and $I_B = I_C = 12.6739 \times 10^{-39}\ g·cm^2$.

Shimanouchi[6] selected vibrational frequencies from gas–phase infrared spectra of SiH_3X (X=F, Cl, Br) observed by Newman *et al.*[7] These authors' assignments for SiH_3F and SiH_3Br have been modified slightly by new data[1] obtained at higher resolution. Unpublished gas–phase frequencies of SiH_3X from the thesis of Robiette were quoted by Ball *et al.*[8] These are more consistent with the new data for SiH_3F and SiH_3Br, so we adopt them for SiH_3Cl. Monfils also obtianed partially resolved spectra of SiH_3Cl; his final paper[9] is not available to us.

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3Cl.[10] Electronic absorption bands of SiH_3Cl were observed at ≥67000 cm^{-1} [11] and the absorption maximum in the lowest transition was estimated to be at ~62000 cm^{-1}.[12] Contributions of these high–lying states would be negligible.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.441	−132.769	−132.769	INFINITE
100	33.561	207.803	288.915	−8.111	−135.660	−131.498	68.688
200	40.360	232.644	255.088	−4.489	−138.776	−126.152	32.948
250	45.846	242.233	251.574	−2.335	−140.376	−122.810	25.660
298.15	51.098	250.761	250.761	0.	−141.838	−119.292	20.900
300	51.292	251.078	250.762	0.095	−141.891	−119.152	20.746
350	56.258	259.365	251.406	2.786	−143.268	−115.252	17.200
400	60.660	267.171	252.893	5.711	−144.490	−111.164	14.517
450	64.557	274.545	254.893	8.843	−145.561	−106.932	12.412
500	68.034	281.530	257.210	12.160	−146.489	−102.589	10.717
600	74.008	294.480	262.361	19.272	−147.963	−93.663	8.154
700	78.961	306.272	267.804	26.928	−148.998	−84.525	6.307
800	83.092	317.093	273.298	35.036	−149.677	−75.265	4.914
900	86.538	327.085	278.726	43.523	−150.074	−65.937	3.827
1000	89.411	336.356	284.031	52.325	−150.257	−56.577	2.955
1100	91.809	344.994	289.185	61.390	−150.282	−47.206	2.242
1200	93.817	353.071	294.176	70.674	−150.195	−37.839	1.647
1300	95.504	360.649	299.001	80.142	−150.034	−28.482	1.144
1400	96.929	367.780	303.662	89.766	−149.830	−19.140	0.714
1500	98.140	374.510	308.163	99.521	−149.606	−9.812	0.342
1600	99.174	380.878	312.510	109.388	−149.382	−0.500	0.016
1700	100.062	386.917	316.711	119.351	−199.349	9.245	−0.284
1800	100.829	392.659	320.772	129.396	−198.933	21.504	−0.624
1900	101.496	398.129	324.701	139.513	−198.508	33.738	−0.928
2000	102.077	403.350	328.504	149.693	−198.082	45.951	−1.200
2100	102.587	408.343	332.188	159.926	−197.660	58.142	−1.446
2200	103.037	413.126	335.759	170.208	−197.247	70.313	−1.669
2300	103.435	417.715	339.223	180.532	−196.846	82.466	−1.873
2400	103.789	422.125	342.586	190.894	−196.460	94.602	−2.059
2500	104.105	426.368	345.853	201.289	−196.092	106.722	−2.230
2600	104.388	430.457	349.029	211.714	−195.745	118.828	−2.387
2700	104.642	434.402	352.118	222.165	−195.419	130.920	−2.533
2800	104.872	438.211	355.125	232.641	−195.116	143.001	−2.668
2900	105.079	441.895	358.054	243.139	−194.838	155.072	−2.793
3000	105.268	445.461	360.909	253.656	−194.585	167.133	−2.910
3100	105.439	448.915	363.692	264.192	−194.357	179.187	−3.019
3200	105.596	452.265	366.408	274.744	−194.156	191.233	−3.122
3300	105.739	455.517	369.059	285.311	−193.981	203.274	−3.218
3400	105.870	458.675	371.649	295.891	−193.831	215.310	−3.308
3500	105.991	461.746	374.179	306.484	−193.708	227.341	−3.393
3600	106.102	464.734	376.653	317.089	−577.761	249.831	−3.625
3700	106.205	467.642	379.073	327.705	−577.273	272.813	−3.851
3800	106.300	470.476	381.442	338.330	−576.811	295.782	−4.066
3900	106.388	473.238	383.760	348.964	−576.373	318.739	−4.269
4000	106.470	475.933	386.031	359.607	−575.958	341.685	−4.462
4100	106.546	478.563	388.256	370.258	−575.564	364.621	−4.645
4200	106.617	481.131	390.437	380.916	−575.191	387.548	−4.820
4300	106.683	483.641	392.575	391.581	−574.836	410.466	−4.986
4400	106.745	486.094	394.673	402.253	−574.499	433.376	−5.145
4500	106.803	488.493	396.731	412.930	−574.177	456.279	−5.296
4600	106.857	490.841	398.751	423.613	−573.870	479.174	−5.441
4700	106.908	493.140	400.735	434.302	−573.576	502.063	−5.580
4800	106.955	495.391	402.684	444.995	−573.293	524.947	−5.713
4900	107.000	497.597	404.599	455.693	−573.021	547.824	−5.840
5000	107.043	499.759	406.480	466.395	−572.758	570.696	−5.962
5100	107.083	501.879	408.330	477.101	−572.502	593.562	−6.079
5200	107.120	503.959	410.149	487.811	−572.252	616.424	−6.192
5300	107.156	506.000	411.938	498.525	−572.007	639.280	−6.300
5400	107.190	508.003	413.699	509.242	−571.766	662.133	−6.405
5500	107.222	509.970	415.432	519.963	−571.526	684.980	−6.505
5600	107.252	511.902	417.137	530.687	−571.288	707.824	−6.602
5700	107.280	513.801	418.816	541.413	−571.049	730.663	−6.696
5800	107.308	515.667	420.470	552.143	−570.809	753.498	−6.786
5900	107.334	517.502	422.099	562.875	−570.567	776.328	−6.873
6000	107.358	519.306	423.704	573.609	−570.319	799.155	−6.957

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 94.86 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs2} = 242.6\ K$
$T_{trs1} = 457.7\ K$
$T_{fus} = 793.2\ K$
$T_{dcm} = 612\ K$

$\Delta_f H°(0\ K) = -311.391 \pm 0.84\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -314.553 \pm 0.84\ kJ \cdot mol^{-1}$
$\Delta_{trs2} = 1.046\ kJ \cdot mol^{-1}$
$\Delta_{trs1} = 3.950\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The equilibrium pressures for the reaction $NH_4Cl(cr) = NH_3(g) + HCl(g)$, at 320–636 K, have been measured by many investigators. Smits and de Lange,[2] using the densi–tensimeter, determined the vapor pressure of $NH_4Cl(cr)$ and the density of the saturated vapor simultaneously. The results obtained indicate that within the range 527–626 K the saturated vapor completely dissociates into gaseous NH_3 and HCl. Based on this conclusion, the reported vapor pressure data were employed to evaluate the enthalpy of dissociation of $NH_4Cl(cr)$ by both the 2nd and 3rd law methods. The results are presented as follows.

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
[1]	521.6–619.1	43.18 ± 0.08	42.11	−2.0 ± 0.2
[2]	527.9–625.6	42.16 ± 0.22	42.14	−0.2 ± 0.4
[3]	525.4–615.0	42.02 ± 0.06	42.20	0.2 ± 0.1
[4]	471.3–557.0	42.43 ± 0.09	42.08	−0.3 ± 0.2
[5]	319.0–352.7	43.83 ± 0.38	42.17	−4.9 ± 1.1
[6]	503.4–611.4	41.27 ± 0.38	42.12	1.3 ± 0.8

The value of $\Delta_r H°(298.15\ K)$ adopted is 42.15 ± 0.10 kcal·mol^{-1}, yielding $\Delta_f H°(NH_4Cl, cr, 298.15\ K) = -75.8 \pm 0.20$ kcal·mol^{-1}. The corresponding $\Delta_f H°(298.15\ K)$ value evaluated from solution data, selected by Parker[7] is 42.06 kcal·mol^{-1}.

Heat Capacity and Entropy

The heat capacities (20.1–523.2 K) of $NH_4Cl(cr)$ have been measured by the following investigators: Ewald 138–301 K;[8] Simon 20.1–290.8 K;[9] Klinhardt 323.2–523.2 K;[10] Simon *et al.* 204.5–275.8 K;[11] Ziegler and Messer 107.2–320.2 K;[12] Extermann and Weigle 228.2–248.2[13] and Popov and Galchenko 373.2–523.2 K.[14] These $C_p°$ data were plotted and a smooth $C_p°$ curve was drawn and adopted. The $C_p°$ values above 523 K were obtained by graphical extrapolation of the previous $C_p°$ curve. $S°(298.15\ K)$ was derived from the adopted low temperature data, based on $S°(20.1\ K) = 0.114\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

There are two transitions reported in the literature. The low temperature transition data (T_{trs2} and $\Delta_{trs2}H°$) were derived based on the heat capacity (107–320 K) data reported by Ziegler and Messer,[12] in which the other T_{trs2} values given by previous investigators were reviewed. The high temperature transition data (T_{trs1} and $\Delta_{trs1}H°$) were taken from Klinkhardt.[10] However, $\Delta_{trs1}H° = 1030$ and $\Delta H°(463.5\ K) = 1059.1 \pm 8.0$ cal·mol^{-1} were reported by Scheffer,[13] and Popov and Galchenko,[14] respectively. Markowitz and Boryta[6] determined T_{trs1} to be 459.5 ± 0.5 K.

Fusion Data

T_{fus} was obtained from Rassow.[15]

Decomposition Data

The value of T_{dcm} was calculated as the temperature at which the vapor pressure of the decomposition products (NH_3 and HCl) equals 1 atm. By differential thermal analysis, T_{dcm} for $NH_4Cl(cr)$ was determined to be 611.4 K by Markowitz and Boryta.[6]

References

[1] A. Smith and R. P. Calvert, J. Amer. Chem. Soc. **36**, 1363 (1914), using isoteniscope.
[2] A. Smits and W. D. Lange, J. Chem. Soc. 2944 (1928), using densi–tensimeter.
[3] H. Braune and S. Knoke, Z. Phys. Chem. **135**, 49 (1928), Spiral Manometer.
[4] W. H. Rodebush and J. C. Michalek, J. Amer. Chem. Soc. **51**, 748 (1929), glass diaphragm manometer.
[5] H. Wagner and K. Neumann, Z. Phys. Chem. **28**, 51 (1961), torsion–effusion method.
[6] M. M. Markowitz and D. A. Boryta, J. Phys. Chem. **66**, 1477 (1962), differential thermal analysis.
[7] V. B. Parker, NSRDS–NBS 2, (1965).
[8] R. Ewald, Ann. Physik, **44**, 1213 (1914).
[9] F. Simon, Ann. Physik, **68**, 241 (1922).

Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	.000	.000	INFINITE	−22.698	−311.391	−311.391	INFINITE
100	37.656	24.552	163.795	−13.924	−311.523	−276.392	144.372
200	67.111	59.752	103.140	−8.678	−314.638	−239.828	62.637
298.15	86.441	94.860	94.860	.000	−314.553	−203.092	35.581
300	86.944	95.396	94.861	.160	−314.558	−202.400	35.241
400	102.968	122.642	98.467	9.670	−314.054	−165.049	21.553
457.700	109.956	136.945	102.428	15.798	II <--> III		
457.700	85.898	145.537	102.428	19.731	TRANSITION		
500	90.500	153.330	106.407	23.462	−309.363	−128.299	13.403
600	101.671	170.818	115.701	33.071	−308.920	−92.110	8.019
700	112.801	187.327	124.764	43.795	−307.429	−56.079	4.185
800	123.888	203.114	133.577	55.629	−304.904	−20.332	1.328
900	134.976	218.360	142.155	68.585	−301.346	15.037	−.873
1000	144.557	233.090	150.517	82.573	−296.853	49.958	−2.610
1100	152.716	247.259	158.672	97.446	−291.583	84.389	−4.007
1200	159.829	260.861	166.625	113.083	−285.657	118.312	−5.150
1300	165.686	273.889	174.378	129.364	−279.201	151.717	−6.096
1400	171.000	286.365	181.935	146.203	−272.298	184.609	−6.888
1500	175.728	298.328	189.298	163.544	−265.002	216.992	−7.556

PREVIOUS: December 1960 CURRENT: September 1965

$S°(298.15\ K) = 184.180 \pm 1.26\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 513.15\ K$
$T_{dcm} = [513]\ K$

$\Delta_f H°(0\ K) = -277.78 \pm 0.17\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -295.77 \pm 0.17\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 9.6 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Gilliland and Johnson[1] and Birky and Hepler[2] have derived the enthalpy of formation for NH_4ClO_4(cr) from solution–calorimetric measurements. Thier values are -70.74 ± 0.32 and -70.63 kcal·mol^{-1}, respectively. The mean of these is adopted here.

Heat Capacity and Entropy

Justice and Westrum[3] have measured the heat capacity from 5 to 350 K. The $C_p°$ values above 350 K were extrapolated. From the partial molar entropies of NH_{4+}(aq) and ClO_{4l-}(aq) and the entropy of solution, Birky and Hepler[2] calculated a value of 43.6 cal·K^{-1}·mol^{-1} for $S°(298.15\ K)$. The fair agreement of this value with that derived from $C_p°$ suggests that there is no residual entropy at 0 K, as there would be if the NH_4^+ ion had a random orientation.

Transition and Decomposition Data

T_{trs} and $\Delta_{trs}H°$ were obtained (under a pressure of NH_3) by Markowitz.[4] T_{dcm} was estimated from the report by Markowitz.[4]

References

[1]A. A. Gilliland and W. H. Johnson, J. Res. Nat. Bur. Stand. **65A**, 67 (1961).
[2]M. M. Birky and L. G. Hepler, J. Phys. Chem. **64**, 686 (1960).
[3]B. H. Justice and E. F. Westrum, Univ. of Michigan, Ann Arbor, Mich., personal communication, (April 1961).
[4]M. M. Markowitz, Foote Mineral Company, Exton, Pennsylvania, personal communication, (September 20, 1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−25.238	−277.778	−277.778	INFINITE
100	79.622	72.894	283.140	−21.025	−288.280	−223.321	116.651
200	107.236	137.419	195.200	−11.556	−292.995	−156.325	40.828
298.15	128.072	184.180	184.180	0.	−295.767	−88.607	15.524
300	128.449	184.973	184.182	0.237	−295.804	−87.322	15.204
400	148.699	224.699	189.462	14.095	−296.894	−17.615	2.300
500	168.950	260.052	200.101	29.975	−296.232	52.165	−5.450
513.150	171.628	264.472	201.694	32.215	I <--> II		
513.150	179.996	283.226	201.694	41.838	TRANSITION		
600	197.568	312.708	215.652	58.234	−283.459	119.958	−10.443
700	217.819	344.684	231.823	79.003	−278.431	186.822	−13.941
800	238.070	375.092	247.845	101.797	−271.621	252.842	−16.509
900	258.456	404.312	263.616	126.626	−263.001	317.902	−18.451
1000	278.571	432.586	279.107	153.480	−252.567	381.904	−19.949
1100	299.569	460.142	294.317	182.408	−240.258	444.771	−21.120
1200	317.984	487.016	309.260	213.307	−226.169	506.437	−22.045
1300	333.816	513.111	323.943	245.919	−210.548	566.864	−22.777
1400	347.066	538.350	338.362	279.984	−193.645	626.039	−23.358
1500	357.732	562.674	352.510	315.246	−175.712	683.966	−23.818

PREVIOUS: September 1961 CURRENT: December 1962

$S°(298.15\ K) = 260.005\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 82.54 \pm 9.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 78.45 \pm 9.6\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma^+$	0	2

$\omega_e = 290.94\ cm^{-1}$ $\omega_e x_e = 1.5844\ cm^{-1}$ $\sigma = 1$
$B_e = [0.1121]\ cm^{-1}$ $\alpha_e = [0.0007]\ cm^{-1}$ $r_e = 2.23$ Å

Enthalpy of Formation

Gaydon[1] gives 23 ± 2.3 kcal·mol^{-1} for the heat of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants from Wieland[2] were weighted according to their natural isotopic abundances. Rotational constants were estimated using equation III.[3] Bond length was given by Herzberg.[3]

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall, London (1953).
[2]K. Wieland, Z. Elektrochem. **64**, 761 (1960).
[3]G. Herzberg, "Spectra of Diatomic Molecules," equation III, 123 p. 108, Van Nostrand, New York (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.846	82.537	82.537	INFINITE
100	31.476	222.563	291.359	−6.880	82.342	73.258	−38.266
200	35.116	245.701	263.302	−3.520	81.598	64.458	−16.835
250	35.926	253.632	260.602	−1.743	78.869	60.376	−12.615
298.15	36.420	260.005	260.005	0.	78.450	56.853	−9.960
300	36.435	260.230	260.005	0.067	78.434	56.719	−9.876
350	36.778	265.874	260.450	1.898	78.016	53.133	−7.930
400	37.023	270.802	261.443	3.744	77.610	49.606	−6.478
450	37.207	275.173	262.730	5.599	77.211	46.130	−5.355
500	37.353	279.101	264.174	7.464	76.817	42.697	−4.461
600	37.574	285.932	267.248	11.211	76.034	35.947	−3.129
700	37.740	291.737	270.342	14.977	16.490	35.899	−2.679
800	37.878	296.786	273.339	18.758	16.342	38.682	−2.526
900	37.998	301.254	276.197	22.552	16.198	41.483	−2.408
1000	38.107	305.263	278.907	26.357	16.056	44.300	−2.314
1100	38.209	308.900	281.471	30.173	15.918	47.132	−2.238
1200	38.306	312.229	283.897	33.998	15.784	49.975	−2.175
1300	38.399	315.299	286.196	37.834	15.655	52.830	−2.123
1400	38.490	318.148	288.378	41.678	15.530	55.694	−2.078
1500	38.579	320.806	290.452	45.532	15.409	58.567	−2.039
1600	38.667	323.299	292.428	49.394	15.293	61.448	−2.006
1700	38.753	325.646	294.314	53.265	15.181	64.336	−1.977
1800	38.839	327.863	296.116	57.145	15.073	67.231	−1.951
1900	38.924	329.966	297.843	61.033	14.969	70.131	−1.928
2000	39.009	331.964	299.500	64.929	14.869	73.037	−1.908
2100	39.093	333.870	301.091	68.834	14.771	75.948	−1.889
2200	39.176	335.690	302.623	72.748	14.675	78.863	−1.872
2300	39.260	337.433	304.099	76.670	14.581	81.783	−1.857
2400	39.343	339.106	305.523	80.600	14.489	84.707	−1.844
2500	39.425	340.714	306.898	84.538	14.396	87.635	−1.831
2600	39.508	342.262	308.229	88.485	14.303	90.566	−1.819
2700	39.591	343.754	309.517	92.440	14.209	93.501	−1.809
2800	39.673	345.196	310.766	96.403	14.115	96.439	−1.799
2900	39.755	346.589	311.977	100.374	14.018	99.381	−1.790
3000	39.837	347.938	313.154	104.354	13.920	102.327	−1.782
3100	39.919	349.246	314.297	108.342	13.821	105.275	−1.774
3200	40.001	350.515	315.409	112.338	13.720	108.227	−1.767
3300	40.083	351.747	316.492	116.342	13.619	111.182	−1.760
3400	40.165	352.945	317.546	120.355	13.518	114.140	−1.754
3500	40.247	354.110	318.574	124.375	13.417	117.101	−1.748
3600	40.329	355.245	319.577	128.404	13.317	120.064	−1.742
3700	40.410	356.351	320.556	132.441	13.221	123.031	−1.737
3800	40.492	357.430	321.512	136.486	13.127	126.000	−1.732
3900	40.574	358.483	322.447	140.539	13.039	128.972	−1.727
4000	40.655	359.511	323.361	144.601	12.956	131.945	−1.723
4100	40.737	360.516	324.255	148.670	12.881	134.921	−1.719
4200	40.818	361.498	325.130	152.748	12.815	137.898	−1.715
4300	40.900	362.460	325.987	156.834	12.758	140.877	−1.711
4400	40.981	363.401	326.826	160.928	12.712	143.857	−1.708
4500	41.063	364.323	327.650	165.030	12.678	146.838	−1.704
4600	41.144	365.226	328.457	169.141	12.657	149.820	−1.701
4700	41.226	366.112	329.248	173.259	12.650	152.802	−1.698
4800	41.307	366.981	330.026	177.386	12.658	155.784	−1.695
4900	41.389	367.833	330.788	181.521	12.682	158.765	−1.692
5000	41.470	368.670	331.538	185.664	12.723	161.746	−1.690
5100	41.551	369.492	332.274	189.815	12.781	164.726	−1.687
5200	41.633	370.300	332.997	193.974	12.856	167.705	−1.685
5300	41.714	371.094	333.709	198.141	12.950	170.682	−1.682
5400	41.796	371.874	334.408	202.317	13.062	173.657	−1.680
5500	41.877	372.642	335.097	206.500	13.192	176.630	−1.677
5600	41.958	373.397	335.774	210.692	13.341	179.600	−1.675
5700	42.040	374.141	336.440	214.892	13.509	182.567	−1.673
5800	42.121	374.873	337.097	219.100	13.695	185.532	−1.671
5900	42.202	375.593	337.743	223.316	13.900	188.493	−1.669
6000	42.284	376.303	338.380	227.541	14.122	191.450	−1.667

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

$S°(298.15\ K) = 97.927\ J·K^{-1}·mol^{-1}$
$T_{fus} = 300.53\ K$

$\Delta_f H°(0\ K) = -36.395 \pm 0.105\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -35.422 \pm 0.105\ kJ·mol^{-1}$
$\Delta_{fus} H° = 11.602 \pm 0.008\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is that adopted by Calder and Giauque[1] from an analysis of the equilibrium data of McMorris and Yost[2] and Beeson and Yost.[3] This yielded a enthalpy of formation of ICl(g), from which the heat of formation of ICl(cr) was calculated by using the heat of vaporization determined by Calder and Giauque.[1]

Heat Capacity and Entropy

The heat capacity has been measured by Calder and Giauque[1] from 17–322 K. The entropy was calculated based on $S°(15\ K) = 0.592\ cal·K^{-1}·mol^{-1}$. Above 300 K the heat capacity data was extrapolated smoothly.

Fusion Data

All data were measured by Calder and Giauque.[1]

References

[1]G. V. Calder and W. F. Giauque, J. Phys. Chem. **69**, 2443 (1965).
[2]J. McMorris and D. M. Yost, J. Amer. Chem. Soc. **54**, 2247 (1932).
[3]C. M. Beeson and D. M. Yost, J. Chem. Phys. **7**, 44 (1939).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.163	−36.395	−36.395	INFINITE
100	40.246	45.693	143.013	−9.732	−36.945	−29.015	15.156
200	49.539	77.011	102.805	−5.159	−36.357	−21.267	5.554
298.15	55.229	97.927	97.927	0.	−35.422	−14.049	2.461
300	55.325	98.268	97.928	0.102	−35.401	−13.917	2.423
300.530	55.589	98.366	97.928	0.131	--- CRYSTAL <---> LIQUID ---		
400	60.195	114.866	100.158	5.883	−42.174	−6.656	0.869
500	64.379	128.756	104.525	12.116	−61.826	4.083	−0.427
600	68.145	140.833	109.591	18.745	−58.889	16.995	−1.480
700	71.489	151.594	114.836	25.731	−55.624	29.389	−2.193
800	74.412	161.335	120.049	33.029	−52.065	41.294	−2.696
900	76.914	170.249	125.139	40.599	−48.250	52.737	−3.061
1000	78.994	178.464	130.066	48.398	−44.220	63.743	−3.330

PREVIOUS: September 1963 CURRENT: September 1965

$S°(298.15\ K) = [136.167]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 300.53\ K$

$\Delta_f H°(298.15\ K) = [-23.929]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 11.602 \pm 0.008\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(300.53\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity from 300.53 to 317.76 K has been measured by Calder and Giauque.[1] Above 318 K it was extrapolated in a smooth manner. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Reference

[1]G. V. Calder and W. F. Giauque, J. Phys. Chem. **69**, 2443 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.759	136.167	136.167	0.	−23.929	−13.958	2.445
300	102.851	136.802	136.168	0.190	−23.821	−13.896	2.420
300.530	103.856	136.972	136.170	0.241	--- CRYSTAL <---> LIQUID ---		
400	98.324	165.893	140.170	10.289	−26.275	−11.168	1.458
500	94.140	187.384	147.559	19.913	−42.536	−5.941	0.621
600	89.956	204.178	155.649	29.117	−37.025	0.853	−0.074
700	85.772	217.730	163.582	37.904	−31.958	6.759	−0.504
800	81.588	228.911	171.071	46.272	−27.329	11.969	−0.781
900	77.404	238.279	178.033	54.221	−23.135	16.625	−0.965
1000	73.220	246.217	184.465	61.753	−19.373	20.837	−1.088

PREVIOUS: September 1963 CURRENT: September 1965

0	to 300.53 K	crystal
above	300.53 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−12.163	−36.395	−36.395	INFINITE
100	40.246	45.693	143.013	−9.732	−36.945	−29.015	15.156
200	49.539	77.011	102.805	−5.159	−36.357	−21.267	5.554
298.15	55.229	97.927	97.927	0.	−35.422	−14.049	2.461
300	55.325	98.268	97.928	0.102	−35.401	−13.917	2.423
300.530	55.589	98.366	97.928	0.131	CRYSTAL <--> LIQUID		
300.530	103.856	136.972	97.928	11.734	TRANSITION		
400	98.324	165.893	111.438	21.782	−26.275	−11.168	1.458
500	94.140	187.384	124.573	31.405	−42.536	−5.941	0.621
600	89.956	204.178	136.494	40.610	−37.025	0.853	−0.074
700	85.772	217.730	147.164	49.397	−31.958	6.759	−0.504
800	81.588	228.911	156.705	57.765	−27.329	11.969	−0.781
900	77.404	238.279	165.263	65.714	−23.135	16.625	−0.965
1000	73.220	246.217	172.972	73.245	−19.373	20.837	−1.088

PREVIOUS: CURRENT: September 1965

$S°(298.15\ K) = 247.567\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 19.141 \pm 0.105\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 17.506 \pm 0.105\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 382.18\ cm^{-1}$ $\omega_e x_e = 1.450\ cm^{-1}$ $\sigma = 1$
$B_e = 0.11298\ cm^{-1}$ $\alpha_e = 0.0005275\ cm^{-1}$ $r_e = 2.327$ Å

Enthalpy of Formation

The dissociation energy from spectroscopic measurements of ICl(g) has been summarized by Evans *et al.*[1] from which they adopt $D_0° = 49.64$ kcal·mol^{-1}. *McMorris and Yost*[2] *and Beeson and Yost*[3] *studied the equilibria* $NOCl = NO + 0.5Cl_2$ and $NO + ICl = NOCl + 0.5I_2(g)$ from which the equilibrium constant of $ICl = 1/2\ Cl_2 + 1/2\ I_2(g)$ can be obtained. Calder and Giauque[4] have used 3rd law analysis to obtain $D_0° = 49.578 \pm 0.025$ kcal·mol^{-1}. This value was adopted yielding $\Delta_f H°(298.15\ K) = 4.184 \pm 0.025$ kcal·mol^{-1} (17.506 ± 0.105 kJ·mol^{-1}).

Heat Capacity and Entropy

The molecular and vibrational constants were obtained from Herzberg.[5] The values were then adjusted for the normal isotopic abundance of chlorine.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.555	19.141	19.141	INFINITE
100	30.179	211.592	277.844	−6.625	19.089	10.430	−5.448
200	33.787	233.701	250.772	−3.414	18.315	2.067	−0.540
250	34.859	241.364	248.149	−1.696	17.910	−1.948	0.407
298.15	35.548	247.567	247.567	0.	17.506	−5.737	1.005
300	35.570	247.787	247.568	0.066	17.490	−5.881	1.024
350	36.056	253.309	248.003	1.857	17.016	−9.740	1.454
400	36.401	258.147	248.975	3.669	8.539	−13.255	1.731
450	36.656	262.450	250.237	5.496	7.461	−15.914	1.847
500	36.849	266.323	251.655	7.334	−13.680	−16.554	1.729
600	37.125	273.067	254.678	11.033	−13.674	−17.130	1.491
700	37.313	278.805	257.725	14.756	−13.671	−17.706	1.321
800	37.452	283.797	260.679	18.494	−13.672	−18.283	1.194
900	37.562	288.215	263.498	22.245	−13.676	−18.859	1.095
1000	37.654	292.177	266.171	26.006	−13.685	−19.434	1.015
1100	37.734	295.770	268.701	29.776	−13.698	−20.009	0.950
1200	37.806	299.056	271.096	33.553	−13.718	−20.582	0.896
1300	37.871	302.085	273.364	37.336	−13.748	−21.152	0.850
1400	37.932	304.894	275.517	41.127	−13.792	−21.720	0.810
1500	37.991	307.513	277.564	44.923	−13.855	−22.285	0.776
1600	38.046	309.966	279.513	48.725	−13.942	−22.844	0.746
1700	38.100	312.274	281.373	52.532	−14.057	−23.397	0.719
1800	38.152	314.454	283.151	56.345	−14.204	−23.942	0.695
1900	38.203	316.518	284.853	60.162	−14.384	−24.478	0.673
2000	38.254	318.479	286.486	63.985	−14.600	−25.004	0.653
2100	38.303	320.346	288.054	67.813	−14.851	−25.518	0.635
2200	38.352	322.129	289.563	71.646	−15.134	−26.020	0.618
2300	38.400	323.835	291.016	75.483	−15.446	−26.508	0.602
2400	38.448	325.470	292.418	79.326	−15.783	−26.982	0.587
2500	38.495	327.041	293.772	83.173	−16.140	−27.441	0.573
2600	38.542	328.552	295.081	87.025	−16.513	−27.886	0.560
2700	38.589	330.007	296.347	90.881	−16.894	−28.316	0.548
2800	38.635	331.411	297.575	94.743	−17.281	−28.732	0.536
2900	38.682	332.768	298.765	98.608	−17.666	−29.134	0.525
3000	38.728	334.080	299.920	102.479	−18.046	−29.523	0.514
3100	38.774	335.351	301.043	106.354	−18.416	−29.899	0.504
3200	38.820	336.582	302.134	110.234	−18.773	−30.264	0.494
3300	38.866	337.778	303.196	114.118	−19.112	−30.618	0.485
3400	38.911	338.939	304.231	118.007	−19.431	−30.962	0.476
3500	38.957	340.067	305.239	121.900	−19.727	−31.296	0.467
3600	39.002	341.165	306.221	125.798	−19.997	−31.623	0.459
3700	39.048	342.234	307.180	129.701	−20.239	−31.943	0.451
3800	39.093	343.276	308.117	133.608	−20.453	−32.256	0.443
3900	39.138	344.292	309.031	137.519	−20.635	−32.564	0.436
4000	39.183	345.284	309.925	141.435	−20.785	−32.868	0.429
4100	39.229	346.252	310.799	145.356	−20.901	−33.169	0.423
4200	39.274	347.198	311.655	149.281	−20.984	−33.467	0.416
4300	39.319	348.123	312.492	153.211	−21.031	−33.763	0.410
4400	39.364	349.027	313.312	157.145	−21.042	−34.059	0.404
4500	39.409	349.912	314.116	161.083	−21.017	−34.355	0.399
4600	39.454	350.779	314.903	165.027	−20.955	−34.652	0.393
4700	39.499	351.628	315.676	168.974	−20.856	−34.951	0.388
4800	39.544	352.460	316.433	172.926	−20.720	−35.252	0.384
4900	39.589	353.276	317.177	176.883	−20.546	−35.557	0.379
5000	39.634	354.076	317.907	180.844	−20.335	−35.866	0.375
5100	39.678	354.861	318.624	184.810	−20.087	−36.178	0.371
5200	39.723	355.632	319.328	188.780	−19.801	−36.497	0.367
5300	39.768	356.389	320.020	192.754	−19.478	−36.821	0.363
5400	39.813	357.133	320.701	196.733	−19.118	−37.151	0.359
5500	39.858	357.864	321.370	200.717	−18.721	−37.489	0.356
5600	39.903	358.582	322.028	204.705	−18.288	−37.834	0.353
5700	39.947	359.289	322.676	208.698	−17.819	−38.187	0.350
5800	39.992	359.984	323.313	212.694	−17.314	−38.549	0.347
5900	40.037	360.668	323.940	216.696	−16.774	−38.919	0.345
6000	40.082	361.342	324.558	220.702	−16.199	−39.300	0.342

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 82.55 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1044\ K$

$\Delta_f H°(0\ K) = -436.38 \pm 0.25\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -436.68 \pm 0.25\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 26.284\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from the enthalpy of hydrolysis of K(cr), the enthalpies of solution of HCl(g) and KCl(cr), and the standard enthalpy of neutralization of a strong acid and strong base. Extensive measurements are available for all these quantities. Values used in the calculation, in addition to the enthalpy of formation for HCl(g), are summarized below.

Source	Reaction	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
1-4	$K(cr) + H_2O(l) \rightarrow KOH(\infty H_2O) + 1/2\ H_2(g)$	-46.966 ± 0.05
5, 2, 6	$HCl(g) \rightarrow HCl(\infty H_2O)$	-17.88 ± 0.015
7	$KCl(\infty H_2O) \rightarrow KCl(cr)$	-4.115 ± 0.010
7	$KOH(\infty H_2O) + HCl(\infty H_2O) \rightarrow KCl(\infty H_2O) + H_2O(l)$	-13.345 ± 0.025

Heat Capacity and Entropy

Low temperature heat capacities were obtained from the data (2.8–275 K) of Berg and Morrison.[8] Previous measurements scatter around the selected values and are in good agreement. These include Strelkov *et al.* (12–298 K),[9] Clusius *et al.* (10–273 K),[10] and Southard and Nelson (17–285 K).[11] For other less extensive data see the review by Kelley and King.[12] The entropy is based on the extrapolation $S°(2.8\ K) = 0.0006\ cal \cdot K^{-1} \cdot mol^{-1}$.

High temperature values are based on enthalpy data (373–1038 K) from Douglas.[13] These values join smoothly with the low temperature values and are in excellent agreement with the enthalpy data (673–933 K) of Skuratov and Lapushkin[14] and the adiabatic heat capacities (334–721 K) of Mustajoki.[15]

Fusion Data

The melting point and enthalpy of melting are from Douglas.[13] Values of T_{fus} = 1043 K and 1045 K have been reported by Aukrust *et al.*[16] and Johnson and Bredig,[17] respectively. The enthalpy of melting is confirmed by $\Delta_{fus} H° = 6.34\ kcal \cdot mol^{-1}$ obtained from enthalpy data by Dworkin and Bredig[18] and $\Delta_{fus} H° = 6.4$ and 6.5 $kcal \cdot mol^{-1}$ based on enthalpy and phase diagram studies of Aukrust *et al.*,[16] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.368	−436.379	−436.379	INFINITE
100	39.200	31.773	125.871	−9.410	−437.610	−427.776	223.447
200	48.438	62.630	87.169	−4.908	−437.221	−418.052	109.184
298.15	51.287	82.554	82.554	0.	−436.684	−408.761	71.613
300	51.329	82.872	82.555	0.095	−436.675	−408.587	71.141
400	53.137	97.895	84.592	5.321	−438.662	−398.837	52.083
500	54.752	109.927	88.494	10.717	−438.160	−388.935	40.632
600	56.317	120.048	92.931	16.270	−437.462	−379.152	33.008
700	58.003	128.852	97.447	21.984	−436.580	−369.501	27.573
800	60.078	136.727	101.873	27.883	−435.508	−359.989	23.505
900	62.911	143.957	106.152	34.024	−434.210	−350.625	20.350
1000	66.969	150.782	110.276	40.505	−432.610	−341.420	17.834
1044.000	69.287	153.713	112.045	43.502	--- CRYSTAL <--> LIQUID ---		
1100	71.965	157.406	114.261	47.460	−509.549	−327.785	15.565
1200	76.149	163.853	118.126	54.872	−506.096	−311.410	13.555
1300	79.496	170.086	121.885	62.662	−502.272	−295.339	11.867
1400	82.006	176.075	125.543	70.744	−498.159	−279.574	10.431
1500	83.680	181.794	129.104	79.035	−493.843	−264.111	9.197

PREVIOUS: December 1961 CURRENT: March 1966

$S°(298.15\ K) = [86.657]\ J·K^{-1}·mol^{-1}$
$T_{fus}H° = 1044\ K$

$\Delta_fH°(298.15\ K) = [-421.791]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 26.284\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1044\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The constant heat capacity, 17.59 $cal·K^{-1}·mol^{-1}$, was derived from enthalpy data (1053–1173 K) of Douglas.[1] This value was extrapolated above and below the experimental range. A lower value of 16.7 $cal·K^{-1}·mol^{-1}$ was derived by Dworkin[2] from enthalpy data (1050–1110 K) obtained in an enthalpy of melting study. The entropy of the liquid is calculated in a manner analogous to that used for enthalpy of formation.

Fusion Data

The melting point and enthalpy of melting are from Douglas.[1] Values of T_{fus} = 1043 K and 1045 K have been reported by Aukrust *et al.*[3] and Johnson and Bredig,[4] respectively. The enthalpy of melting is confirmed by $\Delta_{fus}H° = 6.34\ kcal·mol^{-1}$ obtained from enthalpy data by Dworkin and Bredig[5] and $\Delta_{fus}H° = 6.4$ and 6.5 $kcal·mol^{-1}$ based on enthalpy and phase diagram studies of Aukrust *et al.*,[3] respectively.

Vaporization Data

T_{vap}(equilibrium vapor) = ~1710 K is the temperature resulting in unit total pressure based on the calculated partial pressures of KCl(g) and K_2Cl_2(g). This value may be compared with boiling points of 1688 and 1690 K observed respectively by Ruff and Mugdan[6] and von Wartenburg and Albrecht.[7] $\Delta_{vap}H°$ (equilibrium vapor) at the boiling point is calculated as the enthalpy of vaporization of one mole of liquid to vapor containing 22.3 mole percent of dimer. According to the selected functions, the amount of dimer at lower temperatures increases gradually to about 32 mole percent at the melting point then decreases rapidly over the crystal. T_{vap} (monomer) = ~1750 K is taken as the temperature at which the calculated Gibbs energy change is zero for KCl(l) → KCl(g), while $\Delta_{vap}H°$ (monomer) is the corresponding enthalpy of vaporization.

Data on vapor pressures and dimer–monomer equilibrium are reviewed on the tables for KCl(g) and K_2Cl_2(g), respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	73.597	86.657	86.657	0.	−421.791	−395.090	69.218
300	73.597	87.112	86.658	0.136	−421.740	−394.925	68.763
400	73.597	108.285	89.545	7.496	−421.594	−385.925	50.397
500	73.597	124.707	94.996	14.855	−419.128	−377.293	39.415
600	73.597	138.126	101.100	22.215	−416.624	−369.160	32.138
700	73.597	149.471	107.221	29.575	−414.096	−361.449	26.972
800	73.597	159.298	113.130	36.934	−411.563	−354.101	23.120
900	73.597	167.966	118.751	44.294	−409.046	−347.070	20.143
1000	73.597	175.721	124.067	51.654	−406.568	−340.317	17.776
1044.000	73.597	178.890	126.311	54.892	--- CRYSTAL <--> LIQUID ---		
1100	73.597	182.735	129.087	59.013	−483.102	−329.200	15.632
1200	73.597	189.139	133.828	66.373	−479.702	−315.359	13.727
1300	73.597	195.030	138.312	73.733	−476.307	−301.801	12.127
1400	73.597	200.484	142.561	81.092	−472.917	−288.505	10.764
1500	73.597	205.561	146.593	88.452	−469.533	−275.451	9.592
1600	73.597	210.311	150.429	95.812	−466.154	−262.622	8.574
1700	73.597	214.773	154.084	103.171	−462.781	−250.005	7.682
1800	73.597	218.980	157.574	110.531	−459.415	−237.586	6.895
1900	73.597	222.959	160.911	117.891	−456.058	−225.354	6.195
2000	73.597	226.734	164.109	125.250	−452.711	−213.298	5.571

PREVIOUS: December 1961 CURRENT: March 1966

0	to	1044 K	crystal
above		1044 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.368	−436.379	−436.379	INFINITE
100	39.200	31.773	125.871	−9.410	−437.610	−427.776	223.447
200	48.438	62.630	87.169	−4.908	−437.221	−418.052	109.184
298.15	51.287	82.554	82.554	0.	−436.684	−408.761	71.613
300	51.329	82.872	82.555	0.095	−436.675	−408.587	71.141
400	53.137	97.895	84.592	5.321	−438.662	−398.837	52.083
500	54.752	109.927	88.494	10.717	−438.160	−388.935	40.632
600	56.317	120.048	92.931	16.270	−437.462	−379.152	33.008
700	58.003	128.852	97.447	21.984	−436.580	−369.501	27.573
800	60.078	136.727	101.873	27.883	−435.508	−359.989	23.505
900	62.911	143.957	106.152	34.024	−434.210	−350.625	20.350
1000	66.969	150.782	110.276	40.505	−432.610	−341.420	17.834
1044.000	69.287	153.713	112.045	43.502	____ CRYSTAL <--> LIQUID ____		
1044.000	73.597	178.890	112.045	69.786	TRANSITION		
1100	73.597	182.735	115.547	73.907	−483.102	−329.200	15.632
1200	73.597	189.139	121.417	81.267	−479.702	−315.359	13.727
1300	73.597	195.030	126.856	88.626	−476.307	−301.801	12.127
1400	73.597	200.484	131.922	95.986	−472.917	−288.505	10.764
1500	73.597	205.561	136.664	103.346	−469.533	−275.451	9.592
1600	73.597	210.311	141.121	110.705	−466.154	−262.622	8.574
1700	73.597	214.773	145.323	118.065	−462.781	−250.005	7.682
1800	73.597	218.980	149.299	125.425	−459.415	−237.586	6.895
1900	73.597	222.959	153.072	132.784	−456.058	−225.354	6.195
2000	73.597	226.734	156.662	140.144	−452.711	−213.298	5.571

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 239.087\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -212.89 \pm 0.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -214.68 \pm 0.4\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 278.6\ cm^{-1}$ $\omega_e x_e = 1.157\ cm^{-1}$ $\sigma = 1$
$B_e = 0.127536\ cm^{-1}$ $\alpha_e = 0.0007799$ $r_e = 2.6667$ Å

Enthalpy of Formation

The enthalpy of formation was calculated from that of the liquid based on $\Delta_{vap}H°(298.15\ K) = 49.5\ kcal·mol^{-1}$ as selected from vapor pressure analyses summarized below. Partial pressures for the monomer were obtained from data of the first four sources by combination of total vapor pressures with PVT data or with transpiration data. Mass spectrometric values[5] are based on temperature variation of ion intensity. These same five studies were used in selection of $\Delta_f H°(298.15\ K) = 45.0\ kcal·mol^{-1}$ for the dimer–monomer equilibrium (see K_2Cl_2).

The resulting tables were tested by comparison with total pressure data over the range 819–1691 K. Dimer–monomer ratios calculated from the tables were used to convert observed total pressures to the monomer pressures which are analyzed below.[6–11] The results are consistent except near the boiling point where the observed pressures[10, 11] are 6–18% larger than those calculated. Knudsen effusion and transpiration studies over the crystal were not analyzed since they are in essential agreement with the torsion effusion data of source 6.

Source	Method	Data Points	T/K	$\Delta_{vap}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
1	PVT + Vap. Press. (a)	15	1310–1404	51.04 ± 0.40	49.67	−1.0 ± 0.4
2	Trans. + Vap. Press.	10	1253–1352	50.75 ± 0.80	49.49	−1.0 ± 0.6
3	Trans. + Vap. Press. (b)	5	1261–1372	50.26 ± 0.77	49.28	−0.8 ± 0.6
4	Trans. + Vap. Press.	7	1250–1473	49.67 ± 0.66	49.46	−0.1 ± 0.5
5	Mass Spectrometry	–	774–1016	49.6 ± 1.8	—	—
6	Total Vap. Press.	137	819–945	49.5	49.57	0.06
7	Total Vap. Press.	9	847–936	49.0	49.95	1.0 ± 0.6
8	Total Vap. Press.	9	1179–1378	50.3	49.44	−0.8 ± 0.2
9	Total Vap. Press.	9	1170–1466	51.0	49.42	−1.2 ± 0.2
10	Total Vap. Press.	7	1393–1688	53.6	49.48	−2.7 ± 0.4
11	Total Vap. Press.	16	1389–1691	50.2	49.22	−0.8 ± 0.5

(a) Total vapor pressure.[2,3,8] (b) 1235 K was omitted.

Heat Capacity and Entropy

Rotational and vibrational constants are based on the microwave studies of Clouser and Gordy.[12] Earlier microwave data of Honig *et al.*[13] and electric resonance data of Lee *et al.*[14] are in excellent agreement. Infrared spectra of Rice and Klemperer[15] yield $\omega_e = 261 \pm 6\ cm^{-1}$ which is in good agreement. The constants were adjusted to a natural isotopic composition of 24.4% ^{37}Cl and 6.8% ^{41}K.

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Enthalpy Reference Temperature = T_r = 298.15 K — *Standard State Pressure = $p°$ = 0.1 MPa*

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.885	−212.893	−212.893	INFINITE
100	31.699	201.456	270.564	−6.911	−213.108	−220.243	115.043
200	35.270	224.739	242.394	−3.531	−213.841	−227.094	59.311
250	36.034	232.698	239.686	−1.747	−214.241	−230.362	48.131
298.15	36.496	239.087	239.087	0.	−214.681	−233.428	40.896
300	36.510	239.313	239.088	0.068	−214.700	−233.544	40.664
350	36.829	244.967	239.534	1.902	−217.616	−236.547	35.303
400	37.056	249.900	240.528	3.749	−218.231	−239.209	31.237
450	37.228	254.275	241.817	5.606	−218.826	−241.795	28.067
500	37.362	258.205	243.263	7.471	−219.403	−244.316	25.524
600	37.567	265.036	246.339	11.218	−220.511	−249.194	21.694
700	37.721	270.839	249.435	14.983	−221.578	−253.890	18.945
800	37.848	275.884	252.432	18.761	−222.626	−258.434	16.874
900	37.960	280.349	255.291	22.552	−223.679	−262.847	15.255
1000	38.061	284.354	258.000	26.353	−224.759	−267.141	13.954
1100	38.156	287.986	260.564	30.164	−304.842	−266.715	12.665
1200	38.246	291.309	262.989	33.984	−304.981	−263.243	11.459
1300	38.333	294.374	265.287	37.813	−305.117	−259.759	10.437
1400	38.417	297.218	267.468	41.651	−305.250	−256.265	9.561
1500	38.500	299.871	269.541	45.496	−305.379	−252.762	8.802
1600	38.582	302.359	271.515	49.351	−305.505	−249.250	8.137
1700	38.662	304.700	273.399	53.213	−305.630	−245.730	7.550
1800	38.742	306.912	275.200	57.083	−305.753	−242.203	7.029
1900	38.821	309.009	276.924	60.961	−305.878	−238.669	6.561
2000	38.900	311.002	278.579	64.847	−306.005	−235.129	6.141
2100	38.978	312.902	280.168	68.741	−306.136	−231.582	5.760
2200	39.056	314.717	281.698	72.643	−306.276	−228.028	5.414
2300	39.134	316.455	283.172	76.552	−306.425	−224.468	5.098
2400	39.211	318.122	284.593	80.470	−306.587	−220.902	4.808
2500	39.288	319.725	285.967	84.395	−306.766	−217.328	4.541
2600	39.365	321.267	287.295	88.327	−306.965	−213.746	4.294
2700	39.442	322.754	288.581	92.268	−307.187	−210.157	4.066
2800	39.519	324.190	289.827	96.216	−307.436	−206.559	3.853
2900	39.595	325.578	291.036	100.171	−307.714	−202.951	3.656
3000	39.672	326.922	292.210	104.135	−308.027	−199.333	3.471
3100	39.748	328.224	293.351	108.106	−308.376	−195.704	3.298
3200	39.825	329.487	294.461	112.084	−308.766	−192.064	3.135
3300	39.901	330.714	295.541	116.071	−309.190	−188.411	2.982
3400	39.977	331.906	296.593	120.065	−309.667	−184.744	2.838
3500	40.053	333.066	297.618	124.066	−310.191	−181.062	2.702
3600	40.130	334.195	298.619	128.075	−310.770	−177.365	2.573
3700	40.206	335.296	299.595	132.092	−311.404	−173.651	2.452
3800	40.282	336.369	300.549	136.116	−312.099	−169.918	2.336
3900	40.358	337.416	301.481	140.148	−312.856	−166.167	2.226
4000	40.434	338.439	302.392	144.188	−313.673	−162.396	2.121
4100	40.510	339.438	303.283	148.235	−314.560	−158.604	2.021
4200	40.586	340.415	304.156	152.290	−315.524	−154.788	1.925
4300	40.662	341.371	305.010	156.352	−316.565	−150.949	1.834
4400	40.738	342.307	305.847	160.422	−317.408	−147.112	1.746
4500	40.814	343.223	306.668	164.500	−318.543	−143.229	1.663
4600	40.889	344.121	307.472	168.585	−319.751	−139.320	1.582
4700	40.965	345.001	308.261	172.678	−321.016	−135.386	1.505
4800	41.041	345.865	309.036	176.778	−322.247	−131.436	1.430
4900	41.117	346.712	309.796	180.886	−323.658	−127.446	1.359
5000	41.193	347.543	310.543	185.001	−325.144	−123.427	1.289
5100	41.269	348.360	311.276	189.125	−326.705	−119.377	1.223
5200	41.344	349.162	311.997	193.255	−328.343	−115.296	1.158
5300	41.420	349.950	312.706	197.393	−330.056	−111.183	1.096
5400	41.496	350.725	313.403	201.539	−331.844	−107.037	1.035
5500	41.572	351.487	314.088	205.693	−333.706	−102.857	0.977
5600	41.648	352.237	314.763	209.854	−335.640	−98.642	0.920
5700	41.723	352.975	315.427	214.022	−337.300	−94.440	0.865
5800	41.799	353.701	316.080	218.198	−339.330	−90.162	0.812
5900	41.875	354.416	316.724	222.382	−341.422	−85.848	0.760
6000	41.951	355.120	317.358	226.573	−343.575	−81.498	0.710

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = 151.04 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 572.7\ K$
$T_{fus} = 798\ K$

$\Delta_f H°(0\ K) = -422.1 \pm 1.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -430.1 \pm 4.0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 13.77\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy of decomposition of $KClO_4$(cr) to KCl(cr) and O_2(g) was measured by Johnson and Gilliland,[1] yielding $\Delta_f H°(298.15\ K) = -103.22 \pm 0.15\ kcal \cdot mol^{-1}$. Hofmann and Martin[2] burned a mixture of paraffin and potassium perchlorate and obtained $\Delta_f E(298.15\ K) = -1.73\ kcal \cdot mol^{-1}$ for the constant volume process corresponding to the reaction: $KClO_4(cr) = KCl(cr) + 2\ O_2(g)$. Correction of their value for $\Delta(pV)$ gives $\Delta_f H°(298.15\ K) = -0.55\ kcal \cdot mol^{-1}$ which agrees reasonably well to the corresponding value, $-0.96 \pm 0.10\ kcal \cdot mol^{-1}$, reported by Johnson and Gilliland.[1] However, for the same reaction, $\Delta_r H°(298.15\ K) = -2.55 \pm 0.18\ kcal \cdot mol^{-1}$ was determined by Skuratov *et al.*[3] They measured this quantity by two different methods which gave concordant results. The value of $\Delta_f H°(298.15\ K)$ reported was $-101.9 \pm 0.2\ kcal \cdot mol^{-1}$. The value used here is the average of these four results.

Berthelot and Vieille[4] determined the difference between the enthalpy of explosion of ammonium picrate and that of an ammonium picrate–potassium perchlorate mixture, and also the difference between the enthalpy of explosion of potassium picrate and that of a potassium pricrate–potassium perchlorate mixture. They obtained $\Delta_r H° = 7.5\ kcal \cdot mol^{-1}$ for the reaction $KClO_4(cr) = KCl(cr) + 2\ O_2(g)$. From that the value of $\Delta_f H°(298.15\ K)$ was calculated to be $-111.9\ kcal \cdot mol^{-1}$. This value was not used.

Heat Capacity and Entropy

The low temperature heat capacities (12.53–298.07 K) were measured by Latimer and Ahlberg.[5] The heat capacities above 298.15 K were estimated by comparison with those of $NaClO_4$(cr). $S°(298.15\ K)$ was reported by Kelley and King,[6] based on the low temperature heat capacities measured by Latimer and Ahlberg,[5] using $S°(12.59\ K, extrap) = 0.14\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

T_{trs} and $\Delta_{trs} H°$ were obtained from the U. S. National Bureau of Standards.[7]

Fusion Data

T_{fus} was taken from the National Research Council.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.071	−422.147	−422.147	INFINITE
100	64.936	59.404	235.342	−17.594	−427.667	−385.936	201.592
200	88.408	112.278	161.419	−9.828	−429.837	−343.204	89.636
298.15	110.207	151.042	151.042	0.	−430.115	−300.282	52.608
300	112.968	151.733	151.045	0.206	−430.104	−299.477	52.144
400	138.490	187.967	155.809	12.863	−430.602	−255.709	33.392
500	153.971	220.606	165.568	27.519	−426.958	−212.379	22.187
572.700	162.758	242.115	173.939	39.045	I <-- -> II		
572.700	162.661	266.151	173.939	52.810	TRANSITION		
600	165.268	273.786	178.309	57.286	−408.365	−170.557	14.848
700	174.316	299.954	193.849	74.273	−402.719	−131.358	9.802
800	182.422	323.770	208.622	92.118	−396.375	−93.018	6.073
900	189.483	345.671	222.649	110.719	−389.427	−55.510	3.222
1000	195.811	365.969	235.979	129.990	−381.961	−18.803	0.982
1100	201.195	384.887	248.666	149.843	−453.021	21.744	−1.033
1200	206.271	402.613	260.764	170.219	−443.702	64.496	−2.807
1300	211.041	419.314	272.324	191.087	−433.965	106.454	−4.277
1400	215.504	435.119	283.392	212.417	−423.832	147.647	−5.509
1500	219.660	450.131	294.012	234.178	−413.329	188.102	−6.550

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = 59.300 \pm 0.063\ J·K^{-1}·mol^{-1}$
$T_{fus} = 883 \pm 2\ K$

$\Delta_f H°(0\ K) = -408.359 \pm 1.142\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -408.266 \pm 1.142\ kJ·mol^{-1}$
$\Delta_{fus} H° = 19.832 \pm 0.42\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was obtained as follows:

	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}	Source
(1) LiOH(aq, 100 H_2O) → Hcl(aq, 100 H_2O) → LiCl(aq, 201 H_2O)	−13.704 ± 0.014	[1]
(2) Li(cr) + (aq, 1001 H_2O)(l) → LiOH(aq, 1000 H_2O) + 1/2 H_2(g)	−53.142 ± 0.019	[2]
(3) LiOH(aq, 1000 H_2O) → LiOH(aq, 100 H_2O) + (aq, 900 H_2O)(l)	0.153 ± 0.040	[3]
(4) 1/2 H_2(g) + 1/2 Cl_2(g) → HCl(g)	−21.97 ± 0.09	[4]
(5) HCl(g) + (aq, 100 H_2O)(l) → HCl(aq, 100 H_2O)	−17.575 ± 0.100	[5, 6]
(6) LiCl(aq, 201 H_2O) → LiCl(cr) + (aq, 201 H_2O)(l)	8.660 ± 0.010	[7]
(1)+(2)+(3)+(4)+(5)+(6) gives Li(cr) + 1/2 Cl (g) → LiCl(cr)	−97.578 ± 0.273	

A direct calorimetric determination by Siemonsen and Siemonsen[8] gave −94.8 ± 0.6 kcal·mol^{-1}. However, the solution route was thought to be inherently more accurate and was adopted.

Enthalpy Capacity and Entropy

The enthalpy capacity between 15 and 325 K has been measured by Shirley[9] and by Oetting *et al.*[10] The two sets of data are in substantial agreement and were plotted together and used to evalute the entropy at 298. The extrapolation to 0 K was done assuming a T^3 law and yielded $S°(15\ K) = 0.019\ cal·K^{-1}·mol^{-1}$. Above 298, Douglas *et al.*[11] have made enthalpy measurements to 1200 K. Rodigina *et al.*[12] also made enthalpy determinations to 1100 K. These two sets of measurements were averaged and joined smoothly to the low temperature values.

Fusion and Transition Data

The melting point has been reported as follows: 880 K, Douglas *et al.*,[11] 883 K, Rodigina *et al.*;[12] 883 K, Haendler *et al.*;[13] 879 K, Flood *et al.*;[14] 879 K, von Wartenberg and Schulz.[15] The highest value of 883 K was taken as representing the most pure samples. At this temperature the enthalpy equations of Douglas *et al.* yield a enthalpy of fusion of 4.718 kcal·mol^{-1}, those of Rodigina *et al.*, 4.669 kcal·mol^{-1}. Dworkin and Bredig[16] report a value of 4.76 ± 0.10 kcal·mol^{-1} and quote 4.83 kcal·mol^{-1} from a private communication from D. E. Smith. The average value $\Delta_{fus}H° = 4.74 \pm 0.10$ kcal·mol^{-1} was adopted.

A transition at 838 K has been reported by Kislova and Bergman[17] but is not supported by the enthalpy measurements quoted above.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.305	−408.359	−408.359	INFINITE
100	36.313	13.585	98.646	−8.506	−409.511	−400.685	209.296
200	43.350	41.045	63.555	−4.502	−408.867	−392.114	102.410
298.15	48.028	59.300	59.300	0.	−408.266	−384.019	67.279
300	48.095	59.597	59.301	0.089	−408.254	−383.869	66.838
400	50.969	73.853	61.225	5.051	−407.628	−375.837	49.079
500	53.342	85.484	64.948	10.268	−410.130	−367.643	38.407
600	55.593	95.409	69.217	15.715	−409.482	−359.202	31.271
700	57.781	104.144	73.595	21.384	−408.574	−350.891	26.184
800	59.936	112.000	77.912	27.270	−407.434	−342.726	22.378
883.000	*61.702*	*118.003*	*81.402*	32.318	--- CRYSTAL <---> LIQUID ---		
900	62.061	119.183	82.105	33.370	−406.085	−334.716	19.426
1000	64.170	125.831	86.149	39.682	−404.528	−326.868	17.074
1100	66.266	132.045	90.042	46.204	−402.762	−319.185	15.157
1200	68.358	137.901	93.788	52.935	−400.788	−311.673	13.567
1300	70.452	143.455	97.397	59.876	−398.606	−304.334	12.228
1400	72.534	148.752	100.877	67.025	−396.213	−297.170	11.088
1500	74.598	153.827	104.239	74.381	−393.610	−290.186	10.105
1600	76.663	158.707	107.492	81.945	−390.796	−283.381	9.251
1700	78.731	163.417	110.644	89.714	−533.008	−269.583	8.283
1800	80.797	167.976	113.703	97.691	−529.021	−254.202	7.377
1900	82.863	172.399	116.676	105.874	−524.833	−239.047	6.572
2000	84.927	176.702	119.571	114.263	−520.446	−224.119	5.853

PREVIOUS: CURRENT: June 1962

$S°(298.15\ K) = [78.435]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 883 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-390.755]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 19.832 \pm 0.42\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiCl, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(883\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity data from the melting point to 1100 K and 1200 K has been reported by Rodigina *et al.*[1] and Douglas *et al.*[2] The equation given by the former authors for the enthalpy of the liquid does not agree with their measurements and has been replaced by $H°(T;293.15) = 18.000T–1.5 \times 10^{-3}T^2–2279\ cal·mol^{-1}$, which fits to ±0.3%. The two sets of results were averaged and the equations were assumed to hold up to the normal boiling point. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The equilibrium boiling point, T_{vap} = 1656 K, was taken from von Wartenburg and Schultz.[3] The boiling point of the monomeric gas is defined as the temperature at which it reaches 1 bar pressure. This was obtained from the Gibbs energy crossover between liquid and monomeric gas.

References

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[2]T. B. Douglas, J. L. Dever, and A. W. Harman, U.S. Nat. Bur. Stand. Report 6297, (1959).
[3]H. von Wartenburg and H. Schultz, Z. Electrochem. **27**, 568 (1921).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	48.028	78.435	78.435	0.	−390.755	−372.214	65.210
300	48.095	78.732	78.436	0.089	−390.743	−372.099	64.788
400	50.969	92.989	80.360	5.051	−390.117	−365.980	47.792
500	53.342	104.621	84.084	10.269	−392.618	−359.700	37.578
588.000	55.239	113.421	87.830	15.048	GLASS <--> LIQUID		
588.000	67.807	113.421	87.830	15.048	TRANSITION		
600	67.693	114.790	88.355	15.861	−391.825	−353.174	30.747
700	66.747	125.154	92.893	22.583	−389.864	−346.888	25.885
800	65.802	134.005	97.492	29.210	−387.983	−340.878	22.257
883.000	65.015	140.463	101.233	34.639	--- CRYSTAL <--> LIQUID ---		
900	64.856	141.701	101.986	35.743	−386.201	−335.098	19.449
1000	63.911	148.485	106.304	42.182	−384.517	−329.511	17.212
1100	62.965	154.532	110.418	48.525	−382.929	−324.088	15.390
1200	62.015	159.970	114.325	54.774	−381.437	−318.806	13.877
1300	61.070	164.897	118.028	60.929	−380.041	−313.644	12.602
1400	60.124	169.388	121.539	66.988	−378.739	−308.586	11.513
1500	59.165	173.503	124.868	72.953	−377.527	−303.618	10.573
1600	58.216	177.291	128.028	78.822	−376.408	−298.727	9.752
1700	57.284	180.793	131.030	84.597	−520.614	−286.728	8.810
1800	56.346	184.040	133.886	90.278	−518.922	−273.020	7.923
1900	55.403	187.062	136.606	95.866	−517.330	−259.402	7.131
2000	54.455	189.879	139.200	101.359	−515.839	−245.866	6.421

PREVIOUS: CURRENT: June 1962

0 to 883 K crystal
above 883 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K *Standard State Pressure = $p°$ = 0.1 MPa*

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.305	−408.359	−408.359	INFINITE
100	36.313	13.585	98.646	−8.506	−409.511	−400.685	209.296
200	43.350	41.045	63.555	−4.502	−408.867	−392.114	102.410
298.15	48.028	59.300	59.300	0.	−408.266	−384.019	67.279
300	48.095	59.597	59.301	0.089	−408.254	−383.869	66.838
400	50.969	73.853	61.225	5.051	−407.628	−375.837	49.079
500	53.342	85.484	64.948	10.268	−410.130	−367.643	38.407
600	55.593	95.409	69.217	15.715	−409.482	−359.202	31.271
700	57.781	104.144	73.595	21.384	−408.574	−350.891	26.184
800	59.936	112.000	77.912	27.270	−407.434	−342.726	22.378
883.000	61.702	118.003	81.402	32.318	____ CRYSTAL <-- -> LIQUID ____		
883.000	65.015	140.463	81.402	52.150	TRANSITION		
900	64.856	141.701	82.529	53.254	−386.201	−335.098	19.449
1000	63.911	148.485	88.792	59.693	−384.517	−329.511	17.212
1100	62.965	154.532	94.499	66.036	−382.929	−324.088	15.390
1200	62.015	159.970	99.732	72.285	−381.437	−318.806	13.877
1300	61.070	164.897	104.558	78.440	−380.041	−313.644	12.602
1400	60.124	169.388	109.031	84.499	−378.739	−308.586	11.513
1500	59.165	173.503	113.194	90.464	−377.527	−303.618	10.573
1600	58.216	177.291	117.083	96.333	−376.408	−298.727	9.752
1700	57.284	180.793	120.729	102.108	−520.614	−286.728	8.810
1800	56.346	184.040	124.157	107.789	−518.922	−273.020	7.923
1900	55.403	187.062	127.390	113.377	−517.330	−259.402	7.131
2000	54.455	189.879	130.444	118.870	−515.839	−245.866	6.421

PREVIOUS: CURRENT: June 1962

$S°(298.15\ K) = 212.919\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -195.57\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -195.72 \pm 12.6\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0.0	1

$\omega_e = 641.1 \pm 3.0\ cm^{-1}$ $\omega_e x_e = 4.2 \pm 0.3\ cm^{-1}$ $\sigma = 1$
$B_e = 0.7053\ cm^{-1}$ $\alpha_e = 0.0067\ cm^{-1}$ $r_e = 2.022$ Å

Enthalpy of Formation

Klemperer *et al.*[1] quote a private communication from W. H. Evans at the National Bureau of Standards giving $D_0° = 4.35\ cal\cdot K^{-1}\cdot mol^{-1}$ which corresponds to $\Delta_f H°(0\ K) = -45.3 \pm 2.4\ kcal\cdot mol^{-1}$. A 3rd law analysis of the vapor pressure data of Nesmeyanov and Sazonov[2] in conjunction with the relative concentration of monomer, dimer, and trimer at 870 K from the work of Miller and Kusch[3] leads to a monomer enthalpy of sublimation at 298.15 K of 52.56 $kcal\cdot mol^{-1}$, this gives $\Delta_f H°(298.15\ K) = -45.02\ kcal\cdot mol^{-1}$. These values lead, however, to partial vapor pressures of the monomer which are less than half of the total vapor pressure near the boiling point. From the data of Miller and Kusch[3] it would be expected that the monomer would be the predominant species near the boiling point, a fact also substantiated by the work of Beusman,[4] on the average molecular weight of the vapor. Thus it was decided to change the enthalpy of sublimation so as to give the correct normal boiling point and vapor pressures in the region 1400–1600 K and to approximate the relative concentrations of monomer, dimer, and trimer as found by Miller and Kusch at 870 K. A monomer heat of sublimation at 298.15 K of 50.8 $kcal\cdot mol^{-1}$ was chosen, which gives $\Delta_f H°(298.15\ K) = -46.778\ kcal\cdot mol^{-1}$. The normal boiling point was taken as 1656 K as determined by von Wartenburg and Schulz[5] and the boiling point of LiCl(g) was found as 1701 K from the Gibbs energy crossover between liquid and gas.

Heat Capacity and Entropy

The spectroscopic constants were taken from Klemperer *et al.*[1] The value of α_e was calculated by the value of a_1 given by the Rittner potential function and the equation given by Klemperer *et al.*[1] The value of r_e was taken from Douglas *et al.*[6]

References

[1]W. Klemperer, W. G. Norris, A. Buchler and A. G. Emslie, J. Chem. Phys. **33**, 1534 (1960).
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[3]R. C. Miller and P. Kusch, J. Chem. Phys. **25**, 860 (1956); 27, 981 (1957).
[4]C. Beusman, AEC Report ORNL–2323, (1957).
[5]H. Jon Wartenburg and H. Schulz, Z. Electrochem **27**, 568 (1921).
[6]T. B. Douglas, J. L. Dever, and A. W. Harman, U.S. Nat. Bur. Stand. Report 6297, (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.061	−195.567	−195.567	INFINITE
100	29.194	179.425	240.943	−6.152	−194.609	−202.367	105.706
200	31.011	200.100	215.893	−3.159	−194.976	−210.035	54.855
250	32.231	207.153	213.461	−1.577	−195.333	−213.759	44.663
298.15	33.245	212.919	212.919	0.	−195.719	−217.274	38.065
300	33.280	213.125	212.920	0.062	−195.735	−217.408	37.854
350	34.119	218.321	213.328	1.747	−196.171	−220.986	32.980
400	34.778	222.922	214.246	3.470	−196.661	−224.498	29.316
450	35.295	227.049	215.443	5.223	−197.220	−227.945	26.459
500	35.705	230.790	216.793	6.998	−200.852	−231.019	24.134
600	36.304	237.356	219.688	10.601	−202.049	−236.938	20.627
700	36.715	242.985	222.624	14.253	−203.158	−242.664	18.108
800	37.014	247.908	225.483	17.940	−204.217	−248.235	16.208
900	37.242	252.281	228.222	21.653	−205.255	−253.675	14.723
1000	37.425	256.215	230.828	25.387	−206.276	−259.000	13.529
1100	37.577	259.789	233.301	29.137	−207.282	−264.223	12.547
1200	37.707	263.065	235.647	32.901	−208.274	−269.356	11.725
1300	37.821	266.087	237.874	36.678	−209.256	−274.406	11.026
1400	37.924	268.894	239.990	40.465	−210.226	−279.381	10.424
1500	38.019	271.514	242.005	44.262	−211.182	−284.288	9.900
1600	38.107	273.970	243.927	48.069	−212.124	−289.131	9.439
1700	38.189	276.283	245.763	51.884	−358.291	−286.739	8.810
1800	38.268	278.468	247.520	55.706	−358.458	−282.525	8.199
1900	38.344	280.539	249.204	59.537	−358.622	−278.302	7.651
2000	38.417	282.508	250.820	63.375	−358.787	−274.071	7.158
2100	38.487	284.384	252.374	67.220	−358.952	−269.831	6.712
2200	38.556	286.176	253.870	71.073	−359.121	−265.583	6.306
2300	38.624	287.891	255.312	74.932	−359.294	−261.327	5.935
2400	38.690	289.537	256.704	78.797	−359.474	−257.064	5.595
2500	38.755	291.117	258.049	82.670	−359.663	−252.793	5.282
2600	38.820	292.639	259.351	86.548	−359.863	−248.515	4.993
2700	38.883	294.105	260.611	90.433	−360.077	−244.228	4.725
2800	38.946	295.520	261.833	94.325	−360.306	−239.933	4.476
2900	39.009	296.888	263.018	98.223	−360.552	−235.630	4.244
3000	39.071	298.211	264.169	102.127	−360.818	−231.318	4.028
3100	39.132	299.493	265.288	106.037	−361.105	−226.996	3.825
3200	39.193	300.737	266.376	109.953	−361.414	−222.665	3.635
3300	39.254	301.944	267.436	113.875	−361.747	−218.324	3.456
3400	39.314	303.116	268.468	117.804	−362.104	−213.973	3.287
3500	39.375	304.257	269.475	121.738	−362.487	−209.611	3.128
3600	39.435	305.367	270.456	125.679	−362.895	−205.237	2.978
3700	39.494	306.448	271.414	129.625	−363.331	−200.852	2.836
3800	39.554	307.502	272.350	133.578	−363.793	−196.454	2.700
3900	39.613	308.531	273.265	137.536	−364.282	−192.044	2.572
4000	39.673	309.534	274.159	141.500	−364.798	−187.621	2.450
4100	39.732	310.515	275.034	145.471	−365.342	−183.185	2.334
4200	39.791	311.473	275.890	149.447	−365.914	−178.735	2.223
4300	39.850	312.410	276.729	153.429	−366.514	−174.272	2.117
4400	39.909	313.327	277.550	157.417	−367.121	−169.795	2.016
4500	39.967	314.224	278.355	161.410	−367.768	−165.304	1.919
4600	40.026	315.103	279.144	165.410	−368.444	−160.797	1.826
4700	40.084	315.965	279.919	169.416	−369.148	−156.276	1.737
4800	40.143	316.809	280.678	173.427	−369.880	−151.739	1.651
4900	40.201	317.637	281.424	177.444	−370.641	−147.186	1.569
5000	40.260	318.450	282.157	181.467	−371.431	−142.618	1.490
5100	40.318	319.248	282.876	185.496	−372.244	−138.034	1.414
5200	40.376	320.031	283.583	189.531	−373.093	−133.434	1.340
5300	40.434	320.801	284.278	193.571	−373.974	−128.816	1.270
5400	40.492	321.557	284.962	197.618	−374.887	−124.182	1.201
5500	40.550	322.301	285.634	201.670	−375.833	−119.531	1.135
5600	40.608	323.032	286.295	205.728	−376.814	−114.862	1.071
5700	40.666	323.751	286.946	209.791	−377.831	−110.175	1.010
5800	40.724	324.459	287.587	213.861	−378.886	−105.470	0.950
5900	40.782	325.156	288.217	217.936	−379.978	−100.747	0.892
6000	40.840	325.842	288.839	222.018	−381.111	−96.005	0.836

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K)$ = [256.417] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -11.5 \pm 84\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−14.2 ± 84] $kJ·mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
[1150](1)
[500](1)
[700](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [Cs]
Bond Distances: Li–O = 1.82 Å; O–Cl = 1.73 Å
Bond Angle: Li–O–Cl = 115°
Product of the Principal Moments of Inertia: $I_A I_B I_C = 1.83923 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

Data from Hildenbrand.[1]

Enthalpy Capacity and Entropy

Data from Hildenbrand.[1] The principal moments of inertia are: $I_A = 1.4098 \times 10^{-39}$, $I_B = 10.7387 \times 10^{-39}$, and $I_C = 12.1485 \times 10^{-39}$ $g·cm^2$.

Reference

[1]D. L. Hildenbrand, "Tables of Thermodynamic Data for Performance Calculations, "Aeronutronic Division of Ford Motor Company, Newport Beach, Calif., (September 1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.854	−11.525	−11.525	INFINITE
100	33.617	215.894	291.124	−7.523	−11.598	−14.337	7.489
200	37.908	240.313	260.189	−3.975	−12.866	−16.618	4.340
250	40.585	249.062	257.112	−2.012	−13.569	−17.475	3.651
298.15	42.961	256.417	256.417	0.	−14.226	−18.167	3.183
300	43.046	256.683	256.418	0.080	−14.250	−18.191	3.167
350	45.197	263.485	256.950	2.287	−14.903	−18.796	2.805
400	47.028	269.643	258.158	4.594	−15.557	−19.308	2.521
450	48.566	275.273	259.751	6.985	−16.236	−19.736	2.291
500	49.853	280.459	261.566	9.446	−19.953	−19.780	2.066
600	51.826	289.733	265.506	14.536	−21.242	−19.622	1.708
700	53.219	297.833	269.558	19.792	−22.374	−19.260	1.437
800	54.223	305.008	273.550	25.167	−23.414	−18.744	1.224
900	54.963	311.440	277.409	30.628	−24.407	−18.100	1.051
1000	55.520	317.261	281.107	36.153	−25.367	−17.348	0.906
1100	55.948	322.573	284.639	41.728	−26.303	−16.500	0.784
1200	56.284	327.456	288.006	47.340	−27.222	−15.569	0.678
1300	56.551	331.973	291.217	52.982	−28.130	−14.560	0.585
1400	56.767	336.172	294.280	58.649	−29.027	−13.483	0.503
1500	56.944	340.094	297.205	64.334	−29.915	−12.342	0.430
1600	57.090	343.774	300.002	70.036	−30.796	−11.141	0.364
1700	57.213	347.239	302.679	75.752	−176.908	−2.710	0.083
1800	57.316	350.512	305.247	81.478	−177.029	7.540	−0.219
1900	57.404	353.614	307.711	87.214	−177.158	17.798	−0.489
2000	57.480	356.560	310.081	92.959	−177.297	28.062	−0.733
2100	57.545	359.366	312.361	98.710	−177.449	38.334	−0.953
2200	57.602	362.044	314.559	104.467	−177.617	48.613	−1.154
2300	57.652	364.606	316.680	110.230	−177.801	58.900	−1.338
2400	57.696	367.061	318.728	115.998	−178.006	69.196	−1.506
2500	57.735	369.417	320.709	121.769	−178.233	79.501	−1.661
2600	57.770	371.682	322.626	127.545	−178.485	89.815	−1.804
2700	57.801	373.863	324.484	133.323	−178.764	100.139	−1.937
2800	57.828	375.965	326.285	139.105	−179.072	110.475	−2.061
2900	57.853	377.995	328.033	144.889	−179.411	120.821	−2.176
3000	57.876	379.957	329.732	150.675	−179.783	131.180	−2.284
3100	57.896	381.855	331.383	156.464	−180.189	141.553	−2.385
3200	57.915	383.693	332.989	162.254	−180.631	151.938	−2.480
3300	57.932	385.476	334.552	168.047	−181.109	162.338	−2.570
3400	57.947	387.205	336.076	173.841	−181.624	172.753	−2.654
3500	57.961	388.885	337.561	179.636	−182.178	183.184	−2.734
3600	57.974	390.518	339.009	185.433	−182.770	193.631	−2.810
3700	57.986	392.107	340.423	191.231	−183.401	204.095	−2.881
3800	57.997	393.653	341.803	197.030	−184.070	214.578	−2.950
3900	58.008	395.160	343.152	202.830	−184.779	225.078	−3.015
4000	58.017	396.629	344.471	208.632	−185.526	235.596	−3.077
4100	58.026	398.062	345.761	214.434	−186.313	246.134	−3.136
4200	58.034	399.460	347.023	220.237	−187.138	256.691	−3.192
4300	58.042	400.826	348.258	226.041	−188.003	267.269	−3.247
4400	58.049	402.160	349.468	231.845	−188.886	277.865	−3.299
4500	58.056	403.465	350.653	237.650	−189.821	288.483	−3.349
4600	58.062	404.741	351.815	243.456	−190.796	299.123	−3.397
4700	58.068	405.989	352.955	249.263	−191.810	309.784	−3.443
4800	58.073	407.212	354.072	255.070	−192.864	320.467	−3.487
4900	58.078	408.409	355.169	260.877	−193.958	331.173	−3.530
5000	58.083	409.583	356.246	266.685	−195.093	341.901	−3.572
5100	58.088	410.733	357.303	272.494	−196.265	352.653	−3.612
5200	58.092	411.861	358.341	278.303	−197.484	363.427	−3.651
5300	58.096	412.968	359.362	284.112	−198.746	374.226	−3.688
5400	58.100	414.054	360.364	289.922	−200.055	385.049	−3.725
5500	58.103	415.120	361.350	295.732	−201.411	395.896	−3.760
5600	58.107	416.167	362.320	301.543	−202.815	406.770	−3.794
5700	58.110	417.195	363.274	307.354	−204.269	417.668	−3.827
5800	58.113	418.206	364.212	313.165	−205.776	428.592	−3.860
5900	58.116	419.199	365.136	318.976	−207.336	439.542	−3.891
6000	58.119	420.176	366.045	324.788	−208.952	450.520	−3.922

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = [126 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 509\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -380.7 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [29.29]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The heats of reaction ($\Delta_r H°$) involving $LiClO_4$(cr) has been determined by several investigators as follows:

Source	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Gilliland and Johnson[1]	$LiClO_4(cr) + KCl(cr) \rightarrow LiCl(cr) + KClO_4(cr)$	−5.86 ± 0.06	−90.34
Markowitz *et al.*[2]	$LiOH(225\ H_2O) + HClO_4(225\ H_2O) \rightarrow LiClO_4\ (451\ H_2O) + H_2O(l)$	−13.54 ± 0.09	−91.7
Birky and Hepler[3]	$LiClO_4(cr) \rightarrow Li^+(aq) + ClO_4(aq)$	−6.31 ± 0.13	−91.11

The adopted value, $\Delta_f H°(298.15\ K) = -91.0\ kcal \cdot mol^{-1}$, for $LiClO_4$(cr) is the weighted average of the three values listed.

Heat Capacity and Entropy

Heat capacities and $S°(298.15\ K)$ were estimated by comparison with those of $KClO_4$(cr).

Fusion Data

T_{fus} was obtained from Richards and Willard.[4] The value of $\Delta_{fus} H°(509\ K)$ was estimated by comparison with the value, $\Delta_{fus} H°(528\ K) = 5.4\ kcal \cdot mol^{-1}$, for $NaClO_3$(cr) reported by Kelley.[5]

References

[1]A. A. Gilliland and W. H. Johnson, J. Res. Nat. Bur. Stand. **65A**, 67 (1961).
[2]M. M. Markowitz, R. F. Harris and H. Stewart, Jr., J. Phys. Chem. **63**, 1325 (1959).
[3]M. M. Birky and L. G. Hepler, J. Phys. Chem. **64**, 686 (1960).
[4]T. W. Richards and H. H. Willard, J. Amer. Chem. Soc., **32**, 4 (1910).
[5]K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	105.018	125.520	125.520	0.	−380.744	−253.911	44.484
300	105.437	126.171	125.522	0.195	−380.735	−253.125	44.073
400	129.704	160.077	129.980	12.039	−379.169	−210.770	27.524
500	143.511	190.659	139.119	25.770	−379.274	−168.682	17.622
509.000	144.340	193.227	140.053	27.065	--- CRYSTAL <---> LIQUID ---		
600	152.716	217.656	150.004	40.591	−375.571	−126.899	11.048
700	160.038	241.758	161.421	56.236	−371.197	−85.791	6.402
800	166.523	263.561	172.847	72.571	−366.282	−45.349	2.961
900	172.067	283.501	184.050	89.506	−360.909	−5.550	0.322
1000	176.983	301.890	194.926	106.963	−355.130	33.628	−1.757
1100	180.972	318.945	205.435	124.861	−349.006	72.210	−3.429
1200	184.933	334.862	215.564	143.157	−342.565	110.221	−4.798
1300	188.866	349.820	225.322	161.847	−335.799	147.680	−5.934
1400	192.771	363.959	234.724	180.929	−328.701	184.607	−6.888
1500	196.648	377.392	243.791	200.400	−321.266	221.014	−7.696

PREVIOUS: June 1963 CURRENT: March 1964

$S°(298.15\ K) = [164.611]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 509\ K$

$\Delta_f H°(298.15\ K) = [-358.355]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [29.3]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(LiClO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(LiClO_4, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(509\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ for $LiClO_4$(l) was estimated by comparison with that for $NaClO_3$(l). The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature (T_{fus}) was obtained from Richards and Willard.[1] The value of $\Delta_{fus} H°(509\ K)$ was estimated by comparison with the value, $\Delta_{fus} H°(528\ K) = 5.4\ kcal·mol^{-1}$, for $NaClO_3$(cr) reported by Kelley.[2]

References

[1]T. W. Richards and H. H. Willard, J. Amer. Chem. Soc. **32**, 4 (1910).
[2]K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	161.084	164.611	164.611	0.	−358.355	−243.178	42.604
300	161.084	165.608	164.614	0.298	−358.243	−242.463	42.217
400	161.084	211.949	170.933	16.406	−352.412	−204.763	26.739
500	161.084	247.894	182.864	32.515	−350.140	−168.166	17.568
509.000	161.084	250.767	184.039	33.965	--- CRYSTAL <---> LIQUID ---		
600	161.084	277.263	196.224	48.623	−345.150	−132.242	11.513
700	161.084	302.094	209.620	64.732	−340.312	−97.142	7.249
800	161.084	323.604	222.554	80.840	−335.624	−62.725	4.096
900	161.084	342.577	234.856	96.948	−331.077	−28.887	1.677
1000	161.084	359.549	246.492	113.057	−326.647	4.451	−0.232
1100	161.084	374.901	257.479	129.165	−322.313	37.351	−1.774
1200	161.084	388.918	267.856	145.274	−318.059	69.859	−3.041
1300	161.084	401.811	277.671	161.382	−313.876	102.015	−4.099
1400	161.084	413.749	286.970	177.490	−309.751	133.852	−4.994
1500	161.084	424.862	295.797	193.599	−305.678	165.395	−5.760

PREVIOUS: December 1960 CURRENT: March 1964

0 to 509 K crystal
above 500 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0							
100							
200							
298.15	105.018	125.520	125.520	0.	−380.744	−253.911	44.484
300	105.437	126.171	125.522	0.195	−380.735	−253.125	44.073
400	129.704	160.077	129.980	12.039	−379.169	−210.770	27.524
500	143.511	190.659	139.119	25.770	−379.274	−168.682	17.622
509.000	144.340	193.227	140.053	27.065	CRYSTAL <--> LIQUID TRANSITION		
509.000	161.084	250.767	140.053	56.353			
600	161.084	277.263	158.909	71.012	−345.150	−132.242	11.513
700	161.084	302.094	177.636	87.120	−340.312	−97.142	7.249
800	161.084	323.604	194.568	103.229	−335.624	−62.725	4.096
900	161.084	342.577	209.980	119.337	−331.077	−28.887	1.677
1000	161.084	359.549	224.103	135.446	−326.647	4.451	−0.232
1100	161.084	374.901	237.125	151.554	−322.313	37.351	−1.774
1200	161.084	388.918	249.199	167.662	−318.059	69.859	−3.041
1300	161.084	401.811	260.449	183.771	−313.876	102.015	−4.099
1400	161.084	413.749	270.978	199.879	−309.751	133.852	−4.994
1500	161.084	424.862	280.871	215.988	−305.678	165.395	−5.760

PREVIOUS: CURRENT: March 1964

$S°(298.15\ K) = 233.413\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -43.3 \pm 42\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -43.5 \pm 42\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma$	0	2

$\omega_e = 462.4\ cm^{-1}$ $\omega_e x_e = 2.02\ cm^{-1}$ $\sigma = 1$
$B_e = [0.2417]\ cm^{-1}$ $\alpha_e = [0.0014]\ cm^{-1}$ $r_e = 2.199$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from $D_0° = 3.2$ eV reported by Herzberg.[1] $D_0° = 2.7 \pm 0.7$ eV reported by Gaydon,[2] yields $\Delta_f H°(MgCl, g, 298.15\ K) = 1.0 \pm 16\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Spectroscopic constants were reported by Herzberg[1] and adjusted for natural isotopic abundance. The bond length was reported by Morgan and Barrow.[3] B_e and α_e were estimated by the method suggested by Herzberg.[1]

References

[1]G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., D. Van Nostrand Co., Inc., New York, (1950).
[2]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules", 2nd ed., Chapman and Hall, London (1953).
[3]E. Morgan and R. F. Barrow, Nature **192**, 1182, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.361	−43.287	−43.287	INFINITE
100	29.610	198.431	262.874	−6.444	−42.467	−51.910	27.115
200	32.761	219.902	236.542	−3.328	−42.877	−61.232	15.992
250	33.983	227.351	233.982	−1.658	−43.187	−65.786	13.745
298.15	34.828	233.413	233.413	0.	−43.514	−70.109	12.283
300	34.855	233.628	233.413	0.064	−43.527	−70.274	12.236
350	35.477	239.051	233.840	1.824	−43.889	−74.704	11.149
400	35.930	243.819	234.795	3.609	−44.272	−79.080	10.327
450	36.268	248.071	236.039	5.415	−44.675	−83.407	9.682
500	36.528	251.907	237.437	7.235	−45.098	−87.688	9.161
600	36.898	258.602	240.422	10.908	−46.009	−96.122	8.368
700	37.148	264.309	243.437	14.611	−47.014	−104.396	7.790
800	37.330	269.282	246.364	18.335	−48.128	−112.519	7.347
900	37.472	273.687	249.159	22.075	−49.366	−120.495	6.993
1000	37.587	277.642	251.813	25.828	−59.338	−127.613	6.666
1100	37.685	281.229	254.327	29.592	−60.880	−134.365	6.380
1200	37.772	284.512	256.707	33.365	−62.419	−140.978	6.137
1300	37.849	287.538	258.964	37.146	−63.955	−147.462	5.925
1400	37.921	290.346	261.107	40.935	−192.897	−150.661	5.621
1500	37.988	292.964	263.144	44.730	−193.076	−147.638	5.141
1600	38.051	295.418	265.085	48.532	−193.252	−144.603	4.721
1700	38.112	297.727	266.938	52.340	−193.427	−141.557	4.350
1800	38.170	299.907	268.710	56.154	−193.601	−138.501	4.019
1900	38.227	301.972	270.407	59.974	−193.773	−135.435	3.723
2000	38.282	303.934	272.034	63.800	−193.945	−132.361	3.457
2100	38.336	305.803	273.598	67.631	−194.117	−129.277	3.216
2200	38.390	307.588	275.103	71.467	−194.291	−126.185	2.996
2300	38.442	309.296	276.553	75.308	−194.466	−123.086	2.795
2400	38.494	310.933	277.951	79.155	−194.644	−119.979	2.611
2500	38.545	312.505	279.302	83.007	−194.826	−116.864	2.442
2600	38.596	314.018	280.609	86.864	−195.014	−113.741	2.285
2700	38.647	315.476	281.873	90.727	−195.208	−110.612	2.140
2800	38.697	316.882	283.098	94.594	−195.409	−107.475	2.005
2900	38.747	318.241	284.287	98.466	−195.619	−104.331	1.879
3000	38.796	319.555	285.441	102.343	−195.839	−101.179	1.762
3100	38.846	320.828	286.562	106.225	−196.071	−98.020	1.652
3200	38.895	322.062	287.652	110.112	−196.314	−94.854	1.548
3300	38.944	323.260	288.713	114.004	−196.571	−91.679	1.451
3400	38.992	324.423	289.746	117.901	−196.843	−88.496	1.360
3500	39.041	325.554	290.753	121.803	−197.131	−85.306	1.273
3600	39.090	326.655	291.735	125.709	−197.435	−82.106	1.191
3700	39.138	327.726	292.694	129.621	−197.758	−78.898	1.114
3800	39.186	328.771	293.629	133.537	−198.099	−75.681	1.040
3900	39.235	329.789	294.544	137.458	−198.460	−72.455	0.970
4000	39.283	330.783	295.437	141.384	−198.842	−69.219	0.904
4100	39.331	331.754	296.311	145.314	−199.246	−65.974	0.841
4200	39.379	332.702	297.166	149.250	−199.673	−62.718	0.780
4300	39.427	333.629	298.004	153.190	−200.124	−59.452	0.722
4400	39.475	334.536	298.824	157.135	−200.600	−56.175	0.667
4500	39.523	335.424	299.627	161.085	−201.102	−52.887	0.614
4600	39.571	336.293	300.415	165.040	−201.631	−49.588	0.563
4700	39.618	337.145	301.187	168.999	−202.188	−46.277	0.514
4800	39.666	337.979	301.945	172.964	−202.774	−42.953	0.467
4900	39.714	338.797	302.689	176.933	−203.391	−39.617	0.422
5000	39.762	339.600	303.419	180.906	−204.039	−36.269	0.379
5100	39.809	340.388	304.136	184.885	−204.719	−32.906	0.337
5200	39.857	341.162	304.841	188.868	−205.433	−29.531	0.297
5300	39.904	341.921	305.533	192.856	−206.180	−26.141	0.258
5400	39.952	342.668	306.214	196.849	−206.963	−22.737	0.220
5500	40.000	343.401	306.884	200.847	−207.783	−19.317	0.183
5600	40.047	344.122	307.542	204.849	−208.639	−15.883	0.148
5700	40.095	344.832	308.190	208.856	−209.535	−12.433	0.114
5800	40.142	345.529	308.828	212.868	−210.469	−8.967	0.081
5900	40.190	346.216	309.456	216.884	−211.444	−5.485	0.049
6000	40.237	346.892	310.074	220.906	−212.461	−1.986	0.017

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = [228.6 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 646.6 \pm 84\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [652.704] \pm 84\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^{+g}$	0	1
$^3\pi_u$	[9000]	6
$^1\pi_u$	[11000]	2
$^3\Sigma_g^-$	[20000]	3
$^1\Delta$	[25000]	2
$^1\Sigma^+$	[30000]	1

$\omega_e = [400]\ cm^{-1}$ $\omega_e x_e = [2]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.2415]\ cm^{-1}$ $\alpha_e = [0.00164]\ cm^{-1}$ $r_e = [2.2]$ Å

Enthalpy of Formation

The ionization potential of MgCl(g) was reported to be 7.2, 7.5 ± 0.5 and 7 ± 1 eV by Krasnov,[1] Hildenbrand,[9] and Beckett and Cassidy,[2] respectively. The corresponding heats of formation at 298 K for $MgCl^+(g)$ are derived as 156, 163, and 151 $kcal \cdot mol^{-1}$, using $\Delta_f H°(MgCl, g, 0\ K) = -10.34\ kcal \cdot mol^{-1}$ from the JANAF MgCl(g) table (March 31, 1966). The value of $\Delta_f H°(298.15\ K)$ for $MgCl^+(g)$ is tentatively selected as 156 ± 20 $kcal \cdot mol^{-1}$ (652.704 ± 84 $kJ \cdot mol^{-1}$).

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as NaCl(g) which is esoelectronic with $MgCl^+(g)$. The six electronic states are obtained from Fougere.[3] The corresponding electronic levels are estimated by comparison with the isoelectronic molecules BeS,[4] BeO,[5,6] and MgO.[5,7] The bond distance is estimated by the method suggested by Krasnov.[8] The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for MgCl(g) and NaCl(g). B_e and α_e are calculated by the method recommended by Herzberg.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.516	646.579		
100	30.033	192.784	258.681	−6.590			
200	33.588	214.752	231.749	−3.399			
250	34.711	222.375	229.136	−1.690			
298.15	35.446	228.556	228.556	0.	652.704	621.302	−108.849
300	35.470	228.775	228.557	0.066	652.731	621.107	−108.144
350	35.996	234.285	228.991	1.853	653.436	615.780	−91.900
400	36.374	239.117	229.961	3.663	654.116	610.354	−79.704
450	36.655	243.419	231.221	5.489	654.773	604.844	−70.208
500	36.872	247.292	232.638	7.327	655.407	599.262	−62.604
600	37.186	254.045	235.659	11.031	656.606	587.919	−51.183
700	37.405	259.794	238.707	14.761	657.707	576.382	−43.010
800	37.572	264.800	241.662	18.510	658.697	564.696	−36.871
900	37.712	269.234	244.484	22.275	659.561	552.892	−32.089
1000	37.841	273.214	247.161	26.052	651.693	541.712	−28.296
1100	37.977	276.827	249.697	29.843	652.256	530.687	−25.200
1200	38.140	280.138	252.097	33.649	652.828	519.610	−22.618
1300	38.347	283.198	254.373	37.473	653.414	508.485	−20.431
1400	38.618	286.050	256.535	41.320	526.609	500.481	−18.673
1500	38.970	288.726	258.593	45.199	528.592	498.546	−17.361
1600	39.412	291.254	260.556	49.117	530.611	496.478	−16.208
1700	39.954	293.659	262.433	53.085	532.674	494.281	−15.187
1800	40.595	295.961	264.232	57.111	534.792	491.962	−14.276
1900	41.333	298.175	265.961	61.207	536.973	489.523	−13.458
2000	42.158	300.316	267.625	65.381	539.228	486.968	−12.718
2100	43.059	302.394	269.232	69.641	541.564	484.298	−12.046
2200	44.020	304.419	270.785	73.995	543.987	481.515	−11.433
2300	45.025	306.398	272.291	78.447	546.500	478.619	−10.870
2400	46.056	308.336	273.752	83.001	549.108	475.612	−10.351
2500	47.095	310.237	275.174	87.658	551.810	472.495	−9.872
2600	48.124	312.104	276.559	92.419	554.605	469.267	−9.428
2700	49.128	313.940	277.909	97.282	557.490	465.931	−9.014
2800	50.093	315.744	279.228	102.244	560.462	462.485	−8.628
2900	51.007	317.518	280.518	107.299	563.514	458.932	−8.266
3000	51.859	319.262	281.781	112.443	566.639	455.273	−7.927
3100	52.644	320.975	283.017	117.669	569.830	451.509	−7.608
3200	53.354	322.658	284.230	122.969	573.078	447.640	−7.307
3300	53.989	324.309	285.419	128.337	576.376	443.669	−7.023
3400	54.546	325.930	286.587	133.764	579.713	439.598	−6.754
3500	55.026	327.518	287.734	139.244	583.081	435.428	−6.498
3600	55.431	329.074	288.861	144.767	586.473	431.161	−6.256
3700	55.765	330.597	289.968	150.327	589.878	426.800	−6.025
3800	56.030	332.088	291.057	155.918	593.289	422.347	−5.806
3900	56.233	333.546	292.128	161.531	596.700	417.804	−5.596
4000	56.376	334.972	293.181	167.162	600.101	413.174	−5.395
4100	56.467	336.365	294.218	172.805	603.488	408.458	−5.204
4200	56.510	337.727	295.238	178.454	606.853	403.661	−5.020
4300	56.510	339.056	296.241	184.105	610.191	398.784	−4.844
4400	56.472	340.355	297.229	189.755	613.498	393.829	−4.675
4500	56.401	341.624	298.202	195.399	616.769	388.799	−4.513
4600	56.302	342.862	299.159	201.034	619.999	383.698	−4.357
4700	56.179	344.072	300.102	206.658	623.186	378.526	−4.207
4800	56.036	345.253	301.030	212.269	626.325	373.287	−4.062
4900	55.876	346.407	301.945	217.865	629.413	367.984	−3.923
5000	55.702	347.534	302.845	223.444	632.449	362.617	−3.788
5100	55.518	348.635	303.732	229.005	635.430	357.191	−3.658
5200	55.326	349.711	304.606	234.547	638.354	351.707	−3.533
5300	55.128	350.763	305.467	240.070	641.220	346.167	−3.412
5400	54.925	351.792	306.315	245.573	644.025	340.574	−3.294
5500	54.721	352.798	307.151	251.055	646.769	334.929	−3.181
5600	54.516	353.782	307.975	256.517	649.451	329.234	−3.071
5700	54.311	354.745	308.788	261.958	652.068	323.493	−2.964
5800	54.108	355.688	309.588	267.379	654.621	317.706	−2.861
5900	53.907	356.611	310.377	272.780	657.109	311.876	−2.761
6000	53.710	357.516	311.155	278.161	659.531	306.004	−2.664

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 261.680 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 53.622 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 51.714 \pm 0.42\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Degeneracies and Anharmonicity Constants		
ν, cm^{-1}	X_{ii}, cm^{-1}	X_{ii}, cm^{-1}
1799.7(1)	$X_{11} = -17.8$	$X_{12} = 0.0$
595.6(1)	$X_{22} = -2.6$	$X_{23} = -4.3$
330.9(1)	$X_{33} = -1.0$	$X_{13} = -0.6$

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.143 ± 0.012 Å; N–Cl = 1.976 ± 0.005 Å
Bond Angle: O–N–Cl = 113.0° ± 0.7°
Rotational Constants: $A_0 = 2.8492\ cm^{-1}$; $B_0 = 0.19034\ cm^{-1}$; $C_0 = 0.17842\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $\Delta_f H° = 18.43 \pm 0.06\ kcal \cdot mol^{-1}$ derived by 3rd law analysis of equilibrium data[1] for $2ONCl(g) \rightarrow 2NO(g) + Cl_2(g)$. 2nd law analysis yields $\Delta_f H° = 18.39 \pm 0.07$ and an entropy deviation of $-0.09 \pm 0.16\ cal \cdot K^{-1} \cdot mol^{-1}$ from the 3rd law $\Delta_r S°$. Data analyzed cover a temperature range of 372.7 to 491.3 K and consist of a combination of three runs reported by Beeson and Yost.[1] Combination is justified by the mutual consistency of the three runs, which involved excess NO, excess Cl_2, and roughly the stoichiometric ratio of NO and Cl_2, respectively. Earlier data reviewed by Bichowsky and Rossini[2] are considered less reliable.

Heat Capacity and Entropy

We list structural parameters which approximate the adopted rotational constants[3] obtained from microwave spectra of three isotopic molecules. These structural parameters are minor modifications of those given by Millen and Pannell.[3] Changes are well within the ranges specified by the authors but give improved agreement with rotational constant A_0. Literature values include (O–N) = 1.139 ± 0.012[3], 1.14 ± 0.02[4,7] and 1.17 ± 0.06 Å[5,6] (N–Cl) = 1.975 ± 0.005,[3] 1.95 ± 0.01,[4] 1.95 ± 0.06[5,6] and 1.97 ± 0.01 Å;[7,6] and angle (O–N–Cl) = 113.33° ± 0.67°,[3] 116° ± 2°,[4] 114° ± 3°[5,6] and 113° ± 2°.[7,6] The earlier values[4,5,7] resulted from electron–diffraction data by Ketelaar and Palmer[4] and two separate analyses by Rogers and Williams[5] and Whiffen[7] of older microwave data by Rogers *et al.*[6] Rotational constants are adjusted for the natural isotopic abundance of Cl. A_0 is relatively uncertain.

Observed values and anharmonicity constants are from the gas–phase infrared study of Jones *et al.*,[8] who reviewed earlier spectral data. Values of are adjusted for the natural isotopic abundance of chlorine. The anharmonicity constants differ from, and supersede, earlier values by Landau and Fletcher[9] used by Gordon[10] in calculating thermodynamic functions for ONCl.

New functions have been calculated through the courtesy of McBride,[11] who used the above vibrational and rotational constants with first and second order corrections (method NRRA02) in the NASA–Lewis computer program, McBride and Gordon .[12] We adopt these functions directly for 0 to 298.15 K and reproduce the functions at higher temperatures by integration of $C_p°$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.360	53.622	53.622	INFINITE
100	35.016	218.558	298.546	−7.999	52.623	56.874	−29.708
200	40.756	244.629	265.649	−4.204	51.988	61.406	−16.038
298.15	44.589	261.680	261.680	0.	51.714	66.096	−11.580
300	44.643	261.956	261.681	0.083	51.711	66.185	−11.524
400	47.149	275.162	263.465	4.679	51.629	71.027	−9.275
500	49.079	285.898	266.910	9.494	51.658	75.875	−7.927
600	50.687	294.992	270.852	14.484	51.761	80.709	−7.026
700	52.037	302.910	274.878	19.622	51.915	85.522	−6.382
800	53.166	309.934	278.829	24.884	52.104	90.311	−5.897
900	54.106	316.252	282.642	30.249	52.317	95.074	−5.518
1000	54.892	321.995	286.295	35.700	52.549	99.812	−5.214
1100	55.554	327.258	289.783	41.223	52.794	104.527	−4.964
1200	56.117	332.117	293.111	46.807	53.048	109.219	−4.754
1300	56.603	336.628	296.287	52.444	53.310	113.889	−4.576
1400	57.026	340.839	299.320	58.126	53.578	118.539	−4.423
1500	57.399	344.786	302.221	63.847	53.849	123.170	−4.289
1600	57.733	348.501	304.999	69.604	54.123	127.782	−4.172
1700	58.035	352.011	307.662	75.393	54.399	132.377	−4.067
1800	58.311	355.336	310.219	81.210	54.675	136.956	−3.974
1900	58.566	358.495	312.677	87.054	54.951	141.520	−3.891
2000	58.804	361.506	315.044	92.923	55.225	146.069	−3.815
2100	59.027	364.380	317.325	98.815	55.497	150.605	−3.746
2200	59.240	367.131	319.527	104.728	55.766	155.128	−3.683
2300	59.443	369.769	321.655	110.662	56.031	159.638	−3.625
2400	59.637	372.303	323.713	116.616	56.292	164.137	−3.572
2500	59.826	374.741	325.705	122.589	56.547	168.625	−3.523
2600	60.009	377.091	327.637	128.581	56.797	173.103	−3.478
2700	60.188	379.359	329.511	134.591	57.040	177.572	−3.435
2800	60.363	381.551	331.330	140.619	57.277	182.032	−3.396
2900	60.536	383.673	333.099	146.664	57.508	186.483	−3.359
3000	60.706	385.728	334.819	152.726	57.733	190.927	−3.324
3100	60.875	387.721	336.494	158.805	57.952	195.363	−3.292
3200	61.042	389.656	338.125	164.901	58.167	199.792	−3.261
3300	61.208	391.537	339.715	171.013	58.378	204.214	−3.232
3400	61.374	393.367	341.266	177.142	58.586	208.631	−3.205
3500	61.539	395.148	342.780	183.288	58.792	213.041	−3.179
3600	61.704	396.884	344.259	189.450	58.997	217.445	−3.155
3700	61.870	398.577	345.705	195.629	59.204	221.843	−3.132
3800	62.035	400.229	347.118	201.824	59.414	226.236	−3.110
3900	62.201	401.843	348.500	208.036	59.627	230.624	−3.089
4000	62.368	403.420	349.854	214.264	59.847	235.005	−3.069
4100	62.534	404.962	351.179	220.509	60.074	239.382	−3.050
4200	62.702	406.471	352.478	226.771	60.310	243.752	−3.032
4300	62.871	407.948	353.751	233.050	60.556	248.117	−3.014
4400	63.041	409.395	354.999	239.345	60.815	252.476	−2.997
4500	63.212	410.814	356.223	245.658	61.088	256.828	−2.981
4600	63.384	412.205	357.425	251.988	61.375	261.175	−2.966
4700	63.557	413.570	358.605	258.335	61.678	265.515	−2.951
4800	63.731	414.910	359.765	264.699	61.999	269.849	−2.937
4900	63.907	416.226	360.903	271.081	62.338	274.176	−2.923
5000	64.084	417.519	362.023	277.481	62.696	278.495	−2.909
5100	64.262	418.790	363.123	283.898	63.073	282.808	−2.897
5200	64.442	420.039	364.206	290.333	63.471	287.112	−2.884
5300	64.623	421.269	365.271	296.786	63.891	291.409	−2.872
5400	64.806	422.478	366.319	303.258	64.332	295.698	−2.860
5500	64.990	423.669	367.351	309.748	64.794	299.978	−2.849
5600	65.176	424.842	368.367	316.256	65.279	304.250	−2.838
5700	65.363	425.997	369.368	322.783	65.785	308.513	−2.827
5800	65.552	427.135	370.355	329.329	66.313	312.767	−2.817
5900	65.743	428.258	371.326	335.893	66.863	317.011	−2.807
6000	65.935	429.364	372.285	342.477	67.434	321.246	−2.797

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 272.187\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 17.54 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 12.13 \pm 1.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1293(1)	1685(1)
794(1)	411(1)
367(1)	651(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: N–Cl = 1.83 Å; N–O = 1.21 Å
Bond Angles: O–N–O = 129.5°; O–N–Cl = 115.25°
Product of the Moments of Inertia: $I_A I_B I_C = 2.36673 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The selected enthalpy of formation was obtained from the recalculation of the heat of reaction $ClNO_2 + NO = ClNO + NO_2$ which has been measured calorimetrically as $-9.27\ kcal·mol^{-1}$ by Ray and Ogg.[1] Not only the thermal effects of $2NO_2 = N_2O_4$ but also $NO + NO_2 = N_2O_3$ (a minor one) have been considered in calculation. Using all JANAF auxiliary data for ClNO, NO, NO_2, N_2O_3 and N_2O_4, the recalculation gives $\Delta_f H°(298.15\ K) = 2.90 \pm 0.4\ kcal·mol^{-1}$ for $NO_2Cl(g)$. For the reaction $ClNO + N_2O_5 = ClNO_2 + 2NO_2$ also measured by Ray and Ogg,[1] the recalculation gives $\Delta_f H°(NO_2Cl, g, 298.15\ K) = 2.56 \pm 0.4\ kcal·mol^{-1}$.

Martin and Koehlein[2] have determined kinetically the heat of reaction, $\Delta_r H°(273.15\ K) = 3.10\ kcal·mol^{-1}$ for the reaction $NO_2 + NOCl = NO + NO_2Cl$ which gives $\Delta_f H°(298.15\ K) = 1.90 \pm 1\ kcal·mol^{-1}$ for $NO_2Cl(g)$. Cordes and Johnston[3] have also determined kinetically the $\Delta_r H°(0\ K) = 29.5\ kcal·mol^{-1}$ for the reaction $NO_2Cl = NO_2 + Cl$ which gives $\Delta_f H°(298.15\ K) = 6.3 \pm 0.3\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The selected bond distances and bond angles were obtained from microwave spectrum studies by Clayton *et al.*[4] Millen and Sinnott,[5] reported bond distance N–Cl = 1.840 Å, N–O = 1.202 Å and angle ONO = 130° 35' from the microwave measurement. These two are in good agreement.

The selected vibrational frequencies were obtained from infrared and Raman spectrum measurements by Ryason and Wilson.[6] However, the assignment of the fundamental frequencies has been revised by Dodd *et al.*[7] and Morino and Tanaka.[8] Morino and Tanaka's assignment was adopted. The principal moments of inertia are $I_A = 6.3641 \times 10^{-39}$, $I_B = 16.3632 \times 10^{-39}$ and $I_C = 22.7272 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.199	17.544	17.544	INFINITE
100	35.314	225.280	313.645	−8.837	15.094	27.338	−14.280
200	44.951	252.629	276.802	−4.835	13.211	40.377	−10.545
250	49.431	263.152	273.042	−2.473	12.578	47.246	−9.871
298.15	53.187	272.187	272.187	0.	12.134	53.965	−9.454
300	53.321	272.517	272.188	0.099	12.119	54.225	−9.441
350	56.696	280.995	272.850	2.851	11.807	61.269	−9.144
400	59.639	288.763	274.360	5.761	11.617	68.349	−8.925
450	62.214	295.939	276.364	8.809	11.527	75.447	−8.758
500	64.467	302.613	278.659	11.977	11.519	82.551	−8.624
600	68.161	314.709	283.681	18.617	11.691	96.744	−8.422
700	70.985	325.438	288.894	25.580	12.043	110.894	−8.275
800	73.153	335.064	294.074	32.792	12.513	124.985	−8.161
900	74.831	343.781	299.121	40.195	13.062	139.011	−8.068
1000	76.145	351.736	303.990	47.746	13.663	152.974	−7.991
1100	77.185	359.044	308.668	55.415	14.299	166.874	−7.924
1200	78.020	365.798	313.151	63.176	14.956	180.716	−7.866
1300	78.697	372.070	317.445	71.013	15.627	194.502	−7.815
1400	79.252	377.923	321.558	78.912	16.304	208.236	−7.769
1500	79.712	383.407	325.500	86.860	16.982	221.922	−7.728
1600	80.097	388.564	329.282	94.851	17.657	235.563	−7.690
1700	80.422	393.430	332.914	102.878	18.324	249.161	−7.656
1800	80.699	398.035	336.405	110.934	18.981	262.721	−7.624
1900	80.936	402.405	339.764	119.016	19.626	276.244	−7.594
2000	81.141	406.561	343.001	127.120	20.254	289.734	−7.567
2100	81.319	410.525	346.123	135.244	20.865	303.193	−7.542
2200	81.475	414.311	349.137	143.384	21.457	316.624	−7.518
2300	81.612	417.936	352.050	151.538	22.027	330.027	−7.495
2400	81.732	421.412	354.868	159.705	22.574	343.406	−7.474
2500	81.840	424.751	357.597	167.884	23.097	356.764	−7.454
2600	81.935	427.963	360.242	176.073	23.596	370.101	−7.435
2700	82.021	431.056	362.808	184.271	24.068	383.419	−7.418
2800	82.097	434.041	365.299	192.477	24.515	396.720	−7.401
2900	82.167	436.923	367.719	200.690	24.935	410.005	−7.385
3000	82.229	439.710	370.073	208.910	25.329	423.277	−7.370
3100	82.286	442.407	372.363	217.136	25.698	436.536	−7.356
3200	82.338	445.020	374.593	225.367	26.041	449.783	−7.342
3300	82.385	447.554	376.766	233.603	26.360	463.019	−7.329
3400	82.428	450.015	378.884	241.844	26.656	476.247	−7.317
3500	82.468	452.405	380.951	250.089	26.929	489.466	−7.305
3600	82.505	454.728	382.968	258.337	27.182	502.678	−7.294
3700	82.538	456.989	384.938	266.589	27.415	515.883	−7.283
3800	82.569	459.191	386.863	274.845	27.630	529.083	−7.273
3900	82.598	461.336	388.745	283.103	27.829	542.276	−7.263
4000	82.625	463.428	390.586	291.364	28.014	555.464	−7.254
4100	82.649	465.468	392.388	299.628	28.185	568.649	−7.245
4200	82.672	467.460	394.152	307.894	28.345	581.829	−7.236
4300	82.694	469.406	395.879	316.162	28.494	595.006	−7.228
4400	82.714	471.307	397.572	324.433	28.635	608.178	−7.220
4500	82.733	473.166	399.231	332.705	28.768	621.347	−7.212
4600	82.750	474.984	400.859	340.979	28.894	634.514	−7.205
4700	82.766	476.764	402.455	349.255	29.015	647.679	−7.198
4800	82.782	478.507	404.021	357.533	29.131	660.841	−7.191
4900	82.796	480.214	405.559	365.811	29.243	674.001	−7.185
5000	82.810	481.887	407.068	374.092	29.352	687.158	−7.179
5100	82.823	483.527	408.552	382.373	29.456	700.313	−7.173
5200	82.835	485.135	410.009	390.656	29.558	713.465	−7.167
5300	82.847	486.713	411.441	398.940	29.657	726.617	−7.161
5400	82.857	488.262	412.850	407.226	29.752	739.766	−7.156
5500	82.868	489.782	414.235	415.512	29.844	752.913	−7.151
5600	82.877	491.276	415.597	423.799	29.932	766.060	−7.146
5700	82.887	492.743	416.938	432.087	30.015	779.204	−7.141
5800	82.895	494.184	418.257	440.376	30.093	792.348	−7.136
5900	82.904	495.601	419.556	448.666	30.164	805.488	−7.131
6000	82.912	496.995	420.835	456.957	30.228	818.629	−7.127

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = 72.115 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1073.8 \pm 1.0\ K$

$\Delta_f H°(0\ K) = -410.693 \pm 0.34\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -411.120 \pm 0.34\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 28.158 \pm 0.17\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is based on $\Delta_f H°(298.15\ K) = -57.39$ and $-39.95\ kcal \cdot mol^{-1}$ for $Na^+(aq,\infty)$ and $Cl^-(aq,\infty)$, respectively, and on the enthalpy of solution, $\Delta_{sln} H°(298.15\ K) = 0.922\ kcal \cdot mol^{-1}$ for NaCl. These values were reported in a personal communication from Wagman.[1]

Heat Capacity and Entropy

The low temperature values are based on the heat capacities (3–266 K) reported by Barron *et al.*[2] The earlier work of Clusius *et al.*,[3] results in a slightly higher entropy, $S°(298.15\ K) = 17.33\ cal \cdot K^{-1} \cdot mol^{-1}$, but a lower heat capacity at room temperature, $C_p°(298.15\ K) = 11.9\ cal \cdot K^{-1} \cdot mol^{-1}$. The high temperature values have been obtained by re-analysis of the enthalpies (672–1279 K) of Dawson *et al.*,[4] using the new value for $C_p°(298.15\ K)$. The resulting tables agree within $\pm 0.1\ kcal \cdot mol^{-1}$ with the enthalpies (812–1058 K) of Roth and Bertram.[5] The enthalpies (540–1037 K) of Magnus[6] agree well at the lower temperatures but are about 0.3 $kcal \cdot mol^{-1}$ smaller near the melting point.

Fusion Data

The melting temperature was taken from Dawson *et al.*[4] and the heat of melting was obtained by re-analysis of their crystal and liquid enthalpies. Values of $T_{fus} = 1073\ K$ and $\Delta_{fus} H° = 6.69 \pm 0.06\ kcal \cdot mol^{-1}$ were reported by Dworkin and Bredig.[7]

Sublimation Data

The vapor in equilibrium with NaCl contains both monomeric and polymeric forms (for details, see the tables for NaCl gases).

References

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[6]A. Magnus, Physik. Zeitschr. **14**, 5 (1913).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.611	−410.693	−410.693	INFINITE
100	34.932	23.723	114.140	−9.042	−411.920	−402.460	210.224
200	46.873	52.605	76.643	−4.807	−411.660	−393.046	102.653
298.15	50.509	72.115	72.115	0.	−411.120	−384.024	67.279
300	50.543	72.428	72.116	0.093	−411.110	−383.856	66.835
400	52.350	87.226	74.122	5.242	−413.318	−374.636	48.922
500	53.940	99.080	77.966	10.557	−412.890	−365.010	38.132
600	55.476	109.050	82.337	16.028	−412.252	−355.491	30.948
700	57.204	117.727	86.786	21.659	−411.408	−346.095	25.826
800	59.312	125.498	91.147	27.481	−410.346	−336.834	21.993
900	61.869	132.627	95.365	33.536	−409.038	−327.721	19.020
1000	64.865	139.296	99.428	39.868	−407.461	−318.768	16.651
1073.800	67.371	144.002	102.330	44.747	--- CRYSTAL <--> LIQUID ---		
1100	68.325	145.637	103.343	46.524	−405.588	−309.986	14.720
1200	71.965	151.742	107.123	53.542	−500.162	−298.950	13.013
1300	75.145	157.633	110.783	60.905	−496.764	−282.318	11.344
1400	77.530	163.293	114.333	68.544	−493.094	−265.958	9.923
1500	79.245	168.704	117.779	76.388	−489.224	−249.868	8.701

PREVIOUS: December 1960 CURRENT: September 1964

$S°(298.15\ K) = [95.055]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1073.8 \pm 1.0\ K$

$\Delta_f H°(298.15\ K) = [-385.923]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 28.158 \pm 0.17\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(NaCl, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°$(1073.8 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

These were obtained by analysis of the enthalpies (1076–1279 K) of Dawson *et al.*[1] The heat capacity was extrapolated to a constant value of 16.0 at the higher temperatures. A glass transition was assumed at 800 K and below this temperature $C_p°$ was taken to that of the crystal.

$S°$(298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The melting temperature was taken from Dawson *et al.*[1] and the heat of melting was obtained by reanalysis of their crystal and liquid enthalpies. Values of T_{fus} = 1073 K and $\Delta_{fus} H°$ = 6.69 ± 0.06 kcal·mol^{-1} were reported by Dworkin and Bredig.[2]

Sublimation Data

The vapor in equilibrium with NaCl contains both monomeric and polymric forms (for details refer to the tables for NaCl gases).

References

[1]R. Dawson, E. B. Brackett and T. E. Brackett, J. Phys. Chem. **67**, 1669 (1963).
[2]A. S. Dworkin and M. A. Bredig, J. Phys. Chem. **64**, 269 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	50.509	95.055	95.055	0.	−385.923	−365.667	64.063
300	50.543	95.367	95.055	0.093	−385.913	−365.541	63.646
400	52.350	110.165	97.061	5.242	−388.121	−358.615	46.830
500	53.940	122.019	100.905	10.557	−387.693	−351.283	36.698
600	55.476	131.989	105.276	16.028	−387.055	−344.058	29.953
700	57.204	140.666	109.725	21.659	−386.212	−336.955	25.144
800	59.312	148.437	114.086	27.481	−385.149	−329.988	21.546
800.000	59.312	148.437	114.086	27.481	GLASS <--> LIQUID		
800.000	76.400	148.437	114.086	27.481	TRANSITION		
900	74.852	157.354	118.410	35.050	−382.327	−323.264	18.762
1000	72.509	165.127	122.702	42.425	−379.707	−316.845	16.550
1073.800	70.668	170.225	125.796	47.708	--- CRYSTAL <--> LIQUID ---		
1100	70.082	171.921	126.874	49.552	−377.364	−310.674	14.753
1200	68.325	177.937	130.883	56.464	−472.043	−302.265	13.157
1300	67.446	183.367	134.715	63.248	−469.224	−288.232	11.581
1400	67.070	188.351	138.371	69.972	−466.469	−274.413	10.238
1500	66.944	192.973	141.858	76.672	−463.744	−260.790	9.082
1600	66.944	197.293	145.190	83.366	−461.028	−247.349	8.075
1700	66.944	201.352	148.375	90.061	−458.317	−234.077	7.192
1800	66.944	205.178	151.426	96.755	−455.610	−220.964	6.412
1900	66.944	208.798	154.351	103.449	−452.909	−208.002	5.718
2000	66.944	212.232	157.160	110.144	−450.213	−195.182	5.098
2100	66.944	215.498	159.861	116.838	−447.524	−182.497	4.539
2200	66.944	218.612	162.461	123.533	−444.842	−169.939	4.035
2300	66.944	221.588	164.967	130.227	−442.169	−157.503	3.577
2400	66.944	224.437	167.386	136.921	−439.506	−145.184	3.160
2500	66.944	227.170	169.723	143.616	−436.855	−132.975	2.778

PREVIOUS: December 1960 CURRENT: September 1964

0 to 1073.8 K crystal
above 1073.8 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−10.611	−410.693	−410.693	INFINITE
100	34.932	23.723	114.140	−9.042	−411.920	−402.460	210.224
200	46.873	52.605	76.643	−4.807	−411.660	−393.046	102.653
298.15	50.509	72.115	72.115	0.	−411.120	−384.024	67.279
300	50.543	72.428	72.116	0.093	−411.110	−383.856	66.835
400	52.350	87.226	74.122	5.242	−413.318	−374.636	48.922
500	53.940	99.080	77.966	10.557	−412.890	−365.010	38.132
600	55.476	109.050	82.337	16.028	−412.252	−355.491	30.948
700	57.204	117.727	86.786	21.659	−411.408	−346.095	25.826
800	59.312	125.498	91.147	27.481	−410.346	−336.834	21.993
900	61.869	132.627	95.365	33.536	−409.038	−327.721	19.020
1000	64.865	139.296	99.428	39.868	−407.461	−318.768	16.651
1073.800	67.371	144.002	102.330	44.747	CRYSTAL <--> LIQUID TRANSITION		
1073.800	70.668	170.225	102.330	72.905			
1100	70.082	171.921	103.968	74.748	−377.364	−310.674	14.753
1200	68.325	177.937	109.886	81.661	−472.043	−302.265	13.157
1300	67.446	183.367	115.333	88.445	−469.224	−288.232	11.581
1400	67.070	188.351	120.373	95.169	−466.469	−274.413	10.238
1500	66.944	192.973	125.061	101.869	−463.744	−260.790	9.082
1600	66.944	197.293	129.442	108.563	−461.028	−247.349	8.075
1700	66.944	201.352	133.553	115.257	−458.317	−234.077	7.192
1800	66.944	205.178	137.427	121.952	−455.610	−220.964	6.412
1900	66.944	208.798	141.089	128.646	−452.909	−208.002	5.718
2000	66.944	212.232	144.561	135.341	−450.213	−195.182	5.098
2100	66.944	215.498	147.862	142.035	−447.524	−182.497	4.539
2200	66.944	218.612	151.008	148.729	−444.842	−169.939	4.035
2300	66.944	221.588	154.012	155.424	−442.169	−157.503	3.577
2400	66.944	224.437	156.888	162.118	−439.506	−145.184	3.160
2500	66.944	227.170	159.645	168.813	−436.855	−132.975	2.778

PREVIOUS: CURRENT: September 1964

$S°(298.15\ K) = 229.793\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -180.00 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -181.42 \pm 2.1\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 363.62\ cm^{-1}$ $\omega_e x_e = 1.72\ cm^{-1}$ $\sigma = 1$
$B_e = 0.21691\ cm^{-1}$ $\alpha_e = 0.001598\ cm^{-1}$ $r_e = 2.3606$ Å

Enthalpy of Formation

The enthalpy of formation is based on a enthalpy of sublimation $\Delta_{sub}H°(298.15\ K) = 54.9\ kcal·mol^{-1}$ obtained from the more consistent sets of vapor pressure data by correction for the presence of dimer. Observed vapor pressures were converted to monomer pressures by use of dimer–monomer ratios calculated from JANAF Gibbs energy functions and $\Delta_r H°(298.15\ K) = 48.6\ kcal·mol^{-1}$ for the reaction $(NaCl)_2(g) \rightarrow 2\ NaCl(g)$. Higher polymeric species were neglected. Analyses of the resulting monomer pressures are summarized below.

Source	T/K	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
Nesmeyanov and Sazonov[1]	743 – 948*	54.35	54.94
Zimm and Mayer[2]	760 – 897*	55.15	54.91
Mayer and Wintner[3]	890 – 944*	49.6	55.37
Niwa[4]	883 – 973*	52.6	55.03
Barton and Bloom[5]	1340 – 1540**	56.67	54.68
Flock and Rodebush[6]	1250 – 1428**	55.65	54.98
Wartenberg and Albrecht[7]	1429 – 1720**	60.0	54.45
Ruff and Mugden[8]	1433 – 1723**	59.5	54.44

*Knudsen effusion measurements over crystal **total pressures over liquid

Heat Capacity and Entropy

The molecular constants are based on molecular beam studies of the rotational spectra by Clouser and Gordy[9] and on microwave studies by Honig *et al.*[10] The infrared spectra of Rice and Klemperer[11] give a frequency in close agreement (366 cm^{-1}).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.616	−179.997	−179.997	INFINITE
100	30.394	193.507	260.320	−6.681	−179.858	−187.377	97.876
200	34.090	215.819	233.022	−3.440	−180.592	−194.620	50.829
250	35.125	223.546	230.379	−1.708	−180.993	−198.081	41.387
298.15	35.786	229.793	229.793	0.	−181.418	−201.334	35.273
300	35.806	230.014	229.794	0.066	−181.436	−201.458	35.077
350	36.272	235.571	230.231	1.869	−181.945	−204.756	30.558
400	36.604	240.437	231.209	3.691	−185.167	−207.769	27.132
450	36.852	244.764	232.479	5.528	−185.781	−210.557	24.441
500	37.044	248.657	233.906	7.375	−186.370	−213.279	22.281
600	37.324	255.437	236.946	11.095	−187.483	−218.555	19.027
700	37.524	261.206	240.010	14.838	−188.528	−223.650	16.689
800	37.680	266.228	242.980	18.598	−189.526	−228.599	14.926
900	37.809	270.673	245.815	22.373	−190.499	−233.424	13.548
1000	37.921	274.663	248.503	26.159	−191.468	−238.142	12.439
1100	38.022	278.282	251.049	29.957	−192.454	−242.761	11.528
1200	38.116	281.594	253.458	33.764	−290.239	−244.850	10.658
1300	38.205	284.649	255.741	37.580	−290.387	−241.062	9.686
1400	38.289	287.483	257.909	41.404	−290.532	−237.262	8.852
1500	38.371	290.128	259.969	45.237	−290.673	−233.452	8.130
1600	38.450	292.607	261.933	49.079	−290.811	−229.633	7.497
1700	38.528	294.940	263.806	52.927	−290.945	−225.805	6.938
1800	38.604	297.144	265.598	56.784	−291.076	−221.969	6.441
1900	38.679	299.234	267.313	60.648	−291.205	−218.127	5.997
2000	38.754	301.219	268.959	64.520	−291.332	−214.277	5.596
2100	38.828	303.112	270.541	68.399	−291.458	−210.421	5.234
2200	38.901	304.920	272.063	72.285	−291.585	−206.559	4.904
2300	38.973	306.651	273.529	76.179	−291.712	−202.692	4.603
2400	39.045	308.311	274.944	80.080	−291.843	−198.818	4.327
2500	39.117	309.906	276.311	83.988	−291.978	−194.940	4.073
2600	39.189	311.442	277.633	87.903	−292.118	−191.055	3.838
2700	39.260	312.922	278.913	91.826	−292.266	−187.165	3.621
2800	39.331	314.351	280.153	95.756	−292.422	−183.270	3.419
2900	39.402	315.733	281.356	99.692	−292.589	−179.369	3.231
3000	39.473	317.070	282.524	103.636	−292.768	−175.462	3.055
3100	39.544	318.365	283.660	107.587	−292.960	−171.548	2.891
3200	39.614	319.622	284.764	111.545	−293.167	−167.629	2.736
3300	39.685	320.842	285.839	115.510	−293.389	−163.702	2.591
3400	39.755	322.028	286.886	119.482	−293.629	−159.769	2.455
3500	39.825	323.181	287.907	123.461	−293.886	−155.828	2.326
3600	39.895	324.304	288.902	127.447	−294.162	−151.879	2.204
3700	39.965	325.398	289.874	131.440	−294.459	−147.923	2.088
3800	40.035	326.465	290.823	135.440	−294.777	−143.959	1.979
3900	40.105	327.506	291.750	139.447	−295.116	−139.985	1.875
4000	40.175	328.522	292.657	143.461	−295.480	−136.003	1.776
4100	40.245	329.515	293.544	147.482	−295.868	−132.011	1.682
4200	40.315	330.485	294.412	151.510	−296.280	−128.010	1.592
4300	40.385	331.435	295.262	155.545	−296.721	−123.998	1.506
4400	40.455	332.364	296.094	159.587	−297.148	−119.980	1.424
4500	40.524	333.274	296.911	163.636	−297.625	−115.949	1.346
4600	40.594	334.165	297.711	167.692	−298.139	−111.906	1.271
4700	40.664	335.039	298.496	171.755	−298.684	−107.851	1.199
4800	40.733	335.896	299.266	175.825	−299.260	−103.785	1.129
4900	40.803	336.737	300.022	179.901	−299.871	−99.706	1.063
5000	40.873	337.562	300.765	183.985	−300.509	−95.616	0.999
5100	40.942	338.372	301.494	188.076	−301.191	−91.511	0.937
5200	41.012	339.168	302.211	192.174	−301.912	−87.393	0.878
5300	41.082	339.949	302.916	196.278	−302.674	−83.260	0.821
5400	41.151	340.718	303.609	200.390	−303.479	−79.113	0.765
5500	41.221	341.474	304.290	204.509	−304.329	−74.950	0.712
5600	41.290	342.217	304.961	208.634	−305.227	−70.771	0.660
5700	41.360	342.948	305.621	212.767	−306.173	−66.576	0.610
5800	41.429	343.668	306.271	216.906	−307.170	−62.364	0.562
5900	41.499	344.377	306.911	221.052	−308.220	−58.135	0.515
6000	41.568	345.075	307.541	225.206	−309.167	−53.905	0.469

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K)$ = [142.256] $J·K^{-1}·mol^{-1}$
T_{trs} = 581 K
T_{fus} = 755 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −382.752 ± 0.92 $kJ·mol^{-1}$
$\Delta_{trs}H°$ = [13.98] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = Unknown

Enthalpy of Formation

Gilliland and Johnson[1] measured the enthalpy of solution of $NaClO_4$(cr) and gave $\Delta_f H°(298.15\ K)$ = −92.48 ± 0.22 $kcal·mol^{-1}$ for $NaClO_4$(cr). The enthalpy of dilution of $NaClO_4$(cr) was measured by Vanderzee and Swanson.[2] The data led to $\Delta_f H°(298.15\ K)$ = −91.464 $kcal·mol^{-1}$ which agrees very well with the data reported by Gilliland and Johnson.[1] The value of $\Delta_f H°(298.15\ K)$ was reported to be −92.18 $kcal·mol^{-1}$,[3] based upon the data prior to 1950. Vorob'ev *et al.*[4] measured the enthalpy of decomposition of $NaClO_4$(cr) into NaCl(cr) and O_2(g) and gave $\Delta_f H°(298.15\ K)$ = −90.68 ± 0.3 $kcal·mol^{-1}$ for $NaClO_4$(cr). The value reported by Gilliland and Johnson[1] was used.

Heat Capacity and Entropy

Heat capacities and $S°(298.15\ K)$ wee estimated by comparison with those for $NaClO_3$(cr) and $KClO_4$(cr), respectively.

Transition Data

T_{trs} was reported in.[3] $\Delta_{trs}H°$ was estimated from that for $KClO_4$(cr).

Fusion Data

T_{fus} was obtained from.[5]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	111.294	142.256	142.256	0.	−382.752	−254.240	44.542
300	111.713	142.946	142.258	0.206	−382.738	−253.443	44.128
400	135.980	178.647	146.961	12.675	−383.569	−210.358	27.470
500	150.206	210.598	156.559	27.020	−380.228	−167.415	17.490
581.000	158.574	233.798	165.736	39.544	I <-- -> II		
581.000	158.574	257.836	165.736	53.511	TRANSITION		
600	160.247	262.966	168.734	56.539	−361.860	−125.708	10.944
700	168.511	288.302	184.037	72.986	−356.711	−86.747	6.473
800	175.728	311.286	198.528	90.207	−350.923	−48.569	3.171
900	181.586	332.327	212.242	108.076	−344.612	−11.149	0.647
1000	187.025	351.744	225.234	126.510	−337.858	25.544	−1.334
1100	191.962	369.803	237.565	145.461	−330.708	61.542	−2.922
1200	196.648	386.708	249.297	164.894	−419.964	99.312	−4.323
1300	201.083	402.625	260.485	184.782	−411.207	142.232	−5.715
1400	205.267	417.682	271.180	205.102	−402.083	184.465	−6.882
1500	209.200	431.979	281.428	225.828	−392.615	226.032	−7.871

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = [251.9 \pm 13]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 181.92 \pm 4.2\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 182.00 \pm 4.2\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[23108]	[6]
[1507]	[4]	[23796]	[4]
[8394]	[10]	[24788]	[4]
[9330]	[8]	[24836]	[2]
[10116]	[6]	[25036]	[6]
[10664]	[4]	[29071]	[4]
[13550]	[8]	[29593]	[2]
[14996]	[6]	[32500]	[10]
		[32524]	[8]

$\omega_e = [424]\ cm^{-1}$ $\omega_e x_e = [2]\ cm^{-1}$ $\sigma = 1$

$B_e = [10.167]\ cm^{-1}$ $\alpha_e = [0.002]\ cm^{-1}$ $r_e = [2.137]$ Å

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K)$, is based on our third law analysis of unpublished mass spectrometry data (7 points, 1400–1540 K) of Hildenbrand[1] for the reaction Ni(g) + $NiCl_2$(g) = 2NiCl(g). Our analysis of this data yields 2nd and 3rd law values for $\Delta_f H°(298.15\ K)$ of 43.0 ± 1.3 kcal·mol^{-1} and 43.5 ± 1.0 kcal·mol^{-1}, respectively, with a drift of 0.64 ± 1.17 cal·K^{-1}·mol^{-1}. These values are in good agreement with a value of $\Delta_f H°(298.15\ K)$ = 42.9 ± 5.4 kcal·mol^{-1} based on the dissociation energy of 88 ± 5 kcal·mol^{-1} reported by Bulewicz *et al.*[2] using flame photometry. Additional studies include an analysis by Rao and Dadape[3] of the equilibrium $NiCl_2$(g) + Ni(cr) → 2NiCl(g) by the flow method. Our analysis of their data (10 points, 1243–1298 K) using auxiliary JANAF data[4] yields the following values for $\Delta_f H°(298.15\ K)$; 36.9 ± 1.6 kcal·mol^{-1} (2nd law) and 28.5 ± 0.8 kcal·mol^{-1} (3rd law) with a very large drift of −12.85 ± 2.42 cal·K^{-1}·mol^{-1}. The large drift probably indicates an experimental problem such as lack of equilibrium or the presence of side reactions. Other studies on the enthalpy of formation are summarized by Rao and Dadape[3] and are not considered here since the uncertainties in these studies are very large.

Heat Capacity and Entropy

The 18 observed band systems of NiCl(g) are adequately summarized by Suchard.[5] All of these systems have been observed in emission only and the electronic states giving rise to these transitions have not been assigned. The only rotational analysis by Rao and Rao[6] indicates that the upper and lower states are $^2\Delta_{5/2}$ states but the lower state is not definitely identified with the ground state. In view of these difficulties we have chosen to use the electronic energy levels and quantum weights of $Ni^+(g)$[7] as an approximation to those of NiCl(g). This approximation generally gives upper limit values for the thermal functions; we estimate an uncertainty of ± 3 cal·K^{-1}·mol^{-1} for $S°(298.15\ K)$.

Molecular constant data for the ground state are assigned assuming that the lower state of the G band system represents the ground state.[5,6] While this assignment is not certain, the molecular constant data for most of the observed systems are fairly similar[5] so no gross errors will be introduced if this assignment proves incorrect. On this basis the adopted values of B_e and ω_e are from Rao and Rao[6] and Rao *et al.*,[8] respectively, while $\omega_e x_e$ and α_e are our best estimates.

References

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[8]S. V. K. Rao, S. P. Reddy, and P. T. Rao, Z. Physik **166**, 261 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.465	181.915	181.915	INFINITE
100	29.843	216.385	281.814	−6.543	182.874	171.431	−89.546
200	33.290	238.153	255.063	−3.382	182.626	160.032	−41.796
250	34.524	245.720	252.461	−1.685	182.340	154.415	−32.263
298.15	35.443	251.883	251.883	0.	182.004	149.067	−26.116
300	35.475	252.102	251.883	0.066	181.990	148.862	−25.919
350	36.268	257.632	252.318	1.860	181.592	143.372	−21.397
400	36.964	262.521	253.294	3.691	181.152	137.941	−18.013
450	37.586	266.911	254.567	5.555	180.676	132.568	−15.388
500	38.136	270.900	256.004	7.448	180.157	127.250	−13.294
600	39.023	277.936	259.089	11.308	178.923	116.780	−10.167
700	39.645	284.001	262.224	15.244	177.700	106.530	−7.949
800	40.049	289.324	265.286	19.230	176.750	96.427	−6.296
900	40.291	294.056	268.225	23.248	175.778	86.445	−5.017
1000	40.425	298.309	271.024	27.285	174.757	76.573	−4.000
1100	40.496	302.166	273.683	31.331	173.671	66.807	−3.172
1200	40.540	305.691	276.205	35.383	172.512	57.142	−2.487
1300	40.583	308.938	278.600	39.439	171.273	47.578	−1.912
1400	40.646	311.947	280.876	43.500	169.948	38.112	−1.422
1500	40.744	314.755	283.042	47.570	168.536	28.744	−1.001
1600	40.885	317.389	285.107	51.651	167.038	19.473	−0.636
1700	41.076	319.873	287.080	55.748	165.451	10.298	−0.316
1800	41.317	322.227	288.967	59.868	146.630	1.934	−0.056
1900	41.608	324.469	290.777	64.013	144.972	−6.059	0.167
2000	41.945	326.611	292.516	68.191	143.339	−13.966	0.365
2100	42.324	328.667	294.189	72.404	141.737	−21.791	0.542
2200	42.739	330.645	295.801	76.657	140.168	−29.542	0.701
2300	43.183	332.555	297.358	80.952	138.636	−37.221	0.845
2400	43.650	334.402	298.863	85.294	137.142	−44.835	0.976
2500	44.134	336.194	300.321	89.683	135.687	−52.387	1.095
2600	44.627	337.934	301.734	94.121	134.273	−59.882	1.203
2700	45.124	339.628	303.106	98.609	132.900	−67.324	1.302
2800	45.619	341.278	304.440	103.146	131.566	−74.715	1.394
2900	46.107	342.887	305.738	107.732	130.272	−82.059	1.478
3000	46.584	344.458	307.003	112.367	129.017	−89.359	1.556
3100	47.047	345.994	308.236	117.049	127.799	−96.618	1.628
3200	47.491	347.494	309.439	121.776	−250.218	−98.650	1.610
3300	47.916	348.962	310.615	126.546	−249.712	−93.921	1.487
3400	48.318	350.399	311.764	131.358	−249.172	−89.209	1.371
3500	48.698	351.805	312.888	136.209	−248.601	−84.512	1.261
3600	49.053	353.182	313.988	141.097	−248.000	−79.832	1.158
3700	49.384	354.530	315.066	146.019	−247.371	−75.169	1.061
3800	49.690	355.851	316.122	150.973	−246.717	−70.524	0.969
3900	49.973	357.146	317.157	155.956	−246.041	−65.896	0.883
4000	50.232	358.414	318.173	160.967	−245.342	−61.286	0.800
4100	50.468	359.658	319.169	166.002	−244.625	−56.693	0.722
4200	50.683	360.876	320.148	171.059	−243.890	−52.118	0.648
4300	50.877	362.071	321.109	176.138	−243.139	−47.561	0.578
4400	51.051	363.243	322.053	181.234	−242.374	−43.022	0.511
4500	51.207	364.392	322.982	186.347	−241.597	−38.500	0.447
4600	51.346	365.519	323.894	191.475	−240.809	−33.995	0.386
4700	51.469	366.625	324.792	196.616	−240.011	−29.508	0.328
4800	51.578	367.710	325.674	201.768	−239.205	−25.037	0.272
4900	51.672	368.774	326.543	206.931	−238.393	−20.584	0.219
5000	51.755	369.819	327.398	212.103	−237.576	−16.147	0.169
5100	51.826	370.844	328.240	217.282	−236.755	−11.727	0.120
5200	51.887	371.851	329.069	222.467	−235.933	−7.323	0.074
5300	51.939	372.840	329.886	227.659	−235.110	−2.934	0.029
5400	51.983	373.811	330.690	232.855	−234.287	1.439	−0.014
5500	52.019	374.766	331.483	238.055	−233.468	5.797	−0.055
5600	52.048	375.703	332.264	243.258	−232.652	10.140	−0.095
5700	52.072	376.625	333.034	248.465	−231.842	14.468	−0.133
5800	52.090	377.530	333.794	253.673	−231.040	18.782	−0.169
5900	52.104	378.421	334.543	258.882	−230.246	23.083	−0.204
6000	52.114	379.297	335.281	264.093	−229.463	27.370	−0.238

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

D_0° = 22184 ± 3 cm^{-1}
$S°$(298.15 K) = 225.07 ± 0.5 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 101.05 ± 0.1 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 101.63 ± 0.1 $kJ·mol^{-1}$

State	Electronic States and Molecular Constants ($^{35}Cl^{16}O$), cm^{-1}; ϵ_i	g_i	B_e	α_e	Point Group: $C_{\infty v}$ σ = 1 ω_e	$\omega_e x_e$	r_e/Å
$X^2\Pi_{3/2}$	0	2	0.62347334	0.005935	853.72446	5.579573	1.56970
$X^2\Pi_{1/2}$	320.31	2	0.62347334	0.005935	853.72446	5.579573	1.56970
$A^2\Pi_{3/2}$	31650	2	0.4450	0.006	519.5	7.2	1.858
$A^2\Pi_{1/2}$	32169	2	0.4450	0.006	519.5	7.2	1.858

Enthalpy of Formation

The dissociation energy of ClO was measured by Coxon and Ramsay[1] from the convergence limit of the A←X subbands. With respect to this study, the first bound excited state, $A^2\Pi$, dissociates to $Cl(^2P_{3/2}) + O(^1D_2)$. The ground dissociation energy, $D_0° = 22184 \pm 3$ cm^{-1} (265.380 ± 0.036 kJ·mol), gives the value $\Delta_f H°(0\ K) = 101.035 \pm 0.11$ kJ·mol. Additional data needed for the calculations presented here, e. g. thermal functions for the Cl(g) and Cl_2(ref), O(g) and O_2(ref), are taken from JANAF Thermochemical Tables.[2] An earlier study by Durie and Ramsay[3] yielded a dissociation energy of 22152 ± 10 cm^{-1} which is in agreement with our adopted value.

Heat Capacity and Entropy

The spectroscopic results given above are for the $^{35}Cl^{16}O$ isotopic species. Isotopic relationships[4] are used to convert the above constants to those for the normally occuring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X and A states are included in the calculation of the thermal functions; a sum-over-states technique is used.

The high resolution gas phase infrared spectrum of the fundamental of ClO has been measured using laser diode and Fourier transfer infrared spectroscopy.[5–9] The observed spectrum is in agreement with the inertial parameters obtained from the microwave spectrum.[10–14] The spectroscopic parameters for the X states are taken from Burkholder *et al.*[5] These authors utilized their results, microwave results and the results of laser magnetic resonance studies of the vibrational overtone of both $^{35}Cl^{16}O$ and $^{37}Cl^{16}O^{13}$, to obtain precise spectroscopic constants for the X states.[13] These authors also give higher order terms in the rotational vibrational Hamiltonian.

The splitting of the X state, A, is the actual splitting corrected for the lowest lying populated rotational state for both the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components of the X state. The rotational constants given for the X state are B_0 and α_0 values, since they are based on microwave results and results for the first and second vibrational level. Burkholder *et al.*[5] utilized the microwave results, which have been refined by Cohen *et al.*[10] using all available microwave data. The ESR spectrum has been measured.[16,17] Uehara *et al.*[17] interpreted the ESR spectrum including centrifugal distortion effects giving values of the ground state splitting constant, in agreement with the value chosen by Cohen *et al.*,[10] that was obtained from the electronic spectrum by Coxon.[20]

The electronic spectrum has been measured by several workers[18–21] giving electronic levels, including the ground state splitting, vibration and rotation constants and dissociation energies of the ground and first excited state. The dissociation energy, anharmonicity constants and spectroscopic constants for the excited states are obtained from the electronic spectra. Inclusion of the A state increases the entropy 0.1 J mol-1 K^{-1} at temperatures approaching 6000 K. The most recent measurements by Lang *et al.*[22] are in agreement with those of Burkholder *et al.*[5] Results of previous studies are summarized in two references.[5, 22] The other electronic states, which lie about 50,000 cm^{-1}, are not included in the calculations.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.000	0.000	INFINITE	−9.517	101.045	101.045	INFINITE
100	30.834	189.125	254.946	− 6.582	101.072	100.275	− 52.377
200	33.479	211.506	228.195	− 3.338	101.342	99.386	− 25.956
250	34.030	219.038	225.637	− 1.650	101.492	98.879	− 20.659
298.15	34.479	225.071	225.071	0.000	101.630	98.363	− 17.232
300	34.496	225.285	225.072	0.064	101.635	98.343	− 17.123
350	34.919	230.635	225.494	1.799	101.773	97.783	− 14.593
400	35.297	235.323	226.435	3.555	101.906	97.204	− 12.693
450	35.626	239.499	227.659	5.328	102.032	96.609	− 11.214
500	35.909	243.268	229.034	7.117	102.153	96.000	− 10.029
600	36.357	249.857	231.971	10.731	102.371	94.747	− 8.248
700	36.688	255.487	234.938	14.384	102.561	93.461	− 6.974
800	36.941	260.403	237.821	18.066	102.725	92.150	− 6.017
900	37.139	264.766	240.577	21.771	102.866	90.819	− 5.271
1000	37.302	268.688	243.195	25.493	102.989	89.474	− 4.674
1100	37.439	272.250	245.677	29.230	103.097	88.117	− 4.184
1200	37.558	275.513	248.029	32.980	103.191	86.751	− 3.776
1300	37.665	278.523	250.261	36.741	103.275	85.378	− 3.430
1400	37.762	281.318	252.380	40.513	103.349	83.999	− 3.134
1500	37.854	283.927	254.398	44.294	103.413	82.614	− 2.877
1600	37.940	286.372	256.320	48.083	103.470	81.225	− 2.652
1700	38.024	288.675	258.156	51.882	103.518	79.833	− 2.453
1800	38.106	290.851	259.913	55.688	103.558	78.439	− 2.276
1900	38.185	292.913	261.596	59.503	103.589	77.042	− 2.118
2000	38.263	294.874	263.211	63.325	103.612	75.645	− 1.976
2100	38.340	296.742	264.765	67.155	103.624	74.245	− 1.847
2200	38.414	298.528	266.258	70.993	103.627	72.847	− 1.730
2300	38.486	300.237	267.699	74.838	103.620	71.448	− 1.623
2400	38.553	301.876	269.089	78.690	103.601	70.049	− 1.525
2500	38.616	303.451	270.432	82.548	103.570	68.651	− 1.434
2600	38.672	304.967	271.731	86.413	103.525	67.256	− 1.351
2700	38.719	306.427	272.990	90.282	103.466	65.862	− 1.274
2800	38.758	307.836	274.209	94.156	103.392	64.470	− 1.203
2900	38.785	309.197	275.392	98.034	103.302	63.081	− 1.136
3000	38.801	310.512	276.541	101.913	103.194	61.697	− 1.074
3100	38.803	311.784	277.658	105.793	103.067	60.316	− 1.016
3200	38.790	313.016	278.743	109.673	102.922	58.938	− 0.962
3300	38.763	314.209	279.800	113.551	102.757	57.567	− 0.911
3400	38.719	315.366	280.829	117.425	102.572	56.200	− 0.863
3500	38.660	316.488	281.832	121.294	102.367	54.840	− 0.818
3600	38.585	317.576	282.810	125.157	102.140	53.486	− 0.776
3700	38.494	318.632	283.764	129.011	101.892	52.136	− 0.736
3800	38.388	319.657	284.695	132.855	101.623	50.796	− 0.698
3900	38.267	320.652	285.604	136.688	101.332	49.463	− 0.663
4000	38.131	321.620	286.493	140.508	101.019	48.136	− 0.629
4100	37.981	322.559	287.361	144.313	100.685	46.818	− 0.596
4200	37.819	323.473	288.210	148.104	100.330	45.508	− 0.566
4300	37.645	324.361	289.040	151.877	99.954	44.207	− 0.537
4400	37.461	325.224	289.853	155.632	99.557	42.915	− 0.510
4500	37.266	326.064	290.648	159.369	99.139	41.633	− 0.483
4600	37.063	326.880	291.427	163.085	98.701	40.360	− 0.458
4700	36.852	327.675	292.190	166.781	98.243	39.095	− 0.435
4800	36.635	328.449	292.937	170.455	97.764	37.842	− 0.412
4900	36.412	329.202	293.670	174.108	97.267	36.601	− 0.390
5000	36.184	329.935	294.388	177.738	96.750	35.369	− 0.370
5100	35.952	330.650	295.092	181.344	96.213	34.145	− 0.350
5200	35.718	331.345	295.782	184.928	95.659	32.931	− 0.331
5300	35.481	332.024	296.460	188.488	95.084	31.732	− 0.313
5400	35.243	332.685	297.125	192.024	94.491	30.542	− 0.295
5500	35.004	333.329	297.777	195.537	93.880	29.363	− 0.279
5600	34.765	333.958	298.417	199.025	93.249	28.195	− 0.263
5700	34.526	334.571	299.046	202.490	92.600	27.038	− 0.248
5800	34.289	335.169	299.664	205.930	91.931	25.894	− 0.233
5900	34.053	335.753	300.271	209.347	91.244	24.764	− 0.219
6000	33.819	336.324	300.867	212.741	90.538	23.643	− 0.206

PREVIOUS: June 1961 (1 bar) CURRENT: December 1992 (1 bar)

Titanium Chloride Oxide (OTiCl) IDEAL GAS M_r = 99.3324

$S°(298.15\ K)$ = [263.661] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−242.642] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−244.262] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[880](1)
[230](2)
[490](1)

Ground State Quantum Weight: [2] σ = 1
Point Group: [$C_{\infty v}$]
Bond Distances: O–Ti = [1.62] Å; Ti–Cl = [2.17] Å
Bond Angle: O–Ti–Cl = [180]°
Rotational Constant: B_0 = [0.092252] cm^{-1}

Enthalpy of Formation

$\Delta_f H°$(TiOCl, g, 298.15 K) is calculated from an estimated value of $\Delta_f H°$((TiOCl, g, 0 K) = −58 $kcal·mol^{-1}$.[1]

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1]

Reference

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.142	−242.642	−242.642	INFINITE
100	36.633	215.420	305.606	−9.019	−242.987	−245.587	128.282
200	46.229	244.103	268.229	−4.825	−243.685	−247.916	64.749
250	49.321	254.766	264.499	−2.433	−243.995	−248.937	52.012
298.15	51.654	263.661	263.661	0.	−244.262	−249.864	43.775
300	51.733	263.980	263.662	0.096	−244.272	−249.898	43.511
350	53.622	272.103	264.299	2.731	−244.521	−250.816	37.432
400	55.104	279.364	265.736	5.451	−244.750	−251.700	32.869
450	56.272	285.924	267.621	8.237	−244.969	−252.555	29.316
500	57.200	291.903	269.754	11.074	−245.182	−253.387	26.471
600	58.546	302.459	274.349	16.866	−245.612	−254.987	22.199
700	59.444	311.556	279.029	22.769	−246.061	−256.515	19.141
800	60.067	319.537	283.604	28.746	−246.526	−257.977	16.844
900	60.514	326.639	287.998	34.776	−247.050	−259.377	15.054
1000	60.844	333.032	292.187	40.845	−247.702	−260.714	13.618
1100	61.094	338.844	296.169	46.942	−248.549	−261.976	12.440
1200	61.288	344.168	299.950	53.062	−253.579	−263.032	11.449
1300	61.441	349.080	303.543	59.199	−254.101	−263.799	10.600
1400	61.563	353.638	306.960	65.349	−254.707	−264.522	9.869
1500	61.663	357.889	310.215	71.510	−255.412	−265.200	9.235
1600	61.745	361.871	313.321	77.681	−256.230	−265.826	8.678
1700	61.814	365.617	316.288	83.859	−257.174	−266.398	8.185
1800	61.871	369.152	319.127	90.043	−258.260	−266.910	7.746
1900	61.920	372.498	321.849	96.233	−259.502	−267.357	7.350
2000	61.962	375.675	324.462	102.427	−275.600	−267.281	6.981
2100	61.999	378.699	326.973	108.625	−277.943	−266.808	6.636
2200	62.030	381.584	329.390	114.827	−280.299	−266.222	6.321
2300	62.058	384.342	331.720	121.031	−282.671	−265.529	6.030
2400	62.082	386.984	333.968	127.238	−285.059	−264.733	5.762
2500	62.103	389.519	336.140	133.447	−287.463	−263.837	5.513
2600	62.123	391.955	338.240	139.659	−289.884	−262.844	5.281
2700	62.139	394.300	340.273	145.872	−292.324	−261.757	5.064
2800	62.155	396.560	342.243	152.087	−294.781	−260.580	4.861
2900	62.168	398.741	344.154	158.303	−297.256	−259.316	4.671
3000	62.181	400.849	346.009	164.520	−299.750	−257.965	4.492
3100	62.192	402.888	347.811	170.739	−302.262	−256.530	4.323
3200	62.202	404.863	349.563	176.959	−304.790	−255.015	4.163
3300	62.211	406.777	351.268	183.179	−307.336	−253.421	4.011
3400	62.220	408.634	352.928	189.401	−309.897	−251.748	3.868
3500	62.228	410.438	354.546	195.623	−312.473	−250.001	3.731
3600	62.235	412.191	356.123	201.846	−315.063	−248.179	3.601
3700	62.241	413.896	357.661	208.070	−726.763	−238.497	3.367
3800	62.247	415.556	359.163	214.295	−728.142	−225.282	3.097
3900	62.253	417.173	360.630	220.520	−729.586	−212.030	2.840
4000	62.258	418.749	362.063	226.745	−731.091	−198.741	2.595
4100	62.263	420.287	363.465	232.971	−732.657	−185.412	2.362
4200	62.267	421.787	364.835	239.198	−734.278	−172.046	2.140
4300	62.271	423.252	366.177	245.425	−735.952	−158.639	1.927
4400	62.275	424.684	367.490	251.652	−737.677	−145.194	1.724
4500	62.279	426.084	368.777	257.880	−739.448	−131.709	1.529
4600	62.282	427.452	370.038	264.108	−741.263	−118.183	1.342
4700	62.286	428.792	371.274	270.336	−743.119	−104.618	1.163
4800	62.289	430.103	372.486	276.565	−745.013	−91.013	0.990
4900	62.291	431.388	373.675	282.794	−746.942	−77.368	0.825
5000	62.294	432.646	374.842	289.023	−748.903	−63.683	0.665
5100	62.296	433.880	375.987	295.253	−750.893	−49.959	0.512
5200	62.299	435.089	377.112	301.482	−752.911	−36.196	0.364
5300	62.301	436.276	378.217	307.712	−754.954	−22.393	0.221
5400	62.303	437.441	379.303	313.943	−757.019	−8.552	0.083
5500	62.305	438.584	380.371	320.173	−759.105	5.327	−0.051
5600	62.307	439.707	381.420	326.404	−761.210	19.245	−0.180
5700	62.309	440.809	382.453	332.634	−763.331	33.201	−0.304
5800	62.310	441.893	383.468	338.865	−765.468	47.194	−0.425
5900	62.312	442.958	384.467	345.096	−767.619	61.223	−0.542
6000	62.314	444.006	385.451	351.328	−769.783	75.290	−0.655

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$\Delta_a H°(0\ K) = 540.4 \pm 8\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 256.84 \pm 0.1\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta_f H°(0\ K) = 99 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 97 \pm 8\ kJ \cdot mol^{-1}$

			Electronic Levels and Molecular Constants, cm^{-1}					
State	ϵ_i	g_i	ν_1	ν_2	ν_3	r_e/(Å)	<	$I_A I_B I_C$(gm^{3}cm^6)
X^2B_1	0	2	945.580	447.675	1110.1054	1.471	117.6	$1.368837 \times 10^{-115}$
A^2A_2	21013.9	2	708.30	289.56	791.60	1.6270	106°18'	$2.793762 \times 10^{-115}$

Point Group: C_{2v} $\sigma = 2$

Enthalpy of Formation

Clyne and Watson[1] recommended $\Delta_f H°(298.15\ K) = 101.5 \pm 3.1\ kJ \cdot mol^{-1}$, using the techniques of mass spectrometry based on measurements of the equilibrium constant of the gas phase reaction:

$$OClO(g) + Br(g) = BrO(g) + ClO(g)$$

Alqasmi *et al.*[2] obtained $\Delta_f H°(298.15\ K) = 92.9 \pm 2.1\ kJ \cdot mol^{-1}$, from measurements of the enthalpy of the reaction:

$$2ClNO(g) + ClO_2(g) \rightarrow ClNO_2(g) + NO_2(g) + Cl_2(g)$$

The value is calculated using auxiliary data from JANAF.[3] Alqasmi *et al.*[2] summarized the available thermochemical data for this species including the work of Clyne and Watson.[1]

A value of $97 \pm 8\ kJ \cdot mol^{-1}$ is chosen. Within the experimental uncertainty, the values of $\Delta_f H°$ for OClO(g) and ClOO(g) are the same.

Heat Capacity and Entropy

The microwave spectrum of ClO_2 has been investigated in a series of papers by Curl *et al.*[4-9] They have determined the inertial parameters for both chlorine isotopic species in the ground and some excited vibrational states and have identified the ground electronic state as a $^2B_1$ state.[4-9] The results of these studies have been used to compute the moments of inertia for the normally occurring isotopic species from which the structure was derived. The principle moments of inertia in (g·cm^2) are: $I_A = 1.6217 \times 10^{-39}$, $I_B = 8.4128 \times 10^{-39}$, $I_C = 10.0339 \times 10^{-39}$ for the X^2B_1 state and $I_A = 2.6590 \times 10^{-39}$, $I_B = 9.0067 \times 10^{-39}$, $I_C = 11.6657 \times 10^{-39}$ for the A^2A_2 state.

More recent microwave studies have characterized the higher order terms in the rotational Hamiltonian for the ground vibrational state[10] and for the all the vibrational fundamentals and $2\upsilon_2$.[11] The ground state vibrational fundamentals, υ_1 and υ_2, have been determined using high resolution laser diode and Fourier transform spectroscopy.[11, 12] The antisymmetric stretching mode, ν_3, has been determined by IR-microwave double resonance measurements.[13] The electronic spectrum of ClO_2 has been investigated by many workers. The vibrational and rotational constants have been determined for both the ground and excited electronic states.[14-16] Richardson *et al.*[17] have also observed the infrared spectrum for many vibrational levels of the ground electronic state. References to earlier works can be found in the above papers. Fluorescence measurements using a variety of argon ion laser lines have been observed by Curl *et al.*[18] and Sakurai *et al.*[19] Recently Richard *et al.*[20] have observed the fluorescence spectrum of ClO_2 cooled in a supersonic jet. This will probably lead to more accurate spectroscopic constants for this species.[20,21] Wahner *et al.*[22] have measured cross sections for this species as a function of temperature in the wavelength range of 240-480 nm.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−10.796	99.478	99.478	INFINITE
100	33.812	216.512	291.127	−7.462	98.452	103.582	−54.105
200	37.603	241.016	260.538	−3.904	97.579	109.069	−28.486
250	39.822	249.644	257.520	−1.969	97.247	111.982	−23.397
298.15	41.953	256.841	256.841	.000	97.000	114.843	−20.120
300	42.033	257.101	256.842	.078	96.992	114.954	−20.015
350	44.104	263.738	257.361	2.232	96.810	117.963	−17.605
400	45.956	269.751	258.540	4.484	96.693	120.993	−15.800
450	47.563	275.259	260.096	6.823	96.626	124.035	−14.398
500	48.936	280.343	261.870	9.237	96.600	127.082	−13.276
600	51.082	289.466	265.727	14.244	96.632	133.177	−11.594
700	52.619	297.462	269.701	19.433	96.730	139.261	−10.392
800	53.735	304.565	273.623	24.753	96.864	145.328	−9.489
900	54.561	310.944	277.422	30.170	97.015	151.377	−8.786
1000	55.185	316.727	281.068	35.659	97.174	157.409	−8.222
1100	55.666	322.010	284.553	41.202	97.333	163.425	−7.760
1200	56.043	326.870	287.880	46.789	97.490	169.426	−7.375
1300	56.343	331.368	291.054	52.409	97.640	175.415	−7.048
1400	56.586	335.553	294.085	58.055	97.783	181.392	−6.768
1500	56.785	339.464	296.981	63.724	97.915	187.359	−6.524
1600	56.950	343.134	299.752	69.411	98.035	193.318	−6.311
1700	57.088	346.591	302.407	75.113	98.141	199.270	−6.123
1800	57.204	349.858	304.953	80.828	98.231	205.216	−5.955
1900	57.304	352.953	307.399	86.554	98.303	211.158	−5.805
2000	57.390	355.895	309.751	92.288	98.357	217.096	−5.670
2100	57.466	358.697	312.015	98.031	98.390	223.032	−5.548
2200	57.532	361.372	314.198	103.781	98.401	228.968	−5.436
2300	57.593	363.930	316.305	109.538	98.390	234.902	−5.335
2400	57.648	366.383	318.341	115.300	98.355	240.838	−5.242
2500	57.700	368.737	320.310	121.067	98.295	246.776	−5.156
2600	57.751	371.001	322.217	126.840	98.210	252.717	−5.077
2700	57.801	373.182	324.064	132.617	98.101	258.662	−5.004
2800	57.853	375.285	325.856	138.400	97.966	264.611	−4.936
2900	57.906	377.316	327.596	144.188	97.807	270.564	−4.873
3000	57.964	379.280	329.286	149.981	97.625	276.525	−4.815
3100	58.026	381.181	330.929	155.781	97.420	282.492	−4.760
3200	58.093	383.025	332.529	161.587	97.194	288.465	−4.709
3300	58.167	384.813	334.086	167.400	96.949	294.446	−4.661
3400	58.249	386.551	335.604	173.220	96.687	300.435	−4.616
3500	58.339	388.241	337.084	179.050	96.410	306.431	−4.573
3600	58.437	389.886	338.528	184.888	96.120	312.436	−4.533
3700	58.545	391.488	339.937	190.737	95.820	318.448	−4.496
3800	58.662	393.051	341.315	196.598	95.512	324.470	−4.460
3900	58.789	394.576	342.661	202.470	95.199	330.500	−4.427
4000	58.926	396.066	343.977	208.356	94.885	336.537	−4.395
4100	59.072	397.523	345.266	214.256	94.571	342.582	−4.365
4200	59.229	398.949	346.527	220.171	94.260	348.635	−4.336
4300	59.395	400.344	347.762	226.102	93.954	354.695	−4.309
4400	59.571	401.712	348.973	232.050	93.657	360.762	−4.283
4500	59.756	403.052	350.160	238.016	93.370	366.835	−4.258
4600	59.949	404.368	351.324	244.001	93.096	372.915	−4.235
4700	60.151	405.659	352.467	250.006	92.835	379.001	−4.212
4800	60.360	406.928	353.588	256.032	92.591	385.093	−4.191
4900	60.577	408.175	354.689	262.079	92.364	391.190	−4.170
5000	60.800	409.401	355.771	268.147	92.155	397.290	−4.150
5100	61.028	410.607	356.835	274.239	91.966	403.395	−4.132
5200	61.262	411.794	357.880	280.353	91.798	409.502	−4.113
5300	61.500	412.964	358.909	286.491	91.650	415.614	−4.096
5400	61.741	414.115	359.920	292.653	91.524	421.727	−4.079
5500	61.986	415.250	360.916	298.840	91.419	427.843	−4.063
5600	62.233	416.370	361.896	305.051	91.335	433.961	−4.048
5700	62.481	417.473	362.862	311.286	91.272	440.080	−4.033
5800	62.730	418.562	363.813	317.547	91.230	446.200	−4.018
5900	62.980	419.637	364.750	323.832	91.208	452.319	−4.005
6000	63.229	420.697	365.673	330.143	91.204	458.441	−3.991

PREVIOUS: March 1961 (1 bar) CURRENT: December 1992 (1 bar)

$S°(298.15\ K) = 269.32 \pm 0.5\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 99.7 \pm 3.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 98.0 \pm 4.0\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
X^2A''	0.0	2

Vibrational Levels and Degeneracies
ν, cm^{-1}
1442.8 (1)
408.3 (1)
192.4 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Cl-O = [1.83]Å; O-O = [1.23] Å
Bond Angle: Cl-O-O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.418103 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(ClOO, g), has been estimated, calculated and determined experimentally. The reported values are listed below.

Source	Technique (T/K)	Reaction	$\Delta_f H°$(ClOO,g,0 K)
Benson and Buss[4]	$D_0° = 33.5 \pm 8.4$; 0	ClOO = Cl + O_2	[86.1]
Clyne and Coxon[3]			
Clyne *et al.*[1]	mass spectrometry, 298	ClO + ClO ↔ Cl + ClOO	89.8
Clyne and Watson[2]	mass spectrometry, 298	BrO + ClO ↔ Br + ClOO	91.7
Baer *et al.*[11]	laser flash photolysis, 160-300	Cl + O_2 + M = ClOO + M	99.128
Nicovich *et al.*[5]	laser flash photolysis, 181-200	Cl + O_2 + M = ClOO + M	99.7
Mauldin *et al.*[12]	pulse photolysis, 191-250	Cl + O_2 + M = ClOO + M	100.4
Rathman and Schindler[16]	G1 direct isodesmic theory, 0		[121.3]

Based on the above experimental studies we adopt $\Delta_f H°$(ClOO,g,0 K) = 99.7 ± 3 kJ·mol. This corresponds $D_0°$(Cl-OO) = 20 ± 2 kJ·mol. Within the experimental uncertainty, the values of $\Delta_f H°$ for OClO(g) and ClOO(g) are the same.

Heat Capacity and Entropy

Jacox[6] has summarized the IR studies on the three fundamental frequencies (1443, 373, 407)[7-9] and unstructured gas phase absorption[9-12] between 225 and 270 nm. Since her review, there have been two matrix isolation studies which have redefined (reversed the assignment of) ν_2 and ν_3. We adopt the values recommended by Johnston *et al.*[9] (for ν_1) and Johnsson *et al.*[13] (Ar matrix) and Mueller and Willmer[14] (Ne and Ar matrices) for ν_2 and ν_3.

The infrared spectrum of all the fundamentals of ClOO in an argon matrix has been observed by Arkell and Schwager.[8] They observed spectra for the ^{18}O species as well as the ^{16}O species. They did not observe any chlorine isotopic species. Rochkind and Pimentel[7] have observed the stretching fundamentals in a nitrogen matrix isolated infrared spectrum in agreement with Arkell and Schwager.[8] Johnston *et al.*[9] have observed a low resolution gas phase spectrum of the ν_1 fundamental in agreement with Arkell and Schwager's value.[8]

The bond distances and bond angle are from the estimate Arkell and Schwager[8] used in their normal coordinate analysis. Moments of inertia are calculated for the naturally occuring isotopic species. The EPR spectrum has been observed in a Zeolite matrix by Raghunathan and Sur.[15] The spectrum is consistent with a $^2A''$ ground state for the ClOO species. The principle moments of inertia (in $g \cdot cm^2$) are: $I_A = [1.2458 \times 10^{-39}]$, $I_B = [13.3231 \times 10^{-39}]$, $I_C = [14.5689 \times 10^{-39}]$.

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Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.610	99.700	99.700	INFINITE
100	35.208	224.953	307.450	−8.250	98.700	102.986	−53.794
200	42.256	251.656	273.434	−4.356	98.165	107.527	−28.083
250	44.507	261.341	270.075	−2.183	98.070	109.880	−22.958
298.15	46.119	269.324	269.324	.000	98.037	112.158	−19.650
300	46.174	269.609	269.325	.085	98.037	112.246	−19.544
350	47.518	276.831	269.892	2.429	98.044	114.614	−17.105
400	48.668	283.253	271.168	4.834	98.079	116.979	−15.276
450	49.678	289.045	272.838	7.293	98.133	119.338	−13.852
500	50.572	294.326	274.726	9.800	98.200	121.691	−12.713
600	52.059	303.684	278.793	14.934	98.359	126.375	−11.002
700	53.211	311.799	282.941	20.200	98.535	131.030	−9.778
800	54.101	318.965	287.005	25.568	98.716	135.660	−8.858
900	54.792	325.379	290.919	31.014	98.896	140.267	−8.141
1000	55.333	331.181	294.659	36.521	99.073	144.854	−7.566
1100	55.761	336.475	298.224	42.077	99.244	149.424	−7.096
1200	56.104	341.342	301.617	47.671	99.409	153.979	−6.703
1300	56.383	345.845	304.848	53.296	99.564	158.520	−6.369
1400	56.611	350.032	307.928	58.946	99.710	163.049	−6.083
1500	56.799	353.944	310.866	64.616	99.844	167.569	−5.835
1600	56.957	357.615	313.675	70.304	99.965	172.080	−5.618
1700	57.090	361.072	316.362	76.007	100.071	176.583	−5.426
1800	57.204	364.338	318.937	81.722	100.162	181.081	−5.255
1900	57.301	367.434	321.409	87.447	100.234	185.575	−5.102
2000	57.385	370.375	323.784	93.182	100.287	190.065	−4.964
2100	57.457	373.177	326.070	98.924	100.320	194.553	−4.839
2200	57.521	375.851	328.273	104.673	100.330	199.041	−4.726
2300	57.577	378.409	330.397	110.428	100.317	203.527	−4.622
2400	57.626	380.861	332.449	116.188	100.280	208.015	−4.527
2500	57.670	383.214	334.433	121.953	100.218	212.505	−4.440
2600	57.709	385.477	336.353	127.722	100.129	216.998	−4.360
2700	57.744	387.656	338.213	133.495	100.015	221.496	−4.285
2800	57.775	389.756	340.017	139.270	99.874	225.998	−4.216
2900	57.803	391.784	341.767	145.049	99.706	230.504	−4.152
3000	57.829	393.744	343.467	150.831	99.512	235.018	−4.092
3100	57.852	395.641	345.120	156.615	99.291	239.539	−4.036
3200	57.873	397.478	346.727	162.401	99.046	244.066	−3.984
3300	57.893	399.259	348.292	168.190	98.776	248.602	−3.935
3400	57.910	400.987	349.817	173.980	98.484	253.147	−3.889
3500	57.926	402.666	351.303	179.772	98.169	257.700	−3.846
3600	57.941	404.298	352.753	185.565	97.833	262.263	−3.805
3700	57.955	405.886	354.167	191.360	97.479	266.835	−3.767
3800	57.968	407.432	355.549	197.156	97.107	271.418	−3.731
3900	57.979	408.938	356.898	202.953	96.720	276.011	−3.697
4000	57.990	410.406	358.218	208.752	96.318	280.612	−3.664
4100	58.000	411.838	359.508	214.551	95.904	285.225	−3.634
4200	58.010	413.236	360.771	220.352	95.478	289.847	−3.605
4300	58.018	414.601	362.007	226.153	95.043	294.481	−3.577
4400	58.026	415.935	363.217	231.956	94.600	299.124	−3.551
4500	58.034	417.239	364.404	237.759	94.150	303.776	−3.526
4600	58.041	418.514	365.566	243.562	93.694	308.440	−3.502
4700	58.048	419.763	366.706	249.367	93.233	313.113	−3.480
4800	58.054	420.985	367.824	255.172	92.768	317.796	−3.458
4900	58.060	422.182	368.921	260.978	92.299	322.490	−3.438
5000	58.066	423.355	369.998	266.784	91.828	327.193	−3.418
5100	58.071	424.505	371.056	272.591	91.355	331.905	−3.399
5200	58.076	425.633	372.094	278.398	90.879	336.625	−3.381
5300	58.081	426.739	373.115	284.206	90.402	341.357	−3.364
5400	58.085	427.825	374.118	290.014	89.922	346.095	−3.348
5500	58.089	428.890	375.104	295.823	89.439	350.843	−3.332
5600	58.093	429.937	376.074	301.632	88.954	355.602	−3.317
5700	58.097	430.965	377.028	307.442	88.465	360.367	−3.302
5800	58.100	431.976	377.967	313.251	87.972	365.142	−3.288
5900	58.104	432.969	378.891	319.062	87.474	369.924	−3.275
6000	58.107	433.946	379.800	324.872	86.971	374.716	−3.262

PREVIOUS: CURRENT; December 1992 (1bar)

$S°(28{=}98.15\ K) = 270.75 \pm 0.5\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = 200 \pm 10\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = 194 \pm 12\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0.0	2

Vibrational Levels and Degeneracies
ν, cm^{-1}
905.0 (1)
566.6 (1)
1081.3 (2)
475.8 (2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Cl-O = 1.50 ± 0.01 Å
Bond Angle: O-Cl-O = 113.5 ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 13.174066 \times 10^{-115}\ g^3{\cdot}cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(0\ K) = 200 \pm 10$ kJ·mol for ClO_3(g) based on kinetic studies of Colussi et al.[3,4,7] and the quantum mechanical calculations of Rathman and Schindler[6] and Rauk *et al.*[8] Early recommended values for the enthalpy of formation of ClO_3(g), 155 $kJ{\cdot}mol^{-1}$, were based on a calorimetrically determined value of Goodeve and Marsh[1]. This value is now known to be erroneous. The recent determined values are listed in the table below.

Source	Technique	T/K	$\Delta_f H°$(kJ·mol)
Colussi[3]	laser flash photolysis and unimolecular reaction theory	0	238
Colussi *et al.*[4]	second-order rate constants	0	217.1 ± 20.9
Rathman and Schindler[5]	G1 direct isodesmic theory	0	201
Rathman and Schindler(2)[6]	G1 direct isodesmic theory	0	201
Colussi and Grela[7]	adopted value of Rathman and Schindler	0	200.8
Rauk *et al.*[8]	G2 energy calculations	0	197.68

Heat Capacity and Entropy

Jacox[9] has examined the literature pertaining to the structure, vibrational frequencies, and electronic transitions of ClO_3(g). She has recommended a structure and the four vibrational frequencies as derived from the IR study of Grothe and Willner.[10] We adopt her recommendations.

The vibrational frequencies adopted in this calculation are from the experimental study of Grothe and Willner[10]. The authors measured the IR bands of four isotopemers of ^{18}O-enriched ClO_3. From this spectroscopic data, a C_{3v} structure was derived with r(C-lO) = 1.50 ± 0.01 Å and a bond angle of 113.5 ± 2°. The principal moments of inertia are (in $g{\cdot}cm^2$): $I_A = I_B = 8.8757 \times 10^{-39}$ and $I_C = 16.7229 \times 10^{-39}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J{\cdot}K^{-1}{\cdot}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.941	200.000	200.000	INFINITE
100	34.252	225.267	311.275	−8.601	197.527	210.447	−109.926
200	43.422	251.511	275.317	−4.761	195.481	224.220	−58.560
250	48.673	261.770	271.600	−2.458	194.788	231.490	−48.367
298.15	53.328	270.748	270.748	.000	194.325	238.604	−41.802
300	53.496	271.078	270.749	.099	194.311	238.879	−41.592
350	57.731	279.651	271.416	2.882	194.020	246.332	−36.763
400	61.348	287.602	272.948	5.862	193.882	253.816	−33.145
450	64.388	295.009	274.993	9.007	193.864	261.310	−30.332
500	66.926	301.928	277.344	12.292	193.938	268.801	−28.081
600	70.806	314.495	282.511	19.190	194.281	283.745	−24.702
700	73.531	325.626	287.890	26.415	194.788	298.617	−22.283
800	75.485	335.579	293.241	33.871	195.389	313.410	−20.464
900	76.920	344.557	298.452	41.495	196.044	328.124	−19.044
1000	77.999	352.720	303.477	49.243	196.731	342.762	−17.904
1100	78.826	360.194	308.298	57.086	197.436	357.332	−16.968
1200	79.472	367.082	312.913	65.002	198.148	371.836	−16.186
1300	79.986	373.464	317.329	72.976	198.861	386.281	−15.521
1400	80.401	379.407	321.553	80.996	199.570	400.672	−14.949
1500	80.740	384.966	325.597	89.054	200.270	415.011	−14.452
1600	81.021	390.187	329.473	97.142	200.958	429.305	−14.015
1700	81.255	395.106	333.190	105.256	201.630	443.556	−13.629
1800	81.454	399.756	336.760	113.392	202.283	457.768	−13.284
1900	81.622	404.164	340.193	121.546	202.914	471.944	−12.975
2000	81.767	408.355	343.497	129.716	203.521	486.088	−12.695
2100	81.893	412.347	346.681	137.899	204.102	500.202	−12.442
2200	82.002	416.160	349.753	146.094	204.654	514.290	−12.211
2300	82.097	419.807	352.721	154.299	205.176	528.352	−11.999
2400	82.181	423.303	355.589	162.513	205.666	542.392	−11.805
2500	82.255	426.659	358.365	170.735	206.124	556.412	−11.626
2600	82.322	429.886	361.054	178.964	206.547	570.416	−11.460
2700	82.381	432.994	363.662	187.199	206.936	584.404	−11.306
2800	82.434	435.991	366.192	195.439	207.291	598.377	−11.163
2900	82.481	438.885	368.649	203.685	207.611	612.338	−11.029
3000	82.524	441.682	371.037	211.935	207.897	626.290	−10.905
3100	82.563	444.389	373.360	220.190	208.150	640.233	−10.788
3200	82.599	447.010	375.620	228.448	208.369	654.166	−10.678
3300	82.631	449.553	377.822	236.709	208.557	668.094	−10.575
3400	82.660	452.020	379.969	244.974	208.715	682.017	−10.478
3500	82.687	454.416	382.062	253.241	208.844	695.936	−10.386
3600	82.712	456.746	384.104	261.511	208.945	709.851	−10.300
3700	82.735	459.013	386.098	269.784	209.022	723.764	−10.218
3800	82.756	461.219	388.046	278.058	209.074	737.676	−10.140
3900	82.776	463.369	389.950	286.335	209.105	751.587	−10.066
4000	82.794	465.465	391.812	294.614	209.115	765.496	−9.996
4100	82.811	467.510	393.633	302.894	209.107	779.405	−9.930
4200	82.826	469.505	395.416	311.176	209.082	793.315	−9.866
4300	82.841	471.455	397.162	319.459	209.042	807.227	−9.806
4400	82.854	473.359	398.872	327.744	208.989	821.137	−9.748
4500	82.867	475.221	400.548	336.030	208.923	835.050	−9.693
4600	82.879	477.043	402.191	344.317	208.845	848.964	−9.640
4700	82.890	478.825	403.803	352.605	208.757	862.881	−9.590
4800	82.900	480.570	405.384	360.895	208.659	876.800	−9.542
4900	82.910	482.280	406.936	369.186	208.551	890.722	−9.495
5000	82.919	483.955	408.460	377.477	208.435	904.645	−9.451
5100	82.928	485.597	409.956	385.769	208.310	918.571	−9.408
5200	82.936	487.208	411.426	394.063	208.176	932.497	−9.367
5300	82.944	488.787	412.871	402.357	208.033	946.429	−9.328
5400	82.951	490.338	414.291	410.651	207.880	960.362	−9.290
5500	82.958	491.860	415.688	418.947	207.718	974.297	−9.253
5600	82.965	493.355	417.061	427.243	207.543	988.238	−9.218
5700	82.971	494.823	418.413	435.540	207.357	1002.180	−9.184
5800	82.977	496.266	419.743	443.837	207.158	1016.127	−9.151
5900	82.983	497.685	421.052	452.135	206.945	1030.074	−9.120
6000	82.988	499.080	422.341	460.434	206.715	1044.029	−9.089

PREVIOUS: CURRENT: December 1996 (1bar)

$S°(298.15\ K)$ = [237.879] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [129.6] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [129.0] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^3\Sigma]$	0	3

ω_e = [472] cm^{-1} $\omega_e x_e$ = [1.89] cm^{-1} σ = 1
B_e = [0.2443] cm^{-1} α_e = [0.00098] cm^{-1} r_e = [2.04] Å

Enthalpy of Formation

The selected $\Delta_f H°(298.15\ K)$ was calculated by assuming that the second and third bonds in $PCl_3(g)$ are of equal strength, and that the first bond has a strength 20% greater than the other two. These assumptions wee used by Henderson and Scheffee.[1] The selected $\Delta_f H°(298.15\ K)$ was calculated using these bond strengths and auxiliary data from JANAF Tables.

A $\Delta_f H°(298.15\ K)$ = 40 $kcal·mol^{-1}$ was estimated by O'Brien and Perrin.[2]

Sandoval *et al.*[3] have calculated a $\Delta_f H°(298.15\ K)$ for PCl from an appearance potential. They selected the process $PCl_3 \rightarrow Cl^+ + e^- + PCl^+ Cl$ to explain this potential rather than the process $PCl_3 \rightarrow Cl^+ + e^- + P + Cl_2$. The reason for their selection was a calculated $\Delta_f H°$+(Cl), 10 $kcal·mol^{-1}$ lower than the literature value (See Nat. Bur. Stand., Circ 500). Use of the JANAF $\Delta_f H°(298.15\ K)$ for PCl_3 eliminates this difference. Therefore, the process of the reported appearance potential would apparently be the second process which does not involve the neutral PCl radial.

Heat Capacity and Entropy

The molecular constants were estimated by Gordon.[4]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.338	129.612	129.612	INFINITE
100	29.561	203.014	267.234	−6.422	130.185	121.103	−63.258
200	32.631	224.417	240.997	−3.316	129.509	112.047	−29.264
250	33.861	231.837	238.446	−1.652	129.272	107.708	−22.504
298.15	34.718	237.879	237.879	0.	129.000	103.579	−18.147
300	34.745	238.094	237.879	0.064	128.989	103.421	−18.007
350	35.378	243.500	238.305	1.818	127.948	99.256	−14.813
400	35.840	248.256	239.258	3.599	127.537	95.186	−12.430
450	36.185	252.498	240.497	5.400	127.133	91.166	−10.582
500	36.449	256.324	241.892	7.216	126.736	87.191	−9.109
600	36.822	263.005	244.870	10.881	125.952	79.356	−6.909
700	37.073	268.702	247.878	14.577	125.179	71.651	−5.347
800	37.253	273.664	250.797	18.294	124.413	64.057	−4.182
900	37.391	278.060	253.587	22.026	123.653	56.558	−3.283
1000	37.502	282.006	256.235	25.771	122.897	49.144	−2.567
1100	37.595	285.585	258.743	29.526	122.144	41.805	−1.985
1200	37.675	288.859	261.118	33.289	57.822	35.613	−1.550
1300	37.747	291.878	263.370	37.061	57.849	33.761	−1.357
1400	37.812	294.678	265.507	40.839	57.874	31.907	−1.190
1500	37.873	297.288	267.540	44.623	57.896	30.051	−1.046
1600	37.930	299.735	269.476	48.413	57.916	28.194	−0.920
1700	37.983	302.036	271.325	52.209	57.934	26.336	−0.809
1800	38.035	304.208	273.092	56.010	57.949	24.477	−0.710
1900	38.085	306.266	274.784	59.816	57.963	22.617	−0.622
2000	38.133	308.221	276.407	63.627	57.974	20.757	−0.542
2100	38.181	310.082	277.967	67.442	57.982	18.896	−0.470
2200	38.227	311.860	279.468	71.263	57.987	17.034	−0.404
2300	38.272	313.560	280.913	75.088	57.987	15.173	−0.345
2400	38.317	315.190	282.308	78.917	57.983	13.311	−0.290
2500	38.361	316.755	283.654	82.751	57.974	11.450	−0.239
2600	38.405	318.260	284.957	86.589	57.958	9.589	−0.193
2700	38.448	319.710	286.217	90.432	57.937	7.730	−0.150
2800	38.491	321.109	287.438	94.279	57.909	5.870	−0.110
2900	38.534	322.461	288.623	98.130	57.874	4.013	−0.072
3000	38.576	323.768	289.773	101.986	57.831	2.156	−0.038
3100	38.618	325.034	290.890	105.845	57.782	0.301	−0.005
3200	38.660	326.260	291.976	109.709	57.727	−1.552	0.025
3300	38.702	327.451	293.033	113.577	57.665	−3.404	0.054
3400	38.744	328.607	294.063	117.450	57.598	−5.254	0.081
3500	38.785	329.730	295.066	121.326	57.526	−7.101	0.106
3600	38.826	330.823	296.044	125.207	57.450	−8.946	0.130
3700	38.868	331.888	296.998	129.091	57.371	−10.790	0.152
3800	38.909	332.925	297.930	132.980	57.291	−12.631	0.174
3900	38.950	333.936	298.840	136.873	57.211	−14.470	0.194
4000	38.991	334.923	299.730	140.770	57.131	−16.307	0.213
4100	39.031	335.886	300.600	144.671	57.053	−18.142	0.231
4200	39.072	336.827	301.452	148.576	56.979	−19.975	0.248
4300	39.113	337.747	302.285	152.486	56.910	−21.806	0.265
4400	39.154	338.647	303.101	156.399	56.846	−23.636	0.281
4500	39.194	339.527	303.901	160.316	56.790	−25.465	0.296
4600	39.235	340.389	304.685	164.238	56.743	−27.292	0.310
4700	39.275	341.233	305.454	168.163	56.705	−29.119	0.324
4800	39.316	342.060	306.208	172.093	56.677	−30.944	0.337
4900	39.356	342.871	306.948	176.026	56.662	−32.769	0.349
5000	39.397	343.667	307.674	179.964	56.659	−34.595	0.361
5100	39.437	344.447	308.387	183.906	56.669	−36.420	0.373
5200	39.477	345.214	309.088	187.851	56.694	−38.245	0.384
5300	39.518	345.966	309.777	191.801	56.733	−40.071	0.395
5400	39.558	346.705	310.454	195.755	56.788	−41.898	0.405
5500	39.598	347.431	311.120	199.713	56.858	−43.726	0.415
5600	39.639	348.145	311.775	203.675	56.946	−45.556	0.425
5700	39.679	348.847	312.419	207.641	57.050	−47.387	0.434
5800	39.719	349.537	313.053	211.610	57.171	−49.220	0.443
5900	39.759	350.217	313.677	215.584	57.309	−51.056	0.452
6000	39.799	350.885	314.292	219.562	57.465	−52.894	0.460

PREVIOUS: December 1963 (1 atm) CURRENT: December 1963 (1 bar)

$S°(298.15\ K) = 259.61 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 16.74 \pm 50.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 15.06 \pm 50.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X $^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	8274	2
A[$^2\Sigma$]	21866.9	[2]
B $2\Sigma^+$	34937.5	2

$\omega_e = 302.5\ cm^{-1}$ $\omega_e x_e = 0.88\ cm^{-1}$ $\sigma = 1$
$B_e = 0.1172\ cm^{-1}$ $\alpha_e = [0.00047]\ cm^{-1}$ $r_e = 2.180$ Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ is obtained from $D_0°$ (Pb–Cl) = 3.1 ± 0.5 eV (71.5 kcal·mol^{-1}) which is the recommended value given by Gaydon.[1] $D_0°$ is combined with $\Delta_f H°$(Pb, g, 0 K) = 46.91 ± 0.13 kcal·mol^{-1} and $\Delta_f H°$(Cl, g, 0 K) = 28.587 ± 0.002 kcal·mol^{-1}[2] to give $\Delta_f H°$(PbCl, g, 0 K) = 4.0 ± 12.0 kcal·mol^{-1}. $\Delta_f H°$ at 298.15 K is 3.6 ± 12.0 kcal·mol^{-1}. The recommended value for $D_0°$ is based mainly on results ($D_0°$(LBX) = 3.2 eV) of a linear Birge–Sponer extrapolation of the observed vibrational levels (ν, 0–18)[3] for the ground state of PbCl. This same value for $D_0°$(LBX) is obtained from the results of two other spectrometric studies, Morgan[4] and Pannetier and Deschamps,[5] while the results of another similar study Cordes and Gehrke[6] lead to $D_0°$(LBX) = 2.7 eV. The values of $D_0°$(LBX) are increased by only 0.1 eV when corrected for the ionic character of PbCl by application of the Hildenbrand formula.[7] Other spectroscopic values for $D_0°$(LBS) based on linear Birge–Sponer extrapolations include 2.2 eV ($A^2\Sigma$, or $^2\Delta$)[5] and 2.4 eV ($B^2\Sigma$) by Cordes and Gehrke.[6] The dissociation products are assumed to be Pb(^{1}D) + Cl(^{2}P)($A^2\Sigma$, or $^2\Delta$) and Pb(^{3}P) + Cl(^{2}P) ($B^2\Sigma$). Also, Wieland and Newburgh[8] first reported $D_0°$ = 3.12 eV from observations of predissociation, but later work[9] gave 3.05, or possibly 3.40 eV. It is to be noted that our $\Delta_f H°$ values for PbCl and $PbCl_2$, JANAF[2], indicate no significant differences in the binding of these two molecules. The difference $D_0°$(PbCl–Cl)–$D_0°$(Pb–Cl) is equal to only 2.2 kcal·mol^{-1}.

Heat Capacity and Entropy

The vibrational constants, electronic states (except for $A^2\Sigma$), and levels are taken from the compilation of Rosen[10] for $Pb^{35}Cl$. The vibrational constants are adjusted for the natural isotopic abundances of chlorine. It is not clear whether the first excited state for PbCl is $^2\Sigma$ or $^2\Delta$. By analogy with that for PbF,[11] we assume the first excited state to be $^2\Sigma$. However, if this state is $^2\Delta$, the entropy is increased by only 0.006 cal·K^{-1}·mol^{-1} at 4000 K and 0.05 cal·K^{-1}·mol^{-1} at 6000 K. The rotational constant is taken from the results of a rotational analysis of two bands of the A–X system for $^{208}Pb^{35}Cl$ by Singh and Singh.[12] The rotational constant is adjusted for the natural isotopic abundances of lead and chlorine. The value for r_e is obtained from the adopted B_e value. The results of an earlier rotational analysis of the same bands by Rao and Rao[13] are in reasonable agreement with our adopted values. The value for α_e is estimated from the other constants assuming a Morse potential function.

References

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.793	16.738	16.738	INFINITE
100	31.235	222.428	290.774	−6.835	16.474	7.365	−3.847
200	34.890	245.391	262.893	−3.500	15.765	−1.462	0.382
250	35.727	253.274	260.207	−1.733	15.418	−5.729	1.197
298.15	36.234	259.613	259.613	0.	15.062	−9.770	1.712
300	36.250	259.837	259.614	0.067	15.048	−9.924	1.728
350	36.597	265.453	260.056	1.889	14.657	−14.055	2.098
400	36.841	270.356	261.044	3.725	14.242	−18.129	2.367
450	37.021	274.707	262.325	5.572	13.805	−22.150	2.571
500	37.158	278.614	263.762	7.426	13.344	−26.120	2.729
600	37.358	285.408	266.820	11.153	12.366	−33.922	2.953
700	37.500	291.178	269.898	14.896	6.451	−40.757	3.041
800	37.611	296.193	272.878	18.652	5.340	−47.424	3.096
900	37.705	300.629	275.720	22.418	4.260	−53.955	3.131
1000	37.790	304.606	278.413	26.193	3.212	−60.367	3.153
1100	37.873	308.211	280.961	29.976	2.196	−66.675	3.166
1200	37.961	311.510	283.371	33.767	1.212	−72.892	3.173
1300	38.057	314.553	285.654	37.568	0.257	−79.029	3.175
1400	38.166	317.377	287.820	41.379	−0.686	−85.092	3.175
1500	38.289	320.014	289.880	45.202	−1.623	−91.089	3.172
1600	38.429	322.490	291.841	49.038	−2.560	−97.022	3.167
1700	38.585	324.824	293.713	52.888	−3.499	−102.898	3.162
1800	38.756	327.034	295.504	56.755	−4.443	−108.717	3.155
1900	38.941	329.135	297.219	60.640	−5.391	−114.485	3.147
2000	39.138	331.137	298.865	64.544	−6.346	−120.202	3.139
2100	39.345	333.051	300.448	68.468	−184.528	−118.756	2.954
2200	39.560	334.887	301.972	72.413	−185.106	−115.610	2.745
2300	39.780	336.650	303.441	76.380	−185.757	−112.437	2.554
2400	40.002	338.348	304.861	80.369	−186.484	−109.234	2.377
2500	40.225	339.985	306.233	84.380	−187.288	−105.999	2.215
2600	40.448	341.567	307.562	88.414	−188.169	−102.730	2.064
2700	40.668	343.098	308.850	92.470	−189.124	−99.426	1.924
2800	40.884	344.581	310.100	96.548	−190.152	−96.086	1.792
2900	41.095	346.019	311.313	100.647	−191.249	−92.707	1.670
3000	41.300	347.416	312.494	104.766	−192.408	−89.289	1.555
3100	41.499	348.773	313.642	108.906	−193.626	−85.832	1.446
3200	41.692	350.094	314.761	113.066	−194.896	−82.335	1.344
3300	41.877	351.380	315.851	117.244	−196.210	−78.797	1.247
3400	42.055	352.633	316.915	121.441	−197.563	−75.219	1.156
3500	42.226	353.854	317.953	125.655	−198.947	−71.600	1.069
3600	42.389	355.046	318.966	129.886	−200.356	−67.942	0.986
3700	42.546	356.209	319.957	134.133	−201.781	−64.244	0.907
3800	42.696	357.346	320.926	138.395	−203.218	−60.508	0.832
3900	42.840	358.457	321.875	142.672	−204.660	−56.734	0.760
4000	42.978	359.543	322.803	146.963	−206.100	−52.922	0.691
4100	43.110	360.606	323.712	151.267	−207.533	−49.075	0.625
4200	43.236	361.647	324.603	155.585	−208.954	−45.193	0.562
4300	43.358	362.665	325.476	159.914	−210.359	−41.277	0.501
4400	43.474	363.664	326.333	164.256	−211.742	−37.329	0.443
4500	43.586	364.642	327.173	168.609	−213.101	−33.350	0.387
4600	43.695	365.601	327.998	172.973	−214.433	−29.340	0.333
4700	43.799	366.542	328.808	177.348	−215.733	−25.303	0.281
4800	43.900	367.465	329.604	181.733	−217.001	−21.238	0.231
4900	43.997	368.371	330.386	186.128	−218.233	−17.146	0.183
5000	44.092	369.261	331.155	190.532	−219.428	−13.030	0.136
5100	44.184	370.135	331.910	194.946	−220.585	−8.891	0.091
5200	44.274	370.994	332.654	199.369	−221.703	−4.729	0.048
5300	44.361	371.838	333.385	203.801	−222.781	−0.546	0.005
5400	44.446	372.668	334.105	208.241	−223.819	3.657	−0.035
5500	44.529	373.484	334.814	212.690	−224.816	7.879	−0.075
5600	44.611	374.287	335.511	217.147	−225.773	12.118	−0.113
5700	44.691	375.078	336.198	221.612	−226.689	16.374	−0.150
5800	44.769	375.856	336.876	226.085	−227.566	20.646	−0.186
5900	44.846	376.622	337.543	230.566	−228.403	24.933	−0.221
6000	44.922	377.376	338.200	235.054	−229.202	29.233	−0.254

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K) = [255.15 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 741.0 \pm 50.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [745.589]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
$^3\Pi$	[30000]	6

$\omega_e = [283]\ cm^{-1}$ $\omega_e x_e = [0.82]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.1062]\ cm^{-1}$ $\alpha_e = [0.00043]\ cm^{-1}$ $r_e = [2.29]$ Å

Enthalpy of Formation

The $PbCl^+$ ion has been observed in several mass spectrometric studies[1-4] of the vapors in equilibrium with both solid and liquid $PbCl_2$. Electric deflection experiments of mass spectrometrically detected $PbCl_2$ beams by Buchler *et al.*[5] have shown neutral $PbCl_2$ to be the precursor of the ion. Reported values for the AP of $PbCl^+$ are 11.7[1] and 10.7 $cal \cdot K^{-1} \cdot mol^{-1}$.[2,3,4] The higher value of AP was obtained by the method of linear extrapolation; thus, it is judged to be somewhat less reliable. Also, the lower value was obtained with more sensitive equipment. Therefore, we adopt AP = 10.7 ± 0.5 $cal \cdot K^{-1} \cdot mol^{-1}$ for the process $PbCl_2(g) + e^- \rightarrow PbCl^+(g) + Cl(g) + 2e^-$, and we calculate $\Delta_f H°(PbCl^+, g, 0\ K) = 177.1 \pm 12.0\ kcal \cdot mol^{-1}$ by combining the value for AP with $\Delta_f H°(PbCl_2, g, 0\ K) = -41.1 \pm 0.3\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Cl, g, 0\ K) = 28.587 \pm 0.002\ kcal \cdot mol^{-1}$.[6] $\Delta_f H°$ at 298.15 K is 178.2 $kcal \cdot mol^{-1}$, and the corresponding IP for PbCl is 7.5 ± 1.0 $cal \cdot K^{-1} \cdot mol^{-1}$. Our adopted $\Delta_f H°$ is considered a maximum value, since unknown kinetic energy factors could have been involved in the dissociative ionization of $PbCl_2$.

Heat Capacity and Entropy

The dissociation energy of $PbCl^+$ ($D_0° = 69.5\ kcal \cdot mol^{-1}$) is slightly less than that for PbCl ($D_0° = 71.5\ kcal \cdot mol^{-1}$). This implies that somewhat weaker binding occurs in the ion relative to the neutral molecule. Thus, one might expect $r_e(PbCl^+, g) > r_e(PbCl, g)$. We assume an increase in r_e of 5% and obtain $r_e(PbCl^+) = 2.29$ Å with $r_e(PbCl) = 2.180$ Å.[6] The value of B_e is obtained from the estimated value for r_e. Values for ω_e and $\omega_e x_e$ are estimated by a procedure similar to that given for SrF^+.[6] The constant term (d_{ij}) used in Badger's rule[7] is based on molecular data for PbCl, PbS, CsCl, and BaCl.[6] The value of α_e is obtained from the other constants assuming a Morse potential function.

$PbCl^+$ has 10 valence electrons and is isoelectronic with the Group III A monochlorides. By analogy with the electronic states and levels for these isoelectronic molecules,[6,8] we estimate the ground state configuration to be $^1\Sigma$ with a triplet level lying at 30,000 cm^{-1}. The uncertainty in the latter value is believed to be no greater than 5000 cm^{-1}. If the triplet level is decreased to 25,000 cm^{-1}, the entropy increases only 0.01 $cal \cdot K^{-1} \cdot mol^{-1}$ at 4000 K and 1.14 $cal \cdot K^{-1} \cdot mol^{-1}$ at 6000 K. The enthalpy at 0 K is −2.357 $kcal \cdot mol^{-1}$.

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[6] JANAF Thermochemical Tables: $PbCl_2$(g), PbCl(g), and PbS(g), 6-20-73; Cl(g), 6-20-72; SrF^+(g) and BaCl(g), 12-31-72; CSCl(g), 6-30-68; AlCl(g), 6-30-70.
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[8] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., D. Van Nostrand Co., Inc., New York, (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.860	741.001		
100	31.590	217.637	286.530	−6.889			
200	35.163	240.840	258.445	−3.521			
250	35.932	248.776	255.744	−1.742			
298.15	36.394	255.148	255.148	0.	745.589	715.833	−125.411
300	36.408	255.373	255.148	0.067	745.614	715.648	−124.605
350	36.723	261.010	255.593	1.896	746.269	710.602	−106.052
400	36.945	265.929	256.584	3.738	746.899	705.463	−92.124
450	37.108	270.290	257.869	5.590	747.505	700.247	−81.283
500	37.235	274.207	259.310	7.448	748.088	694.965	−72.602
600	37.420	281.013	262.377	11.182	749.195	684.235	−59.568
700	37.554	286.792	265.463	14.931	745.365	674.124	−50.304
800	37.660	291.814	268.449	18.691	746.337	663.881	−43.347
900	37.749	296.255	271.297	22.462	747.341	653.514	−37.929
1000	37.829	300.236	273.995	26.241	748.376	643.033	−33.589
1100	37.901	303.845	276.547	30.028	749.441	632.448	−30.032
1200	37.969	307.146	278.962	33.821	750.538	621.764	−27.065
1300	38.033	310.188	281.248	37.621	751.660	610.987	−24.550
1400	38.095	313.008	283.417	41.428	752.792	600.124	−22.391
1500	38.156	315.639	285.479	45.240	753.923	589.179	−20.517
1600	38.214	318.103	287.441	49.059	755.048	578.160	−18.875
1700	38.272	320.422	289.314	52.883	756.161	567.070	−17.424
1800	38.329	322.611	291.104	56.713	757.259	555.915	−16.132
1900	38.386	324.685	292.817	60.549	758.340	544.700	−14.975
2000	38.442	326.655	294.460	64.390	759.401	533.428	−13.932
2100	38.497	328.532	296.038	68.237	583.221	529.219	−13.164
2200	38.552	330.324	297.556	72.090	584.629	526.614	−12.503
2300	38.607	332.039	299.018	75.948	585.947	523.947	−11.899
2400	38.662	333.683	300.429	79.811	587.173	521.225	−11.344
2500	38.716	335.263	301.791	83.680	588.305	518.453	−10.832
2600	38.771	336.782	303.107	87.554	589.344	515.638	−10.359
2700	38.825	338.246	304.382	91.434	590.291	512.785	−9.920
2800	38.880	339.659	305.617	95.319	591.149	509.899	−9.512
2900	38.935	341.025	306.814	99.210	591.923	506.983	−9.132
3000	38.991	342.346	307.977	103.106	592.619	504.042	−8.776
3100	39.047	343.625	309.106	107.008	593.242	501.079	−8.443
3200	39.105	344.866	310.204	110.916	593.799	498.097	−8.131
3300	39.163	346.070	311.273	114.829	594.298	495.099	−7.837
3400	39.224	347.240	312.314	118.749	594.746	492.086	−7.560
3500	39.286	348.378	313.328	122.674	595.152	489.060	−7.299
3600	39.350	349.485	314.317	126.606	595.523	486.024	−7.052
3700	39.417	350.564	315.282	130.544	595.867	482.977	−6.818
3800	39.487	351.617	316.225	134.489	596.192	479.922	−6.597
3900	39.561	352.643	317.145	138.442	596.505	476.858	−6.387
4000	39.638	353.646	318.045	142.402	596.812	473.786	−6.187
4100	39.720	354.626	318.926	146.370	597.121	470.707	−5.997
4200	39.806	355.584	319.787	150.346	597.437	467.620	−5.816
4300	39.897	356.521	320.631	154.331	597.767	464.525	−5.643
4400	39.994	357.440	321.457	158.325	598.114	461.422	−5.478
4500	40.097	358.340	322.266	162.330	598.485	458.311	−5.320
4600	40.206	359.222	323.060	166.345	598.884	455.192	−5.169
4700	40.321	360.088	323.839	170.371	599.313	452.064	−5.024
4800	40.444	360.938	324.603	174.409	599.778	448.926	−4.885
4900	40.573	361.773	325.353	178.460	600.280	445.778	−4.752
5000	40.710	362.594	326.090	182.524	600.823	442.619	−4.624
5100	40.854	363.402	326.813	186.602	601.409	439.450	−4.501
5200	41.006	364.197	327.525	190.695	602.040	436.268	−4.382
5300	41.165	364.979	328.224	194.804	602.717	433.074	−4.268
5400	41.333	365.750	328.912	198.929	603.443	429.866	−4.158
5500	41.508	366.510	329.588	203.071	604.217	426.645	−4.052
5600	41.691	367.260	330.255	207.230	605.042	423.409	−3.949
5700	41.882	368.000	330.910	211.409	605.917	420.158	−3.850
5800	42.080	368.730	331.556	215.607	606.844	416.891	−3.755
5900	42.286	369.451	332.192	219.825	607.823	413.607	−3.662
6000	42.500	370.163	332.819	224.064	608.854	410.307	−3.572

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K)$ = [237.32 ± 2.5] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [155.65 ± 16.7] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [156.46 ± 16.7] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[400]	[2]
[25000]	[4]

ω_e = [536] cm^{-1} $\omega_e x_e$ = [2.08] cm^{-1} σ = 1
B_e = [0.24060] cm^{-1} α_e = [0.00126] cm^{-1} r_e = [2.04] Å

Enthalpy of Formation

The adopted results are $\Delta_f H°$(SCl, g, 298.15 K) = 37.2 ± 4.0 $kcal·mol^{-1}$ and $D_0°$(S–Cl) = 57.1 ± 4.0 $kcal·mol^{-1}$. We calculate $\Delta_f H°$ from an estimated value for the primary bond dissociation energy of SCl_2 of 69.7 ± 3.0 $kcal·mol^{-1}$, using auxiliary heat of formation data from JANAF.[1] The value of $D_0°$(SCl–Cl) is obtained from the relationship $D_0°(SCl–Cl)/\Delta_{at}H°(SCl_2) = 0.55 \pm 0.03$ with $\Delta_{at}H°(SCl_2)$ = 126.8 ± 0.9 $kcal·mol^{-1}$.[1] The value of the ratio is taken to be the mean of three values calculated[1] for SF_2(0.53 ± 0.05), $SiCl_2$(0.57 ± 0.01), and SiF_2(0.54 ± 0.03). Converting $\Delta_f H°$ to 298.15 K, we obtain $\Delta_f H°$(SCl, g, 298.15 K) = 37.4 $kcal·mol^{-1}$ which is in reasonable agreement with the previous estimate made by Mills (35 ± 5),[2] McBride *et al.* (32.0),[3] and Benson (36.5 ± 2).[4]

Perona *et al.*[5] have measured the hydrogen chloride infrared emission from reactions involving H and D atoms with SCl_2. From the observed highest vibrational level of HCl, they estimated an upper limit to $D_0°$(SCl–Cl) of ≤58 $kcal·mol^{-1}$. From this result, we calculate $\Delta_f H°$(SCl, g, 0 K) ≤25.5 $kcal·mol^{-1}$ and $D_0°$(SCl) ≥68.8 $kcal·mol^{-1}$. We note that the results from this study predict that $D_0°$(S–Cl) > $D_0°$(SCl–Cl) which is inconsistent with established trends in the bond dissociation energies[1] for other mono- and dihalides, such as the silicon chlorides, silicon fluorides, and sulfur fluorides. Factors which can influence the $D_0°$ values estimated from infrared chemiluminescence studies have been discussed by Perona *et al.*[5] It seems likely that their estimate of $D°$ may be too low due to the formation of some HCl in higher vibrational levels by an energy exchange mechanism rather than what is actually produced by the H/SCl_2 chemical reaction. For these reasons, we believe that the $\Delta_f H°$(0 K) value (19 ± 3 $kcal·mol^{-1}$ recently reported by Takacs[6] based primarily on his analysis of the chemiluminscence work of Perona *et al.*[5] is suspect. The results adopted here predict $D_0°$(SCl–Cl) > $D_0°$(S–Cl) by roughly 13 $kcal·mol^{-1}$ which seems reasonable by comparison with bond energy data[1] for other halide systems.

Heat Capacity and Entropy

We estimate the S–Cl bond length to lie between those for SCl_2 and S_2Cl_2.[1] The value of B_e is calculated from the adopted r_e. We use Badger's rule[7] to estimate a value for ω_e. The equation is written as $\omega_e^2 = 3.159 \times 10^6/\mu(r_e–d_{ij})$,[3] and we use molecular data[1] for SiCl to determine the constant d_{ij} = 1.172. The value of x_e is estimated from the expression $x_e\mu^{1/2} = 0.01595$ calculated from data for SiCl.[1] By analogy with SiCl, SiF, and SF, we expect the ground state electronic configuration for SCl to be.[2] The ground state splitting (400 cm^{-1}) and double pi state at 25000 cm^{-1} are estimated from those observed for SF.[1]

McBride *et al.*[3] have previously estimated thermal functions over an extended temperature range (0–6000 K), using molecular data similar to ours. Their entropies are consistently higher than our values by 0.6 $cal·K^{-1}·mol^{-1}$ at 298.15 K and 0.3 $cal·K^{-1}·mol^{-1}$ at 4000 K. The difference at 298.15 K arises primarily from the electronic contribution caused by treating the ground state as a single level[3] with a quantum weight of 4. We believe that the uncertainty in $S°$(298.15 K) should not exceed ± 0.6 $cal·K^{-1}·mol^{-1}$. Their estimate of $\omega_e x_e$ = 5.85 cm^{-1},[3] obtained assuming a linear Birge–Sponer relation, seems rather high in comparison with similar data[1] for SiCl, SiF, and SF.

References

[1]JANAF Thermochemical Tables: SCl_2(g), 6-30-78; SF(g) and SF_2(g), 6-30-76; SiF2(g) and $SiCl_2$(g), 12-31-77; S_2Cl_2(g), 6-30-78; SiF(g) and SiCl(g), 12-31-76; Cl(g), 6-30-72; F(g), 9-30-65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.819	155.648	155.648	INFINITE
100	30.207	200.110	269.024	−6.891	156.430	147.122	−76.848
200	35.382	222.704	240.708	−3.601	156.560	137.743	−35.975
250	36.817	230.770	237.939	−1.792	156.540	133.040	−27.797
298.15	37.541	237.324	237.324	0.	156.465	128.520	−22.516
300	37.560	237.556	237.325	0.069	156.461	128.346	−22.347
350	37.916	243.376	237.783	1.958	156.323	123.671	−18.457
400	38.073	248.451	238.807	3.858	153.917	119.106	−15.554
450	38.130	252.939	240.132	5.763	153.009	114.800	−13.326
500	38.140	256.958	241.618	7.670	152.016	110.610	−11.555
600	38.110	263.909	244.771	11.483	150.428	102.484	−8.922
700	38.068	269.781	247.935	15.292	149.054	94.604	−7.059
800	38.037	274.862	250.991	19.097	147.798	86.912	−5.675
900	38.018	279.341	253.897	22.899	93.484	80.454	−4.669
1000	38.010	283.346	256.645	26.701	93.561	79.002	−4.127
1100	38.011	286.969	259.240	30.502	93.615	77.543	−3.682
1200	38.019	290.276	261.690	34.303	93.649	76.080	−3.312
1300	38.032	293.320	264.008	38.106	93.662	74.616	−2.998
1400	38.050	296.139	266.203	41.910	93.658	73.151	−2.729
1500	38.070	298.765	268.288	45.716	93.635	71.687	−2.496
1600	38.093	301.223	270.270	49.524	93.595	70.225	−2.293
1700	38.118	303.533	272.159	53.335	93.538	68.766	−2.113
1800	38.145	305.712	273.963	57.148	93.466	67.310	−1.953
1900	38.173	307.775	275.689	60.964	93.379	65.860	−1.811
2000	38.202	309.734	277.343	64.782	93.278	64.414	−1.682
2100	38.232	311.599	278.930	68.604	93.163	62.973	−1.566
2200	38.263	313.378	280.456	72.429	93.035	61.539	−1.461
2300	38.295	315.080	281.924	76.257	92.893	60.110	−1.365
2400	38.327	316.710	283.340	80.088	92.739	58.688	−1.277
2500	38.360	318.275	284.706	83.922	92.573	57.273	−1.197
2600	38.394	319.780	286.027	87.760	92.394	55.864	−1.122
2700	38.428	321.230	287.304	91.601	92.203	54.463	−1.054
2800	38.463	322.628	288.541	95.446	92.000	53.069	−0.990
2900	38.498	323.979	289.739	99.294	91.785	51.682	−0.931
3000	38.535	325.284	290.903	103.145	91.559	50.303	−0.876
3100	38.572	326.549	292.032	107.001	91.323	48.932	−0.824
3200	38.610	327.774	293.130	110.860	91.076	47.568	−0.776
3300	38.649	328.962	294.198	114.723	90.820	46.213	−0.731
3400	38.689	330.117	295.238	118.589	90.556	44.865	−0.689
3500	38.731	331.239	296.250	122.460	90.284	43.525	−0.650
3600	38.774	332.331	297.237	126.336	90.005	42.193	−0.612
3700	38.819	333.394	298.200	130.215	89.721	40.869	−0.577
3800	38.865	334.429	299.140	134.100	89.433	39.552	−0.544
3900	38.913	335.440	300.058	137.988	89.142	38.243	−0.512
4000	38.962	336.425	300.955	141.882	88.849	36.942	−0.482
4100	39.014	337.388	301.832	145.781	88.556	35.648	−0.454
4200	39.067	338.329	302.690	149.685	88.264	34.361	−0.427
4300	39.122	339.249	303.529	153.594	87.975	33.081	−0.402
4400	39.179	340.149	304.351	157.509	87.689	31.808	−0.378
4500	39.239	341.030	305.157	161.430	87.407	30.541	−0.355
4600	39.300	341.893	305.946	165.357	87.132	29.280	−0.332
4700	39.363	342.739	306.720	169.290	86.863	28.025	−0.311
4800	39.428	343.568	307.479	173.230	86.603	26.776	−0.291
4900	39.495	344.382	308.224	177.176	86.352	25.533	−0.272
5000	39.564	345.181	308.955	181.129	86.110	24.294	−0.254
5100	39.635	345.965	309.673	185.089	85.880	23.060	−0.236
5200	39.708	346.735	310.378	189.056	85.661	21.830	−0.219
5300	39.783	347.492	311.071	193.031	85.455	20.604	−0.203
5400	39.859	348.236	311.753	197.013	85.262	19.383	−0.187
5500	39.937	348.969	312.423	201.003	85.082	18.165	−0.173
5600	40.017	349.689	313.082	205.000	84.916	16.949	−0.158
5700	40.098	350.398	313.730	209.006	84.765	15.737	−0.144
5800	40.181	351.096	314.368	213.020	84.629	14.527	−0.131
5900	40.265	351.784	314.997	217.042	84.509	13.320	−0.118
6000	40.350	352.461	315.616	221.073	84.404	12.114	−0.105

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

$S°(298.15\ K) = [236.63 \pm 2.5]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1055.66 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1062.037]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[X^3\Sigma]$	0	[3]
$[a^1\Delta]$	[7000]	[2]
$[b^1\Sigma]$	[12000]	[1]
$[A^3\Pi_r]$	[25000]	[6]

$\omega_e = [553]\ cm^{-1}$ $\omega_e x_e = [2.19]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.26333]\ cm^{-1}$ $\alpha_e = [0.00142]\ cm^{-1}$ $r_e = [1.95]$ Å

Enthalpy of Formation

Blais and Cottin[1] have measured the appearance potential (AP) of $SCl^+(g)$ from $SCl_2(g)$ as 12.5 ± 0.2 eV using the electron impact technique. Subsequent work by Hartmann *et al.*[2] using the same method led to $AP(SCl^+/SCl_2) = 12.2 \pm 0.1$ eV which confirms the earlier results. We assume that the fragment ions produced in the dissociative ionization process $e^- + SCl_2(g) = SCl^+(g) + Cl(g) + 2\ e^-$ are formed with no excitation energy or excess kinetic energy, and we calculate the adopted value of $\Delta_f H°(0\ K) = 252.3 \pm 5.0\ kcal \cdot mol^{-1}$ by combining the mean value (284.795 $kcal \cdot mol^{-1}$) of these two AP's with $\Delta_f H°$ data[3] for Cl(g) and $SCl_2(g)$.

Blais and Cottin[1] have also reported the electron impact AP for $SCl^+(g)$ from $S_2Cl_2(g)$ as 13.6 ± 0.2 eV. Assuming that the ionization process is $e^- + S_2Cl_2(g) = SCl^+(g) + SCl(g) + 2e^-$, their AP value gives $\Delta_f H°(SCl^+, g, 0\ K) = 272.8\ kcal \cdot mol^{-1}$ which is about 20 $kcal \cdot mol^{-1}$ higher than the adopted value. Comparison of JANAF IPs[3] for SF (10.09 ± 0.1 eV), SF_2 (10.29 ± 0.3 eV), and SCl_2(9.46 ± 0.02 eV) suggests that the ionization value for SCl should lie near 9.3 eV. Our adopted data for SCl(g) and $SCl^+(g)$ give IP(SCl) = 9.33 ± 0.4 eV. The higher $\Delta_f H°$ value of 272.8 $kcal \cdot mol^{-1}$ corresponds to IP(SCl) = 10.2 ev which appears to be too high by comparison with the difference in the IPs for SF and SF_2 and the highly reliable IP value for SCl_2.[3]

$\Delta_f H°(298.15\ K)$ is obtained from the adopted $\Delta_f H°(0\ K)$ value by using JANAF enthalpies $H°(0\ K) - H°(298.15\ K)$[3] for S(α, cr), $Cl_2(g)$, and $e^-(g)$. $\Delta_r H°(298.15\ K)$ determined for the direct ionization $SCl = SCl^+ + e^-$ from our tables differs from a room-temperature threshold energy due to inclusion of the enthalpies of all the species in this ionization process and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by $-1.481\ kcal \cdot mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron. The S–Cl bond strength to form $S^+(g)$ and Cl(g) by dissociation is calculated to be 80.8 ± 5.0 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The value of r_e has been selected such that when it is substituted into the equation for Badger's rule[5] written as $\omega_{e2} = 3.159 \times 10^6/\mu(r_e - d_{ij})^3$, a value of $\omega_e(553\ cm^{-1})$ is obtained which agrees with that (552.3 cm^{-1}) determined for $P^{35}Cl$ by Coxon and Wickramaaratchi.[6] The value of d_{ij} is taken equal to 1.10 based on the molecular data for SiCl[3] and $P^{35}Cl$.[6] This procedure gives $r_e = 1.95$ Å which is only slightly lower than the S–Cl bond lengths[3] measured for SCl_2(2.015 Å) and S_2Cl_2(2.057 Å). We calculate B_e from the estimated value of r_e. Using the expression $x_e\mu^{1/2} = 0.01623$, x_3 is determined to be 0.00396 which gives $\omega_e x_e = 2.19\ cm^{-1}$ when multiplied by the estimated value of ω_e. The value of the constant in the above expression is based on the values determined for SiCl and PCl. The value of α_e is determined from the other estimated molecular constants assuming a Morse potential function.

Examination of the electronic configurations and levels for diatomic halides having 12 valence electrons, such as PF[3] PCl[6], NCl, and NF[7] suggests that the ground state for SCl^+ is most likely $^3\Sigma$, and several low-lying excited states are expected. We estimate the relative term value for the $a^1\Delta$ state from that observed for PF (7090.41 cm^{-1}). Relative term values for the $b^1\Sigma$ and $A^3\Pi_r$ states are estimated by analogy with those observed for PCl.[6] As discussed by Coxon and Wickramaaratchi[6] for PCl, other singlet ($^1\Pi$) and triplet ($^3\Pi_i$ and $^3\Sigma$) states may be expected to lie in the range 20000–35000 cm^{-1}, similar to those observed for the isoelectronic molecules O_2, S_2, and SO.[3] Inclusion of estimated term values for these additional levels changes our entropy by only about 0.05 $cal \cdot K^{-1} \cdot mol^{-1}$ at 4500 K, and we prefer to omit these levels at this time. The adopted electronic entropy contribution from the excited states amounts to 0.01 $cal \cdot K^{-1} \cdot mol^{-1}$ at 1500 K, and this contribution increases to 0.51 $cal \cdot K^{-1} \cdot mol^{-1}$ at 4500 K.

References

[1] J. C. Blais and M. Cottin, C. R. Acad. Sci. Paris, Series C, **276**, 919 (1973).
[2] O. R. Hartmann, K. H. Lebert, and H. U. Chun, Z. Phys. Chem. **92**, 311 (1974).
[3] JANAF Thermochemical Tables: Cl(g), 6-30-72; SCl_2, SCl_2,(g) and S_2Cl_2(g), 6-30-78; SF^+(g), 6-30-76; SF_2,(g) and SiCl(g), 12-31-76; PF(g) and SO(g), 6-30-77; O_2(g) and e^-(g), 3-31-77; S_2(g) and S(α, cr), 9-30-77; Cl_2(g), 9-30-65.
[4] H. M. Rosenstock *et al.*, J. Phys. Chem. Ref. Data **6**, Suppl. 1, 1977; pp. I-28 and I-35.
[5] R. M. Badger, J. Chem. Phys. **2**, 128 (1934).
[6] J. A. Coxon and M. A. Wickramaaratchi, J. Mol. Spectrosc. **68**, 372 (1977).
[7] S. N. Suchard, "Spectroscopic Data," Volume 1, Part B, IFI/Plenum, New York, (1975).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.183	1055.659		
100	29.303	202.547	265.263	−6.272			
200	31.737	223.512	239.676	−3.233			
250	33.002	230.735	237.187	−1.613			
298.15	33.958	236.633	236.633	0.	1062.037	1028.043	−180.109
300	33.989	236.844	236.634	0.063	1062.065	1027.832	−178.961
350	34.732	242.142	237.051	1.782	1062.798	1022.068	−152.535
400	35.291	246.818	237.985	3.533	1061.282	1016.290	−132.714
450	35.716	251.000	239.203	5.309	1061.283	1010.656	−117.314
500	36.046	254.781	240.575	7.103	1061.217	1005.037	−104.996
600	36.515	261.397	243.509	10.733	1061.524	993.779	−86.516
700	36.829	267.051	246.478	14.401	1062.088	982.446	−73.311
800	37.055	271.985	249.365	18.096	1062.801	971.021	−63.401
900	37.229	276.360	252.126	21.810	1010.477	960.582	−55.751
1000	37.375	280.290	254.749	25.541	1012.561	954.926	−49.880
1100	37.508	283.858	257.236	29.285	1014.638	949.062	−45.067
1200	37.639	287.127	259.592	33.042	1016.706	943.009	−41.048
1300	37.774	290.145	261.828	36.813	1018.766	936.784	−37.640
1400	37.917	292.950	263.952	40.597	1020.820	930.400	−34.714
1500	38.070	295.571	265.973	44.397	1022.870	923.870	−32.172
1600	38.234	298.033	267.901	48.212	1024.915	917.204	−29.944
1700	38.407	300.356	269.743	52.044	1026.959	910.409	−27.973
1800	38.589	302.557	271.505	55.893	1029.002	903.494	−26.219
1900	38.777	304.648	273.195	59.762	1031.046	896.466	−24.646
2000	38.970	306.642	274.818	63.649	1033.091	889.330	−23.227
2100	39.165	308.548	276.379	67.556	1035.140	882.091	−21.941
2200	39.362	310.375	277.883	71.482	1037.192	874.755	−20.769
2300	39.557	312.129	279.334	75.428	1039.248	867.326	−19.698
2400	39.751	313.816	280.736	79.394	1041.307	859.807	−18.713
2500	39.941	315.443	282.092	83.378	1043.369	852.202	−17.806
2600	40.127	317.013	283.405	87.382	1045.434	844.515	−16.967
2700	40.308	318.531	284.678	91.403	1047.502	836.748	−16.188
2800	40.483	320.000	285.913	95.443	1049.573	828.904	−15.463
2900	40.652	321.424	287.113	99.500	1051.646	820.986	−14.788
3000	40.815	322.805	288.280	103.573	1053.720	812.997	−14.156
3100	40.972	324.145	289.416	107.663	1055.796	804.939	−13.563
3200	41.122	325.449	290.521	111.767	1057.874	796.814	−13.007
3300	41.267	326.716	291.599	115.887	1059.953	788.623	−12.483
3400	41.406	327.950	292.650	120.021	1062.034	780.370	−11.989
3500	41.539	329.152	293.676	124.168	1064.117	772.055	−11.522
3600	41.667	330.324	294.678	128.328	1066.202	763.681	−11.081
3700	41.790	331.468	295.657	132.501	1068.290	755.249	−10.662
3800	41.909	332.584	296.614	136.686	1070.381	746.761	−10.265
3900	42.023	333.674	297.550	140.883	1072.477	738.217	−9.887
4000	42.134	334.739	298.467	145.090	1074.577	729.620	−9.528
4100	42.242	335.781	299.364	149.309	1076.682	720.970	−9.185
4200	42.346	336.800	300.243	153.539	1078.794	712.268	−8.858
4300	42.448	337.798	301.105	157.778	1080.914	703.516	−8.546
4400	42.548	338.775	301.950	162.028	1083.041	694.715	−8.247
4500	42.645	339.732	302.779	166.288	1085.177	685.865	−7.961
4600	42.741	340.670	303.593	170.557	1087.322	676.968	−7.687
4700	42.836	341.591	304.391	174.836	1089.478	668.024	−7.424
4800	42.929	342.493	305.176	179.124	1091.645	659.034	−7.172
4900	43.021	343.380	305.947	183.422	1093.824	649.999	−6.929
5000	43.112	344.250	306.704	187.728	1096.015	640.919	−6.696
5100	43.202	345.104	307.448	192.044	1098.219	631.795	−6.471
5200	43.291	345.944	308.181	196.369	1100.436	622.628	−6.254
5300	43.380	346.769	308.901	200.702	1102.668	613.418	−6.046
5400	43.468	347.581	309.610	205.045	1104.913	604.166	−5.844
5500	43.556	348.379	310.308	209.396	1107.173	594.872	−5.650
5600	43.643	349.165	310.994	213.756	1109.449	585.537	−5.462
5700	43.730	349.938	311.671	218.124	1111.739	576.161	−5.280
5800	43.816	350.700	312.337	222.502	1114.045	566.745	−5.104
5900	43.902	351.449	312.994	226.888	1116.367	557.289	−4.934
6000	43.987	352.188	313.641	231.282	1118.704	547.793	−4.769

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = [291.7 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 79.5 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 78.6 \pm 8.4\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2B_1]$	0	[2]
$[^2A_1]$	23000	[2]
$[^2A_1]$	26000	[2]
$[^2A_2]$	30000	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[500](1)
[200](1)
[550](1)

Point Group: $[C_s]$ σ = [1]
Bond Distances: S–Cl = [2.00] Å S–S = [1.90] Å
Bond Angle: S–S–Cl = 105°
Product of Moments of Inertia: $I_A I_B I_C = [4.34028 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.474	79.499	79.499	INFINITE
100	38.122	243.386	333.376	−8.999	80.139	67.755	−35.391
200	45.979	272.300	296.209	−4.782	79.553	55.544	−14.507
250	48.894	282.889	292.515	−2.406	79.080	49.595	−10.362
298.15	50.954	291.686	291.686	0.	78.559	43.963	−7.702
300	51.021	292.002	291.687	0.094	78.538	43.748	−7.617
350	52.557	299.988	292.315	2.686	77.937	37.997	−5.671
400	53.677	307.083	293.726	5.343	72.857	32.511	−4.245
450	54.510	313.456	295.570	8.049	70.824	27.571	−3.200
500	55.140	319.233	297.652	10.791	68.663	22.886	−2.391
600	56.008	329.370	302.117	16.352	65.238	14.065	−1.225
700	56.558	338.048	306.645	21.982	62.339	5.771	−0.431
800	56.927	345.626	311.054	27.657	59.742	−2.131	0.139
900	57.186	352.346	315.276	33.364	−48.925	−7.557	0.439
1000	57.374	358.382	319.290	39.092	−48.777	−2.968	0.155
1100	57.514	363.857	323.096	44.837	−48.650	1.606	−0.076
1200	57.622	368.866	326.705	50.594	−48.548	6.170	−0.269
1300	57.706	373.482	330.128	56.360	−48.473	10.727	−0.431
1400	57.773	377.761	333.379	62.135	−48.426	15.279	−0.570
1500	57.828	381.749	336.472	67.915	−48.408	19.829	−0.690
1600	57.872	385.482	339.420	73.700	−48.419	24.378	−0.796
1700	57.910	388.992	342.234	79.489	−48.460	28.929	−0.889
1800	57.941	392.303	344.924	85.281	−48.529	33.483	−0.972
1900	57.967	395.436	347.501	91.077	−48.626	38.042	−1.046
2000	57.990	398.410	349.973	96.875	−48.749	42.606	−1.113
2100	58.010	401.240	352.347	102.675	−48.898	47.177	−1.173
2200	58.027	403.939	354.631	108.477	−49.072	51.756	−1.229
2300	58.042	406.519	356.832	114.280	−49.270	56.344	−1.280
2400	58.056	408.989	358.954	120.085	−49.490	60.940	−1.326
2500	58.069	411.360	361.003	125.891	−49.734	65.547	−1.370
2600	58.081	413.637	362.984	131.699	−49.999	70.163	−1.410
2700	58.092	415.830	364.901	137.507	−50.284	74.790	−1.447
2800	58.104	417.942	366.758	143.317	−50.590	79.428	−1.482
2900	58.116	419.982	368.558	149.128	−50.915	84.077	−1.514
3000	58.129	421.952	370.305	154.941	−51.259	88.738	−1.545
3100	58.143	423.858	372.002	160.754	−51.621	93.410	−1.574
3200	58.158	425.704	373.652	166.569	−51.999	98.095	−1.601
3300	58.176	427.494	375.256	172.386	−52.393	102.791	−1.627
3400	58.195	429.231	376.818	178.204	−52.802	107.500	−1.652
3500	58.217	430.919	378.340	184.025	−53.225	112.221	−1.675
3600	58.242	432.559	379.823	189.848	−53.661	116.954	−1.697
3700	58.270	434.155	381.270	195.673	−54.107	121.699	−1.718
3800	58.301	435.709	382.683	201.502	−54.564	126.457	−1.738
3900	58.337	437.224	384.062	207.334	−55.029	131.227	−1.758
4000	58.376	438.702	385.409	213.169	−55.501	136.008	−1.776
4100	58.419	440.144	386.727	219.009	−55.980	140.802	−1.794
4200	58.467	441.552	388.016	224.854	−56.463	145.607	−1.811
4300	58.520	442.928	389.277	230.703	−56.949	150.424	−1.827
4400	58.577	444.274	390.511	236.558	−57.437	155.253	−1.843
4500	58.639	445.592	391.721	242.418	−57.925	160.092	−1.858
4600	58.706	446.881	392.906	248.286	−58.413	164.942	−1.873
4700	58.778	448.144	394.068	254.160	−58.899	169.803	−1.887
4800	58.854	449.383	395.207	260.041	−59.383	174.674	−1.901
4900	58.936	450.597	396.325	265.931	−59.862	179.555	−1.914
5000	59.022	451.789	397.423	271.829	−60.336	184.446	−1.927
5100	59.114	452.958	398.500	277.735	−60.804	189.346	−1.939
5200	59.209	454.107	399.559	283.652	−61.265	194.256	−1.951
5300	59.310	455.236	400.599	289.577	−61.718	199.174	−1.963
5400	59.415	456.345	401.621	295.514	−62.163	204.101	−1.974
5500	59.524	457.437	402.626	301.460	−62.598	209.036	−1.985
5600	59.637	458.510	403.614	307.418	−63.023	213.978	−1.996
5700	59.754	459.567	404.586	313.388	−63.438	218.928	−2.006
5800	59.874	460.607	405.543	319.369	−63.841	223.886	−2.016
5900	59.998	461.632	406.485	325.363	−64.233	228.850	−2.026
6000	60.126	462.641	407.413	331.369	−64.612	233.820	−2.036

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

Enthalpy of Formation

Perona *et al.*[1] have studied the infrared emission from vibrationally excited HCl and DCl formed in the reaction of H and D atoms on S_2Cl_2. From their observation that the highest HCl vibrational level occupied was $v = 7$, they obtained an upper limit estimate of the first bond dissociation energy for S_2Cl_2 of $D_0°(S_2Cl–Cl) \leq 53$ kcal·mol^{-1}. Combining this value with $\Delta_f H°$ data for gaseous Cl and S_2Cl_2,[2] we calculate that $\Delta_f H°(S_2Cl, g) = \leq 20.8$ kcal·mol^{-1}. A recent independent analysis of these thermochemical data for S_2Cl_2/S_2Cl was made by Takacs[3] who reported $\Delta_f H°(S_2Cl, g, 0\ K) = 17 \pm 2$ kcal·mol^{-1} based on slightly different auxiliary $\Delta_f H$ datum for S_2Cl_2 (−7.7 kcal·mol^{-1}) than what (−3.6 kcal·mol^{-1}) was used here. In the same paper, Perona *et al.*[1] also used the infrared chemiluminescence technique to measure bond dissociation energies for Cl_2 and the first S–Cl bond in SCl_2. While this technique leads to results in accord with the known thermochemistry of Cl_2/Cl,[2] it appears to give biased results in the case of SCl_2 (see SCl(g) table for discussion). Factors which can adversely influence the $D_0°$ values determined from infrared chemiluminescence studies have been discussed by Perona *et al.*[1]

In a recent review of the thermochemistry of sulfur–containing species, Benson[4] has shown that in R_2S_2 compounds with R equal to H, alkyl, or aryl the first R–S bond dissociation energy exceeds the second one by 9.5 ± 1.0 kcal·mol^{-1}. Assuming this same trend holds for R=Cl, we obtain $\Delta_f H° = 9.5$ kcal·mol^{-1} for $S_2Cl_2(g) + S_2(g) = 2\ S_2Cl(g)$ which leads to $\Delta_f H°(S_2Cl, g, 0\ K) = 18.3 \pm 1.0$ kcal·mol^{-1} by combining the value of $\Delta_f H°$ with JANAF $\Delta_f H°$ values for S_2Cl_2 and S_2.[2]

We choose to adopt a $\Delta_f H°$ value of 19.0 ± 2.0 kcal·mol^{-1} which is a weighted average of the two results derived above. The values of $\Delta_f H°$ at 298.15 K and of $\Delta_a H°(0\ K)$ are 18.8 ± 2.0 kcal·mol^{-1} and 140.9 ± 2.0 kcal·mol^{-1}, respectively. Using JANAF data,[2] we find bond dissociation energies in the S_2Cl radical are $D_0°(S_2–Cl) = 40.2$ kcal·mol^{-1} and $D_0°(S–SCl) = 83.9$ kcal·mol^{-1}.

Heat Capacity and Entropy

S_2Cl has 19 valence electrons, and according to the Walsh correlation diagram,[5] the radical should have a bent structure with a bond angle somewhate greater than that (102°)[2] found for the 20 valence electron molecule SCl_2. We adopt a Cl–S–S angle of 105° which is intermediate between the measured angles for SCl_2 and S_2Cl_2.[2] CNDO and INDO calculations[6] on S_2Cl as a function of bond angle show an energy minimum at 100°, supporting our adopted value. The S–Cl and S–S bond distances are estimated from experimentally measured structural data[2] for S_2Cl_2, SCl_2, and S_2. The principal moments of inertia are: $I_A = 5.0613 \times 10^{-39}$, $I_B = 26.8624 \times 10^{-39}$, and $I_C = 31.9237 \times 10^{-39}$ g·cm^2.

Wight and Andrews[7] have observed an absorption band system at 21930–26178 cm^{-1} during mercury are photolysis of Ar/S_2Cl_2matrices and alkali metal S_2Cl_2 matrix reactions. They assigned this band system to S_2Cl and suggested that the S–Cl stretching frequency was ≥490 cm^{-1} based on the observed vibrational spacing in the absorption spectrum. We estimate $\nu_1 = 500$ cm^{-1}based on the S–Cl stretching frequencies for S_2Cl_2 (466 and 461 cm^{-1}),[2] SCl_2(528 cm^{-1}),[2] and SCl_2+ (530 ± 30 cm^{-1}).[8] The ν_2 bending and ν_3 S–S stretching frequencies are estimated by similar comparisons to that for ν_1. The value of is ν_3 chosen to lie between those[2,9] observed for S_2Cl_2 (546 cm^{-1}) and S_3(590 cm^{-1}).

An absorption band system has been observed at 22000–26000 cm^{-1} when gaseous S_2Cl_2 is flash photolyzed,[10,11] when Ar/S_2Cl_2 matrices are mercury arc photolyzed during deposition,[7] and when S_2Cl_2 is reacted with alkali metal atoms in argon matrices.[7] Wight and Andrews,[7] along with McGrath,[10] have assigned this spectrum to the S_2Cl radical while Donovan *et al.*[11] believe that portions of the spectrum are due

Continued on page 937

$S°(298.15\ K) = 237.833 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 196.25 \pm 6.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 198.32 \pm 6.7\ kJ·mol^{-1}$

Electronic States and Molecular Constants ($\sigma = 1$)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$w_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X\ ^2\Pi_{1/2}$	0	2	533.5	2.15	0.2539	0.00154	2.063	3
$^2\Pi_{3/2}$	207.0	2	533.5	2.15	0.2539	0.00154	2.063	3
$A\ ^2\Sigma^+$	23010	2	295.2	0.72	0.1970	0.0007	2.352	3
$B\ ^2\Sigma^+$	34107	2	703.8	3.9	0.2769	0.0020	1.984	6,7
$B'\ ^2\Delta$	35618	4	509.1	5.6	0.2598	0.00240	2.035	10
$C\ ^2\Pi$	41165	4	671.5	2.2	0.2865	0.0009	1.942	12,13
$D\ ^2\Pi$	44943	4	656.8	3.8	[0.2539]	[0.00154]	[2.063]	15

Enthalpy of Formation

The adopted value is based upon a 3rd law analysis of effusion mass spectrometric data by Farber[1] who obtained $\Delta_f H°(298.15\ K) = 27.1\ kcal·mol^{-1}$ for $Si(g) + SiCl_2(g) = 2\ SiCl(g)$. With auxiliary JANAF data[2] this yields $\Delta_f H°(298.15\ K) = 47.4 \pm 1.6\ kcal·mol^{-1}$. The error estimate is somewhat higher than that given by Farber and should more accurately reflect the uncertainties in relative cross-section values. A value of $88.3 \pm 3.0\ kcal·mol^{-1}$ is obtained for $D_0°$ using auxiliary JANAF data.[2] A linear Birge– Sponer extrapolation of the ground state vibrational data[3] yields $D_0° = 93.8\ kcal·mol^{-1}$ in good agreement with the adopted value. Similar extrapolations for other electronic states yield higher values; Gaydon[4] obtained $104 \pm 12\ kcal·mol^{-1}$ from the B' $^2\Delta$ state. The value of $D_0°$ may be compared to the average (per bond) enthalpies of atomization of 94.7, 96, and 101.9 $kcal·mol^{-1}$ for $SiCl_4$, $SiCl_3$, and $SiCl_2$, respectively.[2]

Heat Capacity and Entropy

Vibrational and rotational constants and splitting for the ground state are taken from the analysis of the A–X system by Singhal and Verma.[3] These are in excellent agreement with those of several other investigators.[5–10,12,13,15] Spectroscopic information for the A $^2\Sigma$ state is also taken from Singhal and Verma[3] and yields different molecular constants than an earlier study by Sanii and Verma.[5] Molecular constants for the $B^2\Sigma$ state are taken from Ovcharenko and Kuzyakov[6] and Rai *et al.*[7] and show good agreement with those of Ovcharenko *et al.*[8] and Mishra and Khanna.[9] The molecular constants for the B' $^2\Delta$ state are taken from Verma[10] and are in good agreement with the less precise measurements by Ovcharenko *et al.*[11] The vibrational properties of the C $^2\pi$ state were taken from Jevons[12] while the rotational constants are from Pandey *et al.*[13] The latter differ slightly from those of Ovcharenko and Kuzyakov.[14] The spin splittings of 2.727 cm^{-1} [10] and 10–12 cm^{-1} [13,14] for the B' and C states, respectively, have been ignored in our calculations. The vibrational constants for the D $^2\Pi$ state were taken from Oldershaw and Robinson;[15] since no rotational study is available, we have used the ground state B_e and α_e as first approximations in our calculations. This introduces a nearly negligible error in the thermal functions. Oldershaw and Robinson[15] has observed two additional sets of high energy levels but these are not included due to uncertainties in their states. It should be recognized that the $^4\Sigma^-$ state observed for SiF and SiI[2] has not been discovered for SiCl; by analogy with SiF and SiI it is expected to lie at $26{,}000 \pm 3{,}000\ cm^{-1}$. The stated uncertainty in the entropy should account for this level as well as the splittings mentioned above. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant ($A = 207.2\ cm^{-1}$). This leads to slightly biased results at low temperatures (below 500 K); the stated uncertainty in $S°(298.15\ K)$ should account for this also. All molecular constant data has been corrected to reflect the natural isotopic abundances of Si and Cl.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.885	196.245	196.245	INFINITE
100	32.744	200.342	268.867	−6.853	197.555	187.355	−97.864
200	34.712	223.757	241.075	−3.463	198.247	176.825	−46.182
298.15	35.780	237.833	237.833	0.	198.322	166.278	−29.131
300	35.795	238.054	237.833	0.066	198.319	166.080	−28.917
400	36.442	248.448	239.246	3.681	198.078	155.364	−20.288
500	36.834	256.626	241.933	7.346	197.679	144.729	−15.120
600	37.088	263.365	244.960	11.043	197.184	134.184	−11.682
700	37.266	269.097	248.009	14.761	196.618	123.728	−9.233
800	37.399	274.082	250.963	18.495	195.993	113.357	−7.401
900	37.504	278.493	253.782	22.240	195.316	103.067	−5.982
1000	37.591	282.449	256.454	25.995	194.592	92.856	−4.850
1100	37.667	286.035	258.983	29.758	193.824	82.719	−3.928
1200	37.734	289.316	261.376	33.528	193.014	72.654	−3.163
1300	37.795	292.339	263.643	37.304	192.164	62.658	−2.518
1400	37.851	295.142	265.794	41.087	191.273	52.729	−1.967
1500	37.905	297.755	267.838	44.875	190.341	42.865	−1.493
1600	37.956	300.203	269.786	48.668	189.369	33.065	−1.079
1700	38.004	302.505	271.643	52.466	138.177	23.774	−0.730
1800	38.052	304.679	273.419	56.269	137.352	17.068	−0.495
1900	38.098	306.738	275.119	60.076	136.526	10.408	−0.286
2000	38.143	308.693	276.749	63.888	135.700	3.792	−0.099
2100	38.187	310.555	278.315	67.705	134.872	−2.783	0.069
2200	38.231	312.332	279.821	71.526	134.043	−9.319	0.221
2300	38.275	314.033	281.272	75.351	133.212	−15.817	0.359
2400	38.318	315.663	282.671	79.180	132.378	−22.278	0.485
2500	38.362	317.228	284.022	83.014	131.540	−28.705	0.600
2600	38.405	318.733	285.328	86.853	130.697	−35.098	0.705
2700	38.449	320.183	286.593	90.695	129.851	−41.459	0.802
2800	38.493	321.583	287.817	94.543	128.999	−47.788	0.892
2900	38.539	322.934	289.005	98.394	128.141	−54.087	0.974
3000	38.585	324.241	290.158	102.250	127.279	−60.356	1.051
3100	38.632	325.507	291.278	106.111	126.412	−66.596	1.122
3200	38.681	326.735	292.367	109.977	125.540	−72.808	1.188
3300	38.732	327.926	293.427	113.847	124.664	−78.993	1.250
3400	38.784	329.083	294.458	117.723	123.785	−85.151	1.308
3500	38.839	330.208	295.464	121.604	122.904	−91.284	1.362
3600	38.896	331.303	296.444	125.491	−262.130	−86.930	1.261
3700	38.955	332.369	297.401	129.384	−262.599	−82.057	1.158
3800	39.017	333.409	298.335	133.282	−263.067	−77.171	1.061
3900	39.082	334.423	299.247	137.187	−263.533	−72.273	0.968
4000	39.151	335.414	300.139	141.099	−263.996	−67.363	0.880
4100	39.222	336.381	301.011	145.017	−264.453	−62.442	0.796
4200	39.296	337.327	301.865	148.943	−264.903	−57.509	0.715
4300	39.374	338.253	302.700	152.877	−265.344	−52.566	0.639
4400	39.456	339.159	303.518	156.818	−265.773	−47.613	0.565
4500	39.541	340.047	304.320	160.768	−266.190	−42.650	0.495
4600	39.630	340.917	305.106	164.727	−266.592	−37.678	0.428
4700	39.722	341.770	305.877	168.694	−266.978	−32.697	0.363
4800	39.819	342.607	306.634	172.671	−267.346	−27.709	0.302
4900	39.919	343.429	307.377	176.658	−267.695	−22.712	0.242
5000	40.023	344.237	308.106	180.655	−268.024	−17.710	0.185
5100	40.131	345.030	308.822	184.663	−268.331	−12.700	0.130
5200	40.242	345.811	309.526	188.681	−268.616	−7.685	0.077
5300	40.358	346.578	310.218	192.711	−268.877	−2.665	0.026
5400	40.477	347.334	310.898	196.753	−269.114	2.361	−0.023
5500	40.600	348.078	311.567	200.807	−269.325	7.390	−0.070
5600	40.726	348.810	312.226	204.873	−269.511	12.423	−0.116
5700	40.856	349.532	312.874	208.952	−269.670	17.459	−0.160
5800	40.990	350.244	313.512	213.045	−269.804	22.497	−0.203
5900	41.128	350.946	314.141	217.150	−269.910	27.538	−0.244
6000	41.268	351.638	314.760	221.270	−269.988	32.580	−0.284

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$\Delta_f H°(0\ K) = -122.49 \pm 8.4$ kJ·mol^{-1}

(298.15 K) = 252.284 ± 0.42 J·K^{-1}·mol^{-1} $\Delta_f H°(298.15\ K) = -123.85 \pm 8.4$ kJ·mol^{-1}

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
X $^2\Sigma^+$	0.0	2	D $^2\Sigma$	28822.9	2
A ^{2}	14818.3	2	E $^2\Sigma$	32201.8	2
	15112.8	2	F $^2\Pi$	32909.4	2
B $^2\Sigma$	15779.5	2		32978.6	2
C $^2\Pi$	25244.7	2	G$^2\Delta$	34086.7	2
	25399.9	2		34112.8	2
			H $^2\Sigma$	34256.7	2

$\omega_e = 300.94$ cm^{-1} $\omega_e x_e = 0.97$ cm^{-1} $\sigma = 1$

$B_e = [0.10271 \pm 0.003]$ cm^{-1} $\alpha_e = [0.00043]$ cm^{-1} $r_e = [2.55 \pm 0.04]$ Å

Enthalpy of Formation

$\Delta_f H°$ is a weighted average of results from three gas–phase equilibrium reactions studied mass spectrometrically by Hildenbrand[1] and Potter *et al.*[2] Analyses of these data are summarized below. The overall range of values is less than 4 kcal·mol^{-1}, suggesting the approximate uncertainty in $\Delta_f H°$. From the adopted $\Delta_f H°$ we calculate $D_0° = 98.2 \pm 2$ kcal·mol^{-1}. Independent methods give 98 ± 4,[3] ≥99,[4] 95.6 ± 1.6,[5] 97 ± 6[6] and 88.1 kcal·mol^{-1}.[7]

Electron–impact data[3] gave $D_0°$(ClSr–Cl) = 112.8 ± 3.3 and we use $\Delta_{at}H°(SrCl_2) = 210.8 \pm 3$ kcal·mol^{-1} to derive $D_0° = 98 \pm 4$ kcal·mol^{-1}. Chemiluminescence from crossed beams of Sr atoms with Cl_2 gave an approximate lower limit of 99 kcal·mol^{-1}.[4] Flame studies gave $D_0° = 95.6 \pm 1.6$ kcal·mol^{-1} [5] and $D_0°$(ClSr–Cl) = 114 ± 5 kcal·mol^{-1};[6] we derive $D_0° = 97 \pm 6$ kcal·mol^{-1} from the latter value using $\Delta_{at}H°(SrCl_2) = 210.8 \pm 3$ kcal·mol^{-1}. Ryabova *et al.*[6,5] considered the flames to involve $SrCl_2$, SrOHCl and SrOH as well as SrCl. Schofield and Sugden[8] inferred that the flames involved mainly $SrCl_2$ rather than SrCl as assumed in earlier flame studies. Gaydon[9] discounted a value of $D_0°$ derived from limited spectroscopic data on the ground state. Novikov and Gurvich[7] published additional emission spectra and derived $D_0° = 88.1$ kcal·mol^{-1} by parabolic extrapolation. This value should be considered as approximate in light of Gaydon's precautionary notes, especially since the observed levels extend only to about 0.3 of the dissociation limit. Hildenbrand[1] found that ionicity corrections bring the Birge–Sponer extrapolation into reasonable agreement with $D_0°$.

Source	Reaction	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$D_0°$
[1] Hildenbrand (1970)	A	1305–1416	16.9 ± 4.2	14.93 ± 0.6	1.5 ± 3.1	−29.49±1.0	98.3
[2] Potter (1970)	A	1235–1540	13.6 ± 1.1	13.97 ± 0.5	−0.3 ± 0.8	−29.97 ± 1.0	98.8
[1] Hildenbrand (1970)	B	1305–1416	19.7 ± 4.5	22.65 ± 0.7	−2.2 ± 3.3	−28.45 ± 2.0	97.3
[2] Potter (1970)	B	1235–1540	7.0 ± 4.7	18.79 ± 2.6	−8.6 ± 3.4	−32.31 ± 3.2	101.1
[1] Hildenbrand (1970)	C	1661		2.07 ± 2	−30.72 ± 3.6	99.6	

Reactions: (A) Sr(g) + $SrCl_2$(g) = 2SrCl(g); (B) Sr(g) + AlCl(g) = SrCl(g) + Al(g); (C) Ca(g) + SrCl(g) = CaCl(g) + Sr(g).

Heat Capacity and Entropy

Electronic levels and vibrational constants are based on the review of Rosen[10] as modified by the additional data of Novikov and Gurvich.[7] Vibrational constants are adjusted for natural isotopic abundances. B_e is calculated from r_e which is estimated by comparison of the bond lengths of MX_2(M=Mg, Ca, Sr, Ba and X=F, Cl) with those of MgCl, CaCl and MF(M=Mg, Ca, Sr, Ba). The value of α_e is estimated from the Morse potential function.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−9.799	−122.487	−122.487	INFINITE
100	31.264	215.070	283.467	−6.840	−122.483	−131.734	68.811
200	34.916	238.054	255.566	−3.503	−123.153	−140.725	36.754
250	35.747	245.942	252.879	−1.734	−123.496	−145.084	30.314
298.15	36.252	252.284	252.284	0.	−123.846	−149.204	26.140
300	36.268	252.509	252.285	0.067	−123.860	−149.362	26.006
350	36.613	258.127	252.728	1.890	−124.250	−153.582	22.921
400	36.856	263.033	253.716	3.727	−124.665	−157.744	20.599
450	37.035	267.385	254.998	5.574	−125.107	−161.852	18.787
500	37.173	271.294	256.435	7.430	−125.575	−165.910	17.333
600	37.374	278.091	259.495	11.158	−126.593	−173.884	15.138
700	37.517	283.863	262.574	14.902	−127.718	−181.678	13.557
800	37.628	288.880	265.555	18.660	−128.950	−189.303	12.360
900	37.721	293.318	268.398	22.427	−130.917	−196.696	11.416
1000	37.803	297.296	271.093	26.204	−132.043	−203.945	10.653
1100	37.877	300.903	273.641	29.988	−141.070	−210.715	10.006
1200	37.945	304.201	276.052	33.779	−143.106	−216.957	9.444
1300	38.010	307.241	278.336	37.577	−145.141	−223.028	8.961
1400	38.073	310.060	280.503	41.381	−147.174	−228.944	8.542
1500	38.135	312.689	282.562	45.191	−149.205	−234.713	8.173
1600	38.196	315.152	284.523	49.008	−151.234	−240.348	7.847
1700	38.259	317.470	286.393	52.831	−290.177	−244.676	7.518
1800	38.324	319.659	288.181	56.660	−290.342	−241.994	7.022
1900	38.394	321.733	289.893	60.496	−290.511	−239.304	6.579
2000	38.469	323.704	291.534	64.339	−290.687	−236.604	6.179
2100	38.552	325.583	293.111	68.190	−290.871	−233.895	5.818
2200	38.644	327.378	294.629	72.049	−291.070	−231.178	5.489
2300	38.746	329.098	296.090	75.919	−291.288	−228.450	5.188
2400	38.861	330.750	297.500	79.799	−291.532	−225.713	4.913
2500	38.990	332.339	298.862	83.691	−291.807	−222.965	4.659
2600	39.133	333.871	300.179	87.597	−292.122	−220.206	4.424
2700	39.291	335.350	301.455	91.518	−292.484	−217.433	4.206
2800	39.466	336.782	302.691	95.456	−292.902	−214.646	4.004
2900	39.656	338.171	303.890	99.412	−293.384	−211.843	3.816
3000	39.863	339.518	305.056	103.388	−293.939	−209.022	3.639
3100	40.087	340.829	306.189	107.385	−294.576	−206.181	3.474
3200	40.327	342.106	307.291	111.406	−295.302	−203.318	3.319
3300	40.582	343.350	308.365	115.451	−296.124	−200.431	3.173
3400	40.852	344.566	309.412	119.523	−297.051	−197.518	3.034
3500	41.137	345.754	310.433	123.622	−298.088	−194.575	2.904
3600	41.435	346.917	311.431	127.751	−299.240	−191.602	2.780
3700	41.746	348.057	312.405	131.910	−300.511	−188.594	2.662
3800	42.069	349.174	313.358	136.100	−301.905	−185.551	2.551
3900	42.403	350.271	314.291	140.324	−303.423	−182.470	2.444
4000	42.746	351.349	315.204	144.581	−305.065	−179.348	2.342
4100	43.099	352.409	316.098	148.873	−306.832	−176.183	2.245
4200	43.460	353.452	316.975	153.201	−308.717	−172.974	2.151
4300	43.827	354.479	317.836	157.565	−310.725	−169.719	2.062
4400	44.201	355.491	318.680	161.967	−312.848	−166.415	1.976
4500	44.580	356.488	319.509	166.406	−315.082	−163.063	1.893
4600	44.963	357.472	320.324	170.883	−317.355	−159.664	1.813
4700	45.349	358.443	321.124	175.398	−319.773	−156.210	1.736
4800	45.737	359.402	321.912	179.953	−322.277	−152.704	1.662
4900	46.128	360.349	322.687	184.546	−324.860	−149.144	1.590
5000	46.518	361.285	323.449	189.178	−327.508	−145.532	1.520
5100	46.909	362.210	324.200	193.850	−330.199	−141.868	1.453
5200	47.299	363.125	324.940	198.560	−332.960	−138.148	1.388
5300	47.688	364.029	325.669	203.310	−335.763	−134.375	1.324
5400	48.074	364.924	326.388	208.098	−338.600	−130.549	1.263
5500	48.458	365.810	327.096	212.924	−341.461	−126.669	1.203
5600	48.838	366.686	327.796	217.789	−344.339	−122.738	1.145
5700	49.214	367.554	328.485	222.692	−347.223	−118.755	1.088
5800	49.585	368.413	329.167	227.632	−350.107	−114.722	1.033
5900	49.952	369.264	329.839	232.609	−352.773	−110.663	0.980
6000	50.312	370.107	330.503	237.622	−355.602	−106.536	0.927

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 249.214 \pm 8.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [154.13 \pm 41.8]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [154.39 \pm 41.8]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^4\Sigma$]	0	[4]
	[1000]	[4]
	[2000]	[4]
	[4000]	[4]
	[6000]	[4]
	[8000]	[4]
	[10000]	[4]

$\omega_e = 379.7\ cm^{-1}$ $\omega_e x_e = 3.41\ cm^{-1}$ $\sigma = 1$

$B_e = [0.146]\ cm^{-1}$ $\alpha_e = [0.0013]\ cm^{-1}$ $r_e = [2.3]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of TiCl(g) is calculated from the dissociation energy which is estimated as 105 kcal·mol^{-1}. This estimate is obtained from the relation $D(TiCl_4) < D°(TiCl) < D(TiCl_3)$, where D represents the average energy per bond, which is valid for the titanium fluorides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF_2(g) by Zmbov and Margrave.[1]

Extrapolations of the vibrational levels reported by Shenyaskaya *et al.*,[2] Rao[3] and Mace and Packer[4] yield values of the dissociation energy which are very low with respect to bond energy relations.

Heat Capacity and Entropy

The vibrational frequency, ω_e, and anharmonic vibrational term, $\omega_e x_e$, were reported by Shenyavskaya *et al.*[2] The interatomic distance is estimated from Guggenheimer's relation.[5] B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+.[6] α_e is estimated from the Morse potential function.

References

[1]K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
[2]E. A. Shenyaskaya, Yu. Ya. Kuzyakov, and V. M. Tatevskii, Opt. Spectrosc. (USSR) **12**, 197 (1962).
[3]V. R. Rao, Indian J. Phys. **23**, 535 (1949).
[4]K. R. Mace and A. H. Packer, Phys. Rev. **52**, 1150 (1937).
[5]K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
[6]C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, (1949).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.680	154.130	154.130	INFINITE
100	30.251	212.708	280.196	−6.749	155.045	144.050	−75.244
200	34.252	234.946	252.532	−3.517	154.840	133.093	−34.760
250	35.893	242.769	249.820	−1.763	154.622	127.681	−26.677
298.15	37.297	249.214	249.214	0.	154.390	122.513	−21.464
300	37.348	249.445	249.215	0.069	154.380	122.315	−21.297
350	38.622	255.300	249.674	1.969	154.134	116.990	−17.460
400	39.709	260.530	250.710	3.928	153.891	111.701	−14.587
450	40.614	265.261	252.068	5.937	153.654	106.441	−12.355
500	41.351	269.580	253.607	7.987	153.424	101.208	−10.573
600	42.402	277.220	256.922	12.179	152.974	90.807	−7.905
700	43.031	283.808	260.303	16.453	152.525	80.481	−6.006
800	43.387	289.579	263.610	20.776	152.073	70.220	−4.585
900	43.581	294.702	266.785	25.125	151.571	60.018	−3.483
1000	43.688	299.300	269.811	29.489	150.945	49.877	−2.605
1100	43.754	303.467	272.684	33.861	150.128	39.808	−1.890
1200	43.804	307.276	275.410	38.239	145.130	29.942	−1.303
1300	43.853	310.784	277.998	42.622	144.646	20.362	−0.818
1400	43.907	314.036	280.457	47.010	144.084	10.823	−0.404
1500	43.969	317.067	282.798	51.404	143.432	1.326	−0.046
1600	44.040	319.907	285.030	55.804	142.678	−8.124	0.265
1700	44.118	322.580	287.161	60.212	141.809	−17.523	0.538
1800	44.201	325.104	289.199	64.628	140.813	−26.867	0.780
1900	44.288	327.496	291.152	69.052	139.675	−36.152	0.994
2000	44.376	329.770	293.027	73.486	123.698	−44.920	1.173
2100	44.465	331.937	294.829	77.928	121.492	−53.297	1.326
2200	44.553	334.007	296.563	82.379	119.289	−61.568	1.462
2300	44.638	335.990	298.234	86.838	117.087	−69.740	1.584
2400	44.721	337.891	299.847	91.306	114.887	−77.816	1.694
2500	44.799	339.719	301.406	95.782	112.687	−85.800	1.793
2600	44.874	341.477	302.913	100.266	110.486	−93.696	1.882
2700	44.943	343.172	304.373	104.757	108.283	−101.507	1.964
2800	45.009	344.808	305.788	109.254	106.078	−109.237	2.038
2900	45.070	346.388	307.161	113.758	103.869	−116.887	2.105
3000	45.126	347.917	308.494	118.268	101.656	−124.462	2.167
3100	45.179	349.398	309.790	122.783	99.439	−131.963	2.224
3200	45.227	350.833	311.050	127.304	97.218	−139.392	2.275
3300	45.272	352.225	312.277	131.829	94.992	−146.751	2.323
3400	45.313	353.577	313.472	136.358	92.762	−154.044	2.367
3500	45.352	354.891	314.637	140.891	90.529	−161.270	2.407
3600	45.388	356.169	315.773	145.428	88.293	−168.433	2.444
3700	45.421	357.413	316.881	149.969	−323.044	−167.745	2.368
3800	45.453	358.625	317.964	154.512	−324.049	−163.534	2.248
3900	45.482	359.806	319.022	159.059	−325.110	−159.297	2.134
4000	45.511	360.958	320.056	163.609	−326.224	−155.031	2.024
4100	45.538	362.082	321.067	168.161	−327.388	−150.737	1.920
4200	45.564	363.180	322.057	172.716	−328.600	−146.413	1.821
4300	45.590	364.252	323.026	177.274	−329.857	−142.061	1.726
4400	45.615	365.301	323.975	181.834	−331.156	−137.679	1.634
4500	45.640	366.326	324.904	186.397	−332.493	−133.267	1.547
4600	45.664	367.329	325.816	190.962	−333.866	−128.824	1.463
4700	45.689	368.312	326.710	195.530	−335.271	−124.352	1.382
4800	45.714	369.274	327.586	200.100	−336.706	−119.849	1.304
4900	45.740	370.217	328.447	204.673	−338.167	−115.316	1.229
5000	45.766	371.141	329.292	209.248	−339.652	−110.753	1.157
5100	45.792	372.048	330.121	213.826	−341.157	−106.160	1.087
5200	45.819	372.937	330.936	218.406	−342.680	−101.538	1.020
5300	45.847	373.810	331.737	222.990	−344.218	−96.886	0.955
5400	45.876	374.667	332.524	227.576	−345.768	−92.204	0.892
5500	45.905	375.509	333.298	232.165	−347.328	−87.494	0.831
5600	45.936	376.337	334.059	236.757	−348.896	−82.756	0.772
5700	45.967	377.150	334.808	241.352	−350.468	−77.989	0.715
5800	46.000	377.950	335.545	245.951	−352.044	−73.195	0.659
5900	46.033	378.737	336.270	250.552	−353.621	−68.374	0.605
6000	46.068	379.511	336.984	255.157	−355.197	−63.526	0.553

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K)$ = [261.895] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [553.74 ± 41.8] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [553.54 ± 41.8] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^2\Delta$]	0	[4]
	[5000]	[2]
	[15000]	[20]

ω_e = [455.4] cm^{-1} $\omega_e x_e$ = [1.46] cm^{-1} σ = 1
B_e = [0.11105] cm^{-1} α_e = [0.00042] cm^{-1} r_e = [2.26] Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(WCl, g, 298.15 K) = 132.3 kcal·mol^{-1}, is calculated from the bond dissociation energy, $D°_0$(W–Cl, 298.15 K) = 100 ± 10 kcal·mol^{-1}. This estimated $\Delta_{at} H°$(298.15 K) is obtained from the average bond dissociation energy for $WCl_x(g) \rightarrow W(g) + xCl(g)$ where x = 2,4,5,6, using all JANAF values.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WCl_6(g). This distance is then used with Guggenheimer's relation for polar molecules to calculate the fundamental vibrational frequency ω_e.[1] The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D° + 0.5\ \omega_e) \approx 0.0032$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the Morse potential function.

The ground state configuration, low lying electronic levels and their quantum weights are assumed to be the same as those estimated for WF(g).[2]

References

[1]K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
[2]JANAF Thermochemical Table; WF(g), 3–31–67.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.370	553.736	553.736	INFINITE
100	29.633	226.867	291.391	−6.452	554.546	542.271	−283.253
200	32.811	248.370	265.027	−3.331	554.141	530.118	−138.453
250	34.017	255.829	262.465	−1.659	553.847	524.145	−109.514
298.15	34.843	261.895	261.895	0.	553.543	518.452	−90.831
300	34.869	262.111	261.896	0.064	553.531	518.234	−90.233
350	35.472	267.534	262.323	1.824	553.207	512.377	−76.468
400	35.908	272.300	263.278	3.609	552.877	506.567	−66.151
450	36.231	276.549	264.521	5.413	552.541	500.798	−58.131
500	36.478	280.380	265.918	7.231	552.199	495.067	−51.719
600	36.826	287.064	268.902	10.897	551.492	483.707	−42.110
700	37.066	292.760	271.913	14.593	550.750	472.467	−35.256
800	37.256	297.722	274.836	18.309	549.972	461.336	−30.122
900	37.426	302.120	277.628	22.043	549.157	450.306	−26.135
1000	37.595	306.072	280.278	25.794	548.306	439.367	−22.950
1100	37.771	309.663	282.788	29.562	547.420	428.516	−20.349
1200	37.955	312.958	285.167	33.349	546.501	417.747	−18.184
1300	38.146	316.003	287.423	37.154	545.550	407.056	−16.356
1400	38.341	318.837	289.567	40.978	544.567	396.439	−14.791
1500	38.537	321.489	291.608	44.822	543.553	385.894	−13.438
1600	38.733	323.982	293.554	48.685	542.507	375.417	−12.256
1700	38.926	326.336	295.414	52.568	541.428	365.007	−11.215
1800	39.116	328.567	297.194	56.470	540.317	354.661	−10.292
1900	39.305	330.687	298.902	60.391	539.172	344.378	−9.468
2000	39.492	332.707	300.542	64.331	537.992	334.156	−8.727
2100	39.682	334.639	302.120	68.290	536.777	323.994	−8.059
2200	39.875	336.489	303.640	72.268	535.525	313.891	−7.453
2300	40.074	338.266	305.107	76.265	534.237	303.845	−6.901
2400	40.281	339.976	306.525	80.283	532.912	293.856	−6.396
2500	40.499	341.625	307.896	84.322	531.550	283.923	−5.932
2600	40.729	343.218	309.224	88.383	530.155	274.046	−5.506
2700	40.972	344.759	310.512	92.468	528.700	264.223	−5.112
2800	41.228	346.254	311.762	96.578	527.152	254.455	−4.747
2900	41.499	347.705	312.976	100.714	525.473	244.745	−4.408
3000	41.783	349.117	314.158	104.878	523.636	235.096	−4.093
3100	42.081	350.492	315.308	109.071	521.601	225.511	−3.800
3200	42.390	351.833	316.428	113.295	519.336	215.995	−3.526
3300	42.711	353.142	317.521	117.550	516.819	206.554	−3.269
3400	43.041	354.422	318.588	121.837	514.015	197.193	−3.030
3500	43.378	355.674	319.629	126.158	510.863	187.920	−2.805
3600	43.722	356.901	320.648	130.513	507.267	178.743	−2.593
3700	44.069	358.104	321.644	134.902	468.364	169.863	−2.398
3800	44.419	359.284	322.619	139.327	467.172	161.811	−2.224
3900	44.768	360.442	323.574	143.786	466.013	153.791	−2.060
4000	45.116	361.580	324.510	148.280	464.886	145.800	−1.904
4100	45.460	362.698	325.428	152.809	463.793	137.836	−1.756
4200	45.798	363.798	326.328	157.372	462.735	129.899	−1.616
4300	46.130	364.879	327.212	161.969	461.712	121.986	−1.482
4400	46.453	365.944	328.080	166.598	460.725	114.097	−1.355
4500	46.767	366.991	328.933	171.259	459.775	106.230	−1.233
4600	47.069	368.022	329.772	175.951	458.861	98.384	−1.117
4700	47.360	369.038	330.597	180.672	457.983	90.557	−1.006
4800	47.637	370.038	331.408	185.422	457.141	82.748	−0.900
4900	47.901	371.023	332.206	190.199	456.336	74.957	−0.799
5000	48.151	371.993	332.993	195.002	455.566	67.181	−0.702
5100	48.387	372.949	333.767	199.829	454.831	59.421	−0.609
5200	48.607	373.891	334.529	204.679	454.129	51.675	−0.519
5300	48.813	374.818	335.281	209.550	453.462	43.942	−0.433
5400	49.003	375.733	336.021	214.441	452.826	36.221	−0.350
5500	49.179	376.633	336.752	219.350	452.222	28.512	−0.271
5600	49.339	377.521	337.472	224.276	451.648	20.813	−0.194
5700	49.485	378.396	338.182	229.218	451.104	13.124	−0.120
5800	49.616	379.257	338.883	234.173	450.587	5.445	−0.049
5900	49.733	380.107	339.574	239.140	450.098	−2.226	0.020
6000	49.837	380.943	340.257	244.119	449.634	−9.888	0.086

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = [254.195 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 206.141 \pm 20.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 205.434 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[4]
[3000]	[4]
[6000]	[4]
[12000]	[4]
[18000]	[4]
[24000]	[4]
[30000]	[4]

Ground State Configuration: [$^4\Sigma$]

ω_e = [437] cm^{-1} $\omega_e x_e$ = [1.1] cm^{-1} σ = 1

B_e = [0.1248] cm^{-1} α_e = [0.00042] cm^{-1} r_e = [2.3] Å

Heat of Formation

Potter[1] investigated mass spectrometrically the gaseous equilibria among ZrCl, $ZrCl_2$, $ZrCl_3$ and $ZrCl_4$. Ion intensities were measured 2.5 eV above the ionization threshold. Using the reported equiilibrium constants for the reaction $ZrCl_3(g) + ZrCl(g) = 2\ ZrCl_2(g)$ in the temperature range 1978–2274 K, second and third law analyses give the heats of reaction at 298 K as −10.36 and −12.83 $kcal \cdot mol^{-1}$, respectively. The third law drift is 1.4 ± 2.5 $cal \cdot K^{-1} \cdot mol^{-1}$. Based on the third law $\Delta_f H°(298.15\ K)$ and $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -44.5\ kcal \cdot mol^{-1}$[2] and $\Delta_f H°(ZrCl_3, g, 298.15\ K) = -125.3\ kcal \cdot mol^{-1}$,[3] we obtain $\Delta_f H°(ZrCl, g, 298.15\ K) = 49.1\ kcal \cdot mol^{-1}$ which is adopted in the tabulation.

Farber *et al.*[4] also studied mass spectrometrically the reaction Zr(cr) + Cl(g). The reported a second law heat of reaction $\Delta_f H°(298.15\ K) = 8.7 \pm 1.4\ kcal \cdot mol^{-1}$. Using the equilibrium constants K = I(ZrCl)/I(Cl) which we calculated from their reported ion intensities of run 3 in the temperature range 1667–1896 K, we obtain $\Delta_f H°(298.15\ K) = 20.3\ kcal \cdot mol^{-1}$ by the third law method. The third law drift is 6.1 ± 2.4 $cal \cdot K^{-1} \cdot mol^{-1}$. The heat of formation is derived as $\Delta_f H°(ZrCl, g, 298.15\ K) = 49.2\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in $ZrCl_4$(g). The bond distance is then used with Guggenheimer's relation[5] for polar molecules to calculate the fundamental vibrational frequency ω_e. The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D° + 0.5\ \omega_e) = 0.0025$. The rotational constant B_e is calculated from the estimated bond distance. The value of α_e is calculated from the More potential function. The moment of inertia is 22.425×10^{-39} $g \cdot cm^2$.

The ground state configuration is taken from the ground state multiplet of Zr^+ reported by Moore.[6] The electronic levels and the quantum weights are estimated to be the same as those of ZrF(g).

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[2]JANAF Thermochemical Tables, $ZrCl_2$(g) and $ZrCl_3$(g), 12–31–69.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.411	206.112	206.112	INFINITE
100	29.736	219.074	283.981	−6.491	206.689	195.638	−102.191
200	33.033	240.706	257.458	−3.350	206.118	184.783	−48.260
250	34.211	248.212	254.882	−1.667	205.775	179.488	−37.502
298.15	35.004	254.309	254.309	0.	205.434	174.456	−30.564
300	35.030	254.526	254.310	0.065	205.421	174.264	−30.342
350	35.607	259.972	254.739	1.831	205.058	169.100	−25.237
400	36.032	264.755	255.698	3.623	204.685	163.989	−21.415
450	36.367	269.019	256.946	5.433	204.302	158.924	−18.447
500	36.655	272.866	258.348	7.259	203.910	153.903	−16.078
600	37.190	279.596	261.345	10.951	203.095	143.978	−12.534
700	37.744	285.370	264.374	14.698	202.239	134.192	−10.014
800	38.336	290.449	267.322	18.501	201.343	124.532	−8.131
900	38.947	294.999	270.149	22.365	200.400	114.986	−6.674
1000	39.553	299.134	272.844	26.291	199.401	105.549	−5.513
1100	40.131	302.932	275.409	30.275	198.339	96.215	−4.569
1200	40.667	306.447	277.851	34.315	193.496	87.202	−3.796
1300	41.155	309.721	280.178	38.407	192.833	78.371	−3.149
1400	41.590	312.788	282.399	42.545	192.169	69.591	−2.596
1500	41.972	315.670	284.522	46.723	191.489	60.859	−2.119
1600	42.302	318.390	286.554	50.937	190.776	52.173	−1.703
1700	42.586	320.963	288.503	55.182	190.016	43.533	−1.338
1800	42.825	323.404	290.375	59.453	189.192	34.940	−1.014
1900	43.025	325.725	292.175	63.746	188.291	26.395	−0.726
2000	43.191	327.937	293.908	68.057	187.296	17.899	−0.467
2100	43.327	330.047	295.579	72.383	186.195	9.456	−0.235
2200	43.438	332.065	297.192	76.721	163.650	1.814	−0.043
2300	43.526	333.998	298.751	81.070	161.877	−5.503	0.125
2400	43.597	335.852	300.258	85.426	160.105	−12.742	0.277
2500	43.653	337.633	301.718	89.789	158.331	−19.908	0.416
2600	43.696	339.346	303.132	94.156	156.554	−27.002	0.542
2700	43.729	340.996	304.504	98.528	154.771	−34.028	0.658
2800	43.755	342.587	305.836	102.902	152.982	−40.988	0.765
2900	43.775	344.123	307.130	107.278	151.185	−47.884	0.862
3000	43.790	345.607	308.388	111.657	149.381	−54.718	0.953
3100	43.801	347.043	309.612	116.036	147.568	−61.491	1.036
3200	43.811	348.434	310.804	120.417	145.746	−68.206	1.113
3300	43.819	349.782	311.964	124.798	143.917	−74.863	1.185
3400	43.825	351.090	313.096	129.180	142.080	−81.466	1.252
3500	43.832	352.361	314.200	133.563	140.236	−88.014	1.314
3600	43.839	353.596	315.277	137.947	138.386	−94.509	1.371
3700	43.846	354.797	316.329	142.331	136.531	−100.953	1.425
3800	43.854	355.966	317.357	146.716	134.673	−107.346	1.476
3900	43.863	357.105	318.361	151.102	132.812	−113.691	1.523
4000	43.873	358.216	319.344	155.489	130.950	−119.988	1.567
4100	43.884	359.300	320.305	159.877	129.088	−126.238	1.608
4200	43.896	360.357	321.246	164.266	127.229	−132.443	1.647
4300	43.909	361.390	322.168	168.656	125.372	−138.604	1.684
4400	43.924	362.400	323.071	173.047	123.520	−144.722	1.718
4500	43.940	363.387	323.956	177.441	121.674	−150.797	1.750
4600	43.957	364.353	324.824	181.835	119.835	−156.832	1.781
4700	43.975	365.299	325.675	186.232	118.005	−162.827	1.810
4800	43.994	366.225	326.510	190.630	−444.752	−157.165	1.710
4900	44.014	367.132	327.330	195.031	−446.213	−151.159	1.611
5000	44.035	368.021	328.135	199.433	−447.680	−145.122	1.516
5100	44.057	368.894	328.925	203.838	−449.150	−139.057	1.424
5200	44.079	369.749	329.702	208.245	−450.621	−132.962	1.336
5300	44.102	370.589	330.466	212.654	−452.090	−126.839	1.250
5400	44.126	371.414	331.217	217.065	−453.556	−120.689	1.167
5500	44.150	372.224	331.955	221.479	−455.016	−114.511	1.088
5600	44.175	373.019	332.681	225.895	−456.470	−108.307	1.010
5700	44.200	373.801	333.396	230.314	−457.915	−102.077	0.935
5800	44.226	374.570	334.099	234.735	−459.349	−95.821	0.863
5900	44.251	375.327	334.791	239.159	−460.772	−89.541	0.793
6000	44.277	376.071	335.473	243.586	−462.182	−83.238	0.725

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

0 to 6000 K Ideal Diatomic Gas

D_0° = 239.242 ± 0.012 kJ·mol^{-1} (natural abundance) $\Delta_f H°(0\ K)$ = 0 kJ·mol^{-1}
$S°(298.15\ K)$ = 223.071 ± 0.040 J·K^{-1}·mol^{-1} $\Delta_f H°(298.15\ K)$ = 0 kJ·mol^{-1}

State	T_e	D_0°	Spectroscopic Data for ^{35}Cl in cm^{-1}[a] ω_e	$\omega_e x_e$[c]	B_e	$10^3 \cdot \alpha_e$[d]	$10^7 \cdot D_e$	r_e, Å	Reference
$^1\Sigma_g^+$	0	19997.28	559.751	2.6943	0.24415	1.5163	1.9195	1.9879	$^1(r_e)$,[2]
$^3\Pi_o^+$	17832.8	20879.64[b]	246.7	2.6747	0.16254	2.022	2.365[e]	2.4354	$^1(r_e)$,[3]

[a] Constants for ground state applicable to v ≤ 40 only.
[b] The $^3\Pi_o^+$ state dissociates to $Cl(^2P_{3/2}) + Cl(^2P_{1/2})$.
[c] $-3.32527 \times 10^{-3}(v + 1/2)^3 - 2.27337 \times 10^{-4}(v + 1/2)^4$ for $^1\Sigma_g^+$; $-0.23826(v + 1/2)^3 + 9.4555 \times 10^{-3}(v + 1/2)^4$ for $^3\Pi_o^+$
[d] $-3.9078 \times 10^{-6}(v + 1/2)^2 + 7.0811 \times 10^{-8}(v + 1/2)^3$ for $^1\Sigma_g^+$; $-1.102 \times 10^{-4}(v + 1/2)^2 + 9.2 \times 10^{-7}(v + 1/2)^3$ for $^3\Pi_o^+$
[e] $+2.25 \times 10^{-8}(v + 1/2) - 1.5 \times 10^{-9}(v + 1/2)^2$

Heat of Formation

Zero by definition. Refer to the monoatomic cholorine gas table for a discussion of the dissociation energy.

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique. Included in the calculation are the ground state plus the $^3\Pi_o^+$ excited state at T_e = 17833 cm^{-1}. To account, in an approximate way, for the presence of the $^3\Pi_g^-$, $^3\Pi_{1u}$, and $^3\Pi_{2u}$ excited states (all near T_e = 17000 cm^{-1}) the rotational states of the $^3\Pi_o^+$ state are artificially weighted byt a factor of six.

For the ground state only, the calculation is performed including the so–called quasi–bound rotational levels above the dissociation limit.[4,5] For a given vibrational quantum number, V, the summation over rotational states is carried out up to a rotational quantum number, J, given by $J = J_{lim}(1–V/V_{max})$, where J_{lim} and V_{max} were determined by Gurvich *et al.*[3] to be 418 and 61, respectively. We adopt the $^{35}Cl_2$ ground state spectroscopic constants and dissociation energy of Douglas and Hoy[1] who gave Dunham type coefficients which fitted the spectroscopic data for $V \leq 40$. For $41 \leq V \leq 60$, we use the exact G_v, B_v, and D_v data as given by Douglas and Hoy.[1]

For the $^3\Pi_o^+$ state, we use the spectroscopic constants given in Gurvich *et al.*[3] as deduced from Clyne and Coxon.[6] The excited states contribute significantly to the heat capacity above 3000 K but the affect on the Gibbs free energy function is considerably smaller (amounting to only 0.4 J·K^{-1}·mol^{-1} at 6000 K). The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[7] who proposed a simpler form of Wooley's method.[8]

The spectroscopic constants of the hypothetical natural abundance species are determined from the $^{35}Cl_2$ data using a standard reduced mass scaling routine. Our adopted value for $S°(298.15\ K)$ differs by 0.003 J·K^{-1}·mol^{-1} from values recommended by CODATA[11] and Gurvich *et al.*[3] and by 0.007 J·K^{-1}·mol^{-1} from the value recommended by Wagman *et al.*[9] For this comparison, the values reported by CODATA[11] and Gurvich *et al.*[3] are increased by 0.1094 J·K^{-1}·mol^{-1} to account for a change in standard–state pressure from 1 atm to 1 bar.

Phase Data

Hultgren *et al.*[10] had recommended a triple point, 172.16 K (0.01374 atm) and a boiling point, 239.10 K (1 atm). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values, the reference state for chlorine is chosen to be the ideal diatomic gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.181	0.	0.	0.
100	29.299	189.007	251.696	−6.269	0.	0.	0.
200	31.720	209.964	226.120	−3.231	0.	0.	0.
250	32.988	217.183	223.633	−1.613	0.	0.	0.
298.15	33.949	223.079	223.079	0.	0.	0.	0.
300	33.981	223.289	223.080	0.063	0.	0.	0.
350	34.731	228.586	223.496	1.782	0.	0.	0.
400	35.296	233.263	224.431	3.533	0.	0.	0.
450	35.728	237.446	225.648	5.309	0.	0.	0.
500	36.064	241.228	227.020	7.104	0.	0.	0.
600	36.546	247.849	229.956	10.736	0.	0.	0.
700	36.872	253.509	232.926	14.408	0.	0.	0.
800	37.109	258.449	235.814	18.108	0.	0.	0.
900	37.291	262.831	238.577	21.828	0.	0.	0.
1000	37.438	266.767	241.203	25.565	0.	0.	0.
1100	37.562	270.342	243.692	29.315	0.	0.	0.
1200	37.672	273.615	246.051	33.077	0.	0.	0.
1300	37.771	276.634	248.289	36.849	0.	0.	0.
1400	37.864	279.437	250.415	40.631	0.	0.	0.
1500	37.954	282.052	252.438	44.422	0.	0.	0.
1600	38.042	284.504	254.366	48.221	0.	0.	0.
1700	38.131	286.813	256.207	52.030	0.	0.	0.
1800	38.223	288.995	257.969	55.848	0.	0.	0.
1900	38.322	291.065	259.657	59.675	0.	0.	0.
2000	38.428	293.033	261.277	63.512	0.	0.	0.
2100	38.544	294.911	262.834	67.361	0.	0.	0.
2200	38.672	296.707	264.333	71.222	0.	0.	0.
2300	38.813	298.429	265.778	75.096	0.	0.	0.
2400	38.966	300.084	267.173	78.985	0.	0.	0.
2500	39.132	301.678	268.522	82.889	0.	0.	0.
2600	39.308	303.216	269.827	86.811	0.	0.	0.
2700	39.493	304.703	271.091	90.751	0.	0.	0.
2800	39.685	306.143	272.317	94.710	0.	0.	0.
2900	39.880	307.539	273.508	98.688	0.	0.	0.
3000	40.075	308.894	274.665	102.686	0.	0.	0.
3100	40.267	310.211	275.791	106.703	0.	0.	0.
3200	40.451	311.492	276.886	110.739	0.	0.	0.
3300	40.624	312.740	277.954	114.793	0.	0.	0.
3400	40.783	313.955	278.995	118.864	0.	0.	0.
3500	40.925	315.139	280.011	122.949	0.	0.	0.
3600	41.048	316.294	281.003	127.048	0.	0.	0.
3700	41.149	317.420	281.972	131.158	0.	0.	0.
3800	41.226	318.518	282.919	135.277	0.	0.	0.
3900	41.278	319.590	283.846	139.402	0.	0.	0.
4000	41.305	320.636	284.753	143.532	0.	0.	0.
4100	41.306	321.656	285.640	147.663	0.	0.	0.
4200	41.280	322.651	286.510	151.792	0.	0.	0.
4300	41.229	323.621	287.361	155.918	0.	0.	0.
4400	41.152	324.568	288.196	160.037	0.	0.	0.
4500	41.051	325.492	289.015	164.147	0.	0.	0.
4600	40.927	326.393	289.818	168.246	0.	0.	0.
4700	40.781	327.272	290.605	172.332	0.	0.	0.
4800	40.615	328.129	291.378	176.402	0.	0.	0.
4900	40.429	328.964	292.137	180.454	0.	0.	0.
5000	40.226	329.779	292.882	184.487	0.	0.	0.
5100	40.007	330.573	293.613	188.499	0.	0.	0.
5200	39.774	331.348	294.331	192.488	0.	0.	0.
5300	39.528	332.103	295.037	196.454	0.	0.	0.
5400	39.271	332.840	295.730	200.394	0.	0.	0.
5500	39.004	333.558	296.411	204.307	0.	0.	0.
5600	38.729	334.258	297.081	208.194	0.	0.	0.
5700	38.447	334.941	297.739	212.053	0.	0.	0.
5800	38.159	335.608	298.386	215.883	0.	0.	0.
5900	37.867	336.257	299.023	219.685	0.	0.	0.
6000	37.571	336.891	299.649	223.456	0.	0.	0.

PREVIOUS: September 1965 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 109.265 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1013 \pm 2\ K$

$\Delta_f H°(0\ K) = -314.39 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -312.54 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{fus} H° = [44.77 \pm 6.3]\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted value for $\Delta_f H°(298.15\ K)$ of $-74.7\ kcal·mol^{-1}$ is that given in NBS Technical Note 270–4.[1] This value is based mainly on results derived from heat of solution measurements on Co(cr)[2] and $CoCl_2$(cr)[3] in aqueous HCl, $\Delta_f H°(CoCl_2, cr, 298.15\ K) = -74.9 \pm 1.0\ kcal·mol^{-1}$, and from a 3rd law analysis of several sets of equilibrium data.[4–11] Results of earlier heat of solution measurements on Co(cr)[12,13] in aqueous HCl are in reasonable agreement ($\pm 0.4\ kcal·mol^{-1}$) with those used in our calculations,[2] while the results of Thomsen[14] are some $2\ kcal·mol^{-1}$ more negative. Results of a 2nd and 3rd law analysis of the equilibrium data with JANAF functions are tabulated below. Auxiliary $\Delta_f H°$ data used in the analysis are (in $kcal·mol^{-1}$): $\Delta_f H°(HCl, g, 298.15\ K) = -22.063 \pm 0.05$ and $\Delta_f H°(FeCl_2, cr, 298.15\ K) = -81.7 \pm 0.1$.[15]

Source	Reaction*	Method	Data Points	T/K	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Crut[4]	A	Static	1	718		23.4		67.5
Jellinek and Uloth[5]	A	Dynamic	3	673–873	36.5	30.46 ± 1.59	−7.8 ± 1.7	74.6 ± 1.7
Sano[6]	A	Static	7	759–831	32.8	30.66 ± 0.16	−2.8 ± 0.4	74.8 ± 0.3
Partington and Towndrow[7]	A	Static	5	673–773	32.9	30.91 ± 0.30	−2.7 ± 1.5	75.0 ± 0.4
Shchukarev *et al.*[8]	A		10	573–973	28.8	29.91 ± 0.39	1.4 ± 0.2	74.0 ± 0.5
Egan[9]	B	emf	2	673;723	−74.1	−75.09 ± 0.10	−1.5	75.1 ± 0.1
Hamby and Scott[10]	B	emf	1	973		−73.09		73.1
Sheldon and Gee[11]	C	emf	Equation	490–760	−6.4	−7.10 ± 0.22	−1.1 ± 0.02	74.6 ± 0.3

*Reactions: (A) $CoCl_2(cr) + H_2(g) = Co(cr) + 2\ HCl(g)$(B) $Co(cr) + Cl_2(g) = CoCl_2(cr)$(C) $Fe(cr) + CoCl_2(cr) = FeCl_2(cr) + Co(cr)$

Three[5–7] of the five sets of equilibrium data on the H_2 reduction of $CoCl_2$(cr) yield $\Delta_f H°$ values which are in good agreement ($\pm 0.3\ kcal·mol^{-1}$) with the value ($-74.9\ kcal·mol^{-1}$) obtained by solution calorimetry.[2,3] Also, the results obtained from our analysis of the recent emf study of reaction (C) provide further confirmation for the adopted value of $\Delta_f H°$.

Heat Capacity and Entropy

$C_p°$ data below 300 K are based on the low temperature measurements of Chisholm and Stout[16] (11–300 K) and Kostryukova[17] (1.8–4 K). The $C_p°$ data of Kostryakova[17] below 3 K involve bias due to the presence of trace amounts of water in the $CoCl_2$ sample. His results[17] contain a small anomaly near 2.8 K which presumably arises from the $CoCl_2·6\ H_2O$ anti-ferromagnetic transition at 2.3 K.[18] The effect of the hexahydrate on the $C_p°$ data above 3 K is judged to be negligible. The $C_p°$ data above 3 K are joined graphically with those of Chisholm and Stout at 11 K.[16] The latter data set contains a lambda peak at 24.71 K. $C_p°$ near the maximum is $4.1\ cal·K^{-1}·mol^{-1}$, and the enthalpy associated with the transition is on the order of a few calories. The existence of this anomaly has been confirmed from heat capacity measurements by Shalyt[19] (30–75 K, $T_{trs} = 24.9$ K) and Trapeznikowa *et al.*[20] (13–130 K, $T_{trs} = 24.90$ K).This anomaly is apparently associated with the cooperative ordering of the magnetic moments of the cobaltous ions.The latter two sets of $C_p°$ data are judged to be less reliable than that of Chisholm and Stout[16] and are not used in the calculation of $S°(298.15\ K)$. $S°(298.15\ K)$ is obtained from integration of the adopted $C_p°$'s and is based on $S°(3\ K) = 0.003\ cal·K^{-1}·mol^{-1}$ $C_p°$ data above 300 K are estimated from C_p curves for $FeCl_2$[15] and $MnCl_2$.[21] The results of the only high temperature enthalpy study[22] reported for $CoCl_2$(cr) have been analyzed by Kelley.[21] However, a comparison of these $C_p°$'s with those for the isostructural chlorides $FeCl_2$[15] and $MnCl_2$[21] indicate that these values are probably too high by 3.5% at 400 K and 27.3% at 1000 K. Other comparisons[21, 15] exist which indicate that it is not unusual for the $C_p°$ data of these Russian workers to be in error by several percent.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−15.801	−314.394	−314.394	INFINITE
100	48.158	36.945	173.312	−13.637	−315.663	−299.689	156.541
200	71.337	79.256	116.256	−7.400	−314.374	−284.115	74.203
298.15	78.492	109.266	109.266	0.	−312.545	−269.647	47.241
300	78.576	109.751	109.267	0.145	−312.508	−269.381	46.903
400	81.714	132.821	112.391	8.172	−310.520	−255.304	33.339
500	83.387	151.243	118.382	16.431	−308.570	−241.727	25.253
600	84.600	166.552	125.170	24.829	−306.698	−228.536	19.896
700	85.939	179.699	132.042	33.360	−304.875	−215.653	16.092
800	86.818	191.234	138.735	41.999	−303.536	−202.967	13.252
900	87.529	201.501	145.149	50.717	−301.883	−190.496	11.056
1000	88.241	210.762	151.255	59.507	−300.401	−178.201	9.308
1013.000	88.316	211.902	152.026	60.655	--- CRYSTAL <---> LIQUID ---		
1100	88.826	219.200	157.054	68.361	−299.134	−166.045	7.885
1200	89.370	226.952	162.560	77.271	−298.121	−153.993	6.703
1300	89.872	234.126	167.793	86.233	−297.514	−142.010	5.706
1400	90.374	240.804	172.772	95.245	−297.441	−130.053	4.852
1500	90.876	247.057	177.518	104.308	−296.317	−118.134	4.114

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = [-149.021]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1013 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-271.514]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [44.8 \pm 6.3\ ]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of the estimated value for $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1013\ K)-H°(298.15\ K)$, between the crystal and liquid. Independent values of $\Delta_f H°(l)$ (or $\Delta_f H°(cr)$) can be obtained from a 2nd and 3rd law analysis of two sets[1,2] of emf data for the formation cell of molten $CoCl_2$. Results of our analysis of these data are tabulated below.

Source	Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(l)$ kcal·mol^{-1}	$\Delta_f H°(cr)$ kcal·mol^{-1}
Devoto and Guzzi[1]	4	1023–1173	−75.8	−65.77 ± 1.2	9.2 ± 1.8	−65.8	−75.6
Hamby and Scott[2]	2	1073–1173	−65.9	−63.67 ± 0.3	2.0	−63.7	−73.5

Even though both data sets contain few points and show significant positive drift, we note that the average $\Delta_f H°(cr)$ value (−74.6 kcal·mol^{-1}) obtained from these results is in excellent agreement with our adopted value (−74.7 kcal·mol^{-1}).

Heat Capacity and Entropy

$C_p°$ is assumed constant at 23.70 cal·K^{-1}·mol^{-1} in the temperature range 700–2000 K and is estimated from liquid heat capacities[3] for $FeCl_2$, $MgCl_2$, $CaCl_2$ and $NiCl_2$.[4] A glass transition is assumed at 700 K below which $C_p°$ is that of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is that obtained by Schafer and Krehl[5] from cooling curve measurements. Other reported values for T_{fus} are 997 K[6] and 1008 K.[7] Our adopted value for T_{fus} is that selected by Brewer *et al.*,[8] while Kelley[9] chose T_{fus} = 1000 K. $\Delta_{fus} H°$ is calculated from $\Delta_{fus} H° = \Delta_{fus} S° \times T_{fus}$ with $\Delta_{fus} S° = 3.51 \pm 0.5$ cal·K^{-1} g·atom^{-1}. $\Delta_{fus} S°$ is estimated from similar data[3,4] for the isostructural chlorides $FeCl_2$, $MgCl_2$, $MnCl_2$, $NiCl_2$, and $CdCl_2$. Kelley[9] has analyzed freezing point depression data for several binary systems which involve $CoCl_2$. Unfortunately, the values of $\Delta_{fus} H°$ derived by Kelley[9] are very discrepant and probably of no use in defining $\Delta_{fus} H°$. Reported values fall in the range 6.71–8.75 kcal·mol^{-1}, and Kelley[9] recommended $\Delta_{fus} H° = 7.39$ kcal·mol^{-1}. This value is 3.31 kcal·mol^{-1} less than our estimated value and is also inconsistent with $\Delta_f H°$ values derived for the crystal and liquid from equilibrium data. See the enthalpy of formation section for $CoCl_2$(cr, l). The discrepancies which arise in Kelley's analysis of the freezing point data may be associated with the ability of the divalent cobalt ion to form complex ions.

Vaporization Data

Refer to the ideal gas table for details.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	78.492	149.021	149.021	0.	−271.514	−240.469	42.129
300	78.576	149.507	149.023	0.145	−271.477	−240.276	41.836
400	81.714	172.577	152.147	8.172	−269.489	−230.175	30.058
500	83.387	190.999	158.137	16.431	−267.539	−220.574	23.043
600	84.600	206.307	164.925	24.829	−265.667	−211.358	18.400
700	85.941	219.448	171.797	33.355	−263.849	−202.451	15.107
700.000	85.941	219.448	171.797	33.355	GLASS <--> LIQUID		
700.000	99.161	219.448	171.797	33.355	TRANSITION		
800	99.161	232.689	178.600	43.271	−261.233	−193.827	12.656
900	99.161	244.368	185.271	53.187	−258.381	−185.575	10.770
1000	99.161	254.816	191.712	63.103	−255.774	−177.628	9.278
1013.000	99.161	256.097	192.530	64.392	--- CRYSTAL <--> LIQUID ---		
1100	99.161	264.267	197.885	73.019	−253.444	−169.928	8.069
1200	99.161	272.895	203.782	82.936	−251.426	−162.428	7.070
1300	99.161	280.832	209.408	92.852	−249.865	−155.078	6.231
1400	99.161	288.181	214.775	102.768	−248.888	−147.827	5.515
1500	99.161	295.022	219.899	112.684	−246.910	−140.675	4.899
1600	99.161	301.422	224.797	122.600	−244.688	−133.664	4.364
1700	99.161	307.433	229.483	132.516	−242.375	−126.796	3.896
1800	99.161	313.101	233.972	142.432	−256.339	−119.770	3.476
1900	99.161	318.462	238.279	152.348	−254.300	−112.238	3.086
2000	99.161	323.549	242.417	162.264	−252.271	−104.814	2.737

PREVIOUS: CURRENT: June 1973

0	to	1013	K crystal
above		1013	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.801	−314.394	−314.394	INFINITE
100	48.158	36.945	173.312	−13.637	−315.663	−299.689	156.541
200	71.337	79.256	116.256	−7.400	−314.374	−284.115	74.203
298.15	78.492	109.266	109.266	0.	−312.545	−269.647	47.241
300	78.576	109.751	109.267	0.145	−312.508	−269.381	46.903
400	81.714	132.821	112.391	8.172	−310.520	−255.304	33.339
500	83.387	151.243	118.382	16.431	−308.570	−241.727	25.253
600	84.600	166.552	125.170	24.829	−306.698	−228.536	19.896
700	85.939	179.699	132.042	33.360	−304.875	−215.653	16.092
800	86.818	191.234	138.735	41.999	−303.536	−202.967	13.252
900	87.529	201.501	145.149	50.717	−301.883	−190.496	11.056
1000	88.241	210.762	151.255	59.507	−300.401	−178.201	9.308
1013.000	88.316	211.902	152.026	60.655	CRYSTAL <--> LIQUID TRANSITION		
1013.000	99.161	256.097	152.026	105.423			
1100	99.161	264.267	160.585	114.050	−253.444	−169.928	8.069
1200	99.161	272.895	169.589	123.967	−251.426	−162.428	7.070
1300	99.161	280.832	177.845	133.883	−249.865	−155.078	6.231
1400	99.161	288.181	185.467	143.799	−248.888	−147.827	5.515
1500	99.161	295.022	192.545	153.715	−246.910	−140.675	4.899
1600	99.161	301.422	199.152	163.631	−244.688	−133.664	4.364
1700	99.161	307.433	205.347	173.547	−242.375	−126.796	3.896
1800	99.161	313.101	211.177	183.463	−256.339	−119.770	3.476
1900	99.161	318.462	216.684	193.379	−254.300	−112.239	3.086
2000	99.161	323.549	221.901	203.295	−252.271	−104.814	2.737

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = [298.51 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -95.0 \pm 8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -93.7 \pm 8\ kJ·mol^{-1}$

State	Electronic Levels and Quantum Weights ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$^4\Sigma_g^-$	0	[4]	$^4\Sigma_g^-$	[10425]	[4]
$^4\phi_g$	[210]	[8]	$^4\Delta_g$	[14197]	[8]
$^4\Pi_g$	[2804]	[8]	$^4\Pi_g$	[21270]	[8]

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[325] (1)
94.5 (2)
493 (1)

Point Group: $D_{\infty h}$
Bond Distance: Co–Cl = 2.117 Å; Bond Angle: Cl–Co–Cl = 180° Rotational constant: $B_0 = 0.053048\ cm^{-1}$; $\sigma = 2$

Enthalpy of Formation

$\Delta_f H°$ is calculated from $\Delta_{sub}H° = 52.3 \pm 1.7\ kcal·mol^{-1}$ by addition of $\Delta_f H°(CoCl_2, cr, 298.15\ K) = -74.7 \pm 0.3\ kcal·mol^{-1}$.[1] The adopted value for $\Delta_{sub}H°$ is based on results of a 2nd and 3rd law analysis of extensive sublimation data reported by Hill *et al.*[2] These studies included both Knudsen–effusion and torsion–effusion measurements which were performed in platinum–10% rhodium effusion cells. Orifice diameters of the cells varied from 0.0518 cm to 0.1645 cm. The extent of dimerization (~1–2%) was also determined from mass spectrometric measurements, and the measured vapor pressures were corrected to represent equilibrium pressure of the monomer. Results of our analysis of sixty–four vapor pressure points measured in five different cells are given below. Derived $\Delta_f H$ values show no significant trends with orifice size; thus, a mean value of the five results is adopted. Also included in this table is a value for $\Delta_f H$ which was obtained from an analysis of equilibrium data[3] for $CoO(cr) + Cl2(g) = CoCl_2(g) + 1/2\ O_2(g)$. Orlov[3] has not reported sufficient information to allow a small correction to be made for dimerization; even so, his results still give a value for $\Delta_f H°(-22.1\ kcal·mol^{-1})$ which agrees fairly well with that adopted.

Source	Method	T/K	Data Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
2	Knudsen–Cell A	680–800	13		52.35 ± 0.13	0.4 ± 0.5	22.4 ± 0.4
2	Knudsen–Cell B	697–814	14[a]	51.9	52.29 ± 0.10	0.5 ± 0.4	22.4 ± 0.4
2	Knudsen–Cell C	715–810	10	52.9	52.14 ± 0.16	−0.9 ± 0.9	22.6 ± 0.5
2	Torsion–Cell A	759–834	10	56.7	52.38 ± 0.52	−5.4 ± 3.2	22.3 ± 0.8
2	Torsion–Cell B	745–824	15	55.0	52.30 ± 0.17	−3.4 ± 0.4	22.4 ± 0.5
3	Transpiration	1323–1523	Equation	16.6	34.77 ± 2.1	12.7	22.1 ± 2.2[b]

[a]Two points rejected due to failure of a statistical test. [b]$\Delta_f H°(CoO, cr, 298.15\ K) = -56.82 \pm 0.10\ kcal·mol^{-1}$.[1]

Other vapor pressures for $CoCl_2(cr, l)$ have been measured by static[4] and transpiration[5,6] methods. In all three studies the presence of a small amount of dimer in the saturated vapor was not considered. JANAF pressures based on (a) selected values of the heats of sublimation and vaporization for the monomer and dimer, (b) the mass spectrometric value of $2\Delta_{sub}H(monomer) - \Delta_{sub}H(dimer) = -38.99\ kcal·mol^{-1}$ (see Co_2Cl_4(g) table) at 298.15 K, and (c) adopted entropies for the condensed and gaseous species are compared with the observed total pressures in the table given below.

Source	Method	Process	T/K	Mole Fraction Dimer Calc. Range	P_{calc}/P_{obs} Range
4	Static	Sublimation	906–997	0.051.0.086	0.073–0.156
4	Static	Vaporization	1022–1256	0.082–0.092	0.198–0.816
5	Transpiration	Vaporization	*1015–1144*	*0.090–0.092*	*0.531–0.743*
6	Transpiration	Sublimation	925–1010	0.057–0.091	0.875–1.096
6	Transpiration	Vaporization	1019–1073	0.092	0.825–0.883

Our predictions agree reasonably well with the transpiration data of Schafer and Krehl,[6] while the static measurements of Maier[4] show significant deviations from our pressures, particularly at lower temperatures. We note that JANAF analysis[1] of Maier's vapor pressures for $BaCl_2$, $AlCl_3$, and $FeCl_2$ indicate the existence of temperature dependent errors in his measurements; thus, the $CoCl_2$ results are probably not reliable. The transpiration data of Kulkarni and Dadape[5] show similar discrepancies.

Heat Capacity and Entropy

Measurements of the infrared[7–9] and electronic[10–12] spectra of both matrix–isolated and gaseous $CoCl_2$ have been interpreted on the basis of a linear structure of $D_{\infty h}$ symmetry. This structure is adopted, and the Co–Cl bond length is taken to be equal to the value determined by

Continued on page 937

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−15.271	−95.041	−95.041	INFINITE
100	51.604	236.844	350.003	−11.316	−94.519	−98.535	51.469
200	57.705	275.056	303.902	−5.769	−93.920	−102.821	26.854
250	58.855	288.064	299.478	−2.853	−93.778	−105.064	21.952
298.15	59.623	298.500	298.500	0.	−93.722	−107.244	18.789
300	59.648	298.869	298.501	0.110	−93.720	−107.328	18.687
350	60.221	308.109	299.230	3.108	−93.704	−109.598	16.357
400	60.657	316.180	300.855	6.130	−93.738	−111.866	14.608
450	61.011	323.346	302.963	9.172	−93.821	−114.128	13.248
500	61.318	329.790	305.329	12.230	−93.947	−116.378	12.158
600	61.872	341.019	310.369	18.390	−94.314	−120.832	10.519
700	62.395	350.596	315.448	24.604	−94.808	−125.214	9.344
800	62.891	358.961	320.375	30.868	−95.843	−129.456	8.453
900	63.344	366.395	325.083	37.181	−96.596	−133.614	7.755
1000	63.737	373.090	329.555	43.535	−97.550	−137.678	7.192
1100	64.064	379.181	333.793	49.926	−98.746	−141.635	6.726
1200	64.324	384.767	337.812	56.346	−100.223	−145.471	6.332
1300	64.522	389.924	341.625	62.789	−102.135	−149.168	5.994
1400	64.666	394.711	345.247	69.249	−104.615	−152.696	5.697
1500	64.765	399.176	348.696	75.720	−106.081	−156.077	5.435
1600	64.828	403.358	351.983	82.200	−107.295	−159.369	5.203
1700	64.862	407.289	355.121	88.685	−108.414	−162.589	4.996
1800	64.875	410.997	358.124	95.172	−125.807	−165.450	4.801
1900	64.873	414.505	361.000	101.660	−127.196	−167.615	4.608
2000	64.860	417.832	363.759	108.146	−128.597	−169.706	4.432
2100	64.842	420.996	366.410	114.631	−130.011	−171.727	4.271
2200	64.821	424.012	368.960	121.115	−131.438	−173.680	4.124
2300	64.799	426.893	371.417	127.595	−132.882	−175.568	3.987
2400	64.779	429.650	373.786	134.074	−134.342	−177.392	3.861
2500	64.762	432.294	376.074	140.551	−135.820	−179.156	3.743
2600	64.748	434.834	378.285	147.027	−137.316	−180.860	3.634
2700	64.738	437.277	380.425	153.501	−138.832	−182.506	3.531
2800	64.733	439.632	382.498	159.975	−140.367	−184.095	3.434
2900	64.733	441.903	384.507	166.448	−141.923	−185.630	3.344
3000	64.738	444.098	386.457	172.921	−143.497	−187.110	3.258
3100	64.747	446.221	388.351	179.396	−145.090	−188.538	3.177
3200	64.761	448.277	390.192	185.871	−521.514	−188.141	3.071
3300	64.778	450.270	391.982	192.348	−521.715	−177.720	2.813
3400	64.800	452.204	393.725	198.827	−521.932	−167.292	2.570
3500	64.825	454.083	395.423	205.308	−522.165	−156.858	2.341
3600	64.853	455.909	397.078	211.792	−522.413	−146.418	2.124
3700	64.884	457.686	398.692	218.279	−522.674	−135.970	1.920
3800	64.917	459.417	400.268	224.769	−522.949	−125.515	1.725
3900	64.952	461.104	401.806	231.262	−523.234	−115.052	1.541
4000	64.989	462.749	403.309	237.759	−523.529	−104.582	1.366
4100	65.028	464.354	404.778	244.260	−523.832	−94.105	1.199
4200	65.068	465.922	406.216	250.765	−524.143	−83.620	1.040
4300	65.108	467.453	407.622	257.274	−524.458	−73.127	0.888
4400	65.149	468.950	408.999	263.786	−524.778	−62.628	0.743
4500	65.191	470.415	410.347	270.303	−525.100	−52.121	0.605
4600	65.232	471.848	411.669	276.825	−525.424	−41.606	0.472
4700	65.274	473.251	412.964	283.350	−525.748	−31.085	0.345
4800	65.315	474.626	414.235	289.879	−526.072	−20.557	0.224
4900	65.356	475.973	415.481	296.413	−526.394	−10.022	0.107
5000	65.396	477.294	416.704	302.950	−526.714	0.519	−0.005
5100	65.435	478.589	417.905	309.492	−527.032	11.067	−0.113
5200	65.474	479.860	419.084	316.037	−527.346	21.621	−0.217
5300	65.511	481.108	420.243	322.587	−527.658	32.181	−0.317
5400	65.548	482.333	421.381	329.140	−527.966	42.747	−0.413
5500	65.583	483.536	422.500	335.696	−528.271	53.319	−0.506
5600	65.617	484.718	423.601	342.256	−528.573	63.896	−0.596
5700	65.650	485.880	424.683	348.820	−528.873	74.478	−0.683
5800	65.681	487.022	425.748	355.386	−529.170	85.066	−0.766
5900	65.711	488.145	426.796	361.956	−529.422	95.656	−0.847
6000	65.740	489.249	427.828	368.528	−529.706	106.252	−0.925

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [383.445 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -656.08 \pm 10.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -659.82 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[140](1)	[76](1)
[67](1)	[151](1)
[141](1)	[156](1)

Ground State Quantum Weight: [1] σ = [4]

Point Group: [D_{2h}]

Bond Distance: Cs–Cl = [3.18] Å

Bond Angle: Cl–Cs–Cl = [93.2]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.62360 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Datz[1] studied the molecular association equilibrium in cesium chloride vapors by measuring the temperature dependence of the molecular weight of gaseous CsCl. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. The pressure sensing element was a fused silica manometer containing Au(l). Based on the reported results, we derive the equilibrium constants for the reaction $Cs_2Cl_2(g) = 2CsCl(g)$ in the temperature range 1224–1418 K. The enthalpy change of this reaction is evaluated by the 2nd and 3rd law method as 39.3 ± 1.1 and 42.9 ± 0.6 $kcal \cdot mol^{-1}$, respectively. The drift in the 3rd law value is equivalent to an entropy error of 2.7 ± 0.8 $cal \cdot K^{-1} \cdot mol^{-1}$. Using the 3rd law $\Delta_r H°$ and $\Delta_f H°$(CsCl, g, 298.15 K) = −57.4 $kcal \cdot mol^{-1}$, we obtain $\Delta_f H°(298.15\ K) = -157.7 \pm 2.5\ kcal \cdot mol^{-1}$ (−659.817 ± 10.5 $kJ \cdot mol^{-1}$) for Cs_2Cl_2(g), which is adopted.

Schrier[2] determined the vapor pressures of molten cesium chloride at temperatures between 1165 and 1387 K by the boiling point or manometric method. The vapor analysis was performed using the transpiration method. An inert gas, N_2, was passed over the CsCl sample at a given temperature. The salt vapor entrained by the carrier gas was collected, weighed and analyzed. The data obtained were combined with the boiling point measurements to yield the average molecular weight of the vapor. Association into dimer was postulated. The mole fraction in the vapor and the partial pressure of CsCl(g) and Cs_2Cl_2(g) were calculated. The equilibrium constants, 1209–1350 K, for dissociation of the Cs_2Cl_2 dimer were derived. Using the reported equilibrium constants, we evaluate the enthalpy change $\Delta_r H°(298.15\ K)$ of the reaction $Cs_2Cl_2(g) = 2CsCl(g)$ to be 34.1 ± 2.9 and 43.2 ± 0.9 $kcal \cdot mol^{-1}$ by the 2nd and 3rd law methods. Based on the 3rd law $\Delta_r H°(298.15\ K)$ value and $\Delta_f H°$(CsCl, g, 298.15 K) = −57.4 $kcal \cdot mol^{-1}$, we obtain $\Delta_f H°(298.15\ K) = -158.0\ kcal \cdot mol^{-1}$ for Cs_2Cl_2(g), which is in agreement with the adopted value.

Miller and Kusch[3] made an analysis of the velocity distribution of the CsCl molecules which escape through an ideal aperture from an isothermal enclosure. They found that there was no definite evidence that any species other than diatomic molecules were present in the beams in measurable amounts, in other words, the dimerization must be small, e.g. <1.5%. However, according to our calculation the concentration of dimer is 15–34% in the temperature range 600–900 K, and 33–20% at the temperatures 1000–1600 K.

Heat Capacity and Entropy

The molecular structure is assumed to be planar, having D_{2h} symmetry. Based on the bond distances of Cs–Cs and Cl–Cl estimated by Berkowitz,[4] the Cs–Cl bond distance and Cl–Cs–Cl bond angle are calculated. The vibrational frequencies were calculated by Berkowitz,[5] on the basis of the potential function for an ionic model. The principal moments of inertia are: $I_A = 62.8570 \times 10^{-39}$, $I_B = 210.7205 \times 10^{-39}$, and $I_C = 273.5775 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.880	−656.082	−656.082	INFINITE
100	71.695	298.145	454.495	−15.635	−658.046	−657.970	343.688
200	79.843	351.168	390.868	−7.940	−658.750	−657.609	171.750
250	80.993	369.121	384.785	−3.916	−659.184	−657.277	137.330
298.15	81.617	383.445	383.445	0.	−659.817	−656.856	115.079
300	81.635	383.950	383.446	0.151	−659.848	−656.838	114.366
350	82.029	396.566	384.442	4.243	−664.864	−655.599	97.843
400	82.287	407.537	386.658	8.352	−665.676	−654.219	85.432
450	82.465	417.240	389.527	12.471	−666.474	−652.739	75.768
500	82.593	425.935	392.741	16.597	−667.266	−651.171	68.027
600	82.760	441.010	399.567	24.866	−668.843	−647.804	56.396
700	82.862	453.776	406.423	33.147	−670.427	−644.172	48.069
800	82.928	464.845	413.049	41.437	−672.023	−640.312	41.808
900	82.973	474.615	419.357	49.732	−673.637	−636.252	36.927
1000	83.005	483.359	425.328	58.031	−809.528	−624.612	32.626
1100	83.029	491.271	430.969	66.333	−809.133	−606.139	28.783
1200	83.048	498.497	436.299	74.637	−808.749	−587.702	25.582
1300	83.062	505.145	441.343	82.942	−808.375	−569.297	22.875
1400	83.073	511.301	446.123	91.249	−808.011	−550.920	20.555
1500	83.082	517.032	450.661	99.557	−807.659	−532.569	18.546
1600	83.090	522.395	454.979	107.865	−807.323	−514.240	16.788
1700	83.096	527.432	459.094	116.175	−807.006	−495.933	15.238
1800	83.101	532.182	463.024	124.485	−806.713	−477.643	13.861
1900	83.106	536.675	466.783	132.795	−806.452	−459.368	12.629
2000	83.109	540.938	470.385	141.106	−806.230	−441.107	11.521
2100	83.113	544.993	473.842	149.417	−806.058	−422.855	10.518
2200	83.115	548.860	477.165	157.728	−805.946	−404.610	9.607
2300	83.118	552.554	480.363	166.040	−805.906	−386.369	8.775
2400	83.120	556.092	483.445	174.352	−805.949	−368.128	8.012
2500	83.122	559.485	486.419	182.664	−806.089	−349.883	7.310
2600	83.124	562.745	489.293	190.976	−806.339	−331.630	6.663
2700	83.125	565.882	492.072	199.289	−806.713	−313.365	6.062
2800	83.126	568.905	494.762	207.601	−807.223	−295.084	5.505
2900	83.128	571.822	497.369	215.914	−807.883	−276.782	4.985
3000	83.129	574.640	499.898	224.227	−808.708	−258.455	4.500
3100	83.130	577.366	502.353	232.540	−809.709	−240.097	4.046
3200	83.131	580.006	504.739	240.853	−810.901	−221.704	3.619
3300	83.131	582.564	507.059	249.166	−812.213	−203.277	3.218
3400	83.132	585.045	509.316	257.479	−813.787	−184.801	2.839
3500	83.133	587.455	511.515	265.792	−815.575	−166.276	2.482
3600	83.133	589.797	513.657	274.105	−817.588	−147.697	2.143
3700	83.134	592.075	515.745	282.419	−819.807	−129.061	1.822
3800	83.134	594.292	517.783	290.732	−822.259	−110.362	1.517
3900	83.135	596.451	519.773	299.046	−824.924	−91.597	1.227
4000	83.135	598.556	521.716	307.359	−827.868	−72.757	0.950
4100	83.136	600.609	523.616	315.673	−831.059	−53.840	0.686
4200	83.136	602.612	525.473	323.986	−834.497	−34.843	0.433
4300	83.137	604.569	527.290	332.300	−838.185	−15.760	0.191
4400	83.137	606.480	529.068	340.614	−841.534	3.344	−0.040
4500	83.137	608.348	530.809	348.927	−844.494	22.462	−0.261
4600	83.138	610.175	532.514	357.241	−848.564	41.772	−0.474
4700	83.138	611.963	534.186	365.555	−852.825	61.172	−0.680
4800	83.138	613.714	535.824	373.869	−857.269	80.666	−0.878
4900	83.138	615.428	537.432	382.183	−861.887	100.254	−1.069
5000	83.139	617.108	539.008	390.496	−866.667	119.937	−1.253
5100	83.139	618.754	540.556	398.810	−871.600	139.718	−1.431
5200	83.139	620.368	542.075	407.124	−875.608	159.442	−1.602
5300	83.139	621.952	543.568	415.438	−880.674	179.395	−1.768
5400	83.139	623.506	545.034	423.752	−885.289	199.358	−1.928
5500	83.140	625.032	546.474	432.066	−890.178	219.442	−2.084
5600	83.140	626.530	547.890	440.380	−895.424	239.664	−2.235
5700	83.140	628.001	549.283	448.694	−900.731	259.981	−2.382
5800	83.140	629.447	550.653	457.008	−906.089	280.391	−2.525
5900	83.140	630.868	552.000	465.322	−911.485	300.893	−2.664
6000	83.140	632.266	553.326	473.636	−916.906	321.487	−2.799

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 108.085\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -206.65 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -205.85 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev and Oranskaya[1] have reported equilibrium constants for the dissociation $CuCl_2(cr) \rightarrow CuCl(cr/l) + 0.5\ Cl_2(g)$, which are in general agreement with earlier reports by Ephraim[2] and Tarasenkov *et al.*[3] These data were subjected to third law analysis which revealed a significant trend of $13 \pm 0.5\ cal·K^{-1}·mol^{-1}$, indicating that equilibrium conditions were not reached. However an average value of $\Delta_f H°(298.15\ K) = 16.5 \pm 1.9\ kcal·mol^{-1}$ yields a heat of formation of $CuCl_2(cr) = -49.5 \pm 2.5\ kcal·mol^{-1}$which is in good agreement with the adopted value taken from NBS Circlular 500.[4]

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 11–300 K by Stout and Chisholm.[5] The integration of this data from $S°(10\ K) = 0.111\ cal·K^{-1}·mol^{-1}$ gave $S°(298.15\ K) = 25.833\ cal·K^{-1}·mol^{-1}$. The heat capacity above 298.15 K was obtained by smooth extrapolation of the above data, since the heat capacities of Krestovnikov and Karetnikov[6] were not compatible with the low temperature data.

Decomposition Data

The temperature of decomposition, T_{dcm} = 766 K, was estimated from the table for $CuCl_2$(cr), CuCl(l) and Cl_2(g) so that the pressure of Cl_2 is 1 bar.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−14.983	−206.648	−206.648	INFINITE
100	46.777	41.020	167.042	−12.602	−207.848	−192.046	100.314
200	65.647	80.525	114.499	−6.795	−207.091	−176.458	46.086
298.15	71.881	108.085	108.085	0.	−205.853	−161.680	28.326
300	71.923	108.530	108.087	0.133	−205.828	−161.405	28.103
400	75.061	129.678	110.949	7.492	−204.433	−146.806	19.171
500	77.278	146.679	116.450	15.115	−202.947	−132.569	13.849
600	78.785	160.906	122.706	22.920	−201.393	−118.638	10.328
700	79.956	173.142	129.057	30.860	−199.800	−104.971	7.833
800	80.885	183.881	135.253	38.903	−198.181	−91.535	5.977
900	81.655	193.453	141.197	47.030	−196.550	−78.302	4.545
1000	82.370	202.093	146.862	55.232	−194.919	−65.251	3.408
1100	83.001	209.974	152.246	63.501	−193.306	−52.362	2.486
1200	83.607	217.222	157.363	71.831	−191.732	−39.619	1.725
1300	84.190	223.937	162.229	80.221	−190.242	−27.004	1.085
1400	84.750	230.197	166.863	88.668	−201.992	−14.093	0.526
1500	85.287	236.063	171.282	97.170	−200.566	−0.721	0.025

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 320.381\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-758.8]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-765.7]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
207 (1)	372 (1)	620 (1)
254 (1)	386 (1)	894 (1)
330 (1)	547 (1)	1331 (1)

Ground State Multiplicity = [1] $\sigma = 1$
Point Group = C_s
Bond Distances: P–Cl = 1.99 ± 0.04 Å; P–F = 1.50 ± 0.03 Å; P–O = 1.54 ± 0.03 Å
Bond Angles: Cl–P–Cl = F–P–Cl = 103°; O–P–Cl = O–P–F = 115.35°
Product of the Moments of Inertia: $I_A I_B I_C = 4.70925 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(298.15\ K)$ of $POFCL_2$ was estimated to be −183 kcal·mol^{-1} from the $\Delta_f H°(298.15\ K)$ of $POCl_3$ by assuming bond energies of 120 kcal·mol^{-1} for $D_0°$(P–F) and 80 kcal·mol^{-1} for $D_0°$(P–Cl). The $D_0°$(P–F) and $D_0°$(P–Cl) values were taken from Neale *et al.*[1,2]

Essentially the same $\Delta_f H°(298.15\ K)$ may be obtained by assuming a $\Delta_f H° = 0$ for the following reaction:

$$POCl_3(g) + POF_3(g) \rightarrow POCl_2F(g) + POF_2Cl(g)$$

Heat Capacity and Entropy

The molecular constants were determined by Brockway and Beach[3] and by Williams *et al.*[4] Brockway and Beach used electron diffraction. Williams *et al.*[4] measured microwave spectra. Brockway and Beach[3] assumed that the F–P–F and F–P–Cl angles were equal in POF_2Cl and $POFCl_2$. An analysis of their data by Williams *et al.*[4] indicates that the angles in POF_2Cl, $POFCl_2$, and $POCl_3$, and POF_3 should be 103° rather than the reported 106° ± 3°. The principal moments of inertia are: $I_A = 26.9230 \times 10^{-39}$, $I_B = 37.9561 \times 10^{-39}$, and $I_C = 46.0837 \times 10^{-39}$ g·cm^6.

The Raman spectra and vibrational frequencies for $POFCl_2$ were reported by Delwaulle and Francois.[5] These frequency assignments are summarized by Delwaulle and Francois.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.431	−758.808	−758.808	INFINITE
100	44.533	253.224	381.368	−12.814	−761.896	−749.365	391.428
200	66.285	291.266	327.264	−7.199	−764.503	−735.924	192.204
250	73.746	306.896	321.658	−3.690	−765.184	−728.696	152.253
298.15	79.319	320.381	320.381	0.	−765.672	−721.622	126.425
300	79.508	320.873	320.383	0.147	−765.688	−721.349	125.598
350	84.039	333.482	321.368	4.240	−766.782	−713.857	106.537
400	87.659	344.949	323.610	8.536	−767.117	−706.272	92.230
450	90.586	355.449	326.573	12.994	−767.342	−698.651	81.097
500	92.977	365.121	329.950	17.585	−767.483	−691.011	72.189
600	96.579	382.412	337.288	27.074	−767.575	−675.704	58.825
700	99.094	397.499	344.835	36.865	−767.492	−660.397	49.279
800	100.901	410.856	352.269	46.870	−767.293	−645.110	42.121
900	102.232	422.821	359.455	57.030	−767.016	−629.853	36.556
1000	103.235	433.646	366.341	67.305	−766.685	−614.630	32.105
1100	104.007	443.523	372.915	77.669	−766.319	−599.442	28.465
1200	104.613	452.600	379.183	88.101	−829.501	−583.210	25.386
1300	105.095	460.993	385.157	98.587	−828.321	−562.734	22.611
1400	105.485	468.797	390.856	109.117	−827.137	−542.349	20.235
1500	105.805	476.086	396.298	119.682	−825.956	−522.048	18.179
1600	106.070	482.923	401.500	130.276	−824.780	−501.826	16.383
1700	106.292	489.360	406.481	140.895	−823.612	−481.677	14.800
1800	106.479	495.441	411.256	151.533	−822.455	−461.597	13.395
1900	106.639	501.202	415.840	162.189	−821.311	−441.580	12.140
2000	106.776	506.676	420.246	172.860	−820.180	−421.624	11.012
2100	106.895	511.888	424.486	183.544	−819.065	−401.723	9.992
2200	106.999	516.864	428.573	194.239	−817.965	−381.875	9.067
2300	107.089	521.622	432.516	204.943	−816.881	−362.078	8.223
2400	107.169	526.181	436.325	215.656	−815.815	−342.327	7.451
2500	107.240	530.558	440.007	226.377	−814.764	−322.620	6.741
2600	107.303	534.765	443.571	237.104	−813.731	−302.954	6.086
2700	107.359	538.816	447.024	247.837	−812.714	−283.328	5.481
2800	107.409	542.721	450.373	258.576	−811.713	−263.740	4.920
2900	107.455	546.491	453.622	269.319	−810.727	−244.187	4.398
3000	107.496	550.135	456.779	280.067	−809.755	−224.668	3.912
3100	107.533	553.660	459.848	290.818	−808.796	−205.180	3.457
3200	107.567	557.075	462.833	301.573	−807.848	−185.725	3.032
3300	107.597	560.385	465.739	312.331	−806.910	−166.298	2.632
3400	107.626	563.598	468.570	323.093	−805.979	−146.899	2.257
3500	107.651	566.718	471.330	333.856	−805.055	−127.528	1.903
3600	107.675	569.751	474.022	344.623	−804.133	−108.183	1.570
3700	107.697	572.701	476.649	355.391	−803.212	−88.864	1.255
3800	107.717	575.574	479.215	366.162	−802.289	−69.569	0.956
3900	107.736	578.372	481.722	376.935	−801.362	−50.299	0.674
4000	107.753	581.100	484.172	387.709	−800.428	−31.053	0.406
4100	107.769	583.761	486.569	398.485	−799.485	−11.830	0.151
4200	107.784	586.358	488.914	409.263	−798.529	7.369	−0.092
4300	107.798	588.894	491.210	420.042	−797.559	26.546	−0.322
4400	107.811	591.372	493.458	430.822	−796.572	45.700	−0.543
4500	107.823	593.795	495.661	441.604	−795.566	64.831	−0.753
4600	107.834	596.165	497.820	452.387	−794.540	83.939	−0.953
4700	107.845	598.484	499.938	463.171	−793.491	103.026	−1.145
4800	107.855	600.755	502.014	473.956	−792.417	122.089	−1.329
4900	107.864	602.979	504.052	484.742	−791.318	141.130	−1.504
5000	107.873	605.158	506.053	495.528	−790.192	160.148	−1.673
5100	107.881	607.295	508.017	506.316	−789.038	179.144	−1.835
5200	107.889	609.389	509.946	517.105	−787.855	198.116	−1.990
5300	107.896	611.445	511.842	527.894	−786.642	217.066	−2.139
5400	107.903	613.462	513.705	538.684	−785.400	235.992	−2.283
5500	107.910	615.442	515.537	549.475	−784.128	254.895	−2.421
5600	107.916	617.386	517.338	560.266	−782.825	273.775	−2.554
5700	107.922	619.296	519.110	571.058	−781.493	292.630	−2.682
5800	107.928	621.173	520.854	581.850	−780.130	311.463	−2.805
5900	107.933	623.018	522.570	592.643	−778.738	330.271	−2.924
6000	107.938	624.832	524.259	603.437	−777.318	349.056	−3.039

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 117.947 \pm 3.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 950\ K$

$\Delta_f H°(0\ K) = -344.419 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -341.833 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 43.012 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Koehler and Coughlin[1] determined $\Delta_r H°(298.15\ K) = -4.06 \pm 0.05\ kcal \cdot mol^{-1}$ for $Fe(\alpha) + 2\ HCl(12.731\ H_2O) = FeCl_2(cr) + H_2(g)$ by solution calorimetry. This leads to $\Delta_f H°(FeCl_2, cr, 298.15\ K) = -81.7 \pm 0.1\ kcal \cdot mol^{-1}$ which is adopted in the tabulation. The value $\Delta_f H°(298.15\ K)\ [HCl(12.731\ H_2O)] = -38.812\ kcal \cdot mol^{-1}$[2] is used in the calculation.

Li and Gregory[3] also determined calorimetrically $\Delta_r H°(298.15\ K) = -19.5 \pm 0.2\ kcal \cdot mol^{-1}$ for $FeCl_2(cr) \rightarrow Fe^{++}(aq) + 2\ Cl^-(aq)$ in aqueous solution at concentrations near 10^{-3} molal. Using $\Delta_f H°(Fe^{++}, aq, \infty\ 298.15\ K) = -21.3\ kcal \cdot mol^{-1}$[4] and $\Delta_f H°(Cl^-, aq, \infty\ 298.15\ K) = -39.952\ kcal \cdot mol^{-1}$,[2] we have obtained $\Delta_f H°(FeCl_2, cr, 298.15\ K) = -81.7\ kcal \cdot mol^{-1}$ which is in excellent agreement with the adopted value.

Kangro and Petersen[5] determined the equilibrium constants for the reaction $FeCl_2(cr) + H_2(g) = Fe(cr) + 2\ HCl(g)$ in the temperature range from 484–662 °C. By use of 2nd and 3rd law analyses, the enthalpy of reaction is evaluated as 37.81 and 38.24 $kcal \cdot mol^{-1}$, respectively. Using the 3rd law $\Delta_r H°(298.15\ K)$, we obtain $\Delta_f H°(FeCl_2, cr, 298.15\ K) = -82.36 \pm 0.5\ kcal \cdot mol^{-1}$ which is in reasonable agreement with the value adopted.

Heat Capacity and Entropy

Kelley and Moore[6] measured the low temperature heat capacities in the temperature range from 53.2–295.0 K and made an extrapolation to 0 K which yielded an entropy of $5.19 \pm 0.8\ cal \cdot K^{-1} \cdot mol^{-1}$ at 50.12 K. This value also includes the uncoupling energy of $Fe^+ + (R \ln 5 = 3.2\ cal \cdot K^{-1} \cdot mol^{-1})$. We have adopted the measured heat capacities, but made a minor adjustment of the entropy at 53.2 K to 4.93 $cal \cdot K^{-1} \cdot mol^{-1}$ which is still within the limit of uncertainty, but yields the entropy at 298.15 K as 28.19 $cal \cdot K^{-1} \cdot mol^{-1}$. The latter was found by E. F. Westrum.[7]

Moore[8] measured high temperature enthalpy data from 670.5 to 941 K by drop calorimetry. The low temperature heat capacities and high temperature enthalpy data were smoothly joined at 298.15 K. The $C_p°$ values above 941 K were obtained by graphical extrapolation. Oetting and Gregory[9] measured high temperature heat capacities in the temperature range from 60 to 500 C in a constant heating adiabatic calorimeter. Their $C_p°$ values are in good agreement with those found by Moore.[8]

Fusion Data

T(fus) and $\Delta_{fus} H°$ were taken from Moore.[8]

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ for the monomer and dimer are calculated from the adopted enthalpies of formation of the crystal and the respective gaseous species.

References

[1] M. F. Koehler and J. P. Coughlin, J. Phys. Chem. **63**, 605 (1959).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] J. C. M. Li and N. W. Gregory, J. Amer. Chem. Soc. **74**, 4670 (1952).
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[5] W. Kangro and E. Petersen, Z. Anorg. Chem. **261**, 157 (1950).
[6] K. K. Kelley and G. E. Moore, J. Amer. Chem. Soc. **65**, 1264 (1943).
[7] E. F. Westrum, Jr., Dept. of Chem., Univ. of Michigan, personal communication to L. E. Wilson and N. W. Gregory as quoted in J. Phys. Chem. **62**, 437 (1958).
[8] G. E. Moore, J. Amer. Chem. Soc. **65**, 1700 (1943).
[9] F. L. Oetting and N. W. Gregory, J. Phys. Chem. **65**, 138 (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−16.273	−344.419	−344.419	INFINITE
100	50.895	44.782	181.905	−13.712	−345.192	−330.163	172.460
200	70.734	88.442	124.802	−7.272	−343.558	−315.664	82.443
298.15	76.664	117.947	117.947	0.	−341.833	−302.342	52.969
300	76.735	118.421	117.948	0.142	−341.800	−302.097	52.600
400	79.668	140.921	120.996	7.970	−340.070	−289.125	37.756
500	81.638	158.919	126.840	16.039	−338.424	−276.581	28.894
600	83.107	173.937	133.473	24.278	−336.904	−264.358	23.014
700	84.375	186.845	140.197	32.654	−335.526	−252.378	18.833
800	85.508	198.187	146.751	41.149	−334.345	−240.583	15.708
900	86.504	208.317	153.039	49.751	−333.492	−228.919	13.286
950.000	86.944	213.006	156.072	54.087	--- CRYSTAL <--> LIQUID ---		
1000	87.354	217.476	159.032	58.445	−333.282	−217.320	11.352
1100	88.013	225.834	164.730	67.214	−333.906	−205.678	9.767
1200	88.554	233.516	170.147	76.043	−333.928	−194.039	8.446
1300	88.962	240.621	175.298	84.920	−332.267	−182.449	7.331
1400	89.287	247.226	180.202	93.833	−330.663	−170.986	6.380
1500	89.507	253.394	184.879	102.773	−329.125	−159.634	5.559
1600	89.684	259.177	189.343	111.733	−327.659	−148.383	4.844
1700	89.817	264.618	193.613	120.708	−327.220	−137.202	4.216
1800	89.907	269.754	197.702	129.695	−326.248	−126.053	3.658
1900	89.953	274.617	201.623	138.688	−339.460	−114.254	3.141
2000	89.956	279.231	205.389	147.684	−338.904	−102.416	2.675

PREVIOUS: June 1965 CURRENT: December 1970

$S°(298.15\ K) = [139.876]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-311.336]\ kJ·mol^{-1}$

$T_{fus} = 950\ K$ $\Delta_{fus}H° = 43.012 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(FeCl_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(950\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Moore[1] derived the constant heat capacity from enthalpy data measured in the temperature range from 950 to 1100 K in a drop calorimeter. The constant $C_P°$ is assumed for all the other temperatures. The entropy is calculated a manner similar to that used for the enthalpy of formation.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were taken from Moore.[1]

Vaporization Data

The boiling point, $T_{vap} = 1297$ K, is the calculated temperature at which the sum of the partial pressures of $FeCl_2$(g) and Fe_2Cl_4(g) over $FeCl_2$(l) reaches one atmosphere. At T_{vap}, the mole fraction of the dimer is 0.1635. The enthalpy of vaporization is calculated to be the difference between the enthalpies of formation at 1297 K for one mole of $FeCl_2$(l) vaporizing to the equilibrium mixture of 0.719 moles of $FeCl_2$(g) and 0.1403 moles of Fe_2Cl_4(g).

Reference

[1]G. E. Moore, J. Amer. Chem. Soc. **65**, 1700 (1943).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.173	139.876	139.876	0.	−311.336	−278.383	48.772
300	102.173	140.508	139.878	0.189	−311.256	−278.179	48.435
400	102.173	169.902	143.886	10.406	−307.137	−267.784	34.969
500	102.173	192.701	151.454	20.624	−303.343	−258.391	26.994
600	102.173	211.330	159.928	30.841	−299.844	−249.734	21.741
700	102.173	227.080	168.425	41.058	−296.624	−241.641	18.031
800	102.173	240.723	176.628	51.276	−293.721	−233.988	15.278
900	102.173	252.757	184.432	61.493	−291.253	−226.675	13.156
950.000	102.173	258.281	188.174	66.602	--- CRYSTAL <---> LIQUID ---		
1000	102.173	263.522	191.812	71.710	−289.520	−219.603	11.471
1100	102.173	273.260	198.781	81.928	−288.695	−212.637	10.097
1200	102.173	282.151	205.363	92.145	−287.330	−205.802	8.958
1300	102.173	290.329	211.589	102.362	−284.328	−199.130	8.001
1400	102.173	297.901	217.487	112.580	−281.420	−192.686	7.189
1500	102.173	304.950	223.085	122.797	−278.604	−186.447	6.493
1600	102.173	311.544	228.410	133.014	−275.881	−180.393	5.889
1700	102.173	317.738	233.484	143.232	−274.200	−174.487	5.361
1800	102.173	323.578	238.329	153.449	−271.997	−168.686	4.895
1900	102.173	329.103	242.962	163.666	−283.985	−162.302	4.462
2000	102.173	334.343	247.402	173.884	−282.207	−155.944	4.073

PREVIOUS: June 1965 CURRENT: December 1970

0 to 950 K crystal
above 950 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.273	−344.419	−344.419	INFINITE
100	50.895	44.782	181.905	−13.712	−345.192	−330.163	172.460
200	70.734	88.442	124.802	−7.272	−343.558	−315.664	82.443
298.15	76.664	117.947	117.947	0.	−341.833	−302.342	52.969
300	76.735	118.421	117.948	0.142	−341.800	−302.097	52.600
400	79.668	140.921	120.996	7.970	−340.070	−289.125	37.756
500	81.638	158.919	126.840	16.039	−338.424	−276.581	28.894
600	83.107	173.937	133.473	24.278	−336.904	−264.358	23.014
700	84.375	186.845	140.197	32.654	−335.526	−252.378	18.833
800	85.508	198.187	146.751	41.149	−334.345	−240.583	15.708
900	86.504	208.317	153.039	49.751	−333.492	−228.919	13.286
950.000	86.944	213.006	156.072	54.087	____ CRYSTAL <--> LIQUID ____		
950.000	102.173	258.281	156.072	97.099	TRANSITION		
1000	102.173	263.522	161.315	102.207	−289.520	−219.603	11.471
1100	102.173	273.260	171.056	112.425	−288.695	−212.637	10.097
1200	102.173	282.151	179.949	122.642	−287.330	−205.802	8.958
1300	102.173	290.329	188.129	132.859	−284.328	−199.130	8.001
1400	102.173	297.901	195.703	143.077	−281.420	−192.686	7.189
1500	102.173	304.950	202.754	153.294	−278.604	−186.447	6.493
1600	102.173	311.544	209.350	163.511	−275.881	−180.393	5.889
1700	102.173	317.738	215.545	173.729	−274.200	−174.487	5.361
1800	102.173	323.578	221.386	183.946	−271.997	−168.686	4.895
1900	102.173	329.103	226.911	194.163	−283.985	−162.302	4.462
2000	102.173	334.343	232.153	204.381	−282.207	−155.944	4.073

PREVIOUS: CURRENT: December 1970

$S°(298.15\ K) = 299.28 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -141.59 \pm 2.1\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = -141.00 \pm 2.1\ kJ{\cdot}mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5\Delta$	0	10
$^5\Pi$	4600	10
$^5\Sigma$	7140	5

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[327](1)
[327](1)
88 (2)
492 (1)

Point Group: [$D_{\infty h}$] $\sigma = 2$
Bond Distance: Fe–Cl = [2.17] Å
Bond Angle: Cl–Fe–Cl = [180]°
Rotational Constant: B_0 = [0.050489] cm^{-1}

Enthalpy of Formation

Using the Gibbs energy functions of monomeric and dimeric $FeCl_2$(g) with the adopted enthalpy of dimerization at 298.15 K, $\Delta_{dim}H° = -35.7\ kcal{\cdot}mol^{-1}$,[1] we have derived partial pressure of monomeric $FeCl_2$ from the reported pressure data.[2-7] Schafer and Krehl[4] determined K_p for the equilibrium reaction C assuming the dimer concentration was insignificant at the equilibrium conditions.

Source	Method	Reaction	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 3rd law	2nd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
2	Static	A	1012–1179	29	40.61 ± 0.11	41.3	−0.6 ± 0.2	−33.80
3	Static	A	972–1268	22	40.70 ± 0.40	39.1	1.1 ± 0.4	−33.71
4	Carrier gas	A	980–1106	6	40.71 ± 0.27	41.7	−0.9 ± 1.3	−33.70
5	Mass spectrometric	B	621–701	8[a]	47.74 ± 0.11	45.7	3.1 ± 0.3	−33.96
6	Torsion effusion	B	685–760	Eqn	43.38 ± 0.11	47.0	1.9	−33.32
7	Torsion effusion	B	725–825	Eqn	48.28 ± 0.17	49.9	−2.2	−33.42
7	Mass effusion (Mo cell)	B	725–825	Eqn	48.53 ± 0.14	49.9	−1.7	−33.17
7	Mass effusion (Fe cell)	B	725–825	Eqn	48.37 ± 0.12	49.5	−1.5	−33.33
14	Torsion effusion	B	643–715	28	48.28 ± 0.08	49.1	−1.1 ± 0.3	−33.42
4	Equilibrium	C	1205–1375	9	≥10.47 ± 0.50	5.1	4.2 ± 0.1	≥−33.66

Reaction: A) $FeCl_2(l) \rightarrow FeCl_2(g)$; B) $FeCl_2(cr) \rightarrow FeCl_2(g)$; C) $Fe(cr) + 2\ HCl(g) + H_2(g)$.
[a] 1 point rejected due to failure of a statistical test.

The adopted value, $\Delta_f H°(FeCl_2, g, 298.15\ K) = -33.7\ kcal^{-1}\ mol$, is in very good agreement with those derived from the reactions A and C. The adopted value is also between the more discrepant results for reaction B derived from mass spectrometry and from effusion studies. This implies that the total pressures calculated from the monomer and dimer tables fit the observed vapor pressures over liquid much better than those over solid. For the liquid, the ratio of the calculated to the observed vapor pressure is about 1.0 ± 0.1 and for the solid, the ratio is about 1.3 ± 0.2

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicated that other transition metal dichlorides are linear.[8] The bond distance is estimated by comparison with that of Fe_2Cl_6(g) reported by Zasorin *et al.*[9] The ground state ($^5\Delta$), low lying electronic levels and the quantum weights were obtained from the work of Dekock and Gruen.[10]

The asymmetric stretching frequency was observed in the infrared spectra of the vapor at 492 cm^{-1} by Leroi[11] and at 494 cm^{-1} in Ar matrices by Thompson and Carlson[12] and Frey *et al.*[13] Normal coordinate analysis yields the stretching force constant k_1 = 2.23 md/Å which leads to the stretching vibrational frequency, ν_1 = 327 cm^{-1}, by a valence force field model. The bending frequency, ν_2 = 88 cm^{-1} was observed in the matrix infrared spectra.[12]

Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−14.277	−141.590	−141.590	INFINITE
100	45.723	242.588	347.586	−10.500	−141.148	−145.899	76.210
200	53.738	277.015	304.447	−5.486	−140.941	−150.761	39.375
250	56.054	289.272	300.223	−2.738	−140.949	−153.217	32.013
298.15	57.570	299.283	299.283	0.	−141.001	−155.575	27.256
300	57.618	299.639	299.284	0.107	−141.004	−155.666	27.104
350	58.695	308.607	299.990	3.016	−141.099	−158.102	23.595
400	59.456	316.497	301.570	5.971	−141.237	−160.522	20.962
450	60.010	323.534	303.626	8.958	−141.423	−162.922	18.912
500	60.425	329.879	305.940	11.970	−141.662	−165.299	17.269
600	60.999	340.950	310.879	18.043	−142.307	−169.969	14.797
700	61.392	350.384	315.865	24.163	−143.184	−174.514	13.022
800	61.713	358.603	320.705	30.319	−144.343	−178.914	11.682
900	62.022	365.890	325.328	36.506	−145.905	−183.147	10.630
1000	62.346	372.441	329.717	42.724	−148.171	−187.173	9.777
1100	62.695	378.399	333.876	48.976	−151.312	−190.907	9.065
1200	63.067	383.870	337.817	55.263	−153.876	−194.412	8.463
1300	63.456	388.934	341.557	61.590	−154.766	−197.754	7.946
1400	63.852	393.651	345.111	67.955	−155.709	−201.026	7.500
1500	64.244	398.069	348.496	74.360	−156.706	−204.229	7.112
1600	64.625	402.228	351.726	80.803	−157.757	−207.363	6.770
1700	64.986	406.157	354.813	87.284	−159.813	−210.411	6.465
1800	65.322	409.881	357.770	93.800	−161.311	−213.344	6.191
1900	65.630	413.421	360.606	100.348	−176.969	−215.491	5.924
2000	65.907	416.795	363.332	106.925	−178.831	−217.470	5.680
2100	66.152	420.016	365.955	113.528	−180.679	−219.356	5.456
2200	66.364	423.099	368.483	120.154	−182.516	−221.155	5.251
2300	66.545	426.053	370.922	126.800	−184.347	−222.870	5.062
2400	66.696	428.888	373.279	133.462	−186.176	−224.506	4.886
2500	66.819	431.613	375.558	140.138	−188.007	−226.066	4.723
2600	66.915	434.236	377.765	146.825	−189.845	−227.552	4.572
2700	66.987	436.763	379.904	153.520	−191.692	−228.967	4.430
2800	67.038	439.200	381.978	160.222	−193.552	−230.313	4.297
2900	67.068	441.553	383.992	166.927	−195.427	−231.593	4.171
3000	67.081	443.827	385.949	173.635	−197.319	−232.808	4.054
3100	67.079	446.027	387.851	180.343	−199.231	−233.960	3.942
3200	67.063	448.156	389.703	187.050	−549.462	−227.626	3.716
3300	67.035	450.219	391.506	193.755	−549.512	−217.567	3.444
3400	66.997	452.220	393.262	200.457	−549.616	−207.507	3.188
3500	66.950	454.161	394.974	207.154	−549.772	−197.443	2.947
3600	66.896	456.047	396.645	213.846	−549.980	−187.373	2.719
3700	66.836	457.879	398.275	220.533	−550.240	−177.298	2.503
3800	66.771	459.660	399.867	227.213	−550.551	−167.214	2.299
3900	66.701	461.394	401.423	233.887	−550.912	−157.122	2.104
4000	66.628	463.082	402.943	240.554	−551.321	−147.019	1.920
4100	66.553	464.726	404.430	247.213	−551.778	−136.906	1.744
4200	66.476	466.329	405.885	253.864	−552.280	−126.781	1.577
4300	66.397	467.892	407.309	260.508	−552.826	−116.644	1.417
4400	66.318	469.418	408.703	267.143	−553.416	−106.494	1.264
4500	66.238	470.907	410.069	273.771	−554.047	−96.329	1.118
4600	66.158	472.362	411.407	280.391	−554.718	−86.150	0.978
4700	66.078	473.784	412.719	287.003	−555.429	−75.957	0.844
4800	65.998	475.174	414.006	293.607	−556.177	−65.747	0.715
4900	65.920	476.534	415.268	300.202	−556.963	−55.522	0.592
5000	65.842	477.865	416.507	306.791	−557.786	−45.280	0.473
5100	65.765	479.168	417.723	313.371	−558.644	−35.021	0.359
5200	65.690	480.445	418.917	319.944	−559.539	−24.746	0.249
5300	65.616	481.695	420.090	326.509	−560.469	−14.452	0.142
5400	65.543	482.921	421.242	333.067	−561.436	−4.141	0.040
5500	65.471	484.123	422.374	339.618	−562.439	6.188	−0.059
5600	65.401	485.302	423.488	346.161	−563.480	16.536	−0.154
5700	65.333	486.459	424.582	352.698	−564.560	26.903	−0.247
5800	65.266	487.595	425.659	359.228	−565.680	37.290	−0.336
5900	65.201	488.710	426.718	365.751	−566.842	47.696	−0.422
6000	65.137	489.805	427.760	372.268	−568.048	58.121	−0.506

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 286.734 \pm 0.34\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-313.01 \pm 12.6]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-320.49 \pm \ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2224(1)	2237(1)
954(1)	602(1)
527(1)	876(1)
188(1)	590(1)
710(1)	

Ground State Quantum Weight = [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: Si–H = 1.480 Å; Si–Cl = 2.033 Å
Bond Angles: H–Si–H = 111.3°; Cl–Si–Cl = 109.72°
Product of the Moments of Inertia: $I_A I_B I_C = 7.53113 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated from values for $SiCl_4$, $SiHCl_3$, and SiH_4.[1] Data for $SiHCl_3$[1] suggest that $\Delta_f H°$ shows minor deviations from linearity in the chlorosilanes. We assume that $\Delta_f H°$ has a cubic variation with a constant third difference of $-1.5\ kcal \cdot mol^{-1}$. $\Delta_f H°$ values of the chloromethanes yield an almost constant third difference of about -2.5 kcal mol $^{-1}$.[1-3] This approximation corresonds to Allen's bond additivity scheme involving near–neighbor interactions taken two and three at a time.[2] Our adopted $\Delta_f H°$ is 1.5 $kcal \cdot mol^{-1}$ more negative than that estimated by linear interpolation between $SiCl_4$ and SiH_4.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Davis and Gerry[4] for three isotopic forms of dichlorosilane. Structural parameters are essentially substitutional (r_s) values. They are in reasonable agreement with an early electron diffraction study.[5] The principal moments of inertia are $I_A = 5.9928 \times 10^{-39}$, $I_B = 33.0411 \times 10^{-39}$ and $I_C = 38.0343 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are those selected by Shimanouchi[6] from a gas–phase infrared study of SiH_2Cl_2, $SiDHCl_2$ and SiD_2Cl_2 done by Christensen and Nielsen.[7] Assignments are based on band contours and isotopic rules and are supported by theoretical calculations.[4,7] Two frequencies, $\nu_4 = 188$ and infrared inactive $\nu_5 = 710\ cm^{-1}$, are from liquid–phase Raman spectra[8] which also support the vibrational assignment. Christensen and Nielsen[7] found a weak infrared band at $\sim 190\ cm^{-1}$ but could not estimate a definite band contour.

We neglect excited states and assume the electronic ground state to be a singlet. A recent vacuum ultraviolet study of Si_2HCl_2[9] is not available to us. We assume that there is little shift in electronic levels between SiH_2Cl_2 and SiH_3Cl,[1] since there is little shift in absorption spectra between CH_2Cl_2 and CH_3Cl.[10] This implies that contributions from the excited states in SiH_2Cl_2 should be unimportant, just as we believe them to be in SiH_3Cl.[1]

References

[1]JANAF Thermochemical Tables: Cl_3HSi(g), 12–31–76; H_4Si(g), 6–30–76; Cl_4Si(g), 12–31–70.
[2]S. A. Kudchadker and A. P. Kudchadker, J. Phys. Chem. Ref. Data **4**, 457 (1975).
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[4]R. W. Davis and M. C. L. Gerry, J. Mol. Spectrosc. **60**, 117 (1976).
[5]L. O. Brockway and I. E. Coop, Trans. Faraday Soc. **34**, 1429 (1938).
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[9]G. C. Causley and B. R. Russell, J. Electron Spectrosc. Relat. Phenom. **8**, 71 (1976).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.385	−313.013	−313.013	INFINITE
100	38.443	234.601	333.516	−9.892	−315.697	−309.800	161.823
200	49.901	264.436	292.044	−5.522	−318.237	−302.916	79.114
250	56.488	276.287	287.727	−2.860	−319.441	−298.945	62.461
298.15	62.174	286.734	286.734	0.	−320.494	−294.900	51.665
300	62.375	287.119	286.735	0.115	−320.532	−294.741	51.319
350	67.358	297.120	287.514	3.362	−321.488	−290.365	43.335
400	71.521	306.394	289.301	6.837	−322.308	−285.861	37.330
450	75.028	315.027	291.686	10.503	−323.002	−281.263	32.648
500	78.029	323.091	294.427	14.332	−323.585	−276.593	28.895
600	82.940	337.770	300.453	22.390	−324.464	−267.106	23.254
700	86.822	350.858	306.735	30.886	−325.026	−257.498	19.215
800	89.965	362.663	313.001	39.730	−325.343	−247.827	16.181
900	92.536	373.413	319.125	48.860	−325.470	−238.128	13.821
1000	94.653	383.276	325.054	58.222	−325.459	−228.422	11.932
1100	96.406	392.382	330.766	67.778	−325.348	−218.723	10.386
1200	97.864	400.835	336.257	77.494	−325.171	−209.038	9.099
1300	99.084	408.718	341.531	87.343	−324.956	−199.368	8.011
1400	100.112	416.100	346.597	97.304	−324.723	−189.717	7.078
1500	100.983	423.037	351.464	107.360	−324.490	−180.081	6.271
1600	101.726	429.579	356.143	117.497	−324.271	−170.462	5.565
1700	102.363	435.765	360.647	127.702	−374.252	−160.408	4.929
1800	102.912	441.632	364.984	137.966	−373.859	−147.840	4.290
1900	103.389	447.209	369.166	148.282	−373.463	−135.294	3.719
2000	103.805	452.523	373.202	158.642	−373.070	−122.769	3.206
2100	104.169	457.597	377.101	169.041	−372.684	−110.264	2.743
2200	104.490	462.451	380.871	179.474	−372.310	−97.776	2.322
2300	104.775	467.102	384.520	189.938	−371.951	−85.305	1.937
2400	105.027	471.566	388.055	200.428	−371.611	−72.850	1.586
2500	105.252	475.858	391.481	210.942	−371.291	−60.408	1.262
2600	105.454	479.991	394.807	221.478	−370.995	−47.979	0.964
2700	105.635	483.974	398.036	232.032	−370.724	−35.560	0.688
2800	105.799	487.819	401.174	242.604	−370.480	−23.152	0.432
2900	105.947	491.534	404.226	253.192	−370.264	−10.751	0.194
3000	106.081	495.128	407.197	263.793	−370.077	1.643	−0.029
3100	106.203	498.608	410.090	274.408	−369.920	14.031	−0.236
3200	106.315	501.982	412.909	285.034	−369.791	26.414	−0.431
3300	106.417	505.255	415.658	295.670	−369.691	38.794	−0.614
3400	106.510	508.433	418.340	306.317	−369.619	51.171	−0.786
3500	106.596	511.522	420.958	316.972	−369.574	63.547	−0.948
3600	106.676	514.526	423.516	327.636	−753.706	86.382	−1.253
3700	106.749	517.450	426.015	338.307	−753.295	109.712	−1.549
3800	106.816	520.298	428.459	348.985	−752.907	133.031	−1.829
3900	106.879	523.073	430.850	359.670	−752.539	156.341	−2.094
4000	106.937	525.780	433.189	370.361	−752.190	179.641	−2.346
4100	106.991	528.421	435.480	381.057	−751.856	202.933	−2.585
4200	107.042	531.000	437.724	391.759	−751.534	226.216	−2.813
4300	107.089	533.519	439.922	402.466	−751.222	249.492	−3.031
4400	107.133	535.981	442.078	413.177	−750.917	272.761	−3.238
4500	107.174	538.389	444.191	423.892	−750.616	296.023	−3.436
4600	107.212	540.745	446.265	434.611	−750.317	319.278	−3.626
4700	107.249	543.052	448.300	445.334	−750.017	342.527	−3.807
4800	107.283	545.310	450.297	456.061	−749.714	365.770	−3.980
4900	107.314	547.522	452.259	466.791	−749.406	389.006	−4.147
5000	107.345	549.691	454.186	477.524	−749.091	412.235	−4.307
5100	107.373	551.817	456.079	488.260	−748.766	435.459	−4.460
5200	107.400	553.902	457.941	498.998	−748.430	458.676	−4.607
5300	107.425	555.948	459.771	509.740	−748.081	481.886	−4.749
5400	107.449	557.956	461.570	520.483	−747.718	505.090	−4.886
5500	107.472	559.928	463.341	531.229	−747.337	528.286	−5.017
5600	107.493	561.865	465.083	541.978	−746.940	551.476	−5.144
5700	107.514	563.767	466.798	552.728	−746.524	574.658	−5.266
5800	107.533	565.637	468.486	563.480	−746.088	597.833	−5.384
5900	107.552	567.476	470.148	574.235	−745.632	621.000	−5.498
6000	107.569	569.284	471.785	584.991	−745.152	644.159	−5.608

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [144.494 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 550\ K$

$\Delta_f H°(298.15\ K) = -230.12 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{fus}H = 19.414 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Taken from.[1]

Heat Capacity and Entropy

C_p° was determined from the enthalpy data of Topol and Ransom[2] and Ewald.[3] Above 550 the curve was smoothly extrapolated. The entropy was estimated by adjusting the value to give the best fit of the melting, sublimation, and vaporization data.

Melting

T_{fus} was taken from.[1] $\Delta_{fus}H$ was given by Topol and Ransom.[2]

References

[1]U. S. Nat. Bur. Stand. Circular 500, (1952).
[2]L. E. Topol and L. D. Ransom, J. Phys. Chem. **64**, 1339 (1960).
[3]R. Ewald, Ann. Phys. Chem. (4) **44**, 1213 (1914).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.906	144.494	144.494	0.	−230.120	−184.022	32.240
300	73.973	144.952	144.496	0.137	−230.098	−183.736	31.991
400	76.986	166.664	147.436	7.691	−228.779	−168.475	22.001
500	79.224	184.075	153.079	15.498	−227.271	−153.570	16.043
550.000	80.500	191.685	156.247	19.491	--- CRYSTAL <--> LIQUID ---		
600	81.672	198.742	159.498	23.546	−225.569	−138.986	12.100
700	83.948	211.509	166.035	31.832	−282.429	−118.132	8.815
800	85.688	222.830	172.441	40.312	−279.728	−94.844	6.193
900	87.646	233.037	178.615	48.979	−276.859	−71.903	4.173
1000	89.508	242.368	184.531	57.837	−273.816	−49.292	2.575
1100	91.287	250.983	190.185	66.878	−270.604	−26.994	1.282
1200	92.968	258.999	195.589	76.092	−267.231	−4.995	0.217
1300	94.563	266.504	200.759	85.469	−263.704	16.716	−0.672
1400	96.065	273.567	205.710	95.000	−260.034	38.150	−1.423
1500	97.571	280.246	210.458	104.682	−256.221	59.316	−2.066

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K)$ = [164.471] $J·K^{-1}·mol^{-1}$
T_{fus} = 550 K

$\Delta_f H°(298.15\ K)$ = [−213.222] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 19.414 ± .21 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(HgCl_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(550\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated to conform with the bromide and iodide, the value given by Topol and Ransom[1] was discounted. A glass type transition was assumed to be 367 K below which the heat capacity was equal to that of the crystal. The entropy was obtained from $S°(cr)$, the entropy of fusion and the estimated heat capacity.

Fusion and Vaporization

T_{fus} and T_{vap} were taken from NBS Circular 500.[2] $\Delta_{fus}H°$ was given by Topol and Ransom[1] and $\Delta_{vap}H$ was obtained from Prideaux[3] and Johnson;[4] T_{vap} = 577 K and $\Delta_{vap}H°$ = 58.9 $kJ·mol^{-1}$.

References

[1]L. E. Topol and L. D. Ransom, J. Phys. Chem. **64**, 1339 (1960).
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[3]E. B. R. Prideaux, J. Chem. Soc. (London) **97**, 2033 (1910).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	102.090	164.471	164.471	0.	−213.222	−173.080	30.323
300	102.090	165.103	164.473	0.189	−213.148	−172.831	30.093
400	102.090	194.472	168.477	10.398	−209.174	−159.994	20.893
500	102.090	217.253	176.039	20.607	−205.264	−148.152	15.477
550.000	102.090	226.983	180.235	25.711	--- CRYSTAL <--> LIQUID ---		
600	102.090	235.866	184.506	30.816	−201.401	−137.093	11.935
700	102.090	251.603	192.996	41.025	−256.338	−120.107	8.962
800	102.090	265.235	201.193	51.234	−251.907	−100.948	6.591
900	102.090	277.260	208.990	61.443	−247.497	−82.343	4.779
1000	102.090	288.016	216.364	71.652	−243.104	−64.228	3.355
1100	102.090	297.746	223.327	81.861	−238.723	−46.552	2.211
1200	102.090	306.629	229.904	92.070	−234.355	−29.275	1.274
1300	102.090	314.800	236.125	102.278	−229.997	−12.362	0.497
1400	102.090	322.366	242.018	112.487	−225.648	4.216	−0.157
1500	102.090	329.409	247.612	122.696	−221.309	20.484	−0.713

PREVIOUS: CURRENT: March 1962

0 to 550 K crystal
above 550 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.906	144.494	144.494	0.	−230.120	−184.022	32.240
300	73.973	144.952	144.496	0.137	−230.098	−183.736	31.991
400	76.986	166.664	147.436	7.691	−228.779	−168.475	22.001
500	79.224	184.075	153.079	15.498	−227.271	−153.570	16.043
550.000	80.500	191.685	156.247	19.491	____ CRYSTAL <--> LIQUID ____		
550.000	*102.090*	226.983	156.247	38.905	TRANSITION		
600	102.090	235.866	162.517	44.009	−205.106	−140.798	12.258
700	102.090	251.603	174.149	54.218	−260.043	−123.811	9.239
800	102.090	265.235	184.701	64.427	−255.612	−104.652	6.833
900	102.090	277.260	194.331	74.636	−251.202	−86.047	4.994
1000	102.090	288.016	203.171	84.845	−246.808	−67.932	3.548
1100	102.090	297.746	211.333	95.054	−242.428	−50.257	2.387
1200	102.090	306.629	218.910	105.263	−238.060	−32.980	1.436
1300	102.090	314.800	225.976	115.472	−233.701	−16.067	0.646
1400	102.090	322.366	232.594	125.681	−229.353	0.511	−0.019
1500	102.090	329.409	238.816	135.890	−225.014	16.779	−0.584

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = 294.793\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -142.31 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -146.29 \pm 6.3\ kJ·mol^{-1}$

Vibrational Levels and Multiplicities ν, cm^{-1}
360 (1)
70 (2)
413 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Hg–Cl = 2.31 Å
Bond Angle: O–Hg–Cl = 180°
Rotational Constant: $B_o = 0.044554\ cm^{-1}$

Enthalpy of Formation

The heat of formation of the crystal as given in NBS Circular 500[1] was combined with the 3rd law enthalpy of sublimation at 298.15 K from the data of Niwa and Zhibata,[2] Ruf and Treadwell[3] and Johnson.[4]

Heat Capacity and Entropy

The vibrational constants were given by Klemperer and Lindeman.[5] The bond length is a weighted average of the values given by Braune and Knoke,[6] Gregg *et al.*,[7] Maxwell and Mosely,[8] and Akishin *et al.*[9]

References

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[3]R. Ruf and W. D. Treadwell, Helv. Chim. Acta **37**, 1941 (1954).
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[5]W. Klemperer and L. Lindeman, J. Chem. Phys. **25**, 397 (1956).
[6]H. Braune and S. Knoke, Naturwiss. **21**, 349 (1933).
[7]A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones and L. E. Sutton, Trans. Faraday Soc. **33**, 852, (1937).
[8]L. R. Maxwell and V. M. Mosley, Phys. Rev. **57**, 21 (1940).
[9]P. A. Akishin, V. P. Spiridinov and A. N. Khodchenkov, Zhur. Fiz. Khim. **33**, 20 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.543	−142.313	−142.313	INFINITE
100	46.437	237.359	343.680	−10.632	−143.019	−144.133	75.287
200	54.452	272.269	300.012	−5.549	−143.559	−145.015	37.874
250	56.690	284.678	295.742	−2.766	−146.092	−145.198	30.338
298.15	58.110	294.793	294.793	0.	−146.294	−145.007	25.405
300	58.154	295.152	294.794	0.108	−146.301	−144.999	25.247
350	59.140	304.196	295.506	3.041	−146.475	−144.768	21.605
400	59.826	312.140	297.099	6.017	−146.627	−144.514	18.872
450	60.319	319.217	299.170	9.021	−146.766	−144.241	16.743
500	60.683	325.592	301.499	12.046	−146.896	−143.954	15.039
600	61.174	336.703	306.467	18.141	−147.147	−143.341	12.479
700	61.478	346.157	311.479	24.275	−206.159	−136.116	10.157
800	61.680	354.381	316.339	30.434	−205.779	−126.136	8.236
900	61.819	361.654	320.977	36.609	−205.403	−116.203	6.744
1000	61.920	368.173	325.376	42.796	−205.031	−106.312	5.553
1100	61.995	374.078	329.540	48.992	−204.663	−96.458	4.580
1200	62.053	379.475	333.479	55.195	−204.301	−86.637	3.771
1300	62.097	384.444	337.211	61.402	−203.945	−76.846	3.088
1400	62.133	389.047	340.751	67.614	−203.593	−67.082	2.503
1500	62.162	393.335	344.115	73.829	−203.248	−57.343	1.997
1600	62.185	397.347	347.318	80.046	−202.909	−47.628	1.555
1700	62.205	401.118	350.373	86.266	−202.577	−37.933	1.166
1800	62.221	404.674	353.292	92.487	−202.252	−28.257	0.820
1900	62.235	408.038	356.086	98.710	−201.935	−18.599	0.511
2000	62.247	411.231	358.764	104.934	−201.626	−8.958	0.234
2100	62.258	414.268	361.335	111.159	−201.328	0.668	−0.017
2200	62.267	417.165	363.808	117.385	−201.041	10.280	−0.244
2300	62.274	419.933	366.188	123.612	−200.767	19.879	−0.451
2400	62.281	422.583	368.483	129.840	−200.507	29.467	−0.641
2500	62.287	425.126	370.698	136.069	−200.262	39.044	−0.816
2600	62.292	427.569	372.839	142.298	−200.033	48.612	−0.977
2700	62.297	429.920	374.910	148.527	−199.822	58.171	−1.125
2800	62.301	432.185	376.915	154.757	−199.630	67.723	−1.263
2900	62.305	434.372	378.859	160.987	−199.457	77.268	−1.392
3000	62.309	436.484	380.745	167.218	−199.302	86.807	−1.511
3100	62.312	438.527	382.576	173.449	−199.167	96.342	−1.623
3200	62.315	440.506	384.355	179.680	−199.050	105.873	−1.728
3300	62.317	442.423	386.086	185.912	−198.951	115.400	−1.827
3400	62.320	444.284	387.771	192.144	−198.868	124.924	−1.919
3500	62.322	446.090	389.411	198.376	−198.801	134.447	−2.007
3600	62.324	447.846	391.010	204.608	−198.746	143.967	−2.089
3700	62.326	449.553	392.569	210.841	−198.702	153.487	−2.167
3800	62.327	451.216	394.091	217.073	−198.667	163.005	−2.241
3900	62.329	452.835	395.577	223.306	−198.639	172.522	−2.311
4000	62.330	454.413	397.028	229.539	−198.615	182.039	−2.377
4100	62.332	455.952	398.446	235.772	−198.592	191.555	−2.440
4200	62.333	457.454	399.833	242.006	−198.568	201.070	−2.501
4300	62.334	458.921	401.191	248.239	−198.540	210.585	−2.558
4400	62.335	460.354	402.519	254.472	−198.506	220.099	−2.613
4500	62.336	461.754	403.820	260.706	−198.464	229.612	−2.665
4600	62.337	463.125	405.094	266.940	−198.411	239.125	−2.715
4700	62.338	464.465	406.343	273.173	−198.346	248.636	−2.763
4800	62.339	465.778	407.568	279.407	−198.265	258.145	−2.809
4900	62.340	467.063	408.769	285.641	−198.168	267.653	−2.853
5000	62.340	468.322	409.947	291.875	−198.053	277.158	−2.895
5100	62.341	469.557	411.104	298.109	−197.918	286.661	−2.936
5200	62.342	470.767	412.240	304.343	−197.762	296.161	−2.975
5300	62.342	471.955	413.355	310.577	−197.584	305.658	−3.012
5400	62.343	473.120	414.451	316.812	−197.384	315.151	−3.048
5500	62.343	474.264	415.529	323.046	−197.160	324.641	−3.083
5600	62.344	475.388	416.588	329.280	−196.911	334.126	−3.117
5700	62.344	476.491	417.629	335.515	−196.639	343.606	−3.149
5800	62.345	477.575	418.653	341.749	−196.341	353.082	−3.180
5900	62.345	478.641	419.661	347.984	−196.019	362.552	−3.210
6000	62.346	479.689	420.653	354.218	−195.672	372.016	−3.239

PREVIOUS: March 1962 (1 atm) CURRENT: March 1962 (1 bar)

Mercury Chloride (Hg_2Cl_2) CRYSTAL M_r = 472.086

$\Delta_f H°(0\ K) = -260.537 \pm 0.21\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 192.535\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -264.927 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is based on the average Gibbs energy of formation, $-50.315\ kcal \cdot mol^{-1}$, as measured by Gerke[1] and Hills and Ives,[2] and the entropy of formation.

Heat Capacity and Entropy

The data of Pollitzer[3] from 22–199 K was treated by Kelley.[4] The heat capacities listed by Kelley were raised by 0.06 to match the entropy data of Gerke.[1] Data above room temperature were obtained by smooth extrapolation. A mean value of the entropy of formation of $-46.614\ cal \cdot K^{-1} \cdot mol^{-1}$ was adopted from the cell measurements of Gerke.[1]

Sublimation

The vapor pressure over mercurous chloride reaches 1 atmosphere at 655 K according to Smith and Menzies.[5] At this point the vapor is dissociated into Hg(g) and $HgCl_2$(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.476	−260.537	−260.537	INFINITE
100	79.245	92.186	278.165	−18.598	−261.981	−244.855	127.899
200	95.479	153.076	201.673	−9.719	−261.310	−227.924	59.528
298.15	101.968	192.535	192.535	0.	−264.927	−210.485	36.876
300	102.048	193.166	192.537	0.189	−264.904	−210.147	36.590
400	106.023	223.084	196.589	10.598	−263.497	−192.096	25.085
500	109.328	247.106	204.367	21.370	−261.751	−174.442	18.224
600	112.131	267.293	213.217	32.446	−259.735	−157.165	13.682
700	114.558	284.762	222.217	43.781	−375.019	−127.101	9.484
800	116.817	300.210	231.019	55.352	−371.305	−91.936	6.003
900	118.826	314.086	239.491	67.136	−367.399	−57.247	3.323
1000	120.667	326.703	247.591	79.112	−363.317	−23.003	1.202
1100	122.340	338.283	255.316	91.264	−359.072	10.824	−0.514
1200	123.846	348.994	262.682	103.574	−354.680	44.258	−1.926
1300	125.169	358.960	269.709	116.027	−350.158	77.320	−3.107
1400	126.311	368.279	276.421	128.602	−345.521	110.030	−4.105
1500	127.277	377.028	282.839	141.283	−340.788	142.405	−4.959

PREVIOUS: CURRENT: December 1961

$S°(298.15\ K)$ = [352.864] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -614.43 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -617.64 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[219](1)	[104](1)
[108](1)	[184](1)
[180](1)	[100](1)

Ground State Quantum Weight: 1 σ = 4
Point Group: D_{2h}
Bond Distance: Cl–K = [2.932] Å
Bond Angle: Cl–K–Cl = [100.8]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.87407 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from that of KCl(g) using $\Delta_r H°(298.15\ K)$ = 45.0 $kcal·mol^{-1}$ for $K_2Cl_2(g) \rightarrow 2\ KCl(g)$ as selected from data analyses summarized below. The three experimental techniques include PVT measurements,[1] combination of total vapor pressure and transpiration data,[2–4] and mass spectrometric studies of the variation of ion intensities with temperature.[5] The results are reasonably consistent, considering the uncertainties inherent in the problem.

The resulting tables were tested by comparison with other data. Calculated total vapor pressures are in satisfactory agreement with the observed values over the range 820–1500 K; however, near the boiling point they are lower by 6–18% [refer to KCl(g)]. Knudsen effusion data and transpiration data over KCl(cr) have been reviewed by Pugh and Barrow.[6] These data suggest negligible dimer formation when combined with the total vapor pressures of Pugh and Barrow[6] but significant dimer formation when combined with the lower (20–30%) total pressures of Dietz.[7] Calculated dimer formation (22 mole percent at 900 K) agrees with the latter combination but calculated total pressures agree with those of Pugh and Barrow.[6] Velocity distribution studies of Miller and Kusch[8] suggest about 10 mole percent of dimer at 900 K. Thus, while minor inconsistencies do exist, it is not apparent that they exceed the combined experimental errors.

Source	Method	Points	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
1	PVT data	15	1310–1404	46.70 ± 2.1	46.01	−0.5 ± 1.6
2	Trans. + Vap. Press.	10	1253–1352	46.24 ± 3.5	44.98	−1.0 ± 2.7
3	Trans. + Vap. Press.	5	1261–1372	43.0 ± 4.5	44.16	0.7 ± 3.4
4	Trans. + Vap. Press.	7	1250–1473	42.54 ± 2.9	45.21	2.2 ± 2.3
5	Mass spectrometry	–	774–1016	41.9 ± 3	—	—

Heat Capacity and Entropy

The structure and vibrational frequencies are those calculated from an ionic model by Berkowitz.[9] The sixth fundamental was arbitrarily lowered from 206 to 100 cm^{-1} since the resulting entropy increase (1.4 $cal·K^{-1}·mol^{-1}$ at 1300 K.) improved the overall agreement with the equilibrium data. Based on electron diffraction studies of the monomer–dimer vapor, Akishin and Rambidi[10] have derived the bond distance and angle to be 2.81 Å and 98°. Interpretation of the diffraction data, however, is complicated by the presence of only about 30 mole percent of dimer at the temperature of measurement. Adoption of this dimer structure would reduce the entropy by 0.23 $cal·K^{-1}·mol^{-1}$. Principal moments of inertia for the Berkowitz structure are I_A = 45.3554 × 10^{-39}, I_B = 60.0935 × 10^{-39}, and I_C = 105.4488 × 10^{-39} $g·cm^2$.

Reference

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−20.133	−614.430	−614.430	INFINITE
100	67.552	269.905	422.606	−15.270	−615.944	−616.913	322.242
200	78.301	321.028	360.199	−7.834	−616.734	−617.550	161.287
250	79.953	338.697	354.191	−3.874	−617.141	−617.708	129.063
298.15	80.865	352.864	352.864	0.	−617.642	−617.774	108.232
300	80.892	353.364	352.866	0.150	−617.665	−617.775	107.564
350	81.473	365.881	353.853	4.210	−623.105	−617.548	92.164
400	81.857	376.787	356.053	8.294	−623.947	−616.696	80.532
450	82.122	386.444	358.903	12.394	−624.751	−615.741	71.473
500	82.314	395.107	362.098	16.505	−625.523	−614.699	64.217
600	82.565	410.139	368.889	24.750	−626.989	−612.395	53.314
700	82.718	422.879	375.715	33.014	−628.388	−609.851	45.508
800	82.817	433.931	382.317	41.292	−629.764	−607.109	39.640
900	82.885	443.690	388.604	49.577	−631.164	−604.194	35.066
1000	82.934	452.425	394.557	57.868	−632.636	−601.119	31.399
1100	82.971	460.332	400.183	66.163	−792.128	−588.672	27.954
1200	82.998	467.552	405.501	74.462	−791.749	−570.192	24.820
1300	83.020	474.197	410.533	82.763	−791.377	−551.745	22.169
1400	83.037	480.350	415.303	91.066	−791.014	−533.325	19.899
1500	83.051	486.079	419.832	99.370	−790.660	−514.931	17.931
1600	83.062	491.439	424.142	107.676	−790.316	−496.560	16.211
1700	83.071	496.475	428.250	115.982	−789.982	−478.211	14.694
1800	83.079	501.224	432.174	124.290	−789.663	−459.881	13.345
1900	83.086	505.716	435.927	132.598	−789.360	−441.568	12.140
2000	83.092	509.978	439.524	140.907	−789.077	−423.270	11.055
2100	83.096	514.032	442.976	149.217	−788.819	−404.986	10.073
2200	83.101	517.898	446.295	157.526	−788.590	−386.714	9.182
2300	83.104	521.592	449.489	165.837	−788.398	−368.452	8.368
2400	83.108	525.129	452.567	174.147	−788.247	−350.197	7.622
2500	83.110	528.521	455.538	182.458	−788.144	−331.947	6.936
2600	83.113	531.781	458.408	190.769	−788.095	−313.700	6.302
2700	83.115	534.918	461.184	199.081	−788.109	−295.454	5.716
2800	83.117	537.941	463.872	207.392	−788.190	−277.206	5.171
2900	83.119	540.857	466.477	215.704	−788.347	−258.954	4.664
3000	83.121	543.675	469.003	224.016	−788.587	−240.695	4.191
3100	83.122	546.401	471.456	232.328	−788.915	−222.427	3.748
3200	83.124	549.040	473.840	240.641	−789.340	−204.147	3.332
3300	83.125	551.598	476.157	248.953	−789.849	−185.853	2.942
3400	83.126	554.079	478.413	257.266	−790.478	−167.541	2.574
3500	83.127	556.489	480.609	265.578	−791.216	−149.209	2.227
3600	83.128	558.831	482.750	273.891	−792.079	−130.854	1.899
3700	83.129	561.108	484.837	282.204	−793.069	−112.474	1.588
3800	83.130	563.325	486.873	290.517	−794.194	−94.065	1.293
3900	83.130	565.484	488.861	298.830	−795.459	−75.624	1.013
4000	83.131	567.589	490.803	307.143	−796.859	−57.150	0.746
4100	83.132	569.642	492.701	315.456	−798.415	−38.639	0.492
4200	83.132	571.645	494.557	323.769	−800.139	−20.087	0.250
4300	83.133	573.601	496.373	332.082	−802.032	−1.493	0.018
4400	83.133	575.512	498.150	340.396	−803.545	17.094	−0.203
4500	83.134	577.381	499.890	348.709	−805.656	35.768	−0.415
4600	83.134	579.208	501.594	357.022	−807.931	54.491	−0.619
4700	83.135	580.996	503.265	365.336	−810.331	73.261	−0.814
4800	83.135	582.746	504.902	373.649	−812.681	92.060	−1.002
4900	83.135	584.460	506.509	381.963	−815.404	110.937	−1.183
5000	83.136	586.140	508.085	390.276	−818.294	129.871	−1.357
5100	83.136	587.786	509.631	398.590	−821.350	148.864	−1.525
5200	83.136	589.400	511.150	406.904	−824.573	167.919	−1.687
5300	83.137	590.984	512.641	415.217	−827.962	187.038	−1.843
5400	83.137	592.538	514.106	423.531	−831.516	206.222	−1.995
5500	83.137	594.064	515.546	431.845	−835.233	225.473	−2.141
5600	83.137	595.562	516.962	440.158	−839.109	244.794	−2.283
5700	83.138	597.033	518.354	448.472	−842.452	264.089	−2.420
5800	83.138	598.479	519.723	456.786	−846.551	283.538	−2.554
5900	83.138	599.900	521.070	465.100	−850.789	303.058	−2.683
6000	83.138	601.298	522.395	473.413	−855.163	322.651	−2.809

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = [288.767]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -595.61 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -598.55 \pm 12.6\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[330](1)	[356](1)
[296](1)	335 (1)
[385](1)	460 (1)

Ground State Quantum Weight: 1 $\sigma = 4$

Point Group: D_{2h}

Bond Distances: Li–Cl = 2.23 Å; Li–Li = 2.62 Å

Bond Angle: Cl–Li–Cl = 108 ± 4°

Product of the Moments of Inertia: $I_A I_B I_C = 6.41793 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

An enthalpy of sublimation at 298.15 K of 52.1 $kcal·mol^{-1}$ was chosen to fit the vapor pressure data and relative concentrations of monomer, dimer and trimer as described in the table for LiCl(g). This value is in reasonable agreement with the value of 53.5 $kcal·mol^{-1}$ from a 3rd law analysis of the vapor pressure data of Nesmeyanov and Sazonov[1] and the relative concentrations of monomer, dimer, and trimer from the work of Miller and Kusch.[2] Also a value of 54.1 $kcal·mol^{-1}$ was found by Milne and Klein[3] from mass spectrometer studies.

Heat Capacity and Entropy

Klemperer and Norris[4] observed two bands in the infrared spectrum and made tentative assignments. The remaining four frequencies were calculated by Berkowitz[5] from a reasonable model. The bond lengths and angles were determined from the electron diffraction experiments of Bauer *et al.*[6] The principal moments of inertia are: $I_A = 3.9605 \times 10^{-39}$, $I_B = 38.3234 \times 10^{-39}$, and $I_C = 42.2839 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.486	−595.607	−595.607	INFINITE
100	41.503	225.773	345.688	−11.991	−596.014	−598.223	312.479
200	62.653	261.707	295.121	−6.683	−597.427	−599.845	156.663
250	68.505	276.364	289.937	−3.393	−598.012	−600.380	125.443
298.15	72.195	288.767	288.767	0.	−598.546	−600.788	105.256
300	72.309	289.214	288.769	0.134	−598.567	−600.802	104.609
350	74.860	300.565	289.659	3.817	−599.128	−601.130	89.714
400	76.631	310.683	291.666	7.607	−599.765	−601.374	78.531
450	77.902	319.786	294.294	11.472	−600.522	−601.531	69.824
500	78.841	328.045	297.262	15.391	−607.417	−600.983	62.784
600	80.103	342.541	303.634	23.344	−609.063	−599.538	52.194
700	80.885	354.952	310.100	31.396	−610.533	−597.832	44.611
800	81.403	365.789	316.398	39.512	−611.909	−595.923	38.910
900	81.761	375.398	322.430	47.672	−613.252	−593.844	34.466
1000	82.020	384.027	328.166	55.861	−614.572	−591.617	30.903
1100	82.213	391.854	333.605	64.073	−615.872	−589.258	27.982
1200	82.360	399.014	338.762	72.302	−617.157	−586.782	25.542
1300	82.475	405.611	343.654	80.544	−618.431	−584.199	23.473
1400	82.567	411.726	348.300	88.797	−619.693	−581.519	21.697
1500	82.640	417.426	352.721	97.057	−620.939	−578.748	20.154
1600	82.701	422.761	356.933	105.324	−622.170	−575.895	18.801
1700	82.751	427.776	360.955	113.597	−913.861	−558.614	17.164
1800	82.794	432.507	364.800	121.874	−913.562	−537.725	15.604
1900	82.829	436.985	368.482	130.155	−913.271	−516.854	14.209
2000	82.860	441.234	372.014	138.440	−912.992	−495.997	12.954
2100	82.886	445.278	375.408	146.727	−912.726	−475.154	11.819
2200	82.909	449.134	378.672	155.017	−912.477	−454.323	10.787
2300	82.929	452.820	381.816	163.309	−912.250	−433.503	9.845
2400	82.947	456.350	384.849	171.603	−912.047	−412.692	8.982
2500	82.962	459.736	387.777	179.898	−911.874	−391.889	8.188
2600	82.976	462.990	390.607	188.195	−911.735	−371.093	7.455
2700	82.988	466.122	393.347	196.493	−911.635	−350.301	6.777
2800	82.999	469.140	396.000	204.793	−911.576	−329.512	6.147
2900	83.009	472.053	398.573	213.093	−911.565	−308.724	5.561
3000	83.018	474.867	401.069	221.394	−911.603	−287.936	5.013
3100	83.026	477.590	403.494	229.697	−911.695	−267.146	4.501
3200	83.033	480.226	405.851	238.000	−911.843	−246.352	4.021
3300	83.039	482.781	408.143	246.303	−912.049	−225.552	3.570
3400	83.046	485.260	410.375	254.607	−912.316	−204.745	3.146
3500	83.051	487.667	412.549	262.912	−912.646	−183.930	2.745
3600	83.056	490.007	414.669	271.218	−913.039	−163.104	2.367
3700	83.061	492.283	416.736	279.523	−913.496	−142.266	2.008
3800	83.065	494.498	418.753	287.830	−914.019	−121.416	1.669
3900	83.069	496.655	420.723	296.137	−914.607	−100.550	1.347
4000	83.073	498.759	422.648	304.444	−915.262	−79.668	1.040
4100	83.076	500.810	424.529	312.751	−915.983	−58.770	0.749
4200	83.079	502.812	426.369	321.059	−916.771	−37.853	0.471
4300	83.082	504.767	428.170	329.367	−917.627	−16.916	0.205
4400	83.085	506.677	429.933	337.675	−918.509	4.038	−0.048
4500	83.088	508.544	431.659	345.984	−919.481	25.015	−0.290
4600	83.090	510.370	433.350	354.293	−920.524	46.016	−0.523
4700	83.092	512.157	435.008	362.602	−921.634	67.039	−0.745
4800	83.095	513.907	436.634	370.911	−922.811	88.087	−0.959
4900	83.097	515.620	438.228	379.221	−924.057	109.160	−1.164
5000	83.098	517.299	439.793	387.531	−925.373	130.259	−1.361
5100	83.100	518.944	441.329	395.841	−926.748	151.385	−1.550
5200	83.102	520.558	442.837	404.151	−928.206	172.538	−1.733
5300	83.104	522.141	444.318	412.461	−929.737	193.721	−1.909
5400	83.105	523.695	445.774	420.771	−931.345	214.934	−2.079
5500	83.106	525.219	447.205	429.082	−933.032	236.176	−2.243
5600	83.108	526.717	448.611	437.393	−934.799	257.450	−2.401
5700	83.109	528.188	449.994	445.704	−936.650	278.757	−2.555
5800	83.110	529.633	451.355	454.015	−938.587	300.097	−2.703
5900	83.111	531.054	452.694	462.326	−940.612	321.471	−2.846
6000	83.112	532.451	454.011	470.637	−942.727	342.879	−2.985

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 89.629\ J·K^{-1}·mol^{-1}$
$T_{fus} = 987\ K$

$\Delta_f H°(0\ K) = -641.196 \pm 0.46\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -641.616 \pm 0.46\ kJ·mol^{-1}$
$\Delta_{fus} H° = 43.095 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -153.35 \pm 0.11\ kcal·mol^{-1}$ is from enthalpy of solution measurements reported by Shomate and Huffman.[1] Shomate and Huffman's enthalpy of solution of Mg in 1 M HCL ($\Delta_f H = -111.322 \pm 0.041\ kcal·mol^{-1}$) has been substantiated for calibration purposes by Gunn and Cunningham[2] ($\Delta_f H = -111.3\ kcal·mol^{-1}$) and by Westrum and Eyring[3] ($\Delta_f H = -111.27\ kcal\ mol^{-1}$). Auxiliary enthalpy of dilution and enthalpy of formation data for HCl were taken from Parker[4] and from Wagman *et al.*[5]

Heat Capacity and Entropy

High temperature heat content data by Moore[6] were joined by Shomate correlation with low temperature heat capacity data reported by Kelley and Moore.[7] $C_p°$(cr) above T_{fus} is a linear extrapolation from 700 K. $S°(298.15\ K)$ is derived from the low temperature data and is based on $S°(53.6\ K) = 2.006\ cal·K^{-1}·mol^{-1}$.

Fusion Data

$\Delta_{fus} H° = 10.30 \pm 0.05\ kcal·mol^{-1}$ is taken from enthalpy measurements of Moore.[6] $T_{fus} = 987$ K is from NBS Circular 500.[8]

Sublimation Data

The value of $\Delta_{sub} H°(298.15\ K)$ was derived by 2nd and 3rd law analyses of vapor pressure data. Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−13.759	−641.196	−641.196	INFINITE
100	40.294	25.956	146.771	−12.081	−643.073	−625.817	326.893
200	63.575	62.664	95.923	−6.652	−642.688	−608.599	158.950
298.15	71.379	89.629	89.629	0.	−641.616	−592.087	103.731
300	71.496	90.071	89.630	0.132	−641.593	−591.780	103.038
400	75.709	111.276	92.493	7.513	−640.237	−575.376	75.136
500	78.145	128.451	98.022	15.215	−638.773	−559.328	58.433
600	79.873	142.857	104.326	23.119	−637.269	−543.580	47.323
700	81.253	155.274	110.737	31.176	−635.756	−528.085	39.406
800	82.550	166.209	117.001	39.366	−634.254	−512.806	33.483
900	83.847	176.007	123.022	47.686	−632.773	−497.714	28.887
987.000	84.977	183.795	128.040	55.030	--- CRYSTAL <--> LIQUID ---		
1000	85.144	184.908	128.773	56.135	−639.916	−482.073	25.181
1100	86.417	193.083	134.252	64.714	−638.519	−466.356	22.145
1200	87.662	200.656	139.474	73.418	−637.007	−450.771	19.622
1300	88.880	207.721	144.455	82.245	−635.383	−435.316	17.491
1400	90.071	214.351	149.213	91.193	−761.057	−416.823	15.552
1500	91.235	220.605	153.766	100.258	−757.861	−392.346	13.663
1600	92.372	226.530	158.131	109.439	−754.559	−368.086	12.017
1700	93.482	232.163	162.321	118.732	−751.153	−344.035	10.571
1800	94.565	237.538	166.352	128.135	−747.647	−320.187	9.292
1900	95.621	242.679	170.235	137.644	−744.043	−296.537	8.152
2000	96.650	247.610	173.981	147.258	−740.346	−273.080	7.132

PREVIOUS: December 1960 CURRENT: December 1965

$S°(298.15\ K) = [129.480]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-601.577]\ kJ·mol^{-1}$

$T_{fus} = 987\ K$ $\Delta_{fus}H° = 43.095 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgCl_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgCl_2, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(987\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A constant $C_p°(l) = 22.0\ cal·K^{-1}·mol^{-1}$ over the temperature range 1006–1428 K is from the high temperature enthalpy data of Moore.[1] This constant value was assumed to hold from an assumed glass transition of 660 K to 3000 K. $C_p°(l)$ below 660 K is taken to be that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the Gibbs energy change of the reaction $MgCl_2(l) = MgCl_2(g)$ is zero. The difference between $\Delta_f H°$ for $MgCl_2(l)$ and $MgCl_2(g)$ at T_{vap} is $\Delta_{vap}H°$.

Reference

[1]G. E. Moore, J. Amer. Chem. Soc. **65**, 1700 (1943).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	71.379	129.480	129.480	0.	−601.577	−563.929	98.798
300	71.496	129.922	129.482	0.132	−601.553	−563.696	98.148
400	75.709	151.128	132.344	7.513	−600.197	−551.276	71.989
500	78.145	168.303	137.873	15.215	−598.733	−539.214	56.331
600	79.873	182.554	144.164	23.034	−597.314	−527.443	45.918
660.000	85.617	190.408	148.013	27.981	GLASS <--> LIQUID TRANSITION		
660.000	92.048	190.415	148.013	27.985			
700	92.048	195.831	150.592	31.667	−595.225	−515.943	38.500
800	92.048	208.122	157.032	40.872	−592.708	−504.791	32.959
900	92.048	218.964	163.323	50.077	−590.342	−493.945	28.668
987.000	92.048	227.458	168.608	58.085	--- CRYSTAL <--> LIQUID ---		
1000	92.048	228.662	169.381	59.282	−596.730	−482.642	25.211
1100	92.048	237.435	175.175	68.486	−594.706	−471.331	22.382
1200	92.048	245.444	180.702	77.691	−592.694	−460.204	20.032
1300	92.048	252.812	185.969	86.896	−590.692	−449.244	18.051
1400	92.048	259.634	190.990	96.101	−716.109	−435.271	16.240
1500	92.048	265.984	195.781	105.306	−712.774	−415.328	14.463
1600	92.048	271.925	200.356	114.510	−709.448	−395.607	12.915
1700	92.048	277.505	204.732	123.715	−706.130	−376.093	11.556
1800	92.048	282.767	208.922	132.920	−702.822	−356.775	10.353
1900	92.048	287.744	212.941	142.125	−699.523	−337.640	9.282
2000	92.048	292.465	216.800	151.330	−696.234	−318.679	8.323
2100	92.048	296.956	220.511	160.534	−692.957	−299.881	7.459
2200	92.048	301.238	224.084	169.739	−689.692	−281.240	6.677
2300	92.048	305.330	227.528	178.944	−686.441	−262.747	5.967
2400	92.048	309.247	230.852	188.149	−683.206	−244.395	5.319
2500	92.048	313.005	234.063	197.354	−679.988	−226.177	4.726

PREVIOUS: December 1960 CURRENT: December 1965

0 to 987 K crystal
above 987 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.759	−641.196	−641.196	INFINITE
100	40.294	25.956	146.771	−12.081	−643.073	−625.817	326.893
200	63.575	62.664	95.923	−6.652	−642.688	−608.599	158.950
298.15	71.379	89.629	89.629	0.	−641.616	−592.087	103.731
300	71.496	90.071	89.630	0.132	−641.593	−591.780	103.038
400	75.709	111.276	92.493	7.513	−640.237	−575.376	75.136
500	78.145	128.451	98.022	15.215	−638.773	−559.328	58.433
600	79.873	142.857	104.326	23.119	−637.269	−543.580	47.323
700	81.253	155.274	110.737	31.176	−635.756	−528.085	39.406
800	82.550	166.209	117.001	39.366	−634.254	−512.806	33.483
900	83.847	176.007	123.022	47.686	−632.773	−497.714	28.887
987.000	84.977	183.795	128.040	55.030	CRYSTAL <--> LIQUID		
987.000	92.048	227.458	128.040	98.125	TRANSITION		
1000	92.048	228.662	129.341	99.321	−596.730	−482.642	25.211
1100	92.048	237.435	138.775	108.526	−594.706	−471.331	22.382
1200	92.048	245.444	147.335	117.731	−592.694	−460.204	20.032
1300	92.048	252.812	155.169	126.936	−590.692	−449.244	18.051
1400	92.048	259.634	162.390	136.141	−716.109	−435.271	16.240
1500	92.048	265.984	169.087	145.345	−712.774	−415.328	14.463
1600	92.048	271.925	175.331	154.550	−709.448	−395.607	12.915
1700	92.048	277.505	181.179	163.755	−706.130	−376.093	11.556
1800	92.048	282.767	186.678	172.960	−702.822	−356.775	10.353
1900	92.048	287.744	191.867	182.165	−699.523	−337.640	9.282
2000	92.048	292.465	196.780	191.369	−696.234	−318.679	8.323
2100	92.048	296.956	201.444	200.574	−692.957	−299.881	7.459
2200	92.048	301.238	205.884	209.779	−689.692	−281.240	6.677
2300	92.048	305.330	210.119	218.984	−686.441	−262.747	5.967
2400	92.048	309.247	214.169	228.189	−683.206	−244.395	5.319
2500	92.048	313.005	218.048	237.393	−679.988	−226.177	4.726

PREVIOUS: CURRENT: December 1965

$S°(298.15\ K) = 277.027 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -392.57 \pm 2.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -392.46 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
590 (1)
88 (2)
[273](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: $D_{\infty h}$
Bond Distance: Mg–Cl = 2.18 Å
Bond Angle: Cl–Mg–Cl = 180°
Rotational Constant: $B_0 = 0.050027\ cm^{-1}$

Enthalpy of Formation

Analysis of vapor pressure data on $MgCl_2$ is clouded by conflicting evidence for the amount of dimer in the vapor. Berkowitz and Marquart[1] by mass spectrometer studies found about 2% dimer at 920 K and derived $\Delta_{dim}H = -39.2\ kcal·mol^{-1}$ and $\Delta_{dim}S = -29.9\ cal·K^{-1}·mol^{-1}$. Schrier and Clark[2] from gas transpiration data calculated about 30% dimer in the saturated vapor at 1300 K with $\Delta_{dim}H = -32.0\ kcal·mol^{-1}$ and $\Delta_{dim}S = -18.8\ cal·K^{-1}·mol^{-1}$. Thermodynamic functions for the gaseous monomer adopted here are clearly not compatible with large amounts of dimer and it is assumed for the present that the mass spectrometer results are correct.

Several vapor pressure studies have been published and third law analyses are given below. Berkowitz and Marquart[1] gave a single point while the remaining publications gave only equations but not individual points. Total pressures calculated from the equations were corrected for dimer.

Source	Method	T/K	$\Delta_{sub}H°(298.15\ K)$ kcal·mol^{-1} 3rd law
Berkowitz and Marquart[1]	Mass spectrometer	920	58.1
Schrier and Clark[2]	Boiling Point	1208–1413	59.55–59.68
Hildenbrand *et al.*[3]	Torsion–effusion	802–985	59.55–59.19
Hildenbrand *et al.*[4]	Torsion–effusion	800–970	59.53–59.38
Fischer *et al.*[5] (total vapor pressures)	"Bell" method	1136–1435	59.30–59.56

The selected value for $\Delta_{sub}H°(298.15\ K)$ is 59.55 kcal·mol^{-1} which is combined with $\Delta_f H°(298.15\ K)$ of the crystal to give $\Delta_f H°(g, 298.15\ K) = -93.80\ kcal·mol^{-1}$.

Heat Capacity and Entropy

White *et al.*[6] by matrix infrared spectroscopy determined the molecule to be linear with the asymmetric stretching frequency at 590 cm^{-1} and the doubly degenerate bending frequency at 88 cm^{-1}. The symmetric stretching frequency was estimated as 273 cm^{-1}. The asymmetric stretching was observed by Buchler and Klemperer[7] at 597 cm^{-1} and by Randall *et al.*[8] at 598 cm^{-1}, both by infrared spectroscopy of the vapor at high temperature. Electric deflection experiments by Klemperer and co-workers as summarized by Hayes[9] and the electron diffraction data of Akishin and Spiridonov[10] agree with the linear structure within their error limits of about 20. The Mg–Cl bond length was determined as 2.18 Å by Akishin and Spiridonov.[10]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.285	−392.565	−392.565	INFINITE
100	46.426	220.299	325.112	−10.481	−392.316	−394.494	206.063
200	53.484	254.921	282.150	−5.446	−392.325	−396.688	103.604
250	55.615	267.097	277.959	−2.715	−392.384	−397.772	83.110
298.15	57.097	277.027	277.027	0.	−392.459	−398.803	69.869
300	57.145	277.380	277.028	0.106	−392.462	−398.842	69.445
350	58.249	286.277	277.728	2.992	−392.557	−399.898	59.682
400	59.057	294.110	279.296	5.926	−392.668	−400.940	52.357
450	59.658	301.102	281.337	8.894	−392.796	−401.966	46.659
500	60.116	307.413	283.635	11.889	−392.942	−402.977	42.099
600	60.747	318.434	288.542	17.935	−393.296	−404.953	35.254
700	61.150	327.830	293.500	24.031	−393.744	−406.862	30.360
800	61.420	336.014	298.314	30.160	−394.302	−408.699	26.685
900	61.610	343.260	302.913	36.312	−394.989	−410.459	23.822
1000	61.748	349.759	307.278	42.481	−404.413	−411.422	21.490
1100	61.851	355.649	311.412	48.661	−405.414	−412.074	19.568
1200	61.931	361.035	315.326	54.850	−406.418	−412.636	17.962
1300	61.993	365.994	319.035	61.046	−407.424	−413.113	16.599
1400	62.042	370.590	322.556	67.248	−535.845	−410.346	15.310
1500	62.082	374.872	325.902	73.455	−535.508	−401.393	13.978
1600	62.115	378.880	329.090	79.665	−535.176	−392.463	12.813
1700	62.143	382.647	332.130	85.878	−534.850	−383.553	11.785
1800	62.166	386.199	335.036	92.093	−534.531	−374.663	10.872
1900	62.185	389.561	337.819	98.311	−534.220	−365.790	10.056
2000	62.202	392.751	340.486	104.530	−533.916	−356.933	9.322
2100	62.217	395.786	343.048	110.751	−533.623	−348.091	8.658
2200	62.229	398.681	345.511	116.973	−533.341	−339.263	8.055
2300	62.240	401.447	347.884	123.197	−533.071	−330.447	7.505
2400	62.250	404.096	350.171	129.421	−532.816	−321.643	7.000
2500	62.258	406.638	352.379	135.647	−532.577	−312.849	6.537
2600	62.266	409.080	354.513	141.873	−532.357	−304.064	6.109
2700	62.272	411.430	356.578	148.100	−532.156	−295.288	5.713
2800	62.278	413.695	358.578	154.327	−531.976	−286.518	5.345
2900	62.284	415.880	360.516	160.555	−531.820	−277.755	5.003
3000	62.288	417.992	362.397	166.784	−531.687	−268.996	4.684
3100	62.293	420.034	364.224	173.013	−531.580	−260.242	4.385
3200	62.297	422.012	365.999	179.242	−531.499	−251.490	4.105
3300	62.301	423.929	367.725	185.472	−531.445	−242.741	3.842
3400	62.304	425.789	369.406	191.703	−531.419	−233.993	3.595
3500	62.307	427.595	371.043	197.933	−531.421	−225.245	3.362
3600	62.310	429.350	372.638	204.164	−531.450	−216.496	3.141
3700	62.312	431.058	374.194	210.395	−531.508	−207.747	2.933
3800	62.315	432.719	375.712	216.626	−531.593	−198.996	2.735
3900	62.317	434.338	377.195	222.858	−531.707	−190.242	2.548
4000	62.319	435.916	378.643	229.090	−531.847	−181.484	2.370
4100	62.321	437.455	380.059	235.322	−532.015	−172.723	2.201
4200	62.323	438.956	381.444	241.554	−532.211	−163.958	2.039
4300	62.324	440.423	382.798	247.786	−532.432	−155.187	1.885
4400	62.326	441.856	384.124	254.019	−532.681	−146.411	1.738
4500	62.327	443.256	385.423	260.251	−532.955	−137.630	1.598
4600	62.328	444.626	386.695	266.484	−533.255	−128.841	1.463
4700	62.330	445.967	387.942	272.717	−533.582	−120.046	1.334
4800	62.331	447.279	389.164	278.950	−533.935	−111.244	1.211
4900	62.332	448.564	390.364	285.183	−534.313	−102.434	1.092
5000	62.333	449.823	391.540	291.416	−534.718	−93.616	0.978
5100	62.334	451.058	392.695	297.650	−535.149	−84.790	0.868
5200	62.335	452.268	393.829	303.883	−535.608	−75.955	0.763
5300	62.336	453.456	394.943	310.117	−536.092	−67.111	0.661
5400	62.337	454.621	396.037	316.350	−536.605	−58.257	0.564
5500	62.337	455.765	397.113	322.584	−537.144	−49.394	0.469
5600	62.338	456.888	398.170	328.818	−537.713	−40.521	0.378
5700	62.339	457.991	399.210	335.052	−538.311	−31.637	0.290
5800	62.339	459.075	400.233	341.286	−538.939	−22.743	0.205
5900	62.340	460.141	401.239	347.520	−539.597	−13.837	0.123
6000	62.341	461.189	402.230	353.754	−540.287	−4.920	0.043

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 337.787 \pm 5.44\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -628.99 \pm 14.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -633.04 \pm 14.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
972 (1)	134 (1)	156 (1)
453 (1)	233 (1)	437 (1)
347 (1)	996 (1)	287 (1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: Mo–O = 1.75 ± 0.10 Å; Mo–Cl = 2.28 ± 0.03 Å

Bond Angles: O–Mo–O = 109.5°; Cl–Mo–Cl = 113°

O–Mo–O plane perpendicular to Cl–Mo–Cl plane

Product of Moments of Inertia: $I_A I_B I_C = 1.09994 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

Graham and Hepler[1] determined calorimetrically $\Delta_r H° = -65.3 \pm 0.5$ kcal·mol^{-1} for the reaction:

$$MoO_2Cl_2(cr) + 4\ NaOH(\infty H_2O) \rightarrow Na_2MoO_4(\infty H_2O) + 2\ NaCl(\infty H_2O) + 2\ H_2O(l).$$

Combining this result with the following enthalpy of formation data; $\Delta_f H°(Na_2MoO_4, \infty H_2O) = -353 \pm 0.4$ kcal·mol^{-1};[2] $\Delta_f H°$(NaCl, ∞H_2O) = −97.33 ± 0.09 kcal·mol^{-1};[3,4] $\Delta_f H°$(NaOH, ∞H_2O) = −112.46 ± 0.1 kcal·mol^{-1};[3,4] $\Delta_f H°(H_2O, l) = -68.315$ kcal·mol^{-1};[5] we derive $\Delta_f H°(MoO_2Cl_2, cr) = -169.6 \pm 1.0$ kcal·mol^{-1}.

Shchukarev *et al.*[6] measured the heats of solution of MoO_3(cr), MoO_2Cl_2(cr) and NaCl(cr) in NaOH(aq) and derived $\Delta_r H° = -45.56 \pm 0.5$ kcal·mol^{-1} for the reaction MoO_2Cl_2(cr) + 2 NaOH·77 $H_2O \rightarrow MoO_3$(cr) + 2 NaCl(cr) + H_2O(l). Using JANAF auxiliary data,[3,4] we obtain $\Delta_f H°(MoO_2Cl_2, cr, 298.15\ K) = -172.86 \pm 1.0$ kcal·mol^{-1}.

The two investigations differ only in the heat of solution of MoO_2Cl_2(cr), both samples were better than 99.9% pure, and multiple determinations on two different samples were employed in each case. We adopt an average of the two values, −171.2 ± 1.7 kcal·mol^{-1} for $\Delta_f H°(MoO_2Cl_2, cr, 298.15\ K)$. Shchukarev *et al.*[8] reported an equation for the vapor pressure over the solid from which we have calcualted a 2nd law $\Delta_{sub} H°(298.15\ K) = 19.9$ kcal·mol^{-1} with an estimated uncertainty of ±2 kcal·mol^{-1}, a ΔC_p correction of −4.1 cal·K^{-1}·mol^{-1} was used.[3] Thus, our adopted value is $\Delta_f H°(MoO_2Cl_2, g, 298.15\ K) = -151.3 \pm 3.5$ kcal·mol^{-1}.

Shchukarev *et al.*[7] reported equilibrium constants for the reaction $MoO_2Cl_2(g) + 0.5\ O_2(g) = MoO_3(cr) + Cl_2(g)$. Shchukarev *et al.*[8] and Hultgren and Brewer[9] reported equilibrium data for the reaction $MoO_3(cr) + 2\ HCl(g) = MoO_2Cl_2(g) + H_2O(g)$. 2nd and 3rd law analysis of these equilibrium data give the following results:

Source	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$-\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[7]	7	−15.6	−30.11 ± 2.0	−15.0	148.0 ± 3.0
[8]	Eqn	12.1	13.8 ± 1.0	2.95	150.6 ± 1.2
[9] Set I	5	27.2	15.2 ± 1.7	−21.37	149.2 ± 2.0
Set II	5	26.5	15.4 ± 3.2	−21.75	149.4 ± 3.5

These equilbrium data are in agreement with the adopted enthalpy of formation but are suspect because of the significant drifts and because the range of validity of the equation[8] is estimated.

Heat Capacity and Entropy

The molecular structural data are from the compilation of Sutton.[10] Infrared data[11–13] for vapor phase MoO_2Cl_2 have indicated that the molecule possesses a distorted tetrahedral structure by reason of the similarity of its spectra to that of CrO_2Cl_2. Principal moments of inertia are $I_A = 32.2143 \times 10^{-39}$, $I_B = 53.4145 \times 10^{-39}$, and $I_C = 63.9238 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies 972, 996, 453, and 437 have been observed in the infrared vapor phase spectra of MoO_2Cl_2 by Barraclough and Stals.[11] These frequencies were assigned to the symmetric and asymmetric Mo–O and Mo–Cl stretches, respectively. Similar infrared data for these four frequencies have been reported by Iorns and Stafford[12] and Ward and Stafford.[13] The rest of the frequencies are from the infrared and Raman studies of crystalline MoO_2Cl_2 by Adams and Churchill.[14] Assignments are made by comparison with data reported for CrO_2Cl_2(l) by Miller *et al.*[15]

Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−18.400	−628.990	−628.990	INFINITE
100	53.401	261.666	405.432	−14.377	−631.275	−620.507	324.120
200	74.277	305.899	345.270	−7.874	−632.563	−609.158	159.096
250	80.563	323.183	339.165	−3.996	−632.879	−603.266	126.046
298.15	85.220	337.787	337.787	0.	−633.039	−597.546	104.688
300	85.378	338.315	337.789	0.158	−633.043	−597.326	104.004
350	89.169	351.772	338.843	4.525	−633.085	−591.368	88.257
400	92.191	363.883	341.228	9.062	−633.036	−585.411	76.447
450	94.615	374.887	344.366	13.734	−632.921	−579.465	67.262
500	96.572	384.960	347.929	18.516	−632.761	−573.533	59.917
600	99.467	402.841	355.629	28.327	−632.357	−561.724	48.902
700	101.440	418.331	363.505	38.378	−631.905	−549.987	41.041
800	102.829	431.973	371.228	48.596	−631.446	−538.316	35.148
900	103.835	444.145	378.666	58.932	−631.002	−526.702	30.569
1000	104.585	455.126	385.772	69.354	−630.591	−515.136	26.908
1100	105.156	465.122	392.538	79.843	−630.224	−503.608	23.914
1200	105.600	474.291	398.974	90.381	−629.915	−492.112	21.421
1300	105.952	482.758	405.097	100.960	−629.673	−480.638	19.312
1400	106.235	490.621	410.929	111.569	−629.508	−469.181	17.505
1500	106.465	497.959	416.489	122.205	−629.430	−457.732	15.940
1600	106.656	504.836	421.798	132.861	−629.448	−446.286	14.570
1700	106.815	511.307	426.875	143.535	−629.570	−434.835	13.361
1800	106.949	517.416	431.737	154.223	−629.806	−423.374	12.286
1900	107.064	523.202	436.400	164.924	−630.167	−411.896	11.324
2000	107.161	528.696	440.878	175.635	−630.661	−400.396	10.457
2100	107.246	533.926	445.186	186.356	−631.302	−388.868	9.673
2200	107.320	538.917	449.334	197.084	−632.098	−377.305	8.958
2300	107.384	543.689	453.333	207.820	−633.062	−365.703	8.305
2400	107.441	548.261	457.194	218.561	−634.206	−354.055	7.706
2500	107.491	552.648	460.925	229.307	−635.542	−342.355	7.153
2600	107.535	556.864	464.534	240.059	−637.094	−330.598	6.642
2700	107.575	560.924	468.029	250.814	−638.903	−318.776	6.167
2800	107.610	564.837	471.417	261.574	−641.032	−306.881	5.725
2900	107.643	568.613	474.704	272.336	−679.446	−294.855	5.311
3000	107.671	572.263	477.896	283.102	−680.420	−281.577	4.903
3100	107.698	575.794	480.997	293.871	−681.430	−268.265	4.520
3200	107.721	579.214	484.013	304.642	−682.475	−254.921	4.161
3300	107.743	582.529	486.949	315.415	−683.552	−241.543	3.823
3400	107.763	585.745	489.807	326.190	−684.660	−228.132	3.505
3500	107.781	588.870	492.593	336.967	−685.798	−214.689	3.204
3600	107.798	591.906	495.310	347.746	−686.963	−201.212	2.920
3700	107.813	594.860	497.961	358.527	−688.152	−187.703	2.650
3800	107.827	597.735	500.549	369.309	−689.363	−174.160	2.394
3900	107.840	600.536	503.077	380.092	−690.593	−160.586	2.151
4000	107.852	603.267	505.547	390.877	−691.839	−146.981	1.919
4100	107.864	605.930	507.963	401.663	−693.098	−133.344	1.699
4200	107.874	608.529	510.327	412.450	−694.367	−119.676	1.488
4300	107.884	611.068	512.640	423.237	−695.644	−105.977	1.287
4400	107.893	613.548	514.906	434.026	−696.926	−92.250	1.095
4500	107.902	615.973	517.125	444.816	−698.210	−78.493	0.911
4600	107.910	618.345	519.300	455.607	−699.495	−64.708	0.735
4700	107.917	620.665	521.432	466.398	−700.777	−50.894	0.566
4800	107.924	622.937	523.523	477.190	−702.056	−37.053	0.403
4900	107.931	625.163	525.574	487.983	−703.329	−23.185	0.247
5000	107.937	627.343	527.588	498.776	−1295.980	−3.561	0.037
5100	107.943	629.481	529.565	509.570	−1298.917	22.317	−0.229
5200	107.948	631.577	531.507	520.365	−1301.991	48.252	−0.485
5300	107.953	633.633	533.414	531.160	−1305.199	74.250	−0.732
5400	107.958	635.651	535.289	541.955	−1308.540	100.308	−0.970
5500	107.963	637.632	537.132	552.751	−1312.010	126.429	−1.201
5600	107.967	639.577	538.944	563.548	−1315.607	152.615	−1.424
5700	107.971	641.488	540.726	574.345	−1319.328	178.866	−1.639
5800	107.975	643.366	542.480	585.142	−1323.171	205.184	−1.848
5900	107.979	645.212	544.205	595.940	−1327.131	231.567	−2.050
6000	107.983	647.027	545.904	606.738	−1331.210	258.020	−2.246

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K)$ = [325.432] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -562.47 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -566.10 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[265](1)	[155](1)
[159](1)	[222](1)
[226](1)	[260](1)

Ground State Quantum Weight = 1 σ = 4
Point Group: D_{2h}
Bond Distance: Cl–Na = [2.624] Å
Bond Angle: Cl–Na–Cl = [108.4]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [6.84195 × 10^{-113}] $g^3·cm^6$

Enthalpy of Formation

An analysis is given below of the more extensive measurements relating to the dimer dissociation, $(NaCl)_2(g) \rightarrow 2\ NaCl(g)$. The mass spectrometric studies suggest that higher polymeric species may be neglected. Velocity distribution analyses are consistent with this procedure. When reduced to 298.15 K, the observed heats of dissociation of the dimer show a range of more than 7 $kcal·mol^{-1}$, reflecting the considerable uncertainty involved in such measurements. A value of $\Delta_r H°(298.15\ K)$ = 48.6 $kcal·mol^{-1}$ was selected for the dissociation; combining this with $\Delta_{sub} H°(298.15\ K)$ = 54.9 $kcal·mol^{-1}$ for sublimation to the monomer leads to $\Delta_{sub} H°(298.15\ K)$ = 61.2 $kcal·mol^{-1}$ for sublimation to the dimer.

Source	Method	T/K	$\Delta_r H°(T)$ $kcal·mol^{-1}$	$\Delta_r H°(298.15\ K)$ $kcal·mol^{-1}$ 2nd law	3rd law
[1]	Molecular weight from vapor pressures	1350	51.0	52.8	52.0
[2]	Molecular weight from P–V–T measurements	1337	50.6	52.4	54.1
[3]	Double oven effusion with mass spectrometer	1002	47.4	48.6	—
[4]	Knudsen effusion with mass spectrometer	870	47.3	48.3	—
[5]	Knudsen effusion with mass spectrometer	930	44.5	45.6	—
[6]	Velocity distribution analysis	940	49.8	50.9	—
[7]	Velocity distribution analysis	980	46.6	47.8	—

Heat Capacity and Entropy

The structure and vibrational frequencies are those calculated from an ionic model by Berkowitz.[8] Electron diffraction studies by Akishin and Rambidi[9] gave a similar bond angle (108°) and a slightly shorter bond distance (2.50 Å); however, interpretation of the diffraction pattern was complicated by uncertainty in the monomer–dimer ratio for the vapor. Principal moments of inertia for the Berkowitz structure are I_A = 17.9886 × 10^{-39}, I_B = 53.3306 × 10^{-39}, and I_C = 71.3192 × 10^{-39} $g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−18.446	−562.467	−562.467	INFINITE
100	57.464	248.550	391.674	−14.312	−563.924	−565.116	295.186
200	74.137	294.802	332.524	−7.544	−565.105	−565.794	147.770
250	77.102	311.696	326.720	−3.756	−565.585	−565.911	118.241
298.15	78.786	325.432	325.432	0.	−566.095	−565.929	99.148
300	78.836	325.919	325.433	0.146	−566.116	−565.928	98.537
350	79.928	338.160	326.397	4.117	−566.770	−565.847	84.448
400	80.656	348.883	328.552	8.133	−572.843	−565.251	73.814
450	81.163	358.414	331.350	12.179	−573.698	−564.250	65.496
500	81.531	366.986	334.492	16.247	−574.503	−563.156	58.833
600	82.016	381.897	341.187	24.426	−575.988	−560.745	48.817
700	82.312	394.564	347.930	32.644	−577.346	−558.096	41.646
800	82.505	405.569	354.462	40.885	−578.623	−555.258	36.255
900	82.639	415.295	360.692	49.143	−579.860	−552.263	32.053
1000	82.734	424.007	366.595	57.412	−581.102	−549.130	28.684
1100	82.805	431.896	372.179	65.689	−582.392	−545.871	25.921
1200	82.859	439.103	377.460	73.972	−777.291	−537.611	23.402
1300	82.901	445.737	382.460	82.260	−776.933	−517.653	20.800
1400	82.934	451.882	387.202	90.552	−776.580	−497.721	18.570
1500	82.961	457.605	391.707	98.847	−776.233	−477.815	16.639
1600	82.983	462.960	395.995	107.144	−775.893	−457.931	14.950
1700	83.002	467.991	400.083	115.443	−775.560	−438.069	13.460
1800	83.017	472.736	403.989	123.744	−775.235	−418.226	12.137
1900	83.030	477.225	407.726	132.047	−774.919	−398.401	10.953
2000	83.041	481.484	411.309	140.350	−774.613	−378.592	9.888
2100	83.051	485.536	414.748	148.655	−774.319	−358.799	8.925
2200	83.059	489.399	418.054	156.960	−774.039	−339.018	8.049
2300	83.066	493.092	421.237	165.267	−773.775	−319.251	7.250
2400	83.073	496.627	424.305	173.574	−773.531	−299.494	6.518
2500	83.078	500.018	427.266	181.881	−773.309	−279.747	5.845
2600	83.083	503.277	430.127	190.189	−773.113	−260.009	5.224
2700	83.088	506.413	432.895	198.498	−772.944	−240.277	4.648
2800	83.092	509.434	435.575	206.807	−772.808	−220.551	4.114
2900	83.095	512.350	438.172	215.116	−772.706	−200.830	3.617
3000	83.098	515.167	440.692	223.426	−772.641	−181.111	3.153
3100	83.101	517.892	443.139	231.736	−772.617	−161.394	2.719
3200	83.104	520.531	445.516	240.046	−772.637	−141.677	2.313
3300	83.106	523.088	447.828	248.356	−772.700	−121.959	1.930
3400	83.108	525.569	450.078	256.667	−772.812	−102.238	1.571
3500	83.110	527.978	452.270	264.978	−772.974	−82.513	1.231
3600	83.112	530.319	454.406	273.289	−773.187	−62.782	0.911
3700	83.114	532.597	456.488	281.601	−773.455	−43.045	0.608
3800	83.116	534.813	458.520	289.912	−773.779	−23.301	0.320
3900	83.117	536.972	460.504	298.224	−774.162	−3.546	0.047
4000	83.118	539.076	462.443	306.536	−774.605	16.219	−0.212
4100	83.120	541.129	464.337	314.847	−775.111	35.996	−0.459
4200	83.121	543.132	466.189	323.159	−775.679	55.785	−0.694
4300	83.122	545.088	468.001	331.472	−776.319	75.589	−0.918
4400	83.123	546.999	469.775	339.784	−776.945	95.402	−1.133
4500	83.124	548.867	471.512	348.096	−777.685	115.235	−1.338
4600	83.125	550.694	473.214	356.409	−778.512	135.087	−1.534
4700	83.125	552.481	474.881	364.721	−779.415	154.957	−1.722
4800	83.126	554.231	476.516	373.034	−780.395	174.847	−1.903
4900	83.127	555.945	478.120	381.346	−781.457	194.759	−2.076
5000	83.128	557.625	479.693	389.659	−782.589	214.692	−2.243
5100	83.128	559.271	481.237	397.972	−783.821	234.650	−2.403
5200	83.129	560.885	482.754	406.285	−785.145	254.632	−2.558
5300	83.129	562.469	484.243	414.598	−786.566	274.642	−2.707
5400	83.130	564.022	485.706	422.911	−788.086	294.678	−2.850
5500	83.130	565.548	487.144	431.224	−789.711	314.745	−2.989
5600	83.131	567.046	488.557	439.537	−791.444	334.841	−3.123
5700	83.131	568.517	489.947	447.850	−793.288	354.969	−3.253
5800	83.132	569.963	491.314	456.163	−795.249	375.131	−3.378
5900	83.132	571.384	492.659	464.476	−797.328	395.328	−3.500
6000	83.133	572.781	493.983	472.789	−799.214	415.524	−3.617

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 98.157 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1304 \pm 4$ K, p 2.5 atm

$\Delta_f H°(0\ K) = -305.389 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -304.930 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 77.170 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of -72.88 ± 0.5 kcal·mol^{-1} is based on our 3rd law analysis of equilibrium data for the reaction $NiCl_2(cr) + H_2(g) \rightarrow Ni(cr) + 2HCl(g)$ of Busey and Giauque.[1] This value is selected from the studies shown below mainly because of the attention to purity of the sample, assurance of equilibrium, and correction for diffusion of hydrogen through pyrex by these authors. The results of Busey and Giauque[1] show excellent agreement between 2nd and 3rd law values with a consequent low drift. Our analysis of the other studies is given below and the large drifts for some of the studies indicate a lack of equilibrium which is attained very slowly in this system; this is certainly the case for Shchukarev *et al.*[2] and possibly also for others.[3–5] The emf results of Egan[6] and Gee and Shelton[7] are about 0.5 kcal·mol^{-1} more negative than the adopted value and we increase the uncertainty in the event that these results prove to be more accurate.

Source	Reaction	Method	Data Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Giauque and Busey[1]	A	static	15	630 – 738	28.86 ± 0.05	28.75 ± 0.02	−0.16 ± 0.08	72.88 ± 0.1
Sano[3]	A	static	5	661 – 792	29.96 ± 0.38	29.26 ± 0.13	−0.96 ± 0.52	73.39 ± 0.1
Egan[6]	B	emf	2	673, 723	−69.73	−73.32 ± 0.36	−5.13	73.32 ± 0.4
Shchukarev *et al.*[2]	A	circulation	7	573 –823	26.52 ± 0.13	28.90 ± 0.58	3.35 ± 0.19	73.03 ± 0.6
Jellinek and Uloth[4]	A	dynamic	3	573 – 723	31.50 ± 3.09	29.81 ± 0.84	−2.64 ± 4.80	73.94 ± 0.8
Berger and Crut[5]	A	static	16	583 – 718	31.84 ± 0.44	29.57 ± 0.46	−3.52 ± 0.67	73.70 ± 0.5
Gee and Shelton[7]	C	emf	Equation	470 – 750	−0.97	−1.20 ± 0.08	−0.39	73.50 ± 0.3
Gee and Shelton[7]	D	emf	Equation	530 – 800	−7.35	−8.34 ± 0.31	−1.51	73.36 ± 0.3

[a]Reactions: A) $NiCl_2(cr) + H_2(g) \rightarrow Ni(cr) + 2HCl(g)$ C) $Co(cr) + NiCl_2(g) \rightarrow CoCl_2(cr) + Ni(cr)$
B) $Ni(cr) + Cl_2(g) \rightarrow NiCl_2(cr)$ D) $Fe(cr) + NiCl_2(g) \rightarrow FeCl_2(cr) + Ni(cr)$

Heat Capacity and Entropy

Heat capacity data below 300 K are based on the measurements of Kostryokova[8] (2–30 K) and Busey and Giauque[9] (14.14–336.36 K). The two sets of data are joined smoothly via a least squares procedure; Kostryokova's values[8] are higher than those of Busey and Giaugue[9] by 5.3% at 15 K and 0.3% at 30 K. The results of Busey and Giauque[9] indicate a sharp lambda peak at 52.35 K which is apparently associated with the cooperative ordering of the magnetic moments of the nickel ions. $C_p°$ near the maximum is 6.74 cal·K^{-1}·mol^{-1} and the enthalpy associated with this transition is of the order of a few calories. The only other measurements in this temperature region are by Trapeznikowa *et al.*[10] (13–129 K) who report three peaks in $C_p°$ at 49.55 K, 57–58 K, and 60–61 K. We put no weight on these results since the authors apparently suffered from an impure sample among other experimental problems;[9] their results range from 4 to 13% higher than those of Busey and Giauque over the temperature range 40–130 K. Earlier results by Kostryokova[11] below 16 K are in good agreement with the adopted $C_p°$ values. $S°(298.15\ K)$ is obtained from integration of the adopted $C_p°$'s and is based on $C_p°(2\ K) = 0.0055$.

$C_p°$ data above 300 K are based on the high temperature enthalpy data of Coughlin[12] (376–1282 K). These data are corrected to IPTS 68[13] and then joined smoothly with the low temperature $C_p°$ data of Busey and Giauque[9] to yield the adopted $C_p°$ values. Data above 1300 K are extrapolated. The high temperature enthalpy data of Krestovnikov and Karetinkov[14] range from 2 to 11% higher than those of Coughlin and are believed to be of lower accuracy.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$T_{sub} = \sim 1245$ K is calculated as the temperature at which $\Delta_r G = 0$ for $NiCl_2(cr) \rightarrow NiCl_2(g)$.[15] See the enthalpy of formation section of the $NiCl_2(g)$ table[15] for the derivation of the adopted enthalpy of sublimation.

References

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Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.426	−305.389	−305.389	INFINITE
52.350	28.361	11.674	278.918	−13.990	____ C_p LAMBDA MAXIMUM ____		
52.350	29.122	11.674	278.918	−13.990	TRANSITION		
100	43.878	32.394	156.473	−12.408	−306.791	−290.384	151.681
200	64.890	70.800	104.534	−6.747	−306.057	−274.184	71.610
298.15	71.660	98.157	98.157	0.	−304.930	−258.779	45.337
300	71.747	98.601	98.159	0.133	−304.908	−258.492	45.008
400	76.289	119.910	101.033	7.551	−303.688	−243.202	31.759
500	78.898	137.244	106.597	15.324	−302.454	−228.225	23.842
600	79.881	151.724	112.945	23.267	−301.421	−213.481	18.585
700	80.313	164.068	119.389	31.275	−300.407	−198.895	14.842
800	80.900	174.824	125.660	39.331	−299.137	−184.480	12.045
900	82.067	184.412	131.664	47.473	−297.846	−170.225	9.880
1000	84.072	193.153	137.382	55.771	−296.473	−156.117	8.155
1100	87.077	201.298	142.826	64.320	−294.932	−142.155	6.750
1200	91.186	209.043	148.024	73.223	−293.120	−128.343	5.587
1300	96.469	216.542	153.007	82.596	−290.929	−114.698	4.609
1304.000	96.705	216.839	153.202	82.982	--- CRYSTAL <--> LIQUID ---		
1400	102.973	223.922	157.809	92.558	−288.244	−101.239	3.777
1500	110.733	231.284	162.462	103.232	−284.946	−87.992	3.064
1600	119.771	238.712	166.995	114.747	−280.911	−74.989	2.448
1700	130.107	246.276	171.435	127.230	−276.016	−62.264	1.913
1800	141.752	254.036	175.808	140.812	−287.283	−49.140	1.426

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = [151.810]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1304 \pm 4\ K,\ p \cong 2.5\ atm$

$\Delta_f H°(298.15) = [-233.516]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 77.170 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NiCl_2, l, 298.15\ K)$ is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1304\ K) - H°(298.15\ K)$, between the crystal and liquid.[1]

Heat Capacity and Entropy

The adopted values of $C_p°$ are obtained from our analysis of the high temperature enthalpy data of Coughlin[2] (1305–1337 K) after correction to IPTS 68.[3] The constant $C_p°$ value obtained from these data is assumed to be valid above an assumed glass transition temperature at 880 K. The assumption of a constant $C_p°$ over such a broad range based on data over a very short range leads to a rather large uncertainty in the thermal functions. Below the glass transition at 880 K, $C_p°$ is assumed to be that of the crystal.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The temperature and heat of melting are obtained from our analysis of Coughlin's[2] measurements after correction to IPTS 68.[3] He observed pre-melting beginning at 1288 K and continuing to 1305 K where the enthalpy change again becomes regular. We adopt a melting point near the upper end of this range, $T_{fus} = 1304 \pm 4$ K. The adopted enthalpy of melting is $18.444 \pm 0.2\ kcal·mol^{-1}$ at T_{fus}.

Phase Data

$NiCl_2(l)$ will not exist as a stable phase at 1 bar pressure according to calculations from our tables.[1] We calculate sublimation at ~1245 K in good agreement with the measured value of 1241 ± 3 K at 730 torr.[4] The adopted melting point of 1304 ± 4 K is from Coughlin's work which was conducted at 2–3.5 atm in the presence of inert gas. These pressures are high enough to increase the sublimation point above the melting point and a relatively short liquid range will be observed. Information on the enthalpy of sublimation is in the enthalpy of formation section of the ideal gas table.[1]

References

[1]JANAF Thermochemical Tables: $NiCl_2$(cr), $NiCl_2$(g), 9-30-77.
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[4]H. Schaefer, Z. anorg. allg. Chem. **278**, 300 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	71.659	151.810	151.810	0.	−233.517	−203.362	35.628
300	71.747	152.253	151.811	0.133	−233.495	−203.175	35.376
400	76.289	173.562	154.685	7.551	−232.275	−193.250	25.236
500	78.898	190.896	160.249	15.324	−231.041	−183.638	19.184
600	79.881	205.376	166.597	23.267	−230.007	−174.259	15.171
700	80.313	217.720	173.041	31.275	−228.993	−165.038	12.315
800	80.900	228.476	179.312	39.331	−227.724	−155.989	10.185
880.000	81.773	236.225	184.139	45.836	GLASS <--> LIQUID TRANSITION		
880.000	101.186	236.225	184.139	45.836			
900	101.186	238.499	185.322	47.860	−226.045	−147.103	8.538
1000	101.186	249.160	191.182	57.978	−222.853	−138.504	7.235
1100	101.186	258.804	196.898	68.097	−219.741	−130.220	6.184
1200	101.186	267.608	202.429	78.215	−216.714	−122.216	5.320
1300	101.186	275.708	207.758	88.334	−213.778	−114.461	4.599
1304.000	101.186	276.018	207.967	88.739	--- CRYSTAL <--> LIQUID ---		
1400	101.186	283.206	212.883	98.453	−210.936	−106.929	3.990
1500	101.186	290.187	217.807	108.571	−208.194	−99.596	3.468
1600	101.186	296.718	222.537	118.690	−205.555	−92.443	3.018
1700	101.186	302.852	227.082	128.808	−203.024	−85.451	2.626
1800	101.186	308.636	231.454	138.927	−217.755	−77.891	2.260

PREVIOUS: CURRENT: September 1977

0 to 1304 K crystal
above 1304 K *liquid*

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.426	−305.389	−305.389	INFINITE
52.350	28.361	11.674	278.918	−13.990	____ C_p LAMBDA MAXIMUM ____		
52.350	29.122	11.674	278.918	−13.990	TRANSITION		
100	43.878	32.394	156.473	−12.408	−306.791	−290.384	151.681
200	64.890	70.800	104.534	−6.747	−306.057	−274.184	71.610
298.15	71.660	98.157	98.157	0.	−304.930	−258.779	45.337
300	71.747	98.601	98.159	0.133	−304.908	−258.492	45.008
400	76.289	119.910	101.033	7.551	−303.688	−243.202	31.759
500	78.898	137.244	106.597	15.324	−302.454	−228.225	23.842
600	79.881	151.724	112.945	23.267	−301.421	−213.481	18.585
700	80.313	164.068	119.389	31.275	−300.407	−198.895	14.842
800	80.900	174.824	125.660	39.331	−299.137	−184.480	12.045
900	82.067	184.412	131.664	47.473	−297.846	−170.225	9.880
1000	84.072	193.153	137.382	55.771	−296.473	−156.117	8.155
1100	87.077	201.298	142.826	64.320	−294.932	−142.155	6.750
1200	91.186	209.043	148.024	73.223	−293.120	−128.343	5.587
1300	96.469	216.542	153.007	82.596	−290.929	−114.698	4.609
1304.000	96.705	216.839	153.202	82.982	____ CRYSTAL <--> LIQUID ____		
1304.000	101.186	276.018	153.202	160.152	TRANSITION		
1400	101.186	283.206	161.873	169.866	−210.936	−106.929	3.990
1500	101.186	290.187	170.198	179.984	−208.194	−99.596	3.468
1600	101.186	296.718	177.903	190.103	−205.555	−92.443	3.018
1700	101.186	302.852	185.075	200.222	−203.024	−85.451	2.626
1800	101.186	308.636	191.780	210.340	−217.755	−77.891	2.260

PREVIOUS: CURRENT: September 1977

$S°$(298.15 K) = 294.233 ± 8.4 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −74.17 ± 0.25 kJ·mol^{-1}
(298.15 K) = −73.932 ± 0.25 kJ·mol^{-1}

Electronic Levels and Quantum Weights					
State	ϵ_i,cm^{-1}	g_i	State	ϵ_i,cm^{-1}	g_i
$^3\Pi_g$	0	6	$^1\Delta_g$	15466	2
$^3\Sigma_g^-$	[879]	3	$^1\Delta_g$	18236	2
$^3\Delta_g$	2454	6	$^3\Sigma_g^-$	21701	3
$^3\phi_g$	5853	6	$^1\Pi_g$	[26740]	2
$^1\Sigma_g^+$	10601	1	$^1\Sigma_g^+$	[27234]	1
$^1\Pi_g$	11727	2	$^1\Gamma_g$	[28825]	2
$^3\Pi_g$	12984	6	$^1\Sigma_g^+$	[55433]	1
$^1\phi_g$	14717	2			

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
360 (1)
87 (2)
523 (1)

Point Group: $D_{\infty h}$ σ = [2]
Bond Distance: Ni–Cl = [2.09] Å
Bond Angle: Cl–Ni–Cl = 180°
Rotational Constant: B_0 = [0.054428] cm^{-1}

Enthalpy of Formation

The adopted value of $\Delta_f H°$(298.15 K) is calculated from $\Delta_{sub}H°$(298.15 K) = 55.21 ± 0.3 kcal·mol^{-1} by addition of $\Delta_f H°$($NiCl_2$, cr, 298.15 K).[1] The adopted value is an average derived from our 3rd law analysis of the sublimation data of Ratkovskii *et al.*,[2] McCreary and Thorn,[3] Schaefer *et al.*,[4] and Hildenbrand.[5] The data of Maier[6] are rejected because there is an apparent temperature dependent error at the high temperature end of his data.

Source	Method	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Ratkovskii *et al.*[2]	Knudsen	973 – 1203	Equation	57.14	55.36 ± 0.29	−1.6	−17.52 ± 0.8
McCreary and Thorn[3]	Torsional Recoil	823 – 881	Equation	55.68	55.01 ± 0.03	−0.80	−17.87 ± 0.5
McCreary and Thorn[3]	Mass Effusion	823 – 881	Equation	54.85	55.08 ± 0.01	0.27	−17.80 ± 0.5
Schaefer *et al.*[4]	Transpiration	973 – 1056	10	55.25 ± 1.50	55.62 ± 0.23	0.36 ± 1.47	−17.26 ± 0.7
Maier[6]	Static (pure sample)	1047 – 1236	18	54.00 ± 0.89	55.39 ± 0.42	1.19 ± 0.75	−17.49 ± 0.7
Hildenbrand[5]	Torsion Effusion	706 – 771	19	55.14 ± 0.34	54.99 ± 0.08	−0.19 ± 0.46	−17.89 ± 0.5

Schoonmaker *et al.*[7] observed no dimers in their Knudsen–mass spectroscopic study while Schaefer and Binnewies[8] observed dimerization to the extent of 0.15% at 796 K by a similar technique. We have not corrected for this small dimerization effect. Of more importance may be the observation of significant quantities of $SiCl_4$(g) and Si_2Cl_6(g) by Schoonmaker *et al.*[7] indicating reaction between $NiCl_2$(g) and the quartz liner in their experiment. Schaefer and Binnewies[8] make no mention of Si_xCl_y species even though their Knudsen cell contains a quartz crucible. Therefore we ignore this effect while recognizing the need for further work in the characterization of the vapor over $NiCl_2$.

Heat Capacity and Entropy

The adopted gas phase values of ν_2 = 87 cm^{-1} and ν_3 = 523 cm^{-1} are from the matrix isolation work of Thompson and Carlson,[9] we have added 2 cm^{-1} to the observed values to account for the matrix effect. The symmetric stretching frequency, ν_1, has not been observed in the infrared spectrum and this is one of the major indications that the molecule is linear. The adopted value of ν_1 (360 cm^{-1}) is from the observed vibrational spacing of the fluorescence spectrum by Gruen *et al.*[10] and is in good agreement with the value of 351 cm^{-1} calculated by Milligan *et al.*[11]

The rotational constant is calculated assuming the molecule is linear with the bond distance estimated to be 2.09 Å in accordance with Brewer *et al.*[12] Further support for a linear structure comes from the molecular beam work of Buchler *et al.*[13] which indicates a zero dipole moment for a number of transition metal difluorides including NiF_2.

Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−14.206	−74.171	−74.171	INFINITE
100	45.245	237.999	342.346	−10.435	−73.819	−77.973	40.729
200	53.251	271.980	299.409	−5.486	−73.797	−82.160	21.458
250	56.051	284.178	295.178	−2.750	−73.854	−84.245	17.602
298.15	58.077	294.233	294.233	0.	−73.931	−86.240	15.109
300	58.144	294.592	294.234	0.108	−73.935	−86.316	15.029
350	59.697	303.677	294.948	3.055	−74.039	−88.372	13.189
400	60.859	311.728	296.552	6.071	−74.170	−90.411	11.806
450	61.749	318.950	298.646	9.137	−74.331	−92.432	10.729
500	62.451	325.494	301.009	12.243	−74.536	−94.432	9.865
600	63.502	336.979	306.073	18.543	−75.146	−98.359	8.563
700	64.265	346.828	311.208	24.933	−75.750	−102.170	7.624
800	64.839	355.448	316.211	31.390	−76.080	−105.922	6.916
900	65.270	363.111	321.004	37.897	−76.423	−109.632	6.363
1000	65.590	370.006	325.565	44.440	−76.805	−113.302	5.918
1100	65.824	376.269	329.894	51.012	−77.241	−116.931	5.553
1200	65.993	382.004	334.001	57.603	−77.741	−120.518	5.246
1300	66.114	387.291	337.900	64.209	−78.317	−124.060	4.985
1400	66.200	392.194	341.605	70.825	−78.979	−127.554	4.759
1500	66.260	396.763	345.132	77.448	−79.732	−130.998	4.562
1600	66.300	401.041	348.494	84.076	−80.583	−134.388	4.387
1700	66.327	405.061	351.704	90.707	−81.540	−137.723	4.232
1800	66.344	408.853	354.775	97.341	−99.755	−140.282	4.071
1900	66.354	412.440	357.716	103.976	−100.838	−142.504	3.918
2000	66.360	415.844	360.538	110.612	−101.931	−144.669	3.778
2100	66.363	419.082	363.250	117.248	−103.035	−146.779	3.651
2200	66.365	422.169	365.858	123.884	−104.150	−148.836	3.534
2300	66.367	425.119	368.371	130.521	−105.279	−150.842	3.426
2400	66.370	427.944	370.795	137.158	−106.422	−152.798	3.326
2500	66.374	430.653	373.135	143.795	−107.581	−154.707	3.232
2600	66.380	433.257	375.398	150.433	−108.756	−156.569	3.146
2700	66.389	435.762	377.587	157.071	−109.949	−158.385	3.064
2800	66.400	438.177	379.709	163.710	−111.159	−160.157	2.988
2900	66.413	440.507	381.765	170.351	−112.388	−161.885	2.916
3000	66.428	442.759	383.761	176.993	−113.635	−163.571	2.848
3100	66.445	444.937	385.699	183.637	−114.900	−165.215	2.784
3200	66.465	447.047	387.584	190.282	−493.016	−161.629	2.638
3300	66.486	449.092	389.417	196.930	−492.660	−151.278	2.395
3400	66.509	451.078	391.201	203.580	−492.318	−140.939	2.165
3500	66.532	453.006	392.940	210.232	−491.988	−130.609	1.949
3600	66.557	454.880	394.634	216.886	−491.670	−120.288	1.745
3700	66.583	456.704	396.287	223.543	−491.361	−109.976	1.553
3800	66.609	458.480	397.901	230.203	−491.061	−99.673	1.370
3900	66.635	460.211	399.476	236.865	−490.768	−89.377	1.197
4000	66.661	461.898	401.016	243.530	−490.481	−79.088	1.033
4100	66.687	463.545	402.521	250.197	−490.196	−68.807	0.877
4200	66.712	465.152	403.993	256.867	−489.914	−58.533	0.728
4300	66.737	466.722	405.434	263.539	−489.632	−48.265	0.586
4400	66.762	468.257	406.844	270.214	−489.348	−38.004	0.451
4500	66.785	469.757	408.226	276.892	−489.062	−27.750	0.322
4600	66.808	471.225	409.579	283.571	−488.771	−17.501	0.199
4700	66.829	472.662	410.906	290.253	−488.475	−7.260	0.081
4800	66.850	474.069	412.208	296.937	−488.173	2.976	−0.032
4900	66.869	475.448	413.484	303.623	−487.863	13.205	−0.141
5000	66.887	476.799	414.737	310.311	−487.546	23.428	−0.245
5100	66.904	478.124	415.967	317.000	−487.221	33.644	−0.345
5200	66.919	479.423	417.175	323.692	−486.888	43.854	−0.441
5300	66.933	480.698	418.361	330.384	−486.546	54.057	−0.533
5400	66.945	481.949	419.527	337.078	−486.196	64.254	−0.622
5500	66.956	483.178	420.674	343.773	−485.838	74.444	−0.707
5600	66.966	484.384	421.800	350.469	−485.474	84.628	−0.789
5700	66.975	485.570	422.909	357.166	−485.102	94.805	−0.869
5800	66.982	486.734	423.999	363.864	−484.725	104.976	−0.945
5900	66.987	487.880	425.072	370.563	−484.343	115.139	−1.019
6000	66.992	489.005	426.129	377.262	−483.959	125.297	−1.091

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$\Delta_{at}H°(0\ K) = 428.3 \pm 2\ kJ·mol^{-1}$
$S°(298.15\ K) = 271.72 \pm 1.5\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = 82.8 \pm 2\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = 81.0 \pm 2\ kJ·mol^{-1}$

Electroninc Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
X^1A	0.0	1

Vibrational Levels and Degeneracies
ν, (cm^{-1})
638 (1)
298 (1)
678 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Cl-O = 1.9697Å
Bond Angle: Cl-O-Cl = 110.893°
Product of the Moments of Inertia: $I_AI_BI_C = 2.824188 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_fH°(298.15\ K)$, was measured by reaction gas phase calorimetry at 298 K. Alqasmi *et al.*[1] measured the enthalpy of the reaction:

$$ClNO + Cl_2O \rightarrow ClNO_2 + Cl_2$$

The value of $\Delta_fH°(298.15K)$ is calculated using auxiliary information from JANAF Thermochemical Tables.[2]

Kustodina *et al.*[3] derived the enthalpy of formation of Cl_2O dissolved in CCl_4 from solution calorimetry at 278, 283, 288 and 308 K. The enthalpy of formation in CCl_4 was interpolated to 285 K. Yost and Felt[4] measured the partial vapor pressure of Cl_2O above its CCl_4 solution at 273 and 298 K which yielded the heat of solution of −6.59 kcal·mol^{-1} at 285 K. Wallace and Goodeve[5] obtained the heat of explosion of Cl_2O(g): their measured data gave $\Delta_fH°(Cl_2O,g,298.15\ K) = 21.4$ kcal·mol^{-1} which is in very good agreement with the above. Also Gunther and Wekua[6] measured the enthalpy of explosion; their data gave $\Delta_fH°(Cl_2O,g,298.15\ K) = 24.7$ kcal·mol^{-1}.

Source	Reaction	T/K	Δ_rH(T) kcal·mol^{-1}	Δ_fH(298.15 K) kcal·mol^{-1}
Kustodina et al.[3]	$Cl_2(g) + 1/2O_2(g) \rightarrow Cl_2O$(in CCl_4)	285	60.16	–
Yost and Felt[4]	Cl_2O(in CCl_4) $\rightarrow Cl_2O(g)$	285	27.57	87.86
Wallace and Goodeve[5]	$Cl_2O(g) \rightarrow Cl_2(g) + 1/2\ O_2(g)$	298	−89.54	89.54
Gunther and Wekua[6]	$Cl_2O(g) \rightarrow Cl_2(g) + 1/2O_2(g)$	298	−103.34	103.34

Heat Capacity and Entropy

The inertial parameters come from the microwave spectrum of Cl_2O which has been measured by several investigators.[7,8,9] The results of Nakata, et. al.[7] obtained for the $^{35}Cl_2{}^{16}O$ isotopic species are used to compute moments of inertia of the naturally occurring isotopic species. The principle moments of inertia (in g·cm^2) are: $I_A = 2.7054 \times 10^{-39}$, $I_B = 30.9855 \times 10^{-39}$, $I_C = 33.6908 \times 10^{-39}$.

The stretching fundamentals, ν_1 and ν_3 have been observed in the infrared gas phase spectrum by Rochkind and Pimentel.[10] Raman spectra of all the fundamentals have been observed in an argon matrix by Chi and Andrews.[11] Their spectrum and assignment, which is given above, is in agreement with earlier results on the Raman spectrum of liquid Cl_2O obtained by Gardiner.[12]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}mol^{-1}	$S°$ J·K^{-1}mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_fH°$ kJ·mol^{-1}	$\Delta_fG°$ kJ·mol^{-1}	log K_f
0	.000	.000	INFINITE	−11.714	82.809	82.809	INFINITE
100	35.535	227.019	310.387	−8.337	81.821	86.686	−45.280
200	42.350	253.700	275.941	−4.448	81.217	91.818	−23.980
250	45.468	263.496	272.497	−2.250	81.067	94.488	−19.742
298.15	47.910	271.721	271.721	.000	81.000	97.080	−17.008
300	47.992	272.018	271.722	.089	80.999	97.179	−16.920
350	49.953	279.570	272.314	2.539	80.993	99.877	−14.906
400	51.458	286.343	273.652	5.076	81.031	102.573	−13.395
450	52.617	292.473	275.408	7.680	81.099	105.262	−12.219
500	53.519	298.066	277.398	10.334	81.188	107.942	−11.277
600	54.796	307.945	281.688	15.754	81.396	113.274	−9.861
700	55.626	316.459	286.061	21.278	81.621	118.569	−8.848
800	56.192	323.926	290.337	26.871	81.845	123.832	−8.085
900	56.593	330.569	294.445	32.511	82.063	129.068	−7.491
1000	56.886	336.547	298.361	38.186	82.270	134.279	−7.014
1100	57.107	341.980	302.083	43.886	82.465	139.471	−6.623
1200	57.277	346.956	305.618	49.606	82.649	144.645	−6.296
1300	57.410	351.546	308.977	55.340	82.819	149.804	−6.019
1400	57.517	355.805	312.172	61.087	82.977	154.951	−5.781
1500	57.604	359.776	315.214	66.843	83.122	160.086	−5.575
1600	57.675	363.496	318.117	72.607	83.253	165.213	−5.394
1700	57.734	366.995	320.890	78.378	83.369	170.332	−5.234
1800	57.784	370.296	323.544	84.154	83.469	175.444	−5.091
1900	57.826	373.422	326.088	89.934	83.553	180.552	−4.964
2000	57.862	376.389	328.529	95.719	83.619	185.655	−4.849
2100	57.894	379.212	330.876	101.506	83.665	190.756	−4.745
2200	57.921	381.906	333.135	107.297	83.691	195.855	−4.650
2300	57.945	384.482	335.312	113.090	83.695	200.953	−4.564
2400	57.965	386.948	337.412	118.886	83.675	206.051	−4.485
2500	57.984	389.315	339.441	124.683	83.630	211.151	−4.412
2600	58.000	391.589	341.404	130.483	83.560	216.253	−4.345
2700	58.015	393.778	343.303	136.283	83.462	221.359	−4.282
2800	58.028	395.889	345.144	142.086	83.336	226.468	−4.225
2900	58.039	397.925	346.929	147.889	83.182	231.582	−4.171
3000	58.050	399.893	348.662	153.693	83.000	236.703	−4.121
3100	58.060	401.796	350.345	159.499	82.791	241.830	−4.075
3200	58.068	403.640	351.982	165.305	82.555	246.963	−4.031
3300	58.076	405.427	353.575	171.113	82.292	252.105	−3.990
3400	58.083	407.161	355.125	176.921	82.006	257.255	−3.952
3500	58.090	408.845	356.636	182.729	81.697	262.414	−3.916
3600	58.096	410.481	358.109	188.539	81.368	267.582	−3.883
3700	58.102	412.073	359.546	194.348	81.021	272.759	−3.851
3800	58.107	413.622	360.949	200.159	80.658	277.947	−3.821
3900	58.112	415.132	362.319	205.970	80.283	283.143	−3.792
4000	58.116	416.603	363.658	211.781	79.897	288.350	−3.765
4100	58.120	418.038	364.967	217.593	79.504	293.566	−3.740
4200	58.124	419.439	366.247	223.405	79.106	298.792	−3.716
4300	58.128	420.807	367.500	229.218	78.706	304.027	−3.693
4400	58.131	422.143	368.727	235.031	78.307	309.272	−3.672
4500	58.134	423.449	369.929	240.844	77.910	314.525	−3.651
4600	58.137	424.727	371.106	246.658	77.520	319.788	−3.631
4700	58.140	425.977	372.260	252.471	77.137	325.058	−3.613
4800	58.142	427.202	373.392	258.285	76.763	330.337	−3.595
4900	58.145	428.400	374.503	264.100	76.401	335.624	−3.578
5000	58.147	429.575	375.592	269.914	76.053	340.918	−3.562
5100	58.149	430.727	376.662	275.729	75.718	346.219	−3.546
5200	58.151	431.856	377.713	281.544	75.400	351.525	−3.531
5300	58.153	432.963	378.745	287.359	75.099	356.839	−3.517
5400	58.155	434.050	379.759	293.175	74.815	362.157	−3.503
5500	58.156	435.118	380.756	298.990	74.549	367.481	−3.490
5600	58.158	436.165	381.736	304.806	74.303	372.809	−3.477
5700	58.159	437.195	382.700	310.622	74.075	378.141	−3.465
5800	58.161	438.206	383.648	316.438	73.867	383.478	−3.454
5900	58.162	439.201	384.581	322.254	73.678	388.817	−3.442
6000	58.164	440.178	385.500	328.070	73.509	394.160	−3.431

PREVIOUS: December 1965 (1 bar) CURRENT: December 1992 (1 bar)

$S°(298.15\ K) = 278.81 \pm 2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 91 \pm 30\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 90 \pm 30\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^3A^{\sim}$	0.0	3

Vibrational Levels and Degeneracies
ν, (cm^{-1})
961.8 (1)
239.4 (1)
375.1 (1)

Point Group: C_s $\sigma = 1$
Bond Distances: Cl-O = [1.587]Å; Cl-Cl = [2.268] Å
Bond Angle: O-Cl-O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.6917819x10^{-114}] $g^3 \cdot cm^6$

Enthalpy of Formation

Browett *et al.*[1] estimated that D_0(OCl-Cl) = ~130 kJ·mol through an interpretation of the infrared spectrum; this implied $\Delta_f H$ = ~91 kJ·mol.

Dekock *et al.*[2] performed molecular orbital calculations using the MNDO method and reported that the enthalpy of formation of ClClO was 175 kJ·mol less stable than ClOCl. However, on an absolute basis, the numbers appeared to be approximately 50 kJ·mol too large in comparison with experimental data for ClOCl. Lee,[3] using a comparative coupled cluster study, calculated that ClClO is less stable than ClOCl by 62.3 ± 3.8 kJ·mol. Luke[4] calculated the energies of the two isomers (ClOCl and ClClO) at the G2 and G2(MP2) levels and concluded that ClClO was less stable that ClOCl by 71 kJ·mol and 68 kJ·mol respectively. In contrast, Luke referred to a Density Functional Theory (DFT) result, which suggested a difference in stability of 22 kJ·mol. This adopted value suggests that this species is less stable (by ~9 $kJ \cdot mol^{-1}$) than ClOCl(g).

Heat Capacity and Entropy

Jacox[5] has summarized the IR studies on the three fundamental frequencies.[6-8] The matrix isolated infrared spectrum of this species formed by the photolysis of Cl_2O or the reaction of Cl + O_3 has been observed by several workers.[6,8] Chi and Andrews[8] have observed the argon matrix isolated Raman spectrum of all the isotopic species involving ^{35}Cl, ^{37}Cl, ^{16}O and ^{18}O. The observations of Rochkind and Pimentel[6] are consistent with the more complete results of Chi and Andrews.[8] Chi and Andrews have fitted the results of all the isotopic species to a force field using the estimated bond distances and angle given above. The vibrational frequencies given by Chi and Andrews[8] for the $^{35}Cl_2{}^{16}O$ are used for the thermodynamic calculations. In determining the UV and IR intensities of the ClClO molecule, Johnsson *et al.*[9] reported ν values (961.9, 240.2, 374.2 cm^{-1}) which agree closely with our adopted values. Lee,[3] Luke[4] and Morris and Bhatia[10] have calculated the three vibrational frequencies which are in good agreement with the experimental values.

The bond distances and angles used by Chi and Andrews in their normal coordinate treatment have been used to compute the moments of inertia for naturally occurring isotopic species. The principle moments of inertia (in $g \cdot cm^2$) are: I_A = [2.5010 × 10^{-39}], I_B = [24.7879 × 10^{-39}], I_C = [27.2889 × 10^{-39}]. In comparison, Lee[3] calculated (CCSD[T]) a bond angle of 114.2° and r(Cl-Cl) = 2.232 Å and r(Cl-O) = 1.545 Å; Luke[4] calculated (MP2/6-31G(D)) a bond angle of 116.7° and r(Cl-Cl) = 2.366 Å and r(Cl-O) = 1.524 Å; Morris and Bhatia[10] calculated (HF/6-31G) a bond angle of 111.3° and r(Cl-Cl) = 2.040 Å and r(Cl-O) = 1.528 Å. The latter results agree with the calculations of Luke[4] who also used this level of calculation.

The reactive scattering work of Browett *et al.*[1] concluded that the bent molecule has a $^3A^{\sim}$ symmetry.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.223	91.300	91.300	INFINITE
100	37.727	231.482	319.302	−8.782	90.376	94.794	−49.515
200	44.869	260.094	283.158	−4.613	90.052	99.375	−25.954
250	47.105	270.357	279.602	−2.311	90.006	101.712	−21.251
298.15	48.841	278.807	278.807	.000	90.000	103.967	−18.215
300	48.901	279.109	278.808	.090	90.000	104.054	−18.117
350	50.370	286.761	279.409	2.573	90.026	106.394	−15.878
400	51.573	293.569	280.761	5.123	90.077	108.729	−14.199
450	52.555	299.702	282.530	7.727	90.147	111.057	−12.891
500	53.358	305.282	284.531	10.376	90.229	113.376	−11.844
600	54.559	315.123	288.831	15.775	90.417	117.988	−10.272
700	55.385	323.600	293.207	21.275	90.618	122.567	−9.146
800	55.970	331.035	297.480	26.844	90.819	127.118	−8.300
900	56.395	337.654	301.583	32.464	91.015	131.643	−7.640
1000	56.712	343.613	305.493	38.120	91.204	136.147	−7.112
1100	56.954	349.030	309.208	43.804	91.383	140.633	−6.678
1200	57.143	353.994	312.736	49.509	91.552	145.103	−6.316
1300	57.292	358.574	316.089	55.231	91.710	149.559	−6.009
1400	57.412	362.824	319.277	60.966	91.857	154.003	−5.746
1500	57.511	366.789	322.314	66.713	91.992	158.437	−5.517
1600	57.592	370.503	325.211	72.468	92.113	162.863	−5.317
1700	57.659	373.997	327.979	78.230	92.222	167.282	−5.140
1800	57.717	377.294	330.628	83.999	92.315	171.694	−4.982
1900	57.765	380.416	333.167	89.773	92.392	176.102	−4.841
2000	57.807	383.380	335.604	95.552	92.452	180.506	−4.714
2100	57.843	386.201	337.947	101.335	92.493	184.908	−4.599
2200	57.874	388.893	340.202	107.121	92.514	189.308	−4.495
2300	57.902	391.466	342.375	112.909	92.514	193.708	−4.399
2400	57.926	393.931	344.472	118.701	92.490	198.107	−4.312
2500	57.947	396.296	346.498	124.494	92.441	202.509	−4.231
2600	57.966	398.569	348.457	130.290	92.367	206.913	−4.157
2700	57.983	400.757	350.354	136.088	92.266	211.321	−4.088
2800	57.998	402.866	352.192	141.887	92.137	215.733	−4.025
2900	58.012	404.901	353.975	147.687	91.981	220.149	−3.965
3000	58.024	406.868	355.705	153.489	91.796	224.572	−3.910
3100	58.035	408.771	357.387	159.292	91.584	229.002	−3.859
3200	58.046	410.614	359.021	165.096	91.345	233.438	−3.810
3300	58.055	412.400	360.612	170.901	91.081	237.882	−3.765
3400	58.063	414.133	362.161	176.707	90.793	242.335	−3.723
3500	58.071	415.817	363.670	182.514	90.482	246.796	−3.683
3600	58.078	417.453	365.141	188.321	90.151	251.267	−3.646
3700	58.085	419.044	366.577	194.129	89.802	255.747	−3.611
3800	58.091	420.593	367.978	199.938	89.437	260.238	−3.577
3900	58.096	422.102	369.346	205.747	89.060	264.737	−3.546
4000	58.101	423.573	370.684	211.557	88.673	269.247	−3.516
4100	58.106	425.008	371.991	217.368	88.278	273.766	−3.488
4200	58.111	426.408	373.270	223.178	87.879	278.295	−3.461
4300	58.115	427.775	374.522	228.990	87.478	282.834	−3.436
4400	58.119	429.111	375.748	234.801	87.077	287.381	−3.412
4500	58.122	430.418	376.948	240.614	86.680	291.938	−3.389
4600	58.126	431.695	378.124	246.426	86.288	296.503	−3.367
4700	58.129	432.945	379.277	252.239	85.904	301.077	−3.346
4800	58.132	434.169	380.408	258.052	85.529	305.659	−3.326
4900	58.135	435.368	381.518	263.865	85.167	310.250	−3.307
5000	58.137	436.542	382.607	269.679	84.817	314.846	−3.289
5100	58.140	437.694	383.675	275.492	84.482	319.451	−3.272
5200	58.142	438.823	384.725	281.307	84.162	324.060	−3.255
5300	58.144	439.930	385.756	287.121	83.860	328.677	−3.239
5400	58.146	441.017	386.770	292.935	83.575	333.299	−3.224
5500	58.148	442.084	387.766	298.750	83.309	337.926	−3.209
5600	58.150	443.132	388.745	304.565	83.062	342.558	−3.195
5700	58.152	444.161	389.708	310.380	82.834	347.193	−3.182
5800	58.154	445.172	390.656	316.196	82.625	351.834	−3.169
5900	58.155	446.166	391.588	322.011	82.435	356.476	−3.156
6000	58.157	447.144	392.506	327.827	82.265	361.122	−3.144

PREVIOUS: CURRENT: December 1995 (1bar)

$S°(298.15\ K) = [321.001]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-543.909]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-545.552]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[455](1)	[250](1)
[849](1)	[250](1)
[120](1)	[180](1)

Ground State Quantum Weights: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: O–Ti = [1.62] Å; Ti–Cl = [2.20] Å
Bond Angle: O–Ti–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.63214 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as −130 kcal·mol^{-1} by Gordon.[1] $\Delta_f H°(298.15\ K)$ was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] Principal moments of inertia are: $I_A = 17.8783 \times 10^{-39}$, $I_B = 42.7411 \times 10^{-39}$, and $I_C = 60.6194 \times 10^{-39}\ g·cm^2$.

Reference

[1] J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., personal communication, (January 10, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.710	−543.909	−543.909	INFINITE
100	51.425	252.861	380.084	−12.722	−544.846	−541.740	282.976
200	65.445	293.526	327.402	−6.775	−545.309	−538.428	140.623
250	69.250	308.562	322.172	−3.403	−545.448	−536.691	112.135
298.15	71.952	321.001	321.001	0.	−545.552	−534.994	93.729
300	72.041	321.447	321.003	0.133	−545.555	−534.929	93.139
350	74.138	332.717	321.888	3.790	−545.643	−533.150	79.568
400	75.739	342.726	323.879	7.539	−545.719	−531.360	69.389
450	76.976	351.721	326.481	11.358	−545.792	−529.561	61.470
500	77.945	359.883	329.420	15.232	−545.867	−527.754	55.134
600	79.330	374.226	335.725	23.101	−546.035	−524.116	45.628
700	80.243	386.528	342.125	31.082	−546.241	−520.447	38.836
800	80.870	397.286	348.362	39.140	−546.476	−516.747	33.740
900	81.318	406.839	354.338	47.250	−546.780	−513.013	29.775
1000	81.647	415.424	360.025	55.399	−547.219	−509.240	26.600
1100	81.896	423.218	365.421	63.577	−547.862	−505.412	24.000
1200	82.088	430.353	370.539	71.777	−552.693	−501.397	21.825
1300	82.240	436.930	375.396	79.993	−553.020	−497.110	19.974
1400	82.361	443.029	380.012	88.224	−553.438	−492.794	18.386
1500	82.459	448.715	384.405	96.465	−553.958	−488.445	17.009
1600	82.541	454.039	388.592	104.715	−554.596	−484.057	15.803
1700	82.608	459.045	392.591	112.973	−555.366	−479.626	14.737
1800	82.665	463.769	396.415	121.236	−556.281	−475.145	13.788
1900	82.714	468.239	400.079	129.505	−557.357	−470.609	12.938
2000	82.755	472.483	403.594	137.779	−573.294	−465.558	12.159
2100	82.791	476.522	406.971	146.056	−575.482	−460.118	11.445
2200	82.822	480.374	410.221	154.337	−577.690	−454.572	10.793
2300	82.849	484.056	413.351	162.620	−579.919	−448.926	10.195
2400	82.873	487.582	416.371	170.907	−582.172	−443.183	9.646
2500	82.894	490.966	419.288	179.195	−584.450	−437.345	9.138
2600	82.913	494.217	422.108	187.485	−586.753	−431.415	8.667
2700	82.929	497.347	424.837	195.777	−589.084	−425.396	8.230
2800	82.944	500.363	427.481	204.071	−591.441	−419.291	7.822
2900	82.958	503.274	430.044	212.366	−593.827	−413.101	7.441
3000	82.970	506.087	432.532	220.663	−596.241	−406.828	7.084
3100	82.981	508.807	434.949	228.960	−598.682	−400.473	6.748
3200	82.991	511.442	437.299	237.259	−601.150	−394.041	6.432
3300	83.000	513.996	439.584	245.558	−603.643	−387.530	6.134
3400	83.008	516.474	441.810	253.859	−606.161	−380.943	5.852
3500	83.016	518.880	443.977	262.160	−608.701	−374.283	5.586
3600	83.023	521.219	446.091	270.462	−611.261	−367.549	5.333
3700	83.029	523.494	448.152	278.764	−1022.938	−352.955	4.983
3800	83.035	525.708	450.164	287.068	−1024.297	−334.829	4.603
3900	83.041	527.865	452.129	295.371	−1025.725	−316.667	4.241
4000	83.046	529.968	454.049	303.676	−1027.217	−298.467	3.898
4100	83.051	532.018	455.925	311.981	−1028.768	−280.229	3.570
4200	83.055	534.020	457.761	320.286	−1030.375	−261.953	3.258
4300	83.059	535.974	459.557	328.592	−1032.034	−243.637	2.960
4400	83.063	537.883	461.316	336.898	−1033.739	−225.283	2.674
4500	83.066	539.750	463.038	345.204	−1035.487	−206.890	2.402
4600	83.070	541.576	464.726	353.511	−1037.273	−188.457	2.140
4700	83.073	543.362	466.380	361.818	−1039.093	−169.985	1.889
4800	83.076	545.111	468.002	370.126	−1040.943	−151.474	1.648
4900	83.079	546.824	469.593	378.433	−1042.819	−132.923	1.417
5000	83.081	548.503	471.155	386.741	−1044.718	−114.335	1.194
5100	83.084	550.148	472.687	395.049	−1046.636	−95.708	0.980
5200	83.086	551.761	474.193	403.358	−1048.570	−77.044	0.774
5300	83.088	553.344	475.671	411.667	−1050.516	−58.342	0.575
5400	83.090	554.897	477.124	419.976	−1052.473	−39.603	0.383
5500	83.092	556.422	478.552	428.285	−1054.437	−20.829	0.198
5600	83.094	557.919	479.956	436.594	−1056.406	−2.018	0.019
5700	83.096	559.390	481.337	444.903	−1058.379	16.828	−0.154
5800	83.097	560.835	482.695	453.213	−1060.352	35.709	−0.322
5900	83.099	562.256	484.031	461.523	−1062.325	54.623	−0.484
6000	83.100	563.652	485.347	469.833	−1064.296	73.571	−0.640

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

S(298.15 K) = 300.98 ± 5 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 136.5 ± 8 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 133.0 ± 8 kJ·mol^{-1}

Vibrational Levels and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
765 (1)	649.9 (1)
647.6 (1)	[440] (1)
[320] (1)	127 (1)

Ground State Quantum Weight = [1] σ = 1
Point Group: C_2
Bond Distances: Cl–O = 1.7044 ± 0.001 Å; O–O = 1.4259 ± 0.0021 Å
Bond Angles: ClOO = 110.07 ± 0.1°; dihedral angle = 81.03 ± 0.8°
Product of the Moments of Inertia: $I_A I_B I_C$ = 8.996135 × 10^{-114} g^3·cm^6

Enthalpy of Formation

The enthalpy of formation has been obtained from kinetic and equilibrium measurements of the rate of self reaction of ClO and the decomposition of the dimer to form the monomer unit. The results of these studies, as summarized by Cox and Hayman[1] indicate the dimer is bound by 17 kcal·mol^{-1} relative to the monomeric ClO. The $\Delta_r H$ and $\Delta_r S$, as determined by a lnK vs 1/T plot in the temperature range of 203–300 K, of the reaction of two monomeric units to form the dimer is −72.5 ± 3.0 kJ·mol^{-1} and −144 ± 11 J·K^{-1}·mol^{-1} respectively.[1] In this study, optical cross sections of the chlorine oxide species were used to determine the equilibrium constants as a function of temperature, from which the thermodynamic properties of the reaction of ClO to form $(ClO)_2$ were determined. These results are in agreement with previous results within combined experimental errors for the enthalpy of this reaction.[2] The cross sections measured by Cox and Hayman[1] are in agreement with recent results of Burkholder *et al.*[3] who measured the ultraviolet cross sections between 210 and 410 nm for $(ClO)_2$. These authors[3] also measured the infrared spectrum of $(ClO)_2$ and Cl_2O_3 in the region of 500 to 2000 cm^{-1} using a Fourier transform infrared spectrometer. Using the enthalpy of reaction given by Cox and Hayman[1] and the dissociation energy of ClO as determined by Coxon and Ramsay,[4] and the $^2\Pi_{1/2}$–$^2\Pi_{3/2}$ splitting A = 320 cm^{-1},[5] gives the value of 133 kJ·mol^{-1} at 298.15 K for the enthalpy of formation of $(ClO)_2$ with an estimated uncertainty of 8 kJ·mol^{-1}.

Heat Capacity and Entropy

The microwave spectrum of this species had been obtained by Birk *et al.*[6] The observered microwave spectrum is in substantial agreement with the earlier theoretical calculations which gave estimates of both the vibrational frequencies and molecular dimensions of the ClO dimer.[7] The molecular dimensions were used to compute the inertial parameters for the normally occuring isotopic species. The computed entropy for the $(ClO)_2$ species at 298.15 K is 300.98 J·K^{-1}·mol^{-1}. The measured entropy for the dimerization of ClO combined with the entropy of formation for ClO gave an $S°$(298.15 K) of 305.92 ± 11 J·mol^{-1}·K^{-1}. The major uncertainty in the computed entropy are the estimated frequencies 320 and 440 cm^{-1}. Lowering these estimated frequencies to 250 and 350 cm^{-1} increases the comuted $S°$(298.15 K) by 3.18 J·K^{-1}·mol^{-1}. This would decrease the calculated $\Delta_r S$, for the dimerization of ClO from −149 to −146 J·K^{-1}·mol^{-1} compared to the measured $\Delta_r S$ of −144 ± 11 J·K^{-1}·mol^{-1}.[1]

The vibrational spectrum of this species in the infrared region of 500 to 2000 cm^{-1} has been observed by Burkholder *et al.*[3] They observed three features that they could assign to $(ClO)_2$ at 750, 653 and 560 cm^{-1}. The two higher frequency absorptions correspond to the 750, 649, and 647 cm^{-1} found by Cheng and Lee[7] in the matrix isolated infrared spectra of the products of the reactions described below. These workers observed the three stretching modes by trapping the molecules formed, in a discharge system, by the reactions: Cl + O_3, Cl + OClO, O + OClO, Cl + ClOCl, and O + ClOCl in an argon matrix at 12 K. They obtained the Cl–O, (649.9 and 647.6 cm^{-1}) and O–O (752.6 cm^{-1}) stretching fundamentals, which have appropriate ^{35}Cl–^{37}Cl isotope shifts. The torsional mode, 127 cm^{-1}, estimated from the microwave measurements,[6] is in excellent agreement with the 119 cm^{-1} obtained in the quantum mechanical calculation.[7] The bending modes, 320 and 440 cm^{-1}, are obtained from the quantum mechanical calculation.[7]

Others have studied the infrared spectrum of the self reaction of ClO by reacting Cl with O_3, Cl_2O, or OClO in a flow system.[8] These workers observed the Cl–O and O–O stretching modes in addition to absorptions in the 1000 to 1250 cm^{-1} region, which they ascribed to $(ClO)_2$. Later workers suggest these bands are due to Cl_2O_3 produced from the termolecular reaction of OClO with ClO, including Burkholder et al.[3] and Cheng and Lee[6] and supported by quantum mechanical calculations of the frequencies of the $-ClO_2$ moiety.[6] Earlier workers who studied the infrared spectrum formed by reacting Cl + O_3 in a matrix have observed other absorptions which are probably due to other chlorine oxygen species.[9-12]

The principle moments of inertia (in g·cm^2) are: I_A = 6.4270 × 10^{-39}, I_B = 35.2686 × 10^{-39}, and I_C = 39.6879 × 10^{-39}.

References

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Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	.000	.000	INFINITE	−14.410	136.454	136.454	INFINITE
100	42.140	244.047	351.478	−10.743	134.305	146.131	−76.331
200	54.797	277.119	306.612	−5.899	133.200	158.466	−41.387
250	60.367	289.965	302.025	−3.015	133.007	164.809	−34.435
298.15	64.703	300.983	300.983	.000	133.000	170.938	−29.948
300	64.850	301.384	300.984	.120	133.003	171.173	−29.804
350	68.331	311.653	301.787	3.453	133.141	177.525	−26.494
400	71.010	320.960	303.611	6.940	133.381	183.851	−24.008
450	73.080	329.449	306.018	10.544	133.693	190.141	−22.071
500	74.694	337.235	308.756	14.240	134.052	196.395	−20.517
600	76.985	351.072	314.684	21.832	134.852	208.789	−18.177
700	78.481	363.059	320.758	29.611	135.704	221.045	−16.495
800	79.502	373.610	326.718	37.513	136.570	233.178	−15.225
900	80.226	383.018	332.461	45.501	137.432	245.202	−14.231
1000	80.757	391.499	337.947	53.552	138.284	257.130	−13.431
1100	81.157	399.216	343.172	61.648	139.121	268.975	−12.773
1200	81.465	406.291	348.141	69.780	139.943	280.743	−12.220
1300	81.707	412.822	352.869	77.939	140.746	292.444	−11.751
1400	81.901	418.884	357.370	86.120	141.532	304.083	−11.345
1500	82.058	424.540	361.662	94.318	142.298	315.667	−10.992
1600	82.187	429.840	365.759	102.531	143.043	327.200	−10.682
1700	82.295	434.826	369.676	110.755	143.767	338.688	−10.407
1800	82.386	439.533	373.428	118.989	144.468	350.133	−10.161
1900	82.463	443.989	377.025	127.231	145.144	361.541	−9.939
2000	82.528	448.221	380.480	135.481	145.793	372.913	−9.739
2100	82.585	452.249	383.803	143.737	146.415	384.254	−9.558
2200	82.634	456.092	387.002	151.998	147.007	395.566	−9.392
2300	82.677	459.766	390.086	160.264	147.568	406.851	−9.240
2400	82.715	463.286	393.063	168.533	148.096	418.112	−9.100
2500	82.749	466.663	395.940	176.806	148.590	429.353	−8.971
2600	82.779	469.909	398.723	185.083	149.048	440.574	−8.851
2700	82.805	473.034	401.418	193.362	149.470	451.779	−8.740
2800	82.829	476.045	404.030	201.644	149.855	462.969	−8.637
2900	82.850	478.952	406.563	209.928	150.203	474.144	−8.540
3000	82.869	481.761	409.024	218.214	150.514	485.310	−8.450
3100	82.887	484.479	411.414	226.502	150.789	496.466	−8.365
3200	82.903	487.111	413.739	234.791	151.029	507.612	−8.286
3300	82.917	489.662	416.001	243.082	151.235	518.752	−8.211
3400	82.930	492.138	418.204	251.374	151.409	529.886	−8.141
3500	82.942	494.542	420.351	259.668	151.553	541.015	−8.074
3600	82.953	496.878	422.444	267.963	151.670	552.141	−8.011
3700	82.963	499.151	424.487	276.259	151.762	563.264	−7.952
3800	82.973	501.364	426.481	284.555	151.831	574.385	−7.895
3900	82.982	503.519	428.429	292.853	151.881	585.505	−7.842
4000	82.990	505.620	430.332	301.152	151.915	596.622	−7.791
4100	82.997	507.670	432.194	309.451	151.935	607.740	−7.743
4200	83.004	509.670	434.015	317.751	151.944	618.857	−7.697
4300	83.011	511.623	435.797	326.052	151.946	629.974	−7.653
4400	83.017	513.531	437.542	334.353	151.942	641.090	−7.611
4500	83.022	515.397	439.252	342.655	151.935	652.207	−7.571
4600	83.027	517.222	440.927	350.958	151.929	663.324	−7.532
4700	83.032	519.008	442.569	359.261	151.923	674.442	−7.496
4800	83.037	520.756	444.180	367.564	151.922	685.559	−7.460
4900	83.041	522.468	445.760	375.868	151.926	696.677	−7.427
5000	83.046	524.146	447.311	384.172	151.936	707.794	−7.394
5100	83.049	525.790	448.834	392.477	151.955	718.912	−7.363
5200	83.053	527.403	450.329	400.782	151.982	730.027	−7.333
5300	83.056	528.985	451.799	409.088	152.020	741.144	−7.304
5400	83.060	530.537	453.242	417.394	152.067	752.259	−7.277
5500	83.063	532.062	454.662	425.700	152.125	763.373	−7.250
5600	83.066	533.558	456.057	434.006	152.194	774.486	−7.224
5700	83.068	535.029	457.430	442.313	152.272	785.598	−7.199
5800	83.071	536.473	458.780	450.620	152.362	796.709	−7.175
5900	83.074	537.893	460.109	458.927	152.460	807.816	−7.152
6000	83.076	539.290	461.417	467.234	152.568	818.923	−7.129

PREVIOUS: CURRENT: December 1992 (1 bar)

$S°(298.15\ K) = 309.17 \pm 2.0\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 178.8 \pm 10\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 176.4 \pm 15\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
952(1)
648(1)
403(1)
341(1)
236(1)
90(1)

Ground State Quantum Weight = [1]
Point Group: C_1
Bond Distances: Cl-O = 1.726 Å; O–Cl' = 1.814 Å; Cl'–O' = 1.532 Å
Bond Angles: ClOCl' = 111.0°; OCl'O' = 113.5°; dihedral angle: = 75.7°
Product of the Moments of Inertia: $I_A I_B I_C = 8.362433 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation has been calculated, by numerous quantum mechanical methods, by McGrath, *et al.*[1,2] and Lee.[3] These calculations suggested that the ClOClO isomer is less stable than the ClOOCl isomer by 31 to 42 $kJ \cdot mol^{-1}$. We adopt the results of Lee[3] which stated that the ClOClO isomer was 10.1 $kcal \cdot mol^{-1}$ or 42.3 $kJ \cdot mol^{-1}$ higher in energy than the ClOOCl isomer at $T/K = 0$.

Heat Capacity and Entropy

The structure and harmonic vibrational frequencies of ClOClO have been calculated, by numerous quantum mechanical methods, by McGrath, *et al.*,[1,2] Lee,[3] and Rendell and Lee.[4] We adopt the results of Lee.[3] The structures (bond distances and bond angles), as presented in these above mentioned studies are in fair agreement: within 5%, except for the dihedral angle where the difference is approximately 11%. The principal moments of inertia are (in $g \cdot cm^2$): $I_A = 6.2905 \times 10^{-39}$, $I_B = 34.7070 \times 10^{-39}$, and $I_C = 38.3028 \times 10^{-39}$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−15.476	178.754	178.754	INFINITE
100	46.365	247.309	363.316	−11.601	176.813	188.313	−98.365
200	59.481	283.809	315.103	−6.259	176.206	200.134	−52.270
250	64.001	297.588	310.257	−3.167	176.221	206.117	−43.066
298.15	67.416	309.165	309.165	.000	176.366	211.864	−37.118
300	67.532	309.583	309.166	.125	176.374	212.084	−36.927
350	70.293	320.209	309.999	3.573	176.627	218.017	−32.537
400	72.460	329.742	311.882	7.144	176.952	223.909	−29.239
450	74.169	338.379	314.353	10.812	177.326	229.756	−26.669
500	75.529	346.267	317.156	14.555	177.733	235.560	−24.609
600	77.505	360.225	323.201	22.214	178.600	247.045	−21.507
700	78.828	372.278	329.371	30.035	179.494	258.382	−19.281
800	79.748	382.868	335.410	37.966	180.389	269.591	−17.602
900	80.408	392.301	341.217	45.976	181.273	280.688	−16.291
1000	80.897	400.799	346.757	54.042	182.141	291.687	−15.236
1100	81.267	408.528	352.026	62.151	182.990	302.601	−14.369
1200	81.554	415.612	357.034	70.293	183.821	313.437	−13.644
1300	81.781	422.149	361.795	78.460	184.633	324.206	−13.027
1400	81.963	428.216	366.325	86.648	185.425	334.912	−12.496
1500	82.111	433.876	370.642	94.852	186.197	345.562	−12.034
1600	82.233	439.180	374.762	103.069	186.948	356.162	−11.628
1700	82.335	444.168	378.699	111.298	187.676	366.716	−11.268
1800	82.421	448.877	382.468	119.535	188.380	377.227	−10.947
1900	82.494	453.335	386.082	127.781	189.060	387.700	−10.659
2000	82.556	457.568	389.551	136.034	189.712	398.137	−10.398
2100	82.610	461.597	392.887	144.292	190.337	408.543	−10.162
2200	82.657	465.442	396.098	152.556	190.931	418.921	−9.946
2300	82.698	469.117	399.193	160.823	191.494	429.271	−9.749
2400	82.734	472.637	402.181	169.095	192.024	439.597	−9.568
2500	82.766	476.015	405.067	177.370	192.519	449.902	−9.400
2600	82.794	479.262	407.859	185.648	192.979	460.188	−9.245
2700	82.820	482.387	410.561	193.929	193.403	470.458	−9.102
2800	82.842	485.399	413.181	202.212	193.789	480.712	−8.968
2900	82.863	488.307	415.721	210.497	194.139	490.952	−8.843
3000	82.881	491.116	418.188	218.785	194.451	501.182	−8.726
3100	82.898	493.834	420.585	227.074	194.727	511.402	−8.617
3200	82.913	496.466	422.915	235.364	194.968	521.613	−8.514
3300	82.927	499.018	425.183	243.656	195.175	531.817	−8.418
3400	82.939	501.494	427.391	251.949	195.350	542.016	−8.327
3500	82.951	503.898	429.543	260.244	195.495	552.210	−8.241
3600	82.961	506.235	431.641	268.539	195.613	562.400	−8.160
3700	82.971	508.508	433.688	276.836	195.705	572.587	−8.083
3800	82.980	510.721	435.686	285.134	195.775	582.773	−8.011
3900	82.988	512.877	437.638	293.432	195.826	592.956	−7.942
4000	82.996	514.978	439.545	301.731	195.860	603.138	−7.876
4100	83.003	517.027	441.410	310.031	195.881	613.320	−7.814
4200	83.010	519.027	443.234	318.332	195.891	623.501	−7.754
4300	83.016	520.981	445.020	326.633	195.893	633.683	−7.698
4400	83.022	522.889	446.768	334.935	195.890	643.864	−7.644
4500	83.027	524.755	448.480	343.238	195.884	654.044	−7.592
4600	83.032	526.580	450.158	351.541	195.877	664.226	−7.543
4700	83.037	528.366	451.803	359.844	195.873	674.407	−7.495
4800	83.042	530.114	453.417	368.148	195.872	684.589	−7.450
4900	83.046	531.826	454.999	376.452	195.876	694.771	−7.406
5000	83.050	533.504	456.553	384.757	195.887	704.952	−7.365
5100	83.053	535.149	458.078	393.062	195.906	715.134	−7.324
5200	83.057	536.762	459.575	401.368	195.934	725.314	−7.286
5300	83.060	538.344	461.047	409.674	195.972	735.495	−7.249
5400	83.063	539.896	462.493	417.980	196.019	745.673	−7.213
5500	83.066	541.420	463.914	426.286	196.078	755.851	−7.178
5600	83.069	542.917	465.311	434.593	196.147	766.029	−7.145
5700	83.072	544.388	466.686	442.900	196.226	776.204	−7.113
5800	83.074	545.832	468.038	451.207	196.315	786.380	−7.082
5900	83.076	547.252	469.369	459.515	196.414	796.551	−7.052
6000	83.079	548.649	470.678	467.823	196.522	806.722	−7.023

PREVIOUS: CURRENT: December 1992 (1 bar)

$S°(298.15\ K) = 294.41 \pm 2.0\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 140.7 \pm 12\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 136.6 \pm 16\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1041.5(1)	271.4(1)
522.7(1)	1281.2(1)
440.5(1)	251.4(1)

Ground State Quantum Weight = [1]
Point Group: C_s
Bond Distances: Cl-O = 1.440 ± 0.005 Å; Cl-Cl = 2.22 ± 0.06 Å
Bond Angles: ∠(ClClO) = 103.5 ± 1°; ∠(OClO) = 116.0 ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 6614.3322 \times 10^{-117}$ $g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation has been calculated, by numerous quantum mechanical methods, by McGrath, *et al.*[1,2], Lee *et al.*,[3] Jensen and Oddershede,[4] and Stanton, *et al.*[5] These calculations suggested that the $ClClO_2$ isomer is less stable than the ClOOCl isomer by 4.2 to 32 $kJ \cdot mol^{-1}$. We adopt the results of Lee[3] which stated that the $ClClO_2$ isomer was 4.2 $kJ \cdot mol^{-1}$ higher in energy than the ClOOCl isomer at $T/K = 0$.

Heat Capacity and Entropy

The vibrational frequencies (ν_1, ν_2, ν_3, and ν_5) are taken from the gas phase infared studies of Müller and Willner,[6,7] while ν_4 and ν_6 are taken from the Ne martrix infrared studies of Müller and Willner.[6,8] The same authors also provided values for all vibrational frequencies in Ne matrices, as well as values for ν_1 and ν_5 in Ar matrices.

The structure is that estimated by Müller and Willner.[6] The results were based on a combination of: use of product rules in the symmetry class A" with vibrational frequencies of four independent isotopomers, in conjunction with expermental and ab initio results of related compounds. The principal moments of inertia are (in $g \cdot cm^2$): $I_A = 9.0179 \times 10^{-39}$, $I_B = 23.8814 \times 10^{-39}$, and $I_C = 30.7121 \times 10^{-39}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.762	140.652	140.652	INFINITE
100	39.852	239.842	342.580	−10.274	138.324	150.571	−78.650
150	47.043	257.397	311.376	−8.097	137.558	156.873	−54.628
200	52.769	271.751	299.727	−5.595	137.054	163.393	−42.674
250	57.214	284.022	295.388	−2.841	136.731	170.019	−35.523
298.15	60.703	294.407	294.407	.000	136.550	176.448	−30.913
300	60.825	294.783	294.408	.112	136.545	176.696	−30.765
350	63.852	304.393	295.160	3.231	136.469	183.395	−27.370
400	66.416	313.092	296.867	6.490	136.482	190.099	−24.824
450	68.589	321.043	299.118	9.867	136.565	196.796	−22.844
500	70.429	328.368	301.681	13.343	136.705	203.482	−21.258
600	73.306	341.477	307.247	20.538	137.108	216.802	−18.874
700	75.381	352.942	312.973	27.978	137.621	230.045	−17.166
800	76.901	363.112	318.617	35.596	138.203	243.209	−15.880
900	78.036	372.238	324.077	43.345	138.826	256.297	−14.875
1000	78.898	380.507	329.313	51.194	139.476	269.315	−14.068
1100	79.566	388.059	334.315	59.118	140.142	282.267	−13.404
1200	80.092	395.006	339.087	67.102	140.815	295.158	−12.848
1300	80.513	401.434	343.639	75.133	141.491	307.992	−12.375
1400	80.854	407.413	347.983	83.202	142.164	320.775	−11.968
1500	81.133	413.001	352.133	91.302	142.832	333.509	−11.614
1600	81.366	418.245	356.103	99.427	143.490	346.200	−11.302
1700	81.560	423.184	359.905	107.574	144.136	358.849	−11.026
1800	81.725	427.851	363.552	115.738	144.767	371.461	−10.780
1900	81.866	432.273	367.053	123.918	145.380	384.038	−10.558
2000	81.987	436.476	370.420	132.111	145.973	396.584	−10.358
2100	82.092	440.478	373.662	140.315	146.543	409.100	−10.176
2200	82.183	444.299	376.786	148.529	147.088	421.591	−10.010
2300	82.263	447.954	379.802	156.751	147.606	434.056	−9.858
2400	82.333	451.457	382.715	164.981	148.094	446.499	−9.718
2500	82.396	454.819	385.532	173.218	148.551	458.923	−9.589
2600	82.451	458.052	388.260	181.460	148.975	471.330	−9.469
2700	82.501	461.165	390.902	189.708	149.365	483.721	−9.358
2800	82.545	464.166	393.466	197.960	149.721	496.098	−9.255
2900	82.585	467.063	395.954	206.217	150.042	508.462	−9.158
3000	82.622	469.863	398.371	214.477	150.327	520.817	−9.068
3100	82.654	472.573	400.721	222.741	150.578	533.163	−8.984
3200	82.684	475.198	403.008	231.008	150.796	545.500	−8.904
3300	82.711	477.743	405.234	239.278	150.981	557.831	−8.830
3400	82.736	480.212	407.403	247.550	151.135	570.158	−8.759
3500	82.759	482.611	409.518	255.825	151.260	582.480	−8.693
3600	82.780	484.942	411.581	264.102	151.359	594.799	−8.630
3700	82.799	487.211	413.594	272.381	151.434	607.116	−8.571
3800	82.817	489.419	415.561	280.662	151.487	619.431	−8.515
3900	82.834	491.571	417.482	288.944	151.522	631.746	−8.461
4000	82.849	493.668	419.361	297.228	151.541	644.058	−8.411
4100	82.863	495.714	421.198	305.514	151.548	656.371	−8.362
4200	82.876	497.711	422.996	313.801	151.544	668.684	−8.316
4300	82.888	499.661	424.757	322.089	151.533	680.997	−8.272
4400	82.900	501.567	426.481	330.378	151.517	693.310	−8.231
4500	82.911	503.430	428.170	338.669	151.499	705.623	−8.191
4600	82.921	505.252	429.826	346.961	151.481	717.937	−8.152
4700	82.930	507.036	431.450	355.253	151.466	730.252	−8.116
4800	82.939	508.782	433.043	363.547	151.454	742.567	−8.081
4900	82.947	510.492	434.606	371.841	151.448	754.882	−8.047
5000	82.955	512.168	436.141	380.136	151.450	767.197	−8.015
5100	82.962	513.811	437.648	388.432	151.459	779.512	−7.984
5200	82.969	515.422	439.128	396.728	151.479	791.826	−7.954
5300	82.976	517.002	440.582	405.026	151.508	804.141	−7.925
5400	82.982	518.553	442.012	413.324	151.547	816.454	−7.898
5500	82.988	520.076	443.417	421.622	151.598	828.766	−7.871
5600	82.993	521.571	444.800	429.921	151.659	841.078	−7.845
5700	82.999	523.040	446.159	438.221	151.730	853.388	−7.820
5800	83.004	524.484	447.497	446.521	151.813	865.698	−7.796
5900	83.008	525.903	448.814	454.821	151.905	878.004	−7.773

PREVIOUS: CURRENT: December 1992 (1 bar)

$S°(298.15\ K) = 311.095 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -348.56 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -354.80 \pm 2.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies (ω, cm^{-1}, all singly degenerate)								
1205	577	406	209	208	1434	388	586	363

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: S–O = 1.404 ± 0.004 Å; S–Cl = 2.011 ± 0.005 Å
Bond Angles: O–S–O = 123.5 ± 0.8°; Cl–S–Cl = 100.0 ± 0.7°
Product of the Moments of Inertia: $I_A I_B I_C = 3.80579 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H° = -84.8 \pm 0.5\ kcal \cdot mol^{-1}$ is based on K_p for dissociation to SO_2 and Cl_2 (see below). The relatively thorough study of Arii[2] gave similar values of K_p near the pressure of SO_2Cl_2 and at reduced pressures. The entropy discrepancy is large ($\delta S = -11\ cal \cdot K^{-1} \cdot mol^{-1}$), but this may be due to the small temperature range and to uncertainties in absorption on the activated charcoal catalyst. Absorption uncertainties probably exist in all of the K_p studies, but the high– temperature data of Trautz[3] have an additional uncertainty; i.e., K_p is very sensitive to small systematic errors in the data since the SO_2Cl_2 is almost completely decomposed. Exclusion of data[3] above 416 K yields a 3rd law $\Delta_f H°$ which agrees satisfactorily with Arii.[2] Data of Londergan[1] yield a 3rd law $\Delta_f H°$ which is smaller by about 0.4 $kcal \cdot mol^{-1}$; these data yield almost no entropy discrepancy, but the experimental method[1] appears to be less satisfactory.

The adopted $\Delta_f H°$ is consistent with old calorimetric data of Thomsen[5] for hydrolysis of the liquid but inconsistent with recent data of Neale and Williams,[4] on which the selections of NBS 270–3[6] are probably based. Consistency tests require $\Delta_v H$; thus, we note that in the absence of a catalyst SO_2Cl_2(g) persists to well above the boiling point even though it is unstable with respect to SO_2 and Cl_2. Evidence for this conclusion includes studies of catalysts,[3,7] vapor densities,[8] boiling point and vapor pressures.[9,10,7] The boiling point (69.5 ± 0.3 °C) and $\Delta_{vap}S$ (20.8 $cal \cdot K^{-1} \cdot mol^{-1}$) are almost exactly those predicted by comparison with SO_2ClF (7.3 °C and 20.6 $cal \cdot K^{-1} \cdot mol^{-1}$) and SO_2F_2 (−55.3°C and 21.1 $cal \cdot K^{-1} \cdot mol^{-1}$), which have normal vapors. Vapor pressure data[9] for SO_2Cl_2 yield $\Delta_v H$ = 7.1 $kcal \cdot mol^{-1}$ at 69.5 °C and $\Delta_v H°$ = 7.8 $kcal \cdot mol^{-1}$ at 25°C. Trautz *et al.*[10] used a condensation method to measure $\Delta_{vap}H$ = 6.67 $kcal \cdot mol^{-1}$ near Tb, but we dismiss this value since the resulting $\Delta_{vap}S$ (19.5 $cal \cdot K^{-1} \cdot mol^{-1}$) is too small for normal vapor and much too small for dissociating vapor.

Source	Data	Reaction[a]	T/K	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	δS, cal·K⁻¹mol⁻¹	$\Delta_f H°$(298.15 K), kcal·mol[b] gas	liquid
1	K_p	A	340–373	13.08 ± 0.05	13.41 ± 0.3	−0.9 ± 0.1	−84.36	(−92.1)
2	K_p	A	303–323	10.41 ± 0.13	13.84 ± 0.2	−10.9 ± 0.4	−84.79	(−92.6)
3	K_p	A	375–464	6.33 ± 0.51	14.2 ± 1.1	−19.2 ± 1.2	−85.2	(−93.0)
			375–416	—	13.91 ± 0.4	—	−84.86	(−92.7)
4	$\Delta_r H$	B	295–296	—	−63.4 ± 0.5[c]	—	(−86.1)	−93.9
5	$\Delta_r H$	B	291–293	—	−63.6 ± 0.5			
6	4?	B?	298?	—	−63.1	—	−87.0	−94.2

[a] A) $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$; B) $SO_2Cl_2(l) + 2\ H_2O(l) \rightarrow [H_2SO_4 + 2HCl](nH_2O)$
[b] Values in parentheses calculated from $\Delta_{vap}H°$ = 7.8 $kcal \cdot mol^{-1}$ at 25°C.
[c] *Calorimetric $\Delta_r H$ adjusted to 25°C.*

Heat Capacity and Entropy

Bond lengths and bond angles are those derived from new electron–diffraction data by Hargittai.[11] These differ significantly from early results of Palmer.[12] Microwave spectra were reported by Abbar,[13] but structural parameters were not derived from the data. The adopted structure has an O–S–Cl angle of 107.7° and principal moments of inertia of $I_A = 24.0520 \times 10^{-39}$, $I_B = 36.0706 \times 10^{-39}$, and $I_C = 43.8672 \times 10^{-39}\ g \cdot cm^2$.

The vibrational assignment is from force–constant calculations of Toyuki and Shimizu.[14] Pfeiffer's assignment[15] is only slightly different and results in negligible change in the thermodynamic functions. Spectral data were summarized by Gillespie and Robinson[16] in their study of the liquid–phase Raman spectra. Only those frequencies above 500 cm^{-1} are based on gas–phase spectra. Trautz *et al.*[10] found $C_p = 15.4 \pm 0.3\ J \cdot K^{-1} \cdot mol^{-1}$ by calorimetry at 43 mmHg and 16 to 99°C; this C_p is too low, like $\Delta_{vap}H$,[10] and the error is almost 20%.

References

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Continued on page 938

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−16.028	−348.555	−348.555	INFINITE
100	43.179	245.860	370.394	−12.453	−351.487	−338.589	176.861
200	64.505	282.771	317.789	−7.004	−353.628	−324.765	84.820
250	71.750	297.982	312.336	−3.589	−354.309	−317.466	66.331
298.15	77.095	311.095	311.095	0.	−354.803	−310.323	54.367
300	77.276	311.573	311.097	0.143	−354.820	−310.047	53.984
350	81.651	323.826	312.055	4.120	−355.204	−302.553	45.154
400	85.216	334.969	314.233	8.294	−357.706	−294.923	38.513
450	88.175	345.182	317.112	12.631	−358.588	−287.030	33.318
500	90.655	354.604	320.396	17.104	−359.455	−279.030	29.150
600	94.520	371.494	327.538	26.373	−360.562	−262.831	22.881
700	97.321	386.286	334.896	35.973	−361.236	−246.485	18.393
800	99.387	399.423	342.156	45.813	−361.643	−230.062	15.021
900	100.940	411.223	349.186	55.833	−415.006	−212.518	12.334
1000	102.128	421.922	355.933	65.989	−413.905	−190.078	9.929
1100	103.052	431.701	362.383	76.250	−412.775	−167.749	7.966
1200	103.783	440.700	368.539	86.593	−411.629	−145.525	6.335
1300	104.370	449.031	374.414	97.002	−410.478	−123.396	4.958
1400	104.847	456.784	380.024	107.463	−409.330	−101.356	3.782
1500	105.240	464.031	385.386	117.968	−408.190	−79.398	2.765
1600	105.566	470.834	390.516	128.509	−407.065	−57.515	1.878
1700	105.840	477.242	395.431	139.080	−405.957	−35.702	1.097
1800	106.073	483.299	400.146	149.676	−404.871	−13.954	0.405
1900	106.271	489.039	404.675	160.293	−403.810	7.735	−0.213
2000	106.442	494.495	409.030	170.929	−402.775	29.368	−0.767
2100	106.590	499.692	413.225	181.581	−401.770	50.950	−1.267
2200	106.719	504.653	417.269	192.246	−400.796	72.486	−1.721
2300	106.833	509.400	421.172	202.924	−399.855	93.977	−2.134
2400	106.933	513.949	424.944	213.613	−398.949	115.428	−2.512
2500	107.021	518.316	428.592	224.310	−398.080	136.843	−2.859
2600	107.100	522.515	432.124	235.016	−397.247	158.223	−3.179
2700	107.170	526.558	435.547	245.730	−396.453	179.573	−3.474
2800	107.233	530.457	438.867	256.450	−395.697	200.893	−3.748
2900	107.290	534.221	442.091	267.176	−394.980	222.186	−4.002
3000	107.342	537.859	445.223	277.908	−394.302	243.457	−4.239
3100	107.388	541.379	448.268	288.645	−393.662	264.705	−4.460
3200	107.431	544.790	451.232	299.386	−393.058	285.932	−4.667
3300	107.469	548.096	454.117	310.131	−392.490	307.142	−4.862
3400	107.505	551.305	456.929	320.879	−391.956	328.335	−5.044
3500	107.537	554.422	459.670	331.632	−391.454	349.512	−5.216
3600	107.567	557.451	462.344	342.387	−390.981	370.676	−5.378
3700	107.594	560.399	464.955	353.145	−390.535	391.827	−5.532
3800	107.620	563.269	467.504	363.906	−390.115	412.967	−5.677
3900	107.643	566.065	469.996	374.669	−389.716	434.095	−5.814
4000	107.665	568.790	472.432	385.434	−389.338	455.214	−5.944
4100	107.685	571.449	474.814	396.202	−388.976	476.323	−6.068
4200	107.704	574.044	477.146	406.971	−388.628	497.423	−6.186
4300	107.721	576.579	479.429	417.742	−388.293	518.516	−6.299
4400	107.738	579.055	481.665	428.515	−387.966	539.601	−6.406
4500	107.753	581.477	483.857	439.290	−387.647	560.678	−6.508
4600	107.767	583.845	486.005	450.066	−387.333	581.748	−6.606
4700	107.781	586.163	488.111	460.843	−387.023	602.812	−6.699
4800	107.793	588.432	490.178	471.622	−386.714	623.869	−6.789
4900	107.805	590.655	492.205	482.402	−386.406	644.920	−6.875
5000	107.816	592.833	494.196	493.183	−386.096	665.964	−6.957
5100	107.827	594.968	496.151	503.965	−385.784	687.003	−7.036
5200	107.836	597.062	498.072	514.748	−385.470	708.034	−7.112
5300	107.846	599.116	499.959	525.532	−385.152	729.060	−7.185
5400	107.855	601.132	501.814	536.317	−384.831	750.080	−7.256
5500	107.863	603.111	503.638	547.103	−384.506	771.093	−7.323
5600	107.871	605.055	505.432	557.890	−384.177	792.102	−7.388
5700	107.878	606.964	507.196	568.678	−383.845	813.104	−7.451
5800	107.885	608.840	508.933	579.466	−383.509	834.101	−7.512
5900	107.892	610.685	510.642	590.255	−383.171	855.089	−7.570
6000	107.899	612.498	512.324	601.044	−382.832	876.075	−7.627

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = [200.832]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -780.32 \pm 5.9\ kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev *et al.*[1] measured calorimetrically the enthalpies of reaction (1) and (2) at 298.15 K at -67.3 ± 0.2 and -13.6 ± 0.11 kcal·mol^{-1}, respectively. The reactions are given as follows: (1) WO_2Cl_2(cr) + 4 NaOH(aq, 16.3 H_2O) → Na_2WO_4(aq, 80000 H_2O) + 2 NaCl(aq, 40000 H_2O) + 2 H_2O(l) and (2) H_2WO_4(cr) + 2 NaOH(aq, 16.3 H_2O) → Na_2WO_4(aq, 20000 H_2O) + 2 H_2O(l).

Based on these data and the enthalpies of dilution for NaOH(aq), NaCl(aq) and Na_2WO_4(aq), we obtain $\Delta_f H°(298.15\ K) = 53.77 \pm 1.0$ kcal·mol^{-1} for WO_2Cl_2(cr) + 2 OH^-(aq, ∞) → H_2WO_4(cr) + 2 Cl^-(aq,∞). This leads to $\Delta_f H°(WO_2Cl_2$, cr, 298.15 K) = -186.5 kcal·mol^{-1} using $\Delta_f H°(H_2WO_4$, cr, 298.15 K) = -270.5 ± 0.4 kcal·mol^{-1}.

Heat Capacity and Entropy

$C_p°(300) = 25.0$ cal·K^{-1}·mol^{-1} *is estimated using Kopp's rule. Heat capacities at higher temperature are estimated from those of* WO_2(cr), WO_3(cr), WCl_6(cr). The entropy $S°(298.15\ K) = 48.0$ cal·K^{-1}·mol^{-1} is calculated from $\Delta S°(598.6\ K) = 32.27 \pm 1.3$ cal·K^{-1}·mol^{-1} for WO_2Cl_2(cr) → WO_2Cl_2(g). The value of $\Delta S°(598.6\ K)$ is obtained from the 2nd law analysis of the vapor pressure data given by Shchukarev and Suvorov.[4]

Decomposition Data

Shchukarev and Suvorov[4] found that WO_2Cl_2(cr) does not melt but decomposes. The saturated vapor over WO_2Cl_2(cr) consists mainly of $WOCl_4$(g) which will disproportionate to form WO_2Cl_2(g) and WCl_6(g). The estimated $T_{dcm} = 642$ K is derived by interpolation to one atmosphere in the total pressures of $WOCl_4$(g), WO_2Cl_2(g) reported by Shchukarev and Suvorov.[4]

References

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[3]We have assumed $\Delta_{dil}H° = 0$ for Na_2WO_4(aq, 20000 H_2O) → Na_2WO_4(aq, 80000 H_2O).
[4]S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev *et al.*, Zh. Neorg. Khim. **3**, 2630 (1958); **5**, 1650 (1960), have been revised and they are not used here.
[5]JANAF Thermochemical Tables: H_2WO_4(cr), 3–31–67.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.408	200.832	200.832	0.	−780.316	−702.781	123.124
300	104.600	201.478	200.834	0.193	−780.285	−702.300	122.281
400	115.060	233.003	205.062	11.176	−778.207	−676.597	88.354
500	125.520	259.809	213.391	23.209	−775.319	−651.511	68.063
600	135.562	283.597	223.145	36.272	−771.605	−627.085	54.593
700	144.557	305.202	233.347	50.298	−767.106	−603.344	45.022
800	151.042	324.947	243.581	65.092	−761.993	−580.292	37.889
900	155.854	343.031	253.641	80.451	−756.449	−557.909	32.380
1000	158.992	359.629	263.422	96.207	−750.625	−536.159	28.006

PREVIOUS: September 1962 CURRENT: March 1967

$S°(298.15\ K)$ = [353.927] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -668.2 \pm 25$ $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -671.5 \pm 25$ $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
984 (1)	[400](1)	[150](1)
972 (1)	[300](1)	[100](1)
[400](1)	[300](1)	[100](1)

Ground State Quantum Weight: 1 σ = [2]
Point Group: [C_{2v}]
Bond Distances: W–Cl = [2.26] Å; W–O = [1.81] Å
Bond Angles: Cl–W–Cl = [113]°; O–W–O = [109.47]°; O–W–Cl = [90]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.16512 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(WO_2Cl_2, g, 298.15\ K) = -160.5$ kcal·mol^{-1} is obtained from $\Delta_r H°(298.15\ K) = 26.0$ kcal·mol^{-1} for $WO_2Cl_2(cr) \rightarrow WO_2Cl_2(g)$. The latter is calculated by the 3rd law method from the partial pressures of $WO_2Cl_2(g)$ given by Shchukarev and Suvorov.[6] 2nd law analysis gives $\Delta_r H°(598.6\ K) = 24.1 \pm 0.8$ kcal·mol^{-1} $\Delta_r H°(298.15\ K) = 26.0$ kcal·mol^{-1}. These reported partial vapor pressures of $WO_2Cl_2(g)$ were derived by the optical tensimetric method from total pressures over $WO_2Cl_2(cr)$ considering the species $WOCl_4(g)$, $WO_2Cl_2(g)$ and $WCl_6(g)$. Since the decomposition of $WO_2Cl_2(cr)$ was very complicated, we tentatively assign 6 kcal·mol^{-1} uncertainty to the adopted enthalpy of formation.

Shchukarev and Suvorov[6] have also derived a log K_p equation for the disproportionation process, 2 $WOCl_4(g) = WO_2Cl_2(g) + WCl_6(g)$. 3rd law analysis gives $\Delta_r H°(298.15\ K) = 10.3$ kcal·mol^{-1} for the above process. This leads to $\Delta_f H°(WO_2Cl_2, g, 298.15\ K) = -145.7 \pm 16$ kcal·mol^{-1}. The 2nd law $\Delta_r H°(590\ K)$ is 11.0 kcal·mol^{-1} $\Delta_r H°(298.15\ K) = 10.1$ kcal·mol^{-1}. The drift in the 3rd law analysis is 0.3 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The molecular configuration is assumed to be a distorted tetrahedron of C_{2v} symmetry, similar to that of $MoO_2Cl_2(g)$,[1] and $CrO_2Cl_2(g)$.[2] The bond distances W–O and W–Cl are estimated to be the same as those in $WO_3(g)$ and $WCl_6(g)$, respectively. The bond angles are assumed to be the same as those in $MoO_2Cl_2(g)$.[1] The principal moments of inertia are: $I_A = 33.9761 \times 10^{-39}$, $I_B = 53.4238 \times 10^{-39}$, and $I_C = 64.1894 \times 10^{-39}$ g·cm.[2]

The vibrational frequencies, 984 cm^{-1} and 972 cm^{-1}, were observed in the infrared spectra Barraclough and Stals.[3] They tentatively assigned these two as the symmetric and asymmetric W–O stretching frequencies. The rest of the frequencies are estimated by comparison with those observed in the infrared and Raman spectra for $CrO_2Cl_2(g)$.[4,5] They are not listed in point group order.

References

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Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−19.504	−668.198	−668.198	INFINITE
100	59.017	273.602	424.320	−15.072	−670.235	−660.403	344.959
200	77.605	320.992	361.629	−8.127	−671.247	−650.101	169.789
250	83.093	338.927	355.341	−4.104	−671.457	−644.787	134.721
298.15	87.199	353.927	353.927	0.	−671.532	−639.642	112.063
300	87.339	354.467	353.929	0.161	−671.533	−639.445	111.337
350	90.723	368.194	355.006	4.616	−671.497	−634.098	94.634
400	93.447	380.493	357.436	9.223	−671.376	−628.762	82.108
450	95.648	391.631	360.627	13.952	−671.192	−623.446	72.368
500	97.435	401.804	364.243	18.781	−670.963	−618.153	64.578
600	100.093	419.820	372.043	28.666	−670.427	−607.640	52.900
700	101.913	435.394	380.006	38.772	−669.848	−597.221	44.565
800	103.198	449.092	387.803	49.031	−669.271	−586.886	38.320
900	104.131	461.303	395.304	59.400	−668.717	−576.621	33.466
1000	104.827	472.312	402.463	69.849	−668.199	−566.417	29.587
1100	105.358	482.329	409.275	80.360	−667.727	−556.261	26.415
1200	105.771	491.515	415.751	90.917	−667.305	−546.147	23.773
1300	106.098	499.995	421.909	101.511	−666.937	−536.066	21.539
1400	106.361	507.867	427.771	112.134	−666.625	−526.011	19.626
1500	106.576	515.213	433.359	122.781	−666.372	−515.977	17.968
1600	106.753	522.097	438.692	133.448	−666.182	−505.957	16.518
1700	106.902	528.574	443.791	144.131	−666.057	−495.947	15.239
1800	107.027	534.688	448.672	154.828	−665.998	−485.943	14.102
1900	107.133	540.477	453.353	165.536	−666.009	−475.940	13.084
2000	107.224	545.975	457.848	176.254	−666.092	−465.934	12.169
2100	107.303	551.208	462.170	186.980	−666.249	−455.923	11.340
2200	107.371	556.201	466.331	197.714	−666.484	−445.901	10.587
2300	107.431	560.976	470.343	208.454	−666.797	−435.869	9.899
2400	107.484	565.549	474.216	219.200	−667.191	−425.821	9.268
2500	107.531	569.938	477.957	229.951	−667.668	−415.754	8.687
2600	107.572	574.156	481.577	240.706	−668.227	−405.666	8.150
2700	107.609	578.217	485.081	251.465	−668.894	−395.555	7.652
2800	107.643	582.131	488.478	262.228	−669.707	−385.417	7.190
2900	107.672	585.909	491.773	272.994	−670.703	−375.248	6.759
3000	107.699	589.559	494.972	283.762	−671.911	−365.039	6.356
3100	107.724	593.091	498.080	294.533	−673.373	−354.786	5.978
3200	107.746	596.512	501.103	305.307	−675.119	−344.483	5.623
3300	107.766	599.827	504.045	316.083	−677.174	−334.120	5.289
3400	107.785	603.045	506.909	326.860	−679.570	−323.689	4.973
3500	107.802	606.169	509.701	337.639	−682.371	−313.182	4.674
3600	107.817	609.207	512.423	348.420	−685.669	−302.589	4.390
3700	107.832	612.161	515.079	359.203	−724.329	−291.705	4.118
3800	107.845	615.037	517.672	369.987	−725.329	−279.999	3.849
3900	107.857	617.838	520.204	380.772	−726.348	−268.266	3.593
4000	107.868	620.569	522.679	391.558	−727.383	−256.507	3.350
4100	107.879	623.233	525.100	402.345	−728.431	−244.722	3.118
4200	107.889	625.832	527.467	413.134	−729.490	−232.912	2.897
4300	107.898	628.371	529.784	423.923	−730.556	−221.076	2.686
4400	107.906	630.852	532.053	434.713	−731.628	−209.215	2.484
4500	107.914	633.277	534.276	445.504	−732.701	−197.331	2.291
4600	107.922	635.649	536.454	456.296	−733.775	−185.422	2.106
4700	107.928	637.970	538.589	467.089	−734.847	−173.490	1.928
4800	107.935	640.242	540.683	477.882	−735.916	−161.534	1.758
4900	107.941	642.468	542.738	488.676	−736.978	−149.556	1.594
5000	107.947	644.649	544.755	499.470	−738.034	−137.558	1.437
5100	107.952	646.786	546.734	510.265	−739.082	−125.537	1.286
5200	107.957	648.882	548.679	521.060	−740.120	−113.498	1.140
5300	107.962	650.939	550.589	531.856	−741.149	−101.437	1.000
5400	107.967	652.957	552.466	542.653	−742.167	−89.358	0.864
5500	107.971	654.938	554.311	553.450	−743.175	−77.260	0.734
5600	107.975	656.884	556.125	564.247	−744.172	−65.142	0.608
5700	107.979	658.795	557.910	575.045	−745.158	−53.008	0.486
5800	107.983	660.673	559.665	585.843	−746.134	−40.856	0.368
5900	107.986	662.519	561.393	596.641	−747.101	−28.690	0.254
6000	107.990	664.334	563.094	607.440	−748.058	−16.504	0.144

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 135.98 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 774\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -359.4 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 21.88 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ of -85.9 ± 0.2 kcal·mol^{-1} is obtained from a 3rd law analysis of six sets of electromotive force data[3,4,6,7] for three different reactions, namely, (A) Pb(cr) + 2 AgCl(cr) = 2 Ag(cr) + $PbCl_2$(cr), (B) Pb(cr) + Hg_2Cl_2(cr) = 2 Hg(l) + $PbCl_2$(cr), and (C) Pb(l) + Cl_2(g) = $PbCl_2$(cr). Seven other sets of similar data[1,2,5] give $\Delta_f H°$ values which are within ± 0.2 kcal·mol^{-1}of adopted value, while one set of emf data[7] for (D) 2CuCl(cr) + Pb(cr) = $PbCl_2$(cr) + 2 Cu(cr) gives a $\Delta_f H°$ value of -85.4 kcal·mol^{-1}. A $\Delta_f H°$ value can be obtained also from a 3rd law analysis of equilibrium data[8] for (E) $PbCl_2$(cr) + H_2(g) = Pb(l) + 2 HCl(g). Auxiliary enthalpies of formation used in our analysis are $\Delta_f H°$(298.15 K), kcal·mol^{-1}: AgCl, cr, = -30.370,[9] CuCl, cr = -33.0 ± 0.4,[10] Pb, l = 1.025,[10] Hg_2Cl_2, cr = -63.319 ± 0.05[10] and HCl, g = -22.063 ± 0.05.[10] We assign an uncertainty of ± 0.2 kcal·mol^{-1} to $\Delta_f H°$ to reflect the estimated error in the adopted value for $S°$(298.15 K).

Source	Reaction	Data Points	T/K	$-\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[1]	A	5	273–298	24.5	25.06 ± 0.04	−1.8 ± 0.3	85.8 ± 0.1
	B	7	273–298	22.0	22.34 ± 0.03	−1.3 ± 0.3	85.7 ± 0.1
[2] Set I	A	5	273–294	24.8	25.26 ± 0.03	−1.7 ± 0.1	86.0 ± 0.1
Set II	A	5	273–294	24.9	25.25 ± 0.03	−1.4 ± 0.2	86.0 ± 0.1
Set I	B	5	273–298	22.2	22.36 ± 0.02	−0.7 ± 0.1	85.7 ± 0.1
Set II	B	5	273–296	22.2	22.36 ± 0.02	−0.7 ± 0.3	85.7 ± 0.1
[3]	A	5	278–318	25.1	25.17 ± 0.03	−0.1 ± 0.5	85.9 ± 0.1
Set I	B	5	278–318	22.7	22.54 ± 0.04	0.4 ± 0.7	85.9 ± 0.1
Set II	B	5	288–308	22.7	25.54 ± 0.04	0.5 ± 0.7	85.9 ± 0.1
[4]	A	3	288–308	25.2	25.17 ± 0.02	0.2 ± 0.9	85.9 ± 0.1
[5]	C	Eqn	673–771	82.1	86.87 ± 0.55	−6.6	85.8 ± 0.6
[6]	C	2	723–773	86.8	86.98 ± 0.02	−0.2	85.9 ± 0.1
[7]	D	Eqn	363–553	19.8	19.44 ± 0.13	0.9	85.4 ± 1.0
	A	Eqn	293–573	24.9	25.20 ± 0.80	−0.7	85.9 ± 0.9
[8]	E	3	633–773	23.3	33.7 ± 2.4	14.7 ± 7.8	76.8 ± 2.5

Heat Capacity and Entropy

$C_p°$ data below 298.15 K have been reported by Nerst (15.6–87.7 K),[11] Eucken (106.5–290.7 K),[12] and Bronsted (283 K).[13] We combine these results with $C_p° = 18.52$ cal·K^{-1}·mol^{-1} [14] at 330 K and obtain $S°(298.15\ K) = 33.7$ cal·K^{-1}·mol^{-1} based on $S°(15.6\ K) = 0.9$ cal·K^{-1}·mol^{-1}. Kelley and King[15] analyzed the same $C_p°$'s and found $S°(298.15\ K) = 34.0 \pm 1.0$ cal·K^{-1}·mol^{-1}. Data obtained from cell measurements on both the crystal and liquid allow independent calculations of $S°$(298.15 K). Thirteen of the 23 sets of emf data htat we have analyzed are more compatible with a value for $S°$(298.15 K) which is at least one cal·K^{-1}·mol^{-1} less than that determined from the low temperature data. Since the cell measurements are judged to be more reliable, we adopt $S°(298.15\ K) = 32.5 \pm 0.5$ cal·K^{-1}·mol^{-1} and omit the $C_p°$ data below 298.25 K.

$C_p°$'s above 300 K are based on the smoothed relative enthalpies of Alim *et al.*[16] Their measurements were made in an isothermal diphenyl ether calorimeter over the temperature range 400 to 950 K. The $PbCl_2$ was reported to have a purity of 99.96%, and samples of this material were sealed in platinum capsules for the drop experiments. Their enthalpies are fitted to a polynomial which represents the data to within ± 0.4%. The calculated $C_p°$'s above 300 K are joined graphically with those of Eucken[12] at 298.15 K by comparison with the $C_p°$–T curve for $BaCl_2$(cr).[10] Our adopted enthalpies are in reasonable agreement with those of Kelley.[17] His results are based on the enthalpy measurements of Krestovnikov and Karetnikov,[18] and most of the points agree with ours to better than a percent but show a maximum deviation of −1.3% at 500 K. Other enthalpy data that have been recently reported are those of Bloom and Tricklebank (693–773 K),[19] and Thompson and Flengas (577–745 K).[20] Both of these studies show rather poor agreement with our adopted results. Deviations from our values are −4.2% at 673 K to −5.0% at 773 K for Bloom and Tricklebank,[19] 0.1% at 680 K and −6.2% at 745 K for Thompson and Flengas.[20] Both drop investigations were conducted with quartz capsules which might have been slowly attacked by the $PbCl_2$ at the higher temperatures. The earlier enthalpy measurements of Goodwin and Kalmus[21] are considered less reliable and not included in our analysis.

Modestova[22] *has reported the existence of a transition for* $PbCl_2$ *at 695 K based on differential thermal analysis and x–ray studies. This* transition has not been observed by other workers, and we prefer not to include it. However, if it does exist, we speculate that the enthalpy associated with it is quite small; thus, our functions would be only slightly altered.

Fusion Data

T_{fus} = 774 K is from the enthalpy study of Alim *et al.*[16] Other values reported for T_{fus} based on enthalpy measurements are 771,[21] 774,[18] 774[19] and 772.[20] DTA measurements[24] gave T_{fus} equal to 774 K, while cryoscopic studies[23] yielded 768 K. $\Delta_{fus} H°$ is calculated to be 5.23 kcal·mol^{-1} from the adopted enthalpies for the crystal and liquid at T_{fus}. Published values (all in kcal·mol^{-1}) include 5.15,[21] 5.70,[23] 2.98,[18] 5.3,[19] 5.56,[20] and 5.03.[24]

Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	77.073	135.980	135.980	0.	−359.406	−314.121	55.033
300	77.170	136.457	135.981	0.143	−359.375	−313.840	54.644
400	80.094	159.059	139.043	8.006	−357.711	−298.911	39.034
500	82.985	177.242	144.922	16.160	−355.942	−284.413	29.712
600	85.881	192.628	151.622	24.603	−354.020	−270.285	23.530
700	88.772	206.083	158.460	33.336	−356.781	−255.694	19.080
774.000	90.915	215.110	163.451	39.984	--- CRYSTAL <--> LIQUID ---		
800	91.667	218.126	165.179	42.358	−354.476	−241.407	15.762
900	94.558	229.090	171.680	51.669	−351.870	−227.427	13.200
1000	97.454	239.203	177.933	61.270	−348.961	−213.753	11.165
1100	100.345	248.626	183.936	71.160	−345.746	−200.385	9.516
1200	103.240	257.482	189.699	81.339	−342.222	−187.324	8.154
1300	106.131	265.860	195.238	91.808	−338.397	−174.569	7.014
1400	109.027	273.831	200.570	102.566	−334.283	−162.119	6.049
1500	111.918	281.451	205.710	113.613	−329.891	−149.973	5.223

PREVIOUS: March 1962 CURRENT: June 1973

$S°(298.15\ K) = [153.396]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 774\ K$

$\Delta_f H°(298.15\ K) = [-344.251]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 21.88 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(PbCl_2, l, 298.15\ K)$ is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(774\ K) - H°(298.15\ K)$, between the crystal and liquid. Independent values of $\Delta_f H°(l)$ (or $\Delta_f H°(cr)$) can be obtained from a 2nd and 3rd analysis of nine sets of emf data[1-9] for the formation cell of molten $PbCl_2$ ((A) $Pb(l) + Cl_2(g) = PbCl_2(l)$) and three sets of equilibrium data[10,11] for (B) $PbCl_2(l) + H_2(g) = Pb(l) + 2\ HCl(g)$. Auxiliary enthalpies of formation used in the analysis are $\Delta_f H°(Pb, l, 298.15\ K) = 1.025\ kcal·mol^{-1}$ [12] and $\Delta_f H°(HCl, g, 298.15\ K) = -22.063 \pm 0.05\ kcal·mol^{-1}$.[12] Five of the nine sets of emf data yield values for $\Delta_f H°(cr)$ which are in good agreement ($\pm 0.2\ kcal·mol^{-1}$) with the adopted value. Also, the results of the extensive emf measurements of Warner and Seifert[8] by the electronic commutator method are quite compatible with our adopted functions.

Source	Reaction	Data Points	T/K	$-\Delta_r H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$-\Delta_f H°(298.15\ K)$ kcal·mol^{-1} (l)	(cr)
Lorenz and Fox[1]	A	14	776–942	86.9	82.45 ± 0.58	5.1 ± 0.5	81.43	85.05
Hildenbrand and Ruhle[2]	A	7	774–880	88.9	82.95 ± 0.62	7.2 ± 0.3	81.93	85.55
Lorenz and Velde[3]	A	47[a]	826–1016	87.1	83.18 ± 0.52	4.4 ± 0.2	82.16	85.78
Wachter and Hildenbrand[4]	A	18	772–855	84.9	83.31 ± 0.11	2.0 ± 0.3	82.29	85.91
Holub *et al.*[5]	A	3	843–923	86.0	83.08 ± 0.27	3.3 ± 0.2	82.06	85.68
Lantratov and Alabyshev[6]	A	47[b]	814–954	82.5	83.69 ± 0.15	1.4 ± 0.1	82.67	86.29
Delimarskii and Roms[7]	A	2	8231, 873	83.5	83.56		82.54	86.16
Warner and Seifert[8]	A	Equation	775–1139	83.4	83.32 ± 0.03	0.1	82.30	85.92
Hagemark and Hengstenberg[9]	A	Equation	773–893	84.6	83.51 ± 0.15	1.3 ± 0.1	82.49	86.11
Bagdasarian[10] Set I	B	10	876–978	40.0	38.89 ± 0.36	−1.2 ± 1.4	81.99	85.61
Set II	B	21	871–1220	44.2	38.08 ± 1.26	−5.8 ± 0.3	81.18	84.80
Jellinek and Rudat[11]	B	5	833–1133	37.8	38.62 ± 0.51	0.8 ± 1.1	81.72	85.34

(3)[a] and (1)[b] points rejected due to failure of a statistical test.

Heat Capacity and Entropy

$C_p°$ is assumed constant at 26.65 $cal·K^{-1}·mol^{-1}$ over the temperature range 500–2000 K and is based on the smoothed relative enthalpies (774–950 K) of Alim *et al.*[13] A glass transition is assumed at 500 K below which $C_p°$ is that of the crystal. The smoothed enthalpies of Kelley[14] (800–1000 K) deviate by +4.0% from our values, while those of Thompson and Flengas[15] (813– 945 K) deviate by ±1%. The enthalpies of Bloom and Tricklebank[16] are consistently lower than our values by −3.1% at 823 K, and the deviation increases to −12.6% at 1073 K. Warner and Seifert[8] have determined $C_p°$ data for $PbCl_2(l)$ from their emf measurements. They reported values of (all in $cal·K^{-1}·mol^{-1}$) 25.7 (800 K), 26.2 (900 K), 26.5 (1000 K) and 26.7 (1100 K). Bizouard and Pauty[17] measured $C_p°$ for the liquid as 24.7 $cal·K^{-1}·mol^{-1}$. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

T_{vap} is the temperature at which $\Delta_r G° = 0$ for the process $PbCl_2(l) \rightarrow PbCl_2(g)$. $\Delta_{vap}H°$ is calculated as the difference between the enthalpies of formation of the gas and liquid at T_{vap}.

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Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	77.073	153.396	153.396	0.	−344.251	−304.160	53.288
300	77.170	153.873	153.398	0.143	−344.221	−303.911	52.916
400	80.094	176.475	156.460	8.006	−342.557	−290.723	37.965
500	82.985	194.659	162.338	16.160	−340.787	−277.967	29.039
500.000	82.985	194.659	162.338	16.160	GLASS <--> LIQUID		
500.000	111.504	194.659	162.338	16.160	TRANSITION		
600	111.504	214.988	169.470	27.311	−336.158	−265.840	23.143
700	111.504	232.177	177.232	38.461	−336.502	−253.680	18.930
774.000	111.504	243.382	183.030	46.712	--- CRYSTAL <--> LIQUID ---		
800	111.504	247.066	185.051	49.611	−332.068	−242.151	15.811
900	111.504	260.199	192.686	60.762	−327.623	−231.178	13.417
1000	111.504	271.947	200.035	71.912	−323.164	−220.701	11.528
1100	111.504	282.575	207.063	83.063	−318.689	−210.671	10.004
1200	111.504	292.277	213.766	94.213	−314.194	−201.050	8.751
1300	111.504	301.202	220.153	105.363	−309.687	−191.804	7.707
1400	111.504	309.465	226.241	116.514	−305.181	−182.905	6.824
1500	111.504	317.158	232.049	127.664	−300.686	−174.328	6.071
1600	111.504	324.354	237.595	138.814	−296.207	−166.050	5.421
1700	111.504	331.114	242.900	149.965	−291.751	−158.052	4.856
1800	111.504	337.488	247.979	161.115	−287.320	−150.315	4.362
1900	111.504	343.516	252.850	172.265	−282.917	−142.824	3.927
2000	111.504	349.236	257.528	183.416	−278.544	−135.564	3.541

PREVIOUS: March 1962 CURRENT: June 1973

0 to 774 K crystal
above 774 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.073	135.980	135.980	0.	−359.406	−314.121	55.033
300	77.170	136.457	135.981	0.143	−359.375	−313.840	54.644
400	80.094	159.059	139.043	8.006	−357.711	−298.911	39.034
500	82.985	177.242	144.922	16.160	−355.942	−284.413	29.712
600	85.881	192.628	151.622	24.603	−354.020	−270.285	23.530
700	88.772	206.083	158.460	33.336	−356.781	−255.694	19.080
774.000	90.915	215.110	163.451	39.984	CRYSTAL <--> LIQUID		
774.000	111.504	243.382	163.451	61.867	TRANSITION		
800	111.504	247.066	166.109	64.766	−332.068	−242.151	15.811
900	111.504	260.199	175.848	75.916	−327.623	−231.178	13.417
1000	111.504	271.947	184.881	87.067	−323.164	−220.701	11.528
1100	111.504	282.575	193.286	98.217	−318.689	−210.671	10.004
1200	111.504	292.277	201.137	109.367	−314.194	−201.050	8.751
1300	111.504	301.202	208.496	120.518	−309.687	−191.804	7.707
1400	111.504	309.465	215.416	131.668	−305.181	−182.905	6.824
1500	111.504	317.158	221.946	142.818	−300.686	−174.328	6.071
1600	111.504	324.354	228.124	153.969	−296.207	−166.050	5.421
1700	111.504	331.114	233.985	165.119	−291.751	−158.052	4.856
1800	111.504	337.488	239.560	176.269	−287.320	−150.315	4.362
1900	111.504	343.516	244.874	187.420	−282.917	−142.824	3.927
2000	111.504	349.236	249.951	198.570	−278.544	−135.564	3.541

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = 317.205 \pm 2.9\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -172.03 \pm 1.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -174.05 \pm 1.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	[22000]	3
$^1B_1$	31000	1

Vibrational Frequencies and Degeneracies
ν_i, cm^{-1}
329 (1)
80 (1)
307 (1)

Point Group: C_{2v} $\sigma = 2$

Bond Distance: Pb–Cl = 2.46 ± 0.02 Å

Bond Angle: Cl–Pb–Cl = 96 + 3°

Product of Moments of Inertia: $I_A I_B I_C = 5.90383 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$ of −41.6 ± 0.3 kcal·mol^{-1} is obtained from $\Delta_f H°$(cr) = −85.9 ± 0.2 kcal·mol^{-1} by addition of $\Delta_{sub} H°$(298.15 K). The adopted value for $\Delta_{sub} H°$(298.15 K) is 44.3 ± 0.1 kcal·mol^{-1} and is based on a 3rd law analysis of six sets of vapor pressure data[4,9,11,14,15] for both the crystal and liquid. Results of our analysis of a total of eighteen sets of Vp data are given below. Seven[1,2,3,7,8,10,12] of the remaining twelve sets yield $\Delta_f H°$(g) values which are within 0.3 kcal·mol^{-1} of the adopted value. Mass spectrometric studies[16] of the equilibrium vapors over the condensed phases indicated that the predominant species is the monomer.

Source	Reaction*	T/K	Data Points	$\Delta_{sub} H°$(or v), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(PbCl_2, g, 298.15\ K)$ kcal·mol^{-1}
1	A	673–748	4	47.6	45.41 ± 0.21	−3.2 ± 0.1	40.5 ± 0.4
	B	773–1223	19	42.5	40.93 ± 0.49	−1.6 ± 0.2	41.3 ± 0.7
2	B	1043–1227	7	37.6	40.62 ± 0.42	2.6 ± 0.8	41.7 ± 0.6
3	B	955–1266	12[a]	39.8	40.75 ± 0.25	0.8 ± 0.3	41.5 ± 0.4
4	A	708–766	5	37.1	44.34 ± 0.53	9.8 ± 3.2	41.6 ± 0.7
	B	783–865	7	44.3	40.69 ± 0.30	−4.4 ± 0.7	41.6 ± 0.5
5	B	1033–1043	2	36.1	40.19 ± 0.06	3.9	42.1 ± 0.3
6	A	653–733	7	49.0	45.13 ± 0.31	−5.6 ± 0.2	40.8 ± 0.5
7	B	953–1215	9[a]	43.6	40.94 ± 0.69	−2.5 ± 0.9	41.3 ± 0.9
8	B	865–1272	18	38.9	40.60 ± 0.50	1.6 ± 0.5	41.7 ± 0.7
9	B	950–1250	Eqn	40.9	40.67 ± 0.04	−0.2	41.6 ± 0.3
10	B	931–1154	4	41.0	40.74 ± 0.24	−0.2 ± 0.8	41.5 ± 0.4
11	B	923	1		40.70		41.6 ± 0.3
12	B	821–1259	56[b]	39.9	40.73 ± 0.24	0.8 ± 0.1	41.5 ± 0.4
13	A	708–758	3	45.1	42.93 ± 0.37	−3.0 ± 6.8	43.0 ± 0.6
	B	793–893	3	31.3	40.24 ± 1.14	10.6 ± 3.8	41.6 ± 0.3
14	B	914–1249	Eqn	40.2	40.69 ± 0.12	0.5	41.6 ± 0.3
15	B	1071	1		40.63		41.6 ± 0.3

*A) $PbCl_2(cr) = PbCl_2(g)$ B) $PbCl_2(l) = PbCl_2(g)$. (1)[a] and (2)[b] points rejected due to failure of a statistical test

Heat Capacity and Entropy

The bond length is taken from the electron diffraction study of Lister and Sutton.[17] Electric deflection experiments by Buchler *et al.*[18] showed that $PbCl_2$ possessed a permanent dipole moment; thus, the molecule must have a bent structure. Infrared studies[19] of matrix isolated $PbCl_2$ have led to a value for the bond angle of 96 ± 3° which we adopt. This value is based on the observed Cl isotopic splitting of the antisymmetrical stretching frequency (ν_3). The principal moments of inertia are: $I_A = 23.7690 \times 10^{-39}$, $I_B = 39.3510 \times 10^{-39}$, and $I_C = 63.1200 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 939

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−14.038	−172.033	−172.033	INFINITE
100	44.386	262.096	363.997	−10.190	−172.863	−176.489	92.189
200	52.288	295.698	322.179	−5.296	−173.532	−179.824	46.965
250	54.098	307.577	318.109	−2.633	−173.793	−181.367	37.895
298.15	55.184	317.205	317.205	0.	−174.054	−182.802	32.026
300	55.218	317.547	317.207	0.102	−174.065	−182.857	31.838
350	55.946	326.117	317.882	2.882	−174.357	−184.299	27.505
400	56.442	333.622	319.390	5.693	−174.673	−185.698	24.250
450	56.793	340.291	321.349	8.524	−175.014	−187.056	21.713
500	57.050	346.289	323.548	11.371	−175.380	−188.375	19.679
600	57.392	356.724	328.233	17.094	−176.178	−190.900	16.619
700	57.602	365.587	332.952	22.845	−181.921	−192.487	14.364
800	57.740	373.289	337.524	28.612	−182.870	−193.932	12.662
900	57.836	380.095	341.883	34.391	−183.797	−195.259	11.333
1000	57.904	386.193	346.014	40.178	−184.701	−196.483	10.263
1100	57.955	391.714	349.922	45.972	−185.583	−197.619	9.384
1200	57.994	396.759	353.618	51.769	−186.441	−198.675	8.648
1300	58.025	401.402	357.117	57.570	−187.283	−199.660	8.022
1400	58.049	405.703	360.436	63.374	−188.124	−200.581	7.484
1500	58.068	409.709	363.589	69.180	−188.973	−201.441	7.015
1600	58.084	413.457	366.590	74.987	−189.838	−202.244	6.603
1700	58.098	416.978	369.451	80.797	−190.723	−202.992	6.237
1800	58.109	420.300	372.185	86.607	−191.631	−203.688	5.911
1900	58.119	423.442	374.800	92.418	−192.567	−204.333	5.617
2000	58.127	426.423	377.308	98.231	−193.532	−204.927	5.352
2100	58.135	429.259	379.715	104.044	−371.749	−198.357	4.934
2200	58.142	431.964	382.029	109.857	−372.389	−190.086	4.513
2300	58.149	434.548	384.256	115.672	−373.130	−181.783	4.128
2400	58.157	437.023	386.404	121.487	−373.975	−173.446	3.775
2500	58.166	439.398	388.476	127.303	−374.927	−165.071	3.449
2600	58.176	441.679	390.479	133.121	−375.985	−156.657	3.147
2700	58.188	443.875	392.416	138.939	−377.148	−148.199	2.867
2800	58.202	445.991	394.292	144.758	−378.414	−139.697	2.606
2900	58.220	448.034	396.110	150.579	−379.777	−131.147	2.362
3000	58.241	450.008	397.874	156.402	−381.232	−122.549	2.134
3100	58.266	451.918	399.587	162.228	−382.773	−113.901	1.919
3200	58.297	453.769	401.251	168.056	−384.392	−105.203	1.717
3300	58.332	455.563	402.870	173.887	−386.081	−96.452	1.527
3400	58.373	457.305	404.445	179.722	−387.830	−87.649	1.347
3500	58.421	458.998	405.980	185.562	−389.632	−78.794	1.176
3600	58.476	460.644	407.476	191.407	−391.476	−69.887	1.014
3700	58.537	462.247	408.934	197.257	−393.353	−60.928	0.860
3800	58.606	463.809	410.358	203.114	−395.254	−51.919	0.714
3900	58.683	465.333	411.748	208.979	−397.171	−42.858	0.574
4000	58.767	466.819	413.107	214.851	−399.094	−33.749	0.441
4100	58.859	468.272	414.434	220.732	−401.016	−24.591	0.313
4200	58.960	469.691	415.733	226.623	−402.928	−15.387	0.191
4300	59.068	471.080	417.004	232.525	−404.824	−6.138	0.075
4400	59.184	472.439	418.249	238.437	−406.697	3.156	−0.037
4500	59.308	473.770	419.468	244.362	−408.539	12.491	−0.145
4600	59.440	475.075	420.662	250.299	−410.347	21.868	−0.248
4700	59.579	476.355	421.834	256.250	−412.114	31.283	−0.348
4800	59.725	477.611	422.983	262.215	−413.836	40.735	−0.443
4900	59.878	478.844	424.110	268.195	−415.509	50.223	−0.535
5000	60.037	480.055	425.217	274.191	−417.130	59.744	−0.624
5100	60.203	481.246	426.304	280.203	−418.695	69.297	−0.710
5200	60.374	482.417	427.372	286.232	−420.201	78.880	−0.792
5300	60.551	483.568	428.421	292.278	−421.647	88.492	−0.872
5400	60.732	484.702	429.453	298.342	−423.031	98.130	−0.949
5500	60.918	485.818	430.468	304.424	−424.352	107.794	−1.024
5600	61.108	486.917	431.466	310.526	−425.608	117.480	−1.096
5700	61.301	488.000	432.448	316.646	−426.798	127.189	−1.166
5800	61.497	489.068	433.415	322.786	−427.924	136.918	−1.233
5900	61.696	490.121	434.368	328.946	−428.982	146.666	−1.298
6000	61.896	491.160	435.306	335.125	−429.976	156.431	−1.362

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K) = [318.57 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 812.26 \pm 50.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [816.298]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2A_1$	0	[2]
$^2B_1$	[20000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[300](1)
[100](1)
[350](1)

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distance: Pb–Cl = [2.30] Å
Bond Angle: Cl–Pb–Cl = [116]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.37567 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The appearance potential for $PbCl_2^+$ from $PbCl_2(g)$ has been determined spectrometrically as (in eV) 11.2 ± 0.2,[1] 10.3 ± 0.2[2] and 10.3 ± 0.5.[3] Hastie *et al.*[2] preferred the lower AP for $PbCl_2^+$, since this value was obtained with more sensitive equipment. Subsequent measurements by Hastie and Swingler[4] confirm the lower result. They reported an ionization efficiency curve for $PbCl_2^+$ from which we obtain AP = 10.0 eV by the linear extrapolation method. Also, molecular orbital calculations by Hastie and Margrave[5] indicated $IP(PbCl_2,g) = 10.3$ eV. We adopt a mean value from[2–4] of 10.2 ± 0.5 eV (235.2 $kcal \cdot mol^{-1}$) for the process $PbCl_2(g) + e^- \rightarrow PbCl_2,(g) + 2\ e^-$ which gives $\Delta_f H°(PbCl_2^+, g, 0\ K) = 194.1 \pm 12.0\ kcal \cdot mol^{-1}$ when AP is combined with $\Delta_f H°(PbCl_2, g, 0\ K) = -41.1 \pm 0.3\ kcal \cdot mol^{-1}$.[6] $\Delta_f H°(298\ K) = 195.1\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The correlation diagram of Walsh[7] predicts a bent configuration for $PbCl_2^+$, since the molecule has seventeen valence electrons. Also, Walsh[7] predicted that the apex angle for a non–hydride AB_2 molecule would decrease markedly in going from a 17– to an 18– electron molecule. We assume that the bond angle in $PbCl_2^+$ is 20° larger than that for $PbCl_2$.[6] The adopted value (116°) is consistent with JANAF bond angles for the isoelectronic molecules BCl_2(112°) and $AlCl_2$(120°).[6] The bond length is assumed to lie between that for PbCl and $PbCl_2$.[6] The principal moments of inertia are: $I_A = 13.0315 \times 10^{-39}$, $I_B = 44.7956 \times 10^{-39}$ and $I_C = 57.8271 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies are estimated by comparison with those for BCl_2, CCl_2, $SiCl_2$, and $PbCl_2$.[6] The ground state is assumed to be $^2A_1$ by analogy with that for the isoelectronic molecule NO_2.[8] MO calculations by Hastie and Margrave[5] for the Group III A dihalides predicted an upper $^2B_1$ state with the $^2A_1$ – $^2B_1$ separation in the energy range 1–2 eV. We have included this state and estimated the $^2A_1$ – $^2B_1$ separation (20,000 cm^{-1}) to be somewhat greater than that for AlO_2 (15,000 cm^{-1}),[6] BCl_2 (11,000 cm^{-1})[6] and NO_2(<15,000 cm^{-1}).[8]

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[6] JANAF Thermochemical Tables: $PbCl_2(g)$ and PbCl(g), 6–30–73; $BCl_2(g)$ and $AlCl_2(g)$, 6–30–72; $CCl_2(g)$, 12–31–68; SiCl2(g), 12–31–70
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.896	812.264		
100	43.788	263.871	365.095	−10.122			
200	51.970	297.156	323.520	−5.273			
250	53.863	308.973	319.465	−2.623			
298.15	55.006	318.566	318.566	0.	816.298	800.890	−140.313
300	55.041	318.906	318.567	0.102	816.326	800.794	−139.431
350	55.809	327.452	319.240	2.874	817.066	798.147	−119.117
400	56.334	334.941	320.744	5.679	817.783	795.395	−103.868
450	56.705	341.599	322.698	8.505	818.476	792.555	−91.997
500	56.978	347.588	324.893	11.348	819.145	789.638	−82.493
600	57.340	358.011	329.569	17.065	820.420	783.616	−68.220
700	57.564	366.868	334.281	22.811	816.751	778.185	−58.069
800	57.711	374.565	338.846	28.575	817.877	772.599	−50.446
900	57.812	381.369	343.200	34.352	819.026	766.870	−44.508
1000	57.885	387.464	347.327	40.137	820.198	761.012	−39.751
1100	57.939	392.983	351.231	45.928	821.394	755.036	−35.854
1200	57.981	398.027	354.923	51.724	822.613	748.950	−32.601
1300	58.013	402.669	358.420	57.524	823.848	742.762	−29.845
1400	58.039	406.969	361.736	63.327	825.085	736.478	−27.478
1500	58.060	410.974	364.886	69.132	826.313	730.106	−25.425
1600	58.077	414.722	367.885	74.938	827.527	723.652	−23.625
1700	58.091	418.243	370.745	80.747	828.719	717.123	−22.035
1800	58.103	421.564	373.477	86.557	829.889	710.525	−20.619
1900	58.113	424.706	376.091	92.367	831.031	703.862	−19.351
2000	58.122	427.687	378.597	98.179	832.144	697.140	−18.207
2100	58.130	430.523	381.003	103.992	656.005	697.479	−17.349
2200	58.138	433.227	383.316	109.805	657.443	699.419	−16.606
2300	58.145	435.811	385.542	115.619	658.781	701.297	−15.927
2400	58.153	438.286	387.689	121.434	660.014	703.119	−15.303
2500	58.161	440.660	389.760	127.250	661.140	704.891	−14.728
2600	58.170	442.942	391.762	133.067	662.160	706.621	−14.196
2700	58.179	445.137	393.699	138.884	663.075	708.313	−13.703
2800	58.190	447.253	395.574	144.702	663.887	709.973	−13.245
2900	58.203	449.295	397.391	150.522	664.601	711.607	−12.817
3000	58.218	451.269	399.154	156.343	665.222	713.217	−12.418
3100	58.234	453.178	400.867	162.166	665.757	714.807	−12.044
3200	58.253	455.027	402.530	167.990	666.213	716.382	−11.694
3300	58.275	456.820	404.148	173.816	666.598	717.944	−11.364
3400	58.299	458.560	405.723	179.645	666.920	719.495	−11.054
3500	58.326	460.250	407.257	185.476	667.189	721.037	−10.761
3600	58.356	461.894	408.752	191.310	667.413	722.572	−10.484
3700	58.388	463.493	410.210	197.148	667.601	724.102	−10.222
3800	58.424	465.051	411.633	202.988	667.762	725.627	−9.974
3900	58.462	466.569	413.022	208.832	667.904	727.147	−9.739
4000	58.504	468.050	414.379	214.681	668.035	728.665	−9.515
4100	58.548	469.495	415.706	220.533	668.163	730.179	−9.303
4200	58.595	470.906	417.004	226.390	668.295	731.690	−9.100
4300	58.644	472.285	418.273	232.252	668.439	733.198	−8.907
4400	58.697	473.634	419.516	238.119	668.600	734.702	−8.722
4500	58.751	474.954	420.734	243.992	668.783	736.202	−8.546
4600	58.808	476.246	421.926	249.870	668.995	737.699	−8.377
4700	58.867	477.511	423.096	255.753	669.239	739.189	−8.215
4800	58.928	478.751	424.242	261.643	669.520	740.675	−8.060
4900	58.990	479.967	425.367	267.539	669.841	742.154	−7.911
5000	59.055	481.159	426.471	273.441	670.206	743.626	−7.769
5100	59.120	482.329	427.555	279.350	670.616	745.090	−7.631
5200	59.187	483.478	428.619	285.265	671.075	746.546	−7.499
5300	59.255	484.606	429.665	291.187	671.583	747.993	−7.372
5400	59.324	485.714	430.693	297.116	672.143	749.429	−7.249
5500	59.393	486.803	431.703	303.052	672.755	750.855	−7.131
5600	59.464	487.874	432.697	308.995	673.419	752.269	−7.017
5700	59.534	488.927	433.674	314.945	674.136	753.671	−6.907
5800	59.605	489.963	434.636	320.902	674.907	755.060	−6.800
5900	59.676	490.983	435.582	326.866	675.731	756.434	−6.697
6000	59.746	491.987	436.514	332.837	676.608	757.795	−6.597

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K) = 183.678 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -49.79 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Trautz and Hoffmann[1] have measured calorimetrically the enthalpy of solution of gaseous chlorine in dichlorodisulfane at 298.15 K. They reported $\Delta_{sln}H° = -9.8 \pm 0.4$ kcal·mol^{-1} for a final state consisting of SCl_2 dissolved in an excess of S_2Cl_2. Combining their measured Δ_{sln}H value with $\Delta_f H°(S_2Cl_2, l, 298.15\ K) = -13.9 \pm 0.5$ kcal·mol^{-1},[2] we obtain the adopted result of $\Delta_f H°(SCl_2, l, 298.15\ K) = -11.9 \pm 0.5$ kcal·mol^{-1}. In arriving at this value, no enthalpy corrections are applied for dissolution of the SCl_2 in the excess S_2Cl_2 and for the temperature difference since we expect both corrections to be small and they tend to cancel. Our adopted value agrees with the selected values of NBS (-12 kcal·mol^{-1})[3] and Mills (-11.8 kcal·mol^{-1}).[4]

Heat Capacity and Entropy

The heat capacity of liquid SCl_2 is estimated as 21.75 cal·K^{-1}·mol^{-1} using the value of 7.25 cal·K^{-1}·g·atom^{-1} recommended by Kubaschewski *et al.*[5] This estimated value of $C_p°$ corresponds to a specific heat of 0.21 cal·g^{-1}·K^{-1} which agrees with the experimentally measured value for S_2Cl_2 of 0.22 cal·g^{-1}·K^{-1}.[2] We assume that $C_p°$ is constant in the temperature range 298–800 K. The value of $S°(298.15\ K)$ is selected as 43.9 ± 1.0 cal·K^{-1}·mol^{-1} which minimizes differences between the second and third law entropies of vaporization determined from vapor pressure data[6] on a pure stabilized sample of SCl_2. Further details on the results of these analyses can be found in the heat of formation section of the SCl_2(g) table.[2]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy of vaporization becomes zero. The value of $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_f H°$ values for the gas and liquid at T_{vap}. The experimental value of T_{vap} determined from vapor pressure measurements is 332.7 K.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.002	183.678	183.678	0.	−49.790	−28.485	4.990
300	91.002	184.241	183.679	0.168	−49.726	−28.353	4.937
400	91.002	210.420	187.249	9.269	−48.693	−21.639	2.826
500	91.002	230.727	193.989	18.369	−47.092	−15.075	1.575
600	91.002	247.318	201.537	27.469	−45.209	−8.843	0.770
700	91.002	261.346	209.105	36.569	−43.127	−2.945	0.220
800	91.002	273.498	216.411	45.669	−40.938	2.647	−0.173

PREVIOUS: CURRENT: June 1978

$S°(298.15\ K) = 281.628 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -16.43 \pm 3.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -17.57 \pm 3.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^1A_2$	25810	1
$^1B_2$	29762	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
528 (1)
205 (1)
525 (1)

Point Group: C_{2v} $\sigma = 2$

Bond Distance: S–Cl = 2.015 ± 0.001 Å

Bond Angle: Cl–S–Cl = 102.73 ± 0.05°

Product of the Moments of Inertia: $I_A I_B I_C = 5.91980 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Rosser and Whitt[1] have reported the results of a vapor pressure study of SCl_2. Measurements were conducted on a sample of SCl_2 stabilized with PCl_3 to suppress decomposition. Using JANAF free energy functions,[2] we analyze their vapor pressure points[1] lying above 298 K by the second and third law methods. In the analysis we select $S°(SCl_2, l, 298.15\ K) = 43.9\ cal \cdot K^{-1} \cdot mol^{-1}$ which minimizes the difference between the 2nd and 3rd law entropies of vaporization. Our results are $\Delta_{vap}H°$ (2nd law) = $\Delta_{vap}H°$ (3rd law) = 7.75 ± 0.02 $kcal \cdot mol^{-1}$ which leads to the adopted heat of formation of $\Delta_f H°(SCl_2, g, 298.15\ K) = -4.2 \pm 0.8\ kcal \cdot mol^{-1}$ when combined with $\Delta_f H°(SCl_2, l, 298.15\ K) = -11.9 \pm 0.5\ kcal \cdot mol^{-1}$.[2] The adopted value of $\Delta_f H°$ is rounded to the nearest 0.1 $kcal \cdot mol^{-1}$. The overall uncertainty is estimated as ±0.8 $kcal \cdot mol^{-1}$ based on contributions from the uncertainty in $\Delta_f H°$ of the liquid (±0.5 $kcal \cdot mol^{-1}$) and from the uncertainty in the entropy (±1.0 $cal \cdot K^{-1} \cdot mol^{-1}$) of the liquid[2] which amounts to roughly 0.3 $kcal \cdot mol^{-1}$ in $\Delta_f H°$.

Barton and Yost[3] have studied the dissociation of S_2Cl_2(g) at various temperatures. Their measured dissociation data above 760 K have been reanalyzed by Yost and Russell[4] who have determined equilibrium constants for the reactions (a) $S_2(g) + Cl_2(g) = S_2Cl_2(g)$ and (b) 0.5 $S_2(g) + Cl_2(g) = SCl_2(g)$ by combining the dissociation pressures with molecular data and an estimated value for the $\Delta_f H°$ of SCl_2. Second and third law analyses of the equilibrium data for reaction (b) give $\Delta_f H°(298.15\ K)$ (2nd law) = $\Delta_f H°(298.15\ K)$ (3rd law) = −20.69 ± 0.01 $kcal \cdot mol^{-1}$ which corresponds to $\Delta_f H°(SCl_2, g, 298.15\ K) = -5.3\ kcal \cdot mol^{-1}$ using the recent JANAF[2] value of $\Delta_f H°$ for S_2(g). This $\Delta_f H°$ value for SCl_2(g) is some 1.1 $kcal \cdot mol^{-1}$ more negative than that obtained from an analysis of vapor pressure data described above. We find a similar discrepancy in the equilibrium data for reaction (a) where the derived $\Delta_f H°$ value of S_2Cl_2(g) is 3 $kcal \cdot mol^{-1}$ more negative than that obtained from an analysis of vapor pressure data. (See S_2Cl_2(g) table for details). We conclude that the equilibrium constants reported by Yost and Russell[4] are biased, and we give no weight to the $\Delta_f H°$ values derived from their data.

Values of $\Delta_f H°$ previously selected by Colwell[5] and Mills[6] have been based primarily on the equilibrium data of Yost and Russell.[4] The value selected by NBS[7] is −4.7 $kcal \cdot mol^{-1}$. Our adopted results give an enthalpy of atomization and mean S–Cl bond dissociation energy of 126.8 ± 0.9 $kcal \cdot mol^{-1}$ and 63.4 $kcal \cdot mol^{-1}$, respectively.

Heat Capacity and Entropy

Early electron diffraction studies[8,9] and more recent microwave measurements[10,11] have shown that the SCl_2 molecule has C_{2v} symmetry. We adopt structural parameters from the microwave work of Davis and Gerry.[11] The bond length and angle refer to an average structure of $^{32}S^{35}Cl_2$ in the (000) vibrational state obtained from a quadratic potential function based solely on microwave data.[11] This average structure is only slightly different from the effective structure determined by Murray *et al.*[10] but quite different from the molecular structure derived from electron diffraction measurements[8,9] which are considered less accurate. The symmetrical stretch (ν_1) and bending (ν_2) frequencies are those observed by Frankiss and Harrison[12] in the Raman spectra of the vapor at 335 K. The asymmetrical stretching frequency (ν_3) was not detected in this recent Raman study[12] and still remains relatively uncertain (±10 cm^{-1}). We use $\nu_3 = 525\ cm^{-1}$ based on the infrared measurements of Savoie and Tremblay,[13] as suggested by Frankiss and Harrison.[12] The electronic levels and configurations are taken from the CNDO/2 MO calculations and electronic absorption spectral measurements of Colton and Rabalais.[14] The principal moments of inertia are: $I_A = 5.8026 \times 10^{-38}$, $I_B = 29.1706 \times 10^{-38}$, and $I_C = 34.9733 \times 10^{-39}\ g \cdot cm^{-2}$.

Our ideal gas thermal functions are essentially an extension of those previously published by Frankiss and Harrison[12] who also reviewed data published prior to their paper. All earlier functions require revision since they are based on liquid state vibrational frequencies and the molecular structure determined by electron diffraction.

Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.445	−16.425	−16.425	INFINITE
100	37.966	233.457	323.231	−8.977	−16.559	−19.752	10.317
200	45.873	262.274	286.144	−4.774	−17.035	−22.770	5.947
250	48.815	272.842	282.455	−2.403	−17.303	−24.173	5.051
298.15	50.895	281.628	281.628	0.	−17.573	−25.472	4.463
300	50.962	281.943	281.629	0.094	−17.583	−25.521	4.444
350	52.512	289.922	282.255	2.683	−17.879	−26.820	4.003
400	53.643	297.011	283.665	5.338	−20.406	−27.989	3.655
450	54.482	303.380	285.508	8.043	−21.404	−28.885	3.353
500	55.117	309.155	287.588	10.783	−22.461	−29.658	3.098
600	55.992	319.288	292.051	16.342	−24.119	−30.935	2.693
700	56.547	327.964	296.576	21.971	−25.508	−31.958	2.385
800	56.919	335.540	300.983	27.646	−26.745	−32.794	2.141
900	57.179	342.260	305.203	33.351	−81.016	−32.400	1.880
1000	57.368	348.295	309.216	39.079	−80.881	−27.005	1.411
1100	57.509	353.770	313.021	44.823	−80.759	−21.624	1.027
1200	57.618	358.778	316.629	50.580	−80.651	−16.253	0.707
1300	57.703	363.394	320.051	56.346	−80.559	−10.890	0.438
1400	57.770	367.673	323.301	62.120	−80.486	−5.534	0.206
1500	57.825	371.660	326.394	67.900	−80.430	−0.182	0.006
1600	57.870	375.394	329.341	73.685	−80.393	5.166	−0.169
1700	57.908	378.903	332.154	79.473	−80.375	10.513	−0.323
1800	57.939	382.214	334.844	85.266	−80.377	15.860	−0.460
1900	57.966	385.347	337.421	91.061	−80.398	21.207	−0.583
2000	57.988	388.321	339.892	96.859	−80.440	26.555	−0.694
2100	58.008	391.151	342.266	102.659	−80.501	31.906	−0.794
2200	58.025	393.850	344.550	108.460	−80.582	37.261	−0.885
2300	58.040	396.430	346.750	114.264	−80.685	42.620	−0.968
2400	58.053	398.900	348.872	120.068	−80.810	47.983	−1.044
2500	58.065	401.270	350.920	125.874	−80.958	53.352	−1.115
2600	58.076	403.548	352.901	131.681	−81.128	58.728	−1.180
2700	58.086	405.740	354.818	137.490	−81.322	64.111	−1.240
2800	58.095	407.852	356.674	143.299	−81.540	69.501	−1.297
2900	58.104	409.891	358.474	149.109	−81.782	74.900	−1.349
3000	58.113	411.861	360.221	154.919	−82.047	80.307	−1.398
3100	58.121	413.767	361.918	160.731	−82.336	85.724	−1.444
3200	58.130	415.612	363.567	166.544	−82.647	91.150	−1.488
3300	58.139	417.401	365.172	172.357	−82.979	96.586	−1.529
3400	58.149	419.137	366.733	178.171	−83.332	102.033	−1.568
3500	58.160	420.823	368.255	183.987	−83.702	107.490	−1.604
3600	58.172	422.461	369.738	189.804	−84.089	112.958	−1.639
3700	58.186	424.055	371.185	195.621	−84.490	118.437	−1.672
3800	58.200	425.607	372.596	201.441	−84.902	123.927	−1.703
3900	58.217	427.119	373.975	207.262	−85.324	129.428	−1.733
4000	58.235	428.593	375.322	213.084	−85.752	134.940	−1.762
4100	58.256	430.032	376.639	218.909	−86.185	140.463	−1.790
4200	58.279	431.436	377.927	224.735	−86.619	145.996	−1.816
4300	58.304	432.807	379.188	230.565	−87.052	151.539	−1.841
4400	58.331	434.148	380.421	236.396	−87.481	157.093	−1.865
4500	58.362	435.459	381.630	242.231	−87.904	162.656	−1.888
4600	58.395	436.742	382.814	248.069	−88.318	168.229	−1.910
4700	58.430	437.998	383.975	253.910	−88.721	173.810	−1.932
4800	58.469	439.229	385.113	259.755	−89.111	179.400	−1.952
4900	58.511	440.435	386.230	265.604	−89.485	184.998	−1.972
5000	58.555	441.618	387.326	271.457	−89.843	190.603	−1.991
5100	58.603	442.778	388.402	277.315	−90.181	196.216	−2.010
5200	58.653	443.916	389.459	283.178	−90.499	201.834	−2.027
5300	58.707	445.034	390.497	289.046	−90.794	207.459	−2.045
5400	58.764	446.132	391.517	294.919	−91.066	213.089	−2.061
5500	58.823	447.210	392.520	300.799	−91.313	218.724	−2.077
5600	58.885	448.271	393.506	306.684	−91.535	224.363	−2.093
5700	58.950	449.314	394.476	312.576	−91.729	230.006	−2.108
5800	59.018	450.340	395.430	318.474	−91.896	235.652	−2.122
5900	59.089	451.349	396.369	324.380	−92.034	241.300	−2.136
6000	59.162	452.343	397.294	330.292	−92.143	246.951	−2.150

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

$S°(298.15\ K) = [287.32 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 896.43 \pm 5.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [901.485]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2B_1$	0	2
$^2A_1$	20325	2
$^2A_1$	[21000]	2
$^2A_2$	22422	2
$^2A_2$	34198	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
530 ± 30 (1)
[200] (1)
[530] (1)

Point Group: $[C_{2v}]$ $\sigma = 2$
Bond Distance: S–Cl = [2.00] Å
Bond Angle: Cl–S–Cl = [105]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.65102 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(0\ K)$ is calculated from IP = 9.46 ± 0.02 eV by addition of the JANAF $\Delta_f H°(0\ K)$ value for SCl_2.[1] The selected value of IP is calculated as the adiabatic IP from the first band system observed in the HeI photoelectron spectrum of SCl_2 by Solouki *et al.*[2] The adiabatic IP is 0.21 eV less than the vertical value determined by photoelectron spectroscopy[2] and 0.24–0.74 eV less than the vertical IP's measured by electron impact.[3,4]

$\Delta_f H°(298.15\ K)$ is obtained from the adopted $\Delta_f H°(0\ K)$ value by using JANAF enthalpies[1] for S(α, cr), Cl_2(g), and e^-(g). $\Delta_r H°(298.15\ K)$ determined for the direct ionization $SCl_2 = SCl_2^+ + e^-$ from our tables differs from a room-temperature threshold energy due to inclusion of the enthalpies of all the species in this ionization process and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by $-1.481\ kcal \cdot mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

We perform bond energy calculations which show that the S–Cl primary bond dissociation energy for SCl_2^+ (66.6 $kcal \cdot mol^{-1}$) is quite similar to that for the neutral dichloride (69.7 $kcal \cdot mol^{-1}$), indicating that the removal of the electron during ionization should produce minimal structural changes. According to the Walsh diagram[6] for AB_2 molecules, the most loosely bound electron in SCl_2 occupies a $4b_1$ orbital which is S–Cl antibonding and Cl–Cl bonding. Thus, we would expect a slight increase in the bond angle and a decrease in the S–Cl bond distance upon removing this electron to form SCl_2^+. We estimate the Cl–S–Cl bond angle as 105° (102.7° for SCl_2) and the S–Cl bond distance as 2.00 Å (2.015 Å for SCl_2). Based on this estimated structure, the principal moments of inertia are: $I_A = 5.4345 \times 10^{-39}$, $I_B = 29.6437 \times 10^{-39}$, and $I_C = 35.0782 \times 10^{-39}\ g \cdot cm^2$.

The photoelectron spectrum of SCl_2 has been measured by Solouki *et al.*[2] who reported observing a vibrational spacing of 530 ± 30 cm^{-1} in the first band system. They assigned this progression to the S–Cl symmetric stretching frequency ν_1. By analogy with the observed vibrational frequencies for SCl_2,[1] the difference between ν_1 and ν_3 is expected to be small. We adopt $\nu_1 = \nu_3 = 530\ cm^{-1}$, and we estimate the bending frequency to be 5 cm^{-1} lower than that for SCl_2 (205 cm^{-1}).[1]

The electronic configurations of the ground and excited states are predicted from Walsh's empirical diagram[6] which correlates well with the observed photoelectron spectra and calculated orbital energies for the related dihalide molecules SCl_2,[2] OCl_2, and OF_2.[7] We use relative term values for three of the four predicted states calculated from the vertical ionization energies reported by Solouki *et al.*[2] We include a second $^2A_1$ state at 21000 cm^{-1} based on the fact that this state has been observed in the PE spectrum of OCl_2,[7] lying 2258 cm^{-1} above the first $^2A_1$ state. Inclusion of this state is also supported by the results of orbital energy calculations[2] on SCl_2. The enthalpy between 0 K and 298.15 K is $-2.9764\ kcal \cdot mol^{-1}$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.453	896.427	896.427	INFINITE
100	38.080	239.130	328.914	−8.978	898.379	894.791	−467.391
200	45.858	267.979	291.835	−4.771	899.985	890.573	−232.594
250	48.783	278.542	288.148	−2.402	900.755	888.131	−185.565
298.15	50.860	287.322	287.322	0.	901.485	885.633	−155.159
300	50.928	287.636	287.323	0.094	901.512	885.535	−154.185
350	52.479	295.610	287.949	2.681	902.254	882.813	−131.753
400	53.613	302.695	289.357	5.335	900.765	880.074	−114.926
450	54.456	309.061	291.199	8.038	900.806	877.476	−101.855
500	55.095	314.833	293.278	10.777	900.787	874.888	−91.399
600	55.975	324.962	297.738	16.334	901.205	869.675	−75.712
700	56.533	333.636	302.262	21.962	901.892	864.369	−64.500
800	56.908	341.211	306.667	27.635	902.733	858.952	−56.084
900	57.170	347.930	310.886	33.340	850.540	854.505	−49.594
1000	57.361	353.964	314.897	39.067	852.753	854.827	−44.652
1100	57.503	359.438	318.701	44.810	854.953	854.928	−40.597
1200	57.613	364.446	322.307	50.566	857.139	854.829	−37.210
1300	57.698	369.061	325.729	56.332	859.308	854.548	−34.336
1400	57.767	373.340	328.979	62.105	861.461	854.101	−31.867
1500	57.822	377.327	332.070	67.885	863.594	853.501	−29.722
1600	57.867	381.060	335.017	73.669	865.709	852.759	−27.840
1700	57.905	384.570	337.829	79.458	867.805	851.885	−26.175
1800	57.937	387.880	340.519	85.250	869.882	850.889	−24.692
1900	57.964	391.013	343.095	91.045	871.939	849.777	−23.362
2000	57.988	393.987	345.566	96.843	873.977	848.558	−22.162
2100	58.009	396.817	347.939	102.643	875.994	847.237	−21.074
2200	58.028	399.516	350.223	108.445	877.991	845.821	−20.082
2300	58.047	402.096	352.423	114.249	879.968	844.314	−19.175
2400	58.065	404.567	354.544	120.054	881.922	842.722	−18.341
2500	58.083	406.937	356.593	125.862	883.855	841.049	−17.573
2600	58.103	409.216	358.573	131.671	885.765	839.299	−16.862
2700	58.124	411.409	360.490	137.482	887.653	837.476	−16.202
2800	58.148	413.523	362.346	143.296	889.518	835.583	−15.588
2900	58.176	415.564	364.146	149.112	891.361	833.625	−15.015
3000	58.208	417.537	365.893	154.931	893.183	831.603	−14.479
3100	58.244	419.446	367.590	160.754	894.983	829.520	−13.977
3200	58.286	421.296	369.240	166.580	896.765	827.380	−13.506
3300	58.334	423.090	370.845	172.411	898.528	825.184	−13.062
3400	58.388	424.833	372.407	178.247	900.276	822.935	−12.643
3500	58.449	426.526	373.929	184.089	902.011	820.635	−12.247
3600	58.517	428.174	375.413	189.937	903.734	818.286	−11.873
3700	58.592	429.778	376.861	195.792	905.450	815.889	−11.518
3800	58.676	431.341	378.274	201.656	907.160	813.445	−11.182
3900	58.767	432.867	379.655	207.528	908.868	810.957	−10.862
4000	58.866	434.356	381.003	213.409	910.577	808.425	−10.557
4100	58.973	435.811	382.323	219.301	912.291	805.850	−10.267
4200	59.088	437.233	383.613	225.204	914.011	803.233	−9.990
4300	59.211	438.625	384.876	231.119	915.743	800.575	−9.725
4400	59.342	439.988	386.113	237.047	917.488	797.876	−9.472
4500	59.479	441.323	387.326	242.988	919.250	795.138	−9.230
4600	59.624	442.632	388.514	248.943	921.032	792.361	−8.998
4700	59.776	443.916	389.679	254.913	922.836	789.544	−8.775
4800	59.934	445.176	390.822	260.898	924.666	786.688	−8.561
4900	60.098	446.413	391.944	266.900	926.522	783.795	−8.355
5000	60.267	447.629	393.045	272.918	928.408	780.863	−8.158
5100	60.442	448.824	394.127	278.953	930.326	777.893	−7.967
5200	60.622	450.000	395.191	285.007	932.277	774.885	−7.784
5300	60.805	451.156	396.236	291.078	934.264	771.839	−7.607
5400	60.993	452.294	397.263	297.168	936.287	768.756	−7.436
5500	61.183	453.415	398.274	303.277	938.348	765.635	−7.271
5600	61.377	454.519	399.269	309.404	940.448	762.475	−7.112
5700	61.573	455.607	400.248	315.552	942.588	759.278	−6.958
5800	61.770	456.680	401.211	321.719	944.768	756.044	−6.809
5900	61.969	457.738	402.160	327.906	946.990	752.771	−6.665
6000	62.169	458.781	403.095	334.113	949.254	749.460	−6.525

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

$S°(298.15\ K) = 223.844 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -58.158 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Feher and Strater[1] have measured calorimetrically the heats of chlorination of sulfur and liquid at 298.15 K. Recalculation of their calorimetric data using 1975 atomic weights[2] and a ΔC_p° of 10.80 $cal \cdot K^{-1} \cdot mol^{-1}$ for the formation reactions $2S(rh) + Cl_2(g) \rightarrow S_2Cl_2(l)$ leads to the adopted $\Delta_f H°$ of -13.9 ± 0.5 $kcal \cdot mol^{-1}$. (-58.158 ± 2.1 $kJ \cdot mol^{-1}$).

Other calorimetric values for $\Delta_f H°$ which were published prior to 1930 have been recently summarized by Mills.[3] Two of these four values, which range from -14.3 to -17.6 $kcal \cdot mol^{-1}$, agree with the adopted $\Delta_f H°$ value within the combined experimental error. Our selected value agrees with that from Mills[3] but is some 0.3 $kcal \cdot mol^{-1}$ less negative than the value (-14.2 $kcal \cdot mol^{-1}$) recommended by NBS.[4]

Heat Capacity and Entropy

C_p° has been measured calorimetrically as 29.706 $cal \cdot K^{-1} \cdot mol^{-1}$ by Trautz and Rick[5] at 295.15 K and by Ogier[6] as the mean C_p° value over the temperature range 285–343 K. We adopt this value and assume C_p° is constant from 298.15 K to 1000 K. The value of $S°(298.15\ K)$ is selected as 53.5 ± 1.0 $cal \cdot K^{-1} \cdot mol^{-1}$ which minimizes differences between the second and third law entropies of vaporization determined from two independent sets[7,8] of vapor pressure data. Further details on the results of these analyses can be found in the heat of formation section of the S_2Cl_2 gas phase table.[9]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy of vaporization becomes zero. The value of $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_f H°$ values for the gas and liquid at T_{vap}. Experimental values of T_{vap} determined from vapor pressure measurements include 411 K[7] and 408.9 K.[8]

References

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[9]JANAF Thermochemical Tables: $S_2Cl_2(g)$, 6–30–78.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	124.290	223.844	223.844	0.	−58.158	−39.271	6.880
300	124.290	224.613	223.846	0.230	−58.075	−39.154	6.817
400	124.290	260.369	228.721	12.659	−58.310	−33.318	4.351
500	124.290	288.103	237.927	25.088	−57.308	−27.213	2.843
600	124.290	310.764	248.236	37.517	−55.681	−21.336	1.857
700	124.290	329.923	258.572	49.946	−53.617	−15.771	1.177
800	124.290	346.520	268.551	62.375	−51.310	−10.519	0.687
900	124.290	361.159	278.044	74.804	−155.115	−3.405	0.198
1000	124.290	374.254	287.022	87.233	−150.135	13.185	−0.689

PREVIOUS: March 1978 CURRENT: June 1978

$S°(298.15\ K) = 327.21 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -15.2 \pm 4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -16.7 \pm 4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
546 (1)	Internal Rotation
466 (1)	461 (1)
202 (1)	244 (1)

Ground State Quantum Weight: 1 σ(overall) = 2
Point Group: C_2
Bond Distances: S–Cl = 2.057 ± 0.002 Å; S–S = 1.931 ± 0.005 Å
Bond Angles: S–S–Cl = 108.2 ± 0.3°; Dihedral Angle = 84.8 ± 1.3°
Product of Moments of Inertia: $I_A I_B I_C = 6.36049 \times 10^{-113}\ g^3\ cm^6$
Reduced Moment of Inertia: $I_{red} = 5.487 \times 10^{-39}\ g \cdot cm^2$
Potential Function for Internal Rotation: $V = 11.99 - 5.60(1-\cos 2\phi) - 0.70(1-\cos 3\phi)\ kcal \cdot mol^{-1}$

Enthalpy of Formation

Harvey and Schuette[1] and Trautz *et al.*[2] have used a static method to measure vapor pressures for liquid S_2Cl_2 at various temperatures below the normal boiling point. Barton and Yost[3] measured the extent of dissociation for gaseous S_2Cl_2 above 760 K. These dissociation data have been reanalyzed by Yost and Russell[4] who reported equilibrium constants for the reaction $S_2(g) + Cl_2(g) = S_2Cl_2(g)$. We analyze these data by the 2nd and 3rd law methods with the results presented below:

Source	Reaction	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	A	12[a]	304–411	9.46	9.89 ± 0.07	1.1 ± 0.2	4.01
2	A	Set 1 20[b]	374–410	10.0	9.93 ± 0.01	−0.1 ± 0.2	3.97
		Set 2 39[c]	329–374	10.15	9.95 ± 0.02	−0.6 ± 0.1	3.95
2	A	22	336–405	10.23	9.98 ± 0.04	−0.8 ± 0.1	3.92
4	B	Equation	760–1100	−35.4	−38.1 ± 0.9	−3.1 ± 7	7.4

Reaction: (A) $S_2Cl_2(l) = S_2Cl_2(g)$ (B) $S_2(g) + Cl_2(g) = S_2Cl_2(g)$.
[a]Points below 298.15 K not analyzed; 2 points rejected due to failure of a statistical test.
[b]Two points rejected due to failure of a statistical test.
[c]Three points rejected.

We adopt $\Delta_f H°(S_2Cl_2, g, 298.15\ K) = -4.0\ kcal \cdot mol^{-1}$ which is the rounded mean value determined from the four 3rd law enthalpies of vaporization. We estimate the uncertainty in the $\Delta_f H°$ value as ± 1.0 kcal·mol^{-1} which includes contributions from the uncertainties in the values of $\Delta_f H°$(298.15 K) and $S°$(298.15 K) for the liquid.[5] $\Delta_f H°(0\ K)$ is − 3.6 kcal·mol^{-1} and the enthalpy of atomization is 192.1 ± 1.0 kcal·mol^{-1}.

Bodewig and Plambeck[6] determined $\Delta_r G = -12.4\ kcal \cdot mol^{-1}$ for $2\ S(l) + 2\ Cl^- = S_2Cl_2(g) + 2\ e^-$ in fused LiCl–KCL eutectic at 693 K. This datum has been analyzed by Mills[7] who reported $\Delta_f H°(298.15\ K)$ value of $-5.8 \pm 2\ kcal \cdot mol^{-1}$. Our selected $\Delta_f H°$ value is some 0.4 kcal·mol^{-1} less negative than that recommended by NBS[8] and is only 0.1 kcal·mol^{-1} less negative than the value adopted by Mills.[7]

Heat Capacity and Entropy

The heat capacity and entropy values from 298.15 K to 1500 K are those calculated by Frankiss and Harrison[9] who used gas-phase infrared ($\nu_1 = 546\ cm^{-1}$)[10] and Raman[9] frequencies and the most recent structural data determined in an electron diffraction study by Beagley *et al.*[11] Contributions to the thermal functions for internal rotation were determined by integration of the potential function from $\phi = 0°$ to 2π. Terms in the potential function were established from the torsional vibration ($\nu_4 = 92\ cm^{-1}$) and the dihedral angle (84.8°)[11] of the two rotamers. Thermal functions are calculated below 298.15 K by treating the torsion as a harmonic oscillator and including its contribution in the vibrational partition function. Justification for this treatment lies in the fact that values of the ratio V_o/RT become extremely large (>20) at these lower temperatures. We add $R\ln 2$ to the calculated entropies below 298.15 K to account for the optical activity of the skew rotamer. The absorption spectra[12] reported for S_2Cl_2 vapor indicate no low-lying electronic states which would contribute to the thermal functions below 1500 K. The principal moments of inertia are: $I_A = 15.2331 \times 10^{-39}$, $I_B = 60.6645 \times 10^{-39}$, and $I_C = 68.8282 \times 10^{-9}\ g \cdot cm^2$.

Thermodynamic functions previously published for S_2Cl_2 have been reviewed by Frankiss and Harrison[9] who concluded that all previous calculations had treated incorrectly the internal rotation of the SCl top. Noble and Mei[13] have discussed the vibrational spectral data on S_2Cl_2 published prior to 1974.

Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−16.479	−15.210	−15.210	INFINITE
100	49.149	260.367	385.447	−12.508	−15.531	−20.162	10.532
200	64.455	299.547	333.379	−6.766	−16.111	−24.572	6.418
298.15	72.768	327.215	327.215	0.	−16.736	−28.669	5.023
300	72.881	327.665	327.216	0.135	−16.748	−28.743	5.005
400	77.032	349.244	330.130	7.646	−21.901	−32.460	4.239
500	79.350	366.698	335.754	15.472	−25.503	−34.705	3.626
600	80.818	381.301	342.162	23.484	−28.292	−36.269	3.158
700	81.839	393.840	348.670	31.619	−30.523	−37.417	2.792
800	82.588	404.819	355.016	39.842	−32.422	−38.270	2.499
900	83.140	414.580	361.102	48.130	−140.368	−36.736	2.132
1000	83.529	423.361	366.897	56.464	−139.482	−25.269	1.320
1100	83.780	431.335	372.398	64.831	−138.609	−13.890	0.660
1200	83.931	438.632	377.618	73.217	−137.758	−2.589	0.113
1300	83.990	445.353	382.573	81.614	−136.939	8.641	−0.347
1400	83.969	451.576	387.282	90.012	−136.158	19.810	−0.739
1500	83.902	457.368	391.764	98.406	−135.422	30.925	−1.077

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

$S°(298.15\ K) = [281.333 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -168.74 \pm 3.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -168.62 \pm 3.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1A_1]$	0	[1]
$[^3B_1]$	[23000]	[3]
	[28300]	[1]
	[29950]	[1]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
514.0 (1)
202.2 (1)
502.7 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Si–Cl = [2.03] Å
Bond Angle: Cl–Si–Cl = 105° ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = [5.55300 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(SiCl_2, g, 298.15\ K) = -40.3\ kcal \cdot mol^{-1}$ is the mean value derived from four studies.[2,3,7,8] JANAF analyses of all the equilibrium data are summarized below. The $\Delta_f H°(298.15\ K)$ values are calculated from the third law $\Delta_r H°(298.15\ K)$ values using auxiliary JANAF data.[1] Four sets of data[2,3,7,8] yield average values of $\Delta_f H°$ (from third law) which agree within 0.4 $kcal \cdot mol^{-1}$ and values of $\Delta_r S°$(second law) which are in reasonable agreement with the JANAF functions. Two of these equilibrium studies used flow techniques, one used mass spectrometry, while the fourth used a static technique. The adopted $\Delta_f H°(298.15\ K)$ value corresponds to $\Delta_{at} H°(0\ K) = 204.2\ kcal \cdot mol^{-1}$ and an average bond energy of 102.1 $kcal \cdot mol^{-1}$. This latter value compares with 94.7 $kcal \cdot mol^{-1}$ for $SiCl_4(g)$, implying that the average bond energy in $SiCl_2(g)$ is 7% larger.

Two other flow studies[4,5] yield large entropy errors, suggesting that there are temperature-dependent errors in $K_p°$. The reported equilibrium constants are reasonable at the lower temperatures but deviate progressively at the higher temperatures. In contrast, the static study of Ishino[6] gave $K_p°$ values which differ by a factor of five from the adopted ones. These data yield a consistent entropy but $\Delta_r H°$ (third law) is lower by 5 $kcal \cdot mol^{-1}$.

Source	Method	Points	T/K	Reaction*	$\Delta_r H°(298.15\ K)$, kcal mol^{-1} 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
Schafer *et al.*[2]	flow	Equation	1273–1473	A	80.56	77.93	−1.9	−40.2
Teichmann and Wolf[3]	flow	Equation	1223–1573	A	80.83	78.06	−2.0	−40.2
Chechentsev *et al.*[4]	flow	3	1473–1573	A	131.78	75.96	−37 ± 6	−41.2
Antipin and Sergeev[5]	flow	5	1273–1673	A	113.99	75.00	−26 ± 3	−41.7
Ishino *et al.*[6]	static	27	1448–1573	A	70.24	72.97	1.8 ± 4	−42.7
Schafer and Nickl[7]	static	Equation	1400–1593	A	79.78	78.38	−0.9	−40.0
Farber and Srivastava[8]	mass spec	10	1593–1792	B	−31.62	−30.95	0.4 ± 2.0	−40.8

*Reactions (A) $Si(cr) + SiCl_4(g) = 2\ SiCl_2(g)$ (B) $Si(g) + SiCl_4(g) = 2\ SiCl_2(g)$

Heat Capacity and Entropy

Maass *et al.*[9] observed the infrared spectra of $SiCl_2$ in argon, neon, and nitrogen matrices. They observed and assigned all three fundamental frequencies. The bond angle was calculated to be 105 ± 3° from the isotopic splitting. The bond length is assumed to be the same as in SiH_2Cl_2.[1] The earlier work of Milligan and Jacox[10] is consistent with these results. The principal moments of inertia are: $I_A = 5.1016 \times 10^{-39}$, $I_B = 30.5397 \times 10^{-39}$, $I_C = 35.6413 \times 10^{-39}\ g \cdot cm^2$.

The ground state is assumed to be $^1A_1$ as suggested by Huckel-molecular-orbital calculation.[12] Singlet excited states[11,12] are included near 28000 and 30000 cm^{-1}, but the values are placed in brackets to emphasize the uncertainty in the analysis. Also tentatively adopted is the suggestion by Hastie *et al.*[13] that the continuous spectrum near 23000 cm^{-1} is due to a triplet excited state.

Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−12.524	−168.740	−168.740	INFINITE
100	38.144	232.778	323.282	−9.050	−168.445	−172.439	90.073
200	46.298	261.819	285.885	−4.813	−168.424	−176.462	46.087
250	49.217	272.481	282.167	−2.421	−168.501	−178.464	37.288
298.15	51.248	281.333	281.333	0.	−168.615	−180.373	31.601
300	51.313	281.651	281.334	0.095	−168.620	−180.446	31.418
350	52.810	289.679	281.965	2.700	−168.769	−182.405	27.222
400	53.893	296.806	283.383	5.369	−168.938	−184.342	24.073
450	54.693	303.202	285.236	8.085	−169.122	−186.256	21.620
500	55.297	308.997	287.327	10.835	−169.321	−188.150	19.656
600	56.125	319.158	291.809	16.410	−169.754	−191.875	16.704
700	56.648	327.852	296.352	22.050	−170.234	−195.525	14.590
800	56.998	335.441	300.774	27.733	−170.759	−199.103	13.000
900	57.243	342.169	305.006	33.446	−171.328	−202.612	11.759
1000	57.421	348.210	309.030	39.180	−171.942	−206.056	10.763
1100	57.553	353.689	312.845	44.929	−172.599	−209.435	9.945
1200	57.655	358.701	316.460	50.689	−173.299	−212.754	9.261
1300	57.734	363.320	319.889	56.459	−174.042	−216.012	8.679
1400	57.798	367.600	323.146	62.236	−174.830	−219.211	8.179
1500	57.849	371.590	326.244	68.018	−175.663	−222.352	7.743
1600	57.891	375.325	329.196	73.805	−176.541	−225.436	7.360
1700	57.926	378.836	332.014	79.596	−227.644	−228.017	7.006
1800	57.956	382.147	334.708	85.390	−228.387	−228.018	6.617
1900	57.981	385.282	337.288	91.187	−229.137	−227.977	6.268
2000	58.003	388.256	339.763	96.987	−229.895	−227.896	5.952
2100	58.021	391.087	342.140	102.788	−230.662	−227.778	5.666
2200	58.038	393.786	344.427	108.591	−231.439	−227.622	5.404
2300	58.053	396.366	346.629	114.395	−232.228	−227.431	5.165
2400	58.068	398.837	348.754	120.201	−233.031	−227.205	4.945
2500	58.081	401.208	350.805	126.009	−233.847	−226.946	4.742
2600	58.095	403.486	352.787	131.818	−234.680	−226.653	4.554
2700	58.110	405.679	354.706	137.628	−235.529	−226.329	4.379
2800	58.126	407.793	356.564	143.440	−236.396	−225.972	4.216
2900	58.144	409.833	358.366	149.253	−237.281	−225.584	4.063
3000	58.164	411.804	360.115	155.069	−238.183	−225.166	3.920
3100	58.188	413.712	361.813	160.886	−239.102	−224.717	3.786
3200	58.215	415.560	363.464	166.706	−240.037	−224.238	3.660
3300	58.247	417.352	365.070	172.529	−240.987	−223.729	3.541
3400	58.284	419.091	366.633	178.356	−241.951	−223.192	3.429
3500	58.326	420.781	368.156	184.186	−242.926	−222.626	3.323
3600	58.374	422.425	369.641	190.021	−628.061	−211.571	3.070
3700	58.429	424.025	371.089	195.861	−628.637	−199.994	2.823
3800	58.492	425.584	372.503	201.707	−629.217	−188.402	2.590
3900	58.561	427.104	373.884	207.560	−629.799	−176.794	2.368
4000	58.639	428.588	375.233	213.420	−630.378	−165.171	2.157
4100	58.725	430.037	376.552	219.288	−630.951	−153.533	1.956
4200	58.819	431.453	377.842	225.165	−631.514	−141.882	1.765
4300	58.922	432.838	379.105	231.052	−632.064	−130.218	1.582
4400	59.033	434.194	380.342	236.950	−632.597	−118.541	1.407
4500	59.154	435.522	381.553	242.859	−633.109	−106.852	1.240
4600	59.283	436.824	382.741	248.781	−633.598	−95.152	1.080
4700	59.421	438.100	383.905	254.716	−634.059	−83.441	0.927
4800	59.567	439.353	385.047	260.665	−634.490	−71.721	0.780
4900	59.722	440.582	386.168	266.630	−634.887	−59.993	0.640
5000	59.885	441.791	387.269	272.610	−635.250	−48.257	0.504
5100	60.055	442.978	388.349	278.607	−635.573	−36.514	0.374
5200	60.234	444.146	389.411	284.621	−635.857	−24.765	0.249
5300	60.420	445.295	390.455	290.654	−636.098	−13.010	0.128
5400	60.612	446.426	391.481	296.705	−636.295	−1.252	0.012
5500	60.811	447.540	392.490	302.776	−636.446	10.510	−0.100
5600	61.016	448.638	393.483	308.868	−636.550	22.273	−0.208
5700	61.227	449.720	394.460	314.980	−636.606	34.039	−0.312
5800	61.442	450.786	395.422	321.113	−636.613	45.805	−0.413
5900	61.663	451.838	396.369	327.268	−636.571	57.570	−0.510
6000	61.887	452.877	397.302	333.446	−636.477	69.334	−0.604

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 114.809 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1000 \pm 10\ K$
$T_{fus} = 1147 \pm 1\ K$

$\Delta_f H°(0\ K) = -829.34 \pm 2.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -828.85 \pm 2.5\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = [6.008 \pm 1.3]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 16.221 \pm 0.63\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is from[1] and was selected by Parker in a manner analogous to that described[2] for $\Delta_f H°(BaCl_2, cr)$. The adopted value is essentially that derived by Ehrlich *et al.*[3] from their measurements of $\Delta_{sol} H°$ of Sr(cr) and $SrCl_2$(cr) in HCl(aq, 550 H_2O). Earlier solution data for Sr[4] and $SrCl_2$[5] are in good agreement.

Parker[2] rejected $\Delta_f H° = -210\ kcal \cdot mol^{-1}$ obtained by Siemonsen[6] from direct chlorination and $\Delta_f H° = -201.0\ kcal \cdot mol^{-1}$ which would result from SrO(cr) based on Mah's direction combustion.[7] Parker noted that these more negative values are inconsistent with data for $SrCl_2$(cr, aq) and related compounds. They are also less consistent with equilibrium data discussed on the tables for $SrCl_2$(*l*, g). Impurity effects are of concern in all these studies involving Sr(cr), but the evidence favors the solution calorimetry.

Heat Capacity and Entropy

$C_p°$ is based on adiabatic calorimetry (7.4–300 K) of Smith *et al.*[8] with omission of the point at 11.22 K which appears to be about 30% low. $S°$ is calculated from $C_p°$ using $S°(7\ K) = 0.012\ cal \cdot K^{-1} \cdot mol^{-1}$. $C_p°$ above 300 K is from constrained fitting of enthalpy data (418–936 K for α–phase and 1034–1134 K for β–phase) from Dworkin and Bredig.[9]

The transition near 1000 K is gradual and may be second order rather than first order as we have treated it. Gradual transitions also are observed for BaF_2, SrF_2 and perhaps CaF_2, all of which have α–phases of the fluorite structure. Reasonable $C_p°$ curves are obtained by omitting from the curve fits those enthalpy data from about 50 below to 30 above T_{trs}. The resulting Gibbs–energy functions agree well with those obtained[9] by second–order analysis.

Deviations of the fitted data[9] from the adopted functions for α–phase are −0.5 to +0.3% except for +2.0% at 417.6 K. Data of Efremova and Matizen[10] deviate by +0.6 to +2.2% (805–959 K), while the equation of Janz *et al.*[11] agrees almost exactly near 850 K but deviates by −4.8% at 600 K. The β–phase deviations are −0.4 to +0.3%[9], 0.0 to −1.0%, (1047–1142 K)[10] and −2 to 0%, (1050–1147 K).[11]

Transition Data

T_{trs} = 1000 K is arbitrarily selected as the peak of the gradual transition. Reported values include 1003,[9] 1002[11] and 990 K.[10] $\Delta_{trs} H°$ is calculated as the difference in the enthalpy curve fits (cf. above) at T_{trs}. $\Delta_{trs} H°$ is assigned an uncertainty of 0.3 $kcal \cdot mol^{-1}$ as a first–order transition, but the result is placed in brackets to emphasize that the transition may be a second order. Reported values of $\Delta_{trs} H°$ include 1.65[9] and 0.65[11] $kcal \cdot mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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[11]G. J. Janz, F. J. Kelly and J. L. Perano, Trans. Faraday Soc. **59**, 2718 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.242	−829.344	−829.344	INFINITE
100	54.296	41.459	178.054	−13.659	−831.172	−813.612	424.988
200	70.735	85.571	121.583	−7.202	−830.241	−796.320	207.978
298.15	75.588	114.809	114.809	0.	−828.850	−779.965	136.647
300	75.659	115.277	114.810	0.140	−828.823	−779.661	135.751
400	78.889	137.512	117.820	7.877	−827.285	−763.503	99.703
500	81.321	155.385	123.603	15.891	−825.670	−747.743	78.116
600	83.659	170.415	130.185	24.138	−823.985	−732.315	63.754
700	86.580	183.518	136.887	32.642	−822.187	−717.177	53.516
800	90.793	195.336	143.465	41.497	−820.171	−702.309	45.856
900	96.977	206.364	149.846	50.866	−818.397	−687.644	39.910
1000	105.826	217.013	156.032	60.981	−815.052	−673.287	35.169
1000.010	105.827	217.014	156.033	60.982	ALPHA <--> BETA		
1000.010	123.010	223.022	156.033	66.990	TRANSITION		
1100	123.010	234.745	162.663	79.290	−811.429	−659.613	31.322
1147.000	123.010	239.892	165.723	85.071	---- BETA <--> LIQUID ----		
1200	123.010	245.448	169.123	91.591	−806.836	−646.014	28.120
1300	123.010	255.294	175.378	103.892	−802.254	−632.798	25.426
1400	123.010	264.410	181.415	116.193	−797.681	−619.935	23.130
1500	123.010	272.897	187.235	128.494	−793.117	−607.398	21.151
1600	123.010	280.836	192.839	140.795	−788.562	−595.166	19.430
1700	123.010	288.293	198.237	153.096	−920.931	−582.038	17.884
1800	123.010	295.324	203.437	165.397	−914.533	−562.288	16.317
1900	123.010	301.975	208.450	177.698	−908.151	−542.893	14.925
2000	123.010	308.285	213.285	189.999	−901.787	−523.833	13.681

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = [135.820]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1147 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-805.352]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 16.221 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of the crystal by addition of $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1147\ K) - H°(298.15\ K)$, between the crystal and liquid. An independent value of $\Delta_f H°$ for liquid (and crystal) may be derived from equilibrium data[1] for $Ca(l) + SrCl_2(l) \rightarrow Sr(l) + CaCl_2(l)$ at 1273 K. Our third-law analysis yields $\Delta_r H°(298.15\ K) = 6.5 \pm 1.3$ kcal·mol^{-1} or $\Delta_f H°(l) = -191.5 \pm 1.5$ kcal·mol^{-1} and $\Delta_f H°(cr) = -197.2 \pm 1.5$ kcal·mol^{-1}. This confirms the adopted values as opposed to the more negative values (cf. $SrCl_2$, cr).

Heat Capacity and Entropy

The constant $C_p°$ of 25.0 cal·K^{-1}·mol^{-1} is a compromise chosen by comparison with $BaCl_2$ and $CaCl_2$. Our fits of the enthalpy data yield 26.8[2] and 23.5[3] cal·K^{-1}·mol^{-1}; the adopted value is roughly their mean. The value 26.7 cal·K^{-1}·mol^{-1} was also reported.[4] Deviations from our adopted functions are ±0.3% (1154–1204 K),[2] +1.1 to −1.7% (1152–1797 K),[3] and −1.1 to −0.2% (equation, 1148–1287 K).[4] $C_p°$ is taken equal to that of the crystal from 298.15 to 800 K, the assumed glass transition. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is selected from 1146,[2] 1147 ± 2[3] and 1148 K[4] reported in the enthalpy studies. $\Delta_{fus} H°$ is obtained from the difference in the adopted enthalpy fits for liquid and β-phases. Published values include 3.85,[2,3] 3.88,[2] 3.65 ± 0.17[4] and 3.73 kcal·mol^{-1},[5] the last value obtained by dynamic differential calorimetry.

Vaporization Data

T_{vap} is calculated as the temperature at which $\Delta_r G° = 0$ for $SrCl_2(l) \rightarrow SrCl_2(g)$. $\Delta_{vap} H°$ is calculated as the corresponding $\Delta_r H°$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
0							
100							
200							
298.15	75.588	135.820	135.820	0.	−805.351	−762.730	133.627
300	75.659	136.288	135.822	0.140	−805.323	−762.465	132.757
400	78.889	158.524	138.832	7.877	−803.786	−748.408	97.732
500	81.321	176.397	144.615	15.891	−802.170	−734.749	76.759
600	83.659	191.426	151.196	24.138	−800.486	−721.422	62.805
700	86.580	204.529	157.898	32.642	−798.687	−708.385	52.860
800	90.793	216.348	164.476	41.497	−796.671	−695.619	45.419
800.010	90.793	216.349	164.477	41.498	GLASS <--> LIQUID		
800.010	104.600	216.349	164.477	41.498	TRANSITION		
900	104.600	228.668	170.938	51.957	−793.806	−683.126	39.648
1000	104.600	239.688	177.271	62.417	−790.116	−671.027	35.051
1100	104.600	249.658	183.406	72.877	−794.343	−658.930	31.290
1147.000	104.600	254.034	186.211	77.793	---- BETA <--> LIQUID		----
1200	104.600	258.759	189.312	83.337	−791.591	−646.742	28.152
1300	104.600	267.132	194.980	93.797	−788.849	−634.782	25.506
1400	104.600	274.883	200.414	104.257	−786.117	−623.033	23.246
1500	104.600	282.100	205.622	114.717	−783.394	−611.480	21.294
1600	104.600	288.851	210.615	125.177	−780.680	−600.107	19.591
1700	104.600	295.192	215.406	135.637	−914.890	−587.725	18.059
1800	104.600	301.171	220.006	146.097	−910.333	−568.611	16.501
1900	104.600	306.826	224.428	156.557	−905.792	−549.751	15.114
2000	104.600	312.191	228.683	167.017	−901.269	−531.129	13.872
2100	104.600	317.295	232.782	177.477	−896.769	−512.732	12.754
2200	104.600	322.161	236.735	187.937	−892.298	−494.550	11.742
2300	104.600	326.811	240.551	198.397	−887.862	−476.570	10.823
2400	104.600	331.262	244.239	208.857	−883.470	−458.782	9.985
2500	104.600	335.532	247.805	219.317	−879.131	−441.176	9.218
2600	104.600	339.635	251.259	229.777	−874.852	−423.742	8.513
2700	104.600	343.582	254.606	240.237	−870.645	−406.472	7.864
2800	104.600	347.386	257.852	250.697	−866.521	−389.356	7.264
2900	104.600	351.057	261.003	261.157	−862.488	−372.386	6.707
3000	104.600	354.603	264.064	271.617	−858.558	−355.553	6.191

PREVIOUS: CURRENT: December 1972

0	to 1000	K	crystal, alpha
1000	to 1147	K	crystal, beta
above	1147	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	0.	−813.101	−813.101	INFINITE
100	65.775	38.171	178.944	−14.077	−831.590	−813.701	425.034
200	71.271	85.512	121.591	−7.216	−830.254	−796.322	207.978
298.15	75.588	114.809	114.809	0.	−828.850	−779.965	136.647
300	75.659	115.277	114.810	0.140	−828.823	−779.661	135.751
400	78.889	137.512	117.820	7.877	−827.285	−763.503	99.703
500	81.321	155.385	123.603	15.891	−825.670	−747.743	78.116
600	83.659	170.415	130.185	24.138	−823.985	−732.315	63.754
700	86.580	183.518	136.887	32.642	−822.187	−717.177	53.516
800	90.793	195.336	143.465	41.497	−820.171	−702.309	45.856
900	96.977	206.364	149.846	50.866	−818.397	−687.644	39.910
1000	105.826	217.013	156.032	60.981	−815.052	−673.287	35.169
1000.010	105.827	217.014	156.033	60.982	ALPHA <--> BETA		
1000.010	123.010	223.022	156.033	66.990	TRANSITION		
1100	123.010	234.745	162.663	79.290	−811.429	−659.613	31.322
1147.000	123.010	239.892	165.723	85.071	BETA <--> LIQUID		
1147.000	104.600	254.034	165.723	101.293	TRANSITION		
1200	104.600	258.759	169.729	106.836	−791.591	−646.742	28.152
1300	104.600	267.132	176.903	117.296	−788.849	−634.782	25.506
1400	104.600	274.883	183.629	127.756	−786.117	−623.033	23.246
1500	104.600	282.100	189.956	138.216	−783.394	−611.480	21.294
1600	104.600	288.851	195.928	148.676	−780.680	−600.107	19.591
1700	104.600	295.192	201.582	159.136	−914.890	−587.725	18.059
1800	104.600	301.171	206.950	169.596	−910.333	−568.611	16.501
1900	104.600	306.826	212.060	180.056	−905.792	−549.751	15.114
2000	104.600	312.191	216.933	190.516	−901.269	−531.129	13.872
2100	104.600	317.295	221.592	200.976	−896.769	−512.732	12.754
2200	104.600	322.161	226.053	211.436	−892.298	−494.550	11.742
2300	104.600	326.811	230.334	221.896	−887.862	−476.570	10.823
2400	104.600	331.262	234.447	232.356	−883.470	−458.782	9.985
2500	104.600	335.532	238.406	242.816	−879.131	−441.176	9.218
2600	104.600	339.635	242.221	253.276	−874.852	−423.742	8.513
2700	104.600	343.582	245.902	263.736	−870.645	−406.472	7.864
2800	104.600	347.386	249.459	274.196	−866.521	−389.356	7.264
2900	104.600	351.057	252.900	284.656	−862.488	−372.386	6.707
3000	104.600	354.603	256.231	295.116	−858.558	−355.553	6.191

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = 316.340 \pm 5.0\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -471.91 \pm 6.3\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -473.21 \pm 6.3\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
270 (1)	44 (1)	300 (1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Sr–Cl = 2.67 ± 0.03 Å

Bond Angle: Cl–Sr–Cl = 120° ± 20°

Product of the Moments of Inertia: $I_A I_B I_C = 5.44364 \times 10^{-113}\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$(298.15 K) is calculated from $\Delta_f H°$(cr) by addition of $\Delta_{sub}H° = 85.0 \pm 1.5\ kcal\cdot mol^{-1}$ derived by third law analysis of the vapor–pressure equation of Hildenbrand *et al.*[1,2] The equation[1] summarized five torsion–effusion runs (102 total points) and is reasonably consistent with three boiling pressures in the mmHg range measured by Novikov and Gavryuchenkov.[3] Effusion studies[4–7] yield lower values of $\Delta_{sub}H°$, but that of Loehman *et al.*[6] is consistent with the adopted value. Langmuir data[6] suggest that the sublimation coefficient is 0.3 ± 0.2. Equilibria derived from flame studies[8,9] and mass–spectrometric effusion[10] confirm the adopted $\Delta_f H°$ via independent paths (cf. below). Mass spectra[11] at 1220 K showed that the saturated vapor consists predominantly of $SrCl_2$ with considerably less than 1% of dimer.

Source	Method	T/K	$\Delta_{sub}H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[1,2]Hildenbrand *et al.* (1965)	Torsion effusion[a]	1220–1425	84.0	85.00	−0.8	−113.1
[3]Novik and Gavryuchenkov	Boiling Point	1620–1710	75.8 ± 9.4	85.52 ± 0.7	−5.8 ± 5.6	−112.6
[4]Novikov *et al.*	Total effusion[a]	1137–1422	75.2	82.3	−5.1	
[5]Naryshkin *et al.*	Effusion[a]	893–1141	75.6	78.0	−2.3	
[6]Loehman *et al.*	Effusion	1195–1307	82.9 ± 3.9	84.2 ± 0.7	−1.0 ± 3.1	−113.9
[6]Loehman *et al.*	Langmuir[b]	968–1119	78.7 ± 3.6	86.3 ± 1.5	−7.4 ± 3.5	−111.8
[7]Van Westenburg	Effusion	1175–1287	80.3 ± 0.5	82.8 ± 0.2	−2.0 ± 0.4	
[8]Schofield and Sugden	Flame K_p[c]	~2134–2350	−9.1 ± 3.7[c]	−1.6 ± 0.8[c]	−3.3 ± 1.6	−110.7 ± 2
[9]Ryabova *et al.*	Flame K_p	1813–2209	9.0 ± 25[c]	−2.0 ± 7.2[c]	5.5 ± 12	−111.1 ± 7
[10]Hildenbrand	Mass spec. K_p[d]	1661		3.7[d]		−112.7 ± 2

[a] Pressures obtained from an equation.

[b] Assuming a sublimation coefficient of 1.0; agreement with[1] requires $\alpha = 0.5$.

[c] $\Delta_r H°$ for $Sr(g) + 2\ HCl(g) = SrCl_2(g) + 2\ H(g)$.

[d] $\Delta_r H°$ for $Sr(g) + CaCl_2(g) = SrCl_2(g) + Ca(g)$.

Heat Capacity and Entropy

Vibrations ν_2 and ν_3 are the values quoted by Hildenbrand[10] and derived from IR spectra of molecules in matrix isolation.[12] The bending mode was observed.[13] Hastie *et al.*[14] failed to observe ν_2 but estimated a higher value of 60 ± 15 cm^{-1}. Agreement is better for $\nu_1 = 269$[10,13] or 274 cm^{-1} [14] and for $\nu_3 = 300 \pm 7$,[15](gas) 300[10,13] or 307 cm^{-1}.[14] We adopt a rounded value of 270 cm^{-1} for ν_1.

Bond length is from gas–phase electron diffraction[16] which also gave the bond angle 180° ± 30°. Later studies[17] of electric deflection of molecular beams revealed a permanent electric dipole moment, leading to the conclusion that $SrCl_2$ is bent. The matrix spectra[10,12] were first interpreted to give an angle of 155° but reanalysis[13] gave the angle 112°, calculated from the three observed fundamentals. An angle of 130° ± 8° was derived by Hastie *et al.*[14] from the Cl–isotope splitting of ν_3. We adopt an intermediate value of 120° ± 20°. $S°$ would change by +0.1 cal·K^{-1}·mol^{-1} for 112° and −1.3 cal·K^{-1}·mol^{-1} for 155°. The singlet ground state is taken by analogy with $BaCl_2$(g). Principal moments of inertia are $I_A = 11.5986 \times 10^{-39}$, $I_B = 62.9539 \times 10^{-39}$, and $I_C = 74.5525 \times 10^{-39}\ g\cdot cm^2$.

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Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−14.449	−471.910	−471.910	INFINITE
100	46.112	259.888	363.999	−10.411	−472.284	−476.567	248.933
200	53.351	294.507	321.380	−5.375	−472.773	−480.640	125.530
250	54.877	306.591	317.253	−2.666	−472.985	−482.588	100.831
298.15	55.775	316.339	316.339	0.	−473.210	−484.411	84.867
300	55.802	316.685	316.341	0.103	−473.220	−484.480	84.356
350	56.397	325.334	317.022	2.909	−473.485	−486.337	72.582
400	56.798	332.893	318.544	5.740	−473.782	−488.153	63.746
450	57.080	339.600	320.518	8.587	−474.112	−489.930	56.870
500	57.286	345.625	322.732	11.446	−474.475	−491.668	51.364
600	57.559	356.096	327.446	17.190	−475.293	−495.032	43.096
700	57.727	364.982	332.190	22.955	−476.234	−498.249	37.180
800	57.836	372.698	336.782	28.733	−477.295	−501.323	32.733
900	57.912	379.515	341.158	34.521	−479.102	−504.185	29.262
1000	57.966	385.620	345.305	40.315	−480.078	−506.920	26.479
1100	58.007	391.146	349.225	46.114	−488.965	−509.191	24.179
1200	58.038	396.195	352.932	51.916	−490.871	−510.945	22.241
1300	58.062	400.842	356.441	57.721	−492.785	−512.541	20.594
1400	58.081	405.145	359.768	63.528	−494.706	−513.988	19.177
1500	58.096	409.153	362.928	69.337	−496.634	−515.298	17.944
1600	58.109	412.903	365.936	75.147	−498.570	−516.480	16.861
1700	58.119	416.426	368.803	80.959	−637.427	−516.360	15.866
1800	58.128	419.748	371.542	86.771	−637.519	−509.236	14.778
1900	58.136	422.891	374.162	92.584	−637.624	−502.106	13.804
2000	58.142	425.873	376.674	98.398	−637.747	−494.970	12.927
2100	58.147	428.710	379.085	104.213	−637.893	−487.828	12.134
2200	58.152	431.415	381.403	110.028	−638.067	−480.678	11.413
2300	58.156	434.000	383.634	115.843	−638.276	−473.520	10.754
2400	58.160	436.475	385.784	121.659	−638.528	−466.351	10.150
2500	58.163	438.850	387.860	127.475	−638.832	−459.171	9.594
2600	58.166	441.131	389.865	133.292	−639.197	−451.978	9.080
2700	58.168	443.326	391.805	139.108	−639.634	−444.769	8.605
2800	58.171	445.442	393.683	144.925	−640.152	−437.542	8.162
2900	58.173	447.483	395.503	150.742	−640.762	−430.296	7.750
3000	58.175	449.455	397.269	156.560	−641.474	−423.026	7.366
3100	58.176	451.363	398.983	162.377	−642.299	−415.732	7.005
3200	58.178	453.210	400.649	168.195	−643.246	−408.408	6.667
3300	58.179	455.000	402.269	174.013	−644.323	−401.053	6.348
3400	58.180	456.737	403.845	179.831	−645.539	−393.664	6.048
3500	58.182	458.423	405.381	185.649	−646.900	−386.236	5.764
3600	58.183	460.062	406.877	191.467	−648.411	−378.767	5.496
3700	58.184	461.657	408.336	197.285	−650.078	−371.255	5.241
3800	58.185	463.208	409.760	203.104	−651.904	−363.695	4.999
3900	58.185	464.720	411.150	208.922	−653.889	−356.085	4.769
4000	58.186	466.193	412.508	214.741	−656.035	−348.422	4.550
4100	58.187	467.630	413.835	220.560	−658.341	−340.703	4.341
4200	58.187	469.032	415.132	226.378	−660.800	−332.927	4.141
4300	58.188	470.401	416.402	232.197	−663.416	−325.090	3.949
4400	58.189	471.739	417.644	238.016	−666.182	−317.190	3.766
4500	58.189	473.046	418.861	243.835	−669.091	−309.226	3.589
4600	58.190	474.325	420.053	249.654	−672.072	−301.201	3.420
4700	58.190	475.577	421.221	255.473	−675.229	−293.105	3.257
4800	58.191	476.802	422.366	261.292	−678.503	−284.940	3.101
4900	58.191	478.002	423.489	267.111	−681.886	−276.706	2.950
5000	58.191	479.177	424.591	272.930	−685.364	−268.402	2.804
5100	58.192	480.330	425.673	278.749	−688.913	−260.030	2.663
5200	58.192	481.460	426.735	284.568	−692.560	−251.585	2.527
5300	58.192	482.568	427.778	290.388	−696.276	−243.069	2.396
5400	58.193	483.656	428.803	296.207	−700.052	−234.483	2.268
5500	58.193	484.724	429.810	302.026	−703.877	−225.826	2.145
5600	58.193	485.772	430.800	307.845	−707.743	−217.099	2.025
5700	58.194	486.802	431.773	313.665	−711.641	−208.303	1.909
5800	58.194	487.814	432.731	319.484	−715.560	−199.438	1.796
5900	58.194	488.809	433.673	325.304	−719.284	−190.530	1.687
6000	58.194	489.787	434.600	331.123	−723.193	−181.536	1.580

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 87.345 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -514.76 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -515.47 \pm 16.7\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of $TiCl_2$(cr) has been measured calorimetrically. The chosen value of $\Delta_f H°(298.15\ K)$ is the average of two such determinations. Values of $\Delta_f H°(298.15\ K)$ are also calculated from the heats of reaction for the processes (A) $2TiCl_3(cr) = TiCl_2(cr) + TiCl_4(g)$, (B) $3TiCl_2(cr) = 2TiCl_3(g) + Ti(cr)$, and (C) $2TiCl_2(cr) = TiCl_4(g) + Ti(cr)$. These enthalpies of reaction are combined with auxiliary JANAF values for the heats of formation of $TiCl_3$(cr), $TiCl_4$(g), $TiCl_3$(cr) and Ti(cr). The following table summarizes the data used to calculate $\Delta_f H°(298.15\ K)$.

Source	Reaction	Method	Data Points	T/K	$\Delta_f H°(298.15\ K)$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
Clifton and MacWood[1]	Calorimetric							−123.4, − 123.8
Krieve *et al.*[2]	Calorimetric							−122.4
Farber and Darnell[3]	A	Effusion	11	615–732	36.0 ± 1.4	38.9	4.2 ± 2.1	−123.7
Sanderson and MacWood[4]	A	Knudsen	22*	593–720	35.6 ± 0.8	39.6	6.1 ± 1.3	−123.0
Sanderson and MacWood[4]	A	Static	15**	679–821	38.5 ± 0.5	35.9	−3.4 ± 0.7	−126.7
Farber and Darnell[5]	B	Effusion	13	798–893	94.4 ± 1.9	112.6	21.4 ± 2.2	−123.1
Farber and Darnell[5]	C	Effusion	11	794–894	51.5 ± 1.4	63.0	13.6 ± 1.7	−122.7
Hartman and Rinds[6]	A	Effusion	20	815–974	38.6 ± 0.5	35.7	−3.3 ± 0.5	−126.9
Skinner and Ruehrwein[7]	A	Manometric	5	802–928	37.6 ± 0.5	36.0	−1.9 ± 0.6	−126.9

*Four points rejected due to failure of a statistical test.
**Two points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The heat capacity for $TiCl_2$(cr) has been measured by Kim and Stout[8] over the range 6 to 300 K. They calculated the adopted value of $S°(298.15\ K)$ from their measurements based on $S°(6\ K) = 0.017\ cal \cdot K^{-1} \cdot mol^{-1}$. The heat capacity above 300 K is estimated by graphical extrapolation. The large uncertainty on $S°(298.15\ K)$ is due to the possibility of sizeable electronic contributions to the heat capacity below 6 K which would account for the rather low value of $S°(298.15\ K)$ reported by Kim and Stout.[8]

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $TiCl_2$(cr) and $TiCl_2$(g). The temperature of sublimation is taken as the point at which $\Delta_r G° = 0$ for the process $TiCl_2(cr) = TiCl_2(g)$. These values are hypothetical since $TiCl_2$ would be decomposed to $TiCl_3$(g) and $TiCl_4$(g) below this temperature.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−13.301	−514.759	−514.759	INFINITE
100	37.777	25.966	142.867	−11.690	−516.621	−499.490	260.907
200	61.505	61.095	93.500	−6.481	−516.366	−482.347	125.976
298.15	69.831	87.345	87.345	0.	−515.469	−465.829	81.611
300	69.899	87.777	87.347	0.129	−515.449	−465.521	81.054
400	73.392	108.374	90.131	7.297	−514.365	−449.040	58.639
500	76.484	125.090	95.502	14.794	−513.179	−432.843	45.219
600	78.375	139.202	101.640	22.537	−511.894	−416.896	36.294
700	80.266	151.426	107.898	30.469	−510.522	−401.170	29.936
800	82.157	162.267	114.029	38.590	−509.025	−385.649	25.180
900	84.048	172.053	119.941	46.901	−507.426	−370.322	21.493
1000	85.939	181.006	125.606	55.400	−505.785	−355.176	18.552
1100	87.831	189.286	131.024	64.088	−504.161	−340.194	16.154
1200	89.722	197.009	136.204	72.966	−506.540	−325.239	14.157
1300	91.613	204.265	141.163	82.033	−504.226	−310.223	12.465
1400	93.504	211.124	145.918	91.289	−501.811	−295.390	11.021
1500	95.395	217.640	150.484	100.734	−499.307	−280.732	9.776
1600	97.286	223.857	154.877	110.368	−496.728	−266.245	8.692
1700	99.178	229.811	159.111	120.191	−494.086	−251.920	7.741
1800	101.069	235.534	163.199	130.203	−491.395	−237.752	6.899
1900	102.960	241.049	167.152	140.405	−488.668	−223.735	6.151
2000	104.851	246.378	170.980	150.795	−500.607	−209.409	5.469

PREVIOUS: June 1968 CURRENT: December 1968

$S°(298.15\ K) = [278.338 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -236.77 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -237.23 \pm 12.6\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[279](1)
[196](2)
[439](1)

Ground State Quantum Weight: 3 $\sigma = 2$

Point Group: [$D_{\infty h}$]

Bond Distance: Ti–Cl = [2.3] Å

Bond Angle: Cl–Ti–Cl = [180]°

Rotational Constant: B_0 = [0.044943] cm^{-1}

Enthalpy of Formation

Gross and Levi[1] have measured the equilibrium $2TiCl_3(g) + Ti(cr) \rightarrow 3TiCl_2(g)$ at 1723 K and obtain $\Delta_r G°(1723) = 21.7\ kcal \cdot mol^{-1}$ from four measurements. This yields $\Delta_f H°(TiCl_2, g, 298.15\ K) = -56.7 \pm 3\ kcal \cdot mol^{-1}$. They discuss the measurements of Farber and Darnell,[2] on the vapor pressure of $TiCl_2(cr)$, and show that the results are probably in error due to disproportionation of $TiCl_3(g)$ on condensation. In the work of Skinner and Ruehrwein[3] on the reaction $2NaCl(g) + Ti(cr) = 2Na(g) + TiCl_2(g)$, Gross and Levi indicate that the basic assumption, of conversion to $TiCl_2$ only, is erroneous. In the 3rd law analysis of both these data sets significant drifts are obtained which tends to confirm the above arguments.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2(cr)$ reported by Benzinger and Rundle.[4] The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to correspond to the inverted states of $NiCl_2(g)$.[5] The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear.[6–9]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.545	−236.767	−236.767	INFINITE
100	41.124	223.342	326.011	−10.267	−236.961	−239.569	125.138
200	53.079	256.188	283.484	−5.459	−237.108	−242.108	63.232
250	55.821	268.352	279.276	−2.731	−237.163	−243.351	50.846
298.15	57.503	278.338	278.338	0.	−237.233	−244.537	42.842
300	57.555	278.694	278.339	0.106	−237.236	−244.583	42.586
350	58.701	287.658	279.044	3.015	−237.333	−245.800	36.684
400	59.490	295.551	280.624	5.971	−237.455	−247.001	32.255
450	60.054	302.592	282.681	8.960	−237.600	−248.186	28.809
500	60.469	308.942	284.995	11.974	−237.764	−249.354	26.050
600	61.025	320.020	289.936	18.051	−238.144	−251.637	21.907
700	61.371	329.455	294.924	24.172	−238.583	−253.852	18.943
800	61.605	337.666	299.765	30.321	−239.058	−256.001	16.715
900	61.782	344.933	304.387	36.491	−239.600	−258.087	14.979
1000	61.938	351.450	308.773	42.677	−240.272	−260.107	13.587
1100	62.098	357.361	312.926	48.878	−241.135	−262.050	12.444
1200	62.280	362.772	316.858	55.097	−246.173	−263.787	11.482
1300	62.496	367.765	320.584	61.336	−246.687	−265.234	10.657
1400	62.750	372.406	324.122	67.598	−247.266	−266.639	9.948
1500	63.044	376.745	327.487	73.887	−247.918	−268.001	9.333
1600	63.373	380.824	330.694	80.208	−248.652	−269.316	8.792
1700	63.732	384.677	333.757	86.563	−249.478	−270.583	8.314
1800	64.115	388.330	336.689	92.955	−250.407	−271.798	7.887
1900	64.513	391.807	339.499	99.386	−251.451	−272.959	7.504
2000	64.919	395.127	342.198	105.858	−267.309	−273.608	7.146
2100	65.326	398.304	344.794	112.370	−269.369	−273.872	6.812
2200	65.728	401.352	347.296	118.923	−271.400	−274.038	6.506
2300	66.120	404.282	349.711	125.515	−273.406	−274.113	6.225
2400	66.499	407.105	352.044	132.146	−275.387	−274.102	5.966
2500	66.861	409.827	354.301	138.814	−277.348	−274.008	5.725
2600	67.206	412.456	356.487	145.518	−279.290	−273.836	5.501
2700	67.531	414.998	358.608	152.255	−281.217	−273.589	5.293
2800	67.837	417.460	360.666	159.023	−283.131	−273.272	5.098
2900	68.125	419.845	362.665	165.822	−285.034	−272.886	4.915
3000	68.394	422.159	364.610	172.648	−286.930	−272.435	4.744
3100	68.647	424.406	366.503	179.500	−288.819	−271.920	4.582
3200	68.884	426.590	368.347	186.377	−290.701	−271.345	4.429
3300	69.107	428.713	370.144	193.276	−292.579	−270.711	4.285
3400	69.317	430.779	371.897	200.198	−294.452	−270.020	4.148
3500	69.516	432.791	373.608	207.139	−296.320	−269.275	4.019
3600	69.705	434.752	375.280	214.101	−298.181	−268.475	3.895
3700	69.884	436.664	376.913	221.080	−709.134	−259.836	3.668
3800	70.056	438.530	378.510	228.077	−709.745	−247.685	3.405
3900	70.220	440.352	380.073	235.091	−710.402	−235.517	3.154
4000	70.378	442.132	381.602	242.121	−711.100	−223.332	2.916
4100	70.531	443.872	383.100	249.167	−711.837	−211.129	2.690
4200	70.679	445.573	384.567	256.227	−712.608	−198.907	2.474
4300	70.822	447.238	386.005	263.302	−713.410	−186.667	2.268
4400	70.960	448.868	387.415	270.391	−714.240	−174.407	2.070
4500	71.094	450.464	388.799	277.494	−715.092	−162.129	1.882
4600	71.224	452.028	390.156	284.610	−715.964	−149.831	1.701
4700	71.350	453.561	391.489	291.739	−716.851	−137.514	1.528
4800	71.472	455.065	392.798	298.880	−717.750	−125.179	1.362
4900	71.590	456.539	394.084	306.033	−718.657	−112.824	1.203
5000	71.703	457.987	395.347	313.198	−719.568	−100.451	1.049
5100	71.812	459.408	396.590	320.373	−720.482	−88.059	0.902
5200	71.916	460.803	397.811	327.560	−721.393	−75.650	0.760
5300	72.016	462.174	399.013	334.757	−722.300	−63.223	0.623
5400	72.111	463.521	400.195	341.963	−723.200	−50.779	0.491
5500	72.201	464.845	401.358	349.179	−724.091	−38.319	0.364
5600	72.286	466.147	402.504	356.403	−724.969	−25.842	0.241
5700	72.365	467.427	403.631	363.635	−725.834	−13.350	0.122
5800	72.439	468.686	404.742	370.876	−726.683	−0.843	0.008
5900	72.508	469.925	405.837	378.123	−727.515	11.679	−0.103
6000	72.571	471.144	406.915	385.377	−728.327	24.214	−0.211

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [130.54]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -257.32 \pm 12.6\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WCl_2, cr, 298.15\ K) = -61.5 \pm 3\ kcal·mol^{-1}$, is derived from the heat of combustion, $\Delta_c H° = -140 \pm 3\ kcal·mol^{-1}$ for $WCl_2(cr) + 3/2\ O_2(g) \rightarrow WO_3(cr) + Cl_2(g)$, reported by Shchukarev *et al.*[1] The value of $\Delta_c H°$ was determined calorimetrically, but no further information about the combustion process was given in the paper.

Heat Capacity and Entropy

$C_p°(298.15\ K) = 6.2\ cal·K^{-1}\ g·atom^{-1}$ and $C_p°(900\ K) = 7.25\ cal·K^{-1}\ g·atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[2] Between 298 and 900, which is near the decomposition temperature, the heat capacity is obtained by linear interpolation.

The entropy, $S°(298.15\ K) = 31.2\ cal·K^{-1}·mol^{-1}$, is estimated by the method of Latimer.[3] Shchukarev *et al.*,[1] have estimated $\Delta_r S° = -30\ cal·K^{-1}·mol^{-1}$ for $W(cr) + Cl_2(g) = WCl_2(cr)$ which leads to $S°(WCl_2, cr, 298.15\ K) = 31.1\ cal·K^{-1}·mol^{-1}$, using JANAF auxiliary data.

Decomposition Data

The decomposition temperature, $T_{dcm} = 862$ K, is obtained by extrapolation to one atmosphere total pressure of a log P versus 1/T fit of the decomposition pressure data reported by Shchukarev *et al.*[4] Decomposition pressure data for Cl:W ratios less than two suggest that the decomposition reaction is not simple.

References

[1]S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zhur. Neorg. Khim. **5**, 1650 (1960).
[2]O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[3]W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, (1952).
[4]S. A. Shchukarev, G. I. Novikov, and N. V. Andreeva, Vestnik Leningrad. Univ. **14**, No. 10, Ser. Fiz. i Khim., No. 2, 78 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	77.822	130.541	130.541	0.	−257.316	−219.988	38.541
300	77.864	131.022	130.542	0.144	−257.280	−219.757	38.263
400	80.052	153.721	133.622	8.040	−255.318	−207.544	27.102
500	82.241	171.817	139.511	16.153	−253.290	−195.833	20.459
600	84.429	187.006	146.194	24.487	−251.145	−184.541	16.066
700	86.617	200.185	152.986	33.039	−248.866	−173.619	12.956
800	88.805	211.893	159.631	41.810	−246.440	−163.033	10.645
900	91.002	222.480	166.035	50.801	−243.859	−152.760	8.866
1000	93.190	232.181	172.171	60.010	−241.119	−142.784	7.458
1100	95.378	241.166	178.040	69.439	−238.220	−133.089	6.320
1200	97.567	249.559	183.654	79.086	−235.159	−123.666	5.383
1300	99.755	257.455	189.030	88.952	−231.935	−114.504	4.601
1400	101.943	264.927	194.187	99.037	−228.548	−105.597	3.940
1500	104.131	272.035	199.142	109.341	−224.998	−96.938	3.376
1600	106.320	278.826	203.911	119.863	−221.285	−88.521	2.890
1700	108.508	285.337	208.511	130.605	−217.409	−80.341	2.469
1800	110.696	291.601	212.954	141.565	−213.371	−72.393	2.101
1900	112.884	297.645	217.253	152.744	−209.172	−64.675	1.778
2000	115.073	303.491	221.420	164.142	−204.812	−57.182	1.493

PREVIOUS: September 1962 CURRENT: December 1966

$S°(298.15\ K) = [309.416]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-13.0 \pm 105]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-12.6 \pm 105]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[5]
[5600]	[10]
[8900]	[10]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[360](1)
[60](2)
[423](1)

Ground State Quantum Weight: [5] σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: W–Cl = [2.26] Å
Bond Angle: Cl–W–Cl = [180]°
Rotational Constant: B_o = [0.046548] cm^{-1}

Enthalpy of Formation

The value of $\Delta_f H°(WCl_2, g, 298.15\ K) = -3 \pm 25\ kcal·mol^{-1}$ is calculated from the heat of formation of the crystal plus the heat of sublimation, $\Delta_{sub} H°(298.15\ K) = 58.5 \pm 25\ kcal·mol^{-1}$. The latter is estimated from the heats of sublimation of $TiCl_2$, $CrCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ given by Brewer *et al.*[1] among the above compounds and also the possible error in transference from the first row transition metal dichlorides to tungsten dichloride.

Heat Capacity and Entropy

The molecular configuration of $WCl_2(g)$ is assumed to be linear. The bond distance is estimated to be the same as that in $WCl_6(g)$. The ground state configuration ($^5\Sigma$), the low lying electronic levels and their quantum weights are assumed to be the same as those for $CrCl_2(g)$, observed by DeKock and Gruen.[3]

The vibrational frequencies are calculated from a valence force field model. The stretching force constant, K_1, is estimated to be the same as that of $HgCl_2(g)$, 2.7 millidyne/Å. The bending force constant is assumed to be one hundredth of the stretching force constant.

References

[1]L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).
[2]S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. **5**, 1650 (1960).
[3]C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.626	−13.024	−13.024	INFINITE
100	46.708	251.950	358.279	−10.633	−12.595	−17.928	9.365
200	54.413	286.912	314.630	−5.544	−12.551	−23.286	6.082
250	56.638	299.310	310.364	−2.764	−12.547	−25.971	5.426
298.15	58.060	309.416	309.416	0.	−12.552	−28.556	5.003
300	58.105	309.775	309.417	0.107	−12.552	−28.655	4.989
350	59.097	318.811	310.128	3.039	−12.564	−31.338	4.677
400	59.789	326.750	311.720	6.012	−12.581	−34.019	4.442
450	60.288	333.823	313.790	9.015	−12.607	−36.697	4.260
500	60.657	340.195	316.117	12.039	−12.640	−39.372	4.113
600	61.159	351.302	321.082	18.132	−12.737	−44.710	3.892
700	61.485	360.756	326.092	24.265	−12.877	−50.029	3.733
800	61.740	368.983	330.950	30.426	−13.060	−55.324	3.612
900	61.984	376.269	335.588	36.612	−13.283	−60.594	3.517
1000	62.261	382.813	339.989	42.824	−13.541	−65.838	3.439
1100	62.595	388.763	344.157	49.067	−13.828	−71.054	3.374
1200	62.996	394.226	348.104	55.346	−14.136	−76.242	3.319
1300	63.465	399.286	351.849	61.668	−14.455	−81.405	3.271
1400	63.997	404.009	355.408	68.041	−14.781	−86.543	3.229
1500	64.579	408.443	358.797	74.469	−15.106	−91.657	3.192
1600	65.198	412.631	362.032	80.958	−15.427	−96.750	3.159
1700	65.838	416.603	365.126	87.509	−15.741	−101.823	3.129
1800	66.486	420.384	368.092	94.126	−16.047	−106.878	3.102
1900	67.126	423.996	370.940	100.806	−16.346	−111.916	3.077
2000	67.748	427.455	373.680	107.550	−16.640	−116.939	3.054
2100	68.339	430.775	376.320	114.355	−16.934	−121.946	3.033
2200	68.892	433.967	378.869	121.217	−17.232	−126.940	3.014
2300	69.401	437.041	381.331	128.132	−17.539	−131.920	2.996
2400	69.860	440.004	383.715	135.095	−17.863	−136.886	2.979
2500	70.268	442.865	386.024	142.102	−18.209	−141.838	2.964
2600	70.622	445.628	388.263	149.147	−18.582	−146.776	2.949
2700	70.924	448.299	390.438	156.225	−19.013	−151.699	2.935
2800	71.174	450.883	392.551	163.330	−19.545	−156.604	2.921
2900	71.374	453.384	394.605	170.458	−20.223	−161.487	2.909
3000	71.527	455.806	396.605	177.603	−21.077	−166.344	2.896
3100	71.637	458.154	398.553	184.762	−22.155	−171.170	2.884
3200	71.707	460.429	400.451	191.930	−23.494	−175.956	2.872
3300	71.740	462.636	402.302	199.102	−25.120	−180.696	2.860
3400	71.740	464.778	404.109	206.276	−27.072	−185.382	2.848
3500	71.711	466.857	405.872	213.449	−29.415	−190.005	2.836
3600	71.656	468.877	407.594	220.618	−32.247	−194.555	2.823
3700	71.578	470.839	409.277	227.780	−70.433	−198.827	2.807
3800	71.481	472.747	410.922	234.933	−70.955	−202.290	2.781
3900	71.367	474.602	412.531	242.075	−71.495	−205.739	2.756
4000	71.238	476.407	414.106	249.206	−72.050	−209.174	2.732
4100	71.098	478.165	415.647	256.323	−72.620	−212.595	2.708
4200	70.948	479.876	417.156	263.425	−73.204	−216.002	2.686
4300	70.791	481.544	418.634	270.512	−73.799	−219.395	2.665
4400	70.627	483.169	420.082	277.583	−74.404	−222.774	2.645
4500	70.459	484.755	421.502	284.637	−75.016	−226.140	2.625
4600	70.288	486.301	422.894	291.675	−75.634	−229.491	2.606
4700	70.114	487.811	424.259	298.695	−76.256	−232.829	2.588
4800	69.940	489.286	425.599	305.697	−76.880	−236.154	2.570
4900	69.765	490.726	426.913	312.683	−77.503	−239.465	2.553
5000	69.591	492.134	428.203	319.651	−78.125	−242.765	2.536
5100	69.419	493.510	429.471	326.601	−78.742	−246.051	2.520
5200	69.248	494.856	430.715	333.534	−79.355	−249.326	2.505
5300	69.079	496.174	431.938	340.451	−79.960	−252.589	2.489
5400	68.912	497.463	433.139	347.350	−80.557	−255.840	2.475
5500	68.749	498.726	434.320	354.233	−81.144	−259.081	2.461
5600	68.589	499.964	435.482	361.100	−81.720	−262.311	2.447
5700	68.432	501.176	436.623	367.951	−82.285	−265.531	2.433
5800	68.278	502.365	437.747	374.787	−82.836	−268.741	2.420
5900	68.128	503.531	438.852	381.607	−83.373	−271.941	2.408
6000	67.982	504.675	439.939	388.412	−83.896	−275.133	2.395

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = [110.039 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [1000]\ K$

$\Delta_f H°(0\ K) = Unknown$
$\Delta_f H°(298.15\ K) = [-430.95 \pm 41.8]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [26.778 \pm 12.6]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(ZrCl_2, cr, 298.15\ K) = -103.0\ kcal \cdot mol^{-1}$ is calculated from the estimated $\Delta_{sub} H°(298.15\ K) = 58.5\ kcal \cdot mol^{-1}$ for $ZrCl_2(cr) \rightarrow ZrCl_2(g)$, using $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -44.5\ kcal \cdot mol^{-1}$.[1] The estimated $\Delta_{sub} H°(298.15\ K)$ is obtained as an average of the heats of sublimation at 298.15 K for $TiCl_2$, VCl_2, $CrCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$ given by Brewer *et al.*[2]

Heat Capacity and Entropy

The heat capacities of $ZrCl_2$(cr) are estimated based on the assumption that $C_p°(ZrCl_2, cr) = 1/2[C_p°(ZrCl_4, cr) + C_p°(Zr, cr)]$. The entropy, $S°(298.15\ K)$, is also estimated in a manner similar to that of the heat capacity.

Fusion Data

The melting point was estimated to be 1000 K by Brewer[3] and the heat of melting was also estimated by Glassner.[4]

References

[1]JANAF Thermochemical Tables: $ZrCl_2$(g), 12–31–69.
[2]L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).
[3]L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L. L. Quill, Ed., McGraw–Hill New York, (1949).
[4]A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500 K," ANL Report 5750, Argonne National Laboratory, (1957).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	72.592	110.039	110.039	0.	−430.952	−385.660	67.566
300	72.710	110.489	110.041	0.134	−430.927	−385.379	67.101
400	76.015	131.884	112.935	7.580	−429.511	−370.407	48.370
500	78.241	149.094	118.502	15.296	−427.991	−355.805	37.171
600	80.040	163.520	124.834	23.211	−426.399	−341.516	29.732
700	81.714	175.987	131.271	31.301	−424.748	−327.498	24.438
800	83.128	186.990	137.562	39.543	−423.055	−313.721	20.484
900	84.542	196.863	143.611	47.927	−421.339	−300.157	17.421
1000	85.923	205.843	149.392	56.450	−419.608	−286.785	14.980
1000.000	85.923	205.843	149.392	56.450	--- CRYSTAL <--> LIQUID ---		
1100	86.692	214.073	154.904	65.086	−417.894	−273.586	12.992
1200	87.446	221.649	160.155	73.793	−419.951	−260.319	11.331
1300	88.199	228.680	165.159	82.578	−417.807	−247.103	9.929
1400	88.617	235.232	169.933	91.420	−415.657	−234.053	8.733
1500	88.910	241.357	174.492	100.297	−413.534	−221.155	7.701

PREVIOUS: June 1962 CURRENT: December 1969

$S°(298.15\ K) = [122.493]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1000]\ K$

$\Delta_f H°(298.15\ K) = [-411.594]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [26.778 \pm 12.6]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrCl_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(ZrCl_2, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1000\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7.25 $cal·K^{-1}$ $g·atom^{-1}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point was estimated to be 1000 K by Brewer,[1] and the heat of melting was also estimated by Glassner.[2]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change approaches zero for the process $ZrCl_2(l) \rightarrow ZrCl_2(g)$. The difference between $\Delta_f H°$ for $ZrCl_2(l)$ and $ZrCl_2(g)$ at T_{vap} is $\Delta_{vap}H°$.

References

[1]L. Brewer, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," L L. Quill, E Ed, McGraw–Hill Book Company, New York, (1949).
[2]A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides and Chlorides to 2500 K," ANL Report 5750, Argonne National Laboratory, (1957).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.002	122.493	122.493	0.	−411.594	−370.015	64.825
300	91.002	123.056	122.495	0.168	−411.535	−369.758	64.381
400	91.002	149.236	126.064	9.269	−408.464	−356.300	46.528
500	91.002	169.542	132.805	18.369	−405.560	−343.598	35.895
600	91.002	186.134	140.352	27.469	−402.783	−331.468	28.857
700	91.002	200.162	147.920	36.569	−400.121	−319.794	23.863
800	91.002	212.314	155.227	45.669	−397.571	−308.495	20.143
900	91.002	223.032	162.177	54.770	−395.138	−297.507	17.267
1000	91.002	232.620	168.750	63.870	−392.831	−286.785	14.980
1000.000	91.002	232.620	168.750	63.870	--- CRYSTAL <--> LIQUID ---		
1100	91.002	241.294	174.957	72.970	−390.652	−276.286	13.120
1200	91.002	249.212	180.820	82.070	−392.315	−265.759	11.568
1300	91.002	256.496	186.365	91.170	−389.856	−255.313	10.259
1400	91.002	263.240	191.618	100.271	−387.448	−245.054	9.143
1500	91.002	269.518	196.604	109.371	−385.103	−234.966	8.182
1600	91.002	275.391	201.347	118.471	−382.829	−225.031	7.347
1700	91.002	280.908	205.866	127.571	−380.638	−215.236	6.613
1800	91.002	286.110	210.181	136.671	−378.541	−205.568	5.965
1900	91.002	291.030	214.308	145.772	−376.549	−196.013	5.389
2000	91.002	295.698	218.262	154.872	−374.673	−186.560	4.872

EVIOUS: June 1962 CURRENT: December 1969

0	to	1000	K crystal
above		1000	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K *Standard State Pressure = $p°$ = 0.1 MPa*

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	72.592	110.039	110.039	0.	−430.952	−385.660	67.566
300	72.710	110.489	110.041	0.134	−430.927	−385.379	67.101
400	76.015	131.884	112.935	7.580	−429.511	−370.407	48.370
500	78.241	149.094	118.502	15.296	−427.991	−355.805	37.171
600	80.040	163.520	124.834	23.211	−426.399	−341.516	29.732
700	81.714	175.987	131.271	31.301	−424.748	−327.498	24.438
800	83.128	186.990	137.562	39.543	−423.055	−313.721	20.484
900	84.542	196.863	143.611	47.927	−421.339	−300.157	17.421
1000	85.923	205.843	149.392	56.450	−419.608	−286.785	14.980
1000.000	85.923	205.843	149.392	56.450	CRYSTAL <--> LIQUID		
1000.000	91.002	232.620	149.392	83.228	TRANSITION		
1100	91.002	241.294	157.359	92.328	−390.652	−276.286	13.120
1200	91.002	249.212	164.688	101.428	−392.315	−265.759	11.568
1300	91.002	256.496	171.474	110.528	−389.856	−255.313	10.259
1400	91.002	263.240	177.791	119.629	−387.448	−245.054	9.143
1500	91.002	269.518	183.699	128.729	−385.103	−234.966	8.182
1600	91.002	275.391	189.248	137.829	−382.829	−225.031	7.347
1700	91.002	280.908	194.479	146.929	−380.638	−215.236	6.613
1800	91.002	286.110	199.427	156.029	−378.541	−205.568	5.965
1900	91.002	291.030	204.120	165.130	−376.549	−196.013	5.389
2000	91.002	295.698	208.583	174.230	−374.673	−186.560	4.872

PREVIOUS: CURRENT: December 1969

$S°(298.15\ K)$ = [292.558 ± 12.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -185.75 \pm 20.9\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -186.19 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[346] (1)
[92] (2)
[461] (1)

Ground State Quantum Weight = [3] σ = [2]
Point Group = [$D_{\infty h}$]
Bond Distance: Zr–Cl = [2.3] Å
Bond Angle: Cl–Zr–Cl = [180]°
Rotational Constant: B_0 = [0.044943] cm^{-1}

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.243	−185.753	−185.753	INFINITE
100	45.422	235.909	340.900	−10.499	−185.807	−189.092	98.771
200	53.791	270.254	297.731	−5.495	−186.034	−192.282	50.219
250	56.153	282.529	293.500	−2.743	−186.116	−193.834	40.499
298.15	57.676	292.558	292.558	0.	−186.188	−195.314	34.218
300	57.724	292.915	292.559	0.107	−186.191	−195.371	34.017
350	58.793	301.898	293.266	3.021	−186.266	−196.895	29.385
400	59.543	309.801	294.849	5.981	−186.346	−198.408	25.909
450	60.085	316.847	296.909	8.972	−186.436	−199.911	23.205
500	60.488	323.199	299.226	11.987	−186.536	−201.402	21.040
600	61.033	334.280	304.171	18.065	−186.781	−204.354	17.791
700	61.374	343.716	309.163	24.187	−187.098	−207.259	15.466
800	61.606	351.927	314.007	30.336	−187.498	−210.112	13.719
900	61.782	359.194	318.631	36.506	−187.996	−212.910	12.357
1000	61.937	365.711	323.019	42.692	−188.603	−215.647	11.264
1100	62.097	371.622	327.173	48.894	−189.322	−218.318	10.367
1200	62.280	377.033	331.106	55.112	−193.867	−220.696	9.607
1300	62.495	382.026	334.833	61.351	−194.270	−222.916	8.957
1400	62.749	386.666	338.372	67.613	−194.700	−225.103	8.399
1500	63.043	391.005	341.737	73.902	−195.166	−227.259	7.914
1600	63.372	395.084	344.945	80.222	−195.672	−229.382	7.489
1700	63.732	398.937	348.009	86.577	−196.226	−231.473	7.112
1800	64.114	402.590	350.941	92.970	−196.837	−233.529	6.777
1900	64.512	406.068	353.751	99.401	−197.514	−235.549	6.476
2000	64.918	409.387	356.451	105.872	−198.267	−237.532	6.204
2100	65.325	412.564	359.048	112.384	−199.106	−239.475	5.957
2200	65.727	415.612	361.550	118.937	−221.368	−240.630	5.713
2300	66.120	418.543	363.965	125.530	−222.833	−241.472	5.484
2400	66.498	421.365	366.298	132.161	−224.275	−242.252	5.272
2500	66.861	424.087	368.555	138.829	−225.696	−242.972	5.077
2600	67.205	426.716	370.742	145.532	−227.098	−243.635	4.895
2700	67.531	429.258	372.863	152.269	−228.485	−244.244	4.725
2800	67.837	431.720	374.921	159.038	−229.860	−244.803	4.567
2900	68.125	434.106	376.921	165.836	−231.224	−245.312	4.419
3000	68.394	436.420	378.866	172.662	−232.579	−245.775	4.279
3100	68.647	438.666	380.759	179.514	−233.928	−246.193	4.148
3200	68.884	440.850	382.603	186.391	−235.272	−246.567	4.025
3300	69.107	442.973	384.400	193.291	−236.610	−246.899	3.908
3400	69.317	445.039	386.153	200.212	−237.943	−247.191	3.798
3500	69.516	447.051	387.865	207.154	−239.271	−247.444	3.693
3600	69.704	449.012	389.536	214.115	−240.593	−247.658	3.593
3700	69.884	450.925	391.169	221.094	−241.907	−247.837	3.499
3800	70.056	452.791	392.767	228.091	−243.213	−247.979	3.409
3900	70.220	454.612	394.329	235.105	−244.509	−248.088	3.323
4000	70.378	456.392	395.858	242.135	−245.792	−248.163	3.241
4100	70.531	458.132	397.356	249.181	−247.061	−248.207	3.162
4200	70.679	459.833	398.824	256.241	−248.314	−248.220	3.087
4300	70.821	461.498	400.262	263.316	−249.549	−248.203	3.015
4400	70.960	463.128	401.672	270.405	−250.763	−248.157	2.946
4500	71.094	464.724	403.056	277.508	−251.955	−248.085	2.880
4600	71.224	466.288	404.413	284.624	−253.122	−247.986	2.816
4700	71.350	467.821	405.746	291.753	−254.263	−247.862	2.755
4800	71.472	469.325	407.055	298.894	−816.312	−236.096	2.569
4900	71.590	470.800	408.341	306.047	−817.047	−224.001	2.388
5000	71.703	472.247	409.605	313.212	−817.768	−211.891	2.214
5100	71.812	473.668	410.847	320.387	−818.473	−199.766	2.046
5200	71.916	475.063	412.069	327.574	−819.158	−187.628	1.885
5300	72.016	476.434	413.270	334.770	−819.822	−175.477	1.729
5400	72.111	477.781	414.452	341.977	−820.463	−163.313	1.580
5500	72.201	479.105	415.616	349.192	−821.079	−151.138	1.435
5600	72.285	480.407	416.761	356.417	−821.668	−138.952	1.296
5700	72.365	481.687	417.889	363.649	−822.228	−126.756	1.162
5800	72.439	482.946	419.000	370.890	−822.759	−114.549	1.032
5900	72.508	484.185	420.094	378.137	−823.259	−102.335	0.906
6000	72.571	485.404	421.173	385.391	−823.728	−90.112	0.784

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

Enthalpy of formation

Potter[1] investigated mass spectrometrically the gaseous equilibria among ZrCl, $ZrCl_2$, $ZrCl_3$ and $ZrCl_4$. Ion intensities were measured 2.5 $cal·K^{-1}·mol^{-1}$ above the ionization threshold. Using the reported equilibrium constants for the reaction $ZrCl_4(g) + ZrCl_2(g) \rightarrow 2\ ZrCl_3(g)$ in the temperature range 1673–2110 K, second and third law analyses give the heat of reaction at 298 K as −15.8 and +1.7 $kcal·mol^{-1}$, respectively. The third law drift is 8.9 ± 3.7 $cal·K^{-1}·mol^{-1}$. Based on the third law heat of reaction and $\Delta_f H°(ZrCl_4, g, 298.15\ K) = -207.77$ $kcal·mol^{-1}$[2] and $\Delta_f H°(ZrCl_3, g, 298.15\ K) = -125.3\ kcal·mol^{-1}$,[2] we obtain $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -44.5\ kcal·mol^{-1}$ (−186.188 ± 20.9 $kJ·mol^{-1}$) which is adopted in the tabulation.

Farber *et al.*[3] also studied mass spectrometrically the reaction (a) $Zr(cr) + ZrCl_4(g) \rightarrow 2\ ZrCl_2(g)$ and the reaction (b) $Zr(cr) + 2\ Cl(g) \rightarrow ZrCl_2(g)$. They reported second law heats of reaction as $\Delta_r H°(298.15\ K) = 28.8 \pm 1.8$ $kcal·mol^{-1}$ for reaction (a); and −141.1 ± 2.2 $kcal·mol^{-1}$ for reaction (b). Third law analysis of the equilibrium constants which were calculated from their ion intensities of run 3 (the only available values) gives $\Delta_f H°(ZrCl_2, g, 298.15\ K) = -43.4\ kcal·mol^{-1}$. Refer to JANAF $ZrCl_3(g)$ table[2] for details.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that other transition metal dichlorides are linear[4–9] even though some fluorides are bent.[10] The bond distance is assumed to be the same as that of $ZrCl_4(g)$. The electronic levels and quantum weights are estimated to be the same as those of $TiCl_2(g)$.[2]

The vibrational frequencies are calculated from a valence force field model. The stretching force constant is estimated to be 2.5 millidyne/Å and the bending force constant 0.05 millidyne/Å.

References

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[10]J. W. Hastie, R. H. Hauge and J. L. Margrave, J. Chem. Phys. **51**, 2648 (1969).

$S°(298.15\ K) = [334.209 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -161.78 \pm 10.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -163.59 \pm 10.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i,cm^{-1}	g_i
0	[5]
[500]	[5]
[1000]	[5]
[5000]	[5]
[10000]	[5]

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[500] (1)
[250] (1)
[550] (2)
[150] (2)

Ground State Quantum Weight = [5] $\sigma = 3$
Point Group: [C_{3v}]
Bond Distance: Co–Cl = [2.09] Å
Bond Angle: Cl–Co–Cl = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.9528 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

Schafer and Krehl[1] studied the reaction of chlorine with $CoCl_2$ by a transpiration method. They ascribed the enhanced volatility of $CoCl_2$(cr,l) in the presence of Cl_2 to the formation of gaseous $CoCl_3$ according to the reaction $Cl_2(g) + 2\ CoCl_2(g) = 2\ CoCl_3(g)$. Partial pressures for the three species involved in the reaction were reported for the temperature range 918–1073 K. No consideration was given to possible dimerization of either the di- or trichloride. Subsequent measurements by Schafer and Breil[2] have confirmed the increased volatility of $CoCl_2$(l) in the presence of Cl_2. However, the latter study was conducted at only one temperature (1056 K). JANAF data[3] for $CoCl_2$(g) and Co_2Cl_4(g) are used to correct their pressures[1, 2] for dimerization of the dichloride. Our corrected $CoCl_2$ pressures are 5% less than those reported by Schafer and Krehl[1] at 918 K and 11.4% less at 1073 K. We tentatively assume that dimerization of the trichloride is negligible over the temperature range investigated and treat the equilibrium pressures by the second and third law methods. Results of the analysis are: $\Delta_r H°(298.15\ K)$ (2nd Law) = −32.9 and $\Delta_r H°(298.15\ K)$ (3rd Law) = -33.36 ± 2.0 kcal·mol^{-1}. The third law drift is -0.5 ± 2.9 cal·K^{-1}·mol^{-1}. The measurements of Schafer and Breil[2] at 1056 K give $\Delta_r H°(298.15\ K)$ (3rd Law) = −33.31 kcal·mol^{-1}. Combining the average value for the third law heats of reaction with $\Delta_f H°(CoCl_2, g, 298.15\ K) = -22.4 \pm 2.0$ kcal·mol^{-1},[3] we obtain $\Delta_f H°(CoCl_3, g, 298.15\ K) = -39.1 \pm 2.5$ kcal·mol^{-1}. This value is adopted and corresponds to a bond dissociation energy of $D°_0$(Cl$_2$–Cl, 298.15 K) = 45.7 kcal·mol^{-1}. A comparison of this value with that for the monochloride ($D°_0$(Co–Cl, 0 K) = 84.4 kcal·mol^{-1}) and dichloride ($D°_0$(CoCl–Cl) = 97.5 kcal·mol^{-1}) clearly reveals the instability of the trichloride molecule.

Heat Capacity and Entropy

The structure of CoCl is not known; however, it can be limited to two possibilities. The molecule has either a pyramidal structure of C_{3v} symmetry, or a planar structure of D_{3h} symmetry. By analogy with the geometries for PCl_3,[3] $SiCl_3$[3] and TiF_3,[3, 4] we adopt the pyramidal structure. The bond length is taken equal to that for CoCl [3]. The Cl–Co–Cl bond angle is estimated as 100°. The principal moments of inertia are: $I_A = I_B = 36.1659 \times 10^{-39}$, and $I_C = 60.3628 \times 10^{-39}$ g·cm^2.

The vibrational frequencies are estimated by comparison with those for PCl_3,[3] $SiCl_3$[3] and TiF_3.[4] The ground state quantum weight is taken equal to that for Co^{+3}.[5] The electronic levels are estimated from those for Fe^{+2},[5] since few levels have been observed in the spectrum of Co^{+3}. The Fe^{+2} ion is isoelectronic with Co^{+3}. The adopted upper levels and quantum weights contribute 0.65 cal·K^{-1}·mol^{-1} at 298.15 K and 2.4 cal·K^{-1}·mol^{-1} at 3000 K to the entropy of $CoCl_3$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.731	−161.783	−161.783	INFINITE
100	48.842	266.224	394.607	−12.838	−162.780	−160.283	83.723
200	66.145	305.685	340.909	−7.045	−163.452	−157.483	41.130
250	72.162	321.128	335.443	−3.579	−163.570	−155.974	32.589
298.15	76.238	334.209	334.209	0.	−163.594	−154.508	27.069
300	76.366	334.681	334.210	0.141	−163.593	−154.451	26.892
350	79.198	346.680	335.152	4.035	−163.540	−152.931	22.824
400	81.067	357.387	337.274	8.045	−163.463	−151.421	19.774
450	82.281	367.010	340.053	12.131	−163.389	−149.920	17.402
500	83.059	375.723	343.191	16.266	−163.337	−148.427	15.506
600	83.853	390.948	349.918	24.618	−163.327	−145.448	12.662
700	84.136	403.899	356.728	33.020	−163.469	−142.459	10.630
800	84.213	415.140	363.342	41.438	−164.200	−139.376	9.100
900	84.219	425.060	369.660	49.860	−164.703	−136.246	7.907
1000	84.212	433.933	375.651	58.282	−165.459	−133.046	6.950
1100	84.214	441.959	381.320	66.703	−166.499	−129.757	6.162
1200	84.233	449.287	386.683	75.125	−167.855	−126.359	5.500
1300	84.268	456.031	391.762	83.550	−169.671	−122.831	4.935
1400	84.317	462.277	396.578	91.979	−172.073	−119.141	4.445
1500	84.375	468.097	401.154	100.414	−173.472	−115.309	4.015
1600	84.440	473.544	405.510	108.854	−174.624	−111.393	3.637
1700	84.509	478.665	409.664	117.302	−175.685	−107.409	3.300
1800	84.580	483.498	413.633	125.756	−193.019	−103.068	2.991
1900	84.651	488.073	417.432	134.218	−194.348	−98.035	2.695
2000	84.721	492.416	421.073	142.686	−195.686	−92.931	2.427
2100	84.789	496.552	424.570	151.162	−197.033	−87.760	2.183
2200	84.854	500.498	427.932	159.644	−198.392	−82.525	1.959
2300	84.917	504.271	431.170	168.133	−199.765	−77.228	1.754
2400	84.975	507.886	434.291	176.627	−201.154	−71.870	1.564
2500	85.031	511.356	437.305	185.128	−202.561	−66.455	1.388
2600	85.082	514.692	440.218	193.633	−203.988	−60.982	1.225
2700	85.129	517.904	443.036	202.144	−205.438	−55.454	1.073
2800	85.173	521.001	445.765	210.659	−206.911	−49.873	0.930
2900	85.212	523.990	448.412	219.178	−208.409	−44.238	0.797
3000	85.248	526.880	450.979	227.701	−209.933	−38.551	0.671
3100	85.280	529.676	453.473	236.228	−211.482	−32.813	0.553
3200	85.308	532.384	455.897	244.757	−587.870	−25.251	0.412
3300	85.333	535.009	458.255	253.289	−588.043	−7.667	0.121
3400	85.354	537.557	460.550	261.824	−588.240	9.923	−0.152
3500	85.372	540.031	462.786	270.360	−588.460	27.519	−0.411
3600	85.387	542.436	464.965	278.898	−588.704	45.122	−0.655
3700	85.399	544.776	467.090	287.437	−588.968	62.732	−0.886
3800	85.408	547.054	469.165	295.978	−589.251	80.349	−1.104
3900	85.415	549.272	471.191	304.519	−589.551	97.974	−1.312
4000	85.419	551.435	473.170	313.060	−589.866	115.607	−1.510
4100	85.420	553.544	475.104	321.602	−590.194	133.248	−1.698
4200	85.420	555.603	476.997	330.144	−590.532	150.897	−1.877
4300	85.417	557.612	478.848	338.686	−590.877	168.554	−2.048
4400	85.413	559.576	480.661	347.228	−591.228	186.220	−2.211
4500	85.406	561.496	482.436	355.769	−591.581	203.893	−2.367
4600	85.399	563.373	484.175	364.309	−591.936	221.574	−2.516
4700	85.389	565.209	485.880	372.848	−592.288	239.263	−2.659
4800	85.379	567.007	487.551	381.387	−592.638	256.959	−2.796
4900	85.367	568.767	489.191	389.924	−592.983	274.663	−2.928
5000	85.353	570.492	490.799	398.460	−593.321	292.373	−3.054
5100	85.339	572.182	492.379	406.995	−593.651	310.090	−3.176
5200	85.324	573.839	493.929	415.528	−593.973	327.814	−3.293
5300	85.308	575.464	495.452	424.060	−594.284	345.543	−3.406
5400	85.292	577.058	496.949	432.590	−594.585	363.279	−3.514
5500	85.274	578.623	498.420	441.118	−594.876	381.020	−3.619
5600	85.256	580.159	499.866	449.644	−595.154	398.766	−3.720
5700	85.238	581.668	501.288	458.169	−595.422	416.517	−3.817
5800	85.219	583.150	502.686	466.692	−595.679	434.273	−3.911
5900	85.199	584.607	504.063	475.213	−595.880	452.029	−4.002
6000	85.179	586.039	505.417	483.732	−596.104	469.792	−4.090

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [429.526]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -258.50 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -258.57 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[100](1)	350 (2)
[150](1)	[300](2)
[250](1)	[60](2)
[200](1)	[80](2)

Ground State Quantum Weight: [1]
Point Group: D_{3h} $\sigma = 6$
Bond Distance: Cu–Cl = 2.16 Å
Bond Angles: Cl–Cu–Cl = 150°; Cu–Cl–Cu = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 2.02938 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The heat of sublimation was determined by second and third law analysis of the following vapor pressure data. Magee[1] measured both vapor pressure by torsion effusion and vapor density in the range 533–644 K and found only trimer present. The second and third law analyses gave $\Delta_{sub}H°(298.15\ K) = 37.37 \pm 0.04$ and $37.24 \pm 0.02\ kcal·mol^{-1}$ with a drift of $-0.25 \pm 0.07\ cal·K^{-1}mol^{-1}$. Shelton,[2] using Knudsen effusion in the range 547–657 K, obtained $\Delta_{sub}H°(298.15\ K) = 40.35 \pm 1.4$ and $37.42 \pm 0.4\ kcal·mol^{-1}$ with a drift of $-4.9\ cal·K^{-1}·mol^{-1}$. Fedorov and Shakhova,[3] using transport methods, obtained vapor pressure over the liquid from 751–1057 K. Using second and third law analysis these gave $\Delta_{sub}H°(298.15\ K) = 38.6 \pm 1.0$ and $39.27 \pm 0.5\ kcal·mol^{-1}$.

Brewer and Lofgren[4] obtained equilibrium constants for the reaction $3\ Cu(cr) + 3\ HCl(g) \rightarrow Cu_3Cl_3(g) + 1.5\ H_2(g)$. Second and third law analysis of these constants gave $\Delta_f H°(298.15\ K) = 3.9 \pm 0.6$ and $4.39 \pm 0.3\ kcal·mol^{-1}$ which leads to $\Delta_f H° = -61.8 \pm 0.5\ kcal·mol^{-1}$ ($-258.571 \pm 2.1\ kJ·mol^{-1}$). *This was the value adopted since it is dependent only on HCl(g) and does not involve three times the uncertainty of CuCl(cr) as do the sublimation experiments, which yield values in good agreement but of larger uncertainty.*

Heat Capacity and Entropy

The structure of the trimer has been investigated by Wong and Schomaker.[5] They conclude that the molecule is planar with D_{3h} symmetry and a Cu–Cl bond length of 2.16 Å. They also state that a very large amplitude of the symetric in–plane bending appears plausible from the diffraction pattern. The infra–red spectrum has been investigated by Klemperer *et al.*[6] They observed one strong absorption with a maximumm at 350 cm^{-1}; they attribute this to bond stretching motion of type E'. They also suggest that the broad absorption may involve another mode of approximately equal frequency.

In order to estimate the remaining frequencies we assumed that the other infra–red active E' mode would be close to the observed 350 cm^{-1} and this was estimated as 300 cm^{-1}. The in–plane bending is the third E' model and since this has a very large amplitude it was estimated as 60 cm^{-1}. By analogy with other D_{3h} rings the A_2' mode was assumed to be in the same region as the E' stretches and was taken to be 250 cm^{-1}. The $2A_1'$ stretches were estimated as 100 and 150 cm^{-1}, while the out of plane A_2'' was taken as 200 cm^{-1} and the E'' as 80 cm^{-1}. These values gave calculated entropies in excellent agreement with the equilibrium data and thus support the estimates.

The principal moments of inertia are: $I_A = I_B = 100.4872 \times 10^{-39}$, $I_C = 200.9745 \times 10^{-39}\ g·cm^2$.

References

[1]D. W. Magee, Ph. D. Thesis, Ohio State University (1955).
[2]R. A. J. Shelton, Trans. Faraday Soc. **57**, 2113 (1961).
[3]P. I. Fedorov and M. N. Shakhova, Izv. Vyssahikh Uchebn. Zavendenii, Khim. i Khim. Tekhnol. **4**, 550 (1961).
[4]L. Brewer and N. L. Lofgren, J. Amer. Chem. Soc. **72**, 3038 (1950).
[5]C. H. Wong and V. Schomaker, J. Phys. Chem. **61**, 358 (1957).
[6]W. Klemperer, S. A. Rice and R. S. Berry, J. Amer. Chem. Soc. **79**, 1810 (1957).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−28.723	−258.503	−258.503	INFINITE
100	91.029	308.854	533.649	−22.480	−258.633	−258.157	134.848
200	116.232	381.296	440.710	−11.883	−258.633	−257.665	67.295
250	121.471	407.846	431.562	−5.929	−258.595	−257.427	53.786
298.15	124.570	429.526	429.526	0.	−258.571	−257.204	45.061
300	124.664	430.297	429.529	0.231	−258.571	−257.196	44.782
350	126.724	449.680	431.055	6.519	−258.570	−256.967	38.350
400	128.120	466.698	434.468	12.892	−258.596	−256.737	33.526
450	129.105	481.849	438.907	19.324	−258.655	−256.501	29.774
500	129.823	495.490	443.894	25.798	−258.743	−256.257	26.771
600	130.778	519.252	454.531	38.832	−259.017	−255.737	22.264
700	131.365	539.459	465.257	51.942	−259.438	−255.159	19.040
800	131.749	557.027	475.654	65.099	−260.002	−254.511	16.618
900	132.015	572.561	485.575	78.288	−260.724	−253.783	14.729
1000	132.206	586.481	494.982	91.499	−261.619	−252.965	13.214
1100	132.348	599.088	503.882	104.727	−262.731	−252.048	11.969
1200	132.457	610.609	512.303	117.968	−264.119	−251.018	10.927
1300	132.541	621.215	520.278	131.218	−265.912	−249.857	10.039
1400	132.608	631.040	527.843	144.475	−307.574	−247.320	9.228
1500	132.662	640.190	535.031	157.739	−309.850	−242.937	8.460
1600	132.707	648.754	541.874	171.008	−312.135	−238.402	7.783
1700	132.744	656.800	548.400	184.280	−314.428	−233.723	7.181
1800	132.775	664.389	554.635	197.556	−316.732	−228.909	6.643
1900	132.801	671.568	560.602	210.835	−319.047	−223.967	6.157
2000	132.823	678.380	566.322	224.116	−321.376	−218.903	5.717
2100	132.842	684.861	571.814	237.399	−323.718	−213.722	5.316
2200	132.859	691.042	577.094	250.684	−326.078	−208.428	4.949
2300	132.874	696.948	582.178	263.971	−328.456	−203.028	4.611
2400	132.886	702.603	587.078	277.259	−330.854	−197.523	4.299
2500	132.898	708.028	591.809	290.548	−333.275	−191.918	4.010
2600	132.908	713.240	596.379	303.839	−335.721	−186.215	3.741
2700	132.917	718.257	600.801	317.130	−338.193	−180.418	3.490
2800	132.925	723.091	605.083	330.422	−340.693	−174.529	3.256
2900	132.932	727.755	609.233	343.715	−1243.833	−150.563	2.712
3000	132.938	732.262	613.259	357.008	−1244.005	−112.861	1.965
3100	132.944	736.621	617.169	370.302	−1244.357	−75.151	1.266
3200	132.949	740.842	620.968	383.597	−1244.888	−37.427	0.611
3300	132.954	744.933	624.663	396.892	−1245.599	0.317	−0.005
3400	132.959	748.902	628.259	410.188	−1246.487	38.085	−0.585
3500	132.963	752.756	631.761	423.484	−1247.548	75.881	−1.132
3600	132.966	756.502	635.174	436.780	−1248.778	113.711	−1.650
3700	132.970	760.145	638.503	450.077	−1250.168	151.576	−2.140
3800	132.973	763.691	641.751	463.374	−1251.710	189.481	−2.605
3900	132.976	767.146	644.922	476.672	−1253.396	227.429	−3.046
4000	132.979	770.512	648.020	489.969	−1255.215	265.422	−3.466
4100	132.981	773.796	651.048	503.267	−1257.157	303.462	−3.866
4200	132.983	777.000	654.009	516.566	−1259.211	341.550	−4.248
4300	132.986	780.130	656.905	529.864	−1261.365	379.689	−4.612
4400	132.988	783.187	659.741	543.163	−1263.609	417.879	−4.961
4500	132.989	786.176	662.517	556.462	−1265.931	456.120	−5.295
4600	132.991	789.098	665.237	569.761	−1268.322	494.415	−5.614
4700	132.993	791.959	667.903	583.060	−1270.770	532.761	−5.921
4800	132.994	794.759	670.517	596.359	−1273.265	571.160	−6.215
4900	132.996	797.501	673.081	609.659	−1275.800	609.612	−6.499
5000	132.997	800.188	675.596	622.958	−1278.365	648.115	−6.771
5100	132.999	802.821	678.065	636.258	−1280.952	686.671	−7.033
5200	133.000	805.404	680.489	649.558	−1283.554	725.277	−7.285
5300	133.001	807.937	682.870	662.858	−1286.164	763.933	−7.529
5400	133.002	810.424	685.209	676.158	−1288.777	802.639	−7.764
5500	133.003	812.864	687.508	689.459	−1291.389	841.393	−7.991
5600	133.004	815.261	689.768	702.759	−1293.994	880.194	−8.210
5700	133.005	817.615	691.990	716.059	−1296.590	919.042	−8.422
5800	133.006	819.928	694.176	729.360	−1299.173	957.936	−8.627
5900	133.007	822.202	696.327	742.661	−1301.743	996.873	−8.826
6000	133.007	824.437	698.443	755.961	−1304.296	1035.854	−9.018

PREVIOUS: March 1966 (1 atm) CURRENT: March 1966 (1 bar)

$S°(298.15\ K) = [336.055 \pm 16.7]\ J \cdot K^{-1} mol^{-1}$

$\Delta_f H°(0\ K) = -838.80 \pm 62.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -840.98 \pm 62.8\ kJ \cdot mol^{-1}$

Vibrational Levels and Quantum Weights ν, cm^{-1}
[925](1)
[350](1)
[500](2)
[270](2)
[200](2)

Ground State Quantum Weight: 1 $\sigma = 3$

Point Group: C_{3v}

Product of the Moments of Inertia: $I_A I_B I_C = [142{,}900 \times 10^{-117}]\ g^3 \cdot cm^6$

Enthalpy of Formation

All data are from Henderson and Scheffee.[1]

Heat Capacity and Entropy

All data are from Henderson and Scheffee.[1]

Reference

[1]C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria,Va., (January 1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.214	−838.796	−838.796	INFINITE
100	55.092	255.734	407.697	−15.196	−840.866	−829.187	433.123
200	78.839	302.234	343.986	−8.350	−841.220	−817.279	213.451
250	85.487	320.584	337.514	−4.233	−841.131	−811.303	169.513
298.15	90.081	336.055	336.055	0.	−840.984	−805.570	141.133
300	90.231	336.613	336.057	0.167	−840.977	−805.351	140.224
350	93.713	350.797	337.169	4.770	−840.782	−799.428	119.308
400	96.325	363.489	339.680	9.524	−840.557	−793.535	103.625
450	98.321	374.955	342.973	14.392	−840.310	−787.672	91.431
500	99.873	385.398	346.701	19.348	−840.050	−781.837	81.678
600	102.076	403.816	354.726	29.454	−839.505	−770.246	67.056
700	103.521	419.667	362.898	39.739	−838.952	−758.746	56.618
800	104.511	433.559	370.880	50.143	−838.410	−747.325	48.795
900	105.217	445.912	378.543	60.631	−837.892	−735.971	42.715
1000	105.735	457.026	385.845	71.180	−837.404	−724.673	37.853
1100	106.126	467.122	392.782	81.774	−836.951	−713.423	33.878
1200	106.429	476.370	399.368	92.403	−836.537	−702.211	30.566
1300	106.667	484.899	405.623	103.058	−836.165	−691.033	27.766
1400	106.857	492.811	411.572	113.734	−835.839	−679.881	25.367
1500	107.012	500.189	417.237	124.428	−835.561	−668.751	23.288
1600	107.140	507.099	422.639	135.136	−835.333	−657.638	21.470
1700	107.246	513.598	427.801	145.855	−885.335	−646.091	19.852
1800	107.335	519.730	432.739	156.585	−884.981	−632.028	18.341
1900	107.411	525.536	437.472	167.322	−884.640	−617.985	16.990
2000	107.476	531.047	442.014	178.066	−884.312	−603.959	15.774
2100	107.532	536.292	446.379	188.817	−883.997	−589.949	14.674
2200	107.581	541.296	450.581	199.573	−883.697	−575.954	13.675
2300	107.624	546.079	454.630	210.333	−883.412	−561.972	12.763
2400	107.661	550.660	458.536	221.097	−883.142	−548.002	11.927
2500	107.694	555.056	462.310	231.865	−882.888	−534.043	11.158
2600	107.724	559.280	465.959	242.636	−882.651	−520.094	10.449
2700	107.750	563.346	469.491	253.410	−882.430	−506.154	9.792
2800	107.774	567.265	472.913	264.186	−882.225	−492.222	9.183
2900	107.795	571.048	476.232	274.964	−882.037	−478.296	8.615
3000	107.814	574.702	479.454	285.745	−881.863	−464.377	8.086
3100	107.831	578.238	482.584	296.527	−881.704	−450.464	7.590
3200	107.847	581.662	485.627	307.311	−881.556	−436.555	7.126
3300	107.861	584.980	488.588	318.096	−881.419	−422.651	6.690
3400	107.874	588.201	491.470	328.883	−881.290	−408.751	6.280
3500	107.886	591.328	494.279	339.671	−881.166	−394.855	5.893
3600	107.897	594.367	497.017	350.460	−1265.195	−370.501	5.376
3700	107.907	597.324	499.688	361.251	−1264.658	−345.656	4.880
3800	107.916	600.201	502.296	372.042	−1264.118	−320.825	4.410
3900	107.925	603.005	504.842	382.834	−1263.571	−296.009	3.965
4000	107.933	605.737	507.331	393.627	−1263.013	−271.206	3.542
4100	107.940	608.403	509.763	404.420	−1262.440	−246.418	3.139
4200	107.947	611.004	512.143	415.215	−1261.849	−221.644	2.757
4300	107.954	613.544	514.472	426.010	−1261.234	−196.885	2.392
4400	107.960	616.026	516.752	436.806	−1260.593	−172.140	2.044
4500	107.965	618.452	518.985	447.602	−1259.922	−147.410	1.711
4600	107.971	620.825	521.173	458.399	−1259.217	−122.695	1.393
4700	107.975	623.147	523.318	469.196	−1258.476	−97.996	1.089
4800	107.980	625.420	525.422	479.994	−1257.695	−73.313	0.798
4900	107.984	627.647	527.485	490.792	−1256.873	−48.647	0.519
5000	107.988	629.828	529.510	501.591	−1256.006	−23.998	0.251
5100	107.992	631.967	531.498	512.390	−1255.093	0.633	−0.006
5200	107.996	634.064	533.451	523.189	−1254.131	25.246	−0.254
5300	107.999	636.121	535.369	533.989	−1253.120	49.840	−0.491
5400	108.003	638.140	537.253	544.789	−1252.059	74.414	−0.720
5500	108.006	640.122	539.105	555.589	−1250.944	98.968	−0.940
5600	108.008	642.068	540.927	566.390	−1249.778	123.502	−1.152
5700	108.011	643.980	542.718	577.191	−1248.558	148.014	−1.356
5800	108.014	645.858	544.480	587.992	−1247.284	172.504	−1.554
5900	108.016	647.705	546.214	598.794	−1245.957	196.972	−1.744
6000	108.019	649.520	547.921	609.596	−1244.576	221.416	−1.928

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = 142.336\ J·K^{-1}·mol^{-1}$
$T_{fus} = 577\ K$

$\Delta_f H°(0\ K) = -400.833 \pm 0.84\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -399.405 \pm 0.84\ kJ·mol^{-1}$
$\Delta_{fus} H° = 43.095\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy change, $\Delta_r H°(298.15\ K) = -24.49 \pm 0.07\ kcal·mol^{-1}$, for the reaction Fe(cr) + 3(HCl·12.731 H_2O)(l) + 1/2(H_2O_2·12.580 H_2O)(l) = $FeCl_3$(cr) + H_2(g) + 45.483 H_2O(l) was determined by Koehler and Coughlin.[1] This leads to $\Delta_f H°(298.15\ K) = -95.46 \pm 0.20\ kcal·mol^{-1}$ for $FeCl_3$(cr), using $\Delta_f H°(298.15\ K) = -38.9 \pm 0.05$ and $-68.32 \pm 0.01\ kcal·mol^{-1}$ for hydrochloric acid and hydrogen peroxide solution, respectively, obtained from Rossini *et al.*[2] From $\Delta_r H°(298.15\ K) = -38.0 \pm 0.2\ kcal·mol^{-1}$ for the reaction $FeCl_3$(cr) = Fe^{+++}(aq) reported by Li and Gregory,[3] the value of $\Delta_f H°(FeCl_3, cr, 298.15\ K)$ was calculated as $-93.26 \pm 0.2\ kcal·mol^{-1}$. The former $\Delta_f H°(298.15\ K)$ value is adopted.

The equilibrium pressures of the reaction 2 $FeCl_2$(cr) + Cl_2(g) = 2$FeCl_3$(cr), in the temperature range of 435.7–482.2 K, were measured by Schafer and Oehler.[4] Using the reported partial pressures for Cl_2(g), the enthalpy change $\Delta_r H°(298.15\ K)$ of the reaction was evaluated as -27.49 ± 0.44 and $-27.21\ kcal·mol^{-1}$ by the 2nd and 3rd law methods, respectively. Based on the 3rd law value for $\Delta_f H°(298.15\ K)$, the value of $\Delta_f H°(FeCl_3, cr, 298.15\ K)$ was derived to be $-95.36 \pm 0.12\ kcal·mol^{-1}$ which is in good agreement with the adopted value.

Heat Capacity and Entropy

The low temperature (51–298.16 K) heat capacities and high temperature (339.6–560.9 K) heat content of $FeCl_3$(cr) were determined by Todd and Coughlin.[5] The low temperature $C_p°$ and the derived high temperature $C_p°$ were plotted. The two $C_p°$ curves were joined smoothly at 298.15 K). The $C_p°$ values above 560.9 K were obtained by graphical extrapolation. The value of $S°(298.15\ K)$ was derived from the low temperature data reported by Todd and Coughlin,[5] using $S°(51\ K) = 6.29\ cal·K^{-1}·mol^{-1}$. The value of $S°(51\ K)$ was selected to make the second and third law values of $\Delta_r H°$, derived from the equilibrium data reported by Schafer and Oehler,[4] in good agreement. The difference in $S°(51\ K)$ between the selected value, 6.29, and the reported value, 4.50 $cal·K^{-1}·mol^{-1}$, by Todd and Coughlin,[5] is assumed to be the magnetic entropy remaining at 51 K which was unaccounted for in the report.

Fusion Data

T_{fus} and $\Delta_{fus} H°$ were obtained from Todd and Coughlin.[5]

Sublimation Data

The difference between $\Delta_f H°(298.15\ K)$ for Fe_2Cl_6(g) and 2$FeCl_3$(cr) is the enthalpy of sublimation at 298.15 K. The former is obtained by the 2nd and 3rd law analyses of related equilibrium data. See Fe_2Cl_6(g) table for details.

References

[1] M. F. Koehler and J. P. Coughlin, J. Phys. Chem. **63**, 605 (1959).
[2] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[3] J. C. M. Li and N. W. Gregory, J. Amer. Chem. Soc. **74**, 4670 (1952).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.706	−400.833	−400.833	INFINITE
100	58.254	54.924	220.004	−16.508	−402.425	−378.960	197.948
200	86.219	105.867	150.854	−8.997	−401.240	−355.834	92.934
298.15	96.650	142.336	142.336	0.	−399.405	−333.930	58.503
300	96.860	142.935	142.338	0.179	−399.366	−333.524	58.072
400	106.692	172.135	146.251	10.354	−397.025	−311.913	40.732
500	119.872	197.194	153.973	21.611	−393.977	−290.964	30.397
577.000	121.754	214.368	160.911	30.845	--- CRYSTAL <--> LIQUID ---		
600	123.428	219.165	163.053	33.667	−390.455	−270.691	23.566
700	128.658	238.611	172.484	46.289	−386.667	−251.027	18.732
800	131.796	256.012	181.857	59.324	−382.796	−231.914	15.142
900	133.470	271.644	190.980	72.598	−379.131	−213.278	12.378
1000	133.888	285.731	199.763	85.968	−376.113	−195.021	10.187
1100	133.888	298.491	208.167	99.357	−373.992	−177.000	8.405
1200	133.888	310.141	216.187	112.745	−371.336	−159.229	6.931
1300	133.888	320.858	223.832	126.134	−367.049	−141.727	5.695
1400	133.888	330.780	231.121	139.523	−362.860	−124.553	4.647
1500	133.888	340.017	238.076	152.912	−358.769	−107.674	3.750

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = [200.657]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 577\ K$

$\Delta_f H°(298.15\ K) = [-362.815]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 43.095\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(FeCl_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(FeCl_3, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(577\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for $FeCl_3$(l) was taken from Todd and Coughlin[1] and assumed as constant between 298.15 and 1500 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} and $\Delta_{fus} H°$ were reported by Todd and Coughlin.[1]

Vaporization Data

The boiling point (T_{vap}) is determined as the temperature at which the Gibbs energy change ($\Delta_r G°$) of the reaction $2FeCl_3(l) = Fe_2Cl_6(g)$ is zero. The corresponding enthalpy change at T_{vap} is the enthalpy vaporization.

References

[1] S. S. Todd and J. P. Coughlin, J. Amer. Chem. Soc. **73**, 4184 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	133.888	200.657	200.657	0.	−362.815	−314.728	55.139
300	133.888	201.485	200.660	0.248	−362.708	−314.430	54.747
400	133.888	240.002	205.911	13.636	−357.152	−299.187	39.070
500	133.888	269.879	215.828	27.025	−351.973	−285.302	29.805
577.000	133.888	289.056	224.351	37.335	--- CRYSTAL <--> LIQUID ---		
600	133.888	294.289	226.932	40.414	−347.118	−272.429	23.717
700	133.888	314.928	238.067	53.803	−342.563	−260.345	19.427
800	133.888	332.806	248.817	67.192	−338.338	−248.892	16.251
900	133.888	348.576	259.042	80.580	−334.558	−237.944	13.810
1000	133.888	362.683	268.713	93.969	−331.522	−227.382	11.877
1100	133.888	375.444	277.845	107.358	−329.401	−217.057	10.307
1200	133.888	387.093	286.471	120.747	−326.745	−206.980	9.010
1300	133.888	397.810	294.629	134.136	−322.458	−197.174	7.923
1400	133.888	407.732	302.358	147.524	−318.269	−187.695	7.003
1500	133.888	416.970	309.694	160.913	−314.177	−178.511	6.216

PREVIOUS: CURRENT: June 1965

0 to 577 K crystal
above 577 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.706	−400.833	−400.833	INFINITE
100	58.254	54.924	220.004	−16.508	−402.425	−378.960	197.948
200	86.219	105.867	150.854	−8.997	−401.240	−355.834	92.934
298.15	96.650	142.336	142.336	0.	−399.405	−333.930	58.503
300	96.860	142.935	142.338	0.179	−399.366	−333.524	58.072
400	106.692	172.135	146.251	10.354	−397.025	−311.913	40.732
500	119.872	197.194	153.973	21.611	−393.977	−290.964	30.397
577.000	121.754	214.368	160.911	30.845	____ CRYSTAL <--> LIQUID ____		
577.000	133.888	289.056	160.911	73.940	TRANSITION		
600	133.888	294.289	165.924	77.019	−347.103	−272.414	23.716
700	133.888	314.928	185.774	90.408	−342.548	−260.330	19.426
800	133.888	332.806	203.060	103.797	−338.323	−248.877	16.250
900	133.888	348.576	218.370	117.186	−334.543	−237.929	13.809
1000	133.888	362.683	232.108	130.574	−331.507	−227.367	11.876
1100	133.888	375.444	244.568	143.963	−329.386	−217.041	10.306
1200	133.888	387.093	255.967	157.352	−326.730	−206.965	9.009
1300	133.888	397.810	266.471	170.741	−322.443	−197.159	7.922
1400	133.888	407.732	276.211	184.130	−318.254	−187.679	7.002
1500	133.888	416.970	285.291	197.518	−314.162	−178.496	6.216

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = [344.206]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -253.07 \pm 5.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -253.13 \pm 5.0\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[350](1)
[160](1)
[310](2)
[130](2)

Ground State Quantum Weight: [6] σ = [6]
Point Group: D_{3h}
Bond Distance: Fe–Cl = [2.17] Å
Bond Angle: Cl–Fe–Cl = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.43810 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The equilibrium pressures for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ were determined by Kangro and Bernstorff[1] and Schafer,[2] respectively. Using their vapor pressure data the corresponding values of $\Delta_r H°(298.15\ K)$ for that reaction were evaluated by both the 2nd and 3rd law methods. Based on the 3rd law values for $\Delta_r H°(298.15\ K)$, the heats of formation $\Delta_f H°(298.15\ K)$ for $FeCl_3$(g) were derived. The results obtained are presented as follows.

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Kangro and Bernstorff[1]	760.2–1014.2	34.99 ± 0.44	35.73	−60.34 ± 0.30
Schafer[2]	673.2–1073.2	34.81 ± 0.02	34.93	−60.74 ± 0.20

The adopted value of $\Delta_f H°(FeCl_3, g, 298.15\ K)$ is -60.5 ± 1.2 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular structure was assumed to be the same as that of $AlCl_3$(g) due to the similarities in structure between Fe_2Cl_6(g) and Al_2Cl_6(g). The Fe–Cl bond distance was estimated by comparison with those for Fe_2Cl_6(g) reported by Zasorin *et al.*[3] and Hassel and Viervoll.[4] Both the ground state quantum weight and vibrational frequencies were estimated so that the second and third law values of $\Delta_r H°(298.15\ K)$, derived from the vapor pressure data, for the reaction $Fe_2Cl_6(g) = 2FeCl_3(g)$ are in reasonable agreement. The principal moments of inertia are: $I_A = I_B = 41.5834 \times 10^{-39}$ and $I_C = 83.1667 \times 10^{-39}\ g·cm^2$.

References

[1]W. Kangro and H. Bernstorff, Z. anorg. allg. Chem. **263**, 316 (1950).
[2]H. Schafer, Z. Anorg. Allg. Chem. **259**, 53 (1949).
[3]E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., **4**, 910 (1963).
[4]O. Hassel and H. Viervoll, Acta Chem. Scand. **1**, 149 (1947).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−18.214	−253.068	−253.068	INFINITE
100	56.528	269.115	409.062	−13.995	−253.639	−251.593	131.419
200	72.371	314.146	351.179	−7.406	−253.377	−249.627	65.196
250	75.716	330.687	345.475	−3.697	−253.233	−248.707	51.964
298.15	77.702	344.206	344.206	0.	−253.132	−247.845	43.421
300	77.762	344.687	344.208	0.144	−253.129	−247.812	43.148
350	79.085	356.780	345.160	4.067	−253.070	−246.931	36.852
400	79.981	367.403	347.290	8.045	−253.060	−246.055	32.132
450	80.615	376.862	350.060	12.061	−253.106	−245.178	28.459
500	81.077	385.381	353.173	16.104	−253.211	−244.292	25.521
600	81.692	400.222	359.814	24.245	−253.604	−242.475	21.109
700	82.070	412.846	366.510	32.435	−254.248	−240.573	17.952
800	82.318	423.822	373.003	40.655	−255.192	−238.559	15.576
900	82.489	433.528	379.199	48.896	−256.560	−236.403	13.720
1000	82.613	442.226	385.075	57.151	−258.657	−234.060	12.226
1100	82.704	450.104	390.634	65.417	−261.659	−231.441	10.990
1200	82.774	457.303	395.894	73.691	−264.118	−228.605	9.951
1300	82.828	463.931	400.876	81.971	−264.939	−225.613	9.065
1400	82.872	470.071	405.602	90.257	−265.854	−222.554	8.304
1500	82.907	475.790	410.093	98.546	−266.862	−219.426	7.641
1600	82.935	481.141	414.368	106.838	−267.964	−216.228	7.059
1700	82.959	486.170	418.445	115.132	−270.111	−212.940	6.543
1800	82.979	490.912	422.341	123.429	−271.737	−209.531	6.080
1900	82.996	495.399	426.069	131.728	−287.557	−205.326	5.645
2000	83.010	499.657	429.643	140.028	−289.615	−200.945	5.248
2100	83.023	503.707	433.074	148.330	−291.689	−196.461	4.887
2200	83.033	507.570	436.373	156.633	−293.779	−191.877	4.556
2300	83.043	511.261	439.549	164.937	−295.889	−187.198	4.251
2400	83.051	514.795	442.611	173.241	−298.020	−182.427	3.970
2500	83.058	518.186	445.567	181.547	−300.174	−177.566	3.710
2600	83.065	521.444	448.423	189.853	−302.353	−172.619	3.468
2700	83.071	524.579	451.186	198.160	−304.559	−167.587	3.242
2800	83.076	527.600	453.861	206.467	−306.792	−162.474	3.031
2900	83.080	530.515	456.455	214.775	−309.054	−157.280	2.833
3000	83.085	533.332	458.971	223.083	−311.345	−152.007	2.647
3100	83.088	536.056	461.414	231.392	−313.664	−146.658	2.471
3200	83.092	538.694	463.788	239.701	−664.312	−133.809	2.184
3300	83.095	541.251	466.096	248.010	−664.785	−117.224	1.855
3400	83.098	543.732	468.343	256.320	−665.316	−100.623	1.546
3500	83.100	546.140	470.532	264.630	−665.902	−84.006	1.254
3600	83.103	548.482	472.665	272.940	−666.542	−67.372	0.978
3700	83.105	550.758	474.745	281.250	−667.233	−50.718	0.716
3800	83.107	552.975	476.775	289.561	−667.974	−34.046	0.468
3900	83.109	555.134	478.756	297.872	−668.760	−17.354	0.232
4000	83.111	557.238	480.692	306.183	−669.589	−0.640	0.008
4100	83.112	559.290	482.584	314.494	−670.459	16.094	−0.205
4200	83.114	561.293	484.434	322.805	−671.366	32.850	−0.409
4300	83.115	563.248	486.245	331.117	−672.308	49.628	−0.603
4400	83.116	565.159	488.017	339.428	−673.281	66.429	−0.789
4500	83.118	567.027	489.752	347.740	−674.283	83.251	−0.966
4600	83.119	568.854	491.451	356.052	−675.312	100.097	−1.137
4700	83.120	570.642	493.117	364.364	−676.365	116.964	−1.300
4800	83.121	572.392	494.751	372.676	−677.441	133.855	−1.457
4900	83.122	574.105	496.353	380.988	−678.537	150.769	−1.607
5000	83.123	575.785	497.925	389.300	−679.651	167.704	−1.752
5100	83.123	577.431	499.468	397.612	−680.784	184.663	−1.891
5200	83.124	579.045	500.982	405.925	−681.933	201.643	−2.026
5300	83.125	580.628	502.470	414.237	−683.099	218.646	−2.155
5400	83.126	582.182	503.932	422.550	−684.281	235.672	−2.280
5500	83.126	583.707	505.369	430.862	−685.479	252.719	−2.400
5600	83.127	585.205	506.781	439.175	−686.695	269.788	−2.516
5700	83.128	586.676	508.170	447.488	−687.928	286.879	−2.629
5800	83.128	588.122	509.536	455.800	−689.180	303.992	−2.738
5900	83.129	589.543	510.880	464.113	−690.453	321.126	−2.843
6000	83.129	590.940	512.203	472.426	−691.749	338.282	−2.945

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K) = 313.717 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -491.15 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -496.22 \pm 4.2\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2261(1)	811(2)
499(1)	600(2)
254(1)	176(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.4655 Å; Si–Cl = 2.0118 Å
Bond Angles: H–Si–Cl = 108.32°; Cl–Si–Cl = 110.60°
Product of the Moments of Inertia: $I_A I_B I_C = 7.59150 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from that of $SiCl_4$(g)[1] using the difference $\Delta(\Delta_f H°) = 39.8\ kcal \cdot mol^{-1}$ taken from the analysis of Hunt and Sirtl.[2] The authors derived $\Delta_f H°(SiHCl_3, g, 298.15\ K) = -116.9 \pm 0.7\ kcal \cdot mol^{-1}$ from six previously reported equilibrium studies. These were at temperatures (773–1200 K) and compositions where the dominant equilibrium was $SiHCl_3 + HCl = SiCl_4 + H_2$. Selected data[2] were either close to or extrapolated to infinite residence time. Equilibria were reduced to $\Delta_f H°(298.15\ K)$ using auxiliary data[2] which are similar to JANAF values,[1] except for $\Delta_f H°(SiCl_4, g, 298.15\ K)$. Since this is now 1.7 $kcal \cdot mol^{-1}$ more negative, we change $\Delta_f H°(SiHCl_3)$ accordingly. Our adopted value is 1.8 $kcal \cdot mol^{-1}$ more negative than that estimated by linear interpolation between $SiCl_4$(g) and SiH_4(g).[1]

We dismiss two calorimetric values due to probable bias. These include $\Delta_f H°(l) = -112\ kcal \cdot mol^{-1}$ from oxygen–bomb calorimetry[3] and $\Delta_f H°(g) = -117.4 \pm 1.7\ kcal \cdot mol^{-1}$ from solution calorimetry[4] in dilute aqueous NaOH. Revised auxiliary data[1,5] change these values to $\Delta_f H°(g) = -115$[3] and $-124\ kcal \cdot mol^{-1}$. Wagman *et al.*[5] adopted $-122.6\ kcal \cdot mol^{-1}$, presumably based on Wolf.[4] The combustion result is suspect because the chemical reaction was determined only qualitatively and included corrosion reactions of the bomb.[3] In our approximate revision of the solution result, we eliminate Na_2SiO_3(cr) by taking the difference between the overall reactions[4] for $SiCl_4$(l) and $SiHCl_3$(g). This yields the difference $\Delta(\Delta_f H°) = \Delta_f H°(SiHCl_3, g) - \Delta_f H°(SiCl_4, g) = 34.6$ compared to 39.8 $kcal \cdot mol^{-1}$.[2] The solution result is suspect due to the possibility that the two hydrolyses did not proceed to equivalent degrees. Solution results[4] for $SiCl_4$, $SiBr_4$(l) and SiI_4(cr) also have a negative bias compared to our adopted values.[1]

Heat Capacity and Entropy

The molecular structure is based on microwave data of Mitzlaff *et al.*[6] for twleve isotopic forms of $SiHCl_3$ and $SiDCl_3$. Structural parameters are substitutional (r_s) values. They are in reasonable agreement with previous data[6] determined by various methods. The principal moments of inertia are $I_A = I_B = 34.3279 \times 10^{-39}$ and $I_C = 64.4220 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are those selected by Shimanouchi[7] from gas–phase infrared spectra of Buerger and Ruoff.[8] Assignments are based on band contours and isotopic splittings and are consistent with recent liquid–phase Raman spectra.[9]

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_2Cl_2, SiH_3Cl and SiH_3Br.[1]

References

[1]JANAF Thermochemical Tables: Cl_4Si(g), 12-31-70; Cl_2H_2Si(g), ClH_3Si(g), BrH3Si(g), $Br_4Si(\ell)$, 12-31-76; I_4Si(cr), H_4Si(g), 6-30-76; 02Si(quartz), 6-30-67; ClH(g), 9-30-64; HNaO(cr), 12-31-70; ClNa(cr), 9-30-64.
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[5]U.S. Nat. Bur. Stand. Tech. Note 270-3, (1968).
[6]M. Mitzlaff, R. Holm and H. Hartmann, Z. Naturforsch. **A22**, 1415 and 288 (1967); Theor. Chim. Acta **12**, 330 (1969).
[7]T. Shimanouchi, J. Phys. Chem. Ref. Data **1**, 205 (1972).
[8]H. Buerger and A. Ruoff, Spectrochim. Acta **A26**, 1449 (1970).
[9]V. S. Dernova *et al.*, Dokl. Akad. Nauk SSSR **222**, 147 (1975).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.151	−491.151	−491.151	INFINITE
100	46.854	248.357	372.097	−12.374	−493.507	−484.572	253.115
200	63.216	286.041	320.258	−6.844	−495.059	−475.003	124.058
250	70.039	300.901	314.931	−3.507	−495.699	−469.914	98.183
298.15	75.455	313.717	313.717	0.	−496.222	−464.899	81.448
300	75.641	314.185	313.719	0.140	−496.241	−464.704	80.912
350	80.107	326.194	314.657	4.038	−496.680	−459.412	68.563
400	83.657	337.131	316.793	8.135	−497.025	−454.063	59.295
450	86.512	347.155	319.617	12.392	−497.286	−448.677	52.081
500	88.851	356.395	322.839	16.778	−497.478	−443.265	46.308
600	92.465	372.932	329.843	25.853	−497.691	−432.399	37.644
700	95.144	387.396	337.053	35.240	−497.729	−421.511	31.454
800	97.212	400.241	344.164	44.862	−497.642	−410.628	26.811
900	98.848	411.789	351.047	54.668	−497.466	−399.761	23.202
1000	100.164	422.275	357.654	64.621	−497.231	−388.917	20.315
1100	101.235	431.873	363.971	74.693	−496.960	−378.099	17.954
1200	102.115	440.721	370.003	84.862	−496.671	−367.306	15.988
1300	102.845	448.924	375.762	95.111	−496.381	−356.537	14.326
1400	103.455	456.569	381.264	105.427	−496.103	−345.790	12.902
1500	103.970	463.724	386.525	115.799	−495.845	−335.063	11.668
1600	104.406	470.449	391.562	126.218	−495.617	−324.352	10.589
1700	104.779	476.790	396.391	136.678	−545.602	−313.207	9.624
1800	105.100	482.788	401.026	147.172	−545.221	−299.548	8.693
1900	105.378	488.478	405.480	157.696	−544.843	−285.909	7.860
2000	105.620	493.890	409.766	168.247	−544.474	−272.291	7.112
2100	105.832	499.048	413.896	178.819	−544.116	−258.691	6.435
2200	106.018	503.976	417.879	189.412	−543.773	−245.107	5.820
2300	106.182	508.692	421.726	200.022	−543.450	−231.539	5.258
2400	106.328	513.214	425.444	210.648	−543.147	−217.984	4.744
2500	106.458	517.558	429.043	221.287	−542.870	−204.441	4.272
2600	106.575	521.735	432.528	231.939	−542.619	−190.909	3.835
2700	106.679	525.759	435.907	242.602	−542.398	−177.386	3.432
2800	106.774	529.641	439.186	253.275	−542.208	−163.871	3.057
2900	106.859	533.389	442.370	263.956	−542.050	−150.361	2.708
3000	106.936	537.013	445.464	274.646	−541.925	−136.857	2.383
3100	107.007	540.521	448.475	285.343	−541.834	−123.357	2.079
3200	107.071	543.919	451.404	296.047	−541.774	−109.859	1.793
3300	107.129	547.215	454.258	306.757	−541.746	−96.361	1.525
3400	107.183	550.414	457.039	317.473	−541.748	−82.865	1.273
3500	107.233	553.521	459.752	328.194	−541.778	−69.368	1.035
3600	107.278	556.543	462.399	338.919	−925.984	−45.409	0.659
3700	107.320	559.483	464.983	349.649	−925.647	−20.953	0.296
3800	107.359	562.345	467.508	360.383	−925.331	3.493	−0.048
3900	107.395	565.135	469.975	371.121	−925.032	27.932	−0.374
4000	107.428	567.854	472.388	381.862	−924.746	52.364	−0.684
4100	107.459	570.507	474.749	392.607	−924.468	76.788	−0.978
4200	107.488	573.097	477.060	403.354	−924.196	101.206	−1.259
4300	107.515	575.627	479.323	414.104	−923.924	125.617	−1.526
4400	107.541	578.099	481.540	424.857	−923.649	150.021	−1.781
4500	107.564	580.516	483.713	435.612	−923.367	174.420	−2.025
4600	107.586	582.880	485.843	446.370	−923.074	198.812	−2.258
4700	107.607	585.194	487.932	457.130	−922.767	223.197	−2.481
4800	107.627	587.460	489.982	467.891	−922.442	247.576	−2.694
4900	107.645	589.679	491.994	478.655	−922.097	271.948	−2.899
5000	107.662	591.854	493.970	489.420	−921.728	296.312	−3.096
5100	107.678	593.986	495.910	500.187	−921.333	320.670	−3.284
5200	107.694	596.077	497.816	510.956	−920.909	345.018	−3.466
5300	107.708	598.129	499.690	521.726	−920.455	369.359	−3.640
5400	107.722	600.142	501.531	532.497	−919.968	393.691	−3.808
5500	107.735	602.119	503.342	543.270	−919.446	418.013	−3.970
5600	107.747	604.060	505.124	554.044	−918.888	442.325	−4.126
5700	107.759	605.967	506.876	564.820	−918.293	466.627	−4.276
5800	107.770	607.841	508.601	575.596	−917.661	490.919	−4.421
5900	107.781	609.684	510.298	586.374	−916.989	515.199	−4.561
6000	107.791	611.495	511.970	597.152	−916.276	539.467	−4.696

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K)$ = [335.747] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -997.47\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1004.72 \pm 20.9\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
[650](6)
[220](6)

Point Group: D_{3h} $\sigma = 6$
Bond Distance: Li–Cl = [2.2] Å
Bond Angle: Li–Cl–Li = [120]°
Product of the Moment of Inertia: $I_A I_B I_C = 2.67006 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

The heat of sublimation at 298.15 K was chosen so as to give the correct ratio of monomer, dimer and trimer at 870 K. The value used was 52.6 kcal·mol^{-1} which compares very well with the value 53.6 kcal·mol^{-1} obtained from a third law analysis of the data of Nesmeyanov and Sazonov[1] in conjunction with the relative concentrations of monomer, dimer, and trimer at 870 K from the work of Miller and Kusch.[2]

Heat Capacity and Entropy

The postulated structure, bond lengths and frequencies were all taken from Hildenbrand *et al.*[3] The principal moments of inertia are: $I_A = I_B = 51.1090 \times 10^{-39}$ and $I_C = 102.2179 \times 10^{-39}$ g·cm^2.

References

[1]An. N. Nesmeyanov and L. A. Sazonov, Zhur. Neorg. Khim. **4**, 231 (1960).
[2]R. C. Miller and P. Kusch, J. Chem. Phys. **25**, 860 (1950).
[3]D. L. Hildenbrand, A. M. Saul, P. R. Basford, S. E. Stephanon, L. Larson and A. Uyehara, Aeronutronic Tenth Quarterly Report on Contract Nord 17980 Report C–898 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−20.383	−997.466	−997.466	INFINITE
100	56.629	250.069	413.649	−16.358	−999.293	−993.747	519.080
200	84.270	298.513	344.567	−9.211	−1002.228	−987.045	257.790
250	94.366	318.444	337.386	−4.735	−1003.565	−983.092	205.406
298.15	102.005	335.747	335.747	0.	−1004.721	−979.042	171.524
300	102.261	336.379	335.749	0.189	−1004.763	−978.883	170.439
350	108.285	352.616	337.017	5.459	−1005.859	−974.482	145.433
400	112.864	367.388	339.904	10.993	−1006.965	−969.925	126.659
450	116.369	380.893	343.719	16.728	−1008.164	−965.224	112.040
500	119.083	393.300	348.066	22.617	−1018.497	−959.462	100.234
600	122.907	415.376	357.491	34.731	−1020.781	−947.432	82.481
700	125.387	434.521	367.158	47.154	−1022.641	−935.055	69.775
800	127.072	451.381	376.653	59.782	−1024.251	−922.431	60.229
900	128.263	466.421	385.807	72.552	−1025.735	−909.613	52.793
1000	129.134	479.982	394.558	85.424	−1027.126	−896.636	46.835
1100	129.788	492.322	402.893	98.372	−1028.447	−883.522	41.955
1200	130.292	503.638	410.823	111.377	−1029.713	−870.291	37.883
1300	130.688	514.083	418.370	124.427	−1030.938	−856.956	34.433
1400	131.004	523.780	425.557	137.512	−1032.124	−843.528	31.472
1500	131.261	532.827	432.410	150.626	−1033.269	−830.017	28.904
1600	131.472	541.305	438.954	163.763	−1034.380	−816.430	26.654
1700	131.647	549.281	445.211	176.919	−1471.169	−781.247	24.005
1800	131.795	556.810	451.204	190.091	−1469.964	−740.698	21.494
1900	131.920	563.940	456.952	203.277	−1468.764	−700.216	19.250
2000	132.027	570.709	462.472	216.475	−1467.574	−659.797	17.232
2100	132.120	577.153	467.780	229.682	−1466.399	−619.437	15.408
2200	132.200	583.301	472.893	242.898	−1465.244	−579.133	13.750
2300	132.270	589.179	477.822	256.122	−1464.117	−538.880	12.238
2400	132.332	594.810	482.580	269.352	−1463.024	−498.676	10.853
2500	132.386	600.213	487.178	282.588	−1461.972	−458.517	9.580
2600	132.435	605.406	491.626	295.829	−1460.968	−418.398	8.406
2700	132.478	610.405	495.933	309.075	−1460.019	−378.318	7.319
2800	132.516	615.224	500.108	322.324	−1459.131	−338.271	6.311
2900	132.551	619.875	504.158	335.578	−1458.310	−298.255	5.372
3000	132.582	624.369	508.091	348.835	−1457.563	−258.266	4.497
3100	132.611	628.717	511.912	362.094	−1456.894	−218.301	3.678
3200	132.636	632.927	515.628	375.357	−1456.308	−178.356	2.911
3300	132.660	637.009	519.245	388.621	−1455.808	−138.428	2.191
3400	132.681	640.970	522.767	401.888	−1455.399	−98.514	1.513
3500	132.701	644.816	526.200	415.158	−1455.081	−58.610	0.875
3600	132.719	648.555	529.547	428.429	−1454.858	−18.714	0.272
3700	132.735	652.191	532.812	441.701	−1454.730	21.177	−0.299
3800	132.751	655.731	536.001	454.976	−1454.699	61.065	−0.839
3900	132.765	659.180	539.115	468.251	−1454.766	100.954	−1.352
4000	132.778	662.541	542.159	481.529	−1454.931	140.847	−1.839
4100	132.790	665.820	545.135	494.807	−1455.196	180.744	−2.303
4200	132.801	669.020	548.047	508.086	−1455.560	220.649	−2.744
4300	132.812	672.145	550.897	521.367	−1456.025	260.564	−3.165
4400	132.822	675.198	553.687	534.649	−1456.528	300.486	−3.567
4500	132.831	678.183	556.421	547.931	−1457.167	340.425	−3.952
4600	132.839	681.103	559.100	561.215	−1457.912	380.380	−4.319
4700	132.847	683.960	561.726	574.499	−1458.756	420.351	−4.672
4800	132.855	686.757	564.302	587.784	−1459.701	460.342	−5.010
4900	132.862	689.496	566.829	601.070	−1460.748	500.354	−5.334
5000	132.869	692.181	569.309	614.357	−1461.900	540.387	−5.645
5100	132.875	694.812	571.744	627.644	−1463.141	580.444	−5.945
5200	132.881	697.392	574.136	640.932	−1464.504	620.527	−6.233
5300	132.886	699.923	576.485	654.220	−1465.979	660.638	−6.511
5400	132.892	702.407	578.794	667.509	−1467.567	700.778	−6.779
5500	132.897	704.846	581.064	680.799	−1469.274	740.948	−7.037
5600	132.901	707.240	583.296	694.088	−1471.101	781.150	−7.286
5700	132.906	709.593	585.491	707.379	−1473.053	821.386	−7.527
5800	132.910	711.904	587.651	720.670	−1475.134	861.657	−7.760
5900	132.914	714.176	589.776	733.961	−1477.346	901.965	−7.985
6000	132.918	716.410	591.868	747.253	−1479.695	942.312	−8.204

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 325.454\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -554.2 \pm 1.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -559.8 \pm 1.7\ kJ·mol^{-1}$

Vibrational Levels and Multiplicities		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1290(1)	486(1)	337(1)
581(2)	267(2)	193(2)

Point Group: C_{3v} $\sigma = 3$

Bond Distances: P–O = 1.45 ± 0.03 Å; P–Cl = 1.99 ± .02 Å

Bond Angle: Cl–P–Cl = 103.6 ± 2°

Product of the Moments of Inertia: $I_A I_B I_C = 1.01841 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

The $\Delta_f H°(298.15\ K)$ for $POCl_3$(g) was derived from the $\Delta_f H°(298.15\ K)$ of $POCl_3$(l) and the $\Delta_{vap} H°(298.15\ K)$. The $\Delta_f H°(298.15\ K)$ of the $POCl_3$(l) was calculated from the heat of hydrolysis observed by Charnley and Skinner[1] for the reaction:

$$POCl_3(l) + (n + 3)\ H_2O(l) \rightarrow [H_3PO_4 + 3\ HCl] \text{ in } n\ H_2O(l)$$

The auxiliary thermochemical data, on the enthalpies of formation of water and aqueous solutions of HCl and of H_3PO_4, were taken from the NBS Circular 500,[2] and were adjusted for consistency with JANAF Tables. The heat of vaporization was measured and corrected to 298.15 K by Ott and Giauque.[3]

Heat Capacity and Entropy

The molecular constants are from the microwave spectral data of Williams *et al.*[4] In order to determine the structure Williams *et al.*[4] assumed the P–Cl distance equal to 1.99 Å. This was the smallest value allowed (2.02 ± 0.03 Å) by the electron diffraction work of Brockway and Beach.[5]

Ott and Giauque[3] have given the moments of inertia obtained from a weighted average of the isotopic species. $I_A \neq I_B$ due to isotopic loss of symmetry. The $S°(298.15\ K)$ calculated from calorimetric data by Ott and Giauque[3] was 77.75 $cal·K^{-1}·mol^{-1}$and the $S°(298.15\ K)$, calculated from the spectral data was 77.77 $cal·K^{-1}·mol^{-1}$.

The principal moments of inertia are: $I_A = I_B = 42.0514 \times 10^{-39}$ and $I_C = 57.5920 \times 10^{-39}\ g·cm^2$.

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[4]Q. Williams, J. Sheridan and W. Gordy, J. Chem. Phys. **20**, 164 (1952).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.880	−554.226	−554.226	INFINITE
100	50.035	251.381	392.051	−14.067	−557.121	−543.474	283.881
200	72.927	293.857	332.888	−7.806	−559.135	−529.144	138.198
250	79.947	310.927	326.826	−3.975	−559.553	−521.594	108.981
298.15	84.917	325.454	325.454	0.	−559.819	−514.257	90.096
300	85.082	325.980	325.456	0.157	−559.828	−513.975	89.491
350	88.953	339.399	326.507	4.512	−560.724	−506.246	75.553
400	91.957	351.481	328.886	9.038	−560.889	−498.451	65.091
450	94.338	362.455	332.016	13.698	−560.969	−490.641	56.952
500	96.257	372.497	335.569	18.464	−560.982	−482.825	50.440
600	99.115	390.317	343.246	28.242	−560.865	−467.202	40.674
700	101.093	405.753	351.098	38.258	−560.616	−451.610	33.700
800	102.506	419.349	358.797	48.442	−560.283	−436.060	28.472
900	103.544	431.485	366.211	58.747	−559.894	−420.555	24.408
1000	104.325	442.437	373.295	69.142	−559.467	−405.095	21.160
1100	104.925	452.410	380.041	79.606	−559.016	−389.680	18.504
1200	105.395	461.560	386.458	90.123	−622.120	−373.228	16.246
1300	105.770	470.012	392.564	100.682	−620.869	−352.537	14.165
1400	106.072	477.862	398.380	111.275	−619.619	−331.943	12.385
1500	106.320	485.189	403.926	121.895	−618.373	−311.439	10.845
1600	106.526	492.057	409.221	132.537	−617.133	−291.017	9.501
1700	106.697	498.521	414.286	143.199	−615.904	−270.672	8.317
1800	106.843	504.624	419.137	153.876	−614.688	−250.400	7.266
1900	106.967	510.404	423.790	164.567	−613.487	−230.194	6.328
2000	107.073	515.893	428.259	175.269	−612.303	−210.052	5.486
2100	107.165	521.119	432.557	185.981	−611.140	−189.968	4.725
2200	107.245	526.107	436.697	196.701	−610.000	−169.938	4.035
2300	107.315	530.876	440.689	207.429	−608.886	−149.961	3.406
2400	107.377	535.444	444.542	218.164	−607.800	−130.031	2.830
2500	107.432	539.829	448.267	228.905	−606.745	−110.146	2.301
2600	107.481	544.043	451.870	239.650	−605.723	−90.302	1.814
2700	107.524	548.100	455.359	250.400	−604.736	−70.497	1.364
2800	107.563	552.011	458.742	261.155	−603.784	−50.728	0.946
2900	107.598	555.787	462.023	271.913	−602.869	−30.992	0.558
3000	107.630	559.435	465.210	282.674	−601.992	−11.287	0.197
3100	107.658	562.965	468.307	293.439	−601.151	8.389	−0.141
3200	107.685	566.383	471.319	304.206	−600.346	28.038	−0.458
3300	107.708	569.697	474.250	314.976	−599.576	47.663	−0.754
3400	107.730	572.913	477.105	325.748	−598.838	67.266	−1.033
3500	107.750	576.036	479.887	336.522	−598.130	86.846	−1.296
3600	107.768	579.071	482.600	347.298	−597.449	106.408	−1.544
3700	107.785	582.024	485.247	358.075	−596.791	125.950	−1.778
3800	107.801	584.899	487.832	368.855	−596.154	145.475	−2.000
3900	107.815	587.699	490.357	379.635	−595.533	164.984	−2.210
4000	107.829	590.429	492.825	390.418	−594.925	184.476	−2.409
4100	107.841	593.092	495.238	401.201	−594.325	203.954	−2.598
4200	107.852	595.691	497.599	411.986	−593.730	223.417	−2.779
4300	107.863	598.229	499.910	422.772	−593.135	242.866	−2.950
4400	107.873	600.709	502.173	433.558	−592.538	262.301	−3.114
4500	107.883	603.133	504.389	444.346	−591.933	281.722	−3.270
4600	107.891	605.504	506.562	455.135	−591.317	301.130	−3.419
4700	107.900	607.825	508.692	465.924	−590.688	320.524	−3.562
4800	107.907	610.096	510.781	476.715	−590.042	339.905	−3.699
4900	107.915	612.321	512.830	487.506	−589.376	359.272	−3.830
5000	107.921	614.502	514.842	498.298	−588.689	378.625	−3.955
5100	107.928	616.639	516.817	509.090	−587.977	397.965	−4.076
5200	107.934	618.735	518.757	519.883	−587.238	417.289	−4.192
5300	107.940	620.791	520.663	530.677	−586.471	436.600	−4.303
5400	107.945	622.808	522.536	541.471	−585.675	455.896	−4.410
5500	107.950	624.789	524.377	552.266	−584.849	475.176	−4.513
5600	107.955	626.734	526.188	563.061	−583.990	494.442	−4.612
5700	107.959	628.645	527.968	573.857	−583.100	513.692	−4.707
5800	107.964	630.523	529.720	584.653	−582.177	532.926	−4.800
5900	107.968	632.368	531.445	595.450	−581.220	552.143	−4.888
6000	107.972	634.183	533.142	606.247	−580.231	571.344	−4.974

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 311.682 \pm .42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -285.50 \pm 5.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -288.70 \pm 5.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
510 (1)	507 (2)
259 (1)	187 (2)

Ground State Quantum Weight = 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distance: P–Cl = 2.039 ± 0.0014 Å
Bond Angle: Cl–P–Cl = 100.27 ± 0.09°
Product of the Moments of Inertia: $I_A I_B I_C = 6.05196 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

Neale and Williams[1] measured the heat of hydrolysis of liquid phosphorus trichloride and reported a $\Delta_f H° = -67.5 \pm 0.3$ kcal·mol^{-1} for the following reaction:

$$PCl_3(l) + (X_2 + 3)\ H_2O \rightarrow H_3PO_3(aq) + 3\ HCl(aq)$$

with X_2 in range 4500 to 7500. Combining this result with enthalpy of formation data for aqueous H_3PO_3, −229.4 kcal·mol^{-1},[2,5,16] H_2O[2] and aqueous HCl,[2] we derive $\Delta_f H°(PCl_3, l, 0\ K) = -76.7$ kcal·mol^{-1}. Charnley and Skinner[3] made an independent investigation of the hydrolysis of liquid phosphorus trichloride and obtained enthalpy data in very good agreement with Neale and Williams' results. Their results lead to $\Delta_f H°(PCl_3, l, 0\ K) = -76.5$ kcal·mol^{-1} when combined with heat of formation data.[2,5,16]

Neale and Williams[4] also investigated the hydrolysis of liquid phosphorus trichloride in aqueous bromine solution with the formation of phosphoric acid rather than phosphorus acid which results when hydrolysis occurs in water. They reported a $\Delta_f H° = -137.9$ kcal·mol^{-1} for the following reaction:

$$PCl_3(l) + Br_2(aq) + (X_2 + 4)H_2O \rightarrow H_3PO_4(aq) + 3\ HCl(aq) + 2\ HBr(aq)$$

with X_2 in range 3500 to 6300. Combining this result with the following enthalpy of formation data: $\Delta_f H°(H_3PO_4 1\ H_2O) = -306.4 \pm 0.5$ kcal·mol^{-1},[5] $\Delta_f H°(Br, aq) = -0.2$ kcal·mol^{-1},[6] HCl(aq) and HBr(aq),[2] along with dilution data for H_3PO_4(aq),[2] we derive $\Delta_f H°(PCl_3, 298.15\ K) = -77.0$ kcal·mol^{-1}.

The enthalpy of formation from white phosphorus of gaseous PCl_3, $\Delta_f H°(PCl_3, g, 298.15\ K) = -69.0 \pm 1.1$ kcal·mol^{-1}, is calculated from $\Delta_f H°(PCl_3, l, 298.15\ K) = -76.7 \pm 1.0$ kcal·mol^{-1}, an average value of the three results given above, and the enthalpy of vaporization of PCl_3. $\Delta_{vap} H°(298.15\ K) = 7.7 \pm 0.1$ kcal·mol^{-1} is determined from a 2nd law analysis of the combined vapor pressure data of Nisel'son and Seryakov[7] and Regnault.[8] The smoothed vapor pressure data of Regnault as reported by Stull[9] were used.

An independent value for the heat of formation can be obtained from the work of Duus and Mykytiuk[17] on the reaction 1.5 $CaF_2 + PCl_3(g) \rightarrow 1.5\ CaCl_2 + PF_3(g)$. The authors reported $\Delta_f H°(630\ K) = -2.97$ kcal·mol^{-1}. From a re-examination of their technique we believe that this heat evolution is likely to be too small, perhaps by 100%. The analytical results indicate that the reaction is 99% complete or better; thus, we can use this with JANAF entropies to calculate $\Delta_f H°(298.15\ K) \leq 3.55$ kcal·mol^{-1}. Finch *et al.*[18] have reported $\Delta_f H°(CaF_2, cr, 0\ K) - \Delta_f H°(CaCl_2, cr, 0\ K) = -100.87 \pm 0.02$ kcal·mol^{-1}; thus, we obtain $\Delta_f H°(PCl_3, g, 298.15\ K) > -70.1 \pm 2.0$ kcal·mol^{-1} from $\Delta_f H°(PF_3, g, 298.15\ K) = -224.9 \pm 0.9$ kcal·mol^{-1}. This value is not adopted because of the lack of calorimeter calibration, but it offers an attractive possibility for further study.

Heat Capacity and Entropy

The molecular structure and bond length given above for PCl_3 are from the electron diffraction studies of Hedberg and Iwasahi.[11] The adopted values are in good agreement within experimental error with the following structural data reported by Kisliuk and Townes[12] from microwave studies: r(P–Cl) = 2.043 ± 0.003 Å, the angle Cl–P–Cl = 100°6′ ± 20′. The vibrational frequencies are from the recent infrared and Raman studies of Frankiss and Miller[13] and are in excellent agreement with those of Muller *et al.*[14] and Davis and Oetjen.[15] The principal moments of inertia are: $I_A = I_B = 32.3918 \times 10^{-39}$ and $I_C = 57.6799 \times 10^{-39}$ g·cm^2.

References

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Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K		J·K^{-1}mol^{-1}		kJ·mol^{-1}		Standard State Pressure = $p°$ = 0.1 MPa	
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.932	−285.497	−285.497	INFINITE
100	46.469	246.997	368.917	−12.192	−287.012	−281.592	147.088
200	62.949	284.738	317.995	−6.651	−288.291	−275.824	72.038
250	68.098	299.372	312.842	−3.368	−288.527	−272.679	56.973
298.15	71.581	311.682	311.682	0.	−288.696	−269.610	47.235
300	71.693	312.125	311.683	0.133	−288.702	−269.492	46.923
350	74.221	323.377	312.566	3.784	−289.564	−266.207	39.729
400	76.036	333.413	314.556	7.543	−289.749	−262.857	34.326
450	77.369	342.450	317.162	11.380	−289.892	−259.487	30.120
500	78.370	350.656	320.107	15.274	−290.007	−256.102	26.755
600	79.738	365.075	326.433	23.185	−290.177	−249.304	21.704
700	80.599	377.436	332.858	31.205	−290.297	−242.482	18.094
800	81.175	388.239	339.119	39.296	−290.388	−235.645	15.386
900	81.576	397.824	345.120	47.434	−290.463	−228.798	13.279
1000	81.867	406.435	350.828	55.607	−290.528	−221.943	11.593
1100	82.085	414.249	356.244	63.805	−290.587	−215.081	10.213
1200	82.251	421.398	361.380	72.022	−354.218	−207.136	9.016
1300	82.381	427.987	366.253	80.254	−353.502	−194.908	7.832
1400	82.485	434.096	370.884	88.498	−352.794	−182.735	6.818
1500	82.569	439.790	375.290	96.751	−352.094	−170.613	5.941
1600	82.638	445.121	379.489	105.011	−351.404	−158.537	5.176
1700	82.696	450.133	383.499	113.278	−350.723	−146.503	4.502
1800	82.744	454.861	387.333	121.550	−350.054	−134.510	3.903
1900	82.784	459.336	391.006	129.826	−349.397	−122.553	3.369
2000	82.819	463.583	394.530	138.107	−348.754	−110.631	2.889
2100	82.849	467.625	397.915	146.390	−348.127	−98.740	2.456
2200	82.875	471.479	401.172	154.676	−347.517	−86.879	2.063
2300	82.898	475.164	404.310	162.965	−346.927	−75.045	1.704
2400	82.918	478.692	407.336	171.256	−346.359	−63.236	1.376
2500	82.936	482.078	410.258	179.549	−345.814	−51.451	1.075
2600	82.951	485.331	413.084	187.843	−345.295	−39.687	0.797
2700	82.965	488.462	415.818	196.139	−344.803	−27.942	0.541
2800	82.978	491.479	418.466	204.436	−344.340	−16.215	0.302
2900	82.989	494.391	421.035	212.734	−343.907	−4.504	0.081
3000	82.999	497.205	423.527	221.034	−343.503	7.193	−0.125
3100	83.008	499.927	425.948	229.334	−343.128	18.877	−0.318
3200	83.017	502.562	428.301	237.635	−342.782	30.548	−0.499
3300	83.024	505.117	430.590	245.938	−342.464	42.210	−0.668
3400	83.031	507.595	432.819	254.240	−342.171	53.862	−0.827
3500	83.038	510.002	434.990	262.544	−341.902	65.506	−0.978
3600	83.043	512.342	437.106	270.848	−341.653	77.143	−1.119
3700	83.049	514.617	439.170	279.152	−341.422	88.773	−1.253
3800	83.054	516.832	441.185	287.458	−341.204	100.397	−1.380
3900	83.058	518.989	443.153	295.763	−340.998	112.015	−1.500
4000	83.063	521.092	445.075	304.069	−340.798	123.629	−1.614
4100	83.066	523.143	446.954	312.376	−340.601	135.237	−1.723
4200	83.070	525.145	448.792	320.682	−340.403	146.840	−1.826
4300	83.073	527.100	450.591	328.990	−340.200	158.439	−1.925
4400	83.077	529.010	452.351	337.297	−339.988	170.033	−2.019
4500	83.080	530.877	454.076	345.605	−339.764	181.622	−2.108
4600	83.082	532.703	455.765	353.913	−339.524	193.206	−2.194
4700	83.085	534.489	457.421	362.221	−339.265	204.784	−2.276
4800	83.087	536.239	459.045	370.530	−338.983	216.356	−2.354
4900	83.090	537.952	460.638	378.839	−338.676	227.923	−2.430
5000	83.092	539.631	462.201	387.148	−338.341	239.482	−2.502
5100	83.094	541.276	463.735	395.457	−337.975	251.036	−2.571
5200	83.096	542.890	465.242	403.767	−337.575	262.581	−2.638
5300	83.098	544.472	466.722	412.076	−337.141	274.118	−2.702
5400	83.099	546.026	468.176	420.386	−336.671	285.647	−2.763
5500	83.101	547.551	469.606	428.696	−336.161	297.167	−2.822
5600	83.102	549.048	471.011	437.007	−335.613	308.677	−2.879
5700	83.104	550.519	472.393	445.317	−335.023	320.177	−2.934
5800	83.105	551.964	473.753	453.627	−334.392	331.667	−2.987
5900	83.107	553.385	475.090	461.938	−333.718	343.145	−3.038
6000	83.108	554.782	476.407	470.249	−333.001	354.610	−3.087

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 337.347\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-376.2]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-380.0]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
169(2)	[247](2)	247(1)
431(1)	540 (2)	751(1)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: P–S = 1.85 ± 0.02 Å; P–Cl = 2.02 ± 0.01 Å
Bond Angle: Cl–P–Cl = 100.5° ± 1°
Product of the Moments of Inertia: $I_A I_B I_C = 2.06885 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was estimated by Henderson and Scheffee.[1] Henderson and Scheffee use white (α) phosphorus as a reference state.

Heat Capacity and Entropy

Ziomek and Piotrowski[2] have chosen the most probable values for the wave numbers from the infrared spectral data of Cilento *et al.*[3] and the Raman spectral data of Simon and Schulze,[4] Thatte,[5] Gerding and Westrick[6] and Delwaulle and Francois.[7] Ziomek and Piotrowski[2] found their normal coordinate treatments gave the listed wave numbers as fundamentals and lent support for the 247 cm^{-1} band missing from the Raman spectral data. The structure (bond distances and angles) was determined from microwave data by Williams *et al.*[8] The principal moments of inertia are: $I_A = 56.7997 \times 10^{-39}$, $I_B = I_C = 60.3519 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.001	−376.202	−376.202	INFINITE
100	54.294	258.141	408.225	−15.008	−378.154	−372.596	194.624
200	77.707	303.800	345.230	−8.286	−379.893	−366.512	95.723
250	84.855	321.951	338.800	−4.212	−380.359	−363.110	75.868
298.15	89.847	337.347	337.347	0.	−380.744	−359.753	63.027
300	90.009	337.903	337.348	0.166	−380.758	−359.622	62.616
350	93.755	352.074	338.459	4.765	−381.839	−356.000	53.130
400	96.516	364.783	340.969	9.526	−384.453	−352.193	45.992
450	98.589	376.276	344.264	14.406	−385.479	−348.107	40.407
500	100.173	386.749	347.996	19.376	−386.520	−343.896	35.927
600	102.377	405.223	356.036	29.512	−388.049	−335.219	29.183
700	103.791	421.118	364.225	39.826	−389.223	−326.318	24.350
800	104.745	435.044	372.225	50.255	−390.187	−317.263	20.715
900	105.418	447.422	379.905	60.765	−444.146	−307.016	17.819
1000	105.908	458.556	387.223	71.333	−443.673	−291.805	15.242
1100	106.275	468.668	394.174	81.943	−443.192	−276.641	13.137
1200	106.558	477.928	400.773	92.585	−506.284	−260.443	11.337
1300	106.779	486.466	407.041	103.253	−505.035	−240.007	9.644
1400	106.956	494.386	413.000	113.940	−503.802	−219.667	8.196
1500	107.100	501.770	418.675	124.643	−502.585	−199.414	6.944
1600	107.218	508.686	424.087	135.359	−501.387	−179.242	5.852
1700	107.316	515.189	429.257	146.086	−500.210	−159.144	4.890
1800	107.398	521.326	434.203	156.821	−499.053	−139.115	4.037
1900	107.468	527.134	438.942	167.565	−497.919	−119.149	3.276
2000	107.528	532.648	443.491	178.315	−496.807	−99.243	2.592
2100	107.580	537.896	447.862	189.070	−495.721	−79.391	1.975
2200	107.625	542.902	452.069	199.830	−494.659	−59.591	1.415
2300	107.664	547.687	456.123	210.595	−493.626	−39.838	0.905
2400	107.698	552.269	460.035	221.363	−492.621	−20.130	0.438
2500	107.728	556.666	463.813	232.134	−491.646	−0.463	0.010
2600	107.755	560.892	467.466	242.909	−490.703	19.165	−0.385
2700	107.779	564.959	471.002	253.685	−489.792	38.759	−0.750
2800	107.801	568.879	474.428	264.464	−488.915	58.318	−1.088
2900	107.820	572.663	477.750	275.245	−488.072	77.847	−1.402
3000	107.838	576.318	480.975	286.028	−487.264	97.348	−1.695
3100	107.853	579.854	484.108	296.813	−486.488	116.822	−1.968
3200	107.868	583.279	487.154	307.599	−485.745	136.271	−2.224
3300	107.881	586.598	490.118	318.386	−485.034	155.699	−2.465
3400	107.893	589.819	493.003	329.175	−484.351	175.104	−2.690
3500	107.904	592.947	495.814	339.965	−483.696	194.491	−2.903
3600	107.914	595.987	498.555	350.756	−483.065	213.858	−3.103
3700	107.923	598.944	501.228	361.548	−482.455	233.209	−3.292
3800	107.931	601.822	503.837	372.340	−481.863	252.543	−3.471
3900	107.939	604.625	506.386	383.134	−481.285	271.862	−3.641
4000	107.947	607.358	508.876	393.928	−480.719	291.166	−3.802
4100	107.953	610.024	511.311	404.723	−480.159	310.457	−3.955
4200	107.960	612.625	513.692	415.519	−479.604	329.733	−4.101
4300	107.966	615.166	516.023	426.315	−479.048	348.997	−4.239
4400	107.971	617.648	518.304	437.112	−478.489	368.247	−4.372
4500	107.976	620.074	520.539	447.909	−477.922	387.484	−4.498
4600	107.981	622.448	522.729	458.707	−477.345	406.710	−4.618
4700	107.985	624.770	524.875	469.506	−476.755	425.922	−4.734
4800	107.990	627.043	526.980	480.304	−476.148	445.121	−4.844
4900	107.993	629.270	529.045	491.103	−475.522	464.308	−4.950
5000	107.997	631.452	531.071	501.903	−474.873	483.481	−5.051
5100	108.001	633.591	533.061	512.703	−474.201	502.642	−5.148
5200	108.004	635.688	535.014	523.503	−473.503	521.789	−5.241
5300	108.007	637.745	536.933	534.304	−472.776	540.922	−5.331
5400	108.010	639.764	538.819	545.104	−472.020	560.042	−5.417
5500	108.013	641.746	540.672	555.906	−471.232	579.147	−5.500
5600	108.015	643.692	542.495	566.707	−470.412	598.237	−5.580
5700	108.018	645.604	544.287	577.509	−469.558	617.313	−5.657
5800	108.020	647.483	546.050	588.311	−468.670	636.373	−5.731
5900	108.023	649.329	547.785	599.113	−467.747	655.418	−5.803
6000	108.025	651.145	549.492	609.915	−466.788	674.446	−5.872

PREVIOUS: September 1962 (1 atm) CURRENT: September 1962 (1 bar)

$S°(298.15\ K) = [-318.189 \pm 4.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -389.25 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -390.37 \pm 16.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
470 (1)
[254](1)
582 (2)
[176](2)

Ground State Quantum Weight = [2] $\sigma = 3$
Point Group: C_{3v}
Bond Distance: Si–Cl = [2.0118] Å
Bond Angle: Cl–Si–Cl = 110.9°
Product of the Moments of Inertia: $I_A I_B I_C = [7.36634 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The adopted value for the heat of formation of $SiCl_3(g)$ is based on the mass spectrometric study of the silicon subchlorides by Farber and Srivastava.[1] Our 2nd and 3rd law analysis of ten data points (1593–1792 K) for the equilibrium $SiCl_4(g) + SiCl_2(g) = 2\ SiCl_3(g)$ yield $\Delta_r H°(298.15\ K)$(2nd law) = 6.4 ± 1.1 kcal·mol^{-1} and $\Delta_r H°(298.15\ K)$(3rd law) = 12.0 ± 0.5 kcal·mol^{-1} with a drift of 3.3 ± 0.6 cal·K^{-1}·mol^{-1}. Using the 3rd law heat of reaction and auxiliary data,[2] we calculate and adopt $\Delta_f H°(SiCl_3, g, 298.15\ K) = -93.3 \pm 2$ kcal·mol^{-1}. This leads to $\Delta_a H°(0\ K) = 285.5 \pm 2$ kcal·mol^{-1} or an average bond energy of 95.2 kcal·mol^{-1}; a value which is within 0.5 kcal·mol^{-1} of the average bond energy in $SiCl_4(g)$.

Many less definitive studies leading to the heat of formation of $SiCl_3(g)$ are reported in the literature. These studies yield values which are 5–10 kcal·mol^{-1} less negative than our adopted value. These works include the relative reaction rates of $SiCl_3$ by Kerr *et al.*,[3] decomposition studies of $SiCl_4$ by adiabatic compression by Vurzel *et al.*,[4] interpretation of electron impact studies on several molecules by Steele *et al.*,[5] examination of infrared emission of a reaction involving $SiCl_3(g)$ by Cadman *et al.*,[6] silane kinetic studies by Walsh and Wells,[7] and negative ion studies by Wang *et al.*[10] and Pabst *et al.*[11]

Heat Capacity and Entropy

Jacox and Milligan[8] studied the formation of $SiCl_3$ by photolysis of $HSiCl_3$ in matrices of argon, nitrogen and CO. The two stretching fundamentals were assigned from the infrared spectra. Isotopic splittings were found to be consistent with an angle of 72 ± 5° between the threefold axis and each of the Si–Cl bonds. This yields a bond angle of 110.9° which is similar to that of $HSiCl_3$. Non-planarity of $SiCl_3$ is consistent with the electron–spin–resonance studies of Roncin.[9]

We adopt the results of Jacox and Milligan[8] and estimate the bond length and two bending vibrations by analogy with $HSiCl_3$.[2] The ground state quantum weight is taken as two, but excited electronic levels are neglected. Jacox and Milligan[8] observed unstructured absorptions corresponding to excitation energies of 30000–34500 cm^{-1} and 41000–46000 cm^{-1}. The principal moments of inertia are: $I_A = I_B = 33.7539 \times 10^{-39}$ and $I_C = 64.6554 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.868	−389.246	−389.246	INFINITE
100	46.997	253.930	374.811	−12.088	−390.100	−386.759	202.022
200	62.205	291.584	324.423	−6.568	−390.315	−383.310	100.110
250	67.220	306.032	319.335	−3.326	−390.351	−381.554	79.721
298.15	70.733	318.189	318.189	0.	−390.367	−379.858	66.549
300	70.847	318.627	318.190	0.131	−390.368	−379.792	66.128
350	73.464	329.755	319.063	3.742	−390.369	−378.030	56.418
400	75.376	339.696	321.032	7.466	−390.359	−376.267	49.135
450	76.798	348.660	323.612	11.272	−390.342	−374.507	43.472
500	77.877	356.810	326.531	15.140	−390.320	−372.748	38.941
600	79.365	371.151	332.805	23.008	−390.276	−369.238	32.145
700	80.311	383.461	339.183	30.995	−390.245	−365.735	27.291
800	80.946	394.230	345.405	39.060	−390.238	−362.234	23.651
900	81.392	403.791	351.371	47.178	−390.263	−358.732	20.820
1000	81.715	412.384	357.050	55.334	−390.322	−355.226	18.555
1100	81.958	420.184	362.440	63.518	−390.419	−351.712	16.701
1200	82.143	427.324	367.554	71.724	−390.555	−348.188	15.156
1300	82.289	433.905	372.408	79.946	−390.732	−344.650	13.848
1400	82.405	440.007	377.021	88.181	−390.953	−341.097	12.727
1500	82.499	445.696	381.412	96.426	−391.218	−337.527	11.754
1600	82.576	451.023	385.598	104.680	−391.530	−333.938	10.902
1700	82.640	456.031	389.595	112.941	−442.066	−329.881	10.136
1800	82.694	460.756	393.419	121.208	−442.246	−323.277	9.381
1900	82.740	465.229	397.082	129.479	−442.434	−316.662	8.706
2000	82.779	469.474	400.596	137.755	−442.634	−310.038	8.097
2100	82.813	473.513	403.973	146.035	−442.847	−303.403	7.547
2200	82.842	477.366	407.222	154.318	−443.075	−296.757	7.046
2300	82.868	481.050	410.352	162.603	−443.320	−290.101	6.588
2400	82.890	484.577	413.372	170.891	−443.585	−283.434	6.169
2500	82.910	487.961	416.288	179.181	−443.872	−276.755	5.782
2600	82.928	491.213	419.108	187.473	−444.182	−270.064	5.426
2700	82.943	494.343	421.837	195.767	−444.518	−263.361	5.095
2800	82.957	497.360	424.481	204.062	−444.881	−256.645	4.788
2900	82.970	500.271	427.044	212.358	−445.272	−249.915	4.501
3000	82.981	503.084	429.532	220.656	−445.691	−243.172	4.234
3100	82.992	505.805	431.949	228.954	−446.137	−236.414	3.984
3200	83.001	508.440	434.298	237.254	−446.611	−229.641	3.749
3300	83.009	510.994	436.584	245.555	−447.111	−222.853	3.527
3400	83.017	513.473	438.809	253.856	−447.635	−216.050	3.319
3500	83.024	515.879	440.977	262.158	−448.181	−209.231	3.123
3600	83.031	518.218	443.090	270.461	−832.898	−191.935	2.785
3700	83.037	520.493	445.152	278.764	−833.065	−174.128	2.458
3800	83.043	522.708	447.164	287.068	−833.247	−156.317	2.149
3900	83.048	524.865	449.128	295.373	−833.439	−138.500	1.855
4000	83.052	526.968	451.048	303.678	−833.638	−120.678	1.576
4100	83.057	529.018	452.925	311.983	−833.839	−102.852	1.310
4200	83.061	531.020	454.761	320.289	−834.038	−85.021	1.057
4300	83.065	532.974	456.557	328.595	−834.232	−67.185	0.816
4400	83.068	534.884	458.315	336.902	−834.415	−49.344	0.586
4500	83.072	536.751	460.038	345.209	−834.585	−31.500	0.366
4600	83.075	538.577	461.725	353.516	−834.737	−13.651	0.155
4700	83.078	540.363	463.380	361.824	−834.869	4.199	−0.047
4800	83.080	542.113	465.002	370.132	−834.976	22.053	−0.240
4900	83.083	543.826	466.593	378.440	−835.056	39.909	−0.425
5000	83.085	545.504	468.154	386.748	−835.107	57.766	−0.603
5100	83.088	547.149	469.687	395.057	−835.125	75.624	−0.775
5200	83.090	548.763	471.193	403.366	−835.108	93.481	−0.939
5300	83.092	550.346	472.671	411.675	−835.056	111.338	−1.097
5400	83.094	551.899	474.124	419.984	−834.965	129.194	−1.250
5500	83.096	553.424	475.552	428.294	−834.834	147.048	−1.397
5600	83.097	554.921	476.956	436.603	−834.664	164.898	−1.538
5700	83.099	556.392	478.337	444.913	−834.451	182.746	−1.675
5800	83.100	557.837	479.695	453.223	−834.197	200.590	−1.807
5900	83.102	559.257	481.031	461.533	−833.900	218.428	−1.934
6000	83.103	560.654	482.347	469.843	−833.560	236.261	−2.057

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 139.750 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 220.1\ K$

$\Delta_f H°(0\ K) = -724.06 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -721.74 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of $TiCl_3$(cr) has been measured by several investigators. The results of these measurements are as follows.

Source	Method	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
[1]Schaffer *et al.* (1954)	Calorimetric, $TiCl_4 + Hg = TiCl_3 + 1/2\ Hg_2Cl_2$	−171.9, − 172.4
[2]Clifton and MacWood (1956)	Solution calorimetric	−172.4
[3]Johnson *et al.* (1956)	Calorimetric, $TiCl_4(\ell) + HI(g) = TiCl_3(cr) + HCl(g) + 1/2\ I_2$	−172.5
[4]Krieve *et al.* (1956)	Solution calorimetric	−171.3
[5]Krieve and Mason (1956)	Equilibrium, $TiCl_3(cr) + HCl(g) = TiCl_4(g) + 1/2\ H_2(g)$	−172.9
[6]Altman *et al.* (1956)	Equilibrium, $Ti(cr) + 3\ TiCl_4(l) = 4\ TiCl_3(cr)$	−169.4, − 171.0
[7]Head (1960)	Equilibrium, $2\ TiCl_4(2) + H_2(g) = 2\ TiCl_3(cr) + 2\ HCl(g)$	−172.3
	$TiCl_4(l) + Hg(l) = 1/2\ Hg_2Cl_2(cr) + TiCl_3(cr)$	
	$TiCl_4(l) + Ag(cr) = AgCl(cr) + TiCl_3(cr)$	

The chosen value of -172.5 ± 1.0 kcal·mol^{-1} is that reported by Johnson *et al.*[3]

Heat Capacity and Entropy

The heat capacity and entropy of $TiCl_3$(cr) has been measured over the temperature range 54 to 1000 K by King *et al.*[8] The value of $S°(298.15\ K)$ is calculated from these data based on $S°(51\ K) = 4.29\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

A second order transition at 220.1 K was observed by King *et al.*[8] The heat capacity at this temperature is in excess of $146.8\ cal \cdot K^{-1} \cdot mol^{-1}$. King *et al.*[8] measured the value of $H°(240\ K) - H°(200\ K)$ as $1.213\ kcal \cdot mol^{-1}$.

Sublimation Data

The enthalpy of sublimation is calculated from the enthalpies of formation of $TiCl_3$(cr) and $TiCl_3$(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_r G° = 0$ for the process $TiCl_3(cr) = TiCl_3(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−20.920	−724.059	−724.059	INFINITE
100	54.438	44.350	227.777	−18.343	−726.410	−701.668	366.514
200	101.926	95.504	149.101	−10.719	−725.260	−677.126	176.847
298.15	97.161	139.750	139.750	0.	−721.740	−654.469	114.660
300	97.195	140.351	139.752	0.180	−721.701	−654.052	113.881
400	98.959	168.557	143.585	9.989	−719.711	−631.807	82.506
500	100.577	190.816	150.882	19.967	−717.830	−610.050	63.731
600	102.048	209.285	159.120	30.099	−715.971	−588.668	51.248
700	103.248	225.106	167.443	40.364	−714.102	−567.598	42.355
800	104.426	238.970	175.535	50.748	−712.193	−546.799	35.702
900	105.583	251.337	183.283	61.249	−710.263	−526.241	30.542
1000	106.704	262.519	190.656	71.863	−708.375	−505.896	26.425
1100	107.818	272.742	197.661	82.589	−706.589	−485.735	23.066
1200	108.926	282.171	204.315	93.426	−708.889	−465.613	20.268
1300	110.029	290.933	210.645	104.374	−706.581	−445.433	17.898
1400	111.125	299.127	216.676	115.432	−704.254	−425.432	15.873
1500	112.215	306.831	222.432	126.599	−701.924	−405.597	14.124

PREVIOUS: March 1964 CURRENT: June 1968

$S°(298.15\ K) = [316.895 \pm 4.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -536.09 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -539.32 \pm 6.3\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[4000]	[2]
[600]	[2]	[10000]	[2]
[1500]	[2]		

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[530](1)	[590](2)
[275](1)	[260](2)

Point Group: [C_{3v}] $\sigma = 3$
Bond Distance: Ti–Cl = [2.3] Å
Bond Angle: Cl–Ti–Cl = [100]°
Products of the Moments of Inertia: $I_A I_B I_C = [1.34297 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiCl_3(g)$ is calculated from the heats of reaction for the processes, (A) $3TiCl_4(g) + Ti(cr) = 4TiCl_3(g)$, and (B) $TiCl_3(cr) = TiCl_3(g)$, combined with auxiliary JANAF heats of formation for $TiCl_4(g)$, $TiCl_3(cr)$ and Ti(cr). Equilibrium measurements of reaction (A) have been reported by Gross and Levi.[1] Vapor pressure measurements for reaction (B) have been reported by Sanderson and MacWood[2] and by Farber and Darnell.[3] Second and third law analyses of these data yield the following results.

Source	Reaction	Data Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Gross and Levi[1]	A	3	1223		31.6 ± 2.0		−128.5
Sanderson and MacWood[2]	B	9*	628–823	42.8 ± 1.1	42.8	−0.1 ± 1.5	−129.3
Farber and Darnell[3]	B	8	636–723	45.3 ± 2.1	45.8	0.8 ± 3.1	−126.2

*One point rejected due to failure of statistical test.

The chosen value of $\Delta_f H°(298.15\ K)$ is − 128.9 kcal·mol^{-1}. This value is the average of the first two determinations.

Heat Capacity and Entropy

The interatomic distance is estimated from that of the solid, given as 2.46 Å by Natta *et al.*,[4] and from comparisons of bond distances of crystal and gas phase tetrahalides of titanium. The pyramidal bond angle is estimated assuming $TiCl_3(g)$ similar to the group V trihalides. The principal moments of inertia are: $I_A = I_B = 42.8614 \times 10^{-39}$ and $I_C = 73.1025 \times 10^{-39}\ g·cm^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3}.[5]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−15.375	−536.091	−536.091	INFINITE
100	42.233	254.787	373.049	−11.826	−537.471	−533.773	278.814
200	61.090	290.122	323.216	−6.619	−538.737	−529.527	138.298
250	67.847	304.518	318.065	−3.387	−539.097	−527.179	110.148
298.15	72.567	316.895	316.895	0.	−539.318	−524.862	91.954
300	72.719	317.344	316.896	0.134	−539.324	−524.773	91.371
350	76.177	328.828	317.795	3.862	−539.462	−522.335	77.954
400	78.645	339.171	319.831	7.736	−539.541	−519.883	67.890
450	80.423	348.542	322.509	11.715	−539.584	−517.423	60.061
500	81.717	357.086	325.546	15.770	−539.604	−514.959	53.797
600	83.362	372.145	332.092	24.032	−539.616	−510.029	44.402
700	84.264	385.070	338.759	32.418	−539.626	−505.097	37.691
800	84.774	396.358	345.268	40.872	−539.646	−500.163	32.657
900	85.073	406.362	351.511	49.366	−539.724	−495.224	28.742
1000	85.258	415.336	357.453	57.883	−539.933	−490.270	25.609
1100	85.378	423.468	363.090	66.415	−540.341	−485.285	23.044
1200	85.457	430.900	368.436	74.957	−544.936	−480.135	20.900
1300	85.509	437.743	373.507	83.506	−545.026	−474.732	19.075
1400	85.543	444.081	378.325	92.059	−545.205	−469.318	17.510
1500	*85.563*	*449.984*	*382.908*	*100.614*	*−545.486*	*−463.889*	*16.154*
1600	85.572	455.506	387.274	109.171	−545.884	−458.437	14.966
1700	85.575	460.694	391.442	117.728	−546.412	−452.956	13.918
1800	85.571	465.585	395.427	126.285	−547.085	−447.439	12.984
1900	85.564	470.212	399.242	134.842	−547.917	−441.882	12.148
2000	85.555	474.600	402.901	143.398	−563.609	−435.822	11.383
2100	85.544	478.774	406.415	151.953	−565.551	−429.385	10.680
2200	*85.533*	*482.753*	*409.796*	*160.507*	*−567.512*	*−422.855*	*10.040*
2300	85.521	486.555	413.051	169.060	−569.494	−416.236	9.453
2400	85.509	490.195	416.190	177.611	−571.499	−409.529	8.913
2500	85.497	493.685	419.221	186.162	−573.530	−402.739	8.415
2600	85.486	497.038	422.149	194.711	−575.587	−395.867	7.953
2700	85.474	500.264	424.983	203.259	−577.673	−388.915	7.524
2800	85.463	503.373	427.728	211.806	−579.788	−381.885	7.124
2900	85.453	506.371	430.388	220.351	−581.934	−374.779	6.751
3000	85.442	509.268	432.969	228.896	−584.109	−367.599	6.400
3100	85.431	512.070	435.476	237.440	−586.315	−360.346	6.072
3200	85.420	514.782	437.912	245.982	−588.550	−353.021	5.762
3300	85.409	517.410	440.282	254.524	−590.813	−345.626	5.471
3400	85.397	519.960	442.588	263.064	−593.103	−338.162	5.195
3500	85.385	522.435	444.834	271.603	−595.416	−330.630	4.934
3600	85.373	524.840	447.023	280.141	−597.750	−323.031	4.687
3700	85.360	527.179	449.158	288.678	−1009.200	−307.580	4.342
3800	85.347	529.455	451.241	297.213	−1010.333	−288.602	3.967
3900	85.333	531.672	453.275	305.747	−1011.531	−269.594	3.611
4000	85.319	533.832	455.262	314.280	−1012.792	−250.554	3.272
4100	85.304	535.939	457.205	322.811	−1014.108	−231.481	2.949
4200	85.289	537.994	459.104	331.341	−1015.475	−212.376	2.641
4300	85.274	540.001	460.962	339.869	−1016.887	−193.238	2.347
4400	85.257	541.961	462.781	348.395	−1018.339	−174.067	2.066
4500	85.241	543.877	464.561	356.920	−1019.824	−154.863	1.798
4600	85.224	545.750	466.306	365.444	−1021.338	−135.624	1.540
4700	85.206	547.583	468.016	373.965	−1022.875	−116.354	1.293
4800	85.188	549.377	469.692	382.485	−1024.431	−97.049	1.056
4900	85.170	551.133	471.337	391.003	−1025.999	−77.712	0.828
5000	85.152	552.854	472.950	399.519	−1027.576	−58.344	0.610
5100	85.133	554.540	474.533	408.033	−1029.156	−38.943	0.399
5200	85.114	556.193	476.088	416.545	−1030.737	−19.512	0.196
5300	85.095	557.814	477.614	425.056	−1032.313	−0.051	0.
5400	85.075	559.404	479.114	433.564	−1033.880	19.441	−0.188
5500	85.056	560.965	480.588	442.071	−1035.437	38.961	−0.370
5600	85.036	562.497	482.037	450.575	−1036.979	58.510	−0.546
5700	85.016	564.002	483.462	459.078	−1038.503	78.085	−0.716
5800	84.996	565.481	484.864	467.579	−1040.007	97.688	−0.880
5900	84.976	566.933	486.242	476.077	−1041.488	117.316	−1.039
6000	84.956	568.361	487.599	484.574	−1042.944	136.969	−1.192

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [145.812 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) =$ Unknown

$\Delta_f H°(298.15\ K) = [-714.21 \pm 62.8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Turnbull and Watts[1] determined the equilibrium pressures for the disproportionation of $ZrCl_3$(cr) in the temperature range from 613 K to 723 K by a modified dew point technique. 2nd and 3rd law analyses of their vapor pressure–temperature equation give the same enthalpy of reaction $\Delta_r H°(298.15\ K) = 30.7\ kcal \cdot mol^{-1}$ for $2ZrCl_3(cr) \rightarrow ZrCl_2(cr) + ZrCl_4(g)$. The adopted value, $\Delta_f H°(ZrCl_3, cr, 298.15\ K) = -170.7\ kcal \cdot mol^{-1}$, is calculated from the enthalpy of reaction at 298.15 K, and $\Delta_f H°(ZrCl_4, g, 298.15\ K) = -207.77\ kcal \cdot mol^{-1}$ [2] and $\Delta_f H°(ZrCl_2, cr, 298.15\ K) = -103\ kcal \cdot mol^{-1}$.[3] The assigned uncertainty, $\pm 15\ kcal \cdot mol^{-1}$ is mainly due to the uncertainty in the enthalpy of formation of $ZrCl_2$(cr), and also the dew point technique used.

Heat Capacity and Entropy

The heat capacities of $ZrCl_3$(cr) are estimated from the $C_p°$ values of $ZrCl_4$(cr) by deduction of one Cl atom $C_p°$ contributions which are calculated as $1/4[C_p°(ZrCl_4, cr) - C_p°(Zr, cr)]$. The $S°(298.15\ K)$ is calculated as $34.85\ cal \cdot K^{-1} \cdot mol^{-1}$ based on the assumption that $S°(ZrCl_3, cr, 298.15\ K) = S°(ZrCl_4, cr, 298.15\ K) - 1/4[S°(ZrCl_4, cr, 298.15\ K) - S°(Zr, cr, 298.15\ K)]$.

Sublimation Data

The enthalpy of sublimation is calculated from the difference in the enthalpies of formation of gas and crystal at 298.15 K. The sublimation temperature is taken as the point at which $\Delta_r G = 0$ for $ZrCl_3(cr) = ZrCl_3(g)$.

References

[1] A. G. Turnbull and J. A. Watts, Aust. J. Chem. **16**, 947 (1963).
[2] JANAF Thermochemical Table: $ZrCl_4$(g), 12–31–69.
[3] JANAF Thermochemical Table: $ZrCl_2$(cr), 12–31–69.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	96.190	145.812	145.812	0.	−714.209	−646.327	113.234
300	96.311	146.408	145.814	0.178	−714.172	−645.906	112.462
400	100.705	174.755	149.649	10.042	−712.072	−623.463	81.416
500	103.470	197.536	157.023	20.257	−709.839	−601.567	62.845
600	105.583	216.593	165.406	30.712	−707.523	−580.129	50.505
700	107.378	233.005	173.918	41.361	−705.149	−559.083	41.719
800	109.052	247.454	182.224	52.184	−702.725	−538.382	35.153
900	110.596	260.388	190.203	63.166	−700.270	−517.986	30.063
1000	112.081	272.121	197.817	74.304	−697.794	−497.865	26.006
1100	113.177	282.855	205.067	85.567	−695.328	−477.992	22.698
1200	114.223	292.748	211.967	96.937	−696.602	−458.120	19.941
1300	115.269	301.932	218.538	108.412	−693.654	−438.366	17.614
1400	116.315	310.514	224.805	119.992	−690.657	−418.840	15.627
1500	117.152	318.567	230.790	131.666	−687.633	−399.530	13.913
1600	117.989	326.155	236.515	143.424	−684.602	−380.422	12.420
1700	118.700	333.329	242.001	155.258	−681.581	−361.504	11.108
1800	119.453	340.137	247.266	167.168	−678.583	−342.762	9.947
1900	119.872	346.607	252.325	179.135	−675.638	−324.186	8.912
2000	120.290	352.766	257.195	191.143	−672.773	−305.763	7.986

PREVIOUS: June 1964 CURRENT: December 1969

$S°(298.15\ K)$ = [339.340 ± 12.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -522.60 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -524.26 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[490](1)	[333](2)
[185](1)	[131](2)

Point Group: [C_{3v}] σ = [3]
Bond Distance: Zr–Cl = [2.3] Å
Bond Angle: Cl–Zr–Cl = [100]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.54256 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

Potter[1] investigated mass spectrometrically the equilibrium $CaCl(g) + ZrCl_4(g) \rightarrow CaCl_2(g) + ZrCl_3(g)$ in the temperature range 1163–1157 K. Ion intensities were measured 2.5 eV above threshold and they were used in the calculation of equilibrium constants. Using the reported equilibrium constants, the enthalpies of reaction at 298 K are evaluated by the 3rd law and 2nd law methods as −3.69 and −16.67 $kcal·mol^{-1}$, respectively. The 3rd law drift is 9.31 ± 1.25 $cal·K^{-1}·mol^{-1}$. Using the 3rd law $\Delta_f H°(298.15\ K)$ = −3.69 $kcal·mol^{-1}$, $\Delta_f H°(ZrCl_4, g, 298.15\ K)$ = −207.77 $kcal·mol^{-1}$,[2] $\Delta_f H°(CaCl, g, 298.15\ K)$ = −28.8 $kcal·mol^{-1}$ [3] and $\Delta_f H°(CaCl_2, g, 298.15\ K)$ = −115.0 $kcal·mol^{-1}$,[4] we obtain $\Delta_f H°(ZrCl_3, g, 298.15\ K)$ = −125.3 $kcal·mol^{-1}$, which is adopted in the tabulation.

Farber *et al.*[5] also studied mass spectrometrically the reaction $Zr(cr) + 3\ ZrCl_4(g) \rightarrow 4\ ZrCl_3(g)$ in the temperature range from 1579 K to 1729 K. They reported a second law heat of reaction as $\Delta_r H°(298.15\ K)$ = 59.2 ± 1.6 $kcal·mol^{-1}$. Since the attainment of equilibrium was questionable in their studies, the heat of reaction obtained from the third law method is generally more reliable. Using their reported ion intensities of run 3 (temperature range from 1667 K to 1896 K, five points), we have calculated the equilibrium constants $K_1 = (I_{ZrCl2})^2/(I_{ZrCl3})(I_{ZrCl})$ for reaction (1) $ZrCl_3(g) + ZrCl(g) \rightarrow 2\ ZrCl_2(g)$; and $K_2 = (I_{ZrCl3})^2/(I_{ZrCl4})(I_{ZrCl2})$ for reaction (2) $ZrCl_4(g) + ZrCl_2 \rightarrow 2\ ZrCl_3(g)$. Third law analyses of the equilibrium constants give $\Delta_r H°(298.15\ K)$ = −11.0 $kcal·mol^{-1}$ for reaction (1) and its drift 4.1 ± 1.7 $cal·K^{-1}·mol^{-1}$; and $\Delta_r H°(298.15\ K)$ = 1.4 $kcal·mol^{-1}$ for reaction (2) and its drift 11.1 ± 1.2 $cal·K^{-1}·mol^{-1}$. Using the 3rd law heats of reaction, and $\Delta_f H°(ZrCl, g, 298.15\ K)$ = 49.1 $kcal·mol^{-1}$ [2] and $\Delta_f H°(ZrCl_4, g, 298.15\ K)$ = −207.77 $kcal·mol^{-1}$,[2] we obtain $\Delta_f H°(ZrCl_3, g, 298.15\ K)$ = −124.9 $kcal·mol^{-1}$ and $\Delta_f H°(ZrCl_2, g, 298.15\ K)$ = −43.4 $kcal·mol^{-1}$ which are in good agreement with the values adopted.

Heat Capacity and Entropy

The molecular structure is assumed to be a pyramid similar to the group VA trichlorides. The bond distance is assumed to be the same as that of $ZrCl_4$(g). The principal moments of inertia are: $I_A = I_B$ = 45.9362 × 10^{-39} and I_C = 73.1025 × 10^{-39} $g·cm^2$. The electronic levels are estimated as three times higher than those of $TiCl_3$(g), based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by Moore.[6] The quantum weights are assumed to be the same as those of $TiCl_3$(g).

Vibrational frequencies are calculated from the estimated force constants by the valence force method.[7] The force constants are estimated from those of PCl_3, $AsCl_3$ and $SbCl_3$ listed by Herzberg.[7]

References

[1]N. D. Potter, Aeronutronic Div., Philco–Ford Corp., Newport Beach, Calif., private communication, dated (December 4, 1969).
[2]JANAF Thermochemical Table: ZrCl(g) and $ZrCl_4$(g), 12–31–69.
[3]The enthalpy of formation and the free energy functions of CaCl(g) are preliminary values calculated by the Physicochemical Laboratory, The Dow Chemical Company, Midland, Michigan.
[4]The enthalpy of formation and the free energy functions of $CaCl_2$(g) are preliminary values calculated by the Physicochemical Studies, The Dow Chemical Company, Midland, Michigan.
[5]M. Farber, M. A. Frisch, G. Grenier and H. C. Ko, Space Sciences, Inc., Monrovia, Calif., Rep. No. AFRPL–TR–67–244, Contract FO4611–67–C–0010, (November, 1967).
[6]C. E. Moore, U.S. Nat. Bur. Stand. Circ. 467, (1949).
[7]G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, (1945).

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−17.615	−522.602	−522.602	INFINITE
100	54.064	267.133	402.036	−13.490	−523.731	−520.688	271.979
200	69.657	310.172	346.126	−7.191	−524.181	−517.416	135.135
250	73.530	326.163	340.579	−3.604	−524.239	−515.717	107.753
298.15	76.025	339.340	339.340	0.	−524.255	−514.074	90.064
300	76.104	339.811	339.342	0.141	−524.255	−514.011	89.497
350	77.945	351.688	340.276	3.994	−524.251	−512.304	76.457
400	79.367	362.192	342.371	7.928	−524.232	−510.598	66.677
450	80.536	371.610	345.106	11.927	−524.203	−508.895	59.071
500	81.533	380.148	348.190	15.979	−524.163	−507.197	52.986
600	83.156	395.163	354.801	24.217	−524.064	−503.812	43.861
700	84.387	408.079	361.511	32.597	−523.959	−500.445	37.344
800	85.308	419.410	368.055	41.084	−523.871	−497.093	32.457
900	85.986	429.499	374.332	49.651	−523.833	−493.748	28.656
1000	86.482	438.586	380.310	58.275	−523.869	−490.404	25.616
1100	86.842	446.846	385.989	66.943	−523.998	−487.053	23.128
1200	87.101	454.414	391.380	75.641	−527.945	−483.463	21.045
1300	87.281	461.394	396.501	84.360	−527.752	−479.764	19.277
1400	87.402	467.867	401.370	93.095	−527.601	−476.079	17.763
1500	87.475	473.899	406.007	101.839	−527.507	−472.402	16.451
1600	87.511	479.546	410.428	110.589	−527.483	−468.730	15.302
1700	87.518	484.852	414.652	119.340	−527.546	−465.056	14.289
1800	87.502	489.854	418.692	128.091	−527.706	−461.376	13.389
1900	87.470	494.584	422.563	136.840	−527.979	−457.684	12.583
2000	87.426	499.070	426.277	145.585	−528.377	−453.975	11.857
2100	87.372	503.334	429.846	154.325	−528.913	−450.242	11.199
2200	87.313	507.397	433.279	163.059	−550.923	−445.735	10.583
2300	87.251	511.277	436.587	171.787	−552.190	−440.925	10.014
2400	87.187	514.989	439.777	180.509	−553.486	−436.060	9.491
2500	87.123	518.547	442.857	189.225	−554.811	−431.140	9.008
2600	87.060	521.963	445.834	197.934	−556.169	−426.166	8.562
2700	86.999	525.247	448.715	206.637	−557.560	−421.140	8.147
2800	86.940	528.410	451.505	215.334	−558.986	−416.061	7.762
2900	86.883	531.460	454.210	224.025	−560.446	−410.931	7.402
3000	86.829	534.404	456.834	232.711	−561.941	−405.750	7.065
3100	86.778	537.251	459.383	241.391	−563.470	−400.519	6.749
3200	86.729	540.005	461.859	250.066	−565.033	−395.238	6.452
3300	86.683	542.673	464.268	258.737	−566.627	−389.907	6.172
3400	86.639	545.260	466.612	267.403	−568.251	−384.527	5.908
3500	86.597	547.771	468.895	276.065	−569.901	−379.100	5.658
3600	86.558	550.210	471.120	284.723	−571.576	−373.624	5.421
3700	86.520	552.581	473.290	293.376	−573.271	−368.103	5.197
3800	86.484	554.888	475.407	302.027	−574.983	−362.535	4.983
3900	86.450	557.134	477.474	310.673	−576.709	−356.922	4.780
4000	86.418	559.322	479.493	319.317	−578.443	−351.264	4.587
4100	86.386	561.456	481.466	327.957	−580.183	−345.563	4.403
4200	86.356	563.537	483.396	336.594	−581.924	−339.819	4.226
4300	86.327	565.569	485.283	345.228	−583.663	−334.034	4.058
4400	86.300	567.553	487.130	353.860	−585.394	−328.209	3.896
4500	86.273	569.492	488.939	362.488	−587.115	−322.345	3.742
4600	86.247	571.388	490.711	371.114	−588.822	−316.442	3.593
4700	86.222	573.243	492.447	379.738	−590.511	−310.502	3.451
4800	86.197	575.058	494.150	388.359	−1153.115	−292.910	3.188
4900	86.174	576.835	495.819	396.977	−1154.411	−274.975	2.931
5000	86.151	578.576	497.457	405.593	−1155.697	−257.015	2.685
5100	86.129	580.281	499.064	414.207	−1156.969	−239.028	2.448
5200	86.107	581.954	500.642	422.819	−1158.224	−221.017	2.220
5300	86.087	583.594	502.192	431.429	−1159.458	−202.982	2.001
5400	86.066	585.203	503.714	440.037	−1160.667	−184.924	1.789
5500	86.047	586.782	505.210	448.642	−1161.850	−166.844	1.585
5600	86.028	588.332	506.681	457.246	−1163.003	−148.742	1.387
5700	86.009	589.854	508.127	465.848	−1164.123	−130.621	1.197
5800	85.991	591.350	509.549	474.448	−1165.210	−112.479	1.013
5900	85.974	592.820	510.948	483.046	−1166.260	−94.320	0.835
6000	85.957	594.265	512.324	491.643	−1167.271	−76.143	0.663

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = [450.400 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -352.91 \pm 29.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -350.62 \pm 29.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i cm^{-1}	g_i
0	[4]
[210]	[8]
[2804]	[8]
[10425]	[4]
[14197]	[8]
[21270]	[8]

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
[50](1)	[125](1)	323 (1)
[75](1)	[150](1)	[143] (1)
[100](1)	[175](1)	289 (1)
[110](1)	[200](1)	432.5(1)

Point Group: [D_{2h}] $\sigma = 4$

Bond Distances: Co–Cl = [2.09] Å; Co–Cl'(bridge) = [2.2] Å

Bond Angles: Co–Cl'(bridge)–Co = [90]°; Cl'(bridge)–Co–Cl = [135]°; Cl'(bridge)–Co–Cl'(bridge) = [90]°

Product of Moments of Inertia: $I_A I_B I_C = [1.34964 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Mass spectrometric studies[1, 2] have indicated the presence of small amounts of dimer in the saturated vapor over $CoCl_2$(cr). The existence of the dimeric species was inferred from the ion current intensities observed for $Co_2Cl_4^+$. This ion is believed to be produced by simple ionization of the dimer molecules. Schoonmaker *et al.*[1] have combined their mass spectral data with results of effusion vapor pressure measurements to give partial pressures for the monomer and dimer at 817 K. These results are analyzed by the third law method with JANAF free energy functions to give ΔH(dimerization, 298.15 K) = −38.99 kcal·mol^{-1} for the process 2 $CoCl_2(g) = Co_2Cl_4(g)$. This result is combined with $\Delta_f H°(CoCl_2, g, 298.15\ K) = -22.4 \pm 2.0$ kcal·mol^{-1} [3] to give $\Delta_f H°(Co_2Cl_4, g, 298.15\ K) = -83.8$ kcal·mol^{-1} (350.619 ± 29.3 kJ·mol^{-1}) which we adopt. The uncertainty assigned to $\Delta_f H°$ is estimated to be ± 7.0 kcal·mol^{-1} and arises mainly from uncertainties in the values of $S°(298.15\ K)$ for dimer and $\Delta_f H°$ for the monomer.

Heat Capacity and Entropy

A bridge–bond structure of D_{2h} symmetry is assigned to Co_2Cl_4. A similar structure has been proposed for Be_2Cl_4[3] and other dimeric transition–metal dihalides.[3–5] The Co_2Cl_2 ring system is assumed to be square and planar. The Cl–Co–Cl'(bridge) bond angle is estimated as 135°. The outer Co–Cl bond lengths are estimated from that for $CoCl_2$,[3] while the ring Co–Cl'(bridge) bond lengths are estimated to be somewhat larger. The principal moments of inertia are: $I_A = 28.4941 \times 10^{-39}$, $I_B = 203.8550 \times 10^{-39}$, and $I_C = 232.3490 \times 10^{-39}$ g·cm^2.

The three observed vibrational frequencies (υ_9, υ_{11}, and υ_{12}) are taken from the matrix–infrared study of Thompson and Carlson.[5] The rest of the frequencies except for υ_{10} are estimated by comparison with similar data for other dimeric molecules.[3] The value for υ_{10} (143 cm^{-1}) was obtained by Thompson and Carlson[5] from a simplified normal coordinate analysis. Also, Leroi *et al.*[4] obseved a band at 422 ± 10 cm^{-1} in the infrared spectrum of gaseous $CoCl_2$ near 1000 K. The band was assigned to an outer–bond stretching frequency of the dimer. This interpretation agrees with our adopted results. The electronic levels and quantum weights are arbitrarily taken equal to those for the monomer.[3]

References

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[3] JANAF Thermochemical Tables: $CoCl_2$(g), 12–31–73; Be_2Cl_4(g), 6–30–65; Fe_2Cl_4(g), 12–31–70; Mg_2Cl_4(g), 12–31–69.

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[5] K. R. Thompson and K. D. Carlson, J. Chem. Phys. **49**, 4379 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−30.198	−352.913	−352.913	INFINITE
100	100.830	322.221	559.182	−23.696	−353.278	−346.163	180.817
200	121.951	400.502	461.920	−12.283	−351.761	−339.640	88.705
250	125.421	428.124	452.488	−6.091	−351.117	−336.687	70.347
298.15	127.432	450.400	450.400	0.	−350.619	−333.955	58.507
300	127.493	451.189	450.403	0.236	−350.601	−333.851	58.129
350	128.835	470.949	451.960	6.646	−350.154	−331.096	49.413
400	129.766	488.217	455.436	13.113	−349.800	−328.399	42.885
450	130.455	503.543	459.946	19.619	−349.543	−325.740	37.811
500	131.001	517.317	465.006	26.156	−349.376	−323.106	33.755
600	131.862	541.281	475.780	39.301	−349.283	−317.865	27.673
700	132.569	561.662	486.629	52.523	−349.477	−312.617	23.328
800	133.183	579.405	497.141	65.811	−350.788	−307.199	20.058
900	133.716	595.123	507.171	79.157	−351.571	−301.707	17.511
1000	134.167	609.236	516.684	92.552	−352.794	−296.106	15.467
1100	134.536	622.041	525.689	105.988	−354.531	−290.358	13.788
1200	134.829	633.760	534.213	119.457	−356.857	−284.426	12.381
1300	135.052	644.562	542.291	132.951	−360.073	−278.267	11.181
1400	135.216	654.576	549.958	146.465	−364.438	−271.817	10.142
1500	135.330	663.909	557.248	159.993	−366.787	−265.114	9.232
1600	135.406	672.646	564.190	173.530	−368.637	−258.274	8.432
1700	135.451	680.856	570.814	187.073	−370.301	−251.325	7.722
1800	135.473	688.599	577.144	200.619	−404.514	−243.691	7.072
1900	135.478	695.924	583.205	214.167	−406.721	−234.696	6.452
2000	135.472	702.873	589.016	227.714	−408.948	−225.585	5.892
2100	135.460	709.483	594.596	241.261	−411.199	−216.362	5.382
2200	135.443	715.784	599.963	254.806	−413.476	−207.030	4.916
2300	135.426	721.804	605.130	268.350	−415.781	−197.595	4.488
2400	135.410	727.567	610.113	281.891	−418.117	−188.059	4.093
2500	135.396	733.095	614.922	295.432	−420.486	−178.424	3.728
2600	135.385	738.405	619.570	308.971	−422.891	−168.695	3.389
2700	135.378	743.514	624.067	322.509	−425.333	−158.871	3.074
2800	135.375	748.438	628.421	336.046	−427.814	−148.957	2.779
2900	135.377	753.188	632.642	349.584	−430.333	−138.954	2.503
3000	135.384	757.778	636.737	363.122	−432.891	−128.863	2.244
3100	135.394	762.217	640.714	376.661	−435.487	−118.686	2.000
3200	135.410	766.516	644.578	390.201	−1187.745	−104.879	1.712
3300	135.429	770.683	648.337	403.743	−1187.558	−71.042	1.125
3400	135.451	774.726	651.995	417.287	−1187.407	−37.211	0.572
3500	135.478	778.653	655.558	430.833	−1187.289	−3.383	0.050
3600	135.507	782.470	659.030	444.382	−1187.203	30.441	−0.442
3700	135.539	786.183	662.417	457.935	−1187.148	64.264	−0.907
3800	135.573	789.798	665.722	471.490	−1187.120	98.085	−1.348
3900	135.609	793.320	668.948	485.049	−1187.119	131.906	−1.767
4000	135.647	796.754	672.101	498.612	−1187.140	165.728	−2.164
4100	135.686	800.104	675.182	512.179	−1187.182	199.550	−2.542
4200	135.726	803.374	678.196	525.749	−1187.242	233.374	−2.902
4300	135.768	806.568	681.144	539.324	−1187.316	267.199	−3.246
4400	135.809	809.690	684.030	552.903	−1187.402	301.026	−3.574
4500	135.851	812.742	686.857	566.486	−1187.498	334.854	−3.887
4600	135.893	815.729	689.626	580.073	−1187.600	368.686	−4.187
4700	135.935	818.652	692.340	593.665	−1187.708	402.519	−4.473
4800	135.977	821.514	695.002	607.260	−1187.818	436.355	−4.749
4900	136.018	824.318	697.612	620.860	−1187.930	470.193	−5.012
5000	136.059	827.067	700.174	634.464	−1188.041	504.033	−5.266
5100	136.098	829.761	702.688	648.072	−1188.152	537.876	−5.509
5200	136.137	832.404	705.158	661.683	−1188.260	571.720	−5.743
5300	136.175	834.998	707.583	675.299	−1188.366	605.567	−5.968
5400	136.212	837.544	709.966	688.918	−1188.468	639.416	−6.185
5500	136.247	840.043	712.309	702.541	−1188.568	673.267	−6.394
5600	136.282	842.499	714.612	716.168	−1188.666	707.119	−6.596
5700	136.315	844.911	716.876	729.798	−1188.762	740.973	−6.790
5800	136.346	847.282	719.104	743.431	−1188.858	774.830	−6.978
5900	136.377	849.613	721.297	757.067	−1188.864	808.680	−7.160
6000	136.406	851.906	723.455	770.706	−1188.939	842.537	−7.335

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K)$ = [464.382 ± 12.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -433.864 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -431.370 \pm 4.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[10]
[4600]	[10]
[7140]	[5]

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[30](1)	[90](1)	[150](1)	249(1)
[50](1)	110 (1)	[180](1)	325(1)
[80](1)	[125](1)	[200](1)	438(1)

Ground State Quantum Weight: [10] σ = [4]
Point Group: [D_{2h}]
Bond Distances: Fe–Cl = [2.17] Å; Fe–Cl'$_{(bridge)}$ = [2.30] Å
Bond Angles: Fe–Cl'$_{(bridge)}$–Fe = [90°]; Cl'$_{(bridge)}$–Fe–Cl'$_{(bridge)}$ = [90°]
Cl–Fe–Cl'$_{(bridge)}$ = [135°]
Product of the Moments of Inertia: $I_A I_B I_C$ [1.7005] × 10^{-111} $g^3·cm^6$

Heat of Formation

Beusman[1] reported the partial pressures of the monomer and dimer in the temperature range from 980–1167 K using both a static method to determine the total pressures of these two species and a transpiration method to determine the ratio of monomer to dimer. Schoonmaker and Porter[2] determined mass spectrometrically the partial pressures of the monomer and dimer in the temperature range from 621–658 K. Based on the combination of these two sets of partial pressure data, we have derived a smoothed equation log K_p(atm) = −7549/T + 6.506 for Fe_2Cl_4(g) = 2 $FeCl_2$(g). Second law analysis of the equilibrium constants gives the heat and the entropy of the dimerization at 298 K as $\Delta_d H°$ = −35.7 $kcal·mol^{-1}$ and $\Delta_d S°$ = −32.0 $cal·K^{-1}·mol^{-1}$ which lead to the adopted $\Delta_f H°$(Fe Cl , g, 298.15 K) = −103.1 $kcal·mol^{-1}$ (−431.370 ± 4.2 $kJ·mol^{-1}$) and $S°$(FeCl,g,298.15K) = 111.0 $cal·K^{-1}·mol^{-1}$, using $\Delta_f H°(FeCl_2, g, 298.15\ K)$ = −33.7 $kcal·mol^{-1}$ and $S°(FeCl_2, g, 298.15\ K)$ = 71.50 $cal·K^{-1}·mol^{-1}$.[3]

The equilibrium constants derived from the two different experimental techniques are reasonably consistent considering the uncertainties inherent in the problems. Combination of these two sets of data leads to reliable second law heat and entropy since the temperature ranges are different by 400 K.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was suggested by Leroi *et al.*,[4] Thompson and Carlson.[5] Two iron and two chlorine atoms form a square. The outer Fe–Cl distance is estimated to be the same as in $FeCl_2$(g) and the square Fe–Cl' distance is assumed to be slightly larger. The Cl–Fe–Cl'$_{bridge}$ angle is estimated to be 135°. The three principal moments of inertia are: $I_A = 31.13 \times 10^{-39}$, $I_B = 218.68 \times 10^{-39}$ $g·cm^2$ and $I_C = I_A + I_B$. The electronic levels and quantum weights were arbitrarily estimated to be the same as in $FeCl_2$(g).

There are only four vibrational frequencies observed in the matrix isolated infrared spectrum, ν_{10} = 110 cm^{-1} and ν_{12} = 436.2 cm^{-1},[5] ν_9 = 325 cm^{-1}, ν_{11} = 249 cm^{-1} and ν_{12} = 438 cm^{-1}.[6] The other eight fundamental vibrational frequencies were estimated by comparison with other dimer molecules and also adjusted so that they give $S°(Fe_2Cl_4, g, 298.15\ K)$ = 111.0 $cal·K^{-1}·mol^{-1}$ which has been discussed in the earlier heat of formation part. The order of the frequencies listed above is arbitrary and not related to their species types.

References

[1]C. Beusman, Oak Ridge National Lab. ORNL−2323, (June 1957).
[2]R. C. Schoonmaker and R. F. Porter, J. Chem. Phys. **29**, 116 (1958).
[3]JANAF Thermochemical Table: $FeCl_2$(g), 12–31–70.
[4]G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. **36**, 2879 (1962).
[5]K. R. Thompson and K. D. Carlson, J. Chem. Phys. **49**, 4379 (1968).
[6]R. A. Frey, R. D. Werder and H. H. Gunthard, J. Mol. Spectrosc. **35**, 260 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−29.849	−433.845	−433.845	INFINITE
100	97.710	339.737	570.950	−23.121	−433.786	−428.745	223.953
200	119.006	415.490	475.843	−12.071	−432.348	−424.281	110.811
250	123.307	442.549	466.563	−6.004	−431.794	−422.331	88.241
298.15	125.875	464.503	464.503	0.	−431.370	−420.548	73.678
300	125.953	465.282	464.506	0.233	−431.356	−420.481	73.212
350	127.673	484.836	466.046	6.576	−431.022	−418.697	62.487
400	128.846	501.966	469.488	12.991	−430.794	−416.953	54.448
450	129.679	517.193	473.958	19.455	−430.676	−415.231	48.199
500	130.290	530.889	478.978	25.955	−430.677	−413.516	43.200
600	131.116	554.723	489.674	39.029	−431.040	−410.058	35.699
700	131.659	574.977	500.450	52.169	−431.895	−406.500	30.333
800	132.077	592.586	510.890	65.357	−433.336	−402.782	26.299
900	132.451	608.164	520.849	78.583	−435.607	−398.837	23.148
1000	132.822	622.138	530.292	91.847	−439.312	−394.572	20.610
1100	133.205	634.816	539.226	105.148	−444.796	−389.804	18.510
1200	133.604	646.423	547.683	118.489	−449.159	−384.650	16.743
1300	134.013	657.133	555.695	131.869	−450.210	−379.233	15.238
1400	134.424	667.080	563.300	145.291	−451.406	−373.729	13.944
1500	134.830	676.368	570.532	158.754	−452.747	−368.135	12.820
1600	135.221	685.082	577.422	172.257	−454.232	−362.447	11.833
1700	135.591	693.291	583.998	185.797	−457.765	−356.623	10.958
1800	135.935	701.051	590.288	199.374	−460.217	−350.604	10.174
1900	136.249	708.409	596.313	212.983	−491.018	−343.040	9.431
2000	136.531	715.405	602.094	226.623	−494.258	−335.168	8.754
2100	136.780	722.073	607.650	240.288	−497.494	−327.134	8.137
2200	136.996	728.441	612.997	253.977	−500.732	−318.945	7.573
2300	137.181	734.535	618.149	267.687	−503.976	−310.610	7.054
2400	137.335	740.376	623.121	281.413	−507.232	−302.133	6.576
2500	137.460	745.985	627.924	295.153	−510.506	−293.520	6.133
2600	137.559	751.379	632.570	308.904	−513.804	−284.775	5.721
2700	137.633	756.572	637.067	322.664	−517.129	−275.903	5.338
2800	137.685	761.578	641.425	336.430	−520.485	−266.908	4.979
2900	137.718	766.410	645.652	350.200	−523.876	−257.792	4.643
3000	137.732	771.079	649.755	363.973	−527.304	−248.558	4.328
3100	137.731	775.596	653.742	377.746	−530.770	−239.209	4.031
3200	137.716	779.968	657.619	391.518	−1230.874	−214.901	3.508
3300	137.690	784.206	661.391	405.289	−1230.615	−183.156	2.899
3400	137.653	788.315	665.064	419.056	−1230.458	−151.417	2.326
3500	137.607	792.305	668.642	432.819	−1230.402	−119.682	1.786
3600	137.554	796.181	672.132	446.577	−1230.445	−87.946	1.276
3700	137.494	799.949	675.535	460.329	−1230.586	−56.209	0.794
3800	137.430	803.615	678.858	474.076	−1230.823	−24.466	0.336
3900	137.361	807.184	682.103	487.815	−1231.152	7.284	−0.098
4000	137.289	810.660	685.273	501.548	−1231.571	39.045	−0.510
4100	137.214	814.050	688.373	515.273	−1232.076	70.816	−0.902
4200	137.137	817.355	691.405	528.990	−1232.666	102.601	−1.276
4300	137.059	820.581	694.372	542.700	−1233.337	134.401	−1.633
4400	136.980	823.731	697.276	556.402	−1234.085	166.217	−1.973
4500	136.901	826.809	700.120	570.096	−1234.909	198.051	−2.299
4600	136.821	829.817	702.907	583.782	−1235.805	229.905	−2.611
4700	136.741	832.758	705.639	597.460	−1236.771	261.778	−2.909
4800	136.662	835.636	708.317	611.131	−1237.806	293.673	−3.196
4900	136.584	838.453	710.945	624.793	−1238.907	325.590	−3.471
5000	136.507	841.212	713.522	638.448	−1240.074	357.530	−3.735
5100	136.430	843.914	716.053	652.094	−1241.305	389.494	−3.989
5200	136.355	846.563	718.537	665.734	−1242.600	421.483	−4.234
5300	136.281	849.160	720.977	679.365	−1243.960	453.497	−4.469
5400	136.209	851.706	723.375	692.990	−1245.384	485.538	−4.697
5500	136.137	854.205	725.731	706.607	−1246.875	517.606	−4.916
5600	136.068	856.657	728.047	720.217	−1248.434	549.702	−5.127
5700	135.999	859.065	730.324	733.821	−1250.064	581.825	−5.332
5800	135.933	861.430	732.565	747.417	−1251.767	613.979	−5.529
5900	135.868	863.753	734.768	761.007	−1253.547	646.162	−5.721
6000	135.804	866.036	736.937	774.591	−1255.409	678.375	−5.906

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$\Delta_f H°(0\ K) = -954.41 \pm 29.3\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [418.810 \pm 20.9]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -954.37 \pm 29.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[500](1)	[240](1)	[130](2)
[400](1)	[200](1)	[100](2)
295 (1)	[150](1)	[80](2)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: $[D_{2h}]$
Bond Distance: Mg–Cl = [2.18] Å; Mg–Cl'(ring) = [2.3] Å
Bond Angles: Cl'–Mg–Cl'(in ring) = [90°]; Cl–Mg–Cl' = [135°]
Product of the Moments of Inertia: $I_A I_B I_C = 1.3313 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

References relative to the monomer–dimer ratio in magnesium chloride vapor are given in the discussion for monomeric ideal gas. The selected best value for the enthalpy of dimerization at 900 K is $-39.2\ kcal \cdot mol^{-1}$. Combined with enthalpy of formation data for the monomer and the heat capacity of the dimer, this yields $\Delta_f H°(298.15\ K) = -228.10\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

A planar structure with D_{2h} symmetry was assumed, with the outer Mg–Cl distance the same as in $MgCl_2$ and the ring Mg–Cl distance slightly larger. The ring was taken to be square, and the Cl–Mg–Cl' angle 135°. This structure gives individual moments of inertia of $I_A = 31.12 \times 10^{-39}$, $I_B = 191.86 \times 10^{-39}$, and $I_C = I_A + I_B\ g \cdot cm^2$.

A reasonable set of frequencies was estimated by comparison with $MgCl_2$ monomer and other dimer molecules. The single observed frequency is from Buchler and Klemperer[1] who erroneously ascribed it to the bending mode of the monomer. The estimated values were adjusted until the entropy of dimerization at 900 K was $-29.9\ kcal \cdot mol^{-1}$, as selected in the discussion for ideal monomeric gas. The calculated thermodynamic properties of monomer and dimer give total vapor pressures in good agreement with experiment and yield a boiling point for magnesium chloride of 1624 K at one atmosphere pressure.

References

[1]A. Buchler and W. Klemperer, J. Chem. Phys. **29**, 121 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−28.396	−954.409	−954.409	INFINITE
100	91.553	298.917	522.238	−22.332	−955.452	−945.642	493.953
200	115.181	371.122	430.020	−11.780	−954.989	−935.971	244.451
250	120.397	397.431	420.950	−5.880	−954.669	−931.253	194.575
298.15	123.611	418.931	418.931	0.	−954.370	−926.771	162.366
300	123.710	419.696	418.933	0.229	−954.359	−926.600	161.335
350	125.913	438.942	420.448	6.473	−954.077	−921.996	137.600
400	127.437	455.861	423.839	12.809	−953.830	−917.430	119.804
450	128.529	470.937	428.250	19.209	−953.622	−912.893	105.966
500	129.335	484.523	433.209	25.657	−953.457	−908.377	94.897
600	130.418	508.208	443.792	38.649	−953.264	−899.382	78.298
700	131.090	528.366	454.470	51.727	−953.274	−890.404	66.443
800	131.534	545.902	464.827	64.860	−953.517	−881.409	57.550
900	131.842	561.413	474.713	78.029	−954.025	−872.368	50.631
1000	132.065	575.316	484.091	91.225	−972.015	−861.830	45.017
1100	132.230	587.911	492.965	104.441	−973.162	−850.756	40.399
1200	132.357	599.422	501.364	117.670	−974.317	−839.577	36.546
1300	132.456	610.021	509.320	130.911	−975.483	−828.302	33.282
1400	132.534	619.840	516.868	144.161	−1231.477	−810.602	30.244
1500	132.598	628.986	524.041	157.417	−1229.960	−780.592	27.183
1600	132.650	637.545	530.870	170.680	−1228.454	−750.683	24.507
1700	132.693	645.588	537.384	183.947	−1226.961	−720.869	22.150
1800	132.729	653.174	543.608	197.218	−1225.482	−691.141	20.056
1900	132.760	660.351	549.566	210.493	−1224.020	−661.496	18.186
2000	132.786	667.161	555.276	223.770	−1222.575	−631.927	16.504
2100	132.809	673.641	560.760	237.050	−1221.150	−602.429	14.985
2200	132.829	679.819	566.032	250.332	−1219.748	−572.999	13.605
2300	132.846	685.724	571.109	263.615	−1218.372	−543.633	12.346
2400	132.861	691.379	576.003	276.901	−1217.026	−514.325	11.194
2500	132.874	696.802	580.727	290.188	−1215.713	−485.073	10.135
2600	132.886	702.014	585.293	303.476	−1214.435	−455.873	9.159
2700	132.896	707.029	589.709	316.765	−1213.198	−426.720	8.255
2800	132.906	711.863	593.986	330.055	−1212.004	−397.614	7.418
2900	132.914	716.527	598.132	343.346	−1210.856	−368.549	6.638
3000	132.922	721.033	602.154	356.638	−1209.756	−339.523	5.912
3100	132.929	725.391	606.059	369.930	−1208.708	−310.532	5.232
3200	132.935	729.612	609.855	383.223	−1207.712	−281.575	4.596
3300	132.941	733.703	613.546	396.517	−1206.770	−252.648	3.999
3400	132.946	737.671	617.139	409.811	−1205.884	−223.749	3.437
3500	132.951	741.525	620.638	423.106	−1205.053	−194.875	2.908
3600	132.955	745.271	624.048	436.401	−1204.279	−166.023	2.409
3700	132.959	748.913	627.374	449.697	−1203.560	−137.193	1.937
3800	132.963	752.459	630.619	462.993	−1202.898	−108.382	1.490
3900	132.966	755.913	633.788	476.290	−1202.291	−79.586	1.066
4000	132.969	759.280	636.883	489.586	−1201.740	−50.806	0.663
4100	132.972	762.563	639.908	502.884	−1201.243	−22.039	0.281
4200	132.975	765.767	642.867	516.181	−1200.800	6.717	−0.084
4300	132.978	768.896	645.762	529.479	−1200.411	35.462	−0.431
4400	132.980	771.953	648.595	542.776	−1200.074	64.200	−0.762
4500	132.982	774.942	651.370	556.075	−1199.790	92.930	−1.079
4600	132.984	777.865	654.088	569.373	−1199.558	121.655	−1.381
4700	132.986	780.725	656.752	582.671	−1199.379	150.374	−1.671
4800	132.988	783.525	659.364	595.970	−1199.251	179.091	−1.949
4900	132.990	786.267	661.926	609.269	−1199.176	207.806	−2.215
5000	132.991	788.953	664.440	622.568	−1199.153	236.519	−2.471
5100	132.993	791.587	666.907	635.867	−1199.183	265.233	−2.717
5200	132.994	794.170	669.330	649.167	−1199.267	293.947	−2.953
5300	132.996	796.703	671.709	662.466	−1199.403	322.664	−3.180
5400	132.997	799.189	674.047	675.766	−1199.596	351.384	−3.399
5500	132.998	801.629	676.345	689.066	−1199.843	380.108	−3.610
5600	132.999	804.026	678.603	702.365	−1200.148	408.837	−3.813
5700	133.000	806.380	680.824	715.665	−1200.512	437.572	−4.010
5800	133.001	808.693	683.009	728.965	−1200.935	466.314	−4.200
5900	133.002	810.966	685.159	742.266	−1201.420	495.064	−4.383
6000	133.003	813.202	687.274	755.566	−1201.967	523.822	−4.560

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = [223.84 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 590\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -477.0 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [16.736 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = 114\ kcal \cdot mol^{-1}$ was determined by Shchukarev *et al.*[1] by solution calorimetry. The authors measured the enthalpy of solution of $MoCl_4$ in the aqueous solvent $FeCl_3$ + HCl and obtained the enthalpy of formation from a comparison with the enthalpy of solution of $MoCl_5$ measured in the same solvent.

The decomposition pressures of $2MoCl_5(cr) = 2MoCl_4(cr) + Cl_2(g)$ (80–150°C) were measured manometrically by Saeki and Matsuzaki[2]. From the reported data we evaluate the enthalpy change for the above reaction by 3rd law analysis. Based on $\Delta_f H°(MoCl_5, cr, 298.15\ K) = -126\ kcal \cdot mol^{-1}$ and the 3rd law $\Delta_r H°(298.15\ K) = 24.132\ kcal \cdot mol^{-1}$, we obtain $\Delta_f H°(MoCl_4, cr, 298.15\ K) = -113.94\ kcal \cdot mol^{-1}$, which is in very good agreement with the value reported by Shchukarev *et al.*[1]

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of WCl_4(cr). The estimated $S°(298.15\ K) = 53.5\ cal \cdot K^{-1} \cdot mol^{-1}$ is based on the assumption that the entropy difference between $MoCl_4$(cr) and $MoCl_5$(cr) is about the same as that between WCl_4(cr) and WCl_5(cr). The entropy obtained from the second law analysis of the data of Saeki and Matsuzaki[2] agrees with the adopted one within the error of the vapor pressure data.

Fusion Data

Refer to the liquid table for details.

References

[1]S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Russ. J. Inorg. Chem. 5, 802 (1960).
[2]Y. Saeki and R. Matsuzaki, Denki Kagaku 33, 155–8 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	129.704	223.844	223.844	0.	−476.976	−402.164	70.458
300	129.704	224.646	223.846	0.240	−476.906	−401.700	69.942
400	135.143	262.705	228.999	13.482	−473.059	−377.207	49.258
500	140.582	293.445	238.908	27.269	−468.964	−353.711	36.952
590.000	145.478	317.108	249.072	40.141	--- CRYSTAL <---> LIQUID ---		
600	146.022	319.557	250.226	41.599	−464.515	−331.072	28.822
700	151.461	342.470	261.799	56.469	−459.661	−309.210	23.074
800	157.318	363.082	273.192	71.912	−454.339	−288.074	18.809
900	162.758	381.937	284.242	87.926	−448.531	−267.635	15.533
1000	166.942	399.306	294.891	104.415	−442.329	−247.865	12.947
1100	170.707	415.397	305.124	121.301	−435.806	−228.731	10.862
1200	174.054	430.400	314.945	138.546	−429.003	−210.205	9.150
1300	176.565	444.434	324.372	156.080	−421.994	−192.255	7.725
1400	178.657	457.595	333.423	173.841	−414.847	−174.850	6.524
1500	180.749	469.993	342.118	191.811	−407.583	−157.960	5.501

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = [245.525]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 590\ K$

$\Delta_f H°(298.15\ K) = [-462.837]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [16.736 \pm 8]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MoCl_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(MoCl_4, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(590\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities are assumed to be constant at 7 $cal·K^{-1}\ g·atom^{-1}$. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is taken from Gutmann.[1] $\Delta_{fus}H°$ is estimated such that the derived $\Delta_f G°$ for $MoCl_4(l)$ yields a reasonable boiling point which is expected to be between 600 and 700 K from comparisons with related compounds.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change ($\Delta_r G°$) of the following process $MoCl_4(l) = MoCl_4(g)$ is zero. The difference between $\Delta_f H°$ for $MoCl_4(l)$ and $MoCl_4(g)$ at T_{vap} is the enthalpy of vaporization.

Reference

[1]V. Gutmann, "Halogen Chemistry," Vol. 3, Academic Press, New York, (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	146.440	245.525	245.525	0.	−462.837	−394.490	69.113
300	146.440	246.431	245.528	0.271	−462.736	−394.066	68.613
400	146.440	288.559	251.271	14.915	−457.488	−371.977	48.575
500	146.440	321.236	262.118	29.559	−452.535	−351.178	36.687
590.000	146.440	345.474	273.036	42.739	--- CRYSTAL <---> LIQUID ---		
600	146.440	347.935	274.264	44.203	−447.772	−331.356	28.847
700	146.440	370.509	286.442	58.847	−443.144	−312.321	23.306
800	146.440	390.063	298.200	73.491	−438.621	−293.941	19.192
900	146.440	407.311	309.384	88.135	−434.184	−276.124	16.026
1000	146.440	422.740	319.961	102.779	−429.826	−258.796	13.518
1100	146.440	436.698	329.950	117.423	−425.545	−241.901	11.487
1200	146.440	449.440	339.384	132.067	−421.343	−225.392	9.811
1300	146.440	461.161	348.306	146.711	−417.224	−209.230	8.407
1400	146.440	472.013	356.760	161.355	−413.194	−193.383	7.215
1500	146.440	482.117	364.784	175.999	−409.257	−177.820	6.192

PREVIOUS: CURRENT: December 1968

0	to	590	K	crystal
above		590	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	129.704	223.844	223.844	0.	−476.976	−402.164	70.458
300	129.704	224.646	223.846	0.240	−476.906	−401.700	69.942
400	135.143	262.705	228.999	13.482	−473.059	−377.207	49.258
500	140.582	293.445	238.908	27.269	−468.964	−353.711	36.952
590.000	145.478	317.108	249.072	40.141	___ CRYSTAL <-- -> LIQUID ___		
590.000	146.440	345.474	249.072	56.877	TRANSITION		
600	146.440	347.935	250.699	58.342	−447.772	−331.356	28.847
700	146.440	370.509	266.244	72.986	−443.144	−312.321	23.306
800	146.440	390.063	280.526	87.630	−438.621	−293.941	19.192
900	146.440	407.311	293.674	102.274	−434.184	−276.124	16.026
1000	146.440	422.740	305.823	116.918	−429.826	−258.796	13.518
1100	146.440	436.698	317.096	131.562	−425.545	−241.901	11.487
1200	146.440	449.440	327.601	146.206	−421.343	−225.392	9.811
1300	146.440	461.161	337.430	160.850	−417.224	−209.230	8.407
1400	146.440	472.013	346.661	175.494	−413.194	−193.383	7.215
1500	146.440	482.117	355.358	190.138	−409.257	−177.820	6.192

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K)$ = [371.941] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−384.25 ± 12.6] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−384.93 ± 12.6] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[10000]	[3]
[30000]	[3]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[390](1)	[410](3)
[120](2)	[120](3)

Point Group: T_d σ = [12]
Bond Distance: Mo–Cl = [2.27] Å
Bond Angle: Cl–Mo–Cl = [109.4712]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [5.29405 × 10^{-112}] $g^3·cm^6$

Enthalpy of Formation

Shchukarev *et al.*,[1] derived the value $\Delta_f H°(MoCl_4, g, 298.15\ K)$ = −89 $kcal·mol^{-1}$ from the decomposition pressures of $2MoCl_3(cr) = MoCl_2(cr) + MoCl_4(g)$, 480–600°C, measured by a transpiration method. However, this value is adjusted to be −92 ± 3 $kcal·mol^{-1}$, in order to obtain a reasonable boiling point (see the liquid table for details).

Heat Capacity and Entropy

Vibrational frequencies and quantum weights are estimated by comparison with those of $WCl_4(g)$. The molecular configuration is assumed to be tetrahedral similar to those of $WCl_4(g)$, $SiCl_4(g)$, $TiCl_4(g)$ and $PbCl_4(g)$. The bond distance is estimated to be the same as that of $MoCl_5(g)$. The principal moments of inertia are $I_A = I_B = I_C$ = 80.8964 × 10^{-39} $g·cm^2$. The low lying electronic levels are estimated to be 0, 10000, and 30000, all triplets, by comparison with those of $WCl_4(g)$.

Reference

[1] S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin and A. K. Baev, Zh, Neorg. Khim. **5**, 1650–4 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−22.265	−384.247	−384.247	INFINITE
100	69.235	279.286	452.572	−17.329	−385.625	−375.050	195.906
200	89.478	334.366	380.690	−9.265	−385.479	−364.471	95.190
250	94.767	354.944	373.540	−4.649	−385.219	−359.248	75.061
298.15	98.109	371.941	371.941	.000	−384.928	−354.272	62.067
300	98.213	372.548	371.943	.182	−384.916	−354.081	61.651
350	100.529	387.873	373.148	5.154	−384.595	−348.967	52.081
400	102.140	401.408	375.851	10.223	−384.271	−343.900	44.909
450	103.298	413.509	379.375	15.360	−383.950	−338.873	39.335
500	104.154	424.439	383.344	20.548	−383.637	−333.881	34.880
600	105.306	443.539	391.830	31.026	−383.040	−323.987	28.206
700	106.021	459.830	400.409	41.594	−382.488	−314.189	23.445
800	106.494	474.020	408.743	52.222	−381.981	−304.467	19.880
900	106.822	486.583	416.707	62.888	−381.521	−294.806	17.110
1000	107.060	497.851	424.268	73.583	−381.112	−285.193	14.897
1100	107.238	508.064	431.429	84.298	−380.760	−275.619	13.088
1200	107.377	517.401	438.210	95.029	−380.471	−266.074	11.582
1300	107.491	526.000	444.636	105.773	−380.253	−256.550	10.308
1400	107.589	533.970	450.736	116.527	−380.113	−247.040	9.217
1500	107.678	541.396	456.535	127.290	−380.056	−237.538	8.272
1600	107.765	548.348	462.059	138.063	−380.091	−228.036	7.445
1700	107.853	554.884	467.329	148.843	−380.222	−218.529	6.715
1800	107.946	561.051	472.366	159.633	−380.459	−209.011	6.065
1900	108.044	566.890	477.188	170.433	−380.809	−199.477	5.484
2000	108.150	572.435	481.813	181.242	−381.280	−189.922	4.960
2100	108.263	577.714	486.255	192.063	−381.883	−180.340	4.486
2200	108.384	582.753	490.528	202.895	−382.628	−170.725	4.054
2300	108.513	587.574	494.643	213.740	−383.526	−161.074	3.658
2400	108.647	592.195	498.612	224.598	−384.589	−151.380	3.295
2500	108.787	596.633	502.445	235.470	−385.830	−141.638	2.959
2600	108.931	600.902	506.150	246.356	−387.274	−131.843	2.649
2700	109.079	605.016	509.736	257.256	−388.961	−121.987	2.360
2800	109.228	608.986	513.210	268.171	−390.954	−112.064	2.091
2900	109.377	612.821	516.579	279.102	−429.221	−102.014	1.837
3000	109.527	616.532	519.850	290.047	−430.037	−90.717	1.580
3100	109.675	620.126	523.027	301.007	−430.877	−79.392	1.338
3200	109.821	623.610	526.116	311.982	−431.739	−68.041	1.111
3300	109.964	626.992	529.122	322.971	−432.624	−56.661	.897
3400	110.103	630.276	532.049	333.974	−433.527	−45.255	.695
3500	110.237	633.470	534.901	344.991	−434.447	−33.822	.505
3600	110.367	636.577	537.682	356.022	−435.380	−22.362	.324
3700	110.492	639.603	540.396	367.065	−436.322	−10.876	.154
3800	110.612	642.551	543.046	378.120	−437.270	.635	−.009
3900	110.726	645.426	545.634	389.187	−438.220	12.171	−.163
4000	110.834	648.231	548.164	400.265	−439.166	23.732	−.310
4100	110.937	650.969	550.639	411.354	−440.105	35.316	−.450
4200	111.034	653.643	553.059	422.452	−441.031	46.923	−.584
4300	111.125	656.257	555.429	433.560	−441.940	58.551	−.711
4400	111.211	658.813	557.750	444.677	−442.827	70.201	−.833
4500	111.291	661.313	560.023	455.802	−443.688	81.870	−.950
4600	111.366	663.760	562.252	466.935	−444.519	93.559	−1.062
4700	111.436	666.155	564.437	478.075	−445.316	105.264	−1.170
4800	111.501	668.502	566.581	489.222	−446.075	116.987	−1.273
4900	111.562	670.802	568.685	500.375	−446.792	128.725	−1.372
5000	111.618	673.056	570.750	511.534	−1038.849	146.208	−1.527
5100	111.670	675.267	572.777	522.699	−1041.153	169.933	−1.740
5200	111.718	677.436	574.769	533.868	−1043.554	193.702	−1.946
5300	111.763	679.565	576.726	545.042	−1046.045	217.519	−2.144
5400	111.804	681.654	578.650	556.221	−1048.625	241.384	−2.335
5500	111.841	683.706	580.542	567.403	−1051.288	265.298	−2.520
5600	111.876	685.721	582.402	578.589	−1054.031	289.260	−2.698
5700	111.907	687.702	584.232	589.778	−1056.849	313.273	−2.871
5800	111.936	689.648	586.033	600.970	−1059.740	337.335	−3.038
5900	111.963	691.562	587.805	612.165	−1062.697	361.447	−3.200
6000	111.987	693.444	589.550	623.363	−1065.721	385.610	−3.357

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [172.8 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 484\ K$

$\Delta_f H°(0\ K) =$ Unknown
$\Delta_f H°(298.15\ K) = -671.11 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 45.380 \pm 12.6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Shchukarev *et al.*[1] measured calorimetrically the enthalpies of reaction (1) and (2) at 298.15 K as -131.5 ± 0.3 and -13.6 ± 0.11 $kcal \cdot mol^{-1}$, respectively. The reactions are given as follows:

(1) $WOCL_4(cr) + 6\ NaOH(aq, 16.3\ H_2O) \rightarrow Na_2WO_4(aq, 190000\ H_2O) + 4\ NaCl(aq, 50000\ H_2O) + 3\ H_2O(l)$
(2) $H_2WO_4(cr) + 2\ NaOH(aq, 16.3\ H_2O) \rightarrow Na_2WO_4(aq, 20000\ H_2O) + 2\ H_2O(l)$

Based on these data and the enthalpies of dilution for NaOH(aq),[2] and $Na_2WO_4(aq)$,[3] we obtain $\Delta_f H°(298.15\ K) = -118.0 \pm 1.6\ kcal \cdot mol^{-1}$ for $WOCl_4(cr) + 4OH^-(aq, \infty) \rightarrow H_2WO_4(cr) + 4\ Cl^-(aq, \infty) + H_2O(l)$. This leads to $\Delta_f H°(WOCl_4, cr, 298.15\ K) = 160.4 \pm 2\ kcal \cdot mol^{-1}$, using $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -270.5 \pm 0.4\ kcal \cdot mol^{-1}$.[5]

Heat Capacity and Entropy

$C_p°(300\ K) = 35.0\ cal \cdot K^{-1} \cdot mol^{-1}$ is estimated using Kopp's rule. Since the melting point of $WOCl_4(cr)$ is approximately 500 K, which is relatively low for oxygen to reach its maximum contribution, we estimate $C_p°(500\ K) = 40.0\ cal \cdot K^{-1} \cdot mol^{-1}$ based on the values for $WO_2(cr)$, $WO_3(cr)$ and $WCl_6(cr)$.

The entropy, $S°(298.15\ K) = 41.3\ cal \cdot K^{-1} \cdot mol^{-1}$, is calculated from $\Delta S°(457\ K) = 44.5\ cal \cdot K^{-1} \cdot mol^{-1}$ for $WOCl_4(cr) \rightarrow WOCl_4(g)$ obtained from the 2nd law analysis of the vapor pressure equation given by Shchukarev and Suvorov.[4] See $WOCl_4(g)$ table (March 31, 1967) for details.

It is surprising that this entropy is smaller than the corresponding value for $WOF_4(cr)$. See $WOF_4(cr)$ table (March 31, 1967) for details.

Fusion Data

T_{fus} is calculated as the temperature at which the Gibbs energies of formation of crystal and liquid are equal. The difference between the enthalpies of formation of crystal and liquid at the melting point is $\Delta_{fus} H°$. This $\Delta_{fus} H°$ is derived from 2nd law analyses of the vapor pressure equation determined by Shchukarev and Suvorov.[4] See $WOCl_4(l, g)$ tables (March 31, 1967) for details.

References

[1]S. A. Shchukarev, I. V. Vasil'kova and G. I. Novikov, Zh. Neorg. Khim. **3**, 2642 (1958).
[2]V. B. Parker, "Thermal Properties of Aqueous Uni–univalent Electrolytes," NSRDS–NBS 2, U. S. Nat. Bur. Stand., (1965).
[3]We have assumed $\Delta H°\ dil = 0 \pm 0.5\ kcal \cdot mol^{-1}$ for $Na_2WO_4(aq, 20000\ H_2O) \rightarrow Na_2WO_4(aq, 190000\ H_2O)$.
[4]S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. 16, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Earlier data reported by Shchukarev *et al.*, Zh. Neorg. Khim **1**, 357 (1956); **3**, 2630 (1958); **5**, 1650 (1960); have been revised and they are not used here.
[5]JANAF Thermochemical Tables: $H_2WO_4(cr)$, 3–31–67.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	146.248	172.799	172.799	0.	−671.114	−549.292	96.234
300	146.440	173.704	172.802	0.271	−671.041	−548.536	95.509
400	156.900	217.265	178.671	15.438	−666.763	−508.327	66.381
484.000	165.686	247.984	188.095	28.986	--- CRYSTAL <--> LIQUID ---		
500	167.360	253.400	190.099	31.651	−661.736	−469.283	49.026
600	177.820	284.879	203.325	48.932	−655.856	−431.331	37.551
700	185.560	312.904	217.015	67.122	−649.238	−394.425	29.432
800	190.790	338.049	230.600	85.959	−642.114	−358.504	23.408
900	193.719	360.694	243.818	105.188	−634.717	−323.495	18.775
1000	196.230	381.238	256.549	124.689	−627.155	−289.319	15.112

PREVIOUS: September 1962 CURRENT: March 1967

$S°(298.15\ K) = [253.565]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 484\ K$

$\Delta_f H°(298.15\ K) = [-630.573]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 45.380 \pm 12.6\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(WOCl_4, l, 298.15\ K)$, is calculated from that of the gas by subtracting the enthalpy of vaporization, $\Delta_{vap}H°(298.15\ K) = 13.643$ kcal·mol^{-1}. The latter is obtained by the 3rd law method from the vapor pressure equation given by Shchukarev and Surorov.[1] 2nd law analysis gives $\Delta_{vap}H°(501.9\ K) = 10.32$ kcal·mol^{-1} [$(\Delta_{vap}H°(298.15\ K) = 13.643$ kcal·mol^{-1}] and the boiling point $T_{vap} = 493$ K. Earlier data reported by Shchukarev *et al.*[2] have been revised and they are not used here.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 cal·K^{-1} g·atom^{-1} as suggested by Kubaschewski and Evans.[3]

The entropy, $S°(298.15\ K) = 60.6$ cal·K^{-1}·mol^{-1}, is calculated from $\Delta S°(501.9\ K) = 20.9$ cal·K^{-1}·mol^{-1} for $WOCl_4(l) \rightarrow WOCl_4(g)$ obtained from the 2nd law analysis of the vapor pressure equation given by Shchukarev and Suvorov.[1]

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the Gibbs energies of formation of liquid and gas are equal. The difference between the enthalpies of formation of liquid and gas at the boiling point is $\Delta_{vap}H°$.

References

[1]S. A. Shchukarev and A. V. Surorov, Vestn. Leningrad. Univ. **16**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).
[2]A. Shchukarev *et al.*, Zh. Neorg. Khim. **1**, 357 (1956); **3**, 2630 (1958); and **5**, 1650 (1960).
[3]O. Kubaschewski and E. Ll. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	182.004	253.565	253.565	0.	−630.573	−532.832	93.350
300	182.004	254.691	253.569	0.337	−630.434	−532.226	92.669
400	182.004	307.050	260.708	18.537	−623.123	−500.601	65.372
484.000	182.004	341.744	271.857	33.825	--- CRYSTAL <---> LIQUID ---		
500	182.004	347.663	274.188	36.738	−616.109	−470.788	49.183
600	182.004	380.847	289.283	54.938	−609.310	−442.365	38.511
700	182.004	408.903	304.419	73.138	−602.682	−415.067	30.973
800	182.004	433.206	319.032	91.339	−596.194	−388.709	25.380
900	182.004	454.643	332.933	109.539	−589.826	−363.157	21.077
1000	182.004	473.819	346.079	127.740	−583.563	−338.309	17.671

PREVIOUS: CURRENT: March 1967

0	to	484	K	crystal
above		484	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
298.15	146.248	172.799	172.799	0.	−671.114	−549.292	96.234
300	146.440	173.704	172.802	0.271	−671.041	−548.536	95.509
400	156.900	217.265	178.671	15.438	−666.763	−508.327	66.381
484.000	165.686	247.984	188.095	28.986	____ CRYSTAL <--> LIQUID ____		
484.000	182.004	341.744	188.095	74.366	TRANSITION		
500	182.004	347.663	193.107	77.278	−616.109	−470.788	49.183
600	182.004	380.847	221.716	95.478	−609.310	−442.365	38.511
700	182.004	408.903	246.504	113.679	−602.682	−415.067	30.973
800	182.004	433.206	268.357	131.879	−596.194	−388.709	25.380
900	182.004	454.643	287.888	150.080	−589.826	−363.158	21.077
1000	182.004	473.819	305.539	168.280	−583.563	−338.309	17.671

PREVIOUS: CURRENT: March 1967

$S°(298.15\ K) = [377.079]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -568.09 \pm 20.9\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -573.49 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[1000](1)	[350](1)	[200](1)
[1000](1)	[350](1)	[200](1)
[480](1)	[300](1)	[100](1)
[480](1)	[300](1)	[100](1)

Ground State Quantum Weight = 1 σ = [2]

Point Group: [C_{2v}]

Bond Distances: W–Cl = [2.26] Å; W–O = [1.81] Å

Bond Angles: Cl*–W–O* = Cl*–W–Cl* = [120]°

Cl*–W–Cl** = Cl**–W–O* = [90]°

Cl**–W–Cl** = [180]°

*Equatorial **Axial

Product of the Moments of Inertia: $I_A I_B I_C = [5.87434 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy formation, $\Delta_f H°(WOCl_4, g, 298.15\ K) = -137.0\ kcal·mol^{-1}$, is calculated from $\Delta_r H°(298.15\ K) = 23.4\ kcal·mol^{-1}$ for $WOCl_4(cr) \rightarrow WOCl_4(g)$. The latter is obtained by the 3rd law method from the vapor pressure equation given by Shchukarev and Suvorov.[1] Second law analysis gives $\Delta_r H°(457.2\ K) = 21.9\ kcal·mol^{-1}$(($\Delta_r H°(298.15\ K) = 23.4\ kcal·mol^{-1}$).

*Earlier data reported by Shchukarev *et al.*[2] have been revised and they are not used here.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of SOF_4(g), reported by Goggin *et al.*[3] The bond distances W–O and W–Cl are estimated to be the same as those in WO_3(g) and WCl_6(g), respectively. The principal moments of inertia are: $I_A = 67.5706 \times 10^{-39}$, $I_B = 82.6053 \times 10^{-39}$ and $I_C = 105.2432 \times 10^{-39}\ g·cm^2$.

All vibrational frequencies are estimated by comparison with those observed in the infrared and Raman spectra for SOF_4(g),[3] $MoOCl_4$(g),[4] WO_2Cl_2(g),[5] CrO_2Cl_2(g),[6,7] WO_3(g),[8] and WCl_6(g).[8] The frequencies are not listed in point group order.

References

[1]S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad Univ. **16**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961).

[2]S. A. Shchukarev *et al.*, Zh. Neorg. Khim. **1**, 357 (1956), **3**, 2630 (1956), **5**, 1650 (1960).

[3]P. L. Goggin, H. L. Roberts and L. A. Woodward, Trans. Faraday Soc. **57**, 1877 (1961).

[4]T. V. Iorns and F. E. Stafford, J. Amer. Chem. Soc. **88**, 4819 (1966).

[5]C. G. Barraclough and J. Stals, Aust. J. Chem. **19**, 741 (1966).

[6]F. A. Miller, G. L. Carlson and W. B. White, Spectrochim. Acta **1959**, 709 (1959).

[7]H. Stammreich, K. Kawai and Y. Tavares, Spectrochim. Acta **1959**, 438 (1959).

[8]JANAF Thermochemical Tables: WO_3(g), 9–30–66; WCl_6(g), 12–31–66.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−22.271	−568.087	−568.087	INFINITE
100	63.815	283.395	460.920	−17.752	−571.497	−552.408	288.549
200	92.057	337.421	386.393	−9.794	−573.077	−532.573	139.094
250	100.261	358.894	378.796	−4.975	−573.382	−522.407	109.151
298.15	106.138	377.079	377.079	0.	−573.493	−512.577	89.801
300	106.335	377.736	377.081	0.197	−573.494	−512.199	89.182
350	110.987	394.492	378.394	5.635	−573.456	−501.984	74.917
400	114.621	409.559	381.364	11.278	−573.301	−491.783	64.220
450	117.495	423.232	385.268	17.084	−573.058	−481.607	55.904
500	119.794	435.735	389.698	23.018	−572.747	−471.462	49.253
600	123.162	457.895	399.265	35.178	−571.990	−451.274	39.287
700	125.440	477.062	409.041	47.615	−571.125	−431.222	32.178
800	127.036	493.922	418.619	60.243	−570.209	−411.298	26.855
900	128.188	508.955	427.836	73.007	−569.277	−391.490	22.721
1000	129.045	522.508	436.637	85.871	−568.352	−371.786	19.420
1100	129.697	534.839	445.012	98.809	−567.447	−352.173	16.723
1200	130.203	546.147	452.975	111.805	−566.573	−332.642	14.480
1300	130.604	556.585	460.549	124.846	−565.738	−313.181	12.584
1400	130.926	566.276	467.759	137.924	−564.948	−293.784	10.961
1500	131.188	575.318	474.632	151.030	−564.207	−274.441	9.557
1600	131.405	583.792	481.192	164.160	−563.520	−255.146	8.330
1700	131.586	591.764	487.464	177.309	−562.890	−235.893	7.248
1800	131.739	599.289	493.469	190.476	−562.321	−216.674	6.288
1900	131.868	606.416	499.228	203.656	−561.817	−197.486	5.429
2000	131.980	613.183	504.758	216.849	−561.382	−178.322	4.657
2100	132.076	619.624	510.076	230.052	−561.019	−159.178	3.959
2200	132.159	625.770	515.196	243.264	−560.731	−140.050	3.325
2300	132.232	631.647	520.132	256.483	−560.524	−120.933	2.746
2400	132.297	637.276	524.897	269.710	−560.400	−101.824	2.216
2500	132.353	642.678	529.501	282.942	−560.363	−82.717	1.728
2600	132.404	647.870	533.954	296.180	−560.412	−63.611	1.278
2700	132.449	652.868	538.266	309.423	−560.578	−44.500	0.861
2800	132.489	657.685	542.446	322.670	−560.896	−25.380	0.473
2900	132.526	662.335	546.500	335.921	−561.407	−6.247	0.113
3000	132.559	666.828	550.437	349.175	−562.138	12.909	−0.225
3100	132.588	671.175	554.262	362.432	−563.133	32.093	−0.541
3200	132.615	675.385	557.981	375.693	−564.422	51.313	−0.838
3300	132.640	679.467	561.601	388.955	−566.028	70.579	−1.117
3400	132.662	683.427	565.126	402.221	−567.983	89.898	−1.381
3500	132.683	687.273	568.562	415.488	−570.349	109.281	−1.631
3600	132.702	691.011	571.911	428.757	−573.218	128.738	−1.868
3700	132.719	694.647	575.180	442.028	−611.453	148.474	−2.096
3800	132.736	698.186	578.370	455.301	−612.028	169.020	−2.323
3900	132.750	701.634	581.487	468.575	−612.622	189.582	−2.539
4000	132.764	704.996	584.533	481.851	−613.230	210.159	−2.744
4100	132.777	708.274	587.511	495.128	−613.845	230.751	−2.940
4200	132.789	711.474	590.425	508.406	−614.462	251.359	−3.126
4300	132.800	714.598	593.276	521.686	−615.077	271.981	−3.304
4400	132.810	717.652	596.068	534.966	−615.685	292.617	−3.474
4500	132.820	720.636	598.803	548.248	−616.279	313.267	−3.636
4600	132.829	723.556	601.484	561.530	−616.857	333.930	−3.792
4700	132.837	726.412	604.112	574.814	−617.412	354.605	−3.941
4800	132.845	729.209	606.689	588.098	−617.942	375.292	−4.084
4900	132.853	731.948	609.217	601.383	−618.442	395.990	−4.221
5000	132.860	734.632	611.699	614.668	−618.909	416.697	−4.353
5100	132.866	737.263	614.135	627.955	−619.340	437.414	−4.480
5200	132.873	739.844	616.528	641.241	−619.732	458.138	−4.602
5300	132.879	742.375	618.879	654.529	−620.083	478.870	−4.720
5400	132.884	744.858	621.189	667.817	−620.390	499.608	−4.833
5500	132.889	747.297	623.459	681.106	−620.653	520.351	−4.942
5600	132.894	749.691	625.692	694.395	−620.869	541.099	−5.047
5700	132.899	752.043	627.888	707.685	−621.038	561.849	−5.149
5800	132.904	754.355	630.049	720.975	−621.159	582.604	−5.247
5900	132.908	756.627	632.175	734.265	−621.231	603.358	−5.342
6000	132.912	758.861	634.268	747.556	−621.254	624.114	−5.433

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = [381.659 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-550.6 \pm 84]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-552.4 \pm 84]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
331 (1)
90 (2)
352 (3)
103 (3)

Ground State Quantum Weight: [1] $\sigma = 12$

Point Group: T_d

Bond Distance: Pb–Cl = 2.43 Å

Bond Angle: Cl–Pb–Cl = [109.4712°]

Product of the Moments of Inertia: $I_A I_B I_C = [7.96655 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -131.6 \pm 20\ kcal \cdot mol^{-1}$ is derived from the dissociation energy for the process $PbCl_4(g) = Pb(g) + 4Cl(g)$. $D° = 12.70$ eV is estimated from an intercomparison of the lead mono–, di–, and tetra– halides.[1] The adopted $D°$ value for $PbCl_4(g)$ is greater than the $D°$ value for $PbCl_2(g)$ by a factor of 2.02. The auxiliary values $\Delta_f H°(Pb, g, 0\ K) = 46.91\ kcal \cdot mol^{-1}$ [1] and $\Delta_f H°(Cl, g, 0\ K) = 28.587$ kcal mol^{-1} [1] are used. $\Delta_f H°(PbCl, g, 298.15\ K) = -132.0 \pm 20\ kcal \cdot mol^{-1}$ is calculated from $\Delta_f H°(0\ K)$.

Heat Capacity and Entropy

The bond distance is given by Lister and Sutton.[2] The vibrational frequencies are those determined by Clark and Hunter[3] from Raman spectra of $PbCl_4$ in n–pentane solution. Clark and Hunter[3] also observed an electronic transition at 35, 250 cm^{-1} which they claim is the lowest allowed electronic transition of the molecule. The present calculations assume a singlet electronic gound state.

The principal moments of inertia are: $I_A = I_B = I_C = 92.7022 \times 10^{-39}\ g \cdot cm^2$.

References

[1]JANAF Thermochemical Tables: PbF(g), PbF_2(g), PBF_4(g), PbBr(g), $PbBr_2$(g), PbI(g), and PbI_2(g),12–31–73; PbCl(g) and $PbCl_2$(g), 6–30–73; Pb(g), 3–31–62;Cl(g), 6–30–72.

[2]M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941).

3. R. J. H. Clark and B. K. Hunter, J. Mol. Struct. **9**, 354 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINTE	−23.449	−550.612	−550.612	INFINITE
100	74.317	284.403	465.502	−18.110	−552.863	−539.819	281.973
200	93.443	342.811	390.673	−9.572	−552.926	−526.648	137.546
250	97.857	364.177	383.300	−4.781	−552.677	−520.106	108.670
298.15	100.536	381.659	381.659	.000	−552.403	−513.857	90.026
300	100.618	382.281	381.661	.186	−552.393	−513.618	89.429
350	102.426	397.936	382.893	5.265	−552.105	−507.179	75.692
400	103.662	411.699	385.651	10.419	−551.829	−500.780	65.395
450	104.540	423.962	389.239	15.625	−551.571	−494.414	57.390
500	105.184	435.011	393.273	20.869	−551.335	−488.076	50.989
600	106.044	454.271	401.881	31.434	−550.923	−475.465	41.393
700	106.573	470.661	410.565	42.067	−555.456	−462.117	34.484
800	106.922	484.916	418.987	52.743	−555.196	−448.800	29.304
900	107.163	497.525	427.027	63.448	−554.917	−435.517	25.277
1000	107.337	508.825	434.651	74.174	−554.620	−422.267	22.057
1100	107.466	519.061	441.867	84.914	−554.304	−409.046	19.424
1200	107.564	528.417	448.695	95.666	−553.970	−395.856	17.231
1300	107.641	537.029	455.163	106.426	−553.625	−382.694	15.377
1400	107.702	545.009	461.299	117.193	−553.284	−369.558	13.788
1500	107.752	552.441	467.130	127.966	−552.957	−356.446	12.413
1600	107.792	559.397	472.682	138.743	−552.652	−343.355	11.209
1700	107.826	565.933	477.977	149.524	−552.374	−330.283	10.148
1800	107.854	572.097	483.036	160.308	−552.127	−317.226	9.206
1900	107.878	577.929	487.879	171.095	−551.914	−304.182	8.363
2000	107.898	583.463	492.521	181.884	−551.740	−291.148	7.604
2100	107.916	588.727	496.978	192.675	−728.828	−271.007	6.741
2200	107.931	593.748	501.263	203.467	−728.350	−249.218	5.917
2300	107.944	598.546	505.389	214.261	−727.986	−227.447	5.165
2400	107.956	603.140	509.367	225.056	−727.740	−205.691	4.477
2500	107.966	607.547	513.207	235.852	−727.617	−183.942	3.843
2600	107.975	611.782	516.917	246.649	−727.617	−162.195	3.259
2700	107.983	615.857	520.507	257.447	−727.740	−140.446	2.717
2800	107.991	619.785	523.983	268.245	−727.985	−118.690	2.214
2900	107.997	623.574	527.352	279.045	−728.349	−96.924	1.746
3000	108.003	627.236	530.621	289.845	−728.825	−75.143	1.308
3100	108.008	630.777	533.795	300.645	−729.408	−53.344	.899
3200	108.013	634.206	536.879	311.447	−730.090	−31.525	.515
3300	108.018	637.530	539.879	322.248	−730.862	−9.683	.153
3400	108.022	640.755	542.799	333.050	−731.715	12.184	−.187
3500	108.025	643.886	545.643	343.852	−732.640	34.076	−.509
3600	108.029	646.929	548.414	354.655	−733.624	55.997	−.812
3700	108.032	649.889	551.117	365.458	−734.659	77.945	−1.100
3800	108.035	652.770	553.754	376.262	−735.733	99.921	−1.374
3900	108.037	655.577	556.329	387.065	−736.836	121.926	−1.633
4000	108.040	658.312	558.845	397.869	−737.957	143.960	−1.880
4100	108.042	660.980	561.303	408.673	−739.087	166.022	−2.115
4200	108.044	663.583	563.708	419.477	−740.215	188.112	−2.340
4300	108.046	666.126	566.060	430.282	−741.334	210.228	−2.554
4400	108.048	668.610	568.363	441.087	−742.433	232.370	−2.759
4500	108.050	671.038	570.617	451.892	−743.506	254.536	−2.955
4600	108.051	673.413	572.826	462.697	−744.545	276.727	−3.142
4700	108.053	675.736	574.991	473.502	−745.543	298.939	−3.322
4800	108.054	678.011	577.114	484.307	−746.495	321.172	−3.495
4900	108.056	680.239	579.196	495.113	−747.395	343.425	−3.661
5000	108.057	682.422	581.239	505.918	−748.239	365.695	−3.820
5100	108.058	684.562	583.244	516.724	−749.022	387.982	−3.974
5200	108.059	686.660	585.212	527.530	−749.740	410.283	−4.121
5300	108.060	688.719	587.146	538.336	−750.392	432.597	−4.264
5400	108.061	690.739	589.046	549.142	−750.974	454.924	−4.401
5500	108.062	692.722	590.913	559.948	−751.484	477.260	−4.533
5600	108.063	694.669	592.748	570.755	−751.922	499.605	−4.660
5700	108.064	696.581	594.553	581.561	−752.285	521.957	−4.783
5800	108.065	698.461	596.328	592.367	−752.574	544.315	−4.902
5900	108.066	700.308	598.075	603.174	−752.787	566.677	−5.017
6000	108.066	702.124	599.794	613.980	−752.926	589.041	−5.128

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 330.945 \pm 0.21\ J \cdot K^{-1}$

$\Delta_f H°(0\ K) = -660.57 \pm 1.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -662.75 \pm 1.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
425 ± 1 (1)	620 ± 1 (3)
149 ± 2 (2)	220 ± 4 (3)

Ground State Quantum Weight: 1 $\sigma = 12$

Point Group: T_d

Bond Distance: Si–Cl = 2.0173 ± 0.0034 Å

Bond Angle: Cl–Si–Cl = 109.4712°

Product of the Moments of Inertia: $I_A I_B I_C = 2.60769 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

Gross *et al.*[1] measured the enthalpy of formation of $SiCl_4$(l) by the direct chlorination of silicon in a bomb calorimeter. Corrections for the difference in enthalpy content between liquid and gaseous chlorine at 25 °C and 1 atm led to the value of $\Delta_f H°(SiCl_4, l, 298.15\ K) = -165.49 \pm 0.16\ kcal \cdot mol^{-1}$. Combination of $\Delta_f H°(l, 298.15\ K)$ with $\Delta_{vap} H°(298.15\ K) = 7.09\ kcal \cdot mol^{-1}$ gives $\Delta_f H°(SiCl_4, g, 298.15\ K) = -158.4 \pm 0.3\ kcal \cdot mol^{-1}$ which is adopted in the tabulation.

Schafer and Heine[2] measured both enthalpy of solution of Si(cr) and $SiCl_4$(l) in HF solution containing AgF which gave $\Delta_f H°(298.15\ K) = 42.7 \pm 0.4\ kcal \cdot mol^{-1}$ for the overall reaction $SiCl_4(l) + 4Ag(cr) = Si(cr) + 4AgCl(cr)$ and led to $\Delta_f H°(SiCl_4, l, 298.15\ K) = -164.18\ kcal \cdot mol^{-1}$ in agreement with the value adopted, using $\Delta_f H°(AgCl, cr, 298.15\ K) = -30.37\ kcal \cdot mol^{-1}$.[3]

Wolf[4] determined the heats of solution of $SiCl_4$(l) and $Na_2SiO_3 \cdot 8H_2O$(cr) in NaOH solution and derived $\Delta_f H°(298.15\ K) = -129.3\ kcal \cdot mol^{-1}$ for $SiCl_4(l) + 13NaOH(27.8\ H_2O) = Na_2SiO_3(cr) + 4NaCl + 3H_2O(l) + 7NaOH(52.14\ H_2O)$ which leads to $\Delta_f H°(SiCl_4, l, 298.15\ K) = -166.7 \pm 2\ kcal \cdot mol^{-1}$, using all JANAF auxiliary data and heats of dilution of NaOH from Parker.[5] However, Wolf's data are suspect due to uncertainties in how he converted his data from Na_2SiO_3(calorimetric solution) to Na_2SiO_3(cr). Beezer and Mortimer[6] measured the heat of solution $\Delta_f H°(298.15\ K) = -97.0\ kcal \cdot mol^{-1}$ for $SiCl_4$(l) + 185 HF(4.335 H_2O) = 4HCl(11 H_2O) + [H_2SiF_6, 179 HF, 758 H_2O] and combined with those of Good *et al.*[7] for [H_2SiF_6, 41 HF, 174 H_2O] solution by neglecting the unknown heats of dilution between the two calorimetric solutions and obtained $\Delta_f H°(l, 298.15\ K) = -169.9\ kcal \cdot mol^{-1}$ which is in poor agreement with the value adopted. In both the measurements of Woof[4] and Beezer and Mortimer,[6] the final state of the calorimetric solution is not well defined or not well known, thus it leads to large uncertainties in their results.

Other calorimetric studies involving aqueous hydrolysis of $SiCl_4$(l) to form SiO_2(colloidal solution) have been reviewed by Gross *et al.*[1] Since the SiO_2(colloidal solution) is an ill–defined state, the heat of formation of $SiCl_4$(l) derived from hydrolysis data is quite unreliable.

Heat Capacity and Entropy

Morino and Murata[8] measured the adopted bond distance by electron diffraction. Their value was confirmed by Ryan and Hedberg.[9] Morino *et al.*[10] observed the adopted vibrational frequencies from the infrared and Raman spectra from the vapor. Infrared data of Smith[11] confirm that ν_3 is about 12 cm^{-1} larger in the vapor than in the liquid. The principal moments of inertia are: $I_A = I_B = I_C = 63.8879 \times 10^{-39}\ g \cdot cm^2$.

Vaporization Data

Vapor pressure data ranging from 20° below T_{fus}(supercooled liquid) to 10° above T_{vap} are in reasonable agreement as summarized below. The analysis is based on fugacities calculated from vapor pressures by the approximation of Lewis *et al.*[19] using $T_c = 506$ K,[20] $P_c = 37.1$ atm[21] and $\omega = 0.26$. At 298.15 K the calculated f/P is 0.982 compared with 0.984 observed by Wood.[22] The analysis also presumes a linear variation of the liquid phase C_p based on 33.3 $cal \cdot K^{-1} \cdot mol^{-1}$ at 210 K and 34.2 at 300 K. The latter value is from data of Vold[17] since earlier data (77–294 K) of Latimer[18] appear to have large positive bias below T_{fus}. The C_p at 210 K assumes Latimer's value to have about 1% bias by analogy with his data for CCl_4(l).

Source	Data Points	T/K	$\Delta_{vap}S°(298.15\ K)$, $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_{vap}H°(298.15\ K)$, $kcal \cdot mol^{-1}$
Combined[14,15,22]	19	275–341	21.45 ± 0.04	7.09 ± 0.01
[12]	Equation	183–204	21.13	7.19
[13]	6	303–323	20.85 ± 0.13	6.89 ± 0.04
[14]	12	298–341	21.48 ± 0.09	7.10 ± 0.03
[15]	6	275–330	21.40 ± 0.05	7.08 ± 0.01
[16]	13	273–333	21.55 ± 0.08	7.13 ± 0.03

Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.404	−660.570	−660.570	INFINITE
100	57.203	250.191	402.620	−15.243	−662.499	−649.333	339.177
200	78.605	297.154	338.877	−8.344	−662.854	−635.967	166.097
250	85.418	315.465	332.406	−4.235	−662.833	−629.246	131.474
298.15	90.261	330.945	330.945	0.	−662.746	−622.784	109.109
300	90.420	331.504	330.947	0.167	−662.741	−622.536	108.393
350	94.081	345.732	332.062	4.784	−662.596	−615.846	91.910
400	96.788	358.480	334.582	9.559	−662.410	−609.179	79.551
450	98.820	370.003	337.888	14.452	−662.194	−602.538	69.941
500	100.372	380.499	341.632	19.433	−661.957	−595.922	62.256
600	102.529	399.005	349.693	29.587	−661.443	−582.763	50.734
700	103.910	414.921	357.901	39.914	−660.908	−569.692	42.511
800	104.841	428.861	365.918	50.354	−660.376	−556.697	36.349
900	105.495	441.249	373.613	60.873	−659.860	−543.769	31.560
1000	105.972	452.390	380.943	71.447	−659.370	−530.896	27.731
1100	106.329	462.508	387.905	82.063	−658.910	−518.071	24.601
1200	106.604	471.772	394.513	92.710	−658.485	−505.287	21.995
1300	106.819	480.314	400.789	103.382	−658.099	−492.536	19.790
1400	106.991	488.236	406.756	114.073	−657.754	−479.814	17.902
1500	107.130	495.623	412.437	124.779	−657.454	−467.114	16.266
1600	107.245	502.541	417.854	135.498	−657.200	−454.434	14.836
1700	107.340	509.045	423.029	146.227	−707.173	−441.320	13.560
1800	107.420	515.183	427.980	156.966	−706.790	−425.693	12.353
1900	107.488	520.993	432.724	167.711	−706.419	−410.087	11.274
2000	107.546	526.508	437.276	178.463	−706.061	−394.500	10.303
2100	107.596	531.756	441.651	189.220	−705.721	−378.930	9.425
2200	107.639	536.762	445.862	199.982	−705.400	−363.376	8.628
2300	107.677	541.548	449.919	210.747	−705.102	−347.837	7.900
2400	107.710	546.131	453.833	221.517	−704.830	−332.309	7.233
2500	107.740	550.529	457.613	232.289	−704.587	−316.793	6.619
2600	107.766	554.755	461.269	243.065	−704.375	−301.285	6.053
2700	107.789	558.823	464.807	253.842	−704.197	−285.785	5.529
2800	107.810	562.743	468.235	264.622	−704.054	−270.291	5.042
2900	107.829	566.527	471.560	275.404	−703.948	−254.802	4.589
3000	107.845	570.182	474.786	286.188	−703.880	−239.315	4.167
3100	107.861	573.719	477.921	296.973	−703.848	−223.830	3.772
3200	107.875	577.144	480.969	307.760	−703.853	−208.346	3.401
3300	107.887	580.463	483.933	318.548	−703.892	−192.860	3.053
3400	107.899	583.684	486.820	329.337	−703.963	−177.374	2.725
3500	107.909	586.812	489.633	340.128	−704.064	−161.885	2.416
3600	107.919	589.852	492.374	350.919	−1088.341	−135.931	1.972
3700	107.928	592.809	495.049	361.712	−1088.075	−109.479	1.546
3800	107.936	595.687	497.660	372.505	−1087.827	−83.034	1.141
3900	107.944	598.491	500.209	383.299	−1087.592	−56.595	0.758
4000	107.951	601.224	502.701	394.094	−1087.366	−30.162	0.394
4100	107.958	603.890	505.136	404.889	−1087.143	−3.735	0.048
4200	107.964	606.491	507.519	415.685	−1086.917	22.687	−0.282
4300	107.969	609.032	509.850	426.482	−1086.683	49.104	−0.596
4400	107.975	611.514	512.133	437.279	−1086.435	75.514	−0.896
4500	107.980	613.941	514.368	448.077	−1086.169	101.919	−1.183
4600	107.984	616.314	516.559	458.875	−1085.880	128.318	−1.457
4700	107.989	618.636	518.706	469.674	−1085.564	154.710	−1.719
4800	107.993	620.910	520.812	480.473	−1085.215	181.096	−1.971
4900	107.996	623.137	522.877	491.272	−1084.830	207.473	−2.212
5000	108.000	625.319	524.904	502.072	−1084.405	233.842	−2.443
5100	108.003	627.457	526.894	512.872	−1083.938	260.203	−2.665
5200	108.007	629.555	528.848	523.673	−1083.424	286.553	−2.878
5300	108.010	631.612	530.768	534.473	−1082.862	312.894	−3.084
5400	108.012	633.631	532.654	545.275	−1082.250	339.223	−3.281
5500	108.015	635.613	534.508	556.076	−1081.584	365.541	−3.472
5600	108.018	637.559	536.331	566.878	−1080.865	391.846	−3.655
5700	108.020	639.471	538.124	577.679	−1080.090	418.137	−3.832
5800	108.022	641.350	539.887	588.482	−1079.259	444.415	−4.002
5900	108.025	643.196	541.623	599.284	−1078.370	470.678	−4.167
6000	108.027	645.012	543.331	610.087	−1077.423	496.924	−4.326

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 209.069 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 249.05\ K$

$\Delta_f H°(0\ K) = [-818.797]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-815.025]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 9.966\ kJ \cdot mol^{-1}$

Heat of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of $TiCl_4$(cr) is calculated from the corresponding quantity for $TiCl_4$(l) and the values of $H°(249.05\ K)-H°(298.15\ K)$ for both crystal and liquid.

Heat Capacity and Entropy

The heat capacity of $TiCl_4$(cr) has been reported by Latimer[1] and by Furukawa.[2] The data from the latter investigation are adopted. These data lead to a value of 44.5 $cal \cdot K^{-1} \cdot mol^{-1}$ for $S°(249.05\ K)$. This compares with Latimer's value[1] of 43.8 $cal \cdot K^{-1} \cdot mol^{-1}$ for the same quantity. The heat capacity of the solid is extrapolated to a value of 18R at 600 K, based on the known heat capacities of $TiBr_4$(cr) and TiI_4(cr). The hypothetical entropy at 298.15 K is base don the integration of the extrapolated curve and the value at the melting point.

Melting Data

The triple point is reported to be 249.05 K, with a measured enthalpy of fusion of 2.382 $kcal \cdot mol^{-1}$, by Furukawa.[2] Latimer[1] reported values of 248.0 K and 2.233 $kcal \cdot mol^{-1}$ for these quantities. The former data are adopted.

References

[1]W. M. Latimer, J. Amer. Chem. Soc. **44**, 90 (1922).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−26.963	−818.797	−818.797	INFINITE
100	84.480	92.582	312.283	−21.970	−820.188	−790.818	413.081
200	112.380	160.341	220.513	−12.034	−818.244	−762.082	199.035
249.046	124.710	186.262	211.264	−6.227	--- CRYSTAL <---> LIQUID ---		
298.15	129.460	209.069	209.069	.000	−815.025	−735.166	128.798
300	129.704	209.871	209.072	.240	−814.958	−734.671	127.918
400	139.540	248.622	214.288	13.733	−811.018	−708.487	92.519
500	145.600	280.480	224.436	28.022	−806.612	−683.357	71.390

PREVIOUS: March 1964 CURRENT: December 1967

$S°(298.15\ K) = 252.38 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 249.05\ K$

$\Delta_f H°(298.15\ K) = -804.2 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 9.966\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(TiCl_4, l, 298.15\ K)$, is calculated from that of $TiCl_4(g)$ and the value of $\Delta_{vap} H°(298.15\ K)$. The value of $\Delta_{vap} H°(298.15\ K)$ is determined from 2nd and 3rd law analyses of fugacity as follows.

Source	Method	T/K	Data Points	$\Delta_{vap} H°(298.15\ K)$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
Pike and Foster[1]	Manometric	363–415	18*	9.82 ± 0.02	9.83	0.0 ± 0.1	−192.2
Seryakov *et al.*[2]	Manometric	358–412	8	9.79 ± 0.03	9.84	0.1 ± 0.1	−192.2
Schafer and Zeppenick[3]	Isoteniscope	313–358	17*	9.86 ± 0.02	9.82	−0.1 ± 0.0	−192.2
Schafer and Zeppenick[3]	Isoteniscope	313–357	16**	9.80 ± 0.01	9.82	0.0 ± 0.0	−192.2
Schafer and Zeppenick[3]	Isoteniscope	313–357	16	9.91 ± 0.02	9.83	−0.2 ± 0.1	−192.2
Schafer and Zeppenick[3]	Isoteniscope	312–359	17	9.90 ± 0.02	9.83	−0.2 ± 0.1	−192.2
Weed[4]	Manometric	298–319	***	9.79 ± 0.01	9.82	0.1 ± 0.0	−192.2
Weed[4]	Manometric	298–319	***	9.81 ± 0.01	9.82	0.0 ± 0.0	−192.2
Weed[4]	Spectra	250–302	***	9.69 ± 0.01	9.80	0.4 ± 0.0	−192.2

* Two Points rejected to failure of a statistical test
** Three points rejected due to failure of a statistical test
*** Selected points from extensive data

3rd law analyses of the several vapor pressure sets result in drifts which are proportional to the mean temperatures. Conversion of these data to fugacity eliminates this temperature dependence and the drifts are then scattered randomly about a constant value. This constant value is made to be essentially zero by methods described on the $TiCl_4(g)$ table. The conversion to fugacity was made using Pitzer's method for normal fluids.[5] The calculation was carried out using the value of 45.7 atm. for the critical pressure, P_c, reported by Minzer[6] and estimated values of 643 ± 15 K for the critical temperature, T_c, and 0.23 ± 0.03 for the acentric constant, ω. Schafer *et al.*[7] reported a calorimetric determination of $\Delta_{vap} H°(298.15\ K)$. Their value of 9.9 ± 0.02 $kcal \cdot mol^{-1}$ was used to check the reliability of their equipment, assuming that the vapor pressure data[3] gave a more accurate determination of $\Delta_{vap} H°(298.15\ K)$. The adopted value of $\Delta_{vap} H°(298.15\ K)$ is 9.82 ± 0.02 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The entropy and heat capacity of $TiCl_4(l)$ has been measured by Furukawa.[8] His reported values are adopted.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is taken as the temperature at which $K_p = 1$ for the reaction $TiCl_4(l) = TiCl_4(g)$. The vapor pressure data are discussed above.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200	144.710	194.513	265.642	−14.226	−809.576	−760.247	198.556
249.046	144.910	226.279	254.876	−7.121	--- CRYSTAL <---> LIQUID ---		
298.15	145.205	252.379	252.379	.000	−804.165	−737.219	129.158
300	145.220	253.277	252.382	.269	−804.069	−736.804	128.289
400	146.170	295.195	258.090	14.842	−799.049	−715.147	93.389
500	147.080	327.909	268.901	29.504	−794.269	−694.728	72.578
600	147.985	354.805	281.043	44.258	−789.606	−675.260	58.787
700	148.892	377.685	293.255	59.101	−784.994	−656.567	48.994
800	149.800	397.626	305.081	74.036	−780.383	−638.535	41.692
900	150.709	415.323	316.365	89.061	−775.789	−621.080	36.047
1000	151.620	431.249	327.071	104.178	−771.267	−604.133	31.557

PREVIOUS: March 1964 CURRENT: December 1967

0 to 249.05 K crystal
above 249.05 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−37.824	−818.798	−818.798	INFINITE
100	84.480	92.582	420.895	−32.831	−820.189	−790.820	413.082
200	112.380	160.341	274.819	−22.896	−818.245	−762.083	199.036
249.046	124.710	186.262	254.876	−17.088	___ CRYSTAL <--> LIQUID ___		
249.046	144.910	226.279	254.876	−7.122	TRANSITION		
298.15	145.205	252.379	252.379	.000	−804.165	−737.219	129.158
300	145.220	253.277	252.382	.269	−804.069	−736.804	128.289
400	146.170	295.195	258.090	14.842	−799.049	−715.147	93.389
500	147.080	327.909	268.901	29.504	−794.269	−694.728	72.578
600	147.985	354.805	281.043	44.258	−789.606	−675.260	58.787
700	148.892	377.685	293.255	59.101	−784.994	−656.567	48.994
800	149.800	397.626	305.081	74.036	−780.383	−638.535	41.692
900	150.709	415.323	316.365	89.061	−775.789	−621.080	36.047
1000	151.620	431.249	327.071	104.178	−771.267	−604.133	31.557

PREVIOUS: CURRENT: December 1967

$S°(298.15\ K) = 354.889 \pm 2.9\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -761.58 \pm 3.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -763.16 \pm 3.8\ kJ·mol^{-1}$

Vibrational Frequences and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
368 (1)	498.5(3)
111 (2)	131 (3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distance: Ti–Cl = 2.185 Å
Bond Angle: Cl–Ti–Cl = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 4.21057 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of $TiCl_4$(g) and $TiCl_4$(l) has been measured by several investigators. The results of these measurements are as follows.

Source	Method	Reaction	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} $TiCl_4$(l)	$TiCl_4$(g)
Johnson *et al.*[1]	Calorimetric	$Ti(cr) + 2\ Cl_2(g) = TiCl_4(g)$	(−192.2)	−182.4 ± 0.7
Farber and Darnell[2]	Equilibrium	$TiO_2(cr) + 4\ HCl(g) = TiCl_4(g) + 2\ H_2O(g)$	(−192.7)	−182.9 ± 0.5
Skinner and Ruehrwein[3]	Calorimetric	$Ti(cr) + xCl_2(g) = [TiCl_4 + (x-2)Cl_2]$ soln	−190.3 ± 3.0	(−180.5)
Gross *et al.*[4]	Calorimetric	$Ti(cr) + xCl_2(\ell) = [TiCl_4 + (x-2)Cl_2]$ soln	−191.5 ± 0.3	(−181.7)
Krieve *et al.*[5]	Calorimetric	$Ti(cr) + xCl_2(g) = [TiCl_4 + (x-2)Cl_2]$ soln	−190.0 ± 0.4	(−180.2)
Thomsen[6]		$TiCl_4(l) + 2\ H_2O(l) = 4\ HCl_{(0.002\ m)} + TiO_2(cr)$	−194.5	(−184.7)

The chosen value of $\Delta_f H°(298.15\ K)$ is that reported by Johnson *et al.*[1] This investigation has the advantage of being independent of the enthalpy of vaporization of chlorine and any heats of solution in deriving the value of the enthalpy of formation.

Heat Capacity and Entropy

The adopted value for the interatomic distance is that reported by Kimura *et al.*[7] The tetrahedral structure was established by the Raman work of Bhagavantam.[8] The vibrational frequencies determined from the infrared and Raman spectra of $TiCl_4$ by Hawkins and Carpenter[9] are adjusted downward 8 cm^{-1} for ν_2 and ν_4 so that the enthalpies of vaporization determined by both 2nd and 3rd law methods are in agreement. See $TiCl_4$(l) table for details. The principal moments of inertia are: $I_A = I_B = I_C = 74.9515 \times 20^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.613	−761.583	−761.583	INFINITE
100	67.436	265.427	432.828	−16.740	−763.094	−751.010	392.287
200	86.118	318.509	363.378	−8.974	−763.321	−738.791	192.953
250	91.800	338.374	356.444	−4.517	−763.265	−732.664	153.082
298.15	95.614	354.889	354.889	0.	−763.162	−726.779	127.329
300	95.735	355.481	354.891	0.177	−763.157	−726.553	126.504
350	98.486	370.458	356.068	5.037	−763.022	−720.463	107.523
400	100.452	383.744	358.712	10.013	−762.875	−714.393	93.290
450	101.892	395.663	362.167	15.073	−762.724	−708.342	82.222
500	102.970	406.457	366.065	20.196	−762.574	−702.307	73.370
600	104.441	425.371	374.417	30.572	−762.288	−690.281	60.094
700	105.366	441.546	382.880	41.066	−762.026	−678.301	50.615
800	105.982	455.658	391.114	51.635	−761.781	−666.358	43.509
900	106.412	468.167	398.994	62.256	−761.591	−654.442	37.983
1000	106.723	479.396	406.482	72.914	−761.528	−642.542	33.563
1100	106.956	489.579	413.581	83.598	−761.659	−630.638	29.947
1200	107.134	498.893	420.307	94.303	−765.972	−618.594	26.927
1300	107.273	507.474	426.687	105.024	−765.777	−606.321	24.362
1400	107.384	515.428	432.745	115.757	−765.666	−594.060	22.165
1500	107.474	522.840	438.507	126.500	−765.655	−581.804	20.260
1600	107.547	529.779	443.997	137.251	−765.758	−569.544	18.594
1700	107.609	536.301	449.237	148.009	−765.990	−557.274	17.123
1800	107.660	542.453	454.246	158.773	−766.366	−544.987	15.815
1900	107.703	548.275	459.043	169.541	−766.900	−532.674	14.644
2000	107.741	553.801	463.644	180.313	−782.294	−519.876	13.578
2100	107.773	559.058	468.063	191.089	−783.940	−506.714	12.604
2200	107.801	564.072	472.314	201.867	−785.606	−493.474	11.717
2300	107.825	568.865	476.409	212.649	−787.297	−480.157	10.905
2400	107.846	573.454	480.357	223.432	−789.015	−466.767	10.159
2500	107.865	577.857	484.170	234.218	−790.762	−453.304	9.471
2600	107.882	582.088	487.855	245.005	−792.542	−439.771	8.835
2700	107.897	586.160	491.421	255.794	−794.357	−426.168	8.245
2800	107.910	590.084	494.875	266.584	−796.208	−412.498	7.695
2900	107.922	593.871	498.224	277.376	−798.097	−398.761	7.182
3000	107.933	597.530	501.474	288.169	−800.024	−384.958	6.703
3100	107.943	601.069	504.630	298.963	−801.988	−371.090	6.253
3200	107.951	604.496	507.697	309.757	−803.989	−357.158	5.830
3300	107.960	607.818	510.681	320.553	−806.025	−343.163	5.432
3400	107.967	611.041	513.586	331.349	−808.093	−329.106	5.056
3500	107.974	614.171	516.415	342.146	−810.191	−314.988	4.701
3600	107.980	617.213	519.173	352.944	−812.315	−300.809	4.365
3700	107.986	620.171	521.863	363.742	−1223.559	−278.783	3.936
3800	107.991	623.051	524.488	374.541	−1224.487	−253.236	3.481
3900	107.996	625.857	527.051	385.340	−1225.483	−227.664	3.049
4000	108.000	628.591	529.556	396.140	−1226.541	−202.066	2.639
4100	108.004	631.258	532.004	406.940	−1227.654	−176.440	2.248
4200	108.008	633.860	534.398	417.741	−1228.815	−150.787	1.875
4300	108.012	636.402	536.741	428.542	−1230.017	−125.105	1.520
4400	108.015	638.885	539.034	439.343	−1231.253	−99.395	1.180
4500	108.019	641.312	541.280	450.145	−1232.517	−73.657	0.855
4600	108.021	643.687	543.481	460.947	−1233.802	−47.890	0.544
4700	108.024	646.010	545.638	471.749	−1235.101	−22.096	0.246
4800	108.027	648.284	547.752	482.552	−1236.408	3.726	−0.041
4900	108.029	650.512	549.827	493.355	−1237.718	29.576	−0.315
5000	108.032	652.694	551.863	504.158	−1239.024	55.452	−0.579
5100	108.034	654.833	553.861	514.961	−1240.322	81.355	−0.833
5200	108.036	656.931	555.823	525.765	−1241.605	107.283	−1.078
5300	108.038	658.989	557.750	536.568	−1242.871	133.235	−1.313
5400	108.040	661.009	559.643	547.372	−1244.113	159.211	−1.540
5500	108.041	662.991	561.504	558.176	−1245.329	185.210	−1.759
5600	108.043	664.938	563.334	568.980	−1246.515	211.230	−1.970
5700	108.044	666.850	565.134	579.785	−1247.666	237.272	−2.174
5800	108.046	668.729	566.904	590.589	−1248.781	263.333	−2.372
5900	108.047	670.576	568.645	601.394	−1249.857	289.413	−2.562
6000	108.049	672.392	570.359	612.199	−1250.891	315.511	−2.747

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K)$ = [198.322] $J·K^{-1}·mol^{-1}$
T_d = [771] K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -443.086 \pm 62.8\ kJ·mol^{-1}$

Heat of Formation

The heat of formation, $\Delta_f H°(WCl_4, cr, 298.15\ K) = -105.9\ kcal·mol^{-1}$, is calculated from $\Delta_r H°(298.15\ K) = 58.9\ kcal·mol^{-1}$ for 3 $WCl_4(cr) = WCl_2(cr) + 2\ WCl_5(g)$. The value of $\Delta_r H°(298.15\ K)$ is calculated by the third law method from decomposition pressure data in the temperature range from 354 °C to 436 °C reported by Shchukarev *et al.*[1] The second law, $\Delta_r H°(298.15\ K) = 73.6 \pm 7.9\ kcal·mol^{-1}$ and the third law drift is $-24 \pm 12\ cal·K^{-1}·mol^{-1}$ which would correspond to a total entropy discrepancy of $-8 \pm 4\ cal·K^{-1}·mol^{-1}$ per mole of WCl_4. This entropy discrepancy is probably within the combined uncertainty of the data and the estimated entropies for the three species. Shchukarev *et al.*[2] have shown that decomposition pressures are essentially independent of the composition in the solid phase until WCl_4(cr) is almost completely decomposed to WCl_2(cr). This is consistent with the assumption of solid phase activities of unity which we have used in the equilibrium analysis.

Heat Capacity and Entropy

$C_p°(298.15\ K) = 6.2\ cal·K^{-1}\ g·atom^{-1}$ and $C_p°(700\ K) = 7.25\ cal·K^{-1}\ g·atom^{-1}$ are estimated using the method described by Kubaschewski and Evans.[3] Between 298 and 700 K, which is near the decomposition temperature, the heat capacity is obtained by linear interporation.

The entropy of WCl_4(cr), $S°(298.15\ K) = 47.4\ cal·K^{-1}·mol^{-1}$, is estimated by the method of Latimer.[4]

Temperature of Decomposition

T_{dcm} = 771 K (f = atm) is calculated as the temperature at which the Gibbs energy change of the reaciton 3 $WCl_4(cr) = WCl_2(cr) + 2\ WCl_5(g)$ approaches zero. We have also derived an approximate value of decomposition temperature, T_{dcm} = 744 K, by extrapolation to one atmosphere total pressure of a log P versus $1/T$ fit of the decomposition pressure data reported by Shchukarev *et al.*[5] The difference between the two decomposition temperatures is related to the second law entropy and the adopted entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	129.704	198.322	198.322	0.	−443.086	−359.456	62.975
300	129.830	199.124	198.324	0.240	−443.016	−358.937	62.496
400	135.290	237.222	203.482	13.496	−439.164	−331.485	43.288
500	140.750	267.997	213.401	27.298	−435.019	−305.038	31.867
600	146.210	294.142	224.732	41.646	−430.492	−279.460	24.329
700	151.670	317.090	236.319	56.540	−425.543	−254.673	19.004
800	157.130	337.700	247.724	71.981	−420.147	−230.626	15.058
900	162.507	356.526	258.782	87.970	−414.287	−207.283	12.030
1000	167.025	373.888	269.436	104.452	−408.012	−184.616	9.643
1100	170.875	389.994	279.672	121.353	−401.390	−162.594	7.721
1200	173.929	404.997	289.498	138.598	−394.493	−141.188	6.146
1300	176.439	419.019	298.928	156.119	−387.387	−120.366	4.836
1400	178.657	432.178	307.981	173.876	−380.110	−100.098	3.735
1500	180.623	444.572	316.678	191.841	−372.689	−80.355	2.798
1600	182.422	456.287	325.040	209.995	−365.145	−61.111	1.995
1700	184.096	467.397	333.090	228.321	−357.493	−42.343	1.301
1800	185.770	477.967	340.848	246.815	−349.738	−24.028	0.697
1900	187.276	488.052	348.332	265.468	−341.892	−6.147	0.169
2000	188.698	497.695	355.561	284.268	−333.969	11.319	−0.296

PREVIOUS: September 1962 CURRENT: December 1966

$S°(298.15\ K) = 379.171\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -335.256 \pm 33\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -335.975 \pm 33\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[10000]	[3]
[30000]	[3]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[380](1)	[390](3)
[110](2)	[115](3)

Ground State Quantum Weight: [3] σ = [12]
Point Group: [T_d]
Bond Distance: W–Cl = [2.26] Å
Bond Angle: Cl–W–Cl = [109.47]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.154 \times 10^{-114}]\ g^3·cm^6$

Heat of Formation

The heat of formation, $\Delta_f H°(WCl_4, g, 298.15\ K) = -80.3\ kcal·mol^{-1}$, is calculated from $\Delta_r H° = 37.7\ kcal·mol^{-1}$ for $WCl_6(g) \rightarrow WCl_4(g) + Cl_2(g)$. The value of $\Delta_r H°(298.15\ K)$ is calculated by the third law method from the equation for log K_p given by Shchukarev and Suvorov.[1] The second law $\Delta_r H°(298.15\ K)$ is 43.6 $kcal·mol^{-1}$ and the third law drift is $-9.6\ cal·K^{-1}·mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be tetrahedral similar to those of $SiCl_4$, $TiCl_4$, VCl_4, $GeCl_4$, $ZrCl_4$, $SnCl_4$, $PbCl_4$. The bond distance is estimated to be the same as that in $WCl_6(g)$. The three principal moments of inertia are: $I_A = I_B = I_C = 80.18 \times 10^{-39}\ g·cm^2$.

All vibrational frequencies are estimated from those of $SiCl_4$, $TiCl_4$, VCl_4, $GeCl_4$, $SnCl_4$ and $PbCl_4$ given by Nakamoto.[2]

If it is considered that the metal atoms are effectively ionized, then the W^{4+} will have 2 d electrons in a field of chloride ions. The electronic splitting would be roughly the inverse of that in $NiCl_2(g)$, as given by DeKock and Gruen,[3] where Ni has a d^8 configuration. By analogy with the splitting in $NiCl_2$, the low lying electronic levels are estimated to be 10000 cm^{-1} and 30000 cm^{-1}, both triplets.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−22.616	−335.256	−335.256	INFINITE
100	70.716	285.257	460.891	−17.563	−336.680	−326.443	170.516
200	90.681	341.319	388.116	−9.359	−336.559	−316.182	82.578
250	95.721	362.138	380.897	−4.690	−336.284	−311.119	65.005
298.15	98.865	379.285	379.285	0.	−335.975	−306.300	53.662
300	98.963	379.897	379.287	0.183	−335.963	−306.115	53.299
350	101.124	395.325	380.501	5.189	−335.619	−301.168	44.947
400	102.620	408.932	383.221	10.284	−335.265	−296.270	38.689
450	103.691	421.084	386.765	15.444	−334.910	−291.417	33.827
500	104.481	432.052	390.754	20.649	−334.557	−286.604	29.941
600	105.540	451.203	399.279	31.154	−333.874	−277.078	24.122
700	106.197	467.525	407.891	41.744	−333.229	−267.664	19.973
800	106.630	481.736	416.253	52.386	−332.630	−258.338	16.868
900	106.931	494.314	424.241	63.065	−332.081	−249.085	14.457
1000	107.148	505.592	431.822	73.770	−331.584	−239.891	12.531
1100	107.312	515.812	439.000	84.493	−331.140	−230.744	10.957
1200	107.439	525.155	445.796	95.231	−330.750	−221.634	9.647
1300	107.544	533.759	452.236	105.980	−330.415	−212.555	8.541
1400	107.635	541.732	458.347	116.739	−330.136	−203.500	7.593
1500	107.719	549.161	464.156	127.507	−329.913	−194.463	6.772
1600	107.801	556.116	469.689	138.283	−329.746	−185.438	6.054
1700	107.885	562.654	474.967	149.067	−329.636	−176.423	5.421
1800	107.974	568.823	480.011	159.860	−329.583	−167.412	4.858
1900	108.069	574.663	484.841	170.662	−329.588	−158.403	4.355
2000	108.173	580.209	489.472	181.474	−329.651	−149.392	3.902
2100	108.284	585.489	493.919	192.297	−329.776	−140.376	3.492
2200	108.403	590.529	498.197	203.131	−329.962	−131.353	3.119
2300	108.530	595.351	502.317	213.978	−330.212	−122.320	2.778
2400	108.663	599.973	506.290	224.838	−330.529	−113.275	2.465
2500	108.802	604.411	510.127	235.711	−330.913	−104.215	2.177
2600	108.945	608.681	513.836	246.598	−331.365	−95.138	1.911
2700	109.091	612.796	517.425	257.500	−331.913	−86.042	1.665
2800	109.239	616.766	520.903	268.416	−332.593	−76.924	1.435
2900	109.388	620.602	524.275	279.348	−333.444	−67.778	1.221
3000	109.537	624.313	527.548	290.294	−334.495	−58.600	1.020
3100	109.684	627.907	530.728	301.255	−335.789	−49.383	0.832
3200	109.830	631.391	533.819	312.231	−337.355	−40.120	0.655
3300	109.972	634.773	536.827	323.221	−339.218	−30.803	0.488
3400	110.110	638.058	539.757	334.225	−341.410	−21.425	0.329
3500	110.245	641.252	542.611	345.243	−343.994	−11.978	0.179
3600	110.374	644.360	545.395	356.274	−347.062	−2.449	0.036
3700	110.499	647.385	548.110	367.318	−385.476	7.363	−0.104
3800	110.618	650.334	550.762	378.373	−386.215	17.990	−0.247
3900	110.732	653.209	553.352	389.441	−386.955	28.636	−0.384
4000	110.840	656.013	555.884	400.520	−387.691	39.302	−0.513
4100	110.942	658.752	558.359	411.609	−388.420	49.986	−0.637
4200	111.039	661.426	560.782	422.708	−389.136	60.688	−0.755
4300	111.130	664.040	563.153	433.816	−389.835	71.406	−0.867
4400	111.215	666.596	565.475	444.934	−390.513	82.141	−0.975
4500	111.295	669.096	567.750	456.059	−391.165	92.890	−1.078
4600	111.370	671.543	569.980	467.193	−391.786	103.654	−1.177
4700	111.440	673.939	572.166	478.333	−392.373	114.430	−1.272
4800	111.505	676.286	574.311	489.480	−392.922	125.219	−1.363
4900	111.566	678.586	576.416	500.634	−393.430	136.020	−1.450
5000	111.622	680.840	578.482	511.793	−393.892	146.829	−1.534
5100	111.674	683.051	580.510	522.958	−394.308	157.648	−1.615
5200	111.722	685.220	582.503	534.128	−394.673	168.474	−1.692
5300	111.766	687.349	584.461	545.302	−394.985	179.307	−1.767
5400	111.807	689.438	586.386	556.481	−395.243	190.145	−1.839
5500	111.844	691.490	588.279	567.664	−395.444	200.988	−1.909
5600	111.879	693.506	590.140	578.850	−395.588	211.833	−1.976
5700	111.910	695.486	591.971	590.039	−395.672	222.681	−2.041
5800	111.939	697.433	593.772	601.232	−395.697	233.530	−2.103
5900	111.966	699.347	595.545	612.427	−395.661	244.378	−2.164
6000	111.990	701.229	597.291	623.625	−395.563	255.225	−2.222

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 181.42 \pm 0.7\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 710 \pm 2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -981.59 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -980.52 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 50.2 \pm 12.6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Gal'chenko *et al.*[1] determined enthalpy of formation of $ZrCl_4$(cr) by the direct chlorination of highly pure Zr metal in a bomb calorimeter. Complete chlorination of the metal was accomplished as indicated by the absence of unreacted metal and of lower chlorides. They reported $\Delta_f H°(ZrCl_4, cr, 298.15\ K) = -234.17 \pm 0.28\ kcal \cdot mol^{-1}$.

Gal'chenko *et al.*[2] had also earlier determined the enthalpy of formation of $ZrCl_4$(cr) by a similar technique and reported -234.35 ± 2.1 kcal·mol^{-1}. Gross *et al.*[6] measured calorimetrically the chlorination of Zr(cr) with liquid chlorine. His results led to $\Delta_f H°(298.15\ K) = -234.7 \pm 0.4\ kcal \cdot mol^{-1}$ for $ZrCl_4$(cr). We adopt $\Delta_f H°(298.15\ K) = -234.35 \pm 0.4\ kcal \cdot mol^{-1}$ which is a weighted mean of these three studies. This adopted value is identical to that suggested by NBS.[4]

Less reliable studies leading to $\Delta_f H°(298.15\ K)$ values have been reported by Siemonsen and Siemonsen,[7] and Beck.[8] Equilibrium studies by Hildenbrand *et al.*[3] and Morozov and Korshunov[5] suggest $\Delta_f H°(298.15\ K)$ values 1–3 kcal·mol^{-1} less negative than our adopted value.

Heat Capacity and Entropy

Todd[9] measured the low temperature heat capacities from 52.6 to 296.7 K, and made an extrapolation to 0 K which yielded an entropy of 8.12 cal·K^{-1}·mol^{-1} at 51 K. We adopt the measured heat capacities but make our own extrapolation to 0 K, based on the ratio of the measured heat capacities of ZrF_4,[10] TiF_4[11] and $TiCl_4$[12] from 6 to 50 K. This extrapolation gives $S°(50\ K) = 6.758 \pm 0.7\ cal \cdot K^{-1} \cdot mol^{-1}$ which is adopted. Coughlin and King[13] measured high temperature enthalpy data from 335.9 to 566.8 K by drop calorimetry. Their data are smoothly joined with Todd's low temperature heat capacities.

Fusion Data

The melting point, $T_{fus} = 710 \pm 2$ K, has been observed by Rahlfs and Fischer,[14] Palko *et al.*,[15] and Denisova *et al.*[16, 17] Nisel'son[18] observed a melting temperature of 708.7 K. Heat of melting data may be extracted from Palko *et al.*[15] and Denisova *et al.*[16, 17] A weighted average $\Delta_{fus} H° = 12 \pm 3\ kcal \cdot mol^{-1}$ is adopted for the heat of melting.

Sublimation Data

Several sets of sublimation studies are summarized below, using a 2nd and 3rd analysis.

Source	Method	Data Points	T/K	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
[14]	static	11	535–607	27.36 ± 0.43	26.31 ± 0.13	−1.9 ± 0.8
[15]	static (diaphragm)	50[a]	503–575	25.75 ± 0.20	26.39 ± 0.17	1.1 ± 0.3
	static (cap. bridge)	36[b]	580–689	25.87 ± 0.28	26.40 ± 0.16	0.8 ± 0.4
[19]	glass Bourdon gage	eqn	503–603	26.19	26.33	0.3
[16]	static	17[c]	625–709	25.51 ± 0.34	26.42 ± 0.11	1.3 ± 0.5
[20]	mass spec.	eqn	373–448	27.14	26.66	−1.2
[21]	—	eqn	376–493	26.59	26.44	−0.4

(a)3, (b)2, (c)1 points rejected due to failure of a statistical test.

A mean of the 3rd law values, $\Delta_{sub}H°(298.15\ K) = 26.42 \pm 0.12\ kcal \cdot mol^{-1}$, is adopted. The sublimation temperature, T_{sub}, is obtained from the Gibbs energy crossover between the crystal and gas. Since T_{sub} is lower than T_{fus}, the liquid phase is thermodynamically unstable at normal conditions.

In analyzing the vapor pressures for the sublimation studies, corrections were made for non-ideality by means of the equation $\Delta G°/T = -R \ln p - Bp/T$. The Bertholet equation of state and the critical constants $T_c = 776.65$ K and $p_c = 57.4$ atm as determined by Nisel'son and Sokolova[22] are used to calculate B.

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Continued on page 940

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−24.924	−981.585	−981.585	INFINITE
100	77.990	70.509	278.997	−20.849	−984.220	−952.064	497.307
200	108.282	135.750	192.067	−11.263	−982.903	−920.258	240.347
298.15	119.788	181.418	181.418	0.	−980.520	−889.999	155.924
300	119.913	182.160	181.421	0.222	−980.471	−889.438	154.865
400	125.394	217.491	186.201	12.516	−977.676	−859.509	112.240
500	128.700	245.848	195.387	25.230	−974.729	−830.306	86.741
600	131.127	269.533	205.825	38.225	−971.690	−801.705	69.795
700	133.135	289.899	216.415	51.439	−968.586	−773.619	57.728
800	134.976	307.799	226.741	64.846	−965.428	−745.981	48.708
900	136.649	323.794	236.652	78.428	−962.235	−718.742	41.715
1000	138.239	338.274	246.101	92.173	−959.019	−691.859	36.139

PREVIOUS: December 1969 CURRENT: June 1975

$S°(298.15\ K) = 367.72 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -868.68 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -869.98 \pm 2.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
377(1)	418(3)
98(2)	113(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: 2.32 ± 0.02 Å
Bond Angle: Cl–Zr–Cl = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = 6.03340 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of gaseous $ZrCl_4$, $\Delta_f H°(298.15\ K) = -207.76 \pm 0.5\ kcal \cdot mol^{-1}$ is calculated from the enthalpies of formation and sublimation of the crystal.[1]

Hildenbrand *et al.*[14] determined the equilibrium constants by the transpiration method for the reaction: $ZrO_2(cr) + 4\ HCl(g) = ZrCl_4(g) + 2\ H_2O(g)$. 2nd and 3rd law analyses for their data are given below. The enthalpy of formation derived from this study is in fair agreement with the value adopted.

Series	Data Points	T/K	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
I	10	1171–1373	28.94 ± 0.44	29.16 ± 0.15	0.17 ± 0.34	−205.80
II	9	1169–1374	31.36 ± 0.60	29.65 ± 0.28	-1.19 ± 0.47	−205.11

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark *et al.*,[2,3] who recorded the Raman spectra of $ZrCl_4$ in the vapor phase (380–420 °C). These studies indicated that $ZrCl_4$ is a tetrahedral monomer in the vapor phase. Shimanouchi,[4] in his compilation of molecular vibrational frequencies, adopted the values of Clark *et al.*[2,3] for $ZrCl_4(g)$. Pontrelli[5] also observed in the Raman spectra all four fundamental vibrational frequencies (376, 99, 418, and 110 cm^{-1}). These values are in excellent agreement with those of Clark *et al.*[2,3]

Other experimental studies involving the vibrational frequencies are as follows. Wilmshurst[6] observed one fundamental vibrational frequency (421 cm^{-1}) in the infrared spectrum of $ZrCl_4$ vapor, while Buchler *et al.*[7] found the same fundamental mode at 423 cm^{-1}. Delwaulle and Francois[8] observed the symmetric stretching vibration (383 cm^{-1}) from the Raman spectra of $ZrCl_4$ in PCl_5 and $POCl_3$. Bobovich[9] reported the symmetric stretching vibration (315 cm^{-1}) from a partially polarized band in his Raman spectrometric studies.

Spiridonov *et al.*[10] measured the bond distance Zr–Cl = 2.32 ± 0.02 Å in the vapor phase by electron diffraction. The molecule was also found to be a regular tetrahedron. The same bond distance was also reported by Lister and Sutton[11] and Kimura *et al.*[12] Rabitz and Fischer,[13] through vapor density measurements, had earlier concluded that $ZrCl_4$ was monomeric in the vapor phase. The principal moments of inertia are $I_A = I_B = I_C = 84.4995 \times 10^{-19}\ g \cdot cm^2$.

Much literature has been published on the inter–relationships between force constants and vibrational frequencies. Since the majority of these articles are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of $ZrCl_4(g)$. One exception is that Clark *et al.*[2] calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is identical to ours in the range 100–1000 K.

References

[1] JANAF Thermochemical Tables: $ZrCl_4$(cr), 6–30–75; ZrO_2(cr), 12–31–65; Hcl(g), 9–30–64; H_2O(g), 3–31–61.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−22.561	−868.681	−868.681	INFINITE
100	70.794	274.385	448.659	−17.427	−870.258	−858.489	448.429
200	89.827	330.054	376.481	−9.285	−870.384	−846.599	221.109
250	94.964	350.691	369.317	−4.656	−870.209	−840.671	175.649
298.15	98.234	367.716	367.716	0.	−869.979	−835.003	146.289
300	98.336	368.324	367.718	0.182	−869.970	−834.786	145.349
350	100.611	383.665	368.925	5.159	−869.701	−828.943	123.713
400	102.199	397.209	371.630	10.232	−869.419	−823.139	107.491
450	103.342	409.316	375.157	15.372	−869.136	−817.371	94.878
500	104.188	420.250	379.128	20.561	−868.857	−811.635	84.791
600	105.328	439.355	387.620	31.041	−868.332	−800.240	69.667
700	106.036	455.649	396.203	41.612	−867.872	−788.929	58.871
800	106.505	469.840	404.540	52.241	−867.492	−777.679	50.777
900	106.831	482.405	412.507	62.908	−867.213	−766.470	44.485
1000	107.066	493.673	420.070	73.604	−867.047	−755.286	39.452
1100	107.241	503.886	427.232	84.320	−867.003	−744.113	35.335
1200	107.374	513.224	434.015	95.051	−870.797	−732.717	31.894
1300	107.479	521.822	440.443	105.793	−870.467	−721.224	28.979
1400	107.562	529.791	446.544	116.546	−870.189	−709.755	26.481
1500	107.629	537.214	452.344	127.305	−869.975	−698.303	24.317
1600	107.684	544.162	457.868	138.071	−869.835	−686.863	22.424
1700	107.730	550.692	463.138	148.842	−869.783	−675.430	20.753
1800	107.768	556.851	468.175	159.617	−869.829	−663.996	19.269
1900	107.801	562.678	472.996	170.395	−869.985	−652.558	17.940
2000	107.829	568.208	477.620	181.177	−870.265	−641.108	16.744
2100	107.853	573.470	482.060	191.961	−870.682	−629.640	15.661
2200	107.874	578.488	486.330	202.747	−892.570	−617.403	14.659
2300	107.892	583.283	490.442	213.536	−893.714	−604.870	13.737
2400	107.908	587.876	494.407	224.326	−894.886	−592.287	12.891
2500	107.922	592.281	498.234	235.117	−896.088	−579.654	12.111
2600	107.934	596.514	501.933	245.910	−897.323	−566.972	11.391
2700	107.945	600.588	505.512	256.704	−898.593	−554.242	10.722
2800	107.955	604.513	508.978	267.499	−899.900	−541.465	10.101
2900	107.964	608.302	512.338	278.295	−901.244	−528.640	9.522
3000	107.972	611.962	515.598	289.092	−902.627	−515.768	8.980
3100	107.979	615.503	518.764	299.889	−904.048	−502.850	8.473
3200	107.986	618.931	521.841	310.688	−905.505	−489.885	7.997
3300	107.992	622.254	524.834	321.487	−906.998	−476.873	7.548
3400	107.998	625.478	527.747	332.286	−908.524	−463.817	7.126
3500	108.003	628.609	530.584	343.086	−910.079	−450.715	6.727
3600	108.007	631.651	533.349	353.887	−911.660	−437.567	6.349
3700	108.012	634.611	536.046	364.687	−913.263	−424.376	5.991
3800	108.016	637.491	538.678	375.489	−914.883	−411.142	5.652
3900	108.019	640.297	541.248	386.291	−916.517	−397.864	5.329
4000	108.023	643.032	543.759	397.093	−918.157	−384.544	5.022
4100	108.026	645.699	546.213	407.895	−919.800	−371.183	4.729
4200	108.029	648.302	548.612	418.698	−921.441	−357.783	4.450
4300	108.031	650.844	550.960	429.501	−923.073	−344.343	4.183
4400	108.034	653.328	553.259	440.304	−924.692	−330.865	3.928
4500	108.036	655.756	555.510	451.108	−926.294	−317.351	3.684
4600	108.038	658.130	557.715	461.911	−927.872	−303.801	3.450
4700	108.040	660.454	559.876	472.715	−929.423	−290.219	3.225
4800	108.042	662.728	561.995	483.519	−1491.880	−264.985	2.884
4900	108.044	664.956	564.074	494.324	−1493.016	−239.413	2.552
5000	108.046	667.139	566.113	505.128	−1494.130	−213.818	2.234
5100	108.047	669.279	568.115	515.933	−1495.217	−188.200	1.928
5200	108.049	671.377	570.081	526.738	−1496.274	−162.563	1.633
5300	108.050	673.435	572.012	537.543	−1497.295	−136.905	1.349
5400	108.052	675.455	573.909	548.348	−1498.277	−111.227	1.076
5500	108.053	677.437	575.773	559.153	−1499.217	−85.532	0.812
5600	108.054	679.384	577.606	569.958	−1500.111	−59.821	0.558
5700	108.055	681.297	579.408	580.764	−1500.958	−34.094	0.312
5800	108.056	683.176	581.181	591.569	−1501.754	−8.352	0.075
5900	108.058	685.023	582.926	602.375	−1502.497	17.402	−0.154
6000	108.058	686.839	584.643	613.181	−1503.185	43.169	−0.376

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K) = [238.488 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 467\ K$

$\Delta_f H°(0\ K) = Unknown$
$\Delta_f H°(298.15\ K) = -527.184 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°[18.8 \pm 6.3]\ kJ \cdot mol^{-1}$

Heat of Formation

The heat of formation is obtained from Shchukarev *et al.*[1] The authors derived the $\Delta_f H°(MoCl_5, cr, 298.15\ K) = -126\ kcal \cdot mol^{-1}$ by measuring the heat of solution of $MoCl_5$ in NaOH(aq), which was compared with the heats of solution of MoO_3 and NaCl measured in the same solvent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with that of WCl_5(cr). $S°(298.15\ K)$ is estimated as $57\ cal \cdot K^{-1} \cdot mol^{-1}$ the vapor pressure data for $MoCl_5(cr) \rightarrow MoCl_5(g)$ measured by Shchukarev *et al.*[2]

Melting Data

Refer to liquid table.

References

[1]S. A. Shchukarev, G. I. Novikov, I. V. Vasil'kova, A. V. Suvorov, N. V. Andreeva, B. N. Sharupin, and A. K. Baev, Zh. Neorg. Khim. **5**, 1650 (1960).
[2]S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR (English Trnsl.) **26**, 2335 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	155.645	238.488	238.488	0.	−527.184	−423.483	74.192
300	155.728	239.451	238.491	0.288	−527.097	−422.840	73.623
400	167.360	285.854	244.739	16.446	−522.070	−388.825	50.775
467.000	174.929	312.345	252.573	27.913	--- CRYSTAL <--> LIQUID ---		
500	178.657	324.413	256.920	33.747	−516.246	−356.170	37.209
600	189.954	358.022	271.026	52.198	−509.492	−324.773	28.274
700	198.740	387.996	285.634	71.654	−501.888	−294.578	21.982
800	205.016	414.962	300.143	91.855	−493.657	−265.517	17.337
900	209.618	439.388	314.279	112.598	−484.982	−237.517	13.785
1000	212.966	461.657	327.920	133.737	−475.997	−210.500	10.995

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride ($MoCl_5$) LIQUID M_r = 273.205

$S°(298.15\ K) = [273.805]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 467\ K$
$T_{vap} = 537\ K$

$\Delta_f H°(298.15\ K) = [-510.117]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [18.828 \pm 6.3]\ kJ·mol^{-1}$
$\Delta_{vap} H° = [50.208]\ kJ·mol^{-1}$

Heat of Formation

The heat of formation is obtained from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus} H°$ and the difference between $H°(T_{fus};298.15)$ for crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed constant and estimated as 42 $cal·K^{-1}·mol^{-1}$ or 7 $cal·K^{-1}\ g·atom^{-1}$. The entropy is obtained in a manner analogous to that of the heat of formation.

Heat of Melting Data

T_{fus} *is taken from Shchukarev et al.*[1] $\Delta_{fus} H°$ *is estimated by comparison with that of* WCl_5(cr).

Heat of Vaporization Data

T_{vap} is the temperature at which the difference between the Gibbs energy of formation for $MoCl_5$(l) and $MoCl_5$(g) approaches zero. The difference between $\Delta_f H°(MoCl_5, l, 537\ K)$ and $\Delta_f H°(MoCl_5, g, 537\ K)$ is $\Delta_{vap} H°$.

Reference

[1]S. A. Shchukarev, G. I. Novikov, A. V. Suvorov and V. K. Moksimov, Russ. J. Inorg. Chem. (English Transl.) **4**, 935 (1959).

Molybdenum Chloride ($MoCl_5$) Cl_5Mo_1(l)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	175.728	273.807	273.807	0.	−510.114	−416.944	73.047
300	175.728	274.894	273.811	0.325	−509.991	−416.366	72.496
400	175.728	325.448	280.703	17.898	−503.548	−386.141	50.425
467.000	175.728	352.662	289.125	29.672	--- CRYSTAL <-- --> LIQUID ---		
500	175.728	364.661	293.719	35.471	−497.452	−357.500	37.348
600	175.728	396.700	308.294	53.043	−491.576	−330.064	28.735
700	175.728	423.788	322.908	70.616	−485.856	−303.600	22.655
800	175.728	447.254	337.017	88.189	−480.253	−277.947	18.148
900	175.728	467.951	350.438	105.762	−474.748	−252.990	14.683
1000	175.728	486.466	363.131	123.335	−469.329	−228.642	11.943
1100	175.728	503.215	375.117	140.907	−463.995	−204.832	9.727
1200	175.728	518.505	386.438	158.480	−458.745	−181.504	7.901

PREVIOUS: CURRENT: December 1968

Molybdenum Chloride ($MoCl_5$) Cl_5Mo_1(l)

0	to	467	K crystal
above		467	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	155.645	238.488	238.488	0.	−527.184	−423.483	74.192
300	155.728	239.451	238.491	0.288	−527.097	−422.840	73.623
400	167.360	285.854	244.739	16.446	−522.070	−388.825	50.775
467.000	174.929	312.345	252.573	27.913	CRYSTAL <--> LIQUID		
467.000	175.728	352.662	252.573	46.741	TRANSITION		
500	175.728	364.661	259.580	52.540	−497.452	−357.500	37.348
600	175.728	396.700	279.844	70.113	−491.576	−330.064	28.735
700	175.728	423.788	298.522	87.686	−485.856	−303.600	22.655
800	175.728	447.254	315.680	105.259	−480.253	−277.947	18.148
900	175.728	467.951	331.472	122.832	−474.748	−252.990	14.683
1000	175.728	486.466	346.062	140.404	−469.329	−228.642	11.943
1100	175.728	503.215	359.599	157.977	−463.995	−204.832	9.727
1200	175.728	518.505	372.213	175.550	−458.745	−181.504	7.901

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = [397.774 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -445.94 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -447.69 \pm 4.2\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[490](1)	[350](2)
[400](1)	[170](2)
[410](1)	[100](2)
[150](1)	[190](2)

Point Group: D_{3h} $\sigma = 6$

Bond Distance: Mo–Cl = 2.27 ± 0.02 Å

Bond Angles: Cl*–Mo–Cl* = 120°; Cl*–Mo–Cl** = 90°; Cl**–Mo–Cl** = 180°

*Equatorial **Axial

Product of the Moments of Inertia: $I_A I_B I_C = 1.02598 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = 107.0\ kcal \cdot mol^{-1}$ is obtained from the vapor pressure data for $MoCl_5(cr) = MoCl_5(g)$ measured by *Shchukarev et al.*[1] and *Saeki and Matsuzaki.*[2]

Source	Method	Reaction	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Shchukarev *et al.*[1]	Transpiration	$MoCl_5(cr) = MoCl_5(g)$	343 – 435	19.04 ± 0.45	19.18	0.3	−106.82
Saeki and Matsuzaki	Manometric	$MoCl_5(cr) = MoCl_5(g)$	298 – 474	16.79 ± 0.06	18.94	5.6	−107.06

*Calculation based on third law $\Delta_f H°(298.15\ K)$

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of $NbCl_5$ obtained from infrared and Raman spectra by Carlson.[3] Structure, bond distance and bond angle are taken from Ewens and Lister.[4] The principal moments of inertia are: $I_A = 91.0085 \times 10^{-39}$ and $I_B = I_C = 106.1766 \times 10^{-39}\ g \cdot cm^2$. *The electronic levels are estimated to be 0, 7000 and 14000 cm^{-1}, all doublets, by comparison with those of WCl_5(g).*

References

[1] S. A. Shchukarev, I. V. Vasil'kova and B. N. Sharupin, J. Gen. Chem. USSR **26**, 2335–9 (1956).

[2] Y. Saeki and R. Matsuzaki, Denki Kagaku **33**, 155–8 (1965).

[3] G. L. Carlson, Spectrochim. Acta **19**, 1291 (1963).

[4] R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. **34**, 1358–62 (1938).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−25.793	−445.945	−445.945	INFINITE
100	77.392	287.812	494.800	−20.699	−448.621	−429.448	224.321
200	107.562	352.265	408.393	−11.226	−448.584	−410.160	107.123
250	114.900	377.117	399.718	−5.650	−448.174	−400.598	83.700
298.15	119.482	397.774	397.774	0.	−447.688	−391.478	68.585
300	119.624	398.514	397.777	0.221	−447.668	−391.129	68.102
350	122.781	417.207	399.246	6.286	−447.114	−381.750	56.973
400	124.971	433.753	402.545	12.483	−446.537	−372.451	48.637
450	126.543	448.568	406.850	18.773	−445.952	−363.226	42.162
500	127.704	461.964	411.702	25.131	−445.366	−354.065	36.989
600	129.265	485.397	422.087	37.986	−444.208	−335.914	29.244
700	130.234	505.402	432.595	50.964	−443.082	−317.955	23.726
800	130.878	522.837	442.809	64.022	−441.994	−300.154	19.598
900	131.332	538.279	452.575	77.134	−440.950	−282.487	16.395
1000	131.674	552.135	461.850	90.285	−439.953	−264.934	13.839
1100	131.950	564.698	470.638	103.466	−439.010	−247.479	11.752
1200	132.192	576.190	478.962	116.674	−438.125	−230.106	10.016
1300	132.417	586.780	486.854	129.904	−437.307	−212.805	8.551
1400	132.639	596.601	494.346	143.157	−436.558	−195.564	7.297
1500	132.862	605.760	501.472	156.432	−435.886	−178.374	6.212
1600	133.092	614.342	508.261	169.730	−435.294	−161.227	5.264
1700	133.328	622.418	514.741	183.051	−434.790	−144.113	4.428
1800	133.570	630.045	520.937	196.395	−434.381	−127.027	3.686
1900	133.817	637.274	526.871	209.765	−434.074	−109.961	3.023
2000	134.067	644.144	532.565	223.159	−433.880	−92.908	2.427
2100	134.317	650.691	538.035	236.578	−433.808	−75.861	1.887
2200	134.566	656.945	543.299	250.022	−433.872	−58.815	1.396
2300	134.811	662.933	548.371	263.491	−434.083	−41.763	0.948
2400	135.053	668.675	553.265	276.984	−434.455	−24.699	0.538
2500	135.288	674.193	557.992	290.501	−435.003	−7.615	0.159
2600	135.516	679.504	562.565	304.042	−435.753	9.495	−0.191
2700	135.736	684.622	566.991	317.604	−436.748	26.638	−0.515
2800	135.947	689.562	571.281	331.189	−438.052	43.823	−0.818
2900	136.150	694.337	575.442	344.794	−475.633	61.111	−1.101
3000	136.342	698.956	579.483	358.418	−475.769	79.622	−1.386
3100	136.525	703.429	583.409	372.062	−475.934	98.137	−1.654
3200	136.697	707.766	587.228	385.723	−476.128	116.659	−1.904
3300	136.860	711.975	590.945	399.401	−476.350	135.187	−2.140
3400	137.012	716.063	594.565	413.094	−476.598	153.722	−2.362
3500	137.155	720.037	598.093	426.803	−476.870	172.265	−2.571
3600	137.287	723.903	601.535	440.525	−477.160	190.816	−2.769
3700	137.410	727.666	604.893	454.260	−477.466	209.375	−2.956
3800	137.523	731.332	608.172	468.007	−477.782	227.942	−3.133
3900	137.627	734.905	611.376	481.764	−478.104	246.518	−3.302
4000	137.722	738.391	614.508	495.532	−478.425	265.102	−3.462
4100	137.808	741.793	617.571	509.308	−478.741	283.694	−3.614
4200	137.885	745.115	620.569	523.093	−479.046	302.294	−3.760
4300	137.955	748.360	623.503	536.885	−479.333	320.901	−3.898
4400	138.017	751.532	626.377	550.684	−479.599	339.514	−4.031
4500	138.071	754.634	629.193	564.488	−479.836	358.132	−4.157
4600	138.118	757.670	631.953	578.298	−480.040	376.757	−4.278
4700	138.159	760.641	634.659	592.112	−480.205	395.384	−4.394
4800	138.193	763.550	637.314	605.929	−480.328	414.015	−4.505
4900	138.221	766.399	639.920	619.750	−480.404	432.649	−4.612
5000	138.243	769.192	642.477	633.573	−1071.814	457.013	−4.774
5100	138.259	771.930	644.989	647.398	−1073.463	487.607	−4.994
5200	138.271	774.615	647.456	661.225	−1075.201	518.232	−5.206
5300	138.278	777.248	649.880	675.052	−1077.021	548.892	−5.410
5400	138.280	779.833	652.263	688.880	−1078.922	579.588	−5.606
5500	138.277	782.371	654.605	702.708	−1080.896	610.319	−5.796
5600	138.271	784.862	656.909	716.536	−1082.941	641.087	−5.980
5700	138.261	787.309	659.176	730.362	−1085.051	671.891	−6.157
5800	138.248	789.714	661.406	744.188	−1087.224	702.734	−6.329
5900	138.231	792.077	663.600	758.012	−1089.452	733.614	−6.495
6000	138.212	794.400	665.761	771.834	−1091.738	764.532	−6.656

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [214.05 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 478.9 \pm 1.5\ K$
$\Delta_{fus}H° = 33.878 \pm 0.96\ kJ \cdot mol^{-1}$

$\Delta_fH°(0\ K) = Unknown$
$\Delta_fH°(298.15\ K) = -797.47 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted value for the enthalpy of formation of $NbCl_5$(cr) is $\Delta_fH°(298.15\ K) = -190.6 \pm 1.0\ kcal \cdot mol^{-1}$ and is based on the study by Gross *et al.*[2] This value was determined from measurements of the enthalpy evolved in the reaction Nb(cr) + 5/2 Cl_2(l) = $NbCl_5$(cr). Schafer and Kahlenberg[1] also determined the enthalpy formation of $NbCl_5$(cr) via calorimetric measurement of the heats of solution of Nb(cr) and $NbCl_5$(cr) *in hydrofluoric acid.* Their procedure consisted of five steps; four were determined experimentally and one was based on literature data. Using their data and auxiliary results,[7] we calculate $\Delta_fH°(298.15\ K) = -190.0 \pm 1.0\ kcal \cdot mol^{-1}$ for $NbCl_5$(cr). This value is in good agreement with our adopted value. Shchukarev *et al.*[3] determined a $\Delta_fH°(298.15\ K)$ value from a heat of hydrolysis for $NbCl_5$(cr). A recalculation of this data, using current auxiliary $\Delta_fH°(298.15\ K)$ data for Nb_2O_5(cr),[10] H_2O(l),[7] and HCl(g),[10] yields $\Delta_fH°(298.15\ K) = -192.8 \pm 0.7\ kcal \cdot mol^{-1}$.

Three compilations on Nb species suggested a similar or closely related $\Delta_fH°(298.15\ K)$ value for $NbCl_5$(cr):[6,8,9] in particular, the NBS Technical Note 270 Series suggested $-190.6\ kcal \cdot mol^{-1}$.[9]

Heat Capacity and Entropy

Keneshea *et al.*[5] measured the saturation enthalpy increments above 298.15 K for the condensed phases of $NbCl_5$ in a drop calorimeter up to the critical point (804 ± 3 K). A figure presented by Keneshea *et al.*[5] indicated roughly 30 data points, the lowest occurring at approximately 360 K. The differences between the saturation and standard enthalpy increments for the crystal phase are negligible, so that the heat capacity values which we adopt are those which are derived from the reported enthalpy equation, $H°(T)-H°(298.15\ K) = [-10.53 + 3.535 \times 10^{-2}T] \pm 0.07\ kcal \cdot mol^{-1}$. This equation is reported to apply to the temerature region 298.15–478.9 K.

Schafer and Kahlenberg[1] estimated the heat capacity of $NbCl_5$(cr) to be given by $C_p° = 38.0\text{–}3 \times 10^5T^{-2}\ cal \cdot K^{-1} \cdot mol^{-1}$. For the crystal range 298.15–478.9 K, these estimated $C_p°$ values vary from 34.63 to 36.69 $cal \cdot K^{-1} \cdot mol^{-1}$. These values are in fair agreement with the adopted values and were estimated by comparison with $ZrCl_4$(cr) and $HfCl_4$(cr). Amosov[4] also estimated the heat capacity of $NbCl_5$ based on Neumann and Koppe's rule, $C_p° = 26.71 + 35.2 \times 10^{-3}T\ cal \cdot K^{-1} \cdot mol^{-1}$. These latter values vary between 37.20 and 43.57 $cal \cdot K^{-1} \cdot mol^{-1}$ over the region 298.15–478.9 K and differ significantly from those $C_p°$ values derived from the experimental data of Keneshea *et al.*[5]

As there is no low temperature heat capacity data reported in the literature, the entropy of $NbCl_5$(cr) at 298.15 K is calculated from the equation $\Delta_{sub}S°(298.15\ K) = S°(g, 298.15\ K) - S°(cr, 298.15\ K)$; $S°(g, 298.15\ K) = 96.56\ cal \cdot K^{-1} \cdot mol^{-1}$ as given in the $NbCl_5$(g) table[10] and $\Delta_{sub}S°(298.15\ K) = 45.40\ cal \cdot K^{-1} \cdot mol^{-1}$ as obtained Keneshea *et al.*[5] based on their evaluation of the available vapor pressure data by a modified Σ approach.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$ is the difference between the $\Delta_fH°(298.15\ K)$ values for $NbCl_5$(g) and $NbCl_5$(cr). For sublimation studies are summarized in the $NbCl_5$(l) table.

References

[1]H. Schafer and F. kahlenberg, Z. anorg. allg. Chem. **305**, 291 (1960).
[2]P. Gross, C. Hayman, D. L. Levi and G. L. Wilson, Trans. Faraday Soc. **56**, 318 (1960).
[3]S. A. Shchukarev, M. A. Oranskaya and T. S. Shemyakina, Russ. J. Inorg. Chem. **5**, 1036 (1960).
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[5]F. J. Keneshea, D. Cubicciotti, G. Withers and H. Eding, J. Phys. Chem. **72**, 1272 (1968).
[6]V. I. Lavrentev and Ya. I. Gerassimov, At. Energy Rev. **1968**, 7 (1968).
[7]U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[8]J. O. Hill, I. G. Worsley and L. G. Hepler, Chem. Rev. **71**, 127 (1971).
[9]U. S. Nat. Bur. Stand. Tech. Note 270–5, (1971).
[10]JANAF Thermochemical Tables: Nb_2O_5(cr), 12–31–72; HCl(g), 9–3–64' $NbCl_5$(g), 12–31–74.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	147.904	214.053	214.053	0.	−797.470	−684.141	119.859
300	147.904	214.968	214.056	0.274	−797.400	−683.438	118.997
400	147.904	257.518	219.858	15.064	−793.792	−646.006	84.360
478.900	147.904	284.145	228.321	26.734	--- CRYSTAL <---> LIQUID ---		
500	147.904	290.522	230.813	29.854	−790.494	−609.446	63.668
600	147.904	317.488	243.080	44.645	−787.397	−573.530	49.930
700	147.904	340.287	255.380	59.435	−784.442	−538.121	40.155

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = [260.970 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 478.9 \pm 1.5\ K$

$\Delta_f H°(298.15\ K) = [-773.354]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 33.878 \pm 0.96\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NbCl_5, l, 298.15\ K)$ is calculated from that of $NbCl_5$(cr) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(478.9\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity values are derived from the enthalpy equation reported by Keneshea *et al.*[5] The equation is used for the region 478.9–600 K, i.e. that region in which the saturation heat capacity and the heat capacity at constant pressure are essentially the same in value. This equation is used also to extrapolate to 700 K and to an assumed glass transition temperature at T_{gls} = 350 K. Below T_{gls} the heat capacity values are those of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°(298.15\ K)$.

Fusion Data

The adopted value of T_{fus} is that reported by Keneshea *et al.*[5] This value, 205.7°C or 478.9 K, was obtained by visual observation on four different samples in evacuated capsules. Other values for T_{fus} reported in the literature are: 205.3 ± 1.5C°,[6] 204.8°C,[4] 206.8 ± 0.3°C,[3] 204.5°C,[2] and 204.7°C.[1] Earlier determinations of melting point have been summarized by Schafer and Pietruck[1] and Meyer *et al.*[3]

The adopted heat of fusion, $\Delta_{fus} H° = 8.097 \pm 0.23\ kcal \cdot mol^{-1}$, is calculated as the difference at 478.9 K in the enthalpy equations for $NbCl_5$(l) and $NbCl_5$(cr) as reported by Keneshea *et al.*[5] Meyer *et al.*,[3] from an examination of the $NbCl_5$–$NbOCl_3$ system, reported a value of 8.30 ± 0.4 kcal mol^{-1} for $\Delta_{fus} H°$. Voitovich *et al.*[4] studied the $NbCl_5$–S_2Cl_2 system and calculated $\Delta_{fus} H° = 8.15\ kcal \cdot mol^{-1}$. These two latter values are in excellent agreement with our adopted value.

Johnson and Cubicciotti,[6] in their study of the orthobaric densities of $NbCl_5$, discussed the possible molecular behavior of $NbCl_5$. The explanation served to explain the large entropy of melting, $\Delta_{fus} S° = 16.91\ kcal \cdot mol^{-1}$. Based on currently available information, they suggested that between the melting point and about 650 K the substance changes from a dimeric solid to a monomeric liquid. This change was suggested to manifest itself in the unusually large volume change[6] (27 ± 2%) and entropy of fusion and in the inverse curvature of the liquid density curve just above the melting point. For additional references, refer to the $NbCl_5$(g) table.

Vaporization Data

T_{vap} is calculated as that temperature for which $\Delta_r G° = 0$ for the process $NbCl_5(l) = NbCl_5(g)$. $\Delta_{vap} H°$ is calculated as the difference between the $\Delta_f H°$ values for $NbCl_5$(g) and $NbCl_5$(l) at T_{vap}. Seven vaporization studies are summarized in the $NbCl_5$(g) table. Sheka *et al.*[2] studied the vapor-liquid equilibrium in the $NbCl_5$–$POCl_3$ system and measured a boiling point (at 760 mm) of 521.7 K for pure $NbCl_5$. The vaporization studies discussed in the $NbCl_5$(g) table which included the boiling point yielded normal boiling points (p = 760 mm) in the range 519.2–520.6 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	147.904	260.970	260.970	0.	−773.354	−674.012	118.084
300	147.904	261.885	260.973	0.274	−773.283	−673.396	117.249
350	147.904	284.684	262.773	7.669	−771.430	−656.897	98.036
350.000	147.904	284.684	262.773	7.669	---- GLASS <--> LIQUID ----		
350.000	228.292	284.684	262.773	7.669	TRANSITION		
400	224.848	314.949	267.451	18.999	−765.740	−640.926	83.696
478.900	218.448	354.886	278.680	36.495	--- CRYSTAL <--> LIQUID ---		
500	216.564	364.264	282.096	41.084	−755.148	−610.971	63.828
600	206.397	402.878	299.132	62.248	−745.678	−583.044	50.759
700	194.430	433.819	316.241	82.304	−737.456	−556.607	41.535
800	180.611	458.900	332.560	101.072	−730.635	−531.254	34.687

PREVIOUS: CURRENT: December 1974

0 to 478.9 K crystal
above 478.9 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	147.904	214.053	214.053	0.	−797.470	−684.141	119.859
300	147.904	214.968	214.056	0.274	−797.400	−683.438	118.997
400	147.904	257.518	219.858	15.064	−793.792	−646.006	84.360
478.900	147.904	284.145	228.321	26.734	CRYSTAL <--> LIQUID TRANSITION		
478.900	218.448	354.886	228.321	60.612			
500	216.564	364.264	233.862	65.201	−755.148	−610.971	63.828
600	206.397	402.878	258.937	86.364	−745.678	−583.044	50.759
700	194.430	433.819	281.789	106.421	−737.456	−556.607	41.535
800	180.611	458.900	302.414	125.189	−730.635	−531.254	34.687

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 404.111 \pm 3.14\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -701.48 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -703.33 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
394.0 (1)	[492.4](2)
317.0 (1)	179.9 (2)
[414.1](1)	54.1 (2)
[143.5](1)	148.0 (2)

Ground State Quantum Weight: [1] $\sigma = 6$

Point Group: D_{3h}

Bond Distance: Nb–Cl = 2.28 ± 0.02 Å

Bond Angles: Cl*–Nb–Cl* = 120°; Cl*–Nb–Cl** = 90°; Cl**–Nb–Cl** = 180°
(* = equatorial ** = axial)

Product of the Moments of Inertia: $I_A I_B I_C = 1.05340 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

The vapor pressures over $NbCl_5$(cr) and $NbCl_5$(l) have been measured by seven investigators. The reported vapor pressures are corrected for vapor non-ideality by means of the equation $\Delta G°/T = -R \ln p - Bp/T$. The Berthelot equation of state and critical constants $T_c = 803.5 \pm 2$ K and $p_c = 48.2$ atm. reported by Johnson *et al.*[9, 10] are used to calculate B. The corrected vapor pressures are used to calculate $\Delta_f H°(298.15\ K)$ by both 2nd and 3rd law methods. By means of comparison, Nisel'son *et al.*[6] measured the orthobaric densities of $NbCl_5$(l), as did Johnson *et al.*,[9] and reported $T_c = 807$ K and $p_c = 46$ atm.

Source	Method	T/K	Data Points	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
$NbCl_5(cr) = NbCl_5(g)$						
Opykhtina and Fleischer[1]	transpiration	373–Tm	Eqn	20.74	22.28	3.6
Tarasenkov and Komandin[2]	static	446–Tm	Eqn	19.20	22.41	7.0
Alexander and Fairbrother[3]	static	402–Tm	7*	22.02 ± 0.30	22.69 ± 0.09	1.5 ± 0.7
Schafer and Polert[7]	flow	351–384	25	22.71 ± 0.10	22.52 ± 0.03	−0.5 ± 0.3
$NbCl\ (l_5) = NbCl\ (g_5)$						
Opykhtina and Fleisher[1]	transpiration	Tm–503	Eqn	16.42	16.55	0.3
Tarasenkov and Komandin[2]	static	Tm–506	Eqn	18.41	16.73	−3.4
	boiling	504–520	Eqn	15.08	16.70	3.2
Alexander and Fairbrother[3]	static	Tm–528	13	16.98 ± 0.05	16.91 ± 0.01	−0.2 ± 0.1
Ainscough *et al.*[4]	boiling	516–530	Eqn	16.65	16.76	0.2
Hart and Meyer[5]	static	544–594	32*	16.45 ± 0.08	16.79 ± 0.03	0.6 ± 0.1
Johnson *et al.*[10]	boiling	503–594	10	16.42 ± 0.04	16.76 ± 0.04	0.6 ± 0.1

*One point is rejected due to statistical test.

The adopted value for $\Delta_f H°(298.15\ K)$ of $NbCl_5$(g) is -168.1 ± 2.0 kcal·mol^{-1} (-703.330 ± 8.4 kJ·mol^{-1}). This value is based on a rounded mean of the 3rd law results for both the sublimation and vaporization studies and the appropriate $\Delta_f H°(298.15\ K)$ value for the crystal or liquid.

Reznitskii[8] measured the enthalpy of chlorination for Nb(cr) and reported $\Delta_f H°(680\ K) = -169.1 \pm 1$ kcal·mol^{-1} for the reaction $Nb(cr) + 5/2\ Cl_2(g) = NbCl_5(g)$. Using auxiliary data for Nb(cr) and Cl_2(g),[11] we calculated $\Delta_f H°(298.15\ K) = -170.1 \pm 1.0$ kcal·mol^{-1} for $NbCl_5$(g).

Heat Capacity and Entropy

Monomeric $NbCl_5$(g) was shown by Spiridonov and Romanov,[19, 20] using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Nb–Cl bond lengths being equal within experimental uncertainty, 2.28 ± 0.2 Å. Skinner and Sutton[12] earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with the experimental results. We adopt the results of Spiridonov and Romanov.[19,20] The principal moments of inertia are: $I_A = 91.8121 \times 10^{-39}$ and $I_B = I_C = 107.1141 \times 10^{-39}\ g \cdot cm^2$.

Continued on page 941

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−26.343	−701.481	−701.481	INFINITE
100	80.548	293.472	501.092	−20.762	−703.961	−684.800	357.703
200	107.409	358.746	414.693	−11.189	−704.080	−665.472	173.803
250	114.494	383.531	406.048	−5.629	−703.751	−655.855	137.033
298.15	119.040	404.111	404.111	0.	−703.330	−646.667	113.293
300	119.183	404.848	404.114	0.220	−703.313	−646.315	112.534
350	122.372	423.475	405.577	6.264	−702.811	−636.855	95.045
400	124.611	439.970	408.865	12.442	−702.274	−627.469	81.939
450	126.230	454.745	413.157	18.715	−701.717	−618.152	71.753
500	127.434	468.110	417.994	25.058	−701.151	−608.897	63.611
600	129.061	491.501	428.351	37.890	−700.012	−590.553	51.412
700	130.076	511.477	438.834	50.850	−698.887	−572.399	42.713
800	130.749	528.893	449.027	63.893	−697.791	−554.404	36.199
900	131.217	544.322	458.774	76.993	−696.731	−536.545	31.140
1000	131.556	558.166	468.033	90.133	−695.713	−518.802	27.099
1100	131.808	570.716	476.806	103.301	−694.740	−501.158	23.798
1200	132.001	582.194	485.117	116.492	−693.814	−483.601	21.051
1300	132.151	592.766	492.996	129.700	−692.935	−466.119	18.729
1400	132.271	602.564	500.477	142.921	−692.106	−448.703	16.741
1500	132.368	611.693	507.591	156.154	−691.333	−431.345	15.021
1600	132.448	620.238	514.367	169.395	−690.624	−414.036	13.517
1700	132.514	628.270	520.833	182.643	−689.989	−396.769	12.191
1800	132.570	635.846	527.014	195.897	−689.434	−379.537	11.014
1900	132.617	643.015	532.933	209.156	−688.969	−362.334	9.961
2000	132.657	649.818	538.608	222.420	−688.602	−345.152	9.014
2100	132.691	656.292	544.059	235.688	−688.341	−327.987	8.158
2200	132.721	662.465	549.302	248.958	−688.194	−310.831	7.380
2300	132.748	668.365	554.352	262.232	−688.174	−293.679	6.670
2400	132.771	674.016	559.221	275.508	−688.294	−276.525	6.018
2500	132.791	679.436	563.922	288.786	−688.573	−259.363	5.419
2600	132.809	684.645	568.465	302.066	−689.038	−242.186	4.866
2700	132.825	689.657	572.862	315.347	−689.729	−224.986	4.353
2800	132.839	694.488	577.120	328.631	−717.062	−207.273	3.867
2900	132.852	699.150	581.248	341.915	−717.071	−189.066	3.405
3000	132.864	703.654	585.253	355.201	−717.126	−170.858	2.975
3100	132.875	708.010	589.143	368.488	−717.230	−152.648	2.572
3200	132.884	712.229	592.924	381.776	−717.379	−134.434	2.194
3300	132.893	716.318	596.602	395.065	−717.572	−116.213	1.839
3400	132.901	720.286	600.182	408.355	−717.805	−97.987	1.505
3500	132.908	724.138	603.668	421.645	−718.076	−79.753	1.190
3600	132.915	727.883	607.067	434.936	−718.379	−61.511	0.892
3700	132.921	731.524	610.382	448.228	−718.710	−43.260	0.611
3800	132.927	735.069	613.617	461.520	−719.062	−25.000	0.344
3900	132.932	738.522	616.775	474.813	−719.430	−6.731	0.090
4000	132.937	741.888	619.861	488.107	−719.807	11.549	−0.151
4100	132.941	745.170	622.878	501.401	−720.187	29.837	−0.380
4200	132.946	748.374	625.828	514.695	−720.564	48.135	−0.599
4300	132.949	751.502	628.714	527.990	−720.930	66.442	−0.807
4400	132.953	754.559	631.540	541.285	−721.280	84.757	−1.006
4500	132.956	757.547	634.307	554.580	−721.608	103.079	−1.197
4600	132.960	760.469	637.018	567.876	−721.907	121.410	−1.379
4700	132.963	763.328	639.675	581.172	−722.173	139.745	−1.553
4800	132.965	766.128	642.280	594.469	−722.398	158.086	−1.720
4900	132.968	768.869	644.836	607.765	−722.580	176.432	−1.881
5000	132.971	771.556	647.343	621.062	−722.712	194.780	−2.035
5100	132.973	774.189	649.805	634.359	−722.792	213.131	−2.183
5200	132.975	776.771	652.222	647.657	−1413.486	240.792	−2.419
5300	132.977	779.304	654.596	660.954	−1413.781	272.608	−2.687
5400	132.979	781.790	656.928	674.252	−1413.986	304.425	−2.945
5500	132.981	784.230	659.221	687.550	−1414.198	336.250	−3.193
5600	132.983	786.626	661.474	700.848	−1414.370	368.077	−3.433
5700	132.984	788.980	663.691	714.147	−1414.501	399.908	−3.665
5800	132.986	791.292	665.871	727.445	−1414.589	431.741	−3.888
5900	132.987	793.566	668.016	740.744	−1414.633	463.574	−4.104
6000	132.989	795.801	670.127	754.043	−1414.633	495.408	−4.313

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 364.288\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -354.72 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -360.18 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
394 (1)	394 (1)	465 (1)
[176] (2)	592 (2)	335 (2)
100 (2)	280 (2)	

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: D_{3h}
Bond Distance: P–Cl* = 2.04 Å; P-Cl** = 2.19 Å
Bond Angle: Cl–P–Cl* = 120°; Cl**–P–Cl** = 180°; Cl*–P–Cl** = 90
(* = equatorial ** = axial)
Product of the Moments of Inertia: $I_A I_B I_C = 6.3873 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from the $\Delta_r H°(298.15\ K)$ for the reaction: $PCl_3(g) + Cl_2(g) \leftarrow PCl_5(g)$. A third law calculation using experimental equilibrium constants, and free energy functions from JANAF Tables gave a $\Delta_r H°(298.15\ K) = -20.884\ kcal·mol^{-1}$. This $\Delta_r H°$ is the average of C. Holland[1] $\Delta_r H°(298.15\ K) = -20.766 \pm 0.26\ kcal·mol^{-1}$ and W. Nernst[2] $\Delta_r H(298.15\ K) = -21.001 \pm 0.24\ kcal·mol^{-1}$. The first, $\Delta_r H°$ C. Holland,[1] was obtained from eleven experimental equillibrium constants measured by Holland[1] as corrected by Nernst.[2] The second, $\Delta_r H°$ W. Nernst,[2] was obtained from thirteen experimental equillibrium constants measured by Fischer and Jubermann.[3]

For the same reaction, $PCl_3(g) + Cl_2(g) = PCl_5(g)$, a 3rd law calculation by Stevenson and Yost[4] gave a $\Delta H°(0\ K) = -21.320 \pm 0.107\ kcal·mol^{-1}$. With a new assignment of fundamental frequencies Wilmshurst and Bernstein[5] reported a $\Delta E°(0\ K) = -20.525 \pm 0.16\ kcal·mol^{-1}$.

The $\Delta_f H°(298.15\ K)$ values corresponding to these heats of reaction are:

$\Delta_f H°(298.15\ K)$	Source
$-82.9\ kcal·mol^{-1}$	[4]
$-82.1\ kcal·mol^{-1}$	[5]
$-81.9\ kcal·mol^{-1}$	Calculated using Gibbs energy function from JANAF Tables

Heat Capacity and Entropy

The fundamental vibrational frequencies were assigned by Wilmshurst and Bernstein[5] from their infrared and Raman spectral data, except the frequency, 176 cm^{-1}, which they calculated. Electron diffraction data of Rouault[6] and Sargent and Schomaker,[7] show the free PCl^5 molecule to be a trigonal bipyramid of D_{3h} symmerty. The bond lengths were calculated from force constants and Badger's rule by Wilmshurst and Bernstein.[5] Their values are in good agreement with the electron diffraction bond lengths of Rouault.[6] The principal moments of inertia are $I_A = 73.5006 \times 10^{-39}$ and $I_B = I_C = 93.2215 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.852	−354.723	−354.723	INFINITE
100	63.002	267.936	451.647	−18.371	−358.410	−336.183	175.604
200	95.704	322.664	374.087	−10.285	−360.181	−313.307	81.827
250	105.426	345.132	366.097	−5.241	−360.276	−301.572	63.010
298.15	111.890	364.288	364.288	0.	−360.184	−290.271	50.854
300	112.096	364.981	364.290	0.207	−360.178	−289.838	50.465
350	116.747	382.631	365.673	5.935	−360.682	−278.059	41.498
400	120.070	398.449	368.799	11.860	−360.452	−266.270	34.771
450	122.505	412.739	372.900	17.927	−360.141	−254.515	29.543
500	124.332	425.745	377.544	24.100	−359.772	−242.799	25.365
600	126.825	448.652	387.538	36.668	−358.917	−219.482	19.108
700	128.396	468.329	397.708	49.435	−357.963	−196.317	14.649
800	129.443	485.547	407.634	62.330	−356.949	−173.293	11.315
900	130.175	500.838	417.156	75.313	−355.900	−150.399	8.729
1000	130.705	514.582	426.223	88.359	−354.829	−127.623	6.666
1100	131.101	527.059	434.832	101.450	−353.745	−104.955	4.984
1200	131.404	538.480	443.000	114.576	−416.229	−81.307	3.539
1300	131.641	549.007	450.755	127.728	−414.364	−53.473	2.149
1400	131.830	558.770	458.126	140.902	−412.508	−25.781	0.962
1500	131.983	567.871	465.142	154.093	−410.661	1.777	−0.062
1600	132.109	576.393	471.832	167.298	−408.826	29.213	−0.954
1700	132.213	584.405	478.220	180.514	−407.005	56.535	−1.737
1800	132.301	591.965	484.332	193.740	−405.199	83.750	−2.430
1900	132.375	599.120	490.186	206.974	−403.412	110.865	−3.048
2000	132.439	605.912	495.804	220.215	−401.646	137.886	−3.601
2100	132.494	612.375	501.203	233.462	−399.904	164.820	−4.100
2200	132.541	618.540	506.397	246.713	−398.190	191.671	−4.551
2300	132.583	624.432	511.402	259.970	−396.506	218.445	−4.961
2400	132.619	630.076	516.230	273.230	−394.857	245.146	−5.335
2500	132.651	635.490	520.893	286.493	−393.247	271.780	−5.679
2600	132.680	640.693	525.401	299.760	−391.677	298.350	−5.994
2700	132.705	645.701	529.764	313.029	−390.152	324.861	−6.285
2800	132.728	650.528	533.992	326.301	−388.674	351.315	−6.554
2900	132.748	655.186	538.091	339.575	−387.243	377.718	−6.803
3000	132.767	659.686	542.070	352.850	−385.860	404.072	−7.036
3100	132.783	664.040	545.934	366.128	−384.526	430.381	−7.252
3200	132.799	668.256	549.691	379.407	−383.238	456.648	−7.454
3300	132.812	672.343	553.346	392.688	−381.995	482.875	−7.643
3400	132.825	676.308	556.905	405.969	−380.793	509.065	−7.821
3500	132.837	680.158	560.372	419.253	−379.630	535.220	−7.988
3600	132.847	683.900	563.751	432.537	−378.500	561.343	−8.145
3700	132.857	687.540	567.048	445.822	−377.398	587.435	−8.293
3800	132.866	691.084	570.266	459.108	−376.319	613.496	−8.433
3900	132.874	694.535	573.408	472.395	−375.256	639.530	−8.566
4000	132.882	697.899	576.478	485.683	−374.204	665.537	−8.691
4100	132.889	701.180	579.480	498.972	−373.155	691.518	−8.810
4200	132.896	704.383	582.416	512.261	−372.104	717.473	−8.923
4300	132.902	707.510	585.289	525.551	−371.045	743.403	−9.031
4400	132.908	710.565	588.102	538.841	−369.969	769.308	−9.133
4500	132.913	713.552	590.856	552.132	−368.872	795.188	−9.230
4600	132.918	716.474	593.555	565.424	−367.748	821.044	−9.323
4700	132.923	719.332	596.201	578.716	−366.591	846.874	−9.412
4800	132.927	722.131	598.796	592.008	−365.395	872.680	−9.497
4900	132.931	724.872	601.341	605.301	−364.156	898.461	−9.578
5000	132.935	727.557	603.838	618.595	−362.869	924.215	−9.655
5100	132.939	730.190	606.290	631.888	−361.531	949.944	−9.729
5200	132.943	732.771	608.698	645.182	−360.136	975.645	−9.800
5300	132.946	735.304	611.063	658.477	−358.682	1001.320	−9.869
5400	132.949	737.789	613.387	671.772	−357.167	1026.966	−9.934
5500	132.952	740.228	615.671	685.067	−355.586	1052.584	−9.997
5600	132.955	742.624	617.916	698.362	−353.939	1078.172	−10.057
5700	132.957	744.977	620.125	711.658	−352.223	1103.730	−10.115
5800	132.960	747.290	622.298	724.953	−350.437	1129.259	−10.170
5900	132.962	749.562	624.435	738.250	−348.579	1154.754	−10.223
6000	132.964	751.797	626.540	751.546	−346.648	1180.218	−10.275

PREVIOUS: September 1962 (1 atm) CURRENT: September 1962 (1 bar)

$S°(298.15\ K)$ = [221.75 ± 6.3] $J·K^{-1}·mol^{-1}$
T_{fus} = 489.7 ± 1.5 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −858.98 ± 4.2 $kJ·mol^{-1}$
$\Delta_{fus} H°$ = 35.146 ± 2.1 $kJ·mol^{-1}$

Enthalpy of Formation

Gross *et al.*[3] measured the heat evolved in the reaction Ta(cr) + 5/2 Cl_2(l) = $TaCl_5$(cr). Using their data for 6 runs we calculate $\Delta_f H°(298.15\ K)$ = −205.6 $kcal·mol^{-1}$ for $TaCl_5$(cr). Gal'chenko *et al.*[4,5] also determined the heat of reaction for the direct chlorination of Ta(15 runs involving 2 samples). They reported $\Delta_f H°(298.15\ K)$ = −205.05 ± 0.18 $kcal·mol^{-1}$. We adopt an intermediate value, $\Delta_f H°(298.15\ K)$ = −205.3 ± 1.0 $kcal·mol^{-1}$ (−858.975 ± 4.2 $kJ·mol^{-1}$), based on these two studies.[3-5]

Schafer and Kahlenberg[1] determined the heat of formation of $TaCl_5$(cr) via calorimetric measurements of the heats of solution of Ta(cr) and $TaCl_5$(cr) in hydrofluoric acid. Their procedure involved eight steps and resulted in $\Delta_f H°(298.15\ K)$ = −205.0 ± 0.3 $kcal·mol^{-1}$. This is in good agreement with our adopted value. In the case of $NbCl_5$(cr) [$TaCl_5$(cr)] the $\Delta_f H°(298.15\ K)$ value derived from the data of Schafer and Kahlenberg[1,2] is 0.6 $kcal·mol^{-1}$ [0.3 $kcal·mol^{-1}$] more positive than that derived from the data of Gross *et al.*[3]

Heat Capacity and Entropy

The heat capacity for $TaCl_5$(cr) is assumed to be the same as that for $NbCl_5$(cr).[6] We adopt $S°(298.15\ K)$ = 53.0 ± 1.5 $cal·K^{-1}·mol^{-1}$ in order to reproduce the sublimation and vaporization data. Schafer and Kahlenberg[1,2] assumed a similar relationship based on a comparison with the corresponding values for the halides of Zr, Hf, and U.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation is discussed in the $TaCl_5$(g) table.[6] Seven sublimation studies are analyzed and lead to a 3rd law result of $\Delta_{sub} H°(298.15\ K)$ = 22.5 $kcal·mol^{-1}$.

References

[1]H. Schafer and F. Kahlenberg, Z. Anorg. Allg. Chem. **294**, 243 (1958).
[2]H. Schafer and F. Kahlenberg, Z. Anorg. Allg. Chem. **305**, 291 (1960).
[3]P. Gross, C. Hayman, D. L. Levi, and G. L. Wilson, Trans. Faraday Soc. **56**, 318 (1960).
[4]G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofiev, S. M. Skuratov, T. I. Serebryakova, and G. V. Samsonov, Dokl. Akad. Nauk. SSSR **170**, 132 (1966).
[5]G. L. Gal'chenko, D. A. Gedakyan, B. I. Timofiev, Russ. J. Inorg. Chem. **13**, 159 (1968).
[6]JANAF Thermochemical Tables: $NbCl_5$(cr) and $TaCl_5$(g), 12-31-74.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	147.904	221.752	221.752	0.	−858.975	−746.448	130.775
300	147.904	222.667	221.755	0.274	−858.905	−745.750	129.847
400	147.904	265.216	227.556	15.064	−855.349	−708.578	92.531
489.700	147.904	295.142	237.288	28.331	--- CRYSTAL <--> LIQUID ---		
500	147.904	298.220	238.511	29.854	−852.096	−672.267	70.231
600	147.904	325.186	250.778	44.645	−849.046	−636.591	55.420
700	147.904	347.986	263.078	59.435	−846.139	−601.413	44.878

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K)$ = [268.135] $J·K^{-1}·mol^{-1}$
T_{fus} = 489.7 ± 1.5 K

$\Delta_fH°(298.15\ K)$ = [−834.347] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 35.146 ± 2.1 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(TaCl_5, l, 298.15K)$ is calculated from that of $TaCl_5$(cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(489.7\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity is assumed to be identical to that for $NbCl_5$(l).[4] As in the case of $NbCl_5$(l), there is a glass transition assumed at 350 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_fH°(298.15\ K)$.

Fusion Data

We adopt T_{fus} = 478.9 ± 1.5 K (216.5°C) based on the work by Schafer and Pietruck (216.5°C),[1] Sheka *et al.* (216.5°C),[2] and Voitovich *et al.* (216.7°C).[3] Earlier reported melting points range between 204°C and 221°C and have been summarized by Schafer and Pietruck.[1]

The adopted heat of fusion, $\Delta_{fus}H°$ = 8.4 ± 0.5 $kcal·mol^{-1}$, is based on the analysis of the S_2Cl_2–$TaCl_5$ system by Voitovich *et al.*[3] A similar study on the S_2Cl_2–$NbCl_5$ system[3] yielded a heat of melting for $NbCl_5$ which was within 0.063 $kcal·mol^{-1}$ of the result determined by drop calorimetry.[4] The discussion of the molecular behavior of $NbCl_5$(l)[4] is assumed to also apply to $TaCl_5$: that is, between the melting point and ~650 K, the substance changes from a dimeric solid to a monomeric liquid.

Vaporization Data

T_{vap} is calculated as that temperature for which $\Delta_rG°$ = 0 for the process $TaCl_5(l) = TaCl_5(g)$. $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_fH°$ values for $TaCl_5$(g) and $TaCl_5$(l) at T_{vap}. Three vaporization studies are summarized in the $TaCl_5$(g) table.[4] Sheka *et al.*[2] studied the vapor–liquid equilibrium in the $TaCl_5$–$POCl_3$ system and measured a boiling point (at 760 mm) of 507.3 K for pure $TaCl_5$. The vaporization studies discussed in the $TaCl_5$(g) table which included the boiling point yielded normal boiling points (p = 760 mm) in the range 506.0–506.9 K.

References

[1]H. Schafer and C. Pietruck, Z. Anorg. Allg. Chem. **267**, 174 (1951).
[2]I. A. Sheka, B. A. Voitovich, and L. A. Nisel'son, Russ. J. Inorg. Chem. **4**, 813 (1959).
[3]B. A. Voitovich, A. S. Barabanova, and N. Kh. Tumanova, Russ. J. Inorg. Chem. **6**, 1286 (1961).
[4]JANAF Thermochemical Tables: $NbCl_5(\ell)$, $NbCl_5$(g) and $TaCl_5$(g), 12-31-74.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	147.904	268.135	268.135	0.	−834.347	−735.649	128.883
300	147.904	269.050	268.138	0.274	−834.277	−735.037	127.981
350	147.904	291.849	269.938	7.669	−832.452	−718.643	107.252
350.000	147.904	291.849	269.938	7.669	---- GLASS <--> LIQUID ----		
350.000	228.280	291.849	269.938	7.669	TRANSITION		
400	224.848	322.113	274.616	18.999	−826.786	−702.774	91.773
489.700	217.482	366.911	287.580	38.849	--- CRYSTAL <-- > LIQUID ---		
500	216.564	371.429	289.261	41.084	−816.238	−673.014	70.309
600	206.397	410.042	306.297	62.247	−806.816	−645.274	56.176
700	194.430	440.983	323.406	82.304	−798.643	−619.014	46.191
800	180.611	466.064	339.725	101.072	−791.858	−593.834	38.773

PREVIOUS: CURRENT: December 1974

0 to 489.7 K crystal
above 489.7 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹			kJ·mol⁻¹		
0							
100							
200							
298.15	147.904	221.752	221.752	0.	−858.975	−746.448	130.775
300	147.904	222.667	221.755	0.274	−858.905	−745.750	129.847
400	147.904	265.216	227.556	15.064	−855.349	−708.578	92.531
489.700	147.904	295.142	237.288	28.331	CRYSTAL <--> LIQUID TRANSITION		
489.700	217.482	366.911	237.288	63.477			
500	216.564	371.429	240.005	65.712	−816.238	−673.014	70.309
600	206.397	410.042	265.250	86.875	−806.816	−645.274	56.176
700	194.430	440.983	288.223	106.932	−798.643	−619.014	46.191
800	180.611	466.064	308.940	125.700	−791.858	−593.834	38.773

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 412.973 \pm 3.14\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -763.07 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -764.84 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
406.0 (1)	[458.0](2)
324.0 (1)	180.9 (2)
[377.2](1)	53.9 (2)
[112.1](1)	127.0 (2)

Ground State Quantum Weight: [1] $\sigma = 6$

Point Group: D_{3h}

Bond Distance: Ta–Cl = 2.27 ± 0.02 Å

Bond Angles: Cl*–Ta–Cl* = 120°; Cl*–Ta–Cl** = 90°; Cl**–Ta–Cl* = 180°
(* = equatorial ** = axial)

Product of the Moments of Inertia: $I_A I_B I_C = 1.02598 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

The vapor pressures over $TaCl_5$(cr) and $TaCl_5$(l) have been measured by eight investigators. The reported vapor pressures are corrected for vapor non–ideality by means of the equation $\Delta G°/T = R \ln p - Bp/T$. The Berthelot equation of state and critical constants T_c = 767 K and P_c = 43 atm. reported by Nisel'son *et al.*[6] are used to calculate B. The corrected vapor pressures are used to calculate $\Delta_r H°(298.15\ K)$ by both 2nd and 3rd law methods.

Source	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
$TaCl_5$(cr) = $TaCl_5$(g)						
Opykhtina and Fleischer[1]	transpiration	393–Tm	Eqn	23.12	22.46	−1.5
Tarasenkov and Komandin[2]	static	301–475	Eqn	20.63	22.26	4.3
Alexander and Fairbrother[3]	static	412–Tm	10*	22.94 ± 0.09	22.76 ± 0.03	−0.4 ± 0.2
Shchukarev and Kurbanov[5]	membrane	425–Tm	Eqn	23.46	22.67	−1.7
Schafer and Polert[7]	flow	350–385	17	22.75 ± 0.06	22.53 ± 0.02	−0.6 ± 0.2
Saeki *et al.*[8]	static	363–Tm	Eqn	22.31	22.53	0.6
Brink and Stevenson[9]	transpiration	431–473	28	21.80 ± 0.20	22.59 ± 0.08	1.8 ± 0.4
$TaCl_5$(l) = $TaCl_5$(g)						
Alexander and Fairbrother[3]	static	Tm–511	6*	17.17 ± 0.13	16.79 ± 0.01	−0.8 ± 0.3
Ainscough *et al.*[4]	boiling point	502–513	Eqn	16.73	16.62	−0.2
Saeki *et al.*[8]	static	490–505	Eqn	17.17	16.66	−1.0

*One point rejected due to a statistical test.

The adopted value for $\Delta_f H°(298.15\ K)$ of $TaCl_5$(g) is −182.8 ± 2.0 kcal·mol^{-1}. This value is calculated using the rounded mean 3rd law result for the seven sublimation studies, $\Delta_{sub} H°(298.15\ K)$ = 22.5 kcal·mol^{-1}. The rounded mean 3rd law result for the three vaporization studies leads to a $\Delta_f H°(298.15\ K)$ value for the gas which is 0.1 kcal·mol^{-1} more positive.

Heat Capacity and Entropy

$TaCl_5$(g) was shown by Spiridonov and Romanov,[15,16] using electron diffraction techniques, to have a trigonal bipyramidal structure of D_{3h} symmetry: all the Ta–Cl bond lengths being equal within experimental uncertainty, Ta–Cl = 2.27 ± 0.02 Å. Skinner and Sutton[10] earlier used electron diffraction techniques and had suggested the same structure although a square pyramidal structure was consistent with their experimental results. We adopt the results of Spiridonov and Romanov.[15,16] The principal moments of inertia are: $I_A = 91.0085 \times 10^{-39}$ and $I_B = I_C = 106.1766 \times 10^{-39}$ g·cm^2. A normal coordinate treatment of $TaCl_5$(g) in the Urey–Bradley force fields was performed by So[18] using the reported vibrational frequencies of Beattie and Ozin.[17] This work by So[18] was intended to check the correctness of the reported fundamental frequencies and predict those frequencies which had not been observed (ν_3, ν_4, ν_5). Beattie and Ozin[17] had recorded the gas phase Raman spectra of $NbCl_5$, $NbBr_5$, $TaCl_5$, and $TaBr_5$. We adopt the results of So[18] which support the work of Beattie and Ozin.[17]

There are many references in the literature to spectroscopic observations (IR and Raman) of $TaCl_5$ in the solid state and in organic solvents. Many problems arise in any attempt in relating the observed spectra. Tantalum pentachloride was shown to be dimeric in the solid phase,[11] while there are indications that it is also dimeric in solution.[12–14]

Continued on page 941

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−26.869	−763.071	−763.071	INFINITE
100	82.867	300.387	511.324	−21.094	−765.570	−746.743	390.059
200	109.077	367.054	423.672	−11.324	−765.647	−727.758	190.071
250	115.849	392.176	414.929	−5.688	−765.283	−718.325	150.086
298.15	120.137	412.973	412.973	0.	−764.835	−709.321	124.270
300	120.271	413.716	412.975	0.222	−764.817	−708.976	123.444
350	123.250	432.494	414.451	6.315	−764.294	−699.710	104.426
400	125.326	449.095	417.764	12.532	−763.741	−690.522	90.173
450	126.821	463.948	422.085	18.838	−763.173	−681.403	79.095
500	127.928	477.370	426.953	25.208	−762.602	−672.348	70.240
600	129.419	500.837	437.367	38.082	−761.469	−654.404	56.971
700	130.346	520.862	447.900	51.073	−760.361	−636.648	47.507
800	130.960	538.310	458.134	64.141	−759.277	−619.049	40.420
900	131.386	553.761	467.917	77.259	−758.215	−601.584	34.915
1000	131.693	567.620	477.206	90.414	−757.182	−584.237	30.517
1100	131.922	580.183	486.006	103.595	−756.186	−566.991	26.924
1200	132.097	591.670	494.339	116.796	−755.237	−549.834	23.934
1300	132.234	602.249	502.239	130.013	−754.334	−532.753	21.406
1400	132.343	612.052	509.737	143.242	−753.470	−515.741	19.243
1500	132.431	621.186	516.866	156.481	−752.635	−498.790	17.369
1600	132.503	629.736	523.656	169.728	−751.825	−481.894	15.732
1700	132.563	637.770	530.134	182.981	−751.048	−465.047	14.289
1800	132.613	645.349	536.327	196.240	−750.323	−448.245	13.008
1900	132.656	652.520	542.255	209.504	−749.666	−431.481	11.862
2000	132.692	659.325	547.940	222.771	−749.085	−414.750	10.832
2100	132.723	665.800	553.399	236.042	−748.581	−398.045	9.901
2200	132.751	671.975	558.650	249.316	−748.157	−381.363	9.055
2300	132.774	677.877	563.706	262.592	−747.820	−364.699	8.283
2400	132.795	683.528	568.582	275.870	−747.577	−348.047	7.575
2500	132.814	688.949	573.289	289.151	−747.439	−331.403	6.924
2600	132.830	694.159	577.838	302.433	−747.418	−314.763	6.324
2700	132.845	699.172	582.240	315.717	−747.526	−298.120	5.767
2800	132.858	704.004	586.503	329.002	−747.779	−281.472	5.251
2900	132.869	708.666	590.635	342.288	−748.192	−264.811	4.770
3000	132.880	713.171	594.645	355.576	−748.782	−248.133	4.320
3100	132.889	717.528	598.539	368.864	−749.569	−231.432	3.900
3200	132.898	721.747	602.324	382.154	−750.570	−214.703	3.505
3300	132.906	725.837	606.005	395.444	−788.263	−197.468	3.126
3400	132.913	729.804	609.588	408.735	−789.332	−179.549	2.758
3500	132.920	733.657	613.078	422.026	−790.439	−161.598	2.412
3600	132.926	737.402	616.480	435.319	−791.578	−143.615	2.084
3700	132.931	741.044	619.798	448.612	−792.744	−125.600	1.773
3800	132.937	744.589	623.035	461.905	−793.932	−107.554	1.478
3900	132.941	748.042	626.196	475.199	−795.135	−89.476	1.198
4000	132.946	751.408	629.285	488.493	−796.349	−71.366	0.932
4100	132.950	754.691	632.304	501.788	−797.565	−53.226	0.678
4200	132.954	757.895	635.256	515.083	−798.777	−35.057	0.436
4300	132.957	761.023	638.144	528.379	−799.980	−16.859	0.205
4400	132.960	764.080	640.972	541.675	−801.166	1.367	−0.016
4500	132.963	767.068	643.741	554.971	−802.330	19.619	−0.228
4600	132.966	769.990	646.454	568.267	−803.465	37.898	−0.430
4700	132.969	772.850	649.113	581.564	−804.566	56.199	−0.625
4800	132.972	775.649	651.720	594.861	−805.628	74.525	−0.811
4900	132.974	778.391	654.277	608.158	−806.646	92.873	−0.990
5000	132.976	781.078	656.786	621.456	−807.615	111.239	−1.162
5100	132.978	783.711	659.249	634.754	−808.531	129.626	−1.328
5200	132.980	786.293	661.668	648.052	−809.390	148.029	−1.487
5300	132.982	788.826	664.043	661.350	−810.188	166.449	−1.640
5400	132.984	791.312	666.377	674.648	−810.924	184.883	−1.788
5500	132.986	793.752	668.671	687.946	−811.594	203.331	−1.931
5600	132.987	796.148	670.926	701.245	−812.196	221.789	−2.069
5700	132.989	798.502	673.144	714.544	−812.729	240.258	−2.202
5800	132.990	800.815	675.325	727.843	−1551.944	261.537	−2.355
5900	132.992	803.088	677.471	741.142	−1552.546	292.809	−2.592
6000	132.993	805.324	679.584	754.441	−1553.118	324.091	−2.821

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [217.56]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 526\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -512.95 \pm 41.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = 20.573 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{sub} H°(298.15\ K) = 10.416\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WCl_5, cr, 298.15\ K) = -122.6\ kcal·mol^{-1}$, is calculated from that of the gas less the enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 24.0\ kcal·mol^{-1}$. The latter is calculated by the third law method from partial pressures of $WCl_5(g)$ derived from the total pressure data* of Shchukarev *et al.*[1] Dimer pressures, calculated from the same authors dimer–monomer dissociation data, are subtracted from the total pressures in order to obtain the monomer pressures. Analyses of the monomer pressures over both crystal and liquid give similar results and the average values for $\Delta_{sub} H°(298.15\ K)$ are 20.6 (second law) and 24.0 $kcal·mol^{-1}$ (third law) with a drift of about 7 $cal·K^{-1}·mol^{-1}$.

*Earlier data reported by Schukarev *et al.*,[2] have been revised and are not used here.

Heat Capacity and Entropy

$C_p° = 6.2\ cal·K^{-1}·mol^{-1}$ and $C_p°(526) = 7.25\ cal·K^{-1}·mol^{-1}$ are estimated using the method described by Kubaschewski and Evans.[3] Between 298.15 and 528, which is the melting point, the heat capacity is obtained by linear interpolation.

The entropy, $S°(298.15\ K) = 52\ cal·K^{-1}·mol^{-1}$, is listed by comparison with those of WCl_2(cr), WCl_4(cr) and WCl_6(cr).

Fusion Data

The melting point was determined from vapor pressure data by Shchukarev *et al.*[1] The heat of melting is the difference at the melting point between the second law enthalpies of vaporization and sublimation derived from total vapor pressure data of Schchukarev *et al.*[1]

Sublimation Data

Refer to the ideal gas table for details.

References

[1]S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. 14, No. 4 Ser. Fiz I Khim., No. 1, 120 (1959).
[2]Shchukarev *et al.*, Zhur. Neorg. Khim. 1, 357 (1956); 3, 2650 (1958).
[3]O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	155.645	217.568	217.568	0.	−512.958	−401.811	70.396
300	155.875	218.531	217.571	0.288	−512.872	−401.122	69.842
400	167.435	264.957	223.823	16.454	−507.845	−364.608	47.613
500	178.996	303.562	236.011	33.775	−501.966	−329.460	34.418
526.000	182.004	312.711	239.577	38.468	--- CRYSTAL <--> LIQUID ---		
600	189.954	337.194	250.129	52.239	−495.140	−295.585	25.733
700	198.531	367.151	264.746	71.684	−487.476	−262.921	19.619
800	205.016	394.106	279.260	91.877	−479.177	−231.402	15.109
900	209.618	418.534	293.399	112.621	−470.422	−200.952	11.663
1000	212.966	440.806	307.043	133.763	−461.356	−171.494	8.958
1100	215.811	461.240	320.145	155.205	−452.069	−142.956	6.788
1200	217.903	480.113	332.699	176.896	−442.606	−115.271	5.018
1300	219.325	497.614	344.720	198.762	−433.042	−88.381	3.551
1400	220.288	513.905	356.230	220.745	−423.429	−62.229	2.322
1500	220.915	529.126	367.254	242.808	−413.806	−36.765	1.280

PREVIOUS: December 1962 CURRENT: December 1966

$S°(298.15\ K)$ = [248.500] $J·K^{-1}·mol^{-1}$
T_{fus} = 526 K

$\Delta_f H°(298.15\ K) = -495.386\ kJ·mol^{-1}$
$\Delta_{fus}H° = 20.573 \pm 4.2\ kJ·mol^{-1}$

Heat of Formation

The heat of formation $\Delta_f H°(WCl_5, l, 298.15\ K) = -118.4\ kcal·mol^{-1}$, is calculated from that of WCl_5(cr) by adding the heat of melting and the difference between $H°(526;298.15)$ for the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 $cal·K^{-1}·mol^{-1}$.

The entropy of WCl_5(l), $S°(298.15\ K) = 59.393\ cal·K^{-1}·mol^{-1}$ is calculated in a manner analogous to that of the heat of formation.

Melting Data

Refer to the crystal table for details.

Vaporization Data

The boiling point (f = 1 atm), 561.4 K, is calculated as the temperature at which the Gibbs energy of formation for both WCl_5(l) and WCl_5(g) are equal. The difference in the enthalpies of formation of WCl_5(l) and WCl_5(g) at the boiling point is the enthalpy of vaporization. Shchukarev *et al.*[1] revised their previous data[2] and derived the boiling point as 561.2 K from their vapor pressure measurements.

References

[1]S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. **14**, No. 4, Ser. Fiz I Khim., No. 1, 120 (1959).
[2]S. A. Shchukarev and G. I. Novikov, Zhur. Neorg. Khim. **1**, 357 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	182.004	248.498	248.498	0.	−495.387	−393.462	68.933
300	182.004	249.624	248.502	0.337	−495.252	−392.830	68.398
400	182.004	301.983	255.641	18.537	−488.190	−359.764	46.980
500	182.004	342.596	269.121	36.738	−481.432	−328.444	34.312
526.000	182.004	351.823	272.983	41.470	--- CRYSTAL <--> LIQUID ---		
600	182.004	375.780	284.216	54.938	−474.870	−298.465	25.984
700	182.004	403.836	299.352	73.138	−468.450	−269.574	20.116
800	182.004	428.139	313.966	91.339	−462.144	−241.595	15.775
900	182.004	449.576	327.866	109.539	−455.933	−214.400	12.443
1000	182.004	468.752	341.012	127.740	−449.808	−187.892	9.814
1100	182.004	486.099	353.426	145.940	−443.762	−161.994	7.692
1200	182.004	501.935	365.152	164.140	−437.791	−136.643	5.948
1300	182.004	516.503	376.241	182.341	−431.891	−111.787	4.492
1400	182.004	529.991	386.748	200.541	−426.061	−87.382	3.260
1500	182.004	542.548	396.721	218.742	−420.301	−63.392	2.208

PREVIOUS: December 1962 CURRENT: December 1966

0 to 526 K crystal
above 526 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	155.645	217.568	217.568	0.	−512.958	−401.811	70.396
300	155.875	218.531	217.571	0.288	−512.872	−401.122	69.842
400	167.435	264.957	223.823	16.454	−507.845	−364.608	47.613
500	178.996	303.562	236.011	33.775	−501.966	−329.460	34.418
526.000	182.004	312.711	239.577	38.468	CRYSTAL <--> LIQUID TRANSITION		
526.000	182.004	351.823	239.577	59.041			
600	182.004	375.780	254.931	72.509	−474.870	−298.465	25.984
700	182.004	403.836	274.250	90.710	−468.450	−269.574	20.116
800	182.004	428.139	292.001	108.910	−462.144	−241.595	15.775
900	182.004	449.576	308.342	127.111	−455.933	−214.400	12.443
1000	182.004	468.752	323.441	145.311	−449.808	−187.892	9.814
1100	182.004	486.099	337.452	163.511	−443.762	−161.994	7.692
1200	182.004	501.935	350.509	181.712	−437.791	−136.643	5.948
1300	182.004	516.503	362.725	199.912	−431.891	−111.787	4.492
1400	182.004	529.991	374.197	218.113	−426.061	−87.382	3.260
1500	182.004	542.548	385.006	236.313	−420.301	−63.392	2.208

PREVIOUS: CURRENT: December 1966

$S°(298.15\ K) = [405.693]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 410.9 \pm 33\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -412.5 \pm 33\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[7000]	[2]
[14000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[480](1)	[350](2)
[400](1)	[150](2)
[380](1)	[100](2)
[130](1)	[180](2)

Ground State Quantum Weight: [2] σ = [6]
Point Group: [D_{3h}]
Bond Distance: W–Cl = [2.26] Å
Bond Angles: Cl*–W–Cl* = [120]°; Cl*–W–Cl** = [90]°; Cl**–W–Cl** = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [9.98 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The heat of formation, $\Delta_f H°(WCl_5, g, 298.15\ K) = -98.6$ kcal·mol^{-1}, is calculated from $\Delta_r H°(298.15\ K) = 19.4$ kcal·mol^{-1} for $WCl_6(g) \rightarrow WCl_5(g) + 1/2\ Cl_2(g)$. The value of $\Delta_r H°(298.15\ K)$ is calculated by the third law method from the equation for log K_p given by Shchukarev.[1] The second law $\Delta_r H°(298.15\ K)$ is 24.6 kcal·mol^{-1} and the third law drift is -8.5 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The molecular configuration is assumed to be a trigonal bipyramid similar to that of $MoCl_5$ determined by electron diffraction by Ewens and Lister.[2] The bond distance is estimated to be the same as that in WCl_6(g). The three principal moments of inertia are: $I_A = 90.2084 \times 10^{-39}$ and $I_B = I_C = 105.2432 \times 10^{-39}$ g·cm^2.

All vibrational frequencies are estimated from those of $SbCl_5$, PCl_5, $NbCl_5$ and $TaCl_5$ obtained from infrared and Raman spectra by Carlson.[3]

If it is considered that the metal atoms are effectively ionized, then the W^{5+} will have a single d electron in a field of chloride ions. The electronic splitting would be roughly the inverse of that in $CuCl_2$(g) as given by DeKock and Gruen,[4] where Cu has a d^9 configuration. By analogy with the splitting in $CuCl_2$, the low lying electronic levels are estimated to be 7000 cm^{-1}, both doublets.

References

[1]S. A. Shchukarev and A. V. Shvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961).
[2]R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. **34**, 1358 (1938).
[3]G. L. Carlson, Spectrochim. Acta **19**, 1291 (1963).
[4]C. W. DeDock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−26.248	−410.866	−410.866	INFINITE
100	79.886	293.996	503.816	−20.982	−413.531	−394.718	206.179
200	108.885	359.776	416.397	−11.324	−413.475	−375.794	98.147
250	115.882	384.884	407.651	−5.692	−413.047	−366.420	76.559
298.15	120.235	405.693	405.693	0.	−412.542	−357.485	62.630
300	120.370	406.438	405.696	0.223	−412.522	−357.143	62.184
350	123.362	425.232	407.173	6.321	−411.945	−347.959	51.930
400	125.434	441.848	410.489	12.544	−411.340	−338.859	44.250
450	126.918	456.712	414.814	18.854	−410.721	−329.836	38.286
500	128.014	470.144	419.686	25.229	−410.097	−320.882	33.522
600	129.486	493.625	430.108	38.110	−408.853	−303.156	26.392
700	130.400	513.659	440.648	51.108	−407.636	−285.637	21.314
800	131.006	531.114	450.889	64.180	−406.458	−268.289	17.517
900	131.434	546.570	460.678	77.303	−405.325	−251.086	14.573
1000	131.757	560.436	469.972	90.463	−404.240	−234.008	12.223
1100	132.019	573.006	478.777	103.652	−403.205	−217.035	10.306
1200	132.250	584.503	487.115	116.866	−402.221	−200.154	8.712
1300	132.467	595.098	495.019	130.102	−401.285	−183.353	7.367
1400	132.681	604.922	502.523	143.359	−400.399	−166.623	6.217
1500	132.900	614.084	509.658	156.638	−399.560	−149.954	5.222
1600	133.125	622.668	516.456	169.940	−398.768	−133.340	4.353
1700	133.357	630.746	522.944	183.264	−398.022	−116.774	3.588
1800	133.596	638.375	529.146	196.611	−397.323	−100.250	2.909
1900	133.841	645.605	535.087	209.983	−396.671	−83.764	2.303
2000	134.088	652.476	540.786	223.380	−396.070	−67.311	1.758
2100	134.336	659.024	546.262	236.801	−395.520	−50.887	1.266
2200	134.583	665.279	551.531	250.247	−395.024	−34.488	0.819
2300	134.827	671.267	556.607	263.717	−394.588	−18.110	0.411
2400	135.067	677.010	561.505	277.212	−394.214	−1.750	0.038
2500	135.301	682.529	566.237	290.730	−393.906	14.596	−0.305
2600	135.528	687.840	570.812	304.272	−393.664	30.932	−0.621
2700	135.748	692.959	575.242	317.836	−393.520	47.260	−0.914
2800	135.958	697.900	579.535	331.421	−393.510	63.584	−1.186
2900	136.160	702.674	583.699	345.027	−393.676	79.911	−1.439
3000	136.352	707.293	587.742	358.653	−394.047	96.247	−1.676
3100	136.534	711.767	591.671	372.297	−394.666	112.600	−1.897
3200	136.706	716.105	595.493	385.959	−395.563	128.976	−2.105
3300	136.868	720.314	599.212	399.638	−396.764	145.387	−2.301
3400	137.020	724.402	602.834	413.332	−398.302	161.837	−2.486
3500	137.162	728.376	606.364	427.042	−400.237	178.339	−2.662
3600	137.294	732.242	609.807	440.764	−402.663	194.903	−2.828
3700	137.416	736.005	613.167	454.500	−440.440	211.733	−2.989
3800	137.529	739.671	616.448	468.247	−440.547	229.360	−3.153
3900	137.632	743.245	619.654	482.005	−440.658	246.991	−3.308
4000	137.727	746.731	622.788	495.774	−440.770	264.624	−3.456
4100	137.813	750.133	625.852	509.551	−440.876	282.261	−3.596
4200	137.890	753.455	628.851	523.336	−440.971	299.899	−3.730
4300	137.960	756.700	631.787	537.128	−441.049	317.540	−3.857
4400	138.021	759.873	634.662	550.927	−441.105	335.182	−3.979
4500	138.075	762.975	637.479	564.732	−441.132	352.825	−4.095
4600	138.122	766.010	640.240	578.542	−441.127	370.469	−4.207
4700	138.163	768.981	642.948	592.357	−441.083	388.112	−4.313
4800	138.196	771.890	645.604	606.175	−440.996	405.753	−4.415
4900	138.224	774.740	648.210	619.996	−440.862	423.393	−4.513
5000	138.246	777.533	650.769	633.819	−440.677	441.028	−4.607
5100	138.263	780.271	653.281	647.645	−440.438	458.661	−4.698
5200	138.274	782.956	655.749	661.472	−440.140	476.287	−4.784
5300	138.281	785.590	658.175	675.299	−439.782	493.907	−4.868
5400	138.283	788.174	660.558	689.128	−439.360	511.520	−4.948
5500	138.280	790.712	662.902	702.956	−438.873	529.126	−5.025
5600	138.274	793.203	665.206	716.783	−438.318	546.720	−5.100
5700	138.264	795.650	667.473	730.610	−437.695	564.305	−5.171
5800	138.251	798.055	669.704	744.436	−437.001	581.878	−5.240
5900	138.234	800.418	671.899	758.260	−436.237	599.438	−5.307
6000	138.214	802.741	674.061	772.083	−435.401	616.984	−5.371

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = [537.016]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -658.290 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -654.378 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[300](1)	[110](1)	[230](1)
[200](1)	[350](1)	[85](1)
[120](1)	[100](1)	[70](1)
[95](1)	[18](1)	[260](1)
[35](1)	[310](1)	[110](1)
[250](1)	[110](1)	[90](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Fe–Cl = 2.11 ± 0.03 Å; $Fe–Cl_{bridge}$ = 2.28 ± 0.03 Å
Bond Angles: Cl–Fe–Cl = 128 ± 3°; Cl_{bridge}–Fe–Cl_{bridge} = 92 ± 3°
Product of the Moments of Inertia: $I_A I_B I_C = 7.35910 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The vaporization of $FeCl_3$(cr) is complex. It involves three possible chemical reactions, i.e. (1) $2FeCl_3(cr) = Fe_2Cl_6(g)$; (2) $FeCl_3(cr) = FeCl_3(g)$; and (3) $2FeCl_3(cr) = 2FeCl_2(cr) + Cl_2(g)$. Although these equilibria have been studied previously by many investigators, a review of their reported data reveals inconsistencies and errors. At room temperature the main vapor species present above $FeCl_3$(cr) is Fe_2Cl_6(g), a dimer of $FeCl_3$(g). As temperature increases, the dimer gradually decomposes into monomers ($FeCl_3$, g). Simultaneously, part of $FeCl_3$(cr) also decomposes into $FeCl_2$(cr) and Cl_2(g). Therefore in order to obtain the partial pressure of Fe_2Cl(g), the partial pressures of other vapor species, e.g. Cl_2(g) and $FeCl_3$(g), must be known and deducted from the observed total pressures. However, only few investigators made such corrections. The total pressures above $FeCl_3$(cr), at 500–600 K, have been determined by Maier[1] and Johnstone *et al.*,[2] respectively. The partial pressures of Fe_2Cl_6(g) were evaluated by the subtraction of the calculated equilibrium pressures of Cl_2(g), obtained from reaction,[3] from the reported total pressures. The partial pressures of $FeCl_3$(g) were found to be insignificant at these temperatures. Using the partial pressures obtained for Fe_2Cl_6(g), the enthalpy change $\Delta_r H°$(298.15 K) of reaction[1] was derived by both the second and third law methods. Then the value of $\Delta_f H°(Fe_2Cl_6, g, 298.15\ K)$ was calculated. The results are given in this table.

Wilson and Gregory[3] have investigated the vaporization and thermal decomposition equilibria of $FeCl_3$(cr) by gas saturation flow and diaphragm gage techniques. Using the partial pressures for Fe_2Cl_6(g), calculated from an equation, the values of $\Delta_r H°$(298.15 K) and $\Delta_f H°$(298.15 K) were also evaluated and listed in the table. Based on the total pressures measured by Stirnemann[4] and Sano,[5] the equations for the pressures of Fe_2Cl_6(g) and Cl_2(g) in equilibrium with $FeCl_3$(cr) and $FeCl_2$(cr) as a function of temperature were reported by Wilson and Gregory.[3] The corresponding values of $\Delta_r H°$(298.15 K) and $\Delta_f H°$(298.15 K) were hence calculated. A brief summary and discussion of results of some other previous investigators were also given in the same report.

Source	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K)* kcal·mol^{-1}
Maier[1]	489.6–591.5	32.18 ± 0.40	34.67	−156.25 ± 0.50
Johnstone *et al.*[2]	505.2–562.2	34.8 ± 0.49	34.50	−156.42 ± 0.50
Wilson and Gregory[3]	463.4–577.2	34.46	34.45	−156.47 ± 0.40
Stirnemann[4]	526.2–574.2	35.04	34.49	−156.42 ± 0.50
Sano[5]	513.2–569.2	30.67	34.76	−156.16 ± 0.50

*Based on the third law values for $\Delta_r H°$(298.15 K).

The value of $\Delta_f H°$(298.15 K) for Fe_2Cl_6(g) is selected as $-156.4 \pm 2.0\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular structure, bond distances and angles were obtained from Zasorin *et al.*[6] The vibrational frequencies were estimated by comparison with those for Al_2Cl_6(g) such that the values of $\Delta H°$ derived from the equilibrium data by the second and third law methods are in reasonable agreement. The three principal moments of inertia are: $I_A = 2.79395 \times 10^{-37}$, $I_B = 1.16349 \times 10^{-37}$ and $I_C = 2.26383 \times 10^{-37}$ g·cm^2.

References

[1]C. G. Maier, U. S. Bur. Mines Tech. Paper 360 (1925).
[2]H. F. Johnstone H. C. Weingartner and W. E. Winsche, J. Amer. Chem. Soc. **64**, 241 (1942).
[3]L. E. Wilson and N. W. Gregory, J. Phys. Chem. **62**, 433 (1958).
[4]E. Stirnemann, Neues Jahrb. Mineral., Geol., Palaont., **52A**, 334 (1925).
[5]K. Sano, J. Chem. Soc. Japan, **59**, 1073 (1938).
[6]E. Z. Zasorin, N. G. Rambidi and P. A. Akishin, Zh. Strukt. Khim., **4**, 910 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−40.447	−658.269	−658.269	INFINITE
100	132.329	365.442	683.671	−31.823	−659.226	−637.855	333.181
200	164.177	469.299	552.585	−16.657	−656.711	−617.413	161.252
250	170.184	506.640	539.778	−8.285	−655.470	−607.734	126.979
298.15	173.663	536.937	536.937	0.	−654.378	−598.641	104.879
300	173.768	538.011	536.940	0.321	−654.338	−598.295	104.172
350	176.052	564.982	539.065	9.071	−653.317	−589.037	87.909
400	177.587	588.597	543.811	17.914	−652.411	−579.917	75.729
450	178.665	609.579	549.975	26.822	−651.626	−570.904	66.269
500	179.449	628.446	556.894	35.776	−650.968	−561.971	58.709
600	180.486	661.263	571.635	53.777	−650.035	−544.268	47.383
700	181.121	689.137	586.480	71.860	−649.620	−526.680	39.301
800	181.537	713.351	600.858	89.994	−649.813	−509.113	33.242
900	181.824	734.751	614.569	108.163	−650.863	−491.473	28.524
1000	182.030	753.919	627.563	126.356	−653.374	−473.648	24.741
1100	182.183	771.276	639.851	144.567	−657.699	−455.437	21.627
1200	182.300	787.133	651.473	162.792	−660.940	−436.946	19.020
1300	182.391	801.729	662.477	181.026	−660.909	−418.282	16.807
1400	182.463	815.248	672.913	199.269	−661.066	−399.613	14.910
1500	182.521	827.839	682.826	217.519	−661.411	−380.927	13.265
1600	182.569	839.620	692.262	235.773	−661.945	−362.212	11.825
1700	182.609	850.689	701.259	254.032	−664.568	−343.420	10.552
1800	182.642	861.128	709.853	272.295	−666.151	−324.484	9.416
1900	182.670	871.003	718.077	290.560	−696.123	−304.051	8.359
2000	182.694	880.374	725.960	308.828	−698.572	−283.353	7.400
2100	182.715	889.288	733.527	327.099	−701.052	−262.531	6.530
2200	182.733	897.788	740.801	345.371	−703.566	−241.590	5.736
2300	182.748	905.911	747.805	363.645	−706.120	−220.534	5.008
2400	182.762	913.689	754.556	381.921	−708.715	−199.367	4.339
2500	182.774	921.150	761.071	400.198	−711.358	−178.090	3.721
2600	182.785	928.319	767.367	418.476	−714.050	−156.706	3.148
2700	182.795	935.218	773.457	436.755	−716.796	−135.217	2.616
2800	182.803	941.866	779.353	455.035	−719.598	−113.626	2.120
2900	182.811	948.281	785.068	473.315	−722.457	−91.934	1.656
3000	182.818	954.478	790.613	491.597	−725.373	−70.143	1.221
3100	182.824	960.473	795.996	509.879	−728.347	−48.253	0.813
3200	182.830	966.278	801.227	528.162	−1427.977	−11.418	0.186
3300	182.835	971.904	806.314	546.445	−1427.259	32.838	−0.520
3400	182.840	977.362	811.265	564.729	−1426.656	77.074	−1.184
3500	182.844	982.662	816.087	583.013	−1426.164	121.294	−1.810
3600	182.848	987.813	820.786	601.297	−1425.780	165.501	−2.401
3700	182.852	992.823	825.368	619.582	−1425.499	209.700	−2.960
3800	182.855	997.699	829.839	637.868	−1425.315	253.891	−3.490
3900	182.858	1002.449	834.205	656.153	−1425.223	298.079	−3.992
4000	182.861	1007.079	838.469	674.439	−1425.218	342.267	−4.470
4100	182.864	1011.594	842.636	692.726	−1425.293	386.455	−4.923
4200	182.866	1016.001	846.712	711.012	−1425.444	430.645	−5.356
4300	182.869	1020.303	850.699	729.299	−1425.663	474.840	−5.768
4400	182.871	1024.508	854.602	747.586	−1425.946	519.041	−6.162
4500	182.873	1028.617	858.423	765.873	−1426.287	563.249	−6.538
4600	182.875	1032.637	862.167	784.160	−1426.681	607.466	−6.898
4700	182.877	1036.570	865.836	802.448	−1427.123	651.690	−7.243
4800	182.878	1040.420	869.433	820.736	−1427.610	695.926	−7.573
4900	182.880	1044.191	872.961	839.024	−1428.138	740.172	−7.890
5000	182.881	1047.885	876.423	857.312	−1428.704	784.428	−8.195
5100	182.883	1051.507	879.821	875.600	−1429.306	828.697	−8.488
5200	182.884	1055.058	883.156	893.888	−1429.941	872.977	−8.769
5300	182.885	1058.542	886.433	912.177	−1430.609	917.270	−9.040
5400	182.886	1061.960	889.652	930.465	−1431.310	961.577	−9.301
5500	182.887	1065.316	892.815	948.754	−1432.043	1005.897	−9.553
5600	182.889	1068.611	895.925	967.043	−1432.810	1050.229	−9.796
5700	182.890	1071.848	898.983	985.332	−1433.613	1094.576	−10.031
5800	182.890	1075.029	901.991	1003.621	−1434.454	1138.938	−10.257
5900	182.891	1078.156	904.951	1021.910	−1435.337	1183.314	−10.476
6000	182.892	1081.230	907.863	1040.199	−1436.265	1227.705	−10.688

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K)$ = [255.224 ± 16.7] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K)$ = [−523.000 ± 41.8] $kJ·mol^{-1}$

Enthalpy of Formation

Novikov and Galitskii,[1] assumed that the equilibrium $MoCl_6(cr) = MoCl_5(g) + 1/2\ Cl_2(g)$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta_r H°(T) = 4$ kcal mol^{-1} and $\Delta_r S(T) = 8$ $cal·K^{-1}·mol^{-1}$, of the equilibrium $MoCl_6(cr) = MoCl_5(cr) + 1/2\ Cl_2(g)$, from which they obtained the $\Delta_f H°(MoCl_6, cr, 298.15\ K) = -125$ $kcal·mol^{-1}$.

Heat Capacity and Entropy

The adopted heat capacity is the same as that of $WCl_6(\alpha, cr)$, since the heat capacities of W and Mo are almost the same. The entropy is estimated from that of $MoCl_5(cr)$ by the addition of 4 $cal·K^{-1}·mol^{-1}$ due to one extra chlorine atom in the molecule.

Vaporization Data

The sublimation point is calculated from the free energy crossover between crystal and gas. However, it should be noted that $MoCl_6(cr)$ is unstable with respect to $MoCl_5(cr)$ at all temperatures and thus sublimation could occur only under an atmosphere of Cl_2.

References

[1]G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. **10**, 576–8 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	175.310	255.224	255.224	0.	−523.000	−391.033	68.507
300	175.728	256.310	255.227	0.325	−522.908	−390.215	67.942
400	192.464	309.156	262.320	18.734	−517.364	−346.787	45.286
500	209.200	353.955	276.271	38.842	−510.519	−304.907	31.853
600	223.007	393.425	292.572	60.512	−502.362	−264.531	23.029
700	229.702	428.347	309.526	83.175	−493.387	−225.594	16.834
800	233.049	459.266	326.350	106.333	−484.049	−187.973	12.273
900	233.886	486.768	342.675	129.684	−474.626	−151.529	8.795
1000	234.304	511.432	358.339	153.093	−465.239	−116.133	6.066
1100	234.722	533.783	373.288	176.544	−455.901	−81.675	3.878
1200	235.141	554.224	387.526	200.037	−446.612	−48.065	2.092
1300	235.559	573.063	401.083	223.574	−437.373	−15.228	0.612
1400	235.840	590.531	413.999	247.145	−428.198	16.900	−0.631
1500	235.978	606.808	426.317	270.737	−419.104	48.375	−1.685

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = [419.538 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-438.253 \pm 83.7]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-439.320 \pm 83.7]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[347](1)	[144](3)
[326](2)	[171](3)
[390](3)	[106](3)

Ground State Quantum Weights = [1]
Point Group = O_h
Bond Distance: Mo–Cl = [2.26] Å
Bond Angle: Cl–Mo–Cl = [90°]; $\sigma = 24$
Product of the Moments of Inertia: $I_A I_B I_C = [1.7396 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Novikov and Galitskii,[1] assumed that the equilibrium $MoCl_6(cr) = MoCl_5(g) + 1/2\ Cl_2(g)$ exists. They then calculated values for the constant of the above equilibrium and estimated the thermodynamic characteristics, $\Delta_T H° = 2.5\ kcal \cdot mol^{-1}$ and $\Delta_T S° = 10\ cal \cdot K^{-1} \cdot mol^{-1}$ of the equilibrium $MoCl_6(g) = MoCl_5(g) + 1/2\ Cl_2(g)$, from which they obtained the $\Delta_f H°(MoCl_6, g, 298.15\ K) = -105\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those of MoF_6 and WF_6, given by Nakamoto[2], and WCl_6 given by Evans and Lo.[3]

Structure, bond distance and bond angle are estimated to be the same as those of WCl_6. The three principal moments of inertia are $I_A = I_B = I_C = 120.2684 \times 10^{-39}\ g \cdot cm^2$.

References

[1]G. I. Novikov and N. V. Galitskii, Zh. Neorg. Khim. **10**, 576–82 (1965).
[2]K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York–London, (1963).
[3]J. C. Evans and G. Y. S. Lo, J. Mol. Spectrosc. **26**, 147 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−31.060	−438.253	−438.253	INFINITE
100	94.690	285.524	537.586	−25.206	−441.626	−412.774	215.611
200	131.116	364.480	432.505	−13.605	−440.980	−384.002	100.291
250	139.219	394.683	422.003	−6.830	−440.179	−369.847	77.275
298.15	144.125	419.654	419.654	0.	−439.320	−356.378	62.436
300	144.276	420.546	419.657	0.267	−439.286	−355.864	61.961
350	147.587	443.052	421.427	7.569	−438.354	−342.033	51.046
400	149.853	462.917	425.396	15.008	−437.410	−328.338	42.876
450	151.463	480.665	430.569	22.543	−436.468	−314.760	36.536
500	152.644	496.687	436.393	30.147	−435.533	−301.287	31.475
600	154.221	524.669	448.840	45.497	−433.696	−274.611	23.907
700	155.193	548.521	461.419	60.972	−431.910	−248.239	18.524
800	155.833	569.289	473.633	76.525	−430.177	−222.119	14.503
900	156.276	587.670	485.302	92.132	−428.498	−196.213	11.388
1000	156.595	604.153	496.377	107.776	−426.876	−170.492	8.906
1100	156.832	619.090	506.864	123.448	−425.317	−144.929	6.882
1200	157.013	632.744	516.794	139.141	−423.829	−119.506	5.202
1300	157.154	645.318	526.203	154.849	−422.418	−94.203	3.785
1400	157.266	656.968	535.132	170.570	−421.092	−69.006	2.575
1500	157.357	667.822	543.620	186.302	−419.859	−43.901	1.529
1600	157.431	677.980	551.704	202.041	−418.726	−18.874	0.616
1700	157.493	687.526	559.415	217.788	−417.700	6.084	−0.187
1800	157.545	696.529	566.785	233.539	−416.793	30.986	−0.899
1900	157.588	705.048	573.840	249.296	−416.012	55.841	−1.535
2000	157.626	713.133	580.604	265.057	−415.370	80.658	−2.107
2100	157.658	720.824	587.100	280.821	−414.878	105.446	−2.623
2200	157.686	728.159	593.346	296.588	−414.549	130.216	−3.092
2300	157.711	735.169	599.361	312.358	−414.396	154.973	−3.520
2400	157.732	741.882	605.161	328.130	−414.433	179.728	−3.912
2500	157.751	748.321	610.759	343.905	−414.677	204.489	−4.273
2600	157.768	754.508	616.170	359.681	−415.152	229.265	−4.606
2700	157.783	760.463	621.404	375.458	−415.902	254.064	−4.915
2800	157.796	766.201	626.474	391.237	−416.991	278.896	−5.203
2900	157.808	771.739	631.388	407.017	−454.386	303.823	−5.472
3000	157.819	777.089	636.156	422.799	−454.363	329.968	−5.745
3100	157.829	782.264	640.786	438.581	−454.398	356.113	−6.000
3200	157.838	787.275	645.286	454.364	−454.488	382.259	−6.240
3300	157.846	792.132	649.663	470.149	−454.631	408.410	−6.465
3400	157.853	796.844	653.923	485.934	−454.823	434.565	−6.676
3500	157.860	801.420	658.072	501.719	−455.060	460.727	−6.876
3600	157.866	805.867	662.116	517.505	−455.336	486.897	−7.065
3700	157.872	810.193	666.060	533.292	−455.645	513.074	−7.243
3800	157.877	814.403	669.908	549.080	−455.979	539.259	−7.413
3900	157.882	818.504	673.666	564.868	−456.333	565.455	−7.573
4000	157.887	822.501	677.337	580.656	−456.699	591.659	−7.726
4100	157.891	826.400	680.925	596.445	−457.068	617.873	−7.872
4200	157.895	830.205	684.435	612.234	−457.432	644.095	−8.010
4300	157.898	833.920	687.868	628.024	−457.785	670.326	−8.143
4400	157.902	837.550	691.229	643.814	−458.119	696.566	−8.269
4500	157.905	841.099	694.520	659.604	−458.425	722.811	−8.390
4600	157.908	844.569	697.744	675.395	−458.698	749.065	−8.506
4700	157.911	847.965	700.904	691.186	−458.929	775.322	−8.617
4800	157.913	851.290	704.003	706.977	−459.113	801.585	−8.723
4900	157.916	854.546	707.042	722.769	−459.245	827.852	−8.825
5000	157.918	857.736	710.024	738.560	−1050.702	859.850	−8.983
5100	157.920	860.864	712.951	754.352	−1052.391	898.079	−9.198
5200	157.922	863.930	715.825	770.144	−1054.158	936.340	−9.406
5300	157.924	866.938	718.648	785.937	−1055.996	974.636	−9.606
5400	157.926	869.890	721.422	801.729	−1057.901	1012.968	−9.799
5500	157.928	872.788	724.148	817.522	−1059.868	1051.336	−9.985
5600	157.929	875.634	726.827	833.315	−1061.891	1089.739	−10.165
5700	157.931	878.429	729.463	849.108	−1063.964	1128.179	−10.339
5800	157.932	881.176	732.055	864.901	−1066.084	1166.657	−10.507
5900	157.934	883.875	734.605	880.694	−1068.244	1205.170	−10.670
6000	157.935	886.530	737.115	896.488	−1070.444	1243.720	−10.828

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [238.488]\ J·K^{-1}·mol^{-1}$
$T_{trs}\ (\alpha_1 \rightarrow \alpha_2) = 450 \pm 10\ K$
$T_{trs}\ (\alpha_2 \rightarrow \beta) = 503 \pm 3\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -593.71 \pm 25.1\ kJ·mol^{-1}$
$\Delta_{trs} H°(\alpha_1 \rightarrow \alpha_2) = [4.2]\ kJ·mol^{-1}$
$\Delta_{trs} H°(\alpha_2 \rightarrow \beta) \approx 15.774\ kJ·mol^{-1}$

Enthalpy of Formation

Shchukarev *et al.*[1] have measured calorimetrically the heat of solution of WCl_6(cr) and also of H_2WO_4(cr) in a 12% solution of NaOH as -188.0 ± 0.3 and -13.6 ± 0.11 kcal·mol^{-1}, respectively. Based on these data and a heat of dilution value for Na_2WO_4 which is essentially zero, we obtain $\Delta_f H°(298.15\ K) = -174.4 \pm 0.3$ kcal·mol^{-1} for WCl_6(cr) + 6 NaOH(aq, 16.3 H_2O) → H_2WO_4(cr) + 6 NaCl(aq, 22000 H_2O) + 2 H_2O(l). This reaction gives $\Delta_f H°(WCl_6, cr, 298.15\ K) = -141.9 \pm 6$ kcal·mol^{-1}, using a revised $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = 270.5$ kcal·mol^{-1}, and other auxiliary data from JANAF Tables and from Parker.[2] The authors have suggested a possible uncertainty of the order of 5 kcal·mol^{-1} due to the slowness of the dissolution of WCl_6(cr).

Heat Capacity and Entropy

Welty[5] has measured the enthalpy changes for $WCl_6(\alpha, cr)$ in the temperature range from 406 to 502.4 K by drop calorimetry. Few points were measured in the region of the $\alpha_1 \rightarrow \alpha_2$ transition and no attempt was made to investigate the phase present at the conclusion of the drop. Thus, these data appear to be inadequate to define the heat capacities of the α_1 and α_2 phase. The adopted heat capacities are estimated so that they are reasonably consistent with the enthalpy data.

The entropy, $S°(298.15\ K) = 57.0$ cal·K^{-1}·mol^{-1}, is calculated from that of the gas using $\Delta S°(298.15\ K) = 43.155$ cal·K^{-1}·mol^{-1} from the vaporization and sublimation data given in the WCl_6(g) table (December 31, 1966).

Transition Data

Transition temperatures and heats of transition have been reported by the following investigators, and their results are summarized as follows:

		$\alpha_1 \rightarrow \alpha_2$ Transition		$\alpha_2 \rightarrow \beta$ Transition	
			$\Delta_{trs}H°$		$\Delta_{trs}H°$
Source	*Method*	*T*/K	kcal·mol^{-1}	*T*/K	kcal·mol^{-1}
Ketelaar *et. al*[3]	Vapor pressure	441	—	500	3.4
Stevenson[4]	Cooling curve	458	—	503	—
	Vapor pressure	—	—	503	1.9
Welty[5]	Drop calorimetric	—	—	504	3.4
Shchukarev *et al.*[6]	Vapor pressure	—	—	504	3.4
Dobrotin *et al.*[7]	Approximate calorimetric	—	—	493 ± 10	5.5

The adopted $\Delta_f H°(450\ K)$ ($\alpha_1 \rightarrow \alpha_2$) and $\Delta_f H°(503\ K)$ ($\alpha_2 \rightarrow \beta$) are calculated as 1.0 and 3.77 kcal·mol^{-1}, respectively, based on the adopted heat capacities and the enthalpy data. The enthalpies are assumed to refer to α_1 phase as the final state, although no experimental evidence for this is given.

Fusion Data

Refer to the β–crystal table for details.

Sublimation Data

Refer to the ideal gas table for details.

References

[1] S. A. Shchukarev, I. V. Vasilkova and G. I. Novikov, Zh. Neorg. Khim. **3**, 2642 (1958).
[2] V. B. Parker, NSRDS–NBS 2, (1965).
[3] J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. **62**, 597 (1943).
[4] F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines RI 6367, (1964).
[5] J. R. Welty, Ph.D. Thesis, Oregon State University (1962).
[6] S. A Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. I Khim., No. 1, 87 (1961).
[7] R. B. Dobrotin, A. V. Suvorov and Y. V. Kondrat'ev Vestnik Leningrad. Univ. **19**, No. 4 Fiz. I Khim. No. 1, 95 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K^{-1}mol^{-1}		kJ·mol^{-1}			
0							
100							
200							
298.15	175.418	238.488	238.488	0.	−593.710	−455.544	79.809
300	175.728	239.574	238.491	0.325	−593.618	−454.687	79.168
400	192.464	292.420	245.584	18.734	−588.082	−409.178	53.433
450	200.832	315.572	252.090	28.567	−584.830	−387.006	44.923
450.000	200.832	324.870	252.090	32.751	- - - - - - - I <- -> II - - - - - - -		
500	209.200	346.463	260.459	43.002	−577.043	−365.681	38.202
503.000	209.702	347.716	260.976	43.630	- - - - - - II <- -> III - - - - - - -		
600	222.170	385.865	278.144	64.633	−568.866	−324.158	28.220
700	229.367	420.706	296.072	87.244	−559.872	−284.076	21.198
800	232.840	451.598	313.620	110.383	−550.476	−245.315	16.017
900	234.095	479.108	330.508	133.740	−540.969	−207.741	12.057
1000	234.304	503.792	346.624	157.168	−531.485	−171.225	8.944

PREVIOUS: December 1962 CURRENT: December 1966

0	to 450	K	crystal, alpha$_1$
450	to 503	K	crystal, alpha$_2$
503	to 555	K	crystal, beta
above	555	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	175.418	238.488	238.488	0.	−593.710	−455.544	79.809
300	175.728	239.574	238.491	0.325	−593.618	−454.687	79.168
400	192.464	292.420	245.584	18.734	−588.082	−409.178	53.433
450	200.832	315.572	252.090	28.567	−584.830	−387.006	44.923
450.000	200.832	324.870	252.090	32.751	- - - - - - - I <- - > II - - - - - - -		
500	209.200	346.463	260.459	43.002	−577.043	−365.681	38.202
503.000	209.702	347.716	260.976	43.630	II <- - > III		
503.000	188.280	379.075	260.976	59.404	TRANSITION		
555.000	188.280	397.597	272.923	69.194	III <- - > LIQUID		
555.000	200.832	409.659	272.923	75.889	TRANSITION		
600	200.832	425.317	283.773	84.926	−548.573	−327.535	28.514
700	200.832	456.275	306.262	105.009	−542.106	−291.209	21.730
800	200.832	483.092	326.727	125.092	−535.767	−255.801	16.702
900	200.832	506.747	345.441	145.176	−529.533	−221.180	12.837
1000	200.832	527.907	362.648	165.259	−523.394	−187.249	9.781
1100	200.832	547.048	378.555	185.342	−517.340	−153.928	7.309
1200	200.832	564.523	393.335	205.425	−511.367	−121.155	5.274
1300	200.832	580.598	407.130	225.508	−505.470	−88.877	3.571
1400	200.832	595.481	420.058	245.592	−499.649	−57.050	2.129
1500	200.832	609.337	432.221	265.675	−493.901	−25.637	0.893

PREVIOUS: CURRENT: December 1966

$S°(298.15\ K)$ = [419.166] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -491.99 \pm 25.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -493.71 \pm 25.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[360](1)	[140](3)
[340](2)	[180](3)
375 (3)	[120](3)

Ground State Quantum Weight = 1 $\sigma = 24$
Point Group: O_h
Bond Distance: W–Cl = 2.26 Å
Bond Angle: Cl–W–Cl = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 1.74003 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of WCl_6(g), $\Delta_f H°(298.15\ K) = -118.0\ kcal·mol^{-1}$, is calculated from that of the crystal plus the adopted heat of sublimation, $\Delta_{sub} H°(298.15\ K) = 23.9\ kcal·mol^{-1}$ for WCl_6(α, cr) → WCl_6(g). The latter was obtained from third law analysis of the vapor pressure data,[1-4] using all JANAF functions (December 31, 1966).

Source	Phase Studied	T/K	Data Points	$\Delta_{sub} H°(298.15\ K)$, kcal mol 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Stevenson[1]	α, cr	462 – 502	38	20.9 ± 0.5	23.74	6.2 ± 1.0	−118.16
	β*, cr	503 – 551	15	23.1 ± 0.2	23.89	1.5 ± 0.3	−118.01
	l*	557 – 598	13	24.2 ± 0.1	23.89	−0.6 ± 0.1	−118.01
Shchukarev *et al.*[2]	α, cr	**	−−	22.0	23.80	4.0	−118.10
	β*, cr		−−	23.8	23.98	0.4	−117.92
	l*		−−	24.1	23.98	−0.2	−117.92
Ketelaar *et al.*[3]	α, cr	425 – 500	21	23.1 ± 0.1	23.94	1.7 ± 0.4	−117.96
	β*, cr	504 – 554	21	24.4 ± 0.1	23.91	−0.8 ± 0.1	−117.99
	l*	523 – 635	21	24.4 ± 0.1	23.85	−1.0 ± 0.1	−118.05
Vernon[4]	α, cr	298 – 423	4	16.1 ± 4.1	21.02	10.8 ± 12.8	−120.88

Vernon[4] has also determined the equilibrium constants in the temperature range from 1360 to 1600 K for the decomposition of WCl_6(g) to W(cr) and Cl_2(g) by reaction of the sample with a hot tungsten filament in a vacuum bulb. Using the reported equilibrium constants, the heat of formation of WCl_6(g) at 298 K is calculated by the second and third law method as $-131.8 \pm 2.9\ kcal·mol^{-1}$ and $-135.2\ kcal·mol^{-1}$, respectively. The third law drift is $2.4 \pm 1.9\ cal·K^{-1}·mol^{-1}$. Unfortunately the reported equilibrium constants may be seriously in error since atomic chlorine is the main species at the pressure and temperature studied.

* Enthalpy changes are converted to $\Delta_{sub} H°(298.15\ K)$ for WCl_6(α, cr) → WCl_6(g).

** Vapor presssure equations for the crystal (α, β) and the liquid to gas are given.

Heat Capacity and Entropy

Ewens and Lister[5] have determined the octahedral structure for WCl_6(g) by electron diffraction and found the bond length to be 2.26 Å.

The vibrational frequency of ν_3, 375 cm^{-1}, was observed in the infrared spectra by Evans.[6] The values of ν_1, ν_2, and ν_5 (360, 340 and 180 cm^{-1}, respectively) are estimated based on those of the aqueous ion $PtCl_6^{2-}$ reported by Woodward and Creighton.[7] The values of ν_4 and ν_6 (140 and 120 cm^{-1}, respectively) are estimated by comparison with those of WF (g_6).

The principal moments of inertia are: $I_A = I_B = I_C = 120.2779 \times 10^{-39}\ g·cm^2$.

References

[1] F. D. Stevenson, Ph.D. Thesis, Oregon State University (1962); U.S. Bur. Mines RI. 6367, (1964).
[2] S. A. Shchukarev and A. V. Suvorov, Vestnik Leningrad. Univ. **16**, No. 4, Ser. Fiz. i Khim., No. 1, 87 (1961). Previous vapor pressure measurements, cited in Zh. Neorg. Khim. **1**, 357 (1956) and **3**, 2630 (1958), have been revised and are not used as reference here.
[3] J. A. A. Ketelaar, G. W. Oosterhout and P. B. Braun, Rec. Trav. Chim. **62**, 597 (1943).
[4] A. A. Vernon, J. Amer. Chem. Soc. **59**, 1832 (1937).
[5] R. V. G. Ewens and M. W. Lister, Trans. Faraday Soc. **34**, 1358 (1938).
[6] J. C. Evans, The Dow Chemical Company, private communication, (December 1, 1966).
[7] L. A. Woodward and J. A. Creighton, Spectrochim. Acta **17**, 594 (1961)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−30.790	−491.987	−491.987	INFINITE
100	93.109	285.822	536.701	−25.088	−495.672	−466.591	243.722
200	130.658	364.112	431.993	−13.576	−495.281	−437.471	114.256
250	138.942	394.234	421.510	−6.819	−494.537	−423.101	88.402
298.15	143.941	419.166	419.166	0.	−493.712	−409.416	71.728
300	144.093	420.057	419.169	0.266	−493.679	−408.893	71.195
350	147.459	442.539	420.936	7.561	−492.765	−394.833	58.926
400	149.758	462.389	424.902	14.995	−491.824	−380.907	49.741
450	151.390	480.127	430.070	22.526	−490.873	−367.100	42.612
500	152.586	496.143	435.889	30.127	−489.921	−353.398	36.919
600	154.182	524.116	448.330	45.472	−488.029	−326.272	28.404
700	155.165	547.963	460.901	60.943	−486.175	−299.459	22.346
800	155.812	568.727	473.110	76.494	−484.368	−272.910	17.819
900	156.259	587.106	484.775	92.099	−482.613	−246.583	14.311
1000	156.581	603.587	495.846	107.741	−480.914	−220.449	11.515
1100	156.821	618.523	506.330	123.412	−479.273	−194.483	9.235
1200	157.003	632.176	516.257	139.104	−477.691	−168.663	7.342
1300	157.146	644.749	525.663	154.811	−476.170	−142.973	5.745
1400	157.259	656.399	534.591	170.532	−474.711	−117.398	4.380
1500	157.351	667.252	543.077	186.263	−473.316	−91.924	3.201
1600	157.426	677.410	551.159	202.002	−471.986	−66.542	2.172
1700	157.488	686.956	558.869	217.747	−470.723	−41.241	1.267
1800	157.541	695.959	566.237	233.499	−469.529	−16.012	0.465
1900	157.585	704.478	573.291	249.255	−468.406	9.152	−0.252
2000	157.623	712.562	580.054	265.016	−467.359	34.260	−0.895
2100	157.655	720.253	586.549	280.780	−466.391	59.317	−1.475
2200	157.683	727.588	592.794	296.547	−465.505	84.329	−2.002
2300	157.708	734.598	598.808	312.316	−464.706	109.303	−2.482
2400	157.730	741.311	604.607	328.088	−463.999	134.245	−2.922
2500	157.749	747.750	610.205	343.862	−463.388	159.159	−3.325
2600	157.766	753.937	615.615	359.638	−462.874	184.050	−3.698
2700	157.781	759.892	620.849	375.415	−462.486	208.924	−4.042
2800	157.794	765.630	625.918	391.194	−462.262	233.787	−4.361
2900	157.807	771.167	630.831	406.974	−462.243	258.644	−4.659
3000	157.818	776.517	635.599	422.755	−462.457	283.505	−4.936
3100	157.827	781.692	640.229	438.537	−462.947	308.378	−5.196
3200	157.836	786.703	644.728	454.321	−463.741	333.271	−5.440
3300	157.845	791.560	649.104	470.105	−464.864	358.195	−5.670
3400	157.852	796.273	653.364	485.890	−466.346	383.157	−5.886
3500	157.859	800.848	657.513	501.675	−468.248	408.169	−6.092
3600	157.865	805.296	661.556	517.461	−470.659	433.242	−6.286
3700	157.871	809.621	665.500	533.248	−508.441	458.581	−6.474
3800	157.876	813.831	669.348	549.036	−508.567	484.718	−6.663
3900	157.881	817.932	673.106	564.823	−508.711	510.859	−6.842
4000	157.886	821.929	676.776	580.612	−508.868	537.004	−7.013
4100	157.890	825.828	680.365	596.401	−509.027	563.153	−7.175
4200	157.894	829.633	683.873	612.190	−509.183	589.306	−7.329
4300	157.898	833.348	687.307	627.979	−509.327	615.462	−7.476
4400	157.901	836.978	690.667	643.769	−509.451	641.622	−7.617
4500	157.904	840.527	693.958	659.560	−509.548	667.783	−7.751
4600	157.907	843.997	697.182	675.350	−509.612	693.948	−7.880
4700	157.910	847.393	700.342	691.141	−509.634	720.111	−8.003
4800	157.913	850.718	703.440	706.932	−509.609	746.276	−8.121
4900	157.915	853.974	706.479	722.724	−509.531	772.440	−8.234
5000	157.917	857.164	709.461	738.515	−509.395	798.601	−8.343
5100	157.920	860.292	712.388	754.307	−509.195	824.759	−8.447
5200	157.922	863.358	715.262	770.099	−508.927	850.912	−8.548
5300	157.924	866.366	718.085	785.891	−508.586	877.060	−8.644
5400	157.926	869.318	720.858	801.684	−508.170	903.201	−8.737
5500	157.927	872.216	723.584	817.476	−507.676	929.333	−8.826
5600	157.929	875.062	726.264	833.269	−507.099	955.455	−8.912
5700	157.930	877.857	728.899	849.062	−506.439	981.567	−8.995
5800	157.932	880.604	731.491	864.855	−505.693	1007.666	−9.075
5900	157.933	883.303	734.041	880.649	−504.860	1033.751	−9.152
6000	157.935	885.958	736.551	896.442	−503.939	1059.821	−9.227

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = [713.581]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -873.16 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(2981.5\ K) = -868.60 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[500](2)	[150](2)	[90](2)
[400](2)	[125](4)	[80](2)
[350](2)	[100](6)	[60](4)
[250](2)		[40](2)

Ground State Quantum Weight: [3] $\sigma = [4]$
Point Group: $[D_{2h}]$
Bond Distance: W–Cl = [2.26] Å
Bond Angles: Cl*–W–Cl* = [90]°; W–$Cl*_{bridge}$–W = [90]°
Cl**–W–Cl** = [180]°; Cl*–W–Cl** = [90]°
* = Equatorial ** = Axial
Product of the Moments of Inertia: $I_A I_B I_C = [6.64026 \times 10^{-110}]\ g^3·cm^6$

Heat of Formation

The heat of formation, $\Delta_f H°(W_2Cl_{10}, g, 298.15\ K) = -207.6\ kcal·mol^{-1}$, is calculated from $\Delta_r H°(298.15\ K) = 10.4\ kcal·mol^{-1}$ for $W_2Cl_{10}(g) = 2\ WCl_5(g)$, using all JANAF functions (December 31, 1966). The value of $\Delta_r H°(2981.5\ K)$ is obtained from third law analysis of the partial pressures of $WCl_5(g)$ and $W_2Cl_{10}(g)$ derived from *PVT* data determined by Shchukarev *et al.*[1] The second law $\Delta_r H°(298.15\ K)$ is $10.4 \pm 0.3\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration is estimated by analogy with that of Mo_2Cl_{10} reported by Sands and Zalkin.[2] Chlorine atoms are placed octahedrally around two tungsten atoms and these two octahedra share one common edge with six chlorine and two tungsten atoms in a plane. The bond length is estimated to be the same as that in $WCl_6(g)$. The three principal moments of inertia re $I_A = 210.4863 \times 10^{-39}$. $I_B = 546.8356 \times 10^{-39}$, and $I_C = 576.9051 \times 10^{-39}\ g·cm^2$.

All vibrational frequencies are estimated based on those of WCl_5, $(AlCl_3)_2$ and Cs_2Cl_2, such that $S°(W_2Cl_{10}, g, 607\ K) = 216.65\ cal·K^{-1}·mol^{-1}$. This entropy is derived from $\Delta S°(607\ K) = 19.92 \pm 0.5\ cal·K^{-1}·mol^{-1}$ for $W_2Cl_{10}(g) = 2WCl_5(g)$, obtained by second law analysis of the data of Shchukarev *et al.*[1] The frequencies are not in point group order.

References

[1]S. A. Shchukarev, G. I. Novikov and N. V. Andreeva, Vestnik Leningrad. Univ. **14**, No. 4, Ser. Fiz. i Khim, No. 1, 120 (1959).
[2]D. Z. Sands and A. Zalkin, Acta Cryst. **12**, 723 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−60.408	−873.157	−873.157	INFINITE
100	200.630	455.551	934.652	−47.910	−876.522	−825.651	431.276
200	246.532	611.501	737.242	−25.148	−872.964	−775.991	202.668
250	256.975	667.725	717.886	−12.540	−870.764	−752.000	157.122
298.15	263.467	713.581	713.581	0.	−868.598	−729.322	127.774
300	263.668	715.212	713.586	0.488	−868.515	−728.459	126.836
350	268.139	756.214	716.814	13.790	−866.254	−705.295	105.259
400	271.243	792.234	724.036	27.279	−864.001	−682.454	89.119
450	273.470	824.317	733.429	40.900	−861.764	−659.895	76.599
500	275.117	853.219	743.987	54.616	−859.548	−637.585	66.608
600	277.333	903.592	766.512	82.248	−855.192	−593.603	51.678
700	278.710	946.454	789.232	110.055	−850.946	−550.342	41.067
800	279.620	983.734	811.266	137.975	−846.815	−507.682	33.148
900	280.252	1016.707	832.296	165.970	−842.799	−465.532	27.019
1000	280.708	1046.260	852.240	194.019	−838.901	−423.824	22.138
1100	281.047	1073.031	871.114	222.108	−835.121	−382.500	18.163
1200	281.307	1097.497	888.975	250.226	−831.461	−341.516	14.866
1300	281.509	1120.021	905.893	278.367	−827.921	−300.831	12.088
1400	281.671	1140.890	921.942	306.527	−824.503	−260.415	9.716
1500	281.801	1160.327	937.194	334.701	−821.209	−220.239	7.669
1600	281.908	1178.518	951.714	362.886	−818.042	−180.278	5.885
1700	281.997	1195.611	965.563	391.082	−815.003	−140.511	4.317
1800	282.071	1211.732	978.796	419.285	−812.097	−100.920	2.929
1900	282.135	1226.985	991.461	447.495	−809.327	−61.486	1.690
2000	282.188	1241.458	1003.602	475.712	−806.700	−22.195	0.580
2100	282.235	1255.227	1015.259	503.933	−804.221	16.969	−0.422
2200	282.275	1268.357	1026.467	532.158	−801.897	56.018	−1.330
2300	282.310	1280.906	1037.259	560.388	−799.736	94.965	−2.157
2400	282.341	1292.921	1047.663	588.620	−797.745	133.822	−2.913
2500	282.369	1304.448	1057.705	616.856	−795.930	172.599	−3.606
2600	282.393	1315.523	1067.410	645.094	−794.292	211.308	−4.245
2700	282.414	1326.181	1076.798	673.334	−792.890	249.958	−4.836
2800	282.434	1336.452	1085.889	701.577	−791.799	288.560	−5.383
2900	282.451	1346.363	1094.701	729.821	−791.100	327.131	−5.892
3000	282.467	1355.939	1103.250	758.067	−790.846	365.685	−6.367
3100	282.481	1365.201	1111.552	786.314	−791.125	404.239	−6.811
3200	282.494	1374.170	1119.619	814.563	−791.996	442.810	−7.228
3300	282.505	1382.863	1127.465	842.813	−793.506	481.421	−7.620
3400	282.516	1391.297	1135.101	871.064	−795.718	520.086	−7.990
3500	282.526	1399.486	1142.539	899.316	−798.755	558.828	−8.340
3600	282.535	1407.445	1149.787	927.569	−802.799	597.671	−8.672
3700	282.543	1415.187	1156.856	955.823	−877.571	637.023	−8.993
3800	282.551	1422.722	1163.754	984.078	−877.024	677.950	−9.319
3900	282.558	1430.061	1170.489	1012.333	−876.508	718.864	−9.628
4000	282.564	1437.215	1177.068	1040.589	−876.012	759.765	−9.922
4100	282.570	1444.192	1183.498	1068.846	−875.522	800.654	−10.200
4200	282.576	1451.002	1189.787	1097.103	−875.025	841.530	−10.466
4300	282.581	1457.651	1195.939	1125.361	−874.508	882.394	−10.719
4400	282.586	1464.147	1201.961	1153.619	−873.959	923.246	−10.960
4500	282.591	1470.498	1207.858	1181.878	−873.365	964.085	−11.191
4600	282.595	1476.709	1213.636	1210.138	−872.714	1004.911	−11.411
4700	282.599	1482.787	1219.298	1238.397	−871.995	1045.720	−11.622
4800	282.603	1488.736	1224.849	1266.657	−871.198	1086.514	−11.824
4900	282.606	1494.563	1230.294	1294.918	−870.312	1127.292	−12.017
5000	282.609	1500.273	1235.637	1323.179	−869.328	1168.048	−12.203
5100	282.613	1505.869	1240.881	1351.440	−868.239	1208.786	−12.380
5200	282.615	1511.357	1246.030	1379.701	−867.037	1249.500	−12.551
5300	282.618	1516.740	1251.087	1407.963	−865.714	1290.190	−12.716
5400	282.621	1522.023	1256.056	1436.225	−864.265	1330.854	−12.873
5500	282.623	1527.209	1260.939	1464.487	−862.684	1371.491	−13.025
5600	282.626	1532.302	1265.739	1492.749	−860.968	1412.096	−13.171
5700	282.628	1537.304	1270.460	1521.012	−859.112	1452.670	−13.312
5800	282.630	1542.219	1275.103	1549.275	−857.114	1493.212	−13.448
5900	282.632	1547.051	1279.671	1577.538	−854.970	1533.716	−13.578
6000	282.634	1551.801	1284.167	1605.801	−852.679	1574.181	−13.704

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

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to SCl and S_3. In addition, Donovan *et al.*[11] observed during flash photolysis of S_2Cl_2 a number of transient bands in the region 30221–34200 cm^{-1} which may be due to S_2Cl. By analogy with the known electronic levels for the isoelectronic radical cations SCl_2^+, OCl_2^+, and OF_2^+,[12] we predict the existence of three excited states for S_2Cl which should give rise to transitions from the ground state in the 20000–30000 cm^{-1} region. No attempt is made here to make definite assignments for the observed absorption spectra[7,10, and 11] assigned to S_2Cl since this will require the results of higher resolution experiments. We prefer to predict the electronic configurations for the ground and excited states from the Walsh correlation diagram[5] and to estimate their relative term values based on the vertical ionization potentials[8,12] observed in the photoelectron spectra of SCl_2, OCl_2, and OF_2. A detailed description of the factors considered in making these estimates can be found on the SF_2^+ gas table.[2]

Additional support for the existence of the S_2Cl radical is provided by the matrix photolysis work of Herring *et al.*[6]

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Tremmel *et al.*[13] The antisymmetric stretching frequency (υ_3) is that observed in the infrared absorption spectra of gaseous CoC_2 by Leroi *et al.*[7] This value has been confirmed from results of two infrared matrix isolation studies.[8,9] The doubly degenerate bending frequency (υ_2) was observed by Thompson and Carlson[8] in the infrared spectra of $CoCl_2$ isolated in an argon matrix. The infrared–inactive symmetric stretching frequency (υ_1) is estimated by comparison with similar data for $FeCl_2$ [1] and $NiCl_2$.[14] Some additional support for this value is provided by calculations of DeKock and Gruen.[11] Assuming linear model, they calculated $\upsilon_1 \approx 332$ cm^{-1} from $\upsilon_3 = 493$ cm^{-1}. Also, Clifton and Gruen[15] observed a vibrational spacing of 332 cm^{-1} in the fluorescence spectrum of argon matrix–isolated $CoCl_2$ which may be υ_1. A similar assignment for $NiCl_2$ was recently proposed[14] based on observations of vibrational spacings in its fluorescence spectrum.

Chlorine

The electronic spectra of $CoCl_2$ have been extensively investigated both in the gas phase[10, 11, 16] and in various matrices.[9, 12, 15, 17] Unfortunately, most of the results are conflicting and difficult to interpret. It is not certain whether the ground state configuration is $^4\phi$ or $^4\Sigma$. Theroretical arguments based on a ligand–field model[12, 18] favor the former, but recently Lever and Hollebone[19] interpreted the electronic spectra of $CoCl_2$ in terms of an "orbital angular over–lap" model and preferred the latter ground state configuration. Other problems associated with band assignments in the $CoCl_2$ spectra have been dealt with by Smith.[18] The adopted states and levels comprise one of two sets of assignments proposed by Lever and Hollebone.[19] The alternate functions derived from their second set of assignments[19] suggest that the adopted entropies may be biased by as much as +2 $cal \cdot K^{-1} \cdot mol^{-1}$ at 298 K and +0.2 $cal \cdot K^{-1} \cdot mol^{-1}$ at 4000 K. Functions based on the assignments of Smith[18] agree with those adopted to better than 1 $cal \cdot K^{-1} \cdot mol^{-1}$ at all temperatures.

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The drift indicated that the entropy of $FeCl_2$(g) is made more consistent by introducing two low lying electronic levels and a relatively low bending frequency. The enthalpies derived by 2nd and 3rd law analyses are in good agreement.

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Continued from page 840

The ground state of the linear $NiCl_2$ molecule is established as $^3\Pi g$ from numerous studies on the Laporte–forbidden d–d transitions[14–16] as well as a study of the Laporte–allowed charge–transfer transitions.[17] The very complex electronic spectra for both the gas phase and matrix isolated $NiCl_2$ have been studied by numerous investigators and interpreted using crystal field or ligand field theory. Our adopted values for the excited states are from Lever and Hollebone[14] who used an "orbital angular overlap" model to fit the spin–allowed and spin–forbidden d–d transition spectra. These assignments are in good agreement with those of DeKock and Gruen[16,18] and Smith[15] but differ from those of Hougen *et al.*[19]

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Continued from page 850

Sublimation Data

Refer to the ideal gas table for details.

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The vibrational frequencies are from the matrix infrared studies of Hastie *et al.*[19] Both of the stretching frequencies (ν_1 and ν_3)were observed in matrices of N_2, Ar, and Ne. The adopted values are gas–phase frequencies which were estimated by Hastie *et al.*[19] from their matrix data. Other matrix infrared[20] and matrix Raman[21] studies have led to stretching frequencies which deviate by less than 30 cm^{-1} from our adopted values. Also, ν_1 is in agreement with the value of 314 cm^{-1} which was observed by Beattie and Perry[22] in a gas–phase Raman study at 1000°C. The bending frequency (ν_2) is somewhat more uncertain that the stretching frequencies. Hastie *et al.*[19] observed a relatively weak band at 80 cm^{-1} when $PbCl_2$ was trapped in a neon matrix and assigned this band to ν_2. Gas–phase[22] and matrix[21] Raman studies have indicated that ν_2 lies much closer to 100 cm^{-1}. The gas–phase Raman spectrum[22] was obtained in the presence of an excess of chlorine to suppress decomposition and subsequent resonance fluorescence. We prefer the lower value (80 cm^{-1}) but assign an uncertainty of ±20 cm^{-1} which corresponds to 0.5 $cal \cdot K^{-1} \cdot mol^{-1}$ in $S°(298.15\ K)$.

The ground state is assumed to be $^1A_1$ based on an analogy with those for other Group IV A dichlorides.[23] The upper $^1B_1$ level at 31000 cm^{-1} was observed by Hastie *et al.*[23] Also included is a triplet level ($^3B_1$) at 22000 cm^{-1}. The energy separation for the $^1B_1$–$^3B_1$ states (9000 cm^{-1}) is assumed to be similar to that observed for other Group IV A dichlorides.[23]

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A normal coordinate treatment of $NbCl_5(g)$ in the Urey–Bradley force fields was performed by So[22] using the reported vibrational frequencies of Beattie and Ozin.[21] This work by So[22] was intended to check the correctness of the reported fundamental frequencies and predict those frequencies which had not been observed (ω_3, ω_4, ω_5). The calculations of So[22] suggested that the ω_5 value reported for $NbCl_5(g)$ was incorrect. Beattie and Ozin[21] had recorded the gas phase Raman spectra of $NbCl_5$, $NbBr_5$, $TaCl_5$ and $TaBr_5$ and has assigned ω_5 only in the case of $NbCl_5$. It was noted that this appeared only very weakly in the spectra. We adopt the results of So[22] which support the work of Beattie and Ozin[21] except for the ω_5 assignment.

There are many references in the literature to spectroscopic observations (IR and Raman) of $NbCl_5$ in the solid state, in organic solvents, and in matrices. Many problems arise in any attempt in relating the observed spectra. Niobium pentachloride was shown to be dimeric in the solid phase.[13] There are also indications that $NbCl_5$ is dimeric in solution.[15–17]

On the basis of these frequencies and the adopted structure, we calculate $S°(298.15\ K) = 96.56 \pm 0.75$ $cal \cdot K^{-1} \cdot mol^{-1}$, as was also calculated by So.[22] This compares to a value of 90.29 $cal \cdot K^{-1} \cdot mol^{-1}$ calculated by Gaunt and Ainscough[14] and 95.52 $cal \cdot K^{-1} \cdot mol^{-1}$ by Werder *et al.*[18]

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[13]D. L. Kepert and R. S. Nyholm, J. Chem. Soc. (London) **1965**, 2871.
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[17]I. R. Beattie and G. A. Ozin, J. Chem. Soc. (London) A **1969**, 1691.
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REFERENCE STATE

0	to 700.1	K	crystal, alpha
700.1	to 1768	K	crystal, beta
1768	to 3184.943	K	liquid
above	3184.943	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹		
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.771	0.	0.	0.
100	13.909	7.681	50.176	−4.249	0.	0.	0.
200	22.226	20.588	32.287	−2.340	0.	0.	0.
298.15	24.802	30.067	30.067	0.	0.	0.	0.
300	24.833	30.221	30.068	0.046	0.	0.	0.
400	26.527	37.597	31.062	2.614	0.	0.	0.
500	28.200	43.700	32.996	5.352	0.	0.	0.
600	29.665	48.973	35.229	8.246	0.	0.	0.
700	31.045	53.650	37.533	11.282	0.	0.	0.
700.100	31.047	53.655	37.535	11.285	ALPHA <--> BETA		
700.100	30.583	54.300	37.535	11.737	TRANSITION		
800	32.426	58.497	39.894	14.883	0.	0.	0.
900	34.518	62.433	42.181	18.227	0.	0.	0.
1000	36.987	66.194	44.396	21.799	0.	0.	0.
1100	39.832	69.849	46.544	25.635	0.	0.	0.
1200	43.221	73.445	48.636	29.771	0.	0.	0.
1300	48.660	77.110	50.685	34.354	0.	0.	0.
1394.000	54.978	80.719	52.587	39.215	C_p LAMBDA MAXIMUM		
1394.000	54.999	80.719	52.587	39.215	TRANSITION		
1400	44.225	80.930	52.708	39.511	0.	0.	0.
1500	39.748	83.794	54.688	43.659	0.	0.	0.
1600	38.284	86.307	56.587	47.552	0.	0.	0.
1700	37.782	88.608	58.404	51.347	0.	0.	0.
1768.000	37.990	90.092	59.594	53.921	BETA <--> LIQUID		
1768.000	40.501	99.251	59.594	70.113	TRANSITION		
1800	40.501	99.977	60.305	71.409	0.	0.	0.
1900	40.501	102.167	62.452	75.459	0.	0.	0.
2000	40.501	104.245	64.490	79.509	0.	0.	0.
2100	40.501	106.221	66.430	83.560	0.	0.	0.
2200	40.501	108.105	68.282	87.610	0.	0.	0.
2300	40.501	109.905	70.053	91.660	0.	0.	0.
2400	40.501	111.629	71.750	95.710	0.	0.	0.
2500	40.501	113.282	73.378	99.760	0.	0.	0.
2600	40.501	114.871	74.944	103.810	0.	0.	0.
2700	40.501	116.399	76.451	107.860	0.	0.	0.
2800	40.501	117.872	77.904	111.910	0.	0.	0.
2900	40.501	119.293	79.307	115.961	0.	0.	0.
3000	40.501	120.666	80.663	120.011	0.	0.	0.
3100	40.501	121.994	81.975	124.061	0.	0.	0.
3184.943	40.501	123.089	83.057	127.501	LIQUID <--> IDEAL GAS		
3184.943	26.233	240.840	83.057	502.529	FUGACITY = 1 bar		
3200	26.233	240.963	83.800	502.924	0.	0.	0.
3300	26.245	241.771	88.574	505.548	0.	0.	0.
3400	26.269	242.555	93.092	508.174	0.	0.	0.
3500	26.305	243.317	97.373	510.802	0.	0.	0.
3600	26.354	244.058	101.437	513.435	0.	0.	0.
3700	26.416	244.781	105.302	516.073	0.	0.	0.
3800	26.491	245.487	108.982	518.719	0.	0.	0.
3900	26.579	246.176	112.491	521.372	0.	0.	0.
4000	26.679	246.850	115.841	524.035	0.	0.	0.
4200	26.919	248.157	122.111	529.394	0.	0.	0.
4400	27.209	249.416	127.869	534.806	0.	0.	0.
4600	27.546	250.633	133.180	540.281	0.	0.	0.
4800	27.930	251.813	138.099	545.827	0.	0.	0.
5000	28.358	252.962	142.671	551.456	0.	0.	0.
5200	28.829	254.083	146.934	557.174	0.	0.	0.
5400	29.342	255.181	150.923	562.990	0.	0.	0.
5600	29.896	256.258	154.666	568.913	0.	0.	0.
5800	30.492	257.317	158.187	574.951	0.	0.	0.
6000	31.003	258.351	161.508	581.056	0.	0.	0.

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 30.067 \pm 0.10\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 700\ K$
$T_{fus} = 923 \pm 1\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.452\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(923\ K) = 16.192 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity of Co(cr) is adopted from Hultgren *et al.*[1] Their selected values are based on the data from nineteen investigations. The entropy values are based on $S°(1\ K) = 0.0011\ cal \cdot K^{-1} \cdot mol^{-1}$. The heat capacity has a maximum value of $13.14\ cal \cdot K^{-1} \cdot mol^{-1}$ at the Curie point (1394 K).

Transition Data

The exact nature of the α(hcp)–β(fcc) transition is yet to be clearly elucidated. Three investigations[2–4] indicate that it is not a simple time- and temperature–dependent phenomenon. Crystalline cobalt exists as pure β–phase above 700 K whereas mixtures of alpha and beta cobalt commonly coexist in varying proportions below this temperature. The values of T_{trs} and $\Delta_{trs}H°$ are those selected by Hultgren *et al.*[1]

Fusion Data

The temperature and enthalpy of melting are those selected by Hultgren *et al.*[1]

Sublimation Data

The enthalpy of sublimation is calculated from the data of Edwards *et al.*[5] See the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.771	0.	0.	0.
100	13.909	7.681	50.176	−4.249	0.	0.	0.
200	22.226	20.588	32.287	−2.340	0.	0.	0.
250	23.984	25.738	30.475	−1.184	0.	0.	0.
298.15	24.802	30.067	30.067	0.	0.	0.	0.
300	24.833	30.221	30.068	0.046	0.	0.	0.
350	25.682	34.113	30.373	1.309	0.	0.	0.
400	26.527	37.597	31.062	2.614	0.	0.	0.
450	27.390	40.772	31.967	3.962	0.	0.	0.
500	28.200	43.700	32.996	5.352	0.	0.	0.
600	29.665	48.973	35.229	8.246	0.	0.	0.
700	31.045	53.650	37.533	11.282	0.	0.	0.
700.100	31.047	53.655	37.535	11.285	ALPHA <--> BETA		
700.100	30.583	54.300	37.535	11.737	TRANSITION		
800	32.426	58.497	39.894	14.883	0.	0.	0.
900	34.518	62.433	42.181	18.227	0.	0.	0.
1000	36.987	66.194	44.396	21.799	0.	0.	0.
1100	39.832	69.849	46.544	25.635	0.	0.	0.
1200	43.221	73.445	48.636	29.771	0.	0.	0.
1300	48.660	77.110	50.685	34.354	0.	0.	0.
1394.000	54.978	80.719	52.587	39.215	C_p LAMBDA MAXIMUM		
1394.000	54.999	80.719	52.587	39.215	TRANSITION		
1400	44.225	80.930	52.708	39.511	0.	0.	0.
1500	39.748	83.794	54.688	43.659	0.	0.	0.
1600	38.284	86.307	56.587	47.552	0.	0.	0.
1700	37.782	88.608	58.404	51.347	0.	0.	0.
1768.000	37.990	90.092	59.594	53.921	BETA <--> LIQUID		
1800	37.656	90.776	60.142	55.141	−16.269	0.293	−0.009
1900	37.656	92.812	61.809	58.906	−16.553	1.221	−0.034
2000	37.656	94.744	63.408	62.672	−16.838	2.164	−0.057
2100	37.656	96.581	64.944	66.437	−17.122	3.121	−0.078
2200	37.656	98.333	66.422	70.203	−17.407	4.092	−0.097
2300	37.656	100.006	67.846	73.969	−17.691	5.076	−0.115
2400	37.656	101.609	69.220	77.734	−17.976	6.071	−0.132
2500	37.656	103.146	70.546	81.500	−18.260	7.079	−0.148

PREVIOUS: CURRENT: September 1967

$S°(298.15\ K)$ = [41.000] $J·K^{-1}·mol^{-1}$
T_{fus} = 1768 K

$\Delta_f H°(298.15\ K)$ = [18.004] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 16.192 ± 0.25 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in $H°(1768\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of Co(l) selected by Hultgren *et al.*[1] is used at temperatures above 1768 K. The capacities at temperatures below the melting point are estimated by assuming a glass transition at 1100 K and heat capacities similar to those of the crystal below 1100 K.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen enthalpy of sublimation at 298.15 K so that the Gibbs energy functions calculated by integration of the crystal liquid data and by statistical methods from the gas phase are equal at the boiling point.

Reference

[1] R. Hultgren, R. L. Orr and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, University of California, Berkeley, Calif. (1966).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	24.811	41.000	41.000	0.	18.004	14.745	−2.583
300	24.842	41.153	41.000	0.046	18.004	14.724	−2.564
350	25.686	45.046	41.306	1.309	18.004	14.178	−2.116
400	26.527	48.531	41.995	2.614	18.005	13.631	−1.780
450	27.390	51.706	42.900	3.963	18.005	13.084	−1.519
500	28.200	54.634	43.929	5.353	18.005	12.538	−1.310
600	29.665	59.909	46.162	8.248	18.006	11.444	−0.996
700	30.878	64.568	48.465	11.272	17.994	10.351	−0.772
800	32.426	68.786	50.745	14.433	17.555	9.323	−0.609
900	34.518	72.723	52.971	17.777	17.555	8.294	−0.481
1000	36.987	76.484	55.135	21.349	17.555	7.265	−0.379
1100	39.832	80.140	57.243	25.187	17.556	6.236	−0.296
1100.000	39.832	80.140	57.243	25.187	____ GLASS <--> LIQUID ____		
1100.000	39.832	80.140	57.243	25.187	TRANSITION		
1200	39.999	83.613	59.297	29.178	17.412	5.211	−0.227
1300	40.166	86.821	61.293	33.187	16.837	4.214	−0.169
1400	40.334	89.804	63.224	37.212	15.705	3.282	−0.122
1500	40.501	92.593	65.090	41.255	15.600	2.401	−0.084
1600	40.501	95.207	66.891	45.305	15.757	1.517	−0.050
1700	40.501	97.662	68.630	49.355	16.012	0.619	−0.019
1768.000	40.501	99.251	69.777	52.109	---- BETA <--> LIQUID ----		
1800	40.501	99.977	70.308	53.405	0.	0.	0.
1900	40.501	102.167	71.928	57.455	0.	0.	0.
2000	40.501	104.245	73.492	61.505	0.	0.	0.
2100	40.501	106.221	75.004	65.555	0.	0.	0.
2200	40.501	108.105	76.466	69.606	0.	0.	0.
2300	40.501	109.905	77.881	73.656	0.	0.	0.
2400	40.501	111.629	79.251	77.706	0.	0.	0.
2500	40.501	113.282	80.580	81.756	0.	0.	0.
2600	40.501	114.871	81.868	85.806	0.	0.	0.
2700	40.501	116.399	83.119	89.856	0.	0.	0.
2800	40.501	117.872	84.334	93.906	0.	0.	0.
2900	40.501	119.293	85.515	97.956	0.	0.	0.
3000	40.501	120.666	86.664	102.006	0.	0.	0.
3100	40.501	121.994	87.783	106.057	0.	0.	0.
3184.943	40.501	123.089	88.710	109.497	---- FUGACITY = 1 bar ----		
3200	40.501	123.280	88.872	110.107	−374.813	1.773	−0.029
3300	40.501	124.526	89.934	114.157	−373.387	13.519	−0.214
3400	40.501	125.736	90.969	118.207	−371.962	25.222	−0.387
3500	40.501	126.910	91.979	122.257	−370.541	36.883	−0.550
3600	40.501	128.051	92.965	126.307	−369.124	48.504	−0.704
3700	40.501	129.160	93.929	130.357	−367.712	60.085	−0.848
3800	40.501	130.240	94.870	134.407	−366.307	71.628	−0.985
3900	40.501	131.292	95.790	138.457	−364.910	83.135	−1.113
4000	40.501	132.318	96.691	142.508	−363.523	94.605	−1.235

PREVIOUS: CURRENT: September 1967

0	to	700.1 K	crystal, alpha
700.1	to	1768 K	crystal, beta
above		1768 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.771	0.	0.	0.
100	13.909	7.681	50.176	−4.249	0.	0.	0.
200	22.226	20.588	32.287	−2.340	0.	0.	0.
250	23.984	25.738	30.475	−1.184	0.	0.	0.
298.15	24.802	30.067	30.067	0.	0.	0.	0.
300	24.833	30.221	30.068	0.046	0.	0.	0.
350	25.682	34.113	30.373	1.309	0.	0.	0.
400	26.527	37.597	31.062	2.614	0.	0.	0.
450	27.390	40.772	31.967	3.962	0.	0.	0.
500	28.200	43.700	32.996	5.352	0.	0.	0.
600	29.665	48.973	35.229	8.246	0.	0.	0.
700	31.045	53.650	37.533	11.282	0.	0.	0.
700.100	31.047	53.655	37.535	11.285	ALPHA <--> BETA		
700.100	30.583	54.300	37.535	11.737	TRANSITION		
800	32.426	58.497	39.894	14.883	0.	0.	0.
900	34.518	62.433	42.181	18.227	0.	0.	0.
1000	36.987	66.194	44.396	21.799	0.	0.	0.
1100	39.832	69.849	46.544	25.635	0.	0.	0.
1200	43.221	73.445	48.636	29.771	0.	0.	0.
1300	48.660	77.111	50.685	34.354	0.	0.	0.
1394.000	54.978	80.719	52.587	39.215	C_p LAMBDA MAXIMUM		
1394.000	54.978	80.719	52.587	39.215	TRANSITION		
1400	44.225	80.930	52.708	39.511	0.	0.	0.
1500	39.748	83.794	54.688	43.659	0.	0.	0.
1600	38.284	86.307	56.587	47.552	0.	0.	0.
1700	37.782	88.608	58.404	51.347	0.	0.	0.
1768.000	37.990	90.092	59.594	53.921	BETA <--> LIQUID		
1768.000	40.501	99.251	59.594	70.113	TRANSITION		
1800	40.501	99.977	60.305	71.409	0.	0.	0.
1900	40.501	102.167	62.452	75.459	0.	0.	0.
2000	40.501	104.244	64.490	79.509	0.	0.	0.
2100	40.501	106.221	66.430	83.560	0.	0.	0.
2200	40.501	108.105	68.282	87.610	0.	0.	0.
2300	40.501	109.905	70.053	91.660	0.	0.	0.
2400	40.501	111.629	71.750	95.710	0.	0.	0.
2500	40.501	113.282	73.378	99.760	0.	0.	0.
2600	40.501	114.871	74.944	103.810	0.	0.	0.
2700	40.501	116.399	76.451	107.860	0.	0.	0.
2800	40.501	117.872	77.904	111.910	0.	0.	0.
2900	40.501	119.293	79.307	115.960	0.	0.	0.
3000	40.501	120.666	80.663	120.011	0.	0.	0.
3100	40.501	121.994	81.975	124.061	0.	0.	0.
3184.943	40.501	123.089	83.057	127.501	----- FUGACITY = 1 bar -----		
3200	40.501	123.280	83.246	128.111	−374.813	1.773	−0.029
3300	40.501	124.526	84.478	132.161	−373.387	13.519	−0.214
3400	40.501	125.735	85.673	136.211	−371.963	25.222	−0.387
3500	40.501	126.910	86.835	140.261	−370.541	36.883	−0.550
3600	40.501	128.050	87.964	144.311	−369.124	48.504	−0.704
3700	40.501	129.160	89.063	148.361	−367.712	60.085	−0.848
3800	40.501	130.240	90.132	152.411	−366.307	71.629	−0.985
3900	40.501	131.292	91.174	156.462	−364.911	83.135	−1.113
4000	40.501	132.318	92.190	160.512	−363.523	94.606	−1.235

PREVIOUS: CURRENT: September 1967

IP(Co, g) = 63430 ± 50 cm^{-1}
$S°(298.15\ K)$ = 179.52 ± 0.01 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 425.1 ± 2.1 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [426.7] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{9/2}$	0	10
$^4F_{7/2}$	816.00	8
$^4F_{5/2}$	1406.84	6
$^4F_{3/2}$	1809.33	4
.	.	.
.	.	.
.	.	.
$^5H_6$	125969.5	13
IP	63430	

Enthalpy of Formation

The enthalpy of formation is the enthalpy of sublimation at 298.15 K. The adopted value is that reported by Edwards *et al.*[1] Their value is used because their vapor pressure measurements for Fe[1] and Cu[2] have proved to be very reliable. The results obtained by Vintaikin and Tomash[3] are rejected because their vapor pressure data for Fe[4] resulted in a value for the enthalpy of sublimation which was higher than the accepted value [refer to JANAF Fe(g) Table for details]. The remaining vapor pressure data are rejected either because the drift was too large or because there were not enough points. Second and third law analyses of the available vapor pressure data gave the following results, with reaction A corresponding to Co(c) = Co(g) and reaction B corresponding to Co(l) = Co(g).

Source	Reaction	Method	Data Points	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Edwards[1]	A	Langmuir	9	1363–1522	101.0 ± 1.0	101.54	±0.4 ± 0.7	101.54
Kornev[5]	A	Knudsen	8*	1323–1523	98.8 ± 0.8	95.37	−2.4 ± 0.6	95.37
Dancy[6]	B	Langmuir	1	1823	—	90.51	—	94.82
Ruff[7]	B	Boiling Pt.	1	2648	—	99.35	—	103.66
Nesmeyanov[8]	A	Knudsen	3	1391–1540	82.4 ± 2.4	82.31	−0.1 ± 1.6	82.31
Nesmeyanov[9]	A	Knudsen	12*	1345–1541	91.7 ± 2.4	83.19	−5.9 ± 1.7	83.19
Vintaikin[3]	A	Knudsen	Eqn	1373–1523	102.9	103.34	+0.3	103.34

*One point rejected due to failure of a statistical test.

Heat Capacity and Entropy

The electronic levels are taken from Moore.[10] All observed levels were used but only the first few levels are listed above. Unobserved levels below 20,000 cm^{-1} are estimated.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.360	425.087	425.087	INFINITE
100	20.793	156.132	198.942	−4.281	426.644	411.799	−215.102
200	21.452	170.670	181.570	−2.180	426.836	396.819	−103.639
250	22.214	175.536	179.892	−1.089	426.771	389.322	−81.344
298.15	23.024	179.518	179.518	0.	426.676	382.117	−66.945
300	23.054	179.660	179.518	0.043	426.673	381.841	−66.484
350	23.841	183.274	179.802	1.215	426.583	374.376	−55.873
400	24.508	186.503	180.441	2.425	426.487	366.924	−47.915
450	25.034	189.421	181.279	3.664	426.378	359.486	−41.728
500	25.425	192.080	182.229	4.926	426.250	352.060	−36.779
600	25.890	196.762	184.271	7.495	425.924	337.251	−29.360
700	26.093	200.771	186.349	10.095	425.489	322.504	−24.066
800	26.186	204.262	188.375	12.710	424.503	307.891	−20.103
900	26.251	207.350	190.315	15.331	423.781	293.356	−17.026
1000	26.320	210.119	192.159	17.960	422.837	278.913	−14.569
1100	26.399	212.631	193.908	20.596	421.637	264.576	−12.564
1200	26.480	214.932	195.565	23.240	420.145	250.361	−10.898
1300	26.558	217.054	197.138	25.892	418.214	236.287	−9.494
1400	26.624	219.025	198.632	28.551	415.716	222.383	−8.297
1500	26.673	220.864	200.053	31.216	414.233	208.628	−7.265
1600	26.705	222.586	201.408	33.885	413.009	194.962	−6.365
1700	26.719	224.206	202.702	36.556	411.885	181.369	−5.573
1800	26.715	225.733	203.939	39.228	394.495	168.135	−4.879
1900	26.697	227.177	205.125	41.899	393.116	155.597	−4.278
2000	26.666	228.546	206.262	44.567	391.734	143.132	−3.738
2100	26.626	229.846	207.354	47.232	390.348	130.736	−3.252
2200	26.579	231.083	208.405	49.892	388.958	118.406	−2.811
2300	26.528	232.264	209.417	52.547	387.564	106.139	−2.410
2400	26.475	233.391	210.392	55.198	386.164	93.933	−2.044
2500	26.423	234.471	211.334	57.842	384.758	81.786	−1.709
2600	26.375	235.507	212.244	60.482	383.348	69.695	−1.400
2700	26.331	236.501	213.124	63.118	381.933	57.658	−1.115
2800	26.293	237.458	213.976	65.749	380.514	45.674	−0.852
2900	26.264	238.380	214.802	68.377	379.092	33.740	−0.608
3000	26.243	239.270	215.603	71.002	377.667	21.856	−0.381
3100	26.233	240.130	216.380	73.626	376.241	10.019	−0.169
3184.943	26.233	240.840	217.023	75.854	----- FUGACITY = 1 bar -----		
3200	26.233	240.963	217.136	76.249	0.	0.	0.
3300	26.245	241.771	217.870	78.873	0.	0.	0.
3400	26.269	242.555	218.584	81.498	0.	0.	0.
3500	26.305	243.317	219.280	84.127	0.	0.	0.
3600	26.354	244.058	219.958	86.760	0.	0.	0.
3700	26.416	244.781	220.619	89.398	0.	0.	0.
3800	26.491	245.487	221.265	92.043	0.	0.	0.
3900	26.579	246.176	221.895	94.697	0.	0.	0.
4000	26.679	246.850	222.510	97.360	0.	0.	0.
4100	26.793	247.510	223.112	100.033	0.	0.	0.
4200	26.919	248.157	223.700	102.719	0.	0.	0.
4300	27.058	248.792	224.277	105.417	0.	0.	0.
4400	27.209	249.416	224.841	108.131	0.	0.	0.
4500	27.372	250.029	225.394	110.859	0.	0.	0.
4600	27.546	250.633	225.936	113.605	0.	0.	0.
4700	27.733	251.227	226.468	116.369	0.	0.	0.
4800	27.930	251.813	226.990	119.152	0.	0.	0.
4900	28.139	252.391	227.502	121.956	0.	0.	0.
5000	28.358	252.962	228.006	124.780	0.	0.	0.
5100	28.589	253.526	228.501	127.628	0.	0.	0.
5200	28.829	254.083	228.987	130.498	0.	0.	0.
5300	29.081	254.635	229.466	133.394	0.	0.	0.
5400	29.342	255.181	229.937	136.315	0.	0.	0.
5500	29.614	255.721	230.401	139.263	0.	0.	0.
5600	29.896	256.258	230.858	142.238	0.	0.	0.
5700	30.189	256.789	231.308	145.242	0.	0.	0.
5800	30.492	257.317	231.752	148.276	0.	0.	0.
5900	30.701	257.833	232.189	151.296	0.	0.	0.
6000	31.003	258.351	232.621	154.381	0.	0.	0.

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

IP(Co^+, g) = 137795 ± 10 cm^{-1}
$S°$(298.15 K) = 178.346 ± 0.05 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1183.88 ± 1.0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1191.597] $kJ·mol^{-1}$

Electronic Level and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_4$	0.00	9
$^3F_3$	950.51	7
$^3F_2$	1597.32	5
$^5F_5$	3350.58	9
.	.	.
.	.	.
.	.	.
$^5H_6$	125969.5	13
IP	137795	

Enthalpy of Formation

$\Delta_f H°(Co^+, g, 0 K)$ is calculated from $\Delta_f H°(Co, g, 0 K)$[1] using the spectroscopic value of IP(Co) = 63430 ± 10 cm^{-1} (758.79 ± 0.12 $kJ·mol^{-1}$) from Sugar and Corliss.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Co^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Co, g, 0 K)$ by using IP(Co) with JANAF[1] enthalpies, $H°(0 K)$–$H°(298.15 K)$, for Co(g), Co^+(g), and e^-(ref). $\Delta_f H°(Co \rightarrow Co^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Sugar and Corliss,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for Co^+(g), all levels listed by Sugar and Corliss,[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Co^+(g), the thermodynamic functions are independent of the estimated missing levels (for n = 3), the cut–off procedure, and the inclusion of n = 7 levels up to 1000 K; the Gibbs energy function showing variations of 0.05% at this temperature. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>7), and use of different fill and cut–off procedures.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.291	1183.879		
100	20.787	155.255	197.384	−4.213			
200	21.116	169.718	180.341	−2.125			
250	21.635	174.482	178.709	−1.057			
298.15	22.272	178.346	178.346	0.	1191.597	1141.133	−199.922
300	22.297	178.484	178.346	0.041	1191.630	1140.819	−198.634
350	22.981	181.973	178.620	1.173	1192.539	1132.279	−168.983
400	23.606	185.083	179.237	2.338	1193.438	1123.609	−146.728
450	24.133	187.895	180.045	3.532	1194.323	1114.827	−129.406
500	24.559	190.461	180.961	4.750	1195.190	1105.947	−115.538
600	25.165	194.996	182.932	7.238	1196.863	1087.940	−94.714
700	25.585	198.908	184.941	9.777	1198.444	1069.660	−79.819
800	25.946	202.348	186.906	12.354	1199.499	1051.222	−68.638
900	26.307	205.425	188.796	14.966	1200.846	1032.605	−59.931
1000	26.681	208.216	190.601	17.615	1202.002	1013.848	−52.958
1100	27.067	210.777	192.320	20.303	1202.932	994.985	−47.248
1200	27.485	213.150	193.958	23.030	1203.602	976.049	−42.486
1300	28.002	215.369	195.521	25.803	1203.871	957.072	−38.456
1400	28.740	217.469	197.014	28.638	1203.626	938.094	−35.001
1500	29.883	219.488	198.445	31.564	1204.484	919.101	−32.006
1600	31.654	221.469	199.822	34.635	1205.740	900.036	−29.383
1700	34.287	223.462	201.154	37.924	1207.312	880.883	−27.066
1800	37.981	225.521	202.450	41.528	1192.933	861.922	−25.012
1900	42.853	227.700	203.721	45.560	1194.993	843.479	−23.189
2000	48.890	230.047	204.978	50.138	1197.599	824.913	−21.545
2100	55.916	232.599	206.232	55.371	1200.861	806.202	−20.053
2200	63.578	235.375	207.492	61.342	1204.861	787.318	−18.693
2300	71.383	238.374	208.769	68.091	1209.639	768.234	−17.447
2400	78.752	241.570	210.069	75.604	1215.180	748.927	−16.300
2500	85.120	244.919	211.395	83.808	1221.413	729.374	−15.239
2600	90.025	248.358	212.751	92.579	1228.212	709.559	−14.255
2700	93.179	251.820	214.134	101.755	1235.416	689.476	−13.339
2800	94.494	255.238	215.541	111.153	1242.843	669.120	−12.483
2900	94.073	258.552	216.967	120.595	1250.314	648.498	−11.681
3000	92.159	261.713	218.406	129.918	1257.665	627.620	−10.928
3100	89.071	264.687	219.852	138.988	1264.763	606.500	−10.219
3200	85.153	267.455	221.297	147.705	896.695	586.930	−9.581
3300	80.724	270.008	222.735	156.002	904.447	577.129	−9.135
3400	76.057	272.349	224.160	163.842	911.740	567.100	−8.712
3500	71.364	274.486	225.568	171.212	918.561	556.863	−8.311
3600	66.801	276.432	226.954	178.119	924.913	546.438	−7.929
3700	62.471	278.202	228.316	184.580	930.815	535.842	−7.565
3800	58.437	279.814	229.650	190.623	936.291	525.093	−7.218
3900	54.728	281.283	230.955	196.279	941.371	514.205	−6.887
4000	51.353	282.626	232.231	201.580	946.088	503.191	−6.571
4100	48.306	283.856	233.475	206.560	950.474	492.064	−6.269
4200	45.568	284.986	234.688	211.251	954.558	480.833	−5.980
4300	43.119	286.029	235.870	215.683	958.370	469.508	−5.703
4400	40.933	286.995	237.021	219.884	961.936	458.098	−5.438
4500	38.985	287.893	238.142	223.878	965.280	446.609	−5.184
4600	37.250	288.730	239.233	227.688	968.422	435.048	−4.940
4700	35.707	289.514	240.294	231.334	971.384	423.420	−4.706
4800	34.332	290.251	241.327	234.835	974.180	411.732	−4.481
4900	33.107	290.946	242.333	238.206	976.826	399.986	−4.264
5000	32.015	291.604	243.312	241.461	979.335	388.189	−4.055
5100	31.040	292.228	244.265	244.613	981.718	376.342	−3.855
5200	30.168	292.822	245.193	247.672	983.985	364.449	−3.661
5300	29.386	293.390	246.097	250.649	986.145	352.514	−3.474
5400	28.686	293.932	246.978	253.552	988.206	340.540	−3.294
5500	28.056	294.453	247.837	256.389	990.173	328.528	−3.120
5600	27.489	294.953	248.673	259.166	992.053	316.481	−2.952
5700	26.978	295.435	249.490	261.889	993.851	304.401	−2.790
5800	26.517	295.900	250.286	264.563	995.570	292.290	−2.632
5900	26.099	296.350	251.063	267.193	997.259	280.147	−2.480
6000	25.721	296.785	251.821	269.784	998.843	267.979	−2.333

PREVIOUS: September 1967 (1 atm) CURRENT: June 1984 (1 bar)

EA(Co, g) = 0.661 ± 0.010 eV
$S°(298.15\ K)$ = 178.412 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 361.31 ± 4.7 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [356.649] $kJ·mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_4$	0	9
$^3F_3$	910	7
$^3F_2$	1560	5

Enthalpy of Formation

$\Delta_f H°(Co^-, g, 0\ K)$ is calculated from $\Delta_f H°(Co, g, 0\ K)$[1] using the adopted electron affinity of EA(Co) = 0.661 ± 0.010 eV (63.776 ± 0.965 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Co^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Co^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Co, g, 0\ K)$ by using EA(Co) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, or Co^-(g), Co(g), and e^-(ref). $\Delta_r H°(Co^- \rightarrow Co + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state and fine-structure separations for Co^-(g) have been experimentally determined by Corderman *et al.*[3] Lacking any experimental evidence as to the existence of stable excited states, we assume no stable excited states exist.

References

[1]JANAF Thermochemical Tables: Co(g), 9–30–67; e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, Volume 14, p. 731 (1985).
[3]R. R. Corderman, P. C. Engelking and W. C. Lineberger, J. Chem. Phys. **70**, 4474 (1979).
[4]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[5]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[6]H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, 741 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.307	361.311		
100	20.788	155.256	197.536	−4.228			
200	21.191	169.734	180.420	−2.137			
250	21.768	174.521	178.777	−1.064			
298.15	22.438	178.412	178.412	0.	356.649	318.675	−55.831
300	22.465	178.550	178.412	0.042	356.607	318.440	−55.445
350	23.154	182.066	178.688	1.182	355.445	312.170	−46.589
400	23.755	185.198	179.310	2.355	354.274	306.068	−39.968
450	24.233	188.025	180.123	3.556	353.087	300.114	−34.836
500	24.582	190.597	181.044	4.777	351.878	294.292	−30.745
600	24.937	195.117	183.024	7.256	349.385	283.007	−24.638
700	24.962	198.966	185.033	9.753	346.767	272.150	−20.308
800	24.794	202.290	186.987	12.242	343.577	261.739	−17.090
900	24.531	205.195	188.852	14.709	340.621	251.684	−14.607
1000	24.233	207.765	190.618	17.147	337.409	241.972	−12.639
1100	23.932	210.060	192.283	19.555	333.902	232.595	−11.045
1200	23.646	212.130	193.852	21.934	330.067	223.552	−9.731
1300	23.383	214.012	195.331	24.285	325.756	214.847	−8.633
1400	23.144	215.736	196.728	26.611	320.846	206.496	−7.704
1500	22.931	217.326	198.049	28.915	316.924	198.467	−6.911
1600	22.740	218.799	199.300	31.198	313.235	190.691	−6.225
1700	22.571	220.173	200.488	33.464	309.627	183.143	−5.627
1800	22.420	221.458	201.618	35.713	289.736	176.101	−5.110
1900	22.286	222.667	202.694	37.948	285.842	169.894	−4.671
2000	22.166	223.807	203.722	40.171	281.936	163.892	−4.280
2100	22.059	224.886	204.704	42.382	278.018	158.086	−3.932
2200	21.964	225.910	205.645	44.583	274.090	152.468	−3.620
2300	21.878	226.884	206.547	46.775	270.154	147.027	−3.339
2400	21.800	227.814	207.414	48.959	266.209	141.758	−3.085
2500	21.731	228.702	208.248	51.135	262.257	136.654	−2.855
2600	21.668	229.553	209.051	53.305	258.298	131.708	−2.646
2700	21.611	230.370	209.826	55.469	254.333	126.915	−2.455
2800	21.559	231.155	210.574	57.627	250.363	122.268	−2.281
2900	21.511	231.910	211.296	59.781	246.387	117.763	−2.121
3000	21.468	232.639	211.996	61.930	242.408	113.396	−1.974
3100	21.429	233.342	212.673	64.074	238.424	109.161	−1.839
3200	21.392	234.022	213.330	66.215	−140.377	106.828	−1.744
3300	21.359	234.680	213.967	68.353	−142.942	114.593	−1.814
3400	21.328	235.317	214.585	70.487	−145.512	122.435	−1.881
3500	21.300	235.935	215.187	72.619	−148.088	130.354	−1.945
3600	21.273	236.534	215.771	74.747	−150.671	138.346	−2.007
3700	21.249	237.117	216.340	76.873	−153.262	146.409	−2.067
3800	21.227	237.683	216.895	78.997	−155.862	154.544	−2.124
3900	21.206	238.234	217.435	81.119	−158.472	162.746	−2.180
4000	21.186	238.771	217.961	83.238	−161.094	171.016	−2.233
4100	21.168	239.294	218.475	85.356	−163.728	179.351	−2.285
4200	21.151	239.804	218.977	87.472	−166.376	187.751	−2.335
4300	21.135	240.301	219.467	89.586	−169.040	196.214	−2.384
4400	21.120	240.787	219.946	91.699	−171.719	204.739	−2.431
4500	21.106	241.262	220.415	93.810	−174.415	213.325	−2.476
4600	21.093	241.725	220.873	95.920	−177.129	221.972	−2.521
4700	21.080	242.179	221.322	98.029	−179.863	230.677	−2.564
4800	21.069	242.622	221.761	100.136	−182.617	239.441	−2.606
4900	21.058	243.057	222.191	102.243	−185.393	248.263	−2.647
5000	21.047	243.482	222.613	104.348	−188.191	257.141	−2.686
5100	21.038	243.899	223.026	106.452	−191.013	266.076	−2.725
5200	21.028	244.307	223.431	108.555	−193.859	275.066	−2.763
5300	21.020	244.708	223.829	110.658	−196.731	284.111	−2.800
5400	21.011	245.100	224.219	112.759	−199.629	293.211	−2.836
5500	21.004	245.486	224.602	114.860	−202.554	302.364	−2.872
5600	20.996	245.864	224.979	116.960	−205.508	311.571	−2.906
5700	20.989	246.236	225.348	119.059	−208.492	320.831	−2.940
5800	20.982	246.601	225.712	121.158	−211.506	330.144	−2.973
5900	20.976	246.959	226.069	123.256	−214.506	339.506	−3.006
6000	20.970	247.312	226.420	125.353	−217.573	348.921	−3.038

PREVIOUS: CURRENT: June 1984 (1 bar)

$S°(298.15\ K) = 82.026 \pm 0.42\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1400 \pm 7.0\ K$

$\Delta_f H°(0\ K) = -670.4 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -671.53 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = 58.819 \pm 12.6\ kJ·mol^{-1}$

Enthalpy of Formation

Heus and Egan[1] measured the emf of a solid state galvanic cell which involved the reactions: Al(cr) + 3/2 CoF_2(cr) → AlF_3(cr) + 3/2 Co(cr), E(873 K) = 1.611 volts; Mg(cr) + CoF_2(cr) → MgF_2(cr) + Co(cr), E(873 K) = 2.231 volts. Combining these results with auxiliary thermodynamic data[2] for the reactants and products, we derive $\Delta_f H°(CoF_2, cr, 298.15\ K) = -160.2$ and $-159.95\ kcal·mol^{-1}$.

Several equilibrium studies[3-5] involving CoF_2(cr) have been reported in the literature. 2nd and 3rd law analyses of these equilibrium data are summarized below, auxiliary data for CoO(cr) and $CoCl_2$(cr) are from.[6]

Source	Reaction	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	*$\Delta_r H°$(298.15 K) kcal·mol^{-1}
[3]	CoF_2(cr) + 2HCl(g) → CoCl ($_2$cr) + 2HF(g)	588–805	3	4.1	1.75 ± 0.4	−1.7 ± 0.1	−162.6 ± 2.0
[4]	CoF_2(cr) + H_2(g) → Co(cr) + 2HF(g)	673–873	3	35.2	31.5 ± 1.0	−4.2 ± 3.5	−161.8 ± 2.0
[5]	CoF_2(cr) + H_2O(g) → CoO(cr) + 2HF(g)	773–1023	5	30.2	31.1 ± 0.2	0.9 ± 0.3	−160.45 ± 1.0

*3rd law values except for the first reaction.

We note that Heus and Egan,[1] in the same paper, measured $\Delta_f H°(AlF_3, cr, 298.15\ K) = -360.2\ kcal·mol^{-1}$ which is in excellent agreement with the JANAF value[2]. Domange[5] also measured similar equilibria for MgF_2 and CaF_2, which were very consistent with the JANAF enthalpies of formation.[2] Jellinek and Rudat[4] reported similar equilibria for PbF_2(cr), which show excellent consistency with the JANAF enthalpy of formation.[2] Thus, it is apparent that these three sets are probably quite reliable, and we adopt $\Delta_f H°(CoF_2, cr, 298.15\ K) = -160.5 \pm 1\ kcal·mol^{-1}$ ($-671.532 \pm 4.2\ kJ·mol^{-1}$).

Heat Capacity and Entropy

Catalano and Stout[7] measured low temperature heat capacities in the temperature range 10 to 300 K. Heat capacity data above 300 K are calculated from the high temperature (468–1400 K) enthalpy data of Binford *et al.*[8] Both sets of data were smoothed by computer and joined at 298.15 K.

The value of $S°(298.15\ K)$ is obtained from the low temperature heat capacity data of Catalano and Stout[7] and is based on $S°(10\ K) = 0.013\ cal·K^{-1}·mol^{-1}$ ($0.05439\ J·K^{-1}·mol^{-1}$).

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Kana'an *et al.*[9] made sublimation studies of CoF_2 using Knudsen and Langmuir techniques over the temperature range 972–1241 K. 2nd and 3rd law analyses of these sublimation pressures are summarized below.

Method	T/K	Data Points	$\Delta_{sub} H°$(298.15 K) kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Knudsen	1058–1242	17	75.0	75.1 ± 0.1	0.1 ± 0.2
Langmuir	972–1032	8	72.8	75.5 ± 0.2	2.6 ± 1.4

The selected value is $\Delta_{sub} H°(298.15\ K) = 75.3 \pm 3.0\ kcal·mol^{-1}$ ($315.055 \pm 12.6\ kJ·mol^{-1}$).

References

[1] R. J. Heus and J. J. Egan, Z. Phys. Chem. **49**, 38 (1966).
[2] JANAF Thermochemical Tables: AlF_3(cr), 6–30–70; MgF_2(cr), 3–31–66; PbF_2(cr), 6–30–69; CaF_2(cr), 12–31–68.
[3] K. Jellinek and R. Koop, Z. Phys. Chem. **A145**, 305 (1929).
[4] K. Jellinek and A. Rudat, Z. Anorg. Chem. **175**, 281 (1928).
[5] L. Domange, Ann. Chim. **7**, 225 (1937).
[6] U. S. Nat. Bur. Stand. Tech. Note 270–4, 141 pp. (1969).
[7] E. Catalano and J. W. Stout, J. Chem. Phys. **23**, 1803 (1955).
[8] J. S. Binford, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem. **71**, 2404 (1967).
[9] A. S. Kana'an, G. Besenbruch, and J. L. Margrave, J. Inorg. Nucl. Chem. **28**, 1035 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.459	−670.395	−670.395	INFINITE
100	33.492	25.002	134.693	−10.969	−672.334	−657.029	343.197
200	57.584	56.746	87.999	−6.250	−672.454	−641.555	167.557
298.15	68.909	82.026	82.026	0.	−671.532	−626.562	109.771
300	69.041	82.453	82.028	0.128	−671.508	−626.283	109.046
400	75.714	103.350	84.831	7.408	−670.016	−611.424	79.844
500	78.927	120.625	90.315	15.155	−668.372	−596.965	62.365
600	80.789	135.193	96.613	23.148	−666.746	−582.837	50.741
700	82.015	147.744	103.041	31.292	−665.190	−568.977	42.458
800	82.902	158.756	109.331	39.540	−664.152	−555.271	36.255
900	83.592	168.562	115.378	47.866	−662.824	−541.742	31.442
1000	84.161	177.400	121.145	56.254	−661.698	−528.351	27.598
1100	84.646	185.444	126.631	64.695	−660.813	−515.062	24.458
1200	85.077	192.828	131.844	73.182	−660.208	−501.841	21.845
1300	85.475	199.654	136.801	81.710	−660.032	−488.654	19.634
1400	85.839	206.002	141.519	90.276	−660.415	−475.460	17.740
1400.000	85.839	206.002	141.519	90.276	--- CRYSTAL <--> LIQUID ---		
1500	86.186	211.936	146.018	98.877	−659.771	−462.269	16.098
1600	86.517	217.509	150.314	107.512	−658.858	−449.131	14.663
1700	86.831	222.764	154.423	116.180	−657.832	−436.054	13.398
1800	87.140	227.736	158.359	124.878	−673.055	−422.744	12.268
1900	87.441	232.455	162.135	133.607	−672.247	−408.860	11.240
2000	87.734	236.948	165.765	142.366	−671.420	−395.019	10.317

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = [86.238]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1400 \pm 7.0\ K$

$\Delta_f H°(298.15\ K) = [-637.691]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 58.819 \pm 12.6\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(CoF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(CoF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion the difference in enthalpy, $H°(1400\ K)–H°(298.15)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid CoF_2 is estimated by comparison with those for $FeCl_2$(l), MgF_2(l), and PbF_2(l) and is assumed constant in the temperature range 298–3000 K. Binford *et al.*[1] reported $C_p = 30.3\ cal·K^{-1}·mol^{-1}$ for liquid CoF_2 at 1444 K. This value is based on only two enthalpy points near the melting point and appears high in comparison with heat capacities for other liquid metal dihalides. Therefore, the value is not adopted.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} = 1400 K is from the high temperature enthalpy studies of Binford *et al.*[1] $\Delta_{fus}H°$ is calculated from their enthalpy data. Premelting of the sample is assumed to be responsible for the rapid rise in enthalpy near the melting point. This enthalpy is included in $\Delta_{fus}H°$.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the process $CoF_2(l) \rightarrow CoF_2(g)$ equals zero. The difference between the enthalpy of formation of the gas and liquid at T_{vap} is $\Delta_{vap}H°$.

Reference

[1] J. S. Bindord, Jr., J. M. Strohmenger, and T. H. Hebert, J. Phys. Chem., **71**, 2404 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.600	86.238	86.238	0.	−637.691	−593.977	104.062
300	104.600	86.885	86.240	0.194	−637.602	−593.706	103.373
400	104.600	116.976	90.343	10.654	−632.929	−579.787	75.712
500	104.600	140.317	98.090	21.114	−628.573	−567.012	59.235
600	104.600	159.388	106.765	31.574	−624.480	−555.088	48.325
700	104.600	175.512	115.464	42.034	−620.608	−543.832	40.581
800	104.600	189.480	123.863	52.494	−617.358	−533.055	34.805
900	104.600	201.800	131.851	62.954	−613.896	−522.728	30.338
1000	104.600	212.820	139.407	73.414	−610.698	−512.772	26.784
1100	104.600	222.790	146.541	83.874	−607.794	−503.123	23.891
1200	104.600	231.891	153.280	94.334	−605.216	−493.723	21.491
1300	104.600	240.264	159.653	104.794	−603.108	−484.522	19.468
1400	104.600	248.015	165.691	115.254	−601.596	−475.460	17.740
1400.000	104.600	248.015	165.691	115.254	--- CRYSTAL <--> LIQUID ---		
1500	104.600	255.232	171.423	125.714	−599.094	−466.535	16.246
1600	104.600	261.983	176.874	136.174	−596.356	−457.786	14.945
1700	104.600	268.324	182.069	146.634	−593.537	−449.212	13.803
1800	104.600	274.303	187.029	157.094	−606.999	−440.510	12.783
1900	104.600	279.958	191.772	167.554	−604.461	−431.330	11.858
2000	104.600	285.324	196.317	178.014	−601.932	−422.283	11.029
2100	104.600	290.427	200.678	188.474	−599.409	−413.362	10.282
2200	104.600	295.293	204.869	198.934	−596.889	−404.562	9.606
2300	104.600	299.943	208.902	209.394	−594.367	−395.876	8.991
2400	104.600	304.394	212.789	219.854	−591.840	−387.301	8.429
2500	104.600	308.664	216.539	230.314	−589.305	−378.830	7.915
2600	104.600	312.767	220.162	240.774	−586.757	−370.461	7.443
2700	104.600	316.714	223.665	251.234	−584.194	−362.191	7.007
2800	104.600	320.519	227.057	261.694	−581.612	−354.016	6.604
2900	104.600	324.189	230.343	272.154	−579.007	−345.933	6.231
3000	104.600	327.735	233.531	282.614	−576.379	−337.941	5.884

PREVIOUS: CURRENT: June 1970

0	to	1400 K	crystal
above		1400 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.459	−670.395	−670.395	INFINITE
100	33.492	25.002	134.693	−10.969	−672.334	−657.029	343.197
200	57.584	56.746	87.999	−6.250	−672.454	−641.555	167.557
298.15	68.909	82.026	82.026	0.	−671.532	−626.562	109.771
300	69.041	82.453	82.028	0.128	−671.508	−626.283	109.046
400	75.714	103.350	84.831	7.408	−670.016	−611.424	79.844
500	78.927	120.625	90.315	15.155	−668.372	−596.965	62.365
600	80.789	135.193	96.613	23.148	−666.746	−582.837	50.741
700	82.015	147.744	103.041	31.292	−665.190	−568.977	42.458
800	82.902	158.756	109.331	39.540	−664.152	−555.271	36.255
900	83.592	168.562	115.378	47.866	−662.824	−541.742	31.442
1000	84.161	177.400	121.145	56.254	−661.698	−528.351	27.598
1100	84.646	185.444	126.631	64.695	−660.813	−515.062	24.458
1200	85.077	192.828	131.844	73.182	−660.208	−501.841	21.845
1300	85.475	199.654	136.801	81.710	−660.032	−488.654	19.634
1400	85.839	206.002	141.519	90.276	−660.415	−475.460	17.740
1400.000	85.839	206.002	141.519	90.276	CRYSTAL <--> LIQUID TRANSITION		
1400.000	104.600	248.015	141.519	149.094			
1500	104.600	255.232	148.862	159.554	−599.094	−466.535	16.246
1600	104.600	261.983	155.724	170.014	−596.356	−457.786	14.945
1700	104.600	268.324	162.163	180.474	−593.537	−449.212	13.803
1800	104.600	274.303	168.228	190.934	−606.999	−440.510	12.783
1900	104.600	279.958	173.961	201.394	−604.461	−431.330	11.858
2000	104.600	285.324	179.396	211.854	−601.932	−422.283	11.029
2100	104.600	290.427	184.563	222.314	−599.409	−413.363	10.282
2200	104.600	295.293	189.487	232.774	−596.889	−404.562	9.606
2300	104.600	299.943	194.189	243.234	−594.367	−395.876	8.991
2400	104.600	304.394	198.688	253.694	−591.840	−387.301	8.429
2500	104.600	308.664	203.003	264.154	−589.305	−378.830	7.915
2600	104.600	312.767	207.146	274.614	−586.757	−370.461	7.443
2700	104.600	316.714	211.131	285.074	−584.194	−362.191	7.007
2800	104.600	320.519	214.971	295.534	−581.612	−354.016	6.604
2900	104.600	324.189	218.674	305.994	−579.007	−345.933	6.231
3000	104.600	327.735	222.250	316.454	−576.379	−337.941	5.884

PREVIOUS: CURRENT: June 1970

$S°(298.15\ K) = 278.04 \pm 12.6\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -355.82 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -356.48 \pm 12.6\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4\Sigma$	0	4
	[300]	[4]
	[4000]	[4]
	[9000]	[4]

Vibrational Frequencies and Degenracies
υ, cm^{-1}
[600](1)
[151](1)
762 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Co–F = [1.72] Å
Bond Angle: F–Co–F = [165]°
Product of Moments of Inertia: $I_A I_B I_C = 6.57815 \times 10^{-116}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(CoF_2, g, 298.15\ K) = -85.2 \pm 3.0\ kcal \cdot mol^{-1}$ ($-355.477 \pm 12.6\ kJ \cdot mol^{-1}$), is calculated from the enthalpy of formation of the crystal, $\Delta_f H°(CoF_2, cr, 298.15\ K) = -160.5 \pm 4.0\ kcal \cdot mol^{-1}$, and the enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 75.3 \pm 3.0\ kcal \cdot mol^{-1}$ The sublimation value is determined from a 3rd law analysis of the vapor pressure data for CoF_2 reported by Kana'an *et al.*[1] Refer to the crystal table for details.

Heat Capacity and Entropy

Buchler *et al.*[2] investigated the deflection of a molecular beam of CoF_2(g) by an electric field and found that within the sensitivity of the apparatus the molecule was nonpolar and consequently possessed a linear structure. Hastie *et al.*[3] recently investigated the infrared absorption spectra of several transition metal difluorides through the use of matrix isolation techniques. Isoptopic shift measurements for matrix isolated NiF_2, ZnF_2, and CuF_2 in neon and argon indicated that these species were slightly bent. Based upon these results, the authors estiamted the F–Co–F angle as 165°. This value is adopted here. The bond length was estimated by Brewer *et al.*[4] The principal moments of inertia are: $I_A = 0.1934 \times 10^{-39}$, $I_B = 18.3484 \times 10^{-39}$, and $I_C = 18.5417 \times 10^{-39}\ g \cdot cm^2$.

Hastie *et al.*[3] isolated CoF_2 in neon and argon matrices and observed the υ_3 fundamental at 762 cm^{-1} They also calculated $\upsilon_1 = 600\ cm^{-1}$ by a valence force field method and estimated υ_2 as 151 cm^{-1} by applying the variation in the frequencies for the chlorides of Co, Ni, Cu, and Zn to the fluorides. The electronic levels and quantum weights are estimated by comparison with the electronic energy levels for Co^{++}(g) ion[5] and those for $CoCl_2$(g) observed by Hougen *et al.*[6]

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−12.940	−355.821	−355.821	INFINITE
100	41.091	227.574	320.907	−9.333	−355.643	−360.595	188.355
200	47.569	258.314	282.621	−4.861	−356.010	−365.424	95.439
250	49.634	269.160	278.877	−2.429	−356.236	−367.752	76.838
298.15	51.210	278.042	278.042	0.	−356.477	−369.949	64.813
300	51.263	278.359	278.043	0.095	−356.486	−370.032	64.428
350	52.536	286.361	278.672	2.691	−356.741	−372.270	55.558
400	53.528	293.444	280.084	5.344	−357.024	−374.470	48.901
450	54.305	299.795	281.928	8.040	−357.343	−376.632	43.718
500	54.920	305.550	284.007	10.772	−357.700	−378.756	39.568
600	55.822	315.648	288.462	16.312	−358.528	−382.892	33.334
700	56.459	324.303	292.979	21.927	−359.500	−386.878	28.869
800	56.956	331.876	297.377	27.599	−361.038	−390.652	25.507
900	57.377	338.609	301.591	33.316	−362.319	−394.279	22.883
1000	57.753	344.674	305.601	39.073	−363.824	−397.752	20.776
1100	58.095	350.195	309.408	44.865	−365.588	−401.062	19.045
1200	58.410	355.263	313.021	50.691	−367.644	−404.198	17.594
1300	58.699	359.950	316.453	56.546	−370.141	−407.147	16.359
1400	58.964	364.310	319.718	62.430	−373.205	−409.882	15.293
1500	59.205	368.387	322.828	68.338	−375.255	−412.428	14.362
1600	59.424	372.215	325.796	74.270	−377.045	−414.847	13.543
1700	59.622	375.823	328.634	80.223	−378.734	−417.157	12.818
1800	59.801	379.236	331.351	86.194	−396.684	−419.075	12.161
1900	59.963	382.474	333.957	92.182	−398.618	−420.267	11.554
2000	60.108	385.554	336.461	98.186	−400.545	−421.356	11.005
2100	60.239	388.489	338.869	104.203	−402.465	−422.350	10.505
2200	60.356	391.295	341.189	110.233	−404.375	−423.252	10.049
2300	60.461	393.980	343.426	116.274	−406.272	−424.067	9.631
2400	60.555	396.555	345.586	122.325	−408.154	−424.800	9.246
2500	60.638	399.029	347.675	128.385	−410.019	−425.455	8.889
2600	60.712	401.409	349.696	134.452	−411.864	−426.036	8.559
2700	60.777	403.701	351.654	140.527	−413.686	−426.547	8.252
2800	60.834	405.912	353.553	146.608	−415.483	−426.990	7.966
2900	60.882	408.048	355.395	152.693	−417.253	−427.370	7.698
3000	60.924	410.113	357.185	158.784	−418.994	−427.689	7.447
3100	60.959	412.111	358.925	164.878	−420.705	−427.951	7.211
3200	60.988	414.047	360.617	170.975	−797.197	−426.385	6.960
3300	61.011	415.924	362.265	177.075	−797.416	−414.793	6.566
3400	61.029	417.746	363.870	183.177	−797.604	−403.196	6.194
3500	61.041	419.515	365.435	189.281	−797.761	−391.593	5.844
3600	61.050	421.235	366.961	195.385	−797.888	−379.986	5.513
3700	61.054	422.907	368.450	201.491	−797.986	−368.377	5.201
3800	61.054	424.536	369.905	207.596	−798.056	−356.765	4.904
3900	61.051	426.121	371.326	213.701	−798.101	−345.151	4.623
4000	61.044	427.667	372.715	219.806	−798.121	−333.536	4.356
4100	61.035	429.174	374.074	225.910	−798.119	−321.922	4.101
4200	61.023	430.645	375.404	232.013	−798.096	−310.307	3.859
4300	61.009	432.081	376.705	238.115	−798.055	−298.694	3.628
4400	60.992	433.483	377.980	244.215	−797.996	−287.082	3.408
4500	60.973	434.853	379.228	250.313	−797.924	−275.471	3.198
4600	60.953	436.193	380.452	256.409	−797.838	−263.862	2.996
4700	60.931	437.504	381.652	262.504	−797.742	−252.254	2.803
4800	60.908	438.787	382.829	268.595	−797.637	−240.649	2.619
4900	60.883	440.042	383.984	274.685	−797.526	−229.047	2.442
5000	60.858	441.272	385.118	280.772	−797.410	−217.446	2.272
5100	60.831	442.477	386.230	286.857	−797.291	−205.848	2.108
5200	60.804	443.658	387.323	292.938	−797.171	−194.252	1.951
5300	60.776	444.816	388.397	299.017	−797.052	−182.659	1.800
5400	60.747	445.951	389.453	305.094	−796.936	−171.068	1.655
5500	60.718	447.066	390.490	311.167	−796.825	−159.479	1.515
5600	60.689	448.160	391.510	317.237	−796.721	−147.891	1.379
5700	60.659	449.234	392.513	323.305	−796.625	−136.306	1.249
5800	60.629	450.288	393.501	329.369	−796.539	−124.723	1.123
5900	60.599	451.324	394.472	335.430	−796.420	−113.143	1.002
6000	60.569	452.343	395.428	341.489	−796.348	−101.563	0.884

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = [94.6 \pm 12.6]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1200 \pm 200]\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -790.36 \pm 12.6\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

Fowler *et al.*[1] determined calorimetrically the enthalpy of fluorination of crystalline CoF_2 at 473.15 K. For the reaction $2\ CoF_2(cr) + F_2(g) \rightarrow 2\ CoF_3(cr)$ they reported $\Delta_r H°(473.15\ K) = -52.0 \pm 3.0\ kcal·mol^{-1}$ which yields $\Delta_r H°(298.15\ K) = -52.4 \pm 3.0\ kcal·mol^{-1}$based upon our functions for $CoF_2(cr)$ and $CoF_3(cr)$. Combining this result with the enthalpy of formation of $CoF_2(cr)$,[2] we derive $\Delta_f H°(CoF_3, cr, 298.15\ K) = -186.7 \pm 3.0\ kcal·mol^{-1}$.

Jessup *et al.*[3] investigated calorimetrically this same fluorination reaction and reported $\Delta_r H°(523.15\ K) = -56.1 \pm 2.0\ kcal·mol^{-1}$. This result leads to $\Delta_f H°(CoF_3, cr, 298.15\ K) = -188.8 \pm 2.0\ kcal·mol^{-1}$. In the same investigation Jessup *et al.*[3] reported $\Delta_r H°(608\ K) = -74.0 \pm 4.0\ kcal·mol^{-1}$ for the reduction reaction $2\ CoF_3(cr) + H_2(g) \rightarrow 2\ CoF_2(cr) + 2\ HF(g)$. Corrected to 298.15 K we calculate $\Delta_r H°(298.15\ K) = -73.3 \pm 4.0\ kcal·mol^{-1}$. Combining this result with enthalpy of formation data for CoF_2cr).[2] and HF(g),[4] we derive $\Delta_f H°(CoF_3, cr, 298.15\ K) = -189.0 \pm 4.0\ kcal·mol^{-1}$. We note that the addition of these two results by Jessup *et al.*[3] leads to $\Delta_r H°(298.15\ K) = -129.9 \pm 6.0\ kcal·mol^{-1}$ for the reaction $H_2(g) + F_2(g) \rightarrow 2\ HF(g)$ which is quite consistent with the result $-130.28 \pm 0.4\ kcal·mol^{-1}$ calculated from the selected value for the enthalpy of formation of HF(g).[4] Thus, it is apparent that these two results are probably quite reliable, and we adopted $\Delta_f H°(CoF_3, cr, 298.15\ K) = -188.9 \pm 3.0\ kcal·mol^{-1}$ ($-790.358 \pm 12.6\ kJ·mol^{-1}$).

Jellinek and Koop[5] reported equilibrium constants for the reduction reaction given above in the temperature range 470–595 K. 2nd and 3rd law analyses of these equilibrium data give $\Delta_r H°(298.15\ K)$ of 31.7 and $29.3 \pm 0.6\ kcal·mol^{-1}$, respectively; the drift is $-4.7 \pm 1.5\ cal·K^{-1}·mol^{-1}$. These values are in considerable disagreement with the calorimetric value of $-73.3 \pm 4.0\ kcal·mol^{-1}$ given by Jessup *et al.* [3], and no weight is given to these equilibrium data.

Heat Capacity and Entropy

Heat capacity data for $CoF_3(cr)$ are estimated by comparison with those for $FeF_2(cr)$, $FeF_3(cr)$, $TiF_3(cr)$, and $CoF_2(cr)$. $S°(298.15\ K)$ is estimated to be $22.6\ cal·K^{-1}·mol^{-1}$ ($94.5584\ J·K^{-1}·mol^{-1}$) from the ionic entropy contributions given by Kubaschewski, Evans, and Alcock.[6] We note that this method leads to $S°(298.15\ K) = 19.4\ cal·K^{-1}·mol^{-1}$ for $CoF_2(cr)$ which is in good agreement with the experimental value of $19.60 \pm 0.10\ cal·K^{-1}·mol^{-1}$.[2]

Fusion Data

T_{fus} is estimated by comparison with those for other transition metal halides. We note that Ruff and Ascher[7] reported $CoF_3(cr)$ being thermally unstable around 900 K, while Stewart[8] recently showed that $CoF_2(cr)$ was formed by hydrolytic reactions and not by thermal decomposition. The derived $\Delta_f G°$ values for $CoF_3(cr)$ indicate that it is thermodynamically more stable than $CoF_2(cr)$ in agreement with the findings of Stewart.[8] In the temperature range 298–900 K, the Gibbs energy change for the decomposition reaction $2\ CoF_3(cr) \rightarrow 2CoF_2(cr) + F_2(g)$ are in the range + 10–20 $kcal·mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.797	94.558	94.558	0.	−790.358	−718.893	125.947
300	92.471	95.128	94.560	0.170	−790.320	−718.450	125.093
400	97.470	122.481	98.255	9.691	−788.197	−694.811	90.733
500	99.701	144.498	105.375	19.561	−786.113	−671.708	70.173
600	100.454	162.742	113.461	29.569	−784.209	−649.010	56.501
700	101.219	178.285	121.638	39.653	−782.489	−626.614	46.759
800	101.981	191.849	129.584	49.812	−781.344	−604.393	39.463
900	102.839	203.909	137.185	60.051	−779.930	−582.361	33.799
1000	103.868	214.796	144.410	70.386	−778.703	−560.477	29.276
1100	105.027	224.750	151.268	80.830	−777.675	−538.706	25.581
1200	106.248	233.940	157.779	91.393	−776.867	−517.019	22.505
1300	107.587	242.497	163.970	102.084	−776.412	−495.386	19.905
1400	108.935	250.519	169.869	112.910	−776.429	−473.771	17.677
1500	110.320	258.082	175.500	123.873	−775.330	−452.188	15.747

PREVIOUS: CURRENT: December 1970

$S°(298.15\ K) = 52.993 \pm 0.34\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2103 \pm 10\ K$

$\Delta_f H°(0\ K) = -238.1 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -237.7 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° =$ Unknown

Enthalpy of Formation

Boyle *et al.*[1] measured the enthalpy of combustion of metallic cobalt at 303.16 K. Their analyses of the combustion products indicated that some overoxidation of the metal had occurred. Correction of their results to correspond to CoO was made on the assumption that the excess oxygen was combined as Co_3O_4. Also the analyses indicated that the combustion products had attacked the silica–glass capsules, used to hold the metal samples, resulting in appreciable amounts of silicate formation. Corrections for these two side reactions amounted to three percent of the total measured energy of combustion. From these data, we derive $\Delta_f H°$(CoO, cr, 298.15 K) = -57.0 ± 0.3 kcal·mol^{-1}. Roth and Havekoss[2] also investigated calorimetrically the combustion of metallic cobalt and reported $\Delta_f H°$(CoO, cr, 298.15 K) = -57.2 ± 0.2 kcal·mol^{-1}.

2nd and 3rd law analyses of several equilibrium studies,[3–12] emf measurements,[13] and mass–spectrometric studies[14] involving CoO(cr) are discussed in the JANAF Thermochemical Tables,[18] $\Delta_f H°$(CoO, cr, 298.15 K) = -56.82 ± 0.10 kcal·mol^{-1}(-237.735 ± 0.4 kJ·mol^{-1}) was adopted. A recent critical evaluation by Cyr *et al.*[19] recommended $\Delta_f H°$(CoO, cr, 298.15 K) = -237.5 ± 0.4 kJ·mol^{-1}, based on 2nd and 3rd law analyses. Since this value differs from the value previously adopted by JANAF by only 0.2 kJ·mol^{-1} and includes ten new references in the evaluation, it is adopted for the current table.

Heat Capacity and Entropy

The adopted heat capacities for CoO(cr) in the temperature range 51–298 K are those of King[15]. These data have a pronounced maximum at 287.3 K, at which point the heat capacity is greater than 17.6 cal·K^{-1}·mol^{-1}. Assayag and Bizette[16] also measured heat capacities for CoO(cr) between 180–400 K and reported a maximum at 298.7 K. Presumably this anomaly is of the magnetic type. Heat capacity data above 300 K are calculated from the high temperature (400–1800 K) enthalpy data of King and Christensen.[17] Both sets of data were smoothed by computer and joined at 298.15 K.

The value of $S°$(298.15 K) is obtained from the low temperature heat capacity dataof King[15] and is based on $S°$(51 K) = 0.42 cal·K^{-1}·mol^{-1}.

Fusion Data

The adopted T_{fus} of 2103 ± 10 K was recommended by IUPAC [20] based on the work of Coutures.[21]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.434	−238.056	−238.056	INFINITE
100	19.038	9.109	97.044	−8.794	−239.390	−230.867	120.593
200	45.376	30.904	58.385	−5.496	−239.458	−222.172	58.025
298.15	55.279	52.993	52.993	0.	−237.735	−213.988	37.490
300	54.831	53.333	52.994	0.102	−237.706	−213.840	37.233
400	52.932	68.698	55.099	5.439	−236.422	−206.088	26.912
500	53.932	80.628	59.052	10.788	−235.342	−198.632	20.751
600	54.312	90.497	63.495	16.201	−234.402	−191.381	16.661
700	54.513	98.883	67.966	21.642	−233.625	−184.275	13.751
800	54.819	106.180	72.297	27.107	−233.428	−177.207	11.570
900	55.312	112.664	76.428	32.612	−232.970	−170.209	9.879
1000	56.011	118.526	80.349	38.176	−232.709	−163.251	8.527
1100	56.886	123.904	84.068	43.820	−232.656	−156.309	7.423
1200	57.915	128.897	87.598	49.559	−232.827	−149.363	6.502
1300	59.070	133.578	90.957	55.407	−233.353	−142.390	5.721
1400	60.329	138.001	94.160	61.377	−234.348	−135.357	5.050
1500	61.672	142.208	97.224	67.476	−234.217	−128.288	4.467
1600	63.086	146.233	100.163	73.713	−233.707	−121.241	3.958
1700	64.559	150.102	102.987	80.095	−232.966	−114.234	3.510
1800	66.078	153.835	105.709	86.627	−248.354	−106.981	3.105
1900	67.639	157.449	108.337	93.312	−247.588	−99.147	2.726
2000	69.233	160.959	110.881	100.156	−246.676	−91.357	2.386
2100	70.856	164.376	113.347	107.160	−245.615	−83.617	2.080
2200	72.505	167.710	115.743	114.328	−244.401	−75.930	1.803
2300	74.174	170.970	118.074	121.662	−243.033	−68.303	1.551
2400	75.860	174.162	120.344	129.163	−241.508	−60.738	1.322
2500	77.563	177.294	122.560	136.834	−239.825	−53.240	1.112
2600	79.283	180.369	124.724	144.676	−237.981	−45.813	0.920
2700	81.011	183.394	126.841	152.691	−235.975	−38.459	0.744
2800	82.747	186.371	128.914	160.879	−233.806	−31.183	0.582
2900	84.496	189.305	130.946	169.241	−231.473	−23.987	0.432
3000	86.253	192.199	132.940	177.778	−228.974	−16.874	0.294

PREVIOUS: CURRENT: December 1970

$S°(298.15\ K) = 117.377 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}\ (\alpha \rightarrow \beta) = 964 \pm 5\ K$

$\Delta_f H°(0\ K) = -878.95 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -888.26 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° \approx 2.134 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Adami and King[1] determined calorimetrically the enthalpies of solution of crystalline CoO and α–$CoSO_4$ in hydrochloric acid solution. From these measurements they derived the enthalpy for the reaction $CoO(cr) + H_2SO_4\ \ 7.068\ H_2O(l \rightarrow CoSO_4(cr) + 8.068\ H_2O\ (l)$ as $\Delta_r H°(298.15\ K) = -14.280 \pm 0.110\ kcal \cdot mol^{-1}$. Combining this result with enthalpies of formation for CoO[2] $H_2SO_4 \cdot 7.068\ H_2O$[3], and H_2O[3], we derive $\Delta_f H°(\alpha\text{–}CoSO_4, cr, 298.15\ K) = -212.3 \pm 0.3\ kcal \cdot mol^{-1} (-888.263 \pm 1.3\ kJ \cdot mol^{-1})$ which is adopted.

The total pressures of $SO_3(g)$, $SO_2(g)$, and $O_2(g)$ over $CoSO_4(cr)$ in the temperature range 1100–1300 K have been determined by manometric[4-7] and transpiration[8] methods. Previous investigators[4-6] analyzed these data solely in terms of two equilibria, namely (A) $CoSO_4(cr) = CoO(cr) + SO_3(g)$ and (B) $SO_3(g) = SO_2(g) + 0.5\ O_2(g)$. However, Warner[10] has shown that $CoSO_4$ takes part in three successive, univariant, decomposition equilibria as the temperature is increased. Co_3O_4 is the decomposition product at low temperatures (<1150 K), a mixture of Co_3O_4 and CoO at intermediate tempertures, and CoO at high temperatures. Second and third law analyses of those points involving only equilibria (A) and (B) are given below. The appearance of Co_3O_4 as a decomposition product was determined by comparing the oxygen partial pressures that were calculated from the total pressure data with those for the decomposition reaction (C) $Co_3O_4(cr) \rightarrow 3\ CoO(cr) + 0.5\ O_2(g)$[2]. Espelund and Flengas[9] measured the Gibbs energy of reaction (A) in a high temperature solid electrolytic cell. Here, no Co_3O_4 was formed over the entire temperature range (827–1133 K), since the oxygen pressures in the cell were too low to oxidize the CoO. Results of an analysis of these data are also given below:

Source	Reaction	Method	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Marchal[4]	A	Manometric	17	1143–1303	54.5	60.4 ± 0.5	4.9 ± 0.6	−211.8 ± 0.8
Schenck and Raub[5]	A	Manometric	14	1099–1243	68.5	60.9 ± 0.7	−6.3 ± 1.1	−212.3 ± 1.0
Warner[6]	A	Manometric	2	1164–1175	56.9	59.3 ± 0.3	2.1	−210.8 ± 0.3
Ingraham[7]	A	Manometric	9	1144–1210	59.1	59.1 ± 0.1	0.04 ± 0.91	−210.6 ± 0.4
Alcock *et al.*[8]	D**	Transpiration	8	1131–1217	−191.1	−166.8 ± 1.4	20.2 ± 5.5	−211.2 ± 1.5
Espelund and Flengas[9]	A	emf	28	827–1177	59.5	59.5 ± 0.3	0.08 ± 0.22	−211.0 ± 0.6

** Reaction: (D) $2\ CoO(cr) + 2\ SO_2(g) + O_2(g) = 2\ CoSO_4(cr)$

These results indicate that the Gibbs energy functions and equilibrium data are consistent within experimental error.

Heat Capacity and Entropy

The low temperature (52–298 K) heat capacities are those reported by Weller.[11] No anomalies appear in these data. Heat capacities in the temperature range 300–2000 K are estimated by comparison with those for $CuSO_4$.[2]

$S°(298.15\ K)$ is determined from the C_p data based on $S°(51\ K) = 1.56 + 2.75\ cal \cdot K^{-1} \cdot mol^{-1}$. The 1.56 is a lattice contribution, while the 2.75 is the entropy associated with the ordering of the Co^{+2} spin moments. In assigning the magnetic entropy, it is assumed that all of the contribution remains to be extracted below the minimum temperature (52 K) of the heat capacity measurements.[11]

Transition Data

The temperature (T_{trs}) and the heat ($\Delta_{trs} H°$) of the α–β transition for $CoSO_4$ are from the differential thermal analysis studies of Ingraham and Marier.[12] Other temperatures reported for the transition are 890[6] and 903 K.[13]

Decomposition Data

T_{dcm} is the temperature at which the Gibbs energy change for the process $CoSO_4(cr) \rightarrow CoO(cr) + SO_3(g)$ is zero.

References

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[2]JANAF Thermochemical Tables: CoO(cr), 2–31–70; $CuSO_4$(cr), 6–30–66; SO_3(g), 9–30–65; SO_2(g), 6–30–61; Co_3O_4(cr), 12–31–71.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−17.238	−878.952	−878.952	INFINITE
100	44.454	37.748	192.584	−15.484	−884.218	−851.311	444.679
200	80.281	80.789	126.133	−9.069	−887.177	−817.096	213.403
298.15	103.219	117.377	117.377	0.	−888.263	−782.408	137.075
300	103.638	118.017	117.379	0.191	−888.269	−781.751	136.115
400	119.286	150.056	121.642	11.366	−890.202	−746.171	97.440
500	131.545	178.049	130.182	23.933	−890.418	−710.133	74.187
600	140.666	202.877	140.269	37.565	−889.584	−674.139	58.689
700	147.277	225.081	150.827	51.977	−888.064	−638.344	47.634
800	152.047	245.074	161.380	66.955	−886.571	−602.736	39.355
900	155.394	263.190	171.702	82.339	−937.599	−566.301	32.867
964.000	156.792	273.916	178.135	92.332	ALPHA <--> BETA		
964.000	157.221	276.129	178.135	94.466	TRANSITION		
1000	158.113	281.910	181.767	100.142	−932.148	−525.304	27.439
1100	160.415	297.089	191.571	116.071	−928.946	−484.775	23.020
1200	162.465	311.137	200.956	132.217	−925.920	−444.531	19.350
1300	164.306	324.215	209.941	148.556	−923.232	−404.528	16.254
1400	165.979	336.453	218.545	165.071	−921.020	−364.713	13.608
1500	167.569	347.959	226.793	181.749	−917.705	−325.090	11.321
1600	169.075	358.822	234.708	198.582	−914.048	−285.700	9.327
1700	170.498	369.115	242.314	215.561	−910.211	−246.545	7.575
1800	171.921	378.901	249.633	232.683	−922.559	−207.326	6.016
1900	173.259	388.232	256.684	249.942	−918.819	−167.692	4.610
2000	174.598	397.153	263.486	267.335	−915.002	−128.257	3.350

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = 114.29 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -896.3 \pm 4.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -910.0 \pm 4.0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Bugden and Pratt[1] measured Gibbs energies of reaction for (a) $2Cu(cr) + Co_3O_4(cr) \rightarrow 3CoO(cr) + Cu_2O(cr)$ and (b) $Ni(cr) + Co_3O_4(cr) \rightarrow 3CoO(cr) + NiO(cr)$ from high temperature solid electrolytic cells. These data were subjected to 2nd and 3rd law analyses with results summarized in the following table:

Source	Reaction	Method	T/K	No. of Points	$\Delta_r H°$(298.15 K) kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298. 15K)*
Bugden and Pratt[1]	a	emf	900–1150	Eqn	5.1	6.3 ± 0.2	1.1	−217.5 ± 0.8
	b	emf	850–1100	Eqn	−12.0	−10.6 ± 0.2	1.3	−217.1 ± 0.8
Foote and Smith[3]	c	Manometric	1073–1243	6	34.5	47.2 ± 1.4	10.6 ± 1.3	−217.7 ± 1.5
Watanabe[4]	c	Manometric	1128–1233	4	38.1	47.9 ± 0.7	8.3 ± 0.8	−218.4 ± 1.0
Chufarov *et al.*[5]	c	Manometric	973–1173	4	27.9	46.4 ± 2.9	17.0 ± 0.6	−216.9 ± 3.0
Balakirev and Chufarov[6]	c	Manometric	923–1173	5	33.8	46.1 ± 2.5	11.3 ± 2.5	−216.6 ± 3.0
Roiter and Paladine[7]	c	Manometric	1139–1220	5	36.4	47.1 ± 0.6	9.0 ± 2.0	−217.6 ± 1.0
Ingraham[8] Set I	c	Manometric	1101–1159	6	41.4	46.8 ± 0.2	4.5 ± 0.4	−217.3 ± 0.5
Set II	c	Manometric	1086–1219	19	35.6	46.9 ± 0.8	9.7 ± 0.2	−217.4 ± 1.0
O'Bryan and Parravano[9]	c	X-ray & Wt. Loss	1073–1243	Eqn	40.3	47.3 ± 0.8	5.9	−217.8 ± 1.0

*3rd law values based on $\Delta_f H°(CoO,cr, 298.15\ K) = -56.82 \pm 0.1\ kcal \cdot mol^{-1}$.[2]

Both sets of emf data are much more compatible with the adopted functions than the dissociation pressure data (refer to the discussion below). The results obtained with the Cu/Cu_2O reference couple are judged to be more reliable and lead to the adopted enthalpy of formation, $\Delta_f H°(Co_3O_4,cr, 298.15\ K) = -217.5 \pm 1.0\ kcal \cdot mol^{-1}$, when used in conjunction with JANAF[2] enthalpies of formation for CoO and Cu_2O.

Equilibrium oxygen pressures for the reaction (c) $Co_3O_4(cr) = 3CoO(cr) + 0.5\ O_2(g)$ have been determined by numerous investigators.[3-9] 2nd and 3rd law analyses of these data are given in the above table. Within each set the 2nd and 3rd law $\Delta_r H°(298.15\ K)$ values are not in agreement, and all sets contain large positive drifts. Warner[10] has suggested that these discrepancies arise as a result of an error in the measured standard entropy[11] for Co_3O_4. However, once the magnetic contribution is included (see entropy write-up) the real error in this value is probably no greater than one cal·K^{-1}·mol^{-1}. The other possible source of error is lack of true equilibrium conditions. Recent thermogravimetric,[9] X-ray,[9] and kinetic,[9, 12] studies of the Co_3O_4–CoO–O_2 system all point to an irreversible reaction. Therefore, no weight has been given to the dissociation pressure data in our evaluation.

Heat Capacity and Entropy

The low temperature heat capacities (54–296.3 K) are those reported by King.[11] Heat capacities in the temperature range 300–1000 K are calculated from the high temperature enthalpy data of King and Christensen;[13] a constrained curve fitting technique was used to join smoothly these data with the low temperature data at 298 K. No anomalies appear in either set of data. Roth[14] observed a maximum in the magnetic susceptibility of Co_3O_4 at 40 K, while Mossbauer studies by Kundig *et al.*[15] indicated a Neel temperature of 33.0 ± 1.0 K. With the assumption that Co_3O_4 is a normal 2–3 spinel,[16] this transition can be associated with the antiferromagnetic ordering of the Co^{+2} ion spin moments. Therefore, the entropy is based on $S°(51\ K) = 1.36 + 2.75 = 4.11\ cal \cdot K^{-1} \cdot mol^{-1}$, where 1.36 is a lattice contribution and 2.75 is the magnetic entropy. In assigning the magnetic entropy, it is assumed that all of the contribution remains to be extracted below the minmum temperature (54 K) of the heat capacity measurements.

Decomposition Data

T_{dcm} is the temperature at which the Gibbs energy change for the process $Co_3O_4(cr \rightarrow 3CoO(cr) + 0.5\ O_2(g)$ is zero.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−17.968	−896.309	−896.309	INFINITE
100	34.368	31.487	198.112	−16.663	−902.377	−868.560	453.689
200	87.595	72.039	124.547	−10.501	−907.767	−832.428	217.408
298.15	123.051	114.286	114.286	0.	−910.020	−794.871	139.258
300	123.512	115.049	114.289	0.228	−910.038	−794.157	138.275
400	142.666	153.657	119.423	13.694	−910.220	−755.468	98.654
500	152.850	186.590	129.647	28.471	−909.774	−716.825	74.886
600	162.808	215.325	141.580	44.247	−908.999	−678.302	59.051
700	173.628	241.224	153.992	61.062	−907.802	−639.941	47.753
800	185.272	265.161	166.410	79.001	−907.337	−601.601	39.280
900	197.552	287.688	178.645	98.139	−905.043	−563.516	32.706
1000	210.296	309.158	190.630	118.528	−902.293	−525.712	27.460
1100	223.384	329.814	202.350	140.210	−899.139	−488.203	23.183
1200	236.727	349.821	213.809	163.214	−895.639	−450.998	19.631
1300	250.262	369.303	225.024	187.562	−892.206	−414.087	16.638
1400	263.943	388.349	236.012	213.272	−889.197	−377.422	14.082
1500	277.742	407.029	246.793	240.355	−881.838	−341.108	11.878

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REFERENCE STATE

0	to 2130	K	crystal
2130	to 2952.078	K	liquid
above	2952.078	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.057	0.	0.	0.
100	9.963	4.286	41.746	−3.746	0.	0.	0.
200	19.860	14.869	25.680	−2.162	0.	0.	0.
298.15	23.434	23.618	23.618	0.	0.	0.	0.
300	23.472	23.764	23.619	0.043	0.	0.	0.
311.500	23.681	24.651	23.641	0.315	___ C_p LAMBDA MAXIMUM ___		
311.500	23.681	24.654	23.641	0.316	TRANSITION		
400	25.230	30.765	24.562	2.481	0.	0.	0.
500	26.631	36.553	26.398	5.078	0.	0.	0.
600	27.719	41.508	28.513	7.797	0.	0.	0.
700	28.577	45.846	30.686	10.612	0.	0.	0.
800	29.434	49.715	32.827	13.511	0.	0.	0.
900	30.501	53.241	34.902	16.505	0.	0.	0.
1000	31.861	56.523	36.901	19.621	0.	0.	0.
1100	33.472	59.634	38.828	22.887	0.	0.	0.
1200	35.187	62.618	40.687	26.318	0.	0.	0.
1300	37.116	65.511	42.485	29.933	0.	0.	0.
1400	39.125	68.334	44.231	33.744	0.	0.	0.
1500	41.200	71.104	45.931	37.760	0.	0.	0.
1600	43.329	73.831	47.589	41.986	0.	0.	0.
1700	45.501	76.523	49.212	46.427	0.	0.	0.
1800	47.706	79.186	50.804	51.087	0.	0.	0.
1900	49.944	81.825	52.367	55.970	0.	0.	0.
2000	52.204	84.444	53.905	61.077	0.	0.	0.
2100	54.488	87.046	55.422	66.411	0.	0.	0.
2130.000	55.174	87.824	55.873	68.056	___ CRYSTAL <--> LIQUID ___		
2130.000	39.330	97.449	55.873	88.558	TRANSITION		
2200	39.330	98.721	57.216	91.311	0.	0.	0.
2300	39.330	100.469	59.059	95.244	0.	0.	0.
2400	39.330	102.143	60.819	99.177	0.	0.	0.
2500	39.330	103.749	62.505	103.110	0.	0.	0.
2600	39.330	105.291	64.121	107.043	0.	0.	0.
2700	39.330	106.775	65.673	110.976	0.	0.	0.
2800	39.330	108.206	67.167	114.909	0.	0.	0.
2900	39.330	109.586	68.606	118.842	0.	0.	0.
2952.078	39.330	110.286	69.335	120.890	___ LIQUID <--> IDEAL GAS ___		
2952.078	30.533	225.302	69.335	460.427	FUGACITY = 1 bar		
3000	30.788	225.796	71.830	461.897	0.	0.	0.
3100	31.302	226.814	76.813	465.001	0.	0.	0.
3200	31.796	227.815	81.517	468.156	0.	0.	0.
3300	32.275	228.801	85.965	471.360	0.	0.	0.
3400	32.745	229.772	90.180	474.611	0.	0.	0.
3500	33.212	230.728	94.182	477.909	0.	0.	0.
3600	33.680	231.670	97.988	481.253	0.	0.	0.
3700	34.156	232.599	101.614	484.645	0.	0.	0.
3800	34.646	233.516	105.073	488.085	0.	0.	0.
3900	35.157	234.423	108.378	491.575	0.	0.	0.
4000	35.692	235.320	111.540	495.117	0.	0.	0.
4100	36.260	236.208	114.570	498.715	0.	0.	0.
4200	36.864	237.089	117.477	502.370	0.	0.	0.
4300	37.511	237.964	120.269	506.089	0.	0.	0.
4400	38.205	238.834	122.954	509.874	0.	0.	0.
4500	38.954	239.701	125.538	513.732	0.	0.	0.
4600	39.760	240.566	128.030	517.667	0.	0.	0.
4700	40.632	241.430	130.433	521.686	0.	0.	0.
4800	41.572	242.295	132.755	525.795	0.	0.	0.
4900	42.587	243.163	134.999	530.003	0.	0.	0.
5000	43.681	244.034	137.171	534.315	0.	0.	0.
5200	44.964	245.697	141.308	542.822	0.	0.	0.
5400	47.221	247.435	145.206	552.036	0.	0.	0.
5600	49.697	249.197	148.889	561.724	0.	0.	0.
5800	52.370	250.986	152.378	571.925	0.	0.	0.
6000	55.230	252.809	155.696	582.682	0.	0.	0.

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K) = 23.618 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{trs} = 311.5\ K$
$T_{fus} = 2130 \pm 20\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0.0008\ kJ·mol^{-1}$
$\Delta_{fus} H° = 20.5 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for $T \leq 10$ K are chosen to be the same as those adopted by Hultgren *et al.*[1] A graphical integration of these $C_p°$ data yields $S°(10\ K) = 0.005\ kcal·mol^{-1}$ and $H°(10\ K) - H°(0\ K) = 0.0252\ cal·mol^{-1}$. These data also match well with the $C_p°$ studies of Clusius and Franzosini.[2] The adopted $C_p°$ values are based on the following studies.

Source	Points	Method	T/K
2	76	$C_p°$	14.10–274.43
3	23	$C_p°$	56.1 –291.1
4	Smooth	$C_p°$	60–300
5	Graph	$C_p°$	268–324
6	Smooth	$C_p°$	273–1073
7	Smooth	drop	400–1500
8	48	drop	1267.2108
9	17	drop	303–1884
10	Smooth	$C_p°$	320–1800
11	26	drop	673–1339

The adopted $C_p°$ values are obtained primarily by graphical techniques to ensure smoothness of the curve and a reasonable representation of the sometimes diverse results. A $\Delta C_p° = 0$ is also adopted across T_{trs}. Below 200 K, there is excellent agreement between three independent studies.[2–4] Above 200 K these three studies drift apart by at most 0.06 $kcal·mol^{-1}$. Above 298 K, there are considerable differences in the various sets of data, differences of the order of 0.2 $kcal·mol^{-1}$ being typical. In terms of enthalpy, the data of Jaeger and Rosenbohm[11] deviates from the adopted values by +150 to +350 $cal·mol^{-1}$; the data of Lucks and Deem[9] by 0 to −450 $cal·mol^{-1}$; the data of Hultgren and Land[7] by −13 to +60 $cal·mol^{-1}$; and the data of Conway and Hein[8] by −190 to +250 $cal·mol^{-1}$. Surprisingly the enthalpy study by Kirillin *et al.*[12] yields enthalpies which are crudely 2 $kcal·mol^{-1}$ less than the adopted values at 2000 K.

Fusion Data

Refer to the liquid table for details.

Transition Data

Beaumont *et al.*[5] measured the heat capacity of 99.998% pure Cr in the region 268–324 K. The detailed $C_p°$ measurements gave evidence of a lambda-type anomaly, the maximum occurring at 311.5 K. Beaument *et al.*[5] estimated the heat associated with this transition to be 1.4 $cal·mol^{-1}$. Garnier and Salamon[13] used an extension of the ac calorimetric method to determine latent heat and heat capacity simultaneously. They concluded that annealing the Cr sample decreases the transition temperature and sharpens the peak. They also concluded that the transition was first order with a latent heat of $0.19 \pm 0.04\ cal·mol^{-1}$ at a transition temperature of 311.5 K. Garnier and Salamon[13] calculated a latent heat of $0.23 \pm 0.05\ cal·mol^{-1}$ and $0.25 \pm 0.08\ cal·mol^{-1}$ from expansivity data and neutron–diffraction data, respectively. Sze and Meaden[14] observed a large step in specific heat measurements (50%) and estimated a latent heat of 0.47 $cal·mol^{-1}$.

We adopt $T_{trs} = 311.5$ K and $\Delta_{fus} H° = 0.0002\ kcal·mol^{-1}$ based on the work by Garnier and Salamon.[13] In addition we adopt $\Delta C_p° = 0$ across the transition. The nature of the transition is not understood at this time.

Sublimation Data

Refer to the ideal gas table for details.

References

[1] R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Cr table, (October 1966).
[2] K. Clusius and P. Franzosini, Z. Naturforsch. **17a**, 522 (1962).
[3] C. T. Anderson, J. Amer. Chem. Soc. **59**, 488 (1937).
[4] G. I. Kalishevich, P. V. Gel'd, and R. P. Krentsis, Russ. J. Phys. Chem. **39**, 1602 (1965).
[5] R. H. Beaumont, H. Chihara, and J. A. Morrison, Phil. Mag. **5**, 188 (1960).
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Continued on page 975

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−4.057	0.	0.	0.
100	9.963	4.286	41.746	−3.746	0.	0.	0.
200	19.860	14.869	25.680	−2.162	0.	0.	0.
250	22.298	19.590	23.998	−1.102	0.	0.	0.
298.15	23.434	23.618	23.618	0.	0.	0.	0.
300	23.472	23.764	23.619	0.043	0.	0.	0.
311.500	23.681	24.651	23.641	0.315	___ C_p LAMBDA MAXIMUM ___		
311.500	23.681	24.654	23.641	0.316	TRANSITION		
350	24.393	27.453	23.908	1.240	0.	0.	0.
400	25.230	30.765	24.562	2.481	0.	0.	0.
450	25.983	33.781	25.421	3.762	0.	0.	0.
500	26.631	36.553	26.398	5.078	0.	0.	0.
600	27.719	41.508	28.513	7.797	0.	0.	0.
700	28.577	45.846	30.686	10.612	0.	0.	0.
800	29.434	49.715	32.827	13.511	0.	0.	0.
900	30.501	53.241	34.902	16.505	0.	0.	0.
1000	31.861	56.523	36.901	19.621	0.	0.	0.
1100	33.472	59.634	38.828	22.887	0.	0.	0.
1200	35.187	62.618	40.687	26.318	0.	0.	0.
1300	37.116	65.511	42.485	29.933	0.	0.	0.
1400	39.125	68.334	44.231	33.744	0.	0.	0.
1500	41.200	71.104	45.931	37.760	0.	0.	0.
1600	43.329	73.831	47.589	41.986	0.	0.	0.
1700	45.501	76.523	49.212	46.427	0.	0.	0.
1800	47.706	79.186	50.804	51.087	0.	0.	0.
1900	49.944	81.825	52.367	55.970	0.	0.	0.
2000	52.204	84.444	53.905	61.077	0.	0.	0.
2100	54.488	87.046	55.422	66.411	0.	0.	0.
2130.000	55.174	87.824	55.873	68.056	--- CRYSTAL <--> LIQUID ---		
2200	56.785	89.634	56.918	71.975	−19.336	0.655	−0.016
2300	59.099	92.209	58.397	77.769	−17.475	1.523	−0.035
2400	61.425	94.774	59.859	83.795	−15.382	2.305	−0.050
2500	63.764	97.328	61.307	90.055	−13.055	2.995	−0.063
2600	66.111	99.875	62.741	96.548	−10.495	3.587	−0.072
2700	68.467	102.414	64.163	103.277	−7.699	4.076	−0.079
2800	70.831	104.947	65.575	110.242	−4.667	4.458	−0.083

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = [36.205]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2130 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [26.068]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 20.5 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Cr(l) at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2130\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for Cr(l) is estimated as 9.4 $cal·K^{-1}·mol^{-1}$ by analogy with other monatomic metals. The same value was adopted by Hutgren *et al.*[1] A glass transition is assumed at 1350 K. Below 1350 K, the $C_p°$ values are those of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The value for the enthalpy of melting is adopted as $\Delta_{fus}H° = 4.9 \pm 1.0\ kcal·mol^{-1}$. This value is calculated from $\Delta_{fus}S° = 2.3\ cal·K^{-1}·mol^{-1}$. This estimated entropy of melting is consistent with the recently accepted $\Delta_{fus}S°$ values for V[2], 2.49 $cal·K - mol^{-1}$), Nb[2], 2.33 $cal·K^{-1}·mol^{-1}$), and Ta[2], 2.68 $cal·K^{-1}·mol^{-1}$). This is in contrast to a value of $\Delta_{fus}S° = 1.9\ cal·K^{-1}·mol^{-1}$ used by Hultgren *et al.*[1]

The melting temperature is adopted as $T_{fus} = 2130$ K as was chosen by Hultgren *et al.*[1] Values reported in the literature are:

Source	Year	T, K
[3]	1949	2133
[4]	1951	2118 ± 10
[5]	1952	2176 ± 10
[6]	1959	2122

Vaporization Data

The value for T_{vap} calculated as the temperature for which the Gibbs energy for the reaction Cr(l) = Cr(g) is zero. The difference in the enthalpy of formation of Cr(l) and Cr(g) at T_{vap} is $\Delta_{vap}H°$.

References

[1] R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Cr table, (October 1966).
[2] JANAF Thermochemical Tables: V(cr), 6–30–73; Nb(cr) and Ta(cr), 12–31–72.
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[5] D. S. Bloom, J. W. Putman, and N. J. Grant, J. Metals **4**, 626 (1952).
[6] C. W. Haworth and W. Hume–Rothery, J. Inst. Metals **87**, 265 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	23.434	36.205	36.205	0.	26.068	22.316	−3.910
300	23.472	36.350	36.205	0.043	26.068	22.292	−3.881
350	24.393	40.036	36.495	1.240	26.067	21.663	−3.233
400	25.230	43.349	37.148	2.481	26.067	21.034	−2.747
450	25.983	46.365	38.007	3.761	26.067	20.405	−2.369
500	26.631	49.137	38.983	5.077	26.067	19.775	−2.066
600	27.722	54.092	41.098	7.797	26.068	18.517	−1.612
700	28.577	58.430	43.271	10.611	26.068	17.259	−1.288
800	29.434	62.299	45.412	13.510	26.068	16.000	−1.045
900	30.501	65.825	47.487	16.505	26.068	14.742	−0.856
1000	31.861	69.107	49.486	19.621	26.068	13.483	−0.704
1100	33.472	72.218	51.412	22.886	26.068	12.225	−0.581
1200	35.187	75.203	53.271	26.318	26.068	10.967	−0.477
1300	37.116	78.095	55.070	29.932	26.068	9.708	−0.390
1350.000	38.112	79.514	55.949	31.813	GLASS <--> LIQUID		
1350.000	39.330	79.514	55.949	31.813	TRANSITION		
1400	39.330	80.944	56.816	33.779	26.103	8.449	−0.315
1500	39.330	83.658	58.516	37.712	26.020	7.190	−0.250
1600	39.330	86.196	60.168	41.645	25.727	5.943	−0.194
1700	39.330	88.581	61.770	45.578	25.219	4.720	−0.145
1800	39.330	90.829	63.322	49.511	24.492	3.535	−0.103
1900	39.330	92.955	64.827	53.444	23.542	2.395	−0.066
2000	39.330	94.972	66.284	57.377	22.368	1.311	−0.034
2100	39.330	96.891	67.696	61.310	20.967	0.292	−0.007
2130.000	39.330	97.449	68.111	62.490	--- CRYSTAL <--> LIQUID ---		
2200	39.330	98.721	69.065	65.243	0.	0.	0.
2300	39.330	100.469	70.393	69.176	0.	0.	0.
2400	39.330	102.143	71.681	73.109	0.	0.	0.
2500	39.330	103.749	72.932	77.042	0.	0.	0.
2600	39.330	105.291	74.147	80.975	0.	0.	0.
2700	39.330	106.775	75.328	84.908	0.	0.	0.
2800	39.330	108.206	76.477	88.841	0.	0.	0.
2900	39.330	109.586	77.595	92.774	0.	0.	0.
2952.078	39.330	110.286	78.165	94.822	----- FUGACITY = 1 bar -----		
3000	39.330	110.919	78.684	96.707	−339.122	5.508	−0.096
3100	39.330	112.209	79.744	100.640	−338.294	16.982	−0.286
3200	39.330	113.457	80.779	104.572	−337.516	28.430	−0.464
3300	39.330	114.668	81.787	108.505	−336.786	39.855	−0.631
3400	39.330	115.842	82.772	112.438	−336.104	51.258	−0.787
3500	39.330	116.982	83.733	116.371	−335.469	62.641	−0.935

PREVIOUS: CURRENT: June 1973

0	to 2130	K	crystal
above	2130	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.057	0.	0.	0.
100	9.963	4.286	41.746	−3.746	0.	0.	0.
200	19.860	14.869	25.680	−2.162	0.	0.	0.
250	22.298	19.590	23.998	−1.102	0.	0.	0.
298.15	23.434	23.618	23.618	0.	0.	0.	0.
300	23.472	23.764	23.619	0.043	0.	0.	0.
311.500	23.681	24.651	23.641	0.315	____ C_p LAMBDA MAXIMUM ____		
311.500	23.681	24.654	23.641	0.316	TRANSITION		
350	24.393	27.453	23.908	1.240	0.	0.	0.
400	25.230	30.765	24.562	2.481	0.	0.	0.
450	25.983	33.781	25.421	3.762	0.	0.	0.
500	26.631	36.553	26.398	5.078	0.	0.	0.
600	27.719	41.508	28.513	7.797	0.	0.	0.
700	28.577	45.846	30.686	10.612	0.	0.	0.
800	29.434	49.715	32.827	13.511	0.	0.	0.
900	30.501	53.241	34.902	16.505	0.	0.	0.
1000	31.861	56.523	36.901	19.621	0.	0.	0.
1100	33.472	59.634	38.828	22.887	0.	0.	0.
1200	35.187	62.618	40.687	26.318	0.	0.	0.
1300	37.116	65.511	42.485	29.933	0.	0.	0.
1400	39.125	68.334	44.231	33.744	0.	0.	0.
1500	41.200	71.104	45.931	37.760	0.	0.	0.
1600	43.329	73.831	47.589	41.986	0.	0.	0.
1700	45.501	76.523	49.212	46.427	0.	0.	0.
1800	47.706	79.186	50.804	51.087	0.	0.	0.
1900	49.944	81.825	52.367	55.970	0.	0.	0.
2000	52.204	84.444	53.905	61.077	0.	0.	0.
2100	54.488	87.046	55.422	66.411	0.	0.	0.
2130.000	55.174	87.824	55.873	68.056	____ CRYSTAL <--> LIQUID ____		
2130.000	39.330	97.449	55.873	88.558	TRANSITION		
2200	39.330	98.721	57.216	91.311	0.	0.	0.
2300	39.330	100.469	59.059	95.244	0.	0.	0.
2400	39.330	102.143	60.819	99.177	0.	0.	0.
2500	39.330	103.749	62.505	103.110	0.	0.	0.
2600	39.330	105.291	64.121	107.043	0.	0.	0.
2700	39.330	106.775	65.673	110.976	0.	0.	0.
2800	39.330	108.206	67.167	114.909	0.	0.	0.
2900	39.330	109.586	68.606	118.842	0.	0.	0.
2952.078	39.330	110.286	69.335	120.890	----- FUGACITY = 1 bar -----		
3000	39.330	110.919	69.994	122.775	−339.122	5.508	−0.096
3100	39.330	112.209	71.335	126.708	−338.294	16.982	−0.286
3200	39.330	113.457	72.632	130.641	−337.516	28.430	−0.464
3300	39.330	114.668	73.888	134.574	−336.786	39.855	−0.631
3400	39.330	115.842	75.105	138.507	−336.104	51.258	−0.787
3500	39.330	116.982	76.285	142.440	−335.469	62.641	−0.935

PREVIOUS: CURRENT: June 1973

IP(Cr, g) = 54570 ± 10 cm^{-1}
$S°(298.15\ K)$ = 174.31 ± 0.4 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 395.34 ± 4.2 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 397.48 ± 4.2 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^7S_3$	0.00	7
$^5S_2$	7593.16	5
$^5D_0$	7750.78	1
$^5D_1$	7810.82	3
$^5D_2$	7927.47	5
$^5D_3$	8095.21	7
$^5D_4$	8307.57	9

Enthalpy of Formation

The many vapor pressure studies are treated by a 2nd and 3rd law analysis and are tabulated below. In all cases the reaction of interest is Cr(cr) → Cr(g).

Source	Data Points	T/K	Method	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
[1]	15*	1283–1562	Langmuir	94.05 ± 0.84	94.82	0.54 ± 0.60
[2]	9	1162–1282	Knudsen	98.51 ± 2.16	95.28	−2.64 ± 1.77
[3]	10	1292–1509	Langmuir	97.60 ± 1.60	92.32	−3.71 ± 1.12
	10**	1187–1550		95.15 ± 1.00	91.82	−2.47 ± 0.74
[4]	9	1381–1505	Knudsen	101.14 ± 2.87	94.90	−4.29 ± 1.97
[5]	eqn	1502–1576	Knudsen	88.08	90.06	1.28
[6]	15	1317–1558	Knudsen	93.14 ± 5.70	93.99	0.59 ± 3.95
[7]	eqn	1441–1672	Knudsen	92.50	94.79	1.48
[8]	9	1273–1373	Knudsen	97.54 ± 2.93	95.97	−1.19 ± 2.23
[9]	eqn	1376–1592	Torsion–effusion	91.79	93.85	1.40
[10]	15**	1559–1805	Knudsen	92.78 ± 3.08	95.50	1.62 ± 1.84

* Two points neglected due to failure of a statistical test.
** One point neglected due to failure of a statistical test.

Early studies by Greenwood[11] and Baur and Brunner[12] are not considered as their work leads to $\Delta_f H°(298.15\ K)$ which are 10–15 kcal·mol^{-1} too low when compared to the results listed above.

We adopt $\Delta_f H°(298.15\ K)$ = 95.0 ± 1.0 kcal·mol^{-1} for Cr(g). This value is representative of the more recent 2nd law values tabulated above.[7-10]

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore;[13] although only the lowest levels are listed above. There are predicted levels which have not been observed and/or classified. It is anticipated that these levels will not significantly alter the entropy below 3000 K. The heat capacity and entropy values are very similar to those adopted bvy Hultgren *et al.*[14]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−6.197	395.340	395.340	INFINITE
100	20.786	151.604	192.791	−4.119	397.107	382.375	−199.732
200	20.786	166.012	176.212	−2.040	397.602	367.374	−95.948
250	20.786	170.650	174.653	−1.001	397.581	359.816	−75.179
298.15	20.786	174.311	174.311	0.	397.480	352.551	−61.765
300	20.786	174.440	174.312	0.038	397.475	352.272	−61.336
350	20.786	177.644	174.565	1.078	397.317	344.750	−51.451
400	20.786	180.419	175.127	2.117	397.116	337.254	−44.041
450	20.786	182.868	175.854	3.156	396.874	329.785	−38.280
500	20.786	185.058	176.666	4.196	396.598	322.346	−33.675
600	20.786	188.847	178.390	6.274	395.957	307.554	−26.775
700	20.787	192.052	180.119	8.353	395.221	292.877	−21.855
800	20.790	194.828	181.788	10.432	394.401	278.311	−18.172
900	20.803	197.277	183.375	12.511	393.486	263.854	−15.314
1000	20.835	199.470	184.877	14.593	392.452	249.504	−13.033
1100	20.901	201.459	186.296	16.679	391.272	235.265	−11.172
1200	21.015	203.282	187.636	18.775	389.937	221.140	−9.626
1300	21.191	204.970	188.905	20.884	388.432	207.134	−8.323
1400	21.440	206.549	190.110	23.015	386.751	193.250	−7.210
1500	21.768	208.039	191.256	25.175	384.895	179.492	−6.250
1600	22.173	209.457	192.350	27.372	382.865	165.864	−5.415
1700	22.653	210.815	193.396	29.612	380.665	152.368	−4.682
1800	23.198	212.125	194.400	31.904	378.297	139.006	−4.034
1900	23.798	213.395	195.367	34.254	375.764	125.780	−3.458
2000	24.439	214.632	196.299	36.665	373.068	112.692	−2.943
2100	25.109	215.840	197.201	39.142	370.211	99.743	−2.481
2200	25.794	217.024	198.075	41.688	347.856	87.589	−2.080
2300	26.483	218.186	198.925	44.301	346.537	75.788	−1.721
2400	27.165	219.328	199.751	46.984	345.287	64.044	−1.394
2500	27.831	220.450	200.557	49.734	344.104	52.350	−1.094
2600	28.476	221.554	201.343	52.549	342.986	40.702	−0.818
2700	29.095	222.641	202.112	55.428	341.932	29.096	−0.563
2800	29.687	223.710	202.864	58.367	340.939	17.528	−0.327
2900	30.250	224.761	203.601	61.364	340.003	5.994	−0.108
2952.078	30.533	225.302	203.979	62.947	----- FUGACITY = 1 bar -----		
3000	30.788	225.796	204.324	64.417	0.	0.	0.
3100	31.302	226.814	205.033	67.521	0.	0.	0.
3200	31.796	227.815	205.729	70.676	0.	0.	0.
3300	32.275	228.801	206.413	73.880	0.	0.	0.
3400	32.745	229.772	207.086	77.131	0.	0.	0.
3500	33.212	230.728	207.748	80.429	0.	0.	0.
3600	33.680	231.670	208.399	83.773	0.	0.	0.
3700	34.156	232.599	209.041	87.165	0.	0.	0.
3800	34.646	233.516	209.673	90.605	0.	0.	0.
3900	35.157	234.423	210.296	94.095	0.	0.	0.
4000	35.692	235.320	210.910	97.637	0.	0.	0.
4100	36.260	236.208	211.517	101.235	0.	0.	0.
4200	36.864	237.089	212.115	104.890	0.	0.	0.
4300	37.511	237.964	212.706	108.609	0.	0.	0.
4400	38.205	238.834	213.290	112.394	0.	0.	0.
4500	38.954	239.701	213.867	116.252	0.	0.	0.
4600	39.760	240.566	214.438	120.187	0.	0.	0.
4700	40.632	241.430	215.003	124.206	0.	0.	0.
4800	41.572	242.295	215.563	128.315	0.	0.	0.
4900	42.587	243.163	216.117	132.523	0.	0.	0.
5000	43.681	244.034	216.667	136.835	0.	0.	0.
5100	43.917	244.834	217.207	140.898	0.	0.	0.
5200	44.964	245.697	217.746	145.342	0.	0.	0.
5300	46.064	246.564	218.282	149.892	0.	0.	0.
5400	47.221	247.435	218.814	154.556	0.	0.	0.
5500	48.432	248.313	219.342	159.338	0.	0.	0.
5600	49.697	249.197	219.867	164.244	0.	0.	0.
5700	51.009	250.087	220.390	169.277	0.	0.	0.
5800	52.370	250.986	220.909	174.445	0.	0.	0.
5900	53.779	251.893	221.427	179.752	0.	0.	0.
6000	55.230	252.809	221.942	185.202	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

IP(Cr^+, g) = 133060 ± 10 cm^{-1}
$S°$(298.15 K) = 173.029 ± 0.05 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1048.14 ± 1.5 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1056.480] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0.00	6
$^6D_{1/2}$	1196.00	2
.	.	.
.	.	.
.	.	.
$^4G_{11/2}$	105421.9	12
IP	133060	

Enthalpy of Formation

$\Delta_f H°(Cr^+, g, 0 K)$ is calculated from $\Delta_f H°(Cr, g, 0 K)$[1] using the spectroscopic value of IP(Cr) = 54570 ± 10 cm^{-1} (652.80 ± 0.12 $kJ·mol^{-1}$) from Sugar and Corliss.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Cr^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Cr, g, 0 K)$ by using IP(Cr) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Cr(g), Cr^+(g), and e^-(ref). $\Delta_f H°(Cr \rightarrow Cr^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for Cr^+(g), all levels listed by Sugar and Corliss,[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Cr^+(g), the tehrmodynamic functions are independent of the estimated missing levels (for n = 4), the cut–off procedure, and the inclusion of n = 6 levels up to 6000 K; the Gibbs energy function showing variations of 0.02% at this temperature. The reported uncertainty is $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>6), and use of different fill and cut–off procedures.[6]

References

[1]JANAF Thermochemical Tables: Cr(g), 3–31–84; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1048.142		
100	20.786	150.322	191.510	−4.119			
200	20.786	164.730	174.931	−2.040			
250	20.786	169.368	173.372	−1.001			
298.15	20.786	173.029	173.029	0.	1056.480	1005.678	−176.191
300	20.786	173.158	173.030	0.038	1056.513	1005.363	−175.049
350	20.786	176.362	173.283	1.078	1057.395	996.767	−148.759
400	20.786	179.138	173.845	2.117	1058.232	988.049	−129.026
450	20.786	181.586	174.572	3.156	1059.030	979.227	−113.666
500	20.786	183.776	175.385	4.196	1059.793	970.319	−101.369
600	20.786	187.566	177.109	6.274	1061.231	952.288	−82.904
700	20.786	190.770	178.837	8.353	1062.573	934.023	−69.698
800	20.786	193.545	180.506	10.431	1063.832	915.572	−59.781
900	20.786	195.994	182.094	12.510	1064.995	896.968	−52.059
1000	20.786	198.184	183.595	14.589	1066.036	878.242	−45.875
1100	20.787	200.165	185.013	16.667	1066.927	859.418	−40.810
1200	20.790	201.974	186.352	18.746	1067.654	840.520	−36.587
1300	20.796	203.638	187.618	20.825	1068.197	821.569	−33.011
1400	20.808	205.180	188.818	22.906	1068.544	802.583	−29.945
1500	20.831	206.616	189.958	24.987	1068.689	783.580	−27.287
1600	20.868	207.961	191.041	27.072	1068.626	764.573	−24.961
1700	20.926	209.228	192.074	29.162	1068.353	745.577	−22.909
1800	21.008	210.426	193.061	31.258	1067.868	726.603	−21.085
1900	21.121	211.565	194.005	33.364	1067.170	707.662	−19.455
2000	21.269	212.652	194.910	35.484	1066.261	688.763	−17.989
2100	21.457	213.694	195.780	37.620	1065.141	669.915	−16.663
2200	21.686	214.698	196.617	39.776	1044.477	651.780	−15.475
2300	21.961	215.667	197.425	41.958	1044.805	633.923	−14.397
2400	22.283	216.609	198.204	44.170	1045.162	616.051	−13.408
2500	22.652	217.526	198.959	46.417	1045.554	598.164	−12.498
2600	23.069	218.422	199.690	48.702	1045.985	580.260	−11.658
2700	23.533	219.301	200.400	51.032	1046.461	562.338	−10.879
2800	24.044	220.166	201.091	53.410	1046.985	544.398	−10.156
2900	24.600	221.019	201.764	55.842	1047.562	526.439	−9.482
3000	25.199	221.863	202.419	58.332	709.076	513.967	−8.949
3100	25.839	222.700	203.060	60.883	710.601	507.438	−8.550
3200	26.517	223.531	203.687	63.501	712.142	500.860	−8.176
3300	27.230	224.358	204.301	66.188	713.704	494.233	−7.823
3400	27.975	225.182	204.903	68.948	715.292	487.559	−7.490
3500	28.750	226.004	205.494	71.784	716.908	480.837	−7.176
3600	29.550	226.825	206.075	74.699	718.557	474.069	−6.879
3700	30.374	227.646	206.647	77.695	720.240	467.255	−6.596
3800	31.218	228.467	207.210	80.774	721.958	460.394	−6.329
3900	32.078	229.289	207.766	83.939	723.712	453.488	−6.074
4000	32.952	230.112	208.314	87.190	725.499	446.537	−5.831
4100	33.838	230.936	208.856	90.530	727.320	439.540	−5.600
4200	34.733	231.763	209.392	93.958	729.171	432.499	−5.379
4300	35.635	232.590	209.921	97.477	731.050	425.413	−5.168
4400	36.542	233.420	210.446	101.085	732.952	418.283	−4.966
4500	37.452	234.251	210.966	104.785	734.873	411.110	−4.772
4600	38.366	235.085	211.481	108.576	736.807	403.894	−4.586
4700	39.282	235.920	211.992	112.458	738.749	396.636	−4.408
4800	40.199	236.756	212.499	116.432	740.692	389.336	−4.237
4900	41.118	237.594	213.003	120.498	742.629	381.996	−4.072
5000	42.040	238.434	213.503	124.656	744.553	374.617	−3.914
5100	42.964	239.276	214.000	128.906	746.819	367.172	−3.761
5200	43.893	240.119	214.494	133.249	748.797	359.709	−3.613
5300	44.827	240.964	214.986	137.685	750.761	352.208	−3.471
5400	45.767	241.811	215.475	142.215	752.705	344.669	−3.334
5500	46.716	242.659	215.961	146.839	754.626	337.095	−3.201
5600	47.675	243.510	216.446	151.558	756.518	329.487	−3.073
5700	48.645	244.362	216.928	156.374	758.379	321.845	−2.949
5800	49.629	245.217	217.408	161.288	760.204	314.170	−2.829
5900	50.627	246.073	217.887	166.300	761.988	306.464	−2.713
6000	51.640	246.933	218.364	171.414	763.730	298.729	−2.601

PREVIOUS: CURRENT: March 1984 (1 bar)

EA(Cr, g) = 0.666 ± 0.012 eV
$S°$(298.15 K) = 173.030 ± 0.003 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 331.081 ± 2 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [327.024] kJ·mol^{-1}

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0.0	6

Enthalpy of Formation

$\Delta_f H°(Cr^-, g, 0 K)$ is calculated from $\Delta_f H°(Cr, g, 0 K)$[1] using the adopted electron affinity of EA(Cr) = 0.666 ± 0.012 eV (64.259 ± 1.158 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Cr^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Cr^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Cr, g, 0 K)$ by using EA(Cr) with JANAF [1] enthalpies, $H°(0 K)-H°(298.15 K)$, or Cr^-(g), Cr(g), and e^-(ref). $\Delta_r H°(Cr^- \rightarrow Cr + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15 K)$ should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity of Entropy

The ground state electronic configuration for Cr^-(g) is given by Hotop and Lineberger[2, 4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	331.081		
100	20.786	150.322	191.510	−4.119			
200	20.786	164.730	174.931	−2.040			
250	20.786	169.368	173.372	−1.001			
298.15	20.786	173.030	173.030	0.	327.024	288.732	−50.585
300	20.786	173.158	173.030	0.038	326.981	288.494	−50.231
350	20.786	176.362	173.283	1.078	325.783	282.174	−42.112
400	20.786	179.138	173.845	2.117	324.543	276.028	−36.046
450	20.786	181.586	174.572	3.156	323.262	270.041	−31.345
500	20.786	183.776	175.385	4.196	321.946	264.197	−27.601
600	20.786	187.566	177.109	6.274	319.227	252.901	−22.017
700	20.786	190.770	178.837	8.353	316.412	242.068	−18.063
800	20.786	193.546	180.506	10.431	313.513	231.644	−15.125
900	20.786	195.994	182.094	12.510	310.519	221.590	−12.861
1000	20.786	198.184	183.595	14.589	307.403	211.874	−11.067
1100	20.786	200.165	185.013	16.667	304.137	202.478	−9.615
1200	20.786	201.974	186.352	18.746	300.706	193.387	−8.418
1300	20.786	203.637	187.619	20.824	297.091	184.589	−7.417
1400	20.786	205.178	188.819	22.903	293.280	176.076	−6.569
1500	20.786	206.612	189.958	24.982	289.264	167.844	−5.845
1600	20.786	207.953	191.041	27.060	285.038	159.886	−5.220
1700	20.786	209.214	192.073	29.139	280.597	152.198	−4.676
1800	20.786	210.402	193.059	31.217	275.937	144.779	−4.201
1900	20.786	211.526	194.001	33.296	271.054	137.625	−3.784
2000	20.786	212.592	194.904	35.375	265.947	130.733	−3.414
2100	20.786	213.606	195.771	37.453	260.612	124.103	−3.087
2200	20.786	214.573	196.604	39.532	235.713	118.387	−2.811
2300	20.786	215.497	197.405	41.610	231.780	113.142	−2.570
2400	20.786	216.381	198.178	43.689	227.847	108.068	−2.352
2500	20.786	217.230	198.923	45.768	223.914	103.158	−2.155
2600	20.786	218.045	199.643	47.846	219.981	98.405	−1.977
2700	20.786	218.830	200.339	49.925	216.048	93.804	−1.815
2800	20.786	219.586	201.013	52.004	212.115	89.348	−1.667
2900	20.786	220.315	201.666	54.082	208.182	85.033	−1.532
3000	20.786	221.020	202.299	56.161	−134.873	86.362	−1.504
3100	20.786	221.701	202.914	58.239	−137.977	93.788	−1.580
3200	20.786	222.361	203.512	60.318	−141.132	101.314	−1.654
3300	20.786	223.001	204.093	62.397	−144.336	108.940	−1.724
3400	20.786	223.621	204.658	64.475	−147.587	116.664	−1.792
3500	20.786	224.224	205.209	66.554	−150.885	124.484	−1.858
3600	20.786	224.809	205.745	68.632	−154.229	132.399	−1.921
3700	20.786	225.379	206.268	70.711	−157.621	140.407	−1.982
3800	20.786	225.933	206.778	72.790	−161.061	148.508	−2.041
3900	20.786	226.473	207.276	74.868	−164.551	156.700	−2.099
4000	20.786	226.999	207.763	76.947	−168.093	164.982	−2.154
4100	20.786	227.513	208.238	79.025	−171.691	173.353	−2.209
4200	20.786	228.014	208.703	81.104	−175.347	181.813	−2.261
4300	20.786	228.503	209.158	83.183	−179.065	190.361	−2.312
4400	20.786	228.981	209.603	85.261	−182.850	198.996	−2.362
4500	20.786	229.448	210.039	87.340	−186.708	207.717	−2.411
4600	20.786	229.905	210.466	89.418	−190.643	216.526	−2.459
4700	20.786	230.352	210.884	91.497	−194.662	225.420	−2.505
4800	20.786	230.789	211.294	93.576	−198.771	234.401	−2.551
4900	20.786	231.218	211.697	95.654	−202.979	243.469	−2.595
5000	20.786	231.638	212.091	97.733	−207.291	252.624	−2.639
5100	20.786	232.049	212.479	99.811	−211.354	261.839	−2.682
5200	20.786	232.453	212.859	101.890	−215.798	271.160	−2.724
5300	20.786	232.849	213.232	103.969	−220.348	280.568	−2.765
5400	20.786	233.237	213.599	106.047	−225.012	290.063	−2.806
5500	20.786	233.619	213.960	108.126	−229.794	299.645	−2.846
5600	20.786	233.993	214.314	110.204	−234.700	309.315	−2.885
5700	20.786	234.361	214.663	112.283	−239.733	319.074	−2.924
5800	20.786	234.723	215.005	114.362	−244.901	328.923	−2.962
5900	20.786	235.078	215.343	116.440	−250.208	338.862	−3.000
6000	20.786	235.428	215.674	118.519	−255.658	348.891	−3.037

PREVIOUS: CURRENT: March 1984 (1 bar)

$S°(298.15\ K) = 37.71 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -116.46 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -117.15 \pm 8.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

2nd and 3rd law analyses of equilibrium nitrogen pressures for the reaction $Cr_2N(cr) + 0.5\ N_2(g) = 2\ CrN(cr)$ cited in a recent review[1] of the thermodynamic properties of the Cr–N system are made using revised thermal functions for Cr_2N [2] and CrN (refer below). We have not taken into account, in our analysis, any variations in the compositions of the two nitrides (see Phase Data Section). Results of our analysis are tabulated below.

Source	Data Points	T/K	$\Delta_f H°$, kcal mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$[a] kcal·mol^{-1}
Valensi[3]	8	1083–1288	−25.9	24.88 ± 0.37	0.8 ± 1.0	−27.4 ± 1.7
Sano[4]	6	1104–1223	−28.5	26.58 ± 0.16	1.7 ± 0.3	−28.3 ± 1.1
Smith[5]	10[b]	1178–1351	−13.0	25.0 ± 1.2	−9.5	−27.5 ± 1.6
Mills[6]	Equation	1173–1323	−25.1	25.26 ± 0.02	−0.2	−27.6 ± 1.0

[a]Third law values; auxiliary data used $\Delta_f H°(Cr_2N, cr, 298.15\ K) = -30.0 \pm 3.0\ kcal \cdot mol^{-1}$.
[b]Data taken from reference[1]; one point rejected due to failure of a statistical test.

The equilibrium pressures of Sano[4] are inconsistent with those of the other investigations, and no weight is given to these results. Reasons for these discrepancies have been presented by DeLuca and Leitnaker.[1] The drifts are both positive and negative which provides support for our revised thermal functions for the two nitrides. Neumann *et al.*[7] measured $\Delta_f H°$ directly by combination of the elements in a bomb calorimeter. Two samples of chromium (99.2–99.7% purity) were heated to temperatures near 1200 K in 25 atmospheres of nitrogen. Under these conditions,[8] it is unlikely that significant amounts of subnitride (Cr_2N) were formed. Neumann *et al.*[7] recommended the value $\Delta_f H°(CrN, cr, 298.15\ K) = -29.5 \pm 0.5\ kcal \cdot mol^{-1}$.

We adopt $\Delta_f H°(CrN, cr, 298.15\ K)$ value of $-28.0 \pm 2.0\ kcal \cdot mol^{-1}$ ($-117.152 \pm 8.4\ kJ \cdot mol^{-1}$) which is based mainly on the results from two equilibrium studies[3,6] and to a lesser extent on the value determined by bomb calorimetry. Our adopted value agrees with that (-28.4 ± 1.5) selected by DeLuca and Leitnaker[1] but is 1.8 kcal·mol^{-1} less negative than the NBS[9] value (−29.8).

Heat Capacity and Entropy

One low temperature heat capacity study[10] has been reported for CrN which covered the temperature range 73–315 K. $C_p°$ values taken from the graph at 25° temperature intervals are used to obtain a value for $S°(298.15\ K)$ by integration. This method leads to $S°(298.15\ K) = 9.0\ cal \cdot K^{-1} \cdot mol^{-1}$ ($37.656\ J \cdot K^{-1} \cdot mol^{-1}$) with $S°(73\ K) = 0.39\ cal \cdot K^{-1} \cdot mol^{-1}$. The latter value is obtained from the Debye function D(530/T). The uncertainty in our value for $S°(298.15\ K)$ is believed to be less than $\pm 0.5\ cal \cdot K^{-1} \cdot mol^{-1}$. Previously published estimates of $S°(298.15\ K)$ are 8.56[1] and 7.85.[11] The low temperature data set[10] contains a lambda peak at 281.7 K with $C_p°$ near the maximum equal to $75.1\ cal \cdot K^{-1} \cdot mol^{-1}$. Other transition temperatures have been reported as 286 K[12] and 287 K.[13] The anomaly arises from an antiferromagnetic–paramagnetic transformation[12, 13] which is accompanied by an orthorhombic to cubic structural change.[14]

Satoh[15] has measured the heat contents of three chromium nitride samples at three temperatures each (372.6, 598.8, and 784.2 K), in an ice calorimeter. DeLuca and Leitnaker[1] have reevaluated his heat contents and presented $C_p°$ data for CrN in the temperature range 298–1400 K. Their values above 400 K are adopted and joined smoothly with the low temperature $C_p°$ data[10] near 350 K. $C_p°$ data above 1400 K are obtained by graphical extrapolation.

Phase Data

The homogeneity range of the CrN phase is not known; however, results of two recent studies[6, 12] indicate that it is probably much smaller than that for Cr_2N.[2] X-ray diffraction patterns[16, 17] for CrN have been interpreted in terms of a cubic structure (NaCl type). Other information on the chromium–chromium nitride system has been reviewed by Storms.[8]

Decomposition Data

No information is available on the melting point of CrN. Upon heating we assume that the compound decomposes to its elements rather than melting. T_{dcm} is the temperature at which $\Delta_r G°$ for the process $CrN(cr) = Cr(cr) + 0.5\ N_2(g)$ equals zero.

References

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Continued on page 975

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−7.705	−116.465	−116.465	INFINITE
100	9.985	3.850	78.059	−7.421	−117.943	−109.909	57.410
200	29.126	16.556	43.947	−5.478	−119.039	−101.378	26.477
298.15	52.677	37.711	37.711	0.	−117.152	−92.790	16.256
300	51.393	38.033	37.712	0.096	−117.126	−92.639	16.130
400	49.078	51.780	39.599	4.873	−116.350	−84.587	11.046
500	49.748	62.804	43.176	9.814	−115.475	−76.749	8.018
600	50.417	71.933	47.229	14.822	−114.678	−69.080	6.014
700	51.087	79.756	51.330	19.898	−113.938	−61.539	4.592
800	51.714	86.618	55.321	25.037	−113.252	−54.101	3.532
900	52.384	92.748	59.145	30.242	−112.630	−46.745	2.713
1000	53.053	98.301	62.787	35.514	−112.094	−39.455	2.061
1100	53.723	103.389	66.250	40.853	−111.670	−32.212	1.530
1200	54.392	108.093	69.544	46.259	−111.369	−25.003	1.088
1300	55.020	112.471	72.679	51.729	−111.211	−17.813	0.716
1400	55.689	116.573	75.669	57.264	−111.204	−10.630	0.397
1500	56.379	120.439	78.526	62.868	−111.350	−3.442	0.120
1600	57.028	124.098	81.261	68.538	−111.655	3.761	−0.123
1700	57.697	127.575	83.884	74.275	−112.123	10.988	−0.338
1800	58.367	130.892	86.404	80.078	−112.755	18.247	−0.530
1900	59.078	134.066	88.830	85.949	−113.550	25.546	−0.702
2000	59.831	137.117	91.168	91.897	−114.504	32.891	−0.859
2100	60.375	140.049	93.427	97.906	−115.632	40.287	−1.002
2200	61.003	142.872	95.610	103.974	−136.273	48.397	−1.149
2300	61.714	145.599	97.725	110.110	−135.887	56.783	−1.290
2400	62.467	148.242	99.775	116.320	−135.433	65.150	−1.418
2500	63.074	150.805	101.765	122.598	−134.915	73.497	−1.536

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 230.553 \pm 8.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 504.62 \pm 20.9\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 505.01 \pm 20.9\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4\Sigma$	0	[4]
	[15000]	[8]
	[20000]	[4]

ω_e = [1000] cm^{-1} $\omega_e x_e$ = [5.0] cm^{-1} σ = 1
B_e = [0.56115] cm^{-1} α_e = [0.00375] cm^{-1} r_e = [1.65] Å

Enthalpy of Formation

Srivastava and Farber[1] have observed mass spectrometrically CrN(g) as one of the vapor species in equilibrium with the Cr–V–N system. A substitution reaction between VN and Cr was employed in the formation of gaseous mononitride in the temperature range 1900 to 2063 K. Ion intensities for the equilibrium species CrN, VN, V, and N_2 were measured and converted to partial pressures by means of an intensity–pressure relationship for Au(g). Results of a 2nd and 3rd law analysis of their pressure data[1] are given below.

Reaction	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd Law	3rd Law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K)[a], kcal·mol^{-1} 2nd Law	3rd Law
A	7	1903–2063	−35.6	−27.18 ± 0.75	4.3 ± 2.3	130.6	122.2
B	7	1903–2063	21.3	22.42 ± 0.33	0.6 ± 1.3	118.1	119.2

Reactions: (A) CrN(g) = Cr(g) + 0.5 N_2(g) (B) VN(g) + Cr(g) = CrN(g) + V(g)
[a]Auxiliary $\Delta_f H°$ data[2] used (in kcal·mol^{-1}): Cr(g), 95.0 ± 1.0; VN(g), 125 ± 5; V(g), 123.2 ± 2.0.

We note that several of the log K_p values listed by Srivastava and Farber[1] for the two gas phase reactions are inconsistent with their reported partial pressure data. Since the 3rd law method is relatively insensitive to errors in the equilibrium constant, we believe the two 3rd law $\Delta_f H°$ values are more reliable than those obtained by the 2nd law. Thus, we adopt the average 3rd law value of $\Delta_f H°$(CrN, g, 298.15 K) = 120.7 ± 5.0 kcal·mol^{-1} (505.009 ± 20.9 kJ·mol^{-1}). Taking into account estimated errors in the pressure determinations and thermal functions, an overall uncertainty of ±5 kcal·mol^{-1} is assigned. The adopted $\Delta_f H°$ value corresponds to a dissociation energy of $\Delta_{at} H°$(CrN, g, 298.15 K) = 87.3 kcal·mol^{-1}.

Although no other experimental value for $\Delta_{at} H°$ is available, two estimations have been reported. Gingerich,[4] using empirical correlations of Colin and Goldfinger[3] and Pauling,[6] predicted a value of $\Delta_{at} H°$(CrN, g, 298.15 K) = 96 kcal·mol^{-1} for CrN(g) by both methods. This predicted value is in reasonable agreement with that determined experimentally by Srivastava and Farber[1] and reaffirms the usefulness of three empirical correlations[3–5] in predicting dissociation energies for gaseous diatomic mononitrides.

Heat Capacity and Entropy

The value of r_e(CrN) is obtained from the expression r_e(MO)–r_e(MN) = −0.023 Å with r_e(CrO) = 1.627 Å.[2] Differences in the bond lengths[7] for the oxides and nitrides of As, B, P, Si, and Ti are used to establish the value of −0.023. B_e is calculated from the estimated value for r_e. The moment of inertia is calculated to be 4.9881×10^{-39} g cm^2. The value of α_e is obtained from the other constants assuming a Morse potential function. The values of ω_e and $\omega_e x_e$ are assumed to lie between those for VO[2] and AsN.[7]

CrN is isoelectronic with VO; therefore, the ground state electronic configuration is taken to be the same as that for VO[2]. Also, the electronic levels and quantum weights are estimated by analogy with those for VO.[2] Futher support for the quartet ground state of CrN is provided by the fact that the atomic levels for Cr^{+3}[8] are also quartets. Our adopted upper levels and quantum weights contribute 0.13 cal·K^{-1}·mol^{-1} to the entropy of CrN at 4000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.778	504.624	504.624	INFINITE
100	29.107	198.342	257.038	−5.870	505.769	494.354	−258.224
200	29.454	218.573	233.318	−2.949	505.651	482.908	−126.123
250	30.032	225.203	231.055	−1.463	505.349	477.256	−99.717
298.15	30.754	230.553	230.553	0.	505.009	471.876	−82.671
300	30.783	230.743	230.553	0.057	504.995	471.670	−82.125
350	31.576	235.548	230.931	1.616	504.525	466.157	−69.570
400	32.327	239.814	231.779	3.214	504.152	460.702	−60.161
450	33.000	243.661	232.889	4.847	503.772	455.293	−52.849
500	33.586	247.169	234.145	6.512	503.384	449.927	−47.004
600	34.517	253.379	236.846	9.920	502.581	439.311	−38.245
700	35.197	258.754	239.601	13.407	501.732	428.832	−32.000
800	35.698	263.488	242.297	16.953	500.824	418.479	−27.324
900	36.077	267.716	244.890	20.543	499.831	408.245	−23.694
1000	36.369	271.533	247.367	24.166	498.718	398.127	−20.796
1100	36.599	275.010	249.724	27.815	497.453	388.127	−18.431
1200	36.786	278.203	251.966	31.484	496.017	378.251	−16.465
1300	36.939	281.154	254.099	35.171	494.392	368.502	−14.807
1400	37.069	283.896	256.131	38.871	492.564	358.885	−13.390
1500	37.180	286.457	258.068	42.584	490.527	349.406	−12.167
1600	37.277	288.860	259.918	46.307	488.274	340.070	−11.102
1700	37.365	291.123	261.688	50.039	485.802	330.882	−10.167
1800	37.447	293.261	263.383	53.780	483.108	321.846	−9.340
1900	37.525	295.287	265.009	57.528	480.189	312.966	−8.604
2000	37.601	297.214	266.572	61.284	477.044	304.245	−7.946
2100	37.679	299.051	268.075	65.048	473.671	295.687	−7.355
2200	37.760	300.805	269.523	68.820	450.734	287.950	−6.837
2300	37.846	302.486	270.920	72.601	448.764	280.595	−6.373
2400	37.938	304.098	272.269	76.390	446.798	273.325	−5.949
2500	38.039	305.649	273.574	80.188	444.835	266.137	−5.561
2600	38.149	307.143	274.836	83.998	442.878	259.028	−5.204
2700	38.269	308.585	276.059	87.819	440.928	251.994	−4.875
2800	38.400	309.979	277.246	91.652	438.987	245.032	−4.571
2900	38.542	311.329	278.398	95.499	437.055	238.139	−4.289
3000	38.695	312.638	279.518	99.361	96.116	235.926	−4.108
3100	38.860	313.910	280.607	103.238	95.036	240.604	−4.054
3200	39.037	315.146	281.667	107.133	93.919	245.317	−4.004
3300	39.224	316.350	282.700	111.046	92.769	250.066	−3.958
3400	39.422	317.524	283.707	114.978	91.588	254.850	−3.915
3500	39.629	318.670	284.690	118.931	90.378	259.670	−3.875
3600	39.846	319.789	285.649	122.904	89.139	264.524	−3.838
3700	40.071	320.884	286.587	126.900	87.874	269.413	−3.803
3800	40.303	321.956	287.503	130.919	86.580	274.337	−3.771
3900	40.541	323.006	288.400	134.961	85.258	279.295	−3.741
4000	40.785	324.035	289.278	139.027	83.905	284.288	−3.712
4100	41.034	325.045	290.138	143.118	82.521	289.314	−3.686
4200	41.286	326.037	290.981	147.234	81.100	294.375	−3.661
4300	41.541	327.012	291.808	151.376	79.641	299.470	−3.638
4400	41.797	327.969	292.619	155.542	78.138	304.600	−3.616
4500	42.054	328.912	293.415	159.735	76.587	309.764	−3.596
4600	42.310	329.839	294.197	163.953	74.982	314.963	−3.577
4700	42.565	330.751	294.965	168.197	73.318	320.198	−3.559
4800	42.819	331.650	295.720	172.466	71.586	325.469	−3.542
4900	43.069	332.536	296.462	176.761	69.780	330.777	−3.526
5000	43.316	333.408	297.192	181.080	67.892	336.122	−3.511
5100	43.559	334.268	297.911	185.424	66.276	341.479	−3.497
5200	43.797	335.117	298.618	189.792	64.302	346.895	−3.485
5300	44.030	335.953	299.315	194.183	62.244	352.349	−3.473
5400	44.257	336.778	300.001	198.597	60.093	357.842	−3.461
5500	44.478	337.592	300.677	203.034	57.844	363.377	−3.451
5600	44.693	338.396	301.343	207.493	55.492	368.953	−3.441
5700	44.900	339.189	302.000	211.973	53.032	374.572	−3.433
5800	45.101	339.971	302.648	216.473	50.456	380.235	−3.424
5900	45.293	340.744	303.288	220.992	47.758	385.944	−3.417
6000	45.479	341.507	303.918	225.531	44.934	391.700	−3.410

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 239.268 \pm 6.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 187.85 \pm 41.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 188.28 \pm 41.8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X^5	0	10
B^5	16584.5	10

$\omega_e = 898.8\ cm{-}1$ $\omega_e x_e = 6.50\ cm^{-1}$ $\sigma = 1$

$B_e = 0.5286\ cm^{-1}$ $\alpha_e = 0.0050\ cm^{-1}$ $r_e = 1.627$ Å

Enthalpy of Formation

Based on the adopted ground state vibrational constants, a linear Birge–Sponer extrapolation yields a dissociation energy, of 3.796 eV (87.54 kcal·mol^{-1}). Applying a correction for the ionicity in the Cr–O bond,[1] we recalculate $D_0° = 4.017$ eV (92.63 kcal·mol^{-1}). This in turn corresponds to $\Delta_f H°(298.15\ K) = 60.95$ kcal·mol^{-1} for CrO(g), using auxiliary data.[2]

Huldt and Lagerqvist,[3] using a spectroscopic flame technique, reported $D_0° = 4.4 \pm 0.5$ eV for CrO(g). This value was later corrected to $D_0° = 5.3$ eV (122.9 kcal·mol^{-1}).[4,5] Grimley *et al.*[6] mentioned that in determining $D_0°$ values by the flame technique of Huldt and Lagerqvist,[3] the calculation assumes that Cr and CrO are the only gaseous species containing Cr and that the CrO_2(g) partial pressure cannot be neglected under these experimental conditions.

Grimley *et al.*[6] studied the vaporization of Cr_2O_3(cr) under neutral and oxidizing conditions using mass spectrometric methods. The reported partial pressure data for Cr(g), CrO(g), CrO_2(g), O(g), and O_2(g) may be analyzed in terms of many different chemical equilibria. Our analyses of four equilibria in the neutral and oxidizing conditions are tabulated below.

	Reaction	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
Neutral conditions	A*	−39.5	−44.9	-2.8 ± 2.1	55.5	50.1
1842–2062 K	B	−108.2	−100.4	4.0 ± 1.4	46.3	54.2
13 points	C	174.0	178.2	2.1 ± 1.2	38.4	42.6
	D*	206.3	205.9	-0.2 ± 1.4	40.9	40.5
Oxidizing conditions	A	−27.2	−43.7	-8.6 ± 13.1	67.8	51.3
1893–1945 K	B	−46.9	−99.3	-27.3 ± 4.0	107.6	55.2
3 points	C	192.2	181.0	-5.8 ± 4.4	56.6	45.4
	D	202.0	208.9	3.6 ± 9.0	36.6	43.5

Reaction A: Cr(g) + 1/2 O_2(g) = CrO(g) C: 1/2 Cr_2O_3(cr) = CrO(g) + 1/4 O_2(g)
B: Cr(g) + O(g) = CrO(g) D: 1/2 Cr_2O_3(cr) = CrO(g) + 1/2 O(g)
*One point rejected due to a statistical test (1842 K).

The drifts are less severe in the netural system so that there is better agreement in the 2nd and 3rd law results for the neutral conditions than in the oxidizing system. Note that the 3rd law $\Delta_f H°(298.15\ K)$ values are slightly more positive for the oxidizing than the netural conditions for corresponding equilibria. The calculated $\Delta_f H°(298.15\ K)$ values for the gas phase (reactions A and B) are about 10 kcal·mol^{-1} higher than those of the condensed phase (reactions C and D) equilibria. Grimley *et al.*[6] prefer the gas phase results while Brewer and Rosenblatt[7] prefer the condensed phase results. We adopt $\Delta_f H°$(CrO, cr, 298.15 K) = 45.0 ± 10.0 kcal·mol^{-1} (188.280 ± 41.8 kJ·mol^{-1}) as a value which is representative of the 2nd and 3rd law results in the neutral system. The adopted $\Delta_f H°$ value leads to $D° = 4.71$ eV (108.6 kcal·mol^{-1}).

Chizhikov *et al.*[8] also studied the vaporization of Cr_2O_3 via mass spectrometry in the range 1690–2020 K. They reported the detection of gaseous Cr, CrO, CrO_2, and O during the evaporation process. The reported smoothed partial pressures of CrO(g) and CrO_2(g) lie higher than those reported by Grimley *et al.*[6] by a factor of 2–5, while the partial pressures of Cr(g) are less than a factor 2 different. These data were not analyzed.

Heat Capacity and Entropy

The spectroscopic work involving CrO(g) has been reviewed and referenced by Rosen.[9] The adopted vibration and rotation constants as well as the electronic levels are those tabulated by Rosen.[9] The ground state has not been firmly established. Weltner[10] suggested a possible $^3\Sigma^-$ ground state. The free energy functions used here are 1.02 cal·K^{-1}·mol^{-1} at 298 K and 1.57 cal·K^{-1}·mol^{-1} at 3000 K lower than those suggested by Brewer and Rosenblatt.[7] The difference arises in that Brewer and Rosenblatt[7] approximated the CrO electronic levels with Cr^{++} electronic levels. The latter has a singlet ground state and many levels lying below 600 cm^{-1}.

Continued on page 975

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.828	187.851	187.851	INFINITE
100	29.111	206.841	266.039	−5.920	188.996	177.405	−92.667
200	29.697	227.123	242.076	−2.991	188.885	165.783	−43.298
250	30.467	233.829	239.778	−1.487	188.599	160.039	−33.438
298.15	31.320	239.268	239.268	0.	188.280	154.567	−27.079
300	31.353	239.461	239.268	0.058	188.267	154.357	−26.876
350	32.214	244.360	239.653	1.647	187.818	148.746	−22.199
400	32.982	248.713	240.518	3.278	187.460	143.188	−18.698
450	33.643	252.637	241.650	4.944	187.087	137.677	−15.981
500	34.201	256.211	242.930	6.640	186.697	132.207	−13.812
600	35.062	262.527	245.684	10.106	185.863	121.387	−10.568
700	35.676	267.981	248.489	13.645	184.959	110.711	−8.261
800	36.125	272.776	251.231	17.236	183.983	100.170	−6.540
900	36.463	277.051	253.867	20.866	182.916	89.756	−5.209
1000	36.725	280.907	256.381	24.526	181.729	79.467	−4.151
1100	36.934	284.417	258.773	28.209	180.392	69.305	−3.291
1200	37.106	287.638	261.046	31.911	178.889	59.271	−2.580
1300	37.250	290.614	263.207	35.629	177.201	49.370	−1.984
1400	37.373	293.379	265.265	39.361	175.314	39.606	−1.478
1500	37.481	295.962	267.226	43.103	173.220	29.984	−1.044
1600	37.576	298.384	269.098	46.856	170.914	20.509	−0.670
1700	37.663	300.664	270.889	50.618	168.388	11.185	−0.344
1800	37.742	302.819	272.603	54.389	165.641	2.016	−0.059
1900	37.816	304.862	274.248	58.167	162.667	−6.994	0.192
2000	37.887	306.803	275.828	61.952	159.463	−15.842	0.414
2100	37.955	308.654	277.347	65.744	156.028	−24.523	0.610
2200	38.021	310.421	278.811	69.543	133.023	−32.381	0.769
2300	38.087	312.112	280.222	73.348	130.980	−39.854	0.905
2400	38.153	313.735	281.585	77.160	128.933	−47.237	1.028
2500	38.220	315.294	282.902	80.979	126.881	−54.536	1.139
2600	38.289	316.794	284.177	84.804	124.825	−61.752	1.241
2700	38.361	318.240	285.412	88.637	122.766	−68.889	1.333
2800	38.435	319.637	286.609	92.476	120.704	−75.949	1.417
2900	38.512	320.987	287.772	96.324	118.640	−82.936	1.494
3000	38.593	322.294	288.901	100.179	−222.444	−85.239	1.484
3100	38.677	323.561	289.999	104.042	−223.683	−80.645	1.359
3200	38.765	324.790	291.067	107.914	−224.973	−76.011	1.241
3300	38.856	325.984	292.107	111.795	−226.311	−71.335	1.129
3400	38.952	327.146	293.120	115.686	−227.696	−66.618	1.023
3500	39.050	328.276	294.109	119.586	−229.126	−61.860	0.923
3600	39.153	329.378	295.073	123.496	−230.600	−57.060	0.828
3700	39.258	330.452	296.015	127.416	−232.118	−52.219	0.737
3800	39.367	331.500	296.935	131.348	−233.681	−47.336	0.651
3900	39.478	332.524	297.834	135.290	−235.290	−42.411	0.568
4000	39.592	333.525	298.714	139.243	−236.946	−37.444	0.489
4100	39.709	334.504	299.575	143.208	−238.653	−32.436	0.413
4200	39.827	335.462	300.418	147.185	−240.413	−27.385	0.341
4300	39.947	336.401	301.244	151.174	−242.229	−22.291	0.271
4400	40.069	337.321	302.054	155.175	−244.107	−17.155	0.204
4500	40.191	338.223	302.848	159.188	−246.050	−11.976	0.139
4600	40.315	339.107	303.626	163.213	−248.065	−6.752	0.077
4700	40.439	339.976	304.390	167.251	−250.158	−1.483	0.016
4800	40.563	340.828	305.141	171.301	−252.335	3.830	−0.042
4900	40.687	341.666	305.878	175.363	−254.603	9.191	−0.098
5000	40.812	342.489	306.602	179.438	−256.971	14.598	−0.153
5100	40.935	343.299	307.313	183.526	−259.084	20.027	−0.205
5200	41.059	344.095	308.013	187.625	−261.572	25.523	−0.256
5300	41.181	344.878	308.701	191.737	−264.162	31.070	−0.306
5400	41.302	345.649	309.378	195.861	−266.861	36.665	−0.355
5500	41.422	346.408	310.045	199.998	−269.674	42.311	−0.402
5600	41.541	347.155	310.701	204.146	−272.608	48.010	−0.448
5700	41.658	347.892	311.347	208.306	−275.665	53.762	−0.493
5800	41.773	348.617	311.983	212.477	−278.855	59.570	−0.536
5900	41.887	349.332	312.610	216.660	−282.182	65.432	−0.579
6000	41.999	350.037	313.228	220.855	−285.652	71.353	−0.621

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 269.24 \pm 12.6\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -73.78 \pm 41.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -75.31 \pm 41.8\ kJ\cdot mol^{-1}$

Vibrational Frequences and Degeneracies υ, cm^{-1}
998 (1)
[300](1)
1008 (1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group : [C_{2v}]
Bond Distance: Cr–O = [1.627] Å
Bond Angle: O–Cr–O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.326337 × 10^{-115}] $g^3\cdot cm^6$

Enthalpy of Formation

Grimley *et al.*[1] studied the vaporization of Cr_2O_3(cr) under neutral and oxidizing conditions using mass spectrometric methods. In the range 1842–2062 K (IPTS-68) this study detected quantitatively Cr(g), CrO(g), CrO_2(g), O(g), and O_2(g). Of the many chemical equilibria which could be analyzed, we tabulated below our 2nd and 3rd law analyses of the equilibrium between CrO(g) and CrO_2(g).

	$\Delta_r H°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal\cdot mol^{-1}$ $kcal\cdot mol^{-1}$
Neutral system, 13 points, 1843–2062 K				
Reaction A**	141.27	119.87	−10.9 ± 3.6	−15.31
Reaction B**	71.11	64.41	−3.4 ± 2.8	−19.41
Oxidizing system, 3 points, 1893–1945 K				
Reaction A	120.97	122.48	0.8 ± 9.2	−17.92
Reaction B	101.21		−17.9 ± 0.1	−21.82

** One point (1865 K) rejected due to a statistical test.
Reactions: (A) $CrO_2(g) = CrO(g) + O(g)$. (B) $CrO_2(g) = CrO(g) + 1/2\ O_2(g)$.

We adopt $\Delta_f H°(298.15\ K) = -18.0 \pm 10.0\ kcal\cdot mol^{-1}$ ($-75.312 \pm 41.8\ kJ\cdot mol^{-1}$). This value is intermediate to the four results tabulated above with extra weight given to those of the neutral conditions. Our analysis of equations analogous to those treated in the CrO(g) table[3] yields the same trends as with CrO(g). The results are consistent with our adopted value.

Using auxiliary data,[3] we calculate $\Delta_{at} H° = 9.98$ eV (230.1 $kcal\cdot mol^{-1}$) corresponding to $CrO_2(g) = Cr(g) + 2\ O(g)$. This value is a factor of 2.12 greater than $D°_0(CrO,g)$.[3]

Chizhikov *et al.*[2] also studied the vaporization of Cr_2O_3 via mass spectrometry in the range 1690–2020 K. They reported the detection of gaseous Cr, CrO, CrO_2, and O during the evaporation process. The reported smoothed partial pressures of CrO(g) and CrO_2(g) lie higher than those of Grimley *et al.*[1] by a factor of 2–5, while the partial pressures of Cr(g) are less than a factor of two difference. This study was not further analyzed.

Mass spectrometric studies were made by Farber and Srivastava[7] on the reactions involved with vanadium and chromium additives in potassium-seeded H_2/O_2 flames. Equilibrium values at an average flame temperature of 2250 K for the reaction for $CrO_2(g) + 2\ H_2O(g) = H_2CrO_4(g) + 2\ H(g)$ were analyzed by Farber and Srivastava.[7] They calculated $\Delta_f H°(298.15\ K) = -3.0 \pm 7\ kcal\cdot mol^{-1}$ for CrO_2(g). The experimental determination of $\Delta_f H°(298.15\ K)$ for H_2CrO_4(g) also required the $\Delta_f H°(298.15\ K)$ value for CrO(g). Adjusting the calculations of Farber and Srivastava[7] to be consistent with the JANAF $\Delta_f H°(298.15\ K)$ value for CrO(g),[3] we recalculate $\Delta_f H°(298.15\ K) = -11.0\ kcal\cdot mol^{-1}$ for CrO_2(g).

Heat Capacity and Entropy

CrO_2(g) is assumed to have a molecular geometry similar to that observed for TiO_2(g), ZrO_2(g), and TaO_2(g).[3] The O–Cr–O bond is estimated as 110° while the Cr–O bond distance is estimated to be the same as that in CrO(g) [3]. The symmetric and asymmetric stretching frequencies are obtained from the infrared spectra of gaseous tetrahedral CrO_2Cl_2 and CrO_2F_2.[4, 5] The bending frequency of 300 cm^{-1} is estimated, based on analogies with TaO_2(g) and WO_2(g).[3, 6] Refer also to the TiO_2ideal gas table.[3] The electronic ground state is assumed to be $^3A_1$ as in WO_2(g).[6] The principal moments of inertia are: $I_A = 2.8646 \times 10^{-39}$, $I_B = 9.4383 \times 10^{-39}$, and $I_C = 12.3029 \times 10^{-39}$ $g\cdot cm^2$.

Continued on page 975

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.210	−73.781	−73.781	INFINITE
100	35.384	226.805	305.163	−7.836	−73.623	−78.544	41.027
200	39.615	252.725	273.086	−4.072	−74.354	−83.229	21.737
250	41.517	261.768	269.945	−2.044	−74.844	−85.391	17.842
298.15	43.390	269.241	269.241	0.	−75.312	−87.380	15.309
300	43.461	269.510	269.242	0.080	−75.329	−87.455	15.227
350	45.324	276.351	269.778	2.301	−75.887	−89.426	13.346
400	47.010	282.515	270.991	4.610	−76.313	−91.331	11.927
450	48.482	288.139	272.588	6.998	−76.723	−93.184	10.816
500	49.742	293.315	274.406	9.454	−77.124	−94.991	9.924
600	51.712	302.568	278.347	14.533	−77.924	−98.490	8.574
700	53.121	310.651	282.396	19.778	−78.748	−101.852	7.600
800	54.142	317.814	286.385	25.144	−79.618	−105.095	6.862
900	54.896	324.237	290.240	30.598	−80.564	−108.223	6.281
1000	55.464	330.052	293.935	36.117	−81.623	−111.241	5.811
1100	55.902	335.360	297.463	41.686	−82.829	−114.145	5.420
1200	56.245	340.239	300.827	47.294	−84.201	−116.933	5.090
1300	56.518	344.752	304.034	52.933	−85.760	−119.599	4.806
1400	56.738	348.949	307.095	58.596	−87.521	−122.137	4.557
1500	56.918	352.870	310.017	64.279	−89.495	−124.543	4.337
1600	57.068	356.548	312.811	69.979	−91.689	−126.809	4.140
1700	57.193	360.012	315.487	75.692	−94.109	−128.931	3.962
1800	57.298	363.284	318.052	81.417	−96.760	−130.904	3.799
1900	57.388	366.384	320.515	87.151	−99.647	−132.723	3.649
2000	57.466	369.330	322.883	92.894	−102.774	−134.384	3.510
2100	57.532	372.135	325.162	98.644	−106.144	−135.883	3.380
2200	57.591	374.813	327.358	104.400	−129.096	−136.559	3.242
2300	57.642	377.374	329.478	110.162	−131.098	−136.854	3.108
2400	57.686	379.828	331.525	115.928	−133.117	−137.062	2.983
2500	57.726	382.184	333.504	121.699	−135.155	−137.184	2.866
2600	57.761	384.449	335.421	127.473	−137.209	−137.225	2.757
2700	57.793	386.629	337.277	133.251	−139.282	−137.186	2.654
2800	57.821	388.732	339.077	139.032	−141.372	−137.070	2.557
2900	57.847	390.761	340.825	144.815	−143.479	−136.880	2.465
3000	57.870	392.723	342.522	150.601	−484.621	−132.003	2.298
3100	57.890	394.620	344.172	156.389	−485.933	−120.227	2.026
3200	57.909	396.459	345.778	162.179	−487.312	−108.409	1.770
3300	57.927	398.241	347.341	167.971	−488.755	−96.546	1.528
3400	57.942	399.970	348.863	173.764	−490.260	−84.638	1.300
3500	57.957	401.650	350.348	179.559	−491.827	−72.686	1.085
3600	57.970	403.283	351.795	185.355	−493.455	−60.687	0.881
3700	57.982	404.872	353.209	191.153	−495.143	−48.643	0.687
3800	57.994	406.418	354.589	196.952	−496.893	−36.552	0.502
3900	58.004	407.925	355.937	202.752	−498.705	−24.414	0.327
4000	58.014	409.393	357.255	208.553	−500.582	−12.229	0.160
4100	58.023	410.826	358.544	214.354	−502.526	0.004	−0.000
4200	58.031	412.224	359.806	220.157	−504.540	12.285	−0.153
4300	58.039	413.590	361.041	225.961	−506.629	24.615	−0.299
4400	58.046	414.924	362.250	231.765	−508.796	36.994	−0.439
4500	58.053	416.229	363.435	237.570	−511.046	49.423	−0.574
4600	58.059	417.505	364.597	243.375	−513.386	61.903	−0.703
4700	58.065	418.753	365.736	249.182	−515.821	74.436	−0.827
4800	58.071	419.976	366.853	254.988	−518.359	87.021	−0.947
4900	58.076	421.173	367.950	260.796	−521.007	99.661	−1.062
5000	58.081	422.347	369.026	266.603	−523.773	112.356	−1.174
5100	58.085	423.497	370.083	272.412	−526.302	125.080	−1.281
5200	58.090	424.625	371.121	278.221	−529.225	137.879	−1.385
5300	58.094	425.731	372.141	284.030	−532.269	150.738	−1.486
5400	58.098	426.817	373.143	289.839	−535.442	163.654	−1.583
5500	58.102	427.883	374.129	295.649	−538.748	176.630	−1.677
5600	58.105	428.930	375.098	301.460	−542.195	189.669	−1.769
5700	58.108	429.959	376.052	307.270	−545.786	202.769	−1.858
5800	58.112	430.969	376.990	313.081	−549.530	215.934	−1.945
5900	58.114	431.963	377.913	318.893	−553.433	229.164	−2.029
6000	58.117	432.940	378.822	324.704	−557.500	242.463	−2.111

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [266.2 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -288.2 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -292.88 \pm 41.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[875](1)
[500](1)
969 (2)
[425](2)

Ground State Quantum Weight: [1]
Point Group: [D_{3h}]
Bond Distance: Cr–O = [1.627] Å
Bond Angle: O–Cr–O = [120]°
Product of the Moments of Inertia = $I_A I_B I_C = [2.348053 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The vaporization of Cr_2O_3 under oxidizing conditions was studied by Grimley, Burns, and Inghram[1] using mass spectrometric methods. The principal gaseous species observed were Cr, CrO, CrO_2, CrO_3, O, and O_2. The vapor pressures at three different temperatures (1893, 1914, and 1942 K, IPTS–68) are analyzed for four different reactions by the 2nd and 3rd law methods.

Reaction	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Cr(g) + 3 O(g) = CrO_3(g)	−279.80	−332.47	−27.5 ± 6.4	−58.79
Cr(g) + 1.5 O_2(g) = CrO_3(g)	−220.52	−165.48	28.7 ± 21.1	−70.48
0.5 Cr_2O_3(cr) + 1.5 O(g) = CrO_3(g)	−30.81	−24.28	3.4 ± 1.4	−70.04
0.5 Cr_2O_3(cr) + 0.75 O_2(g) = CrO_3(g)	−1.17	59.22	31.5 ± 12.4	−75.88

The 2nd law results are considered less reliable due to the small number of data points and the small temperature range studied (52 K). We adopt $\Delta_f H°(CrO_3, g, 298.15\ K) = -70.0 \pm 10\ kcal \cdot mol^{-1}$ ($-292.880 \pm 41.8\ kJ \cdot mol^{-1}$).

Washburn,[3] in a mass spectrometric study of the sublimation of CrO_3(cr), stated that the gaseous Cr–containing molecules are in equilibrium among themselves but not with O(g). If the same situation were to hold in the study by Grimley *et al.*,[1] a value intermediate to −70.04 and −75.88 kcal·mol^{-1} might be more appropriate. However, the adopted value with its assigned uncertainty is still consistent with this possibility.

Mass spectrometric studies were made by Farber and Srivastava[6] on the reactions involved with vanadium and chromium additives in potassium–seeded H_2/O_2 flames. Equilibrium values at an average flame temperature of 2250 K for the reaction $CrO_3(g) + H_2O(g) = H_2CrO_4(g)$ were analyzed by Farber and Srivastava.[6] They calculated $\Delta_f H°(298.15\ K) = -64.6 \pm 7\ kcal \cdot mol^{-1}$ for CrO_3(g). The experimental determination of $\Delta_f H°(298.15\ K)$ for H_2CrO_4(g) also required the $\Delta_f H°(298.15\ K)$ value for CrO(g). Adjusting the calculations of Farber and Srivastava[6] to be consistent with the JANAF $\Delta_f H°(298.15\ K)$ value for CrO(g),[2] we recalculate $\Delta_f H°(289.15\ K) = -72.6\ kcal \cdot mol^{-1}$ for CrO_3(g).

Defining the dissociation by $CrO_3(g) = Cr(g) + 3O(g)$, we calculate $\Delta_{at} H° = 14.8 \pm 0.4$ eV ($340.3 \pm 10\ kcal \cdot mol^{-1}$). This compares with $D_0° = 4.71$ eV for CrO(g) and $\Delta_{at} H° = 9.98$ eV for CrO_2(g) for similar dissociations.[2]

Heat Capacity and Entropy

The molecular structure is assumed to be planar with D_{3h} symmetry. The three Cr–O bond distances are taken to be the same as in CrO(g).[2] The principal moments of inertia are $I_A = I_B = 10.5494 \times 10^{-39}$ and $I_C = 21.0987 \times 10^{-39}\ g \cdot cm^2$.

Barraclough *et al.*[4] observed a vibrational frequency at 969 cm^{-1} in the infrared spectrum of CrO_3(cr) dispersed in a Nujol mull. This frequency was assigned to represent the stretching frequency of the two free Cr–O groups in crystalline CrO_3. We assume this frequency also represents the stretching mode in the vapor phase. This infrared work is supported by the infrared and Raman studies of Mattes.[5] The remaining vibrational frequencies are those suggested by Grimley *et al.*[1] The electronic ground state is assumed to be a singlet.

References

[1]R. F. Grimley, R. P. Burns, and M. G. Inghram, J. Chem. Phys. **34**, 664 (1961).
[2]JANAF Thermochemical Tables: CrO(g) and CrO_2(g), 12–31–73.
[3]C. A. Washburn, U. S. Clearinghouse Fed. Sci. Tech. Inform., PB–183562 (1969); Chem. Abstr. **71**, 755276 (1969).
[4]C. G. Barraclough, J. Lewis and R. S. Nyholm, J. Chem. Soc. **1959**, 3552 (1959).
[5]R. Mattes, Z. Naturforsch **B24**, 772 (1969).
[6]M. Farber and R. D. Srivastava, Combustion and Flame **20**, 43 (1973).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.379	−288.176	−288.176	INFINITE
100	34.969	218.552	308.811	−9.026	−289.492	−284.922	148.828
200	45.791	245.909	270.989	−5.016	−291.432	−279.595	73.023
250	51.301	256.729	267.075	−2.586	−292.250	−276.538	57.779
298.15	56.025	266.178	266.178	0.	−292.880	−273.452	47.908
300	56.193	266.525	266.179	0.104	−292.901	−273.332	47.591
350	60.366	275.510	266.879	3.021	−293.500	−270.016	40.298
400	63.839	283.805	268.483	6.129	−293.875	−266.634	34.819
450	66.695	291.495	270.618	9.394	−294.165	−263.211	30.553
500	69.037	298.647	273.068	12.790	−294.399	−259.759	27.137
600	72.542	311.564	278.431	19.880	−294.767	−252.795	22.008
700	74.953	322.939	283.993	27.262	−295.082	−245.774	18.340
800	76.658	333.065	289.506	34.847	−295.401	−238.709	15.586
900	77.896	342.169	294.860	42.578	−295.772	−231.601	13.442
1000	78.819	350.426	300.010	50.416	−296.243	−224.447	11.724
1100	79.523	357.973	304.942	58.335	−296.854	−217.239	10.316
1200	80.071	364.917	309.654	66.315	−297.628	−209.968	9.140
1300	80.505	371.344	314.155	74.345	−298.587	−202.626	8.142
1400	80.855	377.323	318.456	82.414	−299.750	−195.202	7.283
1500	81.140	382.912	322.569	90.514	−301.128	−187.688	6.536
1600	81.375	388.156	326.506	98.640	−302.729	−180.074	5.879
1700	81.572	393.095	330.279	106.787	−304.560	−172.353	5.296
1800	81.738	397.763	333.900	114.953	−306.628	−164.518	4.774
1900	81.879	402.186	337.379	123.134	−308.939	−156.561	4.304
2000	82.000	406.389	340.725	131.328	−311.496	−148.476	3.878
2100	82.104	410.392	343.948	139.534	−314.303	−140.257	3.489
2200	82.195	414.214	347.055	147.749	−336.700	−131.242	3.116
2300	82.275	417.869	350.055	155.972	−338.155	−121.871	2.768
2400	82.345	421.373	352.955	164.203	−339.637	−112.437	2.447
2500	82.406	424.735	355.759	172.441	−341.144	−102.939	2.151
2600	82.461	427.968	358.474	180.684	−342.678	−93.381	1.876
2700	82.511	431.081	361.106	188.933	−344.238	−83.762	1.620
2800	82.555	434.083	363.659	197.186	−345.825	−74.086	1.382
2900	82.594	436.981	366.138	205.444	−347.436	−64.353	1.159
3000	82.630	439.781	368.546	213.705	−688.092	−49.951	0.870
3100	82.662	442.491	370.888	221.970	−688.925	−28.665	0.483
3200	82.692	445.116	373.167	230.237	−689.833	−7.353	0.120
3300	82.718	447.661	375.386	238.508	−690.813	13.989	−0.221
3400	82.743	450.131	377.548	246.781	−691.862	35.363	−0.543
3500	82.765	452.530	379.657	255.056	−692.981	56.767	−0.847
3600	82.786	454.862	381.713	263.334	−694.166	78.206	−1.135
3700	82.805	457.130	383.721	271.613	−695.420	99.677	−1.407
3800	82.823	459.339	385.682	279.895	−696.741	121.185	−1.666
3900	82.839	461.490	387.598	288.178	−698.131	142.728	−1.912
4000	82.854	463.588	389.472	296.463	−699.592	164.306	−2.146
4100	82.868	465.634	391.305	304.749	−701.126	185.922	−2.369
4200	82.881	467.631	393.098	313.036	−702.736	207.577	−2.582
4300	82.893	469.581	394.854	321.325	−704.427	229.271	−2.785
4400	82.904	471.487	396.575	329.615	−706.201	251.005	−2.980
4500	82.914	473.350	398.260	337.906	−708.065	272.780	−3.166
4600	82.924	475.173	399.912	346.197	−710.023	294.597	−3.345
4700	82.934	476.956	401.533	354.490	−712.083	316.459	−3.517
4800	82.942	478.702	403.122	362.784	−714.251	338.366	−3.682
4900	82.950	480.413	404.682	371.079	−716.536	360.320	−3.841
5000	82.958	482.088	406.214	379.374	−718.944	382.321	−3.994
5100	82.965	483.731	407.718	387.670	−721.123	404.344	−4.141
5200	82.972	485.342	409.195	395.967	−723.702	426.436	−4.284
5300	82.978	486.923	410.647	404.265	−726.409	448.581	−4.421
5400	82.984	488.474	412.074	412.563	−729.253	470.776	−4.554
5500	82.990	489.997	413.476	420.862	−732.237	493.025	−4.682
5600	82.996	491.492	414.856	429.161	−735.371	515.332	−4.807
5700	83.001	492.961	416.214	437.461	−738.658	537.694	−4.927
5800	83.006	494.405	417.549	445.761	−742.106	560.117	−5.044
5900	83.010	495.824	418.864	454.062	−745.723	582.598	−5.158
6000	83.015	497.219	420.158	462.363	−749.514	605.145	−5.268

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [64.85 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -125.52 \pm 12.6\ kJ·mol^{-1}$

Enthalpy of Formation

Mah[1] has measured the enthalpy of combustion of chromium subnitride at 303.15 K. From her data for the process $Cr_2N_{0.969}(cr) + 1.5O_2(g) = Cr_2O_3(cr) + 0.4845\ N_2(g)$, we calculate $\Delta_c H°(298.15\ K) = -241.29 \pm 1.5\ kcal·mol^{-1}$ at unit fugacities of oxygen and nitrogen. Impurity corrections are based on JANAF enthalpy of formation data.[2] When the value for $\Delta_c H°$ is combined with the enthalpy of formation for Cr_2O_3,[2] one obtains $\Delta_f H°(Cr_2N_{0.969}, cr, 298.15\ K) = -29.9 \pm 3.5\ kcal·mol^{-1}$. The large uncertainty arises from impurities in the subnitride sample, as well as from the uncertainty ($\pm 2.0\ kcal·mol^{-1}$) in the $\Delta_f H°$ of Cr_2O_3.[2]

All available equilibrium nitrogen pressures except those of one study[5] have been recently for the reaction $2\ Cr(cr) + 0.5\ N_2(g) = Cr_2N(cr)$. These results are reanalyzed by the 2nd and 3rd law methods using revised thermal functions for Cr_2N (see below). We have not taken into account in our analysis any variations in the composition of the subnitride.

Source	Data Points	T/K	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15\ K)$,kcal·mol⁻¹ 2nd law	3rd law
Sano[4]	6	1229–1395	−3.7 ± 0.2	−24.0	−28.8 ± 0.5
Mozgovai and Samarin[5]	Equation	1600–1750	−14.0	−10.2	−33.8 ± 1.7
Seybolt and Oriani[6]	5	1273–1673	−7.8 ± 5.4	−21.3	−32.8 ± 3.9
Tomilin and Savost'yanova[7]	Equation	1517–1724	−32.6	−20.3	−32.6 ± 5.7
Mills[8]	Equation	1337–1653	−2.1	−29.2	−32.3 ± 0.5
Schwerdtfeger[9]	3	1373–1583	−3.7 ± 0.7	−27.1	−32.5 ± 0.8
Smith[10]	2	1333–1370	−13.4	−13.6	−31.7 ± 0.7

We adopt $\Delta_f H°(Cr_2N, cr, 298.15\ K) = -30.0 \pm 3.0\ kcal·mol^{-1}$ ($-125.52 \pm 12.6\ kJ·mol^{-1}$) which is based on the 2nd and 3rd law results from the two equilibrium studies[8,9] and the $\Delta_f H°$ value determined by combustion calorimetry.[1] Our adopted value agrees with that selected by NBS (-30.5)[11] but is 1.8 $kcal·mol^{-1}$ less negative than the selected value of DeLuca and Leitnaker.[3]

Heat Capacity and Entropy

No low temperature heat capacity data for Cr_2N have been reported. By analogy with entropies[2, 12, 13] for other transition–metal subnitrides, for the reaction $2\ M(cr) + 0.5\ N_2(g) = M_2N(cr)$ where M=Fe, Mo, Nb, Ta, and V, we calculate an average $\Delta_f S°$ of $-18.7\ cal·K^{-1}·mol^{-1}$. This value is combined with entropies for Cr and N_2[2] to give 15.5 $cal·K^{-1}·mol^{-1}$ as $S°(298.15\ K)$ for $Cr_2N(cr)$. Other reported estimates in $cal·K^{-1}·mol^{-1}$ for $S°(298.15\ K)$ are 14.3[3] and 17.7 ± 1.0.[14]

The only high temperature enthalpy study reported for Cr_2N is that of Satoh,[15] who measured heat contents [$H°(T)–H°(273.15\ K)$] three nitride samples at three temperatures each (372.6, 598.8, and 784.2 K) in an ice calorimeter. DeLuca and Leitnaker[3] have shown that the subnitride sample used by Satoh[15] was substoichiometric, reevaluated his heat contents and presented $C_p°$ data for Cr_2N in the temperature range 298–1800 K. A comparison of their value (17.0 $cal·K^{-1}·mol^{-1}$) for $C_p°(298.15\ K)$ with similar data for other transition–metal subnitrides[2, 12, 13] indicates it is probably too large by 1–2 $cal·K^{-1}·mol^{-1}$. We find a $\Delta_f C_p°$ of 1.1 $cal·K^{-1}·mol^{-1}$ for several subnitrides[2, 12, 13] which leads to a $C_p°$ value of 15.79 $cal·K^{-1}·mol^{-1}$ for Cr_2N at 298.15 K. This value is adopted and joined smoothly with the data of Deluca and Leitnaker[3] near 400 K. $C_p°$ data above 1800 K are obtained by graphical extrapolation.

Phase Data

Blix[16] has determined the structure of the subnitride phase as hexagonal by x–ray diffraction methods, and he indicated that the homogeneity limits extend from $CrN_{0.47}$ to $CrN_{0.66}$. Eriksson[17] has reported that the phase exists between $CrN_{0.38}$ and $CrN_{0.50}$. Mills,[8] using a thermogravimetric technique, has examined the homogeneity limits of Cr_2N as a function of temperature. The upper limiting composition was determined to be $CrN_{0.49}$ with only a small variation with temperature. The lower limiting composition of Cr_2N varied widely with temperature in the range 1273–1373 K. Mills[8] reported the limiting composition as $CrN_{0.41}$, at 1273 K and $CrN_{0.37}$ at 1373 K. Other information on the chromium–chromium nitride system has been reviewed by Storms.[18]

Decomposition Data

No information is available on the melting point of Cr_2N. We assume that the subnitride decomposes prior to melting, according to the reaction $Cr_2N(cr) \rightarrow 2\ Cr(cr) + 0.5\ N_2(g)$. T_{dcm} is the temperature at which $\Delta_r G°$ for the decomposition process equals zero.

References

[1] A. D. Mah, U. S. Bur. Mines RI 5529, (1960).
[2] JANAF Thermochemical Tables: $N_2(g)$, 9–30–66; Cr(cr), 6–30–73; $Cr_2O_3(cr)$ and $VN_{0.465}(cr)$, 12–31–73.
[3] J. P. DeLuca and J. M. Leitnaker, J. Amer. Ceram. Soc. **56**, 126 (1973).
[4] K. Sano, Nippon Kagaku Kaishi **58**, 981 (1937).

Continued on page 975

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K⁻¹mol⁻¹)	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	66.065	64.852	64.852	0.	−125.520	−102.208	17.906
300	66.191	65.261	64.853	0.122	−125.511	−102.063	17.771
400	73.429	85.388	67.548	7.136	−125.040	−94.280	12.312
500	76.735	102.139	72.841	14.649	−124.190	−86.688	9.056
600	79.496	116.373	78.939	22.460	−123.309	−79.270	6.901
700	82.257	128.835	85.195	30.548	−122.371	−72.003	5.373
800	84.977	139.996	91.359	38.910	−121.362	−64.876	4.236
900	87.738	150.165	97.336	47.546	−120.304	−57.878	3.359
1000	90.500	159.552	103.094	56.457	−119.244	−50.999	2.664
1100	93.261	168.307	108.629	65.646	−118.236	−44.224	2.100
1200	95.981	176.538	113.949	75.108	−117.311	−37.537	1.634
1300	98.742	184.330	119.066	84.844	−116.500	−30.923	1.243
1400	101.504	191.749	123.994	94.856	−115.828	−24.366	0.909
1500	104.265	198.846	128.749	105.145	−115.305	−17.853	0.622
1600	107.027	205.663	133.345	115.709	−114.942	−11.369	0.371
1700	109.788	212.235	137.793	126.550	−114.746	−4.902	0.151
1800	112.508	218.589	142.106	137.669	−114.722	1.558	−0.045
1900	114.767	224.731	146.294	149.029	−114.912	8.022	−0.221
2000	117.487	230.688	150.366	160.644	−115.306	14.501	−0.379
2100	119.955	236.479	154.329	172.514	−115.907	21.006	−0.522
2200	122.591	242.121	158.192	184.644	−155.386	28.854	−0.685
2300	124.934	247.622	161.961	197.020	−152.693	37.169	−0.844
2400	127.277	252.989	165.643	209.630	−149.771	45.362	−0.987
2500	129.704	258.233	169.242	222.479	−146.617	53.428	−1.116

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 81.15 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2603 \pm 15\ K$

$\Delta_f H°(0\ K) = -1128.84 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1134.70 \pm 8.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = [129.7]\ kJ·mol^{-1}$

Enthalpy of Formation

Two oxygen bomb calorimetric studies on Cr(cr) led to reported values of $\Delta_f H°(Cr_2O_3, cr, 298.15\ K) = -272.6 \pm 0.4\ kcal·mol^{-1}$ by Mah[1] and $-271.0 \pm 1.8\ kcal·mol^{-1}$ by Golutvin and Chin'k'uei.[2] Mah[1] reported that completions of combustion ranged from 95.30 to 98.90% and applied corrections. Of the fourteen runs by Golutvin and Chin'k'uei,[2] seven had a completeness of combustion of 91.88 to 98.96%. Their reported $\Delta_f H°(298.15\ K)$ value is based on an average of the results for these seven runs with no correction for incomplete combustion or impurities. These latter authors[2] also stated that there was no clear dependence between the enthalpy of combustion and completeness of combustion. Early calorimetric studies led to reported values for $\Delta_f H°$ of -267.8 (298 K),[3] -288.9 ± 1.0 (292 K),[4] and $-268.9 \pm 0.6\ kcal·mol^{-1}$ (294 K).[5]

There are many equilibrium studies involving Cr_2O_3(cr). Our analysis of the more recent studies are tabulated below. The free energy of formation equation presented by Richardson and Jeffes[8] is representative of the earlier equilibrium studies.[9]

Source	Reaction	T/K	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
[8]	A	873–1773	Eqn.	−270.62	−268.44	1.7	−270.62	−268.44
[9]	B(transpiration)	871–1427	4	−32.89 ± 0.65	−31.61 ± 0.65	1.1 ± 0.5	−272.05	−268.22
[10]	B(static)	1313–1573	5(47)	−32.17 ± 0.75	−32.36 ± 0.19	−0.1 ± 0.5	−269.89	−270.46
[11]	B(transpiration)	1493–1893	5	−32.85 ± 0.94	−32.79 ± 0.30	0.1 ± 0.6	−271.94	−271.76
[12]	A(emf)	1000–1700	Eqn.	−264.60	−268.91	−3.3	−264.60	−268.91
[13]	A(emf)	1173–1523	Eqn.	−269.71	−270.32	−0.5	−269.71	−270.32

Reactions: (A) 2 Cr(cr) + 3/2 O_2(g) = Cr_2O_3(cr). (B) 2/3 Cr(cr) + H_2O(g) = 1/3 Cr_2O_3(cr) + H_2(g).

We adopt $\Delta_f H°(Cr_2O_3, cr, 298.15\ K) = -271.2 \pm 2.0\ kcal·mol^{-1}$ (1134.701 ± 8.4 kJ·mol^{-1}). This value is an average of two combustion studies,[1,2] and three equilibrium studies which have a small third law drift.[10, 11, 13]

Kelly *et al.*[6] investigated experimentally the thermodynamic properties of the chromium carbides. They measured the CO(g) equilibrium pressure in four distinct systems. A combination of our analyses of these four equilibria[7] leads to $\Delta_f H°(Cr_2O_3, cr, 298.15\ K) = -269.9\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The heat capacity of Cr_2O_3(cr) was measured by Anderson [14 (56–336 K)] and by Volger (graph, 100–350 K).[15] Using the combination of Debye and Einstein functions suggested by Anderson,[14] we calculate $S°(50\ K) = 0.386\ cal·K^{-1}mol^{-1}$ and $H°(50\ K) - 14.3\ cal·mol^{-1}$. Both studies[14, 15] indicated a maximum in the $C_p°$ curve at 205 K. The data of Volger[15] lies considerably higher than that of Anderson.[14] Early heat capacity data by Russell (137–299 K)[16] is in good agreement with that of Anderson.[14] Above 305 K the heat capacity values decrease rapidly (~cal·K^{-1}·mol^{-1}) until 325–340 K, at which point the values show little change with temperature. The adopted $C_p°$ values below $T = 330$ K are based on the study by Anderson.[14]

Enthalpy data on Cr_2O_3(cr) were measured by Kelley *et al.* (298–1774 K)[6] and Laschschenko and Kompanskii (288–1428 K).[17] The adopted heat capacity values are those suggested by Kelley *et al.*,[6] except that the values in the region 350–500 K are shifted slightly so as to join smoothly with the low temperature heat capacity results.[14] The derived enthalpy values agree with the enthalpy data of Kelley *et al.*[6] to within ±0.5%, the maximum deviation of 25 cal or .5% occurring at 479 K.

Phase Data

Brewer[18] summarized the phase data and reported that Cr_2O_3 has a homogeneity range of $x = 1.50$–1.56 for CrO_x. Cr_2O_3has the α–corundum structure and is antiferromagnetic with structural distortion occurring below the Curie temperature of 305 K.

Fusion Data

Refer to the liquid table for details.

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Continued on page 975

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.282	−1128.844	−1128.844	INFINITE
100	24.255	10.093	155.642	−14.555	−1133.096	−1107.252	578.369
200	75.412	43.065	90.567	−9.501	−1135.576	−1080.195	282.118
298.15	120.366	81.154	81.154	0.	−1134.701	−1053.066	184.493
300	121.922	81.904	81.157	0.224	−1134.645	−1052.560	183.267
305.000	126.775	83.958	81.186	0.845	____ C_p LAMBDA MAXIMUM ____		
305.000	126.775	83.958	81.186	0.845	TRANSITION		
400	112.675	113.736	85.534	11.281	−1133.129	−1025.421	133.906
500	117.721	139.503	93.829	22.837	−1131.353	−998.699	104.333
600	120.549	161.232	103.300	34.759	−1129.610	−972.333	84.649
700	122.625	179.977	112.945	46.922	−1127.958	−946.252	70.610
800	124.290	196.463	122.375	59.270	−1126.413	−920.401	60.096
900	125.725	211.187	131.440	71.773	−1125.007	−894.736	51.929
1000	127.009	224.501	140.091	84.410	−1123.795	−869.217	45.403
1100	128.202	236.663	148.325	97.171	−1122.829	−843.808	40.069
1200	129.332	247.867	156.159	110.049	−1122.137	−818.475	35.627
1300	130.411	258.261	163.618	123.036	−1121.754	−793.188	31.871
1400	131.457	267.964	170.729	136.130	−1121.703	−767.918	28.651
1500	132.482	277.069	177.518	149.327	−1121.999	−742.639	25.861
1600	133.486	285.651	184.011	162.625	−1122.654	−717.329	23.418
1700	134.478	293.774	190.230	176.024	−1123.676	−691.967	21.262
1800	135.457	301.486	196.199	189.517	−1125.077	−666.534	19.342
1900	136.880	308.848	201.935	203.135	−1126.833	−641.013	17.623
2000	138.168	315.903	207.459	216.888	−1128.937	−615.391	16.072
2100	139.056	322.665	212.785	230.749	−1131.423	−589.654	14.667
2200	139.947	329.155	217.928	244.699	−1172.985	−562.478	13.355
2300	140.839	335.395	222.900	258.739	−1172.557	−534.738	12.144
2400	141.733	341.408	227.714	272.867	−1172.074	−507.017	11.035
2500	142.628	347.212	232.378	287.085	−1171.534	−479.318	10.015
2600	143.526	352.824	236.903	301.393	−1170.937	−451.640	9.074
2603.000	143.553	352.989	237.037	301.824	--- CRYSTAL <--> LIQUID ---		
2700	144.428	358.257	241.298	315.791	−1170.281	−423.987	8.203
2800	145.333	363.526	245.570	330.279	−1169.566	−396.359	7.394
2900	146.242	368.642	249.726	344.857	−1168.789	−368.759	6.642
3000	147.155	373.615	253.773	359.527	−1845.987	−331.960	5.780

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [125.595]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2603 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-1018.381]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [129.7]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Cr_2O_3, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2603\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for Cr_2O_3(l) is estimated to be 7.5 $cal·K^{-1}·mol^{-1}$. A glass transition is assumed at 1800 K. Below 1800 K, the $C_p°$ values are those of the crystal with the exception that the values below 500 K are a smooth extrapolation to $C_p° = 24.32\ cal·K^{-1}·mol^{-1}$ at 298.15 K.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point is chosen to be $T_{fus} = 2603 \pm 15$ K, as suggested by Charlesworth.[1] This result is based on the work by McNally *et al.*[2] The heat of melting is estimated by analogy with $\Delta_{fus}S° = 12.03$ for corundum.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	101.755	125.595	125.595	0.	−1018.381	−949.997	166.435
300	102.006	126.225	125.597	0.188	−1018.361	−949.572	165.335
400	112.717	157.188	129.745	10.977	−1017.113	−926.786	121.026
500	117.721	182.956	137.888	22.534	−1015.337	−904.409	94.483
600	120.549	204.685	147.258	34.456	−1013.593	−882.388	76.819
700	122.625	223.430	156.831	46.619	−1011.942	−860.653	64.223
800	124.290	239.916	166.207	58.967	−1010.396	−839.147	54.791
900	125.725	254.640	175.229	71.469	−1008.991	−817.827	47.465
1000	127.009	267.954	183.847	84.107	−1007.778	−796.654	41.613
1100	128.202	280.116	192.054	96.868	−1006.812	−775.590	36.830
1200	129.332	291.319	199.865	109.745	−1006.121	−754.602	32.847
1300	130.411	301.714	207.305	122.733	−1005.737	−733.660	29.479
1400	131.457	311.417	214.398	135.826	−1005.687	−712.735	26.592
1500	132.482	320.522	221.173	149.024	−1005.983	−691.802	24.091
1600	133.486	329.104	227.653	162.322	−1006.637	−670.838	21.901
1700	134.478	337.227	233.862	175.720	−1007.659	−649.821	19.967
1800	135.457	344.941	239.820	189.217	−1009.056	−628.733	18.245
1800.000	135.457	344.941	239.820	189.217	GLASS <--> LIQUID		
1800.000	156.900	344.941	239.820	189.217	TRANSITION		
1900	156.900	353.424	245.578	204.907	−1008.740	−607.615	16.705
2000	156.900	361.472	251.173	220.597	−1008.908	−586.501	15.318
2100	156.900	369.127	256.609	236.287	−1009.566	−565.366	14.063
2200	156.900	376.426	261.891	251.977	−1049.387	−542.878	12.890
2300	156.900	383.401	267.024	267.667	−1047.309	−519.902	11.807
2400	156.900	390.078	272.013	283.357	−1045.265	−497.016	10.817
2500	156.900	396.483	276.864	299.047	−1043.253	−474.213	9.908
2600	156.900	402.637	281.584	314.737	−1041.273	−451.491	9.071
2603.000	156.900	402.818	281.724	315.208	--- CRYSTAL <--> LIQUID ---		
2700	156.900	408.558	286.178	330.427	−1039.325	−428.844	8.296
2800	156.900	414.265	290.651	346.117	−1037.407	−406.268	7.579
2900	156.900	419.770	295.009	361.807	−1035.520	−383.762	6.912
3000	156.900	425.090	299.257	377.497	−1711.697	−352.093	6.130
3100	156.900	430.234	303.400	393.187	−1708.210	−306.830	5.170
3200	156.900	435.216	307.441	408.877	−1704.851	−261.679	4.271
3300	156.900	440.044	311.387	424.567	−1701.615	−216.631	3.429
3400	156.900	444.728	315.240	440.257	−1698.498	−171.678	2.638
3500	156.900	449.276	319.005	455.947	−1695.500	−126.816	1.893
3600	156.900	453.696	322.685	471.637	−1692.618	−82.037	1.190
3700	156.900	457.995	326.285	487.327	−1689.852	−37.338	0.527
3800	156.900	462.179	329.806	503.017	−1687.205	7.291	−0.100
3900	156.900	466.254	333.253	518.707	−1684.678	51.850	−0.694
4000	156.900	470.227	336.628	534.397	−1682.276	96.345	−1.258
4100	156.900	474.101	339.933	550.087	−1680.003	140.782	−1.794
4200	156.900	477.882	343.173	565.777	−1677.867	185.165	−2.303
4300	156.900	481.574	346.349	581.467	−1675.874	229.500	−2.788
4400	156.900	485.181	349.463	597.157	−1674.034	273.788	−3.250
4500	156.900	488.707	352.519	612.847	−1672.356	318.037	−3.692

PREVIOUS: CURRENT: December 1973

0	to	2603	K crystal
above		2603	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.282	−1128.844	−1128.844	INFINITE
100	24.255	10.093	155.642	−14.555	−1133.096	−1107.252	578.369
200	75.412	43.065	90.567	−9.501	−1135.576	−1080.195	282.118
298.15	120.366	81.154	81.154	0.	−1134.701	−1053.066	184.493
300	121.922	81.904	81.157	0.224	−1134.645	−1052.560	183.267
305.000	126.775	83.958	81.186	0.845	____ C_p LAMBDA MAXIMUM ____		
305.000	126.775	83.958	81.186	0.845	TRANSITION		
400	112.675	113.736	85.534	11.281	−1133.129	−1025.421	133.906
500	117.721	139.503	93.829	22.837	−1131.353	−998.699	104.333
600	120.549	161.232	103.300	34.759	−1129.610	−972.333	84.649
700	122.625	179.977	112.945	46.922	−1127.958	−946.252	70.610
800	124.290	196.463	122.375	59.270	−1126.413	−920.401	60.096
900	125.725	211.187	131.440	71.773	−1125.007	−894.736	51.929
1000	127.009	224.501	140.091	84.410	−1123.795	−869.217	45.403
1100	128.202	236.663	148.325	97.171	−1122.829	−843.808	40.069
1200	129.332	247.867	156.159	110.049	−1122.137	−818.475	35.627
1300	130.411	258.261	163.618	123.036	−1121.754	−793.188	31.871
1400	131.457	267.964	170.729	136.130	−1121.703	−767.918	28.651
1500	132.482	277.069	177.518	149.327	−1121.999	−742.639	25.861
1600	133.486	285.651	184.011	162.625	−1122.654	−717.329	23.418
1700	134.478	293.774	190.230	176.024	−1123.676	−691.967	21.262
1800	135.457	301.486	196.199	189.517	−1125.077	−666.534	19.342
1900	136.880	308.848	201.935	203.135	−1126.833	−641.013	17.623
2000	138.168	315.903	207.459	216.888	−1128.937	−615.391	16.072
2100	139.056	322.665	212.785	230.749	−1131.423	−589.654	14.667
2200	139.947	329.155	217.928	244.699	−1172.985	−562.478	13.355
2300	140.839	335.395	222.900	258.739	−1172.557	−534.738	12.144
2400	141.733	341.408	227.714	272.867	−1172.074	−507.017	11.035
2500	142.628	347.212	232.378	287.085	−1171.534	−479.318	10.015
2600	143.526	352.824	236.903	301.393	−1170.937	−451.640	9.074
2603.000	143.553	352.989	237.037	301.824	____ CRYSTAL <−−> LIQUID ____		
2603.000	156.900	402.818	237.037	431.528	TRANSITION		
2700	156.900	408.558	243.097	446.747	−1039.325	−428.844	8.296
2800	156.900	414.265	249.109	462.437	−1037.407	−406.268	7.579
2900	156.900	419.770	254.899	478.127	−1035.520	−383.762	6.912
3000	156.900	425.090	260.484	493.817	−1711.697	−352.093	6.130
3100	156.900	430.234	265.877	509.507	−1708.210	−306.830	5.170
3200	156.900	435.216	271.092	525.197	−1704.851	−261.679	4.271
3300	156.900	440.044	276.139	540.887	−1701.615	−216.631	3.429
3400	156.900	444.728	281.029	556.577	−1698.498	−171.678	2.638
3500	156.900	449.276	285.771	572.267	−1695.500	−126.816	1.893
3600	156.900	453.696	290.374	587.957	−1692.618	−82.037	1.190
3700	156.900	457.995	294.847	603.647	−1689.852	−37.338	0.527
3800	156.900	462.179	299.196	619.337	−1687.205	7.291	−0.100
3900	156.900	466.254	303.427	635.027	−1684.678	51.850	−0.694
4000	156.900	470.227	307.548	650.717	−1682.276	96.344	−1.258
4100	156.900	474.101	311.563	666.407	−1680.003	140.782	−1.794
4200	156.900	477.882	315.478	682.097	−1677.867	185.165	−2.303
4300	156.900	481.574	319.298	697.787	−1675.874	229.500	−2.788
4400	156.900	485.181	323.027	713.477	−1674.034	273.788	−3.250
4500	156.900	488.707	326.670	729.167	−1672.356	318.037	−3.692

PREVIOUS: CURRENT: December 1973

Continued from page 960

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0	to 301.55	K	crystal
301.55	to 947.967	K	liquid
above	947.967	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.717	0.	0.	0.
100	25.812	54.952	110.635	−5.568	0.	0.	0.
200	27.804	73.453	87.892	−2.888	0.	0.	0.
298.15	32.195	85.147	85.147	0.	0.	0.	0.
300	32.355	85.347	85.148	0.060	0.	0.	0.
301.550	32.501	85.514	85.149	0.110	CRYSTAL <--> LIQUID TRANSITION		
301.550	32.393	92.436	85.149	2.197			
400	31.518	101.458	88.110	5.339	0.	0.	0.
500	31.154	108.448	91.506	8.471	0.	0.	0.
600	30.999	114.113	94.817	11.578	0.	0.	0.
700	30.941	118.887	97.923	14.674	0.	0.	0.
800	30.932	123.017	100.808	17.768	0.	0.	0.
900	30.957	126.662	103.482	20.862	0.	0.	0.
947.967	30.976	128.270	104.696	22.348	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
947.967	20.786	199.643	104.696	90.007			
1000	20.786	200.754	109.665	91.089	0.	0.	0.
1100	20.788	202.735	118.037	93.167	0.	0.	0.
1200	20.791	204.544	125.172	95.246	0.	0.	0.
1300	20.799	206.208	131.342	97.326	0.	0.	0.
1400	20.814	207.750	136.746	99.406	0.	0.	0.
1500	20.841	209.187	141.528	101.489	0.	0.	0.
1600	20.886	210.533	145.799	103.575	0.	0.	0.
1700	20.952	211.802	149.645	105.667	0.	0.	0.
1800	21.048	213.002	153.131	107.767	0.	0.	0.
1900	21.178	214.143	156.313	109.878	0.	0.	0.
2000	21.349	215.233	159.232	112.004	0.	0.	0.
2100	21.564	216.280	161.924	114.149	0.	0.	0.
2200	21.830	217.289	164.417	116.318	0.	0.	0.
2300	22.150	218.266	166.737	118.517	0.	0.	0.
2400	22.527	219.217	168.904	120.750	0.	0.	0.
2500	22.960	220.145	170.935	123.023	0.	0.	0.
2600	23.456	221.055	172.846	125.344	0.	0.	0.
2700	24.016	221.950	174.648	127.717	0.	0.	0.
2800	24.639	222.835	176.353	130.149	0.	0.	0.
2900	25.326	223.711	177.971	132.646	0.	0.	0.
3000	26.082	224.582	179.510	135.216	0.	0.	0.
3100	26.905	225.451	180.978	137.864	0.	0.	0.
3200	27.796	226.319	182.381	140.599	0.	0.	0.
3300	28.599	227.175	183.725	143.384	0.	0.	0.
3400	29.572	228.043	185.016	146.293	0.	0.	0.
3500	30.600	228.915	186.258	149.301	0.	0.	0.
3600	31.680	229.792	187.455	152.414	0.	0.	0.
3700	32.770	230.671	188.610	155.625	0.	0.	0.
3800	33.902	231.557	189.729	158.949	0.	0.	0.
3900	35.036	232.447	190.812	162.375	0.	0.	0.
4000	36.250	233.349	191.864	165.939	0.	0.	0.
4100	37.488	234.259	192.887	169.626	0.	0.	0.
4200	38.744	235.178	193.883	173.438	0.	0.	0.
4300	40.010	236.104	194.854	177.375	0.	0.	0.
4400	40.717	236.965	195.795	181.147	0.	0.	0.
4500	40.901	237.756	196.706	184.728	0.	0.	0.
4600	41.940	238.667	197.608	188.871	0.	0.	0.
4700	42.950	239.580	198.491	193.115	0.	0.	0.
4800	43.924	240.494	199.357	197.459	0.	0.	0.
4900	44.859	241.409	200.206	201.899	0.	0.	0.
5000	45.748	242.325	201.039	206.430	0.	0.	0.
5100	46.588	243.239	201.857	211.047	0.	0.	0.
5200	46.722	244.034	202.647	215.214	0.	0.	0.
5300	47.407	244.931	203.436	219.921	0.	0.	0.
5400	47.729	245.763	204.205	224.415	0.	0.	0.
5500	48.117	246.611	204.964	229.060	0.	0.	0.
5600	48.599	247.483	205.716	233.896	0.	0.	0.
5700	49.022	248.347	206.456	238.778	0.	0.	0.
5800	49.385	249.203	207.186	243.699	0.	0.	0.
5900	49.689	250.049	207.905	248.653	0.	0.	0.
6000	49.935	250.887	208.614	253.634	0.	0.	0.

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 85.147 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 301.55 \pm 0.01\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(923\ K) = 2.087 \pm 0.004\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities, 0.19–301.55 K, have been measured by Dauphinee,[1] McCollum,[2] Martin,[3] Lien,[4] Filby,[5] and Morgan.[6] The adopted values are derived based on the C_p data reported by Filby[5] and Lien.[4] Lien measured the heat capacities in the temperature range 0.1874 to 1.20K in the adiabatic demagnetization cryostat and at higher temperatures, 1.2 to 4.09 K, in the liquid–helium temperature cryostat. The Cs sample was obtained from a commercial source of 99.8 per cent purity. Filby determined the C_p values in the temperature ranges 0.4–1.5 K, 3–26 K and 20–320 K, using commercial samples of 99.9 per cent purity. These two sets of measurements are joined smoothly at 4 K. $S°(298.15\ K)$ is derived from the adopted heat capacities, based on $S°(0.20\ K) = 0.0002\ cal \cdot K^{-1} \cdot mol^{-1}$. Dauphinee[1] determined the heat capacities of Cs(cr) employing a sample badly contaminated with oxygen. In the temperature range of approximately 100 to 200 K, an anomaly of C_p curve somewhat similar to those found for sodium and potassium was reported. This anomaly was not observed by Filby who used the higher purity cesium sample. The C_p values reported by Dauphines are lower than the adopted ones by about 0.5 to 1.5 per cent in the temperatures 55 to 220 K; above 270 K his reported heat capacities are unreasonably high. Therefore the data are not adopted for evaluation. McCollum[2] calculated the Debye θ values from the measured low temperature heat capacities and plotted them, since no numerical data were reported these were not used. The low temperature C_p values determined by Martin[3] and Morgan[6] are in good agreement with the adopted ones.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference between $\Delta_f H°(298.15\ K)$ for Cs(g) and Cs(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.717	0.	0.	0.
100	25.812	54.952	110.635	−5.568	0.	0.	0.
200	27.804	73.453	87.892	−2.888	0.	0.	0.
250	29.201	79.784	85.656	−1.468	0.	0.	0.
298.15	32.195	85.147	85.147	0.	0.	0.	0.
300	32.355	85.347	85.148	0.060	0.	0.	0.
301.550	32.501	85.514	85.149	0.110	--- CRYSTAL <--> LIQUID ---		
350	34.840	90.550	85.553	1.749	−2.005	0.331	−0.049
400	36.066	95.290	86.479	3.524	−1.815	0.653	−0.085
450	36.777	99.582	87.700	5.347	−1.563	0.946	−0.110
500	37.196	103.480	89.086	7.197	−1.274	1.210	−0.126
600	37.530	110.295	92.069	10.935	−0.643	1.648	−0.144
700	37.614	116.087	95.097	14.693	0.018	1.978	−0.148
800	37.635	121.111	98.042	18.455	0.687	2.212	−0.144
900	37.656	125.545	100.856	22.220	1.358	2.363	−0.137
1000	37.656	129.513	103.527	25.986	−65.103	6.138	−0.321

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K)$ = [92.069] $J·K^{-1}·mol^{-1}$
T_{fus} = 301.55 ± 0.01 K

$\Delta_f H°(298.15\ K)$ = [2.087] $kJ·mol^{-1}$
$\Delta_{fus}H°(301.55\ K)$ = 2.087 ± 0.004 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(Cs, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°(301.55\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The enthalpies of Cs(l) have been measured by Tepper *et al.*,[1] Achener,[2] and Lemmon *et al.*,[3] using drop calorimetry. Lemmon *et al.* used a cesium sample of 99.994 per cent purity and encapsulated in Nb–1Zr alloy. They found that Cs(l) does not behave as a normal liquid from about 100–300°C. The thermal conductivity measurements of Cs(l) show a change of slope at about 200°C and its electrical resistivity also shows scatter in this region. The heat capacities, 301.55–1435.2 K, derived from the reported enthalpies (corrected for vapor condensation), are consistent with the low temperature heat capacity data on Cs(cr) at 298.15 K and are adopted.

Tepper *et al.* measured the enthalpies in the temperature range 351.1–1238 K. The reported enthalpy values are considerably higher, over 20 per cent, at the lower end of the measured temperature range than the adopted ones. However, the agreement becomes better at the higher temperature end. Achener determined the enthalpies of Cs(l) at the temperatures 340.1–1175.7 K. Using the reported enthalpies, the average heat capacity is derived to be 9.75 $kcal·mol^{-1}$, which is unreasonably high by comparison with those for the other alkali metals. The above two sets of data are not used for evaluation. The enthalpies of Cs(l), 773–1423 K, were also measured by Shapiro.[4] [and quoted by 3] The derived constant heat capacity, 7.60 $cal·mol^{-1}$, is in reasonable agreement with the adopted ones.

Heat capacities of Cs(l), 301.55–373.2 K, were reported by Filby,[5] 301.55–320 K, Dauphinee,[6] 310–320 K, and Rengade,[7] 301.7–373.2 K. The values obtained are consistent with the adopted ones.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point and enthalpy of melting have been determined by many investigators. The results reported are presented in the table below. The adopted T_{fus} and $\Delta_{fus}H°$ are obtained from.[5] The two determinations of fraction melted against temperature are in very good agreement with one another and lead to a linear plot of reciprocal fraction melted against temperature thus indicating that the major impurity is solid insoluble. This is confirmed by a graph of excess heat capacity against the reciprocal of $(T_0-T)^2$, where T_0 is the melting point, which indicates an impurity (mainly oxygen) concentration of 0.06 atomic per cent.

T_{fus}/K	$\Delta_{fus}H°$, $kcal·mol^{-1}$	References
299.52	0.496	M. Eckardt and E. Graefe, Z. Anorg. Chem. **23**, 378 (1900)
301.35	—	A. Guntz and W. Broniewski, J. Chim. Phys. **7**, 474 (1909).
301.60 ± 0.05	0.500	E. Rengade[7]
301.75	—	J. H. Boer, J. Broos and H. Emmens, Z. Anorg. Chem. **191**, 118 (1930).
301.45	—	E. Rinck, Compt. Rend. **199**, 1217 (1934).
301.95 ± 0.1	—	L. Losana, Gazz. Chim. Ital. **65**, 855 (1935).
301.75	—	J. B. Taylor and J. Langmuir, Phys. Rev. **51**, 759 (1937).
301.79 ± 0.17	—	K. Clusius and H. Stern, Z. Angew. Physik **6**, 194 (1954).
—	0.510	W. D. Weatherford, Jr., *et al.*, WADD Tech. Rept. 61–96, November 1961.
301.67	0.470	A. W. Lemmon *et al.*[3]
301.55 ± 0.01	0.499 ± 0.01	J. D. Filby and D. L. Martin.[5]

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the reaction Cs(l) = Cs(g) is zero. The differences between $\Delta_f H°$(Cs, g) and $\Delta_f H°$(Cs, l) at T_{vap} is $\Delta_{vap}H°$. Due to the presence of dimer (Cs_2) in the vapor, the boiling point (1 atm) of Cs(l) is calculated to be 941.3 K at which the vapor mixture contains 0.835 mol of monomer/mol of Cs(l) vaporized, or 9.0 per cent of dimer. The corresponding enthalpy of vaporization is evaluated as 15.26 $kcal·mol^{-1}$ of vapor mixture.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	32.439	92.069	92.069	0.	2.087	0.024	−0.004
300	32.413	92.269	92.069	0.060	2.087	0.011	−0.002
301.550	32.393	92.436	92.071	0.110	--- CRYSTAL <--> LIQUID ---		
350	31.898	97.225	92.462	1.667	0.	0.	0.
400	31.518	101.458	93.328	3.252	0.	0.	0.
450	31.310	105.158	94.441	4.822	0.	0.	0.
500	31.154	108.448	95.680	6.384	0.	0.	0.
600	30.999	114.113	98.295	9.491	0.	0.	0.
700	30.941	118.887	100.905	12.587	0.	0.	0.
800	30.932	123.017	103.416	15.681	0.	0.	0.
900	30.957	126.662	105.801	18.775	0.	0.	0.
947.967	30.976	128.270	106.897	20.260	----- FUGACITY = 1 bar -----		
1000	30.999	129.926	108.053	21.873	−67.129	3.699	−0.193
1100	31.054	132.883	110.178	24.975	−66.105	10.733	−0.510
1200	31.116	135.587	112.184	28.084	−65.075	17.673	−0.769
1300	31.188	138.081	114.082	31.199	−64.040	24.526	−0.985
1400	31.263	140.395	115.879	34.321	−62.998	31.300	−1.168
1500	31.342	142.554	117.587	37.452	−61.950	37.999	−1.323

PREVIOUS: CURRENT: June 1968

0	to	301.55	K crystal
above		301.55	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−7.717	0.	0.	0.
100	25.812	54.952	110.635	−5.568	0.	0.	0.
200	27.804	73.453	87.892	−2.888	0.	0.	0.
250	29.201	79.784	85.656	−1.468	0.	0.	0.
298.15	32.195	85.147	85.147	0.	0.	0.	0.
300	32.355	85.347	85.148	0.060	0.	0.	0.
301.550	32.501	85.514	85.149	0.110	CRYSTAL <--> LIQUID TRANSITION		
301.550	32.393	92.436	85.149	2.197			
350	31.898	97.225	86.498	3.754	0.	0.	0.
400	31.518	101.458	88.110	5.339	0.	0.	0.
450	31.310	105.158	89.803	6.910	0.	0.	0.
500	31.154	108.448	91.506	8.471	0.	0.	0.
600	30.999	114.113	94.817	11.578	0.	0.	0.
700	30.941	118.887	97.923	14.674	0.	0.	0.
800	30.932	123.017	100.808	17.768	0.	0.	0.
900	30.957	126.662	103.482	20.862	0.	0.	0.
947.967	30.976	128.270	104.696	22.348	----- FUGACITY = 1 bar -----		
1000	30.999	129.926	105.966	23.960	−67.129	3.699	−0.193
1100	31.054	132.883	108.280	27.062	−66.105	10.733	−0.510
1200	31.116	135.587	110.445	30.171	−65.075	17.673	−0.769
1300	31.188	138.081	112.476	33.286	−64.040	24.526	−0.985
1400	31.263	140.395	114.389	36.409	−62.998	31.300	−1.168
1500	31.342	142.554	116.195	39.539	−61.950	37.999	−1.323

PREVIOUS: CURRENT: June 1968

IP(Cs, g) = 31406.432 ± 0.010 cm^{-1}
$S°(298.15\ K)$ = 175.599 ± 0.025 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = 78.0 ± 1.0 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 76.5 ± 1.0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.0	2
$^2P_{1/2}$	11178.24	2
$^2P_{3/2}$	11732.35	4
$^2S_{1/2}$	18535.51	2
$^2P_{3/2}$	31383.05	4
IP	31406.432	

Enthalpy of Formation

The enthalpy of formation of cesium gas is chosen to be the value recommended by CODATA.[1] This value was obtained from 2nd and 3rd law treatments of vapor pressure data. The reported vapor pressure were corrected for the effects of Cs(g), using D_0^0 = 38.02 $kJ·mol^{-1}$. At higher pressures an alternate virial treatment was employed. As stated by CODATA,[1] the selected value is the weighted average of the 3rd law values of $\Delta_{sub}H°(298.15\ K)$ from the following:

Source	$\Delta_{sub}H°(298.15\ K)$, $kJ·mol^{-1}$
Taylor and Langmuir[2]	76.71 ± 0.64
Bonilla *et al.*[3]	76.20 ± 1.28
Achener[4]	76.66 ± 1.08
Tepper *et al.*[5]	78.08 ± 1.05
Bohdansky and Schins[6]	76.10 ± 0.95
Stone *et al.*[7]	76.52 ± 1.08
Buck and Pauly[8]	76.77 ± 0.75
Shpil'rain and Belova[9]	76.62 ± 1.06
Volyak *et al.*[10]	76.48 ± 0.77
Novikov and Rosupkin[11]	76.57 ± 1.19
Ewing *et al.*[12]	76.44 ± 1.48
Shpil'rain *et al.*[13]	76.50 ± 1.12
Schins *et al.*[14]	76.34 ± 0.90
Shpil'rain and Nikanorov[15]	76.46 ± 1.21
Behrens *et al.*[16]	77.22 ± 1.15

The 2nd law calculations from the above sources led to values somewhat more positive[1]

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP–kT) technique as the cutoff procedure in the energy level summation.[19]

The lowest lying levels for these metals [14904 cm^{-1} (Li), 16956 cm^{-1} (Na), 12985 cm^{-1} (K), 12578 cm^{-1} (Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm^{-1} for Li to 31406.1 cm^{-1} for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.[17]

The atomic energy levels have been taken from the compilation of Moore.[18,19] Our calculated values for the thermal functions are similar to those recommended by CODATA.[1] They do differ for two reasons, however. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 $J·K^{-1}·mol^{-1}$, presumably due to the use of slightly different values for auxiliary data.

References

[1] J. D. Cox, Chairman, CODATA Task Group on Key Values for Thermodynamics, CODATA Special Report No. 8, (1980).

Continued on page 1003

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	78.019	78.019	INFINITE
100	20.786	152.892	194.080	−4.119	77.950	68.156	−35.601
200	20.786	167.300	177.501	−2.040	77.348	58.578	−15.299
250	20.786	171.938	175.942	−1.001	76.967	53.929	−11.268
298.15	20.786	175.599	175.599	0.	76.500	49.532	−8.678
300	20.786	175.728	175.600	0.038	76.479	49.364	−8.595
350	20.786	178.932	175.853	1.078	73.823	45.226	−6.750
400	20.786	181.708	176.415	2.117	73.278	41.178	−5.377
450	20.786	184.156	177.142	3.156	72.747	37.198	−4.318
500	20.786	186.346	177.955	4.196	72.225	33.276	−3.476
600	20.786	190.136	179.679	6.274	71.196	25.583	−2.227
700	20.786	193.340	181.407	8.353	70.178	18.061	−1.348
800	20.786	196.115	183.076	10.431	69.164	10.685	−0.698
900	20.786	198.564	184.664	12.510	68.148	3.436	−0.199
947.967	20.786	199.643	185.395	13.507	----- FUGACITY = 1 bar -----		
1000	20.786	200.754	186.165	14.589	0.	0.	0.
1100	20.788	202.735	187.583	16.667	0.	0.	0.
1200	20.791	204.544	188.922	18.746	0.	0.	0.
1300	20.799	206.208	190.189	20.826	0.	0.	0.
1400	20.814	207.750	191.389	22.906	0.	0.	0.
1500	20.841	209.187	192.528	24.989	0.	0.	0.
1600	20.886	210.533	193.611	27.075	0.	0.	0.
1700	20.952	211.802	194.645	29.167	0.	0.	0.
1800	21.048	213.002	195.631	31.267	0.	0.	0.
1900	21.178	214.143	196.576	33.378	0.	0.	0.
2000	21.349	215.233	197.482	35.504	0.	0.	0.
2100	21.564	216.280	198.352	37.649	0.	0.	0.
2200	21.830	217.289	199.190	39.818	0.	0.	0.
2300	22.150	218.266	199.998	42.017	0.	0.	0.
2400	22.527	219.217	200.779	44.250	0.	0.	0.
2500	22.960	220.145	201.535	46.523	0.	0.	0.
2600	23.456	221.055	202.269	48.844	0.	0.	0.
2700	24.016	221.950	202.981	51.217	0.	0.	0.
2800	24.639	222.835	203.674	53.649	0.	0.	0.
2900	25.326	223.711	204.350	56.146	0.	0.	0.
3000	26.082	224.582	205.010	58.716	0.	0.	0.
3100	26.905	225.451	205.656	61.365	0.	0.	0.
3200	27.796	226.319	206.288	64.099	0.	0.	0.
3300	28.599	227.175	206.907	66.885	0.	0.	0.
3400	29.572	228.043	207.516	69.793	0.	0.	0.
3500	30.600	228.915	208.115	72.801	0.	0.	0.
3600	31.680	229.792	208.705	75.914	0.	0.	0.
3700	32.770	230.671	209.286	79.125	0.	0.	0.
3800	33.902	231.557	209.860	82.449	0.	0.	0.
3900	35.036	232.447	210.428	85.875	0.	0.	0.
4000	36.250	233.349	210.989	89.439	0.	0.	0.
4100	37.488	234.259	211.546	93.126	0.	0.	0.
4200	38.744	235.178	212.097	96.938	0.	0.	0.
4300	40.010	236.104	212.645	100.875	0.	0.	0.
4400	40.717	236.965	213.181	104.647	0.	0.	0.
4500	40.901	237.756	213.706	108.229	0.	0.	0.
4600	41.940	238.667	214.238	112.371	0.	0.	0.
4700	42.950	239.580	214.768	116.616	0.	0.	0.
4800	43.924	240.494	215.294	120.960	0.	0.	0.
4900	44.859	241.409	215.818	125.399	0.	0.	0.
5000	45.748	242.325	216.339	129.930	0.	0.	0.
5100	46.588	243.239	216.857	134.547	0.	0.	0.
5200	46.722	244.034	217.358	138.714	0.	0.	0.
5300	47.407	244.931	217.870	143.421	0.	0.	0.
5400	47.729	245.763	218.372	147.915	0.	0.	0.
5500	48.117	246.611	218.873	152.560	0.	0.	0.
5600	48.599	247.483	219.376	157.396	0.	0.	0.
5700	49.022	248.347	219.877	162.278	0.	0.	0.
5800	49.385	249.203	220.375	167.199	0.	0.	0.
5900	49.689	250.049	220.871	172.153	0.	0.	0.
6000	49.935	250.887	221.364	177.135	0.	0.	0.

PREVIOUS: June 1968 (1 atm) CURRENT: December 1983 (1 bar)

IP(Cs^+, g) = 202263 ± 2 cm^{-1}
$S°$(298.15 K) = 169.836 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 453.72 ± 2.1 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [458.402] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

$\Delta_f H°(Cs^+, g, 0 K)$ is calculated from $\Delta_f H°(Cs, g, 0 K)$[1] using the spectroscopic value of IP(Cs) = 31406.432 ± 0.010 cm^{-1}(375.704 ± 0.001 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Cs^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Cs, g, 0 K)$ by using IP(Cs) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Cs(g), Cs^+(g), and e^-(ref). $\Delta_f H°(Cs \rightarrow Cs^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state; the first excited state is approximately 107392 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

[1]JANAF Thermochemical Tables: Cs(g), 6–30–68; e^-(ref), 3–31–82.
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[6]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–35, Volume III, (1970) [Reprint of NBS Circular 467, Volume III, 1958].
[7]J. R. Downey, Jr., The Dow Chemical Company, AFOSR–TR–78–0960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	453.724		
100	20.786	147.129	188.317	−4.119			
200	20.786	161.537	171.738	−2.040			
250	20.786	166.175	170.178	−1.001			
298.15	20.786	169.836	169.836	0.	458.402	426.897	−74.791
300	20.786	169.965	169.837	0.038	458.419	426.701	−74.295
350	20.786	173.169	170.090	1.078	456.803	421.714	−62.937
400	20.786	175.945	170.652	2.117	457.297	416.667	−54.411
450	20.786	178.393	171.379	3.156	457.805	411.558	−47.772
500	20.786	180.583	172.192	4.196	458.322	406.392	−42.456
600	20.786	184.373	173.915	6.274	459.372	395.908	−34.467
700	20.786	187.577	175.644	8.353	460.433	385.247	−28.747
800	20.786	190.352	177.313	10.431	461.497	374.433	−24.448
900	20.786	192.801	178.900	12.510	462.560	363.486	−21.096
1000	20.786	194.991	180.402	14.589	396.491	356.121	−18.602
1100	20.786	196.972	181.820	16.667	398.569	351.983	−16.714
1200	20.786	198.780	183.159	18.746	400.647	347.656	−15.133
1300	20.786	200.444	184.425	20.824	402.725	343.156	−13.788
1400	20.786	201.985	185.625	22.903	404.802	338.496	−12.629
1500	20.786	203.419	186.764	24.982	406.876	333.687	−11.620
1600	20.786	204.760	187.847	27.060	408.947	328.741	−10.732
1700	20.786	206.020	188.880	29.139	411.013	323.664	−9.945
1800	20.786	207.208	189.865	31.217	413.070	318.467	−9.242
1900	20.786	208.332	190.808	33.296	415.116	313.155	−8.609
2000	20.786	209.398	191.711	35.375	417.148	307.736	−8.037
2100	20.786	210.413	192.578	37.453	419.160	302.216	−7.517
2200	20.786	211.379	193.410	39.532	421.148	296.601	−7.042
2300	20.786	212.303	194.212	41.610	423.106	290.896	−6.606
2400	20.786	213.188	194.984	43.689	425.030	285.106	−6.205
2500	20.786	214.037	195.730	45.768	426.914	279.237	−5.834
2600	20.786	214.852	196.449	47.846	428.751	273.293	−5.491
2700	20.786	215.636	197.146	49.925	430.535	267.280	−5.171
2800	20.786	216.392	197.820	52.004	432.260	261.202	−4.873
2900	20.786	217.122	198.473	54.082	433.920	255.063	−4.594
3000	20.786	217.826	199.106	56.161	435.508	248.868	−4.333
3100	20.786	218.508	199.721	58.239	437.016	242.622	−4.088
3200	20.786	219.168	200.319	60.318	438.439	236.328	−3.858
3300	20.786	219.807	200.899	62.397	439.810	229.988	−3.640
3400	20.786	220.428	201.465	64.475	441.060	223.611	−3.435
3500	20.786	221.031	202.015	66.554	442.209	217.198	−3.242
3600	20.786	221.616	202.552	68.632	443.252	210.755	−3.058
3700	20.786	222.186	203.075	70.711	444.198	204.282	−2.884
3800	20.786	222.740	203.585	72.790	445.032	197.785	−2.719
3900	20.786	223.280	204.083	74.868	445.763	191.267	−2.562
4000	20.786	223.806	204.569	76.947	446.356	184.734	−2.412
4100	20.786	224.319	205.045	79.025	446.826	178.187	−2.270
4200	20.786	224.820	205.510	81.104	447.172	171.631	−2.135
4300	20.786	225.309	205.965	83.183	447.392	165.067	−2.005
4400	20.786	225.787	206.410	85.261	447.777	158.467	−1.881
4500	20.786	226.254	206.846	87.340	448.353	151.826	−1.762
4600	20.786	226.711	207.272	89.418	448.368	145.236	−1.649
4700	20.786	227.158	207.691	91.497	448.280	138.647	−1.541
4800	20.786	227.596	208.101	93.576	448.093	132.061	−1.437
4900	20.786	228.024	208.503	95.654	447.811	125.480	−1.338
5000	20.786	228.444	208.898	97.733	447.438	118.905	−1.242
5100	20.786	228.856	209.285	99.811	446.978	112.339	−1.151
5200	20.786	229.260	209.665	101.890	446.968	105.705	−1.062
5300	20.786	229.656	210.039	103.969	446.418	99.147	−0.977
5400	20.786	230.044	210.406	106.047	446.081	92.558	−0.895
5500	20.786	230.426	210.766	108.126	445.593	85.992	−0.817
5600	20.786	230.800	211.121	110.204	444.914	79.460	−0.741
5700	20.786	231.168	211.469	112.283	444.190	72.940	−0.668
5800	20.786	231.529	211.812	114.362	443.426	66.433	−0.598
5900	20.786	231.885	212.149	116.440	442.629	59.940	−0.531
6000	20.786	232.234	212.481	118.519	441.805	53.461	−0.465

PREVIOUS: December 1970 (1 atm) CURRENT: December 1983 (1 bar)

EA(Cs, g) = 0.471630 ± 0.000025 eV
$S°(298.15\ K)$ = 169.836 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 32.51 ± 0.5 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [24.798] $kJ·mol^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for $Cs^-(g)$ is calculated from the adopted electron affinity, EA(Cs, g) = 0.471630 ± 0.000025 eV, (45.505 ± 0.002 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[7] was measured by a tunable laser photodetachment threshold technique.[4,5] Additional discussion on $Cs^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[1,7] Rosenstock *et al.*,[2] and Massey.[3]

$\Delta_f H°(Cs^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Cs, g, 0\ K)$ by using EA(Cs, g) with JANAF[6] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for $Cs^-(g)$, Cs(g), and e^-(ref). $\Delta_r H°(Cs^- \rightarrow Cs + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[2] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for $Cs^-(g)$ is given by Hotop and Lineberger,[1,7] and Rosenstock *et al.*[2] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

[1] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
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[7] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	32.514		
100	20.786	147.129	188.317	−4.119			
200	20.786	161.537	171.738	−2.040			
250	20.786	166.175	170.179	−1.001			
298.15	20.786	169.836	169.836	0.	24.798	5.802	−1.017
300	20.786	169.965	169.837	0.038	24.738	5.685	−0.990
350	20.786	173.169	170.090	1.078	21.043	2.972	−0.444
400	20.786	175.945	170.652	2.117	19.458	0.499	−0.065
450	20.786	178.393	171.379	3.156	17.888	−1.777	0.206
500	20.786	180.583	172.192	4.196	16.327	−3.878	0.405
600	20.786	184.373	173.916	6.274	13.220	−7.627	0.664
700	20.786	187.577	175.644	8.353	10.123	−10.857	0.810
800	20.786	190.352	177.313	10.431	7.030	−13.642	0.891
900	20.786	192.801	178.901	12.510	3.935	−16.041	0.931
1000	20.786	194.991	180.402	14.589	−66.291	−14.395	0.752
1100	20.786	196.972	181.820	16.667	−68.370	−9.105	0.432
1200	20.786	198.780	183.159	18.746	−70.449	−3.625	0.158
1300	20.786	200.444	184.425	20.824	−72.528	2.028	−0.081
1400	20.786	201.985	185.625	22.903	−74.609	7.841	−0.293
1500	20.786	203.419	186.764	24.982	−76.691	13.803	−0.481
1600	20.786	204.760	187.848	27.060	−78.777	19.904	−0.650
1700	20.786	206.020	188.880	29.139	−80.869	26.135	−0.803
1800	20.786	207.208	189.865	31.217	−82.969	32.490	−0.943
1900	20.786	208.332	190.808	33.296	−85.080	38.962	−1.071
2000	20.786	209.398	191.711	35.375	−87.206	45.546	−1.190
2100	20.786	210.413	192.578	37.453	−89.351	52.236	−1.299
2200	20.786	211.380	193.411	39.532	−91.520	59.029	−1.402
2300	20.786	212.304	194.212	41.610	−93.719	65.921	−1.497
2400	20.786	213.188	194.984	43.689	−95.952	72.910	−1.587
2500	20.786	214.037	195.730	45.768	−98.226	79.992	−1.671
2600	20.786	214.852	196.450	47.846	−100.546	87.167	−1.751
2700	20.786	215.636	197.146	49.925	−102.919	94.431	−1.827
2800	20.786	216.392	197.820	52.004	−105.351	101.785	−1.899
2900	20.786	217.122	198.473	54.082	−107.848	109.226	−1.967
3000	20.786	217.826	199.106	56.161	−110.418	116.755	−2.033
3100	20.786	218.508	199.721	58.239	−113.067	124.371	−2.096
3200	20.786	219.168	200.319	60.318	−115.801	132.074	−2.156
3300	20.786	219.808	200.900	62.397	−118.587	139.860	−2.214
3400	20.786	220.428	201.465	64.475	−121.495	147.735	−2.270
3500	20.786	221.031	202.015	66.554	−124.503	155.697	−2.324
3600	20.786	221.616	202.552	68.632	−127.617	163.747	−2.376
3700	20.786	222.186	203.075	70.711	−130.828	171.883	−2.427
3800	20.786	222.740	203.585	72.790	−134.151	180.108	−2.476
3900	20.786	223.280	204.083	74.868	−137.578	188.420	−2.524
4000	20.786	223.806	204.570	76.947	−141.142	196.824	−2.570
4100	20.786	224.319	205.045	79.025	−144.828	205.319	−2.616
4200	20.786	224.820	205.510	81.104	−148.640	213.905	−2.660
4300	20.786	225.309	205.965	83.183	−152.578	222.583	−2.704
4400	20.786	225.787	206.410	85.261	−156.349	231.321	−2.746
4500	20.786	226.254	206.846	87.340	−159.931	240.113	−2.787
4600	20.786	226.711	207.273	89.418	−164.073	249.048	−2.828
4700	20.786	227.158	207.691	91.497	−168.318	258.075	−2.868
4800	20.786	227.596	208.101	93.576	−172.662	267.193	−2.908
4900	20.786	228.025	208.503	95.654	−177.101	276.402	−2.946
5000	20.786	228.445	208.898	97.733	−181.632	285.703	−2.985
5100	20.786	228.856	209.285	99.811	−186.249	295.096	−3.022
5200	20.786	229.260	209.666	101.890	−190.416	304.502	−3.059
5300	20.786	229.656	210.039	103.969	−195.123	314.064	−3.095
5400	20.786	230.044	210.406	106.047	−199.618	323.673	−3.131
5500	20.786	230.426	210.766	108.126	−204.262	333.383	−3.166
5600	20.786	230.800	211.121	110.204	−209.099	343.202	−3.201
5700	20.786	231.168	211.469	112.283	−213.980	353.107	−3.236
5800	20.786	231.530	211.812	114.362	−218.901	363.099	−3.270
5900	20.786	231.885	212.149	116.440	−223.855	373.176	−3.304
6000	20.786	232.234	212.481	118.519	−228.837	383.337	−3.337

PREVIOUS: CURRENT: December 1983 (1 bar)

$S°(298.15\ K) = [88.3 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 976\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -554.7 \pm 2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 21.7\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution ($\Delta_{sol}H°$) of CsF(cr) in water at 298.15 K has been carefully determined with an adiabatic calorimeter by Somsen.[1] Based on the reported value, $\Delta_{sol}H°(298.15\ K) = -8.62 \pm 0.04\ kcal \cdot mol^{-1}$ and $\Delta_f H°(298.15\ K) = -61.69$[2] and $-79.5\ kcal \cdot mol^{-1}$ [3] for $Cs^+(ag, \infty)$ and $F^-(ag, \infty)$, respectively, the enthalpy of formation for CsF(cr) is calculated to be $-132.57\ kcal \cdot mol^{-1}$ which is adopted.

The value, $\Delta_{sol}H°(298.15\ K) = -8.81 \pm 0.2\ kcal \cdot mol^{-1}$ for CsF(cr), was reported by Parker[4] which is in agreement with the value measured by Somsen.[1]

Heat Capacity and Entropy

The heat capacities of CsF(cr) are estimated according to the method of Kristov,[5] based on $H°(976\ K) - H°(298.15\ K) = 9.4\ kcal \cdot mol^{-1}$ reported by Dworkin.[6] The entropy, $S°(298.15\ K)$, is estimated such that the calculated and observed vapor pressures are in good agreement (refer to CsF(g) and Cs_2F_2(g) tables for details).

Fusion Data

T_{fus} and $\Delta_{fus}H°$ are obtained from Bredig[7] and Dworkin[8]. Buhalova[9] reported $T_{fus} = 958\ K$, which is not adopted.

Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ is calculated as the difference between $\Delta_f H°(298.15\ K)$ for CsF(g) and CsF(cr).

References

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[9] G. A. Bukhalova and D. V. Sementsova, Russ. J. Inorg. Chem. **10**, 1027 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	51.965	88.282	88.282	0.	−554.673	−525.377	92.044
300	52.007	88.604	88.283	0.096	−554.665	−525.195	91.445
400	53.764	103.805	90.344	5.384	−556.266	−514.758	67.221
500	55.564	115.996	94.294	10.851	−555.615	−504.454	52.700
600	57.363	126.286	98.790	16.497	−554.811	−494.295	43.032
700	59.120	135.260	103.372	22.322	−553.860	−484.282	36.138
800	60.877	143.269	107.867	28.321	−552.758	−474.415	30.976
900	62.634	150.541	112.211	34.497	−551.504	−464.696	26.970
976.000	63.952	155.672	115.397	39.308	--- CRYSTAL <---> LIQUID ---		
1000	64.350	157.231	116.383	40.848	−617.224	−451.425	23.580
1100	65.856	163.438	120.382	47.362	−614.649	−434.969	20.655
1200	66.944	169.217	124.213	54.004	−611.958	−418.752	18.228
1300	67.697	174.607	127.885	60.739	−609.188	−402.764	16.183
1400	68.157	179.642	131.404	67.533	−606.370	−386.991	14.439
1500	68.492	184.356	134.779	74.366	−603.525	−371.420	12.934
1600	68.743	188.785	138.017	81.228	−600.663	−356.039	11.623
1700	68.910	192.958	141.127	88.112	−597.794	−340.838	10.473
1800	68.994	196.899	144.117	95.007	−594.928	−325.806	9.455
1900	69.036	200.631	146.994	101.909	−592.073	−310.933	8.548
2000	69.036	204.172	149.766	108.813	−589.236	−296.209	7.736

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = [90.099]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 976\ K$

$\Delta_f H°(298.15\ K) = [-543.849]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 21.7\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(CsF, l, 298.15 K) is calculated from $\Delta_f H°$(CsF, cr, 298.15 K) by adding $\Delta_{fus} H°$ and the difference enthalpy, $H°(976\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Dworkin[1] measured the heat capacity of CsF(l) at the melting point to be 17.7 $cal·K^{-1}·mol^{-1}$ which is adopted and assumed to be constant in the temperature range 298–3000 K.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 1504 K is the temperature at which the calculated vapor pressures of CsF(g) and Cs_2F_2(g) equal one atmosphere. The vapor composition at T_{vap} is calculated as CsF 80.3% and Cs_2F_2 19.7%. The enthalpy required to vaporize one mole of liquid to the above vapor mixture at T_{fus} is $\Delta_{vap} H°$.

T_{vap} has been observed as 1524 and 1526 K by Wartenberg[1] and Ruff,[2] respectively, which are in fair agreement with the calculated one, 1504 K.

References

[1]H. von Wartenberg and H. Schulz, Z. Elektrochem. **22**, 568 F(1921).
[2]O. Ruff, G. Schmidt and S. Mugdan, Z. anorg. allgem. Chem. **123**, 83 (1922).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	74.057	90.099	90.099	0.	−543.849	−515.094	90.242
300	74.057	90.557	90.101	0.137	−543.801	−514.916	89.655
400	74.057	111.862	93.005	7.543	−543.284	−504.999	65.946
500	74.057	128.387	98.491	14.948	−540.693	−495.728	51.788
600	74.057	141.890	104.633	22.354	−538.131	−486.976	42.395
700	74.057	153.305	110.792	29.760	−535.598	−478.651	35.717
800	74.057	163.194	116.738	37.165	−533.090	−470.687	30.733
900	74.057	171.917	122.394	44.571	−530.606	−463.036	26.874
976.000	74.057	177.921	126.487	50.199	--- CRYSTAL <---> LIQUID ---		
1000	74.057	179.720	127.743	51.977	−595.271	−451.961	23.608
1100	74.057	186.778	132.794	59.382	−591.804	−437.798	20.789
1200	74.057	193.222	137.565	66.788	−588.351	−423.950	18.454
1300	74.057	199.150	142.077	74.194	−584.909	−410.390	16.490
1400	74.057	204.638	146.352	81.599	−581.479	−397.094	14.816
1500	74.057	209.747	150.410	89.005	−578.062	−384.043	13.374
1600	74.057	214.527	154.270	96.411	−574.656	−371.220	12.119
1700	74.057	219.016	157.948	103.817	−571.265	−358.609	11.019
1800	74.057	223.249	161.459	111.222	−567.889	−346.197	10.046
1900	74.057	227.253	164.818	118.628	−564.530	−333.973	9.182
2000	74.057	231.052	168.035	126.034	−561.191	−321.924	8.408
2100	74.057	234.665	171.123	133.439	−557.874	−310.043	7.712
2200	74.057	238.110	174.090	140.845	−554.583	−298.319	7.083
2300	74.057	241.402	176.945	148.251	−551.320	−286.743	6.512
2400	74.057	244.554	179.697	155.656	−548.089	−275.310	5.992
2500	74.057	247.577	182.352	163.062	−544.894	−264.010	5.516
2600	74.057	250.482	184.917	170.468	−541.740	−252.837	5.080
2700	74.057	253.277	187.398	177.873	−538.630	−241.784	4.678
2800	74.057	255.970	189.799	185.279	−535.570	−230.846	4.306
2900	74.057	258.569	192.126	192.685	−532.565	−220.016	3.963
3000	74.057	261.079	194.383	200.090	−529.619	−209.289	3.644

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = [98.7 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1}(\alpha–\beta) = 410 \pm 1\ K$
$T_{trs2}(\beta–\gamma) = 493 \pm 1\ K$
$T_{fus} = 588 \pm 1\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -416.73 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = 1.30 \pm 0.13\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 6.07 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 4.56 \pm 0.42\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of CsOH(cr) is obtained from the enthalpy of hydrolysis of metallic cesium, the enthalpy of solution of the hydroxide in water, and appropriate auxiliary data.

Beketov[1] and de Forcrand[2] determined the enthalpy of solution of crystalline CsOH in water. Parker[3] analyzed these data and selected $\Delta_{sol} H°(CsOH, cr) = -17.1 \pm 0.2\ kcal \cdot mol^{-1}$. This value is adopted here.

Discordant values for the enthalpy of hydrolysis of metallic cesium have been reported by Vorob'yev *et al.*[4] and Gunn.[5] For the reaction $Cs(cr) + (n+1)\ H_2O(l) = CsOH \cdot n\ H_2O + 0.5\ H_2(g)$, they reported enthalpies of hydrolysis of -46.5 ± 0.20 (n = 1030) and -48.346 ± 0.20 ($n = 3000$) $kcal \cdot mol^{-1}$, respectively. From these values $\Delta_f H°(CsOH \cdot \infty H_2O, 298.15\ K) = -114.82 \pm 0.20$ and $-116.661 \pm 0.020\ kcal \cdot mol^{-1}$ are calculated based on $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$.[6]

In both investigations the possibility of hydroxide and oxide contamination of the metal samples was reduced by repeated distillation of the metal under vacuum, and spectroscopic analysis of each sample indicated low concentrations of the lighter alkali metals. Vorob'yev *et al.*[4] determined the amount of reaction by both weighing the metal sample and titrating the final hydroxide solution. Gunn[5] determined the amount of reaction by both weighing the sample and recovering the hydrogen formed in the hydrolysis. The systematically high hydrogen yields (0.05–0.16%) obtained by Gunn[5] suggest the presence of lighter alkali metals in higher concentrations than indicated by the spectroscopic analysis of the cesium, and the flame– photometric analyses of the final hydroxide solutions. However, the presence of lighter alkali metals at these concentrations should not introduce any serious error in the enthalpy of hydrolysis, since their heats[5] are quite similar to cesium.

The major difference between the two measurements lies in the instrumentation used to investigate the reaction. Vorob'yev *et al.*[4] used a hermetically sealed static calorimeter which was not stirred. In the absence of proper agitation, temperature gradients and chemical inhomogeneities are likely to arise in the final state. Without any indication of the performance of this calorimeter, the results of Vorob'yev *et al.*[4] are questionable. On the other hand, Gunn [5] carried out the hydrolysis reaction in a closed bomb calorimeter, agitation being effected by rocking the assembly through an angle of approximately 150°.[5,8] Where comparisons are possible, all indications are that the results are quite reliable. Therefore, we adopt $\Delta_f H°(CsOH \cdot \infty H_2O, 298.15\ K) = -116.661 \pm 0.020\ kcal \cdot mol^{-1}$ from the work of Gunn.[5] Combining this result with the enthalpy of solution of CsOH(cr) given above, we derive $\Delta_f H°(CsOH, cr, 298.15\ K) = -99.6 \pm 0.2\ kcal \cdot mol^{-1}$ ($-416.73 \pm 0.8\ kJ \cdot mol^{-1}$).

Heat Capacity and Entropy

Heat capacities for CsOH(cr) over the entire temperature range 298–1000 K are estimated by comparison with similar data for the other alkali metal hydroxides and halides.[9] Likewise, $S°(298.15\ K)$ is estimated to be 23.6 $cal \cdot K^{-1} \cdot mol^{-1}$ (98.7 $J \cdot K^{-1} \cdot mol^{-1}$) for CsOH(cr) by comparison with similar data for the alkali metal halides and lighter hydroxides.[9]

Transition and Fusion Data

The temperatures and enthalpies of the polymorphic transitions and melting of CsOH(cr) are from the work of Reshetnikov and Baranskaya.[10] These data were determined thermographically with $\Delta_{fus} H = 1.575\ kcal \cdot mol^{-1}$ for NaOH(cr) as a standard.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ for the monomer and dimer are calculated from the adopted enthalpies of formation of the crystal and the respective gaseous species.

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[10]N. A. Reshetnikov and E. V. Baranskaya, Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol., **10**, 496 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	67.872	98.742	98.742	0.	−416.726	−370.716	64.948
300	67.990	99.163	98.744	0.126	−416.714	−370.431	64.498
400	74.392	119.617	101.489	7.251	−417.807	−354.453	46.287
410.000	74.990	121.461	101.954	7.998	ALPHA <--> BETA TRANSITION		
410.000	75.228	124.625	101.954	9.295			
493.000	82.174	139.114	107.010	15.827	BETA <--> GAMMA TRANSITION		
493.000	83.680	151.420	107.010	21.894			
500	83.680	152.600	107.640	22.480	−408.701	−339.169	35.433
588.000	83.680	166.166	115.411	29.844	--- GAMMA <--> LIQUID ---		
600	83.680	167.856	116.443	30.848	−406.484	−325.471	28.335
700	83.680	180.756	124.733	39.216	−404.309	−312.142	23.292
800	83.680	191.929	132.450	47.584	−402.179	−299.121	19.531
900	83.680	201.786	139.617	55.952	−400.095	−286.364	16.620
1000	83.680	210.602	146.282	64.320	−465.187	−270.138	14.111

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = [118.513]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-405.970]\ kJ·mol^{-1}$
$T_{fus} = 588 \pm 1\ K$ $\Delta_{fus}H° = 4.56 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(CsOH, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference enthalpy, $H°$(588 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ for liquid CsOH is estimated to be 19.5 $cal·K^{-1}·mol^{-1}$ by comparison with similar data for the other liquid alkali metal hydroxides [1]. It is assumed constant in the temperature range 298–2000 K.

$S°$(298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which $\Delta_r G°$ for the vaporization process is zero. The difference in the enthalpy of formation of CsOH(l) and CsOH(g) at the boiling point is the heat of vaporization.

Reference

[1]JANAF Thermochemical Tables: refer to all alkali metal hydroxide liquid tables.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	81.588	118.513	118.513	0.000	−405.970	−365.855	64.096
300	81.588	119.017	118.514	0.151	−405.933	−365.606	63.658
400	81.588	142.489	121.715	8.310	−405.992	−351.787	45.939
500	81.588	160.695	127.758	16.469	−403.956	−338.472	35.360
588.000	81.588	173.922	133.704	23.648	--- GAMMA <--> LIQUID ---		
600	81.588	175.570	134.524	24.627	−401.949	−325.564	28.343
700	81.588	188.147	141.309	32.786	−399.983	−312.989	23.356
800	81.588	199.041	147.860	40.945	−398.062	−300.694	19.633
900	81.588	208.651	154.091	49.104	−396.187	−288.636	16.752
1000	81.588	217.247	159.985	57.263	−461.488	−273.084	14.264
1100	81.588	225.023	165.549	65.421	−458.682	−254.380	12.080
1200	81.588	232.122	170.806	73.580	−455.916	−235.930	10.270
1300	81.588	238.653	175.777	81.739	−453.188	−217.708	8.748
1400	81.588	244.699	180.487	89.898	−450.499	−199.696	7.451
1500	81.588	250.328	184.957	98.057	−447.847	−181.874	6.333
1600	81.588	255.594	189.209	106.215	−445.234	−164.228	5.361
1700	81.588	260.540	193.261	114.374	−442.659	−146.744	4.509
1800	81.588	265.204	197.130	122.533	−440.125	−129.411	3.755
1900	81.588	269.615	200.830	130.692	−437.633	−112.217	3.085
2000	81.588	273.800	204.374	138.851	−435.187	−95.153	2.485

PREVIOUS: CURRENT: June 1971

0	to	410 K	crystal, alpha
410	to	493 K	crystal, beta
493	to	588 K	crystal, gamma
above		588 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	67.872	98.742	98.742	0.	−416.726	−370.716	64.948
300	67.990	99.163	98.744	0.126	−416.714	−370.431	64.498
400	74.392	119.617	101.489	7.251	−417.807	−354.453	46.287
410.000	74.990	121.461	101.954	7.998	ALPHA <--> BETA TRANSITION		
410.000	75.228	124.625	101.954	9.295			
493.000	82.174	139.114	107.010	15.827	BETA <--> GAMMA TRANSITION		
493.000	83.680	151.420	107.010	21.894			
500	83.680	152.600	107.640	22.480	−408.701	−339.169	35.433
588.000	83.680	166.166	115.411	29.844	GAMMA <--> LIQUID TRANSITION		
588.000	81.588	173.922	115.411	34.404			
600	81.588	175.570	116.598	35.383	−401.949	−325.564	28.343
700	81.588	188.147	125.944	43.542	−399.983	−312.989	23.356
800	81.588	199.041	134.415	51.701	−398.062	−300.694	19.633
900	81.588	208.651	142.140	59.860	−396.187	−288.636	16.752
1000	81.588	217.247	149.229	68.018	−461.488	−273.084	14.264
1100	81.588	225.023	155.771	76.177	−458.682	−254.380	12.080
1200	81.588	232.122	161.842	84.336	−455.916	−235.930	10.270
1300	81.588	238.653	167.503	92.495	−453.188	−217.708	8.748
1400	81.588	244.699	172.804	100.654	−450.499	−199.696	7.451
1500	81.588	250.328	177.787	108.812	−447.847	−181.874	6.333
1600	81.588	255.594	182.487	116.971	−445.234	−164.228	5.361
1700	81.588	260.540	186.934	125.130	−442.659	−146.744	4.509
1800	81.588	265.204	191.154	133.289	−440.125	−129.411	3.755
1900	81.588	269.615	195.169	141.448	−437.633	−112.217	3.085
2000	81.588	273.800	198.996	149.606	−435.187	−95.153	2.485

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = 254.78 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -254.9 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -259.4 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
335.6 (1)
306 (2)
[3610](1)

Ground State Quantum Weight: 1 σ=1
Point Group: $C_{\infty v}$
Bond Distances: Cs–O = 2.391 ± 0.002 Å: O–H = [0.96 ± 0.01] Å
Bond Angle: Cs–O–H = 180°
Rotational Constant: $B_0 = 0.184795\ cm^{-1}$

Enthalpy of Formation

Jensen and Padley[1] determined an equilibrium constant for the reaction Cs(g) + H_2O(g) = CsOH(g) + H(g) at 2475 K by atomic absorption spectroscopy in a hydrogen–oxygen–nitrogen flame. These workers pointed out that interference from ionization of the metal had introduced some uncertainty in their equilibrium data. Using all JANAF functions,[2] 3rd law analysis of the equilibrium constant gives $\Delta_f H°(298.15\ K) = 27.4\ kcal \cdot mol^{-1}$. This leads to an enthalpy of formation, $\Delta_f H°$(CsOH, g, 298.15 K) = −64.2 ± 3.0 $kcal \cdot mol^{-1}$, and a corresponding bond dissociation energy of 91 $kcal \cdot mol^{-1}$. Cotton and Jenkins[3] investigated the same equilibrium in a fuel–rich hydrogen–oxygen–nitrogen flame and eliminated the ionization problem by working at a lower temperature (1570 K). 3rd law analysis of their equilibrium data gives $\Delta_f H°(298.15\ K) = 28.9\ kcal \cdot mol^{-1}$ which results in $\Delta_f H°$(CsOH, g, 298.15 K) = −62.7 ± 2.0 $kcal \cdot mol^{-1}$ corresponding to $D_0°$(Cs–OH) = 89.6 $kcal \cdot mol^{-1}$. Smith and Sugden[4] had earlier reported a $D_0° = 91 \pm 1\ kcal \cdot mol^{-1}$ from flame studies. Electron impact studies[5,6] have also led to values for the bond dissociation energy of CsOH(g). This method resulted in values of 82 ± 3[5] and 86 ± 3 $kcal \cdot mol^{-1}$.[6]

Cotton and Jenkins[3] also reported bond dissociation energies for LiOH(g), KOH(g), and NaOH(g) which are in good agreement with JANAF enthalpy of formation data[7] for these hydroxides. Furthermore, the position of the hydroxides in the order of increasing bond dissociation energy established from their data, i.e. NaOH < KOH < RbOH < CsOH < LiOH, is that predicted by comparison with similar data on the stabilities of the alkali metal halides.[8] However, trends within the bond dissociation energies for the halides suggest that the value $D_0° = 89.6\ kcal \cdot mol^{-1}$ for CsOH may be slightly high. The difference in $D°$ for potassium and sodium compounds is from 0.1 $kcal \cdot mol^{-1}$ for the fluorides to 0.4 $kcal \cdot mol^{-1}$ for the chlorides more than the difference in $D_0°$ for the cesium and potassium compounds. Assuming this same trend in $D_0°$ is prevalent in the hydroxides as well, then $D_0°$(Cs–OH)–D (K–OH) must be less than 3.9 $kcal \cdot mol^{-1}$(see NaOH(g) table). We adopt $D_0°(CsOH) = 89.0 \pm 3.0\ kcal \cdot mol^{-1}$ which results in the difference $D_0°$(Cs–OH)–$D_0°$(K–OH) = 3.6 $kcal \cdot mol^{-1}$.[7] This adopted bond dissociation energy corresponds to $\Delta_f H°$(CsOH, g, 298.15 K) = −62.0 ± 3.0 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The microwave spectra of gaseous CsOH have been studied in a high temperature spectrometer by Kuczkowski *et al.*[9] and Lide *et al.*[10] The spectroscopic data were more consistent with patterns expected from a linear molecule, although a "quasilinear" structure could not be completely eliminated. Acquista *et al.*[11] observed the infrared spectra of CsOH and CsOD in an argon matrix at liquid hydrogen temperatures. The isotope shift of the bending mode, υ_2, was quite large (80 cm^{-1}), and the ratio of υ_2 for CsOH and CsOD was in excellent agreement with the value calculated for a linear molecule and a harmonic oscillator. The infrared results when used in combination with the microwave data indicate a linear equilibrium configuration for CsOH. We adopt this configuration along with the bond distances and angles determined by Lide *et al.*[10] from their microwave data .

The Cs–O stretching mode, υ_1, and the bending frequency, υ_2, are from the matrix isolation studies of Acquista *et al.*[11] The OH stretching frequency, υ_3, is an estimate from the recent work of Jensen.[12]

References

[1]D. E. Jensen and P. J. Padley, Trans. Faraday Soc., **62**, 2132 (1966).
[2]JANAF Thermochemical Tables: Cs(g), 6–30–68; H_2O(g), 3–31–61; H(g), 9–30–65.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.834	−254.950	−254.950	INFINITE
100	34.721	207.752	295.765	−8.801	−257.018	−258.596	135.077
200	45.601	235.675	259.221	−4.709	−258.408	−259.563	67.791
250	48.173	246.150	255.588	−2.360	−258.906	−259.793	54.281
298.15	49.723	254.778	254.778	0.	−259.408	−259.920	45.537
300	49.771	255.085	254.779	0.092	−259.430	−259.923	45.257
350	50.813	262.841	255.389	2.608	−262.071	−259.625	38.747
400	51.525	269.676	256.756	5.168	−262.572	−259.241	33.853
450	52.035	275.775	258.536	7.758	−263.041	−258.797	30.040
500	52.420	281.279	260.540	10.369	−263.493	−258.300	26.984
600	52.991	290.889	264.820	15.641	−264.372	−257.179	22.389
700	53.459	299.093	269.145	20.964	−265.242	−255.912	19.096
800	53.915	306.261	273.345	26.333	−266.112	−254.519	16.618
900	54.388	312.639	277.364	31.748	−266.981	−253.018	14.685
1000	54.877	318.394	281.183	37.211	−334.977	−247.721	12.940
1100	55.371	323.648	284.809	42.723	−334.817	−239.003	11.349
1200	55.857	328.487	288.249	48.285	−334.648	−230.300	10.025
1300	56.325	332.976	291.519	53.894	−334.470	−221.611	8.904
1400	56.769	337.167	294.632	59.549	−334.285	−212.936	7.945
1500	57.184	341.098	297.600	65.247	−334.094	−204.275	7.114
1600	57.568	344.801	300.435	70.985	−333.902	−195.627	6.387
1700	57.922	348.302	303.149	76.759	−333.711	−186.991	5.746
1800	58.246	351.622	305.750	82.568	−333.527	−178.366	5.176
1900	58.543	354.779	308.248	88.408	−333.355	−169.750	4.667
2000	58.813	357.789	310.651	94.276	−333.199	−161.143	4.209
2100	59.060	360.664	312.964	100.170	−333.066	−152.544	3.794
2200	59.285	363.417	315.196	106.087	−332.961	−143.950	3.418
2300	59.490	366.057	317.350	112.026	−332.892	−135.361	3.074
2400	59.677	368.593	319.433	117.985	−332.864	−126.773	2.759
2500	59.848	371.033	321.448	123.961	−332.883	−118.186	2.469
2600	60.005	373.383	323.401	129.954	−332.958	−109.597	2.202
2700	60.148	375.650	325.294	135.961	−333.094	−101.003	1.954
2800	60.279	377.840	327.132	141.983	−333.298	−92.404	1.724
2900	60.400	379.958	328.917	148.017	−333.577	−83.796	1.509
3000	60.511	382.007	330.653	154.063	−333.938	−75.177	1.309
3100	60.614	383.993	332.342	160.119	−334.388	−66.544	1.121
3200	60.708	385.919	333.986	166.185	−334.934	−57.896	0.945
3300	60.796	387.788	335.588	172.260	−335.542	−49.232	0.779
3400	60.876	389.604	337.150	178.344	−336.282	−40.545	0.623
3500	60.951	391.370	338.674	184.435	−337.133	−31.835	0.475
3600	61.021	393.088	340.162	190.534	−338.100	−23.099	0.335
3700	61.086	394.761	341.615	196.639	−339.175	−14.335	0.202
3800	61.146	396.391	343.035	202.751	−340.373	−5.541	0.076
3900	61.203	397.980	344.424	208.869	−341.685	3.286	−0.044
4000	61.255	399.530	345.782	214.992	−343.145	12.149	−0.159
4100	61.304	401.043	347.112	221.120	−344.739	21.051	−0.268
4200	61.350	402.521	348.413	227.252	−346.468	29.994	−0.373
4300	61.394	403.965	349.689	233.390	−348.334	38.979	−0.473
4400	61.434	405.377	350.938	239.531	−350.045	47.975	−0.570
4500	61.472	406.758	352.163	245.676	−351.576	56.979	−0.661
4600	61.508	408.110	353.365	251.825	−353.680	66.081	−0.750
4700	61.542	409.433	354.544	257.978	−355.897	75.230	−0.836
4800	61.573	410.729	355.701	264.134	−358.225	84.428	−0.919
4900	61.604	411.999	356.837	270.292	−360.659	93.675	−0.999
5000	61.632	413.244	357.953	276.454	−363.196	102.973	−1.076
5100	61.659	414.464	359.049	282.619	−365.831	112.322	−1.150
5200	61.684	415.662	360.126	288.786	−368.027	121.646	−1.222
5300	61.708	416.837	361.185	294.956	−370.775	131.089	−1.292
5400	61.731	417.991	362.226	301.128	−373.323	140.541	−1.359
5500	61.753	419.124	363.251	307.302	−376.033	150.058	−1.425
5600	61.773	420.237	364.258	313.478	−378.946	159.650	−1.489
5700	61.793	421.330	365.250	319.656	−381.917	169.294	−1.551
5800	61.811	422.405	366.226	325.836	−384.939	178.991	−1.612
5900	61.829	423.462	367.187	332.018	−388.007	188.740	−1.671
6000	61.846	424.501	368.134	338.202	−391.116	198.542	−1.728

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = [268.7 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 439.32 \pm 41.8\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [441.379]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
υ, cm^{-1}
[300](1)
[275](2)
[3600](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
Bond Distances: Cs–O = [2.40] Å; O–H = [1.03] Å
Bond Angle: Cs–O–H = [180] Å
Rotational Constant: B_O = [0.182583] cm^{-1}

Enthalpy of Formation

The appearance potential of CsOH⁺ has been determined by Emel'yanov *et al.*[1] as 7.21 ± 0.14 eV and by Gorokhov *et al.*[2] as 7.40 ± 0.15 eV. These values correspond to $\Delta_f H°(0\ K) = 166.3 \pm 3.0$ kcal·mol⁻¹ and 170.7 ± 5 kcal·mol⁻¹, respectively, for the process $e^- + CsOH(g) \rightarrow CsOH^+(g) + 2e$. Since there may be excess energy involved, we prefer the lower value. Combining this result with JANAF auxiliary data,[3] we derive $\Delta_f H°(CsOH^+, g, 0\ K) = 105 \pm 10$ kcal·mol⁻¹ (439.32 ± 41.8 kJ·mol⁻¹).

Heat Capacity and Entropy

The correlation diagram of Walsh[4] for HAB molecules predicts that CsOH⁺ (7 valence electrons) should be linear with the unpaired electron in a pi orbital. Therefore, we estimate the ground state of CsOH⁺ to be $^2\Pi$. CsOH⁺ is isoelectronic with OH[3] and SH.[3] A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with these isoelectronic molecules. The bonding in CsOH⁺ is assumed to be weakened relative to that in CsOH by the loss of the bonding electron from the neutral species. The vibrational frequencies are estimated from those for CsOH with somewhat lower values due to the weaker bonding. The Cs–O and O–H bond distances are increased slightly over those for CsOH.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.154	439.320		
100	36.400	220.076	310.754	−9.068			
200	46.942	249.166	273.215	−4.810			
250	49.177	259.903	269.510	−2.402			
298.15	50.492	268.686	268.686	0.	441.379	430.466	−75.416
300	50.532	268.998	268.686	0.093	441.398	430.398	−74.939
350	51.403	276.858	269.305	2.643	439.830	428.860	−64.004
400	51.993	283.762	270.690	5.229	440.394	427.255	−55.794
450	52.414	289.912	272.490	7.840	440.985	425.577	−49.400
500	52.733	295.451	274.514	10.469	441.590	423.833	−44.278
600	53.215	305.110	278.832	15.767	442.816	420.167	−36.579
700	53.628	313.345	283.188	21.110	444.044	416.295	−31.064
800	54.049	320.533	287.416	26.493	445.268	412.247	−26.917
900	54.498	326.925	291.458	31.920	446.489	408.046	−23.682
1000	54.971	332.691	295.297	37.394	380.582	407.409	−21.281
1100	55.452	337.953	298.939	42.915	382.829	409.983	−19.468
1200	55.929	342.798	302.395	48.484	385.084	412.352	−17.949
1300	56.390	347.293	305.678	54.100	387.348	414.532	−16.656
1400	56.827	351.488	308.802	59.761	389.618	416.538	−15.541
1500	57.236	355.423	311.780	65.465	391.892	418.382	−14.569
1600	57.616	359.130	314.625	71.207	394.169	420.073	−13.714
1700	57.966	362.633	317.347	76.987	396.442	421.623	−12.955
1800	58.287	365.956	319.956	82.800	398.709	423.039	−12.276
1900	58.580	369.115	322.461	88.643	400.964	424.329	−11.666
2000	58.848	372.127	324.869	94.515	403.202	425.500	−11.113
2100	59.092	375.004	327.189	100.412	405.417	426.561	−10.610
2200	59.315	377.758	329.425	106.333	407.604	427.516	−10.151
2300	59.518	380.399	331.584	112.274	409.755	428.373	−9.729
2400	59.703	382.936	333.671	118.236	411.864	429.137	−9.340
2500	59.873	385.377	335.691	124.215	413.926	429.814	−8.980
2600	60.027	387.728	337.648	130.210	415.932	430.410	−8.647
2700	60.169	389.996	339.545	136.220	417.877	430.930	−8.337
2800	60.300	392.187	341.386	142.243	419.754	431.379	−8.047
2900	60.419	394.305	343.174	148.279	421.555	431.762	−7.777
3000	60.529	396.355	344.913	154.327	423.274	432.084	−7.523
3100	60.631	398.342	346.605	160.385	424.904	432.351	−7.285
3200	60.725	400.268	348.252	166.453	426.439	432.566	−7.061
3300	60.811	402.138	349.857	172.529	427.911	432.732	−6.850
3400	60.892	403.955	351.421	178.615	429.251	432.858	−6.650
3500	60.967	405.721	352.947	184.708	430.480	432.945	−6.461
3600	61.036	407.439	354.437	190.808	431.593	433.000	−6.283
3700	61.101	409.113	355.892	196.915	432.598	433.024	−6.113
3800	61.161	410.743	357.315	203.028	433.480	433.023	−5.952
3900	61.218	412.332	358.705	209.147	434.249	432.998	−5.799
4000	61.271	413.883	360.065	215.271	434.869	432.958	−5.654
4100	61.322	415.397	361.396	221.401	435.356	432.904	−5.515
4200	61.369	416.875	362.700	227.536	435.707	432.839	−5.383
4300	61.414	418.319	363.976	233.675	435.922	432.769	−5.257
4400	61.456	419.732	365.228	239.818	436.291	432.660	−5.136
4500	61.496	421.113	366.454	245.966	436.840	432.513	−5.020
4600	61.535	422.465	367.657	252.118	436.818	432.416	−4.910
4700	61.572	423.789	368.837	258.273	436.682	432.322	−4.805
4800	61.607	425.086	369.996	264.432	436.437	432.232	−4.704
4900	61.641	426.356	371.133	270.594	436.084	432.148	−4.607
5000	61.674	427.602	372.250	276.760	435.630	432.072	−4.514
5100	61.706	428.824	373.347	282.929	435.078	432.006	−4.425
5200	61.737	430.022	374.426	289.101	434.966	431.874	−4.338
5300	61.767	431.199	375.486	295.276	434.302	431.821	−4.256
5400	61.797	432.353	376.528	301.455	433.839	431.738	−4.176
5500	61.826	433.488	377.554	307.636	433.215	431.681	−4.100
5600	61.854	434.602	378.563	313.820	432.388	431.661	−4.026
5700	61.882	435.697	379.555	320.007	431.504	431.655	−3.956
5800	61.910	436.773	380.533	326.196	430.570	431.667	−3.888
5900	61.937	437.832	381.495	332.389	429.591	431.693	−3.822
6000	61.965	438.873	382.442	338.584	428.572	431.737	−3.759

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = [225.5 \pm 4.2]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [64.9 \pm 41.8]\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [62.8 \pm 41.8]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Pi]$	0	[4]

$\omega_e = [280]\ cm^{-1}$ $\omega_e x_e = [1.0]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.198]\ cm^{-1}$ $\alpha_e = [0.001]\ cm^{-1}$ $r_e = [2.40]$ Å

Enthalpy of Formation

The enthalpy of formation is estimated from three calculated values. The methods of estimation are described as follows. Brewer and Margrave[1] suggested that the $\Delta_f H°$ value for MO(g) from the gaseous ions can be taken as the mean of the corresponding $\Delta_f H°$ values for the alkali fluoride and chloride with a maximum uncertainty of 10 kcal·mol^{-1}. Adopting $\Delta_r H°(298.15\ K) = -131.1$ and -109.6 kcal·mol^{-1} for the reaction $Cs^+(g) + F^-(g) = CsF(g)$ and $Cs^+(g) + Cl^-(g) = CsCl(g)$, respectively, we obtain $\Delta_r H°(298.15\ K) = -120.4$ kcal·mol^{-1} for $Cs^+(g) + O^-(g) = CsO(g)$ which leads to $\Delta_f H°(CsO, g, 298.15\ K) = 12.0$ kcal·mol^{-1}. The $\Delta_f H°(298.15\ K)$ values of the above species are taken from the respective JANAF Thermochemical Tables.

Based on the assumption that $D_0°(Cs–O) = 1/2\ [D_0°(Cs_2) + D_0°(O_2)]$, we derive $D_0°(Cs–O, g, 298.15\ K) = 65.2$ kcal·mol^{-1} and $\Delta_f H°(298.15\ K) = 12.7$ kcal·mol^{-1} for CsO(g).

Adopting the Cs–O bond energy as half of the atomization energy of Cs_2O, we calculate $D_0°(Cs–O) = 60 \pm 10$ kcal·mol^{-1} and $\Delta_f H°(CsO, g, 298.15\ K) = 17 \pm 10$ kcal·mol^{-1}.

The enthalpy of formation for CsO(g) is tentatively selected as 15 ± 10 kcal·mol^{-1}.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of the isoelectronic molecule OH(g). ω_e is estimated from those of LiO(g), CsF(g), and CsCl(g). The bond distance is taken from that in CsOH(g) reported by Lide and Kuczkowski.[2] $\omega_e x_e$ is estimated by comparison with those of the other alkali oxides. The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg.[3]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.879	64.939	64.939	INFINITE
100	31.670	217.938	287.000	−6.906	64.311	56.678	−29.606
200	35.247	241.201	258.847	−3.529	63.552	49.351	−12.889
250	36.016	249.156	256.140	−1.746	63.187	45.843	−9.578
298.15	36.481	255.542	255.542	0.	62.760	42.539	−7.453
300	36.495	255.768	255.543	0.067	62.741	42.414	−7.385
350	36.816	261.419	255.988	1.901	60.141	39.402	−5.880
400	37.044	266.351	256.982	3.748	59.656	36.473	−4.763
450	37.216	270.724	258.270	5.604	59.183	33.604	−3.901
500	37.351	274.653	259.715	7.469	58.715	30.786	−3.216
600	37.555	281.482	262.791	11.214	57.775	25.289	−2.202
700	37.709	287.283	265.886	14.978	56.814	19.950	−1.489
800	37.835	292.326	268.882	18.755	55.830	14.751	−0.963
900	37.945	296.789	271.740	22.544	54.822	9.676	−0.562
1000	38.046	300.793	274.448	26.344	−13.336	8.414	−0.440
1100	38.139	304.423	277.011	30.153	−13.360	10.590	−0.503
1200	38.228	307.745	279.436	33.972	−13.395	12.769	−0.556
1300	38.313	310.809	281.733	37.799	−13.439	14.951	−0.601
1400	38.397	313.651	283.912	41.634	−13.491	17.137	−0.639
1500	38.478	316.303	285.984	45.478	−13.550	19.327	−0.673
1600	38.558	318.789	287.958	49.330	−13.618	21.521	−0.703
1700	38.638	321.129	289.841	53.190	−13.696	23.719	−0.729
1800	38.716	323.340	291.641	57.057	−13.786	25.922	−0.752
1900	38.794	325.435	293.365	60.933	−13.891	28.131	−0.773
2000	38.871	327.427	295.019	64.816	−14.015	30.346	−0.793
2100	38.948	329.325	296.607	68.707	−14.162	32.568	−0.810
2200	39.024	331.139	298.136	72.606	−14.337	34.797	−0.826
2300	39.100	332.875	299.609	76.512	−14.545	37.035	−0.841
2400	39.176	334.541	301.030	80.426	−14.791	39.283	−0.855
2500	39.252	336.142	302.403	84.347	−15.080	41.541	−0.868
2600	39.328	337.683	303.730	88.276	−15.419	43.813	−0.880
2700	39.403	339.168	305.015	92.213	−15.814	46.098	−0.892
2800	39.478	340.603	306.261	96.157	−16.271	48.400	−0.903
2900	39.554	341.989	307.469	100.108	−16.796	50.718	−0.914
3000	39.629	343.331	308.642	104.068	−17.395	53.056	−0.924
3100	39.704	344.632	309.782	108.034	−18.075	55.416	−0.934
3200	39.779	345.894	310.891	112.008	−18.842	57.798	−0.943
3300	39.854	347.119	311.971	115.990	−19.661	60.203	−0.953
3400	39.928	348.310	313.022	119.979	−20.604	62.637	−0.962
3500	40.003	349.468	314.047	123.976	−21.648	65.100	−0.972
3600	40.078	350.596	315.046	127.980	−22.797	67.595	−0.981
3700	40.152	351.695	316.022	131.991	−24.044	70.121	−0.990
3800	40.227	352.767	316.975	136.010	−25.402	72.684	−0.999
3900	40.302	353.813	317.906	140.037	−26.863	75.282	−1.008
4000	40.376	354.834	318.817	144.070	−28.461	77.921	−1.018
4100	40.451	355.832	319.707	148.112	−30.181	80.601	−1.027
4200	40.525	356.808	320.579	152.161	−32.024	83.325	−1.036
4300	40.600	357.762	321.433	156.217	−33.992	86.095	−1.046
4400	40.674	358.697	322.269	160.281	−35.794	88.878	−1.055
4500	40.749	359.612	323.089	164.352	−37.403	91.671	−1.064
4600	40.823	360.508	323.893	168.430	−39.572	94.562	−1.074
4700	40.898	361.387	324.681	172.516	−41.842	97.503	−1.084
4800	40.972	362.249	325.455	176.610	−44.210	100.493	−1.094
4900	41.047	363.094	326.214	180.711	−46.672	103.533	−1.104
5000	41.121	363.924	326.960	184.819	−49.225	106.624	−1.114
5100	41.195	364.739	327.693	188.935	−51.864	109.767	−1.124
5200	41.270	365.540	328.413	193.058	−54.051	112.884	−1.134
5300	41.344	366.327	329.121	197.189	−56.779	116.121	−1.144
5400	41.418	367.100	329.817	201.327	−59.295	119.366	−1.155
5500	41.493	367.861	330.502	205.473	−61.961	122.675	−1.165
5600	41.567	368.609	331.176	209.626	−64.820	126.059	−1.176
5700	41.641	369.346	331.839	213.786	−67.725	129.493	−1.187
5800	41.716	370.070	332.492	217.954	−70.672	132.979	−1.198
5900	41.790	370.784	333.135	222.129	−73.655	136.515	−1.209
6000	41.864	371.487	333.768	226.312	−76.668	140.103	−1.220

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

D_0° = 43.389 ± 0.096 kJ·mol^{-1}
S°(298.15 K) = 284.675 ± 0.084 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 111.77 ± 0.26 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 107.37 ± 0.30 kJ·mol^{-1}

Spectroscopic Constants for Cs_2 in cm^{-1}

State	T_e	ω_e	$10^2\cdot\omega_e x_e$	$10^5\cdot\omega_e y_e$	$10^7\cdot\omega_e z_e$	$10^2\cdot B_e$	$10^5\cdot\alpha_e$	$10^8\cdot\gamma_e$	$10^9\cdot D_e$	$10^{10}\cdot\beta_e$	r_e, Å
$X^1\Sigma_g^+$	0	42.0194	8.191	−9.0404	−3.2912[b]	1.1743	2.215	−8.2448[c]	3.73	1.2608[d]	4.646[e]
$C^1\Pi_u$	15949[a]	29.664	4.202	—	—	1.2360	6.6503	—	[8.5833]	—	4.34[5]

(a) The dissociation energy, D_0°, for the $C^1\Pi_u$ state is 18228 cm^{-1}
(b) $-5.8173\times10^{-9}(v+1/2)^4 - 4.5832\times10^{-12}(v+1/2)^5$ for $^1\Sigma_g^+$
(c) $+5.8751\times10^{-10}(v+1/2)^3 - 3.0391\times10^{-12}(v+1/2)^4 + 1.8161\times10^{-14}(v+1/2)^5$ for $^1\Sigma_g^+$
(d) $+9.2704\times10^{-13}(v+1/2)^2 - 9.7917\times10^{-15}(v+1/2)^3$ for $^1\Sigma_g^+$
(e) As determined from B_e

Enthalpy of Formation

Using the adopted value of the ground state dissociation energy for Cs_2(g), D_0° = 43.389 kJ·mol^{-1},[1] and the recommended $\Delta_f H^\circ$(Cs, g, 0 K) = 155.160 kJ·mol^{-1} from NBS,[6] we calculate the adopted value of $\Delta_f H^\circ(Cs_2, g, 0 K)$ = 111.77 kJ·mol^{-1}. This value is in essential agreement with the NBS recommended value of 111.7 kJ·mol^{-1}. Correcting the adopted $\Delta_f H^\circ$(0 K) to 298.15 K using the current value of H°(298.15 K)−H°(0 K) = 11.029 kJ·mol^{-1} for Cs_2(g) and the NBS value of H°(298.15 K)−H°(0 K) = 7.711 kJ·mol^{-1} for Cs(cr) 6 , we obtain $\Delta_f H^\circ(Cs_2, g, 298.15 K)$ = 107.38 kJ·mol^{-1}.

Heat Capacity and Entropy

The heat capacity and entropy were calculated using a direct summation technique similar to the Li_2(g) calculation[7] using ground state data from Raab *et al.*,[1] as recommended by Stwalley.[2] Spectroscopic data for the $C^1\Pi_u$ state of Cs_2(g) at T_e = 15949 cm^{-1} come from the work of Raab *et. al.*[4] The other low lying states of Cs_2(g) are the $^3\Pi_u$ state at T_e = 7850 cm^{-1},[3] the $B^1\Pi_u$ state at 13044 cm^{-1},[5] and the $^1\Sigma_u^+$ state at T_e = 16720 cm^{-1}.[4] These states have not been characterized satisfactorily to date. To include the excited states in the thermodynamic calculation in an approximate manner, we proceeded as with the Na_2(g) species as follows.[7] The $C^1\Pi_u$ state was included using the spectroscopic data reported by Raab.[1] To account for the $^3\Pi_u$, $B^1\Pi_u$ and $^1\Sigma_u^+$ states, the rotational levels of the $C^1\Pi_u$ state were weighted × 13 to account for the sixfold degeneracy of the $^3\Pi_u$ state, the threefold degeneracy of each of the $^1\Pi_u$ states and the singly degenerate $^1\Sigma_u^+$ state. Note that the $^3\Sigma_u^+$ state is weakly bound and was neglected. Due to the minimal number of vibrational and rotational levels used by[1] to generate Dunham coefficients for the $C^1\Pi_u$ state, we artificially truncated the G(v) expression after the $\omega_e x_e$ term and the B(v) expression after the α_e term. For the same reason, we used Herzberg's method (see Li_2 table) to estimate $D_e = 8.5833\times10^{-9}$ cm^{-1}rather than use the value of 1 .

As with the Na_2(g) calculation, the above method certainly underestimates the $^3\Pi_u$ and $B^1\Pi_u$ contributions but at the same time overestimates the $^1\Sigma_u^+$ contribution to the thermodynamic functions. The contribution of the excited states to the free energy function is negligible at temperatures below 2000 K and only contribute ca. 0.25 J·K^{-1}·mol^{-1} at 6000 K. This method of treating the excited states does result, however, in a more realistic high temperature heat capacity. The rotational levels of the ground state were weighted in accordance with the nuclear spin of the atom (I = 7/2): even J weight = .5833, odd J weight = .4167. The adopted value of S°(298.15 K) is larger than the NBS adopted value 6 by 0.74 J·K^{-1}·mol^{-1} but is in exact agreement with that adopted by Gurvich, *et al.*[8]

References

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[7] JANAF Thermochemical Tables: Li_2(g), 12–31–82; Na_2(g), 12–31–82.
[8] L. V. Gurvich, *et al.*, Thermodynamic Properties of Individual Substances, Vol. IV, 3rd ed., Nauka, Moscow, (1982).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.029	111.770	111.770	INFINITE
100	37.404	243.396	318.414	−7.502	111.000	97.651	−51.008
200	37.872	269.484	288.161	−3.735	109.406	84.890	−22.171
298.15	38.250	284.675	284.675	0.	107.366	73.263	−12.835
300	38.258	284.912	284.676	0.071	107.317	73.052	−12.719
400	38.686	295.977	286.182	3.918	100.605	63.381	−8.277
500	38.962	304.645	289.039	7.803	98.227	54.353	−5.678
600	38.757	311.739	292.249	11.694	95.904	45.796	−3.987
700	37.949	317.660	295.469	15.534	93.551	37.630	−2.808
800	36.671	322.648	298.563	19.268	91.098	29.807	−1.946
900	35.150	326.881	301.481	22.860	88.502	22.300	−1.294
1000	33.582	330.503	304.206	26.297	−48.515	22.490	−1.175
1100	32.089	333.633	306.743	29.579	−49.390	29.631	−1.407
1200	30.734	336.366	309.100	32.719	−50.408	36.859	−1.604
1300	29.537	338.777	311.292	35.731	−51.554	44.177	−1.775
1400	28.497	340.927	313.333	38.632	−52.815	51.587	−1.925
1500	27.602	342.862	315.238	41.436	−54.177	59.091	−2.058
1600	26.836	344.618	317.021	44.156	−55.628	66.690	−2.177
1700	26.183	346.225	318.692	46.807	−57.161	74.381	−2.285
1800	25.631	347.706	320.263	49.396	−58.771	82.165	−2.384
1900	25.166	349.079	321.744	51.936	−60.454	90.040	−2.475
2000	24.781	350.359	323.143	54.432	−62.209	98.006	−2.560
2100	24.468	351.561	324.468	56.894	−64.038	106.061	−2.638
2200	24.221	352.693	325.726	59.328	−65.942	114.206	−2.712
2300	24.037	353.765	326.922	61.741	−67.927	122.438	−2.781
2400	23.912	354.786	328.062	64.138	−69.997	130.759	−2.846
2500	23.842	355.760	329.150	66.525	−72.156	139.168	−2.908
2600	23.826	356.695	330.192	68.908	−74.414	147.665	−2.967
2700	23.861	357.594	331.190	71.292	−76.776	156.251	−3.023
2800	23.944	358.464	332.149	73.682	−79.250	164.927	−3.077
2900	24.073	359.306	333.071	76.082	−81.844	173.693	−3.129
3000	24.245	360.125	333.959	78.498	−84.568	182.550	−3.178
3100	24.456	360.923	334.816	80.932	−87.431	191.501	−3.227
3200	24.704	361.703	335.644	83.390	−90.442	200.546	−3.274
3300	24.986	362.468	336.445	85.874	−93.529	209.682	−3.319
3400	25.297	363.218	337.222	88.388	−96.831	218.919	−3.363
3500	25.634	363.956	337.975	90.935	−100.301	228.256	−3.407
3600	25.994	364.683	338.707	93.516	−103.947	237.694	−3.449
3700	26.371	365.401	339.419	96.134	−107.751	247.235	−3.490
3800	26.764	366.109	340.112	98.791	−111.741	256.880	−3.531
3900	27.168	366.810	340.787	101.487	−115.898	266.630	−3.571
4000	27.579	367.503	341.447	104.224	−120.289	276.494	−3.611
4100	27.994	368.189	342.090	107.003	−124.883	286.470	−3.650
4200	28.410	368.868	342.720	109.823	−129.686	296.561	−3.688
4300	28.824	369.542	343.336	112.685	−134.700	306.769	−3.726
4400	29.232	370.209	343.939	115.588	−139.340	317.028	−3.764
4500	29.632	370.870	344.530	118.531	−143.560	327.330	−3.800
4600	30.022	371.526	345.110	121.514	−148.862	337.852	−3.836
4700	30.400	372.176	345.679	124.535	−154.330	348.492	−3.873
4800	30.763	372.820	346.238	127.593	−159.960	359.249	−3.909
4900	31.110	373.458	346.787	130.687	−165.745	370.126	−3.946
5000	31.440	374.089	347.326	133.815	−171.679	381.122	−3.982
5100	31.752	374.715	347.857	136.975	−177.753	392.238	−4.017
5200	32.043	375.335	348.380	140.165	−182.897	403.319	−4.051
5300	32.315	375.948	348.894	143.383	−189.093	414.651	−4.087
5400	32.566	376.554	349.401	146.627	−194.838	426.015	−4.121
5500	32.795	377.154	349.900	149.895	−200.859	437.521	−4.155
5600	33.004	377.746	350.392	153.185	−207.241	449.185	−4.190
5700	33.192	378.332	350.877	156.495	−213.695	460.965	−4.224
5800	33.358	378.911	351.355	159.823	−220.208	472.857	−4.259
5900	33.505	379.483	351.827	163.166	−226.774	484.863	−4.293
6000	33.630	380.047	352.293	166.523	−233.380	496.980	−4.327

PREVIOUS: June 1968 (1 atm) CURRENT: December 1983 (1 bar)

$S°(298.15\ K) = [352.3 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -885.12 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -890.10 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[200](1)	[120](1)
[110](1)	[220](1)
[210](1)	[230](1)

Ground State Quantum Weight: [1] σ = [4]
Bond Distance: Cs–F = [2.35] Å
Bond Angles: F–Cs–F = [85]°; Cs–F–Cs = [95]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.127422 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Evidence from the velocity distribution in molecular beams[1] has shown that alkali halide vapors contain significant amounts of polymeric species. Using the same method Eisenstadt[2] determined the molecular composition of CsF vapor in the temperature range 838–919 K. Based on the reported equilibrium constants for the reaction $(CsF)_2(g) = 2CsF(g)$, we evaluate the enthalpy change, $\Delta_r H°(298.15\ K)$, by the 2nd and 3rd law methods to be 40.53 ± 1.75 and $42.34 \pm 0.26\ kcal \cdot mol^{-1}$, respectively. Employing $\Delta_r H°(298.15\ K) = 42.34$ and $\Delta_f H°(CsF, g, 298.15\ K) = -85.2\ kcal \cdot mol^{-1}$, we obtained $\Delta_f H°(298.15\ K) = -212.74\ kcal \cdot mol^{-1}$ $(-890.10 \pm 8.4\ kJ \cdot mol^{-1})$ for Cs_2F_2(g), which is adopted.

Heat Capacity and Entropy

The Cs_2F_2 molecule is assumed to have a rhombic configuration of symmetry D_{2h} as Cs_2Cl_2.[3] The Cs–F bond distance is taken as the same as that in CsF(g). The bond angles and vibrational frequencies are estimated by comparison with those of the other dimeric alkali halides.[3,4] The principal moments of inertia are: $I_A = 15.9040 \times 10^{-39}$, $I_B = 132.5032 \times 10^{-39}$, and $I_C = 148.4071 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.273	−885.119	−885.119	INFINITE
100	62.412	272.336	420.380	−14.804	−887.854	−887.060	463.353
200	76.312	321.055	359.539	−7.697	−889.036	−885.736	231.330
250	78.605	338.355	353.628	−3.818	−889.500	−884.858	184.881
298.15	79.888	352.319	352.319	0.	−890.104	−883.913	154.858
300	79.926	352.813	352.320	0.148	−890.134	−883.875	153.896
350	80.750	365.200	353.297	4.166	−895.093	−882.098	131.646
400	81.296	376.021	355.475	8.218	−895.841	−880.190	114.941
450	81.675	385.619	358.301	12.293	−896.575	−878.190	101.938
500	81.950	394.239	361.471	16.384	−897.305	−876.108	91.526
600	82.310	409.215	368.218	24.599	−898.778	−871.730	75.891
700	82.529	421.921	375.005	32.841	−900.280	−867.104	64.704
800	82.672	432.952	381.574	41.102	−901.815	−862.260	56.300
900	82.771	442.695	387.835	49.374	−903.386	−857.222	49.752
1000	82.842	451.420	393.764	57.655	−1039.248	−844.608	44.118
1100	82.894	459.318	399.370	65.942	−1038.838	−825.164	39.184
1200	82.934	466.532	404.671	74.234	−1038.450	−805.756	35.074
1300	82.965	473.172	409.688	82.529	−1038.084	−786.380	31.597
1400	82.989	479.321	414.445	90.826	−1037.738	−767.032	28.618
1500	83.009	485.048	418.963	99.126	−1037.413	−747.707	26.037
1600	83.026	490.405	423.263	107.428	−1037.113	−728.403	23.780
1700	83.039	495.439	427.362	115.731	−1036.838	−709.117	21.789
1800	83.050	500.186	431.277	124.036	−1036.593	−689.847	20.019
1900	83.060	504.676	435.023	132.341	−1036.381	−670.589	18.436
2000	83.068	508.937	438.613	140.648	−1036.208	−651.341	17.011
2100	83.075	512.990	442.059	148.955	−1036.078	−632.101	15.723
2200	83.081	516.855	445.372	157.263	−1035.999	−612.867	14.551
2300	83.087	520.548	448.561	165.571	−1035.976	−593.634	13.482
2400	83.091	524.084	451.634	173.880	−1036.017	−574.401	12.502
2500	83.096	527.477	454.601	182.189	−1036.129	−555.165	11.600
2600	83.099	530.736	457.467	190.499	−1036.322	−535.923	10.767
2700	83.102	533.872	460.239	198.809	−1036.604	−516.672	9.996
2800	83.105	536.894	462.923	207.120	−1036.985	−497.408	9.279
2900	83.108	539.811	465.524	215.430	−1037.475	−478.130	8.612
3000	83.110	542.628	468.048	223.741	−1038.085	−458.832	7.989
3100	83.112	545.353	470.498	232.052	−1038.826	−439.512	7.406
3200	83.114	547.992	472.878	240.364	−1039.709	−420.165	6.858
3300	83.116	550.550	475.193	248.675	−1040.665	−400.795	6.344
3400	83.118	553.031	477.446	256.987	−1041.833	−381.388	5.859
3500	83.119	555.440	479.641	265.299	−1043.170	−361.944	5.402
3600	83.121	557.782	481.779	273.611	−1044.683	−342.460	4.969
3700	83.122	560.059	483.864	281.923	−1046.358	−322.933	4.559
3800	83.123	562.276	485.898	290.235	−1048.223	−303.358	4.170
3900	83.124	564.435	487.885	298.548	−1050.260	−283.734	3.800
4000	83.125	566.540	489.825	306.860	−1052.538	−264.051	3.448
4100	83.126	568.592	491.721	315.173	−1055.027	−244.309	3.113
4200	83.127	570.595	493.575	323.485	−1057.732	−224.503	2.792
4300	83.128	572.551	495.389	331.798	−1060.656	−204.630	2.486
4400	83.128	574.463	497.165	340.111	−1063.216	−184.754	2.193
4500	83.129	576.331	498.903	348.424	−1065.362	−164.881	1.914
4600	83.130	578.158	500.606	356.737	−1068.599	−144.836	1.645
4700	83.130	579.946	502.275	365.050	−1072.010	−124.717	1.386
4800	83.131	581.696	503.912	373.363	−1075.589	−104.524	1.137
4900	83.131	583.410	505.517	381.676	−1079.330	−84.256	0.898
5000	83.132	585.089	507.092	389.989	−1083.224	−63.909	0.668
5100	83.132	586.736	508.637	398.302	−1087.264	−43.483	0.445
5200	83.133	588.350	510.155	406.615	−1090.375	−23.131	0.232
5300	83.133	589.933	511.645	414.929	−1094.540	−2.568	0.025
5400	83.134	591.487	513.109	423.242	−1098.256	17.989	−0.174
5500	83.134	593.013	514.548	431.555	−1102.246	38.650	−0.367
5600	83.134	594.511	515.963	439.869	−1106.596	59.433	−0.554
5700	83.135	595.982	517.354	448.182	−1111.012	80.293	−0.736
5800	83.135	597.428	518.722	456.496	−1115.485	101.232	−0.912
5900	83.135	598.849	520.068	464.809	−1120.003	122.249	−1.082
6000	83.136	600.246	521.393	473.123	−1124.554	143.342	−1.248

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = 360.7 \pm 12.6\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -674.7 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -687.8 \pm 41.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[200](1)	[1250](1)
[110](1)	[1250](1)
[210](1)	[1250](1)
[120](1)	[1250](1)
[220](1)	[3700](1)
[230](1)	[3700](1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2h}

Bond Distances: Cs–O = [2.63] Å; O–H = [0.96] Å

Bond Angles: Cs–O–Cs = [90]°; Cs–O–H = [110]°

Product of Moments of Inertia: $I_A I_B I_C = [5.396347 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Schoonmaker and Porter[1] analyzed the vapors in equilibrium with liquid CsOH and mixed KOH–CsOH condensed phases with a mass spectrometer and reported the presence of appreciable concentrations of dimer in the temperature range 650–700 K. By applying the method of relative equilibrium constants, these workers calculated the difference in the free energies of dimerization for KOH–CsOH. A 3rd law analysis of their free energy data for this pair leads to a difference in the enthalpies of dimerization of 4.9 kcal·mol^{-1} at 298.15 K for CsOH and KOH. Based upon the adopted value for KOH(g), $\Delta_f H°$(dimerization, 298.15 K) = -45.3 ± 3.0 kcal·mol^{-1},[2] we derive $\Delta_f H°$(dimerization, 298.15 K) = -40.4 ± 4.0 kcal·mol^{-1} for 2 CsOH(g) = $Cs_2(OH)_2$(g). Combining this result with the enthalpy of formation for the gaseous monomer,[3] that for the dimer is $\Delta_f H°(Cs_2(OH)_2, g, 298.15\ K) = -164.4 \pm 10.0$ kcal·mol^{-1} (-687.8 ± 41.8 kJ·mol^{-1}).

Heat Capacity and Entropy

Buchler *et al.*[4] investigated the geometries of several molecules containing cesium by the deflection of molecular beams in an inhomogeneous electric field. Their results for $Cs_2(OH)_2$(g) indicated that the molecule was nonpolar which implies a planar configuration for at least the Cs_2O_2 part of the molecule. Several structural models proposed for the dimers of the alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer *et al.*[5] calculated entropies of dimerization for NaOH(g) and KOH(g) with a dimer model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter[1] adopted the same alkali–oxygen configuration but did not allow for hydrogen bonding between the oxygens and hydrogens. Berkowitz *et al.*[6] relied on the apparent similarity of the alkali halides and hydroxides in forming dimeric species to propose a structural model for $Li_2(OH)_2$(g). This model consisted of a trans–configuration with hydrogens above and below the plane of a rhombus formed by the lithium and oxygen atoms, the Li–O–Li bond angle being 100°. We adopt a structure for $Cs_2(OH)_2$(g) which is similar to the model of Berkowitz *et al.*[6] for $Li_2(OH)_2$(g) but with the Cs–O–Cs bond angle equal to 90°. The cesium and oxygen atoms form a square planar configuration. The Cs–O–H bond angle is assumed equal to 110°. The Cs–O bond distance is estimated as being 10% longer than that in CsOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are: $I_A = [20.4212] \times 10^{-39}$, $I_B = [152.8696] \times 10^{-39}$, and $I_C = [172.8610] \times 10^{-39}$ g·cm^2.

Acquista *et al.*[7] observed the infrared spectra of matrix isolated CsOH and reported bands in the region 300–200 cm^{-1}whose relative intensities decreased with increasing temperature. Since the dimer to monomer ratio decreases with increasing temperature, these bands appeared to arise from polymeric species of CsOH, but no definite assignments could be made. Similar results have been reported for RbOH and NaOH from infrared studies[8] of these molecules trapped in inert matrices. Berkowitz *et al.*[6] estimated vibrational frequencies for $Li_2(OH)_2$(g) by comparison with those for dimeric Li_2F_2(g). The frequencies for Li_2F_2(g) had been estimated earlier by Berkowitz[9] using an ionic model and normal coordinate analysis. It has now been established experimentally that these estimated frequencies for Li_2F_2(g) are too low (Refer to Li_2F_2(g) table for details). Until definite assignments for the dimer hydroxides can be made from infrared studies, we tentatively adopt the six estimated frequencies for Cs_2F_2(g) (Refer to CsF_2(g) table for details) and apply them directly to $Cs_2(OH)_2$(g). The remaining O–H stretching and bending frequencies are estimates from the work of Berkowitz *et al.*[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.417	−674.683	−674.683	INFINITE
100	62.412	280.202	429.685	−14.948	−680.415	−670.041	349.994
200	76.646	328.962	368.129	−7.833	−684.265	−658.097	171.877
250	79.900	346.426	362.095	−3.917	−686.043	−651.350	136.092
298.15	82.807	360.748	360.748	0.	−687.850	−644.507	112.915
300	82.919	361.260	360.749	0.153	−687.923	−644.237	112.172
350	85.963	374.271	361.770	4.375	−694.016	−636.132	94.937
400	88.968	385.947	364.074	8.749	−695.764	−627.741	81.975
450	91.824	396.592	367.104	13.270	−697.362	−619.141	71.868
500	94.461	406.406	370.550	17.928	−698.830	−610.370	63.765
600	99.017	424.045	378.029	27.609	−701.451	−592.425	51.575
700	102.729	439.597	385.735	37.703	−703.743	−574.069	42.838
800	105.812	453.521	393.353	48.134	−705.788	−555.402	36.264
900	108.443	466.140	400.751	58.850	−707.641	−536.491	31.137
1000	110.738	477.687	407.875	69.812	−843.598	−509.983	26.639
1100	112.767	488.338	414.712	80.989	−843.126	−476.643	22.634
1200	114.576	498.229	421.264	92.358	−842.542	−443.352	19.299
1300	116.193	507.465	427.544	103.898	−841.865	−410.113	16.479
1400	117.640	516.130	433.565	115.591	−841.111	−376.929	14.063
1500	118.938	524.291	439.344	127.421	−840.295	−343.801	11.972
1600	120.101	532.005	444.897	139.374	−839.433	−310.729	10.144
1700	121.144	539.318	450.238	151.437	−838.539	−277.713	8.533
1800	122.081	546.270	455.381	163.599	−837.626	−244.749	7.102
1900	122.923	552.893	460.341	175.850	−836.709	−211.837	5.824
2000	123.680	559.218	465.128	188.181	−835.803	−178.972	4.674
2100	124.364	565.269	469.753	200.583	−834.921	−146.152	3.635
2200	124.980	571.069	474.227	213.051	−834.079	−113.373	2.692
2300	125.539	576.637	478.560	225.578	−833.292	−80.632	1.831
2400	126.045	581.991	482.759	238.157	−832.573	−47.924	1.043
2500	126.504	587.146	486.832	250.785	−831.937	−15.244	0.318
2600	126.923	592.116	490.786	263.457	−831.400	17.413	−0.350
2700	127.304	596.913	494.628	276.168	−830.976	50.052	−0.968
2800	127.653	601.549	498.365	288.916	−830.679	82.677	−1.542
2900	127.972	606.034	502.000	301.698	−830.523	115.293	−2.077
3000	128.265	610.378	505.541	314.510	−830.525	147.907	−2.575
3100	128.534	614.588	508.991	327.350	−830.698	180.524	−3.042
3200	128.782	618.673	512.355	340.216	−831.057	213.149	−3.479
3300	129.010	622.639	515.637	353.106	−831.532	245.781	−3.890
3400	129.221	626.493	518.841	366.017	−832.269	278.438	−4.278
3500	129.417	630.242	521.971	378.949	−833.222	311.119	−4.643
3600	129.598	633.891	525.029	391.900	−834.402	343.831	−4.989
3700	129.767	637.444	528.020	404.869	−835.795	376.576	−5.316
3800	129.923	640.906	530.945	417.853	−837.430	409.363	−5.627
3900	130.069	644.283	533.808	430.853	−839.288	442.193	−5.923
4000	130.205	647.578	536.611	443.867	−841.441	475.078	−6.204
4100	130.333	650.795	539.357	456.894	−843.856	508.020	−6.472
4200	130.452	653.937	542.048	469.933	−846.541	541.025	−6.729
4300	130.563	657.008	544.686	482.984	−849.496	574.097	−6.974
4400	130.667	660.011	547.273	496.045	−852.140	607.173	−7.208
4500	130.766	662.948	549.811	509.117	−854.422	640.247	−7.432
4600	130.858	665.823	552.302	522.198	−857.846	673.499	−7.648
4700	130.945	668.638	554.747	535.288	−861.495	706.828	−7.856
4800	131.026	671.396	557.149	548.387	−865.363	740.238	−8.055
4900	131.104	674.099	559.508	561.494	−869.443	773.730	−8.248
5000	131.176	676.748	561.826	574.608	−873.727	807.307	−8.434
5100	131.245	679.346	564.105	587.729	−878.205	840.972	−8.613
5200	131.310	681.895	566.346	600.857	−881.803	874.570	−8.785
5300	131.372	684.397	568.550	613.991	−886.504	908.392	−8.953
5400	131.431	686.853	570.718	627.131	−890.804	942.217	−9.114
5500	131.486	689.266	572.852	640.277	−895.425	976.156	−9.271
5600	131.539	691.635	574.952	653.428	−900.453	1010.231	−9.423
5700	131.589	693.964	577.019	666.584	−905.595	1044.396	−9.571
5800	131.636	696.253	579.055	679.746	−910.839	1078.652	−9.714
5900	131.682	698.503	581.061	692.912	−916.174	1112.997	−9.854
6000	131.725	700.717	583.037	706.082	−921.588	1147.437	−9.989

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = [-318.1 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -86.2 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -92.0 \pm 41.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
[290](1)
[130](1)
[300](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Bond Distance: Cs–O = [2.4] Å

Bond Angle: Cs–O–Cs = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.415602 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The appearance potentials of CsOH and Cs_2O ions were investigated by Emel'yanov *et al.*,[1] using the electron–impact method with a mass spectrometer fitted with a heated ion source and a Pt effusion chamber. The enthalpy of atomization of Cs_2O was derived as 117 ± 10 $kcal \cdot mol^{-1}$. Based on this value we calculate the enthalpy of formation $\Delta_f H°(298.15\ K)$ of Cs_2O to be −22 ± 10 $kcal \cdot mol^{-1}$ (−92.0 ± 41.8 $kJ \cdot mol^{-1}$), employing $\Delta_f H°(0\ K)$ = 18.68 and 58.99 $kcal \cdot mol^{-1}$ for Cs(g) and O(g), respectively. Brewer and Mastick[2] calculated theoretically the stability of gaseous alkali oxides according to ionic models and gave the enthalpies of formation from gaseous atoms for Cs_2O(g) as −24 $kcal \cdot mol^{-1}$. The $\Delta_f H°(298.15\ K)$ value is evaluated to be 72.2 $kcal \cdot mol^{-1}$ which is not adopted.

Heat Capacity and Entropy

The molecular structure of Cs_2O(g) has been determined to be nonlinear by Buchler *et al.*,[3] using electric–deflection method. The Cs–O bond distance is assumed to be the same as that in CsOH(g) reported by Lide and Kuczkowski.[4] The bond angle is estimated by comparison with that in the H_2O molecule. Three vibrational frequencies are estimated from those for H_2O(g). The principal moments of inertia are: $I_A = 5.3492 \times 10^{-39}$, $I_B = 160.0237 \times 10^{-39}$, and $I_C = 165.3730 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−13.937	−86.211	−86.211	INFINITE
100	43.945	262.828	365.083	−10.225	−88.248	−94.875	49.557
200	52.568	296.481	323.084	−5.320	−90.159	−100.726	26.307
250	54.345	308.420	318.995	−2.644	−91.051	−103.265	21.576
298.15	55.388	318.088	318.088	0.	−92.048	−105.530	18.488
300	55.420	318.431	318.089	0.102	−92.092	−105.614	18.389
350	56.109	327.029	318.767	2.892	−97.430	−107.104	15.984
400	56.574	334.554	320.280	5.710	−98.529	−108.410	14.157
450	56.902	341.237	322.244	8.547	−99.591	−109.581	12.720
500	57.141	347.246	324.449	11.398	−100.634	−110.635	11.558
600	57.457	357.694	329.145	17.130	−102.696	−112.441	9.789
700	57.651	366.567	333.873	22.886	−104.760	−113.903	8.500
800	57.778	374.274	338.452	28.658	−106.844	−115.067	7.513
900	57.866	381.085	342.818	34.440	−108.953	−115.968	6.731
1000	57.929	387.185	346.955	40.230	−245.346	−109.235	5.706
1100	57.976	392.708	350.867	46.026	−245.463	−95.618	4.541
1200	58.012	397.755	354.567	51.825	−245.596	−81.990	3.569
1300	58.040	402.399	358.070	57.628	−245.744	−68.350	2.746
1400	58.062	406.701	361.392	63.433	−245.906	−54.699	2.041
1500	58.080	410.708	364.548	69.240	−246.085	−41.035	1.429
1600	58.094	414.457	367.551	75.049	−246.283	−27.359	0.893
1700	58.106	417.979	370.415	80.859	−246.502	−13.669	0.420
1800	58.117	421.300	373.151	86.670	−246.748	0.034	−0.001
1900	58.125	424.443	375.768	92.482	−247.028	13.751	−0.378
2000	58.133	427.424	378.277	98.295	−247.348	27.485	−0.718
2100	58.139	430.261	380.686	104.108	−247.718	41.235	−1.026
2200	58.144	432.966	383.001	109.922	−248.146	55.005	−1.306
2300	58.149	435.550	385.230	115.737	−248.644	68.795	−1.562
2400	58.153	438.025	387.379	121.552	−249.222	82.609	−1.798
2500	58.157	440.399	389.452	127.368	−249.891	96.448	−2.015
2600	58.160	442.680	391.456	133.184	−250.663	110.317	−2.216
2700	58.163	444.875	393.394	139.000	−251.552	124.217	−2.403
2800	58.166	446.991	395.271	144.816	−252.568	138.153	−2.577
2900	58.168	449.032	397.089	150.633	−253.725	152.127	−2.740
3000	58.170	451.004	398.854	156.450	−255.036	166.144	−2.893
3100	58.172	452.911	400.567	162.267	−256.514	180.207	−3.036
3200	58.174	454.758	402.232	168.084	−258.173	194.321	−3.172
3300	58.176	456.548	403.851	173.902	−259.942	208.482	−3.300
3400	58.177	458.285	405.426	179.720	−261.964	222.707	−3.421
3500	58.179	459.972	406.961	185.537	−264.195	236.994	−3.537
3600	58.180	461.611	408.456	191.355	−266.644	251.348	−3.647
3700	58.181	463.205	409.915	197.173	−269.295	265.770	−3.752
3800	58.182	464.756	411.337	202.992	−272.178	280.268	−3.853
3900	58.183	466.268	412.727	208.810	−275.273	294.842	−3.949
4000	58.184	467.741	414.084	214.628	−278.651	309.503	−4.042
4100	58.185	469.177	415.410	220.446	−282.280	324.251	−4.131
4200	58.185	470.579	416.707	226.265	−286.165	339.091	−4.217
4300	58.186	471.949	417.976	232.084	−290.309	354.027	−4.301
4400	58.187	473.286	419.218	237.902	−294.127	368.994	−4.381
4500	58.187	474.594	420.434	243.721	−297.570	383.986	−4.457
4600	58.188	475.873	421.625	249.540	−302.141	399.182	−4.533
4700	58.188	477.124	422.793	255.358	−306.923	414.479	−4.606
4800	58.189	478.349	423.937	261.177	−311.910	429.881	−4.678
4900	58.189	479.549	425.060	266.996	−317.094	445.388	−4.748
5000	58.190	480.725	426.162	272.815	−322.467	461.003	−4.816
5100	58.190	481.877	427.243	278.634	−328.019	476.728	−4.883
5200	58.191	483.007	428.304	284.453	−332.678	492.407	−4.946
5300	58.191	484.115	429.347	290.272	−338.424	508.329	−5.010
5400	58.191	485.203	430.371	296.092	−343.754	524.274	−5.071
5500	58.192	486.271	431.378	301.911	−349.391	540.353	−5.132
5600	58.192	487.319	432.368	307.730	−355.420	556.585	−5.192
5700	58.192	488.349	433.341	313.549	−361.548	572.924	−5.250
5800	58.193	489.361	434.298	319.368	−367.764	589.373	−5.308
5900	58.193	490.356	435.240	325.188	−374.057	605.928	−5.364
6000	58.193	491.334	436.166	331.007	−380.415	622.592	−5.420

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [264.834]\ J·K^{-1}·mol^{-1}$
$Tt(II→I) = 940 \pm 5\ K$
$T_{fus}(I→l) = 1278 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [-1410.152]\ kJ·mol^{-1}$
$\Delta_{trs} H°(II→I) = 4.310 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{fus} H°(I→l) = 35.690 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Cs_2SO_4, cr, I, 298.15\ K)$ is calculated from $\Delta_f H°(Cs_2SO_4, cr, II, 298.15\ K)$ by adding the enthalpy of transition (II → I) and the difference in enthaply, $H°(940)–H°(298.15\ K)$, between the II and I crystalline forms.[1]

Heat Capacity and Enthalpy

High–temperature enthalpies of the I–phase of Cs_2SO_4 have been determined by Denielou *et al.*, (960–1260 K)[2] and by Polischcuk *et al.* (950.7–1254.5 K).[3] We have adopted heat capacities based upon the enthalpies of Denielou *et al.*[2] We have extrapolated the heat capacities smoothly to 298.15 K below the II → I transition and extended $C_p°$ above the melting point to 1500 K.

$S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Transition Data

The high–temperature hexagonal modification of cesium sulfate is denoted Cs_2SO_4, cr, I, in accordance with the usual nomenclature. This modification has been referred to as the α–phase in contrast to our use of α to refer to the low–temperature phase for the other members of the alkali metal sulfates.[1]

Fusion Data

The adopted melting point, $T_{fus} = 1278 \pm 5$ K, was determined from the work of Denielou *et al.*, (1274 ± 3 K),[2] Polishchuk *et al.* (1281 K),[3] Rassonskaya and Semendyaeva, (1283 K),[4] and from the compilation of Stern and Weise (1277 K).[5] The enthalpy of fusion, $\Delta_{fus} H° = 8.530 \pm 0.2$ kcal·mol^{-1}, is calculated from the difference between the smoothed relative enthalpy of the liquid and the adopted enthalpy value for the I form at T_{fus}.

References

[1]JANAF Thermochemical Tables: Cs_2SO_4(cr, II), 6–30–79; Na_2SO_4(cr, V), K_2SO_4(cr, α), 6–30–78.
[2]L. Denielou, Y. Fournier, J. P. Petitet, and C. Tequi, C. R. Acad. Sci., Davis **270**, 1854 (1970).
[3]A. F. Polishchuk, T. A. Tishura, and A. N. Buderina, Ukr. Khim. Zh. **40**, 120 (1974).
[4]I. S. Rassonskaya and N. K. Semendyaeva, Russ. J. Inorg. Chem. **15**, 27 (1970).
[5]K. H. Stern and E. L. Weise, NSRDS–NBS 7, (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	108.700	264.834	264.834	0.	−1410.152	−1306.452	228.885
300	108.784	265.506	264.836	0.201	−1410.221	−1305.809	227.361
400	112.131	297.150	269.129	11.209	−1420.312	−1268.991	165.713
500	120.081	322.947	277.379	22.784	−1425.046	−1230.612	128.561
600	132.256	345.866	286.911	35.373	−1428.574	−1191.370	103.718
700	147.737	367.416	296.883	49.373	−1430.624	−1151.653	85.937
800	163.218	388.154	307.003	64.921	−1431.148	−1111.747	72.590
900	178.699	408.272	317.143	82.016	−1483.308	−1070.783	62.147
940.000	184.891	416.177	321.189	89.288	- - - - - - - - II <- - -> I - - - - - - - -		
1000	194.179	427.901	327.241	100.660	−1613.897	−1017.731	53.161
1100	209.660	447.135	337.269	120.852	−1606.752	−958.448	45.513
1200	225.141	466.041	347.214	142.592	−1598.155	−899.880	39.171
1278.000	237.233	480.596	354.911	160.625	- - - - - I <- - -> LIQUID - - - - - -		
1300	240.622	484.675	357.073	165.882	−1588.093	−842.089	33.836
1400	256.103	503.073	366.846	190.718	−1576.563	−785.127	29.293
1500	271.583	521.270	376.535	217.103	−1563.560	−729.041	25.387

PREVIOUS: CURRENT: June 1979

$S°(298.15\ K) = 211.88 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 940 \pm 5\ K$

$\Delta_f H°(0\ K) = -1433.16 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1442.64 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{trs} H°(\alpha \rightarrow \beta) = 4.310 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of solution at infinite dilution of Cs_2SO_4 has been measured by Kuznetsova *et al.*, (3.980 $kcal·mol^{-1}$)[1] and by Borob'ev *et al.*, ($4.11 \pm 0.80\ kcal·mol^{-1}$).[2] We adopt the mean of these values $4.05 \pm 0.1\ kcal·mol^{-1}$. When this result is combined with enthalpies of formation of the infinitely dilute ions from CODATA,[3] we obtain $\Delta_f H°(Cs_2SO_4, \infty H_2O, 298.15\ K) = -340.746 \pm 0.12\ kcal·mol^{-1}$ and $\Delta_f H°(Cs_2SO_4, cr, 298.15\ K) = -344.80 \pm 0.2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The low temperature heat capacities of Cs_2SO_4 were measured by Paukov *et al.*[4] by adiabatic calorimetry over the region 12.82–308.72 K. The curve of C_p–T was graphically extrapolated to 0 K. Our adopted value of $S°(298.15\ K) = 50.64 \pm 0.05\ cal·K^{-1}·mol^{-1}$ is based on $S°(12\ K) = 0.309\ cal·K^{-1}·mol^{-1}$ as estimated by Paukov *et al.*[4] They also estimated $H°(12\ K)$–$H°(0\ K) = 2.83\ cal·K^{-1}·mol^{-1}$ which leads to $H°(298.15\ K)$–$H°(0\ K) = 6.628 \pm 0.006\ kcal·mol^{-1}$. These values of $S°(12\ K)$ and $H°(12\ K)$–$H°(0\ K)$ are almost identical to estimates obtained using a Debye T^3–law extrapolation. We have smoothed the experimental data of Paukov *et al.*[4] by fitting to orthogonal polynomials.

High temperature heat capacities of Cs_2SO_4 have been measured by Shmidt[5] by adiabatic calorimetry over the range 297.5–774.0 K. Enthalpy measurements by drop calorimetry were carried out by Denielou *et al.*,(400–910 K)[6] and by Polishchuk *et al.*,(803.3–933.4 K).[7] We have joined the low temperature $C_p°$ data of Paukov[4] to the high temperature $C_p°$ data of Shmidt[5] and then merged this into $C_p°$ values derived from the measurements of Denielou *et al.*[6] above 700 K. We have extrapolated the data smoothly to 1200 K.

Transition Data

Cs_2SO_4(cr, II) is the low-temperature form of cesium sulfate (often denoted as Cs_2SO_4, β). The crystals are orthohombic, space group D_{2h}^{16}–Pmcn.[8] The transformation to the high-temperature I-phase (hexagonal, Cs_2SO_4, I) occurs at 940 ± 5 K.[5–7] The enthalpy of transition is determined by taking the difference between the adopted enthalpy curves of II- and I-Cs_2SO_4 extended to 940 K.

References

[1] G. P. Kuznetsova, G. A. Lovetskaya, V. M. Presnyakova, and B. O. Stepin, Russ. J. Phys. Chem. **48**, 2141 (1974).
[2] A. F. Borob'ev, N. A. Ibragim, and S. M. Skuratov, Russ. J. Inorg. Chem. **11**, 13 (1966).
[3] ICSU–CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. **10**, 903 (1978).
[4] I. E. Paukov, L. M. Khriplovich, and A. M. Korotkikh, Russ. J. Phys. Chem. **42**, 661 (1968).
[5] N. E. Shmidt, Russ. J. Phys. Chem. **12**, 929 (1967).
[6] L. Denielou, Y. Fournier, J. P. Petitet and C. Tequi, C. R. Acad. Sci., Paris, **270**, 1854 (1970).
[7] A. F. Polishchuk, T. A. Tishura, and A. N. Buderina, Ukr. Khim. Zh., **40**, 120 (1974).
[8] C. N. R. Rao and B. Prakash, NSRDS–NBS 56, (1975).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−27.732	−1433.163	−1433.163	INFINITE
100	89.287	91.922	317.566	−22.564	−1438.791	−1401.080	731.849
200	114.767	162.172	223.551	−12.276	−1441.328	−1362.260	355.786
298.15	135.143	211.878	211.878	0.	−1442.643	−1323.155	231.811
300	135.478	212.715	211.880	0.250	−1442.663	−1322.413	230.253
400	151.293	253.916	217.391	14.610	−1449.401	−1280.787	167.254
500	164.557	289.120	228.298	30.411	−1449.910	−1238.562	129.392
600	176.816	320.158	241.069	47.453	−1448.986	−1196.356	104.152
700	192.255	348.512	254.416	65.867	−1446.621	−1154.417	86.144
800	212.464	375.547	267.877	86.136	−1442.424	−1112.937	72.667
900	228.697	401.504	281.293	108.190	−1489.626	−1071.010	62.160
940.000	235.337	411.592	286.624	117.470	-------- II <--> I --------		
1000	245.266	426.458	294.570	131.888	−1615.161	−1017.551	53.151
1100	261.835	450.612	307.663	157.244	−1602.852	−958.373	45.509
1200	278.362	474.103	320.558	184.254	−1588.984	−900.384	39.193

PREVIOUS: CURRENT: June 1979

$S°(298.15\ K) = [246.449]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-1400.139]\ kJ·mol^{-1}$

$T_{fus}(I \rightarrow l) = 1278 \pm 5\ J·K^{-1}·mol^{-1}$ $\Delta_{fus}H°(I \rightarrow l) = 35.690 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Cs_2SO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(Cs_2SO_4, cr, I, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1278) - H°(298.15\ K)$, between the I crystal and liquid.[1]

Heat Capacity and Entropy

Enthalpies for Cs_2SO_4(l) have been measured by Denielou *et al.*[2] and by Polishchuk *et al.*[3] We adopt enthalpies based on the work of Denielou *et al.*[2] This leads to a constant heat capacity of 49.4 $cal·K^{-1}·mol^{-1}$ at temperatures above an assumed glass transition at 780 K. Below the glass transition, the heat capacity is taken as that of the low temperature II phase. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the I–crystal table for details.

References

[1]JANAF Thermochemical Tables: Cs_2SO_4(cr, I), 6–30–79.
[2]L. Denielou, Y. Fournier, J-P. Petitet, and C. Tequi, C. R. Acad. Sci. Paris **270**, 1854 (1970).
[3]A. F. Polishchuk, T. A. Tishura, and A. N. Budarina, Ukr. Khim. Zh. **40**, 120 (1974).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	135.143	246.449	246.449	0.	−1400.139	−1290.958	226.171
300	135.478	247.286	246.452	0.250	−1400.159	−1290.281	224.658
400	151.293	288.488	251.962	14.610	−1406.897	−1252.112	163.509
500	164.557	323.692	262.869	30.411	−1407.406	−1213.344	126.757
600	176.816	354.729	275.640	47.453	−1406.482	−1174.595	102.258
700	192.255	383.084	288.988	65.867	−1404.117	−1136.113	84.778
800	212.464	409.874	302.434	85.952	−1400.103	−1098.078	71.697
880.000	241.626	431.400	313.174	104.039	GLASS <--> LIQUID		
880.000	206.690	431.400	313.174	104.039	TRANSITION		
900	206.690	436.045	315.853	108.173	−1447.139	−1059.609	61.498
1000	206.690	457.822	328.980	128.842	−1575.703	−1009.458	52.729
1100	206.690	477.521	341.603	149.511	−1568.081	−953.203	45.264
1200	206.690	495.506	353.689	170.180	−1560.555	−897.638	39.073
1278.000	206.690	508.522	362.746	186.301	------ I <--> LIQUID ------		
1300	206.690	512.050	365.243	190.849	−1553.113	−842.697	33.860
1400	206.690	527.367	376.283	211.518	−1545.751	−788.326	29.413
1500	206.690	541.627	386.836	232.187	−1538.463	−734.480	25.577
1600	206.690	554.967	396.932	252.856	−1531.249	−681.116	22.236
1700	206.690	567.497	406.600	273.524	−1524.110	−628.202	19.302
1800	206.690	579.311	415.870	294.193	−1517.048	−575.706	16.707
1900	206.690	590.486	424.769	314.862	−1510.070	−523.600	14.395
2000	206.690	601.088	433.322	335.531	−1503.179	−471.859	12.324
2100	206.690	611.173	441.553	356.200	−1496.384	−420.460	10.458
2200	206.690	620.788	449.484	376.869	−1489.693	−369.382	8.770
2300	206.690	629.975	457.133	397.538	−1483.114	−318.607	7.236
2400	206.690	638.772	464.519	418.207	−1476.658	−268.116	5.835
2500	206.690	647.210	471.659	438.876	−1470.335	−217.891	4.553
2600	206.690	655.316	478.568	459.545	−1464.154	−167.915	3.373
2700	206.690	663.117	485.260	480.214	−1458.128	−118.174	2.286
2800	206.690	670.633	491.747	500.883	−1452.266	−68.654	1.281
2900	206.690	677.886	498.041	521.552	−1446.581	−19.341	0.348
3000	206.690	684.894	504.153	542.221	−1441.084	29.780	−0.519

PREVIOUS: CURRENT: June 1979

0	to	940 K	crystal, II
940	to	1278 K	crystal, I
above		127 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−27.732	−1433.163	−1433.163	INFINITE
100	89.287	91.922	317.566	−22.564	−1438.791	−1401.080	731.849
200	114.767	162.172	223.551	−12.276	−1441.328	−1362.260	355.786
298.15	135.143	211.878	211.878	0.	−1442.643	−1323.155	231.811
300	135.478	212.715	211.880	0.250	−1442.663	−1322.413	230.253
400	151.293	253.916	217.391	14.610	−1449.401	−1280.787	167.254
500	164.557	289.120	228.298	30.411	−1449.910	−1238.562	129.392
600	176.816	320.158	241.069	47.453	−1448.986	−1196.356	104.152
700	192.255	348.512	254.416	65.867	−1446.621	−1154.417	86.144
800	212.464	375.547	267.877	86.136	−1442.424	−1112.937	72.667
900	228.697	401.504	281.293	108.190	−1489.626	−1071.010	62.160
940.000	235.337	411.592	286.624	117.470	II <--> I		
940.000	184.891	416.177	286.624	121.780	TRANSITION		
1000	194.179	427.901	294.750	133.152	−1613.897	−1017.731	53.161
1100	209.660	447.135	307.731	153.344	−1606.752	−958.448	45.513
1200	225.141	466.041	320.138	175.084	−1598.155	−899.880	39.171
1278.000	237.233	480.596	329.488	193.116	I <--> LIQUID		
1278.000	206.690	508.522	329.488	228.806	TRANSITION		
1300	206.690	512.050	332.548	233.353	−1553.113	−842.697	33.860
1400	206.690	527.367	345.923	254.022	−1545.751	−788.326	29.413
1500	206.690	541.627	358.500	274.691	−1538.463	−734.479	25.577
1600	206.690	554.967	370.367	295.360	−1531.249	−681.116	22.236
1700	206.690	567.497	381.598	316.029	−1524.110	−628.202	19.302
1800	206.690	579.311	392.257	336.698	−1517.048	−575.706	16.707
1900	206.690	590.486	402.399	357.367	−1510.069	−523.600	14.395
2000	206.690	601.088	412.070	378.035	−1503.179	−471.859	12.324
2100	206.690	611.173	421.313	398.704	−1496.384	−420.460	10.458
2200	206.690	620.788	430.163	419.373	−1489.693	−369.382	8.770
2300	206.690	629.975	438.653	440.042	−1483.114	−318.607	7.236
2400	206.690	638.772	446.809	460.711	−1476.658	−268.116	5.835
2500	206.690	647.210	454.657	481.380	−1470.335	−217.891	4.553
2600	206.690	655.316	462.220	502.049	−1464.154	−167.915	3.373
2700	206.690	663.117	469.517	522.718	−1458.128	−118.174	2.286
2800	206.690	670.633	476.567	543.387	−1452.266	−68.654	1.281
2900	206.690	677.886	483.384	564.056	−1446.581	−19.341	0.348
3000	206.690	684.894	489.985	584.725	−1441.084	29.780	−0.519

PREVIOUS: CURRENT: June 1979

$S°(298.15\ K) = 406.5 \pm 2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1109.3 \pm 17.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1122.6 \pm 17.0\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Symmetries, and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
A_1 [970](1)	B_1 [460](1)	E 1100 (2)
[510](1)	B_2 1125 (1)	607 (2)
[90](1)	628 (1)	160 (2)
	190 (1)	[40](2)

Ground State Quantum Weight: 1 $\sigma = 4$

Point Group: D_{2d}

Bond Distances: S–O = 1.49 ± 0.02 Å; Ca–O = 2.60 ± 0.07 Å

Bond Angles: O–S–O = 109.47°; O–Ca–O = 55 ± 5°

Product of the Moments of Inertia: $I_A I_B I_C = 3.287254 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

Vaporization experiments on Cs_2SO_4 have been carried out by Ficalora *et al.*,[1] Cubicciotti,[2] Gorokhov and Efimova,[3] and Jaganathan and Wyatt.[4] Cubicciotti[2] carried out Langmuir sublimation experiments which showed that Cs_2SO_4(cr, l) vaporizes congruently and the predominant vapor species is Cs_2SO_4(g). The Knudsen effusion experiments of Cubicciotti[2] are in excellent agreement with the mass spectrometric and effusion data of Gorokhov and Efimova.[3] The Knudsen weight loss results of Jagannathan and Wyatt[4] are in good agreement with the previous studies[2,3] but the data show a substantial drift. The mass spectrometric study of Ficalora *et al.*[1] yields vapor pressures which are much lower than results of the other three studies. The adopted value of the enthalpy of formation, $\Delta_f H°(Cs_2SO_4, g, 298.15\ K) = -268.3 \pm 4.0\ kcal \cdot mol^{-1}$, is based on JANAF analyses of the vaporization data given below. The calculated 3rd law $\Delta_f H°(298.15\ K)$ may have an uncertainty of 4 $kcal \cdot mol^{-1}$ since the JANAF Gibbs energy functions are partially based on the estimated molecular constants of Cs_2SO_4(g).

Source	Method	T/K	Data Points	δS $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_r H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
1	mass spec.	950–1200	graph	−6.2 ± 2.0	75.65 ± 2.0	80.28 ± 2.0	−264.52 ± 4.0
2	Knudsen effusion	1092.6–1260.6	15	5.14 ± 0.5	82.57 ± 0.5	76.54 ± 0.6	−268.26 ± 2.0
2	Knudsen effusion	1148.8–1261.6	7	3.80 ± 0.9	81.05 ± 1.0	76.48 ± 0.4	−268.32 ± 2.0
3	mass spec.	1063–1278	eqn	1.48	78.2 ± 0.5	76.48 ± 0.5	−268.32 ± 2.0
4	Knudsen effusion	1102–1269	eqn	12.84	92.28	76.95 ± 1.8	−267.85 ± 4.0

Reaction: $Cs_2SO_4(cr) = Cs_2SO_4(g)$

Heat Capacity and Entropy

The structure of cesium sulfate is based on the high temperature electron diffraction studies of Ugarov *et al.*[5] and of Spiridonov and Lutoshkin.[6] These studies show a fairly rigid tetrahedral sulfate anion core but with highly mobile cesium atoms as evidenced by the very large amplitudes of vibration, l(CsS) = 0.15 Å, l(CsO) = 0.34 Å.[5] The average structure is of D_{2d} symmetry and can be pictured as having a central sulfur atom surrounded at the corners of a tetrahedron by four oxygen atoms with bridging cesium atoms between two pairs of oxygen atoms. The planar CsO_2S rings are mutually perpendicular. The principal moments of inertia are: $I_A = 15.7294 \times 10^{-39}$ and $I_B = I_C = 457.1516 \times 10^{-39}\ g \cdot cm^2$.

Belyaeva *et al.*[7] investigated the infrared absorption spectra (400–1500 cm^{-1}) of cesium sulfate molecules stabilized in matrices of Ne, Ar, Xe, and H_2 at 4.2 K. The bands listed above at 607, 628, 1100, and 1125 cm^{-1} are from this work. In a later work, Belyaeva *et al.*[8] reported the low frequency (30–1500 cm^{-1}) infrared spectra of K_2SO_4, Rb_2SO_4, and Cs_2SO_4 molecules isolated in matrices of Ar, Kr, and Xe. The bands listed above at 160 and 140 cm^{-1} are from this work. The band estimated at 40 cm^{-1} is based on our upward adjustment of the calculation of Belyaeva *et al.*[8,9] The band estimated at 970 cm^{-1} is based on the Raman work of Atkins and Gingerich[10] on the similar molecules K_2SO_4 and Na_2SO_4. The remaining fundamental frequencies are estimated by analogy with the other alkali metal sulfates.[11]

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Continued on page 1003

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−23.931	−1109.287	−1109.287	INFINITE
100	73.250	308.845	492.557	−18.371	−1114.522	−1098.503	573.799
200	93.381	365.960	416.040	−10.016	−1118.992	−1080.682	282.245
250	102.369	387.780	408.254	−5.118	−1120.869	−1070.882	223.749
298.15	110.070	406.484	406.484	0.	−1122.567	−1061.100	185.900
300	110.346	407.166	406.486	0.204	−1122.634	−1060.719	184.688
350	117.228	424.706	407.856	5.898	−1128.448	−1049.595	156.644
400	123.053	440.751	410.979	11.909	−1132.027	−1038.146	135.568
450	127.929	455.535	415.119	18.187	−1133.849	−1026.309	119.131
500	131.990	469.231	419.854	24.688	−1135.557	−1014.265	105.959
600	138.194	493.878	430.184	38.216	−1138.147	−989.749	86.165
700	142.552	515.527	440.861	52.266	−1140.146	−964.852	71.998
800	145.680	534.777	451.420	66.686	−1141.798	−939.695	61.356
900	147.979	552.075	461.659	81.374	−1196.366	−913.263	53.004
1000	149.708	567.760	471.497	96.263	−1330.710	−874.403	45.674
1100	151.034	582.094	480.909	111.303	−1328.717	−828.868	39.360
1200	152.072	595.282	489.898	126.460	−1326.703	−783.516	34.106
1300	152.897	607.488	498.480	141.710	−1324.680	−738.333	29.667
1400	153.563	618.844	506.676	157.034	−1322.662	−693.305	25.868
1500	154.108	629.458	514.512	172.419	−1320.659	−648.421	22.580
1600	154.559	639.418	522.011	187.853	−1318.680	−603.670	19.708
1700	154.936	648.800	529.195	203.328	−1316.734	−559.041	17.177
1800	155.254	657.665	536.089	218.838	−1314.832	−514.527	14.931
1900	155.526	666.067	542.710	234.377	−1312.983	−470.116	12.924
2000	155.759	674.050	549.080	249.942	−1311.197	−425.801	11.121
2100	155.960	681.655	555.213	265.528	−1309.485	−381.574	9.491
2200	156.136	688.914	561.127	281.133	−1307.857	−337.425	8.011
2300	156.289	695.858	566.835	296.754	−1306.326	−293.350	6.662
2400	156.424	702.513	572.350	312.390	−1304.904	−249.339	5.427
2500	156.544	708.901	577.685	328.038	−1303.600	−205.384	4.291
2600	156.650	715.043	582.851	343.698	−1302.429	−161.479	3.244
2700	156.745	720.956	587.857	359.368	−1301.402	−117.616	2.275
2800	156.830	726.658	592.713	375.047	−1300.530	−73.788	1.377
2900	156.907	732.163	597.427	390.734	−1299.827	−29.990	0.540
3000	156.976	737.484	602.008	406.428	−1299.305	13.789	−0.240
3100	157.039	742.632	606.461	422.129	−1298.976	57.553	−0.970
3200	157.096	747.619	610.795	437.836	−1298.854	101.309	−1.654
3300	157.148	752.454	615.015	453.548	−1298.867	145.057	−2.296
3400	157.195	757.146	619.127	469.265	−1299.157	188.818	−2.901
3500	157.239	761.703	623.135	484.987	−1299.680	232.588	−3.471
3600	157.279	766.133	627.046	500.713	−1300.444	276.377	−4.010
3700	157.315	770.443	630.864	516.442	−1301.433	320.188	−4.520
3800	157.349	774.639	634.592	532.176	−1302.676	364.032	−5.004
3900	157.381	778.726	638.236	547.912	−1304.154	407.908	−5.463
4000	157.410	782.711	641.798	563.652	−1305.936	451.828	−5.900
4100	157.437	786.598	645.283	579.394	−1307.990	495.797	−6.317
4200	157.462	790.393	648.693	595.139	−1310.322	539.819	−6.714
4300	157.485	794.098	652.031	610.887	−1312.933	583.901	−7.093
4400	157.507	797.719	655.302	626.636	−1315.241	627.979	−7.455
4500	157.528	801.259	658.506	642.388	−1317.195	672.046	−7.801
4600	157.547	804.721	661.647	658.142	−1320.299	716.285	−8.134
4700	157.565	808.110	664.727	673.897	−1323.637	760.595	−8.453
4800	157.582	811.427	667.749	689.655	−1327.203	804.977	−8.760
4900	157.597	814.676	670.715	705.414	−1330.990	849.438	−9.055
5000	157.612	817.860	673.626	721.174	−1334.990	893.977	−9.339
5100	157.626	820.982	676.485	736.936	−1339.196	938.598	−9.613
5200	157.639	824.043	679.293	752.699	−1342.534	983.146	−9.876
5300	157.652	827.046	682.052	768.464	−1346.987	1027.914	−10.131
5400	157.664	829.993	684.765	784.230	−1351.053	1072.680	−10.376
5500	157.675	832.886	687.432	799.996	−1355.457	1117.556	−10.614
5600	157.685	835.727	690.055	815.764	−1360.284	1162.565	−10.844
5700	157.695	838.518	692.635	831.534	−1365.243	1207.659	−11.067
5800	157.705	841.260	695.174	847.304	−1370.325	1252.843	−11.283
5900	157.714	843.956	697.673	863.074	−1375.519	1298.111	−11.493
6000	157.722	846.607	700.133	878.846	−1380.816	1343.473	−11.696

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

Continued from page 981

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REFERENCE STATE

0	to	1358	K	crystal
1358	to	2843.261	K	liquid
above		2843.261	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.007	0.	0.	0.
100	16.010	10.034	53.414	−4.338	0.	0.	0.
200	22.631	23.730	35.354	−2.325	0.	0.	0.
298.15	24.442	33.164	33.164	0.	0.	0.	0.
300	24.462	33.315	33.164	0.045	0.	0.	0.
400	25.318	40.484	34.136	2.539	0.	0.	0.
500	25.912	46.206	35.997	5.105	0.	0.	0.
600	26.481	50.982	38.107	7.725	0.	0.	0.
700	26.996	55.103	40.247	10.399	0.	0.	0.
800	27.494	58.739	42.336	13.123	0.	0.	0.
900	28.049	62.009	44.343	15.899	0.	0.	0.
1000	28.662	64.994	46.261	18.733	0.	0.	0.
1100	29.479	67.763	48.091	21.638	0.	0.	0.
1200	30.519	70.368	49.840	24.633	0.	0.	0.
1300	32.143	72.871	51.516	27.762	0.	0.	0.
1358.000	33.353	74.300	52.459	29.660	CRYSTAL <--> LIQUID		
1358.000	32.844	83.974	52.459	42.798	TRANSITION		
1400	32.844	84.974	53.419	44.177	0.	0.	0.
1500	32.844	87.240	55.599	47.462	0.	0.	0.
1600	32.844	89.360	57.644	50.746	0.	0.	0.
1700	32.844	91.351	59.569	54.031	0.	0.	0.
1800	32.844	93.229	61.387	57.315	0.	0.	0.
1900	32.844	95.004	63.110	60.600	0.	0.	0.
2000	32.844	96.689	64.747	63.884	0.	0.	0.
2100	32.844	98.292	66.307	67.168	0.	0.	0.
2200	32.844	99.819	67.795	70.453	0.	0.	0.
2300	32.844	101.279	69.220	73.737	0.	0.	0.
2400	32.844	102.677	70.585	77.022	0.	0.	0.
2500	32.844	104.018	71.896	80.306	0.	0.	0.
2600	32.844	105.306	73.156	83.591	0.	0.	0.
2700	32.844	106.546	74.370	86.875	0.	0.	0.
2800	32.844	107.740	75.540	90.159	0.	0.	0.
2843.261	32.844	108.244	76.034	91.580	LIQUID <--> IDEAL GAS		
2843.261	24.379	213.995	76.034	392.257	FUGACITY = 1 bar		
2900	24.653	214.479	78.738	393.648	0.	0.	0.
3000	25.147	215.323	83.277	396.138	0.	0.	0.
3100	25.652	216.156	87.550	398.678	0.	0.	0.
3200	26.162	216.978	91.582	401.268	0.	0.	0.
3300	26.673	217.791	95.394	403.910	0.	0.	0.
3400	27.180	218.595	99.006	406.603	0.	0.	0.
3500	27.680	219.390	102.434	409.346	0.	0.	0.
3600	28.168	220.177	105.694	412.138	0.	0.	0.
3700	28.641	220.955	108.799	414.979	0.	0.	0.
3800	29.097	221.725	111.760	417.866	0.	0.	0.
3900	29.533	222.486	114.590	420.798	0.	0.	0.
4000	29.948	223.239	117.296	423.772	0.	0.	0.
4100	30.339	223.984	119.889	426.786	0.	0.	0.
4200	30.707	224.719	122.377	429.839	0.	0.	0.
4300	31.051	225.446	124.765	432.927	0.	0.	0.
4400	31.370	226.163	127.062	436.048	0.	0.	0.
4500	31.665	226.872	129.272	439.200	0.	0.	0.
4600	31.936	227.571	131.401	442.380	0.	0.	0.
4700	32.185	228.260	133.455	445.587	0.	0.	0.
4800	32.413	228.940	135.437	448.817	0.	0.	0.
4900	32.621	229.611	137.352	452.069	0.	0.	0.
5000	32.809	230.272	139.204	455.340	0.	0.	0.
5100	32.981	230.923	140.996	458.630	0.	0.	0.
5200	33.137	231.565	142.731	461.936	0.	0.	0.
5300	33.279	232.198	144.413	465.257	0.	0.	0.
5400	33.409	232.821	146.045	468.591	0.	0.	0.
5500	33.530	233.435	147.628	471.938	0.	0.	0.
5600	33.641	234.040	149.166	475.297	0.	0.	0.
5700	33.746	234.637	150.660	478.666	0.	0.	0.
5800	33.845	235.224	152.113	482.046	0.	0.	0.
5900	33.941	235.804	153.527	485.435	0.	0.	0.
6000	34.035	236.375	154.903	488.834	0.	0.	0.

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 33.164 \pm 0.04\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 1358.0 \pm 0.2\ K$

$\Delta_f H°(0\ K) = 0\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 13.138 \pm 0.4\ kJ\cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity and entropy of copper have been well established by the critical review of Furukawa *et al.*[1] Their recommended smoothed values are adopted with minor corrections for a change in the relative atomic mass from 63.54 to 63.546[2] and for a change to the International Practical Temperature Scale of 1968.[3] These corrections increase the entropy at 298.15 K from 7.923 to 7.926 cal $K^{-1}\cdot mol^{-1}$ and the enthalpy difference, $H°(298.15\ K)-H°(0\ K)$, from 1.1962 to 1.1967 $kcal\cdot mol^{-1}$. The values recommended by CODATA[4] are those of Furukawa *et al.*[1]

From 300 K to the melting point, the heat capacity selected by Hultgren *et al.*[5] has been adopted, with correction for relative atomic mass and temperature scale, and has been joined smoothly with the adopted low temperature data. The measurements of Chekhovskoi and Gerasina,[6] as given by their equation (300–900 K), are in excellent agreement with the selection of Hultgren *et al.*[5] Also, while the data given by Brooks *et al.*[7] (313–1193 K) were 1–2% higher than Hultgren's selected values, the later measurements of Yeh and Brooks[8] on the same sample did not totally confirm the earlier results and measurements on a larger sample (370–870 K) are in good agreement with Hultgren *et al.*[5] The same evaluation used by Hultgren *et al.*[5] was used by two other tabulations[9, 10], although there are small differences in the tabulated values.

Fusion Data

Righini *et al.*[11] reviewed the precise measurements of the freezing point of high-purity copper made since 1960. The mean value of five investigations is 1357.99 ± 0.24 (IPTS-68). Ergardt[12] found 1358.41 K and Righini *et al.*[11] measured 1357.98 ± 0.1 K. We adopt 1358.0 ± 0.2 K for the melting point. As a secondary fixed point IPTS-68 uses 1357.6 K.[13] The adopted value for $\Delta_{fus}H°$ is based upon five measured values and an evaluation of $H°(1358\ K)-H°(298.15\ K)$ for the solid and the liquid.

Source	$\Delta_{fus}H°$, $kcal\cdot mol^{-1}$
[14]	3.239
[15]	3.030
[16]	3.080
[17]	3.290 ± 0.275
[18]	3.107 ± 0.048

The average is 3.149 $kcal\cdot mol^{-1}$. Our least squares linear fit of the liquid enthalpy data of Wust, Meuthen, and Durrer[14] leads to $\Delta_{fus}H° = 3.139\ kcal\cdot mol^{-1}$, and with this change, the average of the five measured values is 3.129 $kcal\cdot mol^{-1}$.

We adopt $\Delta_{fus}H° = 3.140 \pm 0.1\ kcal\cdot mol^{-1}$.

Sublimation Data

Refer to the ideal gas Cu(g) table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−5.007	0.	0.	0.
100	16.010	10.034	53.414	−4.338	0.	0.	0.
200	22.631	23.730	35.354	−2.325	0.	0.	0.
250	23.782	28.915	33.563	−1.162	0.	0.	0.
298.15	24.442	33.164	33.164	0.	0.	0.	0.
300	24.462	33.315	33.164	0.045	0.	0.	0.
350	24.975	37.127	33.464	1.282	0.	0.	0.
400	25.318	40.484	34.136	2.539	0.	0.	0.
450	25.686	43.489	35.011	3.815	0.	0.	0.
500	25.912	46.206	35.997	5.105	0.	0.	0.
600	26.481	50.982	38.107	7.725	0.	0.	0.
700	26.996	55.103	40.247	10.399	0.	0.	0.
800	27.494	58.739	42.336	13.123	0.	0.	0.
900	28.049	62.009	44.343	15.899	0.	0.	0.
1000	28.662	64.994	46.261	18.733	0.	0.	0.
1100	29.479	67.763	48.091	21.638	0.	0.	0.
1200	30.519	70.368	49.840	24.633	0.	0.	0.
1300	32.143	72.871	51.516	27.762	0.	0.	0.
1358.000	33.353	74.300	52.459	29.660	---- CRYSTAL <--> LIQUID ----		
1400	34.258	75.330	53.129	31.081	−13.097	0.406	−0.015
1500	36.425	77.767	54.691	34.615	−12.847	1.363	−0.047
1600	38.593	80.187	56.209	38.366	−12.381	2.296	−0.075
1700	40.760	82.592	57.690	42.333	−11.697	3.194	−0.098
1800	42.928	84.983	59.140	46.518	−10.797	4.045	−0.117
1900	45.095	87.362	60.563	50.919	−9.681	4.840	−0.133
2000	47.263	89.730	61.962	55.537	−8.347	5.570	−0.145

PREVIOUS: December 1965 CURRENT: June 1977

$S°(298.15\ K) = [41.620]\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 1358.0 \pm 0.2\ K$

$\Delta_f H°(298.15\ K) = [11.857]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 13.138 \pm 0.4\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation at 298.15 is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1358\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Since the critical evaluation of Hultgren *et al.*[1] and the selection of 7.80 cal $K^{-1}\cdot mol^{-1}$ for the heat capacity of liquid copper, there have been two experimental investigations. Chaudhuri *et al.* [2] measured enthalpies (1386–1887 K) by levitation heating aluminum block drop calorimetry and determined $C_p(l) = 7.89 \pm 0.41$ cal $K^{-1}\cdot mol^{-1}$. Stephens [3] found $C_p(l) = 8$ cal $K^{-1}\cdot mol$ by levitation heating liquid argon calorimetry (1428–2007 K). The scatter in the new liquid argon calorimetry data is large and is considered only in that it tends to support a "chronological increase" in $C_p(l)$ of copper. The enthalpy differences, $H°(1358\ K)-H°(298.15\ K)$, derived from the measurements of Vollmer and Kohlhaus[4] and Chaudhuri *et al.*[2] are in good agreement at about 10.228 kcal·mol^{-1}, which we adopt. The scatter of liquid enthalpy measurements easily accommodates a wide range of values for $C_p(l)$; we adopt 7.85 cal $K^{-1}\cdot mol^{-1}$, an average of the value selected by Hultgren *et al.*[1] and the later measurement of Chaundhuri *et al.*[2] This value is assumed constant from 900 to 4000 K. A glass transition is assumed at 900 K below which the heat capacity is tha of the crystal.

The entropy is calculated in a manner similar to that used to calculate the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is the calculated temperature at which the Gibbs energy difference is zero for the reaction Cu(l) = Cu(g). $\Delta_{vap}H°$ is the difference in $\Delta_f H°$ between gas and liquid at T_{vap}.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0							
100							
200							
298.15	24.442	41.620	41.620	0.	11.857	9.336	−1.636
300	24.460	41.772	41.621	0.045	11.857	9.320	−1.623
350	24.973	45.583	41.921	1.282	11.857	8.898	−1.328
400	25.316	48.939	42.592	2.539	11.857	8.475	−1.107
450	25.684	51.944	43.467	3.814	11.857	8.052	−0.935
500	25.910	54.661	44.453	5.104	11.857	7.629	−0.797
600	26.478	59.436	46.563	7.724	11.857	6.784	−0.591
700	26.993	63.557	48.703	10.398	11.856	5.938	−0.443
800	27.491	67.193	50.791	13.121	11.856	5.093	−0.333
900	28.047	70.463	52.798	15.898	11.856	4.248	−0.247
900.000	28.047	70.463	52.798	15.898	GLASS <--> LIQUID TRANSITION		
900.000	32.844	70.463	52.798	15.898			
1000	32.844	73.923	54.741	19.182	12.306	3.378	−0.176
1100	32.844	77.053	56.629	22.467	12.686	2.466	−0.117
1200	32.844	79.911	58.452	25.751	12.975	1.523	−0.066
1300	32.844	82.540	60.205	29.036	13.131	0.561	−0.023
1358.000	32.844	83.974	61.190	30.941	CRYSTAL <--> LIQUID		
1400	32.844	84.974	61.889	32.320	0.	0.	0.
1500	32.844	87.240	63.504	35.604	0.	0.	0.
1600	32.844	89.360	65.055	38.889	0.	0.	0.
1700	32.844	91.351	66.543	42.173	0.	0.	0.
1800	32.844	93.229	67.974	45.458	0.	0.	0.
1900	32.844	95.004	69.351	48.742	0.	0.	0.
2000	32.844	96.689	70.676	52.027	0.	0.	0.
2100	32.844	98.292	71.953	55.311	0.	0.	0.
2200	32.844	99.819	73.185	58.596	0.	0.	0.
2300	32.844	101.279	74.375	61.880	0.	0.	0.
2400	32.844	102.677	75.525	65.164	0.	0.	0.
2500	32.844	104.018	76.639	68.449	0.	0.	0.
2600	32.844	105.306	77.717	71.733	0.	0.	0.
2700	32.844	106.546	78.761	75.018	0.	0.	0.
2800	32.844	107.740	79.775	78.302	0.	0.	0.
2843.261	32.844	108.244	80.205	79.723	FUGACITY = 1 bar		
2900	32.844	108.893	80.760	81.587	−300.204	5.996	−0.108
3000	32.844	110.006	81.716	84.871	−299.409	16.541	−0.288
3100	32.844	111.083	82.646	88.155	−298.665	27.060	−0.456
3200	32.844	112.126	83.551	91.440	−297.971	37.556	−0.613
3300	32.844	113.137	84.432	94.724	−297.328	48.031	−0.760
3400	32.844	114.117	85.291	98.009	−296.737	58.488	−0.899
3500	32.844	115.069	86.128	101.293	−296.195	68.927	−1.029
3600	32.844	115.995	86.945	104.578	−295.703	79.352	−1.151
3700	32.844	116.894	87.743	107.862	−295.259	89.764	−1.267
3800	32.844	117.770	88.521	111.147	−294.862	100.165	−1.377
3900	32.844	118.624	89.282	114.431	−294.509	110.556	−1.481
4000	32.844	119.455	90.026	117.715	−294.199	120.938	−1.579

PREVIOUS: December 1966 CURRENT: June 1977

0 to 1358 K crystal
above 1358 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.007	0.	0.	0.
100	16.010	10.034	53.414	−4.338	0.	0.	0.
200	22.631	23.730	35.354	−2.325	0.	0.	0.
250	23.782	28.915	33.563	−1.162	0.	0.	0.
298.15	24.442	33.164	33.164	0.	0.	0.	0.
300	24.462	33.315	33.164	0.045	0.	0.	0.
350	24.975	37.127	33.464	1.282	0.	0.	0.
400	25.318	40.484	34.136	2.539	0.	0.	0.
450	25.686	43.489	35.011	3.815	0.	0.	0.
500	25.912	46.206	35.997	5.105	0.	0.	0.
600	26.481	50.982	38.107	7.725	0.	0.	0.
700	26.996	55.103	40.247	10.399	0.	0.	0.
800	27.494	58.739	42.336	13.123	0.	0.	0.
900	28.049	62.009	44.343	15.899	0.	0.	0.
1000	28.662	64.994	46.261	18.733	0.	0.	0.
1100	29.479	67.763	48.091	21.638	0.	0.	0.
1200	30.519	70.368	49.840	24.633	0.	0.	0.
1300	32.143	72.871	51.516	27.762	0.	0.	0.
1358.000	33.353	74.300	52.459	29.660	____ CRYSTAL <-- --> LIQUID ____		
1358.000	32.844	83.974	52.459	42.798	TRANSITION		
1400	32.844	84.974	53.419	44.177	0.	0.	0.
1500	32.844	87.240	55.599	47.462	0.	0.	0.
1600	32.844	89.360	57.644	50.746	0.	0.	0.
1700	32.844	91.351	59.569	54.031	0.	0.	0.
1800	32.844	93.229	61.387	57.315	0.	0.	0.
1900	32.844	95.004	63.110	60.600	0.	0.	0.
2000	32.844	96.689	64.747	63.884	0.	0.	0.
2100	32.844	98.292	66.307	67.168	0.	0.	0.
2200	32.844	99.819	67.795	70.453	0.	0.	0.
2300	32.844	101.279	69.220	73.737	0.	0.	0.
2400	32.844	102.677	70.585	77.022	0.	0.	0.
2500	32.844	104.018	71.896	80.306	0.	0.	0.
2600	32.844	105.306	73.156	83.591	0.	0.	0.
2700	32.844	106.546	74.370	86.875	0.	0.	0.
2800	32.844	107.740	75.540	90.159	0.	0.	0.
2843.261	32.844	108.244	76.034	91.580	----- FUGACITY = 1 bar -----		
2900	32.844	108.893	76.671	93.444	−300.204	5.996	−0.108
3000	32.844	110.006	77.764	96.728	−299.409	16.541	−0.288
3100	32.844	111.083	78.821	100.013	−298.665	27.060	−0.456
3200	32.844	112.126	79.846	103.297	−297.971	37.556	−0.613
3300	32.844	113.137	80.839	106.582	−297.328	48.031	−0.760
3400	32.844	114.117	81.804	109.866	−296.737	58.488	−0.899
3500	32.844	115.069	82.741	113.151	−296.195	68.927	−1.029
3600	32.844	115.995	83.652	116.435	−295.703	79.352	−1.151
3700	32.844	116.894	84.538	119.719	−295.259	89.764	−1.267
3800	32.844	117.770	85.401	123.004	−294.862	100.165	−1.377
3900	32.844	118.624	86.242	126.288	−294.509	110.556	−1.481
4000	32.844	119.455	87.062	129.573	−294.199	120.938	−1.579

PREVIOUS: CURRENT: June 1977

IP(Cu, g) = 62317.2 ± 0.5 cm^{-1}
$S°(298.15\ K)$ = 166.397 ± 0.025 $J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = 336.4 ± 1.2 $kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 337.6 ± 1.2 $kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^1	g_i
$^2S_{1/2}$	0.000	2
$^2D_{5/2}$	11202.565	6
$^2D_{3/2}$	13245.432	4
$^2P_{1/2}$	30535.302	2
$^2P_{3/2}$	30783.683	4

Enthalpy of Formation

The adopted enthalpy of formation for Cu(g), $\Delta_f H°(298.15\ K)$ = 337.6 ± 1.2 $kJ\cdot mol^{-1}$, is the value recommended by CODATA[1]. This value was based on the measurements of Edwards *et al.*,[2] Hersh,[3] Morris and Zellars,[4] Marshall *et al.*,[5] McCormack *et al.*,[6] Myles and Darby,[7] Grieviso *et al.*,[8] Kirschenbaum and Cahill,[9] Krupkowski and Golonka[10] and Ponslit and Bariaux.[11] Additional references are given in Hultgren *et al.*[12]

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[13] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground state and the lowest lying levels, all levels listed by Moore,[13] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Cu(g), the thermodynamic functions are independent of the estimated missing levels (for n = 4−11), the cut off procedure, and the inclusion of n<12 levels up to 6000 K; the Gibbs energy function showing variations of 0.001 $J\ K^{-1}\cdot mol^{-1}$ at this temperature. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>11), and use of different fill and cut off procedures.[14]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	336.409	336.409	INFINITE
100	20.786	143.690	184.877	−4.119	337.819	324.454	−169.477
200	20.786	158.097	168.298	−2.040	337.885	311.011	−81.228
250	20.786	162.736	166.739	−1.001	337.761	304.306	−63.581
298.15	20.786	166.397	166.397	0.	337.600	297.877	−52.187
300	20.786	166.525	166.397	0.038	337.593	297.630	−51.822
350	20.786	169.730	166.650	1.078	337.396	290.985	−43.427
400	20.786	172.505	167.213	2.117	337.178	284.369	−37.135
450	20.786	174.953	167.939	3.156	336.942	277.782	−32.244
500	20.786	177.144	168.752	4.196	336.691	271.222	−28.334
600	20.786	180.933	170.476	6.274	336.150	258.179	−22.476
700	20.786	184.137	172.205	8.353	335.554	245.230	−18.299
800	20.786	186.913	173.874	10.431	334.909	232.370	−15.172
900	20.786	189.361	175.461	12.510	334.211	219.594	−12.745
1000	20.787	191.551	176.963	14.589	333.456	206.898	−10.807
1100	20.788	193.533	178.380	16.667	332.629	194.282	−9.226
1200	20.793	195.342	179.719	18.746	331.713	181.745	−7.911
1300	20.803	197.006	180.986	20.826	330.665	169.289	−6.802
1400	20.823	198.549	182.186	22.907	316.330	157.326	−5.870
1500	20.856	199.986	183.325	24.991	315.130	146.011	−5.085
1600	20.909	201.334	184.409	27.079	313.933	134.775	−4.400
1700	20.985	202.604	185.443	29.174	312.743	123.614	−3.798
1800	21.091	203.806	186.430	31.277	311.562	112.523	−3.265
1900	21.230	204.950	187.375	33.393	310.394	101.497	−2.790
2000	21.407	206.043	188.281	35.525	309.241	90.533	−2.364
2100	21.622	207.093	189.152	37.676	308.107	79.625	−1.981
2200	21.878	208.104	189.990	39.850	306.998	68.771	−1.633
2300	22.173	209.083	190.799	42.053	305.915	57.967	−1.316
2400	22.507	210.034	191.581	44.286	304.865	47.209	−1.027
2500	22.878	210.960	192.338	46.555	303.849	36.495	−0.763
2600	23.282	211.865	193.071	48.863	302.873	25.820	−0.519
2700	23.715	212.752	193.784	51.213	301.938	15.182	−0.294
2800	24.174	213.622	194.477	53.607	301.048	4.578	−0.085
2843.261	24.379	213.995	194.771	54.657	----- FUGACITY = 1 bar -----		
2900	24.653	214.479	195.152	56.048	0.	0.	0.
3000	25.147	215.323	195.810	58.538	0.	0.	0.
3100	25.652	216.156	196.453	61.078	0.	0.	0.
3200	26.162	216.978	197.082	63.669	0.	0.	0.
3300	26.673	217.791	197.697	66.310	0.	0.	0.
3400	27.180	218.595	198.300	69.003	0.	0.	0.
3500	27.680	219.390	198.891	71.746	0.	0.	0.
3600	28.168	220.177	199.472	74.539	0.	0.	0.
3700	28.641	220.955	200.042	77.379	0.	0.	0.
3800	29.097	221.725	200.602	80.266	0.	0.	0.
3900	29.533	222.486	201.154	83.198	0.	0.	0.
4000	29.948	223.239	201.696	86.172	0.	0.	0.
4100	30.339	223.984	202.231	89.187	0.	0.	0.
4200	30.707	224.719	202.758	92.239	0.	0.	0.
4300	31.051	225.446	203.277	95.327	0.	0.	0.
4400	31.370	226.163	203.789	98.449	0.	0.	0.
4500	31.665	226.872	204.294	101.601	0.	0.	0.
4600	31.936	227.571	204.792	104.781	0.	0.	0.
4700	32.185	228.260	205.284	107.987	0.	0.	0.
4800	32.413	228.940	205.770	111.217	0.	0.	0.
4900	32.621	229.611	206.250	114.469	0.	0.	0.
5000	32.809	230.272	206.724	117.741	0.	0.	0.
5100	32.981	230.923	207.192	121.030	0.	0.	0.
5200	33.137	231.565	207.654	124.336	0.	0.	0.
5300	33.279	232.198	208.111	127.657	0.	0.	0.
5400	33.409	232.821	208.563	130.992	0.	0.	0.
5500	33.530	233.435	209.010	134.339	0.	0.	0.
5600	33.641	234.040	209.452	137.697	0.	0.	0.
5700	33.746	234.637	209.888	141.066	0.	0.	0.
5800	33.845	235.224	210.320	144.446	0.	0.	0.
5900	33.941	235.804	210.747	147.835	0.	0.	0.
6000	34.035	236.375	211.169	151.234	0.	0.	0.

PREVIOUS: June 1977 (1 atm) CURRENT: September 1984 (1 bar)

IP(Cu^+,g) = 163669.2 ± 0.5 cm^{-1}
$S°$(298.15 K) = 222.311 ± 0.02 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 1081.9 ± 2.1 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [1089.277] kJ·mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1
$^3D_3$	21928.60	7
$^3D_2$	22847.03	5
$^3D_1$	23998.31	3
$^1D_2$	26264.52	5

Enthalpy of Formation

$\Delta_f H°$(Cu^+, g, 0 K) is calculated from $\Delta_f H°$(Cu, g, 0 K)[1] using the spectroscopic value of IP(Cu) = 62317.2 ± 0.5 cm^{-1} (745.479 ± 0.006 kJ·mol^{-1}) from Moore.[2] The ionization limit is converted from cm^{-1} to kJ·mol^{-1} using the factor, 1 cm^{-1} = 0.01196266 kJ cm^{-1}, which is derived from the 1973 CODATA fundamental constants[3]. Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°$(Cu^+, g, 298.15 K) is calculated from $\Delta_f H°$(Cu, g, 0 K) by using IP(Cu) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for Cu(g), Cu^+(g), and e^-(g). $\Delta_f H°$($Cu \rightarrow Cu^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels, that any reasonable method of filling in these missing levels and cutting off the summation in the partition function,[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states. The next excited state is 66418.65 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions to 6000 K, we list only the ground state and the first four excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

[1]JANAF Thermochemical Tables: Cu(g), 9–30–84 ; e^-(ref), 3–31–82.
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[6]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–35,Volulme I, 1971 [Reprinted from NBS Circular 467, Volume I, 1949].
[7]J. R. Downey, Jr., The Dow Chemical Company, AFOSR–TR–0960, Contract No. F44620–75–1–0048,1978.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1081.889		
100	20.786	199.604	240.792	−4.119			
200	20.786	214.012	224.213	−2.040			
250	20.786	218.650	222.654	−1.001			
298.15	20.786	222.311	222.311	0.	1089.277	1026.628	−179.861
300	20.786	222.440	222.312	0.038	1089.308	1026.239	−178.684
350	20.786	225.644	222.565	1.078	1090.150	1015.660	−151.579
400	20.786	228.420	223.127	2.117	1090.972	1004.963	−131.235
450	20.786	230.868	223.854	3.156	1091.775	994.163	−115.399
500	20.786	233.058	224.667	4.196	1092.564	983.275	−102.722
600	20.786	236.848	226.391	6.274	1094.101	961.272	−83.686
700	20.786	240.052	228.119	8.353	1095.584	939.016	−70.070
800	20.786	242.828	229.788	10.431	1097.017	916.551	−59.845
900	20.786	245.276	231.376	12.510	1098.398	893.909	−51.881
1000	20.786	247.466	232.877	14.589	1099.721	871.116	−45.502
1100	20.786	249.447	234.295	16.667	1100.973	848.195	−40.277
1200	20.786	251.256	235.634	18.746	1102.135	825.163	−35.918
1300	20.786	252.919	236.901	20.824	1103.164	802.039	−32.226
1400	20.786	254.460	238.100	22.903	1090.906	779.248	−29.074
1500	20.786	255.894	239.239	24.982	1091.778	756.957	−26.360
1600	20.786	257.235	240.323	27.060	1092.651	734.607	−23.982
1700	20.786	258.495	241.355	29.139	1093.524	712.202	−21.883
1800	20.786	259.684	242.341	31.217	1094.397	689.746	−20.016
1900	20.786	260.807	243.283	33.296	1095.269	667.242	−18.344
2000	20.786	261.874	244.186	35.375	1096.142	644.692	−16.838
2100	20.786	262.888	245.053	37.453	1097.015	622.098	−15.474
2200	20.786	263.855	245.886	39.532	1097.888	599.462	−14.233
2300	20.786	264.779	246.687	41.610	1098.761	576.787	−13.099
2400	20.786	265.663	247.460	43.689	1099.633	554.074	−12.059
2500	20.786	266.512	248.205	45.768	1100.506	531.324	−11.101
2600	20.786	267.327	248.925	47.846	1101.379	508.539	−10.217
2700	20.786	268.112	249.621	49.925	1102.252	485.721	−9.397
2800	20.786	268.868	250.295	52.004	1103.124	462.871	−8.635
2900	20.786	269.597	250.948	54.082	803.793	445.985	−8.033
3000	20.786	270.302	251.581	56.161	805.461	433.618	−7.550
3100	20.786	270.983	252.196	58.239	807.078	421.197	−7.097
3200	20.786	271.643	252.794	60.318	808.645	408.724	−6.672
3300	20.786	272.283	253.375	62.397	810.160	396.203	−6.271
3400	20.787	272.903	253.940	64.475	811.625	383.637	−5.894
3500	20.787	273.506	254.490	66.554	813.039	371.028	−5.537
3600	20.787	274.091	255.027	68.633	814.404	358.380	−5.200
3700	20.787	274.661	255.550	70.711	815.720	345.694	−4.880
3800	20.787	275.215	256.060	72.790	816.990	332.974	−4.577
3900	20.787	275.755	256.558	74.869	818.216	320.220	−4.289
4000	20.788	276.282	257.045	76.948	819.399	307.436	−4.015
4100	20.788	276.795	257.520	79.026	820.542	294.623	−3.754
4200	20.788	277.296	257.985	81.105	821.647	281.782	−3.504
4300	20.789	277.785	258.440	83.184	822.716	268.915	−3.267
4400	20.789	278.263	258.885	85.263	823.753	256.024	−3.039
4500	20.789	278.730	259.321	87.342	824.758	243.110	−2.822
4600	20.790	279.187	259.748	89.421	825.735	230.174	−2.614
4700	20.790	279.634	260.166	91.500	826.687	217.216	−2.414
4800	20.791	280.072	260.576	93.579	827.614	204.239	−2.223
4900	20.791	280.501	260.979	95.658	828.520	191.243	−2.039
5000	20.792	280.921	261.373	97.737	829.406	178.228	−1.862
5100	20.792	281.332	261.761	99.816	830.274	165.196	−1.692
5200	20.793	281.736	262.141	101.895	831.126	152.147	−1.528
5300	20.793	282.132	262.514	103.975	831.963	139.081	−1.371
5400	20.794	282.521	262.881	106.054	832.787	126.000	−1.219
5500	20.794	282.902	263.242	108.133	833.598	112.904	−1.072
5600	20.795	283.277	263.596	110.213	834.397	99.793	−0.931
5700	20.796	283.645	263.945	112.292	835.186	86.668	−0.794
5800	20.796	284.007	264.288	114.372	835.965	73.530	−0.662
5900	20.797	284.362	264.625	116.452	836.734	60.378	−0.535
6000	20.798	284.712	264.957	118.531	837.493	47.213	−0.411

PREVIOUS: June 1977 (1 atm) CURRENT: September 1984 (1 bar)

EA(Cu, g) = 1.228 ± 0.010 eV
$S°(298.15\ K)$ = 160.634 ± 0.001 J $K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 217.926 kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = [212.920] kJ·mol^{-1}

Electonic level and quantum weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(Cu^-, g, 0\ K)$ is calculated from $\Delta_f H°(Cu, g, 0\ K)$ using the adopted electron affinity of EA(Cu) = 1.228 ± 0.010 eV (118.483 ± 0.965 kJ mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment election spectrometry study[3] Additional information on $Cu^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Cu^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Cu, g, 0\ K)$ by using EA(Cu) with JANAF[1]enthalpies, $H°(0\ K) - H°(298.15\ K)$, for $Cu^-(g)$, Cu(g), and $e^-(g)$. $\Delta_r H°(Cu^- \rightarrow Cu + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Cu^-(g)$ is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

[1]JANAF Thermochemical Tables: Cu(g), 9–30–84; e^-(ref), 3–31–82.
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[5]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
[6]H. S. W. Massey, Negative Ions, 3rd ed., Cambridge University Press, Cambrige, (1976).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	217.926		
100	20.786	137.927	179.114	−4.119			
200	20.786	152.334	162.535	−2.040			
250	20.786	156.973	160.976	−1.001			
298.15	20.786	160.634	160.634	0.	212.920	181.169	−31.740
300	20.786	160.762	160.634	0.038	212.874	180.972	−31.510
350	20.786	163.967	160.887	1.078	211.638	175.753	−26.230
400	20.786	166.742	161.450	2.117	210.381	170.712	−22.293
450	20.786	169.190	162.176	3.156	209.105	165.830	−19.249
500	20.786	171.381	162.989	4.196	207.815	161.091	−16.829
600	20.786	175.170	164.713	6.274	205.195	151.991	−13.232
700	20.786	178.374	166.442	8.353	202.521	143.334	−10.696
800	20.786	181.150	168.111	10.431	199.797	135.064	−8.819
900	20.786	183.598	169.698	12.510	197.020	127.139	−7.379
1000	20.786	185.788	171.200	14.589	194.186	119.525	−6.243
1100	20.786	187.769	172.617	16.667	191.281	112.199	−5.328
1200	20.786	189.578	173.956	18.746	188.286	105.141	−4.577
1300	20.786	191.242	175.223	20.824	185.158	98.338	−3.951
1400	20.786	192.782	176.423	22.903	168.742	92.189	−3.440
1500	20.786	194.216	177.562	24.982	165.458	86.835	−3.024
1600	20.786	195.558	178.645	27.060	162.173	81.701	−2.667
1700	20.786	196.818	179.677	29.139	158.889	76.772	−2.359
1800	20.786	198.006	180.663	31.217	155.605	72.036	−2.090
1900	20.786	199.130	181.606	33.296	152.320	67.483	−1.855
2000	20.786	200.196	182.509	35.375	149.036	63.103	−1.648
2100	20.786	201.210	183.375	37.453	145.751	58.887	−1.465
2200	20.786	202.177	184.208	39.532	142.467	54.828	−1.302
2300	20.786	203.101	185.010	41.610	139.182	50.918	−1.156
2400	20.786	203.986	185.782	43.689	135.898	47.151	−1.026
2500	20.786	204.834	186.527	45.768	132.613	43.521	−0.909
2600	20.786	205.650	187.247	47.846	129.329	40.022	−0.804
2700	20.786	206.434	187.943	49.925	126.045	36.649	−0.709
2800	20.786	207.190	188.617	52.004	122.760	33.398	−0.623
2900	20.786	207.919	189.270	54.082	−180.728	36.261	−0.653
3000	20.786	208.624	189.904	56.161	−183.218	43.785	−0.762
3100	20.786	209.306	190.519	58.239	−185.758	51.394	−0.866
3200	20.786	209.966	191.116	60.318	−188.349	59.085	−0.964
3300	20.786	210.605	191.697	62.397	−190.990	66.858	−1.058
3400	20.786	211.226	192.262	64.475	−193.683	74.712	−1.148
3500	20.786	211.828	192.813	66.554	−196.426	82.646	−1.233
3600	20.786	212.414	193.349	68.632	−199.219	90.658	−1.315
3700	20.786	212.983	193.872	70.711	−202.059	98.750	−1.394
3800	20.786	213.538	194.382	72.790	−204.946	106.918	−1.470
3900	20.786	214.078	194.881	74.868	−207.878	115.163	−1.542
4000	20.786	214.604	195.367	76.947	−210.852	123.484	−1.613
4100	20.786	215.117	195.843	79.025	−213.867	131.880	−1.680
4200	20.786	215.618	196.308	81.104	−216.919	140.349	−1.746
4300	20.786	216.107	196.762	83.183	−220.007	148.892	−1.809
4400	20.786	216.585	197.207	85.261	−223.129	157.507	−1.870
4500	20.786	217.052	197.643	87.340	−226.281	166.194	−1.929
4600	20.786	217.509	198.070	89.418	−229.461	174.950	−1.987
4700	20.786	217.956	198.489	91.497	−232.667	183.776	−2.042
4800	20.786	218.394	198.899	93.576	−235.897	192.671	−2.097
4900	20.786	218.822	199.301	95.654	−239.149	201.633	−2.149
5000	20.786	219.242	199.696	97.733	−242.421	210.662	−2.201
5100	20.786	219.654	200.083	99.811	−245.710	219.756	−2.251
5200	20.786	220.057	200.463	101.890	−249.016	228.915	−2.299
5300	20.786	220.453	200.837	103.969	−252.337	238.138	−2.347
5400	20.786	220.842	201.203	106.047	−255.672	247.423	−2.393
5500	20.786	221.223	201.564	108.126	−259.019	256.771	−2.439
5600	20.786	221.598	201.918	110.204	−262.377	266.179	−2.483
5700	20.786	221.966	202.267	112.283	−265.747	275.647	−2.526
5800	20.786	222.327	202.610	114.362	−269.126	285.175	−2.568
5900	20.786	222.682	202.947	116.440	−272.515	294.761	−2.610
6000	20.786	223.032	203.279	118.519	−275.914	304.404	−2.650

PREVIOUS: CURRENT: September 1984 (1 bar)

Copper Fluoride (CuF) CRYSTAL M_r = 82.544403

$S°(298.15\ K) = [64.852 \pm 2.1]\ J\ K^{-1}\cdot mol^{-1}$
T_{fus} = Unknown

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-280.33 \pm 41.8]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy of formation is calculated by combining the adopted $\Delta_f H°$(CuF, g, 298.15 K) = -3.0 ± 4 kcal mol^{-1} with the estimated enthalpy of sublimation of 64 kcal mol^{-1}. A comparison of enthalpies of sublimation of LiF with LiCl, NaF with NaCl, and KF with KCl[1] along with an enthalpy of sublimation[1] of CuCl of 54.77 kcal mol^{-1} indicates that $\Delta_{sub} H°$(CuF, cr, 298.15 K) might be in the range of 58 to 71 kcal mol^{-1}. The tabulations of King *et al.*[2] lead to $\Delta_{sub} H°(298.15\ K) = 64$ kcal mol^{-1} which we adopt. We derive $\Delta_f H°$(CuF, cr, 298.15 K) = -67 ± 10 kcal mol^{-1}.

Heat Capacity and Entropy

We adopt the heat capacities estimated by King *et al.*[2] and $S°(298.15\ K) = 15.5 \pm 0.5$ cal K$^{-1}\cdot$mol^{-1} estimated by Kelley and King.[3]

References

[1]JANAF Thermochemical Tables: LiCl(cr, g), 9–30–65; NaCl(cr, g), 9–30–64; KCl(cr, g), CuCl(cr, g), 3–31–66; LiF(cr, g), NaF(cr, g), 12–31–68; KF(cr, g), 6–30–69.

[2]E. G. King, A. D. Mah and L. B. Pankratz, Thermodynamic Properties of Copper and Its Inorganic Compounds. INCRA Series on a Metallurgy of Copper, No. 2, INCRA, New York, (1973).

[3]K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	51.882	64.852	64.852	0.	−280.328	−259.545	45.471
300	51.965	65.173	64.853	0.096	−280.306	−259.416	45.168
400	55.145	80.574	66.931	5.457	−279.049	−252.638	32.991
500	57.656	93.160	70.956	11.102	−277.652	−246.194	25.720
600	59.580	103.850	75.570	16.968	−276.142	−240.043	20.898
700	60.961	113.143	80.288	22.998	−274.562	−234.151	17.473
800	62.007	121.354	84.918	29.149	−272.941	−228.488	14.919
900	62.802	128.706	89.382	35.391	−271.302	−223.030	12.944
1000	63.346	135.352	93.652	41.700	−269.672	−217.754	11.374
1100	63.764	141.410	97.722	48.056	−268.081	−212.639	10.097
1200	64.057	146.971	101.598	54.448	−266.557	−207.667	9.040
1300	64.266	152.107	105.288	60.865	−265.153	−202.818	8.149
1400	64.378	156.874	108.805	67.297	−277.031	−197.664	7.375
1500	64.434	161.318	112.159	73.739	−275.780	−192.038	6.687
1600	64.434	165.477	115.363	80.182	−274.536	−186.496	6.088
1700	64.434	169.383	118.427	86.625	−273.299	−181.032	5.562
1800	64.434	173.066	121.361	93.069	−272.070	−175.640	5.097
1900	64.434	176.549	124.175	99.512	−270.847	−170.316	4.682
2000	64.434	179.854	126.877	105.955	−269.629	−165.056	4.311

PREVIOUS: June 1966 CURRENT: December 1977

$D_0^\circ = 425.5 \pm 20.9$ kJ mol^{-1}
$S^\circ(298.15\ K) = 226.495 \pm 0.21$ J K^{-1}·mol^{-1}

$\Delta_f H^\circ(0\ K) = -12.22 \pm 16.7$ kJ·mol^{-1}
$\Delta_f H^\circ(298.15\ K) = -12.55 \pm 16.7$ kJ·mol^{-1}

Electronic levels and quantum weights		
State	ϵ_i, cm^{-1}	g_i
$X(^1\Sigma)$	0	[1]
$A(^1\Pi)$	17546.8	[2]
$B(^1\Sigma)$	19738.5	[1]
$C(^1\Pi)$	20258.8	[2]

$\omega_e = 622.65$ cm^{-1} $\omega_e x_e = 3.950$ cm^{-1} $\sigma = 1$
$B_e = 0.3786$ cm^{-1} $\alpha_e = 0.0032$ cm^{-1} $r_e = 1.7449$ Å

Enthalpy of Formation

Hildenbrand[1] and Ehlert and Wang[2] have reported mass spectrometric measurements of equilibrium pressures of the reactions MgF(g) + Cu(g) = Mg(g) + CuF(g) and 1/2 CuF_2(cr) + 1/2 Cu(cr) = CuF(g), respectively. Our 2nd and 3rd law analyses follow.

Source	Reaction*	T/K	Data points	$\Delta_f H^\circ$(298.15 K), kcal mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H$(298.15 K) kcal·mol^{-1}
[1]	A	1413–1590	12	11.52±2.84	7.08±0.68	−2.9±1.9	−4.15±3
[2]	B	936–948	3	75.97±3.90	62.34±0.19	−14.5±4.1	−2.06±21

*Reactions: (A) MgF(g) + Cu(g) = Mg(g) + CuF(g)
(B) 1/2 CuF_2(cr) + 1/2 Cu(cr) = CuF(g)

We adopt the rounded average, $\Delta_f H^\circ$(CuF, g, 298.15 K) = −3.0 ± 4 kcal·mol^{-1} (−12.552 ± 16.7 kJ·mol^{-1}), which leads to D_0°(CuF, 298.15 K) = 102.5±5 kcal·mol^{-1} and D_0°(CuF) = 101.7±5 kcal·mol^{-1}(425.513 ± 20.9 kJ mol^{-1}).

Another value extant in the literature is D_0°(298.15 K) = 83.6±4.0 kcal·mol^{-1} estimated from the heat of atomization of CuF_2, derived from sublimation studies, and the ratio D_0°(M–F)/$\Delta_a H^\circ(MF_2)$ = 0.46[4]. Hildenbrand[1] has discussed the valence state concept which predicts that D_0°(M–F)>D_0°(MF–F); therefore the ratio D_0°(M–F)/[D(M–F) + D_0°(MF–F) must be greater than 0.5. With $\Delta_{at}H^\circ(CuF_2, 298.15\ K)$ = 182.17 kcal·mol^{-1}[3] and D_0°(CuF, 298.15 K) = −102.5 kcal·mol^{-1}, the ratio based on JANAF values is 0.56. For $\Delta_{at}H^\circ(CuF_2, 298.15\ K)$ = 182.7 kcal mol^{-1}, D_0°(CuF, 298.15 K) must be greater than 91.08 kcal·mol^{-1} to agree with the valence state concept.

Other calculations by Kent *et al.*[4] give D (298.15 K) values ranging from 84.4 to 94.5 kcal mol^{-1}. Gaydon[5] recommends D_0° = 81 kcal·mol^{-1} from a linear Birge–Sponer extrapolation of spectroscopic data but suggests that it is probably higher. King *et al.*[6] used $\Delta_f H^\circ$(298.15 K) = 14 kcal·mol^{-1}, $\Delta_{at}H^\circ$(298.15 K) = 84.7 kcal·mol^{-1} in their recent tabulation.

Heat Capacity and Entropy

The values of B_e and r_e are from the microwave data of Hoeft *et al.*[7] adjusted for normal isotopic abundance; the electronic levels, ω_e and $\omega_e x_e$ are taken from Rosen.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

T/K	C_p°	S° (J·K^{-1}·mol^{-1})	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$ (kJ·mol^{-1})	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−9.083	−12.216	−12.216	INFINITE
100	29.204	192.900	254.629	−6.173	−11.428	−21.196	11.072
200	31.140	213.620	229.482	−3.172	−11.905	−30.818	8.049
250	32.375	220.704	227.040	−1.584	−12.231	−35.509	7.419
298.15	33.379	226.495	226.495	0.	−12.552	−39.963	7.001
300	33.414	226.702	226.496	0.062	−12.564	−40.133	6.988
350	34.234	231.917	226.906	1.754	−12.903	−44.701	6.671
400	34.871	236.532	227.826	3.482	−13.248	−49.220	6.427
450	35.367	240.669	229.027	5.239	−13.600	−53.696	6.233
500	35.759	244.416	230.382	7.017	−13.961	−58.131	6.073
600	36.327	250.989	233.284	10.623	−14.712	−66.896	5.824
700	36.713	256.620	236.225	14.276	−15.508	−75.531	5.636
800	36.992	261.541	239.088	17.962	−16.351	−84.048	5.488
900	37.203	265.911	241.831	21.673	−17.245	−92.457	5.366
1000	37.371	269.840	244.438	25.402	−18.194	−100.764	5.263
1100	37.509	273.408	246.912	29.146	−19.215	−108.972	5.175
1200	37.627	276.677	249.258	32.903	−20.326	−117.084	5.097
1300	37.730	279.693	251.485	36.671	−21.571	−125.098	5.026
1400	37.822	282.493	253.601	40.448	−36.105	−132.603	4.947
1500	37.906	285.105	255.615	44.235	−37.508	−139.447	4.856
1600	37.984	287.554	257.536	48.029	−38.912	−146.197	4.773
1700	38.058	289.859	259.370	51.831	−40.317	−152.859	4.697
1800	38.129	292.036	261.125	55.641	−41.722	−159.439	4.627
1900	38.198	294.100	262.806	59.457	−43.126	−165.940	4.562
2000	38.267	296.061	264.421	63.280	−44.528	−172.368	4.502
2100	38.336	297.930	265.972	67.111	−45.926	−178.725	4.446
2200	38.408	299.715	267.466	70.948	−47.318	−185.016	4.393
2300	38.483	301.424	268.905	74.792	−48.702	−191.244	4.343
2400	38.564	303.063	270.294	78.645	−50.075	−197.412	4.297
2500	38.651	304.639	271.637	82.505	−51.437	−203.523	4.252
2600	38.746	306.157	272.936	86.375	−52.782	−209.580	4.211
2700	38.850	307.621	274.193	90.255	−54.110	−215.586	4.171
2800	38.965	309.036	275.413	94.145	−55.418	−221.542	4.133
2900	39.092	310.405	276.596	98.048	−356.906	−221.457	3.989
3000	39.233	311.733	277.745	101.964	−357.371	−216.778	3.774
3100	39.387	313.022	278.862	105.895	−357.857	−212.084	3.574
3200	39.556	314.275	279.949	109.842	−358.364	−207.374	3.385
3300	39.740	315.495	281.008	113.807	−358.889	−202.647	3.208
3400	39.940	316.684	282.040	117.791	−359.430	−197.904	3.040
3500	40.156	317.845	283.046	121.795	−359.984	−193.146	2.883
3600	40.387	318.980	284.029	125.822	−360.549	−188.371	2.733
3700	40.634	320.089	284.989	129.873	−361.121	−183.580	2.592
3800	40.896	321.177	285.927	133.950	−361.697	−178.774	2.457
3900	41.173	322.242	286.844	138.053	−362.273	−173.953	2.330
4000	41.464	323.288	287.742	142.185	−362.847	−169.117	2.208
4100	41.767	324.316	288.622	146.346	−363.414	−164.267	2.093
4200	42.083	325.326	289.484	150.539	−363.971	−159.402	1.982
4300	42.410	326.320	290.329	154.763	−364.516	−154.525	1.877
4400	42.746	327.299	291.158	159.021	−365.044	−149.636	1.776
4500	43.092	328.264	291.972	163.313	−365.552	−144.734	1.680
4600	43.445	329.215	292.771	167.640	−366.038	−139.822	1.588
4700	43.804	330.153	293.557	172.002	−366.499	−134.899	1.499
4800	44.168	331.079	294.329	176.400	−366.933	−129.967	1.414
4900	44.536	331.993	295.088	180.836	−367.337	−125.026	1.333
5000	44.907	332.897	295.835	185.308	−367.709	−120.077	1.254
5100	45.279	333.790	296.571	189.817	−368.049	−115.121	1.179
5200	45.651	334.673	297.295	194.364	−368.354	−110.158	1.107
5300	46.021	335.546	298.008	198.947	−368.623	−105.190	1.037
5400	46.390	336.409	298.712	203.568	−368.857	−100.218	0.969
5500	46.755	337.264	299.405	208.225	−369.054	−95.241	0.905
5600	47.115	338.110	300.088	212.919	−369.214	−90.261	0.842
5700	47.470	338.947	300.763	217.648	−369.338	−85.279	0.781
5800	47.819	339.775	301.428	222.412	−369.425	−80.295	0.723
5900	48.161	340.596	302.085	227.211	−369.477	−75.309	0.667
6000	48.496	341.408	302.734	232.044	−369.493	−70.323	0.612

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 77.452 \pm 0.08\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 1109 \pm 10\ K$

$\Delta_f H°(0\ K) = -537.2 \pm 8.4\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -538.9 \pm 8.4\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 55.229 \pm 20.1\ kJ\cdot mol^{-1}$

Enthalpy of Formation

Pervov *et al.*[1] have measured a enthalpy of formation of -128.8 ± 0.3 kcal·mol^{-1} by direct fluorine combustion calorimetry. In view of the spread of values obtained from the equilibrium pressure and the emf data discussed below, we adopt $\Delta_f H°(CuF_2, cr, 298.15\ K) = -128.8\pm2$ kcal·mol^{-1} (-538.899 ± 8.4 kJ·mol^{-1}).

Jellinek and Rudat[2] and Domange[3] have measured equilibrium partial pressures for reactions of CuF_2(cr) with hydrogen and with water, respectively. Koerber and De Vries[4] and Skelton and Patterson[5] have derived $\Delta_r G°$ from emf studies. Our 2nd and 3rd law analyses are as follows, using auxiliary data from the JANAF Thermochemical Tables[6]

Source	Reactions*	T/K	Data points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1} mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
2	A	423	1	—	22.6	—	−152.9
3	B	573–723	4	23.3±1.3	20.8±0.6	−3.9±2.0	−130.6±2
4	C	273–283	2	−1.9	−10.6±0.4	−31.4	−126.6±4
5	D	661–918	Equation	−132.1	−136.4	−5.5	−136.4

*Reactions: (A) $CuF_2(cr) + H_2(g) = Cu(cr) + 2\ HF(g)$ (B) $CuF_2(cr) + H_2O(g) = CuO(cr) + 2\ HF(g)$ (C) $Cu(cr) + Hg_2F_2 = CuF_2(cr) + 2\ Hg(l)$ (D) $Cu(cr) + F_2(g) = CuF_2(cr)$

The evaluation of King *et al.*,[7] $\Delta_f H°(CuF_2, cr, 298.15\ K) = -130.2$ kcal·mol^{-1}, preceded the direct fluorination study of Pervov *et al.*[1] and is based mainly on the work of Domange[3] and Koerber and De Vries.[4] We place greater reliance on the direct fluorination work.[1]

Heat Capacity and Entropy

The heat capacity is based on smoothed values from the unpublished low temperature measurements of Boo and Stout[8] (10–300 K) and the differential scanning calorimetric measurements of heat capacity by Ehlert[9] (300–710 K). Our graphical joining and smoothing of the two data sets produces data which are 1 to 2% lower than Ehlert's measurements[9] in the 350–500 K range and are in agreement from 520–700 K; our extrapolation to 1000 K yields 21.60 cal·K^{-1}·mol^{-1} compared to 22.4 cal·K^{-1}·mol^{-1} by Ehlert[9].

Boo and Stout[8] show an anomaly in the heat capacity at 70.90 K. $S°(298.15\ K) = 18.51$ cal·K^{-1}·mol^{-1} is based on $S°(10\ K) = 0.009$ cal·K^{-1}·mol^{-1} by Boo and Stout.[8]

Fusion Data

Ehlert and Wang[1] interpret their DTA measurements as indicating a solid state transition at 1065 ± 10 K and a fusion point of 1109 ± 10 K. They believe the observed transitions at 1028 K and 1040 K are caused by Cu_2O–CuF_2 and 10 CuO_2–20Cu–70CuF_2 weight percent eutectics, respectively. Based on the latter, and ignoring the 1065 K solid state transition, they calculated a enthalpy of fusion of 13.2 ± 2 kcal·mol^{-1}. We adopt $T_{fus} = 1109\pm10$ K and $\Delta_{fus} H° = 13.2\pm5$ kcal·mol^{-1} and await confirmation of the solid state transition.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−12.103	−537.170	−537.170	INFINITE
100	34.229	21.852	128.307	−10.646	−539.289	−523.434	273.414
200	55.731	53.151	83.178	−6.005	−539.591	−507.345	132.505
298.15	65.552	77.452	77.452	0.	−538.899	−491.642	86.134
300	65.689	77.858	77.453	0.121	−538.881	−491.349	85.551
400	72.383	97.697	80.113	7.034	−537.682	−475.674	62.117
500	77.739	114.446	85.347	14.549	−536.097	−460.348	48.092
600	81.923	129.001	91.436	22.539	−534.201	−445.372	38.773
700	84.810	141.857	97.739	30.883	−532.083	−430.732	32.142
800	87.027	153.332	103.984	39.479	−529.821	−416.406	27.189
900	88.868	163.692	110.052	48.276	−527.454	−402.371	23.353
1000	90.374	173.136	115.895	57.241	−525.013	−388.603	20.299
1100	91.588	181.807	121.498	66.340	−522.539	−375.081	17.811
1109.000	91.713	182.554	121.991	67.164	---- CRYSTAL <--> LIQUID ----		
1200	92.550	189.820	126.862	75.550	−520.070	−361.785	15.748
1300	93.303	197.259	131.995	84.844	−517.673	−348.693	14.011
1400	93.847	204.195	136.907	94.203	−528.521	−335.374	12.513
1500	94.224	210.683	141.611	103.608	−526.211	−321.659	11.201
1600	94.433	216.771	146.121	113.041	−523.891	−308.097	10.058
1700	94.558	222.501	150.447	122.492	−521.570	−294.681	9.054
1800	94.558	227.906	154.601	131.948	−519.258	−281.402	8.166
1900	94.558	233.018	158.595	141.404	−516.959	−268.250	7.375
2000	94.558	237.868	162.439	150.859	−514.668	−255.220	6.666

PREVIOUS: June 1966 CURRENT: December 1977

$S°(298.15\ K) = [122.585]\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 1109 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-487.854]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 55.229 \pm 20.1\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(CuF_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1109\ K) - H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

The heat capacity is estimated from an average heat capacity of 8 cal K^{-1} g–atom^{-1} for several difluorides and dichlorides. A glass transition is assumed at 740 K below which the heat capacity is that of the crystal.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 1948.9 K is the calculated temperature at which the fugacity of CuF_2(g) is 1 atm for the reaction CuF_2(l) = CuF_2(g). $\Delta_{vap} H°$ = 81.132 kJ mol^{-1} is the difference in $\Delta_f H°$ between the ideal gas and liquid at T_{vap}.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	65.551	122.585	122.585	0.	−487.854	−454.053	79.548
300	65.689	122.990	122.586	0.121	−487.836	−453.844	79.021
400	72.383	142.830	125.246	7.034	−486.637	−442.682	57.808
500	77.739	159.579	130.480	14.549	−485.052	−431.870	45.117
600	81.923	174.134	136.569	22.539	−483.156	−421.407	36.687
700	84.810	186.990	142.872	30.883	−481.038	−411.280	30.690
740.000	85.772	191.730	145.386	34.295	GLASS <--> LIQUID		
740.000	100 .416	191.730	145.386	34.295	TRANSITION		
800	100.416	199.558	149.159	40.320	−477.935	−401.501	26.215
900	100.416	211.386	155.429	50.361	−474.324	−392.165	22.761
1000	100.416	221.965	161.563	60.403	−470.806	−383.226	20.018
1100	100.416	231.536	167.496	70.444	−467.390	−374.634	17.790
1109.000	100 .416	232.354	168.019	71.348	CRYSTAL <--> LIQUID		
1200	100.416	240.273	173.202	80.486	−464.089	−366.348	15.947
1300	100.416	248.311	178.674	90.528	−460.945	−358.332	14.398
1400	100.416	255.753	183.917	100.569	−471.110	−350.144	13.064
1500	100.416	262.681	188.940	110.611	−468.163	−341.607	11.896
1600	100.416	269.161	193.754	120.652	−465.235	−333.265	10.880
1700	100.416	275.249	198.370	130.694	−462.323	−325.106	9.989
1800	100.416	280.989	202.802	140.736	−459.426	−317.118	9.203
1900	100.416	286.418	207.061	150.777	−456.540	−309.291	8.503
2000	100.416	291.568	211.159	160.819	−453.664	−301.616	7.877
2100	100.416	296.468	215.106	170.860	−450.794	−294.084	7.315
2200	100.416	301.139	218.911	180.902	−447.926	−286.689	6.807
2300	100.416	305.603	222.584	190.944	−445.058	−279.424	6.346
2400	100.416	309.876	226.133	200.985	−442.184	−272.284	5.926
2500	100.416	313.976	229.565	211.027	−439.301	−265.264	5.542

PREVIOUS: June 1966 CURRENT: December 1977

CRYSTAL-LIQUID

0	to	1109 K	crystal
above		1109 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−12.103	−537.170	−537.170	INFINITE
100	34.229	21.852	128.307	−10.646	−539.289	−523.434	273.414
200	55.731	53.151	83.178	−6.005	−539.591	−507.345	132.505
298.15	65.552	77.452	77.452	0.	−538.899	−491.642	86.134
300	65.689	77.858	77.453	0.121	−538.881	−491.349	85.551
400	72.383	97.697	80.113	7.034	−537.682	−475.674	62.117
500	77.739	114.446	85.347	14.549	−536.097	−460.348	48.092
600	81.923	129.001	91.436	22.539	−534.201	−445.372	38.773
700	84.810	141.857	97.739	30.883	−532.083	−430.732	32.142
800	87.027	153.332	103.984	39.479	−529.821	−416.406	27.189
900	88.868	163.692	110.052	48.276	−527.454	−402.371	23.353
1000	90.374	173.136	115.895	57.241	−525.013	−388.603	20.299
1100	91.588	181.807	121.498	66.340	−522.539	−375.081	17.811
1109.000	91.713	182.554	121.991	67.164	CRYSTAL <--> LIQUID		
1109.000	100 .416	232.354	121.991	122.393	TRANSITION		
1200	100.416	240.273	130.664	131.531	−464.089	−366.348	15.947
1300	100.416	248.311	139.409	141.573	−460.945	−358.331	14.398
1400	100.416	255.753	147.457	151.614	−471.109	−350.144	13.064
1500	100.416	262.681	154.910	161.656	−468.163	−341.607	11.896
1600	100.416	269.161	161.850	171.698	−465.234	−333.265	10.880
1700	100.416	275.249	168.344	181.739	−462.323	−325.106	9.989
1800	100.416	280.989	174.444	191.781	−459.425	−317.118	9.203
1900	100.416	286.418	180.196	201.822	−456.540	−309.291	8.503
2000	100.416	291.568	185.637	211.864	−453.664	−301.615	7.877
2100	100.416	296.468	190.798	221.906	−450.794	−294.084	7.315
2200	100.416	301.139	195.709	231.947	−447.926	−286.689	6.807
2300	100.416	305.603	200.390	241.989	−445.057	−279.424	6.346
2400	100.416	309.876	204.864	252.030	−442.183	−272.284	5.926
2500	100.416	313.976	209.147	262.072	−439.301	−265.264	5.542

PREVIOUS: CURRENT: December 1977

$S°(298.15\ K) = [267.09 \pm 2.1]\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 265.16 \pm 12.6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 266.94 \pm 12.6\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma^+_g]$	0	[2]
$[^2\Pi_g]$	[9000]	[4]
$[^2\Delta_g]$	[18000]	[4]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
625 (1)
185±5 (1)
782 (1)

Ground State Quantum Weight: [2] $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Cu–F = [1.72]Å
Bond Angle: F–Cu–F = 165 ± 8°
Product of the Moments of Inertia: $I_A I_B I_C = [6.77288 \times 10^{116}]\ g^3\cdot cm^6$

Enthalpy of Formation

Sublimation pressures, $CuF_2(cr) = CuF_2(g)$, have been measured by Kent *et al.*[1] (897–1026 K) and by Ehlert and Wang[2] (874–1005 K) by effusion cell mass spectrometric techniques. Using JANAF data[6] for $CuF_2(cr)$, we derive the following by 2nd and 3rd law analysis:

Source	T/K	Data points	$\Delta_{sub}H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	Drift cal $K^{-1}\cdot mol^{-1}$	$\Delta_f H°(g, 298.15\ K)$ kcal·mol⁻¹
[1]	897–1026	26[a]	63.20±0.50	62.74±0.17	−0.5±0.5	−66.1
[2] via CuF^+	874–1005	33[b]	65.82±0.72	64.992±0.33	−0.9±0.8	−63.8
[2] via CuF^+	874–1005	33[b]	65.92±0.67	65.085±0.30	−0.9±0.7	

[a]Two data points eliminated by a statistical test.
[b]One data point eliminated by a statistical test.

We adopt $\Delta_f H°(CuF_2, g, 298.15\ K) = -63.8 \pm 3$ kcal·mol⁻¹ (266.4 ± 12.6 kJ mol^{-1}).

Heat Capacity and Entropy

The bond distance is taken from Brewer *et al.*[3] The bond distances for all of the transition metal difluorides from chromium through copper were estimated to be the same with the assessment that an error of 0.5 Å would lead to an error of less than 1 cal·K^{-1}·mol^{-1} in the entropy. The bond angle and vibrational frequencies are those derived by Hastie *et al.*[4] from infrared studies of matrix isolated isotopic species. The electronic states and levels are assumed the same as those assigned to $CuCl_2$.[5] The principal moments of inertia are $I_A = 0.1990 \times 10^{-39}$, $I_B = 18.3484 \times 10^{-39}$, $I_C = 18.5474 \times 10^{-39}$ g·cm^2.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.056	−265.163	−265.163	INFINITE
100	38.109	220.861	306.489	−8.563	−265.246	−269.292	140.664
200	43.318	248.878	271.334	−4.491	−266.117	−273.016	71.304
250	45.858	258.822	267.865	−2.261	−266.552	−274.690	57.393
298.15	47.987	267.086	267.086	0.	−266.939	−276.222	48.393
300	48.061	267.384	267.087	0.089	−266.954	−276.279	48.104
350	49.859	274.932	267.679	2.539	−267.329	−277.803	41.460
400	51.289	281.687	269.016	5.069	−267.687	−279.275	36.470
450	52.419	287.796	270.768	7.662	−268.036	−280.703	32.583
500	53.315	293.367	272.754	10.307	−268.380	−282.091	29.470
600	54.609	303.210	277.031	15.707	−269.073	−284.769	24.791
700	55.466	311.697	281.391	21.214	−269.792	−287.329	21.441
800	56.057	319.144	285.654	26.792	−270.547	−289.783	18.921
900	56.481	325.773	289.751	32.420	−271.350	−292.140	16.955
1000	56.796	331.741	293.656	38.084	−272.210	−294.404	15.378
1100	57.042	337.166	297.369	43.777	−273.142	−296.579	14.083
1200	57.245	342.138	300.895	49.491	−274.169	−298.665	13.001
1300	57.426	346.727	304.246	55.225	−275.332	−300.660	12.081
1400	57.599	350.989	307.435	60.976	−289.787	−302.153	11.273
1500	57.776	354.969	310.473	66.745	−291.114	−302.990	10.551
1600	57.965	358.704	313.372	72.532	−292.440	−303.739	9.916
1700	58.170	362.224	316.143	78.339	−293.763	−304.405	9.353
1800	58.396	365.555	318.796	84.167	−295.079	−304.992	8.851
1900	58.642	368.719	321.341	90.018	−296.384	−305.508	8.399
2000	58.909	371.734	323.786	95.896	−297.672	−305.954	7.991
2100	59.195	374.615	326.138	101.801	−298.938	−306.337	7.620
2200	59.498	377.376	328.405	107.735	−300.178	−306.660	7.281
2300	59.814	380.027	330.592	113.701	−301.385	−306.928	6.971
2400	60.141	382.580	332.705	119.698	−302.555	−307.144	6.685
2500	60.476	385.042	334.750	125.729	−303.683	−307.311	6.421
2600	60.816	387.420	336.730	131.794	−304.765	−307.435	6.176
2700	61.158	389.722	338.650	137.893	−305.798	−307.518	5.949
2800	61.498	391.952	340.514	144.025	−306.777	−307.564	5.738
2900	61.836	394.116	342.326	150.192	−607.904	−301.579	5.432
3000	62.168	396.218	344.087	156.392	−607.975	−291.015	5.067
3100	62.493	398.262	345.802	162.625	−608.036	−280.449	4.726
3200	62.808	400.251	347.473	168.891	−608.088	−269.881	4.405
3300	63.114	402.188	349.101	175.187	−608.129	−259.311	4.105
3400	63.408	404.077	350.691	181.513	−608.160	−248.741	3.821
3500	63.690	405.919	352.242	187.868	−608.180	−238.169	3.554
3600	63.958	407.717	353.758	194.251	−608.188	−227.597	3.302
3700	64.214	409.473	355.241	200.659	−608.185	−217.025	3.064
3800	64.455	411.189	356.690	207.093	−608.169	−206.454	2.838
3900	64.682	412.866	358.109	213.550	−608.140	−195.882	2.624
4000	64.895	414.506	359.499	220.029	−608.098	−185.312	2.420
4100	65.094	416.111	360.860	226.528	−608.041	−174.743	2.226
4200	65.278	417.682	362.194	233.047	−607.970	−164.176	2.042
4300	65.449	419.220	363.503	239.583	−607.883	−153.610	1.866
4400	65.606	420.726	364.786	246.136	−607.780	−143.047	1.698
4500	65.749	422.202	366.046	252.704	−607.660	−132.486	1.538
4600	65.880	423.649	367.282	259.286	−607.524	−121.928	1.385
4700	65.997	425.067	368.497	265.880	−607.371	−111.373	1.238
4800	66.103	426.458	369.690	272.485	−607.200	−100.822	1.097
4900	66.197	427.822	370.862	279.100	−607.011	−90.274	0.962
5000	66.279	429.160	372.015	285.724	−606.805	−79.731	0.833
5100	66.350	430.473	373.148	292.355	−606.582	−69.191	0.709
5200	66.411	431.762	374.263	298.993	−606.341	−58.656	0.589
5300	66.462	433.027	375.360	305.637	−606.083	−48.127	0.474
5400	66.504	434.270	376.440	312.286	−605.808	−37.602	0.364
5500	66.537	435.491	377.502	318.938	−605.517	−27.082	0.257
5600	66.561	436.690	378.548	325.593	−605.211	−16.568	0.155
5700	66.577	437.868	379.579	332.249	−604.891	−6.059	0.056
5800	66.585	439.026	380.594	338.908	−604.557	4.443	−0.040
5900	66.587	440.164	381.594	345.566	−604.210	14.941	−0.132
6000	66.581	441.284	382.579	352.225	−603.852	25.432	−0.221

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = [108.366]\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -450.37 \pm 8.4\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy change, $\Delta_r H°(433\ K)$, for the reaction $Cu(OH)_2(cr) = CuO(cr) + H_2O(g)$ has been determined by My.[1] Based on the reported value, $\Delta_r H°(433\ K) = 12\ kcal\cdot mol^{-1}$. The adopted $\Delta_f H°(Cu(OH)_2, cr, 298.15\ K)$ value was derived as $-107.64\ kcal\cdot mol^{-1}$, using $\Delta_f H°(298.15\ K) = -37.250$ and $-57.798\ kcal\cdot mol^{-1}$ for CuO(cr) and $H_2O(g)$, respectively.

The Gibbs energy change, $\Delta_r G°(298.15\ K)$, of the reaction $Cu(OH)_2(cr) = Cu^{++}(aq) + 2\ OH^-\ (aq)$ was evaluated to be 26.36 and 26.26 $kcal\cdot mol^{-1}$, based on the solubility product for $Cu(OH)_2(cr)$ reported by Ganelina[2] and Zhuk,[3] respectively. Using values of $S°(298.15\ K)$ and $\Delta_f H°(298.15\ K)$ for $Cu^{++}(aq)$ and OH (aq) from NBS[4] and NBS,[5] the corresponding enthalpy change $\Delta_r H°(298.15\ K)$ and enthalpy of formation, $\Delta_f H°(298.15\ K)$ for $Cu(OH)_2(cr)$ are derived. The results obtained are presented as follows:

Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	Source
$Cu(OH)_2(cr) = Cu^{++}(aq) + 2\ OH^-(aq)$	10.06	−104.61	1
$Cu(OH)_2(cr) = Cu^{++}(aq) + 2\ OH^-(aq)$	9.97	−104.52	2
$CuO(cr) + H_2O(l) = Cu(OH)_2(cr)$	−1.9	−107.5	3
$CuO(cr) + H_2O(l) = Cu(OH)_2(cr)$	0.3	−105.3	4

The enthalpies of solution of CuO(cr) and $Cu(OH)_2(cr)$ in $HNO_3(aq)$ have been determined by de Forcrand[6] to be −16.38 and −14.46 $kcal\cdot mol^{-1}$, respectively. From these data, the enthalpy change for the reaction $CuO(cr) + H_2O(l) = Cu(OH)_2(cr)$ was derived as $-1.9\ kcal\cdot mol^{-1}$. For the same reaction, the enthalpy change was reported to be $0.3\ kcal\cdot mol^{-1}$ by Sabatier[7]. Based on $\Delta_f H°(298.15\ K) = -37.25$ and $-68.315\ kcal\cdot mol^{-1}$ for CuO(cr) and $H_2O(l)$, respectively, the enthalpy of formation for $Cu(OH)_2$ was evaluated. The results obtained are presented in the above table.

Heat Capacity and Entropy

Heat capacities, 298.15−700 K, were estimated by comparison with those for CuO(cr), CaO(cr) and $Ca(OH)_2(cr)$. The $C_p°$ values above 700 K were obtained by graphical extrapolation. $S°(298.15\ K)$ was estimated such that the derived $\Delta_f G°(Cu(OH)_2, cr) = \Delta_f G°(CuO, cr) + \Delta_f G°(H_2O, g)$ at 433 K.

Decomposition Data

T_{dcm} = 433 K is the temperature at which the Gibbs energy change for the reaction $Cu(OH)_2(cr) = CuO(cr) + H_2O(g)$ is such that the fugacity of water is 1 atm.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	95.186	108.366	108.366	0.	−450.366	−372.660	65.289
300	95.228	108.955	108.367	0.176	−450.343	−372.178	64.802
400	99.496	136.934	112.154	9.912	−448.977	−346.323	45.225
500	103.763	159.595	119.444	20.075	−447.361	−320.841	33.518
600	108.031	178.893	127.782	30.666	−445.479	−295.709	25.744
700	112.131	195.862	136.319	41.680	−443.332	−270.913	20.216
800	115.562	211.070	144.729	53.073	−440.952	−246.442	16.091
900	117.989	224.829	152.877	64.757	−438.425	−222.279	12.901
1000	119.662	237.352	160.708	76.644	−435.838	−198.401	10.363
1100	120.750	248.811	168.204	88.668	−433.267	−174.782	8.300
1200	121.503	259.353	175.366	100.784	−430.774	−151.395	6.590
1300	121.880	269.094	182.206	112.954	−428.435	−128.209	5.152
1400	122.047	278.133	188.739	125.151	−439.431	−104.790	3.910
1500	122.173	286.558	194.983	137.363	−437.354	−80.960	2.819

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 42.59 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -153.81 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -156.06 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of CuO(cr) has been investigated calorimetrically (both oxidation and reduction reactions) and by extensive study of the $Cu_2O(cr) + 1/2\ O_2(g) = 2\ CuO(cr)$ equilibrium by pressure and by emf measurement. The more consistent data leading to the adopted value are summarized below.

Source	Method	Reaction*	T/K	Data points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K)** kcal·mol^{-1}
[1]	Aq Calorim	A	291	—	31.15		—	−37.16
[2]	Calorimetric	A	295	—	30.27±0.2		—	−38.04
[3]	Calorimetric	See Text	298.15	—	—		—	−37.23±0.15
[4]	Calorimetric	A	297.9	(Coarse grain CuO)	—		—	−38.72±0.30
		A	298	(Fine powder CuO)	—		—	−36.50±0.2
		B	297.9	(Coarse grain CuO)	—		—	−38.59±0.35
[5]	Equil Press	B	1011–1156	5	−33.84±0.31	−37.73±0.43	−3.6±0.3	−37.73
[6]	emf	B	845–1270	Equation	−37.26	−37.38	−0.1±0.0	−37.38
[7]	Equil Press	C	1223–1322	7	−32.52±0.18	−33.65±0.06	−0.9±0.1	−37.23
[8]	Equil Press	C	1189–1358	20	−33.28±0.06	−33.68±0.04	−0.3±0.0	−37.24
[9]	Equil Press	C	1193–1293	6	−33.23±0.28	−33.68±0.04	−0.4±0.2	−37.24
[10]	Equil Press	C	1047–1342	11	−32.79±0.14	−33.69±0.17	−0.7±0.1	−37.25
[11]	Equil Press	C	1026–1072	3	−35.50±0.37	−33.62±0.07	1.4±0.3	−37.21
[12]	emf	C	973–1273	Equation	−33.57	−33.64	−0.6	−37.22
[13]	emf	C	892–1320	Equation	−33.53	−33.58	−0.6	−37.19
[14]	emf	C	1023–1294	Equation	−33.39	−33.58	0.2	−37.19
[15]	emf	C	870–1170	Equation	−34.37	−35.00	0.6	−37.90
[16]	Press	C	993–1021	4	−34.18±0.06	−34.12±0.0	−0.1±0.1	−37.46
[17]	Equil Press	C	800–950	Equation	−29.92	−34.30	10.0	−37.55
[18]	Equil Press	C	873–1073	Equation	−40.06	−35.26	4.9	−38.03

*Reactions: (A) $Cu(cr) + H_2O(l) = CuO(cr) + H_2(g)$
(B) $Cu(cr) + 1/2\ O_2(g) = CuO(cr)$
(C) $Cu_2O(cr) + 1/2\ O_2(g) = 2\ CuO(cr)$

**Based on third law where possible and $\Delta_f H°(Cu_2O, cr, 298.15\ K)$ = $-40.8\ kcal \cdot mol^{-1}$ in Reaction C.

Thomsen's data[1] may be reduced to the enthalpy of reduction of CuO(cr) with H_2 by combining enthalpies of reaction for $CuO + H_2SO_4$, $Fe + H_2SO_4$, and $Fe + CuSO_4(aq)$. Wartenberg and Werth[2] and Nunez *et al.*[4] have measured the direct enthalpy of reduction of CuO(cr) by H_2; Mah *et al.*[3] and Nunez *et al.*[4] have measured the direct enthalpy of oxidation of copper by O_2. Mah *et al.*[3] obtained a mixed Cu_2O and CuO product and used $\Delta_f H°(298.15\ K) = -33.63 \pm 0.05\ kcal \cdot mol^{-1}$ for the equilibrium reaction $Cu_2O(cr) + 1/2\ O_2(g) = 2\ CuO(cr)$ to resolve their results into $\Delta_f H°(CuO, cr, 298.15\ K)$ and $\Delta_f H°(Cu_2O, cr, 298.15\ K)$. From the measurment of the reduction of coarse and fine CuO(cr), Nunez *et al.*[4] conclude that $\Delta_f H°$ of the copper oxides is influenced by material history, state of subdivision, and non stoichiometry.

Eliminating three studies[5,17,18] from our 3rd law analysis because of large drift and poor 2nd and 3rd law agreement, the average of the eleven remaining studies is $-37.32\ kcal\ mol^{-1}$. We adopt $\Delta_f H°(298.15\ K) = -37.3 \pm 0.5\ kcal\ mol^{-1}$.

Heat Capacity and Entropy

The adopted values are based on the low temperature heat capacities by Hu and Johnston[19] (15–297 K) and the high temperature enthalpies by Mah *et al.*[3] (410–1400 K). Changes are made where appropriate to adjust to the 1975 atomic weights[20] and the IPTS 68 temperature scale[21]. A small anomaly in the heat capacity was observed in the 210–230 K region. Magnetic measurements of O'Keefe and Stone[22] and neutron diffraction studies of Brockhouse[23] suggest that this is a Neel point associated with antiferromagnetism.

The entropy is obtained from the adopted heat capacities based on a T^3 extrapolation to obtain $S°(15\ K) = 0.016\ cal\ K^{-1}$.

Decomposition Data

T_{dcm} = 1397 K is the temperature at which fugacity (O_2) = 1 atm for the reaction $2\ CuO(cr) = Cu_2O(cr) + 1/2\ O_2(g)$.

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Continued on page 1027

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−7.092	−153.807	−153.807	INFINITE
100	16.499	9.768	74.176	−6.441	−155.277	−146.585	76.568
200	34.795	27.018	46.256	−3.848	−156.152	−137.461	35.901
298.15	42.246	42.594	42.594	0.	−156.063	−128.292	22.476
300	42.364	42.856	42.595	0.078	−156.057	−128.120	22.308
400	46.806	55.723	44.319	4.562	−155.553	−118.875	15.523
500	49.261	66.451	47.703	9.374	−154.836	−109.785	11.469
600	50.935	75.588	51.608	14.388	−154.022	−100.851	8.780
700	52.240	83.541	55.614	19.549	−153.162	−92.056	6.869
800	53.349	90.591	59.554	24.829	−152.274	−83.387	5.445
900	54.340	96.932	63.361	30.215	−151.368	−74.830	4.343
1000	55.262	102.706	67.011	35.695	−150.453	−66.375	3.467
1100	56.135	108.014	70.500	41.265	−149.542	−58.012	2.755
1200	56.978	112.935	73.834	46.921	−148.656	−49.730	2.165
1300	57.800	117.528	77.020	52.660	−147.837	−41.520	1.668
1400	58.601	121.841	80.069	58.480	−160.239	−32.963	1.230
1500	59.395	125.911	82.991	64.380	−159.444	−23.899	0.832
1600	60.181	129.769	85.795	70.359	−158.583	−14.891	0.486
1700	60.958	133.441	88.491	76.416	−157.657	−5.938	0.182
1800	61.726	136.947	91.086	82.550	−156.665	2.958	−0.086
1900	62.494	140.305	93.589	88.761	−155.608	11.798	−0.324
2000	63.259	143.530	96.006	95.049	−154.486	20.580	−0.537

PREVIOUS: June 1966 CURRENT: December 1977

$S°(298.15\ K) = 234.617\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 305.87 \pm 41.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 306.27 \pm 41.8\ kJ\cdot mol^{-1}$

Electronic levels and quantum weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{3/2}$	0	2
$X^2\Pi_{1/2}$	277.0	2
$A'^2\Sigma^+$	15531.9	2
$A^2\Sigma^+$	16492.4	2
$C^2\Pi_i$	18811.4	4
$E^2\Delta_{5/2}$	21103.7	4
$F^2\Pi_i$	21222	4
$G^2\Sigma^-$	21594.0	2
$M^2\Pi_{3/2}$	23898	4

$\omega_e = 640.14\ cm^{-1}$ $\omega_e x_e = 4.43\ cm^{-1}$ $\sigma = 1$
$B_e = 0.44454\ cm^{-1}$ $\alpha_e = 0.0046\ cm^{-1}$ $r_e = 1.7246$ Å

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = 73.2 \pm 10\ kcal\cdot mol^{-1}$ comes from our 3rd law analysis of the mass spectrometric Knudsen cell measurements of the equilibrium reaction CuO(g) + Ni(g) = Cu(g) + NiO(g) (1611–1828 K)[1]. Auxiliary data[2, 3] are used in the analysis. Also considered in the evaluation are: the unpublished but quoted[4] and others] value of Burns, $D_0° = 62.7 \pm 3\ kcal\cdot mol^{-1}$, the sublimation measurement of,[5] the linear Birge Sponer extrapolation of the ground state to obtain $D_0°$, and the linear Birge Sponer extrapolation corrected for the ionic character of CuO according to Hildenbrand.[6]

Source	$D_0°$ (0 K) $kcal\cdot mol^{-1}$	$\Delta_f H°$(298.15 K) kcal mol^{-1}
Smoes *et al.*[1], Equilibrium	66.3	73.2
Burns[4], Mass spec.	62.7±3	76.8±3
Mack *et al.*[5], Transpiration (1273 K)	80.2	59.02
Linear Birge Sponer	65.2	74.2
Modified Linear Birge Sponer	61.0±12	78.5±12

Mack *et al.*[5] report measurements at 873, 1073, and 1173 K which lead to higher dissociation energies. Because of the scatter of the measurements and the suspect nature of the analytical measurement recognized by the authors, the $D_0°$ value of 80.2 $kcal\cdot mol^{-1}$ is discounted.

Heat Capacity and Entropy

The molecular constants and electronic levels are taken from the work of Appelblad and Lagerqvist,[7, 8, 9] Lefebvre *et al.*,[10] and Lefebvre *et al.*[11] The spectrum of CuO is complex and there are almost certainly excited states missing among those already analyzed;[9] in fact some doubt still exists that the $X^2\Pi_i$ state is really the ground state[9] although the absence of esr signals in the matrix isolation study of Thompson *et al.*[12] supports this assignment. Because of the uncertain and incomplete spectral analysis, we choose to calculate the thermodynamic functions with first order anharmonic corrections assuming the ground state vibrational rotational constants for all states. Use of the actual constants for each state increases the entropy at 6000 K by 0.045 $cal\cdot K^{-1}\cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.751	305.866	305.866	INFINITE
100	31.554	197.630	265.437	−6.781	306.715	296.621	−154.939
200	34.498	220.596	237.849	−3.451	306.577	286.552	−74.840
250	35.198	228.373	235.202	−1.707	306.428	281.563	−58.829
298.15	35.693	234.617	234.617	0.	306.269	276.788	−48.492
300	35.710	234.838	234.618	0.066	306.262	276.605	−48.161
350	36.098	240.373	235.054	1.862	306.083	271.676	−40.545
400	36.399	245.214	236.028	3.674	305.891	266.774	−34.837
450	36.636	249.515	237.292	5.501	305.683	261.896	−30.400
500	36.827	253.386	238.711	7.337	305.459	257.043	−26.853
600	37.114	260.127	241.735	11.035	304.957	247.405	−21.539
700	37.320	265.864	244.782	14.757	304.378	237.858	−17.749
800	37.478	270.858	247.736	18.498	303.726	228.399	−14.913
900	37.606	275.280	250.556	22.252	303.001	219.026	−12.712
1000	37.715	279.248	253.230	26.018	302.202	209.737	−10.956
1100	37.810	282.847	255.762	29.795	301.319	200.533	−9.523
1200	37.896	286.141	258.158	33.580	300.335	191.413	−8.332
1300	37.975	289.178	260.429	37.374	299.209	182.381	−7.328
1400	38.050	291.995	262.584	41.175	284.788	173.848	−6.486
1500	38.121	294.622	264.633	44.983	283.491	165.969	−5.780
1600	38.189	297.085	266.585	48.799	282.189	158.177	−5.164
1700	38.256	299.402	268.448	52.621	280.881	150.466	−4.623
1800	38.322	301.590	270.229	56.450	279.567	142.832	−4.145
1900	38.389	303.664	271.935	60.286	278.248	135.272	−3.719
2000	38.456	305.635	273.571	64.128	276.925	127.781	−3.337
2100	38.526	307.513	275.143	67.977	275.597	120.356	−2.994
2200	38.599	309.307	276.655	71.833	274.265	112.996	−2.683
2300	38.677	311.024	278.113	75.697	272.929	105.695	−2.400
2400	38.760	312.672	279.519	79.569	271.590	98.452	−2.143
2500	38.850	314.256	280.877	83.449	270.248	91.266	−1.907
2600	38.949	315.782	282.190	87.339	268.906	84.133	−1.690
2700	39.056	317.254	283.461	91.239	267.563	77.052	−1.491
2800	39.174	318.676	284.694	95.151	266.221	70.021	−1.306
2900	39.303	320.053	285.890	99.074	−35.323	69.033	−1.243
3000	39.444	321.388	287.051	103.012	−35.864	72.640	−1.265
3100	39.598	322.684	288.179	106.964	−36.450	76.267	−1.285
3200	39.766	323.944	289.277	110.932	−37.079	79.913	−1.304
3300	39.949	325.170	290.347	114.918	−37.751	83.579	−1.323
3400	40.145	326.366	291.388	118.922	−38.463	87.266	−1.341
3500	40.357	327.532	292.404	122.947	−39.213	90.975	−1.358
3600	40.583	328.672	293.396	126.994	−39.998	94.706	−1.374
3700	40.824	329.787	294.365	131.064	−40.815	98.458	−1.390
3800	41.079	330.880	295.311	135.159	−41.662	102.234	−1.405
3900	41.348	331.950	296.237	139.280	−42.533	106.032	−1.420
4000	41.631	333.000	297.143	143.429	−43.426	109.853	−1.435
4100	41.926	334.032	298.030	147.607	−44.337	113.696	−1.449
4200	42.234	335.046	298.900	151.815	−45.263	117.562	−1.462
4300	42.552	336.043	299.752	156.054	−46.198	121.450	−1.475
4400	42.881	337.025	300.588	160.326	−47.141	125.359	−1.488
4500	43.220	337.993	301.408	164.631	−48.087	129.290	−1.501
4600	43.566	338.947	302.214	168.970	−49.033	133.242	−1.513
4700	43.920	339.887	303.006	173.344	−49.976	137.215	−1.525
4800	44.279	340.816	303.784	177.754	−50.914	141.208	−1.537
4900	44.644	341.732	304.549	182.200	−51.844	145.220	−1.548
5000	45.012	342.638	305.302	186.683	−52.763	149.251	−1.559
5100	45.383	343.533	306.042	191.203	−53.670	153.301	−1.570
5200	45.756	344.418	306.772	195.760	−54.563	157.367	−1.581
5300	46.129	345.293	307.490	200.354	−55.441	161.451	−1.591
5400	46.501	346.159	308.199	204.986	−56.303	165.552	−1.601
5500	46.872	347.015	308.897	209.654	−57.149	169.668	−1.611
5600	47.240	347.863	309.585	214.360	−57.977	173.799	−1.621
5700	47.604	348.703	310.264	219.102	−58.789	177.945	−1.631
5800	47.964	349.534	310.934	223.881	−59.584	182.106	−1.640
5900	48.319	350.357	311.595	228.695	−60.362	186.279	−1.649
6000	48.667	351.172	312.248	233.544	−61.126	190.466	−1.658

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 109.254 \pm 0.42\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -760.059 \pm 0.84\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -769.982 \pm 0.84\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution, $\Delta_r H°(298.15\ K)$, of CuO(cr) in sulfuric acid to form $CuSO_4$(cr) has been measured by Adami and King.[1] From the reported value, $\Delta_r H° = 5.61 \pm 0.09$ kcal·mol^{-1} for the reacton $CuO(cr) + H_2SO_4 \cdot 7.068\ H_2O(aq) = CuSO_4(cr) + 8.068\ H_2O(l)$, the enthalpy of formation, $\Delta_f H°(298.15\ K)$, for $CuSO_4$(cr) was evaluated as -184.03 kcal·mol^{-1}, using $\Delta_f H°(298.15\ K) = -37.25$, -209.49 and -68.315 kcal·mol^{-1} for CuO(cr), $H_2SO_4 \cdot 7.068\ H_2O$(aq) and H_2O(l), respectively. See $Fe_2(SO_4)_3$(cr) table for the sources of the last two $\Delta_f H°(298.15\ K)$ values.

The equilibrium pressure for the following chemical reactons: (A) $2\ CuSO_4(cr) = CuOCuSO_4(cr) + SO_3(g)$, (B) $3\ Cu(cr) + CuSO_4(cr) = 2\ Cu_2O(cr) + SO_2(g)$, and (C) $4\ CuSO_4(cr) + Cu_2O(cr) = 3\ CuO\cdot CuSO_4(cr) + SO_2(g)$, were determined by several investigators. For reaction (A), the partial pressures of SO_3(g) at different temperatures were calculated from the measured total pressures exerted by SO_3(g), SO_2(g) and O_2(g) produced by the reaction $SO_3(g) = SO_2(g) + 1/2\ O_2(g)$. From these vapor pressure data, the corresponding enthalpy changes, $\Delta_r H°(298.15\ K)$, for the three reactions were evaluated by the 2nd and 3rd law methods. The results obtained are presented in the following table. The value of $\Delta_f H°(CuSO_4, cr, 298.15\ K)$ adopted was -184.03 ± 0.2 kcal·mol^{-1}.

Source	Reaction	T/K	$\Delta_r H°(298.15\ K)$,kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[2]	(A)	819.15–1004.15	25.90±3.60	47.45	22±4	−181.87
[3]	(A)	953.15–1053.15	56.54±0.77	51.96	−4.55±0.79	−184.13
	(C)	825.15–921.15	42.84±1.38	42.34	−0.55±1.57	−184.42
[4]	(A)	880.15–1071.75	51.59±0.41	51.75	0.07±0.43	−184.02
[5]	(B)	525.1 – 608.1	31.71±0.76	32.27	0.84±1.30	−184.62

Heat Capacity and Entropy

Low temperature heat capacities, 52.67–296.29 K were obtained from Weller.[6] The high temperature heat capacities were measured by Schottky[7] (282°C), Ewald[8] (275–373 K), Krestovnikov and Feigina[9] (288–873 K), and Chiznikov and Khirik[10] (373–1273 K). The heat capacities below 51 K were obtained from Stout.[11] In that paper, the $C_p°$ values, 15–58 K, were plotted as function of temperature and the $C_p°$ curve shows a maximum at 34.8 K. In an attempt to evaluate the entropy due to the anomalous portion of the curve, a "normal" heat capacity curve was drawn. The entropy above the normal $C_p°$ curve is reported to be 0.48 cal K^{-1}·mol^{-1} rather than a magnetic entropy of Rln2 = 1.377 cal K^{-1}·mol^{-1}. Apparently the magnetic entropy increases gradually above 40 K so that it is not feasible to separate the heat capacity due to magnetic effects from that of the crystal lattice.

The $C_p°$ values above 298.15 K were extrapolated smoothly by comparison with those for $MnSO_4$(cr) (refer to $FeSO_4$(cr) table for details). The adopted $C_p°$ values are close to the average of the reported $C_p°$ values.

The value of $S°(298.15\ K)$ was derived using the low temperature $C_p°$ data reported by Weller,[6] based on $S°(51\ K) = 2.851$ cal K^{-1}·mol^{-1} evaluated from $C_p°$ data determined by Stout.[11]

Decomposition Data

$T_{dcm} = 1078$ K is the temperature at which the total pressure of the gaseous decomposition products equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for $CuSO_4$(cr), determined by Ingraham.[4]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−16.863	−760.059	−760.059	INFINITE
100	43.718	32.670	181.424	−14.875	−765.239	−731.589	382.143
200	77.008	74.167	117.649	−8.696	−768.538	−696.504	181.908
298.15	98.868	109.254	109.254	0.	−769.982	−660.781	115.766
300	99.286	109.867	109.256	0.183	−769.994	−660.104	114.934
400	114.934	140.654	113.347	10.923	−772.288	−623.342	81.400
500	127.194	167.676	121.566	23.055	−772.767	−586.042	61.223
600	136.315	191.710	131.291	36.251	−772.095	−548.744	47.772
700	142.925	213.244	141.488	50.229	−770.647	−511.625	38.178
800	147.695	232.656	151.691	64.772	−768.713	−474.750	30.998
900	151.042	250.251	161.680	79.714	−819.616	−437.054	25.366
1000	153.762	266.309	171.352	94.958	−815.986	−394.741	20.619
1100	156.063	281.074	180.665	110.451	−812.287	−352.795	16.753
1200	158.113	294.743	189.609	126.161	−808.556	−311.188	13.546
1300	159.954	307.473	198.191	142.066	−804.849	−269.891	10.844
1400	161.628	319.388	206.427	158.146	−814.329	−228.471	8.524
1500	163.218	330.594	214.335	174.389	−810.587	−186.755	6.503
1600	164.724	341.177	221.935	190.787	−806.756	−145.290	4.743
1700	166.147	351.206	229.247	207.330	−802.843	−104.068	3.198
1800	167.569	360.743	236.289	224.017	−798.849	−63.079	1.831
1900	168.908	369.839	243.081	240.841	−794.778	−22.313	0.613
2000	170.247	378.537	249.638	257.798	−790.631	18.236	−0.476

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 241.72\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1485.43 \pm 12.6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 485.34 \pm 12.6\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma_g^+]$	0	[1]
	20433	[1]
	21758	[1]

$\omega_e = 265.34\ cm^{-1}$ $\omega_e x_e = 1.015\ cm^{-1}$ $\sigma = 2$
$B_e = 0.10776\ cm^{-1}$ $\alpha_e = 0.000608\ cm^{-1}$ $r_e = 2.219$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from that of Cu(g) using $\Delta_f H°(298.15\ K) = 46.0\ kcal\cdot mol^{-1}$ for $Cu_2(g) \rightarrow 2\ Cu(g)$ obtained by 3rd law analysis of the mass spectrometric data of Ackerman *et al.*[1] Earlier studies of mass spectra and of the electronic band spectra yield values in reasonable agreement as shown below. The selected $\Delta_f H°$ corresponds to D_0^0 (0 K) = 1.97 eV compared with the linear Birge–Sponer extrapolation of 2.1 eV.

Source	Method	T/K	$\Delta_r H°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\ K^{-1}\cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal\cdot mol^{-1}$
[1]	Mass Spect.	1549–1709	47.8±2.6	45.99	−1.0±1.6	116.0
[2]	Mass Spect.	1575–1720	50.3±3.7	46.76	−2.1±2.3	115.0
[3]	Mass Spect.	1440–1560	—	46.5	—	115.5
[4]	Band Spectra	—	—	49.0	—	113.0

Heat Capacity and Entropy

Molecular constants, except for $\omega_e x_e$, were taken from the rotational analysis of bands of the B–X system given by Travis and Barrow.[5] The value for $\omega_e x_e$ was obtained from the earlier study of Kleman and Lindkvist[4] who showed by means of the vibrational isotope effect that the emitter was Cu_2. The spectroscopic characters of the ground and excited states are uncertain, but Travis and Barrow indicate that the transition is probably $^1\Sigma_u^+ - {}^1\Sigma_g^+$ for the B–X system. Vibrational and rotational constants were adjusted for 30.91% ^{65}Cu.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.930	485.428	485.428	INFINITE
100	31.964	203.874	273.337	−6.946	487.074	468.693	−244.820
200	35.442	227.321	245.038	−3.543	486.450	450.478	−117.653
250	36.156	235.313	242.321	−1.752	485.916	441.545	−92.256
298.15	36.585	241.721	241.721	0.	485.344	433.051	−75.869
300	36.598	241.947	241.722	0.068	485.321	432.726	−75.344
350	36.893	247.612	242.168	1.905	484.686	424.010	−63.280
400	37.103	252.553	243.164	3.756	484.021	415.387	−54.244
450	37.261	256.933	244.455	5.615	483.329	406.849	−47.226
500	37.386	260.865	245.903	7.481	482.616	398.390	−41.619
600	37.576	267.699	248.983	11.230	481.124	381.683	−33.228
700	37.720	273.503	252.082	14.995	479.541	365.233	−27.254
800	37.840	278.548	255.082	18.773	477.872	349.016	−22.788
900	37.945	283.011	257.942	22.562	476.108	333.014	−19.328
1000	38.041	287.014	260.652	26.362	474.239	317.214	−16.570
1100	38.131	290.644	263.216	30.170	472.237	301.607	−14.322
1200	38.216	293.965	265.642	33.988	470.065	286.190	−12.458
1300	38.299	297.027	267.940	37.813	467.634	270.963	−10.887
1400	38.380	299.869	270.121	41.647	438.637	256.749	−9.579
1500	38.459	302.519	272.193	45.489	435.910	243.852	−8.492
1600	38.537	305.004	274.167	49.339	433.191	231.137	−7.546
1700	38.614	307.343	276.050	53.197	430.479	218.591	−6.716
1800	38.691	309.552	277.851	57.062	427.776	206.205	−5.984
1900	38.767	311.646	279.575	60.935	425.080	193.969	−5.333
2000	38.843	313.636	281.229	64.815	422.392	181.875	−4.750
2100	38.919	315.533	282.817	68.704	419.711	169.915	−4.226
2200	38.995	317.346	284.346	72.599	417.038	158.083	−3.753
2300	39.071	319.081	285.819	76.503	414.372	146.372	−3.324
2400	39.149	320.745	287.239	80.414	411.714	134.777	−2.933
2500	39.228	322.345	288.612	84.332	409.064	123.292	−2.576
2600	39.308	323.885	289.939	88.259	406.422	111.914	−2.248
2700	39.390	325.370	291.224	92.194	403.788	100.637	−1.947
2800	39.475	326.804	292.469	96.137	401.162	89.457	−1.669
2900	39.562	328.191	293.677	100.089	−201.863	90.362	−1.628
3000	39.653	329.533	294.850	104.050	−202.882	100.456	−1.749
3100	39.747	330.835	295.990	108.020	−203.991	110.585	−1.863
3200	39.845	332.099	297.099	111.999	−205.193	120.752	−1.971
3300	39.948	333.326	298.178	115.989	−206.487	130.958	−2.073
3400	40.055	334.520	299.230	119.989	−207.872	141.204	−2.169
3500	40.166	335.683	300.255	124.000	−209.348	151.492	−2.261
3600	40.283	336.816	301.255	128.022	−210.910	161.823	−2.348
3700	40.405	337.922	302.231	132.057	−212.557	172.200	−2.431
3800	40.533	339.001	303.184	136.104	−214.284	182.621	−2.510
3900	40.666	340.055	304.116	140.164	−216.088	193.090	−2.586
4000	40.804	341.087	305.027	144.237	−217.963	203.605	−2.659
4100	40.947	342.096	305.919	148.324	−219.904	214.168	−2.729
4200	41.096	343.085	306.793	152.427	−221.907	224.779	−2.796
4300	41.250	344.053	307.648	156.544	−223.966	235.439	−2.860
4400	41.409	345.003	308.486	160.677	−226.076	246.147	−2.922
4500	41.572	345.936	309.308	164.826	−228.231	256.904	−2.982
4600	41.740	346.851	310.114	168.991	−230.426	267.709	−3.040
4700	41.913	347.751	310.905	173.174	−232.656	278.562	−3.096
4800	42.089	348.635	311.682	177.374	−234.916	289.462	−3.150
4900	42.270	349.505	312.445	181.592	−237.201	300.411	−3.202
5000	42.454	350.361	313.195	185.828	−239.509	311.406	−3.253
5100	42.641	351.203	313.932	190.083	−241.833	322.447	−3.303
5200	42.831	352.033	314.657	194.356	−244.172	333.534	−3.350
5300	43.023	352.851	315.370	198.649	−246.521	344.666	−3.397
5400	43.218	353.657	316.071	202.961	−248.878	355.843	−3.442
5500	43.414	354.452	316.762	207.293	−251.240	367.063	−3.486
5600	43.612	355.236	317.442	211.644	−253.606	378.326	−3.529
5700	43.811	356.009	318.112	216.015	−255.973	389.632	−3.571
5800	44.012	356.773	318.772	220.406	−258.341	400.979	−3.611
5900	44.212	357.527	319.422	224.817	−260.709	412.367	−3.651
6000	44.414	358.272	320.064	229.249	−263.075	423.795	−3.689

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = 92.36 \pm 0.34\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1516.7\ K$

$\Delta_f H°(0\ K) = -168.95 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -170.71 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus} H° = 64.768 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Cu_2O(cr) has been investigated calorimetrically (both oxidation and reduction reactions) and the oxidation reaction 2 Cu(cr) + 1/2 O_2(g) = Cu_2O(cr) has been studied extensively by pressure and by emf measurement. The more consistent data leading to the adopted value are summarized below.

Source	Method	Reaction*	T/K	Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	Aq Calorim.	A	291	—	27.61		—	−40.70
2	Calorimetric	See Text	298.15	—	—		—	−40.83±0.30
3	Calorimetric	A	297.90	—	26.93		—	−41.39±0.32
4	Aq emf	A	273–318	5	27.47±0.04	27.58±0.02	0.4±0.1	−40.74
5*	q emf	A	298–318	7	29.97±0.38	28.02±0.14	−6.4±1.3	−40.30
6	Aq emf	A	288–308	3	29.54±0.73	28.25±0.10	−4.3±2.5	−40.06
7	Equil Press	B	1011–1156	5	−35.79±0.86	−41.55±0.66	−5.3±0.8	−41.55
8	emf vs Fe/FexO	B	1073–1323	4	−42.29±0.59	−40.96±0.23	1.1±0.5	−40.96
9	Fused Salt emf	B	987	1		−41.72		−41.72
10	emf	B	1100–1200	2	−60.17	−39.77±2.03	14.3	−39.77
11	emf	B	973–1273	Eqn	−41.10	−40.75	0.31	−40.75
12	emf	B	892–1320	Eqn	−40.75	−40.77	−0.01	−40.77
13	Equil Press	B	1200–1420	Eqn	−33.37	−40.30	5.4	−40.30
14	Equil Press	B	1280–1450	Eqn	−36.82	−40.24	5.0	−40.24
15	emf	B	973–1373	Eqn	−41.83	−41.01	1.4	−41.01
16	emf	B	845–1270	Eqn	−40.83	−40.88	−0.1	−40.88
17	emf	B	976–1234	Eqn	−39.84	−40.59	−0.7	−40.59
18	emf	B	1073–1273	Eqn	−41.07	−39.12	1.7	−39.12
19	Equil Press	B	1013–1243	Eqn	−43.07	−43.86	1.4	−43.86
20	emf	B	973–1273	Eqn	−42.62	−41.23	1.2	−41.23
21	emf	B	1173–1356	Eqn	−40.71	−40.90	−0.2	−40.90

*Reactions: (A) 2 Cu(cr) + H_2O(l) = Cu_2O(cr) + H_2(g) (B) 2 Cu(cr) + 0.5 O_2(g) = Cu_2O(cr)

Thomsen[1] obtained $\Delta_f H°(298.15\ K)$ values of −40.18, −40.87, and −41.51 kcal·mol^{-1} from aqueous calorimetry using three different paths. He favored the first path which is recalculated by combination of the heats of reaction of $Cu_2O + H_2SO_4$, $Fe + H_2SO_4$, and $Fe + CuSO_4$(aq) to yield the heat of reduction of Cu_2O with H_2. Nunez *et al.*[3] measured the direct heat of reduction of Cu_2O by H_2; to conclude that the heats of formation of the copper oxides are influenced by material history, state of subdivision, and non stoichiometry. Mah *et al.*[2] measured the direct heat of oxidation of copper by O_2, but they obtained a mixed product of Cu_2O and CuO and used $\Delta_f H°(298.15\ K) = -33.63 \pm 0.05$ kcal·mol^{-1} for the equilibrium reaction Cu_2O(cr) + 1/2 O_2(g) = 2 CuO(cr) to resolve their results into $\Delta_f H°(Cu_2O, cr, 298.15\ K)$ and $\Delta_f H°$(CuO, cr, 298.15 K). The overall average from our 3rd law analyses is −40.82 kcal·mol^{-1}; without the outlier[10,18,19] the average is 40.81; the average of the six data sets with an absolute drift less than 1 is −40.77. We adopt $\Delta_f H°(Cu_2O, cr, 298.15\ K) = -40.8 \pm 0.5$ kcal·mol^{-1}.

Heat Capacity and Entropy

The heat capacities are smoothed values adopted from a consideration of the work of Gregor[22] (2.8–21 K), Hu and Johnston[23] (15–300 K) and Mah *et al.*[2] (52–296 K, 406–1464 K). The data of Mah *et al.*[2] are favored over that of Hu and Johnston[23] above 120 K. Adjustment is made to the IPTS 68 temperature scale[24].

The entropy is based on a T^3 extrapolation to obtain $S°(2.8\ K) = 0.0015$ cal K^{-1}·mol^{-1}.

Fusion Data

Refer to the liquid table for details.

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Continued on page 1027

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.600	−168.952	−168.952	INFINITE
100	39.499	37.092	141.510	−10.442	−169.584	−162.621	84.944
200	53.619	69.143	97.826	−5.737	−170.360	−155.348	40.573
298.15	62.543	92.360	92.360	0.	−170.707	−147.886	25.909
300	62.664	92.747	92.361	0.116	−170.709	−147.745	25.725
400	67.688	111.531	94.888	6.657	−170.641	−140.092	18.294
500	70.922	127.000	99.809	13.596	−170.363	−132.484	13.840
600	73.448	140.161	105.465	20.818	−169.961	−124.944	10.877
700	75.645	151.651	111.259	28.274	−169.479	−117.478	8.766
800	77.666	161.886	116.959	35.941	−168.929	−110.087	7.188
900	79.493	171.141	122.473	43.801	−168.325	−102.767	5.964
1000	81.245	179.606	127.769	51.837	−167.688	−95.517	4.989
1100	83.385	187.443	132.842	60.061	−167.029	−88.331	4.194
1200	86.110	194.812	137.702	68.532	−166.322	−81.208	3.535
1300	89.173	201.824	142.367	77.294	−165.608	−74.144	2.979
1400	92.489	208.552	146.855	86.375	−191.165	−66.321	2.474
1500	95.987	215.052	151.186	95.798	−190.132	−57.438	2.000
1516.700	96.587	216.118	151.895	97.406	---- CRYSTAL <--> LIQUID ----		
1600	99.631	221.362	155.376	105.578	−188.755	−48.635	1.588
1700	103.380	227.514	159.439	115.728	−187.020	−39.928	1.227
1800	107.212	233.532	163.389	126.257	−184.917	−31.335	0.909
1900	111.115	239.433	167.236	137.173	−182.440	−22.868	0.629
2000	115.068	245.232	170.992	148.481	−179.581	−14.542	0.380

PREVIOUS: June 1966 CURRENT: December 1977

$S°(298.15\ K) = [129.957]\ J\ K^{-1}\cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-111.995]\ kJ\cdot mol^{-1}$

$T_{fus} = 1516.7\ K$ $\Delta_{fus}H° = 64.768 \pm 0.63\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Cu_2O, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1516.7\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is taken from the enthalpy measurements of Mah *et al.*[1] (1521–1600 K) and is assumed constant at 23.88 cal $K^{-1}\cdot mol^{-1}$ from 1000 to 2000 K. A glass transition is assumed at 1000 K below which the heat capacity is that of the crystal.

The entropy is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The melting point, 1515 K, was determined by drop calorimetry by Mah *et al.*[1] Correcting to the IPTS–68 temperature scale,[2] we adopt $T_{fus} = 1516.7$ K.

$\Delta_{fus} H° = 15.48 \pm 0.15\ kcal\cdot mol^{-1}$ is based on our smoothing through the pre–melt region of the enthalpy measurements of Mah *et al.*[1]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	62.542	129.957	129.957	0.	−111.995	−100.384	17.587
300	62.664	130.345	129.959	0.116	−111.997	−100.312	17.466
400	67.688	149.128	132.486	6.657	−111.929	−96.419	12.591
500	70.922	164.598	137.407	13.596	−111.651	−92.570	9.671
600	73.448	177.758	143.062	20.818	−111.249	−88.791	7.730
700	75.645	189.249	148.857	28.274	−110.767	−85.085	6.349
800	77.666	199.483	154.557	35.941	−110.217	−81.452	5.318
900	79.493	208.739	160.071	43.801	−109.613	−77.893	4.521
1000	81.245	217.203	165.367	51.837	−108.976	−74.402	3.886
1000.000	81.245	217.203	165.367	51.837	GLASS <--> LIQUID		
1000.000	99.914	217.203	165.367	51.837	TRANSITION		
1100	99.914	226.726	170.519	61.828	−106.550	−71.064	3.375
1200	99.914	235.420	175.570	71.819	−104.323	−67.938	2.957
1300	99.914	243.417	180.486	81.811	−102.380	−64.987	2.611
1400	99.914	250.822	185.249	91.802	−127.026	−61.360	2.289
1500	99.914	257.715	189.853	101.794	−125.424	−56.725	1.975
1516.700	99.914	258.821	190.606	103.462	---- CRYSTAL <--> LIQUID ----		
1600	99.914	264.163	194.298	111.785	−123.836	−52.197	1.704
1700	99.914	270.220	198.587	121.776	−122.259	−47.768	1.468
1800	99.914	275.931	202.727	131.768	−120.694	−43.431	1.260
1900	99.914	281.333	206.723	141.759	−119.142	−39.181	1.077
2000	99.914	286.458	210.583	151.751	−117.600	−35.013	0.914

PREVIOUS: June 1966 CURRENT: December 1977

0 to	1516.7 K	crystal
above	1516.7 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.600	−168.952	−168.952	INFINITE
100	39.499	37.092	141.510	−10.442	−169.584	−162.621	84.944
200	53.619	69.143	97.826	−5.737	−170.360	−155.348	40.573
298.15	62.543	92.360	92.360	0.	−170.707	−147.886	25.909
300	62.664	92.747	92.361	0.116	−170.709	−147.745	25.725
400	67.688	111.531	94.888	6.657	−170.641	−140.092	18.294
500	70.922	127.000	99.809	13.596	−170.363	−132.484	13.840
600	73.448	140.161	105.465	20.818	−169.961	−124.944	10.877
700	75.645	151.651	111.259	28.274	−169.479	−117.478	8.766
800	77.666	161.886	116.959	35.941	−168.929	−110.087	7.188
900	79.493	171.141	122.473	43.801	−168.325	−102.767	5.964
1000	81.245	179.606	127.769	51.837	−167.688	−95.517	4.989
1100	83.385	187.443	132.842	60.061	−167.029	−88.331	4.194
1200	86.110	194.812	137.702	68.532	−166.322	−81.208	3.535
1300	89.173	201.824	142.367	77.294	−165.608	−74.144	2.979
1400	92.489	208.552	146.855	86.375	−191.165	−66.321	2.474
1500	95.987	215.052	151.186	95.798	−190.132	−57.438	2.000
1516.700	96.587	216.118	151.895	97.406	CRYSTAL <--> LIQUID		
1516.700	99.914	258.821	151.895	162.174	TRANSITION		
1600	99.914	264.163	157.603	170.497	−123.836	−52.197	1.704
1700	99.914	270.220	164.051	180.488	−122.259	−47.768	1.468
1800	99.914	275.931	170.109	190.480	−120.694	−43.431	1.260
1900	99.914	281.333	175.822	200.471	−119.142	−39.181	1.077
2000	99.914	286.458	181.227	210.463	−117.600	−35.013	0.914

PREVIOUS: CURRENT: December 1977

$S°(298.15\ K) = [157.318 \pm 8.4]\ J\ K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) \approx$ Unknown

$\Delta_f H°(298.15\ K) = -927.593 \pm 1.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The equilibrium pressures for the following reactions: (A) $CuO \cdot CuSO_4(cr) = 2\ CuO(cr) + SO_3(g)$ and $SO_3(g) = SO_2(g) + 0.5\ O_2(g)$ and (B) $CuO \cdot CuSO_4(cr) + Cu_2O(cr) = 4\ CuO(cr) + SO_2(g)$, were determined by Reinders[1] and Ingraham.[2] Using the reported vapor pressures, the corresponding enthalpy changes were evaluated by both the 2nd and 3rd law methods. The results obtained are presented as follows:

Reference	Reaction	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	A*	1013–1093	53.03±2.53	52.43	−0.7±2.4	−221.5
1	B	917–1027	41.72±1.42	42.43	0.5±1.4	−221.7
2	A*	969–1138	50.92±0.16	52.57	1.5±0.2	−221.7

*Partial pressures were calculated from JANAF values for the $SO_3 - SO_2$ equilibrium.

The value of $\Delta_f H°(CuO \cdot CuSO_4, cr, 298.15\ K)$ adopted is $-221.7 \pm 0.3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacities are calculated as the sum of those for CuO(cr) and $CuSO_4$(cr). The value of $S°(298.15\ K)$ is estimated by comparison with those for CuO(cr) and $CuSO_4$(cr) and adjusted so that, using the derived free energy functions, the 2nd and 3rd law values for $\Delta_r H°(298.15\ K)$ agree reasonably.

Decomposition Data

$T_{dcm} = 1138$ K is the temperature at which the total pressure of the gaseous decomposition products of reaction (A) equals one atmosphere. It was obtained by graphical extrapolation of the decomposition pressures for $CuOCuSO_4$(cr), determined by Ingraham.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	141.043	157.318	157.318	0.	−927.593	−792.253	138.799
300	141.419	158.192	157.321	0.261	−927.600	−791.413	137.797
400	162.339	201.891	163.137	15.501	−929.372	−745.953	97.411
500	176.983	239.760	174.761	32.499	−929.081	−700.122	73.141
600	187.820	273.029	188.423	50.763	−927.541	−654.457	56.976
700	195.811	302.603	202.662	69.959	−925.177	−609.121	45.453
800	202.129	329.172	216.843	89.863	−922.273	−564.163	36.836
900	207.526	353.295	230.685	110.349	−972.111	−518.512	30.094
1000	212.547	375.424	244.067	131.356	−967.283	−468.369	24.465
1100	217.150	395.897	256.951	152.841	−962.253	−418.719	19.883
1200	221.752	414.990	269.334	174.787	−957.056	−369.536	16.085
1300	226.313	432.923	281.235	197.194	−951.765	−320.790	12.889
1400	230.329	449.842	292.680	220.027	−972.716	−271.639	10.135
1500	234.304	465.869	303.696	243.259	−967.089	−221.757	7.722

PREVIOUS: CURRENT: June 1966

Continued from Page 1019

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$S°(298.15\ K) = 123.350 \pm 0.017\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 219.807 \pm 0.004\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = 221.720 \pm 0.004\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2

Enthalpy of Formation

The adopted value for $\Delta_f H°$(D, g, 298.15 K) is derived using $D_0° = 36748.9 \pm 0.4\ cm^{-1}$ from Herzberg[1] and auxiliary data for D_2.[2] An earlier value for the dissociation energy was reported by Herzberg and Monfils[3] as $D_0° = 36743.6 \pm 0.5\ cm^{-1}$. Two theoretical studies by Kolos and Wolniewicz[4] and Bunker[5] yielded a vlue of 36748.2 cm^{-1}. More recently, LeRoy and Barwell,[6] using a relationship involving the near–dissociation behavior of the rotational constants and the long range intermolecular potential, calculated $D_0° = 36748.88(\pm 0.3)\ cm^{-1}$.

Heat Capacity and Entropy

The electronic levels for D(g) are given in the compilation by Moore.[7] Our calculations indicate that the inclusion of levels up to $n = 12$ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the first excited state lies at 82281 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the gram formula weight and the fundamental constants. The gram formula weight is that recommended by IUPAC.[8] Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of prope fill and cut off procedures.[9]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	219.807	219.807	INFINITE
100	20.786	100.643	141.830	−4.119	220.511	216.086	−112.872
200	20.786	115.051	125.251	−2.040	221.112	211.433	−55.221
250	20.786	119.689	123.692	−1.001	221.422	208.977	−43.663
298.15	20.786	123.350	123.350	0.	221.720	206.553	−36.187
300	20.786	123.479	123.350	0.038	221.732	206.459	−35.948
350	20.786	126.683	123.603	1.078	222.041	203.889	−30.429
400	20.786	129.458	124.166	2.117	222.350	201.275	−26.284
450	20.786	131.907	124.892	3.156	222.657	198.622	−23.055
500	20.786	134.097	125.705	4.196	222.963	195.935	−20.469
600	20.786	137.886	127.429	6.274	223.568	190.473	−16.582
700	20.786	141.091	129.158	8.353	224.156	184.910	−13.798
800	20.786	143.866	130.827	10.431	224.723	179.265	−11.705
900	20.786	146.314	132.414	12.510	225.262	173.550	−10.073
1000	20.786	148.504	133.916	14.589	225.774	167.776	−8.764
1100	20.786	150.485	135.333	16.667	226.256	161.953	−7.690
1200	20.786	152.294	136.673	18.746	226.710	156.087	−6.794
1300	20.786	153.958	137.939	20.824	227.138	150.184	−6.034
1400	20.786	155.498	139.139	22.903	227.540	144.249	−5.382
1500	20.786	156.932	140.278	24.982	227.919	138.287	−4.816
1600	20.786	158.274	141.361	27.060	228.276	132.299	−4.319
1700	20.786	159.534	142.394	29.139	228.614	126.290	−3.880
1800	20.786	160.722	143.379	31.217	228.934	120.262	−3.490
1900	20.786	161.846	144.322	33.296	229.237	114.216	−3.140
2000	20.786	162.912	145.225	35.375	229.524	108.155	−2.825
2100	20.786	163.926	146.091	37.453	229.797	102.080	−2.539
2200	20.786	164.893	146.924	39.532	230.056	95.992	−2.279
2300	20.786	165.817	147.726	41.610	230.303	89.893	−2.042
2400	20.786	166.702	148.498	43.689	230.538	83.783	−1.823
2500	20.786	167.550	149.243	45.768	230.762	77.663	−1.623
2600	20.786	168.366	149.963	47.846	230.975	71.535	−1.437
2700	20.786	169.150	150.659	49.925	231.179	65.399	−1.265
2800	20.786	169.906	151.333	52.004	231.372	59.255	−1.105
2900	20.786	170.635	151.986	54.082	231.556	53.105	−0.957
3000	20.786	171.340	152.620	56.161	231.732	46.949	−0.817
3100	20.786	172.022	153.235	58.239	231.898	40.786	−0.687
3200	20.786	172.682	153.832	60.318	232.056	34.619	−0.565
3300	20.786	173.321	154.413	62.397	232.206	28.447	−0.450
3400	20.786	173.942	154.979	64.475	232.347	22.270	−0.342
3500	20.786	174.544	155.529	66.554	232.480	16.089	−0.240
3600	20.786	175.130	156.065	68.632	232.605	9.905	−0.144
3700	20.786	175.699	156.588	70.711	232.722	3.717	−0.052
3800	20.786	176.254	157.099	72.790	232.831	−2.473	0.034
3900	20.786	176.794	157.597	74.868	232.932	−8.667	0.116
4000	20.786	177.320	158.083	76.947	233.025	−14.863	0.194
4100	20.786	177.833	158.559	79.025	233.111	−21.061	0.268
4200	20.786	178.334	159.024	81.104	233.188	−27.262	0.339
4300	20.786	178.823	159.478	83.183	233.258	−33.464	0.407
4400	20.786	179.301	159.924	85.261	233.321	−39.667	0.471
4500	20.786	179.768	160.359	87.340	233.375	−45.872	0.532
4600	20.786	180.225	160.786	89.418	233.423	−52.078	0.591
4700	20.786	180.672	161.205	91.497	233.462	−58.285	0.648
4800	20.786	181.110	161.615	93.576	233.495	−64.493	0.702
4900	20.786	181.538	162.017	95.654	233.521	−70.701	0.754
5000	20.786	181.958	162.412	97.733	233.540	−76.910	0.803
5100	20.786	182.370	162.799	99.811	233.552	−83.119	0.851
5200	20.786	182.773	163.179	101.890	233.558	−89.328	0.897
5300	20.786	183.169	163.553	103.969	233.558	−95.538	0.942
5400	20.786	183.558	163.920	106.047	233.552	−101.747	0.984
5500	20.786	183.939	164.280	108.126	233.541	−107.956	1.025
5600	20.786	184.314	164.634	110.204	233.524	−114.165	1.065
5700	20.786	184.682	164.983	112.283	233.503	−120.374	1.103
5800	20.786	185.043	165.326	114.362	233.478	−126.582	1.140
5900	20.786	185.399	165.663	116.440	233.449	−132.790	1.176
6000	20.786	185.748	165.995	118.519	233.416	−138.997	1.210

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

$S°(298.15\ K) = 117.583 \pm 0.02\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1532.21 \pm 0.04\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1540.324]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(D^+, g, 0\ K)$ is calculated from $\Delta_f H°(D, g, 0\ K)$[1] using the spectroscopic value of IP(D) = 109708.608 ± 0.005 cm^{-1}(313.6727 ± 0.0001 $kJ \cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot cm^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(D^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(D, g, 0\ K)$ by using IP(D) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for D(g), $D^+(g)$, and $e^-(g)$. $\Delta_f H°(D \rightarrow D^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by $-6.197\ kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The thermodynamic functions of the proton gas are calculated using the recent CODAT fundamental constants (2) and assuming that the proton is an ideal monatomic gas. Since there is no electron associated with this species, there is only a translational contribution to the thermochemical function.

References

[1]JANAF Thermochemical Tables: D(g), 3–31–82 ; e^-(g), 3–31–82.
[2]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–3, Section 6, 1972.
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[4]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1532.214		
100	20.786	94.876	136.064	−4.119			
200	20.786	109.284	119.485	−2.040			
250	20.786	113.922	117.926	−1.001			
298.15	20.786	117.583	117.583	0.	1540.324	1520.622	−266.407
300	20.786	117.712	117.584	0.038	1540.374	1520.500	−264.743
350	20.786	120.916	117.837	1.078	1541.723	1517.081	−226.412
400	20.786	123.692	118.399	2.117	1543.071	1513.468	−197.639
450	20.786	126.140	119.126	3.156	1544.418	1509.687	−175.240
500	20.786	128.330	119.939	4.196	1545.763	1505.756	−157.305
600	20.786	132.120	121.663	6.274	1548.446	1497.502	−130.369
700	20.786	135.324	123.391	8.353	1551.113	1488.800	−111.096
800	20.786	138.100	125.060	10.431	1553.758	1479.718	−96.616
900	20.786	140.548	126.648	12.510	1556.377	1470.305	−85.334
1000	20.786	142.738	128.149	14.589	1558.967	1460.603	−76.294
1100	20.786	144.719	129.567	16.667	1561.528	1450.642	−68.885
1200	20.786	146.528	130.906	18.746	1564.060	1440.449	−62.701
1300	20.786	148.191	132.173	20.824	1566.566	1430.047	−57.460
1400	20.786	149.732	133.372	22.903	1569.047	1419.452	−52.960
1500	20.786	151.166	134.511	24.982	1571.505	1408.681	−49.055
1600	20.786	152.507	135.595	27.060	1573.941	1397.746	−45.632
1700	20.786	153.768	136.627	29.139	1576.357	1386.660	−42.607
1800	20.786	154.956	137.613	31.217	1578.755	1375.432	−39.914
1900	20.786	156.079	138.555	33.296	1581.137	1364.071	−37.501
2000	20.786	157.146	139.458	35.375	1583.503	1352.585	−35.326
2100	20.786	158.160	140.325	37.453	1585.854	1340.982	−33.355
2200	20.786	159.127	141.158	39.532	1588.192	1329.266	−31.561
2300	20.786	160.051	141.959	41.610	1590.518	1317.445	−29.920
2400	20.786	160.935	142.732	43.689	1592.831	1305.522	−28.414
2500	20.786	161.784	143.477	45.768	1595.134	1293.504	−27.026
2600	20.786	162.599	144.197	47.846	1597.426	1281.393	−25.744
2700	20.786	163.384	144.893	49.925	1599.708	1269.195	−24.554
2800	20.786	164.140	145.567	52.004	1601.980	1256.912	−23.448
2900	20.786	164.869	146.220	54.082	1604.243	1244.548	−22.417
3000	20.786	165.574	146.853	56.161	1606.497	1232.107	−21.453
3100	20.786	166.255	147.468	58.239	1608.742	1219.590	−20.550
3200	20.786	166.915	148.066	60.318	1610.978	1207.001	−19.702
3300	20.786	167.555	148.647	62.397	1613.206	1194.342	−18.905
3400	20.786	168.175	149.212	64.475	1615.426	1181.616	−18.153
3500	20.786	168.778	149.762	66.554	1617.638	1168.825	−17.444
3600	20.786	169.363	150.299	68.632	1619.841	1155.970	−16.773
3700	20.786	169.933	150.822	70.711	1622.037	1143.055	−16.137
3800	20.786	170.487	151.332	72.790	1624.225	1130.080	−15.534
3900	20.786	171.027	151.830	74.868	1626.404	1117.048	−14.961
4000	20.786	171.553	152.317	76.947	1628.576	1103.960	−14.416
4100	20.786	172.067	152.792	79.025	1630.740	1090.817	−13.897
4200	20.786	172.568	153.257	81.104	1632.896	1077.622	−13.402
4300	20.786	173.057	153.712	83.183	1635.045	1064.376	−12.930
4400	20.786	173.535	154.157	85.261	1637.186	1051.080	−12.478
4500	20.786	174.002	154.593	87.340	1639.319	1037.735	−12.046
4600	20.786	174.459	155.020	89.418	1641.445	1024.344	−11.632
4700	20.786	174.906	155.438	91.497	1643.564	1010.905	−11.235
4800	20.786	175.343	155.848	93.576	1645.675	997.422	−10.854
4900	20.786	175.772	156.250	95.654	1647.779	983.895	−10.488
5000	20.786	176.192	156.645	97.733	1649.877	970.325	−10.137
5100	20.786	176.603	157.032	99.811	1651.967	956.713	−9.799
5200	20.786	177.007	157.413	101.890	1654.052	943.061	−9.473
5300	20.786	177.403	157.786	103.969	1656.130	929.368	−9.159
5400	20.786	177.791	158.153	106.047	1658.203	915.636	−8.857
5500	20.786	178.173	158.514	108.126	1660.270	901.866	−8.565
5600	20.786	178.547	158.868	110.204	1662.333	888.058	−8.283
5700	20.786	178.915	159.216	112.283	1664.390	874.213	−8.011
5800	20.786	179.277	159.559	114.362	1666.444	860.332	−7.748
5900	20.786	179.632	159.896	116.440	1668.493	846.417	−7.494
6000	20.786	179.981	160.228	118.519	1670.539	832.466	−7.247

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

EA(D, g) = 0.754209 ± 0.000003 eV
$S°$(298.15 K) = 117.590 ± 0.017 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 147.038 ± 0.04 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [142.753] kJ·mol^{-1}

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(D^-, g, 0 K)$ is calculated from $\Delta_f H°(D, g, 0 K)$[1] using the adopted electron affinity of EA(D) = 0.754209 ± 0.000003 eV (72.7696 ± 0.0003 kJ·mol^{-1}). This value is assumed to be the same as that recommended by Hotop and Lineberger[2] for H(g). Additional information on D^-(g) and H^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 3] Rosenstock *et al.*[4] and Massey.[5]

$\Delta_f H°(D^-, g, 298.15 K)$ is obtained from $\Delta_f H°(D, g, 0 K)$ by using EA(D) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for D^-(g), D(g), and e^-(ref). $\Delta_r H°(D^- \rightarrow D + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for D^-(g) is given by Hotop and Lineberger[2, 3] and Rosenstock *et al.*[4]

A comparison of the isoelectronic sequence – H^-(g), He(g), and Li^+(g) – would suggest that stable electronic states may exist at 0.8 EA(H) or roughly 6400 cm^{-1}. This would greatly affect the entropy. However, Pekeris[6] states that he was unable to find any bound states. In addition, Seman and Branscom[7] state that theoretical and semiempirical evidence suggests that atomic negative ions have very few if any excited states below the continuum. We assume that the same arguments apply for D^-(g) and that no stable excited states exist.

References

[1]JANAF Thermochemical Tables: D(g), 3–31–82; e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731, (1985).
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[4]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	147.038		
100	20.786	94.883	136.071	−4.119			
200	20.786	109.291	119.492	−2.040			
250	20.786	113.929	117.933	−1.001			
298.15	20.786	117.590	117.590	0.	142.753	135.559	−23.749
300	20.786	117.719	117.591	0.038	142.726	135.514	−23.595
350	20.786	120.923	117.844	1.078	141.996	134.370	−20.054
400	20.786	123.699	118.406	2.117	141.266	133.330	−17.411
450	20.786	126.147	119.133	3.156	140.534	132.382	−15.366
500	20.786	128.337	119.946	4.196	139.801	131.515	−13.739
600	20.786	132.127	121.670	6.274	138.327	129.997	−11.317
700	20.786	135.331	123.398	8.353	136.837	128.726	−9.606
800	20.786	138.106	125.067	10.431	135.324	127.670	−8.336
900	20.786	140.555	126.655	12.510	133.785	126.805	−7.360
1000	20.786	142.745	128.156	14.589	132.218	126.113	−6.587
1100	20.786	144.726	129.574	16.667	130.622	125.580	−5.963
1200	20.786	146.534	130.913	18.746	128.998	125.193	−5.450
1300	20.786	148.198	132.179	20.824	127.346	124.943	−5.020
1400	20.786	149.739	133.379	22.903	125.670	124.821	−4.657
1500	20.786	151.173	134.518	24.982	123.970	124.819	−4.347
1600	20.786	152.514	135.601	27.060	122.249	124.932	−4.079
1700	20.786	153.774	136.634	29.139	120.508	125.153	−3.845
1800	20.786	154.962	137.619	31.217	118.749	125.477	−3.641
1900	20.786	156.086	138.562	33.296	116.974	125.899	−3.461
2000	20.786	157.152	139.465	35.375	115.182	126.415	−3.302
2100	20.786	158.167	140.332	37.453	113.376	127.021	−3.159
2200	20.786	159.134	141.165	39.532	111.557	127.713	−3.032
2300	20.786	160.058	141.966	41.610	109.726	128.488	−2.918
2400	20.786	160.942	142.738	43.689	107.882	129.343	−2.815
2500	20.786	161.791	143.484	45.768	106.027	130.276	−2.722
2600	20.786	162.606	144.204	47.846	104.162	131.282	−2.637
2700	20.786	163.390	144.900	49.925	102.287	132.361	−2.561
2800	20.786	164.146	145.574	52.004	100.402	133.509	−2.491
2900	20.786	164.876	146.227	54.082	98.507	134.725	−2.427
3000	20.786	165.580	146.860	56.161	96.604	136.006	−2.368
3100	20.786	166.262	147.475	58.239	94.692	137.351	−2.314
3200	20.786	166.922	148.073	60.318	92.771	138.758	−2.265
3300	20.786	167.562	148.654	62.397	90.842	140.225	−2.220
3400	20.786	168.182	149.219	64.475	88.905	141.751	−2.178
3500	20.786	168.785	149.769	66.554	86.959	143.333	−2.139
3600	20.786	169.370	150.306	68.632	85.006	144.972	−2.103
3700	20.786	169.940	150.829	70.711	83.044	146.664	−2.071
3800	20.786	170.494	151.339	72.790	81.075	148.410	−2.040
3900	20.786	171.034	151.837	74.868	79.097	150.208	−2.012
4000	20.786	171.560	152.324	76.947	77.112	152.056	−1.986
4100	20.786	172.073	152.799	79.025	75.119	153.955	−1.961
4200	20.786	172.574	153.264	81.104	73.118	155.902	−1.939
4300	20.786	173.063	153.719	83.183	71.109	157.896	−1.918
4400	20.786	173.541	154.164	85.261	69.093	159.938	−1.899
4500	20.786	174.008	154.600	87.340	67.069	162.025	−1.881
4600	20.786	174.465	155.027	89.418	65.037	164.158	−1.864
4700	20.786	174.912	155.445	91.497	62.999	166.335	−1.849
4800	20.786	175.350	155.855	93.576	60.953	168.555	−1.834
4900	20.786	175.779	156.257	95.654	58.900	170.818	−1.821
5000	20.786	176.198	156.652	97.733	56.840	173.123	−1.809
5100	20.786	176.610	157.039	99.811	54.774	175.469	−1.797
5200	20.786	177.014	157.419	101.890	52.701	177.856	−1.787
5300	20.786	177.410	157.793	103.969	50.622	180.283	−1.777
5400	20.786	177.798	158.160	106.047	48.538	182.749	−1.768
5500	20.786	178.180	158.520	108.126	46.448	185.253	−1.759
5600	20.786	178.554	158.875	110.204	44.353	187.796	−1.752
5700	20.786	178.922	159.223	112.283	42.253	190.376	−1.745
5800	20.786	179.284	159.566	114.362	40.149	192.993	−1.738
5900	20.786	179.639	159.903	116.440	38.042	195.646	−1.732
6000	20.786	179.988	160.235	118.519	35.931	198.335	−1.727

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

$S°(298.15\ K) = 179.702\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -275.458 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -275.516 \pm 0.8\ kJ·mol^{-1}$

State	Electronic States and Molecular Constants σ = 1						
	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	2998.19	45.76	11.000	0.2907	0.9187
$V^1\Sigma^+$	83755	1	839.4	8.90	2.121	0.00712	2.088

Enthalpy of Formation

The enthalpy of formation was calculated from $\Delta_f H°(298.15\ K)$ of HF(g), -65.13 ± 0.2 kcal·mol^{-1}, given in JANAF Thermochemical Tables[1] the appropriate thermal functions (see tables for H_2, D_2, DF and HF,[1] and the estimated zero point energies. The energies for H_2(g) and D_2(g) are those given by Herzberg and Monfils.[2] The energies for HF(g) and DF(g) include the Dunham correction and were calculated from the data given by Mann *et al.*[3] and Spanbauer *et al.*[4]

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[5] The National Bureau of Standards prepared this table[6] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[6] we recalculate the table in terms of 1973 fundamental constants,[7] 1975 atomic weights,[8] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.638	−275.458	−275.458	INFINITE
100	29.117	147.887	205.599	−5.771	−275.419	−276.050	144.194
200	29.125	168.071	182.367	−2.859	−275.449	−276.667	72.258
250	29.130	174.571	180.182	−1.403	−275.473	−276.969	57.870
298.15	29.137	179.702	179.702	0.	−275.516	−277.254	48.574
300	29.137	179.882	179.703	0.054	−275.518	−277.265	48.276
350	29.150	184.375	180.057	1.511	−275.586	−277.551	41.422
400	29.174	188.268	180.846	2.969	−275.674	−277.825	36.280
450	29.221	191.707	181.865	4.429	−275.779	−278.088	32.280
500	29.298	194.790	183.006	5.892	−275.899	−278.339	29.078
600	29.561	200.152	185.430	8.833	−276.168	−278.802	24.272
700	29.962	204.738	187.868	11.809	−276.458	−279.218	20.836
800	30.463	208.770	190.234	14.829	−276.755	−279.592	18.255
900	31.016	212.390	192.498	17.903	−277.047	−279.929	16.247
1000	31.583	215.687	194.654	21.033	−277.329	−280.234	14.638
1100	32.137	218.724	196.706	24.219	−277.599	−280.511	13.320
1200	32.661	221.543	198.660	27.459	−277.857	−280.764	12.221
1300	33.148	224.176	200.523	30.750	−278.102	−280.997	11.291
1400	33.594	226.649	202.301	34.087	−278.336	−281.211	10.492
1500	34.001	228.981	204.003	37.468	−278.561	−281.408	9.800
1600	34.370	231.188	205.634	40.886	−278.777	−281.591	9.193
1700	34.705	233.282	207.199	44.340	−278.987	−281.760	8.657
1800	35.008	235.274	208.704	47.826	−279.190	−281.917	8.181
1900	35.284	237.174	210.153	51.341	−279.387	−282.064	7.754
2000	35.534	238.991	211.549	54.882	−279.578	−282.199	7.370
2100	35.762	240.730	212.898	58.447	−279.762	−282.326	7.022
2200	35.971	242.398	214.201	62.034	−279.939	−282.444	6.706
2300	36.162	244.002	215.462	65.641	−280.108	−282.554	6.417
2400	36.339	245.545	216.684	69.266	−280.268	−282.657	6.152
2500	36.501	247.031	217.868	72.908	−280.418	−282.753	5.908
2600	36.652	248.466	219.017	76.566	−280.556	−282.844	5.682
2700	36.792	249.852	220.134	80.238	−280.683	−282.929	5.474
2800	36.923	251.192	221.219	83.924	−280.796	−283.011	5.280
2900	37.045	252.490	222.275	87.623	−280.894	−283.088	5.099
3000	37.160	253.748	223.304	91.333	−280.978	−283.162	4.930
3100	37.269	254.968	224.306	95.054	−281.046	−283.234	4.772
3200	37.371	256.153	225.282	98.786	−281.098	−283.303	4.624
3300	37.468	257.305	226.235	102.528	−281.133	−283.372	4.485
3400	37.560	258.424	227.166	106.280	−281.151	−283.439	4.355
3500	37.647	259.514	228.074	110.040	−281.152	−283.507	4.231
3600	37.731	260.576	228.963	113.809	−281.136	−283.574	4.115
3700	37.811	261.611	229.831	117.586	−281.102	−283.642	4.004
3800	37.888	262.620	230.681	121.371	−281.052	−283.712	3.900
3900	37.961	263.606	231.512	125.164	−280.986	−283.782	3.801
4000	38.033	264.568	232.327	128.963	−280.902	−283.855	3.707
4100	38.101	265.508	233.125	132.770	−280.803	−283.930	3.617
4200	38.168	266.427	233.907	136.584	−280.688	−284.008	3.532
4300	38.232	267.325	234.673	140.404	−280.557	−284.088	3.451
4400	38.295	268.205	235.425	144.230	−280.411	−284.172	3.374
4500	38.355	269.066	236.164	148.062	−280.251	−284.259	3.300
4600	38.414	269.910	236.888	151.901	−280.077	−284.350	3.229
4700	38.472	270.737	237.599	155.745	−279.888	−284.445	3.161
4800	38.528	271.547	238.298	159.595	−279.686	−284.544	3.096
4900	38.583	272.342	238.985	163.451	−279.471	−284.648	3.034
5000	38.637	273.122	239.660	167.312	−279.242	−284.755	2.975
5100	38.690	273.888	240.324	171.178	−279.002	−284.868	2.918
5200	38.742	274.640	240.976	175.050	−278.748	−284.985	2.863
5300	38.793	275.378	241.618	178.927	−278.483	−285.108	2.810
5400	38.843	276.104	242.250	182.808	−278.205	−285.236	2.759
5500	38.892	276.817	242.872	186.695	−277.915	−285.369	2.710
5600	38.940	277.518	243.485	190.587	−277.614	−285.507	2.663
5700	38.988	278.208	244.088	194.483	−277.301	−285.651	2.618
5800	39.035	278.886	244.682	198.384	−276.976	−285.800	2.574
5900	39.081	279.554	245.267	202.290	−276.639	−285.955	2.532
6000	39.127	280.211	245.844	206.200	−276.291	−286.116	2.491

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 143.803 \pm 0.033\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 0.330 \pm 0.008\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 0.321 \pm 0.013\ kJ\cdot mol^{-1}$

Vibrational and Rotational Levels (cm^{-1})

Direction Summmation of Electronic Ground State:

$$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H^2Z^3/(H+LZ),$$

where $Z = J(J+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L

$$G = 3815.403Y - 93.61504Y^2 + 1.39630Y^3 - 0.118666Y^4 + 5.97675 \times 10^{-3}Y^5 - 2.08092 \times 10^{-4}Y^6$$

$$B = 45.66910 - 2.031845Y + 7.27360 \times 10H^{-2}Y^2 - 1.82824 \times 10^{-2}Y^3 + 3.06318 \times 10^{-3}Y^4$$
$$- 3.00453 \times 10^{-4}Y^5 + 1.47623 \times 10^{-5}Y^6 - 2.9887 \times 10^{-7}Y^7$$

$$D = 2.6527 \times 10^{-2} - 1.1534 \times 10^{-3}Y + 1.7075 \times 10^{-4}Y^2 - 2.1142 \times 10^{-5}Y^3 + 9.9570 \times 10^{-7}Y^4$$

$$H = 2.206 \times 10^{-5} - 2.648 \times 10^{-6}Y + 3.047 \times 10^{-7}Y^2 - 1.327 \times 10^{-8}Y^3$$

$$L = 2.122 \times 10^{-8} - 3.912 \times 10^{-9}Y + 3.298 \times 10^{-10}Y^2$$

$$v_{max} = 17, \quad J_{max} = 46 - 42\ v/v_{max}$$

Ground State Configuration: $^1\Sigma^+$ Symmetry Number = 1

Enthalpy of Formation

$\Delta_f H°(0\ K)$ is derived from $D_0° = 36406.0 \pm 0.4\ cm^{-1}$ ($104.090 \pm 0.001\ kcal\cdot mol^{-1}$) based on absorption limits analyzed by Herzberg.[1] He derived $D_0°$ values of 36406.6 and 36405.8 cm^{-1} from lower and upper absorption edges. Thorson,[2] by theoretical treatment of absorption–edge doubling, concluded that the value from the upper edge is more accurate. We adopt a value closer to that from the upper edge and essentially the same as that selected by the National Bureau of Standards.[3]

Heat Capacity and Entropy

These are calculated by direct summation[4] over vibrational–rotational energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U. S. National Bureau of Standards. Contributions of excited states ($T_0 > 9000\ cm^{-1}$)[5] are negligible at 6000 K.

Vibrational–rotational levels are represented by the polynomials given above. G, B, and D are our fits of data from Dabrowski and Herzberg.[5] Data from Durie and Herzberg,[6] McKellar *et al.*,[7] Brannon *et al.*[8] and Stoicheff[9] were also used where appropriate. Observed HD data extend to $v_{max} = 17$ for G and B, $v = 16$ for D, but only $v = 1$ for H. We estimate polynomials H and L by isotopic relations from those of H_2[4] in order to provide a similar extrapolation to high J values. Our H polynomial differs from H_0 and H_1[8,9] by less than the experimental uncertainty. Our combination of H and L should be consistent with our adopted approximation for the infinite series (F) of rotational levels. We assume that F has the form proposed by Khachkuruzov[10] and Woolley *et al.*[11] We assume a linear approximation[10] for the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated by comparison with H_2 and D_2[4] so that J_{max} is consistent with observation for HD[5] of a rovibrational level at $J = 6$, $v = 16$.

Thermodynamic functions are calculated using 1973 fundamental constants,[12] 1975 atomic weight of H, and 1973 isotopic mass of D.[13] Results apply either to $^1H^2H$ or to HD containing H of natural abundance, even though the vibrational–rotational constants are for $^1H^2H$. Maximum difference between thermodynamic functions for $^1H^2H$ and HD is 0.0002 $cal\cdot K^{-1}\cdot mol^{-1}$ in $S°(298.15\ K)$. Our calculations agree to within 0.002 $cal\cdot K^{-1}\cdot mol^{-1}$ (or $kcal\cdot mol^{-1}$) with those of Woolley *et al.*[11] up to 2000 K. The more approximate $C_p°$ values of NBS[3] differ by less than 0.04 $cal\cdot K^{-1}\cdot mol^{-1}$ in the range 3000 to 6000 K. We omit the nuclear–spin contribution (R ln 6) to entropy and Gibbs–energy function.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.509	0.330	0.330	INFINITE
100	29.288	111.898	169.759	−5.786	0.178	−0.336	0.176
200	29.188	132.147	146.473	−2.865	0.275	−0.883	0.231
298.15	29.200	143.803	143.803	0.	0.320	−1.463	0.256
300	29.202	143.983	143.803	0.054	0.321	−1.474	0.257
400	29.231	152.388	144.949	2.976	0.329	−2.074	0.271
500	29.283	158.915	147.114	5.901	0.328	−2.675	0.279
600	29.395	164.263	149.539	8.834	0.323	−3.275	0.285
700	29.594	168.808	151.975	11.783	0.312	−3.874	0.289
800	29.890	172.778	154.333	14.756	0.297	−4.471	0.292
900	30.269	176.320	156.582	17.764	0.278	−5.066	0.294
1000	30.708	179.531	158.719	20.812	0.258	−5.659	0.296
1100	31.183	182.480	160.747	23.907	0.236	−6.250	0.297
1200	31.674	185.215	162.673	27.050	0.216	−6.838	0.298
1300	32.164	187.769	164.507	30.242	0.196	−7.425	0.298
1400	32.641	190.171	166.255	33.482	0.178	−8.011	0.299
1500	33.101	192.438	167.926	36.769	0.162	−8.595	0.299
1600	33.539	194.589	169.525	40.102	0.147	−9.179	0.300
1700	33.951	196.635	171.060	43.476	0.135	−9.761	0.300
1800	34.341	198.586	172.536	46.891	0.123	−10.343	0.300
1900	34.706	200.453	173.956	50.344	0.114	−10.924	0.300
2000	35.050	202.242	175.326	53.832	0.105	−11.505	0.300
2100	35.371	203.960	176.649	57.353	0.098	−12.085	0.301
2200	35.676	205.612	177.928	60.905	0.092	−12.665	0.301
2300	35.962	207.205	179.167	64.487	0.087	−13.245	0.301
2400	36.234	208.741	180.367	68.097	0.082	−13.824	0.301
2500	36.491	210.225	181.532	71.734	0.079	−14.403	0.301
2600	36.738	211.661	182.663	75.395	0.077	−14.983	0.301
2700	36.972	213.052	183.763	79.081	0.075	−15.562	0.301
2800	37.198	214.401	184.834	82.789	0.073	−16.141	0.301
2900	37.414	215.710	185.876	86.520	0.073	−16.720	0.301
3000	37.625	216.982	186.892	90.272	0.073	−17.299	0.301
3100	37.829	218.219	187.882	94.045	0.074	−17.878	0.301
3200	38.028	219.423	188.849	97.837	0.075	−18.457	0.301
3300	38.223	220.597	189.794	101.650	0.077	−19.036	0.301
3400	38.414	221.740	190.716	105.482	0.079	−19.616	0.301
3500	38.602	222.857	191.619	109.333	0.082	−20.195	0.301
3600	38.788	223.947	192.502	113.202	0.085	−20.774	0.301
3700	38.971	225.012	193.366	117.090	0.089	−21.354	0.301
3800	39.153	226.054	194.213	120.996	0.094	−21.933	0.301
3900	39.334	227.073	195.042	124.921	0.099	−22.513	0.302
4000	39.513	228.071	195.855	128.863	0.105	−23.093	0.302
4100	39.690	229.049	196.653	132.823	0.112	−23.673	0.302
4200	39.866	230.008	197.436	136.801	0.119	−24.253	0.302
4300	40.041	230.948	198.204	140.797	0.127	−24.834	0.302
4400	40.213	231.870	198.959	144.809	0.136	−25.414	0.302
4500	40.384	232.776	199.701	148.839	0.145	−25.995	0.302
4600	40.551	233.665	200.429	152.886	0.155	−26.576	0.302
4700	40.715	234.539	201.146	156.949	0.166	−27.157	0.302
4800	40.876	235.398	201.850	161.029	0.178	−27.739	0.302
4900	41.033	236.243	202.544	165.124	0.191	−28.321	0.302
5000	41.185	237.073	203.226	169.235	0.204	−28.902	0.302
5100	41.333	237.890	203.898	173.361	0.219	−29.485	0.302
5200	41.474	238.694	204.559	177.502	0.234	−30.067	0.302
5300	41.610	239.485	205.211	181.656	0.250	−30.650	0.302
5400	41.738	240.264	205.853	185.823	0.268	−31.233	0.302
5500	41.859	241.031	206.485	190.003	0.286	−31.817	0.302
5600	41.972	241.787	207.109	194.195	0.305	−32.401	0.302
5700	42.078	242.530	207.724	198.398	0.324	−32.985	0.302
5800	42.174	243.263	208.330	202.610	0.345	−33.570	0.302
5900	42.261	243.985	208.929	206.832	0.367	−34.155	0.302
6000	42.339	244.696	209.519	211.062	0.389	−34.740	0.302

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 155.552 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1490.499 \pm 0{,}021\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [1496.793]\ kJ·mol^{-1}$

Vibrational and Rotational Levels (cm^{-1})

Direct Summation using Energy–Level Equations for the $^2\Sigma_g^+$ Electronic Ground State:

$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_o + BZ - DZ^2 + H Z^2 I^3(H+LZ)$

where $Z = N(N+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L

$G = 2012.19\ Y - 50.5532\ Y^2 + 0.0604244\ Y^3 - 0.0163194\ Y^4$

$B = 22.4643 - 1.03566\ Y + 0.0180076\ Y^2 - 0.000633616\ Y^3$ $\qquad r_e = 1.057$ Å

$D = 1.12041 \times 10^{-2} - 4.24035 \times 10^{-4}\ Y + 1.26643 \times 10^{-5}\ Y^2$

$H = 7.26086 \times 10^{-6} - 2.19375 \times 10^{-7}\ Y$ and $L = 5.06679 \times 10^{-9}$

$v_{max} = 21$ and $N_{max} = 47 - 38v/v_{max}$

Electronic statistical weight = 2 and rotational statistical weights = 1(even and odd N)

Enthalpy of Formation

$\Delta_f H°(0\ K) = 356.238 \pm 0.005$ kcal·mol^{-1} is obtained from that of HD(g)[1] using IP(HD) = 124568.5 ± 1.2 cm^{-1}(356.159 ± 0.004 kcal·mol^{-1}). Takezawa and Tanaka[2] determined IP = 124569.5 ± 0.6 cm^{-1} from Rydberg spectra of HD. Similar studies on H_2 by Herzberg and Jungen[3] revealed a bias of ~1.0 cm^{-1} attributed to a pressure shift in the spectra. We assume an equal shift for HD, adjust IP by −1.0 cm^{-1} and increase the uncertainty due to this adjustment. $\Delta_f H°(0\ K)$ is converted to $\Delta_f H°(298.15\ K)$ by use of JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for H_2, D_2, HD^+ and $e^-(g)$. The difference in $\Delta_f H°(298.15\ K)$ between HD^+ and HD should not be interpreted as a room-temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by Rosenstock *et al.*[4]

The adopted spectroscopic IP(HD) receives strong support from a value calculated indirectly from experimental values[1] of $D_0°(HD)$ and IP(H) combined with the theoretical value[5] of $D_0°(HD^+)$; this indirect value differs by only 0.3 cm^{-1}. Furthermore, IP(HD) can be predicted[6] approximately from that of H_2 (or D_2) using differences in zero-point energies[1] of the diatomic molecules and their ions. Predicted values of IP(HD) deviate from the observed value by −16 cm^{-1} (based on H_2) and +16 cm^{-1}(based on D_2). Inclusion of an empirical adjustment for the difference IP(D)–IP(H) overcorrects the predictions, giving deviations of +14 cm^{-1} (based on H_2) and −14 cm^{-1} (based on D_2). The average of deviations derived from H_2 and D_2 is zero, suggesting that the slight discrepancies are due to the approximate nature of the prediction. An approximate photoionization result, reviewed by Rosenstock *et al.*,[4] deviates from the spectroscopic result by ~130 cm^{-1}.

Heat Capacity and Entropy

Thermodynamic functions for ortho–para "equilibrium" HD^+ are calculated by direct summation using the energy–level equations listed above. We use 1973 fundamental constants[7] in an extended version of a computer program written by W. H. Evans and provided by D. D. Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they do not contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect the very small rotational splitting.[8]

Coefficients of the energy–level polynomials are calculated from the theoretical values of H_2^+ [1] using rho = 0.866117 n isotopic equations. These polynomials are confirmed by six rotation–vibration transitions ($v \leq 3$, $N \leq 2$) observed between 1642 and 1869 cm^{-1} by an infrared laser–resonance method.[8] Our polynomials predict these transitions within 0.1 cm^{-1}. We give the polynomial coefficients, especially higher order ones, to many more digits than are justified by their accuracy. The equations are very approximate near N_{max} but, judging by H_2^+,[1] this should have little effect on the thermodynamic functions even at 6000 K. The approximate v_{max} is derived from the G polynomial.

The thermodynamic functions include contributions from quasi–bound levels lying above $D_0°(HD^+ \rightarrow H^+ + D) = 21516$ cm^{-1}. At 6000 K these levels contribute 0.39 cal·K^{-1}·mol^{-1} to $C_p°$ and 0.048 cal·K^{-1}·mol^{-1} to the Gibbs–energy function. Their contribution is negligible below 3000 K. Limiting rotational quantum numbers N_{max} are estimated from H_2^+, H_2 and HD[1] by comparing energy increments and rotational quanta found above the respective values of $D°$. The crudity of these estimates makes $C_p°$ at 6000 K somewhat more uncertain than in the case of H_2^+.[1]

References

[1]JANAF Thermochemical Tables: $H_2(g)$, $D_2(g)$, $H^+(g)$, $D^+(g)$, $e^-(g)$, 3–31–77; HD(g), 6–30–77; $H_{2+}(g)$, $HD^+(g)$, $D_2^+(g)$, 9–30–77.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S° - [G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.614	1490.499	
100	29.179	123.637	181.549	−5.791		
200	29.213	143.870	158.230	−2.872		
298.15	29.334	155.552	155.552	0.	1496.793	1485.251	−260.210
300	29.339	155.733	155.552	0.054	1496.832	1485.179	−258.593
400	29.742	164.221	156.707	3.005	1498.948	1480.977	−193.396
500	30.461	170.930	158.903	6.014	1501.108	1476.235	−154.221
600	31.354	176.561	161.389	9.104	1503.338	1471.052	−128.067
700	32.281	181.464	163.914	12.286	1505.640	1465.491	−109.356
800	33.161	185.833	166.385	15.558	1508.002	1459.594	−95.302
900	33.960	189.786	168.769	18.915	1510.412	1453.399	−84.353
1000	34.672	193.402	171.054	22.347	1512.853	1446.934	−75.580
1100	35.304	196.737	173.239	25.847	1515.316	1440.223	−68.390
1200	35.865	199.833	175.328	29.406	1517.790	1433.287	−62.389
1300	36.369	202.724	177.325	33.018	1520.269	1426.144	−57.303
1400	36.825	205.436	179.237	36.678	1522.749	1418.811	−52.936
1500	37.244	207.991	181.070	40.382	1525.228	1411.300	−49.146
1600	37.633	210.407	182.829	44.126	1527.704	1403.624	−45.824
1700	38.001	212.700	184.519	47.907	1530.177	1395.794	−42.888
1800	38.351	214.882	186.146	51.725	1532.647	1387.817	−40.273
1900	38.692	216.965	187.713	55.577	1535.115	1379.704	−37.931
2000	39.024	218.958	189.226	59.463	1537.584	1371.461	−35.819
2100	39.353	220.870	190.688	63.382	1540.053	1363.094	−33.905
2200	39.681	222.708	192.102	67.334	1542.524	1354.609	−32.163
2300	40.008	224.479	193.471	71.318	1545.000	1346.012	−30.569
2400	40.335	226.189	194.799	75.335	1547.482	1337.307	−29.106
2500	40.661	227.842	196.088	79.385	1549.970	1328.499	−27.757
2600	40.984	229.443	197.340	83.467	1552.467	1319.591	−26.511
2700	41.303	230.996	198.558	87.582	1554.973	1310.587	−25.355
2800	41.614	232.503	199.744	91.728	1557.488	1301.489	−24.280
2900	41.914	233.969	200.899	95.904	1560.012	1292.302	−23.277
3000	42.199	235.395	202.025	100.110	1562.544	1283.027	−22.339
3100	42.466	236.783	203.124	104.344	1565.084	1273.668	−21.461
3200	42.710	238.135	204.197	108.603	1567.630	1264.227	−20.636
3300	42.929	239.453	205.245	112.885	1570.180	1254.707	−19.860
3400	43.119	240.737	206.270	117.187	1572.731	1245.108	−19.129
3500	43.278	241.990	207.273	121.507	1575.282	1235.435	−18.438
3600	43.403	243.211	208.254	125.842	1577.829	1225.689	−17.784
3700	43.494	244.401	209.215	130.187	1580.369	1215.873	−17.165
3800	43.549	245.562	210.157	134.539	1582.898	1205.988	−16.577
3900	43.568	246.693	211.079	138.896	1585.414	1196.036	−16.019
4000	43.551	247.796	211.983	143.252	1587.912	1186.020	−15.488
4100	43.499	248.871	212.870	147.605	1590.390	1175.942	−14.982
4200	43.412	249.918	213.740	151.950	1592.844	1165.804	−14.499
4300	43.292	250.938	214.593	156.286	1595.271	1155.608	−14.038
4400	43.140	251.932	215.430	160.608	1597.667	1145.355	−13.597
4500	42.959	252.899	216.252	164.913	1600.030	1135.048	−13.175
4600	42.751	253.841	217.059	169.199	1602.358	1124.690	−12.771
4700	42.517	254.758	217.852	173.462	1604.648	1114.281	−12.384
4800	42.260	255.651	218.630	177.701	1606.898	1103.824	−12.012
4900	41.983	256.519	219.394	181.914	1609.106	1093.320	−11.655
5000	41.687	257.365	220.145	186.097	1611.271	1082.772	−11.312
5100	41.375	258.187	220.883	190.250	1613.391	1072.181	−10.981
5200	41.049	258.987	221.608	194.372	1615.466	1061.549	−10.663
5300	40.711	259.766	222.321	198.460	1617.495	1050.877	−10.357
5400	40.363	260.524	223.021	202.514	1619.477	1040.167	−10.062
5500	40.008	261.261	223.710	206.532	1621.412	1029.421	−9.777
5600	39.645	261.979	224.387	210.515	1623.301	1018.641	−9.501
5700	39.279	262.677	225.053	214.461	1625.143	1007.827	−9.236
5800	38.909	263.357	225.707	218.371	1626.939	996.981	−8.979
5900	38.538	264.019	226.351	222.243	1628.690	986.105	−8.730
6000	38.166	264.664	226.984	226.078	1630.396	975.199	−8.490

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K)$ = [151.206 ± 0.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [241.543 ± 41.8] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [235.484] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma_u^+$	0	2

ω_e = [1473] cm^{-1} $\omega_e x_e$ = [26.3] cm^{-1} σ = 2
B_e = [19.0] cm^{-1} α_e = [0.259] cm^{-1} r_e = [1.15] Å

Enthalpy of Formation

The enthalpy of formation at 0 K for HD^-(g) is based on the electron affinity value from a Rydberg–Klein–Rees configuration–interaction calculation for H_2^-.[1] This study by Sharpe[1] led to EA(H_2) = −2.5 eV. Assuming this value is valid for HD^-(g) and using auxiliary data,[2] we calculate $\Delta_f H°(0\ K)$ = 57.73 ± 10 $kcal·mol^{-1}$ and $D°(HD^-)$ = 29.0 ± 10 $kcal·mol^{-1}$; the latter value is calculated for dissociation into ground state D(g) and H^-(g) or D^-(g) and H(g). The adopted EA (H_2) value is suggested to be the more reliable value of eight studies considered by Rosenstock *et al.*[3]

In terms of molecular orbitals, the ground state for HD^-(g) is the $(1s\sigma_g)^2\ (2p\sigma_u)\ ^2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron. We would expect, however, the ground state to be $(1s\sigma_g)^2\ (1s\sigma_u)$. As stated by Massey,[4] we should expect only a weakly-bound molecule as compared with HD(g) for which the ground state has no electron in an antibonding orbital. Our adopted calculated EA (HD) value is consitent with this viewpoint. Further discussion of the HD^-(g) ion may be found in Massey.[4]

$\Delta_f H°(0\ K)$ is converted to $\Delta_f H°(298.15\ K)$ by use of JANAF[2] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for D_2(g), H_2(g), DH^-(g), and e^-(g). $\Delta_f H°(298.15\ K)$ should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3]

Heat Capacity and Entropy

The vibrational constants for H_2^-(g) are estimated to be the same as in the isoelectronic species He_2^+.[5] The vibrational constants for HD^-(g) are calculated from those for H_2^-(g) using isotopic relations. The internuclear distance is estimated to be ~8% larger than that for He_2^+(g). The same relationship appeared to exist for the (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey.[4] No excited state contributions are included in this calculation.

References

[1]T. E. Sharpe, Lockheed Report LMSC 5-10-69-9 (1969).
[2]JANAF Thermochemical Tables: H(g), H^-(g), D_2(g), H_2(g), and e^-(g), 3-31-77; H_2^-(g), 9-30-77; HD(g), 6-30-77.
[3]H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[4]H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, 741 pp. (1976).
[5]B. Rosen, Ed., Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.656	241.543		
100	29.198	119.174	177.359	−5.818			
200	29.304	139.437	153.910	−2.895			
250	29.471	145.992	151.695	−1.426			
298.15	29.771	151.206	151.206	0.	235.484	237.747	−41.652
300	29.786	151.391	151.207	0.055	235.447	237.762	−41.398
350	30.239	156.015	151.571	1.555	234.453	238.226	−35.553
400	30.787	160.087	152.386	3.081	233.480	238.832	−31.188
450	31.383	163.748	153.449	4.635	232.533	239.558	−27.807
500	31.985	167.086	154.648	6.219	231.614	240.388	−25.113
600	33.121	173.020	157.227	9.475	229.853	242.310	−21.095
700	34.102	178.201	159.861	12.838	228.178	244.520	−18.246
800	34.921	182.810	162.447	16.290	226.563	246.965	−16.125
900	35.603	186.963	164.944	19.817	224.985	249.610	−14.487
1000	36.172	190.745	167.338	23.407	223.427	252.430	−13.186
1100	36.655	194.216	169.626	27.049	221.875	255.406	−12.128
1200	37.069	197.423	171.810	30.736	220.319	258.522	−11.253
1300	37.430	200.405	173.896	34.461	218.755	261.769	−10.518
1400	37.750	203.191	175.891	38.220	217.177	265.137	−9.892
1500	38.038	205.805	177.799	42.010	215.584	268.619	−9.354
1600	38.299	208.269	179.627	45.827	213.976	272.206	−8.887
1700	38.539	210.598	181.381	49.669	212.352	275.896	−8.477
1800	38.762	212.807	183.066	53.534	210.713	279.681	−8.116
1900	38.972	214.908	184.687	57.421	209.058	283.557	−7.796
2000	39.169	216.913	186.248	61.328	207.391	287.521	−7.509
2100	39.358	218.828	187.755	65.255	205.710	291.569	−7.252
2200	39.538	220.663	189.209	69.199	204.018	295.697	−7.021
2300	39.711	222.425	190.615	73.162	202.314	299.903	−6.811
2400	39.879	224.118	191.976	77.142	200.601	304.182	−6.620
2500	40.042	225.750	193.295	81.138	198.879	308.534	−6.446
2600	40.201	227.323	194.573	85.150	197.148	312.954	−6.287
2700	40.356	228.843	195.814	89.178	195.410	317.441	−6.141
2800	40.508	230.314	197.020	93.221	193.665	321.992	−6.007
2900	40.657	231.738	198.193	97.279	191.914	326.606	−5.883
3000	40.804	233.119	199.335	101.352	190.156	331.281	−5.768
3100	40.949	234.459	200.446	105.440	188.393	336.014	−5.662
3200	41.092	235.761	201.529	109.542	186.625	340.804	−5.563
3300	41.233	237.028	202.586	113.658	184.852	345.650	−5.471
3400	41.373	238.261	203.617	117.789	183.074	350.549	−5.386
3500	41.511	239.462	204.624	121.933	181.291	355.501	−5.306
3600	41.649	240.634	205.608	126.091	179.505	360.504	−5.231
3700	41.785	241.777	206.570	130.262	177.714	365.556	−5.161
3800	41.921	242.893	207.512	134.448	175.919	370.657	−5.095
3900	42.055	243.983	208.433	138.647	174.120	375.805	−5.033
4000	42.189	245.050	209.335	142.859	172.317	380.999	−4.975
4100	42.322	246.093	210.219	147.084	170.511	386.239	−4.921
4200	42.455	247.115	211.085	151.323	168.700	391.522	−4.869
4300	42.587	248.115	211.935	155.575	166.886	396.849	−4.821
4400	42.718	249.096	212.768	159.841	165.069	402.218	−4.775
4500	42.849	250.057	213.586	164.119	163.248	407.628	−4.732
4600	42.980	251.000	214.389	168.410	161.425	413.079	−4.691
4700	43.110	251.926	215.178	172.715	159.598	418.569	−4.652
4800	43.239	252.835	215.953	177.032	157.769	424.099	−4.615
4900	43.369	253.728	216.715	181.363	155.938	429.666	−4.580
5000	43.498	254.605	217.464	185.706	154.106	435.271	−4.547
5100	43.627	255.468	218.201	190.062	152.272	440.912	−4.516
5200	43.755	256.316	218.926	194.431	150.437	446.590	−4.486
5300	43.884	257.151	219.639	198.813	148.603	452.303	−4.458
5400	44.012	257.973	220.341	203.208	146.769	458.050	−4.431
5500	44.140	258.781	221.033	207.616	144.936	463.831	−4.405
5600	44.267	259.578	221.714	212.036	143.105	469.646	−4.381
5700	44.395	260.362	222.385	216.469	141.277	475.494	−4.357
5800	44.522	261.136	223.047	220.915	139.452	481.373	−4.335
5900	44.649	261.898	223.699	225.374	137.632	487.284	−4.314
6000	44.776	262.649	224.342	229.845	135.817	493.225	−4.294

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 199.512\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -242.435 \pm 0.063\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -245.371 \pm 0.063\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
2723.66(1)
1402.80(1)
3707.47(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_h
Bond Distances: O–H = 0.9584 Å; O–D = 0.9854 Å
Bond Angle: H–O–D = 104.45°
Product of the Moments of Inertia: $I_A I_B I_C = 1.59584 \times 10^{-119}\ g^3·cm^6$

Enthalpy of Formation

3rd and 2nd law (where possible) analyses of the more recent determinations[1–5] of the experimental equilibrium constants, Keq, were made for the reacitons: (A) $H_2O(g) + HD(g) = HDO(g) + H_2(g)$, and (B) $H_2O(g) + D_2O(g)$. Spectroscopic values for the heats of reaction, $\Delta_r H°(298.15\ K)$, of (A) and (B) were based on the zero point energies of H_2O, D_2O, and HDO given by Hulston[6] and Wolfsberg[7] and H_2, HD given by Herzberg and Monfils.[8] The earlier work on (A) cited by Kirshenbaum[9] is in poor agreement except for that of Herrick, Kirshenbaum, Brown and Herrick, Crist, Davis $\Delta_f H°(298.15\ K) = 928 \pm 30$, 921 $kcal·mol^{-1}$, respectively). $\Delta_r H°(298.15\ K)$ for the reaction (C) $H_2O(l) + D_2O(l) = 2\ HDO(l)$ has been determined to be $-32 \pm 1\ cal·K^{-1}·mol^{-1}$ [10–12] assuming ideal solutions (see[13]) and $K_{eq}(C) \sim 3.8$. (We calculate $K_{eq}(C) = 3.76 \pm 0.04$ from $K_{eq}(B) = 3.76 \pm 0.02$, $P°(H_2O)/P°(D_2O) = 1.151 \pm 0.006$[14] at 298.15 K, and $P°(H_2O)/P°(HDO) = 1.073 \pm 0.004$[15] at 298.15 K.) $\Delta_f H°(298.15\ K)$ of (B) was calculated from the difference in enthalpies of vaporization at 298.15 K of $D_2O(l) - H_2O(l) = 331 \pm 8$ cal (see D_2O table), and $HDO(l) - H_2O(l) = 183 \pm 20\ cal·K^{-1}·mol^{-1}$.[14] Values selected for $\Delta_r H°(298.15\ K)$ based on non–spectroscopic and spectroscopic work for (A) and (B), underlined in the table, were used to calculate values of $\Delta_f H°(298.15\ K)$ of $HDO(g) - H_2O(g)$ of -845 ± 6, -852 ± 12, and $-851 \pm 10\ cal·K^{-1}·mol^{-1}$, respectively (see D_2O and HD tables). An average value of $-850 \pm 10\ cal·K^{-1}·mol^{-1}$ was added to $\Delta_f H°(298.15\ K)$ of $H_2O(g)$ to obtain $\Delta_f H°(HDO, g, 298.15\ K)$.

Source	Reaction	T/K	$\Delta_r H°(298.15-K1)$, $kcal·mol^{-1}$	Drift $cal·K^{-1}·mol^{-1}$
Cerrai *et al.*[1]	A	324–1015	-915 ± 20	0.04 ± 0.10 (-864 ± 30, 0.12 ± 0.07)[a]
Suess[2]	A	353–473	-921 ± 6	0.05 ± 0.05 ($-9\ 55 \pm 29$, 0.09 ± 0.09)[a]
Hulston[6]	A	Spectroscopic	-928 ± 10	
Wolfsberg[7]	A	Spectroscopic	-937 ± 10	
Pyper, Newbury and Barton[3]	B	273.15	56 ± 11	(3.75 ± 0.08)[b]
		297.95	63 ± 11	(3.74 ± 0.04)[b]
Friedman and Shiner[4]	B	273.15	58 ± 3	(3.74 ± 0.02)[b]
		298.15	60 ± 3	(3.76 ± 0.02)[b]
		358.15	62 ± 7	(3.80 ± 0.04)[b]
Kresge, Chiang[5]	B	298.15	46 ± 5	(3.85 ± 0.03)[b]
Reaction C, see text	B	298.15	57 ± 22	
Hulston[6]	B	Spectroscopic	65 ± 10	
Wolfsberg[7]	B	Spectroscopic	70 ± 10	

[a]Second law: $\Delta_r H°(298.15\ K)$, $S°(298.15\ K)$ (obsv.–calc.); [b]Keq at temperature cited.

Heat Capacity and Entropy

The thermodynamic functions of this table are analogous to those in the JANAF table for $H_2O(g)$ (March 31, 1961): both tables are tablen from Friedman and Haar.[16] Friedman and Haar[16] applied their non–rigid–rotor, anharmonic–oscillator treatment (with vibrational–rotational coupling terms and low–temperature rotational corrections) to the infrared–spectra analyses of Benedict *et al.*[17, 18] In the present table for HDO, the values of $C_p°$ of Friedman and Haar[16] between 4000 and 5000 K were extrapolated linearly (except with a term in T^{-2}) from 5000 to 6000 K. $I_A = 0.1213 \times 10^{-39}$, $I_B = 0.3071 \times 10^{-39}$, $I_C = 0.4284 \times 10^{-39}\ g·cm^2$ from Friedman and Haar.[16] The National Bureau of Standards prepared this table[19] by critical analysis of data existing in 1972.

References

[1]I. Cerrai, C. Marchetti, R. Renzoni, L. Roseo, M. Silvestri, and S. Villani, Chem. Eng. Prog. Symp. Ser. **50**, (11), 271 (1954).
[2]H. Suess, Z. Naturforsch. **4a**, 328 (1949).

Continued on page 1048

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.924	−242.435	−242.435	INFINITE
100	33.300	163.034	229.267	−6.623	−243.461	−240.424	125.584
200	33.363	186.126	202.590	−3.293	−244.410	−237.015	61.902
298.15	33.786	199.511	199.511	0.	−245.371	−233.181	40.852
300	33.798	199.720	199.511	0.063	−245.389	−233.106	40.587
400	34.773	209.569	200.848	3.489	−246.362	−228.863	29.886
500	36.045	217.463	203.406	7.028	−247.278	−224.381	23.441
600	37.451	224.158	206.320	10.703	−248.122	−219.722	19.128
700	38.920	230.041	209.297	14.521	−248.890	−214.926	16.038
800	40.405	235.335	212.226	18.487	−249.581	−210.026	13.713
900	41.873	240.180	215.066	22.602	−250.195	−205.044	11.900
1000	43.283	244.665	217.805	26.860	−250.737	−199.998	10.447
1100	44.622	248.854	220.439	31.256	−251.211	−194.900	9.255
1200	45.873	252.791	222.972	35.782	−251.624	−189.763	8.260
1300	47.028	256.509	225.411	40.428	−251.981	−184.593	7.417
1400	48.087	260.033	227.759	45.184	−252.289	−179.397	6.693
1500	49.053	263.384	230.023	50.042	−252.556	−174.181	6.066
1600	49.936	266.579	232.209	54.992	−252.786	−168.949	5.516
1700	50.735	269.631	234.321	60.026	−252.985	−163.702	5.030
1800	51.463	272.551	236.364	65.137	−253.159	−158.445	4.598
1900	52.124	275.352	238.343	70.317	−253.311	−153.179	4.211
2000	52.731	278.041	240.261	75.560	−253.445	−147.906	3.863
2100	53.279	280.627	242.122	80.861	−253.566	−142.626	3.548
2200	53.785	283.118	243.929	86.214	−253.675	−137.340	3.261
2300	54.246	285.519	245.686	91.616	−253.775	−132.050	2.999
2400	54.668	287.837	247.394	97.062	−253.870	−126.756	2.759
2500	55.061	290.076	249.057	102.549	−253.961	−121.457	2.538
2600	55.421	292.243	250.676	108.073	−254.048	−116.155	2.334
2700	55.752	294.341	252.255	113.632	−254.136	−110.850	2.145
2800	56.061	296.374	253.794	119.223	−254.223	−105.541	1.969
2900	56.350	298.346	255.297	124.844	−254.313	−100.230	1.805
3000	56.618	300.261	256.764	130.492	−254.405	−94.915	1.653
3100	56.869	302.122	258.197	136.167	−254.500	−89.597	1.510
3200	57.103	303.931	259.598	141.865	−254.600	−84.276	1.376
3300	57.325	305.692	260.968	147.587	−254.705	−78.952	1.250
3400	57.530	307.406	262.309	153.330	−254.815	−73.625	1.131
3500	57.727	309.077	263.622	159.093	−254.932	−68.294	1.019
3600	57.911	310.706	264.907	164.875	−255.056	−62.960	0.914
3700	58.086	312.295	266.166	170.675	−255.187	−57.622	0.813
3800	58.250	313.846	267.401	176.491	−255.326	−52.280	0.719
3900	58.409	315.361	268.611	182.324	−255.473	−46.935	0.629
4000	58.559	316.842	269.799	188.173	−255.629	−41.586	0.543
4100	58.702	318.289	270.964	194.036	−255.794	−36.233	0.462
4200	58.835	319.706	272.107	199.913	−255.968	−30.876	0.384
4300	58.965	321.092	273.230	205.803	−256.152	−25.514	0.310
4400	59.091	322.449	274.334	211.706	−256.346	−20.148	0.239
4500	59.208	323.778	275.418	217.621	−256.551	−14.778	0.172
4600	59.321	325.080	276.483	223.547	−256.766	−9.403	0.107
4700	59.430	326.357	277.531	229.485	−256.992	−4.023	0.045
4800	59.538	327.610	278.561	235.433	−257.229	1.362	−0.015
4900	59.639	328.838	279.575	241.392	−257.477	6.752	−0.072
5000	59.739	330.044	280.572	247.361	−257.735	12.147	−0.127
5100	59.831	331.228	281.554	253.340	−258.006	17.547	−0.180
5200	59.923	332.391	282.520	259.327	−258.287	22.953	−0.231
5300	60.015	333.533	283.472	265.324	−258.580	28.364	−0.280
5400	60.099	334.656	284.410	271.330	−258.883	33.781	−0.327
5500	60.187	335.759	285.333	277.344	−259.198	39.203	−0.372
5600	60.271	336.845	286.243	283.367	−259.524	44.632	−0.416
5700	60.350	337.912	287.140	289.398	−259.860	50.066	−0.459
5800	60.430	338.962	288.025	295.437	−260.206	55.507	−0.500
5900	60.505	339.996	288.897	301.484	−260.563	60.952	−0.540
6000	60.580	341.014	289.757	307.538	−260.931	66.406	−0.578

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 187.234\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 375.276 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 375.305 \pm 20.9\ kJ·mol^{-1}$

Electronic State and Molecular Constants							
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^3\Sigma^-$	0	3	2422	50.6	8.993	0.252	1.040

Symmetry Number = 1

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of ND(g) minus NH(g) was calculated from the JANAF thermal functions and the zero point energies of H_2(g), D_2(g) [given by Herzberg and Monfils],[1] NH(g), and ND(g) [given by Haar, *et al.*][2] $\Delta_f H°(298.15\ K)$ of ND(g) was calculated from this value and the JANAF selection for $\Delta_f H°(298.15\ K)$ of NH(g).[3]

Heat Capacity and Entropy

The molecular constants which are given for NH in the JANAF Thermochemical Tables[3] were adjusted for the isotope effect. The National Bureau of Standards prepared this table[4] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[4] we recalculate the table in terms of 1973 fundamental constants,[5] 1975 atomic weights,[6] and current JANAF reference states for the elements.

References

[1]G. Herzberg and A. Monfils, J. Mol. Spectrosc. **5**, 482 (1960).
[2]L. Haar, A. S. Friedman, and C. W. Beckett, NBS Monograph 20, (1961).
[3]JANAF Thermochemical Tables, 2nd Edition, NSRDS–NBS 37, (June 1971).
[4]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand., Rept. 10904, 239, (July 1972).
[5]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
[6]IUPAC Commission on Atomic Weights, Pure Appl. Chem. **47**, 75 (1976); **37**, 589 (1974).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.648	375.276	375.276	INFINITE
100	29.118	155.412	213.138	−5.773	375.325	373.414	−195.052
200	29.131	175.599	189.900	−2.860	375.306	371.515	−97.030
250	29.140	182.100	187.714	−1.403	375.305	370.567	−77.426
298.15	29.159	187.234	187.234	0.	375.305	369.655	−64.762
300	29.160	187.414	187.234	0.054	375.305	369.620	−64.357
350	29.208	191.912	187.590	1.513	375.305	368.673	−55.021
400	29.300	195.818	188.379	2.975	375.307	367.725	−48.020
450	29.449	199.277	189.402	4.444	375.311	366.777	−42.574
500	29.655	202.390	190.547	5.921	375.318	365.828	−38.218
600	30.213	207.844	192.988	8.913	375.345	363.928	−31.683
700	30.891	212.551	195.454	11.968	375.388	362.022	−27.014
800	31.604	216.722	197.857	15.093	375.445	360.109	−23.513
900	32.298	220.485	200.165	18.288	375.514	358.188	−20.789
1000	32.943	223.922	202.372	21.551	375.589	356.259	−18.609
1100	33.528	227.090	204.477	24.875	375.668	354.322	−16.825
1200	34.050	230.030	206.485	28.254	375.749	352.378	−15.339
1300	34.514	232.774	208.403	31.683	375.829	350.427	−14.080
1400	34.925	235.347	210.236	35.155	375.908	348.470	−13.002
1500	35.290	237.770	211.992	38.666	375.986	346.508	−12.066
1600	35.615	240.058	213.675	42.212	376.061	344.540	−11.248
1700	35.905	242.226	215.292	45.788	376.134	342.568	−10.526
1800	36.166	244.286	216.846	49.392	376.204	340.591	−9.884
1900	36.401	246.247	218.342	53.020	376.271	338.611	−9.309
2000	36.614	248.120	219.784	56.671	376.337	336.627	−8.792
2100	36.809	249.911	221.177	60.343	376.400	334.640	−8.324
2200	36.987	251.628	222.522	64.033	376.461	332.650	−7.898
2300	37.152	253.276	223.823	67.740	376.519	330.657	−7.509
2400	37.304	254.860	225.084	71.463	376.576	328.662	−7.153
2500	37.446	256.386	226.306	75.200	376.631	326.664	−6.825
2600	37.579	257.857	227.491	78.952	376.684	324.665	−6.523
2700	37.703	259.278	228.642	82.716	376.735	322.663	−6.242
2800	37.821	260.651	229.761	86.492	376.784	320.659	−5.982
2900	37.932	261.980	230.849	90.280	376.831	318.654	−5.740
3000	38.038	263.268	231.908	94.078	376.877	316.647	−5.513
3100	38.139	264.517	232.940	97.887	376.920	314.639	−5.302
3200	38.235	265.729	233.946	101.706	376.962	312.629	−5.103
3300	38.328	266.907	234.927	105.534	377.001	310.618	−4.917
3400	38.417	268.053	235.885	109.371	377.039	308.606	−4.741
3500	38.503	269.167	236.820	113.217	377.075	306.593	−4.576
3600	38.586	270.253	237.733	117.072	377.108	304.578	−4.419
3700	38.667	271.312	238.627	120.934	377.140	302.563	−4.271
3800	38.745	272.344	239.500	124.805	377.169	300.547	−4.131
3900	38.822	273.351	240.356	128.683	377.195	298.531	−3.998
4000	38.896	274.335	241.193	132.569	377.219	296.513	−3.872
4100	38.969	275.296	242.013	136.463	377.241	294.495	−3.752
4200	39.040	276.236	242.817	140.363	377.260	292.477	−3.637
4300	39.110	277.156	243.605	144.271	377.276	290.458	−3.528
4400	39.178	278.056	244.377	148.185	377.290	288.439	−3.424
4500	39.246	278.937	245.136	152.106	377.302	286.419	−3.325
4600	39.312	279.800	245.880	156.034	377.310	284.400	−3.229
4700	39.377	280.646	246.611	159.969	377.316	282.380	−3.138
4800	39.441	281.476	247.328	163.910	377.320	280.360	−3.051
4900	39.505	282.290	248.034	167.857	377.322	278.340	−2.967
5000	39.567	283.089	248.727	171.810	377.321	276.320	−2.887
5100	39.629	283.873	249.408	175.770	377.318	274.300	−2.809
5200	39.690	284.643	250.078	179.736	377.313	272.280	−2.735
5300	39.751	285.400	250.738	183.708	377.306	270.260	−2.664
5400	39.811	286.143	251.386	187.686	377.298	268.240	−2.595
5500	39.870	286.874	252.025	191.670	377.289	266.221	−2.528
5600	39.929	287.593	252.654	195.660	377.279	264.202	−2.464
5700	39.987	288.300	253.273	199.656	377.269	262.182	−2.403
5800	40.045	288.996	253.883	203.658	377.258	260.163	−2.343
5900	40.103	289.681	254.484	207.665	377.247	258.144	−2.285
6000	40.160	290.356	255.076	211.678	377.236	256.126	−2.230

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Hydroxyl–d_1 (OD) IDEAL GAS M_r = 18.013502

$S°(298.15\ K) = 189.651\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 36.021 \pm 1.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 36.602 \pm 1.21\ kJ·mol^{-1}$

			Electronic States and Molecular Constants				
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0	2	2720.9	44.2	10.02	0.29	0.970
	139.7	2					
$A^2\Sigma^+$	35474	2	2322.6	55.4	9.198	0.322	1.012
$B^2\Sigma^+$	68769	2	684.3	55.6	2.91	0.25	1.80
			Symmetry Number = 1				

Enthalpy of Formation

The enthalpy of formation was calculated from the selected value for $\Delta_f H°(298.15\ K)$ of OH(g), $-0.27 \pm 3\ kcal·mol^{-1}$,[8] the appropriate thermal functions, and zero point energies of H_2(g), D_2(g), OH(g), and OD(g). The zero point energies of H_2(g) and D_2(g) were taken from Herzberg and Monfils.[1] The zero point energies of OH and OD include the Dunham correction (see Herzberg and Monfils).[1] The molecular constants are those given by Rosen[2] with the exception of the spin–coupling constants taken from Herzberg.[3]

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[2] Comparison of the results with those from a more exact treatment given by Haar *et al.*[4] indicates errors in the table above 400 K are negligible. Below this, they may be appreciable. In particular, it is recommended that $H°(0\ K)–H°(298.15\ K)$, $S°(298.15\ K)$ and $C_p°(298.15\ K)$ be taken as $-2.151\ kcal·mol^{-1}$, $45.307\ cal·K^{-1}·mol^{-1}$, and $7.156\ cal·K^{-1}·mol^{-1}$, respectively. These errors result from dealing with the ground state ($X^2\Pi_i$) as two different electronic states separated by $139.7\ cm^{-1}$.

The National Bureau of Standards prepared this table[5] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[5] we recalculate the table in terms of 1973 fundamental constants,[6] 1975 atomic weights,[7] and current JANAF reference states for the elements.

References

[1]G. Herzberg and A. Monfils, J. Mol. Spectrosc. **5**, 482 (1960).
[2]B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[3]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, pp. 232, 561, (1950).
[4]L. Haar, A. S. Friedman, and C. W. Beckett, U. S. Nat. Bur. Stand. Monograph 20, (1961).
[5]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand., Rept. 10904, 239, (July 1972).
[6]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
[7]IUPAC Commission on Atomic Weights, Pure Appl. Chem. **47**, 75 (1976); **37**, 589 (1974).
[8]JANAF Thermochemical Tables: OH(g), 6-30-77.

Hydroxyl–D_1(OD) D_1O_1(g)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.207	36.021	36.021	INFINITE
100	32.617	155.537	216.921	−6.138	36.262	35.013	−18.289
200	30.775	177.535	192.414	−2.976	36.492	33.664	−8.792
250	30.282	184.345	190.147	−1.450	36.559	32.949	−6.884
298.15	29.989	189.651	189.651	0.	36.602	32.249	−5.650
300	29.980	189.837	189.652	0.055	36.603	32.222	−5.610
350	29.798	194.443	190.016	1.549	36.629	31.490	−4.700
400	29.705	198.415	190.823	3.037	36.638	30.755	−4.016
450	29.688	201.912	191.865	4.521	36.632	30.020	−3.485
500	29.740	205.042	193.029	6.007	36.614	29.286	−3.059
600	30.026	210.487	195.498	8.993	36.546	27.826	−2.422
700	30.491	215.148	197.980	12.018	36.454	26.380	−1.969
800	31.056	219.256	200.388	15.095	36.350	24.948	−1.629
900	31.657	222.949	202.693	18.230	36.244	23.529	−1.366
1000	32.252	226.315	204.889	21.426	36.141	22.122	−1.156
1100	32.815	229.416	206.980	24.680	36.044	20.725	−0.984
1200	33.335	232.293	208.971	27.987	35.953	19.336	−0.842
1300	33.809	234.981	210.869	31.345	35.868	17.955	−0.721
1400	34.237	237.502	212.682	34.748	35.787	16.580	−0.619
1500	34.622	239.878	214.417	38.191	35.710	15.211	−0.530
1600	34.968	242.123	216.079	41.671	35.635	13.847	−0.452
1700	35.279	244.253	217.674	45.183	35.561	12.487	−0.384
1800	35.559	246.277	219.208	48.726	35.486	11.132	−0.323
1900	35.813	248.207	220.683	52.294	35.410	9.781	−0.269
2000	36.043	250.050	222.106	55.887	35.330	8.434	−0.220
2100	36.252	251.813	223.479	59.502	35.246	7.092	−0.176
2200	36.444	253.504	224.806	63.137	35.158	5.753	−0.137
2300	36.619	255.128	226.089	66.790	35.064	4.419	−0.100
2400	36.782	256.690	227.332	70.461	34.965	3.088	−0.067
2500	36.932	258.195	228.536	74.146	34.858	1.762	−0.037
2600	37.071	259.646	229.705	77.846	34.745	0.440	−0.009
2700	37.201	261.047	230.840	81.560	34.625	−0.877	0.017
2800	37.323	262.403	231.943	85.286	34.497	−2.189	0.041
2900	37.438	263.714	233.016	89.025	34.362	−3.497	0.063
3000	37.546	264.985	234.061	92.774	34.219	−4.800	0.084
3100	37.648	266.218	235.078	96.534	34.069	−6.098	0.103
3200	37.745	267.415	236.070	100.303	33.911	−7.392	0.121
3300	37.838	268.578	237.038	104.082	33.746	−8.680	0.137
3400	37.926	269.709	237.982	107.871	33.573	−9.963	0.153
3500	38.011	270.809	238.904	111.668	33.392	−11.241	0.168
3600	38.092	271.881	239.806	115.473	33.204	−12.513	0.182
3700	38.171	272.926	240.687	119.286	33.009	−13.781	0.195
3800	38.246	273.945	241.549	123.107	32.806	−15.042	0.207
3900	38.320	274.940	242.392	126.935	32.596	−16.299	0.218
4000	38.391	275.911	243.218	130.771	32.378	−17.550	0.229
4100	38.460	276.859	244.027	134.613	32.153	−18.795	0.239
4200	38.528	277.787	244.820	138.463	31.921	−20.035	0.249
4300	38.594	278.694	245.597	142.319	31.682	−21.269	0.258
4400	38.659	279.582	246.359	146.181	31.435	−22.498	0.267
4500	38.722	280.452	247.107	150.050	31.181	−23.721	0.275
4600	38.784	281.304	247.842	153.926	30.920	−24.938	0.283
4700	38.846	282.138	248.562	157.807	30.652	−26.150	0.291
4800	38.907	282.957	249.270	161.695	30.376	−27.355	0.298
4900	38.967	283.760	249.966	165.589	30.093	−28.555	0.304
5000	39.026	284.548	250.650	169.488	29.802	−29.749	0.311
5100	39.085	285.321	251.322	173.394	29.504	−30.937	0.317
5200	39.144	286.081	251.983	177.305	29.199	−32.119	0.323
5300	39.202	286.827	252.634	181.223	28.886	−33.295	0.328
5400	39.261	287.560	253.274	185.146	28.565	−34.466	0.333
5500	39.319	288.281	253.904	189.075	28.237	−35.630	0.338
5600	39.378	288.990	254.524	193.010	27.902	−36.788	0.343
5700	39.437	289.687	255.135	196.950	27.558	−37.940	0.348
5800	39.496	290.374	255.736	200.897	27.207	−39.086	0.352
5900	39.555	291.049	256.329	204.849	26.849	−40.227	0.356
6000	39.615	291.715	256.913	208.808	26.482	−41.360	0.360

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Hydroxyl–D_1(OD) D_1O_1(g)

$S°(298.15\ K) = 201.484\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 137.893 \pm 5.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 138.490 \pm 5.0\ kJ·mol^{-1}$

State	ϵ_i, cm^{-1}	Electronic States and Molecular Constants (σ = 1) g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0	2					
	376.8	2					
$A^2\Sigma^+$	30769	2	1417	48.85	4.392	0.172	1.423
$B^2\Sigma$	59566	2	1917.7	29.3	4.532	0.105	1.405
$C^2\Delta$	63872	4					
$D^2\Delta$	71205	4					
$E^2\Sigma$	71328	2	[1930.4]	[23.44]	[4.949]	[0.101]	
$F^2\Delta$	76717	4					
$G^2\Delta$	79320	4					
$H^2\Delta$	80858	4					

Enthalpy of Formation

The enthalpy of formation was calculated from the appropriate thermal functions (see tables for HS, DS, H_2, D_2)[1] the selected value for $\Delta_f H°(298.15\ K)$ of HS(g) (33.3 ± 1.2 kcal·mol^{-1}, refer to table for HS(g),[1] and the zero point energies of H_2(g),[2] D_2(g),[2] HS(g),[3] and DS(g).[3] The Dunham corrections were made in Herzberg and Monfils.[2] for H_2(g) and D_2(g). Spectroscopic constants tabulated in Rosen.[3] were used to calculate the zero point energies of HS and DS including Dunham corrections.

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[3] From a comparison of this approximate calculation with more exact methods (see HS(g) table),[1] it is concluded that the errors are negligible above 400 K. Below this, they may be appreciable. In particular, it is recommended that $H°(0\ K)-H°(298.15\ K)$, $S°(298.15\ K)$ and $C_p°(298.15\ K)$ be taken as −2.171 kcal·mol^{-1}, 48.138 cal·K^{-1}·mol^{-1}, and 7.760 cal·K^{-1}·mol^{-1}, respectively. These errors result from dealing with the ground state ($^2\Pi_i$) as two different electronic states separated by 376.8 cm^{-1}.

The National Bureau of Standards prepared this table[4] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[4] we recalculate the table in terms of 1973 fundamental constants,[5] 1975 atomic weights,[6] and current JANAF reference states for the elements. Our calculated $C_p°$ values agree with the NBS table up to 4000 K; above 4000 K our values trend slightly higher and at 6000 K the difference from the original NBS table is 0.017 cal·K^{-1}·mol^{-1}.

References

[1]JANAF Thermochemical Tables: HS(g), DS(g), 6-30-77; H_2(g), D_2(g), 3-31-77.
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[5]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.294	137.893	137.893	INFINITE
100	30.185	166.532	230.367	−6.383	138.738	128.977	−67.371
200	32.699	188.421	204.473	−3.210	138.793	119.167	−31.123
250	32.752	195.733	202.021	−1.572	138.682	114.271	−23.876
298.15	32.520	201.484	201.484	0.	138.490	109.585	−19.199
300	32.509	201.685	201.484	0.060	138.482	109.406	−19.049
350	32.249	206.676	201.879	1.679	138.204	104.581	−15.608
400	32.086	210.970	202.753	3.287	135.650	99.888	−13.044
450	32.049	214.746	203.880	4.890	134.596	95.472	−11.082
500	32.125	218.126	205.139	6.493	133.464	91.188	−9.526
600	32.510	224.013	207.808	9.723	131.635	82.911	−7.218
700	33.047	229.064	210.492	13.000	130.075	74.916	−5.590
800	33.613	233.514	213.097	16.334	128.685	67.133	−4.383
900	34.148	237.504	215.591	19.722	74.278	60.598	−3.517
1000	34.630	241.127	217.966	23.161	74.294	59.077	−3.086
1100	35.055	244.448	220.225	26.646	74.311	57.554	−2.733
1200	35.425	247.515	222.373	30.171	74.324	56.030	−2.439
1300	35.747	250.363	224.418	33.730	74.329	54.505	−2.190
1400	36.029	253.023	226.367	37.319	74.324	52.981	−1.977
1500	36.276	255.517	228.228	40.934	74.307	51.457	−1.792
1600	36.493	257.866	230.008	44.573	74.276	49.934	−1.630
1700	36.687	260.084	231.712	48.232	74.231	48.414	−1.488
1800	36.860	262.186	233.347	51.909	74.173	46.897	−1.361
1900	37.016	264.183	234.918	55.603	74.102	45.384	−1.248
2000	37.157	266.085	236.429	59.312	74.018	43.874	−1.146
2100	37.286	267.901	237.885	63.034	73.922	42.370	−1.054
2200	37.405	269.639	239.289	66.769	73.815	40.870	−0.970
2300	37.514	271.304	240.645	70.515	73.697	39.375	−0.894
2400	37.616	272.903	241.956	74.272	73.570	37.885	−0.825
2500	37.712	274.440	243.225	78.038	73.433	36.401	−0.761
2600	37.802	275.921	244.454	81.814	73.287	34.923	−0.702
2700	37.886	277.349	245.646	85.598	73.135	33.450	−0.647
2800	37.967	278.729	246.803	89.391	72.974	31.983	−0.597
2900	38.044	280.062	247.927	93.191	72.807	30.522	−0.550
3000	38.117	281.353	249.020	97.000	72.633	29.067	−0.506
3100	38.188	282.604	250.083	100.815	72.453	27.617	−0.465
3200	38.256	283.818	251.119	104.637	72.267	26.174	−0.427
3300	38.322	284.996	252.128	108.466	72.074	24.737	−0.392
3400	38.386	286.141	253.111	112.301	71.876	23.305	−0.358
3500	38.448	287.255	254.071	116.143	71.672	21.880	−0.327
3600	38.509	288.339	255.008	119.991	71.462	20.460	−0.297
3700	38.569	289.394	255.923	123.845	71.246	19.046	−0.269
3800	38.628	290.424	256.817	127.705	71.023	17.638	−0.242
3900	38.686	291.428	257.692	131.570	70.794	16.236	−0.217
4000	38.744	292.408	258.548	135.442	70.559	14.841	−0.194
4100	38.801	293.365	259.385	139.319	70.316	13.451	−0.171
4200	38.858	294.301	260.205	143.202	70.067	12.066	−0.150
4300	38.915	295.216	261.009	147.091	69.811	10.689	−0.130
4400	38.972	296.111	261.797	150.985	69.547	9.317	−0.111
4500	39.029	296.988	262.569	154.885	69.276	7.951	−0.092
4600	39.087	297.846	263.327	158.791	68.998	6.591	−0.075
4700	39.145	298.688	264.070	162.702	68.712	5.238	−0.058
4800	39.204	299.512	264.800	166.620	68.419	3.890	−0.042
4900	39.264	300.321	265.517	170.543	68.118	2.549	−0.027
5000	39.324	301.115	266.221	174.473	67.810	1.214	−0.013
5100	39.385	301.895	266.913	178.408	67.495	−0.115	0.001
5200	39.448	302.660	267.593	182.350	67.172	−1.438	0.014
5300	39.511	303.412	268.261	186.298	66.843	−2.754	0.027
5400	39.576	304.151	268.919	190.252	66.508	−4.064	0.039
5500	39.642	304.878	269.566	194.213	66.166	−5.368	0.051
5600	39.709	305.593	270.203	198.180	65.819	−6.665	0.062
5700	39.778	306.296	270.830	202.155	65.466	−7.956	0.073
5800	39.848	306.989	271.448	206.136	65.109	−9.242	0.083
5900	39.920	307.670	272.056	210.125	64.747	−10.520	0.093
6000	39.993	308.342	272.655	214.120	64.382	−11.793	0.103

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

0 to 6000 K Ideal Gas

$D_0^\circ = 439.615 \pm 0.005$ kJ·mol^{-1} $\Delta_f H^\circ(0\ K) = 0$ kJ·mol^{-1}

$S^\circ(298.15\ K) = 144.960 \pm 0.04$ J·K^{-1}·mol^{-1} $\Delta_f H^\circ(298.15\ K) = 0$ kJ·mol^{-1}

Vibrational and Rotational Levels (cm^{-1})

Direct Summation of Electronic Ground State

$E = G - G_0 + F = G - G_0 + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots - G - G_0 + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = J(J+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L

$G = 3116.334Y - 62.50516Y^2 + 0.7797565Y^3 - 5.48262 \times 10^{-2}Y^4 + 2.25748 \times 10^{-3}Y^5 - 6.30154 \times 10^{-5}Y^6$

$B = 30.45273 - 1.102045Y + 0.0295505Y^2 - 5.99912 \times 10^{-3}Y^3 + 8.37740 \times 10^{-4}Y^4$
$- 6.87040 \times 10^{-5}Y^5 + 2.80134 \times 10^{-6}Y^6 - 4.68952 \times 10^{-8}Y^7$

$D = 0.011525 - 3.6876 \times 10^{-4}Y + 4.1199 \times 10^{-5}Y^2 - 4.4723 \times 10^{-6}Y^3 + 1.7858 \times 10^{-7}Y^4$

$H = 6.55 \times 10^{-6} - 6.42 \times 10^{-7}Y + 6.03 \times 10^{-8}Y^2 - 2.15 \times 10^{-9}Y^3$

$L = 4.20 \times 10^{-9} - 6.32 \times 10^{-10}Y + 4.35 \times 10^{-11}Y^2$

$v_{max} = 21$, $J_{max} = 54 - 47v/v_{max}$

Normalized statistical weights = 2/3 (even J) and 1/3 (odd J)

Ground State Configuration: $^1\Sigma_g^+$ $r_e = 0.7415$ Å

Enthalpy of Formation

Zero by definition. Refer to the monatomic deuterium gas table for a discussion of the dissociation energy.

Heat Capacity and Entropy

These are calculated by direct summation[1] over vibration–rotation energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U. S. National Bureau of Standards. Contributions of excited states ($T_0 > 90000$ cm^{-1}) are negligible at 6000 K. Polynomials G, B and D are our fits of data from Stoicheff[2] and Bredohl and Herzberg[3]. Polynomials H and L are estimated by isotopic relations from those of H_2[1] in order to provide a similar extrapolation to high J values. The adopted H polynomial is not more accurate than the relatively scattered data,[2–4] but it should be more consistent with our adopted approximation for the infinite-series (F) equation for rotational levels. We assume that F has the form proposed by Khachkuruzov[5] and Woolley *et al.*[6] We use a linear approximation for the limiting values (J_{max}) of rotational quantum number. The J_{max} equation is estimated; its second value has been revised from 52 (in the 1977 table) to 47 in order to yield C_p° and S° values that agree more closely with theory[8] near 6000 K. We omit the nuclear-spin contribution (R ln 9) to entropy and Gibbs energy function.

We adopt ortho–para "equilibrium" D_2 as the reference state at all temperatures. Values differ from "normal" D_2 only at 100 K.[6,7] Our values can be compared with the theoretical results of Kosloff *et al.*[8] and Gurvich *et al.*[9] and with the earlier table of NBS.[7] Our S° values deviate by 0.001[8] or −0.005[9] cal·K^{-1}·mol^{-1} at 6000 K. Our C_p° values deviate by 0.011[8], −0.002[9] or 0.002[7] at 5000 K and by 0.001[8] or −0.005[9] cal·K^{-1}·mol^{-1} at 6000 K.

References

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[3]H. Bredohl and G. Herzberg, Can. J. Phys. **51**, 867 (1973).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.569	0.	0.	0.
100	30.317	112.789	170.973	−5.818	0.	0.	0.
200	29.204	133.306	147.630	−2.865	0.	0.	0.
250	29.185	139.819	145.441	−1.405	0.	0.	0.
298.15	29.194	144.960	144.960	0.	0.	0.	0.
300	29.195	145.141	144.961	0.054	0.	0.	0.
350	29.213	149.642	145.316	1.514	0.	0.	0.
400	29.242	153.545	146.106	2.975	0.	0.	0.
450	29.290	156.992	147.128	4.439	0.	0.	0.
500	29.366	160.081	148.272	5.905	0.	0.	0.
600	29.619	165.456	150.701	8.853	0.	0.	0.
700	30.008	170.049	153.144	11.833	0.	0.	0.
800	30.502	174.087	155.515	14.858	0.	0.	0.
900	31.057	177.712	157.783	17.936	0.	0.	0.
1000	31.636	181.014	159.943	21.070	0.	0.	0.
1100	32.210	184.056	161.999	24.263	0.	0.	0.
1200	32.762	186.882	163.956	27.512	0.	0.	0.
1300	33.282	189.526	165.823	30.814	0.	0.	0.
1400	33.766	192.010	167.605	34.167	0.	0.	0.
1500	34.213	194.355	169.311	37.566	0.	0.	0.
1600	34.625	196.576	170.946	41.008	0.	0.	0.
1700	35.004	198.687	172.517	44.490	0.	0.	0.
1800	35.353	200.698	174.027	48.008	0.	0.	0.
1900	35.676	202.618	175.481	51.560	0.	0.	0.
2000	35.975	204.456	176.885	55.142	0.	0.	0.
2100	36.252	206.218	178.240	58.754	0.	0.	0.
2200	36.512	207.910	179.550	62.392	0.	0.	0.
2300	36.755	209.539	180.819	66.056	0.	0.	0.
2400	36.984	211.108	182.048	69.743	0.	0.	0.
2500	37.201	212.622	183.241	73.452	0.	0.	0.
2600	37.407	214.085	184.400	77.182	0.	0.	0.
2700	37.605	215.501	185.525	80.933	0.	0.	0.
2800	37.795	216.872	186.620	84.703	0.	0.	0.
2900	37.978	218.201	187.687	88.492	0.	0.	0.
3000	38.156	219.492	188.725	92.298	0.	0.	0.
3100	38.329	220.746	189.738	96.123	0.	0.	0.
3200	38.498	221.965	190.726	99.964	0.	0.	0.
3300	38.665	223.152	191.691	103.822	0.	0.	0.
3400	38.829	224.309	192.633	107.697	0.	0.	0.
3500	38.991	225.437	193.555	111.588	0.	0.	0.
3600	39.152	226.533	194.456	115.495	0.	0.	0.
3700	39.312	227.613	195.337	119.419	0.	0.	0.
3800	39.470	228.663	196.200	123.358	0.	0.	0.
3900	39.628	229.690	197.046	127.313	0.	0.	0.
4000	39.785	230.696	197.875	131.283	0.	0.	0.
4100	39.941	231.680	198.687	135.270	0.	0.	0.
4200	40.096	232.644	199.484	139.271	0.	0.	0.
4300	40.250	233.590	200.267	143.289	0.	0.	0.
4400	40.402	234.517	201.035	147.321	0.	0.	0.
4500	40.553	235.426	201.789	151.369	0.	0.	0.
4600	40.701	236.319	202.530	155.432	0.	0.	0.
4700	40.847	237.196	203.258	159.509	0.	0.	0.
4800	40.989	238.058	203.974	163.601	0.	0.	0.
4900	41.127	238.904	204.678	167.707	0.	0.	0.
5000	41.262	239.736	205.371	171.826	0.	0.	0.
5100	41.391	240.555	206.053	175.959	0.	0.	0.
5200	41.515	241.360	206.724	180.105	0.	0.	0.
5300	41.633	242.152	207.385	184.262	0.	0.	0.
5400	41.745	242.931	208.036	188.431	0.	0.	0.
5500	41.850	243.698	208.678	192.611	0.	0.	0.
5600	41.947	244.453	209.310	196.801	0.	0.	0.
5700	42.036	245.196	209.933	201.000	0.	0.	0.
5800	42.117	245.928	210.547	205.208	0.	0.	0.
5900	42.190	246.648	211.153	209.423	0.	0.	0.
6000	42.253	247.358	211.751	213.645	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

$S°(298.15\ K) = 156.735 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1492.287 \pm 0.013\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [1498.567]\ kJ·mol^{-1}$

Vibrational and Rotational Levels (cm^{-1})

Direct Summation using Energy–Level Equations for the $^2\Sigma_g^+$ Electronic Ground State:

$E = G - G_o + F = G - G_o + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots\ G - G_o + BZ - DZ^2 + H Z^2 /^3(H+LZ)$,
where $Z = N(N+1)$, $Y = v+1/2$, and we omit subscript v on G, F, B, D, H, and L
$G = 1643.29\ Y - 33.7163\ Y^2 + 0.329116\ Y^3 - 0.00725916\ Y^4$
$B = 14.9825 - 0.564098\ Y + 0.00801011\ Y^2 - 0.000230173\ Y^3$ $\quad r_3 = 1.057$ Å
$D = 4.98379 \times 10^{-3} - 1.54039 \times 10^{-4}\ Y + 3.75711 \times 10^{-6}\ Y^2$
$H = 2.15408 \times 10^{-6} - 5.31503 \times 10^{-8}\ Y$ and $L = 1.00253 \times 10^{-9}$
$v_{max} = 26$ and $N_{max} = 57 - 46v/v_{max}$
electronic statistical weight = 2 and normalized rotational statistical weights = 2/3 (even N) or 1/3 (odd N)

Enthalpy of Formation

$\Delta_f H°(0\ K) = 356.666 \pm 0.003\ kcal·mol^{-1}$ is the ionization potential $IP(D_2) = 124745.6 \pm 1.2\ cm^{-1}$. Takezawa and Tanaka[1] determined $IP = 124746.6 \pm 0.6\ cm^{-1}$ from Rydberg spectra of D_2. Similar studies on H_2 by Herzberg and Jungen[2] revealed a bias of $-1.0\ cm^{-1}$ attributed to a pressure shift in the spectra. We assume an equal shift for D_2, adjust IP by $-1.0\ cm^{-1}$ and increase the uncertainty due to this adjustment. $\Delta_f H°(0\ K)$ is converted to $\Delta_f H°(298.15\ K)$ by use of JANAF[3] enthalpies $H°(0\ K)–H°(298.15\ K)$ for D_2, D_2^+ and e^-(ref). $\Delta_f H°(298.15\ K)$ should not be interpreted as a room–temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by Rosenstock *et al.*[4]

The adopted spectroscopic $IP(D_2)$ receives strong support from a value calculated indirectly from experimental values[3] of $D_0°(D_2)$ and IP(D) combined with the theoretical value[5] of $D_0°(D_2^+)$; this indirect value differs by only $0.4\ cm^{-1}$. Rosenstock *et al.*[4] review several less accurate determinations of $IP(D_2)$ and recommend a value calculated from $IP(H_2)$ using differences in zero–point energies of the diatomic molecules and their ions. Repeating this calculation with JANAF values,[3] we predict an IP (D_2) which differs from the observed value by $-32\ cm^{-1}$. Inclusion of an empirical adjustment for IP(D)–IP(H) overcorrects the prediction, giving a deviation of $+28\ cm^{-1}$. These slight discrepancies are due,[3] (refer to HD^+, g) to the approximate nature of the prediction. Villarejo's average photoionization result,[6] $IP(D_2) = 124757 \pm 180\ cm^{-1}$, deviates by $+11\ cm^{-1}$ from the spectroscopic value.

Heat Capacity and Entropy

Thermodynamic functions for ortho–para "equilibrium" D_2^+ are calculated by direct summation using the energy–level equations listed above. We use 1973 fundamental constants[7] in an extended version of a computer program written by W. H. Evans and provided by D.D. Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they do not contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect rotational splitting which should be very small (see HD^+ and H_2^+).[3]

Coefficients of the energy–level polynomials are calculated from the theoretical values of H_2^+[3] using rho = 0.707330 in isotopic equations. Theoretical calculations[5] on D_2^+ provide confirmation of B_e, ω_e and $\omega_e x_e$; the latter two are confirmed by vibrational structure observed[6] in the photoionization threshold of D_2^+. We give the polynomial coefficients, especially higher order ones, to many more digits than are justified by their accuracy. The equations are very approximate near N_{max} but, judging by H_2^+,[3] this should have little effect on the thermodynamic functions even at 6000 K. The approximate v_{max} is derived from the G polynomial.

The thermodynamic functions include contributions from quasi–bound levels lying above $D_0° = 21712\ cm^{-1}$. At 6000 K these levels contribute 0.33 cal $K^{-1}·mol^{-1}$ to $C_p°$ and 0.041 $cal·K^{-1}·mol^{-1}$ to the Gibbs–energy function. Their contribution is negligible below 3000 K. Limiting rotational quantum numbers N_{max} are estimated from H_2^+, H_2 and D_2[3] by comparing energy increments and rotational quanta found above the respective values of $D_0°$. The crudity of these estimates makes $C_p°$ at 6000 K somewhat more uncertain than in the case of H_2^+.[3]

References

[1] S. Takezawa and Y. Tanaka, J. Mol. Spectrosc. **54**, 379 (1975).
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[3] JANAF Thermochemical Tables: H_2(ref), D_2(ref), H^+(g), D^+(g), e^-(ref) 3–31–77; H_2^+(g), HD^+(g), D_2^+(g) 9–30–77.
[4] H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹·mol⁻¹)	$S°$ (J·K⁻¹·mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹·mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−8.651	1492.287		
100	29.192	124.796	182.774	−5.798			
200	29.221	145.027	159.422	−2.879			
298.15	29.510	156.735	156.735	0.	1498.567	1488.801	−260.832
300	29.519	156.917	156.735	0.055	1498.606	1488.741	−259.213
400	30.282	165.504	157.901	3.041	1500.749	1485.131	−193.938
500	31.332	172.371	160.130	6.121	1502.978	1480.971	−154.716
600	32.420	178.181	162.666	9.309	1505.297	1476.353	−128.528
700	33.417	183.255	165.252	12.602	1507.688	1471.340	−109.793
800	34.285	187.775	167.790	15.988	1510.128	1465.982	−95.719
900	35.028	191.857	170.241	19.454	1512.595	1460.316	−84.755
1000	35.664	195.582	172.592	22.990	1515.075	1454.374	−75.969
1100	36.214	199.007	174.839	26.584	1517.556	1448.184	−68.769
1200	36.695	202.179	176.987	30.230	1520.031	1441.768	−62.759
1300	37.123	205.133	179.040	33.922	1522.499	1435.146	−57.665
1400	37.510	207.899	181.004	37.653	1524.956	1428.334	−53.292
1500	37.867	210.499	182.884	41.423	1527.405	1421.347	−49.496
1600	38.201	212.954	184.688	45.226	1529.845	1414.197	−46.169
1700	38.518	215.279	186.419	49.062	1532.278	1406.894	−43.229
1800	38.825	217.490	188.084	52.929	1534.705	1399.449	−40.611
1900	39.125	219.597	189.688	56.827	1537.130	1391.869	−38.265
2000	39.422	221.611	191.234	60.754	1539.553	1384.160	−36.151
2100	39.719	223.542	192.727	64.711	1541.977	1376.331	−34.234
2200	40.017	225.396	194.170	68.698	1544.404	1368.386	−32.490
2300	40.317	227.182	195.567	72.715	1546.836	1360.331	−30.894
2400	40.620	228.904	196.920	76.761	1549.275	1352.170	−29.429
2500	40.923	230.568	198.233	80.839	1551.721	1343.907	−28.079
2600	41.225	232.179	199.508	84.946	1554.176	1335.546	−26.831
2700	41.523	233.741	200.747	89.083	1556.642	1327.091	−25.674
2800	41.814	235.256	201.952	93.250	1559.117	1318.543	−24.598
2900	42.094	236.728	203.126	97.446	1561.603	1309.908	−23.594
3000	42.360	238.160	204.270	101.669	1564.097	1301.186	−22.656
3100	42.607	239.553	205.386	105.917	1566.600	1292.381	−21.776
3200	42.832	240.909	206.475	110.189	1569.110	1283.495	−20.951
3300	43.032	242.231	207.539	114.483	1571.624	1274.531	−20.174
3400	43.204	243.518	208.578	118.795	1574.140	1265.490	−19.442
3500	43.345	244.772	209.594	123.123	1576.655	1256.376	−18.750
3600	43.453	245.995	210.589	127.463	1579.166	1247.190	−18.096
3700	43.526	247.187	211.562	131.812	1581.671	1237.933	−17.476
3800	43.565	248.348	212.515	136.167	1584.165	1228.610	−16.888
3900	43.567	249.480	213.448	140.524	1586.646	1219.221	−16.330
4000	43.534	250.582	214.363	144.879	1589.109	1209.768	−15.798
4100	43.467	251.657	215.259	149.230	1591.552	1200.254	−15.291
4200	43.365	252.703	216.138	153.571	1593.970	1190.681	−14.808
4300	43.232	253.722	217.001	157.902	1596.362	1181.051	−14.347
4400	43.068	254.714	217.846	162.217	1598.723	1171.365	−13.906
4500	42.875	255.680	218.676	166.514	1601.051	1161.626	−13.484
4600	42.655	256.620	219.491	170.791	1603.344	1151.836	−13.080
4700	42.411	257.534	220.291	175.044	1605.598	1141.996	−12.692
4800	42.145	258.424	221.076	179.272	1607.813	1132.108	−12.320
4900	41.859	259.291	221.847	183.473	1609.986	1122.175	−11.963
5000	41.556	260.133	222.605	187.643	1612.116	1112.199	−11.619
5100	41.237	260.953	223.348	191.783	1614.202	1102.179	−11.289
5200	40.905	261.751	224.079	195.890	1616.242	1092.120	−10.970
5300	40.562	262.526	224.797	199.964	1618.237	1082.021	−10.664
5400	40.210	263.281	225.503	204.002	1620.185	1071.886	−10.368
5500	39.850	264.016	226.197	208.006	1622.087	1061.714	−10.083
5600	39.485	264.731	226.879	211.972	1623.943	1051.509	−9.808
5700	39.116	265.426	227.549	215.902	1625.752	1041.271	−9.542
5800	38.744	266.103	228.208	219.795	1627.516	1031.001	−9.285
5900	38.371	266.763	228.856	223.651	1629.235	1020.701	−9.037
6000	37.998	267.404	229.493	227.470	1630.910	1010.373	−8.796

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 158.26 \pm 0.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [241.4 \pm 42]\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [235.365]\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma_u^+$	0	2

$\omega_e = [1202]\ cm^{-1}$ $\omega_e x_e = [17.5]\ cm^{-1}$ $\sigma = 2$
$B_e = [12.7]\ cm^{-1}$ $\alpha_e = [0.141]\ cm^{-1}$ $r_e = [1.15]$Å

Enthalpy of Formation

The enthalpy of formation at 0 K for D_2^-(g) is based on the electron affinity (EA) value derived from a Rydberg–Klein–Rees configuration interaction calculation for H_2^-.[1] This study by Sharpe[1] led to $EA(H_2) = -2.5$ eV. Assuming the same value for D_2 and using auxiliary data,[2] we calculate $\Delta_f H°(0\ K) = 57.7 \pm 10\ kcal\cdot mol^{-1}$ and $D_0°(D_2^-) = 30.0 \pm 10\ kcal\cdot mol^{-1}$, the latter value assumes dissociation into ground state D(g) and D^-(g). The adopted $EA(H_2)$ value is suggested to be the more reliable value of eight studies considered by Rosenstock *et al.*[3]

In terms of molecular orbitals, the ground state for D_2^-(g) is the $(1s\sigma_g)^2(2p\sigma_u)^2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron. As stated by Massey,[4] we should expect only a weakly-bound molecule as compared with D_2(g) for which the ground state has no electrons in an antibonding orbital. We would expect, however, the ground state to be $(1s\sigma_g)^2(1s\sigma_u)$. Our calculated $EA(D_2)$ value is consistent with this viewpoint. Further discussion of the D_2^-(g) ion may be found in Massey.[4]

$\Delta_f H(0\ K)$ is converted to $\Delta_f H°(298.15\ K)$ by use of JANAF[2] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for D_2(g), D_2^-(g), and e^-(ref). $\Delta_f H°(298.15\ K)$ should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to thereshold effects discussed by Rosenstock *et al.*[3]

Heat Capacity and Entropy

The vibrational constants for H_2^-(g) are estimated to be the same as in the isoelectronic species He_2^+.[5] The vibrational constants for D_2^-(g) are calculated from those of H_2^-(g) using isotopic relations.[2] The internuclear distance is estimated to be ~8% larger than that for He_2^+(g). The same relationship appeared to exist for the (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey.[4] No excited state contributions are included in this calculation.

References

[1]T. E. Sharpe, Lockheed Report LMSC 5–10–69–9 (1969).
[2]JANAF Thermochemical Tables: D(g), D^-(g), D_2(g) and e^-(ref), 3–31–77; H_2^-(g), 9–30–77.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−8.714	241.418		
100	29.190	126.100	184.605	−5.850			
200	29.403	146.375	160.997	−2.924			
250	29.771	152.971	158.755	−1.446			
298.15	30.315	158.259	158.259	0.	235.365	237.655	−41.636
300	30.338	158.447	158.260	0.056	235.329	237.669	−41.382
350	31.023	163.174	158.632	1.590	234.363	238.136	−35.540
400	31.745	167.364	159.466	3.159	233.432	238.739	−31.176
450	32.447	171.144	160.557	4.764	232.534	239.457	−27.795
500	33.101	174.597	161.791	6.403	231.667	240.272	−25.101
600	34.226	180.735	164.449	9.771	230.009	242.151	−21.081
700	35.121	186.081	167.166	13.240	228.419	244.301	−18.230
800	35.832	190.819	169.832	16.789	226.865	246.676	−16.106
900	36.404	195.073	172.404	20.402	225.322	249.245	−14.466
1000	36.875	198.934	174.867	24.067	223.773	251.986	−13.162
1100	37.270	202.468	177.218	27.775	222.210	254.883	−12.103
1200	37.610	205.725	179.459	31.519	220.627	257.923	−11.227
1300	37.907	208.748	181.598	35.295	219.022	261.095	−10.491
1400	38.173	211.567	183.639	39.100	217.395	264.393	−9.865
1500	38.413	214.209	185.590	42.929	215.746	267.807	−9.326
1600	38.634	216.695	187.457	46.782	214.078	271.332	−8.858
1700	38.840	219.044	189.246	50.655	212.392	274.962	−8.449
1800	39.033	221.269	190.964	54.549	210.689	278.692	−8.087
1900	39.216	223.384	192.615	58.462	208.971	282.517	−7.767
2000	39.390	225.400	194.204	62.392	207.240	286.432	−7.481
2100	39.558	227.326	195.736	66.339	205.497	290.435	−7.224
2200	39.721	229.170	197.214	70.303	203.744	294.520	−6.993
2300	39.878	230.940	198.642	74.283	201.982	298.686	−6.783
2400	40.032	232.640	200.024	78.279	200.212	302.928	−6.593
2500	40.182	234.277	201.361	82.290	198.435	307.245	−6.420
2600	40.329	235.856	202.658	86.315	196.652	311.632	−6.261
2700	40.474	237.381	203.916	90.355	194.862	316.089	−6.115
2800	40.616	238.855	205.138	94.410	193.068	320.611	−5.981
2900	40.757	240.283	206.325	98.479	191.270	325.198	−5.857
3000	40.896	241.667	207.480	102.561	189.467	329.847	−5.743
3100	41.034	243.010	208.605	106.658	187.661	334.556	−5.637
3200	41.170	244.315	209.700	110.768	185.851	339.324	−5.539
3300	41.305	245.584	210.769	114.892	184.038	344.147	−5.447
3400	41.439	246.819	211.811	119.029	182.222	349.027	−5.362
3500	41.573	248.022	212.828	123.180	180.403	353.959	−5.283
3600	41.705	249.195	213.822	127.344	178.581	358.944	−5.208
3700	41.837	250.340	214.794	131.521	176.756	363.979	−5.138
3800	41.968	251.457	215.744	135.711	174.929	369.063	−5.073
3900	42.099	252.549	216.674	139.914	173.099	374.196	−5.012
4000	42.229	253.617	217.584	144.131	171.266	379.376	−4.954
4100	42.359	254.661	218.476	148.360	169.430	384.601	−4.900
4200	42.488	255.683	219.349	152.602	167.592	389.871	−4.849
4300	42.617	256.685	220.206	156.858	165.751	395.185	−4.801
4400	42.745	257.666	221.046	161.126	163.908	400.542	−4.755
4500	42.873	258.628	221.871	165.407	162.063	405.941	−4.712
4600	43.001	259.572	222.680	169.700	160.215	411.381	−4.671
4700	43.129	260.498	223.475	174.007	158.366	416.861	−4.633
4800	43.256	261.407	224.256	178.326	156.514	422.381	−4.596
4900	43.383	262.300	225.023	182.658	154.662	427.939	−4.562
5000	43.510	263.178	225.778	187.003	152.809	433.535	−4.529
5100	43.637	264.041	226.519	191.360	150.955	439.167	−4.498
5200	43.763	264.889	227.249	195.730	149.101	444.837	−4.468
5300	43.890	265.724	227.967	200.113	147.247	450.542	−4.440
5400	44.016	266.546	228.674	204.508	145.395	456.282	−4.414
5500	44.142	267.355	229.370	208.916	143.544	462.056	−4.388
5600	44.268	268.151	230.055	213.336	141.696	467.864	−4.364
5700	44.394	268.936	230.731	217.769	139.852	473.704	−4.341
5800	44.519	269.709	231.396	222.215	138.011	479.577	−4.319
5900	44.645	270.471	232.052	226.673	136.175	485.482	−4.298
6000	44.770	271.222	232.698	231.144	134.345	491.419	−4.278

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 204.291\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 188.276 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 185.351 \pm 8.4\ kJ·mol^{-1}$

Electronic Levels (Quantum Weights) and Vibrational Frequencies (Degeneracies)

State	ϵ_i, cm^{-1}	g_i	ν_1, cm−1	υ_2, cm^{-1}	υ_3, cm^{-1}
$\tilde{X}^2B_1$	0	(2)	[2305](1)	1110(1)	[2367](1)
$\tilde{A}^2A_1(\pi)$	10393	(2)	[2305](1)	[500](1)	[2367](1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: N–D = 1.024 Å
Bond Angle: D–N–D = 103.4°
Product of the Moments of Inertia: $I_A I_B I_C = 5.7948 \times 10^{-119}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ of $ND_2(g)$ was calculated from the JANAF selection[1] for $\Delta_f H°(298.15\ K)$ of $NH_2(g)$, the JANAF thermal functions,[1] and the zero point energies of $H_2(g)$, $D_2(g)$, $NH_2(g)$, and $ND_2(g)$. The zero point energies of $H_2(g)$ and $D_2(g)$ were those given by Herzberg and Monfils.[2] The zero point energies of $NH_2(g)$ and $ND_2(g)$ were estimated from vibrational frequencies given by Milligan and Jacox[3] who observed the infrared and visible spectrum of matrix-isolated NH_2 and ND_2.

Heat Capacity and Entropy

The bond distance and angle are from the electronic absorption spectrum of NH_2 as summarized by Herzberg.[4] The vibrational frequencies for the ground state are from Milligan and Jacox;[3] those for the excited state are estimated by comparison with NH_2.[1,4]

The National Bureau of Standards prepared this table[5] by critical analysis of data existing in 1972. Using $S°$, $C_p°$ and $\Delta_f H°$ selected by NBS,[5] we recalculate the table in terms of current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables: $NH_2(g)$, 7-31-72 (NBS)/6-30-77.
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[4]G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, (1966).
[5]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Report 10904, 239, (July 1972).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.979	188.276	188.276	INFINITE
100	33.259	167.708	234.234	−6.653	187.401	189.900	−99.193
200	33.439	190.787	207.397	−3.322	186.323	192.825	−50.361
298.15	34.422	204.291	204.291	0.	185.351	196.226	−34.378
300	34.447	204.504	204.292	0.064	185.334	196.293	−34.178
400	36.062	214.625	205.661	3.586	184.476	200.080	−26.128
500	37.949	222.871	208.302	7.285	183.775	204.065	−21.319
600	39.953	229.967	211.334	11.179	183.231	208.177	−18.123
700	41.945	236.277	214.455	15.275	182.825	212.369	−15.847
800	43.815	242.002	217.546	19.565	182.535	216.610	−14.143
900	45.509	247.262	220.559	24.033	182.337	220.882	−12.820
1000	47.007	252.136	223.476	28.660	182.210	225.173	−11.762
1100	48.308	256.679	226.290	33.427	182.136	229.473	−10.897
1200	49.442	260.932	229.002	38.316	182.101	233.778	−10.176
1300	50.421	264.929	231.613	43.310	182.096	238.085	−9.566
1400	51.279	268.697	234.129	48.396	182.112	242.391	−9.044
1500	52.036	272.262	236.553	53.563	182.145	246.696	−8.591
1600	52.714	275.642	238.892	58.801	182.192	250.997	−8.194
1700	53.329	278.856	241.149	64.103	182.250	255.296	−7.844
1800	53.898	281.921	243.329	69.465	182.319	259.591	−7.533
1900	54.430	284.849	245.438	74.881	182.399	263.882	−7.255
2000	54.936	287.654	247.479	80.350	182.490	268.168	−7.004
2100	55.424	290.346	249.457	85.868	182.595	272.449	−6.777
2200	55.902	292.936	251.375	91.434	182.713	276.725	−6.570
2300	56.368	295.431	253.236	97.048	182.846	280.996	−6.382
2400	56.827	297.840	255.045	102.708	182.996	285.260	−6.209
2500	57.278	300.169	256.804	108.413	183.164	289.518	−6.049
2600	57.722	302.424	258.515	114.163	183.351	293.768	−5.902
2700	58.160	304.611	260.182	119.957	183.556	298.011	−5.765
2800	58.589	306.734	261.807	125.795	183.782	302.246	−5.638
2900	59.009	308.797	263.392	131.675	184.027	306.473	−5.520
3000	59.417	310.804	264.939	137.596	184.292	310.690	−5.410
3100	59.813	312.759	266.450	143.558	184.576	314.899	−5.306
3200	60.195	314.664	267.927	149.558	184.879	319.098	−5.209
3300	60.565	316.522	269.372	155.597	185.199	323.288	−5.117
3400	60.919	318.335	270.785	161.671	185.537	327.467	−5.031
3500	61.259	320.106	272.169	167.780	185.890	331.637	−4.949
3600	61.580	321.837	273.525	173.922	186.257	335.796	−4.872
3700	61.883	323.528	274.854	180.095	186.638	339.944	−4.799
3800	62.169	325.182	276.156	186.298	187.029	344.082	−4.730
3900	62.436	326.801	277.434	192.529	187.430	348.210	−4.664
4000	62.685	328.384	278.688	198.785	187.839	352.328	−4.601
4100	62.915	329.935	279.919	205.065	188.255	356.435	−4.541
4200	63.128	331.454	281.128	211.367	188.675	360.531	−4.484
4300	63.322	332.942	282.316	217.690	189.098	364.618	−4.429
4400	63.499	334.399	283.483	224.031	189.522	368.695	−4.377
4500	63.660	335.828	284.631	230.389	189.946	372.762	−4.327
4600	63.803	337.229	285.759	236.762	190.369	376.821	−4.279
4700	63.932	338.603	286.869	243.149	190.789	380.869	−4.233
4800	64.045	339.950	287.961	249.548	191.205	384.909	−4.189
4900	64.146	341.271	289.035	255.958	191.615	388.940	−4.146
5000	64.233	342.568	290.093	262.377	192.020	392.964	−4.105
5100	64.303	343.841	291.134	268.804	192.418	396.978	−4.066
5200	64.363	345.090	292.160	275.237	192.808	400.985	−4.028
5300	64.413	346.317	293.170	281.676	193.189	404.985	−3.991
5400	64.451	347.521	294.166	288.119	193.562	408.978	−3.956
5500	64.480	348.704	295.146	294.566	193.926	412.963	−3.922
5600	64.499	349.866	296.113	301.015	194.280	416.943	−3.889
5700	64.509	351.008	297.066	307.465	194.625	420.916	−3.857
5800	64.509	352.130	298.006	313.916	194.959	424.883	−3.826
5900	64.503	353.232	298.933	320.367	195.284	428.844	−3.797
6000	64.492	354.316	299.847	326.817	195.598	432.801	−3.768

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Diazene–d_2, Cis (N_2D_2) — IDEAL GAS — M_r = 32.041604

$S°(298.15\ K) = 224.092\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 214.039 \pm 2.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 207.108 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
υ, cm^{-1}	υ, cm^{-1}
[2300](1)	[2400](1)
[1490](1)	[1150](1)
[1058](1)	[750](1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: N–N = [1.230] Å; N–D = [1.014] Å

Bond Angle: D–N–N = [100]°

Product of Moments of Inertia: $I_A I_B I_C = 3.8165 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(N_2D_2, g, 298.15\ K)$ was estimated from $\Delta_f H°(N_2H_2, g, 298.15\ K) = 50.9 \pm 5\ kcal·mol^{-1}$, given in the JANAF Thermochemical Tables,[1] the appropriate thermal functions (see tables for N_2D_2, H_2, D_2, and N_2H_2)[1] and the estimated zero point energies. The zero point energies for $H_2(g)$, $D_2(g)$ are those given by Herzberg and Monfils.[2] The zero point energies for $N_2D_2(g)$ and $N_2H_2(g)$ are taken to be one half the sum of the vibrational frequencies given above and for $N_2H_2(g)$.[1]

Heat Capacity and Entropy

The bond distances and angle are assumed the same as were obtained from a quantum mechanical calculation for N_2H_2 by Wheland and Chen.[3] The principal moments of inertia are: $I_A = 0.5832$, $I_B = 2.1780$, $I_C = 2.7612 \times 10^{-39}\ g·cm^2$. The infrared spectrum of $N_2H_2(g)$ has been observed using matrix isolation techniques by Rosengren and Pimentel;[4] they also observed absorptions at 1481 and 1058 cm^{-1} attributed to trans–HNND and at 946 cm^{-1} attributed to trans–DNND. For cis–HNNH, they assigned υ_1 or $\upsilon_4 = 3074$ cm and $\upsilon_3 = 1279\ cm^{-1}$. Based on these observations and the vibrational frequencies adopted for $N_2H_2(g)$,[1] the vibrational frequencies for N_2D_2 are estimated.

The National Bureau of Standards prepared this table[5] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[5] we recalculate the table in terms of 1973 fundamental constants,[6] 1975 atomic weights,[7] and current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables: $N_2H_2(g)$, 12–31–65; H_2(ref. st.), 3–31–77; $N_2D_2(g)$, 6–30–77.

[2]G. Herzberg and A. Monfils, J. Mol. Spectrosc. **5**, 482 (1960).

[3]G. W. Wheland and P. S. K. Chen, J. Chem. Phys. **24**, 482 (1960).

[4]K. Rosengren and G. Pimentel, J. Chem. Phys. **24**, 67 (1956).

[5]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand., Report 10904, p. 239, (July 1972).

[6]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).

[7]IUPAC Commission on Atomic Weights, Pure Appl. Chem. **47**, 75 (1976); **37**, 589 (1974).

Diazene–D_2, Cis (DNND) — $D_2N_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.308	214.039	214.039	INFINITE
100	33.278	186.132	255.951	−6.982	211.712	220.359	−115.104
200	34.771	209.482	227.508	−3.605	209.225	229.987	−60.066
250	36.691	217.435	224.721	−1.821	208.094	235.310	−49.165
298.15	39.024	224.092	224.092	0.	207.108	240.643	−42.160
300	39.119	224.333	224.092	0.072	207.072	240.851	−41.936
350	41.779	230.562	224.578	2.094	206.177	246.554	−36.796
400	44.483	236.317	225.690	4.251	205.412	252.376	−32.957
450	47.125	241.710	227.174	6.541	204.774	258.286	−29.981
500	49.652	246.807	228.884	8.961	204.254	264.260	−27.607
600	54.274	256.278	232.673	14.163	203.524	276.337	−24.057
700	58.283	264.953	236.673	19.796	203.134	288.507	−21.529
800	61.703	272.965	240.715	25.800	203.004	300.715	−19.635
900	64.591	280.404	244.717	32.119	203.068	312.927	−18.162
1000	67.018	287.339	248.636	38.703	203.278	325.123	−16.983
1100	69.056	293.825	252.453	45.509	203.595	337.293	−16.017
1200	70.770	299.909	256.157	52.503	203.991	349.430	−15.210
1300	72.215	305.633	259.745	59.654	204.446	361.532	−14.527
1400	73.440	311.030	263.217	66.939	204.944	373.597	−13.939
1500	74.483	316.134	266.576	74.336	205.474	385.626	−13.429
1600	75.375	320.970	269.826	81.830	206.027	397.618	−12.981
1700	76.143	325.563	272.971	89.407	206.596	409.575	−12.585
1800	76.808	329.935	276.015	97.056	207.177	421.498	−12.232
1900	77.386	334.103	278.963	104.766	207.766	433.389	−11.915
2000	77.891	338.086	281.821	112.530	208.359	445.248	−11.629
2100	78.335	341.897	284.591	120.342	208.955	457.078	−11.369
2200	78.726	345.550	287.280	128.195	209.550	468.879	−11.133
2300	79.073	349.058	289.890	136.086	210.144	480.654	−10.916
2400	79.381	352.430	292.426	144.009	210.734	492.402	−10.717
2500	79.656	355.676	294.891	151.961	211.321	504.127	−10.533
2600	79.903	358.805	297.290	159.939	211.902	515.827	−10.363
2700	80.125	361.825	299.624	167.941	212.477	527.506	−10.205
2800	80.326	364.742	301.898	175.963	213.045	539.163	−10.058
2900	80.507	367.564	304.114	184.005	213.606	550.800	−9.921
3000	80.672	370.296	306.275	192.064	214.159	562.418	−9.793
3100	80.822	372.944	308.383	200.139	214.704	574.018	−9.672
3200	80.959	375.512	310.441	208.228	215.239	585.600	−9.559
3300	81.084	378.006	312.451	216.331	215.764	597.166	−9.452
3400	81.199	380.428	314.415	224.445	216.279	608.716	−9.352
3500	81.305	382.783	316.335	232.570	216.784	620.250	−9.257
3600	81.402	385.075	318.212	240.706	217.277	631.771	−9.167
3700	81.492	387.307	320.050	248.850	217.759	643.278	−9.081
3800	81.576	389.481	321.848	257.004	218.229	654.772	−9.000
3900	81.653	391.601	323.610	265.165	218.687	666.254	−8.923
4000	81.724	393.669	325.336	273.334	219.132	677.725	−8.850
4100	81.791	395.688	327.027	281.510	219.565	689.184	−8.780
4200	81.853	397.660	328.685	289.692	219.984	700.633	−8.714
4300	81.911	399.586	330.312	297.880	220.390	712.072	−8.650
4400	81.965	401.470	331.908	306.074	220.783	723.502	−8.589
4500	82.016	403.313	333.474	314.273	221.162	734.923	−8.531
4600	82.064	405.116	335.012	322.477	221.528	746.336	−8.475
4700	82.108	406.881	336.522	330.686	221.880	757.742	−8.421
4800	82.150	408.610	338.006	338.899	222.219	769.139	−8.370
4900	82.189	410.305	339.465	347.116	222.544	780.530	−8.321
5000	82.227	411.965	340.898	355.337	222.856	791.914	−8.273
5100	82.262	413.594	342.308	363.561	223.154	803.292	−8.227
5200	82.295	415.192	343.694	371.789	223.440	814.665	−8.183
5300	82.326	416.760	345.058	380.020	223.714	826.032	−8.141
5400	82.356	418.299	346.400	388.254	223.977	837.394	−8.100
5500	82.384	419.810	347.721	396.491	224.227	848.751	−8.061
5600	82.410	421.295	349.021	404.731	224.467	860.104	−8.023
5700	82.435	422.754	350.302	412.973	224.697	871.452	−7.986
5800	82.459	424.188	351.564	421.218	224.917	882.797	−7.950
5900	82.482	425.597	352.807	429.465	225.127	894.138	−7.916
6000	82.504	426.984	354.031	437.714	225.328	905.476	−7.883

PREVIOUS: June 1977 (1 atm) — CURRENT: June 1977 (1 bar)

Diazene–D_2, Cis (DNND) — $D_2N_2(g)$

$S°$(298.15 K) = 198.339 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −246.251 ± 0.067 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −249.203 ± 0.067 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2671.69(1)	1178.33(1)	2788.02(1)

Ground State Quantum Weight: 1 σ = 2
Point Group: C_{2v}
Bond Distance: O–D = 0.958 Å
Bond Angle: D–O–D = 104.45°
Product of the Moments of Inertia: $I_A I_B I_C$ = 3.9948 × 10^{-119} g^3·cm^6

Enthalpy of Formation

Rossini *et al.*[1] measured the ratio of the heats of formation of D_2O(l)/H_2O(l). Recalculation of their results using $\Delta_f H°$(298.15 K) of H_2O(l) = −68.315 ± 0.010 kcal·mol^{-1} (refer to H_2O(g) table,[15] yields $\Delta_f H°$(298.15 K) of D_2O(l)–H_2O(l) = −2.1098 ± 0.01492 × $\Delta_f H°$[HDO(l)–H_2O(l), 298.15 K] ± .016 kcal·mol^{-1}. Using a value of 32 ± 30 kcal·mol^{-1} for the reaction H_2D_2O(l) = 2 HDO(l) from[2] (some justification that the uncertainty may be smaller is given by Van Hook,[3] refer also to HDO table,[15] one obtains $\Delta_f H°$[D_2O(l)–H_2O(l), 298.15 K] = −2.094 ± 0.016 kcal·mol^{-1}.

The difference between the heats of vaporization of D_2O(l) and H_2O(l) at 298.15 K were evaluated as follows. A) By direct calorimetry, Rossini *et al.*[1] determined the ratio of the heats of vaporization of H_2O(l)/D_2O(l) at 298.15 K and zero pressure to be 0.969503 ± 0.00070. B) Bartholome and Clusius[4] determined the heat of vaporization of D_2O(l) by direct calorimetry at 0°C. Recalculation of their results, using the energy equivalent of a Bunsen ice calorimetergiven by[5] (compression correction assumed zero) and neglecting gas imperfection corrections, yields 12.637 ± 0.026 kcal·mol^{-1}. The heat of vaporization of D_2O(l) at 25°C was calculated using a heat of fusion of D_2O(l) selected by[6] and,[7] the condensed phase of heat capacity data of D_2O(l) given by Long and Kemp[8] and the gas phase thermal functions of Friedman and Haar (refer to the next section). C) The difference in heats of vaporization of D_2O(l) and H_2O(l) was derived by differentiating the formula given by Jones[9] (refer to Liu and Lindsay[10] for a comparison with other measurements) for the ratio of the vapor pressures of H_2O(l)/D_2O(l) as a function of temperature and assuming negligible corrections for gas imperfection (refer to Kell, Laurin and Whalley,[11] however).

Source	Method	$\Delta_{vap}H°$[D_2O(l)–H_2O(l), 298.15 K], kcal·mol^{-1}
Knowlton, Johnston, Rossini	Calorimetry	0.331 ± 0.008*
Bartholome and Clusius	Calorimetry	0.340 ± 0.028*
Jones	Vapor Pressure	0.307 ± 0.020

*Calculated from $\Delta_{vap}H°$(298.15 K) of H_2O(l) = 10.520 ± 0.002 kcal·mol^{-1}.[12]

Selecting 0.331 ± .008 kcal·mol^{-1} for the difference in the heats of vaporization, one obtains −1.763 ± 0.018 kcal·mol^{-1} for $\Delta_f H°$(298.15 K) of D_2O(g)–H_2O(g). The "spectroscopic" value for this difference was calculated to be −1.768 ± 0.015 kcal·mol^{-1} based on the zero point energies given by Hulston[13] for H_2O(g) and D_2O(g), and by Herzberg and Monfils[14] for H_2(g) and D_2(g), and the appropriate thermal functions (H_2O(g), H_2(ref. st.), D_2(ref. st.), D_2O(g)).[15] To close the consistency check, the "spectroscopic" value of $\Delta_f H°$(298.15 K) of D_2O(g) minus HDO(g) is −0.916 ± 0.0015 kcal·mol^{-1} and the "nonspectroscopic" value for this difference (refer to HDO table, reaction A)[15] is (−1.763 ± 0.0018) + (0.846 ± 0.006) = −0.917 ± 0.019 kcal·mol^{-1}. The average value of −1.766 ± 0.016 kcal·mol^{-1} for $\Delta_f H°$(298.15 K) of D_2O(g)–H_2O(g) and $\Delta_f H°$(298.15 K) of H_2O(g) = −57.795 ± 0.010 kcal·mol^{-1} [12] are used to obtain $\Delta_f H°$(298.15 K) for D_2O(g) = −59.561 ± 0.016 kcal·mol^{-1}.

Heat Capacity and Entropy

The thermodynamic functions of this table are analogous to those in the JANAF table for H_2O(g);[15] both tables are taken from Friedman and Haar.[16] Friedman and Haar applied their non–rigid–rotor, anharmonic–oscillator treatment (with vibrational–rotational coupling terms and low–temperature rotational corrections) to the infrared–spectra analyses of Benedict *et al.*,[17] and of Benedict *et al.*[18] In the present table for D_2O, the values of $C_p°$ of Friedman and Haar between 4000 and 5000 K were extrapolated linearly (except with a term in T^{-2}) from 5000 to 6000 K.

The National Bureau of Standards prepared this table[19] by critical analysis of data existing in 1972. Using $S°$(298.15 K) and $C_p°$ values selected by NBS,[19] we recalculate the table in terms of the current JANAF reference states for the elements.[15]

References

[1]F. D. Rossini, J. W. Knowlton, and H. L. Johnston, J. Res. Nat. Bur. Stand. **24**, 369 (1940).
[2]W. C. Duer and G. L. Bertrand, J. Chem. Phys. **53**, 3020 (1970).

Continued on page 1048

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.958	−246.251	−246.251	INFINITE
100	33.299	161.756	228.282	−6.653	−247.148	−243.379	127.128
200	33.449	184.861	201.451	−3.318	−248.222	−239.185	62.469
298.15	34.255	198.339	198.339	0.	−249.203	−234.536	41.090
300	34.278	198.551	198.340	0.063	−249.221	−234.445	40.820
400	35.635	208.591	199.699	3.557	−250.135	−229.379	29.954
500	37.184	216.707	202.314	7.197	−250.954	−224.093	23.411
600	38.835	223.631	205.303	10.997	−251.681	−218.651	19.035
700	40.545	229.745	208.366	14.966	−252.320	−213.094	15.901
800	42.251	235.271	211.389	19.106	−252.873	−207.452	13.545
900	43.892	240.343	214.328	23.414	−253.346	−201.745	11.709
1000	45.424	245.048	217.168	27.881	−253.744	−195.990	10.237
1100	46.826	249.444	219.904	32.494	−254.078	−190.198	9.032
1200	48.091	253.574	222.540	37.241	−254.354	−184.378	8.026
1300	49.225	257.469	225.078	42.108	−254.581	−178.537	7.174
1400	50.236	261.155	227.525	47.082	−254.767	−172.680	6.443
1500	51.136	264.652	229.884	52.151	−254.917	−166.811	5.809
1600	51.938	267.978	232.162	57.306	−255.038	−160.934	5.254
1700	52.653	271.149	234.363	62.536	−255.136	−155.049	4.764
1800	53.292	274.177	236.491	67.834	−255.214	−149.159	4.328
1900	53.866	277.074	238.551	73.192	−255.277	−143.266	3.939
2000	54.382	279.850	240.547	78.605	−255.328	−137.369	3.588
2100	54.848	282.515	242.483	84.067	−255.371	−131.470	3.270
2200	55.270	285.076	244.361	89.573	−255.407	−125.569	2.981
2300	55.654	287.541	246.185	95.119	−255.439	−119.666	2.718
2400	56.004	289.918	247.958	100.702	−255.470	−113.763	2.476
2500	56.326	292.210	249.683	106.319	−255.500	−107.858	2.254
2600	56.621	294.425	251.361	111.967	−255.531	−101.951	2.048
2700	56.894	296.567	252.996	117.643	−255.564	−96.044	1.858
2800	57.146	298.641	254.589	123.345	−255.601	−90.135	1.681
2900	57.380	300.651	256.143	129.071	−255.642	−84.225	1.517
3000	57.598	302.600	257.660	134.820	−255.688	−78.313	1.364
3100	57.802	304.492	259.140	140.590	−255.740	−72.399	1.220
3200	57.993	306.330	260.586	146.380	−255.799	−66.484	1.085
3300	58.172	308.117	261.999	152.189	−255.864	−60.568	0.959
3400	58.342	309.856	263.381	158.014	−255.937	−54.648	0.840
3500	58.501	311.550	264.734	163.856	−256.018	−48.727	0.727
3600	58.652	313.200	266.057	169.714	−256.107	−42.803	0.621
3700	58.795	314.809	267.353	175.587	−256.205	−36.877	0.521
3800	58.931	316.379	268.623	181.473	−256.312	−30.947	0.425
3900	59.060	317.911	269.867	187.373	−256.428	−25.015	0.335
4000	59.184	319.408	271.087	193.285	−256.554	−19.080	0.249
4100	59.301	320.871	272.283	199.209	−256.690	−13.141	0.167
4200	59.414	322.301	273.457	205.145	−256.837	−7.200	0.090
4300	59.522	323.700	274.609	211.092	−256.994	−1.254	0.015
4400	59.626	325.070	275.741	217.049	−257.163	4.695	−0.056
4500	59.726	326.411	276.852	223.017	−257.342	10.648	−0.124
4600	59.822	327.725	277.944	228.994	−257.532	16.606	−0.189
4700	59.914	329.012	279.016	234.981	−257.734	22.568	−0.251
4800	60.003	330.275	280.071	240.977	−257.947	28.534	−0.311
4900	60.089	331.513	281.108	246.982	−258.173	34.505	−0.368
5000	60.172	332.728	282.129	252.995	−258.409	40.480	−0.423
5100	60.254	333.920	283.133	259.016	−258.658	46.460	−0.476
5200	60.333	335.091	284.121	265.045	−258.918	52.445	−0.527
5300	60.410	336.241	285.093	271.083	−259.190	58.436	−0.576
5400	60.484	337.371	286.051	277.127	−259.473	64.432	−0.623
5500	60.556	338.481	286.994	283.179	−259.768	70.432	−0.669
5600	60.626	339.573	287.923	289.238	−260.075	76.439	−0.713
5700	60.696	340.647	288.839	295.304	−260.392	82.450	−0.756
5800	60.764	341.703	289.741	301.377	−260.721	88.468	−0.797
5900	60.832	342.742	290.631	307.457	−261.060	94.491	−0.837
6000	60.898	343.765	291.508	313.544	−261.410	100.521	−0.875

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Hydrogen Sulfide–d_2 (D_2S) IDEAL GAS $M_r = 36.088204$

$S°(298.15\ K) = 215.284\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -20.997 \pm 0.8\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -23.891 \pm 0.8\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
1896.38(1)
855.45(1)
1999 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distance: S–D = 1.328 Å
Bond Angle: D–S–D = 92.2°
Product of the Moments of Inertia: $I_A I_B I_C = 0.3445 \times 10^{-117}\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(D_2S, g, 298.15\ K)$ was determined by Kapustinskii and Kankovskii[1] to be $-5.692 \pm 0.06\ kcal\cdot mol^{-1}$ (recalculated) from the reaction: (a+b) $D_2S(g)$ + (1.5a+0.5b) $O_2(g)$ = a $SO_2(g)$ + (a+b) $D_2O(g)$ + b S(rhombic). The difference of $\Delta_f H°(D_2S, g, 298.15\ K)$ minus $H_2S(g)$ for their work was calculated using their results for $\Delta_f H°(H_2S, g, 298.15\ K)$, $-4.92 \pm 0.08\ kcal\cdot mol^{-1}$ (recalculated), in the hope of eliminating possible systematic error due to uncertainty in the product formed.

The "spectroscopic" value of $\Delta_f H°(D_2S, g, 298.15\ K)$–$H_2S(g)$ was calculated from the appropriate thermal functions (see H_2, D_2, H_2S)[5] and the zero point energies of $H_2S(g)$, $D_2S(g)$,[2,3] $D_2(g)$,[4] and $H_2(g)$.[4]

The equilibrium data of Grafe *et al.*[5] for the exchange reaction $H_2(g) + D_2S(g) = D_2(g) + H_2S(g)$ were analyzed by third and second law methods.

Source	$\Delta_f H°(298.15\ K)$ of $D_{2\,S}(g)$–$H_{2\,S}(g)$, $kcal\cdot mol^{-1}$
Kapustinskii and Kankovskii[1]	-0.771 ± 0.10
Spectroscopic[2–4]	-0.810 ± 0.01
Grafe, Clusius, and Kruis[5] Third Law	-0.826 ± 0.05
Second Law	-0.887 ± 0.02

A weighted average of $-0.81 \pm 0.02\ kcal\cdot mol^{-1}$ was selected for $\Delta_f H°(298.15\ K)$ of $D_2S(g)$ minus $H_2S(g)$ and was added to the selected value of $\Delta_f H°(298.15\ K)$ of $H_2S(g)$[6] to determine $\Delta_f H°(298.15\ K)$ of D_2

Heat Capacity and Entropy

The thermodynamic functions were estimated from those in the present table for $H_2S(g)$[6] by adding those for $D_2S(g)$ and subtracting those for $H_2S(g)$, where both the added and subtracted functions were generated using the rigid–rotor harmonic oscillator approximation. In this calculation the molecular constants for D_2S were taken from Miller, Leroi and Meggers.[2]

The National Bureau of Standards prepared this table[7] by critical analysis of data existing in 1972. Using $S°(298.15\ K)$ and $C_p°$ values selected by NBS,[7] we recalculate the table in terms of the current JANAF reference states for the elements.

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Hydrogen Sulfide–D_2(D_2S) $D_2S_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−10.088	−20.997	−20.997	INFINITE
100	33.263	177.971	245.585	−6.761	−21.111	−26.377	13.778
200	33.932	201.151	218.221	−3.414	−22.360	−31.201	8.149
298.15	35.761	215.284	215.284	0.	−23.891	−35.300	6.184
300	35.794	215.506	215.285	0.066	−23.920	−35.371	6.159
400	37.999	226.102	216.715	3.755	−27.750	−38.856	5.074
500	40.342	234.833	219.489	7.672	−30.691	−41.300	4.315
600	42.673	242.396	222.690	11.824	−33.072	−43.189	3.760
700	44.836	249.140	225.995	16.202	−35.021	−44.717	3.337
800	46.748	255.254	229.276	20.782	−36.677	−45.986	3.003
900	48.488	260.864	232.479	25.547	−91.246	−45.980	2.669
1000	49.827	266.044	235.579	30.464	−91.320	−40.946	2.139
1100	51.028	270.850	238.570	35.508	−91.339	−35.907	1.705
1200	52.049	275.335	241.449	40.664	−91.320	−30.869	1.344
1300	52.923	279.537	244.219	45.913	−91.275	−25.833	1.038
1400	53.672	283.487	246.884	51.244	−91.215	−20.801	0.776
1500	54.321	287.212	249.450	56.644	−91.147	−15.773	0.549
1600	54.886	290.737	251.921	62.105	−91.077	−10.751	0.351
1700	55.379	294.079	254.303	67.619	−91.008	−5.733	0.176
1800	55.823	297.257	256.602	73.179	−90.942	−0.718	0.021
1900	56.208	300.286	258.822	78.781	−90.881	4.292	−0.118
2000	56.568	303.178	260.968	84.420	−90.826	9.300	−0.243
2100	56.881	305.946	263.045	90.093	−90.777	14.305	−0.356
2200	57.166	308.599	265.055	95.796	−90.736	19.308	−0.458
2300	57.430	311.146	267.004	101.525	−90.701	24.309	−0.552
2400	57.676	313.595	268.895	107.281	−90.673	29.309	−0.638
2500	57.902	315.955	270.730	113.060	−90.652	34.308	−0.717
2600	58.107	318.230	272.514	118.861	−90.638	39.306	−0.790
2700	58.300	320.426	274.248	124.681	−90.630	44.304	−0.857
2800	58.480	322.550	275.935	130.520	−90.629	49.301	−0.920
2900	58.647	324.605	277.578	136.377	−90.635	54.299	−0.978
3000	58.810	326.596	279.179	142.250	−90.647	59.296	−1.032
3100	58.965	328.527	280.740	148.138	−90.666	64.295	−1.083
3200	59.112	330.401	282.263	154.042	−90.691	69.294	−1.131
3300	59.245	332.222	283.749	159.960	−90.723	74.294	−1.176
3400	59.379	333.993	285.201	165.891	−90.763	79.295	−1.218
3500	59.509	335.716	286.620	171.836	−90.810	84.297	−1.258
3600	59.630	337.394	288.007	177.793	−90.865	89.301	−1.296
3700	59.748	339.029	289.364	183.762	−90.928	94.307	−1.331
3800	59.860	340.624	290.692	189.742	−90.999	99.314	−1.365
3900	59.973	342.181	291.992	195.734	−91.079	104.323	−1.397
4000	60.082	343.700	293.266	201.737	−91.169	109.335	−1.428
4100	60.187	345.185	294.515	207.750	−91.268	114.349	−1.457
4200	60.291	346.637	295.738	213.774	−91.377	119.365	−1.485
4300	60.392	348.057	296.939	219.808	−91.497	124.384	−1.511
4400	60.488	349.446	298.116	225.852	−91.627	129.406	−1.536
4500	60.588	350.807	299.272	231.906	−91.768	134.431	−1.560
4600	60.676	352.139	300.407	237.970	−91.920	139.459	−1.584
4700	60.768	353.445	301.522	244.042	−92.084	144.491	−1.606
4800	60.865	354.726	302.617	250.123	−92.259	149.526	−1.627
4900	60.953	355.982	303.693	256.214	−92.445	154.565	−1.648
5000	61.045	357.214	304.751	262.314	−92.643	159.609	−1.667
5100	61.124	358.424	305.792	268.423	−92.851	164.655	−1.686
5200	61.216	359.611	306.815	274.540	−93.071	169.707	−1.705
5300	61.300	360.778	307.822	280.665	−93.301	174.762	−1.722
5400	61.383	361.925	308.814	286.800	−93.541	179.823	−1.739
5500	61.467	363.052	309.790	292.942	−93.791	184.887	−1.756
5600	61.551	364.160	310.751	299.093	−94.050	189.956	−1.772
5700	61.634	365.250	311.697	305.252	−94.317	195.030	−1.787
5800	61.710	366.323	312.630	311.419	−94.593	200.109	−1.802
5900	61.798	367.379	313.549	317.595	−94.875	205.192	−1.817
6000	61.873	368.418	314.455	323.779	−95.163	210.281	−1.831

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Hydrogen Sulfide–D_2(D_2S) $D_2S_1(g)$

$S°(298.15\ K) = 203.931\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -51.622 \pm 0.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -58.576 \pm 0.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies υ, cm^{-1}
2495(1)
793(1)
2652(2)
1225(2)

Ground State Quantum Weight: 1 σ(external) = 3
Point Group: C_{3v} σ(internal) = 2
Bond Length: N–D = 1.0124 Å
Bond Angle: 106.67°
Product of the Moments of Inertia; $I_A I_B I_C = 2.5775 \times 10^{-118}\ g^3·cm^6$

Enthalpy of Formation

A "spectroscopic" value for the difference in $\Delta_f H°(298.15\ K)$ of $ND_3(g)$ minus $NH_3(g)$ of $-3.029 \pm 0.01\ kcal·mol^{-1}$ was calculated from the appropraite thermal functions (refer to H_2, D_2, NH_3,[6,7] zero point energies of $ND_3(g)$ and $NH_3(g)$,[1,2] and the zero point energies of $H_2(g)$ and $D_2(g)$ given by Herzberg and Monfils.[3]

Analysis of the equilibrium data of Schulz and Schaefer[4] for $K_p°$ (1 atm, 660–773 K) for $1/2N_2(g) + 3/2D_2(g) = ND_3(g)$ gave the following:

	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$	Drift $cal·K^{-1}·mol^{-1}$	$\Delta S°$(obsv.-calc., 298.15 K)
third law	−13.80	−1.2	—
second law[a]	−13.0 ± 0.38	—	$+1.3 \pm 0.5\ cal·K^{-1}·mol^{-1}$

[a]Asuming $\Delta C_p° = 1.237–0.00608(T–700)\ cal\ K^{-1}·mol^{-1}$

Using the results from the same authors' data for NH(g),[6] one obtains a difference in $\Delta_f H°(298.15K)$ for $ND_3(g)$ minus $NH_3(g)$ of $-2.93 \pm 0.14\ kcal·mol^{-1}$ (third law) and $-2.22 \pm 0.4\ kcal·mol^{-1}$ (second law). The third law value agrees with the "spectroscopic" value within combined uncertainty intervals.

A value of $-3.03 \pm 0.1\ kcal·mol^{-1}$ was added to the JANAF selection for $\Delta_f H°(298.15\ K)$ of $NH_3(g)$, $-10.97 \pm 0.10\ kcal·mol^{-1}$,[5,6] to obtain $\Delta_f H°(298.15\ K)$ of $ND_3(g)$.

Heat Capacity and Entropy

The thermodynamic functions were estimated from those in the present table for $NH_3(g)$[6] by adding those for $ND_3(g)$ and subtracting those for $NH_3(g)$, where both the added and subtracted functions were generated using the rigid–rotor harmonicoscillator approximation. In this calculation the molecular constants for ND_3 were taken from Duncan and Mills[1] and Benedict and Plyler.[2]

The National Bureau of Standards prepared this table[7] by critical analysis of data existing in 1972. Using $S°$, $C_p°$ and $\Delta_f H°$ selected by NBS,[7] we recalculate the table in terms of current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.234	−51.622	−51.622	INFINITE
100	33.296	166.193	235.480	−6.929	−53.893	−45.604	23.821
200	34.551	189.507	207.289	−3.556	−56.406	−36.317	9.485
298.15	38.225	203.931	203.931	0.	−58.576	−25.984	4.552
300	38.305	204.168	203.932	0.071	−58.613	−25.782	4.489
400	42.924	215.822	205.490	4.133	−60.392	−14.558	1.901
500	47.375	225.883	208.583	8.650	−61.739	−2.934	0.307
600	51.472	234.888	212.229	13.595	−62.707	8.923	−0.777
700	55.208	243.108	216.061	18.932	−63.362	20.917	−1.561
800	58.589	250.704	219.923	24.625	−63.761	32.987	−2.154
900	61.601	257.782	223.741	30.638	−63.953	45.094	−2.617
1000	64.258	264.413	227.480	36.933	−63.979	57.213	−2.989
1100	66.576	270.649	231.124	43.478	−63.873	69.328	−3.292
1200	68.592	276.530	234.665	50.238	−63.660	81.429	−3.544
1300	70.346	282.091	238.101	57.187	−63.361	93.508	−3.757
1400	71.869	287.361	241.433	64.299	−62.995	105.561	−3.939
1500	73.199	292.366	244.663	71.554	−62.573	117.587	−4.095
1600	74.362	297.128	247.795	78.933	−62.107	129.582	−4.230
1700	75.379	301.667	250.831	86.421	−61.604	141.548	−4.349
1800	76.278	306.002	253.777	94.005	−61.072	153.483	−4.454
1900	77.069	310.148	256.635	101.673	−60.516	165.387	−4.547
2000	77.768	314.119	259.411	109.416	−59.942	177.262	−4.630
2100	78.387	317.928	262.107	117.224	−59.353	189.108	−4.704
2200	78.940	321.588	264.728	125.091	−58.754	200.925	−4.771
2300	79.429	325.108	267.278	133.010	−58.147	212.715	−4.831
2400	79.868	328.498	269.758	140.975	−57.535	224.479	−4.886
2500	80.257	331.766	272.174	148.982	−56.920	236.217	−4.935
2600	80.601	334.921	274.527	157.025	−56.306	247.930	−4.981
2700	80.906	337.969	276.820	165.101	−55.694	259.620	−5.023
2800	81.182	340.916	279.057	173.205	−55.087	271.287	−5.061
2900	81.416	343.769	281.240	181.335	−54.486	282.933	−5.096
3000	81.634	346.533	283.370	189.488	−53.893	294.557	−5.129
3100	81.814	349.213	285.451	197.661	−53.310	306.163	−5.159
3200	81.973	351.813	287.484	205.850	−52.739	317.750	−5.187
3300	82.107	354.337	289.472	214.055	−52.181	329.319	−5.213
3400	82.224	356.790	291.416	222.271	−51.639	340.871	−5.237
3500	82.326	359.175	293.318	230.499	−51.112	352.408	−5.259
3600	82.408	361.496	295.180	238.736	−50.604	363.930	−5.280
3700	82.466	363.754	297.003	246.980	−50.115	375.438	−5.300
3800	82.508	365.954	298.789	255.228	−49.647	386.933	−5.319
3900	82.537	368.098	300.539	263.481	−49.201	398.416	−5.336
4000	82.550	370.188	302.254	271.735	−48.779	409.888	−5.353
4100	82.548	372.226	303.936	279.990	−48.382	421.350	−5.368
4200	82.534	374.215	305.585	288.245	−48.011	432.802	−5.383
4300	82.506	376.157	307.204	296.497	−47.667	444.246	−5.397
4400	82.467	378.053	308.793	304.745	−47.352	455.682	−5.410
4500	82.414	379.906	310.353	312.990	−47.065	467.111	−5.422
4600	82.349	381.716	311.884	321.228	−46.809	478.535	−5.434
4700	82.276	383.487	313.389	329.459	−46.583	489.953	−5.445
4800	82.186	385.218	314.868	337.682	−46.389	501.366	−5.456
4900	82.082	386.912	316.321	345.896	−46.227	512.776	−5.466
5000	81.965	388.569	317.749	354.098	−46.099	524.183	−5.476
5100	81.818	390.190	319.154	362.287	−46.006	535.587	−5.486
5200	81.780	391.779	320.535	370.467	−45.942	546.991	−5.495
5300	81.746	393.336	321.894	378.643	−45.902	558.393	−5.503
5400	81.712	394.864	323.231	386.816	−45.884	569.795	−5.512
5500	81.680	396.363	324.547	394.985	−45.887	581.196	−5.520
5600	81.649	397.834	325.843	403.152	−45.911	592.598	−5.528
5700	81.619	399.279	327.119	411.315	−45.953	603.999	−5.535
5800	81.591	400.698	328.375	419.476	−46.013	615.403	−5.542
5900	81.564	402.093	329.613	427.633	−46.089	626.807	−5.549
6000	81.538	403.464	330.832	435.789	−46.180	638.213	−5.556

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Continued from page 1036

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Continued from page 1045

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0 to 6000 K Ideal Gas

$S°(298.15\ K) = 20.979 \pm 0.013\ (\pm 2.0)\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 0\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

As shown by Sommerfeld,[1] the electron gas is a degenerate Fermi–Dirac gas and its properties will differ from the classical (Boltzmann) gas. These deviations will increase as the temperature decreases or as the density increases.[2,3] Due to the low mass of the electron, these departures from classical behavior will persist to higher temperatures and lower densities than for atomic systems. Under conditions of 1 atm pressure, Gordon[3] showed that the deviation of the Fermi–Dirac gas from the Boltzmann gas is negligible above 1250 K. Below this temperature the deviation between classical and quantum statistics will be significant; Mitchell[4] calculates $S°(298.15\ K) = 22.72\ J\cdot K^{-1}\cdot mol^{-1}$ for the Fermi–Dirac gas compared to the classical value of $20.87\ J\cdot K^{-1}\cdot mol^{-1}$ for a pressure of 1 atm.

Despite these known deviations we have chosen to present the classical (Boltzmann) values here since the primary purpose of this table is to serve as a reference state for the calculation of tables of thermodynamic properties for atomic and molecular ions. When ionization equilibria are considered, the density (or partial pressure) of the electron gas will be extremely low except at very high temperatures. At an electron partial pressure of 10^{-6} bar, the deviation between classical and quantum statistics will be significant only below 5 K.[3] Deviations from classical statistics are encountered at about this same temperature in some atomic and molecular systems at 1 bar pressure; these are usually ignored since the deviations in the enthalpy and entropy are quite small. Therefore, although this ideal-gas table has the formalism of 1 bar as the standard reference state, it should not be applied to real systems where the electron partial pressure exceeds 10^{-6} bar. An equivalent statement is that the electron gas will behave as an ideal gas only at electron partial pressures less than about 10^{-6} bar, with deviations from ideal gas behavior at higher pressures as a result of the departure from classical statistics.

The thermodynamic functions are calculated here via Boltzmann statistics assuming the electron gas to be an ideal monatomic gas with two equivalent spin states. The relative ionic mass is the electron rest mass as reported in the 1973 CODATA fundamental constants.[5] The first uncertainty in $S°(298.15\ K)$ represents the uncertainty in the fundamental constants and electron rest mass (i.e., the uncertainty below 10^{-6} bar where classical statistics is valid) while the value given in parenthesis represents the uncertainty due to the use of classical rather than quantum statistics at 1 atm pressure. Values below 298.15 K are omitted from the table since the classical calculation (at 1 bar pressure) results in negative values of entropy below 109 K.[4] The values of the thermodynamic functions agree with those published by Gurvich *et al.*[6] except for two minor differences. First, the entropy differs by $0.1094\ J\cdot K^{-1}\cdot mol^{-1}$ because this table uses a standard state pressure of 1 bar, whereas Gurvich *et al.*[6] used 1 atm. Second, smaller entropy differences occur due to the use of slightly different values of R.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
0				−6.197			
100							
200							
250							
298.15	20.786	20.979	20.979	0.	0.	0.	0.
300	20.786	21.107	20.979	0.038	0.	0.	0.
350	20.786	24.311	21.232	1.078	0.	0.	0.
400	20.786	27.087	21.794	2.117	0.	0.	0.
450	20.786	29.535	22.521	3.156	0.	0.	0.
500	20.786	31.725	23.334	4.196	0.	0.	0.
600	20.786	35.515	25.058	6.274	0.	0.	0.
700	20.786	38.719	26.786	8.353	0.	0.	0.
800	20.786	41.495	28.455	10.431	0.	0.	0.
900	20.786	43.943	30.043	12.510	0.	0.	0.
1000	20.786	46.133	31.544	14.589	0.	0.	0.
1100	20.786	48.114	32.962	16.667	0.	0.	0.
1200	20.786	49.923	34.301	18.746	0.	0.	0.
1300	20.786	51.587	35.568	20.824	0.	0.	0.
1400	20.786	53.127	36.768	22.903	0.	0.	0.
1500	20.786	54.561	37.907	24.982	0.	0.	0.
1600	20.786	55.903	38.990	27.060	0.	0.	0.
1700	20.786	57.163	40.022	29.139	0.	0.	0.
1800	20.786	58.351	41.008	31.217	0.	0.	0.
1900	20.786	59.475	41.950	33.296	0.	0.	0.
2000	20.786	60.541	42.853	35.375	0.	0.	0.
2100	20.786	61.555	43.720	37.453	0.	0.	0.
2200	20.786	62.522	44.553	39.532	0.	0.	0.
2300	20.786	63.446	45.354	41.610	0.	0.	0.
2400	20.786	64.331	46.127	43.689	0.	0.	0.
2500	20.786	65.179	46.872	45.768	0.	0.	0.
2600	20.786	65.994	47.592	47.846	0.	0.	0.
2700	20.786	66.779	48.288	49.925	0.	0.	0.
2800	20.786	67.535	48.962	52.004	0.	0.	0.
2900	20.786	68.264	49.615	54.082	0.	0.	0.
3000	20.786	68.969	50.249	56.161	0.	0.	0.
3100	20.786	69.650	50.863	58.239	0.	0.	0.
3200	20.786	70.310	51.461	60.318	0.	0.	0.
3300	20.786	70.950	52.042	62.397	0.	0.	0.
3400	20.786	71.570	52.607	64.475	0.	0.	0.
3500	20.786	72.173	53.158	66.554	0.	0.	0.
3600	20.786	72.759	53.694	68.632	0.	0.	0.
3700	20.786	73.328	54.217	70.711	0.	0.	0.
3800	20.786	73.882	54.727	72.790	0.	0.	0.
3900	20.786	74.422	55.225	74.868	0.	0.	0.
4000	20.786	74.949	55.712	76.947	0.	0.	0.
4100	20.786	75.462	56.187	79.025	0.	0.	0.
4200	20.786	75.963	56.652	81.104	0.	0.	0.
4300	20.786	76.452	57.107	83.183	0.	0.	0.
4400	20.786	76.930	57.552	85.261	0.	0.	0.
4500	20.786	77.397	57.988	87.340	0.	0.	0.
4600	20.786	77.854	58.415	89.418	0.	0.	0.
4700	20.786	78.301	58.833	91.497	0.	0.	0.
4800	20.786	78.738	59.243	93.576	0.	0.	0.
4900	20.786	79.167	59.646	95.654	0.	0.	0.
5000	20.786	79.587	60.040	97.733	0.	0.	0.
5100	20.786	79.998	60.428	99.811	0.	0.	0.
5200	20.786	80.402	60.808	101.890	0.	0.	0.
5300	20.786	80.798	61.181	103.969	0.	0.	0.
5400	20.786	81.187	61.548	106.047	0.	0.	0.
5500	20.786	81.568	61.909	108.126	0.	0.	0.
5600	20.786	81.942	62.263	110.204	0.	0.	0.
5700	20.786	82.310	62.612	112.283	0.	0.	0.
5800	20.786	82.672	62.954	114.362	0.	0.	0.
5900	20.786	83.027	63.292	116.440	0.	0.	0.
6000	20.786	83.377	63.623	118.519	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

IP(F, g) = 140524.5 ± 0.4 cm^{-1}
$S°$(298.15 K) = 158.750 ± 0.003 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 77.28 ± 0.30 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 79.39 ± 0.30 kJ·mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P°_{3/2}$	0.0	4
$^2P°_{1/2}$	404.1	2

Enthalpy of Formation

The adopted value for the enthalpy of formation of F(g) is the value proposed by CODATA;[1] $\Delta_f H°$(F, g, 298.15 K) = 79.38 ± 0.30 kJ·mol^{-1}. This value is calculated from the dissociation energy of F_2(g), $D_0°$ = 12920 ± 50 cm^{-1} (154.56 ± 0.60 kJ·mol^{-1}), obtained from the extensive spectroscopic measurements of Colbourn *et al.*[2] This value is in satisfactory agreement with the results of the equilibrium measurements of Doescher[3] and the photoionization measurements of Berkowitz *et al.*[4] It is also in good agreement with the value calculated from the enthalpies of formation[5] and vaporization[6] of HF(l) and the spectroscopic data for the dissociation energy of HF(g).[4,7,8] This same value is recommended by Brewer and Winn,[9] Huber and Herzberg[10] and Gurvich *et al.*,[13] whereas Wagman *et al.*[21] adopted a dissociation energy which is approximately 0.76 kJ·mol^{-1} smaller.

Additional discussions on the enthalpy of formation may be found in the earlier reviews by the JANAF[11] and NBS[12] groups and a recent review by Gurvich *et al.*[13] Coxon[14] has summarized the spectroscopic information on the lower electronic states of the halogens as of 1973. The more recent spectroscopic studies are discussed by Colbourn *et al.*[2]

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[15,16] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 100000 cm^{-1}. Our calculations indicate that any reasonable method of filling in the missing levels and cutting off the summation in the partition function[17] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels. Therefore, we list only the ground state and the first excited state. Extension to higher temperatures may require consideration of the higher excited states and utilization of different fill and cutoff procedures.

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations[1] except for two minor differences. First, the entropy differs by 0.1094 J K^{-1}·mol^{-1} because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 J K^{-1}·mol^{-1} for the monatomic halogens arise due to the use of slightly different values for the relative atomic mass and for R; this table uses R = 8.31441 J K^{-1}·mol^{-1}. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[18] Gurvich *et al.*[13] and Wagman *et al.*[21] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[19] and the 1973 values,[20] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.518	77.284	77.284	INFINITE
100	21.205	134.479	178.805	−4.433	77.916	72.987	−38.124
200	22.605	149.670	160.833	−2.233	78.652	67.783	−17.703
250	22.783	154.738	159.125	−1.097	79.037	65.021	−13.585
298.15	22.746	158.750	158.750	0.	79.390	62.289	−10.913
300	22.742	158.891	158.751	0.042	79.403	62.183	−10.827
350	22.603	162.387	159.027	1.176	79.743	59.286	−8.848
400	22.431	165.394	159.639	2.302	80.053	56.342	−7.358
450	22.259	168.026	160.428	3.419	80.337	53.361	−6.194
500	22.100	170.363	161.307	4.528	80.597	50.350	−5.260
600	21.832	174.368	163.161	6.724	81.056	44.256	−3.853
700	21.628	177.717	165.008	8.897	81.453	38.090	−2.842
800	21.474	180.594	166.780	11.051	81.803	31.871	−2.081
900	21.357	183.117	168.458	13.193	82.117	25.611	−1.486
1000	21.266	185.362	170.038	15.324	82.403	19.317	−1.009
1100	21.194	187.385	171.525	17.446	82.666	12.995	−0.617
1200	21.137	189.227	172.924	19.563	82.909	6.651	−0.290
1300	21.091	190.917	174.244	21.674	83.136	0.287	−0.012
1400	21.053	192.478	175.492	23.781	83.348	−6.095	0.227
1500	21.022	193.930	176.673	25.885	83.546	−12.490	0.435
1600	20.996	195.286	177.795	27.986	83.733	−18.899	0.617
1700	20.974	196.558	178.861	30.085	83.909	−25.319	0.778
1800	20.955	197.756	179.878	32.181	84.075	−31.749	0.921
1900	20.939	198.889	180.849	34.276	84.234	−38.188	1.050
2000	20.925	199.963	181.778	36.369	84.387	−44.635	1.166
2100	20.913	200.983	182.669	38.461	84.535	−51.090	1.271
2200	20.902	201.956	183.523	40.551	84.681	−57.551	1.366
2300	20.893	202.885	184.345	42.641	84.827	−64.020	1.454
2400	20.885	203.774	185.136	44.730	84.974	−70.494	1.534
2500	20.877	204.626	185.899	46.818	85.125	−76.975	1.608
2600	20.871	205.445	186.635	48.906	85.281	−83.462	1.677
2700	20.865	206.232	187.346	50.992	85.444	−89.956	1.740
2800	20.860	206.991	188.034	53.079	85.617	−96.455	1.799
2900	20.855	207.723	188.701	55.164	85.800	−102.961	1.855
3000	20.851	208.430	189.347	57.250	85.994	−109.473	1.906
3100	20.847	209.114	189.973	59.334	86.202	−115.992	1.954
3200	20.843	209.775	190.582	61.419	86.423	−122.518	2.000
3300	20.840	210.417	191.173	63.503	86.660	−129.051	2.043
3400	20.837	211.039	191.748	65.587	86.911	−135.592	2.083
3500	20.834	211.643	192.308	67.670	87.179	−142.140	2.121
3600	20.831	212.230	192.854	69.754	87.463	−148.695	2.158
3700	20.829	212.800	193.385	71.837	87.764	−155.259	2.192
3800	20.827	213.356	193.903	73.920	88.081	−161.832	2.225
3900	20.825	213.897	194.409	76.002	88.416	−168.413	2.256
4000	20.823	214.424	194.903	78.084	88.767	−175.003	2.285
4100	20.821	214.938	195.385	80.167	89.135	−181.602	2.314
4200	20.820	215.440	195.857	82.249	89.520	−188.209	2.341
4300	20.818	215.930	196.318	84.331	89.921	−194.827	2.367
4400	20.817	216.408	196.769	86.412	90.338	−201.454	2.392
4500	20.815	216.876	197.211	88.494	90.771	−208.090	2.415
4600	20.814	217.334	197.643	90.575	91.220	−214.736	2.438
4700	20.813	217.781	198.067	92.657	91.685	−221.392	2.461
4800	20.812	218.219	198.482	94.738	92.164	−228.059	2.482
4900	20.811	218.648	198.889	96.819	92.658	−234.735	2.502
5000	20.810	219.069	199.289	98.900	93.166	−241.422	2.522
5100	20.809	219.481	199.681	100.981	93.687	−248.119	2.541
5200	20.808	219.885	200.065	103.062	94.223	−254.826	2.560
5300	20.807	220.281	200.443	105.143	94.771	−261.544	2.578
5400	20.807	220.670	200.814	107.224	95.332	−268.272	2.595
5500	20.806	221.052	201.179	109.304	95.905	−275.011	2.612
5600	20.805	221.427	201.537	111.385	96.491	−281.760	2.628
5700	20.805	221.795	201.889	113.465	97.088	−288.520	2.644
5800	20.804	222.157	202.235	115.546	97.696	−295.290	2.659
5900	20.803	222.513	202.576	117.626	98.315	−302.071	2.674
6000	20.803	222.862	202.911	119.706	98.944	−308.862	2.689

PREVIOUS: September 1965 (1 atm) CURRENT: June 1982 (1 bar)

$IP(F^+, g) = 282058.6 \pm 1.5\ cm^{-1}$
$S°(298.15\ K) = 161.728 \pm 0.005\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1758.33 \pm 0.3\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1766.826]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.0	5
$^3P_1$	341.0	3
$^3P_0$	489.9	1
$^1D_2$	20873.4	5
$^1S_0$	44918.1	1

Enthalpy of Formation

$\Delta_f H°(F^+, g, 0\ K)$ is calculated from $\Delta_f H°(F, g, 0\ K)$[1] using the spectroscopic value of IP(F) = 140524.5 ± 0.4 cm^{-1}(1681.047 ± 0.005 $kJ\cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ\cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ\cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization potential and appearance potential data.

$\Delta_f H°(F^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(F, g, 0\ K)$ by using IP(F) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for F(g), $F^+(g)$, and e^-(ref). $\Delta_f H°(F \rightarrow F^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ\cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the lowest four excited states; the next lowest level is approximately 164797 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and four excited states, with the energy of these states taken from recent study by Moore.[2] The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass, the fundamental constants, and the position of the four lowest excited states. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[7]

References

[1]JANAF Thermochemical Tables: F(g), 3–31–82; e^-(ref), 3–31–82.
[2]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–34, (1970).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.711	1758.331		
100	21.738	136.478	182.608	−4.613			
200	23.642	152.281	163.889	−2.322			
250	23.694	157.569	162.116	−1.137			
298.15	23.497	161.728	161.728	0.	1766.826	1742.583	−305.293
300	23.487	161.873	161.728	0.043	1766.879	1742.433	−303.385
350	23.197	165.472	162.013	1.211	1768.291	1738.246	−259.419
400	22.904	168.550	162.643	2.363	1769.668	1733.860	−226.419
450	22.636	171.232	163.451	3.502	1771.012	1729.303	−200.732
500	22.404	173.605	164.350	4.627	1772.328	1724.597	−180.167
600	22.035	177.655	166.241	6.848	1774.891	1714.809	−149.287
700	21.770	181.031	168.120	9.038	1777.383	1704.598	−127.199
800	21.577	183.925	169.919	11.205	1779.824	1694.033	−110.609
900	21.433	186.457	171.619	13.355	1782.225	1683.164	−97.688
1000	21.324	188.710	173.217	15.492	1784.597	1672.030	−87.338
1100	21.240	190.738	174.719	17.621	1786.943	1660.659	−78.858
1200	21.174	192.583	176.132	19.741	1789.270	1649.076	−71.782
1300	21.121	194.276	177.464	21.856	1791.578	1637.300	−65.788
1400	21.078	195.840	178.721	23.966	1793.872	1625.346	−60.642
1500	21.043	197.293	179.911	26.072	1796.151	1613.229	−56.178
1600	21.014	198.650	181.041	28.174	1798.418	1600.960	−52.266
1700	20.989	199.923	182.114	30.275	1800.674	1588.550	−48.810
1800	20.968	201.122	183.137	32.372	1802.920	1576.007	−45.735
1900	20.951	202.255	184.114	34.468	1805.159	1563.340	−42.979
2000	20.935	203.329	185.048	36.563	1807.391	1550.555	−40.496
2100	20.922	204.350	185.943	38.656	1809.619	1537.658	−38.247
2200	20.911	205.324	186.802	40.747	1811.845	1524.655	−36.200
2300	20.902	206.253	187.628	42.838	1814.070	1511.551	−34.328
2400	20.894	207.142	188.422	44.928	1816.297	1498.351	−32.611
2500	20.887	207.995	189.188	47.017	1818.527	1485.057	−31.029
2600	20.882	208.814	189.928	49.105	1820.763	1471.674	−29.566
2700	20.879	209.602	190.642	51.193	1823.006	1458.205	−28.211
2800	20.876	210.361	191.333	53.281	1825.259	1444.653	−26.950
2900	20.876	211.094	192.001	55.368	1827.522	1431.020	−25.775
3000	20.876	211.802	192.650	57.456	1829.798	1417.309	−24.678
3100	20.878	212.486	193.279	59.544	1832.087	1403.521	−23.649
3200	20.882	213.149	193.889	61.632	1834.391	1389.660	−22.684
3300	20.888	213.792	194.483	63.720	1836.710	1375.726	−21.776
3400	20.895	214.416	195.060	65.809	1839.045	1361.722	−20.920
3500	20.904	215.021	195.622	67.899	1841.398	1347.649	−20.113
3600	20.914	215.610	196.169	69.990	1843.768	1333.508	−19.349
3700	20.926	216.184	196.702	72.082	1846.156	1319.302	−18.625
3800	20.940	216.742	197.222	74.175	1848.563	1305.030	−17.939
3900	20.956	217.286	197.729	76.270	1850.988	1290.695	−17.287
4000	20.974	217.817	198.225	78.367	1853.432	1276.297	−16.667
4100	20.993	218.335	198.709	80.465	1855.895	1261.839	−16.076
4200	21.014	218.841	199.183	82.565	1858.377	1247.319	−15.513
4300	21.037	219.336	199.645	84.668	1860.877	1232.741	−14.975
4400	21.061	219.820	200.099	86.773	1863.396	1218.104	−14.461
4500	21.086	220.293	200.542	88.880	1865.934	1203.410	−13.969
4600	21.113	220.757	200.976	90.990	1868.490	1188.659	−13.498
4700	21.141	221.211	201.402	93.103	1871.064	1173.852	−13.046
4800	21.171	221.657	201.820	95.218	1873.656	1158.991	−12.612
4900	21.202	222.094	202.229	97.337	1876.266	1144.075	−12.196
5000	21.234	222.522	202.630	99.459	1878.893	1129.105	−11.796
5100	21.267	222.943	203.025	101.584	1881.538	1114.083	−11.411
5200	21.300	223.356	203.412	103.712	1884.199	1099.009	−11.040
5300	21.335	223.762	203.792	105.844	1886.877	1083.884	−10.682
5400	21.371	224.162	204.165	107.979	1889.571	1068.708	−10.338
5500	21.407	224.554	204.532	110.118	1892.282	1053.482	−10.005
5600	21.443	224.940	204.893	112.261	1895.007	1038.206	−9.684
5700	21.480	225.320	205.248	114.407	1897.749	1022.882	−9.374
5800	21.518	225.694	205.598	116.557	1900.505	1007.509	−9.074
5900	21.556	226.062	205.942	118.710	1903.276	992.089	−8.783
6000	21.594	226.425	206.280	120.868	1906.061	976.622	−8.502

PREVIOUS: CURRENT: June 1982 (1 bar)

EA(F, g) = 3.399 ± 0.003 eV
$S°(298.15\ K)$ = 145.576 ± 0.005 J K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = −250.67 ± 0.6 kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = [−265.085] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(F^-, g, 0\ K)$ is calculated from $\Delta_f H°(F, g, 0\ K)$[1] using the adopted electron affinity of EA (F) = 3.399 ± 0.003 eV (327.951 ± 0.289 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[10] is based on plasma absorption and plasma emission studies.[5, 6] Additional information on $F^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H°(F^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(F, g, 0\ K)$ by using EA(F) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for $F^-(g)$, F(g), and e^-(ref). $\Delta_r H°(F^- \rightarrow F + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for $F^-(g)$ is given by Hotop and Lineberger,[2, 10] Rosenstock *et al.*[3] and Massey.[4] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

entropy at all temperatures (0–6000 K) agrees within 0.001 J K^{-1}·mol^{-1} with the values of Gurvich *et al.*[8] except for one minor difference. The entropy differs by 0.1094 J K^{-1}·mol^{-1} because this table uses a standard-state pressure of 1 bar, whereas the tabulation of Gurvich *et al.*[8] is based on 1 atm. The estimated uncertainty is due to uncertainties in the relative ionic mass and the fundamental constants which are based on the 1981 scale[9] and the 1973 values,[7] respectively.

References

[1]JANAF Thermochemical Tables: F(g), 6–30–82; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	−250.667		
100	20.786	122.869	164.056	−4.119			
200	20.786	137.276	147.477	−2.040			
250	20.786	141.915	145.918	−1.001			
298.15	20.786	145.576	145.576	0.	−255.079	−261.997	45.901
300	20.786	145.704	145.576	0.038	−255.108	−262.040	45.625
350	20.786	148.909	145.829	1.078	−255.903	−263.133	39.270
400	20.786	151.684	146.392	2.117	−256.718	−264.110	34.489
450	20.786	154.132	147.118	3.156	−257.552	−264.984	30.759
500	20.786	156.322	147.931	4.196	−258.401	−265.765	27.764
600	20.786	160.112	149.655	6.274	−260.138	−267.075	23.251
700	20.786	163.316	151.384	8.353	−261.913	−268.092	20.005
800	20.786	166.092	153.053	10.431	−263.718	−268.852	17.554
900	20.786	168.540	154.640	12.510	−265.545	−269.384	15.635
1000	20.786	170.730	156.142	14.589	−267.390	−269.711	14.088
1100	20.786	172.711	157.559	16.667	−269.250	−269.854	12.814
1200	20.786	174.520	158.898	18.746	−271.123	−269.826	11.745
1300	20.786	176.184	160.165	20.824	−273.008	−269.641	10.834
1400	20.786	177.724	161.365	22.903	−274.903	−269.312	10.048
1500	20.786	179.158	162.504	24.982	−276.808	−268.846	9.362
1600	20.786	180.500	163.587	27.060	−278.723	−268.253	8.758
1700	20.786	181.760	164.619	29.139	−280.645	−267.539	8.220
1800	20.786	182.948	165.605	31.217	−282.575	−266.713	7.740
1900	20.786	184.072	166.548	33.296	−284.511	−265.779	7.307
2000	20.786	185.138	167.451	35.375	−286.452	−264.743	6.914
2100	20.786	186.152	168.317	37.453	−288.395	−263.609	6.557
2200	20.786	187.119	169.150	39.532	−290.340	−262.383	6.230
2300	20.786	188.043	169.952	41.610	−292.284	−261.069	5.929
2400	20.786	188.928	170.724	43.689	−294.226	−259.670	5.652
2500	20.786	189.776	171.469	45.768	−296.163	−258.191	5.395
2600	20.786	190.591	172.189	47.846	−298.094	−256.634	5.156
2700	20.786	191.376	172.885	49.925	−300.017	−255.002	4.933
2800	20.786	192.132	173.559	52.004	−301.931	−253.300	4.725
2900	20.786	192.861	174.212	54.082	−303.834	−251.530	4.531
3000	20.786	193.566	174.846	56.161	−305.725	−249.694	4.348
3100	20.786	194.248	175.461	58.239	−307.602	−247.795	4.175
3200	20.786	194.907	176.058	60.318	−309.465	−245.836	4.013
3300	20.786	195.547	176.639	62.397	−311.313	−243.819	3.859
3400	20.786	196.168	177.204	64.475	−313.145	−241.746	3.714
3500	20.786	196.770	177.755	66.554	−314.961	−239.620	3.576
3600	20.786	197.356	178.291	68.632	−316.760	−237.442	3.445
3700	20.786	197.925	178.814	70.711	−318.542	−235.214	3.321
3800	20.786	198.480	179.324	72.790	−320.308	−232.938	3.202
3900	20.786	199.019	179.823	74.868	−322.056	−230.616	3.089
4000	20.786	199.546	180.309	76.947	−323.787	−228.249	2.981
4100	20.786	200.059	180.785	79.025	−325.501	−225.840	2.877
4200	20.786	200.560	181.249	81.104	−327.199	−223.388	2.778
4300	20.786	201.049	181.704	83.183	−328.879	−220.897	2.683
4400	20.786	201.527	182.149	85.261	−330.544	−218.367	2.592
4500	20.786	201.994	182.585	87.340	−332.192	−215.798	2.505
4600	20.786	202.451	183.012	89.418	−333.825	−213.194	2.421
4700	20.786	202.898	183.430	91.497	−335.442	−210.554	2.340
4800	20.786	203.335	183.841	93.576	−337.044	−207.880	2.262
4900	20.786	203.764	184.243	95.654	−338.631	−205.172	2.187
5000	20.786	204.184	184.637	97.733	−340.204	−202.433	2.115
5100	20.786	204.596	185.025	99.811	−341.763	−199.662	2.045
5200	20.786	204.999	185.405	101.890	−343.309	−196.860	1.977
5300	20.786	205.395	185.778	103.969	−344.841	−194.029	1.912
5400	20.786	205.784	186.145	106.047	−346.361	−191.170	1.849
5500	20.786	206.165	186.506	108.126	−347.868	−188.282	1.788
5600	20.786	206.540	186.860	110.204	−349.363	−185.367	1.729
5700	20.786	206.908	187.209	112.283	−350.847	−182.425	1.672
5800	20.786	207.269	187.552	114.362	−352.319	−179.458	1.616
5900	20.786	207.624	187.889	116.440	−353.781	−176.465	1.562
6000	20.786	207.974	188.221	118.519	−355.231	−173.447	1.510

PREVIOUS: December 1971 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K)$ = [240.337] J K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = [47.549 ± 20.9] kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = [47.698 ± 20.9] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
[$^6\Sigma$]	0	[6]

ω_e = [630.0] cm^{-1} $\omega_e x_e$ = [2.7] cm^{-1} σ = 1
B_e = [0.3670] cm^{-1} α_e = [0.0017] cm^{-1} r_e = [1.8] Å

Enthalpy of Formation

The dissociation energy of FeF(g) was estimated as 4.64±0.22 eV or 107±5 kcal·mol^{-1} by Margrave.[1] From the value of $D_0°$(FeF), the enthalpy of formation, $\Delta_f H°$(298.15 K), for FeF(g) is derived to be 11.4±5.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The ground state configuration and bond distance (r_e) were estimated by comparison with those for FeCl(g). The value of B_e was calculated using the relationship $B_e = (2.79889 \times 10^{-39})/I$ where I = moment of inertia of FeF(g), and α_e was estimated by comparison with those for AlF(g), AlCl(g) and FeCl(g). The value of ω_e was derived from the bond distance, reduced mass and number of valence electrons according to the method given by Guggenheimer[2] and the $\omega_e x_e$ was estimated from those for AlF(g), AlCl(g) and FeCl(g).

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.067	47.549	47.549	INFINITE
100	29.193	206.817	268.389	−6.157	48.583	37.027	−19.341
200	31.049	227.505	243.314	−3.162	48.345	25.499	−6.660
250	32.266	234.566	240.880	−1.578	48.040	19.822	−4.142
298.15	33.264	240.337	240.337	0.	47.698	14.418	−2.526
300	33.298	240.543	240.338	0.062	47.684	14.211	−2.474
350	34.117	245.740	240.747	1.748	47.289	8.663	−1.293
400	34.754	250.339	241.664	3.470	46.855	3.174	−0.414
450	35.249	254.463	242.861	5.221	46.374	−2.258	0.262
500	35.639	258.197	244.211	6.993	45.842	−7.633	0.797
600	36.201	264.749	247.103	10.587	44.614	−18.217	1.586
700	36.578	270.359	250.034	14.228	43.152	−28.576	2.132
800	36.846	275.262	252.888	17.899	41.405	−38.708	2.527
900	37.045	279.614	255.620	21.594	39.244	−48.598	2.821
1000	37.200	283.525	258.218	25.307	36.364	−58.213	3.041
1100	37.324	287.077	260.683	29.033	32.588	−67.474	3.204
1200	37.428	290.329	263.020	32.771	29.363	−76.447	3.328
1300	37.516	293.328	265.237	36.518	27.782	−85.201	3.423
1400	37.594	296.111	267.344	40.274	26.115	−93.830	3.501
1500	37.663	298.708	269.350	44.037	24.362	−102.337	3.564
1600	37.725	301.140	271.261	47.806	22.523	−110.724	3.615
1700	37.783	303.429	273.087	51.582	19.647	−118.975	3.656
1800	37.837	305.590	274.833	55.363	17.302	−127.062	3.687
1900	37.887	307.637	276.506	59.149	0.774	−134.314	3.693
2000	37.935	309.582	278.112	62.940	−1.978	−141.353	3.692
2100	37.981	311.434	279.655	66.736	−4.728	−148.254	3.688
2200	38.026	313.202	281.140	70.536	−7.474	−155.024	3.681
2300	38.068	314.893	282.571	74.341	−10.216	−161.670	3.672
2400	38.110	316.514	283.952	78.150	−12.951	−168.196	3.661
2500	38.151	318.071	285.285	81.963	−15.678	−174.609	3.648
2600	38.191	319.568	286.575	85.780	−18.394	−180.912	3.635
2700	38.230	321.010	287.824	89.601	−21.099	−187.111	3.620
2800	38.268	322.401	289.034	93.426	−23.790	−193.211	3.604
2900	38.306	323.744	290.208	97.255	−26.467	−199.214	3.588
3000	38.344	325.044	291.348	101.087	−29.127	−205.126	3.572
3100	38.381	326.302	292.455	104.923	−31.771	−210.949	3.554
3200	38.417	327.521	293.532	108.763	−382.696	−209.263	3.416
3300	38.454	328.703	294.580	112.607	−383.402	−203.832	3.226
3400	38.490	329.852	295.601	116.454	−384.122	−198.380	3.048
3500	38.525	330.968	296.595	120.305	−384.855	−192.906	2.879
3600	38.561	332.054	297.565	124.159	−385.602	−187.411	2.719
3700	38.596	333.111	298.512	128.017	−386.363	−181.895	2.568
3800	38.632	334.141	299.436	131.878	−387.139	−176.359	2.424
3900	38.667	335.145	300.339	135.743	−387.931	−170.802	2.288
4000	38.702	336.124	301.221	139.612	−388.740	−165.224	2.158
4100	38.736	337.080	302.084	143.484	−389.567	−159.626	2.034
4200	38.771	338.014	302.928	147.359	−390.414	−154.007	1.915
4300	38.806	338.927	303.755	151.238	−391.280	−148.369	1.802
4400	38.840	339.819	304.565	155.120	−392.168	−142.709	1.694
4500	38.874	340.692	305.358	159.006	−393.079	−137.030	1.591
4600	38.909	341.547	306.135	162.895	−394.014	−131.329	1.491
4700	38.943	342.384	306.898	166.788	−394.976	−125.608	1.396
4800	38.977	343.205	307.645	170.684	−395.964	−119.867	1.304
4900	39.011	344.009	308.379	174.583	−396.982	−114.104	1.216
5000	39.045	344.797	309.100	178.486	−398.030	−108.321	1.132
5100	39.079	345.571	309.807	182.392	−399.110	−102.516	1.050
5200	39.113	346.330	310.503	186.301	−400.224	−96.689	0.971
5300	39.147	347.075	311.186	190.214	−401.374	−90.841	0.895
5400	39.180	347.807	311.857	194.131	−402.561	−84.971	0.822
5500	39.214	348.526	312.517	198.050	−403.789	−79.079	0.751
5600	39.248	349.233	313.167	201.974	−405.059	−73.163	0.682
5700	39.281	349.928	313.805	205.900	−406.374	−67.225	0.616
5800	39.315	350.612	314.434	209.830	−407.736	−61.264	0.552
5900	39.349	351.284	315.053	213.763	−409.148	−55.278	0.489
6000	39.382	351.946	315.662	217.700	−410.613	−49.268	0.429

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 173.780 \pm 0.033\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -272.499 \pm 0.8\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -272.546 \pm 0.8\ kJ\cdot mol^{-1}$

Electronic States and Molecular Constants (σ = 1)

State	T_o,cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^1\Sigma^+$	0	1	4138.73	90.05	20.9555	0.7958	0.9168
$B^1\Sigma^+$	83275	1	1158.46	17.718	4.0263	0.0173	2.091

Enthalpy of Formation

The enthalpy of formation was adopted from the 1968 JANAF Thermochemical Table.[1] This value was obtained by simultaneous selection[2] of $\Delta_f H°(298.15\ K)$ for HF(g), BF_3(g), NF_3(g), CF_4(g), NaF(cr), and C_2F_4(polymer). Subsequent data have led CODATA[3] to recommend the more negative value of -65.32 ± 0.17 kcal·mol^{-1} for HF(g).

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[4] These constants do not differ appreciably from those given in the 1968 JANAF Tables.[1] The values of $\Delta_f H°$, $\Delta_f G°$, and log Kp are appreciably different because of the new thermal functions for the reference state F_2.[5]

The National Bureau of Standards prepared this table[6] from data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[6] we recalculate the table in terms of 1973 fundamental constants,[7] 1975 atomic weights,[8] and current JANAF reference states for the elements.[5] A more complete analysis of electronic states and molecular constants is now available.[9]

References

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[7]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.599	−272.499	−272.499	INFINITE
100	29.128	141.959	199.679	−5.772	−272.625	−273.266	142.739
200	29.128	162.148	176.445	−2.859	−272.524	−273.947	71.548
250	29.133	168.648	174.260	−1.403	−272.516	−274.304	57.313
298.15	29.138	173.780	173.780	0.	−272.546	−274.646	48.117
300	29.138	173.960	173.780	0.054	−272.548	−274.659	47.822
350	29.143	178.452	174.135	1.511	−272.609	−275.007	41.043
400	29.150	182.344	174.923	2.968	−272.696	−275.344	35.956
450	29.159	185.778	175.943	4.426	−272.802	−275.669	31.999
500	29.173	188.851	177.082	5.884	−272.924	−275.981	28.831
600	29.230	194.174	179.501	8.804	−273.205	−276.566	24.077
700	29.351	198.688	181.927	11.732	−273.522	−277.102	20.678
800	29.550	202.619	184.273	14.677	−273.858	−277.590	18.125
900	29.827	206.115	186.510	17.645	−274.205	−278.036	16.137
1000	30.169	209.275	188.631	20.644	−274.552	−278.443	14.544
1100	30.556	212.168	190.641	23.680	−274.896	−278.816	13.240
1200	30.971	214.845	192.547	26.757	−275.231	−279.157	12.151
1300	31.397	217.340	194.360	29.875	−275.558	−279.471	11.229
1400	31.822	219.683	196.086	33.036	−275.874	−279.760	10.438
1500	32.237	221.893	197.733	36.239	−276.181	−280.027	9.751
1600	32.636	223.986	199.309	39.483	−276.477	−280.273	9.150
1700	33.017	225.976	200.820	42.766	−276.763	−280.502	8.619
1800	33.376	227.873	202.270	46.085	−277.040	−280.714	8.146
1900	33.713	229.687	203.666	49.440	−277.308	−280.911	7.723
2000	34.029	231.424	205.011	52.827	−277.566	−281.093	7.341
2100	34.325	233.092	206.309	56.245	−277.815	−281.264	6.996
2200	34.601	234.695	207.563	59.692	−278.053	−281.422	6.682
2300	34.858	236.239	208.776	63.165	−278.279	−281.570	6.395
2400	35.099	237.728	209.952	66.663	−278.493	−281.709	6.131
2500	35.323	239.165	211.092	70.184	−278.694	−281.838	5.889
2600	35.533	240.555	212.198	73.727	−278.882	−281.961	5.665
2700	35.730	241.899	213.273	77.290	−279.054	−282.076	5.457
2800	35.914	243.202	214.319	80.872	−279.210	−282.185	5.264
2900	36.088	244.466	215.337	84.473	−279.349	−282.288	5.085
3000	36.251	245.692	216.329	88.090	−279.472	−282.388	4.917
3100	36.405	246.883	217.295	91.723	−279.576	−282.483	4.760
3200	36.550	248.041	218.238	95.370	−279.662	−282.575	4.613
3300	36.687	249.168	219.158	99.032	−279.730	−282.665	4.474
3400	36.818	250.265	220.057	102.708	−279.779	−282.754	4.344
3500	36.941	251.334	220.935	106.395	−279.809	−282.841	4.221
3600	37.059	252.376	221.794	110.096	−279.821	−282.927	4.105
3700	37.171	253.393	222.635	113.807	−279.814	−283.013	3.995
3800	37.279	254.386	223.457	117.530	−279.789	−283.100	3.891
3900	37.381	255.356	224.263	121.263	−279.746	−283.188	3.793
4000	37.480	256.303	225.052	125.006	−279.685	−283.277	3.699
4100	37.574	257.230	225.826	128.759	−279.607	−283.367	3.610
4200	37.665	258.137	226.584	132.521	−279.512	−283.460	3.525
4300	37.753	259.024	227.328	136.292	−279.400	−283.556	3.445
4400	37.837	259.893	228.059	140.071	−279.273	−283.654	3.367
4500	37.919	260.744	228.775	143.859	−279.130	−283.755	3.294
4600	37.998	261.578	229.479	147.655	−278.971	−283.859	3.223
4700	38.074	262.396	230.171	151.458	−278.798	−283.967	3.156
4800	38.149	263.199	230.851	155.270	−278.611	−284.079	3.091
4900	38.221	263.986	231.519	159.088	−278.410	−284.195	3.030
5000	38.291	264.759	232.176	162.914	−278.195	−284.315	2.970
5100	38.359	265.518	232.823	166.746	−277.967	−284.440	2.913
5200	38.426	266.263	233.459	170.585	−277.725	−284.569	2.859
5300	38.491	266.996	234.084	174.431	−277.471	−284.703	2.806
5400	38.555	267.716	234.701	178.284	−277.204	−284.842	2.755
5500	38.617	268.424	235.307	182.142	−276.925	−284.987	2.707
5600	38.678	269.120	235.905	186.007	−276.633	−285.135	2.660
5700	38.737	269.806	236.494	189.878	−276.329	−285.290	2.614
5800	38.796	270.480	237.074	193.754	−276.013	−285.450	2.571
5900	38.853	271.143	237.646	197.637	−275.684	−285.616	2.529
6000	38.910	271.797	238.209	201.525	−275.343	−285.787	2.488

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Hypofluorous Acid (HOF) IDEAL GAS $M_r = 56.005743$

$S°(298.15\ K) = 226.772 \pm 0.21\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -95.423 \pm 4.2\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -98.324 \pm 4.2\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
3578.5(1)
1354.8(1)
889.0(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: H–O = 0.966 Å; O–F = 1.442 Å
Bond Angle: H–O–F = 96.78°
Product of the Moments of Inertia: $I_A I_B I_C = 1.4723 \times 10^{-117}\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(0\ K)$ is the value derived by Berkowitz *et al.*[1] from photoionization data which gave 14.34 eV as the threshold of O^+ formation, $HOF + h + O^+ HF + e^-$. The threshold of OH^+ formation, 15.07 eV for $HOF + h \rightarrow + OH^+ + F + e^-$, yields $\Delta_f H°(0\ K) = -21.7\ kcal\cdot mol^{-1}$ assuming $\Delta_f H°(OH^+, 0\ K) = 307.5 \pm 0.5\ kcal\cdot mol^{-1}$ from Dibeler *et al.*[2] The latter authors found 18.05 eV for $H_2O + h \rightarrow OH^+ + H^+ + e.^-$ Our adopted value for HOF differs by only 2.5 $kcal\cdot mol^{-1}$ from the mean $\Delta_f H°(0\ K)$ of H_2O and F_2O, namely $-25.3\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

Vibrational frequencies are from gas-phase infrared spectra of Appelman and Kim;[3] the values are confirmed by IR spectra of HOF isolated in a matrix of N_2.[4] Structural parameters are those derived by Pearson and Kim[5] from centrifugal distortion analysis of mm wave rotational spectra[5, 6] of HOF and DOF. We use the atomic coordinates[5] to derive the principal moments of inertia are $I_A = 0.1431 \times 10^{-39}$, $I_B = 3.1363 \times 10^{-39}$, and $I_C = 3.2795 \times 10^{-39}\ g\cdot cm^2$ and their product; the corresponding bond distances are 0.96648 and 1.44215 Å, i.e., slightly longer than the rounded values[5] listed above. The earlier study[6] gave 0.964 ± 0.01 and 1.442 ± 0.001 Å and a bond angle of 97.2 ± 0.6°.

References

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Hypofluorous Acid (HOF) $F_1H_1O_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.087	−95.423	−95.423	INFINITE
100	33.261	189.739	257.352	−6.761	−96.503	−93.257	48.712
200	33.873	212.899	229.983	−3.417	−97.425	−89.650	23.414
250	34.787	220.549	227.357	−1.702	−97.889	−87.653	18.314
298.15	35.929	226.772	226.772	0.	−98.324	−85.642	15.004
300	35.976	226.994	226.772	0.067	−98.340	−85.563	14.898
350	37.277	232.637	227.215	1.898	−98.766	−83.399	12.447
400	38.571	237.700	228.215	3.794	−99.161	−81.177	10.601
450	39.790	242.314	229.528	5.753	−99.524	−78.907	9.159
500	40.907	246.565	231.022	7.771	−99.857	−76.598	8.002
600	42.830	254.199	234.263	11.962	−100.448	−71.889	6.258
700	44.409	260.924	237.601	16.326	−100.956	−67.088	5.006
800	45.744	266.943	240.899	20.835	−101.396	−62.219	4.062
900	46.906	272.400	244.101	25.469	−101.779	−57.298	3.325
1000	47.936	277.396	247.184	30.212	−102.114	−52.337	2.734
1100	48.858	282.009	250.143	35.053	−102.408	−47.345	2.248
1200	49.687	286.296	252.979	39.981	−102.666	−42.328	1.842
1300	50.432	290.303	255.698	44.987	−102.896	−37.290	1.498
1400	51.102	294.066	258.305	50.065	−103.103	−32.235	1.203
1500	51.703	297.612	260.809	55.205	−103.292	−27.167	0.946
1600	52.242	300.967	263.215	60.403	−103.468	−22.086	0.721
1700	52.726	304.148	265.530	65.652	−103.634	−16.995	0.522
1800	53.160	307.175	267.760	70.946	−103.794	−11.894	0.345
1900	53.550	310.060	269.911	76.282	−103.951	−6.784	0.186
2000	53.901	312.815	271.988	81.655	−104.105	−1.666	0.043
2100	54.217	315.453	273.995	87.061	−104.257	3.460	−0.086
2200	54.503	317.982	275.938	92.498	−104.409	8.593	−0.204
2300	54.761	320.410	277.819	97.961	−104.561	13.733	−0.312
2400	54.994	322.746	279.642	103.449	−104.712	18.879	−0.411
2500	55.206	324.995	281.412	108.959	−104.861	24.032	−0.502
2600	55.399	327.164	283.130	114.489	−105.009	29.191	−0.586
2700	55.575	329.259	284.800	120.038	−105.154	34.355	−0.665
2800	55.736	331.283	286.424	125.604	−105.296	39.525	−0.737
2900	55.883	333.241	288.005	131.185	−105.433	44.699	−0.805
3000	56.018	335.138	289.545	136.780	−105.566	49.879	−0.868
3100	56.141	336.977	291.045	142.388	−105.693	55.062	−0.928
3200	56.255	338.761	292.508	148.008	−105.814	60.250	−0.983
3300	56.360	340.494	293.936	153.639	−105.928	65.441	−1.036
3400	56.457	342.178	295.331	159.280	−106.035	70.636	−1.085
3500	56.547	343.816	296.693	164.930	−106.135	75.833	−1.132
3600	56.630	345.410	298.024	170.589	−106.228	81.034	−1.176
3700	56.708	346.962	299.326	176.256	−106.313	86.236	−1.217
3800	56.780	348.476	300.599	181.930	−106.390	91.442	−1.257
3900	56.847	349.951	301.846	187.612	−106.459	96.649	−1.294
4000	56.909	351.391	303.067	193.300	−106.522	101.858	−1.330
4100	56.967	352.797	304.262	198.994	−106.577	107.068	−1.364
4200	57.022	354.171	305.434	204.693	−106.625	112.279	−1.396
4300	57.073	355.513	306.583	210.398	−106.666	117.492	−1.427
4400	57.121	356.826	307.710	216.107	−106.702	122.705	−1.457
4500	57.166	358.110	308.816	221.822	−106.731	127.919	−1.485
4600	57.208	359.367	309.902	227.541	−106.755	133.133	−1.512
4700	57.248	360.598	310.967	233.263	−106.774	138.349	−1.538
4800	57.285	361.803	312.014	238.990	−106.789	143.565	−1.562
4900	57.320	362.985	313.042	244.720	−106.800	148.781	−1.586
5000	57.354	364.143	314.052	250.454	−106.807	153.997	−1.609
5100	57.385	365.279	315.046	256.191	−106.812	159.213	−1.631
5200	57.415	366.394	316.023	261.931	−106.814	164.429	−1.652
5300	57.443	367.488	316.983	267.674	−106.814	169.645	−1.672
5400	57.470	368.562	317.929	273.420	−106.813	174.861	−1.691
5500	57.496	369.617	318.859	279.168	−106.811	180.077	−1.710
5600	57.520	370.653	319.774	284.919	−106.809	185.294	−1.728
5700	57.543	371.671	320.676	290.672	−106.807	190.509	−1.746
5800	57.564	372.672	321.564	296.427	−106.806	195.726	−1.763
5900	57.585	373.656	322.438	302.185	−106.805	200.941	−1.779
6000	57.605	374.624	323.300	307.944	−106.807	206.158	−1.795

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 297.267 \pm 3.3$ J K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = -742.051 \pm 8.4$ kJ·mol^{-1}

$\Delta_f H°(298.15\ K) = -753.120 \pm 8.4$ kJ·mol^{-1}

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3602(1)	825(1)	1486(1)
1243(1)	550(1)	562(1)
1150(1)	410(1)	390(1)
896(1)	390(1)	265(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $[C_s]$
Bond Distances: O–S = [1.405] Å; S–OH = S–F = [1.53] Å; O–H = [1.00] Å
Bond Angles: O–S–O = [124°]; F–S–OH = S–O–H = [100°]
Product of the Moments of Inertia: $I_A I_B I_C = [4.2743 \times 10^{-114}]$ g^3·cm^6

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) may be derived from calorimetric data of Richards and Woolf[1] which yield $\Delta_f H°(298.15\ K) = -14.94 \pm 0.2$ kcal·mol^{-1} for SO_3(l) + HF (real gas, 1 atm) → HSO_3F(l). Using $\Delta_f H°(SO_3, l, 0\ K) = -105.41$[2] and $\Delta_f H°$(HF, real gas, 0 K) = −70.12[3,4] kcal·mol^{-1}, we derive $\Delta_f H° = -190.5$ kcal·mol^{-1} for HSO_3F(l) ar.d −180.3 ± 1.5 kcal·mol^{-1} for the ideal gas. The latter value agrees well with −179.2 ± 3 kcal·mol^{-1} estimated for HSO_3F(g) from the related molecules SO_2F_2 and H_2SO_4.[4] We adopt $\Delta_f H° = -180 \pm 2$ kcal·mol^{-1} (−753.120 ± 8.4 kJ·mol^{-1}).

Derivation of $\Delta_f H°$(g) presumes that the heat of vaporization is 10.2 ± 1.0 kcal·mol^{-1} at 25°C. Measurements of the heat of condensation[5] yield 12.8 ± 0.8 kcal·mol^{-1} for the enthalpy difference between real gas at 164.4°C and the liquid at 25°C. Added to this value should be ±0.2 kcal·mol^{-1} (estimated correction for gas imperfection) and −2.8 kcal·mol^{-1} (calculated enthalpy difference for the ideal gas between 25°C and 164.4°C, the approximate normal boiling point).

Other calorimetric data bearing on $\Delta_f H°$ were reported by Lenskii *et al.*[5] and Woolf,[6] but these results are much more uncertain[1] due to experimental error and to inadequate definition of the states of the reactants and products.

Heat Capacity and Entropy

Savoie and Giguere[7] reviewed possible molecular structures and preferred eclipsed (cis) forms, arbitrarily selecting one in which F–S–O–H is coplanar. We adopt this structure since the choice changes the thermodynamic functions very little. Possible structures all have $\sigma = 1$ (C_s or C_1 symmetry) and similar values of the product of the moments of inertia. Bond lengths and angles are estimated by comparison with SO_2ClF,[8]

SO_2Cl_2 and H_2SO_4.[4] These parameters yield O = S–F and O = S–OH angles of 107.56° and principal moments of inertia are: $I_A = 15.9647 \times 10^{-39}$, $I_B = 16.1688 \times 10^{-39}$, and $I_C = 16.5588 \times 10^{-39}$ g·cm^2.

Vibrational fundamentals are from the assignment of Savoie and Giguere[7] as modified by Chackalackal and Stafford.[9] Data include Raman spectra of the liquid[1] and infrared spectra of all three phases[7] plus the superheated vapor.[9] Spectra of the superheated vapor helped to clarify the vibrational distinction between the monomer and associated molecules. Savoie and Giguere derived a barrier of about 1.3 kcal·mol^{-1} for hindered interal rotation of the OH group and used this to calculate $C_p° = 17.64$ and $S° = 71.38$ cal K^{-1}·mol^{-1} at 298.15 K. We calculated $C_p° = 17.98$ and $S° = 71.02$ cal K^{-1}·mol^{-1} using the OH–torsional frequency (265 cm^{-1}) instead of hindered rotation.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.014	−742.051	−742.051	INFINITE
100	39.145	237.149	352.791	−11.564	−746.601	−729.513	381.058
200	59.278	270.467	303.667	−6.640	−750.497	−710.811	185.645
250	67.997	284.656	298.466	−3.453	−751.965	−700.713	146.406
298.15	75.243	297.267	297.267	0.	−753.120	−690.734	121.014
300	75.501	297.733	297.268	0.139	−753.160	−690.347	120.200
350	81.950	309.869	298.212	4.080	−754.119	−679.799	101.454
400	87.477	321.182	300.384	8.319	−757.096	−669.040	87.368
450	92.198	331.765	303.290	12.814	−758.366	−657.964	76.374
500	96.227	341.693	306.639	17.527	−759.549	−646.741	67.565
600	102.624	359.833	314.023	27.486	−761.115	−624.019	54.326
700	107.389	376.027	321.745	37.998	−762.077	−601.087	44.854
800	111.041	390.616	329.457	48.927	−762.646	−578.046	37.743
900	113.926	403.867	337.000	60.181	−816.071	−553.870	32.146
1000	116.264	415.996	344.302	71.694	−814.954	−524.795	27.412
1100	118.199	427.170	351.334	83.420	−813.742	−495.837	23.545
1200	119.826	437.527	358.090	95.324	−812.461	−466.992	20.328
1300	121.210	447.174	364.576	107.377	−811.130	−438.257	17.609
1400	122.397	456.201	370.802	119.559	−809.764	−409.626	15.283
1500	123.425	464.682	376.781	131.851	−808.376	−381.093	13.271
1600	124.318	472.676	382.527	144.239	−806.977	−352.653	11.513
1700	125.100	480.237	388.054	156.711	−805.575	−324.301	9.965
1800	125.786	487.407	393.376	169.256	−804.177	−296.031	8.591
1900	126.392	494.225	398.506	181.866	−802.788	−267.839	7.363
2000	126.929	500.722	403.456	194.532	−801.412	−239.719	6.261
2100	127.406	506.927	408.236	207.250	−800.052	−211.668	5.265
2200	127.832	512.864	412.858	220.012	−798.708	−183.680	4.361
2300	128.214	518.554	417.331	232.815	−797.383	−155.755	3.537
2400	128.556	524.019	421.663	245.653	−796.077	−127.887	2.783
2500	128.865	529.273	425.863	258.525	−794.789	−100.072	2.091
2600	129.144	534.333	429.938	271.425	−793.518	−72.308	1.453
2700	129.397	539.211	433.895	284.353	−792.264	−44.593	0.863
2800	129.626	543.921	437.741	297.304	−791.026	−16.924	0.316
2900	129.836	548.474	441.482	310.277	−789.802	10.700	−0.193
3000	130.027	552.879	445.122	323.271	−788.593	38.284	−0.667
3100	130.202	557.145	448.667	336.282	−787.395	65.827	−1.109
3200	130.362	561.281	452.122	349.310	−786.209	93.330	−1.523
3300	130.510	565.295	455.491	362.354	−785.034	120.798	−1.912
3400	130.645	569.193	458.778	375.412	−783.868	148.230	−2.277
3500	130.771	572.982	461.987	388.483	−782.711	175.627	−2.621
3600	130.887	576.668	465.122	401.566	−781.564	202.993	−2.945
3700	130.994	580.256	468.185	414.660	−780.424	230.325	−3.252
3800	131.094	583.750	471.181	427.764	−779.292	257.629	−3.541
3900	131.187	587.157	474.111	440.878	−778.168	284.902	−3.816
4000	131.273	590.479	476.979	454.001	−777.053	312.145	−4.076
4100	131.353	593.722	479.787	467.133	−775.945	339.361	−4.324
4200	131.429	596.888	482.537	480.272	−774.846	366.551	−4.559
4300	131.499	599.981	485.233	493.418	−773.756	393.714	−4.783
4400	131.565	603.005	487.875	506.572	−772.675	420.852	−4.996
4500	131.626	605.962	490.467	519.731	−771.604	447.964	−5.200
4600	131.684	608.856	493.009	532.897	−770.545	475.054	−5.394
4700	131.739	611.689	495.504	546.068	−769.497	502.121	−5.580
4800	131.790	614.463	497.954	559.244	−768.462	529.166	−5.759
4900	131.838	617.181	500.359	572.426	−767.440	556.190	−5.929
5000	131.884	619.845	502.722	585.612	−766.434	583.193	−6.093
5100	131.927	622.457	505.044	598.803	−765.443	610.176	−6.249
5200	131.968	625.019	507.327	611.997	−764.470	637.138	−6.400
5300	132.006	627.533	509.572	625.196	−763.516	664.084	−6.545
5400	132.043	630.001	511.779	638.399	−762.582	691.011	−6.684
5500	132.077	632.424	513.950	651.605	−761.669	717.919	−6.818
5600	132.110	634.804	516.087	664.814	−760.780	744.815	−6.947
5700	132.141	637.143	518.191	678.027	−759.915	771.692	−7.072
5800	132.171	639.441	520.261	691.242	−759.075	798.556	−7.192
5900	132.199	641.701	522.301	704.461	−758.264	825.402	−7.308
6000	132.226	643.923	524.309	717.682	−757.482	852.239	−7.419

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = 238.402 \pm 0.8\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-367.16 \pm 20.9]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-376.560 \pm 20.9]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2206(1)	2209(2)
991(1)	961(2)
875(1)	729(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.468 Å; Si–F = 1.593 Å
Bond Angles: H–Si–H = 110.43°; H–Si–F = 108.50°
Product of the Moments of Inertia: $I_A I_B I_C = 3.42403 \times 10^{-116}\ g^3\cdot cm^6$

Enthalpy of Formation

There are no reported experimental studies leading to the heat of formation of SiH_3F(g). We estimate this value via a linear interpolation between the established $\Delta_f H°(298.15\ K)$ values of SiH_4(g) and SiF_4(g).[1] The reasonableness of this approach has been demonstrated by Lapidus *et al.*,[2] Hunt and Sirtl,[3] and Seiter and Sirtl.[4] Lapidus *et al.*[2] examined the trends in the thermodynamic properties of halogenated silanes and methanes. Hunt and Sirtl[3] and Seiter and Sirtl[4] studied the chlorinated silanes and proposed a linear $\Delta_f H$ relationship within the sequence SiH_4(g) to $SiCl_4$(g).

Heat Capacity and Entropy

The adopted vibrational frequencies are from the gas phase infrared spectra of SiH_3F and SiD_3F as documented by Robiette *et al.*[5] Except for ν_4 and ν_5 these values are within $\pm 3\ cm^{-1}$ of those suggested in the compilation by Shimanouchi.[6] In particular, based on earlier work, Shimanouchi[6] suggested $\nu_4 = 2196\ cm^{-1}$ and $\nu_5 = 956\ cm^{-1}$. The work of Robiette *et al.*[5] is judged to yield more accurate frequencies than the earlier work.

The adopted bond angles and bond distances are obtained from the microwave spectra study on SiH_3F and various isotopic derivatives by Kewley *et al.*[7] This work is deemed more accurate than earlier studies.[8–11] The individual moments of inertia are calculated to be $I_A = 0.9972 \times 10^{-39}\ g\cdot cm^2$ and $I_B = I_C = 5.8599 \times 10^{-39}\ g\cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.931	−367.160	−367.160	INFINITE
100	33.317	197.814	273.865	−7.605	−370.052	−365.823	191.086
200	37.439	221.708	242.386	−4.136	−373.267	−360.386	94.123
250	42.143	230.548	239.150	−2.150	−374.977	−356.968	74.584
298.15	47.196	238.402	238.402	0.	−376.560	−353.354	61.906
300	47.391	238.694	238.402	0.087	−376.619	−353.210	61.499
350	52.495	246.387	238.998	2.586	−378.123	−349.188	52.113
400	57.187	253.708	240.383	5.330	−379.466	−344.960	45.047
450	61.420	260.693	242.255	8.297	−380.647	−340.575	39.533
500	65.229	267.364	244.435	11.465	−381.676	−336.066	35.109
600	71.784	279.856	249.312	18.326	−383.321	−326.781	28.449
700	77.185	291.340	254.507	25.783	−384.494	−317.258	23.674
800	81.656	301.948	259.783	33.732	−385.288	−307.595	20.084
900	85.359	311.787	265.021	42.089	−385.782	−297.851	17.287
1000	88.429	320.944	270.161	50.783	−386.050	−288.065	15.047
1100	90.981	329.496	275.171	59.758	−386.150	−278.260	13.213
1200	93.109	337.506	280.035	68.965	−386.131	−268.452	11.685
1300	94.894	345.031	284.748	78.368	−386.034	−258.649	10.393
1400	96.398	352.120	289.310	87.935	−385.892	−248.856	9.285
1500	97.673	358.816	293.722	97.640	−385.728	−239.073	8.325
1600	98.761	365.155	297.991	107.463	−385.562	−229.301	7.486
1700	99.694	371.171	302.120	117.387	−435.586	−219.093	6.732
1800	100.500	376.893	306.116	127.398	−435.226	−206.369	5.989
1900	101.199	382.346	309.986	137.483	−434.855	−193.664	5.324
2000	101.808	387.552	313.735	147.634	−434.479	−180.980	4.727
2100	102.343	392.533	317.370	157.843	−434.102	−168.314	4.187
2200	102.814	397.305	320.895	168.101	−433.726	−155.667	3.696
2300	103.230	401.885	324.318	178.404	−433.354	−143.036	3.248
2400	103.601	406.286	327.642	188.745	−432.985	−130.421	2.839
2500	103.931	410.522	330.873	199.122	−432.620	−117.822	2.462
2600	104.227	414.604	334.016	209.530	−432.259	−105.237	2.114
2700	104.493	418.543	337.074	219.967	−431.902	−92.666	1.793
2800	104.732	422.347	340.052	230.428	−431.548	−80.108	1.494
2900	104.949	426.026	342.953	240.912	−431.197	−67.563	1.217
3000	105.146	429.588	345.782	251.417	−430.848	−55.030	0.958
3100	105.325	433.038	348.541	261.941	−430.501	−42.508	0.716
3200	105.489	436.385	351.234	272.482	−430.156	−29.998	0.490
3300	105.638	439.633	353.864	283.038	−429.812	−17.498	0.277
3400	105.776	442.789	356.433	293.609	−429.470	−5.009	0.077
3500	105.902	445.857	358.945	304.193	−429.128	7.470	−0.111
3600	106.018	448.842	361.401	314.789	−812.940	30.400	−0.441
3700	106.125	451.748	363.803	325.396	−812.188	53.816	−0.760
3800	106.224	454.580	366.155	336.014	−811.439	77.212	−1.061
3900	106.316	457.340	368.458	346.641	−810.694	100.588	−1.347
4000	106.401	460.033	370.714	357.277	−809.953	123.944	−1.619
4100	106.481	462.661	372.924	367.921	−809.215	147.282	−1.876
4200	106.554	465.228	375.092	378.573	−808.480	170.603	−2.122
4300	106.623	467.736	377.217	389.232	−807.749	193.906	−2.355
4400	106.688	470.188	379.302	399.897	−807.022	217.192	−2.578
4500	106.748	472.586	381.349	410.569	−806.300	240.461	−2.791
4600	106.805	474.933	383.358	421.247	−805.581	263.714	−2.995
4700	106.858	477.231	385.331	431.930	−804.866	286.952	−3.189
4800	106.908	479.481	387.269	442.618	−804.156	310.175	−3.375
4900	106.954	481.686	389.173	453.311	−803.449	333.383	−3.554
5000	106.999	483.847	391.045	464.009	−802.747	356.577	−3.725
5100	107.040	485.966	392.886	474.711	−802.049	379.755	−3.889
5200	107.079	488.045	394.696	485.417	−801.354	402.922	−4.047
5300	107.117	490.085	396.476	496.127	−800.663	426.074	−4.199
5400	107.152	492.088	398.229	506.840	−799.975	449.214	−4.345
5500	107.185	494.054	399.953	517.557	−799.289	472.340	−4.486
5600	107.217	495.986	401.651	528.277	−798.607	495.455	−4.621
5700	107.246	497.884	403.322	539.000	−797.926	518.557	−4.752
5800	107.275	499.749	404.969	549.726	−797.246	541.648	−4.878
5900	107.302	501.583	406.591	560.455	−796.567	564.726	−5.000
6000	107.328	503.387	408.189	571.187	−795.888	587.792	−5.117

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 248.373\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 7.370\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 2.929 \pm 50.2\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma$	0	2

$\omega_e = 490.8\ cm^{-1}$ $\omega_e x_e = 4.05\ cm^{-1}$ $\sigma = 1$
$B_e = [0.2732]\ cm^{-1}$ $\alpha_e = [0.0026]\ cm^{-1}$ $r_e = [1.89]$ Å

Enthalpy of Formation

Gaydon[1] gives 32±12 kcal·mol^{-1} for the enthalpy of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants are from Herzberg.[2] Rotational constants were estimated using relationships in Herzberg.[2] Bond length estimated by comparison of the mercurous halides with thalium and cesium halides.

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall, London (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, equation III, 123 p. 108, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.314	7.370	7.370	INFINITE
100	29.502	213.636	277.625	−6.399	7.126	−1.997	1.043
200	32.488	234.956	251.483	−3.305	6.170	−10.751	2.808
250	33.752	242.348	248.939	−1.648	3.380	−14.771	3.086
298.15	34.651	248.373	248.373	0.	2.929	−18.225	3.193
300	34.680	248.588	248.374	0.064	2.912	−18.356	3.196
350	35.356	253.987	248.799	1.816	2.480	−21.867	3.263
400	35.857	258.743	249.751	3.597	2.070	−25.316	3.306
450	36.236	262.989	250.990	5.400	1.672	−28.716	3.333
500	36.532	266.823	252.385	7.219	1.282	−32.071	3.350
600	36.960	273.524	255.365	10.895	0.507	−38.669	3.366
700	37.258	279.245	258.378	14.607	−59.031	−38.566	2.878
800	37.481	284.235	261.305	18.344	−59.177	−35.632	2.327
900	37.659	288.660	264.103	22.102	−59.325	−32.680	1.897
1000	37.809	292.636	266.761	25.875	−59.475	−29.711	1.552
1100	37.939	296.246	269.280	29.663	−59.626	−26.728	1.269
1200	38.055	299.552	271.667	33.462	−59.778	−23.730	1.033
1300	38.162	302.602	273.931	37.273	−59.930	−20.720	0.833
1400	38.263	305.434	276.081	41.095	−60.083	−17.698	0.660
1500	38.358	308.077	278.127	44.926	−60.236	−14.665	0.511
1600	38.449	310.556	280.077	48.766	−60.389	−11.622	0.379
1700	38.537	312.889	281.939	52.615	−60.540	−8.569	0.263
1800	38.623	315.095	283.720	56.473	−60.691	−5.508	0.160
1900	38.706	317.185	285.427	60.340	−60.839	−2.438	0.067
2000	38.788	319.173	287.065	64.215	−60.983	0.639	−0.017
2100	38.869	321.067	288.640	68.098	−61.123	3.724	−0.093
2200	38.949	322.877	290.155	71.988	−61.255	6.815	−0.162
2300	39.028	324.610	291.616	75.887	−61.379	9.912	−0.225
2400	39.106	326.273	293.025	79.794	−61.492	13.014	−0.283
2500	39.184	327.871	294.387	83.709	−61.594	16.120	−0.337
2600	39.261	329.409	295.705	87.631	−61.681	19.231	−0.386
2700	39.338	330.892	296.981	91.561	−61.753	22.344	−0.432
2800	39.414	332.324	298.218	95.498	−61.808	25.460	−0.475
2900	39.490	333.709	299.418	99.444	−61.844	28.577	−0.515
3000	39.566	335.049	300.583	103.396	−61.861	31.696	−0.552
3100	39.641	336.347	301.716	107.357	−61.856	34.814	−0.587
3200	39.716	337.607	302.818	111.325	−61.830	37.932	−0.619
3300	39.791	338.830	303.891	115.300	−61.781	41.049	−0.650
3400	39.866	340.019	304.936	119.283	−61.709	44.164	−0.678
3500	39.940	341.176	305.955	123.273	−61.613	47.277	−0.706
3600	40.015	342.302	306.949	127.271	−61.494	50.386	−0.731
3700	40.089	343.400	307.920	131.276	−61.350	53.492	−0.755
3800	40.164	344.470	308.867	135.289	−61.181	56.594	−0.778
3900	40.238	345.514	309.794	139.309	−60.988	59.691	−0.799
4000	40.312	346.534	310.700	143.336	−60.771	62.782	−0.820
4100	40.386	347.530	311.586	147.371	−60.530	65.868	−0.839
4200	40.460	348.504	312.453	151.413	−60.265	68.948	−0.857
4300	40.534	349.457	313.303	155.463	−59.976	72.021	−0.875
4400	40.607	350.390	314.135	159.520	−59.663	75.087	−0.891
4500	40.681	351.303	314.951	163.585	−59.328	78.146	−0.907
4600	40.755	352.198	315.751	167.656	−58.971	81.197	−0.922
4700	40.829	353.075	316.536	171.736	−58.591	84.240	−0.936
4800	40.902	353.936	317.306	175.822	−58.190	87.275	−0.950
4900	40.976	354.780	318.062	179.916	−57.768	90.301	−0.963
5000	41.049	355.608	318.805	184.017	−57.326	93.318	−0.975
5100	41.123	356.422	319.534	188.126	−56.864	96.327	−0.987
5200	41.196	357.221	320.252	192.242	−56.382	99.326	−0.998
5300	41.270	358.006	320.956	196.365	−55.883	102.315	−1.008
5400	41.343	358.779	321.650	200.496	−55.365	105.295	−1.019
5500	41.416	359.538	322.332	204.634	−54.831	108.266	−1.028
5600	41.490	360.285	323.003	208.779	−54.280	111.226	−1.037
5700	41.563	361.020	323.663	212.932	−53.714	114.176	−1.046
5800	41.637	361.743	324.314	217.092	−53.133	117.117	−1.055
5900	41.710	362.456	324.954	221.259	−52.538	120.047	−1.063
6000	41.783	363.157	325.585	225.434	−51.929	122.967	−1.071

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

$S°(298.15\ K) = 236.296\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 92.854 \pm 3.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 94.759 \pm 3.8\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma$	0	2

$\omega_e = 612\ cm^{-1}$ $\omega_e x_e = 4\ cm^{-1}$ $\sigma = 1$
$B_e = 0.2799\ cm$ $\alpha_e = 0.00763\ cm^{-1}$ $r_e = 1.906$ Å

Enthalpy of Formation

Durie and Gaydon[1] have obtained the dissociation limit (from the spectra) of IF as 23570 $cm.^{-1}$ The first excited states of F and I are 404 and 7598 cm^{-1} above the ground state, respectively. There are two sets of dissociation products possible: $I(^2P_{1/2}) + F(^2P_{3/2})$ or $I(^2P_{3/2}) + F(^2P_{1/2})$. When corrected to the normal atoms, the observed limit gives $D_0°$ (IF) 2.87 ± 0.04 eV or 66.18 ± 0.9 $kcal·mol^{-1}$ and 1.98 ± 0.04 eV or 45.66 ± 0.9 $kcal·mol^{-1}$ for dissociation energy, respectively. Durie and Gaydon[1] favored the lower value. However, Slutsky and Bauer[2] have pointed out a numerical error in their calculations which removes the chief support for the lower value and presented additional evidence favoring the higher value. More weight was given to the higher value which gives $\Delta_f H°(298.15\ K) = 22.648 \pm 0.9$ $kcal·mol^{-1}$ for the reaction 1/2 I_2(cr) + 1/2 F_2(g) = IF(g).

Heat Capacity and Entropy

All molecular constants were obtained from Evans *et al.*[3] except r_e = 1.906 Å which was obtained from Cole and Elverun[4] and ground state configuration which was estimated by comparison with that for IBr and ICl from Herzberg.[5]

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[5]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.106	−92.854	−92.854	INFINITE
100	29.216	202.594	264.549	−6.196	−92.922	−101.613	53.077
200	31.268	223.358	239.297	−3.188	−93.845	−109.955	28.717
250	32.537	230.474	236.843	−1.592	−94.314	−113.929	23.804
298.15	33.561	236.296	236.296	0.	−94.759	−117.666	20.615
300	33.596	236.503	236.296	0.062	−94.776	−117.808	20.512
350	34.429	241.748	236.709	1.764	−95.275	−121.609	18.149
400	35.076	246.389	237.634	3.502	−103.765	−125.062	16.331
450	35.583	250.551	238.842	5.269	−104.849	−127.659	14.818
500	35.986	254.321	240.204	7.058	−125.990	−128.236	13.397
600	36.577	260.938	243.124	10.689	−125.974	−128.687	11.203
700	36.991	266.609	246.084	14.368	−125.954	−129.141	9.637
800	37.298	271.570	248.966	18.083	−125.933	−129.597	8.462
900	37.541	275.977	251.727	21.826	−125.913	−130.057	7.548
1000	37.740	279.943	254.353	25.590	−125.894	−130.518	6.818
1100	37.911	283.549	256.846	29.373	−125.879	−130.981	6.220
1200	38.062	286.854	259.211	33.172	−125.870	−131.446	5.722
1300	38.199	289.906	261.456	36.985	−125.869	−131.910	5.300
1400	38.325	292.742	263.591	40.811	−125.881	−132.375	4.939
1500	38.443	295.390	265.623	44.649	−125.912	−132.838	4.626
1600	38.555	297.874	267.562	48.499	−125.965	−133.298	4.352
1700	38.663	300.215	269.415	52.360	−126.045	−133.754	4.110
1800	38.766	302.428	271.188	56.232	−126.153	−134.204	3.895
1900	38.867	304.527	272.888	60.113	−126.293	−134.648	3.702
2000	38.965	306.523	274.520	64.005	−126.462	−135.083	3.528
2100	39.062	308.426	276.090	67.906	−126.658	−135.510	3.371
2200	39.157	310.246	277.601	71.817	−126.877	−135.926	3.227
2300	39.250	311.988	279.059	75.738	−127.114	−136.332	3.096
2400	39.342	313.661	280.466	79.667	−127.361	−136.728	2.976
2500	39.434	315.269	281.826	83.606	−127.611	−137.113	2.865
2600	39.524	316.817	283.142	87.554	−127.857	−137.488	2.762
2700	39.614	318.310	284.417	91.511	−128.092	−137.854	2.667
2800	39.704	319.753	285.654	95.477	−128.308	−138.211	2.578
2900	39.792	321.147	286.854	99.452	−128.498	−138.562	2.496
3000	39.881	322.498	288.019	103.435	−128.657	−138.906	2.419
3100	39.969	323.807	289.153	107.428	−128.778	−139.245	2.346
3200	40.056	325.077	290.256	111.429	−128.858	−139.582	2.278
3300	40.144	326.311	291.330	115.439	−128.893	−139.916	2.215
3400	40.231	327.511	292.376	119.458	−128.879	−140.250	2.155
3500	40.317	328.678	293.397	123.485	−128.813	−140.585	2.098
3600	40.404	329.815	294.393	127.521	−128.695	−140.923	2.045
3700	40.490	330.924	295.365	131.566	−128.523	−141.265	1.994
3800	40.576	332.005	296.315	135.619	−128.296	−141.612	1.947
3900	40.662	333.060	297.244	139.681	−128.013	−141.966	1.901
4000	40.748	334.090	298.152	143.752	−127.675	−142.328	1.859
4100	40.834	335.097	299.041	147.831	−127.282	−142.700	1.818
4200	40.920	336.082	299.911	151.919	−126.834	−143.081	1.779
4300	41.005	337.046	300.764	156.015	−126.333	−143.474	1.743
4400	41.091	337.990	301.599	160.120	−125.778	−143.879	1.708
4500	41.176	338.914	302.418	164.233	−125.171	−144.296	1.675
4600	41.262	339.820	303.221	168.355	−124.514	−144.729	1.643
4700	41.347	340.709	304.010	172.485	−123.806	−145.176	1.613
4800	41.432	341.580	304.783	176.624	−123.050	−145.638	1.585
4900	41.517	342.435	305.543	180.772	−122.247	−146.117	1.558
5000	41.602	343.275	306.289	184.928	−121.398	−146.613	1.532
5100	41.687	344.099	307.023	189.092	−120.504	−147.126	1.507
5200	41.772	344.910	307.743	193.265	−119.566	−147.657	1.483
5300	41.857	345.706	308.452	197.447	−118.586	−148.206	1.461
5400	41.942	346.489	309.149	201.637	−117.564	−148.775	1.439
5500	42.027	347.260	309.835	205.835	−116.503	−149.363	1.419
5600	42.112	348.018	310.510	210.042	−115.403	−149.970	1.399
5700	42.196	348.764	311.175	214.257	−114.265	−150.597	1.380
5800	42.281	349.499	311.829	218.481	−113.090	−151.245	1.362
5900	42.366	350.222	312.474	222.714	−111.880	−151.913	1.345
6000	42.450	350.935	313.109	226.954	−110.635	−152.602	1.329

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = 66.547 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1131\ K$

$\Delta_f H°(0\ K) = -567.111 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -568.606 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 27.196\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution of KF(cr) in water has been measured by several investigators. Their results have been converted to $\Delta_{sol}H°(aq, \infty)$ by Parker[5] and listed in the table below. Using $\Delta_{sol}H°(aq, \infty) = -4.24$, $\Delta_f H°(K^+, aq, \infty, 298.15\ K) = -60.32$,[6] and $\Delta_f H°(F^-, aq, \infty, 298.15\ K) = -79.82\ kcal \cdot mol^{-1}$,[7] we obtain $\Delta_f H°(298.15\ K) = -135.9 \pm 0.1\ kcal \cdot mol^{-1}$ ($-568.606 \pm 0.4\ kJ \cdot mol^{-1}$) which is adopted.

Source	T/K	Concentration Molality	No. of Determinations	$\Delta_{sol}H°(aq,\infty)$ kcal·mol^{-1}
Guntz (1884)[1]	291	0.28	1	−3.95
Forcrand (1911)[2]	288	0.50	1	−4.54
Lange and Eichler (1927)[3]	298	3.16 – 0.21	8	−4.24±0.4
Lange and Martin (1937)[4]	298	0.31	1	−4.01

Heat Capacity and Entropy

The low temperature heat capacities, 16–323 K, were measured by Westrum and Pitzer.[8] The high temperature enthalpies, 298.15–530 K and 291–1187 K, were determined by Westrum and Pitzer,[8] and Lyashenko,[9] respectively. However, the high temperature $C_p°$ values derived from both sets appear to be inconsistent with the low temperature $C_p°$ values. The heat capacities derived from the enthalpy data of Westrum and Pitzer are too high (3% at 530 K and less at lower temperatures) to be joined smoothly with their low temperature $C_p°$'s. The adopted enthalpy at 530 K is about 1.4% lower than the reported value. The heat capacity derived from the enthalpy data of Lyashenko is 2.5% lower than the adopted one at 900 K. The differences are smaller at lower temperatures. At 900 K, the adopted enthalpy is 1.3% higher than the reported value. The adopted heat capacities in the temperature range, 323–2000 K, are estimated by graphical comparison with other alkali fluorides and chlorides, and joined smoothly with the low temperature data at 298.15 K.

$S°(298.15\ K)$ is derived based on the adopted low temperature heat capacities.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The value of $\Delta_{sub}H°(298.15\ K) = 241.835\ kJ \cdot mol^{-1}$ for the process KF(cr) = KF(g) for the process KF(cr) = KF(g) is obtained as the difference between $\Delta_f H°(298.15\ K)$ for KF(cr) and KF(g).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.000	−567.111	−567.111	INFINITE
100	31.606	20.497	107.023	−8.653	−568.949	−558.920	291.950
200	45.187	47.660	70.944	−4.657	−569.013	−548.781	143.327
298.15	48.982	66.547	66.547	0.	−568.606	−538.934	94.419
300	49.022	66.850	66.547	0.091	−568.599	−538.750	93.805
400	51.045	81.245	68.496	5.099	−570.678	−528.399	69.002
500	52.718	92.820	72.240	10.290	−570.278	−517.872	54.102
600	54.266	102.571	76.504	15.640	−569.704	−507.442	44.177
700	55.856	111.056	80.846	21.147	−568.969	−497.121	37.096
800	57.404	118.614	85.103	26.808	−568.089	−486.915	31.792
900	59.078	125.468	89.213	32.630	−567.077	−476.828	27.674
1000	61.170	131.797	93.159	38.639	−565.926	−466.860	24.386
1100	63.848	137.748	96.944	44.884	−643.560	−452.406	21.483
1131.000	64.852	139.536	98.087	46.878	--- CRYSTAL <--> LIQUID ---		
1200	66.777	143.436	100.583	51.423	−640.972	−435.140	18.941
1300	68.618	148.858	104.090	58.198	−638.160	−418.101	16.799
1400	69.789	153.989	107.472	65.123	−635.210	−401.283	14.972
1500	70.500	158.830	110.736	72.140	−632.178	−384.679	13.396
1600	70.919	163.394	113.886	79.212	−629.101	−368.280	12.023
1700	71.128	167.701	116.926	86.316	−626.002	−352.073	10.818
1800	71.128	171.766	119.861	93.429	−622.904	−336.049	9.752
1900	71.128	175.612	122.695	100.542	−619.816	−320.197	8.803
2000	71.128	179.260	125.433	107.655	−616.738	−304.507	7.953

PREVIOUS: December 1963 CURRENT: June 1969

$S°(298.15\ K) = [67.634]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-554.467]\ kJ·mol^{-1}$

$T_{fus} = 1131\ K$ $\Delta_{fus}H° = 27.196\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(KF,l, 298.15 K) is calculated from $\Delta_f H°$(KF, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°$(1131 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those of the alkali fluorides and chlorides, and is assumed to be constant in the temperature range, 298–3000 K. The $C_p°$ value, 16 cal $K^{-1}·mol^{-1}$, derived from the enthalpy data of Lyashenko[12] appears low and is not adopted.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} has been reported as 1119,[1,2] 1129,[3,4] 1131,[5,6] and 1153 K.[7] The value 1131 K is adopted. Kelley[8] evaluated the following freezing–point data of binary systems: KF-AlF_3,[9] KF-K_2SO_4,[10] KF-KCl,[11] KF-K_2CO_3,[13] and KF- K_3PO_4,[14] and derived the values of $\Delta_{fus}H°$ (in $kcal·mol^{-1}$) as 5.5, 5.55, 6.51, 7.1, and 7.1, respectively. The best value is recommended as 6.50 $kcal·mol^{-1}$. Other reported $\Delta_{fus}H°$ values are 6.70[7] and 6.75±0.1 $kcal·mol^{-1}$.[12] The value of heat of melting is tentatively adopted as 6.50 $kcal·mol^{-1}$.

Vaporization Data

The boiling point (T_{vap}=1790K) is calculated to be the temperature at which the partial pressures of KF(g) and K_2F_2(g) equal one atmosphere. The composition of the gaseous mixture in equilibrium with KF(l) at T_{fus} is calculated as K_2F_2 21.1% and KF 78.9%. The heat required to vaporize one mole of liquid at T_{vap} is evaluated to be 33.9 $kcal·mol^{-1}$ (141.838 $kJ·mol^{-1}$).

The experimental values for the boiling point are 1778 K^{-1} and 1771 K.[15]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	71.965	67.634	67.634	0.	−554.467	−525.120	91.999
300	71.965	68.079	67.635	0.133	−554.418	−524.938	91.400
400	71.965	88.782	70.458	7.330	−554.309	−515.045	67.258
500	71.965	104.840	75.788	14.526	−551.903	−505.507	52.810
600	71.965	117.961	81.757	21.723	−549.483	−496.455	43.220
700	71.965	129.055	87.742	28.919	−547.058	−487.809	36.401
800	71.965	138.664	93.520	36.116	−544.643	−479.510	31.309
900	71.965	147.140	99.016	43.312	−542.256	−471.512	27.366
1000	71.965	154.723	104.214	50.508	−539.918	−463.777	24.225
1100	71.965	161.582	109.123	57.705	−616.600	−451.664	21.448
1131.000	71.965	163.582	110.588	59.936	--- CRYSTAL <---> LIQUID ---		
1200	71.965	167.843	113.759	64.901	−613.355	−436.813	19.014
1300	71.965	173.604	118.144	72.098	−610.122	−422.232	16.965
1400	71.965	178.937	122.298	79.294	−606.900	−407.900	15.219
1500	71.965	183.902	126.241	86.491	−603.688	−393.798	13.713
1600	71.965	188.546	129.992	93.687	−600.487	−379.910	12.403
1700	71.965	192.909	133.566	100.884	−597.296	−366.221	11.253
1800	71.965	197.023	136.978	108.080	−594.114	−352.720	10.236
1900	71.965	200.914	140.242	115.277	−590.942	−339.396	9.331
2000	71.965	204.605	143.368	122.473	−587.781	−326.239	8.520
2100	71.965	208.116	146.368	129.670	−584.629	−313.239	7.791
2200	71.965	211.464	149.252	136.866	−581.488	−300.390	7.132
2300	71.965	214.663	152.027	144.063	−578.357	−287.683	6.533
2400	71.965	217.726	154.701	151.259	−575.238	−275.111	5.988
2500	71.965	220.663	157.281	158.456	−572.130	−262.670	5.488
2600	71.965	223.486	159.773	165.652	−569.035	−250.353	5.030
2700	71.965	226.202	162.184	172.849	−565.954	−238.154	4.607
2800	71.965	228.819	164.517	180.045	−562.889	−226.070	4.217
2900	71.965	231.344	166.778	187.242	−559.841	−214.094	3.856
3000	71.965	233.784	168.971	194.438	−556.811	−202.224	3.521

PREVIOUS: December 1963 CURRENT: June 1969

0	to	1131	K crystal
above		1131	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.000	−567.111	−567.111	INFINITE
100	31.606	20.497	107.023	−8.653	−568.949	−558.920	291.950
200	45.187	47.660	70.944	−4.657	−569.013	−548.781	143.327
298.15	48.982	66.547	66.547	0.	−568.606	−538.934	94.419
300	49.022	66.850	66.547	0.091	−568.599	−538.750	93.805
400	51.045	81.245	68.496	5.099	−570.678	−528.399	69.002
500	52.718	92.820	72.240	10.290	−570.278	−517.872	54.102
600	54.266	102.571	76.504	15.640	−569.704	−507.442	44.177
700	55.856	111.056	80.846	21.147	−568.969	−497.121	37.096
800	57.404	118.614	85.103	26.808	−568.089	−486.915	31.792
900	59.078	125.468	89.213	32.630	−567.077	−476.828	27.674
1000	61.170	131.797	93.159	38.639	−565.926	−466.860	24.386
1100	63.848	137.748	96.944	44.884	−643.560	−452.406	21.483
1131.000	64.852	139.536	98.087	46.878	CRYSTAL <--> LIQUID		
1131.000	71.965	163.582	98.087	74.074	TRANSITION		
1200	71.965	167.843	101.977	79.040	−613.355	−436.813	19.014
1300	71.965	173.604	107.268	86.236	−610.122	−422.232	16.965
1400	71.965	178.937	112.199	93.433	−606.900	−407.900	15.219
1500	71.965	183.902	116.816	100.629	−603.688	−393.798	13.713
1600	71.965	188.546	121.155	107.826	−600.487	−379.910	12.403
1700	71.965	192.909	125.249	115.022	−597.296	−366.221	11.253
1800	71.965	197.023	129.123	122.219	−594.114	−352.720	10.236
1900	71.965	200.914	132.800	129.415	−590.942	−339.396	9.331
2000	71.965	204.605	136.299	136.612	−587.781	−326.239	8.520
2100	71.965	208.116	139.636	143.808	−584.629	−313.239	7.791
2200	71.965	211.464	142.825	151.005	−581.488	−300.390	7.132
2300	71.965	214.663	145.880	158.201	−578.357	−287.683	6.533
2400	71.965	217.726	148.810	165.398	−575.238	−275.111	5.988
2500	71.965	220.663	151.626	172.594	−572.130	−262.670	5.488
2600	71.965	223.486	154.336	179.791	−569.035	−250.353	5.030
2700	71.965	226.202	156.947	186.987	−565.954	−238.154	4.607
2800	71.965	228.819	159.468	194.184	−562.889	−226.070	4.217
2900	71.965	231.344	161.903	201.380	−559.841	−214.094	3.856
3000	71.965	233.784	164.258	208.577	−556.811	−202.224	3.521

PREVIOUS: CURRENT: June 1969

$S°(298.15\ K) = 226.612 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -324.729 \pm 2.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -326.770 \pm 2.1\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 426.04\ cm^{-1}$ $\omega_e x_e = 2.43\ cm^{-1}$ $\sigma = 1$

$B_e = 0.27994\ cm^{-1}$ $\alpha_e = 0.002335\ cm^{-1}$ $r_e = 2.17155$ Å

Enthalpy of Formation

The total vapor pressures of KF(g) and $K_2F_2(g)$ over KF(cr, l) have been determined by many investigators using the boiling point,[1, 2, 5] Knudsen–effusion,[3] transpiration,[4] and torsion–effusion 6 methods. A method of trial and error is employed to select the appropriate values for $\Delta_{sub}H°$(KF, cr, 298.15 K) and $\Delta_{vap}H°$(KF, l, 298.15 K) such that by use of these two values and $\Delta_f H°(298.15\ K) = 50\ kcal·mol^{-1}$ for the reaction $K_2F_2(g) = 2\ KF(g)$ and the Gibbs energy functions for KF(cr), KF(l), KF(g), and $K_2F_2(g)$, the calculated total pressures of KF(g) and $K_2F_2(g)$ are consistent with the measured ones. Adopting $\Delta_{sub}H°(298.15\ K) = 57.8$ and $\Delta_{vap}H°(298.15\ K) = 54.42\ kcal·mol^{-1}$, we evaluate the partial pressures of KF(g) and $K_2F_2(g)$ from the reported total pressure measurements. Based on the derived partial pressures for KF(g), the enthalpy changes for the processes: A) KF(cr) = KF(g), and B) KF(l) = KF(g) are calculated by the 2nd and 3rd law methods. Using the 3rd law $\Delta_f H°(298.15\ K)$ and $\Delta_f H°(298.15\ K) = -135.90$ and $-132.519\ kcal·mol^{-1}$ for KF(cr) and KF(l), respectively, we obtain the $\Delta_f H°(298.15\ K)$ for KF(g). The results are presented in the table below.

The dissociation energy of KF(g) has been determined as $117 \pm 8\ kcal·mol^{-1}$ by flame photometry by Page and Sugden,[7] and Bulewicz, Phillips, and Sugden,[8] yielding $\Delta_f H°$(KF, g, 298.15 K) = $-77.6 \pm 8\ kcal·mol^{-1}$. Barrow and Caunt[9] measured the fluctuation bands in the ultraviolet absorption spectra of KF and reported the upper limit for the $D_0°$(KF, g) value to be $121.8\ kcal·mol^{-1}$ which leads to $\Delta_f H°$(KF, g, 298.15 K) = $-81.4\ kcal·mol^{-1}$ as the lower limit. Gaydon[1] reported $D_0° = 116.9 \pm 4.6\ kcal·mol^{-1}$ for KF(g). The corresponding value of $\Delta_f H°(298.15\ K)$ is calculated as $-77.5 \pm 4.6\ kcal·mol^{-1}$.

The enthalpy of formation for KF(g) at 298.15 K is adopted as $.78.1 \pm 0.5\ kcal·mol^{-1}$.

Source	Method	T/K	Data Points	Process	$\Delta_f H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal $K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Wartenberg[1]	boiling point	1624–1776	5	B	54.4±0.9	54.16	−0.1±0.5	−78.36
Ruff[2]	boiling point	1551–1773	6	B	58.1±2.5	54.14	−2.4±1.5	−78.38
Niwa[3]	Knudsen–effusion	913–973	6	A	56.2±0.3	55.67	−0.6±0.3	−80.23
Naryshkin[4]	transpiration	1023–1108	2	A	—	57.23	—	−78.67
		1188–1233	2**	B	—	54.60	—	−77.92
Cantor[5]	boiling point	1200–1500	7*	B	54.4	54.38	−0.02	−78.14
Pugh[6]	torsion–effusion	910–1020	6*	A	57.7	58.12	0.47	−77.78

* Data points calculated from the given vapor pressure equation.

** Only the data point at 1233 K is adopted for evaluation.

Heat Capacity and Entropy

The rotational transition spectrum of KF(g) has been measured in the millimeter– and submillimeter–wave region with a high resolution molecular–beam absorption spectrometer by Veazey and Gordy.[15] From the derived potential constants the vibrational constants were calculated. The reported values for ω_e, $\omega_e x_e$, B_e, α_e and r_e are adopted.

Other values of ω_e reported are (in cm^{-1}): 390 ± 39,[11] 405 ± 25,[9] 429 ± 3,[12] and 426 ± 4.[13] The value of $\omega_e x_e$ has been determined as 1.45 cm^{-1} by Barrow and Caunt,[9] and 2.4 cm^{-1} by Ritchie and Lew[12] and Baikov and Vasilevskii.[13] Using the molecular beam electric resonance method, Green and Lew[14] measured the rotational transitions between the J = 0 and J = 1 states of $K^{39}F$ and reported the following values: $B_e = 0.27994\ cm^{-1}$, $\alpha_e = 0.002335\ cm^{-1}$, and $r_e = 2.17144 \pm 0.00005$ Å which are in excellent agreement with the adopted values. By use of the same method, Grabner and Hughes[11] investigated the rotational Stark spectrum of $K^{39}F$ and reported the K–F bond distance for the zeroth vibrational state as 2.55 ± 0.06 Å.

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Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−9.453	−324.729	−324.729	INFINITE
100	29.837	191.161	256.478	−6.532	−324.993	−332.031	173.435
200	33.260	212.918	229.781	−3.373	−325.893	−338.713	88.463
250	34.438	220.474	227.187	−1.678	−326.325	−341.868	71.429
298.15	35.228	226.612	226.612	0.	−326.770	−344.822	60.411
300	35.253	226.830	226.612	0.065	−326.789	−344.934	60.058
350	35.826	232.309	227.044	1.843	−329.697	−347.821	51.909
400	36.242	237.122	228.009	3.645	−330.297	−350.369	45.753
450	36.553	241.409	229.264	5.465	−330.874	−352.843	40.957
500	36.793	245.273	230.675	7.299	−331.433	−355.254	37.113
600	37.141	252.015	233.686	10.997	−332.511	−359.916	31.333
700	37.385	257.759	236.725	14.724	−333.556	−364.400	27.192
800	37.570	262.764	239.673	18.472	−334.590	−368.736	24.076
900	37.719	267.198	242.490	22.237	−335.635	−372.942	21.645
1000	37.846	271.179	245.163	26.015	−336.714	−377.030	19.694
1100	37.958	274.791	247.695	29.806	−416.803	−376.397	17.874
1200	38.060	278.098	250.093	33.607	−416.953	−372.717	16.224
1300	38.155	281.148	252.366	37.417	−417.106	−369.024	14.828
1400	38.244	283.979	254.524	41.237	−417.260	−365.320	13.630
1500	38.329	286.621	256.577	45.066	−417.417	−361.604	12.592
1600	38.412	289.097	258.533	48.903	−417.574	−357.878	11.684
1700	38.492	291.428	260.400	52.748	−417.734	−354.143	10.881
1800	38.570	293.631	262.185	56.601	−417.896	−350.397	10.168
1900	38.647	295.718	263.896	60.462	−418.060	−346.643	9.530
2000	38.722	297.702	265.537	64.331	−418.227	−342.880	8.955
2100	38.797	299.593	267.114	68.207	−418.396	−339.108	8.435
2200	38.871	301.400	268.632	72.090	−418.567	−335.329	7.962
2300	38.944	303.129	270.094	75.981	−418.743	−331.541	7.530
2400	39.017	304.788	271.506	79.879	−418.921	−327.746	7.133
2500	39.089	306.383	272.869	83.784	−419.105	−323.943	6.768
2600	39.160	307.917	274.188	87.697	−419.294	−320.133	6.432
2700	39.232	309.396	275.464	91.616	−419.490	−316.315	6.119
2800	39.303	310.824	276.702	95.543	−419.694	−312.490	5.830
2900	39.374	312.205	277.902	99.477	−419.909	−308.658	5.560
3000	39.444	313.541	279.068	103.418	−420.135	−304.818	5.307
3100	39.515	314.835	280.201	107.366	−420.376	−300.970	5.071
3200	39.585	316.091	281.303	111.321	−420.635	−297.114	4.850
3300	39.655	317.310	282.376	115.283	−420.905	−293.251	4.642
3400	39.725	318.495	283.421	119.252	−421.203	−289.378	4.446
3500	39.795	319.648	284.440	123.228	−421.526	−285.496	4.261
3600	39.865	320.770	285.433	127.211	−421.880	−281.605	4.086
3700	39.935	321.863	286.403	131.201	−422.269	−277.703	3.920
3800	40.004	322.929	287.350	135.198	−422.696	−273.790	3.764
3900	40.074	323.969	288.276	139.202	−423.167	−269.865	3.614
4000	40.143	324.984	289.181	143.213	−423.679	−265.929	3.473
4100	40.213	325.976	290.067	147.230	−424.245	−261.979	3.338
4200	40.282	326.946	290.933	151.255	−424.872	−258.013	3.209
4300	40.351	327.895	291.782	155.287	−425.561	−254.033	3.086
4400	40.421	328.823	292.613	159.325	−426.040	−250.062	2.969
4500	40.490	329.733	293.428	163.371	−426.800	−246.054	2.856
4600	40.559	330.623	294.227	167.423	−427.624	−242.029	2.748
4700	40.628	331.496	295.011	171.483	−428.496	−237.986	2.645
4800	40.697	332.352	295.780	175.549	−429.329	−233.937	2.546
4900	40.766	333.192	296.535	179.622	−430.335	−229.856	2.450
5000	40.835	334.016	297.276	183.702	−431.413	−225.754	2.358
5100	40.904	334.826	298.004	187.789	−432.564	−221.629	2.270
5200	40.973	335.621	298.720	191.883	−433.790	−217.481	2.185
5300	41.042	336.402	299.424	195.984	−435.090	−213.309	2.102
5400	41.111	337.170	300.116	200.091	−436.466	−209.112	2.023
5500	41.180	337.925	300.796	204.206	−437.917	−204.889	1.946
5600	41.249	338.667	301.466	208.327	−439.442	−200.638	1.871
5700	41.318	339.398	302.125	212.456	−440.697	−196.407	1.800
5800	41.387	340.117	302.774	216.591	−442.325	−192.108	1.730
5900	41.456	340.825	303.413	220.733	−444.020	−187.779	1.662
6000	41.525	341.523	304.042	224.882	−445.779	−183.421	1.597

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

$S°(298.15\ K) = 35.660 \pm 0.021\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1121.3 \pm 1.0\ K$

$\Delta_f H°(0\ K) = -614.369 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 616.931 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 27.087 \pm 0.021\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpies of solution and reaction of LiF(cr) in water and hydrochloric acid have been measured by many investigators. The reported $\Delta_{sln}H°$ values are listed in the table below. Using $\Delta_f H°(Li,^+ aq, \infty, 298.15\ K) = -66.56\ kcal \cdot mol^{-1}$,[8] and $\Delta_f H°(F,^- aq, \infty, 298.15\ K) = -79.82\ kcal \cdot mol^{-1}$,[9] we calculate the corresponding $\Delta_f H°(298.15\ K)$ values for LiF(cr). Based on the enthalpy of solution of LiOH(cr) in excess HF solution measured by Sinke,[7] the value, $\Delta_f H°(LiF, cr, 298.15\ K) = 146.65 \pm 0.5\ kcal \cdot mol^{-1}$ is derived. The value of $\Delta_f H°(298.15\ K)$ for LiF(cr) is adopted as $147.45 \pm 0.2\ kcal \cdot mol^{-1}$.

Source	Solvent	T/K	Concentration ($LiF \cdot nH_2O$)	$\Delta_r H°$, kcal·mol^{-1}	$\Delta_\infty H°$, kcal·mol^{-1}*	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
R.de Forcrand (1911)[1]	H_2O	288.2	unavailable	1.04	–	–
Kolesov–Skuratov (1961)[2]	H_2O	294.7	3800 H_2O	1.25 ± 0.02	1.13 ± 0.05	−147.50
Wulff (1962)[3]	HCl	298.2	unavailable	unavailable	1.10 ± 0.10	−147.47
Stephenson *et al.*(1964)[4]	H_2O	298.2	2780–5560 H_2O	unavailable	1.07 ± 0.05	−147.44
Cox and Harrop (1964)[5]	H_2O	298.2	60400 H_2O	1.059 ± 0.028	1.014 ± 0.055	−147.38

*The enthalpy of dilution data of Parker[6] are used to convert $\Delta_r H°$ to $\Delta_\infty H°$

Heat Capacity and Entropy

Clusius, *et al.*[10] measured the low temperature heat capacities in the temperature range 19 to 272 K and Clusius and Eishenauer[11] from 10 to 111 K. Below 20 K a number of investigators have reported values of θ_D, and the average value of 729 ± 6 is used here. The high temperature enthalpies from 298.15 K to the melting point 1121.3 K were measured by Douglas and Dever,[12] and Voskresenskaya *et al.*[13] All these data are taken and smoothed by computer to 400 K. Above 400 K the $C_p°$ values are obtained graphically by drawing a smooth line through the data points.

$S°(298.15\ K)$ is derived from the adopted low temperature heat capacities, based on $S°(20\ K) = 0.064\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K) = 276.144\ kJ \cdot mol^{-1}$, is calculated as the difference between $\Delta_f H°(298.15\ K)$ for LiF(g) and LiF(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−6.473	−614.369	−614.369	INFINITE
100	12.816	4.858	65.944	−6.109	−615.953	−607.186	317.162
200	32.803	20.690	39.225	−3.707	−616.858	−597.965	156.172
298.15	41.815	35.660	35.660	0.	−616.931	−588.660	103.131
300	41.936	35.919	35.661	0.077	−616.928	−588.485	102.464
400	46.543	48.706	37.373	4.533	−616.682	−579.039	75.615
500	49.329	59.401	40.738	9.331	−619.500	−569.345	59.479
600	51.589	68.597	44.633	14.378	−619.173	−559.341	48.695
700	53.723	76.711	48.647	19.645	−618.607	−549.410	40.997
800	55.731	84.016	52.619	25.118	−617.835	−539.575	35.231
900	57.697	90.695	56.483	30.790	−616.881	−529.848	30.752
1000	59.580	96.871	60.217	36.654	−615.749	−520.237	27.174
1100	61.505	102.642	63.814	42.710	−614.434	−510.748	24.253
1121.300	61.883	103.825	64.563	44.02	--- CRYSTAL <---> LIQUID ---		
1200	63.245	108.068	67.278	48.948	−612.944	−501.386	21.825
1300	64.892	113.196	70.615	55.356	−611.294	−492.155	19.775
1400	66.445	118.063	73.832	61.923	−609.487	−483.058	18.023
1500	67.906	122.697	76.936	68.642	−607.532	−474.094	16.509
1600	69.274	127.124	79.936	75.502	−605.436	−465.266	15.189
1700	70.549	131.363	82.837	82.494	−748.444	−449.397	13.808
1800	71.731	135.429	85.647	89.608	−745.339	−431.895	12.533
1900	72.821	139.337	88.370	96.837	−742.129	−414.569	11.397
2000	73.817	143.098	91.013	104.169	−738.820	−397.414	10.379
2100	74.720	146.722	93.580	111.597	−735.423	−380.427	9.463
2200	75.530	150.217	96.076	119.110	−731.944	−363.603	8.633
2300	76.248	153.590	98.503	126.700	−728.394	−346.940	7.879
2400	76.872	156.849	100.867	134.357	−724.780	−330.432	7.192
2500	77.404	159.998	103.170	142.071	−721.112	−314.076	6.562

PREVIOUS: December 1963 CURRENT: December 1968

$S°(298.15\ K) = [42.962]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1121.3 \pm 1.0\ K$

$\Delta_f H°(298.15\ K) = [-598.651]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 27.087 \pm 0.021\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiF, l, 298.15 K) is calculated from $\Delta_f H°$(LiF, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1121.3\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Douglas and Dever[1] and Voskresenskaya *et al.*[2] have measured the enthalpies of LiF liquid to 1200 and 1400 K, respectively. Using the reported enthalpy data, a constant heat capacity is derived for each set. The adopted $C_p°$ for LiF(l) is the mean of the two derived heat capacities, and is extended arbitrarily to the temperatures above T_{vap} and below T_{fus}. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point has been determined by many investigators. See the table below for details. The adopted value, 1121.3±1.0 K, is that reported by Douglas and Dever.[1] The heat of melting is the mean of the $\Delta_{fus}H°$ values reported by Douglas and Dever[1] and Voskresenskaya *et al.*[2]

T_{fus}/K	Source
1115	von Wartenberg and Schulz[3]
1115	Petit and Cremieu[4]
1119	Flood *et al.*[5]
1120	Goryacheva *et al.*[6]
1121	Haendler *et al.*[7]
1121.2	Mateiko and Bukhalova[8]
1121.3	Douglas and Dever[9]
1123	Bukhalova and Sementsova[10]

Vaporization Data

T_{vap} = 1990 K is the temperature at which the partial pressures of LiF(g), Li_2F_2(g), and Li_3F_3(g), in equilibrium with LiF(l), equal one atmosphere. The vapor composition at the boiling point is evaluated as LiF 69%, Li_2F_2 26.6%, and Li_3F_3 4.4%. The heat required to vaporize one mole of liquid to form 0.739 mole of vapor mixture of the above composition at T_{vap} is calculated to be 35.08 $kcal·mol^{-1}$ (146.775 $kJ·mol^{-1}$).

The value of T_{vap} for LiF(l) has been reported to be 1943 and 1949 K by Ruff *et al.*[3] and von Wartenberg and Schulz,[1] respectively, which were obtained by extrapolation of their vapor pressure data, measured by the boiling point method.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	64.183	42.962	42.962	0.	−598.651	−572.558	100.310
300	64.183	43.359	42.964	0.119	−598.607	−572.396	99.663
400	64.183	61.824	45.481	6.537	−596.399	−564.003	73.651
500	64.183	76.146	50.235	12.955	−597.597	−555.814	58.065
600	64.183	87.847	55.558	19.374	−595.898	−547.617	47.674
700	64.183	97.741	60.896	25.792	−594.181	−539.705	40.273
800	64.183	106.312	66.049	32.210	−592.464	−532.040	34.739
900	64.183	113.871	70.951	38.628	−590.764	−524.589	30.446
1000	64.183	120.634	75.587	45.047	−589.077	−517.327	27.022
1100	64.183	126.751	79.965	51.465	−587.399	−510.234	24.229
1121.300	64.183	127.982	80.865	52.832	--- CRYSTAL <---> LIQUID ---		
1200	64.183	132.335	84.100	57.883	−585.730	−503.292	21.908
1300	64.183	137.473	88.010	64.301	−584.069	−496.490	19.949
1400	64.183	142.229	91.715	70.720	−582.412	−489.815	18.275
1500	64.183	146.657	95.232	77.138	−580.757	−483.259	16.829
1600	64.183	150.800	98.577	83.556	−579.102	−476.813	15.566
1700	64.183	154.691	101.765	89.974	−722.684	−463.294	14.235
1800	64.183	158.359	104.808	96.393	−720.276	−448.106	13.004
1900	64.183	161.829	107.718	102.811	−717.875	−433.051	11.905
2000	64.183	165.122	110.507	109.229	−715.481	−418.122	10.920
2100	64.183	168.253	113.183	115.647	−713.093	−403.313	10.032
2200	64.183	171.239	115.754	122.066	−710.710	−388.617	9.227
2300	64.183	174.092	118.229	128.484	−708.331	−374.030	8.494
2400	64.183	176.823	120.614	134.902	−705.955	−359.546	7.825
2500	64.183	179.443	122.915	141.320	−703.583	−345.161	7.212
2600	64.183	181.961	125.138	147.739	−701.214	−330.871	6.647
2700	64.183	184.383	127.288	154.157	−698.848	−316.672	6.126
2800	64.183	186.717	129.369	160.575	−696.484	−302.560	5.644
2900	64.183	188.969	131.385	166.993	−694.124	−288.533	5.197
3000	64.183	191.145	133.341	173.412	−691.768	−274.588	4.781

PREVIOUS: December 1963 CURRENT: December 1968

0 to 1121.3 K crystal
above 1121.3 K liquid

Refer to individual tables for details

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.473	−614.369	−614.369	INFINITE
100	12.816	4.858	65.944	−6.109	−615.953	−607.186	317.162
200	32.803	20.690	39.225	−3.707	−616.858	−597.965	156.172
298.15	41.815	35.660	35.660	0.	−616.931	−588.660	103.131
300	41.936	35.919	35.661	0.077	−616.928	−588.485	102.464
400	46.543	48.706	37.373	4.533	−616.682	−579.039	75.615
500	49.329	59.401	40.738	9.331	−619.500	−569.345	59.479
600	51.589	68.597	44.633	14.378	−619.173	−559.341	48.695
700	53.723	76.711	48.647	19.645	−618.607	−549.410	40.997
800	55.731	84.016	52.619	25.118	−617.835	−539.575	35.231
900	57.697	90.695	56.483	30.790	−616.881	−529.848	30.752
1000	59.580	96.871	60.217	36.654	−615.749	−520.237	27.174
1100	61.505	102.642	63.814	42.710	−614.434	−510.748	24.253
1121.300	61.883	103.825	64.563	44.024	CRYSTAL <--> LIQUID TRANSITION		
1121.300	64.183	127.982	64.563	71.111			
1200	64.183	132.335	68.867	76.162	−585.730	−503.292	21.908
1300	64.183	137.473	73.949	82.581	−584.069	−496.490	19.949
1400	64.183	142.229	78.659	88.999	−582.412	−489.815	18.275
1500	64.183	146.657	83.046	95.417	−580.757	−483.259	16.829
1600	64.183	150.800	87.152	101.835	−579.102	−476.813	15.566
1700	64.183	154.691	91.012	108.254	−722.684	−463.294	14.235
1800	64.183	158.359	94.653	114.672	−720.276	−448.106	13.004
1900	64.183	161.829	98.098	121.090	−717.875	−433.051	11.905
2000	64.183	165.122	101.367	127.508	−715.481	−418.122	10.920
2100	64.183	168.253	104.478	133.927	−713.093	−403.313	10.032
2200	64.183	171.239	107.446	140.345	−710.710	−388.617	9.227
2300	64.183	174.092	110.282	146.763	−708.331	−374.030	8.494
2400	64.183	176.823	112.998	153.181	−705.955	−359.546	7.825
2500	64.183	179.443	115.604	159.600	−703.583	−345.161	7.212
2600	64.183	181.961	118.108	166.018	−701.214	−330.871	6.647
2700	64.183	184.383	120.518	172.436	−698.848	−316.672	6.126
2800	64.183	186.717	122.841	178.854	−696.485	−302.560	5.644
2900	64.183	188.969	125.082	185.273	−694.124	−288.533	5.197
3000	64.183	191.145	127.248	191.691	−691.768	−274.588	4.781

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = 200.278 \pm 0.008\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -340.575 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -340.787 \pm 8.4\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 914.33\ cm^{-1}$ $\omega_e x_e = 8.00\ cm^{-1}$ $\sigma = 1$

$B_e = 1.3588\ cm^{-1}$ $\alpha_e = 0.0203\ cm^{-1}$ $r_e = 1.5631$Å

Enthalpy of Formation

The molecular species produced on vaporization of lithium fluoride have been studied by many investigators during the last ten years. The occurrence of dimer and trimer molecules in addition to the monomer has been established by use of mass spectrometric,[4,7,8] torsion effusion,[3,6] molecular beam[9,10] and transpiration[11] methods. To evaluate $\Delta_{vap}H°$(LiF, g) we have used a trial and error variation of $\Delta_{sub}H°$ and $\Delta_{vap}H°$ for the monomer, dimer and trimer in order to obtain reasonable agreement with the observed total pressures, 997–1939 K.[1,2,3,5,6] Using as guidelines these total pressures and the equilibrium data for dimer and trimer (refer to these tables), we adopt $\Delta_{sub}H°(298.15\ K) = 66.0$, 69.57 and 79.73 and $\Delta_{vap}H°(298.15\ K) = 61.63$, 60.83 and 66.62 $kcal·mol^{-1}$ for LiF, Li_2F_2 and Li_3F_3, respectively. The adopted value $\Delta_{sub}H°(1000\ K) = 63.1\ kcal·mol^{-1}$ is in agreement with the reported values: 64.8 ± 2[12], 63.6 ± 1[6] and 63.0 ± 1.5[8] $kcal·mol^{-1}$ at 1000 K.

A 2nd and 3rd law analysis of the total pressure data is given below. Monomer pressures for this analysis are obtained by deducing dimer and trimer pressures calcualted from JANAF free energy functions and the adopted values of $\Delta_{sub}H°(298.15\ K)$ and $\Delta_{vap}H°(298.15\ K)$.

The vapor pressure data reported by Eisenstadt *et al.*[9,10] are too low and so not consistent with the others and are not used for evaluation. The transpiration data of Sense and Stone[11] and Knudsen effusion data of Evseev *et al.*[13] are not considered for analysis because of the complications involved in converting the report apparent pressures to the real total pressures of the gaseous mixtures containing monomer, dimer and trimer.

Herzberg[14] and Gaydon[15] reported the dissociation energies ($D_0°$) of LiF(g) to be <6.6 and 5.95 ± 0.3 eV, respectively. Using these $D_0°$ values, we derive $\Delta_f H°$(LiF, g, 298.15 K) as −95.9 and −80.9 ± 6.9 $kcal·mol^{-1}$. By use of flame photometric method, Page and Sugden[16] and Bulewicz *et al.*[17] gave $D_0° = 141$ and 136 ± 8 $kcal·mol^{-1}$, yielding $\Delta_f H°$(LiF, g, 298.15 K) = −84.7 and −79.7 ± 8 $kcal·mol^{-1}$.

Source	T/K	Method	Reaction*	Data Points	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal\ K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
von Wartenberg (1921)[1]	1626–1820	boiling point	I	5	67.6±2.4	61.4	−3.6±1.4	−81.68
Ruff (1922)[2]	1671–1939	boiling point	I	14	65.8±0.7	60.8	−2.7±0.4	−82.28
Pugh (1958)*[3]	1020–1120	torsion effusion	II	6	69.1	66.8	−2.2	−80.65
Porter (1958)[4]	1073	mass spectrometry	II	1	–	67.7	–	−79.75
Cantor (1958)*[5]	1328–1575	boiling point	I	10	64.5	61.6	−2.0	−81.48
Hildenbrand (1964)*[6]	997–1119	torsion effusion	II	24	69.9	66.8	−3.0	−80.65
	1125–1159	torsion effusion	I	19	67.1	62.3	−4.2	−80.78

*Data points are calculated from the given vapor pressure equation.
Reaction I: LiF(l) = LiF(g); II: LiF(cr) = LiF(g).

Heat Capacity and Entropy

The infrared spectrum of LiF(g) and microwave spectrum of Li^6F have been observed by Vidale[19] and Wharten and Klemperer,[21] respectively. The reported vibrational and rotational constants for Li^7F and Li^6F(g) are adopted and corrected to the average isotopic species. Veazey and Gordy[18] measured the rotational transitions of Li^7F with a high resolution molecular beam absorption spectrometer. By use of the electric resonance method of molecular beam spectroscopy, Braunstein and Trischka[22] observed the transitions between $v = 0$ and $v = 1$ vibrational states. The infrared spectrum of LiF(g) have also been measured by Vasilevskii and Baikov.[20]

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Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.823	−340.575	−340.575	INFINITE
100	29.119	167.860	227.033	−5.917	−339.618	−347.151	181.333
200	29.683	188.144	203.084	−2.988	−339.995	−354.593	92.610
250	30.438	194.845	200.788	−1.486	−340.372	−358.200	74.842
298.15	31.287	200.278	200.278	0.	−340.787	−361.597	63.350
300	31.320	200.471	200.278	0.058	−340.803	−361.726	62.982
350	32.185	205.365	200.663	1.646	−341.273	−365.177	54.500
400	32.965	209.715	201.527	3.275	−341.797	−368.557	48.129
450	33.641	213.638	202.659	4.941	−342.388	−371.867	43.165
500	34.215	217.213	203.938	6.637	−346.050	−374.801	39.155
600	35.110	223.534	206.691	10.106	−347.301	−380.431	33.120
700	35.756	228.998	209.496	13.651	−348.457	−385.861	28.793
800	36.234	233.805	212.240	17.252	−349.557	−391.128	25.538
900	36.600	238.095	214.879	20.894	−350.633	−396.260	22.998
1000	36.888	241.967	217.397	24.569	−351.689	−401.273	20.960
1100	37.122	245.494	219.794	28.270	−352.729	−406.181	19.288
1200	37.318	248.733	222.072	31.992	−353.756	−410.995	17.890
1300	37.484	251.726	224.240	35.733	−354.773	−415.723	16.704
1400	37.630	254.510	226.303	39.489	−355.778	−420.374	15.684
1500	37.759	257.110	228.271	43.258	−356.771	−424.953	14.798
1600	37.876	259.551	230.151	47.040	−357.753	−429.467	14.021
1700	37.983	261.850	231.949	50.833	−503.960	−426.743	13.112
1800	38.082	264.024	233.671	54.636	−504.167	−422.195	12.252
1900	38.175	266.086	235.323	58.449	−504.372	−417.635	11.482
2000	38.263	268.046	236.911	62.271	−504.574	−413.065	10.788
2100	38.347	269.915	238.438	66.102	−504.774	−408.484	10.160
2200	38.427	271.701	239.910	69.940	−504.970	−403.894	9.590
2300	38.504	273.411	241.329	73.787	−505.163	−399.296	9.068
2400	38.579	275.051	242.701	77.641	−505.352	−394.689	8.590
2500	38.652	276.627	244.026	81.503	−505.536	−390.074	8.150
2600	38.723	278.145	245.310	85.372	−505.717	−385.452	7.744
2700	38.793	279.607	246.553	89.247	−505.893	−380.823	7.367
2800	38.861	281.020	247.759	93.130	−506.065	−376.188	7.018
2900	38.928	282.384	248.929	97.019	−506.234	−371.546	6.692
3000	38.994	283.705	250.067	100.916	−506.399	−366.899	6.388
3100	39.059	284.985	251.173	104.818	−506.562	−362.246	6.104
3200	39.124	286.226	252.249	108.727	−506.723	−357.588	5.837
3300	39.188	287.431	253.297	112.643	−506.884	−352.925	5.586
3400	39.251	288.602	254.318	116.565	−507.044	−348.257	5.350
3500	39.314	289.740	255.314	120.493	−507.206	−343.585	5.128
3600	39.376	290.849	256.286	124.428	−507.371	−338.908	4.917
3700	39.438	291.928	257.234	128.368	−507.539	−334.226	4.718
3800	39.500	292.981	258.161	132.315	−507.713	−329.539	4.530
3900	39.561	294.008	259.067	136.268	−507.893	−324.848	4.351
4000	39.622	295.010	259.953	140.227	−508.081	−320.152	4.181
4100	39.682	295.989	260.820	144.193	−508.279	−315.452	4.019
4200	39.743	296.946	261.669	148.164	−508.488	−310.746	3.865
4300	39.803	297.882	262.500	152.141	−508.711	−306.036	3.718
4400	39.863	298.798	263.315	156.124	−508.927	−301.321	3.577
4500	39.922	299.694	264.114	160.114	−509.171	−296.600	3.443
4600	39.982	300.572	264.897	164.109	−509.435	−291.873	3.314
4700	40.041	301.433	265.665	168.110	−509.718	−287.141	3.191
4800	40.101	302.277	266.419	172.117	−510.021	−282.402	3.073
4900	40.160	303.104	267.159	176.130	−510.347	−277.657	2.960
5000	40.219	303.916	267.886	180.149	−510.697	−272.904	2.851
5100	40.278	304.713	268.600	184.174	−511.069	−268.145	2.746
5200	40.336	305.496	269.303	188.205	−511.473	−263.378	2.646
5300	40.395	306.265	269.993	192.241	−511.907	−258.603	2.549
5400	40.454	307.020	270.671	196.284	−512.373	−253.819	2.455
5500	40.512	307.763	271.339	200.332	−512.874	−249.027	2.365
5600	40.570	308.494	271.996	204.386	−513.411	−244.225	2.278
5700	40.629	309.212	272.643	208.446	−513.986	−239.413	2.194
5800	40.687	309.919	273.279	212.512	−514.601	−234.591	2.113
5900	40.745	310.615	273.906	216.583	−515.258	−229.757	2.034
6000	40.803	311.301	274.524	220.661	−515.959	−224.912	1.958

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [246.022]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [89.499 \pm 41.8]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-92.048 \pm 41.8]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[800](1)
[500](1)
[950](1)

Ground State Quantum Weight: [1] $\sigma = 1$

Point Group: C_s

Bond Distance: Li–O = [1.59] Å; F–O = [1.41] Å

Bond Angle: F–O–Li = [104]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.21997 \times 10^{-116}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(LiFO, g, 298.15 K), is calculated from $\Delta_r H°(298.15\ K) = 139\ kcal·mol^{-1}$ for the reaction LiFO(g) = Li(g) + F(g) + O(g) where the value of $\Delta_r H°(298.15\ K)$ is estimated to be the sum of the F–O and Li–O bond energies. The values of the F–O and Li–O bond energies are obtained from those in F_2O(g) and Li_2O(g) molecules, respectively.

Heat Capacity and Entropy

The F–O and Li–O bond distances are assumed to be the same as those in F_2O(g) and Li_2O(g) molecules, respectively. The F–O–Li bond angle and vibrational frequencies are estimated by comparison with the corresponding values for the same oxide molecules. The three principal moments of inertia are: $I_A = 1.2732 \times 10^{-39}$, $I_B = 5.1556 \times 10^{-39}$, and $I_C = 6.4288 \times 10^{-39}\ g·cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.827	−89.499	−89.499	INFINITE
100	33.594	205.644	280.612	−7.497	−89.569	−92.216	48.168
200	37.671	229.966	249.788	−3.964	−90.799	−94.413	24.658
250	40.466	238.672	246.717	−2.011	−91.454	−95.240	19.899
298.15	43.031	246.022	246.022	0.	−92.048	−95.915	16.804
300	43.124	246.289	246.023	0.080	−92.070	−95.939	16.704
350	45.452	253.116	246.557	2.296	−92.650	−96.537	14.407
400	47.406	259.317	247.770	4.619	−93.227	−97.053	12.674
450	49.017	264.997	249.373	7.031	−93.830	−97.496	11.317
500	50.336	270.232	251.201	9.515	−97.475	−97.562	10.192
500	52.306	279.595	255.171	14.654	−98.637	−97.468	8.485
700	53.656	287.765	259.257	19.956	−99.663	−97.190	7.252
800	54.607	294.996	263.281	25.372	−100.616	−96.771	6.319
900	55.296	301.469	267.171	30.869	−101.540	−96.235	5.585
1000	55.809	307.323	270.898	36.425	−102.446	−95.597	4.993
1100	56.200	312.662	274.456	42.027	−103.340	−94.869	4.505
1200	56.504	317.565	277.846	47.662	−104.228	−94.059	4.094
1300	56.744	322.098	281.078	53.325	−105.113	−93.176	3.744
1400	56.937	326.310	284.160	59.010	−105.997	−92.225	3.441
1500	57.095	330.244	287.103	64.712	−106.879	−91.210	3.176
1600	57.225	333.933	289.916	70.428	−107.760	−90.137	2.943
1700	57.334	337.406	292.608	76.156	−253.878	−81.832	2.514
1800	57.425	340.686	295.189	81.894	−254.008	−71.709	2.081
1900	57.503	343.793	297.666	87.640	−254.149	−61.577	1.693
2000	57.570	346.744	300.047	93.394	−254.300	−51.438	1.343
2100	57.628	349.554	302.338	99.154	−254.463	−41.291	1.027
2200	57.678	352.236	304.545	104.919	−254.637	−31.135	0.739
2300	57.722	354.801	306.675	110.689	−254.822	−20.972	0.476
2400	57.760	357.258	308.732	116.464	−255.017	−10.801	0.235
2500	57.794	359.617	310.720	122.241	−255.223	−0.621	0.013
2600	57.825	361.884	312.645	128.022	−255.439	9.567	−0.192
2700	57.852	364.067	314.509	133.806	−255.666	19.764	−0.382
2800	57.876	366.172	316.317	139.593	−255.903	29.970	−0.559
2900	57.898	368.203	318.071	145.381	−256.151	40.183	−0.724
3000	57.918	370.166	319.775	151.172	−256.410	50.406	−0.878
3100	57.935	372.065	321.432	156.965	−256.681	60.638	−1.022
3200	57.952	373.905	323.043	162.759	−256.964	70.879	−1.157
3300	57.966	375.689	324.611	168.555	−257.260	81.128	−1.284
3400	57.980	377.419	326.139	174.352	−257.569	91.387	−1.404
3500	57.992	379.100	327.628	180.151	−257.893	101.655	−1.517
3600	58.004	380.734	329.081	185.951	−258.231	111.933	−1.624
3700	58.014	382.323	330.499	191.752	−258.587	122.220	−1.725
3800	58.024	383.871	331.883	197.554	−258.959	132.517	−1.822
3900	58.033	385.378	333.235	203.356	−259.351	142.824	−1.913
4000	58.041	386.847	334.557	209.160	−259.762	153.141	−2.000
4100	58.049	388.281	335.850	214.965	−260.195	163.469	−2.083
4200	58.056	389.679	337.115	220.770	−260.651	173.808	−2.162
4300	58.062	391.046	338.354	226.576	−261.131	184.158	−2.237
4400	58.069	392.381	339.566	232.382	−261.618	194.518	−2.309
4500	58.074	393.686	340.755	238.189	−262.143	204.890	−2.378
4600	58.080	394.962	341.919	243.997	−262.699	215.274	−2.445
4700	58.085	396.211	343.061	249.805	−263.286	225.671	−2.508
4800	58.090	397.434	344.181	255.614	−263.905	236.081	−2.569
4900	58.094	398.632	345.280	261.423	−264.559	246.505	−2.628
5000	58.098	399.806	346.359	267.233	−265.249	256.941	−2.684
5100	58.102	400.956	347.418	273.043	−265.972	267.392	−2.739
5200	58.106	402.084	348.459	278.853	−266.741	277.857	−2.791
5300	58.110	403.191	349.481	284.664	−267.552	288.338	−2.842
5400	58.113	404.278	350.486	290.475	−268.409	298.835	−2.891
5500	58.116	405.344	351.474	296.287	−269.314	309.347	−2.938
5600	58.119	406.391	352.445	302.098	−270.269	319.877	−2.984
5700	58.122	407.420	353.400	307.910	−271.276	330.424	−3.028
5800	58.125	408.431	354.340	313.723	−272.338	340.990	−3.071
5900	58.127	409.424	355.266	319.535	−273.458	351.573	−3.113
6000	58.130	410.401	356.177	325.348	−274.637	362.177	−3.153

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 221.085 \pm 0.08\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -236.371 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -236.814 \pm 8.4\ kJ·mol^{-1}$

		Electronic Levels and Molecular Constants					
State	T_0, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Sigma^+$	0	2	719.56	4.91	1.7498		
$A^2\pi$	27829.60	4	743.89	3.95	0.51711	0.00324	1.7485
$B^2\Sigma^+$	37187.45	2	759.94	5.57	0.53542	0.00507	1.7183
$C^2\Sigma^+$	42589.64	2	820.77	5.01	0.54792	0.00445	1.6986

Enthalpy of Formation

We calculated $\Delta_f H°$(MgF, g, 298.15 K) = −56.6 ± 2.0 kcal·mol^{-1} from an adopted. $\Delta_{at} H°$(MgF, 298.15 K) = 110.7 ± 2 kcal·mol^{-1} which is derived from a 3rd law analysis of three sets of mass spectral–equilibrium data reported by Murad *et al.*[1] and Hildenbrand.[2] Also included in the analysis are independent mass spectrometer–equilibrium measurements on MgF(g) by Ehlert.[3,4]

Source	Reaction	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K)[c] kcal·mol^{-1}	$D_0°$(298.15 K) kcal·mol^{-1}
Murad *et al.*[1]	(A)	4	1546–1585	6.2	5.6[b]±1.3	−0.4±26	−57.5±2.0	111.6
Hildenbrand[2] Set 1	(B)	4	1280–1345	22.1	25.8±0.7	2.9±8.7	−56.3±0.8	110.4
Set 2	(B)	7	1413–1493	24.3	26.58±0.2	1.6±3.7	−55.9±0.7	110.0
Ehlert[3]	(B)	5	1205–1253	−90.0	−31.5±2.1	47±18	−53.5±1.5	107.6
Ehlert *et al.*[4]	(C)	5	1238–1301	63.0	47.6±26	−12.2±26	−53.7±2.0	107.8
Ehlert *et al.*[4]	(D)	5	1238–1301	−91.9	−126.7±1.8	−28.3±17	−53.4±1.0	107.5

Reactions: (A) Tl(g) + MgF(g) = TiF(g) + Mg(g) (B) Mg(g) + MgF_2(g) = 2 MgF(g) (C) AlF_3(g) + 2 Mg(g) = AlF(g) + 2 MgF(g)
(D) 2 MgF(g) = Mg(g) + MgF_2(cr)

[a]One point rejected due to failure of a statistical test.

[b]Free–energy functions (FEF) for TiF(g) are calculated from spectral data;[5] FEF for Tl(g) are from Hultgren.[6]

[c]3rd law Values; all auxillary $\Delta_f H°$(298.15 K) from JANAF Thermochemical Table[8] except for Tl and TlF.[7]

We dismiss the measurements of Ehlert[3] and Ehlert *et al.*[4] since our analyses show that their equilibrium data most likely contain temperature dependent errors. Furthermore, their results[3,4] yield $D_0°$ values which are less than that predicted by the Rittner ionic model. Krasnov and Karaseva[9] have applied this potential function to all the alkaline earth monohalides and found that it establishes a lower limit for $D_0°$. Recalculation of their results[9] sets $\Delta_{at} H°$(MgF, 298.15 K) > 110.4 kcal·mol^{-1}. Application of this ionic model to MgF is justified since the spin densities calculated from the ESR spectra[10] of matrix–isolated MgF show that the molecule is indeed highly ionic.

Trends in the well–established values of the ratio $\Delta_{at} H°(MX, 298.15\ K)/\Delta_{at} H°(MX_2, 298.15\ K)$ for the majority of the alkaline earth halides[8] suggests a value for MgF/MgF_2 which is less than or equal to 0.45. This sets the upper limit of $\Delta_{at} H°$(MgF, 298.15 K) at 111 kcal·mol^{-1} when $\Delta_{at} H°$(MgF_2, 298.15 K) = 246.7 kcal·mol^{-1}.[8] If MgF_2(g) is linear then the maximum $\Delta_{at} H°$(298.15 K) value increases to 112.6 kcal·mol^{-1} suggesting a possible uncertainty in the adopted $D_0°$ of ±2 kcal·mol^{-1}. Our adopted results give $\Delta_{at} H°$(MgF, 298.15 K)/Δ_{at}H(MgF_2, 298.15 K) = 0.44_9.

Our selected thermochemical $\Delta_{at} H°$(298.15 K) value converted to 0 K is 4.76 eV (109.8 kcal·mol^{-1}). Other values for $D_0°$ which were considered but believed less reliable are (all in ev 4.0,[11] 5.0 or 4.7[11] and 4.2.[12] These spectroscopic values have been derived from linear Birge–Sponer extrapolations of the ground state ($X^2\Sigma^+$) and first excited state ($^2\pi$) vibrational levels. We obtain $D_0° = 3.2_2$ eV from a linear Birge–Sponer extrapolation with our adopted ground state vibrational constants. This value adjusts to 3.59 eV when corrected for the ionicity[2] of the Mg–F bond. The corrected $D_0°$ value is 1.2 eV less than the thermochemical result. This discrepancy is most likely due to the use of an inaccurate value for the anharmonic constant, $\omega_e x_e$, in the Birge–Sponer extrapolation. The use of lower reported values[12,15] for $\omega_e x_e$ brings the spectroscopic and thermochemical $D_0°$ values into much better agreement but leaves the thermodynamic functions for MgF unaltered. In addition, Singh *et al.*[10] have employed a method to fit an electronegative potential energy function to the expermimental potential energy curves which yields $D_0° = 4.45$ eV. This value agrees with our results within probable error limits.

Heat Capacity and Entropy

The electronic levels and vibrational–rotational constants are taken from the compilation of Rosen.[5] Values of these constants, tabulated for $Mg^{24}F$, are corrected for the natural isotopic abundances of magnesium. The value of α_e listed by Rosen for the $C^2\Sigma^+$ state is incorrect. The rotational constants are based on an analysis[14] of the rotational structure in the bands of the A–X, B–X, and C–X systems. Barrow and Beale[14] used the Pekeris relation[12] to calculate $\omega_e x_e$ values from their spectroscopic α_e's. These $\omega_e x_e$ values were combined with $\Delta G_{1/2}$ values to give ω_e. These estimates of ω_e and $\omega_e x_e$ differ somewhat from those obtained from a vibrational analysis[15] of band head measurements.

Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.968	−236.371	−236.371	INFINITE
100	29.142	188.032	248.620	−6.059	−235.558	−244.892	127.919
200	30.463	208.521	223.998	−3.095	−236.066	−254.077	66.358
250	31.569	215.437	221.616	−1.545	−236.438	−258.537	54.018
298.15	32.569	221.085	221.085	0.	−236.814	−262.759	46.034
300	32.605	221.287	221.086	0.060	−236.829	−262.920	45.778
350	33.481	226.381	221.486	1.713	−237.233	−267.237	39.883
400	34.194	230.900	222.386	3.406	−237.649	−271.495	35.454
450	34.768	234.962	223.561	5.130	−238.078	−275.700	32.002
500	35.229	238.649	224.888	6.881	−238.523	−279.857	29.236
600	35.912	245.137	227.737	10.440	−239.468	−288.036	25.076
700	36.381	250.710	230.630	14.056	−240.500	−296.050	22.092
800	36.720	255.591	233.452	17.712	−241.637	−303.910	19.843
900	36.975	259.932	236.157	21.397	−242.897	−311.620	18.086
1000	37.175	263.838	238.733	25.105	−252.890	−318.470	16.635
1100	37.338	267.389	241.179	28.831	−254.455	−324.952	15.431
1200	37.474	270.644	243.501	32.572	−256.018	−331.292	14.421
1300	37.592	273.649	245.706	36.325	−257.580	−337.501	13.561
1400	37.695	276.438	247.803	40.090	−386.551	−340.423	12.701
1500	37.787	279.042	249.800	43.864	−386.761	−337.121	11.740
1600	37.872	281.484	251.704	47.647	−386.971	−333.805	10.898
1700	37.950	283.782	253.524	51.438	−387.181	−330.475	10.154
1800	38.023	285.953	255.266	55.237	−387.391	−327.134	9.493
1900	38.092	288.011	256.936	59.042	−387.600	−323.780	8.901
2000	38.157	289.966	258.539	62.855	−387.807	−320.416	8.368
2100	38.221	291.830	260.080	66.674	−388.010	−317.042	7.886
2200	38.281	293.609	261.564	70.499	−388.209	−313.657	7.447
2300	38.341	295.312	262.995	74.330	−388.402	−310.264	7.046
2400	38.398	296.945	264.375	78.167	−388.587	−306.863	6.679
2500	38.454	298.514	265.710	82.010	−388.764	−303.454	6.340
2600	38.510	300.023	267.001	85.858	−388.930	−300.038	6.028
2700	38.564	301.477	268.251	89.712	−389.086	−296.616	5.738
2800	38.619	302.881	269.463	93.571	−389.230	−293.189	5.470
2900	38.672	304.237	270.639	97.435	−389.361	−289.757	5.219
3000	38.726	305.549	271.780	101.305	−389.480	−286.320	4.985
3100	38.779	306.820	272.890	105.180	−389.587	−282.880	4.766
3200	38.833	308.052	273.970	109.061	−389.682	−279.436	4.561
3300	38.887	309.247	275.021	112.947	−389.766	−275.989	4.369
3400	38.941	310.409	276.045	116.838	−389.840	−272.540	4.187
3500	38.997	311.539	277.043	120.735	−389.906	−269.089	4.016
3600	39.053	312.638	278.016	124.638	−389.964	−265.637	3.854
3700	39.110	313.709	278.967	128.546	−390.017	−262.182	3.701
3800	39.169	314.753	279.895	132.460	−390.066	−258.727	3.556
3900	39.230	315.771	280.802	136.380	−390.114	−255.270	3.419
4000	39.292	316.765	281.688	140.306	−390.162	−251.811	3.288
4100	39.357	317.736	282.556	144.238	−390.213	−248.352	3.164
4200	39.423	318.685	283.405	148.177	−390.270	−244.891	3.046
4300	39.492	319.613	284.236	152.123	−390.333	−241.429	2.933
4400	39.563	320.522	285.050	156.076	−390.406	−237.966	2.825
4500	39.637	321.412	285.849	160.036	−390.491	−234.500	2.722
4600	39.714	322.284	286.631	164.003	−390.590	−231.033	2.623
4700	39.794	323.139	287.399	167.979	−390.706	−227.563	2.529
4800	39.877	323.978	288.152	171.962	−390.840	−224.090	2.439
4900	39.963	324.801	288.892	175.954	−390.995	−220.615	2.352
5000	40.052	325.609	289.618	179.955	−391.172	−217.136	2.268
5100	40.145	326.403	290.332	183.965	−391.374	−213.653	2.188
5200	40.241	327.184	291.033	187.984	−391.603	−210.166	2.111
5300	40.340	327.951	291.722	192.013	−391.859	−206.675	2.037
5400	40.443	328.706	292.400	196.052	−392.146	−203.178	1.965
5500	40.549	329.449	293.067	200.101	−392.464	−199.676	1.896
5600	40.659	330.181	293.723	204.162	−392.814	−196.167	1.830
5700	40.772	330.901	294.369	208.233	−393.199	−192.653	1.765
5800	40.888	331.611	295.005	212.316	−393.620	−189.131	1.703
5900	41.008	332.311	295.632	216.411	−394.077	−185.601	1.643
6000	41.131	333.002	296.249	220.518	−394.573	−182.063	1.585

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [215.330 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 506.533 \pm 46.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [512.289]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	[1]	$B^1\Sigma^+$	[20000]	[1]
$^3\Pi$	[2600]	[6]	$^3\Pi$	[28000]	[3]
$A^1\Pi$	[3500]	[2]	$^3\Delta$	[29000]	[6]
$^3\Sigma^+$	[15000]	[3]	$D^1\Delta$	[30000]	[2]

$\omega_e = [718.5]\ cm^{-1}$ $B_e = [0.5162]\ cm^{-1}$
$\omega_e x_e = [4.90]\ cm^{-1}$ $\alpha_e = [0.00463]\ cm^{-1}$
$\sigma = 1$ $r_e = [1.75]$ Å

Enthalpy of Formation

MgF^+ ionization–efficiency curves obtained from mass spectral observations on the MgF_2[1] and MgF_2–Al[2] systems are of the two–process type. Evidence[1,2] has been presented which shows that the low–energy portion (<13 eV) of the curve arises from the direct ionization (A) of MgF(g). These curves also show an inflection point at higher energies (~14 eV) which has been interpreted[1-3] as due to the onset of the dissociative ionization (B) of MgF_2(g). The appearance potentials, in eV, which have been observed for these two processes from measurements on various MgF_2 systems are tabulated below.

Source	Year	System	(A) Direct Ionization	(B) Dissociative Ionization
Berkowitz and Marquart[4]	1962	MgF_2		13.5±0.4
Green *et al.*[1]	1964	MgF_2		13.6±0.3
Ehlert *et al.*[2]	1964	MgF_2–Al	7.8±0.3	13.7±0.4
Murad *et al.*[5]	1966	MgF_2–Tl–Pd	8.0±0.5	
Hildenbrand[6]	1968	MgF_2–Cu	7.5±0.3	
Hildenbrand[3]	1968	MgF_2	7.5±0.5	

(A) $MgF(g) + e^- \rightarrow MgF^+(g) + 2\ e^-$ (B) $MgF_2(g) + e^- \rightarrow MgF^+(g) + F(g) + 2\ e^-$

Both sets of data show the normal scatter (0.5 eV) expected for such measurements. The mean value (7.7 ± 0.4 eV) of the four AP's for the direct ionization (A) is supported by the spectroscopic ionization potential of 7.68 eV.[7] We adopt $\Delta_f H° = 177.56 \pm 9\ kcal·mol^{-1}$ (7.7 eV) for process (A), and we obtain $\Delta_f H°(MgF,^+ g) = 121.1 \pm 11.0\ kcal·mol^{-1}$ when the $\Delta_r H°$ value is combined with $\Delta_f H°(MgF, g) = -56.5 \pm 2.0\ kcal·mol.^{-1}$[8] The fragmentation process (B) is likely to involve unknown kinetic energy factors and would not be expected to yield as reliable $\Delta_f H°$ value as obtained from direct ionization. However, the mean value (13.58 ± 0.5 eV) of the four AP's for process (B) leads to $\Delta_f H°(MgF^+, g, 0\ K) = 121.5 \pm 13.0\ kcal·mol^{-1}$ which is in remarkably good with the $\Delta_f H°$ value from direct ionization (121.1 $kcal·mol^{-1}$). This implies that the excess kinetic energy of the fragment MgF^+ is small.

Heat Capacity and Entropy

The bond dissociation energy for MgF^+ (108.6 $kcal·mol^{-1}$) is nearly the same as that for MgF(109.8 $kcal·mol^{-1}$)[8] which implies that the bonding in these two molecules is quite similar. Thus, it is reasonable to assume that $r_e(MgF^+) = r_e(MgF)$. We adopt the measured r_e value (1.75 Å) for MgF.[8] B_e is calculated from the adopted value for r_e. The value of ω_e is obtained from Badger's rule[9] which is written in the form $\omega_e^2 = 3.159 \times 10^6/\mu$ ($r_e = d_{ij}$).[3] Molecular data[8] for NaF, MgF, and MgO are used to determine the constant d_{ij}. Barrow and Caunt[10] have shown that the product $x_e^{1/2}$ is fairly constant within a group of similar molecules. We assume $x_e(MgF^+) = x_e(MgF)$ since $^1/_2(MgF^+) = {}^1/_2(MgF)$. These estimates of ω_e and $\omega_e x_e$ are only slightly different from those observed for MgF.[8] α_e is obtained from the other constants assuming a Morse potential function.

Novikov and Gurvich[11] have observed a band system in the emission spectrum of MgF near 54000 cm^{-1}. An analysis of the vibrational structure showed that the system did not belong to any of those known for MgF, and they[11] assigned it to the $^1\Sigma$–$^1\Sigma$ transition of MgF^+. Band systems have appeared in the absorption spectra[12,13] of MgF which are now known to arise from AlF. A comparison of the vibrational constants reported by Novikov and Gurvich[11] with those for AlF[8] strongly suggests that this system is the $B^1\Sigma$–$X^1\Sigma$ transition of AlF. Barrow[14] has come to the same conclusion.

MgF^+ (8 valence elecrons) is isoelectronic with the alkaline earth monoxides. We estimate the electronic states and levels for MgF^+ by analogy with those for these isoelectronic molecules,[8] particularly MgO. The $^1\pi^{-3}\pi$ splitting of MgO has recently been reported as 900 ± 200 $cm.^{-1}$.[15] We believe that our adopted electronic entropies represent minimal values. Probable upper limits for the electronic contributions can be established by decreasing the two lowest triplet levels to 1000 cm^{-1} ($^3\pi$) and 5000 cm^{-1} ($^3\Sigma$) and neglecting the other excited states. This increases the entropy to 65.1 and 78.6 cal $K^{-1}·mol^{-1}$ at 1000 K and 4000 K, respectively. The enthalpy is much more uncertain, approaching ±3.0 $kcal·mol^{-1}$ at temperatures in excess of 2000 K.

Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.969	506.533	
100	29.142	182.270	242.875	−6.060		
200	30.469	202.761	218.245	−3.097		
250	31.580	209.679	215.862	−1.546		
298.15	32.605	215.330	215.330	0.	512.289	481.805	−84.410
300	32.643	215.532	215.331	0.060	512.313	481.616	−83.857
350	33.621	220.638	215.732	1.717	512.952	476.449	−71.106
400	34.589	225.191	216.635	3.422	513.588	471.191	−61.531
450	35.646	229.324	217.819	5.178	514.229	465.853	−54.075
500	36.868	233.142	219.162	6.990	514.885	460.443	−48.102
600	39.885	240.119	222.084	10.821	516.291	449.425	−39.126
700	43.407	246.529	225.123	14.984	517.884	438.157	−32.696
800	46.861	252.555	228.179	19.500	519.687	426.647	−27.857
900	49.709	258.246	231.207	24.336	521.655	414.900	−24.080
1000	51.662	263.593	234.181	29.412	515.109	403.642	−21.084
1100	52.688	268.572	237.084	34.637	517.121	392.398	−18.633
1200	52.931	273.172	239.902	39.923	519.183	380.969	−16.583
1300	52.600	277.399	242.626	45.204	521.226	369.368	−14.841
1400	51.901	281.273	245.251	50.431	395.797	360.779	−13.461
1500	51.001	284.824	247.772	55.577	399.038	358.164	−12.472
1600	50.020	288.084	250.191	60.629	402.175	355.336	−11.601
1700	49.035	291.087	252.510	65.581	405.204	352.315	−10.825
1800	48.095	293.863	254.731	70.437	408.131	349.119	−10.131
1900	47.225	296.439	256.859	75.203	410.960	345.763	−9.506
2000	46.436	298.841	258.899	79.885	413.701	342.261	−8.939
2100	45.731	301.090	260.855	84.493	416.365	338.623	−8.423
2200	45.107	303.202	262.732	89.034	418.961	334.860	−7.951
2300	44.559	305.195	264.536	93.517	421.498	330.980	−7.517
2400	44.081	307.081	266.269	97.948	423.986	326.991	−7.117
2500	43.665	308.872	267.938	102.335	426.432	322.899	−6.747
2600	43.306	310.577	269.545	106.683	428.844	318.710	−6.403
2700	42.997	312.206	271.095	110.998	431.229	314.428	−6.083
2800	42.732	313.765	272.592	115.284	433.590	310.059	−5.784
2900	42.506	315.260	274.037	119.545	435.935	305.606	−5.505
3000	42.315	316.698	275.436	123.786	438.265	301.072	−5.242
3100	42.154	318.082	276.789	128.009	440.585	296.461	−4.995
3200	42.021	319.419	278.101	132.218	442.896	291.775	−4.763
3300	41.913	320.710	279.372	136.414	445.201	287.017	−4.543
3400	41.825	321.960	280.607	140.601	447.501	282.189	−4.335
3500	41.757	323.171	281.806	144.780	449.796	277.293	−4.138
3600	41.706	324.347	282.971	148.953	452.087	272.332	−3.951
3700	41.670	325.489	284.105	153.122	454.373	267.307	−3.774
3800	41.648	326.600	285.208	157.288	456.654	262.221	−3.604
3900	41.638	327.682	286.284	161.452	458.929	257.075	−3.443
4000	41.639	328.736	287.332	165.616	461.197	251.870	−3.289
4100	41.651	329.764	288.354	169.780	463.457	246.609	−3.142
4200	41.671	330.768	289.352	173.946	465.707	241.293	−3.001
4300	41.700	331.749	290.327	178.114	467.944	235.923	−2.866
4400	41.736	332.708	291.279	182.286	470.169	230.501	−2.736
4500	41.780	333.646	292.210	186.462	472.379	225.029	−2.612
4600	41.829	334.565	293.121	190.642	474.571	219.508	−2.493
4700	41.884	335.465	294.013	194.828	476.744	213.940	−2.378
4800	41.944	336.348	294.885	199.019	478.896	208.326	−2.267
4900	42.009	337.213	295.740	203.217	481.026	202.667	−2.160
5000	42.079	338.063	296.578	207.421	483.130	196.965	−2.058
5100	42.152	338.897	297.400	211.633	485.209	191.221	−1.958
5200	42.229	339.716	298.206	215.852	487.258	185.436	−1.863
5300	42.309	340.521	298.997	220.079	489.278	179.613	−1.770
5400	42.393	341.313	299.773	224.314	491.266	173.751	−1.681
5500	42.479	342.091	300.535	228.557	493.222	167.853	−1.594
5600	42.567	342.858	301.284	232.810	495.142	161.920	−1.510
5700	42.658	343.612	302.020	237.071	497.025	155.953	−1.429
5800	42.751	344.354	302.744	241.341	498.870	149.953	−1.350
5900	42.845	345.086	303.455	245.621	500.676	143.922	−1.274
6000	42.941	345.807	304.155	249.910	502.441	137.860	−1.200

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

Molybdenum Fluoride (MoF) **IDEAL GAS** M_r = 114.938403 **Molybdenum Fluoride (MoF)** **F_1Mo_1(g)**

D_0° = [451.454 ± 16.7] kJ·mol^{-1}
$S°$(298.15 K) = [246.399 ± 8.4] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = [282.853 ± 12.6] kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 282.838 ± 12.6 kJ·mol^{-1}

Electronic Levels and Quantum Weights					
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[15199]	[6]	[15890]	[2]
[11783]	[2]	[15331]	[8]	[16796]	[2]
[12034]	[4]	[15428]	[10]	[16947]	[8]
[12417]	[6]	[15447]	[12]	[17174]	[4]
[12900]	[8]	[15691]	[6]	[17344]	[6]
[13461]	[10]	[15699]	[4]		

ω_e = [700] cm^{-1} $\omega_e x_e$ = [3.05] cm^{-1} σ = 1
B_e = [0.3209] cm^{-1} α_e = [0.0019] cm^{-1} r_e = [1.82] Å

Enthalpy of Formation

The adopted enthalpy of formation at 298.15 K is that derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous molybdenum fluorides by Hildenbrand [2054–2242 K].[2] The value of $\Delta_f H°$(0 K) combined with JANAF data[3] for Mo(g) and F(g) gives D_0°(MoF) = 107.9±4 kcal·mol^{-1}.

Heat Capacity and Entropy

We use the ground state vibrational frequency of 700 cm^{-1} estimated by Hildenbrand[2] and adopted by Brewer.[1] The Mo–F bond distance, 1.82 Å, is the Mo–F bond distance in MoF_6(g) used by Brewer.[1] The electronic contributions are assumed to be the same as those for the free gaseous Mo^+ ion, as suggested by Brewer.[1] All states up to 17344 cm^{-1} as listed by Moore[4] are included in the calculation. Our thermodynamic functions differ slightly from those reported by Brewer[1] because of the use of non zero values for $\omega_e x_e$ and α_e. The estimates for $\omega_e x_e$ and α_e are based on the empirical correlations of Calder and Ruedenberg.[5]

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

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[3]JANAF Thermochemical Tables: Mo(g), 3–31–78; F(g), 9–30–65.
[4]C. E. Moore, U.S. Nat. Bur. Stand., NSRDS NBS 34 (1970); NSRDS NBS 35, Vol. III, 1971 [Reprint of NBS Circular 467, Vol. III, 1958].
[5]G. V. Calder and K. Ruedenberg, J. Chem. Phys. **49**, 5399 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.982	282.853	282.853	INFINITE
100	29.145	213.279	274.009	−6.073	283.818	271.711	−141.927
200	30.549	233.795	249.321	−3.105	283.479	259.681	−67.822
250	31.674	240.733	246.931	−1.550	283.165	253.767	−53.022
298.15	32.671	246.399	246.399	0.	282.838	248.134	−43.472
300	32.706	246.601	246.399	0.060	282.826	247.919	−43.166
350	33.567	251.710	246.801	1.718	282.475	242.129	−36.136
400	34.260	256.239	247.703	3.414	282.114	236.389	−30.869
450	34.812	260.307	248.881	5.142	281.743	230.696	−26.778
500	35.253	263.999	250.211	6.894	281.362	225.044	−23.510
600	35.897	270.487	253.065	10.453	280.568	213.854	−18.618
700	36.334	276.055	255.961	14.066	279.733	202.801	−15.133
800	36.645	280.928	258.783	17.716	278.857	191.870	−12.528
900	36.875	285.258	261.489	21.393	277.940	181.051	−10.508
1000	37.053	289.153	264.064	25.089	276.979	170.337	−8.897
1100	37.195	292.692	266.508	28.802	275.969	159.721	−7.585
1200	37.313	295.933	268.827	32.527	274.903	149.200	−6.495
1300	37.416	298.924	271.029	36.264	273.774	138.770	−5.576
1400	37.511	301.700	273.121	40.010	272.575	128.430	−4.792
1500	37.605	304.291	275.114	43.766	271.300	118.177	−4.115
1600	37.707	306.722	277.014	47.532	269.944	108.013	−3.526
1700	37.825	309.011	278.830	51.308	268.503	97.936	−3.009
1800	37.967	311.177	280.567	55.097	266.971	87.946	−2.552
1900	38.144	313.234	282.233	58.903	265.346	78.044	−2.146
2000	38.363	315.196	283.832	62.728	263.624	68.231	−1.782
2100	38.634	317.074	285.371	66.577	261.803	58.505	−1.455
2200	38.965	318.879	286.853	70.457	259.882	48.869	−1.160
2300	39.362	320.619	288.284	74.372	257.859	39.323	−0.893
2400	39.830	322.304	289.666	78.331	255.733	29.866	−0.650
2500	40.373	323.941	291.005	82.341	253.502	20.501	−0.428
2600	40.993	325.536	292.302	86.408	251.153	11.226	−0.226
2700	41.688	327.096	293.562	90.542	248.656	2.045	−0.040
2800	42.457	328.626	294.787	94.749	245.958	−7.040	0.131
2900	43.296	330.130	295.980	99.036	207.102	−15.974	0.288
3000	44.198	331.613	297.143	103.410	205.820	−23.645	0.412
3100	45.157	333.078	298.279	107.877	204.644	−31.274	0.527
3200	46.163	334.527	299.389	112.443	203.581	−38.867	0.634
3300	47.206	335.964	300.476	117.111	202.636	−46.428	0.735
3400	48.277	337.389	301.540	121.885	201.812	−53.963	0.829
3500	49.363	338.804	302.585	126.767	201.112	−61.475	0.917
3600	50.453	340.210	303.610	131.758	200.538	−68.969	1.001
3700	51.537	341.607	304.618	136.857	200.090	−76.449	1.079
3800	52.603	342.995	305.610	142.064	199.766	−83.919	1.154
3900	53.640	344.375	306.586	147.377	199.565	−91.381	1.224
4000	54.640	345.746	307.548	152.791	199.482	−98.840	1.291
4100	55.593	347.107	308.497	158.303	199.515	−106.298	1.354
4200	56.491	348.458	309.432	163.908	199.656	−113.759	1.415
4300	57.330	349.797	310.355	169.599	199.902	−121.224	1.473
4400	58.102	351.124	311.267	175.372	200.244	−128.695	1.528
4500	58.805	352.438	312.167	181.218	200.676	−136.176	1.581
4600	59.436	353.737	313.057	187.130	201.190	−143.667	1.631
4700	59.992	355.021	313.936	193.102	201.780	−151.170	1.680
4800	60.474	356.290	314.805	199.126	202.436	−158.687	1.727
4900	60.882	357.541	315.664	205.195	203.151	−166.217	1.772
5000	61.217	358.774	316.514	211.300	−387.467	−168.032	1.755
5100	61.481	359.989	317.355	217.436	−388.335	−163.635	1.676
5200	61.677	361.185	318.186	223.594	−389.314	−159.219	1.599
5300	61.808	362.361	319.009	229.769	−390.406	−154.784	1.525
5400	61.879	363.517	319.822	235.954	−391.619	−150.327	1.454
5500	61.892	364.653	320.627	242.143	−392.955	−145.847	1.385
5600	61.853	365.768	321.423	248.330	−394.419	−141.341	1.318
5700	61.765	366.862	322.211	254.512	−396.011	−136.808	1.254
5800	61.632	367.935	322.990	260.682	−397.735	−132.246	1.191
5900	61.459	368.987	323.761	266.837	−399.591	−127.653	1.130
6000	61.251	370.019	324.523	272.973	−401.584	−123.028	1.071

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

$S°(298.15\ K) = 215.276\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 248.953 \pm 33\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 248.948 \pm 33\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^3\Sigma]$	0	3

$\omega_e = 1115\ cm^{-1}$ $\omega_e x_e = [12.175]\ cm^{-1}$ $\sigma = 1$
$B_e = [.923]\ cm^{-1}$ $\alpha_e = [.0120]\ cm^{-1}$ $r_e = [1.51\ Å]$

Enthalpy of Formation

The enthalpy of formation is obtained by taking an average of two estimates of the dissociation energy of NF. The first estimate of 3.15 eV (72.4 kcal·mol^{-1}) was obtained from Price *et al.*[1] The second estimate of 70.4 kcal·mol^{-1} is obtained by taking one half the dissociation energy of NF_2(g) calculated from JANAF values. The $\Delta_f H°$(298.15 K) for NF(g) was then calculated with auxiliary JANAF data from a dissociation energy of 71.4 kcal·mol^{-1}.

Heat Capacity and Entropy

The ω_e value was obtained from infrared studies of Milligan and Jacox.[2] The r_e value was estimated from Guggenheimer's[3] relation for single bonded molecules. The anharmonicity constant x_e is estimated by assuming the separation of the vibrational levels to be a linear function of the vibrational quantum number. The α_e value is then calculated using the Morse potential function; B_e is determined from the bond length. The ground state configuration is assumed to be the same as that in NBr.

References

[1]W. C. Price, T. R. Passmore and D. M. Roessler, Disc. Faraday Soc. **35**, 201 11 (1963).
[2]D. E. Milligan and M. E. Jacox, J. Chem. Phys. **40**, 2461 (1964).
[3]K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.745	248.953	248.953	INFINITE
100	29.108	183.197	241.576	−5.838	248.953	247.142	−129.094
200	29.318	203.404	218.012	−2.922	248.949	245.332	−64.074
250	29.745	209.987	215.772	−1.446	248.946	244.429	−51.071
298.15	30.345	215.276	215.276	0.	248.948	243.558	−42.670
300	30.370	215.464	215.276	0.056	248.948	243.525	−42.401
350	31.089	220.199	215.649	1.592	248.962	242.620	−36.209
400	31.813	224.397	216.485	3.165	248.989	241.713	−31.564
450	32.492	228.184	217.578	4.773	249.030	240.801	−27.951
500	33.106	231.640	218.814	6.413	249.084	239.884	−25.060
600	34.122	237.770	221.475	9.777	249.220	238.031	−20.722
700	34.893	243.090	224.191	13.229	249.375	236.154	−17.622
800	35.480	247.790	226.853	16.749	249.536	234.255	−15.295
900	35.933	251.996	229.417	20.321	249.692	232.335	−13.484
1000	36.291	255.801	231.868	23.933	249.839	230.399	−12.035
1100	36.578	259.274	234.204	27.577	249.974	228.448	−10.848
1200	36.815	262.467	236.428	31.247	250.097	226.486	−9.859
1300	37.013	265.422	238.546	34.938	250.207	224.513	−9.021
1400	37.182	268.171	240.565	38.648	250.305	222.533	−8.303
1500	37.329	270.742	242.492	42.374	250.391	220.546	−7.680
1600	37.459	273.155	244.334	46.114	250.467	218.554	−7.135
1700	37.575	275.430	246.097	49.865	250.533	216.558	−6.654
1800	37.679	277.580	247.787	53.628	250.591	214.558	−6.226
1900	37.775	279.620	249.409	57.401	250.643	212.554	−5.844
2000	37.864	281.560	250.969	61.183	250.690	210.548	−5.499
2100	37.947	283.409	252.470	64.974	250.735	208.540	−5.187
2200	38.024	285.177	253.916	68.772	250.779	206.530	−4.904
2300	38.098	286.868	255.313	72.578	250.824	204.517	−4.645
2400	38.168	288.491	256.662	76.392	250.873	202.503	−4.407
2500	38.235	290.051	257.966	80.212	250.928	200.487	−4.189
2600	38.299	291.552	259.229	84.039	250.990	198.468	−3.987
2700	38.362	292.998	260.453	87.872	251.062	196.446	−3.800
2800	38.422	294.395	261.641	91.711	251.146	194.422	−3.627
2900	38.481	295.744	262.793	95.556	251.242	192.394	−3.465
3000	38.538	297.049	263.914	99.407	251.352	190.363	−3.315
3100	38.594	298.314	265.003	103.264	251.479	188.328	−3.173
3200	38.649	299.540	266.063	107.126	251.622	186.289	−3.041
3300	38.704	300.730	267.096	110.993	251.782	184.245	−2.916
3400	38.757	301.886	268.102	114.867	251.961	182.196	−2.799
3500	38.809	303.011	269.084	118.745	252.158	180.141	−2.688
3600	38.861	304.105	270.041	122.628	252.375	178.080	−2.584
3700	38.912	305.170	270.976	126.517	252.611	176.013	−2.485
3800	38.962	306.209	271.890	130.411	252.868	173.940	−2.391
3900	39.013	307.221	272.783	134.309	253.144	171.859	−2.302
4000	39.062	308.210	273.656	138.213	253.440	169.771	−2.217
4100	39.111	309.175	274.511	142.122	253.756	167.676	−2.136
4200	39.160	310.118	275.347	146.035	254.092	165.572	−2.059
4300	39.209	311.040	276.167	149.954	254.447	163.460	−1.986
4400	39.257	311.942	276.970	153.877	254.822	161.340	−1.915
4500	39.305	312.825	277.757	157.805	255.216	159.211	−1.848
4600	39.352	313.689	278.528	161.738	255.628	157.073	−1.784
4700	39.400	314.536	279.286	165.676	256.059	154.926	−1.722
4800	39.447	315.366	280.029	169.618	256.508	152.770	−1.662
4900	39.494	316.180	280.758	173.565	256.975	150.604	−1.605
5000	39.541	316.978	281.475	177.517	257.459	148.428	−1.551
5100	39.588	317.761	282.178	181.473	257.960	146.242	−1.498
5200	39.634	318.531	282.870	185.434	258.477	144.047	−1.447
5300	39.680	319.286	283.550	189.400	259.010	141.841	−1.398
5400	39.727	320.028	284.219	193.370	259.560	139.625	−1.351
5500	39.773	320.758	284.877	197.345	260.124	137.399	−1.305
5600	39.819	321.475	285.524	201.325	260.704	135.162	−1.261
5700	39.865	322.180	286.161	205.309	261.298	132.915	−1.218
5800	39.911	322.873	286.788	209.298	261.905	130.658	−1.177
5900	39.956	323.556	287.405	213.291	262.527	128.390	−1.137
6000	40.002	324.228	288.013	217.289	263.161	126.111	−1.098

PREVIOUS: June 1965 (1 atm) CURRENT: June 1965 (1 bar)

$S°(298.15\ K) = 248.082\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -63.300 \pm 1.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -65.689 \pm 1.7\ kJ·mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
1844.03(1)
521
765.85(1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_s

Bond Distances: N–O = 1.13 Å; N–F = 1.52 Å

Bond Angle: O–N–F = 110.2°

Product of the Moments of Inertia: $I_A I_B I_C = 49.6113 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

For the reaction $2NO(g) + F_2(g) \rightarrow 2ONF(g)$, Johnston and Bertin[1] report $\Delta_f H°(298.15\ K) = 74.8 \pm 0.8\ kcal·mol^{-1}$, determined calorimetrically. This yields $15.7 \pm 0.4\ kcal·mol^{-1}$ for $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

Stephenson and Jones,[2] report the frequencies, obtained from the infrared spectrum, and moments of inertia, obtained from the microwave spectrum. The principal moments of inertia are: $I_A = 0.8778 \times 10^{-39}$, $I_B = 7.0919 \times 10^{-39}$, and $I_C = 7.9697 \times 10^{-39}\ g·cm^2$.

References

[1]H. S. Johnston and H. J. Bertin, J. Amer. Chem. Soc. **81,** 6402 (1959).

[2]C. V. Stephenson and E. A. Jones, J. Chem. Phys. **20,** 135 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.701	−63.300	−63.300	INFINITE
100	33.534	208.247	281.961	−7.371	−64.328	−59.978	31.329
200	37.177	232.429	251.737	−3.862	−65.193	−55.267	14.434
250	39.427	240.969	248.753	−1.946	−65.485	−52.750	11.021
298.15	41.348	248.082	248.082	0.	−65.689	−50.277	8.808
300	41.416	248.338	248.083	0.077	−65.695	−50.182	8.737
350	43.115	254.854	248.594	2.191	−65.842	−47.584	7.101
400	44.574	260.708	249.748	4.384	−65.942	−44.968	5.872
450	45.850	266.034	251.266	6.645	−66.005	−42.342	4.915
500	46.980	270.924	252.991	8.967	−66.041	−39.711	4.149
600	48.895	279.665	256.725	13.764	−66.052	−34.442	2.998
700	50.437	287.322	260.561	18.733	−66.007	−29.177	2.177
800	51.678	294.141	264.340	23.841	−65.927	−23.921	1.562
900	52.678	300.288	267.998	29.061	−65.826	−18.676	1.084
1000	53.486	305.881	271.511	34.370	−65.712	−13.443	0.702
1100	54.142	311.011	274.872	39.753	−65.593	−8.222	0.390
1200	54.679	315.746	278.083	45.195	−65.473	−3.012	0.131
1300	55.122	320.140	281.152	50.686	−65.355	2.188	−0.088
1400	55.491	324.239	284.085	56.217	−65.243	7.380	−0.275
1500	55.799	328.079	286.891	61.782	−65.138	12.563	−0.437
1600	56.060	331.688	289.579	67.375	−65.042	17.740	−0.579
1700	56.282	335.094	292.157	72.992	−64.956	22.911	−0.704
1800	56.472	338.316	294.633	78.630	−64.880	28.078	−0.815
1900	56.636	341.374	297.013	84.286	−64.815	33.240	−0.914
2000	56.778	344.283	299.304	89.957	−64.760	38.400	−1.003
2100	56.902	347.056	301.513	95.641	−64.715	43.556	−1.083
2200	57.011	349.706	303.644	101.337	−64.678	48.712	−1.157
2300	57.107	352.242	305.702	107.043	−64.648	53.865	−1.223
2400	57.192	354.674	307.692	112.758	−64.624	59.017	−1.284
2500	57.267	357.011	309.618	118.481	−64.604	64.168	−1.341
2600	57.335	359.258	311.485	124.211	−64.586	69.319	−1.393
2700	57.395	361.423	313.294	129.947	−64.569	74.469	−1.441
2800	57.450	363.511	315.051	135.690	−64.552	79.618	−1.485
2900	57.499	365.528	316.757	141.437	−64.532	84.766	−1.527
3000	57.544	367.478	318.415	147.189	−64.509	89.914	−1.566
3100	57.584	369.366	320.029	152.946	−64.481	95.061	−1.602
3200	57.621	371.195	321.599	158.706	−64.447	100.207	−1.636
3300	57.655	372.968	323.129	164.470	−64.406	105.352	−1.668
3400	57.686	374.690	324.620	170.237	−64.357	110.496	−1.698
3500	57.714	376.363	326.075	176.007	−64.299	115.637	−1.726
3600	57.740	377.989	327.494	181.780	−64.233	120.778	−1.752
3700	57.764	379.571	328.881	187.555	−64.157	125.915	−1.778
3800	57.786	381.112	330.235	193.332	−64.071	131.052	−1.801
3900	57.807	382.613	331.559	199.112	−63.975	136.186	−1.824
4000	57.826	384.077	332.854	204.894	−63.869	141.316	−1.845
4100	57.844	385.505	334.120	210.677	−63.752	146.444	−1.866
4200	57.860	386.899	335.360	216.462	−63.625	151.570	−1.885
4300	57.876	388.261	336.575	222.249	−63.489	156.692	−1.903
4400	57.890	389.591	337.765	228.037	−63.342	161.811	−1.921
4500	57.904	390.893	338.931	233.827	−63.185	166.926	−1.938
4600	57.916	392.165	340.074	239.618	−63.020	172.037	−1.954
4700	57.928	393.411	341.196	245.410	−62.846	177.146	−1.969
4800	57.939	394.631	342.297	251.204	−62.663	182.250	−1.983
4900	57.950	395.826	343.377	256.998	−62.473	187.351	−1.997
5000	57.959	396.996	344.438	262.794	−62.276	192.447	−2.010
5100	57.969	398.144	345.480	268.590	−62.072	197.540	−2.023
5200	57.977	399.270	346.503	274.387	−61.863	202.628	−2.035
5300	57.986	400.374	347.509	280.185	−61.648	207.712	−2.047
5400	57.993	401.458	348.498	285.984	−61.430	212.792	−2.058
5500	58.001	402.523	349.471	291.784	−61.207	217.868	−2.069
5600	58.008	403.568	350.428	297.585	−60.983	222.941	−2.080
5700	58.015	404.594	351.369	303.386	−60.756	228.008	−2.089
5800	58.021	405.603	352.295	309.187	−60.529	233.073	−2.099
5900	58.027	406.595	353.207	314.990	−60.303	238.132	−2.108
6000	58.033	407.571	354.105	320.793	−60.077	243.189	−2.117

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 260.250\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 102.881 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -108.784 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1312(1)	1793(1)
822(1)	570(1)
460(1)	742(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: N–F = 1.40 Å; N–O = 1.21 Å
Bond Angles: O–N–O = 129.5°; F–N–O = 115.25°
Product of the Moments of Inertia: $I_A I_B I_C = 6.400639 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of reaction at 25°C for direct synthesis of nitryl fluoride from nitrogen dioxide with fluorine ($NO_2(g) + 1/2\ F_2(g) = NO_2F(g)$) has been measured calorimetrically as $-33.9\ kcal·mol^{-1}$ by Breazeale and MacLaren.[1] The enthalpy of formation, $\Delta_f H°(298.15\ K) = -26.0\ kcal·mol^{-1}$, for $NO_2F(g)$ was then drived. The values of $\Delta_f H°(298.15\ K) = -20 \pm 5$ and $-19 \pm 2\ kcal·mol^{-1}$ were issued in their second and third quarterly technical reports and have been quoted in the literature by Tschuikow-Roux.[2]

Hetherington and Robinson[3] quoted $\Delta_f H° = 26\ kcal·mol^{-1}$ (presumably it has a minus sign) for $NO_2F(g)$ which was derived from the heat of solution measured by Nichols and Robinson.[4]

Heat Capacity and Entropy

Smith and Magnuson[5] have measured the moments of inertia from microwave spectrum of $NO_2F(g)$. In order to calculate the bond distances, given as N–F = 1.35 Å and N–O = 1.23 Å, the bond angle O–N–O was assumed to be 125°. The selected bond distances and angle were obtained from Clayton *et al.*[6] Clayton *et al.* assumed the bond angle O–N–O in $NO_2F(g)$ should be the same as that in $NO_2Cl(g)$ and then calculated the bond distances N–F and N–O from Smith and Magnuson[5] data of the moments of inertia.

The selected vibrational frequencies were obtained from the infrared and Raman spectra measurements by Dodd *et al.*[7]

The three principal moments of inertia are: $I_A = 6.3641 \times 10^{-39}$, $I_B = 7.3394 \times 10^{-39}$, and $I_C = 13.7034 \times 10^{-39}\ g·cm^2$.

References

[1]J. D. Breazeale and R. O. MacLaren, "Thermochemistry of Oxygen Fluorine Bonding", Final Tech. Summary Report, Contract No. Nonr 3433(00), ARPA Order No. 184–62, United Technology Corporation, Sunnyvale, Calif., (March 1963).
[2]E. Tschuikow Roux, J. Phys. Chem. **66**, 1636 (1962).
[3]G. Hetherington and P. L. Robinson, Special Publication No. 10, The Chem. Soc., London, (1957).
[4]Nichols and Robinson, personal communication to Hetherington and Robinson.
[5]D. F. Smith and D. W. Magnuson, Phys. Rev. **87**, 226 (1952).
[6]L. Clayton, Q. Williams, and T. Weatherly, J. Chem. Phys. **30**, 1328 (1959).
[7]R. Dodd, J. Rolfe and L. Woodward, Trans. Faraday Soc. **52**, 145 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.528	−102.881	−102.881	INFINITE
100	33.929	216.706	298.630	−8.192	−105.355	−93.186	48.675
200	41.239	242.134	264.542	−4.482	−107.475	−80.141	20.931
250	45.801	251.830	261.049	−2.305	−108.235	−73.215	15.298
298.15	49.865	260.250	260.250	0.	−108.784	−66.418	11.636
300	50.013	260.559	260.251	0.092	−108.802	−66.155	11.519
350	53.744	268.555	260.874	2.688	−109.205	−59.013	8.807
400	57.010	275.950	262.302	5.459	−109.475	−51.823	6.767
450	59.862	282.833	264.206	8.382	−109.635	−44.606	5.178
500	62.352	289.272	266.394	11.439	−109.706	−37.376	3.905
600	66.424	301.017	271.205	17.887	−109.646	−22.912	1.995
700	69.537	311.500	276.226	24.692	−109.393	−8.474	0.632
800	71.933	320.949	281.236	31.771	−109.011	5.918	−0.386
900	73.795	329.534	286.133	39.061	−108.541	20.256	−1.176
1000	75.256	337.387	290.871	46.516	−108.013	34.539	−1.804
1100	76.417	344.616	295.433	54.102	−107.445	48.767	−2.316
1200	77.351	351.307	299.814	61.792	−106.851	62.942	−2.740
1300	78.110	357.529	304.017	69.567	−106.241	77.067	−3.097
1400	78.734	363.342	308.049	77.410	−105.623	91.145	−3.401
1500	79.252	368.792	311.919	85.310	−105.004	105.178	−3.663
1600	79.687	373.921	315.635	93.257	−104.387	119.170	−3.890
1700	80.054	378.763	319.207	101.245	−103.777	133.123	−4.090
1800	80.366	383.348	322.645	109.266	−103.176	147.041	−4.267
1900	80.635	387.701	325.955	117.317	−102.586	160.926	−4.424
2000	80.867	391.843	329.147	125.392	−102.008	174.780	−4.565
2100	81.069	395.793	332.227	133.489	−101.442	188.605	−4.691
2200	81.245	399.569	335.203	141.605	−100.889	202.405	−4.806
2300	81.400	403.184	338.081	149.737	−100.348	216.178	−4.910
2400	81.537	406.651	340.866	157.884	−99.819	229.929	−5.004
2500	81.659	409.982	343.564	166.044	−99.299	243.658	−5.091
2600	81.767	413.187	346.181	174.216	−98.788	257.366	−5.171
2700	81.865	416.275	348.720	182.397	−98.285	271.055	−5.244
2800	81.952	419.254	351.186	190.588	−97.788	284.725	−5.312
2900	82.031	422.131	353.583	198.788	−97.295	298.377	−5.374
3000	82.102	424.913	355.915	206.994	−96.806	312.013	−5.433
3100	82.167	427.606	358.184	215.208	−96.318	325.632	−5.487
3200	82.225	430.216	360.395	223.427	−95.832	339.235	−5.537
3300	82.279	432.747	362.549	231.653	−95.345	352.823	−5.585
3400	82.328	435.204	364.650	239.883	−94.856	366.397	−5.629
3500	82.374	437.591	366.700	248.118	−94.366	379.956	−5.671
3600	82.415	439.912	368.702	256.358	−93.872	393.501	−5.710
3700	82.453	442.171	370.657	264.601	−93.375	407.032	−5.746
3800	82.489	444.370	372.568	272.848	−92.874	420.551	−5.781
3900	82.521	446.513	374.437	281.099	−92.368	434.056	−5.814
4000	82.552	448.603	376.265	289.352	−91.858	447.547	−5.844
4100	82.580	450.642	378.054	297.609	−91.342	461.026	−5.874
4200	82.606	452.632	379.806	305.868	−90.822	474.492	−5.901
4300	82.631	454.576	381.522	314.130	−90.297	487.946	−5.927
4400	82.653	456.476	383.204	322.394	−89.767	501.386	−5.952
4500	82.675	458.334	384.853	330.661	−89.233	514.816	−5.976
4600	82.695	460.151	386.471	338.929	−88.695	528.233	−5.998
4700	82.713	461.930	388.057	347.200	−88.154	541.639	−6.020
4800	82.731	463.671	389.614	355.472	−87.610	555.033	−6.040
4900	82.748	465.377	391.143	363.746	−87.064	568.416	−6.059
5000	82.763	467.049	392.645	372.021	−86.517	581.788	−6.078
5100	82.778	468.688	394.120	380.298	−85.970	595.149	−6.096
5200	82.792	470.296	395.569	388.577	−85.424	608.498	−6.112
5300	82.805	471.873	396.994	396.857	−84.879	621.838	−6.129
5400	82.817	473.421	398.395	405.138	−84.338	635.167	−6.144
5500	82.829	474.940	399.773	413.420	−83.800	648.485	−6.159
5600	82.840	476.433	401.129	421.704	−83.268	661.796	−6.173
5700	82.850	477.899	402.463	429.988	−82.743	675.095	−6.187
5800	82.860	479.340	403.776	438.274	−82.226	688.387	−6.200
5900	82.870	480.757	405.069	446.560	−81.719	701.667	−6.212
6000	82.879	482.150	406.342	454.848	−81.223	714.942	−6.224

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

Fluorine Nitrate (FNO_3) IDEAL GAS $M_r = 81.003303$

$S°(298.15\ K) = [292.933]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [18.049 \pm 2.1]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [10.460 \pm 2.1]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[1300](1)	[760](1)
[800](1)	[980](1)
[680](1)	[370](1)
[1700](1)	[130](1)
[450](1)	

Ground State Quantum Weight: [1] $\sigma = 1$

Point Group: C_s

Bond Distances: O–N = 1.29 ± 0.05 Å; N–O' = 1.39 ± 0.05 Å; O'–F = 1.42 ± 0.05 Å

Bond Angles: O–N–O = 125° ± 5°; F–O'–N = 105° ± 5°

Angle between NO'F plane and O_2NO' plane = 90°

Product of the Moments of Inertia: $I_A I_B I_C = 3.88611 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The value, 2.5 ± 0.5 kcal·mol^{-1}, for the enthalpy of formation of FNO_3(g) was obtained from Anderson, *et al.*[1] The value of $\Delta_f H°$ reported by Talakin, *et al.*[2] was 4.2 ± 0.9 kcal·mol^{-1} at 294 K.

Heat Capacity and Entropy

Vibrational frequencies were estimated by comparison with those of HNO_3(g) reported by Palm and Kilpatrick.[3] Bond distances and angles were taken from Pauling and Brockway.[4] The three principal moments of inertia are: $I_A = 8.8638 \times 10^{-39}$, $I_B = 18.5651 \times 10^{-39}$, and $I_C = 23.6154 \times 10^{-39}\ g·cm^2$. The possible existence of restricted internal rotation in the molecule was not considered. Thus the calculated values of $C_p°$ and $S°$ may be low.

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Fluorine Nitrate ($FONO_2$) $F_1N_1O_3$(g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.184	18.049	18.049	INFINITE
100	41.294	237.188	342.626	−10.544	14.427	33.213	−17.349
200	53.333	269.363	298.527	−5.833	11.852	53.088	−13.865
250	59.618	281.944	293.975	−3.008	11.011	63.501	−13.268
298.15	65.223	292.933	292.933	0.	10.460	73.664	−12.906
300	65.427	293.337	292.934	0.121	10.443	74.056	−12.894
350	70.594	303.819	293.750	3.524	10.109	84.688	−12.639
400	75.105	313.547	295.624	7.169	9.967	95.354	−12.452
450	79.008	322.624	298.125	11.025	9.980	106.028	−12.307
500	82.371	331.127	301.005	15.061	10.118	116.693	−12.191
600	87.757	346.645	307.344	23.581	10.670	137.962	−12.011
700	91.766	360.489	313.965	32.567	11.477	159.116	−11.873
800	94.781	372.949	320.573	41.901	12.446	180.143	−11.762
900	97.080	384.251	327.030	51.499	13.521	201.041	−11.668
1000	98.860	394.575	333.276	61.300	14.663	221.816	−11.586
1100	100.258	404.066	339.286	71.258	15.850	242.475	−11.514
1200	101.372	412.839	345.054	81.342	17.063	263.023	−11.449
1300	102.271	420.990	350.586	91.526	18.290	283.470	−11.390
1400	103.006	428.597	355.889	101.791	19.523	303.823	−11.336
1500	103.613	435.725	360.976	112.123	20.753	324.086	−11.286
1600	104.120	442.429	365.860	122.510	21.976	344.269	−11.239
1700	104.546	448.754	370.552	132.944	23.187	364.375	−11.196
1800	104.909	454.740	375.064	143.417	24.382	384.410	−11.155
1900	105.219	460.421	379.408	153.924	25.559	404.379	−11.117
2000	105.487	465.825	383.595	164.460	26.716	424.287	−11.081
2100	105.719	470.977	387.634	175.020	27.852	444.138	−11.047
2200	105.922	475.900	391.535	185.602	28.968	463.936	−11.015
2300	106.100	480.613	395.307	196.204	30.062	483.682	−10.985
2400	106.258	485.132	398.956	206.822	31.136	503.381	−10.956
2500	106.397	489.472	402.490	217.455	32.191	523.036	−10.928
2600	106.521	493.648	405.917	228.101	33.229	542.649	−10.902
2700	106.632	497.670	409.241	238.758	34.250	562.223	−10.877
2800	106.732	501.550	412.469	249.427	35.255	581.760	−10.853
2900	106.822	505.297	415.605	260.105	36.248	601.259	−10.830
3000	106.903	508.919	418.656	270.791	37.228	620.726	−10.808
3100	106.977	512.426	421.624	281.485	38.198	640.161	−10.787
3200	107.044	515.824	424.515	292.186	39.159	659.563	−10.766
3300	107.106	519.118	427.332	302.894	40.113	678.935	−10.747
3400	107.162	522.317	430.079	313.607	41.061	698.280	−10.728
3500	107.213	525.424	432.759	324.326	42.003	717.595	−10.710
3600	107.260	528.445	435.375	335.050	42.941	736.885	−10.692
3700	107.304	531.384	437.931	345.778	43.876	756.148	−10.675
3800	107.344	534.246	440.428	356.510	44.808	775.387	−10.658
3900	107.381	537.035	442.869	367.247	45.739	794.601	−10.642
4000	107.416	539.754	445.258	377.986	46.668	813.790	−10.627
4100	107.448	542.407	447.595	388.730	47.595	832.957	−10.612
4200	107.477	544.997	449.883	399.476	48.522	852.101	−10.597
4300	107.505	547.526	452.125	410.225	49.448	871.223	−10.583
4400	107.531	549.998	454.321	420.977	50.372	890.323	−10.569
4500	107.555	552.414	456.474	431.731	51.295	909.402	−10.556
4600	107.578	554.779	458.586	442.488	52.216	928.460	−10.543
4700	107.599	557.092	460.657	453.247	53.134	947.500	−10.530
4800	107.619	559.358	462.690	464.008	54.050	966.519	−10.518
4900	107.638	561.577	464.685	474.771	54.960	985.520	−10.506
5000	107.656	563.752	466.645	485.535	55.866	1004.502	−10.494
5100	107.672	565.884	468.570	496.302	56.765	1023.466	−10.482
5200	107.688	567.975	470.462	507.070	57.657	1042.411	−10.471
5300	107.703	570.026	472.321	517.839	58.540	1061.342	−10.460
5400	107.717	572.040	474.149	528.610	59.412	1080.253	−10.449
5500	107.730	574.016	475.947	539.383	60.273	1099.149	−10.439
5600	107.743	575.958	477.715	550.156	61.119	1118.031	−10.429
5700	107.755	577.865	479.456	560.931	61.950	1136.896	−10.418
5800	107.766	579.739	481.169	571.707	62.764	1155.749	−10.409
5900	107.777	581.581	482.855	582.484	63.559	1174.585	−10.399
6000	107.787	583.393	484.516	593.263	64.331	1193.411	−10.390

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

Fluorine Nitrate ($FONO_2$) $F_1N_1O_3$(g)

$S°(298.15\ K) = 51.212 \pm 0.08\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1269 \pm 2\ K$

$\Delta_f H°(0\ K) = -573.013 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -575.384 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = 33.346\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpies of solution and reaction of NaF(cr) have been determined by many investigators. Incorporating their reported data with auxiliary $\Delta_f H°$(298.15 K) values,[1,2] we calculate the corresponding values of $\Delta_f H°$(NaF, cr, 298.15 K). The results are presented in the table below. The adopted $\Delta_f H°$(NaF, cr, 298.15 K) is $-137.52 \pm 0.2\ kcal·mol^{-1}$ ($-575.384 \pm 0.8\ kJ·mol^{-1}$).

Source	Reaction*	T/K	Concentration NaF·nH$_2$O	No. of Determination	$\Delta r H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Guntz (1884)[1]	A	285	400	1	0.13	−137.42
Latimer–Jolly (1953)[2]	A	298	1850	2	0.23±0.01	−137.52
Hepler *et al.* (1953)[3]	A	298	1540	1	0.22±0.01	−137.51
Davies–Benson (1965)[4]	A	298	222	1	0.24±0.01	−137.53
Thomsen (1882)[5]	B	291		2	16.24±0.15	−137.38
Wartenberg–Fitzner (1926)[6]	C	293	—	1	−39.3 ±0.1	−137.62
Schmitz–Schumaker (1947)[7]	C	291	—	1	−39.5	−137.82
Coughlin (1958)[8]	D	298		6	−1.40±0.06	−137.58
Vorob'yev–Skuratov (1960)[9]	E	298	—	5	−325.5 ±2.2	−137.13

*Reaction A) NaF(cr) = NaF(n H_2O) and $\Delta_r H°(298.15\ K) = \Delta_{sol} H°$; B) NaOH($H_2O$, 200 K) + HF($H_2O$, 200 K) + H_2O(NaF401 H_2O);
C) NaCl(cr) + 1/2 F_2(g) = NaF(cr) + 1/2 Cl_2(g); D) NaCl(cr) + HF(H_2O, 5.716 K) = NaF(cr) + HCl(H_2O, 2.731K);
E) 4 Na(cr) + CF_4(g) = 4 NaF(cr) + C (graphite).

Heat Capacity and Entropy

The low temperature heat capacities, 0.05–15 K and 54.01 –295.86 K, were measured by Harrison *et al.*[10] and King,[11] respectively. These two sets of data are joined smoothly with the high temperature heat capacities at 298 K which were derived from the enthalpy measurements, 406.1–1282.2 K, determined by O'Brien and Kelley.[12] The $C_p°$ values above 1282.2 K are obtained by linear extrapolation. $S°$(298.15 K) is calculated using the adopted low temperature heat capacities and $S°(54\ K) = 0.555\ cal\ K^{-1}·mol^{-1}$.

Frank[13] commented that the temperature measurements of O'Brien and Kelley[12] seemed to be about 20 K high at 1000 with a smaller error at lower temperatures. A correction for the assumed error in the temperature measurement was used in the previous JANAF table. However, Douglas and Ditmars[14] have questioned this correction, since new enthalpy data for AlF_3 yielded $C_p°$ values in better agreement with the original $C_p°$ values of O'Brien and Kelley than with the corrected values of Frank. The $\alpha \rightarrow \beta$ transition of AlF_3(cr) was found in the range 723–6 K, while O'Brien and Kelley selected 727 K based on a point at 728.1 K in the β region and a point at 724.9 K in the pretransition region. Frank's correction yields an error of 9 at 727 K, yet the true error appears to be negligible (≤2) for AlF_3(cr). Based on the above reasoning and the comparison of the $C_p°$ curve of NaF(cr) with those of NaCl(cr), LiCl(cr) and LiF(cr) in the temperature range 300–1300 K, we adopt the high temperature enthalpy data of O'Brien and Kelley without any correction.

The low temperature heat capacities in the temperature ranges 81–190 and 198–273 K were also measured by Koref;[15] and high temperature enthalpies at temperatures 288–1073 and 290–1287 K were reported by Krestovnikov and Karetnikov,[16] and Lyashenko,[17] respectively. They are not used for evaluation.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K) = 284.93\ kJ·mol^{-1}$ is calculated as the difference between $\Delta_f H°$(298.15 K) for NaF(g) and NaF(cr).

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Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.488	−573.013	−573.013	INFINITE
100	22.836	11.067	88.086	−7.702	−575.020	−565.226	295.244
200	40.811	33.606	55.340	−4.347	−575.585	−555.101	144.978
298.15	46.852	51.212	51.212	0.	−575.384	−545.081	95.496
300	46.924	51.502	51.213	0.087	−575.378	−544.892	94.874
400	49.597	65.409	53.091	4.927	−577.769	−534.566	69.807
500	51.262	76.664	56.716	9.974	−577.506	−523.791	54.720
600	52.677	86.136	60.850	15.171	−577.062	−513.087	44.668
700	54.124	94.363	65.063	20.510	−576.451	−502.471	37.495
800	55.710	101.692	69.191	26.001	−575.674	−491.953	32.121
900	57.492	108.355	73.178	31.659	−574.730	−481.543	27.948
1000	59.505	114.514	77.007	37.507	−573.615	−471.247	24.615
1100	61.756	120.289	80.682	43.568	−572.322	−461.071	21.894
1200	64.266	125.768	84.213	49.866	−667.607	−448.581	19.526
1269.000	66.149	129.412	86.572	54.364	--- CRYSTAL <--> LIQUID ---		
1300	66.944	131.018	87.612	56.427	−665.009	−430.433	17.295
1400	69.162	136.065	90.894	63.239	−662.172	−412.494	15.390
1500	70.626	140.892	94.068	70.236	−659.158	−394.764	13.747
1600	71.128	145.469	97.139	77.328	−656.059	−377.238	12.316
1700	71.128	149.781	100.110	84.441	−652.948	−359.907	11.059
1800	71.128	153.846	102.983	91.554	−649.844	−342.759	9.947
1900	71.128	157.692	105.762	98.666	−646.747	−325.783	8.956
2000	71.128	161.340	108.451	105.779	−643.655	−308.971	8.069
2100	71.128	164.811	111.053	112.892	−640.566	−292.312	7.271
2200	71.128	168.120	113.572	120.005	−637.481	−275.801	6.548
2300	71.128	171.281	116.013	127.118	−634.396	−259.430	5.892
2400	71.128	174.309	118.379	134.230	−631.312	−243.193	5.293
2500	71.128	177.212	120.675	141.343	−628.227	−227.085	4.745
2600	71.128	180.002	122.903	148.456	−625.140	−211.101	4.241
2700	71.128	182.686	125.068	155.569	−622.051	−195.235	3.777
2800	71.128	185.273	127.172	162.682	−618.958	−179.483	3.348
2900	71.128	187.769	129.219	169.794	−615.863	−163.842	2.951
3000	71.128	190.180	131.211	176.907	−612.765	−148.308	2.582

PREVIOUS: December 1963 CURRENT: December 1968

Sodium Fluoride (NaF) LIQUID M_r = 41.988173 Sodium Fluoride (NaF) $F_1Na_1(l)$

$S°(298.15\ K)$ = [73.464] $J·K^{-1}·mol^{-1}$
T_{fus} = 1269 ± 2 K

$\Delta_f H°(298.15\ K)$ = [−546.204] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 33.346 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NaF_3,l, 298.15\ K)$ is calculated from $\Delta_f H°$(NaF, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1269\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities of NaF(l) are derived from the enthalpy data, 1287.6–1746.5 K, determined by O'Brien and Kelley.[1] A glass transition temperature is assumed at 900 K. The heat capacities below 900 K are taken from those for NaF(cr). The $C_p°$ values above 1746.5 K are obtained by extrapolation. The entropy is calculated in a manner analogous to that used for the enthalpy formation.

Fusion Data

The value of T_{fus} has been reported as (K): 1313,[2] 1285,[1] 1270,[3,4,5] 1269,[6] 1268,[7,8,9] 1267,[10,11,12] 1265,[13] 1263,[14] and 1253.[15] We select T_{fus} = 1269 K. The value 1285 K reported by O'Brien and Kelley seems unreasonably high and is not adopted. The cause of this discrepancy is still unresolved.[17] The heat of melting is calculated as the difference between the adopted enthalpies for NaF(cr) and NaF(l) at 1269 K. Kelley[18] derived $\Delta_{fus}H°(1265\ K)$ to be 5.82 8.43 $kcal·mol^{-1}$, based on 13 sets of molten salts equilibrium data involving NaF. The value $\Delta_{fus}H°(1285\ K)$ = 8.03 $kcal·mol^{-1}$ reported by O'Brien and Kelley is not used.

Vaporization Data

T_{vap} = 2060 K is the temperature at which the partial pressures of NaF(g) and Na_2F_2(g) in equilibrium with NaF(l) equal one atmosphere. The vapor composition at T_{vap} is evaluated as NaF 84.8% and Na_2F_2 15.2%. The heat required to vaporize one mole of liquid to form 0.868 mole of vapor mixture of the above composition at T_{vap} is calculated to be 42.1 $kcal·mol^{-1}$ (176.146 $kJ·mol^{-1}$).

Ruff *et al.*[16] measured the vapor pressure of NaF(l) in the temperature range of 1699–1974 K and reported T_{vap} = 1978 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	46.852	73.464	73.464	0.000	−546.204	−522.536	91.546
300	46.924	73.754	73.465	0.087	−546.199	−522.389	90.956
400	49.597	87.661	75.343	4.927	−548.589	−514.287	67.159
500	51.262	98.915	78.968	9.974	−548.327	−505.738	52.834
600	52.677	108.387	83.102	15.171	−547.883	−497.259	43.290
700	54.124	116.615	87.314	20.510	−547.271	−488.868	36.480
800	55.710	123.944	91.443	26.001	−546.495	−480.575	31.378
900	57.492	130.606	95.430	31.659	−545.551	−472.390	27.417
900.000	57.492	130.606	95.430	31.659	GLASS <--> LIQUID		
900.000	76.525	130.606	95.430	31.659	TRANSITION		
1000	74.099	138.538	99.353	39.185	−542.757	−464.413	24.258
1100	72.300	145.512	103.239	46.501	−540.209	−456.704	21.687
1200	70.961	151.744	107.026	53.662	−634.632	−446.778	19.448
1269.000	70.208	155.689	109.566	58.531	--- CRYSTAL <--> LIQUID ---		
1300	69.873	157.380	110.686	60.702	−631.555	−431.249	17.328
1400	69.036	162.526	114.207	67.646	−628.585	−415.953	15.519
1500	68.367	167.266	117.589	74.515	−625.699	−400.866	13.959
1600	67.823	171.660	120.833	81.324	−622.884	−385.969	12.601
1700	67.362	175.758	123.944	88.083	−620.127	−371.247	11.407
1800	66.986	179.597	126.931	94.800	−617.419	−356.685	10.351
1900	66.651	183.210	129.798	101.481	−614.752	−342.273	9.410
2000	66.358	186.621	132.555	108.131	−612.123	−328.000	8.566
2100	66.107	189.852	135.207	114.754	−609.525	−313.858	7.807
2200	65.898	192.923	137.761	121.354	−606.952	−299.839	7.119
2300	65.731	195.848	140.224	127.936	−604.399	−285.936	6.494
2400	65.563	198.642	142.600	134.500	−601.863	−272.144	5.923
2500	65.438	201.316	144.896	141.050	−599.341	−258.458	5.400
2600	65.312	203.880	147.115	147.588	−596.829	−244.872	4.920
2700	65.187	206.342	149.264	154.112	−594.328	−231.383	4.476
2800	65.103	208.711	151.345	160.627	−591.834	−217.986	4.067
2900	65.019	210.995	153.363	167.133	−589.345	−204.679	3.687
3000	64.936	213.197	155.321	173.631	−586.862	−191.457	3.334
3100	64.852	215.325	157.222	180.120	−584.385	−178.317	3.005
3200	64.810	217.384	159.070	186.603	−581.911	−165.258	2.698
3300	64.726	219.376	160.868	193.080	−579.442	−152.276	2.410
3400	64.685	221.308	162.617	199.550	−576.980	−139.368	2.141
3500	64.643	223.183	164.321	206.016	−574.523	−126.533	1.888

PREVIOUS: June 1964 CURRENT: December 1968

0 to 1269 K crystal
above 1269 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.488	−573.013	−573.013	INFINITE
100	22.836	11.067	88.086	−7.702	−575.020	−565.226	295.244
200	40.811	33.606	55.340	−4.347	−575.585	−555.101	144.978
298.15	46.852	51.212	51.212	0.	−575.384	−545.081	95.496
300	46.924	51.502	51.213	0.087	−575.378	−544.892	94.874
400	49.597	65.409	53.091	4.927	−577.769	−534.566	69.807
500	51.262	76.664	56.716	9.974	−577.506	−523.791	54.720
600	52.677	86.136	60.850	15.171	−577.062	−513.087	44.668
700	54.124	94.363	65.063	20.510	−576.451	−502.471	37.495
800	55.710	101.692	69.191	26.001	−575.674	−491.953	32.121
900	57.492	108.355	73.178	31.659	−574.730	−481.543	27.948
1000	59.505	114.514	77.007	37.507	−573.615	−471.247	24.615
1100	61.756	120.289	80.682	43.568	−572.322	−461.071	21.894
1200	64.266	125.768	84.213	49.866	−667.607	−448.581	19.526
1269.000	66.149	129.412	86.572	54.364	CRYSTAL <--> LIQUID		
1269.000	70.208	155.689	86.572	87.710	TRANSITION		
1300	69.873	157.380	88.240	89.882	−631.555	−431.249	17.328
1400	69.036	162.526	93.365	96.826	−628.585	−415.953	15.519
1500	68.367	167.266	98.136	103.695	−625.699	−400.866	13.959
1600	67.823	171.660	102.595	110.504	−622.884	−385.969	12.601
1700	67.362	175.758	106.780	117.262	−620.127	−371.247	11.407
1800	66.986	179.597	110.720	123.979	−617.419	−356.685	10.351
1900	66.651	183.210	114.441	130.661	−614.752	−342.273	9.410
2000	66.358	186.621	117.965	137.311	−612.123	−328.000	8.566
2100	66.107	189.852	121.312	143.934	−609.525	−313.858	7.807
2200	65.898	192.923	124.498	150.534	−606.952	−299.839	7.119
2300	65.731	195.848	127.537	157.115	−604.399	−285.936	6.494
2400	65.563	198.642	130.442	163.679	−601.863	−272.144	5.923
2500	65.438	201.316	133.224	170.229	−599.341	−258.458	5.400
2600	65.312	203.880	135.893	176.767	−596.829	−244.872	4.920
2700	65.187	206.342	138.456	183.292	−594.328	−231.383	4.476
2800	65.103	208.711	140.924	189.806	−591.834	−217.986	4.067
2900	65.019	210.995	143.301	196.312	−589.345	−204.679	3.687
3000	64.936	213.197	145.594	202.810	−586.862	−191.457	3.334
3100	64.852	215.325	147.809	209.299	−584.385	−178.317	3.005
3200	64.810	217.384	149.952	215.782	−581.911	−165.258	2.698
3300	64.726	219.376	152.025	222.259	−579.442	−152.276	2.410
3400	64.685	221.308	154.035	228.729	−576.980	−139.368	2.141
3500	64.643	223.183	155.984	235.196	−574.523	−126.533	1.888

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = 217.610 \pm 0.008\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -288.819 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -290.453 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 536.10 \pm 0.35\ cm^{-1}$ $\omega_e x_e = 3.83 \pm 0.14\ cm^{-1}$ $\sigma = 1$

$B_e = 0.4369\ cm^{-1}$ $\alpha_e = 0.00456\ cm^{-1}$ $r_e = 1.99260$ Å

Enthalpy of Formation

The total pressure of NaF(g) and Na_2F_2(g), in equilibrium with NaF(cr,l) at temperatures 1020–1974 K, have been determined by many investigators, using manometric,[1, 2, 5] torsion–effusion,[6, 8] Knudsen effusion,[3, 7] transpiration,[4] and molecular–beam velocity–selector[9, 10] methods. In order to evaluate $\Delta_{vap}H°$(LiF, g) we have used a trial and error variation of $\Delta_{sub}H°$ and $\Delta_{vap}H°$ for the monomer and dimer such that the $\Delta_f H°$(298.15 K) values derived by the 2nd and 3rd law methods are in reasonable agreement.

Incorporating $\Delta_{sub}H°(298.15\ K) = 68.1$ and 72.7, and $\Delta_{vap}H°(298.15\ K) = 61.12$ and 58.75 kcal·mol^{-1} for NaF and Na_2F_2, respectively, with JANAF functions for NaF(cr), NaF(l), NaF(g) and Na_2F_2(g), we derive the partial pressures of NaF monomer from the reported total pressures. Based on the calculated partial pressures of NaF(g), the corresponding enthalpy of vaporization are evaluated by the 2nd and 3rd law methods. Using the 3rd law $\Delta_f H°(298.15\ K)$ and $\Delta_f H°(298.15\ K) = -137.52$ and -130.545 kcal·mol^{-1}for NaF(cr) and NaF(l), we obtain values of $\Delta_f H°$(298.15 K) for NaF(g). The results are presented in the table below. The $\Delta_f H°$(NaF, g, 298.15 K) value adopted is -69.42 kcal·mol^{-1} (-290.453 ± 2.1 kJ·mol^{-1}).

Gaydon[11] and Herzberg[12] reported $D_0° = 114.2 \pm 6.9$ (4.95±0.3 eV) and < 122.2 kcal·mol^{-1} (5.3 eV), respectivley. Using JANAF $\Delta_f H°(298.15\ K)$ values for Na(g) and F(g), we obtain $\Delta_f H°$(NaF, g, 298.15 K) = -70.5 ± 5.8 and >-78.5 kcal·mol.$^{-1}$ Employing flame–photometric method, Bulewicz *et al.*[13] and Page and Sugden[14] derived $D_0° = 121 \pm 7$ and 119–120 kcal·mol^{-1} for NaF(g), which lead to $\Delta_f H°$(NaF, g, 298.15 K) = -77.3 ± 7 and -75 to -76 kcal·mol.$^{-1}$

Source	T/K	Reaction**	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
vonWartenberg Schulz (1921)[1]	1669–1830	B	5	67.76±0.11	59.90	−4.5±0.1	−70.65
Ruff *et al.* (1922)[2]	1699–1974	B	14	64.07±0.58	59.54	−2.4±0.3	−71.01
Niwa (1938)[3]	1053–1112	A	5	63.18±1.04	66.68	3.2±1.0	−70.84
Sense *et al.* (1957)[4]	1208–1265	A	7	71.26±0.63	68.25	−2.4±0.5	−69.27
	1274–1348	B	9	65.88±0.76	61.14	−3.6±0.6	−69.41
Cantor Blankenship (1958)[5]	1381–1592	B	6*	66.13	60.84	−3.6	−69.71
Pugh Barrow (1958)[6]	1023–1166	A	7*	68.13	68.14	0.0	−69.38
Porter Schoonmaker (1958)[7]	1121	A	1	–	68.82	–	−68.70
Entner Neckel (1967)[8]	1016–1236	A	6*	68.54±0.10	67.74	−0.7±0.1	−69.78

*Data points calculated from a given total pressure equation.

**Reaction A) NaF(cr) = NaF(g) B) NaF(l) = NaF(g).

Heat Capacity and Entropy

Veazey and Gordy[15] have measured the rotational transitions of NaF in the millimeter– and sub–millimeter–wave region with a high resolution molecular–beam absorption spectrometer. The derived values of ω_e, $\omega_e x_e$, B_e, α_e and r_e are adopted here.

Using the molecular beam electric resonance method, Bauer and Lew[16] measured the transition between the J = 0 and J = 1 rotational levels of $Na^{23}F^{19}$ in the three lowest vibrational states. Radio–frequency transitions for $Na^{23}F^{19}$ have been observed by Hollowell *et al.*[19] Infrared spectra of NaF have been analyzed by Snelson and Pitzer,[17] Ritchie and Lew,[18] and Baikov and Vasilevskii.[20] The molecular constants derived by the above authors are similar to the values adopted, except the value ω_e= 550 cm^{-1} [17] which is different from the value 536.1 cm^{-1} reported by Veazey and Gordy.[15]

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Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.225	−288.819	−288.819	INFINITE
100	29.357	183.316	246.446	−6.313	−288.700	−296.132	154.683
200	31.978	204.387	220.675	−3.258	−289.565	−303.238	79.198
250	33.261	211.666	218.168	−1.626	−290.009	−306.605	64.062
298.15	34.215	217.610	217.610	0.	−290.453	−309.761	54.269
300	34.247	217.821	217.610	0.063	−290.471	−309.881	53.955
350	34.984	223.159	218.030	1.795	−290.987	−313.077	46.724
400	35.538	227.868	218.971	3.559	−294.207	−315.987	41.264
450	35.962	232.079	220.198	5.347	−294.815	−318.673	36.991
500	36.293	235.886	221.579	7.153	−295.396	−321.293	33.565
600	36.773	242.548	224.535	10.808	−296.494	−326.367	28.413
700	37.103	248.243	227.525	14.503	−297.528	−331.264	24.719
800	37.348	253.214	230.432	18.226	−298.518	−336.015	21.940
900	37.541	257.625	233.213	21.971	−299.488	−340.644	19.770
1000	37.699	261.589	235.856	25.733	−300.458	−345.165	18.030
1100	37.835	265.188	238.361	29.510	−301.449	−349.588	16.601
1200	37.955	268.486	240.736	33.300	−399.243	−351.479	15.299
1300	38.064	271.528	242.989	37.101	−399.405	−347.492	13.962
1400	38.165	274.353	245.130	40.912	−399.568	−343.493	12.816
1500	38.259	276.989	247.167	44.733	−399.730	−339.482	11.822
1600	38.349	279.461	249.109	48.564	−399.893	−335.460	10.952
1700	38.436	281.789	250.963	52.403	−400.055	−331.428	10.184
1800	38.519	283.988	252.737	56.251	−400.216	−327.386	9.500
1900	38.600	286.073	254.437	60.107	−400.376	−323.336	8.889
2000	38.679	288.055	256.069	63.971	−400.532	−319.277	8.339
2100	38.757	289.944	257.638	67.843	−400.685	−315.210	7.840
2200	38.834	291.748	259.147	71.722	−400.833	−311.137	7.387
2300	38.909	293.476	260.603	75.609	−400.974	−307.056	6.973
2400	38.984	295.134	262.007	79.504	−401.108	−302.970	6.594
2500	39.058	296.727	263.364	83.406	−401.234	−298.878	6.245
2600	39.131	298.260	264.677	87.316	−401.350	−294.782	5.922
2700	39.204	299.738	265.948	91.232	−401.457	−290.681	5.624
2800	39.276	301.165	267.181	95.156	−401.553	−286.576	5.346
2900	39.348	302.545	268.377	99.088	−401.639	−282.468	5.088
3000	39.419	303.880	269.538	103.026	−401.715	−278.358	4.847
3100	39.491	305.174	270.667	106.971	−401.782	−274.245	4.621
3200	39.562	306.429	271.765	110.924	−401.839	−270.130	4.409
3300	39.632	307.647	272.834	114.884	−401.887	−266.013	4.211
3400	39.703	308.831	273.875	118.850	−401.929	−261.895	4.024
3500	39.773	309.983	274.890	122.824	−401.964	−257.776	3.847
3600	39.843	311.105	275.881	126.805	−401.996	−253.656	3.680
3700	39.913	312.197	276.848	130.793	−402.025	−249.535	3.523
3800	39.983	313.262	277.792	134.788	−402.054	−245.413	3.373
3900	40.053	314.302	278.715	138.790	−402.084	−241.291	3.232
4000	40.123	315.317	279.617	142.798	−402.119	−237.167	3.097
4100	40.192	316.308	280.500	146.814	−402.161	−233.043	2.969
4200	40.262	317.278	281.364	150.837	−402.211	−228.918	2.847
4300	40.331	318.226	282.211	154.866	−402.275	−224.791	2.731
4400	40.400	319.154	283.040	158.903	−402.313	−220.666	2.620
4500	40.470	320.063	283.852	162.946	−402.388	−216.537	2.514
4600	40.539	320.953	284.649	166.997	−402.491	−212.406	2.412
4700	40.608	321.826	285.431	171.054	−402.615	−208.273	2.315
4800	40.677	322.681	286.198	175.118	−402.765	−204.136	2.221
4900	40.746	323.521	286.951	179.190	−402.942	−199.996	2.132
5000	40.815	324.345	287.691	183.268	−403.143	−195.853	2.046
5100	40.884	325.153	288.418	187.353	−403.384	−191.705	1.963
5200	40.953	325.948	289.132	191.445	−403.661	−187.552	1.884
5300	41.022	326.729	289.834	195.543	−403.979	−183.393	1.807
5400	41.091	327.496	290.524	199.649	−404.340	−179.228	1.734
5500	41.160	328.251	291.203	203.761	−404.747	−175.056	1.663
5600	41.229	328.993	291.871	207.881	−405.202	−170.875	1.594
5700	41.297	329.723	292.529	212.007	−405.709	−166.686	1.528
5800	41.366	330.442	293.177	216.140	−406.269	−162.488	1.463
5900	41.435	331.150	293.814	220.280	−406.886	−158.280	1.401
6000	41.504	331.847	294.442	224.427	−407.404	−154.079	1.341

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

D_0° = 18030 ± 850 cm^{-1}
$S°$(298.15 K) = 216.40 ± 0.3 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 108 ± 10 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 109 ± 10 kJ·mol^{-1}

Electronic Levels and Molecular Constants ($^{16}O^{19}F$, cm^{-1}

State	T_e	g_i	ω_e	$\omega_e x_e$*	B_e	α_e**	D_e
10^6**	r_e/Å						
$X^2\Pi_{3/2}$	0	2	1052.99376	9.90030	1.05870547		
	−0.0138015	4.28739	1.35412				
$X^2\Pi_{1/2}$	193.80	2	1052.99376	9.90030	1.05870547		
	−0.0138015	4.28739	1.35412				

* $\omega_e y_e$ = −0.068456, $\omega_e z_e$ = −0.0010881, $\omega_e a_e \times 10^{-5}$ = −5.945
** 3 additional higher order terms are also available

σ=1

Enthalpy of Formation

The dissociation energy has been calculated by many different techniques. The derived values range from 106.3 to 403.7 kJ·mol^{-1}. The values may be grouped into two types: (1) derived from a molecular orbital calculation and (2) extracted from reaction studies involving F_2O. We adopt D_0°(OF) = 18030 ± 850 cm^{-1} (215.687 ± 10 kJ·mol^{-1}) based on the experimental studies of Clyne and Watson,[1] Czarnowski and Schumacher,[2] Berkowitz *et al.*,[3] and Zhang *et al.*[4] These four studies are all dependent on the enthalpy of formation of OF_2(g) and are mass spectrometric studies except for the thermal decomposition of OF_2 by Czarnowski and Schumacher.[2] From the adopted value, we calculate $\Delta_f H°$(OF,g, 298K) = 109 ± 10 kJ·mol^{-1}. Additional data needed for the calculations presented here, e.g. thermal functions for the F(g) and F_2(ref), O(g) and O_2(ref), are taken from the JANAF Thermochemical Tables.[5]

Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{16}O^{19}F$ isotopomer. Isotopic relationships[6] are used to convert the above constants to those for the normally occurring, i.e. natural abundance, species. The latter values are then used in the calculation of the thermal functions. Only the X state is included in the calculation of the thermal functions; a sum–over–states technique is used.

The ground state, $X^2\Pi_{3/2}$, has been characterized by Burkholder *et al.*[7] The observations were made using a high resolution Fourier transform spectrometer and a multiple reflection absorption cell equipped to study short–lived molecules under fast flow conditions. Hammer *et al.*[8] used a high resolution Fourier transform spectrometer to study the OF infrared chemiluminescence. This latter study, the results of which we have adopted, provided values which were slightly different from the Burkholder *et al.*[7] work.

The value of A, the splitting of the ground state, has been determined experimentally by five authors: McKellar[9] (177.3 ± 5.6 cm^{-1}), Dyke *et al.*[10] (160 ± 30 cm^{-1}), McKellar *et al.*[11] (177.3 cm^{-1}), Burkholder *et al.*[7] (198.3 ± 6.7 cm^{-1}), and Hammer *et al.*[8] (193.80 ± 0.97 cm^{-1}). We adopt the value of Hammer *et al.* as determined by high resolution Fourier transform spectroscopy.

An $A^2\Pi$ state is assumed to exist at approximately 35,000 cm^{-1} but has not been observed. This state would not contribute significantly to the thermal functions below 6000 K.

References

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[5]JANAF Thermochemical Tables: F(g), June 1982; F_2(ref), June 1982; O(g), Sept. 1982; O_2(ref), Sept. 1982).
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[9]A.R.W. McKellar, Can. J. Phys. **57**, 2106 (1979).
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[11]A.R.W. McKellar, C. Yamada and E. Hirota, J. Mol. Spectrosc. **97** (2), 425 (1983).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−9.388	108.392	108.392	INFINITE
50	30.058	159.390	318.327	−7.947	108.382	107.996	−112.819
100	32.600	181.178	244.853	−6.367	108.506	107.572	−56.188
150	32.472	194.419	225.985	−4.735	108.682	107.066	−37.283
200	31.935	203.681	219.310	−3.126	108.828	106.505	−27.816
250	31.788	210.783	216.922	−1.535	108.939	105.911	−22.128
298.15	31.995	216.396	216.396	0.000	109.025	105.320	−18.451
300	32.007	216.594	216.397	0.059	109.028	105.297	−18.333
400	32.917	225.920	217.662	3.303	109.177	104.030	−13.585
500	33.860	233.369	220.083	6.643	109.304	102.728	−10.732
600	34.620	239.612	222.831	10.069	109.414	101.402	−8.828
700	35.193	244.994	225.622	13.561	109.502	100.059	−7.466
800	35.621	249.723	228.345	17.102	109.571	98.705	−6.445
900	35.941	253.938	230.959	20.681	109.620	97.344	−5.650
1000	36.183	257.738	233.450	24.288	109.651	95.978	−5.013
1100	36.367	261.195	235.817	27.916	109.664	94.610	−4.493
1200	36.509	264.366	238.066	31.560	109.661	93.241	−4.059
1300	36.619	267.293	240.203	35.217	109.641	91.874	−3.691
1400	36.704	270.010	242.236	38.883	109.606	90.509	−3.377
1500	36.770	272.544	244.173	42.557	109.553	89.146	−3.104
1600	36.821	274.919	246.021	46.236	109.485	87.788	−2.866
1700	36.859	277.153	247.788	49.921	109.401	86.434	−2.656
1800	36.886	279.260	249.478	53.608	109.300	85.086	−2.469
1900	36.903	281.255	251.099	57.297	109.184	83.744	−2.302
2000	36.910	283.148	252.654	60.988	109.053	82.408	−2.152
2100	36.906	284.949	254.149	64.679	108.908	81.079	−2.017
2200	36.891	286.666	255.589	68.369	108.749	79.758	−1.894
2300	36.865	288.305	256.976	72.057	108.577	78.445	−1.781
2400	36.826	289.873	258.314	75.742	108.394	77.138	−1.679
2500	36.774	291.375	259.607	79.422	108.199	75.838	−1.585
2600	36.707	292.816	260.856	83.096	107.994	74.549	−1.498
2700	36.626	294.200	262.066	86.763	107.779	73.266	−1.417
2800	36.530	295.531	263.238	90.420	107.554	71.992	−1.343
2900	36.418	296.811	264.373	94.068	107.321	70.725	−1.274
3000	36.292	298.043	265.475	97.704	107.077	69.469	−1.210
3100	36.151	299.231	266.545	101.326	106.824	68.220	−1.149
3200	35.996	300.376	267.584	104.933	106.561	66.977	−1.093
3300	35.828	301.481	268.595	108.525	106.289	65.745	−1.041
3400	35.647	302.548	269.578	112.098	106.007	64.521	−0.991
3500	35.454	303.579	270.535	115.654	105.715	63.305	−0.945
3600	35.251	304.575	271.467	119.189	105.411	62.098	−0.901
3700	35.038	305.538	272.375	122.703	105.096	60.897	−0.860
3800	34.818	306.469	273.260	126.196	104.769	59.710	−0.821
3900	34.589	307.371	274.123	129.667	104.431	58.529	−0.784
4000	34.355	308.243	274.965	133.114	104.079	57.353	−0.749
4100	34.116	309.089	275.787	136.538	103.714	56.193	−0.716
4200	33.873	309.908	276.590	139.937	103.336	55.036	−0.684
4300	33.627	310.702	277.374	143.312	102.943	53.891	−0.655
4400	33.379	311.472	278.140	146.662	102.536	52.755	−0.626
4500	33.129	312.220	278.889	149.988	102.114	51.629	−0.599
4600	32.879	312.945	279.622	153.288	101.677	50.510	−0.574
4700	32.630	313.650	280.338	156.564	101.224	49.403	−0.549
4800	32.381	314.334	281.039	159.814	100.755	48.306	−0.526
4900	32.134	314.999	281.726	163.040	100.270	47.221	−0.503
5000	31.889	315.646	282.398	166.241	99.767	46.142	−0.482
5100	31.646	316.275	283.056	169.418	99.247	45.075	−0.462
5200	31.407	316.887	283.700	172.571	98.711	44.015	−0.442
5300	31.170	317.483	284.332	175.699	98.155	42.970	−0.423
5400	30.937	318.064	284.952	178.805	97.582	41.935	−0.406
5500	30.708	318.629	285.559	181.887	96.990	40.909	−0.389
5600	30.483	319.180	286.154	184.947	96.379	39.895	−0.372
5700	30.263	319.718	286.738	187.984	95.748	38.890	−0.356
5800	30.046	320.242	287.312	190.999	95.097	37.900	−0.341
5900	29.834	320.754	287.874	193.993	94.426	36.918	−0.327
6000	29.627	321.254	288.426	196.966	93.734	35.950	−0.313

PREVIOUS: December 1966 (1 bar) CURRENT: September 1995 (1 bar)

Titanium Fluoride Oxide (OTiF) IDEAL GAS M_r = 82.877803

$S°(298.15\ K)$ = [250.667] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−430.918] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−433.211] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[880](1)
[300](1)
[740](1)

Ground State Quantum Weight: [2] σ = 1
Point Group: [$C_{\infty v}$]
Bond Distances: Ti–O = [1.62] Å; Ti–F = [1.74] Å
Bond Angle: O–Ti–F = [180°]
Rotational Constant: B_0 = [0.170462] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as −103 $kcal·mol^{-1}$ by Gordon.[1] $\Delta_f H°(298.15\ K)$ was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] Principal moment was 16.419 × 10^{-39} $g·cm^2$.

Reference

[1]J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., personal communication, (January 10, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.291	−430.918	−430.918	INFINITE
100	33.375	206.489	289.330	−8.284	−431.378	−434.017	226.707
200	42.295	232.558	254.917	−4.472	−432.402	−436.255	113.938
250	45.706	242.373	251.450	−2.269	−432.844	−437.166	91.341
298.15	48.472	250.667	250.667	0.	−433.211	−437.964	76.729
300	48.568	250.967	250.668	0.090	−433.224	−437.993	76.261
350	50.908	258.636	251.268	2.579	−433.555	−438.761	65.482
400	52.791	265.561	252.629	5.173	−433.850	−439.484	57.391
450	54.299	271.870	254.422	7.852	−434.121	−440.172	51.094
500	55.509	277.656	256.460	10.598	−434.378	−440.831	46.053
600	57.279	287.944	260.871	16.243	−434.874	−442.075	38.486
700	58.469	296.868	265.390	22.035	−435.374	−443.235	33.075
800	59.297	304.733	269.826	27.925	−435.882	−444.324	29.011
900	59.892	311.753	274.102	33.886	−436.441	−445.347	25.847
1000	60.332	318.088	278.189	39.898	−437.126	−446.301	23.312
1100	60.666	323.854	282.082	45.949	−438.005	−447.178	21.235
1200	60.925	329.144	285.787	52.029	−443.067	−447.845	19.494
1300	61.129	334.029	289.312	58.132	−443.620	−448.222	18.010
1400	61.293	338.566	292.670	64.254	−444.260	−448.552	16.736
1500	61.427	342.799	295.873	70.390	−445.000	−448.834	15.630
1600	61.537	346.767	298.931	76.538	−445.854	−449.062	14.660
1700	61.629	350.501	301.856	82.697	−446.837	−449.233	13.803
1800	61.706	354.026	304.657	88.864	−447.962	−449.343	13.040
1900	61.772	357.364	307.344	95.038	−449.241	−449.385	12.354
2000	61.828	360.534	309.925	101.218	−465.375	−448.902	11.724
2100	61.876	363.551	312.407	107.403	−467.750	−448.020	11.144
2200	61.919	366.431	314.798	113.593	−470.133	−447.025	10.614
2300	61.956	369.184	317.103	119.786	−472.522	−445.921	10.127
2400	61.988	371.822	319.328	125.984	−474.917	−444.713	9.679
2500	62.017	374.353	321.479	132.184	−477.315	−443.406	9.264
2600	62.042	376.786	323.560	138.387	−479.715	−442.002	8.880
2700	62.065	379.127	325.575	144.592	−482.115	−440.506	8.522
2800	62.085	381.385	327.528	150.800	−484.514	−438.921	8.188
2900	62.104	383.564	329.423	157.009	−486.910	−437.250	7.876
3000	62.120	385.670	331.263	163.221	−489.301	−435.497	7.583
3100	62.135	387.707	333.051	169.433	−491.687	−433.664	7.307
3200	62.149	389.680	334.790	175.648	−494.067	−431.755	7.048
3300	62.161	391.592	336.482	181.863	−496.438	−429.771	6.803
3400	62.173	393.448	338.131	188.080	−498.801	−427.715	6.571
3500	62.183	395.251	339.737	194.298	−501.155	−425.590	6.352
3600	62.193	397.003	341.304	200.516	−503.499	−423.398	6.143
3700	62.201	398.707	342.832	206.736	−914.931	−413.352	5.835
3800	62.210	400.366	344.324	212.957	−916.019	−399.781	5.495
3900	62.217	401.982	345.782	219.178	−917.152	−386.181	5.172
4000	62.224	403.557	347.207	225.400	−918.328	−372.552	4.865
4100	62.230	405.093	348.600	231.623	−919.545	−358.893	4.572
4200	62.236	406.593	349.963	237.846	−920.802	−345.203	4.293
4300	62.242	408.058	351.297	244.070	−922.097	−331.483	4.027
4400	62.247	409.489	352.604	250.295	−923.429	−317.733	3.772
4500	62.252	410.888	353.883	256.519	−924.796	−303.951	3.528
4600	62.257	412.256	355.137	262.745	−926.197	−290.140	3.295
4700	62.261	413.595	356.367	268.971	−927.630	−276.297	3.071
4800	62.265	414.906	357.573	275.197	−929.093	−262.423	2.856
4900	62.269	416.190	358.756	281.424	−930.586	−248.519	2.649
5000	62.272	417.448	359.917	287.651	−932.105	−234.583	2.451
5100	62.275	418.681	361.058	293.878	−933.652	−220.618	2.260
5200	62.279	419.890	362.177	300.106	−935.222	−206.622	2.076
5300	62.282	421.076	363.278	306.334	−936.817	−192.594	1.898
5400	62.284	422.241	364.359	312.562	−938.434	−178.538	1.727
5500	62.287	423.383	365.422	318.791	−940.072	−164.451	1.562
5600	62.290	424.506	366.467	325.020	−941.730	−150.333	1.402
5700	62.292	425.608	367.495	331.249	−943.408	−136.187	1.248
5800	62.294	426.692	368.506	337.478	−945.103	−122.010	1.099
5900	62.296	427.757	369.501	343.707	−946.816	−107.804	0.954
6000	62.298	428.804	370.481	349.937	−948.546	−93.569	0.815

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$\Delta_{at}H°(0\ K)$ = [790 ± 20] kJ·mol^{-1}
$S°(298.15\ K)$ = [251 ± 1] J·K^{-1} mol^{-1}

$\Delta_fH°(0\ K)$ = [381.2 ± 20] kJ·mol^{-1}
$\Delta_fH°(298.15\ K)$ = [378.6 ± 20] kJ·mol^{-1}

Electronic Levels and Quantum Weights		
State	cm^{-1}	g_i
[$^2B_2$]	0	[2]
[$^2B_1$]	[1049.3]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1050](1)
[600](1)
[1200](1)

Point Group: [C_{2v}] σ = 2
Bond Distance: F–O = [1.5591]Å
Bond Angle: O–F–O = [76.75]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [116.8132 × 10^{-117}] g^3·cm^6

Enthalpy of Formation

The enthalpy of formation was calculated based on the molecular geometry optimization of Gosavi *et al.*[1] This calculation yielded the result Δ_fH(OFO) – Δ_fH(FOO) = 356 kJ·mol^{-1}. It is assumed that this calculated difference referred to 0 K. In contrast, Gole and Hayes[2] earlier calculated difference of >418 kJ·mol^{-1}.

Heat Capacity and Entropy

The molecular geometry adopted here is that used by Gosavi *et al.*[1] in their quantum mechanical calculations (6–31G basis sets). The structure was calculated to be bent with a O–F–O angle of [76.75°]. The bond length was calculated to be [1.5591]Å. The principle moments of inertia (in g·cm^2) are: I_A = 2.9573×10^{-39}, I_B = 4.9779×10^{-39}, and I_C = 7.9351×10^{-39}.

Gosavi *et al.*[1] examined the molecular geometry optimization of four electronic states of OFO at the RHF–SCF level with 6–31G and 6–31G* basis sets. In contrast, earlier calculations by Gole and Hayes[2] were based on a double–zeta sp basis set SCF total energy calculations as a function of the OFO bond angle. This latter study suggested a $^2B_1$ ground state with a bond angle of 128.22° (assuming a O–F bond distance of 1.19 Å).

The vibrational frequencies are estimated from the corresponding vibrational frequencies which describe the other OXO(g) molecules, where X = Cl and Br.

References

[1]R.K. Gosavi, P. Raghunathan and O.P. Stauz, J. Mol. Struct. **133**, 25 (1985).
[2]J.L. Gole and E.F. Hayes, Intern. J. Quantum Chem. Symp. No. **5**, 519 (1969).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−10.538	381.180	381.180	INFINITE
50	33.258	189.213	366.723	−8.875	380.667	382.618	−399.719
100	33.370	212.280	284.393	−7.211	380.149	384.770	−200.983
150	34.218	225.938	262.776	−5.526	379.650	387.190	−134.832
200	35.991	236.005	254.874	−3.774	379.210	389.772	−101.798
250	38.446	244.290	251.951	−1.915	378.860	392.454	−81.999
298.15	41.126	251.289	251.289	.000	378.622	395.096	−69.219
300	41.230	251.544	251.290	.076	378.615	395.198	−68.810
400	46.544	264.155	252.973	4.473	378.431	400.764	−52.334
500	50.581	275.001	256.319	9.341	378.557	406.338	−42.450
600	53.294	284.481	260.240	14.544	378.864	411.867	−35.856
700	55.036	292.837	264.312	19.967	379.257	417.337	−31.142
800	56.142	300.264	268.351	25.530	379.678	422.748	−27.603
900	56.849	306.920	272.273	31.183	380.098	428.107	−24.847
1000	57.306	312.935	276.043	36.892	380.501	433.419	−22.640
1100	57.606	318.412	279.650	42.639	380.878	438.693	−20.832
1200	57.806	323.434	283.092	48.410	381.228	443.933	−19.324
1300	57.942	328.066	286.376	54.198	381.548	449.146	−18.047
1400	58.034	332.364	289.509	59.997	381.838	454.334	−16.951
1500	58.098	336.370	292.501	65.804	382.098	459.503	−16.001
1600	58.143	340.121	295.361	71.616	382.329	464.656	−15.169
1700	58.174	343.647	298.099	77.432	382.531	469.795	−14.435
1800	58.196	346.973	300.723	83.250	382.703	474.923	−13.782
1900	58.211	350.120	303.240	89.071	382.848	480.042	−13.197
2000	58.222	353.106	305.660	94.892	382.967	485.154	−12.671
2100	58.230	355.947	307.987	100.715	383.061	490.261	−12.195
2200	58.235	358.656	310.229	106.538	383.131	495.365	−11.761
2300	58.238	361.244	312.391	112.362	383.180	500.465	−11.366
2400	58.240	363.723	314.479	118.186	383.209	505.563	−11.003
2500	58.241	366.101	316.497	124.010	383.221	510.661	−10.670
2600	58.242	368.385	318.449	129.834	383.218	515.759	−10.362
2700	58.242	370.583	320.339	135.658	383.201	520.857	−10.077
2800	58.241	372.701	322.172	141.482	383.174	525.956	−9.812
2900	58.240	374.745	323.949	147.307	383.138	531.055	−9.565
3000	58.240	376.719	325.676	153.131	383.094	536.157	−9.335
3100	58.239	378.629	327.353	158.954	383.045	541.260	−9.120
3200	58.238	380.478	328.985	164.778	382.992	546.364	−8.918
3300	58.237	382.270	330.572	170.602	382.937	551.470	−8.729
3400	58.235	384.008	332.119	176.426	382.881	556.579	−8.551
3500	58.234	385.697	333.625	182.249	382.824	561.688	−8.383
3600	58.233	387.337	335.095	188.072	382.769	566.799	−8.224
3700	58.232	388.933	336.528	193.896	382.716	571.911	−8.074
3800	58.231	390.485	337.928	199.719	382.665	577.026	−7.932
3900	58.230	391.998	339.295	205.542	382.618	582.142	−7.797
4000	58.229	393.472	340.631	211.365	382.574	587.258	−7.669
4100	58.228	394.910	341.937	217.188	382.535	592.376	−7.547
4200	58.227	396.313	343.216	223.011	382.499	597.494	−7.431
4300	58.226	397.683	344.466	228.833	382.467	602.614	−7.320
4400	58.226	399.022	345.691	234.656	382.439	607.733	−7.215
4500	58.225	400.330	346.891	240.478	382.416	612.854	−7.114
4600	58.224	401.610	348.066	246.301	382.395	617.974	−7.017
4700	58.223	402.862	349.219	252.123	382.378	623.096	−6.925
4800	58.222	404.088	350.349	257.945	382.363	628.218	−6.836
4900	58.222	405.289	351.458	263.768	382.350	633.341	−6.751
5000	58.221	406.465	352.547	269.590	382.339	638.463	−6.670
5100	58.220	407.618	353.615	275.412	382.327	643.586	−6.592
5200	58.220	408.748	354.665	281.234	382.315	648.708	−6.516
5300	58.219	409.857	355.696	287.056	382.302	653.832	−6.444
5400	58.219	410.945	356.709	292.878	382.286	658.955	−6.374
5500	58.218	412.014	357.705	298.700	382.266	664.078	−6.307
5600	58.218	413.063	358.684	304.521	382.241	669.203	−6.242
5700	58.217	414.093	359.647	310.343	382.210	674.327	−6.180
5800	58.217	415.106	360.594	316.165	382.172	679.453	−6.119
5900	58.216	416.101	361.527	321.986	382.125	684.577	−6.061
6000	58.216	417.079	362.445	327.808	382.068	689.705	−6.004

PREVIOUS: CURRENT: September 1995 (1 bar)

$S°(298.15\ K) = 259.5 \pm 0.2\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 27.2 \pm 2\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 25.4 \pm 2\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X^2A''	0	2
$^2A'$	8630	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1486.93(1)
376 (1)
579.32(1)

Point Group: C_s $\sigma = 1$
Bond Distances: F–O = 1.649Å ; O–O = 1.200Å
Bond Angle: F–O–O = 111.2°
Product of the Moments of Inertia: $I_A I_B I_C = 84.3487 \times 10^{-117}\ g^3\cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of O_2F(g) at 298.15 K, 25.4 ± 2 kJ·mol^{-1}, is based on six experimental results.[1-6] Two earlier studies[7,8] are not included in this analysis. The review by Lyman[4] recommended an enthalpy of formation value based on three experimental studies.[1,7,8] These six experimental studies and their recommended values are:

Author	$\Delta_f H°$(298 K), kJ·mol^{-1}	T/K of study	Technique
Lyman and Holland[1]	23.0 ± 1.7	298 K	Kinetic study of reaction F+O_2
Holland *et al.*[2]	24.1		Unpublished; kinetic study of reaction F+O_2
Shamonima and Kotov[3]	21.6	223–293 K	EPR measurement of rate constants
Lyman[4]	22.9		Review
Pagsberg *et al.*[5]	26.1 ± 2.1	295–359 K	Spectrokinetic study
Campuzano–Jost *et al.*[6]	24.7 ± 4	100–420 K	Spectrokinetic study

Heat Capacity and Entropy

The structure of this molecule is bent with a F–O–O angle of 111.2° based on the diode–laser spectrum as obtained by Yamada and Hirota.[9] The bond length is F–O = 1.649Å and O–O = 1.200 Å. Supporting structural information is available from the infrared study of McKellar *et al.*,[10] a microwave study by Bogey *et al.*,[11] and a laser magnetic resonance study by Bley *et al.*[12] The principle moments of inertia (in g·cm^2) are: $I_A = 1.0714 \times 10^{-39}$, $I_B = 8.3532 \times 10^{-39}$, and $I_C = 9.4246 \times 10^{-39}$.

There are numerous studies from which vibrational frequencies are derived: Yamada and Hirota,[9] Mckellar *et al.*,[10] Arkell,[13] Noble and Pimentel,[14] Spratley *et al.*,[15] Jacox,[16] and Kim and Campbell.[17] We adopt the recommendations of Jacox,[18] using gas phase values for ν_1 and ν_3 and the nitrogen matrix X value for ν_2.[15] Similar vibrational frequencies were recommended by Lyman[4] in an earlier review.

Lyman stated that the published absorption spectra of O_2F Glissman and Schumacher[19] and Matchuk *et al.*[20] indicated no electronic states at energies below the dissociation energy of the molecule. Jacox[18] in her review, discussed four absorption studies in which a maximum has been observed at 205nm by Chegodaev and Tupikov,[21] 420nm by Fessenden and Schuler,[22] and 445nm Matchuk *et al.*[20] Jacox[16] observed the onset of dissociation near 490nm. Only the X and A states are used in the calculation.

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Continued on page 1214

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−11.256	27.240	27.240	INFINITE
50	33.278	193.625	385.481	−9.593	26.728	28.458	−29.730
100	34.495	216.933	296.015	−7.908	26.230	30.385	−15.872
150	37.360	231.437	272.202	−6.115	25.839	32.554	−11.336
200	40.260	242.593	263.455	−4.172	25.590	34.833	−9.098
250	42.627	251.841	260.233	−2.098	25.455	37.162	−7.765
298.15	44.453	259.511	259.511	.000	25.400	39.422	−6.907
300	44.516	259.786	259.511	.082	25.399	39.509	−6.879
400	47.417	273.011	261.295	4.687	25.422	44.213	−5.774
500	49.606	283.838	264.753	9.542	25.537	48.899	−5.108
600	51.295	293.038	268.720	14.591	25.689	53.557	−4.663
700	52.594	301.047	272.778	19.788	25.856	58.189	−4.342
800	53.595	308.138	276.763	25.100	26.026	62.796	−4.100
900	54.372	314.498	280.609	30.500	26.193	67.382	−3.911
1000	54.983	320.259	284.290	35.969	26.355	71.950	−3.758
1100	55.472	325.523	287.803	41.492	26.510	76.502	−3.633
1200	55.872	330.368	291.151	47.060	26.656	81.040	−3.528
1300	56.210	334.854	294.342	52.665	26.793	85.567	−3.438
1400	56.504	339.030	297.387	58.301	26.920	90.083	−3.361
1500	56.769	342.938	300.295	63.965	27.037	94.590	−3.294
1600	57.015	346.609	303.076	69.654	27.145	99.090	−3.235
1700	57.250	350.073	305.739	75.367	27.244	103.584	−3.183
1800	57.478	353.352	308.294	81.104	27.334	108.072	−3.136
1900	57.702	356.466	310.748	86.863	27.418	112.555	−3.094
2000	57.925	359.431	313.109	92.644	27.496	117.034	−3.057
2100	58.146	362.262	315.383	98.448	27.571	121.509	−3.022
2200	58.366	364.972	317.575	104.273	27.644	125.981	−2.991
2300	58.585	367.572	319.693	110.121	27.716	130.449	−2.963
2400	58.800	370.070	321.740	115.990	27.791	134.913	−2.936
2500	59.012	372.474	323.722	121.881	27.870	139.375	−2.912
2600	59.220	374.793	325.642	127.793	27.954	143.834	−2.890
2700	59.421	377.032	327.504	133.725	28.046	148.289	−2.869
2800	59.616	379.196	329.312	139.677	28.146	152.741	−2.849
2900	59.803	381.292	331.068	145.648	28.257	157.189	−2.831
3000	59.982	383.322	332.776	151.637	28.378	161.633	−2.814
3100	60.152	385.292	334.439	157.644	28.512	166.073	−2.798
3200	60.313	387.204	336.058	163.667	28.659	170.507	−2.783
3300	60.465	389.062	337.636	169.706	28.819	174.937	−2.769
3400	60.606	390.869	339.175	175.760	28.992	179.363	−2.756
3500	60.738	392.628	340.678	181.827	29.180	183.783	−2.743
3600	60.861	394.341	342.145	187.907	29.382	188.197	−2.731
3700	60.973	396.010	343.578	193.999	29.597	192.606	−2.719
3800	61.077	397.637	344.979	200.101	29.826	197.009	−2.708
3900	61.171	399.225	346.350	206.214	30.068	201.406	−2.698
4000	61.256	400.775	347.691	212.335	30.323	205.795	−2.687
4100	61.332	402.289	349.004	218.465	30.589	210.179	−2.678
4200	61.400	403.767	350.291	224.601	30.867	214.556	−2.668
4300	61.461	405.213	351.551	230.744	31.156	218.926	−2.659
4400	61.513	406.626	352.787	236.893	31.455	223.289	−2.651
4500	61.559	408.009	353.999	243.047	31.762	227.645	−2.642
4600	61.598	409.363	355.188	249.205	32.077	231.994	−2.634
4700	61.631	410.688	356.355	255.366	32.399	236.337	−2.627
4800	61.657	411.986	357.500	261.531	32.726	240.673	−2.619
4900	61.678	413.257	358.625	267.698	33.058	245.002	−2.612
5000	61.694	414.503	359.730	273.866	33.393	249.324	−2.605
5100	61.705	415.725	360.816	280.036	33.729	253.640	−2.598
5200	61.712	416.924	361.884	286.207	34.066	257.948	−2.591
5300	61.714	418.099	362.933	292.379	34.402	262.251	−2.585
5400	61.713	419.253	363.966	298.550	34.736	266.546	−2.578
5500	61.708	420.385	364.981	304.721	35.065	270.835	−2.572
5600	61.700	421.497	365.980	310.891	35.389	275.120	−2.566
5700	61.688	422.589	366.964	317.061	35.706	279.398	−2.560
5800	61.674	423.661	367.932	323.229	36.014	283.671	−2.555
5900	61.658	424.716	368.886	329.396	36.312	287.937	−2.549
6000	61.639	425.752	369.825	335.560	36.598	292.200	−2.544

PREVIOUS: September 1966 (1 bar) CURRENT: September 1995 (1 bar)

D_0° = 443.881 ± 19.2 kJ·mol^{-1}
$S°$(298.15 K) = 224.968 ± 0.04 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −51.335 ± 20.9 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −52.250 ± 20.9 kJ·mol^{-1}

State	T_0, cm^{-1}	g_i	Electronic and Molecular Constants (σ = 1) ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^3\Sigma$	0	3	846.75	4.489	0.5665	0.00456	1.5896
$a^1\Delta$	7090.41	2	858.79	4.438	0.5699	0.00467	1.5849
$b^1\Sigma$	13353.9	1	866.14	4.51	0.5725	0.0045	1.5812
$B^3\Pi_0$	29338.69	2	436	[1.5]	0.4632	0.004	1.752
$B^3\Pi_1$	29481.80	2	436	[1.5]	0.4663	0.0038	1.752
$B^3\Pi_2$	29623.06	2	436	[1.5]	0.4693	0.0037	1.752
$d^1\Pi$	35812.29	2	413	[1.5]	0.4848	0.0062	1.721

Enthalpy of Formation

There has been no report of a direct experimental determination of $\Delta_f H°$. Sufficient information is available, however, to allow a reasonable estimate of the P–F bond energy (D_0°) to be made.

linear Birge–Sponer extrapolation of the ground state vibrational constants leads to D''(LBX) = 4.90 eV. This value can be refined by taking into account the ionic character of the P–F bond. Using relationships developed by Hildenbrand,[1] we adjust the value of D''(LBX) to obtain D'' = 4.25 eV. A similar treatment of spectroscopic data[5] for related molecules (AlF, SiF, and ClF) which have well established bond energies indicates that the true D_0° value could be higher than D'' by roughly 0.3 eV. Additional support for this is provided by the results of two molecular orbital studies[2,3] which have led to estimates of D_0° of 4.5 eV and 4.65 ± 0.2 eV. The latter value, obtained from Hartree–Fock energies and estimated corrections for correlation effects, is believed to be reliable within the quoted uncertainty. A CNDO/2 MO study,[4] employing energy partitioning concepts, has led to a much higher estimate of D_0° equal to 5.17 eV.

We adopt D_0°(PF) = 4.60 ± 0.2 eV (106.08 kcal·mol^{-1}) which gives $\Delta_f H°$(PF) = −8.546 ± 5.0 kcal·mol^{-1} when combined with JANAF auxiliary data[5] for P and F. The adopted D_0° value lies midway between the well established bond energies[5] for SiF (130.3 kcal·mol^{-1}) and SF (81.2 kcal·mol^{-1}) and is near the mean bond energy (D = 109.1 kcal·mol^{-1}) in PF_5.[5] $\Delta_f H°$ at 298.15 K is −8.345 kcal·mol^{-1}.

Heat Capacity and Entropy

The thermal functions are calculated from the partition function $Q = Q_t \Sigma g_i Q_r^i Q_v^i \exp(-c_2\epsilon_i/T)$ in which Q_r^i and Q_v^i contain first order corrections for anharmonicity. The electronic and molecular constants are taken from the compilation of Suchard.[6] Values of $\omega_e x_e$ placed in brackets are estimates obtained from data on isoconfigurational states of SO ($A^3\Pi$[6]) and PF($B^3\Pi$). Our entropies may contain significant errors, amounting to several tenths of a cal K^{-1}·mol^{-1}, above 3500 K due to the omission of many unobserved electronic levels which have been predicted[7] to lie above the $b^1\Sigma$ state at 13353.91 cm^{-1}. In addition, Skolnik and Goodfriend[8] recently observed in emission a triple headed band system near 5600Å which was tentatively assigned to a $^3\Delta_{inv} - {}^3\Pi_{inv}$ transition of PF. These inverted triplet levels are also omitted since we are unable to estimate their term values with respect to the $X^3\Sigma^-$ ground state.

Our calculations essentially update and extend those previously made on PF by O'Hare.[9] The most significant difference is that our calculations are based on solid phosphorus (Red, V) as the reference state below 704 K rather than the ideal diatomic gas selected by O'Hare.[9]

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[5]JANAF Thermochemical Tables: AlF(g), 12–31–75; SiF(g), 12–31–76; ClF(g) and F(g), 9–30–65; P(g), 6–30–62; SF(g), 6–30–76; PF_5(g), 12–31–69.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	C_p° (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.858	−51.335	−51.335	INFINITE
100	29.115	192.409	251.908	−5.950	−50.768	−59.722	31.195
200	29.854	212.729	227.801	−3.014	−51.560	−68.616	17.921
250	30.716	219.480	225.484	−1.501	−51.890	−72.843	15.220
298.15	31.620	224.968	224.968	0.	−52.250	−76.846	13.463
300	31.654	225.164	224.969	0.059	−52.264	−76.999	13.407
350	32.528	230.110	225.357	1.663	−53.390	−81.018	12.091
400	33.289	234.505	226.231	3.309	−53.875	−84.932	11.091
450	33.928	238.464	227.374	4.990	−54.344	−88.785	10.306
500	34.461	242.067	228.666	6.700	−54.799	−92.588	9.673
600	35.270	248.426	231.443	10.189	−55.680	−100.062	8.711
700	35.838	253.908	234.270	13.746	−56.531	−107.391	8.014
800	36.250	258.721	237.032	17.352	−57.363	−114.600	7.483
900	36.563	263.010	239.684	20.993	−58.181	−121.706	7.064
1000	36.813	266.876	242.213	24.662	−58.990	−128.720	6.724
1100	37.025	270.394	244.617	28.355	−59.790	−135.655	6.442
1200	37.215	273.624	246.902	32.067	−124.156	−141.438	6.157
1300	37.395	276.610	249.074	35.797	−124.168	−142.878	5.741
1400	37.573	279.388	251.141	39.546	−124.177	−144.317	5.385
1500	37.751	281.986	253.112	43.312	−124.183	−145.755	5.076
1600	37.933	284.429	254.993	47.096	−124.183	−147.193	4.805
1700	38.120	286.734	256.793	50.899	−124.177	−148.631	4.567
1800	38.310	288.918	258.518	54.720	−124.162	−150.070	4.355
1900	38.503	290.994	260.173	58.561	−124.136	−151.510	4.165
2000	38.697	292.974	261.764	62.421	−124.098	−152.952	3.995
2100	38.892	294.867	263.296	66.300	−124.045	−154.396	3.840
2200	39.085	296.681	264.772	70.199	−123.977	−155.843	3.700
2300	39.276	298.422	266.198	74.117	−123.890	−157.293	3.572
2400	39.464	300.098	267.575	78.054	−123.784	−158.747	3.455
2500	39.647	301.713	268.909	82.010	−123.656	−160.207	3.347
2600	39.825	303.271	270.201	85.983	−123.506	−161.672	3.248
2700	39.998	304.777	271.454	89.975	−123.333	−163.143	3.156
2800	40.164	306.235	272.670	93.983	−123.134	−164.621	3.071
2900	40.324	307.647	273.852	98.007	−122.910	−166.106	2.992
3000	40.478	309.017	275.001	102.047	−122.659	−167.600	2.918
3100	40.626	310.347	276.120	106.103	−122.381	−169.103	2.849
3200	40.767	311.639	277.210	110.172	−122.076	−170.614	2.785
3300	40.902	312.895	278.272	114.256	−121.743	−172.136	2.725
3400	41.032	314.118	279.309	118.353	−121.383	−173.669	2.668
3500	41.157	315.310	280.320	122.462	−120.995	−175.212	2.615
3600	41.277	316.471	281.308	126.584	−120.579	−176.767	2.565
3700	41.393	317.603	282.274	130.717	−120.136	−178.334	2.518
3800	41.506	318.709	283.218	134.862	−119.666	−179.913	2.473
3900	41.615	319.788	284.142	139.019	−119.169	−181.505	2.431
4000	41.723	320.843	285.047	143.185	−118.645	−183.110	2.391
4100	41.828	321.875	285.932	147.363	−118.095	−184.728	2.353
4200	41.933	322.884	286.800	151.551	−117.519	−186.360	2.318
4300	42.037	323.872	287.651	155.750	−116.917	−188.006	2.284
4400	42.141	324.839	288.485	159.958	−116.290	−189.667	2.252
4500	42.245	325.788	289.304	164.178	−115.637	−191.342	2.221
4600	42.351	326.717	290.107	168.408	−114.959	−193.032	2.192
4700	42.459	327.629	290.896	172.648	−114.256	−194.736	2.164
4800	42.569	328.524	291.670	176.899	−113.529	−196.456	2.138
4900	42.682	329.403	292.431	181.162	−112.777	−198.192	2.113
5000	42.798	330.267	293.179	185.436	−112.000	−199.943	2.089
5100	42.917	331.115	293.915	189.722	−111.199	−201.709	2.066
5200	43.040	331.950	294.638	194.019	−110.374	−203.492	2.044
5300	43.167	332.771	295.350	198.330	−109.523	−205.291	2.023
5400	43.298	333.579	296.051	202.653	−108.649	−207.106	2.003
5500	43.434	334.375	296.740	206.989	−107.750	−208.938	1.984
5600	43.575	335.159	297.419	211.340	−106.826	−210.785	1.966
5700	43.720	335.931	298.088	215.705	−105.877	−212.651	1.949
5800	43.870	336.693	298.747	220.084	−104.904	−214.532	1.932
5900	44.025	337.444	299.397	224.479	−103.905	−216.431	1.916
6000	44.185	338.185	300.037	228.889	−102.881	−218.347	1.901

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Phosphorus Fluoride, Ion (PF^+) IDEAL GAS $M_r = 49.971614$ Phosphorus Fluoride, Ion (PF^+) $F_1P_1^+(g)$

$D_0^\circ = 508.356 \pm 41.8$ kJ·mol^{-1}
$S°(298.15\ K) = 224.035 \pm 0.21$ J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = 895.664 \pm 37.7$ kJ·mol^{-1}
$\Delta_f H°(298.15\ K) = 901.518 \pm 37.7$ kJ·mol^{-1}

Electronic States and Molecular Constants ($\sigma = 1$)

State	T_0, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_{1/2}$	0	2	1053.25	5.047	0.6360	0.0048	1.5003
$X^2\Pi_{3/2}$	323.95	2	1053.25	5.047	0.6360	0.0048	1.5003
$^2\Sigma$	35434.64	2	619.0	4.615	0.5593	0.0079	1.5998

Enthalpy of Formation

Harland *et al.*[1] and Torgerson and Westmore[2] reported the appearance potential of PF^+ from PF_3 as 21.0 ± 0.3 eV and 20.5 ± 0.2 eV, respectively. We use the mean value of $AP(PF^+/PF_3) = 20.75 \pm 0.3$ eV (478.50 kcal·mol^{-1}) in the expression $\Delta_r H°(0\ K) = AP\text{-}E^*$ for the process $PF_3(g) + e^- = PF^+(g) + 2\ F(g) + 2e^-$. With the assumption $E^* = 0$, the value of $\Delta_r H°(0\ K)$ gives $\Delta_f H°(PF^+, g, 0\ K) = 217.823 \pm 9.0$ kcal·mol^{-1} with $\Delta_f H°(PF_3, g, 0\ K) = -223.97 \pm 0.9$ kcal·mol^{-1} and $\Delta_f H°(F, g, 0\ K) = 18.36 \pm 0.4$ kcal·mol^{-1}.[3] We adopted this value. In the same paper, Harland *et al.*[1] also reported $AP(PF^+/PF_2CN) = 19.1 \pm 0.2$ eV which leads to $\Delta_f H°(PF^+, g, 0\ K) = 233.56 \pm 21.3$ kcal·mol^{-1}, in reasonable accord with the adopted result.

$\Delta_f H°$ at 298.15 K is 219.641 ± 9.0 kcal·mol^{-1}, and the adopted ionization potential (IP) is 9.82 ± 0.61 eV. This IP compares favorably with values predicted from quantum mechanical calculations. These have included (all in eV) 9.5 ± 0.2,[4] 9.6,[5] and 10.35.[6] The latter value is based on IP(P) = 10.98 eV which is 0.5 eV higher than the current best value of 10.486 eV.[7] Recalculation of the results of Companion and Hsia[6] gives IP(PF) = 9.85 eV.

The primary bond dissociation energy $D_0^\circ(PF^+)$ is calculated to be 121.5 kcal·mol^{-1} which can be compared with 106.1 kcal·mol^{-1},[3] in the neutral molecule. The stronger P–F bond in the ion is consistent with theoretical predictions[4–6] that the electron lost from PF occupies an antibonding orbital.

Heat Capacity and Entropy

The thermal functions are calculated from the partition function $Q = Q_t \Sigma g_i Q_r^i Q_v^i \exp(-c_2\epsilon_i/T)$ in which Q_r^i and Q_v^i contain first order corrections for anharmonicity. The electronic and molecular constants are taken from Douglas and Frackowiak[8] who observed one band system in the emission spectrum of PF^+ formed by passing a discharge through a mixture of PF_3 and He. We treat the ground state as two distinct electronic levels with a splitting of 323.95 cm^{-1}. This procedure gives functions which are slightly biased below 400 K. The uncertainty in the value of $S°(298.15\ K)$ includes this error. By analogy with the isoelectronic molecules SiF and PO,[3] other excited states are predicted to lie in the range 20000–30000 cm^{-1}. We prefer to omit these levels, but if they do exist our entropies could be slightly low above 4500 K.

References

[1] P. W.Harland, D. W.H. Rankin and J. C. J. Thynne, Int. J. Mass Spectr. Ion Phys. **13**, 395 (1974).
[2] D. F. Torgerson and J. B. Westmore, Can. J. Chem. **53**, 933 (1975).
[3] JANAF Thermochemical Tables: PF_3(g), 12–31–69; F(g), 9–30–65; SiF(g), 12–31–76; PO(g), 6–30–71; PF(g), 6–30–77.
[4] P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. **54**, 4563 (1971).
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[7] H. M. Rosenstock, K. Draxl, et al, J. Phys. Chem. Ref. Data **6**, Suppl. 1 (1977).
[8] A. E. Douglas and M. Frackowiak, Can. J. Phys. **40**, 832 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.430	895.664		
100	30.783	188.512	253.369	−6.486			
200	33.019	210.776	227.079	−3.261			
250	33.221	218.167	224.584	−1.604			
298.15	33.428	224.035	224.035	0.	901.518	870.945	−152.586
300	33.438	224.242	224.036	0.062	901.545	870.755	−151.612
350	33.734	229.418	224.444	1.741	901.533	865.638	−129.189
400	34.078	233.945	225.354	3.436	902.136	860.469	−112.366
450	34.431	237.979	226.537	5.149	902.739	855.225	−99.272
500	34.767	241.624	227.866	6.879	903.343	849.913	−88.790
600	35.352	248.017	230.707	10.386	904.559	839.113	−73.051
700	35.812	253.502	233.581	13.945	905.788	828.108	−61.794
800	36.168	258.308	236.377	17.545	907.029	816.927	−53.340
900	36.446	262.585	239.056	21.176	908.279	805.589	−46.755
1000	36.666	266.437	241.605	24.832	909.536	794.112	−41.480
1100	36.843	269.940	244.024	28.508	910.798	782.508	−37.158
1200	36.989	273.152	246.319	32.200	848.491	771.868	−33.599
1300	37.111	276.118	248.499	35.905	850.533	765.400	−30.754
1400	37.215	278.872	250.571	39.621	852.570	758.775	−28.310
1500	37.305	281.443	252.545	43.347	854.602	752.004	−26.187
1600	37.383	283.853	254.427	47.082	856.631	745.098	−24.325
1700	37.454	286.121	256.225	50.824	858.655	738.065	−22.678
1800	37.517	288.264	257.946	54.572	860.676	730.913	−21.211
1900	37.574	290.294	259.596	58.327	862.694	723.649	−19.895
2000	37.627	292.223	261.179	62.087	864.711	716.279	−18.707
2100	37.676	294.060	262.702	65.852	866.728	708.808	−17.631
2200	37.722	295.814	264.167	69.622	868.746	701.240	−16.650
2300	37.765	297.491	265.580	73.397	870.768	693.581	−15.752
2400	37.806	299.099	266.943	77.175	872.794	685.834	−14.927
2500	37.845	300.644	268.260	80.958	874.827	678.002	−14.166
2600	37.883	302.129	269.535	84.744	876.868	670.089	−13.462
2700	37.919	303.559	270.769	88.534	878.920	662.097	−12.809
2800	37.954	304.939	271.964	92.328	880.982	654.029	−12.201
2900	37.987	306.271	273.125	96.125	883.058	645.887	−11.634
3000	38.020	307.559	274.251	99.925	885.148	637.673	−11.103
3100	38.053	308.807	275.346	103.729	887.252	629.389	−10.605
3200	38.084	310.015	276.410	107.536	889.373	621.037	−10.137
3300	38.115	311.188	277.447	111.346	891.511	612.619	−9.697
3400	38.145	312.326	278.456	115.159	893.666	604.135	−9.281
3500	38.176	313.432	279.439	118.975	895.839	595.588	−8.889
3600	38.205	314.508	280.399	122.794	898.031	586.978	−8.517
3700	38.235	315.555	281.335	126.616	900.241	578.308	−8.164
3800	38.264	316.575	282.249	130.441	902.470	569.577	−7.829
3900	38.293	317.570	283.142	134.269	904.717	560.787	−7.511
4000	38.322	318.539	284.015	138.099	906.983	551.940	−7.208
4100	38.351	319.486	284.868	141.933	909.268	543.035	−6.918
4200	38.380	320.411	285.703	145.769	911.571	534.075	−6.642
4300	38.409	321.314	286.521	149.609	913.893	525.059	−6.378
4400	38.438	322.197	287.322	153.451	916.232	515.990	−6.126
4500	38.468	323.061	288.107	157.297	918.590	506.867	−5.884
4600	38.498	323.907	288.876	161.145	920.965	497.691	−5.651
4700	38.528	324.736	289.630	164.996	923.357	488.464	−5.429
4800	38.559	325.547	290.370	168.851	925.766	479.186	−5.215
4900	38.591	326.342	291.096	172.708	928.191	469.857	−5.009
5000	38.622	327.122	291.809	176.569	930.633	460.478	−4.811
5100	38.655	327.887	292.509	180.433	933.091	451.051	−4.620
5200	38.688	328.638	293.196	184.300	935.565	441.575	−4.436
5300	38.722	329.376	293.872	188.170	938.054	432.051	−4.258
5400	38.757	330.100	294.536	192.044	940.558	422.481	−4.087
5500	38.793	330.811	295.189	195.922	943.076	412.863	−3.921
5600	38.830	331.511	295.832	199.803	945.609	403.201	−3.761
5700	38.867	332.198	296.464	203.688	948.157	393.492	−3.606
5800	38.906	332.875	297.085	207.576	950.718	383.739	−3.456
5900	38.946	333.540	297.698	211.469	953.293	373.941	−3.311
6000	38.987	334.195	298.301	215.366	955.882	364.100	−3.170

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

D_0° = 222.170 ± 71.1 kJ·mol^{-1}
$S°$(298.15 K) = [225.218 ± 2.1] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −157.592 ± 69.0 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [−164.046 ± 69.0] kJ·mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^2\Pi_{3/2}$]	0	[2]
	[350]	[2]
	[25000]	[4]

ω_e = [840] cm^{-1} $\omega_e x_e$ = [4.6] cm^{-1} σ = 1
B_e = [0.56626] cm^{-1} α_e = [0.00424] cm^{-1} r_e = [1.59] Å

Enthalpy of Formation

We calculate the enthalpy of formation at 0 K as the difference between $\Delta_f H°(PF, g, 0 K) = -8.55 \pm 5.0$ kcal·mol^{-1},[1] and the selected value of 1.1±0.5 eV (25.366 kcal·mol^{-1}) for the electron affinity (EA) of PF. The value of EA refers to the vertical electron detachment process $PF^-(g) = PF(g) + e^-$ and is taken from the molecular orbital study of O'Hare.[2] This value was obtained from Hartree Fock energies and estimated corrections for correlation effects. The estimated uncertainty in EA is 0.5 eV which should be adequate to cover the possibility that the adiabatic value is lower than the vertical EA. Other theoretical predictions of EA include 2.55 eV[3] and 1.4 eV.[4]

$\Delta_f H°$ at 298.15 K is −35.035 kcal·mol^{-1}, and the primary bond dissociation energy (Products P(g) + F^- (g)) is 53.1 kcal·mol^{-1}. The latter value can be compared with $D_0^\circ(PF)$ = 106.1 kcal·mol^{-1},[1] indicating that the P–F bond is much weaker in the anion relative to the neutral molecule. This is consistent with MO predictions[24] which indicate that the electron captured by PF occupies an antibonding orbital located primarily on the phosphorus atom.

Our thermal functions indicate that PF^- is thermodynamically stable with respect to dissociation (P + F^-) below 2500 K. These predictions agree qualitatively with the results of MacNeil and Thynne[5] who observed PF^- in the negative ion mass spectrum of PF_3. Their reported appearance potential, $AP(PF^-/PF_3)$ = 11.4 ± 0.1 eV, gives EA(PF) = −0.47 eV assuming that the dissociative electron capture process is $PF_3(g) + e^- = PF^-(g) + 2F(g)$. We believe this value is too low probably because of excess kinetic and/or excitation energies amounting to roughly 1.5 eV.

Heat Capacity and Entropy

The bond length and vibrational constants are assumed to lie between those for PF and SF.[1] The value of B_e is obtained from r_e. We calculate α_e from the other constants assuming a Morse potential function.

The ground state electronic configuration ($^2\Pi_{3/2}$), ground state splitting (A = 350 cm^{-1}), and excited state ($^2\Pi$) at 25000 cm^{-1} are estimated by analogy with those for the isoelectronic molecule SF.[1] The major source of error in our calculations below 500 K arises from the uncertainty in the ground state splitting. With A = 0 cm^{-1}, the value of $S°$(298.15 K) increases by 0.5 cal K^{-1}·mol^{-1}. At higher temperatures the differences in S become smaller, indicating that the uncertainty in the adopted entropies above 1000 K is less than 0.2 cal K^{-1}·mol^{-1}.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.516	−157.592		
100	30.469	189.364	255.166	−6.580			
200	33.518	211.573	228.364	−3.358			
250	34.258	219.137	225.788	−1.663			
298.15	34.786	225.218	225.218	0.	−164.046	−182.462	31.967
300	34.804	225.433	225.218	0.064	−164.093	−182.576	31.789
350	35.242	230.832	225.644	1.816	−166.111	−185.484	27.682
400	35.603	235.562	226.594	3.587	−167.511	−188.156	24.571
450	35.903	239.774	227.829	5.375	−168.912	−190.652	22.130
500	36.152	243.570	229.216	7.177	−170.315	−192.992	20.162
600	36.535	250.197	232.177	10.812	−173.128	−197.264	17.173
700	36.810	255.850	235.165	14.480	−175.947	−201.064	15.004
800	37.016	260.780	238.065	18.172	−178.771	−204.459	13.350
900	37.175	265.149	240.836	21.882	−181.599	−207.500	12.043
1000	37.302	269.073	243.467	25.606	−184.432	−210.226	10.981
1100	37.407	272.633	245.959	29.341	−187.267	−212.669	10.099
1200	37.496	275.892	248.320	33.087	−253.678	−213.774	9.305
1300	37.574	278.896	250.558	36.840	−255.746	−210.365	8.453
1400	37.643	281.683	252.683	40.601	−257.821	−206.797	7.716
1500	37.705	284.283	254.704	44.369	−259.904	−203.079	7.072
1600	37.763	286.718	256.629	48.142	−261.994	−199.223	6.504
1700	37.816	289.009	258.467	51.921	−264.090	−195.235	5.999
1800	37.866	291.172	260.224	55.705	−266.191	−191.124	5.546
1900	37.914	293.220	261.908	59.494	−268.295	−186.897	5.138
2000	37.960	295.166	263.522	63.288	−270.402	−182.558	4.768
2100	38.004	297.019	265.074	67.086	−272.509	−178.114	4.430
2200	38.046	298.788	266.566	70.889	−274.615	−173.570	4.121
2300	38.088	300.481	268.004	74.695	−276.719	−168.930	3.837
2400	38.128	302.102	269.391	78.506	−278.817	−164.198	3.574
2500	38.168	303.660	270.731	82.321	−280.909	−159.379	3.330
2600	38.208	305.157	272.027	86.140	−282.993	−154.477	3.103
2700	38.247	306.600	273.281	89.963	−285.066	−149.495	2.892
2800	38.286	307.992	274.496	93.789	−287.128	−144.436	2.694
2900	38.325	309.336	275.674	97.620	−289.176	−139.303	2.509
3000	38.364	310.636	276.818	101.454	−291.209	−134.101	2.335
3100	38.404	311.895	277.929	105.293	−293.227	−128.831	2.171
3200	38.444	313.114	279.010	109.135	−295.228	−123.495	2.016
3300	38.484	314.298	280.061	112.981	−297.211	−118.098	1.869
3400	38.526	315.448	281.085	116.832	−299.175	−112.641	1.731
3500	38.568	316.565	282.083	120.687	−301.121	−107.126	1.599
3600	38.611	317.652	283.056	124.545	−303.046	−101.556	1.474
3700	38.656	318.710	284.005	128.409	−304.952	−95.933	1.354
3800	38.702	319.742	284.932	132.277	−306.838	−90.259	1.241
3900	38.750	320.748	285.838	136.149	−308.703	−84.535	1.132
4000	38.799	321.730	286.723	140.027	−310.547	−78.763	1.029
4100	38.849	322.688	287.588	143.909	−312.371	−72.946	0.929
4200	38.902	323.625	288.435	147.797	−314.174	−67.084	0.834
4300	38.956	324.541	289.264	151.689	−315.956	−61.180	0.743
4400	39.012	325.437	290.076	155.588	−317.718	−55.235	0.656
4500	39.070	326.315	290.872	159.492	−319.459	−49.250	0.572
4600	39.130	327.174	291.652	163.402	−321.180	−43.226	0.491
4700	39.191	328.016	292.417	167.318	−322.880	−37.165	0.413
4800	39.255	328.842	293.167	171.240	−324.560	−31.068	0.338
4900	39.320	329.652	293.903	175.169	−326.220	−24.937	0.266
5000	39.388	330.447	294.626	179.104	−327.861	−18.771	0.196
5100	39.457	331.228	295.336	183.047	−329.482	−12.574	0.129
5200	39.528	331.995	296.034	186.996	−331.084	−6.344	0.064
5300	39.601	332.748	296.719	190.952	−332.666	−0.084	0.001
5400	39.675	333.489	297.394	194.916	−334.229	6.206	−0.060
5500	39.751	334.218	298.057	198.887	−335.774	12.524	−0.119
5600	39.828	334.935	298.709	202.866	−337.300	18.871	−0.176
5700	39.907	335.640	299.350	206.853	−338.808	25.245	−0.231
5800	39.988	336.335	299.982	210.848	−340.298	31.644	−0.285
5900	40.069	337.019	300.604	214.850	−341.770	38.070	−0.337
6000	40.152	337.694	301.217	218.862	−343.224	44.520	−0.388

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Thiophosphoryl Fluoride (PSF) IDEAL GAS M_r = 82.032163

$S°(298.15\ K) = [277.717 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-169.189 \pm 62.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-172.268 \pm 62.8]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[940](1)
[740](1)
[400](1)

Ground State Quantum Weight: 1 $\sigma = 1$

Point Group: C_s

Product of the Moments of Inertia: $I_A I_B I_C = [7.999 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The $\Delta_f H°(298.15\ K)$ was estimated by Henderson and Scheffee.[1]

Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with the corresponding frequencies of PF(g), PS(g), and PF_2(g). The vibrational levels of PF_2(g) in turn were estimated by Gordon.[2] The entropy was estimated by Henderson and Scheffee.[1] The product of the moment of inertia was derived from the estimated entropy.

References

[1]C. B. Henderson and R. S. Scheffee, "Survey of Thermochemical Data," Atlantic Research Corp., Alexandria, Virginia, (January 1960).
[2]J. S. Gordon, "Thermodynamic Data for Combustion Products," Thiokol Corp., Reaction Motors Division, Denville, New Jersey, (January 1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.106	−169.189	−169.189	INFINITE
100	34.160	235.944	313.591	−7.765	−168.879	−180.934	94.510
200	39.208	261.056	281.619	−4.113	−170.596	−192.590	50.299
250	41.993	270.107	278.435	−2.082	−171.428	−197.993	41.368
298.15	44.439	277.717	277.717	0.	−172.268	−203.034	35.571
300	44.526	277.992	277.718	0.082	−172.301	−203.224	35.385
350	46.695	285.023	278.268	2.364	−173.915	−208.237	31.078
400	48.493	291.380	279.516	4.746	−177.096	−212.986	27.813
450	49.962	297.179	281.161	7.208	−178.709	−217.384	25.233
500	51.159	302.508	283.033	9.737	−180.348	−221.590	23.149
600	52.936	312.003	287.090	14.948	−183.091	−229.573	19.986
700	54.148	320.259	291.251	20.306	−185.489	−237.127	17.695
800	54.999	327.549	295.342	25.765	−187.677	−244.352	15.955
900	55.615	334.064	299.289	31.298	−242.862	−250.231	14.523
1000	56.073	339.949	303.065	36.883	−243.610	−251.010	13.111
1100	56.421	345.310	306.666	42.509	−244.348	−251.714	11.953
1200	56.692	350.231	310.094	48.165	−308.657	−251.273	10.938
1300	56.906	354.778	313.358	53.845	−308.621	−246.492	9.904
1400	57.078	359.002	316.470	59.545	−308.598	−241.714	9.018
1500	57.218	362.944	319.438	65.260	−308.588	−236.937	8.251
1600	57.334	366.641	322.274	70.988	−308.593	−232.160	7.579
1700	57.430	370.120	324.987	76.726	−308.614	−227.383	6.987
1800	57.512	373.405	327.586	82.473	−308.649	−222.604	6.460
1900	57.581	376.516	330.081	88.228	−308.699	−217.822	5.988
2000	57.640	379.471	332.477	93.989	−308.761	−213.037	5.564
2100	57.692	382.285	334.782	99.756	−308.834	−208.250	5.180
2200	57.736	384.970	337.003	105.527	−308.915	−203.458	4.831
2300	57.775	387.537	339.145	111.303	−309.003	−198.662	4.512
2400	57.810	389.997	341.213	117.082	−309.095	−193.863	4.219
2500	57.840	392.357	343.211	122.864	−309.189	−189.060	3.950
2600	57.867	394.626	345.146	128.650	−309.284	−184.253	3.702
2700	57.891	396.811	347.019	134.438	−309.375	−179.442	3.472
2800	57.912	398.916	348.835	140.228	−309.462	−174.628	3.258
2900	57.932	400.949	350.597	146.020	−309.544	−169.811	3.059
3000	57.949	402.913	352.309	151.814	−309.618	−164.992	2.873
3100	57.965	404.814	353.972	157.610	−309.683	−160.170	2.699
3200	57.980	406.654	355.589	163.407	−309.738	−155.346	2.536
3300	57.993	408.439	357.164	169.206	−309.782	−150.520	2.383
3400	58.005	410.170	358.698	175.006	−309.815	−145.694	2.238
3500	58.016	411.852	360.193	180.807	−309.835	−140.866	2.102
3600	58.026	413.486	361.650	186.609	−309.844	−136.038	1.974
3700	58.035	415.076	363.073	192.412	−309.840	−131.210	1.852
3800	58.044	416.624	364.462	198.216	−309.824	−126.383	1.737
3900	58.052	418.132	365.819	204.021	−309.795	−121.556	1.628
4000	58.059	419.601	367.145	209.826	−309.755	−116.730	1.524
4100	58.066	421.035	368.442	215.632	−309.702	−111.905	1.426
4200	58.072	422.435	369.711	221.439	−309.638	−107.081	1.332
4300	58.078	423.801	370.953	227.247	−309.564	−102.259	1.242
4400	58.083	425.136	372.169	233.055	−309.479	−97.439	1.157
4500	58.089	426.442	373.361	238.863	−309.384	−92.621	1.075
4600	58.093	427.718	374.529	244.672	−309.279	−87.805	0.997
4700	58.098	428.968	375.674	250.482	−309.166	−82.992	0.922
4800	58.102	430.191	376.797	256.292	−309.045	−78.181	0.851
4900	58.106	431.389	377.899	262.102	−308.916	−73.372	0.782
5000	58.110	432.563	378.980	267.913	−308.781	−68.567	0.716
5100	58.113	433.714	380.042	273.724	−308.638	−63.764	0.653
5200	58.117	434.842	381.085	279.536	−308.490	−58.964	0.592
5300	58.120	435.949	382.110	285.348	−308.337	−54.167	0.534
5400	58.123	437.036	383.117	291.160	−308.179	−49.372	0.478
5500	58.126	438.102	384.107	296.972	−308.017	−44.581	0.423
5600	58.128	439.150	385.081	302.785	−307.851	−39.793	0.371
5700	58.131	440.179	386.039	308.598	−307.681	−35.008	0.321
5800	58.133	441.190	386.981	314.411	−307.508	−30.226	0.272
5900	58.135	442.183	387.908	320.225	−307.333	−25.446	0.225
6000	58.138	443.160	388.821	326.038	−307.156	−20.670	0.180

PREVIOUS: September 1962 (1 atm) CURRENT: September 1962 (1 bar)

$S°(298.15\ K) = 249.957 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -78.243 \pm 10.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -80.266 \pm 10.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	8264.7	2
$A[^2\Sigma]$	22566.6	[2]
$B^2\Sigma^+$	35643	2

$\omega_e = 507.2\ cm^{-1}$ $\omega_e x_e = 2.30\ cm^{-1}$ $\sigma = 1$
$B_e = 0.2288\ cm^{-1}$ $\alpha_e = [0.0013]\ cm^{-1}$ $r_e = 2.058$ Å

Enthalpy of Formation

Rosen[1] lists $D° = 84.0 \pm 2$ kcal·mol^{-1} derived from the mass spectrometric work of Zmbov *et al.*[2] The partial pressures and log K for the $PbF_2(g) + Pb(g) = 2PbF(g)$ reaction in the latter reference are inconsistent. 3rd law calculations show that the log K value corresponds to the heat of reaction given. The dissociation energy calculated by the linear Birge–Sponer extrapolation of the adopted ground state vibrational constants, as derived from emission and absorption spectra (ν, 0–13),[3, 4] is 3.44 eV. Correcting this value for the ionic character of PbF as suggested by Hildenbrand[5] gives $D_0° = 3.64$ eV (83.9 kcal·mol^{-1}). The upper limit of the value recommended by Gaydon[6] (3 ± 0.5 eV) falls at 80.7 kcal·mol^{-1}. An intercomparison of the dissociation energies of the lead,[7] mercury,[1] and potassium[7] monohalides indicates that $D_0° = 84.0 \pm 2$ kcal·mol^{-1} is reasonable. Combining this with $\Delta_f H°$(Pb, g, 0 K) = 46.91 ± 0.13 kcal·mol^{-1},[7] and $\Delta_f H°$(F, g, 0 K) = 18.36 ± 0.40 kcal·mol^{-1},[7] gives $\Delta_f H°$(PbF, g, 0 K) = −18.73 ± 2.5 kcal·mol^{-1}. We adopt $\Delta_f H°$(PbF, g, 0 K) = −18.70 ± 2.5 kcal·mol^{-1} which is consistent with the above. $\Delta_f H°$(PbF, g, 298.15 K) = −19.18 ± 2.5 kcal·mol^{-1} is calculated from $\Delta_f H°$(0 K).

Heat Capacity and Entropy

The vibrational constants, the electronic states and levels, and the rotational constant are those recommended in Rosen[1] with the following modifications. The first excited state, unassigned in Rosen,[1] is tentatively classed as a $^2\Sigma$ state in accordance with the preference for $^2\Sigma$ over $^2\Delta$ expressed by Barrow *et al.*[8] If the state is $^2\Delta$ rather than $^2\Sigma$, the entropy is increased by 0.005 cal K^{-1}·mol^{-1} at 4000 K and 0.05 cal K^{-1}·mol^{-1} at 6000 K. The *C* and higher electronic states[1] have been omitted; inclusion increases the entropy only by approximately 0.005 cal K^{-1}·mol^{-1} at 6000 K. The adopted $B_e = 0.2288\ cm^{-1}$ is obtained by an approximate correction to $B_0 = 0.2281\ cm^{-1}$ given in Rosen,[1] and $r_e = 2.058$ Å calculated from B_e compares with $r_0 = 2.061$ Å given in Rosen.[1] The value for α_e is calculated assuming a Morse potential function.

References

[1] B. Rosen, Ed., "Spectroscopic Data Relative to Diatomic Molecules," Pergamon Press, New York, (1970).
[2] K. Zmbov, J. W. Hastie, and J. L. Margrave, Trans. Faraday Soc. **64,** 861 (1968).
[3] G. D. Rochester, Proc. Roy. Soc. (London) A **153,** 407 (1936).
[4] G. D. Rochester, proc. Roy. Soc. (London) A **167,** 569 (1938).
[5] D. L. Hildenbrand in "Advances in High Temperature Chemistry," Vol. 1, L. Eyring, editor, Academic Press, New York, pp. 193–215, (1967).
[6] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed., Chapman and Hall, London, (1968).
[7] JANAF Thermochemical Tables: Pb(g), 3–31–62; F(g), 9–30–65; PbCl(g), 6–30–73; PbBr(g), 12–31–73; PbI(g), 12–31–73; KF(g), 6–30–69; KCl(g), 3–31–66; KBr(g), 3–31–67; KI(g), 6–30–67.
[8] R. F. Barrow, D. Butler, J. W. C. Johns, and J. L. Powell, Proc. Phys. Soc. (London) **73,** 317 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.268	−78.243	−78.243	INFINITE
100	29.426	215.448	278.991	−6.354	−78.549	−87.893	45.910
200	32.232	236.643	253.043	−3.280	−79.464	−96.873	25.301
250	33.491	243.976	250.519	−1.636	−79.876	−101.177	21.140
298.15	34.399	249.957	249.957	0.	−80.266	−105.244	18.438
300	34.429	250.170	249.958	0.064	−80.281	−105.399	18.352
350	35.115	255.531	250.380	1.803	−80.689	−109.553	16.350
400	35.622	260.255	251.325	3.572	−81.111	−113.648	14.841
450	36.004	264.474	252.555	5.363	−81.550	−117.689	13.661
500	36.298	268.283	253.941	7.171	−82.009	−121.680	12.712
600	36.717	274.941	256.902	10.823	−82.982	−129.524	11.276
700	36.998	280.623	259.895	14.510	−88.893	−136.401	10.178
800	37.201	285.578	262.802	18.220	−90.005	−143.112	9.344
900	37.357	289.969	265.581	21.949	−91.089	−149.685	8.687
1000	37.486	293.911	268.220	25.691	−92.146	−156.138	8.156
1100	37.601	297.490	270.721	29.445	−93.176	−162.488	7.716
1200	37.711	300.766	273.090	33.211	−94.178	−168.744	7.345
1300	37.823	303.789	275.337	36.988	−95.156	−174.918	7.028
1400	37.943	306.596	277.471	40.776	−96.126	−181.017	6.754
1500	38.075	309.219	279.501	44.577	−97.095	−187.047	6.514
1600	38.219	311.680	281.436	48.391	−98.067	−193.012	6.301
1700	38.378	314.002	283.284	52.221	−99.045	−198.917	6.112
1800	38.551	316.201	285.052	56.067	−100.030	−204.763	5.942
1900	38.737	318.290	286.747	59.932	−101.022	−210.555	5.789
2000	38.933	320.282	288.374	63.815	−102.019	−216.294	5.649
2100	39.138	322.186	289.939	67.719	−280.241	−214.868	5.345
2200	39.350	324.012	291.447	71.643	−280.854	−211.741	5.027
2300	39.567	325.766	292.901	75.589	−281.533	−208.584	4.737
2400	39.785	327.454	294.306	79.557	−282.279	−205.397	4.470
2500	40.004	329.083	295.664	83.546	−283.090	−202.177	4.224
2600	40.222	330.656	296.980	87.557	−283.963	−198.923	3.996
2700	40.436	332.178	298.256	91.590	−284.895	−195.635	3.785
2800	40.646	333.652	299.494	95.644	−285.880	−192.311	3.588
2900	40.850	335.082	300.696	99.719	−286.915	−188.951	3.403
3000	41.049	336.471	301.866	103.814	−287.991	−185.555	3.231
3100	41.240	337.820	303.004	107.929	−289.103	−182.122	3.069
3200	41.425	339.132	304.113	112.062	−290.244	−178.653	2.916
3300	41.602	340.409	305.193	116.213	−291.406	−175.148	2.772
3400	41.771	341.654	306.247	120.382	−292.584	−171.607	2.636
3500	41.933	342.867	307.276	124.567	−293.770	−168.032	2.508
3600	42.087	344.051	308.282	128.768	−294.958	−164.422	2.386
3700	42.234	345.206	309.264	132.985	−296.142	−160.780	2.270
3800	42.374	346.334	310.225	137.215	−297.316	−157.106	2.160
3900	42.508	347.436	311.165	141.459	−298.476	−153.401	2.055
4000	42.635	348.514	312.085	145.716	−299.616	−149.667	1.954
4100	42.756	349.568	312.986	149.986	−300.733	−145.904	1.859
4200	42.872	350.600	313.870	154.268	−301.823	−142.114	1.767
4300	42.983	351.610	314.736	158.560	−302.882	−138.299	1.680
4400	43.088	352.600	315.585	162.864	−303.909	−134.460	1.596
4500	43.189	353.569	316.418	167.178	−304.900	−130.597	1.516
4600	43.286	354.519	317.236	171.502	−305.855	−126.714	1.439
4700	43.379	355.451	318.040	175.835	−306.771	−122.809	1.365
4800	43.469	356.366	318.829	180.177	−307.648	−118.886	1.294
4900	43.555	357.263	319.604	184.529	−308.485	−114.944	1.225
5000	43.639	358.144	320.366	188.888	−309.281	−110.987	1.159
5100	43.720	359.009	321.115	193.256	−310.038	−107.013	1.096
5200	43.798	359.858	321.852	197.632	−310.753	−103.025	1.035
5300	43.874	360.693	322.577	202.016	−311.429	−99.024	0.976
5400	43.949	361.514	323.291	206.407	−312.066	−95.010	0.919
5500	44.021	362.321	323.993	210.805	−312.663	−90.985	0.864
5600	44.092	363.115	324.684	215.211	−313.223	−86.949	0.811
5700	44.162	363.896	325.365	219.624	−313.746	−82.904	0.760
5800	44.230	364.665	326.036	224.043	−314.234	−78.850	0.710
5900	44.297	365.421	326.698	228.470	−314.686	−74.788	0.662
6000	44.363	366.166	327.349	232.903	−315.105	−70.718	0.616

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [225.275 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 12.316 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 12.970 \pm 6.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^1	g_i
$X^2\Pi_{3/2}$	0	2
$^2\Pi_{1/2}$	398	2
$A^2\Pi_{3/2}$	24991	2
$^2\Pi_{1/2}$	25601	2

$\omega_e = [830 \pm 20]\ cm^1$ $\omega_e x_e = [4.7 \pm 0.4]\ cm^{-1}$ $\sigma = 1$

$B = 0.55427 \pm 0.0005\ cm^{-1}$ $\alpha = [0.0042]\ cm^{-1}$ $r_e = 1.5967 \pm 0.001$

Enthalpy of Formation

Hildenbrand[1] has investigated the isomolecular reaction $CS_2(g) + 2SF(g) = CF_2(g) + 2S_2(g)$ by mass spectrometry. The various molecular species were found to be formed as products of the reaction of gaseous SF_6 with graphite at temperatures in the range 1436–1611 K. This study employed three different effusion cell configurations which were used to optimize the reaction conditions, and ion abundances for each species were measured at 2 eV above their appearance potentials in order to eliminate fragmentation effects. We analyze the reported equilibrium data by the 2nd and 3rd law methods with the results being presented below.

Series	Cell Configuration	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	Mo cell/C liner/packed	2	1529–1611	−11.6	−16.2	2.9	3.2
	with C cloth				±0.3		±1.2
3	C cell/wound Pt wire	4	1436–1564	6.8	−16.0	−15.1	3.1
					±1.8	±5.0	±2.0
3	C cell/Pt partition/packed	7	1478 1588	−37.2	−15.8	13.9	3.0
	with C cloth and Pt wire				±1.4	±5.0	±1.8

The three cell configurations used by Hildenbrand[1] yield almost identical 3rd law $\Delta_f H°$ values. We adopt the mean value of 3.1±1.5 kcal·mol^{-1}. This value corresponds to a $D_0°$ of 81.2±2.0 kcal·mol^{-1} which is close to the average bond energies (80.0 kcal·mol^{-1}) for SF_4 and SF_3[2]. Other reported $D_0°$ values include 96.9 kcal·mol^{-1} [3] and <76.1 kcal·mol^{-1}.[4] The former value is based on Hartree Foch binding energies[3] which were combined with an estimate of the extra molecular correlation energy. This estimate now appears to be about 20% too high. The upper limit value for $D_0°$ was obtained from predissociation observed in the $A^2\Pi$ state by Di Lonardo and Trombetti.[4]

Heat Capacity and Entropy

The electronic states and levels (T_e) are taken from the recent compilation of Barrow.[5] His results were derived from the spectral measurements of Di Lonardo and Trombetti.[4] Further confirmation that the ground state is inverted $^2\Pi$ is provided by the results of an analysis of the gas phase electron resonance spectra by Carrington *et al*.[6] The rotational constant (B_e) is calculated from the microwave data (B_{eff}) of Amano and Hirota.[7] Other values for B_e determined from EPR[6] measurements and from a rotational analysis[4] of the $A^2\Pi$ $X^2\Pi$ band system agree with the microwave results but are less precise. The value of r_e is calculated from B_e.

The ground state vibrational constants have not been determined experimentally. O'Hare[8] computed Hartree Fock total energies for the ground states of NF, SiF, PF, and SF and derived spectroscopic constants for each monofluoride by a Dunham analysis. He adjusted the computed values for SF for differences found between calculated and experimental data for the other three monofluorides. We adopt his predicted vibrational constants along with his computed value for α_e. We do not include the rotational and vibrational constants[4, 5] for the $A^2\Pi$ state since they have a negligible effect.

Thermal functions have been previously reported for SF by Wilkins[9] and O'Hare.[10] These two sets of functions agree reasonably well, and presumably they are both based on a ground state quantum weight of 2. Our entropies are consistently higher than the literature data[9, 10] at all temperatures by roughly 1.0 1.5 cal K^{-1}·mol^{-1}. This increase can be attributed primarily to the entropy contribution from the $X\ ^2\Pi_{1/2}$ state which lies at 398 cm^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.478	12.316	12.316	INFINITE
100	29.999	189.668	255.214	−6.555	13.097	3.901	−2.038
200	33.400	211.569	228.443	−3.375	13.170	−5.351	1.398
250	34.454	219.143	225.850	−1.677	13.098	−9.974	2.084
298.15	35.152	225.275	225.275	0.	12.970	−14.407	2.524
300	35.174	225.493	225.276	0.065	12.964	−14.577	2.538
350	35.683	230.955	225.706	1.837	12.776	−19.153	2.858
400	36.055	235.745	226.668	3.631	10.324	−23.611	3.083
450	36.337	240.009	227.917	5.441	9.375	−27.805	3.227
500	36.556	243.849	229.322	7.264	8.346	−31.878	3.330
600	36.872	250.544	232.317	10.936	6.697	−39.763	3.462
700	37.088	256.245	235.338	14.635	5.273	−47.391	3.536
800	37.246	261.209	238.269	18.352	3.974	−54.825	3.580
900	37.368	265.603	241.066	22.083	−50.379	−61.019	3.541
1000	37.466	269.545	243.720	25.825	−50.338	−62.204	3.249
1100	37.549	273.120	246.233	29.576	−50.319	−63.392	3.010
1200	37.620	276.390	248.612	33.334	−50.320	−64.580	2.811
1300	37.684	279.404	250.866	37.099	−50.342	−65.768	2.643
1400	37.741	282.199	253.006	40.871	−50.384	−66.953	2.498
1500	37.795	284.805	255.040	44.648	−50.446	−68.135	2.373
1600	37.844	287.245	256.977	48.430	−50.527	−69.311	2.263
1700	37.892	289.541	258.826	52.216	−50.625	−70.482	2.166
1800	37.937	291.708	260.593	56.008	−50.740	−71.647	2.079
1900	37.980	293.761	262.285	59.804	−50.870	−72.805	2.002
2000	38.023	295.710	263.908	63.604	−51.011	−73.956	1.932
2100	38.064	297.566	265.467	67.408	−51.163	−75.100	1.868
2200	38.104	299.338	266.966	71.217	−51.322	−76.236	1.810
2300	38.143	301.032	268.411	75.029	−51.486	−77.365	1.757
2400	38.182	302.657	269.804	78.845	−51.652	−78.486	1.708
2500	38.221	304.216	271.150	82.665	−51.818	−79.601	1.663
2600	38.259	305.716	272.451	86.489	−51.981	−80.709	1.621
2700	38.298	307.160	273.710	90.317	−52.138	−81.811	1.583
2800	38.336	308.554	274.929	94.149	−52.288	−82.907	1.547
2900	38.374	309.900	276.112	97.984	−52.429	−83.998	1.513
3000	38.413	311.201	277.260	101.824	−52.559	−85.085	1.481
3100	38.452	312.462	278.375	105.667	−52.676	−86.167	1.452
3200	38.491	313.683	279.460	109.514	−52.780	−87.246	1.424
3300	38.531	314.868	280.515	113.365	−52.868	−88.321	1.398
3400	38.573	316.019	281.542	117.220	−52.941	−89.394	1.373
3500	38.615	317.138	282.543	121.080	−52.998	−90.466	1.350
3600	38.658	318.226	283.520	124.943	−53.039	−91.535	1.328
3700	38.702	319.286	284.472	128.811	−53.061	−92.604	1.307
3800	38.748	320.319	285.402	132.684	−53.067	−93.673	1.288
3900	38.795	321.326	286.310	136.561	−53.055	−94.742	1.269
4000	38.843	322.308	287.198	140.443	−53.026	−95.811	1.251
4100	38.893	323.268	288.066	144.330	−52.980	−96.881	1.234
4200	38.945	324.206	288.915	148.222	−52.917	−97.953	1.218
4300	38.999	325.123	289.747	152.119	−52.836	−99.026	1.203
4400	39.055	326.020	290.561	156.021	−52.740	−100.101	1.188
4500	39.112	326.899	291.359	159.930	−52.627	−101.179	1.174
4600	39.171	327.759	292.141	163.844	−52.498	−102.259	1.161
4700	39.232	328.602	292.907	167.764	−52.354	−103.342	1.149
4800	39.295	329.429	293.660	171.690	−52.194	−104.429	1.136
4900	39.360	330.239	294.398	175.623	−52.020	−105.519	1.125
5000	39.427	331.035	295.123	179.562	−51.832	−106.613	1.114
5100	39.495	331.817	295.835	183.508	−51.629	−107.710	1.103
5200	39.565	332.584	296.534	187.461	−51.413	−108.812	1.093
5300	39.638	333.339	297.221	191.422	−51.184	−109.918	1.083
5400	39.711	334.080	297.897	195.389	−50.941	−111.028	1.074
5500	39.787	334.810	298.562	199.364	−50.686	−112.143	1.065
5600	39.863	335.527	299.215	203.346	−50.419	−113.263	1.056
5700	39.942	336.233	299.859	207.337	−50.140	−114.388	1.048
5800	40.022	336.929	300.492	211.335	−49.848	−115.518	1.040
5900	40.103	337.614	301.115	215.341	−49.546	−116.652	1.033
6000	40.185	338.288	301.729	219.355	−49.232	−117.793	1.025

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K)$ = [225.405 ± 9.2] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 985.664 ± 16.7 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [991.901] mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[X^3\Sigma]$	0	[3]
$[a\ ^1\Delta]$	[8000]	[2]
$[b\ ^1\Sigma]$	[14500]	[1]
$[B\ ^3\Pi]$	[30000]	[6]

ω_e = [838] cm^{-1} $\omega_e x_e$ = [4.6] cm^{-1} σ = 1
B_e = [0.55686] cm^{-1} α_e = [0.0044] cm^{-1} r_e = [1.593] Å

Enthalpy of Formation

The electron impact appearance potential of SF^+ from SF has been measured by Hildenbrand[1] as 10.09 ± 0.1 eV. Normally, this measured AP would be identical to the vertical ionization potential of SF; however, formation of SF^+ involves the loss of an antibonding electron which appears to be situated primarily on the sulfur atom (IP(S) = 10.36 eV,)[2]. Thus, the geometrical changes produced upon ionization should be minimal, and therefore, the measured AP is probably very close to the true (adiabatic) ionization potential, as suggested by Hildenbrand.[1] We employ the experimental IP value as the heat of reaction, $\Delta_r H°$ = 232.68 ± 2.3 $kcal·mol^{-1}$, for the process $SF(g) + e = SF^+(g) + 2e^-$ at 0 K, and we calculate $\Delta_f H°(SF^+, g, 0\ K)$ = 235.6 ± 4.0 $kcal·mol^{-1}$ by combining the value of $\Delta_r H°(0\ K)$ with $\Delta_f H°(SF, g, 0\ K)$ = 2.9 ± 1.5 $kcal·mol^{-1}$.[1,3] Independent values of IP include 10.0 eV[4] and 9.9 eV.[5] Both of these values were obtained from semiempirical molecular orbital calculations and are in excellent agreement with the results adopted here.

Earlier electron impact studies which can also be used to derive $\Delta_f H°$ of SF^+ have been previously analyzed by O'Hare and Wahl.[6] We do not reanalyze these results since their analysis[6] has shown that the data are seriously in error.

Heat Capacity and Entropy

As discussed in the enthalpy of formation section, one would expect that the bonding in SF^+ is probably not very different from that in SF, since the ionizing orbital is antibonding. Additional support for this is provided by the fact that the bond dissociation energies for SF^+ (87.4 $kcal·mol^{-1}$) and SF (81.2 $kcal·mol^{-1}$) are very similar. In addition, SF^+ is isoelectronic with PF, and one might therefore expect that the molecular characteristics of these two isoelectronic molecules would be quite similar. We estimate the vibrational and rotational constants to be intermediate between those for SF^3 and PF.[7] By analogy with other twelve valence electron molecules,[7] we predict that the ground state is $^3\Sigma$ and expect several excited states to exist below 35000 cm^{-1}. The two singlet levels are estimated from those observed for NF and O_2.[7] We also include a triplet level at 30000 cm^{-1} based on that observed for PF.[7] We assume that the vibrational and rotational constants for the excited states are identical with those for the ground state since a comparison of the constants[7] that are available for the various states of NF and PF shows that they are not significantly different. The uncertainty in our value of $S°(298.15\ K)$ is estimated as ±2.2 cal $K^{-1}·mol^{-1}$ and arises primarily from the effect of the ground state quantum weight. If the SF^+ ground state is singlet, then our entropy value at 298.15 K should be decreased by 2.18 cal $K^{-1}·mol^{-1}$. The electronic contribution to the entropy from the estimated excited states is negligible below 2000 K but increases to 0.4 cal $K^{-1}·mol^{-1}$ at 4500 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.864	985.664		
100	29.116	192.820	252.379	−5.956			
200	29.886	213.148	228.243	−3.019			
250	30.766	219.908	225.922	−1.503			
298.15	31.679	225.405	225.405	0.	991.901	958.230	−167.878
300	31.713	225.601	225.406	0.059	991.927	958.021	−166.806
350	32.590	230.557	225.795	1.667	992.614	952.315	−142.125
400	33.348	234.960	226.671	3.316	991.056	946.601	−123.613
450	33.985	238.926	227.816	4.999	991.020	941.037	−109.233
500	34.513	242.535	229.110	6.712	990.920	935.491	−97.730
600	35.313	248.902	231.892	10.206	991.171	924.388	−80.475
700	35.874	254.390	234.723	13.767	991.688	913.219	−68.145
800	36.280	259.208	237.489	17.376	992.359	901.965	−58.892
900	36.585	263.500	240.145	21.020	939.998	891.702	−51.753
1000	36.824	267.367	242.677	24.691	942.047	886.225	−46.292
1100	37.021	270.887	245.084	28.383	944.086	880.544	−41.814
1200	37.191	274.115	247.371	32.094	946.116	874.678	−38.074
1300	37.346	277.098	249.544	35.821	948.134	868.643	−34.903
1400	37.494	279.871	251.612	39.563	950.141	862.453	−32.179
1500	37.640	282.463	253.584	43.319	952.138	856.120	−29.813
1600	37.789	284.897	255.465	47.091	954.125	849.654	−27.738
1700	37.942	287.193	257.265	50.877	956.105	843.064	−25.904
1800	38.100	289.366	258.988	54.679	958.079	836.357	−24.270
1900	38.263	291.430	260.642	58.498	960.051	829.541	−22.806
2000	38.431	293.397	262.231	62.332	962.022	822.621	−21.485
2100	38.602	295.276	263.760	66.184	963.996	815.603	−20.287
2200	38.776	297.076	265.234	70.053	965.977	808.490	−19.196
2300	38.952	298.804	266.656	73.939	967.965	801.287	−18.198
2400	39.129	300.465	268.030	77.843	969.966	793.997	−17.281
2500	39.305	302.066	269.360	81.765	971.980	786.624	−16.436
2600	39.480	303.611	270.648	85.704	974.011	779.170	−15.654
2700	39.653	305.104	271.897	89.661	976.061	771.637	−14.928
2800	39.823	306.549	273.108	93.635	978.132	764.028	−14.253
2900	39.989	307.950	274.286	97.625	980.225	756.344	−13.623
3000	40.152	309.308	275.431	101.632	982.341	748.588	−13.034
3100	40.310	310.627	276.545	105.656	984.482	740.761	−12.482
3200	40.463	311.910	277.630	109.694	986.649	732.865	−11.963
3300	40.611	313.157	278.688	113.748	988.841	724.900	−11.474
3400	40.755	314.371	279.720	117.816	991.060	716.869	−11.013
3500	40.893	315.555	280.727	121.899	993.305	708.772	−10.578
3600	41.026	316.709	281.710	125.995	995.575	700.610	−10.166
3700	41.155	317.835	282.671	130.104	997.872	692.385	−9.775
3800	41.278	318.934	283.611	134.225	1000.195	684.098	−9.404
3900	41.397	320.008	284.531	138.359	1002.542	675.749	−9.051
4000	41.512	321.057	285.431	142.505	1004.913	667.340	−8.715
4100	41.623	322.083	286.312	146.662	1007.308	658.871	−8.394
4200	41.729	323.088	287.176	150.829	1009.725	650.343	−8.088
4300	41.832	324.071	288.023	155.007	1012.165	641.757	−7.796
4400	41.932	325.034	288.853	159.196	1014.626	633.115	−7.516
4500	42.029	325.977	289.667	163.394	1017.107	624.416	−7.248
4600	42.122	326.902	290.467	167.601	1019.608	615.662	−6.991
4700	42.213	327.809	291.252	171.818	1022.128	606.854	−6.744
4800	42.302	328.699	292.023	176.044	1024.665	597.991	−6.507
4900	42.388	329.572	292.780	180.278	1027.220	589.076	−6.280
5000	42.473	330.429	293.525	184.521	1029.791	580.108	−6.060
5100	42.556	331.271	294.256	188.773	1032.377	571.089	−5.849
5200	42.638	332.098	294.976	193.033	1034.979	562.019	−5.646
5300	42.718	332.911	295.684	197.300	1037.594	552.898	−5.449
5400	42.797	333.710	296.381	201.576	1040.223	543.728	−5.260
5500	42.875	334.496	297.067	205.860	1042.866	534.510	−5.076
5600	42.952	335.269	297.742	210.151	1045.521	525.243	−4.899
5700	43.029	336.030	298.407	214.450	1048.187	515.928	−4.728
5800	43.105	336.779	299.063	218.757	1050.866	506.567	−4.562
5900	43.180	337.517	299.708	223.071	1053.555	497.160	−4.402
6000	43.255	338.243	300.344	227.393	1056.255	487.707	−4.246

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

Sulfur Fluoride, Ion (SF^-) — IDEAL GAS — M_r = 51.058952 — $F_1S_1^-$(g)

$S°(298.15\ K) = [218.956 \pm 0.8]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-180.649 \pm 54.4]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-186.590]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[X^1\Sigma^+]$	[0]	[1]
$[A^3\Pi]$	[20000]	[6]

$\omega_e = [627]\ cm^{-1}$ $\quad \omega_e x_e = [5.06]\ cm^{-1}$ $\quad \sigma = 1$

$B_e = [0.45620]\ cm^{-1}$ $\quad \alpha = [0.0046]\ cm^{-1}$ $\quad r_e = [1.76]$ Å

Enthalpy of Formation

The adopted value of $\Delta_f H°(0\ K) = 43.2 \pm 13.0\ kcal·mol^{-1}$ is calculated as the difference between the $\Delta_f H°(SF, g, 0\ K) = 2.94 \pm 1.5\ kcal·mol^{-1}$ [1] and an estimated EA (SF) = 2.0 ± 0.5 eV (46.121 $kcal·mol^{-1}$). We estimate EA based on a consideration of trends in the electron affinities for other S–F Species.[1] These data follow a regular pattern among the even– and odd– electron molecules, with the odd electron molecules having, as expected, the higher EA's. Within each even– and odd–electron series, the EA values become progressively larger as the number of fluorine atoms in the ion is increased. Our $\Delta_f H°(0\ K)$ value corresponds to a fluoride ion affinity IA (S) and bond dissociation energy ($SF^- = S + F^-$) of 48.9 ± 13.5 $kcal·mol^{-1}$. Correcting $\Delta_f H°(0\ K)$ to a temperature of 298.15 K, we obtain the value of −44.6 $kcal·mol^{-1}$.

Several pieces of information are available which tend to provide support for our estimated EA value. Formation of SF^- involves the addition of an electron to an antibonding orbital of SF^2 which is located primarily on the sulfur atom. It is reasonable, therefore, to assume that EA(SF)≃EA(S) = 2.0772 ± 0.005 eV.[3] O'Hare[2] has pointed out that Koopmans' theorem[4] gives reliable estimates of electron affinities and ionization potentials provided that the parent molecule or ion have a closed shell electronic configuration. Application of this theorem to SF^- which has the required closed–shell structure leads to EA = 1.7 eV.[2] Other estimates of EA based on MO calculations have included (all in eV) 2.8,[5] 2.5 ± 0.5,[6] and <3.2.[2]

JANAF data[1] suggest that SF^- should be reasonably stable at moderate temperatures, with dissociative ionization becoming thermodynamically favorable above 2000 K. These predictions are supported qualitatively by the observations of Harland and Thynne[7, 8] who have identified SF^- in the negative ion mass spectra of SF_4, SF_6, and SF_5Cl. The temperature of the ion source was reported as around 325 K.[8]

Heat Capacity and Entropy

The additional antibonding electron in SF^- should weaken the bonding in the ion relative to the parent molecule, as evidenced by a reduction (~32 $kcal·mol^{-1}$) in the S–F bond strength for SF when compared with that for SF.[1] In addition, MO calculations[9] on OF and OF^- show that the O–F bond length in OF increases by 0.159 Å upon forming the negative ion. We apply this difference to $r_e(SF)$ = 1.5967 Å,[1] and we obtain $r_e(SF^-)$ = 1.76 Å. The value of B_e is calculated from our estimate of r_e. We use Badger's rule[10] to estimate a value for ω_e. We write the equation in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e\ d_{ij})$,[3] and we set d_{ij} equal to 0.8833 based on molecular data for ClF.[11] Barrow and Caunt[12] have shown that the product $x_e\mu^{1/2}$ is reasonably constant for a series of similar molecules. Using $x_e\mu^{1/2} = 0.0279$ from ClF,[11] we calculate x_e= 0.008068 and $\omega_e x_e = 5.06\ cm^{-1}$ for SF^-. The value of α_e is obtained from the other constants, assuming a Morse potential function.[13]

The electronic states and levels are estimated by analogy with those for ClF.[11] The effect of the triplet level at 20000 cm^{-1} on our entropies is insignificant below 3000 K, but this level does contribute 0.15 cal $K^{-1}·mol^{-1}$ to S at 4500 K. We assign an uncertainty of ±0.2 cal $K^{-1}·mol^{-1}$ to the value of $S°(298.15\ K)$ based on conservative estimates of the uncertainties in the vibrational and rotational data.

References

[1] JANAF Thermochemical Tables: SF(g), 6–30–76; SF_2^-(g), SF_3^-(g), SF_4^-(g), and SF_5^-(g), 12–31–76; F^-(g), 12–31–71; S(g), 6–30–71; SF_6^-(g), 6–30–77.

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Sulfur Fluoride, Ion (SF^-) — $F_1S_1^-$(g)

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−9.082	−180.649		
100	29.204	185.367	247.084	−6.172			
200	31.130	206.084	221.942	−3.172			
250	32.368	213.166	219.500	−1.584			
298.15	33.380	218.956	218.956	0.	−186.590	−205.828	36.060
300	33.414	219.163	218.957	0.062	−186.637	−205.948	35.859
350	34.243	224.379	219.367	1.754	−187.945	−209.063	31.201
400	34.889	228.995	220.287	3.483	−191.501	−211.901	27.671
450	35.395	233.135	221.489	5.241	−193.542	−214.337	24.880
500	35.795	236.886	222.844	7.021	−195.653	−216.533	22.621
600	36.378	243.467	225.748	10.631	−199.443	−220.346	19.183
700	36.779	249.106	228.692	14.290	−202.985	−223.548	16.681
800	37.071	254.038	231.558	17.984	−206.386	−226.252	14.773
900	37.295	258.417	234.304	21.702	−262.830	−227.455	13.201
1000	37.476	262.356	236.915	25.441	−264.871	−223.415	11.670
1100	37.626	265.936	239.393	29.196	−266.925	−219.170	10.408
1200	37.756	269.215	241.744	32.966	−268.995	−214.737	9.347
1300	37.871	272.242	243.975	36.747	−271.079	−210.131	8.443
1400	37.974	275.052	246.095	40.539	−273.179	−205.364	7.662
1500	38.070	277.675	248.114	44.342	−275.294	−200.447	6.980
1600	38.159	280.135	250.040	48.153	−277.423	−195.388	6.379
1700	38.244	282.451	251.879	51.973	−279.567	−190.195	5.844
1800	38.326	284.640	253.638	55.802	−281.724	−184.875	5.365
1900	38.404	286.714	255.325	59.638	−283.891	−179.436	4.933
2000	38.482	288.686	256.944	63.483	−286.067	−173.882	4.541
2100	38.560	290.565	258.501	67.335	−288.250	−168.219	4.184
2200	38.638	292.361	259.999	71.195	−290.436	−162.452	3.857
2300	38.719	294.080	261.444	75.063	−292.623	−156.586	3.556
2400	38.803	295.730	262.839	78.939	−294.807	−150.624	3.278
2500	38.893	297.315	264.186	82.823	−296.987	−144.572	3.021
2600	38.988	298.843	265.490	86.717	−299.159	−138.432	2.781
2700	39.092	300.316	266.753	90.621	−301.319	−132.209	2.558
2800	39.206	301.740	267.977	94.536	−303.464	−125.907	2.349
2900	39.330	303.118	269.165	98.463	−305.592	−119.528	2.153
3000	39.467	304.453	270.319	102.403	−307.701	−113.076	1.969
3100	39.617	305.750	271.441	106.357	−309.786	−106.554	1.795
3200	39.782	307.010	272.533	110.327	−311.845	−99.965	1.632
3300	39.963	308.237	273.597	114.314	−313.877	−93.313	1.477
3400	40.160	309.433	274.633	118.320	−315.877	−86.599	1.330
3500	40.374	310.600	275.644	122.346	−317.846	−79.826	1.191
3600	40.605	311.741	276.631	126.395	−319.779	−72.998	1.059
3700	40.854	312.857	277.595	130.468	−321.676	−66.117	0.933
3800	41.120	313.950	278.537	134.566	−323.534	−59.185	0.814
3900	41.403	315.021	279.459	138.692	−325.352	−52.205	0.699
4000	41.703	316.073	280.361	142.847	−327.128	−45.178	0.590
4100	42.019	317.107	281.245	147.033	−328.862	−38.108	0.486
4200	42.351	318.123	282.111	151.252	−330.550	−30.996	0.385
4300	42.697	319.124	282.960	155.504	−332.194	−23.844	0.290
4400	43.057	320.110	283.793	159.792	−333.791	−16.655	0.198
4500	43.429	321.081	284.611	164.116	−335.340	−9.429	0.109
4600	43.813	322.040	285.415	168.478	−336.842	−2.171	0.025
4700	44.206	322.987	286.204	172.879	−338.296	5.121	−0.057
4800	44.608	323.921	286.980	177.319	−339.701	12.442	−0.135
4900	45.018	324.845	287.743	181.801	−341.057	19.793	−0.211
5000	45.433	325.759	288.494	186.323	−342.364	27.171	−0.284
5100	45.853	326.663	289.234	190.887	−343.622	34.574	−0.354
5200	46.275	327.557	289.962	195.494	−344.831	42.001	−0.422
5300	46.700	328.443	290.680	200.143	−345.991	49.452	−0.487
5400	47.125	329.320	291.388	204.834	−347.104	56.923	−0.551
5500	47.548	330.188	292.085	209.567	−348.169	64.415	−0.612
5600	47.970	331.049	292.773	214.343	−349.186	71.926	−0.671
5700	48.388	331.902	293.452	219.161	−350.158	79.454	−0.728
5800	48.801	332.747	294.123	224.021	−351.084	86.999	−0.784
5900	49.208	333.584	294.784	228.921	−351.966	94.560	−0.837
6000	49.608	334.415	295.438	233.862	−352.804	102.136	−0.889

PREVIOUS: December 1976 (1 atm) — CURRENT: December 1976 (1 bar)

Sulfur Fluoride, Ion (SF^-) — $F_1S_1^-$(g)

$S°(298.15\ K) = 225.786 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -21.912 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -20.083 \pm 12.6\ kJ \cdot mol^{-1}$

State	Electronic Levels and Molecular Constants (σ = 1) ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
$X^2\Pi_{1/2}$	0	2	1.6008	0.58138	0.00494	857.20	4.735
$^2\Pi_{3/2}$	161.93	2	1.6008	0.58138	0.00494	857.20	4.735
$A^2\Sigma^+$	22858.84	2	1.6049	0.57839	0.00941	718.5	10.167
$a^4\Sigma$	29805.06	4	1.604	0.5786	0.00502	863.16	5.730
$B^2\Sigma^+$	34561.5	2	1.5714	0.62707	0.00462	1011.2	4.825
$C^2\Delta$	39438.4	4	1.5714	0.60338	0.00539	829.41	7.01
$C'^2\Pi$	41964.9	4	—	0.6376	0.0039	1031.9	4.45
$D'^2\Pi$	46606.7	4	—	0.6329	0.0044	1032.9	5.28
$D^2\Sigma^+$	47418.6	2	1.54	0.625	0.005	1003.2	5.64

Enthalpy of Formation

Ehlert and Margrave[1] have studied mass spectrometrically the reaction $Si(g) + SiF_2(g) \rightarrow 2\ SiF(g)$ by monitoring the intensities of the Si^+, SiF_2^+ and SiF^+ ions in an equilibrium system containing CaF_2 and Si. The ionization cross sections are assumed to cancel so that equilibrium constants can be obtained directly from the ion intensities. Eleven data points were reported in the 1395 to 1543 K range. We have analyzed their data using present JANAF functions[2] and obtain $\Delta_r H°(298.15\ K) = 23.5 \pm 3$ kcal·mol^{-1} by the 3rd law technique with a drift of -0.8 ± 11 cal $K^{-1} \cdot mol^{-1}$; the 2nd law value is 23.9 ± 7 kcal·mol^{-1}. Farber[6] also has determined equilibrium constants mass-spectrometrically for the $Si(g) + SiF_2(g) = 2\ SiF(g)$ reaction; ten data points over a 1590 to 1782 K range were obtained. Our analysis yields a 3rd law $\Delta_r H°(298.15\ K) = 21.08 \pm 0.59$ kcal·mol^{-1} with a drift of -1.9 ± 1.5 cal $K^{-1} \cdot mol^{-1}$; the 2nd law value is 24.18 ± 2.5 kcal·mol^{-1}. The two groups of data are in good agreement. We adopt an average value and calculate $\Delta_f H°(SiF, g, 298.15\ K) = -4.8 \pm 3$ kcal·mol^{-1}.

$D_0° = 130 \pm 4$ kcal·mol^{-1} is calculated from the resulting $\Delta_f H°(0\ K)$ and auxiliary data.[2] Johns and Barrow[3] recommended 125 ± 10 kcal·mol^{-1} from Birge–Sponer extrapolations of several states. Gaydon[4] preferred 115 ± 12 kcal·mol^{-1} from a Birge–Sponer extrapolation of the ground state.

Heat Capacity and Entropy

The molecular constants and electronic levels are those given by Suchard.[5] Five higher levels are given but are not used since they do not significantly affect the calculations. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant (A=161.93 cm^{-1}). This approximation gives slightly biased results at lower temperatures. An error of ± 0.04 cal $K^{-1} \cdot mol^{-1}$ has been assigned to $S°(298.15\ K)$ to allow for this.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.460	−21.912	−21.912	INFINITE
100	32.762	190.572	254.370	−6.380	−20.552	−30.708	16.040
200	31.864	212.954	228.738	−3.157	−19.972	−41.165	10.751
250	32.126	220.085	226.320	−1.559	−19.976	−46.466	9.709
298.15	32.650	225.786	225.786	0.	−20.083	−51.559	9.033
300	32.672	225.988	225.786	0.060	−20.089	−51.755	9.011
350	33.289	231.070	226.186	1.709	−20.269	−57.019	8.510
400	33.874	235.554	227.083	3.389	−20.492	−62.254	8.130
450	34.392	239.575	228.251	5.096	−20.742	−67.459	7.830
500	34.836	243.222	229.569	6.827	−21.014	−72.636	7.588
600	35.530	249.638	232.393	10.347	−21.607	−82.905	7.218
700	36.029	255.155	235.260	13.926	−22.251	−93.071	6.945
800	36.396	259.991	238.055	17.548	−22.943	−103.142	6.734
900	36.674	264.295	240.736	21.203	−23.678	−113.123	6.565
1000	36.891	268.170	243.289	24.881	−24.455	−123.020	6.426
1100	37.065	271.695	245.714	28.579	−25.273	−132.837	6.308
1200	37.208	274.926	248.015	32.293	−26.131	−142.578	6.206
1300	37.329	277.909	250.201	36.020	−27.029	−152.246	6.117
1400	37.432	280.679	252.281	39.758	−27.968	−161.844	6.038
1500	37.523	283.265	254.261	43.506	−28.950	−171.372	5.968
1600	37.604	285.690	256.150	47.263	−29.974	−180.834	5.904
1700	37.678	287.972	257.956	51.027	−81.217	−189.783	5.831
1800	37.745	290.127	259.684	54.798	−82.096	−196.144	5.692
1900	37.807	292.170	261.340	58.576	−82.973	−202.456	5.566
2000	37.866	294.110	262.931	62.359	−83.850	−208.722	5.451
2100	37.921	295.959	264.460	66.149	−84.724	−214.944	5.346
2200	37.973	297.724	265.932	69.943	−85.593	−221.125	5.250
2300	38.024	299.414	267.351	73.743	−86.457	−227.266	5.161
2400	38.072	301.033	268.721	77.548	−87.314	−233.370	5.079
2500	38.120	302.588	270.045	81.358	−88.161	−239.438	5.003
2600	38.166	304.084	271.325	85.172	−88.997	−245.472	4.932
2700	38.211	305.525	272.566	88.991	−89.821	−251.475	4.865
2800	38.256	306.916	273.768	92.814	−90.631	−257.447	4.803
2900	38.301	308.259	274.934	96.642	−91.426	−263.391	4.744
3000	38.346	309.558	276.067	100.474	−92.204	−269.307	4.689
3100	38.391	310.816	277.167	104.311	−92.964	−275.198	4.637
3200	38.436	312.036	278.238	108.153	−93.705	−281.065	4.588
3300	38.483	313.219	279.280	111.998	−94.427	−286.909	4.541
3400	38.530	314.369	280.295	115.849	−95.128	−292.731	4.497
3500	38.579	315.486	281.285	119.705	−95.808	−298.533	4.455
3600	38.629	316.574	282.250	123.565	−480.618	−293.855	4.264
3700	38.681	317.633	283.192	127.430	−480.841	−288.664	4.075
3800	38.735	318.665	284.112	131.301	−481.042	−283.467	3.897
3900	38.791	319.672	285.011	135.177	−481.223	−278.265	3.727
4000	38.850	320.655	285.890	139.060	−481.382	−273.059	3.566
4100	38.911	321.615	286.750	142.947	−481.519	−267.849	3.412
4200	38.974	322.553	287.591	146.842	−481.633	−262.637	3.266
4300	39.041	323.471	288.415	150.742	−481.724	−257.421	3.127
4400	39.111	324.370	289.222	154.650	−481.792	−252.204	2.994
4500	39.184	325.249	290.013	158.565	−481.837	−246.986	2.867
4600	39.260	326.111	290.788	162.487	−481.858	−241.766	2.745
4700	39.340	326.957	291.549	166.417	−481.856	−236.547	2.629
4800	39.423	327.786	292.295	170.355	−481.830	−231.328	2.517
4900	39.510	328.599	293.028	174.302	−481.781	−226.110	2.410
5000	39.601	329.399	293.747	178.257	−481.708	−220.893	2.308
5100	39.696	330.184	294.454	182.222	−481.611	−215.677	2.209
5200	39.794	330.955	295.148	186.196	−481.491	−210.464	2.114
5300	39.897	331.714	295.831	190.181	−481.347	−205.253	2.023
5400	40.004	332.461	296.503	194.176	−481.180	−200.045	1.935
5500	40.114	333.196	297.163	198.182	−480.990	−194.841	1.850
5600	40.229	333.920	297.813	202.199	−480.777	−189.640	1.769
5700	40.348	334.633	298.453	206.228	−480.541	−184.443	1.690
5800	40.471	335.336	299.083	210.269	−480.282	−179.251	1.614
5900	40.597	336.029	299.703	214.322	−480.002	−174.063	1.541
6000	40.728	336.712	300.314	218.388	−479.698	−168.880	1.470

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 239.919 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -292.859 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -294.554 \pm 8.4\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights					
State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2	$D\ ^2\Sigma$	28296.6	2
$A^2\Pi$	15067.8	2	$E^2\Pi$	31528.7	2
	15348.5	2		31614.8	2
$B^2\Sigma$	17303.4	2	$F^2\Sigma$	32822.0	2
$C^2\Pi$	27383.7	4	$G^2\Pi$	34759.2	4

$\omega_e = 498.0\ cm^{-1}$ $\omega_e x_e = 2.15\ cm^{-1}$ $\sigma = 1$

$B_e = 0.2506\ cm^{-1}$ $\alpha_e = [0.00148]\ cm^{-1}$ $r_e = 2.0757 \pm 0.0005$ Å

Enthalpy of Formation

Equilibrium constants for four dissociation equilibria have been determined from observations made on the condensed phase systems SrF_2–B,[1] SrF_2–Al,[2] and SrF_2–BaF_2–Al[2] by the mass spectrometric Knudsen effusion method. Enthalpies of reaction have been calculated from these Kp data by both the 2nd and 3rd law methods. Results of our analysis are given below, using JANAF auxiliary data.[4] Also included below is a value for the enthalpy of dissociation of SrF which was determined from spectrophotometric studies[3] of reaction equilibria in H_2–O_2–N_2 flames.

Source	Reaction	T/K	Data Points	$\Delta_f H°$(298.15), kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Hildenbrand[1]	A	1476–1585	10	23.4	25.1±0.9	1.2±4.7	−70.1±2.7
Hildenbrand[1]	B	1436–1525	9	4.3	2.0±0.7	−1.5±4.0	−71.0±1.0
Ehlert *et al.*[2]	C	1174–1290	9[a]	8.1	10.6±0.3	2.0±1.0	−70.0±4.0
Ehlert *et al.*[2]	D	1125–1292	10	127.6	−116.5±1.5	9.1±2.7	−67.6±1.3
Ryabova and Gurvich[3]	E			132 ± 7			−73.9±8.0

Reactions: (A) $2Sr(g) + BF_3(g) = 2SrF(g) + BF(g)$ (D) $2SrF(g) = Sr(g) + SrF_2(cr)$

(B) $Sr(g) + SrF_2(g) = 2SrF(g)$ (E) $SrF(g) = Sr(g) + F(g)$

(C) $Sr(g) + BaF(g) = Ba(g) + SrF(g)$

[a]One point rejected due to failure of a statistical test.

It is believed that the Kp data for the three homogeneous reactions (A, B, and C) are more reliable than those for the heterogeneous reaction (D) due to the need for a machine calibration constant which appears in the equilibrium expression for the latter. Ehlert *et al.*[2] determined this constant from vaporization experiments performed with silver contained in their Knudsen cell. This belief is further substantiated by the appearance of the rather large positive drift in the third law analysis of their Kp data for reaction (D). Also, it is felt that the $\Delta_f H°$ value obtained from the flame spectrophotometric studies[3] is perhaps somewhat less reliable than the three values derived from the Kp data for the homogeneous reactions. Thus, a median value $\Delta_f H°$(SrF, g, 298.15 K) = −70.4±2.0 kcal·mol^{-1} of the latter results is adopted. The adopted value corresponds to a dissociation energy of $D_0°$ (Sr–F) = 127.7 kcal·mol^{-1} (5.54 cal K^{-1}·mol^{-1}).

Spectroscopic values for $D_0°$ based on a linear Birge–Sponer extrapolation of the ground state ($X^2\Sigma$) vibrational levels (v, 0–4) have been reported as 3.2[5] and 3.5 eV.[6] However, it is well established now that the linear extrapolation[5, 6] generally underestimates $D_0°$ if the binding of the molecule is partially ionic. Based on the ionic character correction suggested by Hildenbrand,[6] these values adjust to 4.9 and 5.4 eV. The latter value is now in reasonable agreement with the adopted thermochemical value. Other spectroscopic values[7] include 4.6 (from $X^2\Sigma$), 4.7 (from $A^2\Pi$), and 5.2 eV (from $C^2\Pi$). The products of dissociation from the two excited states of SrF were assumed to be $Sr(^3P) + F(^2P)$.

Heat Capacity and Entropy

The spectroscopic data with the exception of the value for α_e are those given by Rosen.[8] α_e is calculated from the other constants assuming a Morse potential function. The electronic states and levels are also taken from the compilation of Rosen.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.286	−292.859	−292.859	INFINITE
100	29.458	205.319	269.038	−6.372	−292.898	−302.106	157.804
200	32.336	226.565	243.014	−3.290	−293.768	−310.974	81.218
250	33.590	233.922	240.482	−1.640	−294.172	−315.234	65.865
298.15	34.487	239.919	239.919	0.	−294.554	−319.250	55.931
300	34.516	240.133	239.920	0.064	−294.568	−319.403	55.613
350	35.190	245.507	240.343	1.807	−294.972	−323.510	48.281
400	35.687	250.240	241.290	3.580	−295.391	−327.559	42.775
450	36.060	254.466	242.523	5.374	−295.832	−331.554	38.486
500	36.347	258.280	243.911	7.184	−296.297	−335.498	35.049
600	36.756	264.946	246.878	10.841	−297.307	−343.245	29.882
700	37.031	270.634	249.875	14.531	−298.426	−350.814	26.178
800	37.229	275.592	252.786	18.245	−299.657	−358.216	23.389
900	37.381	279.987	255.569	21.976	−301.628	−365.384	21.206
1000	37.503	283.932	258.212	25.720	−302.762	−372.407	19.453
1100	37.606	287.511	260.715	29.476	−311.803	−378.951	17.995
1200	37.694	290.787	263.086	33.241	−313.857	−384.965	16.757
1300	37.773	293.807	265.335	37.014	−315.914	−390.807	15.703
1400	37.845	296.609	267.470	40.795	−317.975	−396.491	14.793
1500	37.912	299.223	269.501	44.583	−320.038	−402.027	14.000
1600	37.977	301.671	271.436	48.377	−322.104	−407.426	13.301
1700	38.040	303.976	273.283	52.178	−461.087	−411.516	12.644
1800	38.103	306.152	275.049	55.985	−461.296	−408.594	11.857
1900	38.168	308.214	276.740	59.799	−461.509	−405.660	11.152
2000	38.236	310.173	278.364	63.619	−461.729	−402.715	10.518
2100	38.310	312.040	279.923	67.446	−461.957	−399.759	9.943
2200	38.390	313.824	281.424	71.281	−462.195	−396.791	9.421
2300	38.479	315.533	282.870	75.125	−462.447	−393.813	8.944
2400	38.577	317.172	284.265	78.977	−462.715	−390.823	8.506
2500	38.686	318.749	285.613	82.840	−463.004	−387.822	8.103
2600	38.808	320.269	286.917	86.715	−463.321	−384.808	7.731
2700	38.942	321.736	288.180	90.602	−463.670	−381.782	7.386
2800	39.091	323.155	289.404	94.504	−464.058	−378.742	7.066
2900	39.253	324.530	290.591	98.421	−464.493	−375.687	6.767
3000	39.431	325.863	291.745	102.355	−464.981	−372.617	6.488
3100	39.623	327.159	292.867	106.308	−465.532	−369.529	6.227
3200	39.829	328.421	293.958	110.280	−466.151	−366.423	5.981
3300	40.051	329.649	295.021	114.274	−466.846	−363.296	5.750
3400	40.286	330.849	296.057	118.291	−467.624	−360.147	5.533
3500	40.536	332.020	297.068	122.332	−468.492	−356.973	5.328
3600	40.798	333.166	298.055	126.398	−469.456	−353.773	5.133
3700	41.073	334.287	299.019	130.492	−470.520	−350.545	4.949
3800	41.360	335.386	299.962	134.613	−471.689	−347.288	4.774
3900	41.658	336.464	300.884	138.764	−472.965	−343.997	4.607
4000	41.966	337.523	301.787	142.945	−474.350	−340.673	4.449
4100	42.284	338.563	302.671	147.158	−475.845	−337.313	4.297
4200	42.611	339.586	303.538	151.402	−477.447	−333.915	4.153
4300	42.946	340.592	304.388	155.680	−479.159	−330.478	4.015
4400	43.288	341.584	305.222	159.992	−480.976	−326.999	3.882
4500	43.636	342.560	306.041	164.338	−482.896	−323.478	3.755
4600	43.990	343.523	306.845	168.719	−484.848	−319.919	3.633
4700	44.348	344.473	307.636	173.136	−486.939	−316.311	3.515
4800	44.711	345.411	308.413	177.589	−489.111	−312.658	3.402
4900	45.076	346.336	309.177	182.078	−491.359	−308.959	3.294
5000	45.444	347.251	309.930	186.604	−493.670	−305.213	3.189
5100	45.813	348.154	310.670	191.167	−496.023	−301.423	3.087
5200	46.183	349.047	311.400	195.767	−498.445	−297.583	2.989
5300	46.553	349.931	312.119	200.404	−500.911	−293.697	2.895
5400	46.923	350.804	312.827	205.078	−503.412	−289.764	2.803
5500	47.291	351.669	313.525	209.788	−505.940	−285.785	2.714
5600	47.658	352.524	314.214	214.536	−508.486	−281.759	2.628
5700	48.021	353.371	314.894	219.320	−511.043	−277.687	2.545
5800	48.382	354.209	315.564	224.140	−513.604	−273.571	2.464
5900	48.739	355.039	316.226	228.996	−515.951	−269.435	2.385
6000	49.092	355.861	316.880	233.888	−518.467	−265.235	2.309

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K)$ = [232.846 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 192.679 ± 41.8 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [197.066] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$a^3\Pi$	[1000]	6
$A'^1\Pi$	[12000]	2
$B'^1\Delta$	[15000]	2
$A^1\Sigma^+$	[18000]	1
$b^3\Sigma^-$	[20000]	3
$B^1\Sigma^+$	[35000]	1

ω_e = [561] cm^{-1} $\omega_e x_e$ = [2.42] cm^{-1} σ = 1
B_e = [0.27265] cm^{-1} α_e = [0.00157] cm^{-1} r_e = [1.99] Å

Enthalpy of Formation

The appearance potential of SrF^+ from SrF(g) has been measured mass spectrometrically by Hildenbrand,[1] Green *et al.*[2] and Ehlert *et al.*[3] as 5.0 ± 0.3 eV, 4.9 ± 0.3 eV, and 5.2 ± 0.3 eV, respectively. For the process $e^- + SrF(g) \rightarrow SrF^+(g) + 2e^-$, the corresponding $\Delta_f H°(SrF^+, g, 0\ K)$ are derived to be 45.3 ± 9.0, and 49.9± 9.0 $kcal·mol^{-1}$ with $\Delta_f H°(SrF, g, 0\ K) = -70.0 \pm 2.0\ kcal·mol^{-1}$.[4]

Hildenbrand[1] has also reported AP = 13.0 ± 1.0 eV for SrF^+ from $SrF_2(g)$. Green *et al.*[2] obtained an ionization efficiency curve for SrF^+ which extrapolates (high–energy portion) to 10.5 eV at zero ion current. Assuming the process to be $e^- + SrF_2(g) \rightarrow SrF^+(g) + F(g) + 2e^-$, we obtain $\Delta_f H°(SrF^+, g, 0\ K)$ equal to 98.7 ± 25.0 and 41.1 $kcal·mol^{-1}$ by combining the above results with $\Delta_f H°(SrF_2, g, 0\ K) = 182.7 \pm 1.0$ $kcal·mol^{-1}$ and $\Delta_f H°(F, g, 0\ K) = 18.36 \pm 0.4\ kcal·mol^{-1}$.[4]

The adopted $\Delta_f H°(0\ K)$ is based on the three mass spectral results[1, 2, 3] for the direct ionization process of SrF(g). The value of $\Delta_f H°$ at 298.15 K is 47.1 ± 10.0 $kcal·mol^{-1}$, and the corresponding ionization potential for SrF(g) is 5.03 eV.

Heat Capacity and Entropy

The internuclear distance (r_e) is the value estimated by Barrow and Beale[5] from spectroscopic work on SrF. The value of ω_e is calculated from Badger's rule[6] which can be written in the form $\omega_e^2 = 3.159 \times 10^6/\mu(r_e - d_{ij})$.[3] Molecular data for the ground states of SrF,[4] SrO,[7] and RbF[8] were used to determine the constant d_{ij}. The product $x_e\mu^{1/2}$ has been shown to be constant within a group of similar molecules by Barrow and Caunt.[9] Since $\mu^{1/2}(SrF^+) \cong \mu^{1/2}(SrF)$, we assume $x_e(SrF^+) = x_e(SrF)$ and obtain $\omega_e x_e$ equal to 2.42 cm^{-1} with our estimated value ω_e = 561 cm^{-1}. The value of α_e is obtained from the other constants assuming a Morse potential function.

SrF^+ has eight valence electrons; thus, the ground state configuration ($^1\Sigma^+$) and electronic level for the B state are estimated from those for the isoelectronic molecule SrS.[7] By analogy with the gaseous alkaline earth oxides,[10] C_2,[4] BeS,[11] and BaS,[12] low lying triplet states are to be expected. The two estimated triplet levels are based on those which have been observed directly in C_2,[4] BeS,[11] and indirectly (through perturbative effects) in BaS.[12] Also included are additional states at 12,000 cm^{-1} ($^1\Pi$), 15,000 cm^{-1} ($^1\Delta$), and 18,000 cm^{-1} ($^1\Sigma$). These three levels are also estimated from those for C_2,[4] Bes,[11] and BaS.[12] The adopted electronic entropies are believed to represent minimal values. Probable upper limits for the electronic contributions can be established by decreasing the two triplet levels to 1000 cm^{-1} ($^3\Pi$) and 5000 cm^{-1} ($^3\Sigma$) and neglecting the other excited states. This increases the entropy by 3.9 cal $K^{-1}·mol^{-1}$ and 2.6 cal $K^{-1}·mol^{-1}$ at 2000 K and 4000 K, respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.171	192.679		
100	29.288	198.822	261.416	−6.259			
200	31.664	219.755	235.882	−3.225			
250	32.928	226.961	233.399	−1.610			
298.15	33.891	232.846	232.846	0.	197.066	168.224	−29.472
300	33.923	233.056	232.847	0.063	197.089	168.045	−29.259
350	34.677	238.345	233.263	1.779	197.697	163.157	−24.350
400	35.245	243.014	234.196	3.527	198.294	158.181	−20.656
450	35.679	247.191	235.412	5.301	198.871	153.132	−17.775
500	36.016	250.969	236.782	7.094	199.428	148.020	−15.464
600	36.497	257.581	239.713	10.721	200.467	137.639	−11.983
700	36.819	263.233	242.679	14.388	201.403	127.093	−9.484
800	37.049	268.165	245.563	18.082	202.231	116.419	−7.601
900	37.223	272.539	248.322	21.796	202.322	105.720	−6.136
1000	37.364	276.469	250.943	25.526	203.252	94.936	−4.959
1100	37.488	280.036	253.428	29.268	196.277	84.426	−4.009
1200	37.611	283.303	255.784	33.023	196.292	74.257	−3.232
1300	37.748	286.319	258.018	36.791	196.307	64.086	−2.575
1400	37.913	289.122	260.141	40.574	196.327	53.915	−2.012
1500	38.124	291.745	262.161	44.375	196.355	43.742	−1.523
1600	38.394	294.213	264.088	48.200	196.399	33.566	−1.096
1700	38.734	296.551	265.930	52.056	59.550	24.567	−0.755
1800	39.153	298.776	267.693	55.950	61.506	22.453	−0.652
1900	39.657	300.906	269.385	59.890	63.497	20.229	−0.556
2000	40.247	302.955	271.013	63.884	65.530	17.899	−0.467
2100	40.923	304.935	272.581	67.942	67.611	15.467	−0.385
2200	41.678	306.856	274.096	72.071	69.746	12.934	−0.307
2300	42.506	308.726	275.561	76.280	71.939	10.303	−0.234
2400	43.398	310.554	276.981	80.575	74.192	7.575	−0.165
2500	44.340	312.344	278.360	84.961	76.504	4.752	−0.099
2600	45.322	314.103	279.701	89.444	78.875	1.835	−0.037
2700	46.328	315.832	281.007	94.026	81.299	−1.174	0.023
2800	47.345	317.535	282.281	98.710	83.771	−4.273	0.080
2900	48.361	319.214	283.526	103.495	86.284	−7.462	0.134
3000	49.361	320.871	284.743	108.382	88.826	−10.738	0.187
3100	50.335	322.505	285.935	113.367	91.387	−14.099	0.238
3200	51.271	324.118	287.103	118.447	93.955	−17.543	0.286
3300	52.160	325.709	288.249	123.619	96.516	−21.067	0.333
3400	52.994	327.279	289.374	128.877	99.058	−24.668	0.379
3500	53.768	328.827	290.479	134.216	101.566	−28.344	0.423
3600	54.475	330.351	291.566	139.629	104.027	−32.090	0.466
3700	55.114	331.853	292.634	145.109	106.428	−35.905	0.507
3800	55.682	333.330	293.686	150.649	108.757	−39.783	0.547
3900	56.179	334.783	294.721	156.243	111.002	−43.721	0.586
4000	56.606	336.211	295.740	161.883	113.154	−47.716	0.623
4100	56.963	337.613	296.745	167.562	115.204	−51.763	0.659
4200	57.253	338.990	297.734	173.273	117.148	−55.860	0.695
4300	57.481	340.340	298.709	179.010	118.974	−60.001	0.729
4400	57.647	341.663	299.671	184.767	120.680	−64.183	0.762
4500	57.758	342.960	300.618	190.538	122.264	−68.402	0.794
4600	57.817	344.230	301.553	196.317	123.788	−72.661	0.825
4700	57.828	345.474	302.474	202.100	125.142	−76.946	0.855
4800	57.796	346.691	303.382	207.881	126.377	−81.259	0.884
4900	57.724	347.882	304.278	213.658	127.494	−85.597	0.912
5000	57.618	349.047	305.162	219.425	128.503	−89.957	0.940
5100	57.480	350.187	306.034	225.180	129.422	−94.337	0.966
5200	57.315	351.302	306.894	230.920	130.218	−98.732	0.992
5300	57.127	352.392	307.742	236.642	130.916	−103.142	1.017
5400	56.919	353.457	308.579	242.345	131.522	−107.564	1.040
5500	56.693	354.500	309.404	248.026	132.043	−111.997	1.064
5600	56.454	355.519	310.219	253.683	132.486	−116.438	1.086
5700	56.203	356.516	311.022	259.316	132.856	−120.886	1.108
5800	55.942	357.491	311.815	264.923	133.161	−125.341	1.129
5900	55.675	358.445	312.597	270.504	133.617	−129.824	1.149
6000	55.403	359.379	313.369	276.058	133.842	−134.291	1.169

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 237.31 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-66.941 \pm 41.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-66.944 \pm 41.8]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[4]	[6000]	[4]
[1000]	[4]	[8000]	[4]
[2000]	[4]	[10000]	[4]
[4000]	[4]		

$\omega_e = [590] cm^{-1}$ $\omega_e x_e = [6.6]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.328]\ cm^{-1}$ $\alpha_e = [0.0036]\ cm^{-1}$ $r_e = [1.95]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(TiF, g, 298.15 K), is calculated from the dissociation energy. The dissociation energy is estimated as 148 ± 6 kcal·mol^{-1} using the corresponding quantity for TiF_2(g) and the relation $D_0°(MF)/\Delta_{at}H°(MF_2) = 0.46 \pm 0.02$ which Zmbov and Margrave[1] found held for other mono– and di–fluorides.

Heat Capacity and Entropy

The vibrational frequency, ω_e, and anharmonic vibrational term, $\omega_e x_e$, are estimated from those of the alkali and mercury monohalides. The interatomic distance, r_e, is estimated from those of TiCl(g), TiF_2(g) and TiF_3(g). B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^+.[2]

References

[1]K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
[2]C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, (1949).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.239	−66.941	−66.941	INFINITE
100	29.254	203.037	266.316	−6.328	−66.044	−77.003	40.222
200	31.809	223.943	240.429	−3.297	−66.394	−87.872	22.950
250	33.638	231.236	237.881	−1.661	−66.673	−93.210	19.475
298.15	35.339	237.309	237.309	0.	−66.944	−98.296	17.221
300	35.401	237.528	237.309	0.065	−66.954	−98.490	17.149
350	36.971	243.105	237.746	1.876	−67.226	−103.725	15.480
400	38.309	248.132	238.736	3.759	−67.484	−108.921	14.224
450	39.417	252.711	240.038	5.703	−67.731	−114.086	13.243
500	40.316	256.912	241.518	7.697	−67.969	−119.224	12.455
600	41.599	264.385	244.722	11.798	−68.430	−129.431	11.268
700	42.376	270.861	248.004	16.000	−68.892	−139.561	10.414
800	42.830	276.552	251.224	20.262	−69.359	−149.625	9.770
900	43.089	281.613	254.325	24.559	−69.880	−159.628	9.265
1000	43.240	286.161	257.285	28.876	−70.529	−169.567	8.857
1100	43.333	290.287	260.100	33.205	−71.375	−179.432	8.521
1200	43.402	294.061	262.775	37.542	−76.406	−189.090	8.231
1300	43.461	297.537	265.318	41.885	−76.928	−198.460	7.974
1400	43.520	300.760	267.735	46.235	−77.533	−207.786	7.753
1500	43.584	303.765	270.038	50.590	−78.233	−217.066	7.559
1600	43.652	306.580	272.235	54.951	−79.041	−226.296	7.388
1700	43.725	309.228	274.334	59.320	−79.967	−235.472	7.235
1800	43.801	311.730	276.343	63.696	−81.025	−244.589	7.098
1900	43.879	314.100	278.268	68.080	−82.224	−253.644	6.973
2000	43.958	316.353	280.117	72.472	−98.265	−262.178	6.847
2100	44.037	318.499	281.894	76.872	−100.533	−270.318	6.724
2200	44.113	320.550	283.604	81.280	−102.794	−278.350	6.609
2300	44.186	322.512	285.254	85.695	−105.047	−286.280	6.502
2400	44.255	324.394	286.846	90.117	−107.290	−294.111	6.401
2500	44.320	326.202	288.384	94.545	−109.522	−301.850	6.307
2600	44.381	327.942	289.872	98.981	−111.742	−309.499	6.218
2700	44.437	329.618	291.313	103.422	−113.948	−317.063	6.134
2800	44.488	331.235	292.710	107.868	−116.139	−324.546	6.054
2900	44.534	332.797	294.066	112.319	−118.315	−331.950	5.979
3000	44.575	334.307	295.382	116.774	−120.474	−339.280	5.907
3100	44.612	335.769	296.662	121.234	−122.615	−346.539	5.839
3200	44.645	337.186	297.906	125.697	−124.739	−353.728	5.774
3300	44.674	338.560	299.117	130.163	−126.845	−360.851	5.712
3400	44.700	339.894	300.297	134.631	−128.932	−367.911	5.652
3500	44.723	341.191	301.447	139.103	−131.000	−374.910	5.595
3600	44.742	342.451	302.569	143.576	−133.050	−381.849	5.540
3700	44.760	343.677	303.663	148.051	−544.179	−380.944	5.378
3800	44.775	344.871	304.732	152.528	−544.957	−376.522	5.176
3900	44.789	346.034	305.776	157.006	−545.772	−372.079	4.983
4000	44.800	347.168	306.797	161.485	−546.623	−367.614	4.801
4100	44.811	348.274	307.795	165.966	−547.508	−363.128	4.626
4200	44.821	349.354	308.772	170.448	−548.426	−358.620	4.460
4300	44.830	350.409	309.728	174.930	−549.376	−354.090	4.301
4400	44.838	351.440	310.664	179.414	−550.356	−349.537	4.150
4500	44.847	352.448	311.581	183.898	−551.364	−344.962	4.004
4600	44.855	353.433	312.481	188.383	−552.400	−340.364	3.865
4700	44.863	354.398	313.362	192.869	−553.462	−335.743	3.731
4800	44.871	355.343	314.227	197.355	−554.547	−331.099	3.603
4900	44.880	356.268	315.076	201.843	−555.655	−326.432	3.480
5000	44.889	357.175	315.909	206.331	−556.783	−321.743	3.361
5100	44.899	358.064	316.726	210.821	−557.930	−317.031	3.247
5200	44.909	358.936	317.530	215.311	−559.094	−312.296	3.137
5300	44.920	359.791	318.319	219.803	−560.274	−307.539	3.031
5400	44.932	360.631	319.095	224.295	−561.467	−302.759	2.929
5500	44.944	361.456	319.858	228.789	−562.673	−297.957	2.830
5600	44.958	362.266	320.608	233.284	−563.889	−293.133	2.734
5700	44.972	363.061	321.346	237.781	−565.115	−288.287	2.642
5800	44.988	363.844	322.072	242.279	−566.348	−283.420	2.552
5900	45.004	364.613	322.786	246.778	−567.587	−278.531	2.466
6000	45.021	365.369	323.490	251.279	−568.832	−273.621	2.382

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K)$ = [251.141] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [386.518 ± 62.8] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [386.183 ± 62.8] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^2\Delta$]	0	[4]
	[5000]	[2]
	[15000]	[20]

ω_e = [726.5] cm^{-1} $\omega_e x_e$ = [2.9] cm^{-1} σ = 1
B_e = [0.292 3] cm^{-1} α_e = [0.0015] cm^{-1} r_e = [1.83] Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(WF, g, 298.15 K) = 92.3 kcal·mol^{-1}, is calculated from the bond dissociation energy $\Delta_{at} H°$(WF, 298.15 K) = 130 ± 15 kcal·mol^{-1}. This value of $\Delta_{at} H°(298.15\ K)$ is estimated to be slightly higher than the average bond dissociation energy of WF_6(g) by analogy with the WCl_x system.

Heat Capacity and Entropy

The bond distance is estimated to be the same as that in WF_6(g). This distance is then used with Guggenheimer's[1] relation to calculate the fundamental vibrational frequency, ω_e.[1] The anharmonicity correction x_e is estimated roughly by assuming $x_e = \omega_e/4(D_0^o + 0.5\ \omega_e) = 0.0042$. The rotational constant, B_e, is calculated from the estimated bond distance. The value of α_e is calculated form the Morse potential function.

The ground state configuration, low lying electronic levels and their quantum weights are estimated based on the tentative molecular orbital diagram for TaO given by Weltner and McLeod.[2] Using this scheme, we obtain the ground state configuration as $\Pi^4\sigma\delta^4$ which yields a $^2\Sigma$ state. Higher levels are considered to be formed by transition to Π^* antibonding orbitals, and by analogy with TaO these are assumed to lie in the 15000 cm^{-1} region. The degeneracy of these levels is estimated roughly from the large number of possible configurations.

References

[1]K. M. Guggenheimer, Proc. Phys. Soc. **58**, 456 (1946).
[2]W. Weltner, Jr., and D. McLeod, Jr., J. Chem. Phys. **42**, 882 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.051	386.518	386.518	INFINITE
100	29.135	217.762	279.175	−6.141	387.322	375.025	−195.893
200	30.708	238.278	254.142	−3.173	386.818	362.882	−94.775
250	32.340	245.300	251.691	−1.598	386.485	356.937	−74.578
298.15	34.026	251.141	251.141	0.	386.183	351.274	−61.542
300	34.090	251.351	251.141	0.063	386.172	351.057	−61.125
350	35.728	256.732	251.563	1.809	385.900	345.227	−51.522
400	37.157	261.598	252.518	3.632	385.668	339.433	−44.325
450	38.353	266.046	253.777	5.521	385.472	333.665	−38.731
500	39.326	270.139	255.212	7.464	385.303	327.918	−34.257
600	40.693	277.441	258.323	11.471	385.015	316.469	−27.551
700	41.464	283.778	261.517	15.583	384.751	305.066	−22.764
800	41.824	289.342	264.655	19.750	384.468	293.701	−19.177
900	41.920	294.275	267.677	23.939	384.141	282.375	−16.389
1000	41.854	298.690	270.561	28.128	383.752	271.088	−14.160
1100	41.697	302.672	273.303	32.306	383.291	259.843	−12.339
1200	41.493	306.292	275.903	36.466	382.753	248.643	−10.823
1300	41.271	309.604	278.370	40.604	382.137	237.492	−9.543
1400	41.049	312.654	280.711	44.720	381.441	226.391	−8.447
1500	40.835	315.479	282.936	48.815	380.668	215.343	−7.499
1600	40.635	318.108	285.053	52.888	379.817	204.348	−6.671
1700	40.451	320.566	287.071	56.942	378.891	193.409	−5.943
1800	40.284	322.873	288.996	60.979	377.893	182.527	−5.297
1900	40.133	325.047	290.837	64.999	376.826	171.702	−4.720
2000	39.998	327.102	292.599	69.006	375.691	160.935	−4.203
2100	39.877	329.051	294.289	72.999	374.491	150.227	−3.737
2200	39.769	330.903	295.912	76.982	373.229	139.577	−3.314
2300	39.674	332.669	297.472	80.954	371.909	128.986	−2.929
2400	39.589	334.356	298.974	84.917	370.532	118.453	−2.578
2500	39.514	335.970	300.422	88.872	369.101	107.979	−2.256
2600	39.449	337.519	301.819	92.820	367.623	97.563	−1.960
2700	39.391	339.006	303.169	96.762	366.072	87.206	−1.687
2800	39.340	340.438	304.474	100.698	364.416	76.907	−1.435
2900	39.295	341.818	305.738	104.630	362.618	66.670	−1.201
3000	39.257	343.149	306.963	108.558	360.654	56.498	−0.984
3100	39.223	344.436	308.152	112.481	358.480	46.395	−0.782
3200	39.195	345.681	309.305	116.402	356.068	36.365	−0.594
3300	39.170	346.886	310.426	120.321	353.393	26.415	−0.418
3400	39.149	348.055	311.515	124.236	350.421	16.550	−0.254
3500	39.132	349.190	312.576	128.151	347.089	6.778	−0.101
3600	39.118	350.292	313.608	132.063	343.301	−2.892	0.042
3700	39.107	351.364	314.614	135.974	304.192	−12.260	0.173
3800	39.098	352.407	315.595	139.885	302.780	−20.794	0.286
3900	39.092	353.422	316.552	143.794	301.385	−29.290	0.392
4000	39.088	354.412	317.486	147.703	300.007	−37.752	0.493
4100	39.086	355.377	318.399	151.612	298.645	−46.179	0.588
4200	39.086	356.319	319.290	155.520	297.300	−54.573	0.679
4300	39.088	357.239	320.162	159.429	295.971	−62.935	0.765
4400	39.091	358.137	321.015	163.338	294.659	−71.267	0.846
4500	39.095	359.016	321.850	167.247	293.364	−79.568	0.924
4600	39.101	359.875	322.667	171.157	292.085	−87.842	0.997
4700	39.108	360.716	323.468	175.067	290.822	−96.087	1.068
4800	39.116	361.540	324.252	178.979	289.574	−104.306	1.135
4900	39.125	362.346	325.022	182.891	288.343	−112.499	1.199
5000	39.135	363.137	325.776	186.804	287.126	−120.667	1.261
5100	39.146	363.912	326.516	190.718	285.925	−128.811	1.319
5200	39.158	364.672	327.243	194.633	284.738	−136.932	1.375
5300	39.170	365.418	327.956	198.549	283.565	−145.030	1.429
5400	39.183	366.150	328.656	202.467	282.407	−153.105	1.481
5500	39.197	366.869	329.345	206.386	281.262	−161.160	1.531
5600	39.212	367.576	330.021	210.306	280.131	−169.194	1.578
5700	39.227	368.270	330.686	214.228	279.013	−177.208	1.624
5800	39.242	368.952	331.340	218.152	277.908	−185.202	1.668
5900	39.259	369.623	331.983	222.077	276.815	−193.177	1.710
6000	39.275	370.283	332.616	226.003	275.735	−201.134	1.751

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = [243.736 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°[83.669 \pm 20.9]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [82.843 \pm 20.9]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[4]	[18000]	[4]
[3000]	[4]	[24000]	[4]
[6000]	[4]	[30000]	[4]
[12000]	[4]		

$\omega_e = [828.0]\ cm^{-1}$ $\omega_e x_e = [4.0]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.29699]\ cm^{-1}$ $\alpha_e = [0.009]\ cm^{-1}$ $r_e = [1.90]$ Å

Enthalpy of Formation

Based on $[D_0°(ZrF)/\Delta_{at}H°(ZrF_2)] = 0.46$, as indicated by recent work on the fluorides of Groups II and IV elements,[1, 2, 3, 4, 5] and $\Delta_{at}H°(ZrF_2) = 318.1\ kcal·mol^{-1}$, the $D_0°(ZrF)$ is calculated as 146.3 $kcal·mol^{-1}$. Using $\Delta_f H°(ZrF, g, 0\ K) = 147.99$, $\Delta_f H°(F, g, 0\ K) = 18.36$, and $D_0°(ZrF, g) = 146.3\ kcal·mol^{-1}$, we derive $\Delta_f H°(ZrF, g, 0\ K) = 20.0$ or $\Delta_f H°(ZrF, g, 298.15\ K) = 19.8 \pm 5\ kcal·mol^{-1}$ (82.843 ± 20.9 $kJ·mol^{-1}$) which is adopted.

The $\Delta_f H°(ZrF, g, 298.15\ K)$ was evaluated as approximately 16 ± 5 $kcal·mol^{-1}$ by Murad and Hildenbrand,[8] employing a different $\Delta_{at}H°(ZrF_2)$ value. Their value is in agreement with the adopted one, within the assigned uncertainty.

Heat Capacity and Entropy

The ground state configuration is taken from the ground state multiplet of Zr^+.[6] The electronic levels are estimated as three times higher than those of TiF(g) and the quantum weights are assumed to be the same. ω_e is taken to be approximately the same as the ZrF_2 stretching frequency ν_1 for ZrF_4(g). B_e is calculated from the formula $B_e = 2.799076 \times 10^{-39}/I_e$ where $I_e = \mu r_e$, μ = reduced mass of ZrF(g), $r_e = 1.90$ Å which is estimated from those of ZrF_4, CF_4, CF and other related gaseous molecules, α_e is derived from B_e, ω_e and $\omega_e x_e$ (estimated), according to the method suggested by Herzberg.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.084	83.669	83.669	INFINITE
100	29.199	210.139	271.878	−6.174	84.239	73.149	−38.209
200	31.136	230.853	246.724	−3.174	83.581	62.286	−16.267
250	32.394	237.939	244.280	−1.585	83.203	57.006	−11.911
298.15	33.427	243.736	243.736	0.	82.843	51.993	−9.109
300	33.462	243.942	243.736	0.062	82.829	51.802	−9.019
350	34.316	249.167	244.147	1.757	82.459	46.660	−6.964
400	34.996	253.796	245.069	3.491	82.089	41.571	−5.429
450	35.552	257.951	246.274	5.255	81.715	36.528	−4.240
500	36.027	261.722	247.633	7.044	81.335	31.528	−3.294
600	36.856	268.365	250.549	10.689	80.552	21.639	−1.884
700	37.629	274.105	253.513	14.414	79.734	11.885	−0.887
800	38.392	279.179	256.410	18.215	78.881	2.250	−0.147
900	39.142	283.744	259.198	22.092	77.983	−7.276	0.422
1000	39.866	287.906	261.864	26.042	77.033	−16.698	0.872
1100	40.548	291.738	264.408	30.064	76.023	−26.023	1.236
1200	41.178	295.294	266.835	34.150	71.235	−35.031	1.525
1300	41.752	298.613	269.153	38.297	70.629	−43.862	1.762
1400	42.268	301.726	271.370	42.499	70.024	−52.647	1.964
1500	42.727	304.659	273.492	46.749	69.406	−61.387	2.138
1600	43.132	307.429	275.528	51.042	68.758	−70.086	2.288
1700	43.486	310.055	277.482	55.374	68.066	−78.743	2.419
1800	43.794	312.549	279.362	59.738	67.314	−87.357	2.535
1900	44.063	314.925	281.171	64.131	66.491	−95.928	2.637
2000	44.295	317.191	282.916	68.549	65.582	−104.453	2.728
2100	44.496	319.357	284.600	72.989	64.575	−112.931	2.809
2200	44.671	321.431	286.228	77.448	42.135	−120.612	2.864
2300	44.824	323.420	287.802	81.923	40.482	−127.973	2.906
2400	44.957	325.331	289.326	86.412	38.846	−135.262	2.944
2500	45.076	327.168	290.803	90.914	37.226	−142.483	2.977
2600	45.181	328.938	292.236	95.427	35.624	−149.639	3.006
2700	45.276	330.645	293.627	99.950	34.040	−156.735	3.032
2800	45.364	332.294	294.979	104.482	32.474	−163.772	3.055
2900	45.445	333.887	296.293	109.022	30.927	−170.753	3.076
3000	45.521	335.429	297.572	113.570	29.401	−177.682	3.094
3100	45.593	336.923	298.817	118.126	27.896	−184.560	3.110
3200	45.663	338.371	300.031	122.689	26.411	−191.389	3.124
3300	45.731	339.777	301.214	127.259	24.949	−198.173	3.137
3400	45.798	341.144	302.369	131.835	23.510	−204.912	3.148
3500	45.865	342.472	303.496	136.418	22.093	−211.610	3.158
3600	45.932	343.765	304.596	141.008	20.699	−218.267	3.167
3700	45.999	345.025	305.672	145.605	19.330	−224.886	3.175
3800	46.067	346.252	306.724	150.208	17.984	−231.469	3.182
3900	46.136	347.450	307.753	154.818	16.662	−238.016	3.188
4000	46.205	348.619	308.760	159.435	15.363	−244.530	3.193
4100	46.276	349.760	309.746	164.059	14.089	−251.011	3.198
4200	46.348	350.876	310.712	168.690	12.839	−257.462	3.202
4300	46.421	351.968	311.659	173.329	11.613	−263.883	3.206
4400	46.495	353.036	312.587	177.975	10.410	−270.276	3.209
4500	46.570	354.082	313.498	182.628	9.231	−276.642	3.211
4600	46.646	355.106	314.391	187.289	8.075	−282.982	3.213
4700	46.724	356.110	315.268	191.957	6.943	−289.297	3.215
4800	46.802	357.095	316.129	196.633	−555.103	−283.971	3.090
4900	46.881	358.060	316.975	201.317	−555.842	−278.315	2.967
5000	46.962	359.008	317.806	206.010	−556.576	−272.643	2.848
5100	47.043	359.939	318.623	210.710	−557.303	−266.957	2.734
5200	47.124	360.853	319.427	215.418	−558.023	−261.257	2.624
5300	47.207	361.752	320.217	220.135	−558.735	−255.543	2.519
5400	47.290	362.635	320.994	224.859	−559.437	−249.816	2.416
5500	47.373	363.503	321.759	229.593	−560.129	−244.076	2.318
5600	47.457	364.358	322.512	234.334	−560.809	−238.324	2.223
5700	47.541	365.198	323.254	239.084	−561.477	−232.559	2.131
5800	47.625	366.026	323.984	243.842	−562.132	−226.783	2.042
5900	47.710	366.841	324.704	248.609	−562.773	−220.995	1.957
6000	47.795	367.643	325.413	253.384	−563.398	−215.197	1.873

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

0 to 6000 K Ideal Diatomic Gas

D_0° = 154.56 ± 0.60 kJ·mol^{-1}
S°(298.15 K) = 202.789 ± 0.040 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 0 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 0 kJ·mol^{-1}

Spectroscopic Data for F_2 in cm^{-1}

v =	0	1	2	3	4	5	6	7	8	9	10	11
G(v)−G(0)	0.00	893.90	1764.15	2610.22	3431.53	4227.43	4997.19	5740.05	6455.17	7141.63	7798.48	8424.67
B_v	0.8833	0.8696	0.8560	0.8423	0.8284	0.8142	0.7996	0.7484	0.7685	0.7518	0.7343	0.7156
$D_v \times 10^6$	3.3	3.1	2.7	4.4	3.6	2.2	4.6	4.5	5.2	5.4	6.5	6.7

v =	12	13	14	15	16	17	18	19	20	21	22
G(v)−G(0)	9019.11	9580.63	10108.02	10599.62	11053.90	11468.96	11842.62	12172.25	12452.98	12678.00	12830.38
B_v	0.6958	0.6747	0.6522	0.6282	0.6025	0.5750	0.5449	0.5094	0.4711	0.4185	0.3865
D_v x 10^6	3.7	9.2	8.5	5.5	8.6	7.0	9.8	15.0	19.6	32.7	86.4

r_e = 1.41193 Å[10]

Heat of Formation

Zero by definition. Refer to monatomic fluorine gas table for a discussion of the discussion energy.

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique. Due to the absence of known low lying bound excited states (i.e. <93000 cm^{-1}) only the ground state is included in the calculation.

The G(v), B_v and D_v spectroscopic constants for the ground state and the dissociation energy were determined by Colbourn *et al.*[1] These are used in the computation as given (and not as the usual fitting coefficients ω_e, $\omega_e x_e$, etc.). The rotational levels are weighted in accordance with the nuclear spin–rotation interaction[5] as follows: even J weight = 0.75, odd J weight = 0.25. Also, the rotational levels are extrapolated to high J values according to the method of Khachkuruzov[6] who proposed a simpler form of Wooley's method.[7] Note that there is only one stable isotope of fluorine, ^{19}F.

The so-called quasibound rotational levels above the dissociation limit[2,3] are also included. For a given vibrational quantum number, v, the summation over rotational states is carried out up to a rotational quantum number, J, given by $J = J_{lim}(1-v/v_{max})$ where J_{lim} amd v_{max} were determined by Gurvich *et al.*[4] to be 178 and 23, respectively. Our adopted value for S°(298.15 K) differs from values recommended by CODATA,[9] Gurvich *et al.*[3] and Wagman *et al.*[11] by less than 0.01 J K^{-1}·mol^{-1}. For this comparison, the entropy values reported by CODATA[9] and Gurvich *et al.*[3] are increased by 0.1094 J K^{-1}·mol^{-1}to account for a change in the standard–state pressure from 1 atm to 1 bar.

Phase Data

Hultgren *et al.*[8] had recommended the α→β transition temperature, 45.55 K, the triple point, 53.48 K (0.000249 atm) and the boiling point, 84.95 K (1 atm). These values should prove reasonably accurate, although they have not been evaluated by the present authors, and are furnished for the convenience of the reader. As a result of the low values, the reference state for fluorine is chosen to be the ideal diatomic gas at all temperatures. This may differ from the choice of other authors.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p° (J·K^{-1}·mol^{-1})	S° (J·K^{-1}·mol^{-1})	$-[G^\circ-H^\circ(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H^\circ-H^\circ(T_r)$ (kJ·mol^{-1})	$\Delta_f H^\circ$ (kJ·mol^{-1})	$\Delta_f G^\circ$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.825	0.	0.	0.
100	29.114	170.370	229.549	−5.918	0.	0.	0.
200	29.685	190.652	205.596	−2.989	0.	0.	0.
250	30.447	197.354	203.300	−1.486	0.	0.	0.
298.15	31.302	202.789	202.789	0.	0.	0.	0.
300	31.336	202.983	202.790	0.058	0.	0.	0.
350	32.207	207.880	203.175	1.647	0.	0.	0.
400	32.992	212.233	204.040	3.277	0.	0.	0.
450	33.674	216.159	205.172	4.944	0.	0.	0.
500	34.255	219.738	206.452	6.643	0.	0.	0.
600	35.166	226.068	209.208	10.116	0.	0.	0.
700	35.832	231.542	212.016	13.668	0.	0.	0.
800	36.336	236.361	214.764	17.277	0.	0.	0.
900	36.732	240.664	217.407	20.932	0.	0.	0.
1000	37.057	244.552	219.930	24.622	0.	0.	0.
1100	37.334	248.097	222.332	28.341	0.	0.	0.
1200	37.579	251.356	224.617	32.087	0.	0.	0.
1300	37.802	254.373	226.791	35.857	0.	0.	0.
1400	38.008	257.182	228.863	39.647	0.	0.	0.
1500	38.199	259.811	230.839	43.458	0.	0.	0.
1600	38.374	262.282	232.728	47.287	0.	0.	0.
1700	38.530	264.613	234.536	51.132	0.	0.	0.
1800	38.663	266.819	236.268	54.992	0.	0.	0.
1900	38.770	268.913	237.932	58.864	0.	0.	0.
2000	38.846	270.904	239.531	62.745	0.	0.	0.
2100	38.889	272.800	241.071	66.632	0.	0.	0.
2200	38.895	274.609	242.554	70.521	0.	0.	0.
2300	38.864	276.338	243.986	74.409	0.	0.	0.
2400	38.795	277.991	245.369	78.293	0.	0.	0.
2500	38.690	279.572	246.705	82.167	0.	0.	0.
2600	38.549	281.087	247.999	86.030	0.	0.	0.
2700	38.375	282.539	249.251	89.876	0.	0.	0.
2800	38.170	283.931	250.465	93.704	0.	0.	0.
2900	37.939	285.266	251.642	97.509	0.	0.	0.
3000	37.683	286.548	252.785	101.290	0.	0.	0.
3100	37.406	287.779	253.894	105.045	0.	0.	0.
3200	37.111	288.962	254.971	108.771	0.	0.	0.
3300	36.802	290.100	256.019	112.467	0.	0.	0.
3400	36.482	291.193	257.037	116.131	0.	0.	0.
3500	36.152	292.246	258.028	119.763	0.	0.	0.
3600	35.817	293.260	258.993	123.361	0.	0.	0.
3700	35.477	294.237	259.932	126.926	0.	0.	0.
3800	35.135	295.178	260.848	130.457	0.	0.	0.
3900	34.793	296.087	261.740	133.953	0.	0.	0.
4000	34.452	296.963	262.609	137.415	0.	0.	0.
4100	34.114	297.810	263.458	140.844	0.	0.	0.
4200	33.780	298.628	264.285	144.238	0.	0.	0.
4300	33.450	299.419	265.093	147.600	0.	0.	0.
4400	33.125	300.184	265.882	150.929	0.	0.	0.
4500	32.807	300.925	266.653	154.225	0.	0.	0.
4600	32.495	301.642	267.405	157.490	0.	0.	0.
4700	32.191	302.338	268.141	160.724	0.	0.	0.
4800	31.893	303.013	268.861	163.929	0.	0.	0.
4900	31.603	303.667	269.565	167.103	0.	0.	0.
5000	31.321	304.303	270.253	170.249	0.	0.	0.
5100	31.046	304.920	270.927	173.368	0.	0.	0.
5200	30.779	305.521	271.586	176.459	0.	0.	0.
5300	30.519	306.104	272.232	179.524	0.	0.	0.
5400	30.268	306.673	272.865	182.563	0.	0.	0.
5500	30.023	307.226	273.484	185.577	0.	0.	0.
5600	29.787	307.765	274.092	188.568	0.	0.	0.
5700	29.557	308.290	274.687	191.535	0.	0.	0.
5800	29.335	308.802	275.271	194.480	0.	0.	0.
5900	29.119	309.301	275.843	197.402	0.	0.	0.
6000	28.911	309.789	276.405	200.304	0.	0.	0.

PREVIOUS: June 1977 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 86.985 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [1373]\ K$

$\Delta_f H°(0\ K) = 705.266 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 705.841 \pm 41.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [51.882]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The equilibrium pressures for the reaction $FeF_2(cr) + H_2(g) = Fe(cr) + 2HF(g)$ have been measured by Jellinek and Rudat[1] at 773, 873 and 973 K. The enthalpy change of the reaction, $\Delta_r H°(298.15\ K)$, was evaluated by the 2nd and 3rd law methods to be 27.19 and 39.08 $kcal \cdot mol^{-1}$, respectively. Based on the 3rd law value of $\Delta_r H°(298.15\ K)$, the $\Delta_f H°(FeF_2, cr, 298.15\ K)$ was calculated to be 168.7 ± 10 $kcal \cdot mol^{-1}$. The drift in the 3rd law values of $\Delta_r H°(298.15\ K)$ was evaluated to be 13.3 ± 1.8 cal $K^{-1} \cdot mol^{-1}$.

Heat Capacity and Entropy

The low temperature (11.33–307.30 K) heat capacities were determined by Catalano and Stout.[2] The heat capacities above 307 K were estimated by comparison with those of $FeCl_2(cr)$, $MgCl_2(cr)$ and $MgF_2(cr)$. The value of $S°(298.15\ K)$ was obtained from Catalano and Stout,[2] in which a sharp maximum $C_p°$ of 17.8 cal $K^{-1} \cdot mol^{-1}$ at 78.35 K was reported. The $S°(298.15\ K)$ value was based on $S°(15\ K) = 0.039$ cal $K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was estimated as 1100°C based on the data reported by Biltz and Rahlfs.[3] The value of $\Delta_{fus} H°$ was calculated using $\Delta_m S° = 9$ cal $K^{-1} \cdot mol^{-1}$ which was assumed to be the same as the corresponding value for $MgF_2(cr)$.

Sublimation Data

The value of $\Delta_{sub} H°(298.15\ K) = 316.31 \pm 8.4\ kJ \cdot mol^{-1}$ was obtained from Margrave.[4] See $FeF_2(g)$ table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.757	−705.266	−705.266	INFINITE
100	33.447	30.853	138.926	−10.807	−706.646	−692.088	361.510
200	56.610	62.024	92.902	−6.176	−706.712	−677.397	176.918
298.15	68.116	86.985	86.985	0.	−705.841	−663.168	116.184
300	68.199	87.407	86.987	0.126	−705.819	−662.903	115.422
400	71.965	107.562	89.709	7.141	−704.651	−648.774	84.721
500	74.894	123.948	94.968	14.490	−703.521	−634.937	66.331
600	77.153	137.811	100.983	22.097	−702.473	−621.321	54.091
700	78.868	149.837	107.122	29.900	−701.547	−607.871	45.360
800	80.249	160.462	113.138	37.859	−700.813	−594.541	38.820
900	81.337	169.979	118.934	45.941	−700.414	−581.286	33.737
1000	82.132	178.592	124.476	54.115	−700.676	−568.045	29.672
1100	82.717	186.448	129.758	62.359	−701.795	−554.713	26.341
1200	83.178	193.666	134.787	70.655	−702.335	−541.337	23.564
1300	83.516	200.338	139.576	78.990	−701.212	−527.966	21.214
1373.000	83.685	204.906	142.929	85.094	--- CRYSTAL <--> LIQUID ---		
1400	83.764	206.536	144.140	87.354	−700.166	−514.679	19.203
1500	83.983	212.323	148.495	95.742	−699.200	−501.464	17.463
1600	84.182	217.750	152.656	104.150	−698.315	−488.311	15.942
1700	84.365	222.859	156.636	112.578	−698.461	−475.192	14.601
1800	84.517	227.685	160.451	121.022	−698.073	−462.071	13.409
1900	84.637	232.258	164.111	129.480	−711.865	−448.266	12.324
2000	84.726	236.602	167.628	137.949	−711.880	−434.392	11.345

PREVIOUS: CURRENT: September 1965

$S°(298.15\ K) = [92.537]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1373]\ K$

$\Delta_f H°(298.15\ K) = [-674.549]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [51.882]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(FeF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(FeF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1373\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for FeF_2(l) is estimated by comparison with those for $FeCl_2$(cr), $MgCl_2$(cr), MgF_2(cr), $CaCl_2$(cr) and CaF_2(cr). The $C_p°$ (FeF_2, l) value is assumed to be constant in the temperature range, 298.15–3000 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

$T_{vap} = 2110$ K is calculated as the temperature at which the fugacity of the reaction $FeF_2(l) = FeF_2(g)$ is 1 atm. The difference between $\Delta_f H°$ for FeF_2 (l) and FeF_2(g) at T_{vap} is $\Delta_{vap}H° = 224.43\ kJ·mol^{-1}$.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	98.324	92.537	92.537	0.	−674.549	−633.532	110.992
300	98.324	93.145	92.539	0.182	−674.472	−633.277	110.263
400	98.324	121.431	96.395	10.014	−670.486	−620.157	80.984
500	98.324	143.371	103.678	19.847	−666.872	−608.000	63.517
600	98.324	161.298	111.833	29.679	−663.599	−596.539	51.933
700	98.324	176.455	120.010	39.511	−660.644	−585.600	43.698
800	98.324	189.584	127.904	49.344	−658.036	−575.062	37.548
900	98.324	201.165	135.413	59.176	−655.886	−564.825	32.782
1000	98.324	211.524	142.516	69.009	−654.491	−554.792	28.979
1100	98.324	220.896	149.222	78.841	−654.021	−544.831	25.872
1200	98.324	229.451	155.556	88.673	−653.025	−534.968	23.287
1300	98.324	237.321	161.547	98.506	−650.405	−525.237	21.104
1373.000	98.324	242.693	165.720	105.684	--- CRYSTAL <--> LIQUID ---		
1400	98.324	244.608	167.223	108.338	−647.891	−515.703	19.241
1500	98.324	251.391	172.611	118.171	−645.480	−506.346	17.633
1600	98.324	257.737	177.735	128.003	−643.170	−497.147	16.230
1700	98.324	263.698	182.618	137.835	−641.911	−488.069	14.997
1800	98.324	269.318	187.280	147.668	−640.135	−479.072	13.902
1900	98.324	274.634	191.739	157.500	−652.553	−469.468	12.907
2000	98.324	279.677	196.011	167.333	−651.204	−459.867	12.010
2100	98.324	284.475	200.110	177.165	−649.861	−450.333	11.201
2200	98.324	289.049	204.050	186.997	−648.521	−440.863	10.467
2300	98.324	293.419	207.841	196.830	−647.179	−431.454	9.799
2400	98.324	297.604	211.495	206.662	−645.832	−422.104	9.187
2500	98.324	301.618	215.020	216.495	−644.477	−412.809	8.625
2600	98.324	305.474	218.425	226.327	−643.109	−403.570	8.108
2700	98.324	309.185	221.718	236.159	−641.725	−394.383	7.630
2800	98.324	312.761	224.906	245.992	−640.323	−385.248	7.187
2900	98.324	316.211	227.996	255.824	−638.899	−376.163	6.775
3000	98.324	319.544	230.992	265.657	−637.450	−367.128	6.392

PREVIOUS: CURRENT: September 1965

0 to 1373 K crystal
above 1373 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.757	−705.266	−705.266	INFINITE
100	33.447	30.853	138.926	−10.807	−706.646	−692.088	361.510
200	56.610	62.024	92.902	−6.176	−706.712	−677.397	176.918
298.15	68.116	86.985	86.985	0.	−705.841	−663.168	116.184
300	68.199	87.407	86.987	0.126	−705.819	−662.903	115.422
400	71.965	107.562	89.709	7.141	−704.651	−648.774	84.721
500	74.894	123.948	94.968	14.490	−703.521	−634.937	66.331
600	77.153	137.811	100.983	22.097	−702.473	−621.321	54.091
700	78.868	149.837	107.122	29.900	−701.547	−607.871	45.360
800	80.249	160.462	113.138	37.859	−700.813	−594.541	38.820
900	81.337	169.979	118.934	45.941	−700.414	−581.286	33.737
1000	82.132	178.592	124.476	54.115	−700.676	−568.045	29.672
1100	82.717	186.448	129.758	62.359	−701.795	−554.713	26.341
1200	83.178	193.666	134.787	70.655	−702.335	−541.337	23.564
1300	83.516	200.338	139.576	78.990	−701.212	−527.966	21.214
1373.000	83.685	204.906	142.929	85.094	CRYSTAL <--> LIQUID TRANSITION		
1373.000	98.324	242.693	142.929	136.975			
1400	98.324	244.608	144.872	139.630	−647.891	−515.703	19.241
1500	98.324	251.391	151.750	149.462	−645.480	−506.346	17.633
1600	98.324	257.737	158.178	159.295	−643.170	−497.147	16.230
1700	98.324	263.698	164.211	169.127	−641.911	−488.069	14.997
1800	98.324	269.318	169.896	178.960	−640.135	−479.072	13.902
1900	98.324	274.634	175.270	188.792	−652.553	−469.468	12.907
2000	98.324	279.677	180.365	198.624	−651.204	−459.867	12.010
2100	98.324	284.475	185.209	208.457	−649.861	−450.333	11.201
2200	98.324	289.049	189.826	218.289	−648.521	−440.863	10.467
2300	98.324	293.419	194.236	228.122	−647.179	−431.454	9.799
2400	98.324	297.604	198.456	237.954	−645.832	−422.104	9.187
2500	98.324	301.618	202.503	247.786	−644.477	−412.809	8.625
2600	98.324	305.474	206.390	257.619	−643.109	−403.570	8.108
2700	98.324	309.185	210.129	267.451	−641.725	−394.383	7.630
2800	98.324	312.761	213.731	277.284	−640.323	−385.248	7.187
2900	98.324	316.211	217.205	287.116	−638.899	−376.163	6.775
3000	98.324	319.544	220.561	296.948	−637.450	−367.128	6.392

PREVIOUS: CURRENT: September 1965

$S°(298.15\ K)$ = [265.205] J K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = −388.870 ± 14.2 kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = −389.530 ± 14.2 kJ·mol^{-1}

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[5]
[1000]	[10]
[4000]	[5]
[6000]	

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[550](1)
[190](2)
[714](1)

Point Group: [$D_{\infty h}$] σ = 2
Bond Distance: Fe–F = [1.8] Å
Bond Angle: F–Fe–F = [180]°
Rotational constant: B_o = 0.136932 cm^{-1}

Enthalpy of Formation

The rate of sublimation of FeF_2(cr) was measured between 965 and 1149 K by the Knudsen technique employing the high temperature magnetic mass spectrometer by Margrave.[1] The only vapor species of importance is FeF_2(g). From the vapor pressure data, the 3rd law enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, was reported as 75.6 ± 2.0 kcal·mol^{-1}. The sum of the values $\Delta_{sub}H°(298.15\ K)$ and $\Delta_f H°(298.15\ K)$ for FeF_2(cr) is $\Delta_f H°(FeF_2, g, 298.15\ K)$.

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The Fe–F bond distance was estimated from that in FeF_2(cr) reported by Baur.[2] The vibrational frequencies, ν_1 and ν_3, were estimated by Brewer *et al.*[3] The values of ν_2, electronic levels and quantum weights were estimated by comparison with those for $FeCl_2$(g). See the ideal gas table for details.

References

[1]J. L. Margrave, "Research in Fluorine Chemistry," William Marsh Rice University, Houston, Texas, Progress Report No. 7, Jan. 1 to March 31, (1965).
[2]W. H. Baur, Acta Cryst. **11**, 488 (1958).
[3]L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.671	−388.870	−388.870	INFINITE
100	38.559	214.824	309.258	−9.443	−388.972	−392.811	205.183
200	47.902	244.563	270.063	−5.100	−389.326	−396.519	103.560
250	52.104	255.709	266.103	−2.599	−389.465	−398.300	83.220
298.15	55.747	265.205	265.205	0.	−389.530	−399.994	70.077
300	55.876	265.551	265.206	0.103	−389.532	−400.059	69.656
350	58.995	274.407	265.899	2.978	−389.532	−401.813	59.967
400	61.390	282.449	267.473	5.991	−389.491	−403.570	52.701
450	63.115	289.786	269.551	9.106	−389.441	−405.332	47.050
500	64.284	296.500	271.915	12.293	−389.408	−407.100	42.529
600	65.466	308.344	277.026	18.791	−389.469	−410.636	35.749
700	65.785	318.466	282.241	25.358	−389.780	−414.144	30.904
800	65.747	327.251	287.331	31.936	−390.425	−417.585	27.265
900	65.601	334.986	292.205	38.504	−391.541	−420.919	24.429
1000	65.452	341.890	296.834	45.056	−393.425	−424.092	22.152
1100	65.339	348.123	301.218	51.595	−396.248	−427.008	20.277
1200	65.266	353.805	305.367	58.125	−398.555	−429.722	18.705
1300	65.229	359.027	309.296	64.650	−399.243	−432.292	17.370
1400	65.219	363.861	313.023	71.172	−400.038	−434.805	16.223
1500	65.226	368.360	316.564	77.694	−400.937	−437.258	15.227
1600	65.244	372.570	319.935	84.218	−401.937	−439.647	14.353
1700	65.265	376.526	323.148	90.743	−403.985	−441.952	13.580
1800	65.286	380.257	326.218	97.270	−405.514	−444.142	12.889
1900	65.304	383.788	329.156	103.800	−421.235	−445.542	12.249
2000	65.316	387.138	331.972	110.331	−423.187	−446.771	11.668
2100	65.323	390.325	334.676	116.863	−425.144	−447.902	11.141
2200	65.323	393.364	337.275	123.395	−427.104	−448.940	10.659
2300	65.316	396.267	339.777	129.927	−429.063	−449.888	10.217
2400	65.302	399.047	342.189	136.458	−431.017	−450.752	9.810
2500	65.283	401.712	344.517	142.988	−432.965	−451.534	9.434
2600	65.258	404.272	346.766	149.515	−434.903	−452.239	9.086
2700	65.228	406.734	348.942	156.039	−436.827	−452.869	8.761
2800	65.193	409.106	351.049	162.560	−438.736	−453.428	8.459
2900	65.155	411.393	353.090	169.078	−440.627	−453.919	8.176
3000	65.114	413.601	355.071	175.591	−442.497	−454.346	7.911
3100	65.070	415.736	356.994	182.100	−444.345	−454.710	7.662
3200	65.024	417.801	358.862	188.605	−794.468	−447.591	7.306
3300	64.976	419.801	360.678	195.105	−794.366	−436.753	6.913
3400	64.927	421.740	362.446	201.600	−794.269	−425.918	6.543
3500	64.877	423.621	364.167	208.090	−794.179	−415.085	6.195
3600	64.827	425.448	365.844	214.576	−794.094	−404.255	5.866
3700	64.776	427.224	367.479	221.056	−794.015	−393.427	5.554
3800	64.726	428.951	369.074	227.531	−793.943	−382.602	5.259
3900	64.675	430.631	370.631	234.001	−793.879	−371.778	4.979
4000	64.625	432.268	372.151	240.466	−793.822	−360.955	4.714
4100	64.575	433.863	373.637	246.926	−793.775	−350.134	4.461
4200	64.525	435.419	375.090	253.381	−793.739	−339.314	4.220
4300	64.477	436.936	376.511	259.831	−793.715	−328.495	3.990
4400	64.429	438.418	377.901	266.276	−793.704	−317.676	3.771
4500	64.382	439.865	379.262	272.717	−793.709	−306.857	3.562
4600	64.336	441.280	380.595	279.152	−793.730	−296.038	3.362
4700	64.290	442.663	381.901	285.584	−793.770	−285.218	3.170
4800	64.246	444.016	383.181	292.011	−793.829	−274.397	2.986
4900	64.203	445.340	384.436	298.433	−793.911	−263.575	2.810
5000	64.161	446.637	385.667	304.851	−794.017	−252.751	2.640
5100	64.119	447.907	386.875	311.265	−794.148	−241.924	2.478
5200	64.079	449.152	388.061	317.675	−794.308	−231.095	2.321
5300	64.040	450.372	389.225	324.081	−794.497	−220.262	2.171
5400	64.002	451.569	390.368	330.483	−794.719	−209.425	2.026
5500	63.965	452.743	391.492	336.881	−794.975	−198.584	1.886
5600	63.928	453.895	392.596	343.276	−795.269	−187.738	1.751
5700	63.893	455.026	393.681	349.667	−795.602	−176.887	1.621
5800	63.859	456.137	394.748	356.055	−795.979	−166.029	1.495
5900	63.825	457.228	395.798	362.439	−796.401	−155.164	1.374
6000	63.793	458.301	396.831	368.820	−796.873	−144.292	1.256

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 104.264 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 469.85\ K$
$T_{fus} = 511.95\ K$

$\Delta_f H°(0\ K) = -926.386 \pm 1.26\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -931.233 \pm 1.26\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 11.221 \pm 0.04\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 6.619 \pm 0.013\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Davis and Westrum[1] measured directly the enthalpy of the decomposition reaction $KHF_2(cr) \rightarrow KF(cr) + HF(g)$ in an adiabatic calorimeter as $\Delta_{dcm}H° = 18.52 \pm 0.05\ kcal \cdot mol^{-1}$ at 500 K. Reducing to 298.15 K, we obtain $\Delta_{dcm}H°(298.15\ K) = 21.533 \pm 0.05\ kcal \cdot mol^{-1}$ which leads to the enthalpy of formation, $\Delta_f H°(KHF_2, cr, 298.15\ K) = -222.57 \pm 0.3\ kcal \cdot mol^{-1}$, using JANAF auxiliary data. This value is adopted in the tabulation.

Westrum and Pitzer[3] measured the dissociation vapor pressures of KHF_2 (cr, l) by a static method. Their pressure data have been analyzed by both 2nd law and 3rd law methods as given below. The enthalpy of formation derived from the 3rd law analysis differs by about 0.3 $kcal \cdot mol^{-1}$ from the value adopted, which is greater than the combined experimental errors.

Reaction	T/K	Data Points	$\Delta_{dcm}H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\ K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
$KHF_2(cr) \rightarrow KF(cr) + HF(g)$	478–500	14	21.21 ± 0.12	21.31 ± 0.01	0.2 ± 0.2	−222.35
$KHF_2(l) \rightarrow KF(cr) + HF(g)$	504–577	5	19.82 ± 0.08	17.73 ± 0.24	−3.9 ± 0.2	−222.28**

**This value is derived from the adopted heat of melting, $\Delta_{fus}H°(298.15\ K) = 3.504\ kcal \cdot mol^{-1}$ and $\Delta_f H°(KHF_2,l,298.15\ K) = -218.773\ kcal \cdot mol^{-1}$. The latter is calculated from the 3rd law $\Delta_{dcm}H°(298.15\ K)$.

Heat Capacity and Entropy

Westrum and Pitzer[3] measured both low temperature $C_p°$ data (16–315 K) in an adiabatic calorimeter and high temperature enthalpy data (321.6–465 K for α phase and 471.3–505.9 K for β phase) in a drop calorimeter. We use their experimental $C_p°$ data to derive $S°(298.15\ K) = 24.92 \pm 0.1\ cal\ K^{-1} \cdot mol^{-1}$, based on $S° = 0.0643\ cal\ K^{-1} \cdot mol^{-1}$ at 15 K. The low temperature $C_p°$ and high temperature enthalpy data for the α phase are smoothly joined at 298.15 K by a polynomial curve fitting method. The deviations of the observed enthalpy data from the adopted values are 0.68% at 321.6 K and 0.09% at 463.7 K. The constant heat capacity, 23.96 $cal\ K^{-1} \cdot mol^{-1}$, in the β phase is derived from the measured enthalpy data,[3] and is assumed to be the same when the temperature is above the melting point.

Transition and Fusion Data

Davis and Westrum[1] measured the heat of the αβ transition, $\Delta_{trs}H° = 2.682 \pm 0.01\ kcal \cdot mol^{-1}$ at 196.7°C, and the heat of melting, $\Delta_{fus}H° = 1.582 \pm 0.003\ kcal \cdot mol^{-1}$ at 238.8°C in an adiabatic calorimeter. Their data are adopted in the tabulation. Based on the drop calorimetric measurements,[3] we have derived $\Delta_{fus}H° = 1.554\ kcal \cdot mol^{-1}$ which is in good agreement with the value adopted.

References

[1]M. L. Davis and E. F. Westrum, Jr., J. Phys. Chem. **65**, 338 (1961).
[2]JANAF Thermochemical Tables: HF(g), 12–31–68; KF(cr), 6–30–69.
[3]E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. **71**, 1940 (1949).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−15.294	−926.386	−926.386	INFINITE
100	48.961	34.988	165.420	−13.043	−930.274	−908.140	474.363
200	67.070	75.565	110.999	−7.087	−931.188	−885.531	231.277
298.15	76.940	104.264	104.264	0.	−931.233	−863.095	151.211
300	77.111	104.741	104.266	0.142	−931.230	−862.672	150.205
400	86.065	128.152	107.398	8.302	−933.221	−839.415	109.616
469.850	92.450	142.501	111.566	14.535	ALPHA <--> BETA		
469.850	100 .249	166.384	111.566	25.757	TRANSITION		
500	100.249	172.619	115.061	28.779	−920.678	−816.803	85.331
511.950	100.249	174.987	116.432	29.977	---- BETA <--> LIQUID ----		
600	100.249	190.897	126.224	38.804	−918.631	−796.221	69.317
700	100.249	206.350	136.595	48.829	−916.622	−775.979	57.904
800	100.249	219.737	146.169	58.854	−914.660	−756.021	49.363
900	100.249	231.544	155.012	68.879	−912.760	−736.306	42.734
1000	100.249	242.106	163.203	78.903	−910.939	−716.799	37.442
1100	100.249	251.661	170.817	88.928	−988.173	−692.859	32.901
1200	100.249	260.384	177.923	98.953	−985.512	−666.130	28.996
1300	100.249	268.408	184.579	108.978	−982.895	−639.621	25.700
1400	100.249	275.837	190.835	119.003	−980.322	−613.312	22.883
1500	100.249	282.754	196.735	129.028	−977.791	−587.186	20.448
1600	100.249	289.224	202.316	139.053	−975.301	−561.227	18.322
1700	100.249	295.301	207.609	149.077	−972.851	−535.423	16.452
1800	100.249	301.031	212.641	159.102	−970.438	−509.761	14.793
1900	100.249	306.451	217.437	169.127	−968.060	−484.233	13.313
2000	100.249	311.594	222.017	179.152	−965.716	−458.829	11.983

PREVIOUS: December 1963 CURRENT: June 1971

$S°(298.15\ K) = [132.764]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-916.573]\ kJ·mol^{-1}$
$T_{fus} = 511.95\ K$ $\Delta_{fus}H° = 6.619 \pm 0.013\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(511.95\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Westrum and Pitzer[1] measured high temperature enthalpy data by drop calorimetry in a narrow range of 510.6–523.2 K and derived a constant heat capacity of approximately 25 cal $K^{-1}·mol^{-1}$ which is adopted in the tabulation.

A glass transition is assumed at 314 K. Below 314 K, the heat capacities are assumed to be the same as those of the crystal. Between 314 K and the melting point, the $C_p°$ is assumed to be the same as that of the liquid.

The entropy is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

The decomposition temperature, $T_{dcm} = 750$ K, is calculated as the temperature at which $\Delta_f G = 0$ for $KHF_2(l) \rightarrow KF(cr) + HF(g)$. At T_{dcm}, the vapor pressure of HF(g) reaches one atmosphere.

Westrum and Pitzer[1] determined the decomposition vapor pressures of KHF_2(cr, l) by a static method. Their data lead to the decomposition temperature, 700 K when the pressure of HF reaches one atmosphere. JANAF analyses of their data are given in KHF_2(cr) table. Their data over the crystal phase are suspected to be high by approximately 11.5%; and the data over the liquid phase are probably in error as indicated by the 3rd law drift (3.9 cal $K^{-1}·mol^{-1}$) in the JANAF analyses.

Reference

[1]E. F. Westrum, Jr. and K. S. Pitzer, J. Amer. Chem. Soc. **71**, 1940 (1949).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	76.944	132.764	132.764	0.	−916.573	−856.932	150.131
300	76.944	133.240	132.766	0.142	−916.569	−856.562	149.141
314.000	78.408	136.784	132.866	1.230	GLASS <--> LIQUID		
314.000	104.600	136.784	132.866	1.230	TRANSITION		
400	104.600	162.105	136.540	10.226	−916.636	−836.412	109.224
500	104.600	185.446	144.074	20.686	−914.111	−816.649	85.315
511.950	104.600	187.916	145.069	21.936	---- BETA <--> LIQUID ----		
600	104.600	204.517	152.607	31.146	−911.629	−797.391	69.419
700	104.600	220.641	161.204	41.606	−909.185	−778.545	58.096
800	104.600	234.608	169.526	52.066	−906.788	−760.046	49.626
900	104.600	246.928	177.455	62.526	−904.452	−741.844	43.056
1000	104.600	257.949	184.963	72.986	−902.197	−723.898	37.813
1100	104.600	267.918	192.059	83.446	−978.995	−701.564	33.314
1200	104.600	277.020	198.765	93.906	−975.898	−676.480	29.446
1300	104.600	285.392	205.111	104.366	−972.847	−651.652	26.184
1400	104.600	293.144	211.125	114.826	−969.839	−627.058	23.396
1500	104.600	300.361	216.837	125.286	−966.873	−602.678	20.987
1600	104.600	307.111	222.270	135.746	−963.948	−578.494	18.886
1700	104.600	313.453	227.449	146.206	−961.062	−554.491	17.037
1800	104.600	319.431	232.395	156.666	−958.214	−530.658	15.399
1900	104.600	325.087	237.126	167.126	−955.401	−506.982	13.938
2000	104.600	330.452	241.659	177.586	−952.622	−483.452	12.626

PREVIOUS: December 1963 CURRENT: June 1971

Potassium Fluoride ($K(HF_2)$) **CRYSTAL(α–β)-LIQUID** M_r = 78.103046

0	to	469.85 K	crystal, alpha
467.85	to	511.95 K	crystal, beta
above		511.95 K	liquid

Refer to the individual tables for details.

Potassium Fluoride ($K(HF_2)$) $F_2H_1K_1$(cr,l)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.294	−926.386	−926.386	INFINITE
100	48.961	34.988	165.420	−13.043	−930.274	−908.140	474.363
200	67.070	75.565	110.999	−7.087	−931.188	−885.531	231.277
298.15	76.940	104.264	104.264	0.	−931.233	−863.095	151.211
300	77.111	104.741	104.266	0.142	−931.230	−862.672	150.205
400	86.065	128.152	107.398	8.302	−933.221	−839.415	109.616
469.850	92.450	142.501	111.566	14.535	ALPHA <--> BETA		
469.850	100.249	166.384	111.566	25.757	TRANSITION		
500	100.249	172.619	115.061	28.779	−920.678	−816.803	85.331
511.950	100.249	174.987	116.432	29.977	BETA <--> LIQUID		
511.950	104.600	187.916	116.432	36.596	TRANSITION		
600	104.600	204.517	128.173	45.806	−911.629	−797.391	69.419
700	104.600	220.641	140.261	56.266	−909.185	−778.545	58.096
800	104.600	234.608	151.200	66.726	−906.788	−760.046	49.626
900	104.600	246.928	161.166	77.186	−904.452	−741.844	43.056
1000	104.600	257.949	170.303	87.646	−902.197	−723.898	37.813
1100	104.600	267.918	178.731	98.106	−978.995	−701.564	33.314
1200	104.600	277.020	186.548	108.566	−975.898	−676.480	29.446
1300	104.600	285.392	193.834	119.026	−972.847	−651.652	26.184
1400	104.600	293.144	200.654	129.486	−969.839	−627.058	23.396
1500	104.600	300.361	207.063	139.946	−966.873	−602.678	20.987
1600	104.600	307.111	213.107	150.406	−963.948	−578.494	18.886
1700	104.600	313.453	218.826	160.866	−961.062	−554.491	17.037
1800	104.600	319.431	224.250	171.326	−958.214	−530.658	15.399
1900	104.600	325.087	229.410	181.786	−955.401	−506.982	13.938
2000	104.600	330.452	234.329	192.246	−952.622	−483.452	12.626

PREVIOUS: CURRENT: June 1971

Potassium Fluoride ($K(HF_2)$) $F_2H_1K_1$(cr,l)

$S°(298.15\ K) = 238.849 \pm 8.4\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -566.600 \pm 3.3\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -572.664 \pm 3.3\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[4000](1)
[3400](1)
[1200](2)
[720](1)
[350](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_s
Bond Distances: F–H = 0.92 Å; H ··· F = 1.87 Å
Bond Angles: H ··· F–H = 108°; F–H ··· F = 180°
Product of the Moments of Inertia: $I_A I_B I_C = 1.98556 \times 10^{-116}\ g^3\cdot cm^6$

Enthalpy of Formation

The enthalpy of 2 HF(g) → H_2F_2(g) was taken as the mean of the 3rd law values which were obtained from the following equilibrium data. Briegleb and Strohmeier[1] measured the vapor density of associated HF(g) between 26 and 56°C and between 30 and 700 torr. Franck and Meyer[2] measured the heat capacity between 20 and 100°C and between 100 and 700 torr. Their 2nd law values differed by 1.2 kcal·mol^{-1}; and using the molecular constants discussed below gave respectively mean 3rd law values which differed by 0.34 kcal·mol^{-1}, a 0.14 kcal·mol^{-1} temperature trend for Briegleb and Strohmeier,[1] and a 0.02 kcal·mol^{-1} temperature trend for Franck and Meyer.[2] $\Delta_f H°(H_2F_2, g, 298.15\ K)$ was calculated using auxiliary JANAF data.[3]

Heat Capacity and Entropy

The structure of the semi rigid hydrogen bonded dimer is taken from Dyke *et al.*[4] Using bond distances and angles given by these authors we obtain $I_A = 0.1203 \times 10^{-39}$, $I_B = 12.7869 \times 10^{-39}$, and $I_C = 12.9022 \times 10^{-39}$ ·cm^2. Dyke *et al.*[4] observed a doubling of the rotational energy levels of the dimer and attributed this to a tunneling motion involving breaking of the hydrogen bond, interchange of the two HF units, and formation of a new hydrogen bond. Thus there are two identical configurations for the dimer separated by a low energy barrier so that quantum mechanical tunneling occurs at a significant rate. Therefore the overall symmetry number is 2 even though the external symmetry number is 1.

Reliable experimental values of the vibrational frequencies of H_2F_2(g) are not available. The estimated frequencies are similar to those used for the higher polymers which were obtained from data on HF solid. The infrared absorption bands observed in the vapor (350 to 400 cm^{-1}, 700 to 800 cm^{-1}, and 1000–1200 cm^{-1} regions) are largely due to the higher polymers, such as the tetramer and hexamer. Calculated values (610, 443, and 144 cm^{-1}) were obtained from force constants given in a paper on theory of molecular interactions of the HF polymers by Del Bene and Pople.[5] The potential energy surface computed for the dimer suggests very anharmonic low frequency motions for the external hydrogen (estimated at 600 ± 200 cm^{-1}) and for the hydrogen bond stretching mode.

The National Bureau of Standards prepared this table[6] by critical analysis of data existing in 1972. Using our $I_A I_B I_C$ with other molecular constants and $\Delta_f H°$ selected by NBS,[6] we recalculate the table in terms of 1973 fundamental constants,[7] 1975 atomic weights[8] and current JANAF reference states for the elements.

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[7]CODATA Task Group on Fundamental Constants, CODATA Bulletin **11**, (December 1973).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.228	−566.600	−566.600	INFINITE
100	34.675	196.439	275.181	−7.874	−569.152	−561.686	293.395
200	39.777	222.014	242.789	−4.155	−571.056	−553.446	144.545
250	42.385	231.170	239.574	−2.101	−571.901	−548.945	114.696
298.15	44.874	238.849	238.849	0.	−572.664	−544.453	95.386
300	44.968	239.127	238.850	0.083	−572.692	−544.278	94.767
350	47.433	246.246	239.407	2.394	−573.419	−539.484	80.514
400	49.702	252.731	240.673	4.823	−574.077	−534.590	69.810
450	51.736	258.705	242.349	7.360	−574.668	−529.618	61.477
500	53.536	264.251	244.265	9.993	−575.196	−524.584	54.803
600	56.536	274.287	248.450	15.502	−576.089	−514.374	44.780
700	58.952	283.190	252.789	21.281	−576.800	−504.030	37.611
800	61.000	291.199	257.098	27.281	−577.363	−493.594	32.228
900	62.809	298.490	261.298	33.473	−577.799	−483.096	28.038
1000	64.449	305.194	265.357	39.837	−578.129	−472.555	24.684
1100	65.953	311.408	269.264	46.358	−578.366	−461.985	21.938
1200	67.335	317.207	273.020	53.023	−578.525	−451.397	19.649
1300	68.602	322.647	276.631	59.821	−578.617	−440.799	17.712
1400	69.761	327.774	280.103	66.740	−578.653	−430.196	16.051
1500	70.818	332.624	283.444	73.770	−578.642	−419.592	14.611
1600	71.778	337.225	286.663	80.900	−578.591	−408.990	13.352
1700	72.651	341.603	289.767	88.123	−578.508	−398.392	12.241
1800	73.442	345.779	292.763	95.428	−578.396	−387.801	11.254
1900	74.159	349.769	295.659	102.808	−578.261	−377.216	10.370
2000	74.809	353.590	298.461	110.257	−578.103	−366.638	9.576
2100	75.399	357.254	301.174	117.768	−577.924	−356.069	8.857
2200	75.934	360.774	303.804	125.335	−577.726	−345.509	8.203
2300	76.421	364.161	306.355	132.953	−577.507	−334.959	7.607
2400	76.864	367.423	308.832	140.618	−577.267	−324.418	7.061
2500	77.268	370.569	311.239	148.325	−577.004	−313.888	6.558
2600	77.637	373.606	313.579	156.071	−576.719	−303.369	6.095
2700	77.975	376.543	315.857	163.852	−576.409	−292.862	5.666
2800	78.284	379.384	318.076	171.665	−576.072	−282.366	5.268
2900	78.568	382.137	320.237	179.507	−575.709	−271.883	4.897
3000	78.829	384.805	322.345	187.377	−575.317	−261.413	4.552
3100	79.069	387.393	324.402	195.273	−574.897	−250.956	4.229
3200	79.291	389.907	326.410	203.191	−574.447	−240.514	3.926
3300	79.495	392.350	328.371	211.130	−573.967	−230.085	3.642
3400	79.685	394.726	330.288	219.089	−573.456	−219.672	3.375
3500	79.860	397.039	332.163	227.067	−572.915	−209.275	3.123
3600	80.023	399.291	333.996	235.061	−572.344	−198.893	2.886
3700	80.175	401.485	335.791	243.071	−571.744	−188.527	2.662
3800	80.316	403.625	337.548	251.095	−571.114	−178.179	2.449
3900	80.448	405.713	339.269	259.134	−570.455	−167.847	2.248
4000	80.571	407.752	340.956	267.185	−569.769	−157.532	2.057
4100	80.686	409.743	342.609	275.248	−569.055	−147.235	1.876
4200	80.793	411.688	344.231	283.322	−568.315	−136.955	1.703
4300	80.894	413.591	345.822	291.406	−567.550	−126.694	1.539
4400	80.989	415.451	347.383	299.500	−566.760	−116.451	1.382
4500	81.077	417.272	348.916	307.604	−565.946	−106.226	1.233
4600	81.161	419.055	350.422	315.716	−565.109	−96.019	1.090
4700	81.240	420.802	351.900	323.836	−564.251	−85.830	0.954
4800	81.314	422.513	353.354	331.963	−563.371	−75.660	0.823
4900	81.384	424.190	354.782	340.098	−562.470	−65.509	0.698
5000	81.450	425.835	356.187	348.240	−561.550	−55.376	0.579
5100	81.513	427.449	357.569	356.388	−560.610	−45.262	0.464
5200	81.572	429.032	358.928	364.542	−559.652	−35.166	0.353
5300	81.628	430.586	360.265	372.703	−558.675	−25.089	0.247
5400	81.681	432.113	361.582	380.868	−557.681	−15.031	0.145
5500	81.732	433.612	362.878	389.039	−556.668	−4.992	0.047
5600	81.780	435.085	364.154	397.214	−555.639	5.030	−0.047
5700	81.825	436.533	365.411	405.395	−554.592	15.032	−0.138
5800	81.869	437.956	366.650	413.579	−553.527	25.016	−0.225
5900	81.910	439.356	367.870	421.768	−552.446	34.982	−0.310
6000	81.949	440.733	369.073	429.961	−551.347	44.929	−0.391

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 262.130 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-782.254 \pm 20.9]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-790.776 \pm 20.9]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
2246(1)	322(1)	730(1)
982(1)	730(1)	981(1)
869(1)	2251(1)	903(1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distances: Si–H = 1.471 Å; Si–F = 1.5767 Å

Bond Angles: H–Si–H = 112.02°; F–Si–F = 107.93°

Product of the Moments of Inertia: $I_A I_B I_C = 4.815754 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

There are no reported experimental studies leading to the enthalpy of formation of SiH_2F_2(g). We estimate this value via a linear interpolation between the established $\Delta_f H°(298.15\ K)$ values of SiH_4(g) and SiF_4(g).[1] The reasonableness of this approach has been demonstrated by Lapidus *et al.*,[2] Hunt and Sirtl,[3] and Seiter and Sirtl.[4]

Heat Capacity and Entropy

The adopted vibrational frequencies are from the gas phase infrared study of Cradock *et al.*[6] Two frequencies (ν_5 and ν_6) were quite uncertain and were discussed in terms of a strong Coriolis interaction.

These frequencies appear quite reasonable when a comparison of the dihalosilanes and dihalomethanes (halogen is fluorine, chlorine, and bromine) is made.[1,5]

The adopted bond distances and bond angles are obtained from the microwave spectrum study by Laurie.[7] The individual moments of inertia are: $I_A = 3.4021 \times 10^{-39}$, $I_B = 10.7552 \times 10^{-39}$, and $I_C = 13.1614 \times 10^{-39}\ g \cdot cm^2$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.988	−782.254	−782.254	INFINITE
100	35.089	216.460	302.698	−8.624	−785.062	−779.215	407.020
200	42.974	242.890	266.723	−4.766	−788.006	−772.238	201.688
250	48.646	253.078	262.992	−2.478	−789.467	−768.126	160.491
298.15	54.268	262.130	262.130	0.	−790.776	−763.895	133.831
300	54.479	262.466	262.131	0.101	−790.824	−763.728	132.977
350	59.903	271.278	262.814	2.962	−792.035	−759.114	113.292
400	64.714	279.598	264.397	6.081	−793.090	−754.338	98.506
450	68.914	287.469	266.527	9.424	−793.999	−749.437	86.992
500	72.575	294.923	268.998	12.963	−794.774	−744.443	77.771
600	78.609	308.712	274.487	20.535	−795.981	−734.257	63.923
700	83.350	321.200	280.283	28.642	−796.811	−723.899	54.018
800	87.139	332.586	286.120	37.173	−797.351	−713.443	46.583
900	90.201	343.033	291.871	46.045	−797.670	−702.934	40.797
1000	92.697	352.670	297.475	55.195	−797.825	−692.398	36.167
1100	94.746	361.604	302.904	64.570	−797.865	−681.853	32.378
1200	96.440	369.923	308.146	74.132	−797.826	−671.307	29.221
1300	97.850	377.699	313.201	83.848	−797.739	−660.767	26.550
1400	99.033	384.995	318.071	93.694	−797.631	−650.235	24.261
1500	100.033	391.863	322.764	103.649	−797.519	−639.711	22.277
1600	100.882	398.347	327.287	113.696	−797.418	−629.194	20.541
1700	101.609	404.485	331.649	123.821	−847.516	−618.235	18.996
1800	102.236	410.311	335.859	134.014	−847.236	−604.756	17.550
1900	102.778	415.854	339.924	144.266	−846.949	−591.293	16.256
2000	103.251	421.138	343.854	154.568	−846.658	−577.845	15.092
2100	103.665	426.186	347.655	164.914	−846.364	−564.411	14.039
2200	104.029	431.017	351.335	175.299	−846.067	−550.992	13.082
2300	104.351	435.648	354.901	185.718	−845.766	−537.586	12.209
2400	104.637	440.096	358.359	196.168	−845.461	−524.194	11.409
2500	104.892	444.372	361.714	206.645	−845.148	−510.814	10.673
2600	105.120	448.491	364.973	217.145	−844.827	−497.447	9.994
2700	105.325	452.462	368.140	227.668	−844.495	−484.092	9.365
2800	105.510	456.296	371.221	238.210	−844.150	−470.750	8.782
2900	105.677	460.001	374.219	248.769	−843.789	−457.421	8.239
3000	105.828	463.586	377.138	259.345	−843.412	−444.104	7.733
3100	105.966	467.059	379.983	269.934	−843.016	−430.801	7.259
3200	106.092	470.425	382.757	280.537	−842.601	−417.510	6.815
3300	106.207	473.691	385.463	291.152	−842.165	−404.232	6.398
3400	106.313	476.864	388.105	301.779	−841.707	−390.969	6.007
3500	106.410	479.947	390.685	312.415	−841.227	−377.719	5.637
3600	106.499	482.946	393.207	323.060	−1224.876	−354.022	5.137
3700	106.581	485.865	395.672	333.714	−1223.937	−329.844	4.657
3800	106.657	488.708	398.083	344.376	−1222.977	−305.692	4.202
3900	106.728	491.480	400.442	355.046	−1221.996	−281.566	3.771
4000	106.794	494.183	402.752	365.722	−1220.994	−257.465	3.362
4100	106.855	496.820	405.014	376.404	−1219.972	−233.389	2.973
4200	106.911	499.396	407.231	387.092	−1218.928	−209.339	2.604
4300	106.964	501.912	409.404	397.786	−1217.865	−185.314	2.251
4400	107.014	504.372	411.534	408.485	−1216.781	−161.313	1.915
4500	107.060	506.777	413.624	419.189	−1215.678	−137.338	1.594
4600	107.103	509.131	415.675	429.897	−1214.556	−113.387	1.288
4700	107.144	511.435	417.688	440.609	−1213.416	−89.461	0.994
4800	107.182	513.691	419.665	451.326	−1212.258	−65.559	0.713
4900	107.218	515.901	421.606	462.046	−1211.082	−41.682	0.444
5000	107.252	518.068	423.514	472.769	−1209.889	−17.828	0.186
5100	107.284	520.192	425.389	483.496	−1208.680	6.001	−0.061
5200	107.314	522.275	427.232	494.226	−1207.455	29.806	−0.299
5300	107.343	524.320	429.045	504.959	−1206.214	53.588	−0.528
5400	107.370	526.327	430.828	515.695	−1204.957	77.346	−0.748
5500	107.395	528.297	432.582	526.433	−1203.686	101.080	−0.960
5600	107.420	530.232	434.308	537.174	−1202.400	124.792	−1.164
5700	107.443	532.134	436.008	547.917	−1201.099	148.480	−1.361
5800	107.464	534.003	437.681	558.662	−1199.785	172.146	−1.550
5900	107.485	535.840	439.330	569.410	−1198.456	195.788	−1.733
6000	107.505	537.646	440.953	580.159	−1197.113	219.408	−1.910

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [116.315 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-422.584 \pm 41.8]\ kJ \cdot mol^{-1}$

$T_{fus} = 918\ K$ $\Delta_{fus} H° = [23.012 \pm 4.2]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Estimated by comparison of the mercurous and mercuric halides.

Heat Capacity and Entropy

The heat capacity is assumed to be a linear function of temperature and was estimated to be 7.0 cal $K^{-1} \cdot g\text{-atom}^{-1}$ at the melting point. The entropy is estimated by comparison with the other mercuric and mercurous halides and use of additive entropy constants for the halogens.[1]

Fusion Data

T_{fus} was given by Ruff and Bahlau.[2] The heat of melting was from Brewer.[3]

References

[1]K. K. Kelley, U.S. Bur. Mines, personal communication, (1960).
[2]O. Ruff and G. Bahlau, Ber. **51**, 1752 (1918).
[3]L. Brewer, in 'Thermodynamics,' McGraw Hill, National Nuclear Energy Series 4–19B paper 7 (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.856	116.315	116.315	0.	−422.584	−374.134	65.547
300	74.894	116.778	116.317	0.139	−422.555	−373.833	65.090
400	76.986	138.610	119.279	7.732	−420.946	−357.833	46.728
500	79.078	156.014	124.943	15.536	−419.236	−342.250	35.755
600	81.170	170.616	131.370	23.548	−417.411	−327.022	28.470
700	83.262	183.286	137.901	31.770	−474.215	−305.539	22.800
800	85.354	194.541	144.290	40.200	−471.472	−281.627	18.388
900	87.446	204.714	150.448	48.840	−468.565	−258.070	14.978
918.000	87.822	206.450	151.529	50.418	--- CRYSTAL <--> LIQUID ---		
1000	89.538	214.036	156.347	57.689	−465.485	−234.845	12.267
1100	91.630	222.668	161.988	66.748	−462.225	−211.937	10.064
1200	93.722	230.731	167.384	76.015	−458.782	−189.334	8.241
1300	95.814	238.315	172.552	85.492	−455.153	−167.026	6.711
1400	97.906	245.492	177.508	95.178	−451.336	−145.004	5.410
1500	99.998	252.318	182.269	105.073	−447.330	−123.262	4.292
1600	102.090	258.839	186.853	115.178	−443.133	−101.793	3.323
1700	104.182	265.091	191.272	125.491	−438.743	−80.593	2.476
1800	106.274	271.105	195.541	136.014	−434.159	−59.657	1.731
1900	108.366	276.907	199.672	146.746	−429.378	−38.981	1.072
2000	110.458	282.518	203.675	157.687	−424.396	−18.561	0.485

PREVIOUS: CURRENT: March 1962

Mercury Fluoride (HgF_2) LIQUID $M_r = 238.586806$

$S°(298.15\ K) = [134.246]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 918\ K$

$\Delta_f H°(298.15\ K) = [-404.897]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [23.012 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(HgF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(HgF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(918\ K)\ H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated by analogy with mercuric iodide and bromide. A glass type transitiion is assumed at 613 K below which the heat capacity is that of HgF_2(cr). The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion and Vaporization Data

T_{fus} was given by Ruff and Bahlan.[1] $T_{vap} = 920\ K$, $\Delta_{fus}H° = 23.0 \pm 4.2\ kJ·mol^{-1}$, and $\Delta_{vap}H° = 92.0 \pm 16.7\ kJ·mol^{-1}$ were all taken from Brewer.[2]

References

[1]O. Ruff and G. Bahlan, Ber. **51**, 1752 (1918).
[2]L. Brewer, in 'Thermodynamics' McGraw Hill, New York, National Nuclear Energy Series 4–19B paper 7, (1950).

Mercury Fluoride (HgF_2) $F_2Hg_1(l)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.856	134.246	134.246	0.	−404.897	−361.793	63.385
300	74.894	134.709	134.248	0.139	−404.868	−361.525	62.947
400	76.986	156.541	137.210	7.732	−403.259	−347.318	45.355
500	79.078	173.945	142.874	15.536	−401.549	−333.528	34.843
600	81.170	188.548	149.301	23.548	−399.724	−320.093	27.867
613.000	81.442	190.290	150.152	24.605	GLASS <--> LIQUID		
613.000	102.090	190.290	150.152	24.605	TRANSITION		
700	102.090	203.839	156.001	33.487	−454.810	−300.521	22.425
800	102.090	217.471	162.852	43.696	−450.290	−278.789	18.203
900	102.090	229.496	169.602	53.905	−445.813	−257.621	14.952
918.000	102.090	231.517	170.796	55.742	--- CRYSTAL <--> LIQUID ---		
1000	102.090	240.252	176.138	64.114	−441.373	−236.949	12.377
1100	102.090	249.982	182.416	74.323	−436.963	−216.720	10.291
1200	102.090	258.865	188.422	84.532	−432.578	−196.892	8.570
1300	102.090	267.037	194.159	94.741	−428.217	−177.428	7.129
1400	102.090	274.602	199.638	104.949	−423.877	−158.300	5.906
1500	102.090	281.646	204.873	115.158	−419.557	−139.481	4.857
1600	102.090	288.234	209.880	125.367	−415.256	−120.950	3.949
1700	102.090	294.424	214.673	135.576	−410.971	−102.687	3.155
1800	102.090	300.259	219.267	145.785	−406.700	−84.676	2.457
1900	102.090	305.779	223.676	155.994	−402.442	−66.902	1.839
2000	102.090	311.015	227.913	166.203	−398.193	−49.351	1.289

PREVIOUS: CURRENT: March 1962

Mercury Fluoride (HgF_2) $F_2Hg_1(l)$

0 to 918 K crystal
above 918 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.856	116.315	116.315	0.	−422.584	−374.134	65.547
300	74.894	116.778	116.317	0.139	−422.555	−373.833	65.090
400	76.986	138.610	119.279	7.732	−420.946	−357.833	46.728
500	79.078	156.014	124.943	15.536	−419.236	−342.250	35.755
600	81.170	170.616	131.370	23.548	−417.411	−327.022	28.470
700	83.262	183.286	137.901	31.770	−474.215	−305.539	22.800
800	85.354	194.541	144.290	40.200	−471.472	−281.627	18.388
900	87.446	204.714	150.448	48.840	−468.565	−258.070	14.978
918.000	87.822	206.450	151.529	50.418	CRYSTAL <--> LIQUID TRANSITION		
918.000	102.090	231.517	151.529	73.430			
1000	102.090	240.252	158.451	81.801	−441.373	−236.949	12.377
1100	102.090	249.982	166.337	92.010	−436.963	−216.720	10.291
1200	102.090	258.865	173.683	102.219	−432.578	−196.892	8.570
1300	102.090	267.037	180.554	112.428	−428.217	−177.428	7.129
1400	102.090	274.602	187.005	122.637	−423.877	−158.300	5.906
1500	102.090	281.646	193.082	132.846	−419.557	−139.481	4.857
1600	102.090	288.234	198.825	143.055	−415.256	−120.950	3.949
1700	102.090	294.424	204.268	153.264	−410.971	−102.687	3.155
1800	102.090	300.259	209.441	163.473	−406.700	−84.676	2.457
1900	102.090	305.779	214.367	173.682	−402.442	−66.902	1.839
2000	102.090	311.015	219.070	183.891	−398.193	−49.351	1.289

PREVIOUS: CURRENT: March 1962

Mercury Fluoride (HgF_2) IDEAL GAS $M_r = 238.586806$

$S°(298.15\ K) = 271.737\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -288.672\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-293.654 \pm 41.8]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[600](1)
[120](2)
[593](1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: $D_{\infty h}$

Bond Distance: Hg–F = [1.96] Å

Bond Angle: F–Hg–F = [180°]

Rotational Constant: $B_0 = [0.115488]\ cm^{-1}$

Enthalpy of Formation

Estimated by comparison with the other gaseous mercuric halides and with the crystalline mercurous mercuric fluorides.

Heat Capacity and Entropy

Vibrational constants were estimated by analogy with the other mercuric halides and the mercurous halides. The bond length was estimated by assuming the mercurous bond to be 0.965 of the mercuric bond by analogy with the mercury chlorides.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.186	−288.672	−288.672	INFINITE
100	42.378	219.689	316.215	−9.653	−289.751	−290.961	151.983
200	49.043	251.161	276.531	−5.074	−290.687	−291.784	76.206
250	51.842	262.416	272.614	−2.550	−293.362	−291.860	60.981
298.15	53.968	271.737	271.737	0.	−293.654	−291.543	51.077
300	54.040	272.071	271.738	0.100	−293.664	−291.530	50.760
350	55.705	280.532	272.402	2.845	−293.897	−291.155	43.453
400	56.961	288.056	273.897	5.664	−294.085	−290.750	37.968
450	57.915	294.823	275.853	8.537	−294.246	−290.323	33.700
500	58.649	300.965	278.062	11.451	−294.390	−289.880	30.284
600	59.677	311.756	282.803	17.372	−294.658	−288.952	25.156
700	60.339	321.008	287.616	23.375	−353.680	−281.409	20.999
800	60.787	329.096	292.306	29.432	−353.311	−271.110	17.702
900	61.102	336.275	296.800	35.528	−352.948	−260.857	15.140
1000	61.333	342.725	301.075	41.650	−352.594	−250.643	13.092
1100	61.505	348.579	305.132	47.792	−352.250	−240.465	11.419
1200	61.638	353.937	308.979	53.950	−351.917	−230.318	10.025
1300	61.743	358.875	312.630	60.119	−351.596	−220.197	8.848
1400	61.826	363.454	316.098	66.298	−351.287	−210.102	7.839
1500	61.893	367.722	319.399	72.484	−350.990	−200.027	6.966
1600	61.949	371.718	322.546	78.676	−350.705	−189.972	6.202
1700	61.995	375.475	325.550	84.873	−350.432	−179.935	5.529
1800	62.034	379.020	328.423	91.075	−350.168	−169.913	4.931
1900	62.067	382.375	331.175	97.280	−349.914	−159.906	4.396
2000	62.095	385.559	333.815	103.488	−349.665	−149.912	3.915
2100	62.119	388.589	336.352	109.699	−349.420	−139.931	3.481
2200	62.140	391.480	338.793	115.912	−349.175	−129.961	3.086
2300	62.159	394.242	341.144	122.126	−348.927	−120.002	2.725
2400	62.175	396.888	343.412	128.343	−348.673	−110.054	2.395
2500	62.189	399.426	345.602	134.561	−348.408	−100.117	2.092
2600	62.202	401.866	347.719	140.781	−348.129	−90.191	1.812
2700	62.213	404.214	349.768	147.002	−347.833	−80.276	1.553
2800	62.223	406.476	351.754	153.224	−347.517	−70.372	1.313
2900	62.232	408.660	353.678	159.446	−347.179	−60.480	1.089
3000	62.241	410.770	355.546	165.670	−346.815	−50.600	0.881
3100	62.248	412.811	357.361	171.894	−346.424	−40.733	0.686
3200	62.255	414.787	359.125	178.120	−346.003	−30.878	0.504
3300	62.261	416.703	360.841	184.345	−345.552	−21.037	0.333
3400	62.266	418.562	362.511	190.572	−345.069	−11.211	0.172
3500	62.272	420.367	364.139	196.799	−344.552	−1.399	0.021
3600	62.276	422.121	365.725	203.026	−344.002	8.398	−0.122
3700	62.281	423.827	367.272	209.254	−343.418	18.179	−0.257
3800	62.285	425.488	368.783	215.482	−342.799	27.943	−0.384
3900	62.288	427.106	370.257	221.711	−342.146	37.692	−0.505
4000	62.292	428.683	371.698	227.940	−341.458	47.422	−0.619
4100	62.295	430.222	373.107	234.169	−340.737	57.135	−0.728
4200	62.298	431.723	374.485	240.399	−339.981	66.831	−0.831
4300	62.301	433.189	375.833	246.629	−339.193	76.507	−0.929
4400	62.303	434.621	377.153	252.859	−338.372	86.165	−1.023
4500	62.306	436.021	378.446	259.089	−337.519	95.805	−1.112
4600	62.308	437.391	379.712	265.320	−336.635	105.424	−1.197
4700	62.310	438.731	380.954	271.551	−335.721	115.024	−1.278
4800	62.312	440.042	382.171	277.782	−334.777	124.605	−1.356
4900	62.314	441.327	383.365	284.013	−333.805	134.165	−1.430
5000	62.316	442.586	384.537	290.245	−332.806	143.705	−1.501
5100	62.317	443.820	385.688	296.477	−331.780	153.225	−1.569
5200	62.319	445.030	386.817	302.708	−330.728	162.725	−1.635
5300	62.320	446.217	387.927	308.940	−329.652	172.205	−1.697
5400	62.322	447.382	389.017	315.172	−328.553	181.663	−1.757
5500	62.323	448.526	390.089	321.405	−327.432	191.101	−1.815
5600	62.324	449.649	391.142	327.637	−326.289	200.519	−1.870
5700	62.325	450.752	392.178	333.869	−325.126	209.916	−1.924
5800	62.327	451.836	393.198	340.102	−323.945	219.292	−1.975
5900	62.328	452.901	394.201	346.335	−322.746	228.648	−2.024
6000	62.329	453.949	395.188	352.568	−321.530	237.984	−2.072

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

$\Delta_f H°(0\ K)$ = unknown

$S°(298.15\ K)$ = [160.666 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−485.344 ± 12.6] $kJ·mol^{-1}$

Enthalpy of Formation

A value of $\Delta_f G°(298.15\ K)$ was obtained from the cell measurements of Koerber and de Vries.[1] This was combined with $\Delta_f S°$ from the estimated entropy.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with mercurous chloride. The entropy is estimated by comparison with the other mercurous and mercuric halides and use of additive entropy constants for the halogens from Kelley.[2]

Sublimation Data

Sublimation with decomposition to Hg(g) and HgF_2(g) is assumed at 949 K from the Gibbs energy change of the reaction.

References

[1]G. G. Koerber and T. de Vries, J. Amer. Chem. Soc. **74**, 5008 (1952).
[2]K. K. Kelley, U.S. Bur. Mines, personal communication, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	100.416	160.666	160.666	.000	−485.344	−427.449	74.887
300	100.500	161.287	160.668	.186	−485.320	−427.090	74.363
400	104.684	190.783	164.661	10.449	−483.807	−407.898	53.266
500	108.407	214.551	172.337	21.107	−481.969	−389.128	40.652
600	111.671	234.611	181.086	32.115	−479.863	−370.753	32.277
700	114.516	252.044	190.005	43.427	−595.050	−339.607	25.342
800	116.943	267.499	198.744	55.004	−591.240	−303.373	19.808
900	118.951	281.391	207.168	66.800	−587.255	−267.627	15.533
1000	120.748	294.018	215.231	78.787	−583.115	−232.333	12.136
1100	122.334	305.603	222.927	90.943	−578.837	−197.461	9.377
1200	123.709	316.308	230.269	103.247	−574.436	−162.984	7.095
1300	124.872	326.257	237.274	115.678	−569.932	−128.878	5.178
1400	125.825	335.547	243.966	128.214	−565.343	−95.123	3.549
1500	126.566	344.255	250.364	140.836	−560.689	−61.698	2.149

PREVIOUS: CURRENT: March 1962

Potassium Fluoride, Ion (KF_2^-) IDEAL GAS $M_r = 77.095655$

$S°(298.15\ K) = [261.868 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -686.217 \pm 41.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -694.544 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[350](1)
[130](1)
[500](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: $[D_{\infty h}]$

Bond Distance: K–F = [2.17] Å

Bond Angle: F–K–F = [180°]

Rotational Constant: $B_0 = [0.094216]\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation is estimated from three calculated values. The methods of calculation are described as follows. In a manner analogous to $LiF_2^-(g)$, the first reaction considered is $KF(g) + F^-(g) = KF_2^-(g)$ and the $\Delta_f H°(298.15\ K)$ value is evaluated to be between 0 and $1/2(-50) = 25\ kcal·mol^{-1}$ (see $LiF_2^-(g)$ table for details), yielding $\Delta_f H°(KF_2^-, g, 298.15\ K)$ between -140 and $-165\ kcal·mol^{-1}$. The $\Delta_f H°(298.15\ K)$ values for the other species involved are taken from JANAF tables.

The second reaction employed for estimation is $K_2F_2(g) = KF_2^-(g) + K^+(g)$. The enthalpy change of this reaction is calculated as $\Delta_r H°(298.15\ K) = (1/2)(50.0) + 138.8 = 163.8\ kcal·mol^{-1}$ where the KF_2^- ion is considered to be converted from $K_2F_2(g)$ by breaking one of the two dimer association bonds, $\Delta_r H°(298.15\ K) = 50.0\ kcal·mol^{-1}$, and one K^+–F^- ionic bond, $\Delta_r H°(298.15\ K) = 138.8\ kcal·mol^{-1}$. Using $\Delta_f H°(298.15\ K) = -206.2$ and $122.9\ kcal·mol^{-1}$ for $K_2F_2(g)$ and $K^+(g)$, we obtain the enthalpy of formation for $KF_2^-(g)$ as $-165\ kcal·mol^{-1}$.

Based on an assumption that the electron affinity of $KF_2(g)$ is similar to that of F (refer to $LiF_2^-(g)$ table for details), i.e., $\Delta_r H°(298.15\ K) = 83.5\ kcal·mol^{-1}$ for the reaction $KF_2^-(g) = KF_2(g) + e^-(g)$, we derive $\Delta_f H°(KF_2^-, g, 298.15\ K) = -167.7\ kcal·mol^{-1}$. The $\Delta_f H°(KF_2, g, 298.15\ K)$ is calculated as $-84.2\ kcal·mol^{-1}$ from the value $\Delta_r H°(298.15\ K) = 143.3\ kcal·mol^{-1}$ for the reaction $K_2F_2(g) = KF_2(g) + K(g)$ where the $\Delta_r H°(298.15\ K)$ value is calculated as the sum of two enthalpy changes, i.e. half of the heat of dimer dissociation into two monomers or $1/2(50.0) = 25.0\ kcal·mol^{-1}$, and the heat of dissociation of KF(g) or $118.3\ kcal·mol^{-1}$.

The value of $\Delta_f H°(KF_2^-\ 298.15\ K)$ is tentatively adopted as $-166 \pm 10\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion given by Walsh[2] that molecules with not more than 16 valency electrons are linear in their ground states. The K–F bond distance is taken to be the same as that of KF(g) reported by Veazey and Gordy.[3] The vibrational frequencies are estimated from the vibrational frequency of KF(g) using the method suggested by Herzberg.[4]

References

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[3]S. E. Veazey and W. Gordy, Phys. Rev. **138**, A1303 (1965).

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Potassium Fluoride, Ion (KF_2^-) $F_2K_1^-(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−13.777	−686.217		
100	43.337	206.619	309.310	−10.269			
200	52.713	239.908	266.969	−5.412			
250	55.318	251.970	262.798	−2.707			
298.15	57.015	261.868	261.868	0.	−694.544	−686.622	120.293
300	57.069	262.221	261.869	0.106	−694.589	−686.573	119.543
350	58.272	271.114	262.569	2.991	−698.224	−685.041	102.237
400	59.122	278.954	264.137	5.927	−699.544	−683.068	89.200
450	59.739	285.955	266.179	8.899	−700.842	−680.930	79.040
500	60.200	292.274	268.478	11.898	−702.125	−678.649	70.898
600	60.824	303.310	273.390	17.952	−704.663	−673.715	58.652
700	61.215	312.717	278.352	24.055	−707.185	−668.357	49.873
800	61.475	320.909	283.171	30.191	−709.715	−662.638	43.266
900	61.656	328.161	287.775	36.348	−712.273	−656.600	38.108
1000	61.787	334.664	292.144	42.520	−714.882	−650.275	33.967
1100	61.884	340.558	296.282	48.704	−796.516	−639.075	30.347
1200	61.959	345.946	300.199	54.896	−798.227	−624.687	27.192
1300	62.017	350.908	303.912	61.095	−799.954	−610.155	24.516
1400	62.064	355.506	307.435	67.299	−801.699	−595.490	22.218
1500	62.101	359.789	310.784	73.508	−803.459	−580.699	20.222
1600	62.132	363.798	313.973	79.719	−805.235	−565.791	18.471
1700	62.158	367.565	317.016	85.934	−807.027	−550.771	16.923
1800	62.179	371.119	319.924	92.151	−808.834	−535.645	15.544
1900	62.198	374.481	322.708	98.370	−810.654	−520.418	14.307
2000	62.213	377.672	325.377	104.590	−812.488	−505.095	13.192
2100	62.227	380.708	327.940	110.812	−814.333	−489.680	12.180
2200	62.238	383.603	330.405	117.036	−816.188	−474.177	11.258
2300	62.248	386.370	332.778	123.260	−818.052	−458.589	10.415
2400	62.257	389.019	335.067	129.485	−819.924	−442.920	9.640
2500	62.265	391.561	337.276	135.711	−821.803	−427.173	8.925
2600	62.272	394.003	339.411	141.938	−823.687	−411.351	8.264
2700	62.278	396.353	341.477	148.166	−825.577	−395.456	7.651
2800	62.284	398.618	343.477	154.394	−827.473	−379.491	7.079
2900	62.289	400.804	345.417	160.622	−829.373	−363.458	6.547
3000	62.293	402.916	347.298	166.852	−831.281	−347.359	6.048
3100	62.298	404.958	349.126	173.081	−833.196	−331.197	5.581
3200	62.301	406.936	350.902	179.311	−835.122	−314.973	5.141
3300	62.305	408.853	352.629	185.541	−837.050	−298.689	4.728
3400	62.308	410.713	354.310	191.772	−838.997	−282.346	4.338
3500	62.311	412.520	355.947	198.003	−840.959	−265.945	3.969
3600	62.313	414.275	357.543	204.234	−842.944	−249.488	3.620
3700	62.316	415.982	359.100	210.466	−844.952	−232.976	3.289
3800	62.318	417.644	360.619	216.697	−846.989	−216.409	2.975
3900	62.320	419.263	362.102	222.929	−849.058	−199.788	2.676
4000	62.322	420.841	363.550	229.161	−851.159	−183.113	2.391
4100	62.323	422.380	364.967	235.393	−853.303	−166.386	2.120
4200	62.325	423.882	366.352	241.626	−855.498	−149.606	1.861
4300	62.327	425.348	367.707	247.858	−857.745	−132.773	1.613
4400	62.328	426.781	369.033	254.091	−859.773	−115.913	1.376
4500	62.329	428.182	370.332	260.324	−862.073	−98.981	1.149
4600	62.331	429.552	371.604	266.557	−864.428	−81.998	0.931
4700	62.332	430.892	372.852	272.790	−866.822	−64.965	0.722
4800	62.333	432.204	374.075	279.023	−869.168	−47.892	0.521
4900	62.334	433.490	375.274	285.257	−871.680	−30.756	0.328
5000	62.335	434.749	376.451	291.490	−874.256	−13.569	0.142
5100	62.336	435.983	377.606	297.724	−876.899	3.671	−0.038
5200	62.337	437.194	378.741	303.957	−879.609	20.964	−0.211
5300	62.337	438.381	379.855	310.191	−882.387	38.309	−0.378
5400	62.338	439.547	380.949	316.425	−885.235	55.707	−0.539
5500	62.339	440.690	382.025	322.659	−888.153	73.158	−0.695
5600	62.339	441.814	383.083	328.892	−891.139	90.664	−0.846
5700	62.340	442.917	384.123	335.126	−893.850	108.175	−0.991
5800	62.341	444.001	385.146	341.361	−896.930	125.781	−1.133
5900	62.341	445.067	386.153	347.595	−900.073	143.442	−1.270
6000	62.342	446.115	387.143	353.829	−903.277	161.155	−1.403

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

Potassium Fluoride, Ion (KF_2^-) $F_2K_1^-(g)$

$\Delta_f H°(0\ K) = -858.080 \pm 8.4\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [319.955 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -862.741 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[273](1)	[150](1)
[150](1)	[255](1)
[235](1)	[258](1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: D_{2h}
Bond Distance: K–F = 2.2 Å
Bond Angles: F–K–F = [90°]: K–F–K = [90°]
Product of the Moments of Inertia: $I_A I_B I_C = [2.240426 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The equilibrium constants (K_c) for the reaction $K_2F_2(g) = 2\ KF(g)$, in the temperature range 974–1052 K, were determined by Eisenstadt *et al.*[1] Although the reported absolute values of the vapor pressures of KF(cr) are not adopted for evaluation, the reported K_c values are used to calculate the enthalpy change, $\Delta_r H°(298.15\ K)$, for the above reaction. The 2nd and 3rd law values of $\Delta_r H°(298.15\ K)$ are derived as 51.0 ± 1.6 and 50.0 $kcal \cdot mol^{-1}$, respectively. Based on the 3rd law $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(KF, g, 298.15\ K) = -78.1\ kcal \cdot mol^{-1}$, we obtain $\Delta_f H°(298.15\ K) = -206.2\ kcal \cdot mol^{-1}$ ($-862.74 \pm 8.4\ kJ \cdot mol^{-1}$) for $K_2F_2(g)$ which is tentatively adopted.

Heat Capacity and Enthalpy

The molecular structure and K–F bond distance were determined by Akishin and Rambidi,[2] using electron diffraction with sector microphotometry. The bond angles are estimated by comparison with other alkali halide dimers. The vibrational frequencies are taken from Berkowitz[3] which were calculated based on an ionic model. The three principal moments of inertia are: $I_A = 15.2693 \times 10^{-39}$, $I_B = 31.4238 \times 10^{-39}$, and $I_C = 46.6931 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.329	−858.080	−858.080	INFINITE
100	56.735	243.679	385.805	−14.213	−860.336	−860.546	449.503
200	73.655	289.471	327.017	−7.509	−861.750	−860.117	224.640
250	76.754	306.272	321.238	−3.742	−862.234	−859.652	179.615
298.15	78.525	319.955	319.955	0.	−862.741	−859.111	150.513
300	78.578	320.440	319.956	0.145	−862.763	−859.088	149.581
350	79.731	332.646	320.917	4.105	−868.174	−858.232	128.084
400	80.500	343.346	323.066	8.112	−868.972	−856.757	111.881
450	81.039	352.861	325.858	12.151	−869.727	−855.184	99.267
500	81.429	361.420	328.993	16.213	−870.451	−853.529	89.168
600	81.944	376.316	335.675	24.384	−871.833	−850.014	74.000
700	82.259	388.973	342.408	32.596	−873.165	−846.272	63.150
800	82.464	399.972	348.931	40.833	−874.492	−842.339	54.999
900	82.606	409.693	355.153	49.086	−875.857	−838.239	48.650
1000	82.707	418.402	361.050	57.352	−877.307	−833.982	43.563
1100	82.783	426.289	366.628	65.627	−1036.789	−820.355	38.955
1200	82.840	433.494	371.904	73.908	−1036.411	−800.696	34.853
1300	82.885	440.127	376.900	82.195	−1036.052	−781.068	31.384
1400	82.921	446.271	381.639	90.485	−1035.710	−761.467	28.411
1500	82.949	451.993	386.140	98.779	−1035.386	−741.889	25.835
1600	82.973	457.347	390.425	107.075	−1035.080	−722.333	23.582
1700	82.992	462.378	394.511	115.373	−1034.792	−702.795	21.594
1800	83.009	467.122	398.415	123.673	−1034.522	−683.273	19.828
1900	83.023	471.610	402.150	131.975	−1034.271	−663.767	18.248
2000	83.034	475.869	405.730	140.278	−1034.037	−644.272	16.827
2100	83.045	479.921	409.168	148.582	−1033.823	−624.790	15.541
2200	83.053	483.784	412.472	156.886	−1033.629	−605.316	14.372
2300	83.061	487.476	415.653	165.192	−1033.455	−585.852	13.305
2400	83.068	491.011	418.720	173.499	−1033.302	−566.394	12.327
2500	83.074	494.402	421.680	181.806	−1033.173	−546.942	11.428
2600	83.079	497.661	424.540	190.113	−1033.068	−527.495	10.598
2700	83.084	500.796	427.307	198.422	−1032.991	−508.052	9.829
2800	83.088	503.818	429.986	206.730	−1032.945	−488.610	9.115
2900	83.092	506.734	432.582	215.039	−1032.932	−469.170	8.451
3000	83.095	509.551	435.101	223.349	−1032.957	−449.730	7.830
3100	83.098	512.275	437.547	231.658	−1033.026	−430.288	7.250
3200	83.101	514.914	439.924	239.968	−1033.143	−410.843	6.706
3300	83.104	517.471	442.235	248.278	−1033.296	−391.395	6.195
3400	83.106	519.952	444.485	256.589	−1033.521	−371.940	5.714
3500	83.108	522.361	446.675	264.900	−1033.807	−352.478	5.260
3600	83.110	524.702	448.810	273.211	−1034.172	−333.007	4.832
3700	83.112	526.979	450.892	281.522	−1034.618	−313.524	4.426
3800	83.114	529.196	452.924	289.833	−1035.156	−294.028	4.042
3900	83.115	531.355	454.907	298.144	−1035.794	−274.516	3.677
4000	83.117	533.459	456.845	306.456	−1036.528	−254.988	3.330
4100	83.118	535.511	458.739	314.768	−1037.383	−235.441	3.000
4200	83.119	537.514	460.591	323.080	−1038.374	−215.869	2.685
4300	83.120	539.470	462.402	331.392	−1039.503	−196.273	2.384
4400	83.121	541.381	464.176	339.704	−1040.227	−176.703	2.098
4500	83.122	543.249	465.912	348.016	−1041.525	−157.062	1.823
4600	83.123	545.076	467.613	356.328	−1042.967	−137.392	1.560
4700	83.124	546.864	469.281	364.641	−1044.518	−117.693	1.308
4800	83.125	548.614	470.915	372.953	−1046.002	−97.983	1.066
4900	83.126	550.328	472.519	381.266	−1047.849	−78.214	0.834
5000	83.127	552.007	474.092	389.578	−1049.853	−58.406	0.610
5100	83.127	553.653	475.636	397.891	−1052.016	−38.555	0.395
5200	83.128	555.268	477.151	406.204	−1054.342	−18.661	0.187
5300	83.128	556.851	478.640	414.516	−1056.832	1.279	−0.013
5400	83.129	558.405	480.103	422.829	−1059.486	21.268	−0.206
5500	83.130	559.930	481.541	431.142	−1062.304	41.308	−0.392
5600	83.130	561.428	482.954	439.455	−1065.285	61.400	−0.573
5700	83.131	562.899	484.344	447.768	−1067.737	81.452	−0.746
5800	83.131	564.345	485.711	456.081	−1070.950	101.641	−0.915
5900	83.131	565.766	487.055	464.394	−1074.311	121.887	−1.079
6000	83.132	567.164	488.379	472.708	−1077.815	142.190	−1.238

PREVIOUS: June 1969 (1 atm) CURRENT: June 1969 (1 bar)

Lithium Fluoride, Ion (LiF_2^-) IDEAL GAS $M_r = 44.938355$

$S°(298.15\ K) = [229.618 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-702.735 \pm 62.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-711.280 \pm 62.8]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1300](1)
[350](2)
[550](1)

Ground State Quantum Weight: [1] $\sigma = [2]$

Point Group: $[D_{\infty h}]$

Bond Distance: Li–F = [1.57] Å

Bond Angle: F–Li–F = [180]°

Rotational Constant: $B_0 = [0.179988]\ cm^{-1}$

Enthalpy of Formation

Due to lack of thermal data, the enthalpy of formation for LiF_2^- (g) is arbitrarily selected from the following three estimated values. For the reaction (1) LiF(g) + F^-(g) = LiF_2(g), we expect the enthalpy change would be between 0 to −31 K cal·mol^{-1}. Comparison with the other molecules like CO_2, BOF, BeF_2, etc. having 16 valence electrons leads us to assume that the isoelectronic molecule LiF_2^- should also be quite stable. This indicates that reaction (1) is favorable or $\Delta_r H°(298.15\ K)$ is negative. However, the LiF–F^- bond strength is expected to be weaker than half of the two ionic bonds between Li^+ and F^- in Li_2F_2 molecule (refer to Li_2F_2(g) table for the molecular structure). In other words, the $\Delta_r H°(298.15\ K)$ value of reaction (1) is less negative than half of the enthalpy of dimerization (−62.4 K cal·mol^{-1}). Incorporating $\Delta_r H°(298.15\ K) = 0$ and −31 K cal·mol^{-1}, respectively, for reaction (1), with $\Delta_f H°(298.15\ K) = -81.45$ and −62.2 kcal·mol^{-1} for LiF(g) and F^- (g), we derived the corresponding values for $\Delta_f H°(LiF_2^-, g, 298.15\ K)$ as −144 and −175 K cal·mol^{-1}, which are the upper and lower limits.

The electron affinities of Li and F atoms are reported as 0.7 and 3.448 eV, respectively, by Beckett and Cassidy.[1] From this data we estimate that the electron affinity of LiF_2(g) should be closer to that of F atom than to that of Li. Assuming $\Delta_r H°(298.15\ K)$ = electron affinity of F atom = 83.5 kcal·mol^{-1} for the reaction LiF_2^- (g) = LiF_2(g) + e^- (g), we obtain the enthalpy of formation for LiF_2^- (g) as 177.3 kcal·mol^{-1}. The $\Delta_f H°(LiF_2, g, 298.15\ K)$ used for calculation is derived from an estimated $\Delta_r H°(298.15\ K) = 169.9$ kcal·mol^{-1} for the decomposition of LiF dimer of Li_2F_2(g) = LiF_2(g) + Li(g) as the sum of two enthalpy changes, namely, half of the enthalpy of dissociation of the dimer and the enthalpy of dissociation of the monomer.

The third estimated value for the enthalpy of formation of LiF_2^- (g) is calculated as follows. Based on the two enthalpies of reaction, i.e. $\Delta_r H°(298.15\ K) = 62.4$ kcal·mol^{-1} for Li_2F_2(g) = LiF(g), and $\Delta_r H°(298.15\ K) = 183.5$ kcal·mol^{-1} for LiF(g) = Li^+(g) + F^- (g), we assume the enthalpy change of the reaction Li_2F_2(g) = LiF_2^- (g) + Li^+(g) to be 1/2(62.4) + 183.5 = 214.7 kcal·mol^{-1}. In other words, we consider the LiF_2^- (g) molecule is formed by breaking half of the dimer dissociation bonds and one monomer dissociation bond to produce two ions. Using $\Delta_f H°(298.15\ K) = -225.33$ and 164.24 K cal·mol^{-1} for Li_2F_2(g) and Li^+(g), we evaluate $\Delta_f H°(LiF_2^-, g, 298.15\ K) = -174.9$ kcal·mol^{-1}.

From the above three estimated values, we tentatively choose $\Delta_f H°(LiF_2^-, g, 298.15\ K)$ as -170 ± 15 K cal·mol^{-1}.

Heat Capacity and Entropy

According to Walsh,[3] molecules with not more than 16 valence electrons are linear in their ground states. Since LiF_2^- (g) has 16 valence electrons, we assume its molecular structure is linear. The Li–F bond distance is estimated by comparison with that of LiF(g) reported by Wharton *et al.*[2] The vibrational frequencies are estimated from those of the isoelectronic gaseous molecules, CO_2 and BeF_2.

References

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Lithium Fluoride, Ion (LiF_2^-) $F_2Li_1^-$(g)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.100	−702.735		
100	32.069	186.362	267.697	−8.133			
200	41.808	211.729	233.812	−4.417			
250	45.181	221.439	230.390	−2.238			
298.15	47.670	229.618	229.618	0.	−711.280	−704.353	123.400
300	47.754	229.914	229.619	0.088	−711.334	−704.309	122.631
350	49.802	237.434	230.209	2.529	−712.784	−703.024	104.921
400	51.483	244.198	231.542	5.062	−714.258	−701.530	91.610
450	52.886	250.345	233.295	7.673	−715.777	−699.848	81.236
500	54.066	255.980	235.285	10.347	−720.350	−697.687	72.887
600	55.910	266.009	239.591	15.851	−723.382	−692.868	60.319
700	57.248	274.734	244.002	21.513	−726.276	−687.551	51.306
800	58.233	282.446	248.334	27.289	−729.084	−681.827	44.519
900	58.973	289.349	252.515	33.151	−731.845	−675.754	39.220
1000	59.538	295.593	256.516	39.078	−734.573	−669.375	34.965
1100	59.977	301.289	260.331	45.054	−737.276	−662.724	31.470
1200	60.324	306.523	263.965	51.070	−739.961	−655.828	28.547
1300	60.602	311.363	267.427	57.117	−742.634	−648.708	26.065
1400	60.828	315.863	270.728	63.189	−745.298	−641.383	23.930
1500	61.014	320.066	273.879	69.281	−747.952	−633.868	22.073
1600	61.169	324.009	276.890	75.391	−750.599	−626.176	20.443
1700	61.298	327.721	279.772	81.514	−898.477	−611.142	18.778
1800	61.408	331.228	282.534	87.650	−900.361	−594.186	17.243
1900	61.502	334.551	285.185	93.795	−902.247	−577.125	15.866
2000	61.582	337.708	287.733	99.950	−904.136	−559.964	14.625
2100	61.652	340.714	290.185	106.111	−906.027	−542.710	13.499
2200	61.713	343.584	292.547	112.280	−907.916	−525.364	12.474
2300	61.767	346.328	294.827	118.454	−909.804	−507.933	11.536
2400	61.814	348.958	297.028	124.633	−911.689	−490.420	10.674
2500	61.856	351.482	299.156	130.816	−913.567	−472.829	9.879
2600	61.893	353.909	301.215	137.004	−915.438	−455.162	9.144
2700	61.926	356.245	303.210	143.195	−917.301	−437.424	8.462
2800	61.956	358.498	305.145	149.389	−919.154	−419.617	7.828
2900	61.983	360.673	307.022	155.586	−920.997	−401.744	7.236
3000	62.007	362.774	308.846	161.785	−922.828	−383.807	6.683
3100	62.029	364.808	310.619	167.987	−924.648	−365.810	6.164
3200	62.049	366.778	312.343	174.191	−926.456	−347.754	5.676
3300	62.067	368.687	314.022	180.397	−928.253	−329.641	5.218
3400	62.084	370.540	315.657	186.605	−930.039	−311.475	4.785
3500	62.099	372.340	317.251	192.814	−931.814	−293.256	4.377
3600	62.113	374.090	318.805	199.024	−933.581	−274.986	3.990
3700	62.126	375.792	320.323	205.236	−935.339	−256.668	3.624
3800	62.138	377.449	321.804	211.449	−937.090	−238.302	3.276
3900	62.149	379.063	323.252	217.664	−938.835	−219.890	2.945
4000	62.159	380.637	324.667	223.879	−940.577	−201.433	2.630
4100	62.169	382.172	326.051	230.096	−942.316	−182.933	2.331
4200	62.178	383.670	327.405	236.313	−944.055	−164.391	2.044
4300	62.186	385.133	328.730	242.531	−945.796	−145.807	1.771
4400	62.193	386.563	330.029	248.750	−947.520	−127.184	1.510
4500	62.201	387.960	331.301	254.970	−949.261	−108.520	1.260
4600	62.207	389.328	332.547	261.190	−951.010	−89.818	1.020
4700	62.214	390.666	333.770	267.411	−952.769	−71.077	0.790
4800	62.220	391.975	334.969	273.633	−954.538	−52.299	0.569
4900	62.225	393.258	336.145	279.855	−956.321	−33.484	0.357
5000	62.230	394.516	337.300	286.078	−958.119	−14.633	0.153
5100	62.235	395.748	338.434	292.301	−959.930	4.254	−0.044
5200	62.240	396.956	339.548	298.525	−961.765	23.178	−0.233
5300	62.244	398.142	340.642	304.749	−963.622	42.137	−0.415
5400	62.249	399.306	341.718	310.974	−965.505	61.131	−0.591
5500	62.252	400.448	342.775	317.199	−967.414	80.160	−0.761
5600	62.256	401.570	343.815	323.424	−969.354	99.225	−0.926
5700	62.260	402.672	344.838	329.650	−971.325	118.324	−1.084
5800	62.263	403.754	345.845	335.876	−973.331	137.458	−1.238
5900	62.266	404.819	346.835	342.103	−975.373	156.627	−1.387
6000	62.269	405.865	347.810	348.330	−977.454	175.831	−1.531

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

Lithium Fluoride, Ion (LiF_2^-) $F_2Li_1^-$(g)

$S°(298.15\ K) = 258.627 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -938.070 \pm 16.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -942.781 \pm 16.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[570](1)	301.5(1)
[570](1)	571.5(1)
[490](1)	658.0(1)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: D_{2h}

Bond Distances: Li–F = 1.68Å: F–F = 2.67 Å

Bond Angles: Li–F–Li = 74.76°: F–Li–F = 105.24°

Product of the Moments of Inertia: $I_A I_B I_C = 3.678682 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(Li_2F_2, g, 298.15\ K)$ is calculated based on the adopted value $\Delta_f H°(1000) = 61.4\ kcal \cdot mol^{-1}$ for the reaction $Li_2F_2(g) = 2LiF(g)$ which is consistent with the literature values listed in the table below. Due to lack of Knowledge of the fragmentation patterns, the relative ionization cross sections of the ionic species formed in the mass spectrometer, and the molecular constants of the LiF polymers, the evaluation of equilibrium constants used to calculate $\Delta_f H°$ involves considerable uncertainty. In order to solve this problem more research work seems necessary.

Source	$\Delta_f H°(1000\ K)$, kcal·mol^{-1}	Method
Berkowitz *et al.*[1]	61.6 ± 2	mass spectrometry with a double–oven apparatus
Buchler and Stauffer[2]	61.3 ± 3	mass spectrometry with a two–piece Ni Knudsen cell
Eisenstadt *et al.*[3]	61.2	molecular–beam velocity–selector
Hildenbrand *et al.*[4]	60.4 ± 3	torsion effusion
Akishin *et al.*[5]	59.5 ± 3	mass spectrometry with a double effusion chamber
Porter and Schoonmaker[6]	65.0 *	mass spectrometry with a Mo Knudsen cell

*derived from reported vapor pressures of LiF(g) and Li_2F_2(g) at 1073 K.

Heat Capacity and Entropy

The molecular structure of Li_2F_2(g) was determined as D_{2h} by Bushler *et al.*,[12] using electric deflection and mass spectrometric detection. Akishin and Rambidi[7] studied the structure of Li_2F_2(g) by electron deflection with sector microphotometry and assigned the bond distances of Li–F and F–F which are adopted. Evidence for a matrix stabilized linear structure of Li_2F_2 has been obtained by extending the spectral measurements for matrix isolated lithium fluoride into the far infrared region by Redington[8] and Abramowitz *et al.*[9]

Klemperer and Norris[10] observed two infrared active vibrational frequencies, 640 and 460 cm^{-1}, and assigned them as $\nu_5(B_{2u})$ and $\nu_6(B_{3u})$ The infrared absorption spectra of lithium fluoride monomer and dimer isolated in solid inert gas matrices were investigated by Linevsky,[11] Snelson and Pitzer,[13] and Schlick and Schnepp.[14] Redington[8] obtained infrared spectra of LiF species suspended in solid Ne, O_2, CO, and CH_4 at liquid helium temperature. The observed solvent shifts for LiF and Li_2F_2 spectra exhibit several regularities. The vibrational frequencies used for calculation are those reported by Snelson[1] who re–examined the spectrum of LiF species over the range 200–4000 cm^{-1}, using sample purity of 99.3%. The saturated vapor was isolated at 900°C and the superheated unsaturated vapor at 1200°C. A variety of deposition rates and matrix dilutions was tried. Based on the frequencies assigned to the isotopic species, the vibrational frequencies of the natural isotopic Li_2F_2(g) are calculated. It appears that the vibrational frequencies calculated on the basis of the potential function for an ionic model by Berkowitz[1] are too low.

The three principal moments of inertia are: $I_A = 2.3980 \times 10^{-39}$, $I_B = 11.2447 \times 10^{-39}$ and $I_C = 13.6427 \times 10^{-39}\ g \cdot cm^2$.

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Continued on page 1215

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.359	−938.070	−938.070	INFINITE
100	36.231	206.434	306.175	−9.974	−938.582	−940.720	491.382
200	51.023	235.802	264.055	−5.651	−940.871	−941.971	246.017
250	57.938	247.958	259.639	−2.920	−941.900	−942.124	196.846
298.15	63.131	258.627	258.627	0.	−942.781	−942.086	165.049
300	63.304	259.018	258.629	0.117	−942.813	−942.081	164.031
350	67.331	269.094	259.415	3.388	−943.657	−941.892	140.570
400	70.346	278.291	261.208	6.833	−944.517	−941.582	122.958
450	72.626	286.715	263.581	10.410	−945.454	−941.160	109.247
500	74.375	294.461	266.287	14.087	−952.495	−940.014	98.203
600	76.816	308.254	272.161	21.656	−954.366	−937.337	81.602
700	78.383	320.222	278.191	29.421	−956.002	−934.367	69.723
800	79.442	330.762	284.117	37.316	−957.510	−931.173	60.799
900	80.187	340.164	289.831	45.299	−958.962	−927.793	53.848
1000	80.730	348.642	295.296	53.347	−960.377	−924.254	48.278
1100	81.138	356.357	300.501	61.441	−961.765	−920.574	43.714
1200	81.451	363.430	305.455	69.571	−963.133	−916.769	39.906
1300	81.696	369.960	310.169	77.729	−964.489	−912.850	36.679
1400	81.892	376.022	314.659	85.909	−965.832	−908.827	33.909
1500	82.051	381.677	318.940	94.106	−967.160	−904.709	31.505
1600	82.182	386.977	323.028	102.318	−968.476	−900.503	29.398
1700	82.290	391.963	326.938	110.542	−1260.252	−881.862	27.096
1800	82.382	396.669	330.683	118.775	−1260.039	−859.610	24.945
1900	82.459	401.125	334.274	127.018	−1259.832	−837.370	23.021
2000	82.525	405.357	337.723	135.267	−1259.631	−815.140	21.289
2100	82.582	409.385	341.041	143.522	−1259.436	−792.921	19.723
2200	82.632	413.227	344.235	151.783	−1259.245	−770.710	18.299
2300	82.675	416.902	347.315	160.049	−1259.058	−748.508	16.999
2400	82.713	420.421	350.288	168.318	−1258.875	−726.314	15.808
2500	82.747	423.798	353.162	176.591	−1258.694	−704.128	14.712
2600	82.777	427.044	355.941	184.867	−1258.516	−681.949	13.701
2700	82.803	430.169	358.633	193.146	−1258.341	−659.776	12.764
2800	82.827	433.180	361.242	201.428	−1258.169	−637.610	11.895
2900	82.848	436.087	363.773	209.712	−1258.002	−615.450	11.085
3000	82.868	438.896	366.231	217.997	−1257.839	−593.296	10.330
3100	82.885	441.614	368.619	226.285	−1257.683	−571.148	9.624
3200	82.901	444.246	370.941	234.574	−1257.534	−549.004	8.962
3300	82.916	446.797	373.201	242.865	−1257.395	−526.864	8.340
3400	82.929	449.272	375.403	251.158	−1257.268	−504.729	7.754
3500	82.941	451.676	377.548	259.451	−1257.155	−482.597	7.202
3600	82.952	454.013	379.639	267.746	−1257.059	−460.468	6.681
3700	82.962	456.286	381.680	276.041	−1256.981	−438.342	6.188
3800	82.972	458.499	383.673	284.338	−1256.925	−416.218	5.721
3900	82.980	460.654	385.619	292.636	−1256.893	−394.094	5.278
4000	82.988	462.755	387.521	300.934	−1256.890	−371.971	4.857
4100	82.996	464.804	389.382	309.233	−1256.917	−349.848	4.457
4200	83.003	466.804	391.201	317.533	−1256.978	−327.723	4.076
4300	83.009	468.758	392.982	325.834	−1257.077	−305.597	3.712
4400	83.015	470.666	394.726	334.135	−1257.175	−283.472	3.365
4500	83.021	472.532	396.434	342.437	−1257.340	−261.340	3.034
4600	83.026	474.356	398.109	350.739	−1257.556	−239.205	2.716
4700	83.031	476.142	399.750	359.042	−1257.820	−217.064	2.412
4800	83.036	477.890	401.360	367.346	−1258.138	−194.917	2.121
4900	83.040	479.602	402.939	375.649	−1258.512	−172.763	1.842
5000	83.044	481.280	404.489	383.954	−1258.946	−150.600	1.573
5100	83.048	482.925	406.011	392.258	−1259.434	−128.430	1.315
5200	83.052	484.537	407.506	400.563	−1259.998	−106.248	1.067
5300	83.055	486.119	408.974	408.869	−1260.634	−84.054	0.828
5400	83.059	487.672	410.417	417.174	−1261.346	−61.848	0.598
5500	83.062	489.196	411.836	425.480	−1262.138	−39.628	0.376
5600	83.065	490.693	413.231	433.787	−1263.014	−17.393	0.162
5700	83.067	492.163	414.603	442.093	−1263.977	4.859	−0.045
5800	83.070	493.607	415.952	450.400	−1265.032	27.128	−0.244
5900	83.072	495.028	417.281	458.707	−1266.182	49.417	−0.438
6000	83.075	496.424	418.588	467.015	−1267.431	71.725	−0.624

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = 57.255 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1536 \pm 5\ K$

$\Delta_f H°(0\ K) = -1120.332 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1124.241 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 58.702 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Rudzitis *et al.*[1] used fluorine bomb calorimetry to study the heat of combustion of a highly pure (99.91 mole %) sample of magnesium. Six combustion experiments were performed, and the sole combustion product was identified as MgF_2 by x-ray diffraction. Values for the completeness of combustion ranged from 98.4 to 99.99%. Corrections for the unburned magnesium were based on analysis performed by hydrogen evolution. This study gave $\Delta_f H°(MgF_2, cr, 298.15\ K) = -268.7 \pm 0.3\ kcal \cdot mol^{-1} (-1124.241 \pm 1.3\ kJ \cdot mol^{-1})$ which is adopted. The quoted uncertainty is twice the combined standard deviation arising from the scatter in the six results and from the analytical and calibration data.

More uncertain values for $\Delta_f H°$ derived indirectly from reaction calorimetry,[2,3] high temperature equilibria,[4] and emf's of solid electrolyte galvanic cells[5,6] are tabulated below. The original data are reanalyzed with the use of the most recent auxiliary data. These sources are included in the table.

Source	Method	Reaction	T/K	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
	Reaction					
2	Calorimetry	$Mg(OH)_2(cr)+2(HF4.5H_2O)=MgF_2(cr)+H_2O(l)$	346.9	−30.85[b]		268.4±1.0
	Reaction					
3	Calorimetry	$Mg(cr)+2(HF8OH_2O)=MgF_2(cr)+H_2(g)$	293	109.46±0.7[b]		−263.1±1.0
4	Equilibria	$MgF_2(cr)+H_2O(g)=MgO(cr)+2HF(g)$	1173–1373	51.58±0.9[a]	4.6±0.3	−268.0±1.5
5	emf	$AlF_3(cr)+1.5Mg(cr)=Al(cr)+1.5MgF_2(cr)$	720–860	41.5±0.2[a]	−1.5	−268.3±1.6
6	emf	$AlF_3(cr)+1.5Mg(cr)=Al(cr)+1.5MgF_2(cr)$	750–900	−40.6±0.2[a]	1.8	−267.7±1.8

[a] 3rd Law Values
[b] $\Delta_f H°$(HF, aq) consistent with JANAF value for HF(g); also, ϕ_c(HF, aq) taken from reference 9.

Auxiliary $\Delta_f H°(298.15\ K)$ values (kcal·mol^{-1}): $Mg(OH)_2$(cr), −221.0 ± 0.5;[7] HF4.5 H_2O, −76.6 ± 0.1;[c] H_2O(l), −68.315;[8] $HF8OH_2O$, −76.8 ± 0.1;[c] H_2O(g), −57.7979;[7] MgO(cr), −143.7 + 0.15;[7] HF(g), −65.14 ± 0.2;[7] AlF_3(cr), −361.0 ± 0.3[7] With the exception of the older calorimetric measurements of Wartenberg,[3] these results are in reasonable agreement with the directly measured $\Delta_f H°$ value.[1]

Heat Capacity and Entropy

Todd[10] measured the low temperature heat capacities (54.2−296.5 K) by adiabatic calorimetry. These $C_p°$ data extrapolate to 14.71 cal·K^{-1}·mol^{-1} at 298.15 K. Integration of these $C_p°$'s gives $S°(298.15\ K) = 13.68$ cal K^{-1}·mol^{-1} when combined with $S°(51\ K) = 0.539$ cal·K^{-1}·mol^{-1}. The latter value is calculated from a combination of Debye and Einstein functions which fits all the experimental $C_p°$ data with an average deviation of ±1.0%.

Relative enthalpies $H°(T;298.15)$ have been measured (411.3−1516 K) by the "drop" method[11] on a portion of the same sample used for the $C_p°$ study.[10] Gravimetric analysis for Mg as $MgSO_4$ indicated a MgF_2 purity of 99.87 wt%. However, premelting effects which appear in the experimental enthalpies about 80° below the melting point suggest that the sample was probably somewhat less pure. Insufficient information is reported to attempt to correct for the impurities. High temperature heat capacities (300–2000 K) are derived from the measured enthalpies[11] by curve fitting with orthogonal polynomials. The curve is constrained to join smoothly with the low-temperature $C_p°$ data near 298.15 K. Three enthalpy points which appear to involve premelting are not included in the fit. Also, we omit the enthalpy point at 411.3 K which shows an usually large positive deviation (+2.9%) from the adopted curve. The maximum deviation of the seven enthalpy points used in the fit is −0.5% and occurs at 1032.7 K. The older heat capacity measurements (288–1278 K) reported by Krestovnikov and Karentnikov[12] are considered less reliable and are not included in our evaluation.

Fusion Data

T_{fus} is the value measured by drop calorimetry.[11] Melting point determinations (1529 and 1534 K) on two commercially available materials which had been further purified by hydrofluorination[13] suggest an uncertainty in the adopted T_{fus} value (1536 K) of ±5 K. Other literature values include 1525 K[14] and 1528 K.[15]

$\Delta_{fus} H°$ is calculated as the difference between JANAF enthalpies for the liquid and crystal at T_{fus}. Other reported values for $\Delta_{fus} H°$ are 13.9[11] and 13.15 kcal·mol^{-1}.[14]

Sublimation Data

Refer to the ideal gas table for details.

Continued on page 1215

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.914	−1120.332	−1120.332	INFINITE
100	21.722	10.686	102.413	−9.173	−1123.140	−1106.221	577.830
200	48.817	35.056	62.549	−5.499	−1124.402	−1088.654	284.327
298.15	61.547	57.255	57.255	0.	−1124.241	−1071.109	187.654
300	61.689	57.636	57.256	0.114	−1124.231	−1070.779	186.439
400	68.484	76.377	59.765	6.645	−1123.475	−1053.065	137.516
500	72.634	92.132	64.706	13.713	−1122.439	−1035.579	108.186
600	75.320	105.624	70.429	21.117	−1121.275	−1018.315	88.652
700	77.178	117.381	76.315	28.746	−1120.070	−1001.250	74.714
800	78.555	127.780	82.110	36.535	−1118.878	−984.358	64.272
900	79.626	137.096	87.711	44.446	−1117.740	−967.612	56.159
1000	80.496	145.532	93.078	52.453	−1125.279	−950.276	49.637
1100	81.237	153.239	98.202	60.541	−1124.342	−932.821	44.296
1200	81.877	160.336	103.088	68.697	−1123.363	−915.452	39.849
1300	82.454	166.912	107.748	76.914	−1122.346	−898.167	36.089
1400	82.977	173.042	112.195	85.186	−1248.705	−877.795	32.751
1500	83.467	178.784	116.445	93.508	−1246.272	−851.386	29.648
1536.000	83.635	180.766	117.929	96.516	---- CRYSTAL <--> LIQUID ----		
1600	83.923	184.186	120.512	101.878	−1243.809	−825.141	26.938
1700	84.358	189.286	124.409	110.292	−1241.319	−799.050	24.552
1800	84.776	194.120	128.148	118.749	−1238.801	−773.107	22.435
1900	85.178	198.715	131.743	127.247	−1236.254	−747.304	20.545
2000	85.567	203.094	135.201	135.784	−1233.676	−721.636	18.847

PREVIOUS: March 1966 CURRENT: June 1975

$S°(298.15\ K) = [89.967]\ J·K^{-1}·mol^{-1}$ $\Delta_fH°(298.15\ K) = [-1072.356]\ kJ·mol^{-1}$
$T_{fus} = 1536 \pm 5\ K$ $\Delta_{fus}H° = 8.702 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(MgF_2, l, 298.15\ K)$ is calculated from $\Delta_fH°(MgF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1536\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Naylor[1] has measured relative enthalpies (1539–1760 K) for the liquid by drop calorimetry. These results give a $C_p°(l)$ equal to 22.687 $cal\ K^{-1}·mol^{-1}$. This value is used in the temperature range 1000–3000 K. Below 1000 K, the assumed glass transition temperature, $C_p°$ is assumed to be that of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 2536 K is the temperature at which $\Delta_rG°$ for the process MgF (l) = MgF_2 (g) is zero. $\Delta_{vap}H° = 274.052\ kJ·mol^{-1}$ is the difference between the $\Delta_fH°$ values for the gas and liquid at T_{vap}. Several methods[2-6] predict an insignificant amount of dimer (–1%) in the saturated vapor below 2000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
		$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
0							
100							
200							
298.15	61.547	89.967	89.967	0.	−1072.356	−1028.977	180.272
300	61.689	90.348	89.968	0.114	−1072.345	−1028.707	179.114
400	68.484	109.088	92.477	6.645	−1071.589	−1014.265	132.449
500	72.634	124.843	97.418	13.713	−1070.553	−1000.049	104.474
600	75.320	138.336	103.140	21.117	−1069.390	−986.057	85.844
700	77.178	150.092	109.026	28.746	−1068.184	−972.263	72.551
800	78.555	160.491	114.822	36.535	−1066.993	−958.642	62.593
900	79.626	169.807	120.423	44.446	−1065.855	−945.167	54.856
1000	80.496	178.244	125.790	52.454	−1073.393	−931.102	48.636
1000.000	80.496	178.244	125.790	52.454	GLASS <--> LIQUID TRANSITION		
1000.000	94.922	178.244	125.790	52.454			
1100	94.922	187.291	130.976	61.946	−1071.052	−916.987	43.544
1200	94.922	195.550	136.018	71.438	−1068.736	−903.083	39.310
1300	94.922	203.148	140.894	80.931	−1066.444	−889.372	35.735
1400	94.922	210.182	145.595	90.423	−1191.583	−872.669	32.560
1500	94.922	216.731	150.121	99.915	−1187.980	−850.015	29.600
1536.000	94.922	218.983	151.709	103.332	--- CRYSTAL <--> LIQUID ---		
1600	94.922	222.858	154.478	109.407	−1184.395	−827.601	27.018
1700	94.922	228.612	158.671	118.900	−1180.826	−805.411	24.747
1800	94.922	234.038	162.709	128.392	−1177.273	−783.430	22.735
1900	94.922	239.170	166.599	137.884	−1173.731	−761.647	20.939
2000	94.922	244.039	170.351	147.376	−1170.199	−740.049	19.328
2100	94.922	248.670	173.971	156.869	−1166.672	−718.629	17.875
2200	94.922	253.086	177.467	166.361	−1163.149	−697.376	16.558
2300	94.922	257.305	180.848	175.853	−1159.625	−676.283	15.359
2400	94.922	261.345	184.118	185.345	−1156.097	−655.344	14.263
2500	94.922	265.220	187.285	194.838	−1152.561	−634.552	13.258
2600	94.922	268.943	190.355	204.330	−1149.014	−613.902	12.333
2700	94.922	272.526	193.332	213.822	−1145.455	−593.388	11.480
2800	94.922	275.978	196.223	223.314	−1141.879	−573.006	10.690
2900	94.922	279.309	199.030	232.807	−1138.285	−552.753	9.956
3000	94.922	282.527	201.760	242.299	−1134.673	−532.624	9.274

PREVIOUS: March 1966 CURRENT: June 1975

0 to 1536 K crystal
above 1536 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.914	−1120.332	−1120.332	INFINITE
100	21.722	10.686	102.413	−9.173	−1123.140	−1106.221	577.830
200	48.817	35.056	62.549	−5.499	−1124.402	−1088.654	284.327
298.15	61.547	57.255	57.255	0.	−1124.241	−1071.109	187.654
300	61.689	57.636	57.256	0.114	−1124.231	−1070.779	186.439
400	68.484	76.377	59.765	6.645	−1123.475	−1053.065	137.516
500	72.634	92.132	64.706	13.713	−1122.439	−1035.579	108.186
600	75.320	105.624	70.429	21.117	−1121.275	−1018.315	88.652
700	77.178	117.381	76.315	28.746	−1120.070	−1001.250	74.714
800	78.555	127.780	82.110	36.535	−1118.878	−984.358	64.272
900	79.626	137.096	87.711	44.446	−1117.740	−967.612	56.159
1000	80.496	145.532	93.078	52.453	−1125.279	−950.276	49.637
1100	81.237	153.239	98.202	60.541	−1124.342	−932.821	44.296
1200	81.877	160.336	103.088	68.697	−1123.363	−915.452	39.849
1300	82.454	166.912	107.748	76.914	−1122.346	−898.167	36.089
1400	82.977	173.042	112.195	85.186	−1248.705	−877.795	32.751
1500	83.467	178.784	116.445	93.508	−1246.272	−851.386	29.648
1536.000	83.635	180.766	117.929	96.516	CRYSTAL <--> LIQUID TRANSITION		
1536.000	94.922	218.983	117.929	155.218			
1600	94.922	222.858	122.050	161.293	−1184.395	−827.601	27.018
1700	94.922	228.612	128.150	170.785	−1180.826	−805.411	24.747
1800	94.922	234.038	133.884	180.277	−1177.273	−783.430	22.735
1900	94.922	239.170	139.291	189.769	−1173.731	−761.647	20.939
2000	94.922	244.039	144.408	199.262	−1170.199	−740.049	19.328
2100	94.922	248.670	149.264	208.754	−1166.672	−718.629	17.875
2200	94.922	253.086	153.883	218.246	−1163.149	−697.376	16.558
2300	94.922	257.305	158.289	227.738	−1159.625	−676.283	15.359
2400	94.922	261.345	162.499	237.231	−1156.097	−655.344	14.263
2500	94.922	265.220	166.531	246.723	−1152.561	−634.552	13.258
2600	94.922	268.943	170.399	256.215	−1149.014	−613.902	12.333
2700	94.922	272.526	174.115	265.707	−1145.454	−593.388	11.480
2800	94.922	275.978	177.692	275.200	−1141.879	−573.006	10.690
2900	94.922	279.309	181.139	284.692	−1138.285	−552.753	9.956
3000	94.922	282.527	184.465	294.184	−1134.673	−532.624	9.274

PREVIOUS: CURRENT: June 1975

$S°(298.15\ K) = 256.508 \pm 2.1$ (or ± 12.6) $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -724.994 \pm 3.3$ (or ± 16.7) $kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -726.761 \pm 3.3$ (or 16.7) $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
υ, cm^{-1}	υ, cm^{-1}	υ, cm^{-1}
508 (1)	215 (1)	875 (1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Mg–F = 1.77 ± 0.02 Å

Bond Angle: F–Mg–F = 158°

Product of the Principal Moments of Inertia: $I_A I_B I_C = 1.033673 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_{sub}H°(298.15\ K)$ is added to $\Delta_f H°(MgF_2, cr, 298.15\ K)$ to give $\Delta_f H°(g, 298.15\ K) = 173.7 \pm 0.8\ kcal \cdot mol^{-1}$. $\Delta_{sub}H°(298.15\ K)$ is selected from the results of a 3rd law analysis of twenty sets[19] of vapor pressure data for MgF_2(cr, l). These measurements cover an extended temperature range (~1200°) and include the use of manometric,[1, 4] Knudsen effusion,[2, 5, 6] torsion effusion[5–8] and mass spectrometric[3, 9] methods. The amount of dimer present in the saturated vapor is predicted not to exceed 1% below 2000 K by several methods.[3, 6, 7–9]

Source		Reaction	Method	T/K	Data Points	$\Delta_f H°$ kcal·mol^{-1} 2nd law	$\Delta_f H°$ kcal·mol^{-1} 3rd law	Drift cal $K^{-1} \cdot mol^{-1}$	$-\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1		A	Manometric	1934–2129	6	89.2	82.5±1.0	−3.3±3.4	173.8±1.5
2	Set 1	B	Knudsen Effusion	1337–1480	8	93.7	94.6±0.7	0.6±2.6	174.1±1.0
	2	B	"	1440–1530	4	91.3	95.0±0.4	2.5±2.9	173.7±0.7
	3	B	"	1284–1357	6	100.3	94.8±0.3	−4.1±1.9	173.9±0.6
3		B	Mass Spec	1450	1	91.4[a]	93.9	174.8	
4	Set 1	A	Manometric	2155–2327	Equation	82.9	82.40±0.03	−0.2	173.9±0.5
	2	A	Manometric	2087–2357	Equation	84.8	82.53±0.2	−1.0	173.8±0.7
5, 6	Set 1	B	Knudsen Effusion	1451–1533	6	98.7	95.3±0.5	−2.3±3.5	173.4±0.8
	2	A	"	1568–1613	4	81.9	82.9±0.2	0.6±4.2	
	3	B	Torsion Effusion	1413–1518	11[b]	92.9	95.3±0.6	1.7±2.3	173.4±0.9
	4	A	"	1539–1614	11[c]	80.6	82.8±0.3	1.4±1.6	173.5±0.8
7	Set 1	B	"	1273–1433	21	72.7	90.6±1.4	13.2±1.0	178.1±1.7
	2	B	"	1373–1513	18[b]	76.6	91.0±1.0	10.0±0.8	177.7±1.3
8	Set 1	B	"	1340–1500	Equation	97.7	95.8±0.2	−1.4	172.9±0.5
	2	B	"	1348–1482	"	98.3	96.0±0.2	−1.6	172.7±0.5
	3	B	"	1324–1465	"	96.7	95.7±0.1	−0.7	173.0±0.4
	4	B	"	1376–1517	"	98.9	95.6±0.3	−2.2	173.1±0.7
	5	B	"	1345–1515	"	97.9	95.7±0.2	−1.5	173.0±0.5
	6	B	"	1341–1520	"	96.9	95.6±0.1	−1.0	173.1±0.4
9		B	Mass Spec	1241–1492	Equation	93.9	95.4±0.2	1.1	173.3±0.5

Reactions: (A) $MgF_2(l) = Mg + F_2(g)$; (B) $MgF_2(cr) = MgF_2(g)$.

[a]2nd law value by slope method. [b]One point rejected due to failure of a statistical test.

[c]Two points rejected due to failure of a statistical test.

These data are in agreement on $\Delta_{sub}H°(298.15\ K) = 95.0 \pm 0.5\ kcal \cdot mol^{-1}$. We adopt this value but assign an alternate uncertainty to $\Delta_f H°$ to include the possibility that MgF_2 is linear (refer below).

Heat Capacity and Entropy

Considerable confusion exists as to whether MgF_2 is bent or linear. Electron diffraction,[11] electric deflection,[12] matrix isolation Raman[23] and infrared[13, 22, 23] spectral studies, and MO calculations[14–16, 24] predict a linear configuration. Other matrix isolation IR studies[17, 18] and MO calculations[19, 24] favor the nonlinear structure. Isotopic shifts[18] in the matrix frequencies suggest that the most probable value of the apex angle

Continued on page 1215

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.056	−724.994	−724.994	INFINITE
100	37.519	210.143	296.182	−8.604	−725.091	−728.117	380.330
200	43.734	238.149	260.788	−4.528	−725.951	−730.821	190.871
250	46.242	248.185	257.291	−2.277	−726.373	−731.990	152.941
298.15	48.259	256.508	256.508	0.	−726.761	−733.036	128.425
300	48.329	256.806	256.509	0.089	−726.775	−733.075	127.640
350	50.021	264.388	257.103	2.550	−727.166	−734.094	109.558
400	51.375	271.159	258.445	5.086	−727.553	−735.057	95.989
450	52.455	277.275	260.203	7.683	−727.944	−735.972	85.429
500	53.320	282.848	262.193	10.328	−728.344	−736.842	76.977
600	54.583	292.689	266.477	15.727	−729.185	−738.464	64.289
700	55.431	301.171	270.842	21.231	−730.106	−739.939	55.215
800	56.020	308.613	275.107	26.805	−731.129	−741.275	48.400
900	56.444	315.237	279.205	32.429	−732.277	−742.476	43.092
1000	56.758	321.201	283.111	38.090	−742.162	−742.829	38.801
1100	56.996	326.623	286.824	43.778	−743.625	−742.825	35.274
1200	57.180	331.590	290.351	49.487	−745.093	−742.687	32.328
1300	57.326	336.173	293.702	55.213	−746.567	−742.427	29.831
1400	57.442	340.426	296.889	60.952	−875.459	−738.886	27.568
1500	57.538	344.392	299.925	66.701	−875.599	−729.126	25.390
1600	57.616	348.108	302.822	72.459	−875.749	−719.356	23.485
1700	57.681	351.603	305.589	78.224	−875.908	−709.577	21.803
1800	57.736	354.902	308.238	83.994	−876.075	−699.788	20.307
1900	57.783	358.025	310.777	89.771	−876.250	−689.990	18.969
2000	57.823	360.990	313.214	95.551	−876.429	−680.182	17.765
2100	57.858	363.812	315.557	101.335	−876.611	−670.365	16.674
2200	57.888	366.504	317.812	107.122	−876.793	−660.539	15.683
2300	57.914	369.078	319.985	112.912	−876.971	−650.706	14.778
2400	57.937	371.543	322.083	118.705	−877.142	−640.864	13.948
2500	57.958	373.909	324.109	124.500	−877.304	−631.016	13.184
2600	57.976	376.182	326.068	130.297	−877.453	−621.162	12.479
2700	57.992	378.370	327.965	136.095	−877.587	−611.302	11.826
2800	58.007	380.480	329.803	141.895	−877.704	−601.437	11.220
2900	58.020	382.516	331.586	147.696	−877.801	−591.569	10.655
3000	58.032	384.483	333.316	153.499	−877.878	−581.697	10.128
3100	58.042	386.386	334.998	159.302	−877.934	−571.824	9.635
3200	58.052	388.229	336.633	165.107	−877.968	−561.948	9.173
3300	58.061	390.015	338.223	170.913	−877.980	−552.072	8.739
3400	58.069	391.749	339.772	176.719	−877.971	−542.197	8.330
3500	58.076	393.432	341.281	182.527	−877.942	−532.321	7.944
3600	58.083	395.068	342.753	188.335	−877.894	−522.447	7.581
3700	58.089	396.660	344.188	194.143	−877.829	−512.574	7.236
3800	58.095	398.209	345.590	199.952	−877.748	−502.704	6.910
3900	58.100	399.718	346.958	205.762	−877.655	−492.835	6.601
4000	58.105	401.189	348.296	211.572	−877.550	−482.969	6.307
4100	58.110	402.624	349.603	217.383	−877.437	−473.106	6.027
4200	58.114	404.024	350.883	223.194	−877.318	−463.246	5.761
4300	58.118	405.392	352.134	229.006	−877.196	−453.389	5.508
4400	58.122	406.728	353.360	234.818	−877.075	−443.534	5.265
4500	58.125	408.034	354.561	240.630	−876.955	−433.682	5.034
4600	58.129	409.312	355.737	246.443	−876.842	−423.833	4.813
4700	58.132	410.562	356.890	252.256	−876.737	−413.986	4.601
4800	58.134	411.786	358.021	258.069	−876.643	−404.141	4.398
4900	58.137	412.984	359.131	263.883	−876.564	−394.298	4.203
5000	58.140	414.159	360.219	269.697	−876.501	−384.457	4.016
5100	58.142	415.310	361.288	275.511	−876.458	−374.616	3.837
5200	58.144	416.439	362.338	281.325	−876.438	−364.776	3.664
5300	58.146	417.547	363.369	287.140	−876.441	−354.937	3.498
5400	58.148	418.634	364.383	292.955	−876.471	−345.097	3.338
5500	58.150	419.701	365.379	298.769	−876.531	−335.256	3.184
5600	58.152	420.748	366.358	304.585	−876.622	−325.414	3.035
5700	58.154	421.778	367.322	310.400	−876.747	−315.570	2.892
5800	58.155	422.789	368.269	316.215	−876.907	−305.724	2.753
5900	58.157	423.783	369.202	322.031	−877.105	−295.874	2.619
6000	58.158	424.761	370.120	327.847	−877.343	−286.021	2.490

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K) = [258.145 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 587.193 \pm 20.9$ (or ± 37.7) $kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 591.982 \pm 20.9$ (or ± 37.7) $kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Pi$	[20000]	4
$^2\Sigma$	[25000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[500](1)
[200](2)
[800](1)

Point Group: $[D_{\infty h}]$ $\sigma = 2$
Bond Distance: Mg–F = [1.95] Å
Bond Angle: F–Mg–F = [180]°
Rotational Constant: B_0 = [0.116677] cm^{-1}

Enthalpy of Formation

The MgF_2^+ ion has been identified as an important species in the vapor mass spectra of the MgF_2,[1-3] MgF_2–Tl–Pd[4] and MgF_2–Cu[5] systems. The observed appearance potentials (AP) for this ion are tabulated below.

Source	Year	AP, eV
Berkowitz and Marquart[1]	1962	13.5±0.4
Green *et al.*[2]	1964	13.6
Murad *et al.*[4]	1966	14.0±0.5
Hildenbrand[5]	1968	13.5
Hildenbrand[3]	1968	13.3±0.3

These results show the normal scatter expected for such measurements; the largest deviation is 0.7 eV. We adopt an average value of 13.6±0.2 eV (313.62±4.6 $kcal \cdot mol^{-1}$), and we assume that this value refers to the direct ionization process $MgF_2(g) + e^- = MgF_2^+(g) + 2e^-$ occurring at 0 K. Combining the selected AP value with $\Delta_f H°(MgF_2, g) = -173.3 \pm 0.8\ kcal \cdot mol^{-1}$,[6] we obtain $\Delta_f H°(MgF_2^+, g, 0\ K) = 140.3 \pm 5\ kcal \cdot mol^{-1}$. The $\Delta_f H°$ value at 298.15 K is 141.5 $kcal \cdot mol^{-1}$. An alternate uncertainty of $\pm 9\ kcal \cdot mol^{-1}$ is included to cover the possibility that the MgF_2 molecule is linear.[6]

Heat Capacity and Entropy

A comparison of the atomization energies, $\Delta_{at} H°(0\ K)$ in $kcal \cdot mol^{-1}$, for MgF_2(245)[6] and MgF_2^+ (107.7) suggests weaker bonding in the ion relative to the neutral molecule. One might therefore expect that the fundamental frequencies of MgF_2^+ would be somewhat less than those for MgF_2. We assume a slight decrease in the three vibrational frequencies of MgF_2.[6] MgF_2^+ (fifteen valence electrons) is isoelectronic with the molecules BO_2, N_3, NCO, and N_2O^+. By analogy with the ground states[6] for these isoelectronic molecules, we assume that the ground state for MgF_2^+ is $^2\Pi$. We also include two excited states ($^2\Pi$ and $^2\Sigma$) which would be expected to exist based on those observed for BO_2.[6]

According to the diagram of Walsh,[7] MgF_2^+ is predicted to be linear. This prediction is supported by the fact that several other fifteen valence electron molecules (BO_2, NCO, N_2O^+, and N_3) are now known to be linear in their ground states. We adopt a linear configuration. Due to the weaker bonding in MgF_2^+ relative to MgF_2, it is reasonable to assume that $r_e(MgF_2^+) > r_e(MgF_2)$. We assume a 10% increase in the bond length for MgF_2.[6]

References

[1] J. Berkowitz and J. R. Marquart, J. Chem. Phys. **37**, 1853 (1962).
[2] J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, J. Chem. Phys. **41**, 2245 (1964).
[3] D. L. Hildenbrand, J. Chem. Phys. **48**, 3657 (1968).
[4] E. Murad, D. L. Hildenbrand, and R. P. Main, J. Chem. Phys. **45**, 263 (1966).
[5] D. L. Hildenbrand, J. Chem. Phys. **48**, 2457 (1968).
[6] JANAF Thermochemical Tables: MgF_2(g), 6-30-75; BO_2(g), 6-30-68; CNO(g), N_2O^+(g) and N_3(g), 12-31-70.
[7] A. D. Walsh, J. Chem. Soc. **1953**, 2266 (1953).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.414	587.193		
100	38.135	208.753	300.902	−9.215			
200	47.129	238.250	262.789	−4.908			
250	50.159	249.106	258.996	−2.473			
298.15	52.449	258.145	258.145	0.	591.982	578.963	−101.432
300	52.526	258.469	258.146	0.097	592.013	578.883	−100.792
350	54.358	266.710	258.792	2.771	592.876	576.626	−86.057
400	55.774	274.065	260.250	5.526	593.746	574.245	−74.989
450	56.875	280.700	262.160	8.343	594.615	571.756	−66.368
500	57.738	286.739	264.320	11.210	595.476	569.169	−59.461
600	58.973	297.384	268.967	17.050	597.154	563.749	−49.079
700	59.786	306.539	273.696	22.990	598.749	558.054	−41.643
800	60.344	314.561	278.313	28.998	600.239	552.138	−36.051
900	60.742	321.693	282.745	35.054	601.600	546.042	−31.691
1000	61.034	328.109	286.966	41.143	594.222	540.515	−28.234
1100	61.255	333.937	290.975	47.258	595.265	535.094	−25.409
1200	61.425	339.274	294.780	53.393	596.301	529.578	−23.052
1300	61.559	344.196	298.395	59.542	597.329	523.976	−21.054
1400	61.666	348.763	301.831	65.703	470.938	521.462	−19.456
1500	61.753	353.020	305.104	71.875	473.299	524.989	−18.282
1600	61.825	357.008	308.224	78.054	475.649	528.358	−17.249
1700	61.885	360.758	311.205	84.239	477.989	531.580	−16.333
1800	61.936	364.297	314.058	90.430	480.320	534.666	−15.516
1900	61.979	367.647	316.791	96.626	482.644	537.621	−14.780
2000	62.016	370.827	319.414	102.826	484.963	540.455	−14.115
2100	62.048	373.853	321.935	109.029	487.278	543.172	−13.511
2200	62.077	376.740	324.361	115.235	489.595	545.780	−12.958
2300	62.103	379.500	326.698	121.444	491.914	548.282	−12.452
2400	62.126	382.144	328.954	127.656	494.240	550.683	−11.985
2500	62.149	384.680	331.133	133.870	496.576	552.987	−11.554
2600	62.170	387.118	333.239	140.086	498.925	555.197	−11.154
2700	62.192	389.465	335.279	146.304	501.289	557.316	−10.782
2800	62.214	391.727	337.254	152.524	503.671	559.348	−10.435
2900	62.236	393.911	339.171	158.746	506.074	561.294	−10.110
3000	62.260	396.021	341.031	164.971	508.497	563.157	−9.805
3100	62.286	398.063	342.838	171.199	510.944	564.938	−9.519
3200	62.313	400.041	344.595	177.428	513.414	566.641	−9.249
3300	62.343	401.959	346.304	183.661	515.907	568.266	−8.995
3400	62.376	403.820	347.968	189.897	518.424	569.815	−8.754
3500	62.411	405.629	349.590	196.137	520.964	571.289	−8.526
3600	62.449	407.388	351.171	202.380	523.525	572.691	−8.310
3700	62.491	409.099	352.714	208.627	526.108	574.021	−8.104
3800	62.536	410.767	354.220	214.878	528.709	575.281	−7.908
3900	62.584	412.392	355.691	221.134	531.328	576.473	−7.721
4000	62.636	413.977	357.128	227.395	533.962	577.597	−7.543
4100	62.691	415.524	358.534	233.661	536.609	578.655	−7.372
4200	62.749	417.035	359.908	239.933	539.267	579.648	−7.209
4300	62.811	418.513	361.254	246.211	541.934	580.578	−7.053
4400	62.876	419.957	362.572	252.495	544.606	581.446	−6.903
4500	62.945	421.371	363.863	258.786	547.283	582.253	−6.759
4600	63.016	422.755	365.128	265.084	549.960	583.001	−6.620
4700	63.090	424.111	366.369	271.390	552.636	583.690	−6.487
4800	63.167	425.440	367.586	277.703	555.308	584.323	−6.359
4900	63.247	426.744	368.780	284.023	557.973	584.900	−6.235
5000	63.329	428.022	369.952	290.352	560.629	585.422	−6.116
5100	63.413	429.277	371.103	296.689	563.274	585.892	−6.001
5200	63.499	430.509	372.234	303.035	565.904	586.310	−5.890
5300	63.587	431.720	373.345	309.389	568.520	586.677	−5.782
5400	63.677	432.909	374.437	315.752	571.116	586.995	−5.678
5500	63.767	434.078	375.510	322.124	573.692	587.265	−5.577
5600	63.859	435.228	376.567	328.506	576.246	587.489	−5.480
5700	63.953	436.359	377.606	334.896	578.775	587.667	−5.385
5800	64.046	437.472	378.628	341.296	581.278	587.801	−5.294
5900	64.141	438.568	379.635	347.706	583.752	587.893	−5.205
6000	64.235	439.647	380.626	354.124	586.196	587.942	−5.118

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$\Delta_{at}H°(0\ K) = 974.035 \pm 25.1\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [271.932 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_fH°(0\ K) = [-162.853 \pm 16.7]\ kJ \cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = [-162.758 \pm 16.7]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[450]	[5]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[700](1)
[150](2)
[700](1)

Point Group: [$D_{\infty h}$] σ = [2]
Bond Distance: Mo–F = [1.82] Å
Bond Angle: F–Mo–F = [180]°
Rotational Constant: B_0 = [0.133939] cm^{-1}

Enthalpy of Formation

The adopted enthalpy of formation at 298.15 K is that derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous fluorides by Hildenbrand (1818–2242 K).[2] The value of $\Delta_fH°(0\ K)$ combined with JANAF data[3] for Mo(g) and F(g) gives $\Delta_{at}H°(0\ K) = 232.8 \pm 6\ kcal \cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_{at}H°(0\ K)/2 = 116.4 \pm 3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

We use the vibrational frequencies of 700(2) and 150(2) cm^{-1} estimated by Hildenbrand[2] and adopted by Brewer.[1] Brewer[1] assumed a linear molecule with a Mo–F distance of 1.82 Å as in MoF_6(g). No electronic level data are available for the dihalides of molybdenum. Brewer[1] uses g = 3 for the ground state and one excited level at 450 cm^{-1} with g = 5. Additional electronic contributions are expected, but the electronic contribution was kept small[1] to be as consistent as possible with the smaller entropy values derived for MoF(g) and MoF_2(g) from the 2nd law treatment of Hildenbrand's equilibria data.[2]

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, (Sept. 1978), of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]D. L. Hildenbrand, J. Chem. Phys. **65**, 614 (1976).
[3]JANAF Thermochemical Tables: Mo(g), 3–31–78; F(g), 9–30–65.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−13.505	−162.853	−162.853	INFINITE
100	41.502	217.787	318.908	−10.112	−162.858	−166.897	87.178
200	52.007	250.046	277.031	−5.397	−162.914	−170.897	44.634
250	55.223	262.022	272.864	−2.711	−162.848	−172.900	36.125
298.15	57.221	271.932	271.932	0.	−162.758	−174.844	30.632
300	57.282	272.286	271.933	0.106	−162.754	−174.919	30.456
350	58.594	281.222	272.636	3.005	−162.657	−176.954	26.409
400	59.454	289.106	274.212	5.958	−162.577	−179.002	23.375
450	60.042	296.145	276.265	8.946	−162.521	−181.059	21.017
500	60.460	302.494	278.575	11.959	−162.490	−183.121	19.131
600	61.005	313.569	283.511	18.035	−162.504	−187.247	16.301
700	61.337	323.000	288.496	24.153	−162.610	−191.364	14.280
800	61.557	331.206	293.333	30.298	−162.796	−195.460	12.762
900	61.711	338.466	297.952	36.462	−163.052	−199.528	11.580
1000	61.824	344.974	302.334	42.639	−163.378	−203.564	10.633
1100	61.909	350.870	306.483	48.826	−163.774	−207.564	9.856
1200	61.976	356.260	310.410	55.021	−164.244	−211.525	9.207
1300	62.028	361.223	314.130	61.221	−164.794	−215.444	8.657
1400	62.071	365.821	317.660	67.426	−165.429	−219.316	8.183
1500	62.105	370.105	321.015	73.635	−166.156	−223.141	7.770
1600	62.134	374.114	324.210	79.847	−166.980	−226.913	7.408
1700	62.158	377.882	327.257	86.061	−167.906	−230.631	7.086
1800	62.178	381.435	330.169	92.278	−168.940	−234.292	6.799
1900	62.196	384.797	332.957	98.497	−170.088	−237.892	6.540
2000	62.211	387.988	335.629	104.717	−171.355	−241.428	6.305
2100	62.224	391.024	338.195	110.939	−172.747	−244.898	6.092
2200	62.235	393.918	340.663	117.162	−174.269	−248.299	5.895
2300	62.245	396.685	343.039	123.386	−175.928	−251.627	5.715
2400	62.254	399.335	345.330	129.611	−177.729	−254.880	5.547
2500	62.262	401.876	347.541	135.837	−179.682	−258.055	5.392
2600	62.269	404.318	349.678	142.063	−181.803	−261.149	5.247
2700	62.275	406.668	351.746	148.291	−184.129	−264.157	5.110
2800	62.281	408.933	353.748	154.518	−186.720	−267.075	4.982
2900	62.286	411.119	355.689	160.747	−225.538	−269.845	4.860
3000	62.290	413.230	357.572	166.975	−226.856	−271.350	4.725
3100	62.294	415.273	359.401	173.205	−228.147	−272.812	4.597
3200	62.298	417.251	361.178	179.434	−229.409	−274.232	4.476
3300	62.302	419.168	362.906	185.664	−230.640	−275.614	4.363
3400	62.305	421.028	364.588	191.895	−231.840	−276.959	4.255
3500	62.308	422.834	366.227	198.125	−233.007	−278.269	4.153
3600	62.310	424.589	367.824	204.356	−234.140	−279.546	4.056
3700	62.313	426.297	369.381	210.587	−235.239	−280.792	3.964
3800	62.315	427.958	370.901	216.819	−236.304	−282.009	3.876
3900	62.317	429.577	372.385	223.050	−237.334	−283.198	3.793
4000	62.319	431.155	373.834	229.282	−238.330	−284.361	3.713
4100	62.321	432.694	375.251	235.514	−239.292	−285.500	3.637
4200	62.323	434.195	376.637	241.747	−240.220	−286.615	3.565
4300	62.324	435.662	377.992	247.979	−241.115	−287.710	3.495
4400	62.326	437.095	379.319	254.211	−241.977	−288.783	3.428
4500	62.327	438.495	380.619	260.444	−242.806	−289.837	3.364
4600	62.329	439.865	381.892	266.677	−243.604	−290.874	3.303
4700	62.330	441.206	383.140	272.910	−244.371	−291.893	3.244
4800	62.331	442.518	384.363	279.143	−245.108	−292.896	3.187
4900	62.332	443.803	385.563	285.376	−245.815	−293.885	3.133
5000	62.333	445.063	386.741	291.609	−837.878	−289.127	3.020
5100	62.334	446.297	387.896	297.843	−840.208	−278.130	2.849
5200	62.335	447.507	389.031	304.076	−842.657	−267.084	2.683
5300	62.336	448.695	390.146	310.310	−845.224	−255.991	2.523
5400	62.337	449.860	391.241	316.543	−847.907	−244.849	2.368
5500	62.337	451.004	392.317	322.777	−850.706	−233.656	2.219
5600	62.338	452.127	393.375	329.011	−853.618	−222.410	2.075
5700	62.339	453.230	394.416	335.244	−856.641	−211.113	1.935
5800	62.339	454.315	395.439	341.478	−859.774	−199.761	1.799
5900	62.340	455.380	396.446	347.712	−863.012	−188.353	1.668
6000	62.341	456.428	397.437	353.946	−866.358	−176.891	1.540

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

$S°(298.15\ K) = 249.950\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 44.8 \pm 8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 42.3 \pm 8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1074(1)
573(1)
931(1)

Ground State Quantum Weight: 2 $\sigma = 2$

Point Group: C_{2v}

Bond Distance: N–F = 1.37 Å

Bond Angle: F–N–F = 104.2°

Product of the Moments of Inertia: $I_A I_B I_C = 7.61262 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

Colburn and Johnson[1] reported the study of the dissociation reaction $N_2F_4(g) = 2\ NF_2(l)$ by two independent methods: (a) measurement of the pressure variation with temperature at constant volume and (b) a spectrophotometric method based on the temperature dependence of the ultraviolet absorption of NF_2 radical. The authors gave a more detailed account of their data in a later publication.[2] The contents of these articles indicate that 2 $NF_2(l)$ should read 2 $NF_2(g)$ in the above reaction. The first method gave a value of 19.85 $kcal·mol^{-1}$ for the enthalpy of dissociation in the temperature range 373 to 423 K which corresponds to 19.87 $kcal·mol^{-1}$ at 298.15 K. From their ΔH and ΔS data, ΔG was calculated and used in a 3rd law evaluation of the enthalpy of dissociation. The $\Delta_f H°(298.15\ K)$ so calculated showed an increasing trend with increasing temperature; the average value was 22.87 $kcal·mol^{-1}$ which is not in agreement with their value of 19.87 $kcal·mol^{-1}$. The spectrophotometric value of 21.7 $kcal·mol^{-1}$ at 298.15 K was obtained from the integrated Van't Hoff equation.

Piette, Johnson, Booman and Colburn[3] studied the temperature dependence of the EPR spectrum of the NF_2 radical. They obtained a 2nd law value of 19.3 $kcal·mol^{-1}$ for the enthalpy of dissociation. This value, however, depends upon the degree of dissociation of N_2F_4 which they calculated from the (dP/dT) measurements of Colburn and Johnson.[1] Any error in the (dP/dT) measurements would manifest itself in like manner here.

Doorenbos and Loy[4] investigated the ESR spectrum of the N_2F_4–NF_2 equilibrium from which they calculated a 2nd law value of 19.8 $kcal·mol^{-1}$ for the enthalpy of dissociation. They report that at 25°C and 13 atm, N_2F_4 is 0.022% dissociated in the vapor phase. A 3rd law calculation using this datum and the relationship $K_p = (4\alpha^2/1-\alpha^2)P_T$, where α is the degree of dissociation of N_2F_4 and P_T is the total pressure, gave a heat of dissociation of 21.79 $kcal·mol^{-1}$ at 298.15 K; this is not in agreement with their 2nd law value.

Herron and Diebler[5] report thermal dissociation data for N_2F_4. From their data they calculated a 2nd law value of 21.5 $kcal·mol^{-1}$ for the heat of dissociation of N_2F_4. A 2nd and 3rd law evaluation of their data was performed. It is found that if the k factor, relating their measured ion abundances to partial pressure, is taken as 4.72×10^{-8}, a 3rd law is obtained that shows slight scatter but no temperature dependence. Excluding those points that showed scatter, the 3rd law heat of dissociation at 298.15 K is 22.27 $kcal·mol^{-1}$. A 2nd law plot gives a heat value of 22.23 $kcal·mol^{-1}$ at an average temperature of 400 K or 22.25 $kcal·mol^{-1}$ at 298.15 K. Those points that deviated from the chosen straight line in the 2nd law plot shows corresponding deviations in the 3rd law calculation. Those points lying on the 2nd law slope give a constant 3rd law value.

The enthalpy of dissociation for $N_2F_4(g) = 2\ NF_2(g)$ is taken to be 22.26 $kcal·mol^{-1}$. Utilizing the enthalpy of formation of $N_2F_4(g)$, the enthalpy of formation of the difluoroamino radical becomes $10.1 \pm 2.0\ kcal·mol^{-1}$. All values for the enthalpy of dissociation fall within the limits of error assigned to the enthalpy of formation of NF_2.

Heat Capacity and Entropy

Refer to table on tetrafluorohydrazine, $N_2F_4(g)$, for discussion.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.575	44.844	44.844	INFINITE
100	33.409	210.747	283.220	−7.247	43.813	47.766	−24.950
200	36.304	234.591	253.546	−3.791	42.885	52.096	−13.606
250	38.656	242.940	250.612	−1.918	42.528	54.441	−11.375
298.15	41.005	249.950	249.950	0.	42.258	56.762	−9.944
300	41.093	250.204	249.951	0.076	42.249	56.852	−9.899
350	43.377	256.713	250.460	2.189	42.045	59.302	−8.850
400	45.399	262.640	251.617	4.409	41.905	61.778	−8.067
450	47.136	268.091	253.149	6.724	41.820	64.268	−7.460
500	48.604	273.135	254.898	9.118	41.779	66.765	−6.975
600	50.874	282.209	258.711	14.099	41.794	71.762	−6.247
700	52.481	290.179	262.649	19.271	41.893	76.750	−5.727
800	53.639	297.267	266.542	24.580	42.038	81.720	−5.336
900	54.491	303.636	270.315	29.989	42.204	86.670	−5.030
1000	55.132	309.412	273.941	35.471	42.377	91.602	−4.785
1100	55.625	314.691	277.409	41.010	42.547	96.516	−4.583
1200	56.010	319.548	280.721	46.593	42.709	101.415	−4.414
1300	56.316	324.044	283.883	52.210	42.860	106.301	−4.271
1400	56.563	328.227	286.902	57.854	42.997	111.176	−4.148
1500	56.766	332.136	289.789	63.521	43.119	116.041	−4.041
1600	56.933	335.805	292.552	69.206	43.226	120.899	−3.947
1700	57.073	339.261	295.199	74.907	43.319	125.751	−3.864
1800	57.191	342.527	297.738	80.620	43.398	130.598	−3.790
1900	57.292	345.622	300.177	86.344	43.465	135.440	−3.724
2000	57.379	348.563	302.524	92.078	43.523	140.279	−3.664
2100	57.453	351.364	304.783	97.820	43.575	145.116	−3.610
2200	57.519	354.038	306.962	103.568	43.625	149.950	−3.560
2300	57.576	356.596	309.065	109.323	43.675	154.782	−3.515
2400	57.626	359.048	311.097	115.083	43.729	159.611	−3.474
2500	57.670	361.401	313.062	120.848	43.791	164.439	−3.436
2600	57.710	363.664	314.965	126.617	43.864	169.263	−3.401
2700	57.745	365.843	316.809	132.390	43.953	174.085	−3.368
2800	57.776	367.943	318.598	138.166	44.059	178.902	−3.337
2900	57.805	369.971	320.335	143.945	44.187	183.716	−3.309
3000	57.831	371.931	322.022	149.727	44.337	188.525	−3.283
3100	57.854	373.828	323.663	155.511	44.514	193.328	−3.258
3200	57.875	375.665	325.260	161.297	44.718	198.125	−3.234
3300	57.894	377.446	326.814	167.086	44.951	202.916	−3.212
3400	57.912	379.175	328.329	172.876	45.215	207.699	−3.191
3500	57.928	380.854	329.806	178.668	45.510	212.474	−3.171
3600	57.943	382.486	331.246	184.462	45.838	217.240	−3.152
3700	57.957	384.074	332.653	190.257	46.199	221.996	−3.134
3800	57.969	385.619	334.027	196.053	46.592	226.742	−3.117
3900	57.981	387.125	335.369	201.851	47.019	231.477	−3.100
4000	57.992	388.593	336.681	207.649	47.479	236.201	−3.084
4100	58.002	390.026	337.965	213.449	47.972	240.913	−3.069
4200	58.011	391.423	339.221	219.249	48.497	245.613	−3.055
4300	58.020	392.788	340.451	225.051	49.055	250.299	−3.041
4400	58.028	394.122	341.656	230.853	49.644	254.973	−3.027
4500	58.035	395.427	342.836	236.656	50.265	259.632	−3.014
4600	58.042	396.702	343.993	242.460	50.916	264.278	−3.001
4700	58.049	397.950	345.128	248.265	51.597	268.909	−2.989
4800	58.055	399.173	346.241	254.070	52.306	273.525	−2.977
4900	58.061	400.370	347.334	259.876	53.045	278.126	−2.965
5000	58.067	401.543	348.406	265.682	53.810	282.712	−2.953
5100	58.072	402.693	349.460	271.489	54.602	287.282	−2.942
5200	58.077	403.820	350.494	277.297	55.420	291.837	−2.932
5300	58.081	404.927	351.511	283.105	56.264	296.375	−2.921
5400	58.086	406.012	352.510	288.913	57.131	300.897	−2.911
5500	58.090	407.078	353.493	294.722	58.022	305.403	−2.900
5600	58.094	408.125	354.459	300.531	58.936	309.893	−2.891
5700	58.097	409.153	355.409	306.341	59.872	314.366	−2.881
5800	58.101	410.164	356.345	312.150	60.829	318.822	−2.871
5900	58.104	411.157	357.265	317.961	61.805	323.263	−2.862
6000	58.108	412.134	358.172	323.771	62.802	327.685	−2.853

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

$S°(298.15\ K) = 259.810\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 74.711 \pm 5.0\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 68.618 \pm 5.0\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights ν, $cm^{-1}\nu$, cm^{-1}	
896(1)	952(1)
1524(1)	573(1)
552(1)	737(1)

Ground State Quantum Weight: = 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distances: N–F = 1.384 Å; N–N = 1.214 Å

Bond Angle: F–N–N = 114.5 ± 0.5°

Product of the Moments of Inertia: $I_A I_B I_C = 6.590443 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation was derived from the heat of reaction $N_2F_2(g) + 8/3\ NH_3(g) = 2\ NH_4F(cr) + 4/3\ N_2(g)$ which was measured calorimetrically by Armstrong and Marantz.[1] There are two isomers, the trans and the active form of difluoridiazine. The enthalpy of formation were determined to be 19.4 and 16.4 kcal·mol^{-1} for the trans and the active isomers, respectively. The active form of N_2F_2 has been interpreted here as the cis isomer which will be discussed later. The enthalpy of isomerization has also been reported as 3.0 kcal·mol^{-1} by Armstrong and Marantz. The value, $\Delta_f H°$(cis N_2F_2, g, 298.15 K) = 16.4 kcal·mol^{-1}, is adopted in the tabulation.

Pankratov *et al.*[2] have measured the enthalpy of reaction $N_2F_2(g) + 3\ KI = 2\ KF + N_2 + KI_3$ in acidic solution (pH = 3), and reported $\Delta_f H°$(active N_2F_2, g, 298.15 K) = 25.3 ± 2.0 kcal·mol^{-1}.

The "heat of isomerization" has been reported as 27.5 ± 5.0 kcal·mol^{-1} by Colburn *et al.*[9] The derivation of this value is unknown. The authors observed three values of the equilibrium constant for the isomerization reaction. Third law analysis of their data gives $\Delta_r H°(298.15\ K) = 2.52 \pm 0.05$ kcal·mol^{-1} for the reaction *cis* $N_2F_2(g) \rightarrow$ trans $N_2F_2(g)$ which is in good agreement with Armstrong and Sidney's data.

Heat Capacity and Entropy

Although the infrared spectrum[7,8] of the active form of $N_2F_2(g)$ has been interpreted as favoring the 1,1–di–flurodiazine over the *cis* configuration,[3,4] NMR[5] and microwave[6] studies definitely indicate the latter. The vibrational frequencies[7] previously assigned to the 1,1–difluorodiazine have been adopted here for the *cis* isomer. The selected bond distances and angle were taken from the isotopic nitrogen microwave studies.[6] The principal moments of inertia were: $I_A = 4.2469 \times 10^{-39}$, $I_B = 10.5134 \times 10^{-39}$, and $I_C = 14.7603 \times 10^{-39}$ g·cm^2.

Refer to the trans–N_2F_2(g) table for the comparison of the different physical properties between *trans* and *cis* isomers.

References

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[8] R. H. Sanborn, J. Chem. Phys. **34**, 2188 (1961).
[9] C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger and C. O. Parker, J. Amer. Chem. Soc. **81**, 6397 (1959).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.402	74.711	74.711	INFINITE
100	33.621	216.960	297.678	−8.072	72.232	83.554	−43.644
200	40.350	241.888	264.073	−4.437	70.027	95.777	−25.014
250	45.327	251.424	260.607	−2.296	69.210	102.313	−21.377
298.15	49.961	259.810	259.810	0.	68.618	108.745	−19.052
300	50.131	260.119	259.811	0.093	68.598	108.994	−18.978
350	54.432	268.177	260.437	2.709	68.169	115.763	−17.277
400	58.158	275.695	261.880	5.526	67.895	122.583	−16.008
450	61.339	282.734	263.810	8.516	67.752	129.429	−15.024
500	64.039	289.340	266.036	11.652	67.716	136.284	−14.238
600	68.275	301.411	270.946	18.279	67.887	149.987	−13.057
700	71.349	312.179	276.081	25.268	68.281	163.641	−12.211
800	73.616	321.862	281.209	32.522	68.816	177.229	−11.572
900	75.317	330.635	286.221	39.973	69.436	190.744	−11.070
1000	76.619	338.641	291.069	47.572	70.106	204.187	−10.666
1100	77.631	345.993	295.732	55.287	70.803	217.561	−10.331
1200	78.432	352.784	300.207	63.092	71.513	230.872	−10.050
1300	79.074	359.088	304.497	70.968	72.226	244.123	−9.809
1400	79.596	364.968	308.609	78.902	72.936	257.319	−9.601
1500	80.026	370.474	312.551	86.884	73.639	270.464	−9.418
1600	80.383	375.651	316.335	94.905	74.333	283.564	−9.257
1700	80.683	380.533	319.969	102.959	75.016	296.620	−9.114
1800	80.938	385.152	323.463	111.040	75.688	309.636	−8.985
1900	81.155	389.534	326.826	119.145	76.351	322.614	−8.869
2000	81.342	393.702	330.067	127.270	77.007	335.559	−8.764
2100	81.505	397.675	333.192	135.413	77.657	348.470	−8.668
2200	81.646	401.470	336.210	143.571	78.306	361.351	−8.580
2300	81.770	405.102	339.127	151.742	78.955	374.202	−8.498
2400	81.879	408.584	341.949	159.924	79.609	387.025	−8.423
2500	81.976	411.929	344.682	168.117	80.271	399.820	−8.354
2600	82.062	415.146	347.331	176.319	80.944	412.589	−8.289
2700	82.140	418.244	349.900	184.529	81.632	425.332	−8.229
2800	82.209	421.233	352.394	192.747	82.338	438.049	−8.172
2900	82.271	424.119	354.818	200.971	83.064	450.740	−8.119
3000	82.327	426.909	357.175	209.201	83.813	463.405	−8.069
3100	82.378	429.609	359.468	217.436	84.588	476.046	−8.021
3200	82.425	432.225	361.701	225.676	85.389	488.661	−7.977
3300	82.467	434.762	363.877	233.921	86.219	501.250	−7.934
3400	82.506	437.225	365.998	242.170	87.079	513.814	−7.894
3500	82.542	439.617	368.068	250.422	87.970	526.352	−7.855
3600	82.574	441.942	370.088	258.678	88.893	538.865	−7.819
3700	82.604	444.205	372.060	266.937	89.847	551.351	−7.784
3800	82.632	446.409	373.988	275.199	90.834	563.810	−7.750
3900	82.658	448.555	375.873	283.463	91.854	576.244	−7.718
4000	82.681	450.648	377.716	291.730	92.905	588.651	−7.687
4100	82.704	452.690	379.520	299.999	93.989	601.031	−7.657
4200	82.724	454.683	381.286	308.271	95.105	613.385	−7.629
4300	82.743	456.630	383.015	316.544	96.252	625.711	−7.601
4400	82.761	458.533	384.710	324.819	97.430	638.011	−7.574
4500	82.778	460.393	386.371	333.096	98.639	650.283	−7.548
4600	82.794	462.212	388.000	341.375	99.877	662.528	−7.523
4700	82.808	463.993	389.598	349.655	101.144	674.746	−7.499
4800	82.822	465.737	391.166	357.936	102.438	686.937	−7.475
4900	82.835	467.444	392.706	366.219	103.760	699.100	−7.453
5000	82.847	469.118	394.217	374.503	105.109	711.236	−7.430
5100	82.859	470.759	395.702	382.789	106.483	723.345	−7.409
5200	82.869	472.368	397.161	391.075	107.882	735.427	−7.387
5300	82.880	473.946	398.595	399.362	109.305	747.482	−7.367
5400	82.889	475.496	400.005	407.651	110.751	759.509	−7.347
5500	82.898	477.017	401.391	415.940	112.220	771.510	−7.327
5600	82.907	478.511	402.755	424.231	113.710	783.484	−7.308
5700	82.915	479.978	404.097	432.522	115.220	795.430	−7.289
5800	82.923	481.420	405.418	440.814	116.750	807.350	−7.271
5900	82.930	482.838	406.718	449.106	118.299	819.244	−7.253
6000	82.937	484.232	407.998	457.400	119.865	831.111	−7.235

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

Nitrogen Fluoride, Trans (N_2F_2) — IDEAL GAS — M_r = 66.010206 — Nitrogen Fluoride, Trans (FNNF) — F_2N_2(g)

$S°(298.15\ K) = 262.660\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 86.436 \pm 5.0\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 81.170 \pm 5.0\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1010(1)	989(1)
1636(1)	421(1)
592(1)	360(1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2h}

Bond Distances: N–F = 1.44 Å; N–N = 1.25 Å

Bond Angle: F–N–N = 115°

Product of the Moments of Inertia: $I_A I_B I_C = 4.328461 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

Armstrong and Marantz[1] have measured calorimetrically the enthalpy of reaction $N_2F_2(g) + 8/3\ NH_3(g) = 2\ NH_4F(cr) + 4/3\ N_2(g)$, and reported $\Delta_f H°$(*trans* N_2F_2, g, 298.15 K) = 19.4 ± 1.2 kcal·mol^{-1} which is adopted in this tabulation.

Heat Capacity and Entropy

The bond distances and bond angle were obtained from Bauer[2] by electron diffraction. The fundamental vibrational frequencies were obtained from Sanborn[3] by infrared spectroscopy. The three principal moments of inertia are $I_A = 0.9191 \times 10^{-39}$, $I_B = 21.2461 \times 10^{-39}$, and $I_C = 22.1652 \times 10^{-39}\ g·cm^2$.

As pointed out by Ettinger *et al.*,[4] the *trans* N_2F_2 is the less active isomer which is different from the active isomer by its (1) vapor pressure (2) boiling point (3) heat of vaporization (4) critical temperature (5) melting point (6) mass spectral cracking pattern (7) NMR spectrum (8) infrared spectrum (9) heat of isomerization (10) reactivity with mercury and glass.

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[4]R. Ettinger, F. A. Johnson and C. B. Colburn, J. Chem. Phys. **34**, 2187 (1961).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.229	86.436	86.436	INFINITE
100	35.368	215.607	304.259	−8.865	83.990	95.448	−49.857
200	45.076	243.033	267.293	−4.852	82.164	107.685	−28.124
250	49.593	253.586	263.519	−2.483	81.575	114.137	−23.848
298.15	53.466	262.660	262.660	0.	81.170	120.448	−21.102
300	53.606	262.991	262.661	0.099	81.157	120.691	−21.014
350	57.134	271.525	263.326	2.870	80.881	127.304	−18.999
400	60.214	279.360	264.848	5.805	80.726	133.948	−17.492
450	62.886	286.610	266.868	8.884	80.673	140.605	−16.321
500	65.199	293.359	269.183	12.088	80.704	147.263	−15.384
600	68.922	305.591	274.254	18.803	80.962	160.554	−13.977
700	71.707	316.435	279.520	25.841	81.406	173.786	−12.968
800	73.810	326.154	284.752	33.121	81.967	186.946	−12.206
900	75.417	334.944	289.849	40.586	82.601	200.031	−11.610
1000	76.663	342.958	294.765	48.193	83.278	213.043	−11.128
1100	77.643	350.312	299.485	55.910	83.978	225.986	−10.731
1200	78.424	357.103	304.007	63.715	84.688	238.864	−10.397
1300	79.055	363.406	308.337	71.590	85.400	251.683	−10.113
1400	79.571	369.284	312.482	79.522	86.108	264.448	−9.867
1500	79.998	374.789	316.455	87.501	86.808	277.162	−9.652
1600	80.354	379.963	320.264	95.519	87.499	289.829	−9.462
1700	80.654	384.844	323.920	103.570	88.179	302.454	−9.293
1800	80.908	389.462	327.435	111.649	88.848	315.039	−9.142
1900	81.127	393.842	330.815	119.751	89.508	327.587	−9.006
2000	81.315	398.008	334.072	127.873	90.161	340.101	−8.883
2100	81.478	401.980	337.212	136.013	90.809	352.582	−8.770
2200	81.621	405.773	340.242	144.168	91.455	365.032	−8.667
2300	81.746	409.404	343.171	152.336	92.102	377.453	−8.572
2400	81.857	412.886	346.004	160.517	92.753	389.846	−8.485
2500	81.955	416.229	348.746	168.707	93.413	402.211	−8.404
2600	82.042	419.445	351.404	176.907	94.084	414.550	−8.328
2700	82.120	422.543	353.982	185.115	94.770	426.862	−8.258
2800	82.191	425.531	356.484	193.331	95.474	439.149	−8.192
2900	82.254	428.416	358.915	201.553	96.199	451.411	−8.131
3000	82.311	431.206	361.279	209.782	96.946	463.647	−8.073
3100	82.363	433.906	363.578	218.015	97.719	475.857	−8.018
3200	82.410	436.521	365.817	226.254	98.519	488.042	−7.966
3300	82.453	439.058	367.998	234.497	99.348	500.202	−7.918
3400	82.493	441.520	370.125	242.745	100.206	512.337	−7.871
3500	82.529	443.912	372.199	250.996	101.096	524.445	−7.827
3600	82.562	446.237	374.223	259.250	102.017	536.528	−7.785
3700	82.593	448.500	376.200	267.508	102.971	548.585	−7.745
3800	82.621	450.703	378.132	275.769	103.956	560.615	−7.706
3900	82.647	452.849	380.020	284.032	104.975	572.619	−7.669
4000	82.671	454.942	381.867	292.298	106.026	584.597	−7.634
4100	82.694	456.984	383.675	300.566	107.108	596.548	−7.600
4200	82.715	458.977	385.444	308.837	108.223	608.472	−7.567
4300	82.734	460.923	387.177	317.109	109.370	620.369	−7.536
4400	82.753	462.825	388.875	325.384	110.547	632.239	−7.506
4500	82.770	464.685	390.539	333.660	111.754	644.083	−7.476
4600	82.786	466.505	392.170	341.938	112.992	655.898	−7.448
4700	82.801	468.285	393.771	350.217	114.258	667.687	−7.421
4800	82.815	470.029	395.342	358.498	115.552	679.449	−7.394
4900	82.828	471.736	396.883	366.780	116.873	691.183	−7.368
5000	82.840	473.410	398.397	375.063	118.221	702.890	−7.343
5100	82.852	475.050	399.884	383.348	119.594	714.570	−7.319
5200	82.863	476.659	401.345	391.634	120.992	726.222	−7.295
5300	82.874	478.238	402.781	399.921	122.415	737.848	−7.272
5400	82.883	479.787	404.193	408.208	123.860	749.446	−7.249
5500	82.893	481.308	405.581	416.497	125.328	761.017	−7.228
5600	82.902	482.802	406.947	424.787	126.818	772.562	−7.206
5700	82.910	484.269	408.290	433.078	128.328	784.080	−7.185
5800	82.918	485.711	409.613	441.369	129.857	795.571	−7.165
5900	82.926	487.128	410.915	449.661	131.406	807.036	−7.145
6000	82.933	488.522	412.197	457.954	132.972	818.474	−7.125

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [250.672 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -661.011 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -669.440 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[400](1)
[170](2)
[650](1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [$D_{\infty h}$]
Bond Distance: Na–F = [1.93] Å
Bond Angle: F–Na–F = [180]°
Rotational Constant: B_0 = [0.119105] cm^{-1}

Enthalpy of Formation

The enthalpy of formation for NaF_2^-(g) is estimated from three calculated values. The methods of calculation are described as follows. The first reaction we take into consideration is NaF(g) + F^-(g) = NaF_2 (g). In a manner analogous to LiF_2 (g) molecule (see LiF_2^-(g) table for details), we assume NaF_2^-(g) is stable and $\Delta_f H°$(298.15 K) for the reaction NaF(g) + F^-(g) = NaF_2^-(g) is somewhere between 0 to 1/2(−64) = −32 kcal·mol^{-1} where the value −56 kcal·mol^{-1} is the enthalpy of dimerization. Based on $\Delta_f H°(298.15\ K) = 0$ and −28 kcal·mol^{-1}, respectively, with JANAF $\Delta_f H°$(298.15 K) values for the species involved, we obtain $\Delta_f H°(NaF_2^-, g, 298.15\ K)$ = −132 and −164 kcal·mol^{-1} as the upper and lower limits.

The enthalpy of formation, based on the reaction $NaF_2^-(g) = NaF_2(g) + e^-(g)$, is −165.8 kcal·$mol^{-1}$, using $\Delta_r H°$(298.15 K) and $\Delta_f H°(NaF_2, g, 298.15\ K)$ estimated as 83.5 and −82.3 kcal·mol^{-1}, respectively. The $\Delta_r H°$(298.15 K) value is obtained from an assumption that the enthalpy change for removing an electron from NaF_2^-(g) is comparable to that from F^-(g). Due to the fact that the Na atom has smaller electronegativity (0.9) than that of the F atom (4.0), we expect that there is less possibility that the electron will associate with Na atom in the NaF_2^- molecule. Therefore, we adopt EA(F,g), reported by Pritchard,[1] or $\Delta_r H°(298.15\ K) = 83.5$ kcal·mol^{-1} for the reaction $F^-(g) = F(g) + e^-(g)$ as the $\Delta_r H°$(298.15 K) for NaF_2^- (g) = NaF_2(g) + e^-(g). The value of $\Delta_f H°$(298.15 K) for NaF_2(g) is calculated using the enthalpy change for the reaction $Na_2F_2(g) = NaF_2(g) + Na(g)$ as 145.8 kcal·mol^{-1} which is derived from the sum of two enthalpy changes, namely, half of the $\Delta_r H°$(298.15 K) value for the dimer dissociation reaction $Na_2F_2(g) = 2NaF(g)$, and the $\Delta_r H°$(298.15 K) for the monomer dissociation reaction NaF(g) = Na(g) + F(g).

Employing $\Delta_r H°(298.15\ K) = 63.5$ kcal·mol^{-1} for $Na_2F_2(g) = 2NaF(g)$ and 153.0 kcal·mol^{-1} for NaF(g) = Na^+(g) + F^-(g), we estimate $\Delta_r H°(298.15\ K) = (1/2)(63.5) + 153.0 = 184.7$ kcal·mol^{-1} for the reaction $Na_2F_2(g) = NaF_2(g) + Na^+(g)$, which leads to $\Delta_f H°(298.15\ K)$ = 163.4 kcal·mol^{-1} for NaF_2 (g). For all calculations the $\Delta_f H°$(298.15 K) values of the chemical species involved are taken from JANAF Thermochemical Tables.

$\Delta_f H°(NaF_2^-, g, 298.15\ K)$ is tentatively adopted as −160±10 kcal·mol^{-1} (−669.440±41.8 kJ·mol^{-1}).

Heat Capacity and Entropy

The molecular structure is assumed to be linear, according to the suggestion by Walsh[2] that molecules with not more than 16 valence electrons are linear in their ground state. The Na–F bond distance is estimated by comparison with that of NaF(g) reported by Veazey and Gordy.[3] The vibrational frequencies are estimated from those for the isoelectronic molecule SiO_2(g).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−13.040	−661.011		
100	40.374	198.472	295.762	−9.729			
200	49.878	229.724	255.552	−5.166			
250	52.805	241.186	251.564	−2.595			
298.15	54.860	250.672	250.672	0.	−669.440	−662.120	116.001
300	54.927	251.011	250.673	0.102	−669.487	−662.074	115.277
350	56.473	259.600	251.347	2.889	−670.781	−660.738	98.610
400	57.612	267.219	252.864	5.742	−674.766	−659.006	86.057
450	58.466	274.057	254.846	8.645	−676.132	−656.953	76.257
500	59.118	280.252	257.081	11.585	−677.468	−654.750	68.401
600	60.024	291.117	261.874	17.546	−680.076	−649.960	56.584
700	60.603	300.416	266.732	23.579	−682.625	−644.739	48.111
800	60.994	308.536	271.460	29.660	−685.141	−639.155	41.733
900	61.269	315.737	275.987	35.774	−687.647	−633.256	36.753
1000	61.469	322.203	280.291	41.912	−690.166	−627.078	32.755
1100	61.619	328.069	284.372	48.066	−692.718	−620.646	29.472
1200	61.735	333.436	288.240	54.234	−792.085	−611.540	26.620
1300	61.825	338.381	291.910	60.413	−793.833	−596.423	23.965
1400	61.897	342.965	295.395	66.599	−795.595	−581.172	21.684
1500	61.956	347.238	298.710	72.792	−797.370	−565.794	19.703
1600	62.004	351.238	301.869	78.990	−799.158	−550.298	17.965
1700	62.044	354.998	304.885	85.192	−800.958	−534.689	16.429
1800	62.077	358.545	307.769	91.398	−802.769	−518.974	15.060
1900	62.106	361.903	310.530	97.607	−804.590	−503.158	13.833
2000	62.130	365.089	313.179	103.819	−806.418	−487.246	12.726
2100	62.151	368.121	315.724	110.033	−808.250	−471.242	11.722
2200	62.170	371.012	318.172	116.250	−810.085	−455.151	10.807
2300	62.186	373.776	320.530	122.467	−811.918	−438.976	9.969
2400	62.200	376.423	322.804	128.687	−813.748	−422.722	9.200
2500	62.212	378.963	325.000	134.907	−815.571	−406.392	8.491
2600	62.223	381.403	327.122	141.129	−817.385	−389.989	7.835
2700	62.233	383.751	329.177	147.352	−819.187	−373.517	7.226
2800	62.241	386.015	331.166	153.575	−820.976	−356.978	6.659
2900	62.249	388.199	333.096	159.800	−822.751	−340.375	6.131
3000	62.256	390.309	334.968	166.025	−824.509	−323.711	5.636
3100	62.263	392.351	336.786	172.251	−826.251	−306.989	5.173
3200	62.269	394.328	338.554	178.478	−827.975	−290.211	4.737
3300	62.274	396.244	340.273	184.705	−829.683	−273.380	4.327
3400	62.279	398.103	341.947	190.933	−831.374	−256.497	3.941
3500	62.283	399.909	343.577	197.161	−833.050	−239.564	3.575
3600	62.287	401.663	345.166	203.389	−834.711	−222.584	3.230
3700	62.291	403.370	346.716	209.618	−836.360	−205.557	2.902
3800	62.295	405.031	348.229	215.847	−837.998	−188.487	2.591
3900	62.298	406.649	349.706	222.077	−839.628	−171.373	2.295
4000	62.301	408.227	351.150	228.307	−841.252	−154.218	2.014
4100	62.304	409.765	352.561	234.537	−842.872	−137.022	1.746
4200	62.306	411.266	353.941	240.768	−844.490	−119.786	1.490
4300	62.308	412.732	355.291	246.998	−846.112	−102.513	1.245
4400	62.311	414.165	356.613	253.229	−847.699	−85.204	1.012
4500	62.313	415.565	357.907	259.461	−849.313	−67.857	0.788
4600	62.315	416.935	359.176	265.692	−850.946	−50.474	0.573
4700	62.317	418.275	360.419	271.923	−852.592	−33.054	0.367
4800	62.318	419.587	361.638	278.155	−854.255	−15.600	0.170
4900	62.320	420.872	362.834	284.387	−855.937	1.890	−0.020
5000	62.321	422.131	364.007	290.619	−857.635	19.413	−0.203
5100	62.323	423.365	365.159	296.851	−859.367	36.971	−0.379
5200	62.324	424.575	366.290	303.084	−861.128	54.564	−0.548
5300	62.325	425.763	367.401	309.316	−862.923	72.190	−0.711
5400	62.327	426.928	368.493	315.549	−864.755	89.851	−0.869
5500	62.328	428.071	369.565	321.782	−866.628	107.546	−1.021
5600	62.329	429.194	370.620	328.014	−868.543	125.275	−1.169
5700	62.330	430.297	371.658	334.247	−870.506	143.039	−1.311
5800	62.331	431.381	372.678	340.480	−872.517	160.838	−1.449
5900	62.332	432.447	373.682	346.713	−874.581	178.672	−1.582
6000	62.333	433.495	374.670	352.947	−876.542	196.523	−1.711

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [287.366 \pm 16.7]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-839.955 \pm 12.6]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-846.423 \pm 12.6]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[420](1)	[200](1)
[400](1)	[425](1)
[350](1)	[500](1)

Ground State Quantum Weight: [1] σ = [4]
Point Group: $[D_{2h}]$
Bond Distance: Na–F = 2.02 Å
Bond Angle: Na–F–Na = [85]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.614743 \times 10^{-114}]\ g^3\cdot cm^6$

Enthalpy of Formation

Although the absolute values of the vapor pressure measurements are not used for evaluation, the ratios of the numbers of dimeric and monomeric NaF molecules that effuse from the oven at the temperatures 1115–1191 K determined by Eisenstadt *et al.*[1] by use of the electron beam velocity selector method are used. Based on the reported equilibrium data, we evaluate the enthalpy change of the reaction (A) $Na_2F_2(g) = 2\ NaF(g)$ by the 2nd and 3rd law methods. The results are presented in the table below.

Porter and Schoonmaker[2] analyzed the vapor effusing from a Knudsen cell at 1121 K mass spectrometrically and derived the partial pressures of NaF(g) and $Na_2F_2(g)$ at that temperature. Using these reported partial pressures we calculate, by the 3rd law method, the value $\Delta_f H°(298.15\ K) = 64.1\ kcal\cdot mol^{-1}$ for reaction (A).

Sidorov *et al.*[3] studied the NaF–ZrF_4 system by the mass spectrometric method and derived the partial pressures of NaF(g) and $Na_2F_2(g)$ as a function of composition and temperature. Employing the data points reported at 1074 and 1167 K we obtain the 3rd law value $\Delta_f H°(298.15\ K) = 62.0 \pm 1.6\ kcal\cdot mol^{-1}$ for the same reaction.

The $\Delta_f H°(Na_2F_2, g, 298.15\ K)$ is calculated based on the adopted 3rd law value $\Delta_f H°(298.15\ K) = 63.5\ kcal\cdot mol^{-1}$ for the reaction $Na_2F_2(g) = 2\ NaF(g)$, using $\Delta_f H°(NaF, g, 298.15\ K) = -69.5\ kcal\cdot mol^{-1}$. Brewer and Brackett[9] reported $\Delta_f H°(1000\ K) = 56.9\ kcal\cdot mol^{-1}$ for the above reaction. According to our tables the $\Delta_f H°(1000\ K)$ value is 62.5 $kcal\cdot mol^{-1}$.

Source	T/K	Data Points	$\Delta_r H°(298.15\ K)$, $kcal\cdot mol^{-1}$ 2nd law	3rd law	Drift $cal\ K^{-1}\cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal\cdot mol^{-1}$
Eisenstadt *et al.*[1]	1115–1191	6	58.1 ± 2.9	63.5	4.7 ± 2.5	−202.4
Porter and Schoonmaker[2]	1121	1	—	64.1	—	−203.0
Sidorov *et al.*[3]	1074–1167	8	—	62.0 ± 1.6	—	−200.9

Heat Capacity and Entropy

The $Na_2F_2(g)$ molecule is assumed to have a rhombic structure with D_{2h} (ν_h) symmetry.[4,5] The Na–F bond distance is reported by Akishin and Rambidi,[5] who studied the molecular structure of alkali halide vapors by electron diffraction with sector microphotometry. The bond angle is estimated by comparison with those of the other alkali halides. Berkowitz[4,6] has calculated the vibration frequencies of Na_2F_2 based on an ionic model. By comparison of the calculated frequencies of Li_2F_2[6] with those of the observed ones (see Li_2F_2(g) table for details), we re-estimate the vibrational frequencies for $Na_2F_2(g)$ to be higher than the ones reported by Berkowitz.[6] Bauer *et al.*[7] used a pseudo electrostatic model, similar to the one suggested by O'Konski and Higuchi,[8] to calculate the entropies of dimerization for a number of gaseous alkali halides and estimated the six vibrational frequencies as 477, 318, 291, 477, 291 and 291 cm^{-1}. Bauer *et al.*[7] calculated $\Delta_{sub}H°(1146\ K) = -32.5$ $cal\ K^{-1}\cdot mol^{-1}$ for the reaction $2\ NaF(g) = Na_2F_2(g)$, in reasonable agreement with the value $-33.5\ cal\ K^{-1}\cdot mol^{-1}$ which is derived using JANAF $S°(1146\ K)$ values for NaF(g) and $Na_2F_2(g)$.

The three principal moments of inertia are: $I_A = 13.9948 \times 10^{-39}$, $I_B = 14.2197 \times 10^{-39}$, and $I_C = 28.2145 \times 10^{-39}\ g\cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−15.250	−839.955	−839.955	INFINITE
100	41.612	225.792	342.904	−11.711	−842.002	−842.782	440.224
200	60.880	260.954	293.579	−6.525	−844.657	−842.438	220.022
250	66.886	275.228	288.512	−3.321	−845.604	−841.771	175.878
298.15	70.821	287.366	287.366	0.	−846.423	−840.957	147.332
300	70.945	287.805	287.368	0.131	−846.454	−840.923	146.418
350	73.732	298.963	288.243	3.752	−847.327	−839.934	125.353
400	75.698	308.945	290.218	7.491	−853.557	−838.401	109.484
450	77.125	317.947	292.807	11.313	−854.527	−836.448	97.092
500	78.187	326.131	295.736	15.197	−855.419	−834.391	87.168
600	79.625	340.524	302.034	23.094	−857.028	−830.030	72.261
700	80.524	352.871	308.436	31.105	−858.473	−825.415	61.593
800	81.120	363.665	314.679	39.189	−859.817	−820.599	53.580
900	81.536	373.245	320.664	47.323	−861.111	−815.619	47.337
1000	81.835	381.852	326.360	55.492	−862.407	−810.495	42.336
1100	82.059	389.662	331.765	63.687	−863.748	−805.240	38.238
1200	82.230	396.810	336.892	71.902	−1058.700	−794.979	34.605
1300	82.364	403.398	341.758	80.132	−1058.397	−773.014	31.060
1400	82.470	409.505	346.381	88.374	−1058.103	−751.073	28.023
1500	82.556	415.198	350.781	96.625	−1057.819	−729.152	25.391
1600	82.627	420.529	354.976	104.885	−1057.546	−707.250	23.089
1700	82.686	425.540	358.981	113.150	−1057.283	−685.365	21.059
1800	82.735	430.267	362.811	121.422	−1057.030	−663.494	19.254
1900	82.777	434.742	366.480	129.697	−1056.785	−641.638	17.640
2000	82.812	438.989	370.000	137.977	−1056.547	−619.794	16.187
2100	82.843	443.030	373.382	146.260	−1056.313	−597.963	14.874
2200	82.870	446.884	376.637	154.545	−1056.081	−576.142	13.679
2300	82.893	450.569	379.771	162.833	−1055.850	−554.331	12.589
2400	82.913	454.097	382.795	171.124	−1055.617	−532.531	11.590
2500	82.931	457.482	385.716	179.416	−1055.380	−510.741	10.671
2600	82.947	460.735	388.539	187.710	−1055.138	−488.960	9.823
2700	82.962	463.866	391.271	196.005	−1054.890	−467.189	9.038
2800	82.974	466.883	393.918	204.302	−1054.634	−445.427	8.310
2900	82.986	469.795	396.484	212.600	−1054.370	−423.674	7.631
3000	82.996	472.608	398.975	220.899	−1054.100	−401.930	6.998
3100	83.006	475.330	401.395	229.199	−1053.823	−380.196	6.406
3200	83.014	477.965	403.747	237.500	−1053.542	−358.471	5.851
3300	83.022	480.520	406.035	245.802	−1053.256	−336.754	5.330
3400	83.029	482.999	408.262	254.105	−1052.970	−315.046	4.840
3500	83.035	485.406	410.432	262.408	−1052.686	−293.347	4.378
3600	83.041	487.745	412.547	270.712	−1052.406	−271.655	3.942
3700	83.047	490.020	414.610	279.016	−1052.136	−249.971	3.529
3800	83.052	492.235	416.624	287.321	−1051.878	−228.295	3.138
3900	83.057	494.392	418.591	295.627	−1051.637	−206.625	2.767
4000	83.061	496.495	420.512	303.932	−1051.419	−184.961	2.415
4100	83.065	498.546	422.390	312.239	−1051.229	−163.302	2.080
4200	83.069	500.548	424.228	320.545	−1051.067	−141.647	1.762
4300	83.072	502.503	426.025	328.852	−1050.948	−119.996	1.458
4400	83.075	504.412	427.785	337.160	−1050.788	−98.354	1.168
4500	83.078	506.279	429.509	345.468	−1050.719	−76.710	0.890
4600	83.081	508.105	431.198	353.776	−1050.717	−55.065	0.625
4700	83.084	509.892	432.853	362.084	−1050.772	−33.420	0.371
4800	83.086	511.641	434.476	370.392	−1050.891	−11.773	0.128
4900	83.089	513.355	436.069	378.701	−1051.079	9.877	−0.105
5000	83.091	515.033	437.631	387.010	−1051.328	31.530	−0.329
5100	83.093	516.679	439.165	395.319	−1051.670	53.191	−0.545
5200	83.095	518.292	440.671	403.629	−1052.100	74.859	−0.752
5300	83.097	519.875	442.151	411.938	−1052.623	96.536	−0.951
5400	83.098	521.428	443.605	420.248	−1053.246	118.224	−1.144
5500	83.100	522.953	445.033	428.558	−1053.975	139.924	−1.329
5600	83.102	524.450	446.438	436.868	−1054.814	161.639	−1.508
5700	83.103	525.921	447.820	445.178	−1055.770	183.369	−1.680
5800	83.104	527.367	449.179	453.489	−1056.847	205.118	−1.847
5900	83.106	528.787	450.516	461.799	−1058.051	226.886	−2.009
6000	83.107	530.184	451.832	470.110	−1059.069	248.639	−2.165

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$\Delta_{at}H°(0\ K) = 375 \pm 2\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 247.46 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_fH°(0\ K) = 26.8 \pm 2\ kJ \cdot mol^{-1}$
$\Delta_fH°(298.15\ K) = 24.5 \pm 2\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[X^1A]$	0.0	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
928(1)
461(1)
831(1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: F–O = 1.412 Å
Bond Angle: F–O–F = 103° 10'
Product of the Moments of Inertia: $I_AI_BI_C = 101.8236 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

King and Armstrong[1] have established the enthalpy of formation with a series of reactions in a flame calorimeter. They burned OF_2 in hydrogen to give HF aqueous; in addition they burned F_2 in hydrogen and O_2 in hydrogen so that the enthalpy of formation, 24.52 $kJ \cdot mol^{-1}$, was directly obtainable. This value was in good agreement with the recalculated values of Wartenberg and Klinkott,[2] 23.85 ± 12.6 $kJ \cdot mol^{-1}$, and of Ruff and Menzel,[3] 19.66 ± 8.45 $kJ \cdot mol^{-1}$ but differed from that of Bisbee *et al.*,[4] −16.99 ± 8.4 $kJ \cdot mol^{-1}$. There are several factors in the experiments of Bisbee *et al.* that might cause the enthalpy of formation to be too negative. We adopt the value of 24.52 $kJ \cdot mol^{-1}$, reported by King and Armstrong.[1]

Heat Capacity and Entropy

The structural parameters are those reported by Pierce *et al.*[5] for the average ground state molecule from the microwave spectrum. Earlier measurements of Hilton *et al.*[6] disagree but according to Pierce *et al.*,[7] the line assignments used by Hilton *et al.* are incorrect. The microwave study of Morino and Saito[8] yielded r_e = 1.4053 Å and an angle of 103°4' which is in agreement with our adopted values. The principle moments of inertia (in $g \cdot cm^2$) are: $I_A = 1.4392 \times 10^{-39}$, $I_B = 7.7225 \times 10^{-39}$, and $I_C = 9.1617 \times 10^{-39}$.

We adopt the vibrational frequencies reported by Jones *et al.*,[9] several other investigators reported similar values.[10–12] Nebgen *et al.*[13] obtained the harmonic frequencies and the anharmonic constants for the three vibrations.

There are numerous more recent studies focusing on Fermi resonance and Coriolis coupling but the results support our adopted values.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−10.895	26.791	26.791	INFINITE
50	33.261	183.592	368.242	−9.232	26.278	28.436	−29.707
100	33.751	206.729	282.351	−7.562	25.765	30.795	−16.085
150	35.531	220.714	259.612	−5.835	25.307	33.412	−11.635
200	38.056	231.271	251.255	−3.997	24.946	36.171	−9.447
250	40.796	240.057	248.159	−2.026	24.686	39.009	−8.150
298.15	43.302	247.460	247.460	.000	24.520	41.784	−7.320
300	43.393	247.728	247.461	.080	24.515	41.891	−7.294
400	47.586	260.820	249.217	4.641	24.371	47.711	−6.230
500	50.463	271.769	252.663	9.553	24.388	53.546	−5.594
600	52.400	281.152	256.648	14.702	24.484	59.369	−5.169
700	53.728	289.336	260.746	20.013	24.616	65.173	−4.863
800	54.664	296.574	264.781	25.435	24.760	70.957	−4.633
900	55.343	303.054	268.680	30.937	24.905	76.723	−4.453
1000	55.847	308.912	272.415	36.498	25.045	82.473	−4.308
1100	56.232	314.254	275.979	42.103	25.175	88.210	−4.189
1200	56.531	319.160	279.376	47.741	25.294	93.935	−4.089
1300	56.768	323.695	282.613	53.407	25.398	99.651	−4.004
1400	56.958	327.909	285.699	59.093	25.487	105.359	−3.931
1500	57.113	331.844	288.646	64.797	25.560	111.061	−3.867
1600	57.241	335.534	291.462	70.515	25.616	116.759	−3.812
1700	57.348	339.008	294.158	76.245	25.654	122.455	−3.763
1800	57.438	342.288	296.742	81.984	25.676	128.148	−3.719
1900	57.515	345.396	299.221	87.732	25.682	133.841	−3.680
2000	57.580	348.348	301.605	93.487	25.674	139.534	−3.644
2100	57.637	351.159	303.898	99.248	25.656	145.227	−3.612
2200	57.687	353.841	306.108	105.014	25.628	150.922	−3.583
2300	57.730	356.406	308.239	110.785	25.595	156.617	−3.557
2400	57.768	358.864	310.298	116.560	25.561	162.314	−3.533
2500	57.801	361.223	312.288	122.338	25.527	168.013	−3.510
2600	57.831	363.491	314.214	128.120	25.498	173.713	−3.490
2700	57.858	365.674	316.080	133.904	25.478	179.414	−3.471
2800	57.882	367.778	317.889	139.691	25.468	185.116	−3.453
2900	57.903	369.810	319.644	145.481	25.473	190.817	−3.437
3000	57.923	371.773	321.349	151.272	25.495	196.519	−3.422
3100	57.940	373.673	323.007	157.065	25.535	202.219	−3.407
3200	57.956	375.513	324.619	162.860	25.597	207.917	−3.394
3300	57.971	377.296	326.188	168.656	25.682	213.614	−3.381
3400	57.984	379.027	327.717	174.454	25.792	219.307	−3.369
3500	57.996	380.708	329.207	180.253	25.927	224.997	−3.358
3600	58.007	382.342	330.660	186.053	26.090	230.682	−3.347
3700	58.018	383.931	332.079	191.855	26.279	236.363	−3.337
3800	58.027	385.479	333.464	197.657	26.496	242.038	−3.327
3900	58.036	386.986	334.817	203.460	26.742	247.707	−3.318
4000	58.044	388.456	336.140	209.264	27.016	253.369	−3.309
4100	58.052	389.889	337.433	215.069	27.318	259.024	−3.300
4200	58.059	391.288	338.699	220.874	27.649	264.672	−3.292
4300	58.065	392.654	339.938	226.681	28.006	270.311	−3.284
4400	58.071	393.989	341.151	232.487	28.392	275.942	−3.276
4500	58.077	395.294	342.340	238.295	28.803	281.563	−3.268
4600	58.082	396.571	343.505	244.103	29.241	287.175	−3.261
4700	58.087	397.820	344.647	249.911	29.704	292.778	−3.254
4800	58.092	399.043	345.768	255.720	30.192	298.370	−3.247
4900	58.097	400.241	346.867	261.530	30.702	303.952	−3.240
5000	58.101	401.415	347.947	267.339	31.236	309.523	−3.234
5100	58.105	402.565	349.006	273.150	31.790	315.083	−3.227
5200	58.108	403.694	350.047	278.960	32.366	320.632	−3.221
5300	58.112	404.800	351.070	284.771	32.961	326.171	−3.215
5400	58.115	405.887	352.075	290.583	33.573	331.697	−3.209
5500	58.118	406.953	353.063	296.394	34.203	337.211	−3.203
5600	58.121	408.000	354.035	302.206	34.849	342.716	−3.197
5700	58.124	409.029	354.991	308.019	35.510	348.207	−3.191
5800	58.127	410.040	355.931	313.831	36.184	353.687	−3.185
5900	58.129	411.034	356.857	319.644	36.871	359.155	−3.180
6000	58.131	412.011	357.768	325.457	37.568	364.612	−3.174

PREVIOUS: December 1969 (1 bar) CURRENT: September 1995 (1 bar)

$S°(298.15\ K) = 279.132\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-538.967 \pm 105]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-543.920 \pm 105]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1330 (1)	377.8(1)
808.2(1)	747.0(1)
530.4(1)	392.5(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: O–S = 1.412 Å; S–F = 1.585 Å
Bond Angles: O–S–F = 106.82°; F–S–F = 92.82°
Product of the Moments of Inertia: $I_A I_B I_C = 1.655344 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The increment in $\Delta_f H°$ at 298.15 K between gaseous SOF_2 and SO_2F_2 is estimated from increments for the four pairs a) S and SO, b) SO and SO_2, c) SO_2 and SO_3, and d) $SOCl_2$ and SO_2Cl_2. Based on $\Delta_f H° = -181.3\ kcal·mol^{-1}$ for SO_2F_2[1], we derive a) −116, b) −109, c) −158, and d) −148 for $\Delta_f H°$ of SOF_2(g). The derivation is based on $\Delta_f H°(SOCl_2, g, 298.15\ K)$.[1,2] Giving lesser weight to c) which involves SO_3, we adopt an average of $-130 \pm 25\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular structure is from the microwave study of Ferguson.[3] Principal moments of inertia are $I_A = 9.7369 \times 10^{-39}$, $I_B = 10.0399 \times 10^{-39}$, and $I_C = 16.9332 \times 10^{-39}\ g·cm^2$. Vibrational frequencies are those assigned by Pace and Samuelson[4] from their gas phase infrared spectra. These authors also measured Raman spectra of liquid and gas and summarized earlier spectral studies. We adopt ν_1 as the lower wave number of the Fermi resonance doublet at 1330 and 1340 cm^{-1}. Uncertainty is greatest for the overlapping bands near 378 and 392 cm^{-1}.

Pace and Turnbull[5] derived $S° = 63.56 \pm 0.15\ cal\ K^{-1}·mol^{-1}$ for the ideal gas at $T_{vap} = 228.84$ K from calorimetric measurements of heat capacity (12 to 230 K), $\Delta_{fus}H°$, and $\Delta_{vap}H°$. Spectroscopic data of this table yield the corresponding value of $S° = 63.29$ which is 0.27 cal $K^{-1}·mol^{-1}$ smaller than observed. Pace and Turnbull attributed the minor discrepancy to bias in the measurements of $\Delta_{vap}H°$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−12.625	−538.967	−538.967	INFINITE
100	35.545	230.278	322.875	−9.260	−540.650	−536.723	280.356
200	47.164	258.341	284.057	−5.143	−542.560	−532.022	138.950
250	52.631	269.468	280.048	−2.645	−543.313	−529.298	110.591
298.15	57.105	279.132	279.132	0.	−543.920	−526.542	92.248
300	57.262	279.485	279.133	0.106	−543.941	−526.434	91.660
350	61.105	288.610	279.844	3.068	−544.472	−523.473	78.124
400	64.276	296.983	281.471	6.205	−547.144	−520.353	67.951
450	66.894	304.710	283.629	9.486	−548.214	−516.948	60.006
500	69.060	311.874	286.100	12.887	−549.285	−513.414	53.636
600	72.365	324.775	291.495	19.968	−550.842	−506.084	44.059
700	74.697	336.115	297.076	27.328	−552.008	−498.528	37.201
800	76.381	346.206	302.598	34.886	−552.939	−490.823	32.047
900	77.626	355.277	307.956	42.589	−606.849	−481.929	27.970
1000	78.568	363.507	313.106	50.401	−606.315	−468.077	24.450
1100	79.293	371.031	318.035	58.296	−605.766	−454.280	21.572
1200	79.863	377.956	322.743	66.255	−605.214	−440.533	19.176
1300	80.317	384.367	327.240	74.265	−604.668	−426.832	17.150
1400	80.685	390.333	331.536	82.315	−604.132	−413.172	15.416
1500	80.987	395.910	335.644	90.399	−603.613	−399.551	13.914
1600	81.237	401.145	339.576	98.511	−603.112	−385.963	12.600
1700	81.446	406.077	343.344	106.645	−602.631	−372.406	11.443
1800	81.623	410.737	346.960	114.799	−602.172	−358.877	10.414
1900	81.774	415.154	350.434	122.969	−601.733	−345.372	9.495
2000	81.904	419.352	353.776	131.153	−601.312	−331.891	8.668
2100	82.016	423.351	356.994	139.349	−600.909	−318.430	7.921
2200	82.114	427.169	360.098	147.556	−600.518	−304.987	7.241
2300	82.200	430.821	363.094	155.772	−600.138	−291.562	6.622
2400	82.276	434.321	365.989	163.996	−599.764	−278.154	6.054
2500	82.342	437.681	368.790	172.227	−599.394	−264.762	5.532
2600	82.402	440.912	371.502	180.464	−599.023	−251.384	5.050
2700	82.455	444.023	374.131	188.707	−598.647	−238.020	4.605
2800	82.503	447.022	376.681	196.955	−598.264	−224.670	4.191
2900	82.546	449.918	379.157	205.207	−597.869	−211.335	3.807
3000	82.584	452.717	381.563	213.464	−597.461	−198.013	3.448
3100	82.619	455.426	383.902	221.724	−597.037	−184.705	3.112
3200	82.651	458.049	386.178	229.988	−596.594	−171.411	2.798
3300	82.680	460.593	388.395	238.254	−596.130	−158.131	2.503
3400	82.707	463.062	390.555	246.524	−595.645	−144.865	2.226
3500	82.731	465.459	392.661	254.795	−595.137	−131.615	1.964
3600	82.754	467.790	394.715	263.070	−594.606	−118.378	1.718
3700	82.774	470.058	396.721	271.346	−594.050	−105.158	1.485
3800	82.793	472.266	398.680	279.625	−593.469	−91.952	1.264
3900	82.811	474.417	400.595	287.905	−592.863	−78.762	1.055
4000	82.827	476.513	402.467	296.187	−592.233	−65.588	0.856
4100	82.843	478.559	404.298	304.470	−591.578	−52.430	0.668
4200	82.857	480.555	406.090	312.755	−590.900	−39.288	0.489
4300	82.870	482.505	407.844	321.042	−590.198	−26.163	0.318
4400	82.882	484.410	409.563	329.329	−589.474	−13.054	0.155
4500	82.894	486.273	411.247	337.618	−588.728	0.038	−0.000
4600	82.904	488.095	412.898	345.908	−587.961	13.113	−0.149
4700	82.914	489.878	414.517	354.199	−587.174	26.172	−0.291
4800	82.924	491.624	416.105	362.491	−586.369	39.213	−0.427
4900	82.933	493.334	417.664	370.783	−585.546	52.238	−0.557
5000	82.941	495.009	419.194	379.077	−584.706	65.245	−0.682
5100	82.949	496.652	420.697	387.372	−583.852	78.236	−0.801
5200	82.956	498.263	422.173	395.667	−582.983	91.210	−0.916
5300	82.963	499.843	423.624	403.963	−582.102	104.167	−1.027
5400	82.970	501.394	425.049	412.259	−581.209	117.107	−1.133
5500	82.976	502.916	426.451	420.557	−580.306	130.030	−1.235
5600	82.982	504.411	427.830	428.855	−579.394	142.937	−1.333
5700	82.988	505.880	429.187	437.153	−578.475	155.827	−1.428
5800	82.993	507.324	430.521	445.452	−577.549	168.702	−1.519
5900	82.998	508.742	431.835	453.752	−576.618	181.560	−1.607
6000	83.003	510.137	433.129	462.052	−575.683	194.403	−1.692

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K)$ = [271.247] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−962.125 ± 25.1] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−966.504 ± 25.1] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm	ν, cm
[440](1)	[760](1)
[490](1)	[980](1)
[610](1)	[1420](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: Si–O = [1.60] Å; Si–F = [1.54] Å
Bond Angles: F–Si–O = [120]°; F–Si–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.565383 × 10^{-114}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(SiOF_2, g, 298.15\ K)$ is estimated by comparison with those for SiF_4(g) and SiO_2(g).

Heat Capacity and Entropy

The vibrational frequencies were estimated by comparison with those for COF_2(g) and TiOF(g). The vibrational frequencies for COF_2(g) and $TiOF_2$(g) were obtained from Lovell *et al.*[1] and Gordon,[2] respectively. The bond distances of Si–O and Si–F were assumed to be the same as those for SiO(g) and SiF_4(g), respectively. Point group, ground state multiplicity, and bond angles were estimated.

References

[1]R. J. Lovell, C. V. Stephenson, and E. A. Jones, J. Chem. Phys. **22,** 1953 (1954).
[2]J. S. Gordon, personal communication, (May 12, 1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.006	−962.125	−962.125	INFINITE
100	34.330	225.460	312.100	−8.664	−963.409	−959.869	501.384
200	43.808	251.839	275.855	−4.803	−965.111	−955.667	249.595
250	49.127	262.195	272.106	−2.478	−965.867	−953.217	199.164
298.15	53.689	271.247	271.247	0.	−966.504	−950.721	166.562
300	53.851	271.579	271.248	0.099	−966.527	−950.623	165.518
350	57.899	280.193	271.919	2.896	−967.092	−947.927	141.470
400	61.320	288.154	273.457	5.879	−967.574	−945.155	123.425
450	64.198	295.548	275.506	9.019	−967.983	−942.327	109.383
500	66.615	302.441	277.858	12.291	−968.334	−939.457	98.144
600	70.366	314.937	283.019	19.151	−968.904	−933.626	81.279
700	73.058	325.997	288.384	26.329	−969.352	−927.709	69.227
800	75.027	335.888	293.715	33.738	−969.730	−921.734	60.183
900	76.497	344.814	298.905	41.318	−970.069	−915.714	53.147
1000	77.615	352.934	303.908	49.026	−970.393	−909.657	47.516
1100	78.481	360.374	308.708	56.833	−970.717	−903.568	42.907
1200	79.164	367.233	313.303	64.716	−971.052	−897.448	39.065
1300	79.710	373.592	317.699	72.661	−971.409	−891.301	35.813
1400	80.154	379.516	321.905	80.655	−971.795	−885.124	33.024
1500	80.518	385.058	325.932	88.689	−972.216	−878.919	30.607
1600	80.821	390.265	329.792	96.756	−972.677	−872.684	28.490
1700	81.074	395.172	333.495	104.851	−1023.358	−865.973	26.608
1800	81.289	399.813	337.052	112.970	−1023.677	−856.706	24.861
1900	81.473	404.213	340.472	121.108	−1024.000	−847.421	23.297
2000	81.630	408.396	343.764	129.264	−1024.326	−838.119	21.889
2100	81.767	412.382	346.938	137.434	−1024.656	−828.800	20.615
2200	81.886	416.189	349.999	145.616	−1024.986	−819.466	19.457
2300	81.991	419.831	352.957	153.810	−1025.315	−810.117	18.398
2400	82.083	423.323	355.817	162.014	−1025.641	−800.753	17.428
2500	82.164	426.675	358.584	170.227	−1025.960	−791.376	16.535
2600	82.237	429.899	361.266	178.447	−1026.270	−781.987	15.710
2700	82.301	433.004	363.866	186.674	−1026.568	−772.586	14.947
2800	82.360	435.998	366.389	194.907	−1026.851	−763.174	14.237
2900	82.412	438.889	368.839	203.145	−1027.116	−753.752	13.577
3000	82.459	441.684	371.221	211.389	−1027.362	−744.321	12.960
3100	82.502	444.388	373.538	219.637	−1027.586	−734.883	12.383
3200	82.541	447.008	375.793	227.889	−1027.786	−725.438	11.842
3300	82.577	449.549	377.990	236.145	−1027.961	−715.987	11.333
3400	82.609	452.014	380.131	244.405	−1028.110	−706.530	10.855
3500	82.639	454.410	382.219	252.667	−1028.230	−697.071	10.403
3600	82.666	456.738	384.257	260.932	−1412.475	−677.146	9.825
3700	82.692	459.003	386.246	269.200	−1412.124	−656.726	9.271
3800	82.715	461.209	388.190	277.471	−1411.746	−636.314	8.747
3900	82.736	463.358	390.090	285.743	−1411.340	−615.913	8.249
4000	82.756	465.453	391.948	294.018	−1410.905	−595.523	7.777
4100	82.775	467.496	393.766	302.294	−1410.441	−575.145	7.327
4200	82.792	469.491	395.545	310.573	−1409.949	−554.777	6.900
4300	82.808	471.440	397.288	318.853	−1409.429	−534.422	6.492
4400	82.823	473.343	398.995	327.134	−1408.880	−514.080	6.103
4500	82.837	475.205	400.668	335.417	−1408.304	−493.750	5.731
4600	82.850	477.026	402.308	343.702	−1407.700	−473.433	5.376
4700	82.863	478.808	403.917	351.987	−1407.071	−453.129	5.036
4800	82.874	480.552	405.495	360.274	−1406.416	−432.840	4.710
4900	82.885	482.261	407.044	368.562	−1405.736	−412.564	4.398
5000	82.895	483.936	408.566	376.851	−1405.033	−392.302	4.098
5100	82.905	485.577	410.060	385.141	−1404.308	−372.054	3.811
5200	82.914	487.187	411.527	393.432	−1403.561	−351.821	3.534
5300	82.922	488.767	412.970	401.724	−1402.794	−331.603	3.268
5400	82.931	490.317	414.388	410.017	−1402.008	−311.399	3.012
5500	82.938	491.839	415.782	418.310	−1401.205	−291.211	2.766
5600	82.946	493.333	417.154	426.604	−1400.385	−271.035	2.528
5700	82.952	494.801	418.503	434.899	−1399.551	−250.877	2.299
5800	82.959	496.244	419.831	443.195	−1398.704	−230.731	2.078
5900	82.965	497.662	421.138	451.491	−1397.846	−210.602	1.865
6000	82.971	499.057	422.425	459.788	−1396.976	−190.486	1.658

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K) = [284.678]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-920.454]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-924.873]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[553](1)	[715](1)
[888](1)	[300](1)
[350](1)	[452](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: [C_{2v}]

Bond Distances: Ti–O = [1.62] Å; Ti–F = [1.74] Å

Bond Angle: O–Ti–F = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.344131 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as $-220\ kcal·mol^{-1}$ by Gordon.[1] $\Delta_f H°(298.15\ K)$ was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] The principal moments of inertia are: $I_A = 11.6652 \times 10^{-39}$, $I_B = 14.3272 \times 10^{-39}$, and $I_C = 25.9925 \times 10^{-39}\ g·cm^2$.

Reference

[1] J. S. Gordon, Astrosystems, Inc., Caldwell Twp., N. J., personal communication, (January 10, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.577	−920.454	−920.454	INFINITE
100	37.517	231.211	332.858	−10.165	−921.961	−918.554	479.803
200	52.117	261.723	290.111	−5.678	−923.776	−914.396	238.816
250	58.147	274.024	285.687	−2.916	−924.409	−911.974	190.547
298.15	62.779	284.678	284.678	0.	−924.873	−909.535	159.347
300	62.936	285.067	284.679	0.116	−924.889	−909.440	158.348
350	66.665	295.060	285.460	3.360	−925.259	−906.835	135.338
400	69.558	304.159	287.237	6.769	−925.555	−904.182	118.074
450	71.812	312.488	289.587	10.305	−925.801	−901.495	104.643
500	73.585	320.149	292.265	13.942	−926.017	−898.782	93.895
600	76.128	333.807	298.079	21.437	−926.401	−893.299	77.769
700	77.806	345.676	304.049	29.139	−926.765	−887.753	66.245
800	78.961	356.146	309.920	36.981	−927.126	−882.155	57.599
900	79.784	365.496	315.585	44.920	−927.535	−876.510	50.871
1000	80.390	373.935	321.005	52.930	−928.067	−870.813	45.487
1100	80.848	381.620	326.171	60.993	−928.793	−865.055	41.078
1200	81.202	388.670	331.090	69.097	−933.705	−859.101	37.396
1300	81.480	395.181	335.773	77.231	−934.112	−852.868	34.269
1400	81.703	401.228	340.235	85.391	−934.608	−846.600	31.587
1500	81.885	406.871	344.491	93.571	−935.210	−840.294	29.262
1600	82.034	412.161	348.557	101.767	−935.931	−833.943	27.225
1700	82.159	417.138	352.446	109.977	−936.785	−827.544	25.427
1800	82.263	421.837	356.172	118.198	−937.785	−821.090	23.827
1900	82.352	426.288	359.746	126.429	−938.944	−814.576	22.394
2000	82.428	430.514	363.180	134.668	−954.959	−807.543	21.091
2100	82.494	434.537	366.483	142.914	−957.216	−800.117	19.902
2200	82.551	438.376	369.664	151.166	−959.481	−792.582	18.818
2300	82.601	442.047	372.732	159.424	−961.751	−784.945	17.827
2400	82.645	445.563	375.694	167.686	−964.022	−777.210	16.916
2500	82.684	448.938	378.556	175.953	−966.291	−769.379	16.075
2600	82.718	452.181	381.326	184.223	−968.555	−761.458	15.298
2700	82.749	455.304	384.009	192.496	−970.811	−753.449	14.576
2800	82.777	458.313	386.609	200.773	−973.055	−745.358	13.905
2900	82.801	461.219	389.132	209.052	−975.284	−737.187	13.278
3000	82.824	464.026	391.582	217.333	−977.496	−728.939	12.692
3100	82.844	466.742	393.963	225.616	−979.689	−720.617	12.142
3200	82.862	469.373	396.278	233.902	−981.860	−712.226	11.626
3300	82.879	471.923	398.532	242.189	−984.008	−703.766	11.140
3400	82.894	474.397	400.727	250.477	−986.131	−695.242	10.681
3500	82.908	476.800	402.867	258.768	−988.229	−686.656	10.248
3600	82.921	479.136	404.953	267.059	−990.299	−678.010	9.838
3700	82.933	481.408	406.989	275.352	−1401.440	−661.519	9.339
3800	82.944	483.620	408.976	283.646	−1402.221	−641.511	8.818
3900	82.954	485.775	410.918	291.941	−1403.028	−621.481	8.324
4000	82.963	487.875	412.816	300.236	−1403.861	−601.431	7.854
4100	82.972	489.924	414.672	308.533	−1404.718	−581.360	7.407
4200	82.980	491.923	416.487	316.831	−1405.598	−561.267	6.980
4300	82.988	493.876	418.264	325.129	−1406.500	−541.154	6.574
4400	82.995	495.784	420.005	333.428	−1407.422	−521.019	6.185
4500	83.001	497.649	421.709	341.728	−1408.362	−500.863	5.814
4600	83.007	499.473	423.380	350.029	−1409.320	−480.686	5.458
4700	83.013	501.259	425.018	358.330	−1410.295	−460.487	5.118
4800	83.018	503.006	426.625	366.631	−1411.285	−440.268	4.791
4900	83.024	504.718	428.201	374.933	−1412.290	−420.028	4.478
5000	83.028	506.396	429.748	383.236	−1413.307	−399.768	4.176
5100	83.033	508.040	431.267	391.539	−1414.336	−379.486	3.887
5200	83.037	509.652	432.759	399.842	−1415.377	−359.185	3.608
5300	83.041	511.234	434.225	408.146	−1416.428	−338.864	3.340
5400	83.045	512.786	435.666	416.451	−1417.489	−318.523	3.081
5500	83.048	514.310	437.082	424.755	−1418.558	−298.162	2.832
5600	83.052	515.806	438.474	433.060	−1419.635	−277.781	2.591
5700	83.055	517.276	439.844	441.366	−1420.720	−257.382	2.359
5800	83.058	518.721	441.191	449.671	−1421.812	−236.962	2.134
5900	83.061	520.141	442.518	457.977	−1422.910	−216.525	1.917
6000	83.064	521.537	443.823	466.283	−1424.014	−196.068	1.707

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

$S°(298.15\ K) = 277.2 \pm 0.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 22.9 \pm 2.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 19.2 \pm 2.0\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight

State	ϵ_i, cm^{-1}	g_i
	0.0	1

Vibrational Frequencies and Degeneracies

ν, cm^{-1}	ν,cm^{-1}
1210(1)	202(1)
630(1)	614(1)
360(1)	466(1)

Point Group: C_s $\sigma = 1$

Bond Distances: F–O = 1.575 Å; O–O = 1.217 Å

Bond Angles: O–O–F = 109°30'; dihedral angle = 87°30'

Product of the Moments of Inertia: $I_A I_B I_C = 1.3348 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

A critical measurement for the calculation of the thermodynamic functions for both O_2F and O_2F_2 is the standard enthalpy of formation of O_2F_2 by Kirshenbaum *et al.*[1] These authors made a calorimetric measurement at 190 K for decomposition of O_2F_2 into O_2 and F_2. Conversion of that measurement from 190 K to the standard enthalpy of formation at 298 K required knowledge of the difference in constant–volume heat capacity between the reactant (O_2F_2) and the products (O_2 and F_2). The authors assumed that difference to be zero over the entire range. With the published heat capacities for fluorine and oxygen, plus that for O_2F_2 reported here, we find that the average heat capacity difference over the 190 to 298 K temperature range to be 1.41 cal $K^{-1} \cdot mol^{-1}$. The standard enthalpy of formation that Kirshenbaum *et al.*[1] reported was $\Delta_f H°(O_2F_2, 298.15\ K) = 19.8 \pm 1.3\ kJ \cdot mol^{-1}$. With the heat capacity correction suggested by Lyman,[2] it became $\Delta_f H°(O_2F_2, 298.15\ K) = 19.2 \pm 0.84\ kJ \cdot mol^{-1}$ as suggested by Lyman.[2]

The value adopted is that recommended by the evaluation of Lyman,[2] with an increased uncertainty.

Heat Capacity and Entropy

The structure of this molecule is estimated to be a nonlinear chain with an O–O–F bond angle of 109°30' and a dihedral angle 87°30'. The adopted bond lengths are r(F–O) = 1.575 Å and r(O–O) = 1.217 Å from the microwave study of Jackson.[3] The principle moments of inertia (in $g \cdot cm^2$) are: $I_A = 4.1409 \times 10^{-39}$, $I_B = 1.6747 \times 10^{-38}$, $I_C = 1.9247 \times 10^{-38}$.

The vibrational frequencies are those recommended in the review by Jacox.[4] For $\nu_1 - \nu_5$ we adopt the gas phase results (rather than the matrix isolation matrix) of Kim and Campbell.[5] For ν_6 we adopt the results of Spratley *et al.*[6] which were derived from oxygen matrix isolation studies. For ν_2, ν_3 and ν_5, these matrix isolation studies agree within 6 cm^{-1} of the gas phase results. The matrix isolation results of Arkell,[7] Gardiner *et al.*[8] and Jacox[4] are in support of these values.

References

[1]A.D. Kirshenbaum, A.V. Grosse and J.G. Aston, J. Am. Chem. Soc. **81**, 6398 (1959).
[2]J.L. Lyman, J. Phys. Chem. Ref. Data **18(2)**, 799 (1989).
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[5]K.C. Kim and G.M. Campbell, Appl. Spectrosc. **39(4)**, 625–8 (1985).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.778	22.930	22.930	INFINITE
50	34.134	197.692	439.855	−12.108	21.699	26.981	−28.187
100	39.458	222.827	325.625	−10.280	20.617	32.702	−17.082
150	46.225	240.092	294.354	−8.139	19.844	38.925	−13.555
200	52.643	254.291	282.610	−5.664	19.393	45.362	−11.847
250	57.967	266.632	278.206	−2.894	19.203	51.881	−10.840
298.15	62.073	277.206	277.206	.000	19.200	58.177	−10.192
300	62.213	277.591	277.207	.115	19.203	58.419	−10.172
400	68.291	296.385	279.729	6.663	19.560	71.448	−9.330
500	72.244	312.079	284.673	13.703	20.176	84.352	−8.812
600	74.896	325.500	290.386	21.068	20.908	97.119	−8.455
700	76.732	337.192	296.256	28.655	21.689	109.760	−8.190
800	78.040	347.528	302.031	36.397	22.484	122.287	−7.985
900	78.997	356.778	307.609	44.251	23.279	134.715	−7.819
1000	79.716	365.140	312.951	52.189	24.064	147.054	−7.681
1100	80.267	372.764	318.047	60.189	24.836	159.316	−7.565
1200	80.697	379.768	322.903	68.238	25.590	171.508	−7.466
1300	81.039	386.241	327.529	76.326	26.325	183.638	−7.379
1400	81.316	392.257	331.940	84.444	27.039	195.712	−7.302
1500	81.542	397.875	336.151	92.587	27.731	207.736	−7.234
1600	81.729	403.144	340.175	100.751	28.398	219.714	−7.173
1700	81.885	408.104	344.026	108.932	29.042	231.652	−7.118
1800	82.017	412.788	347.717	117.127	29.662	243.552	−7.068
1900	82.130	417.225	351.260	125.334	30.258	255.418	−7.022
2000	82.226	421.441	354.664	133.552	30.832	267.254	−6.980
2100	82.310	425.455	357.941	141.779	31.387	279.061	−6.941
2200	82.383	429.285	361.097	150.014	31.924	290.843	−6.905
2300	82.446	432.949	364.142	158.256	32.446	302.600	−6.872
2400	82.502	436.459	367.083	166.503	32.958	314.334	−6.841
2500	82.552	439.828	369.926	174.756	33.461	326.048	−6.812
2600	82.596	443.066	372.677	183.013	33.960	337.742	−6.785
2700	82.635	446.184	375.342	191.275	34.458	349.417	−6.760
2800	82.671	449.190	377.926	199.540	34.958	361.073	−6.736
2900	82.703	452.092	380.434	207.809	35.463	372.710	−6.713
3000	82.731	454.896	382.869	216.081	35.977	384.331	−6.692
3100	82.757	457.609	385.237	224.355	36.501	395.935	−6.671
3200	82.781	460.237	387.540	232.632	37.038	407.520	−6.652
3300	82.802	462.785	389.781	240.911	37.590	419.089	−6.634
3400	82.822	465.257	391.965	249.192	38.160	430.641	−6.616
3500	82.840	467.658	394.094	257.475	38.747	442.176	−6.599
3600	82.857	469.992	396.170	265.760	39.354	453.695	−6.583
3700	82.872	472.262	398.196	274.047	39.982	465.195	−6.567
3800	82.886	474.473	400.174	282.335	40.631	476.679	−6.552
3900	82.899	476.626	402.107	290.624	41.301	488.146	−6.538
4000	82.911	478.725	403.996	298.914	41.994	499.594	−6.524
4100	82.922	480.772	405.844	307.206	42.709	511.025	−6.511
4200	82.933	482.771	407.652	315.499	43.446	522.439	−6.497
4300	82.943	484.722	409.421	323.793	44.204	533.835	−6.485
4400	82.952	486.629	411.155	332.087	44.984	545.212	−6.472
4500	82.960	488.493	412.853	340.383	45.786	556.572	−6.461
4600	82.968	490.317	414.517	348.679	46.607	567.913	−6.449
4700	82.975	492.101	416.149	356.977	47.447	579.237	−6.438
4800	82.982	493.848	417.749	365.274	48.306	590.543	−6.426
4900	82.989	495.559	419.320	373.573	49.182	601.831	−6.416
5000	82.995	497.236	420.861	381.872	50.074	613.101	−6.405
5100	83.001	498.879	422.375	390.172	50.981	624.352	−6.395
5200	83.006	500.491	423.862	398.472	51.902	635.585	−6.385
5300	83.012	502.072	425.323	406.773	52.835	646.802	−6.375
5400	83.016	503.624	426.758	415.075	53.779	657.999	−6.365
5500	83.021	505.147	428.170	423.377	54.732	669.179	−6.355
5600	83.025	506.643	429.558	431.679	55.693	680.343	−6.346
5700	83.030	508.113	430.923	439.982	56.659	691.488	−6.337
5800	83.033	509.557	432.267	448.285	57.630	702.618	−6.328
5900	83.037	510.976	433.589	456.588	58.604	713.729	−6.319
6000	83.041	512.372	434.890	464.892	59.578	724.825	−6.310

PREVIOUS: CURRENT: September 1995 (1 bar)

$S°(298.15\ K) = 283.623 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -750.138 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -758.559 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1269(1)	1502(1)
848(1)	553(1)
544(1)	885(1)
384(1)	539(1)
388(1)	

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: C_{2v}
Bond Distances: S–O = 1.405 ± 0.003 Å; S–F = 1.530 ± 0.003 Å
Bond Angles: O–S–O = 123.97 ± 0.20°; F–S–F = 96.12 ± 0.17°
Product of the Moments of Inertia: $I_A I_B I_C = 4.490464 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Ruh *et al.*[1] reported percent conversions for the reaction $SO_2(g) + Cl_2(g) + 2\ HF(g) \rightarrow SO_2F_2(g) + 2\ HCl(g)$ at 110 to 700°C and at pressures slightly above atmospheric. The data allow calculation of apparent values of K_p from the assumption of exact stoichiometry. Two temperatures may be excluded, namely 110°C for failure to approach equilibrium and 597°C due to power failure. The remaining values (503 to 973 K) yield $\Delta_r H°$(3rd law) = −24.15 ± 2 and $\Delta_r H°$(2nd law) = −20.7 ± 1.6 $kcal \cdot mol^{-1}$ at 298.15 K. The 3rd law values show a minor trend with temperature, corresponding to $\Delta_r S°$(2nd law) $-\Delta_r S°$(3rd law) = 5.4 ± 2.5 cal $K^{-1} \cdot mol^{-1}$, but this inconsistency is small enough to suggest that there was reasonable approach to equilibrium. An example given in the text of the patent[1] reveals that the actual recovery of SO_2 was somewhat less than that predicted on the assumption of stoichiometry. Use of this actual recovery of SO_2 would make $\Delta_f H°$(3rd law) more negative by less than 0.4 $kcal \cdot mol^{-1}$. We adopt $\Delta_f H° = -24.15\ kcal \cdot mol^{-1}$ and $\Delta_f H° = -181.3 \pm 2\ kcal \cdot mol^{-1}$ at 298.15 K.

Reese *et al.*[2] derived $\Delta_f H° = -205\ kcal \cdot mol^{-1}$ from electron impact studies. They measured potentials of 12.44 ± 0.1 and 19.9 ± 0.3 eV for the appearance of SO_2^+ from SO_2 and SO_2F_2, respectively. Combination of these values implies that $\Delta_f H°$ of SO_2F_2 should be about 1.0 eV more negative than the adopted value. This discrepancy could reasonably arise from neglect of the unknown excess energies of the products of the two reactions. Bond–energy comparisons tend to confirm this view. Average values of $D_0°$(S–F) may be calculated from $\Delta_f H°/2$ for $SF_6 \rightarrow SF_4 + 2\ F$ and $SO_2F_2 \rightarrow SO_2 + 2F$. $D_0°$(S–F) = 72 $kcal \cdot mol^{-1}$ from SF_6 is much more consistent with $D_0°$(S–F) = 74 $kcal \cdot mol^{-1}$ from the adopted $\Delta_f H°$ than with $D_0°$(S–F) = 86 $kcal \cdot mol^{-1}$ from the electron impact value.

Heat Capacity and Entropy

Bond lengths and bond angles are from the microwave study of Lide *et al.*[3] The resulting O–S–F angle is 108.3° and the principal moments of inertia are $I_A = 16.3467 \times 10^{-39}$, $I_B = 16.5727 \times 10^{-39}$, and $I_C = 16.5756 \times 10^{-39}\ g \cdot cm^2$. An early electron–diffraction study[4] is in reasonable agreement.

Vibrational frequencies are those assigned by Lide *et al.*[5] based on additional microwave and infrared data for the gaseous and matrix–isolated phases. Assignment of the three fundamentals near 544 cm^{-1} and the two near 388 cm^{-1} is supported by gas phase Raman spectra,[6] by combination and overtones in the infrared[6] and by force–field calculations.[7]

Calculated values of $C_p°$ agree within 0.1% with those derived by Gehri[8] from measurements of $C_p°$ at temperatures of 273 to 323 K and pressures up to 1 atm. The calculated entropy, $S° = 63.25$ cal $K^{-1} \cdot mol^{-1}$ at the normal boiling point of 217.78 K, may be compared with 62.66 ± 0.15 cal $K^{-1} \cdot mol^{-1}$ derived from low–temperature calorimetric data by Bockhoff *et al.*[9] The discrepancy is 0.59 cal $K^{-1} \cdot mol^{-1}$; it was attributed[9] to randomness in the solid at absolute zero. Bockhoff and Pace[10] later reported an entropy discrepancy of 1.48 cal $K^{-1} \cdot mol^{-1}$, but this value resulted from an incorrect vibrational assignment.[5–7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.499	−750.138	−750.138	INFINITE
100	35.872	230.833	332.132	−10.130	−753.270	−740.734	386.920
200	51.609	260.231	289.215	−5.797	−756.419	−726.911	189.850
250	59.368	272.600	284.672	−3.018	−757.620	−719.389	150.308
298.15	65.825	283.623	283.623	0.	−758.559	−711.938	124.729
300	66.054	284.031	283.625	0.122	−758.592	−711.648	123.909
350	71.723	294.651	284.450	3.570	−759.375	−703.760	105.030
400	76.513	304.550	286.351	7.280	−762.221	−695.683	90.847
450	80.558	313.803	288.893	11.209	−763.401	−687.302	79.780
500	83.975	322.472	291.822	15.325	−764.529	−678.783	70.912
600	89.324	338.282	298.274	24.005	−766.067	−661.478	57.587
700	93.205	352.358	305.014	33.141	−767.083	−643.960	48.053
800	96.066	365.000	311.736	42.612	−767.770	−626.321	40.895
900	98.215	376.445	318.300	52.331	−821.368	−607.529	35.260
1000	99.858	386.882	324.644	62.238	−820.469	−583.817	30.495
1100	101.136	396.462	330.744	72.290	−819.517	−560.198	26.602
1200	102.146	405.307	336.593	82.456	−818.532	−536.666	23.360
1300	102.956	413.516	342.198	92.713	−817.531	−513.218	20.621
1400	103.615	421.171	347.569	103.042	−816.523	−489.847	18.276
1500	104.157	428.339	352.717	113.432	−815.519	−466.549	16.247
1600	104.608	435.075	357.656	123.871	−814.524	−443.316	14.473
1700	104.986	441.429	362.399	134.351	−813.544	−420.146	12.910
1800	105.307	447.439	366.958	144.866	−812.581	−397.033	11.522
1900	105.581	453.140	371.345	155.411	−811.637	−373.973	10.281
2000	105.817	458.562	375.572	165.981	−810.712	−350.962	9.166
2100	106.021	463.730	379.648	176.573	−809.804	−327.997	8.158
2200	106.200	468.666	383.582	187.184	−808.913	−305.074	7.243
2300	106.356	473.391	387.385	197.812	−808.036	−282.192	6.409
2400	106.494	477.920	391.064	208.455	−807.171	−259.348	5.645
2500	106.616	482.270	394.626	219.111	−806.313	−236.540	4.942
2600	106.725	486.454	398.078	229.778	−805.460	−213.766	4.295
2700	106.822	490.483	401.426	240.455	−804.609	−191.024	3.696
2800	106.909	494.370	404.676	251.142	−803.755	−168.314	3.140
2900	106.988	498.123	407.834	261.837	−802.897	−145.635	2.623
3000	107.058	501.751	410.905	272.539	−802.032	−122.986	2.141
3100	107.123	505.262	413.892	283.248	−801.156	−100.365	1.691
3200	107.181	508.664	416.801	293.963	−800.268	−77.773	1.270
3300	107.235	511.963	419.635	304.684	−799.366	−55.210	0.874
3400	107.284	515.165	422.398	315.410	−798.448	−32.673	0.502
3500	107.328	518.276	425.093	326.141	−797.514	−10.164	0.152
3600	107.369	521.300	427.723	336.876	−796.561	12.319	−0.179
3700	107.407	524.242	430.292	347.615	−795.590	34.774	−0.491
3800	107.442	527.107	432.803	358.357	−794.599	57.204	−0.786
3900	107.475	529.898	435.257	369.103	−793.589	79.607	−1.066
4000	107.505	532.620	437.657	379.852	−792.559	101.983	−1.332
4100	107.532	535.275	440.006	390.604	−791.511	124.333	−1.584
4200	107.558	537.866	442.305	401.358	−790.443	146.658	−1.824
4300	107.582	540.398	444.557	412.115	−789.358	168.958	−2.052
4400	107.605	542.871	446.763	422.875	−788.255	191.231	−2.270
4500	107.626	545.290	448.926	433.636	−787.135	213.479	−2.478
4600	107.646	547.655	451.047	444.400	−785.999	235.702	−2.676
4700	107.664	549.971	453.127	455.165	−784.849	257.901	−2.866
4800	107.682	552.237	455.168	465.933	−783.686	280.075	−3.048
4900	107.698	554.458	457.172	476.702	−782.511	302.225	−3.222
5000	107.713	556.634	459.139	487.472	−781.325	324.351	−3.388
5100	107.728	558.767	461.072	498.244	−780.130	346.452	−3.548
5200	107.741	560.859	462.971	509.018	−778.927	368.530	−3.702
5300	107.754	562.911	464.837	519.793	−777.718	390.586	−3.849
5400	107.766	564.926	466.672	530.569	−776.506	412.617	−3.991
5500	107.778	566.903	468.477	541.346	−775.290	434.626	−4.128
5600	107.789	568.845	470.252	552.124	−774.073	456.615	−4.259
5700	107.799	570.753	471.998	562.904	−772.857	478.580	−4.386
5800	107.809	572.628	473.717	573.684	−771.644	500.525	−4.508
5900	107.818	574.471	475.409	584.465	−770.434	522.447	−4.625
6000	107.827	576.283	477.075	595.248	−769.232	544.351	−4.739

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$\Delta_{at}H°(0\ K)$ = [954.370 ± 25.1] kJ·mol^{-1}
$S°(298.15\ K)$ = [262.957 ± 0.8] J·K^{-1}·mol^{-1}

$\Delta_fH°(0\ K)$ = [−485.280 ± 20.9] kJ·mol^{-1}
$\Delta_fH°(298.15\ K)$ = [−488.256 ± 20.9] kJ·mol^{-1}

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
[25000]	[2]
[28000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
831 (1)
[353](1)
852 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: P–F = [1.58] Å
Bond Angle: F–P–F = [99]°
Product of the Moments of Inertia: $I_AI_BI_C$ = [3.285613 × 10^{-115}] g^3·cm^6

Enthalpy of Formation

The adopted results are $\Delta_fH°(0\ K)$ = 112.2 ± 5.0 kcal·mol^{-1}, $D_0°$ (PF-F) = 122.0±10.0 kcal·mol^{-1}, and $\Delta_{at}H°$ = 228.1 ± 6.0 kcal·mol^{-1}. We estimate $\Delta_fH°$ such that the value gives $D_0°$ (PF–F)/$\Delta_{at}H°(0\ K)$ = 0.535. The value of this ratio is selected from those for SiF_2(0.54 ± 0.03) and SF_2(0.53 ± 0.05) which are calculated from the most recent JANAF tables.[1] Two previous estimates of $\Delta_fH°$ are available for comparison. O'Hare[2] used the relationship $D_0°$ (PF_2–F) = 1.1 $\Delta_{at}H°(PF_3)$ to obtain a $\Delta_fH°$ of −115.7 ± 5 kcal·mol^{-1}. This estimate agrees quite well with the results adopted here. An earlier JANAF table[3] gives $\Delta_fH°(PF_2)$ = −104.7 ± 15.0 kcal·mol^{-1} which was based on an estimate value for the $\Delta_{at}H°$ of PF_3. We estimate that the uncertainty in the value of the ratio $D_0°/\Delta_{at}H°$ should not exceed ±0.06 which corresponds to an uncertainty in $\Delta_fH°$ of ±5.0 kcal·mol^{-1}.

Heat Capacity and Entropy

The results of electron spin resonance experiments[4,5] and molecular orbital calculations[4,6,7] are consistent with PF_2 having C_{2v} symmetry; however, no experimental determination of the structural parameters has been reported. Numerous values for the bond length and angle have been proposed based on energy optimization[6,7] and other estimation techniques.[2,4,8,9] These estimates are widely scattered with the bond lengths ranging from (1.52 to 1.73 Å) and the bond angles ranging from 98.6 to 112°. We prefer to use molecular parameters similar to those measured[10] for the related molecule PF_2H. The adopted values appear quite reasonable by comparison with structural data[1] for SiF_2 and SF_2. The principal moments of inertia are: I_A = 2.9836 × 10^{-39}, I_B= 9.1077 × 10^{-39}, and I_C = 12.0913 × 10^{-39} g·cm^2.

The two stretching frequencies (ν_1 and ν_3) have been observed[11] in the infrared spectrum of PF_2 formed in an argon matrix by photolysis of PF_2H. The adopted values are rounded to the nearest cm^{-1}. The bending frequency (ν_2) is calculated from the force constant f_α/r^2 = 0.495 mdyn/Å. We obtain the bending force constant from the ratio $f_r/(f_\alpha/r^2)$ equal to 9.59 which is the value calculated for SiF_2.[1]

The ground state is expected to be $^2B_1$, as shown by Wei *et al.*[4] We assume that the upper electronic levels and their corresponding quantum weights are the same as those previously estimated for the isoelectronic SF_2^+ ion. The procedure used to estimate these levels is thoroughly discussed on the SF_2^+ table.[1]

This table essentially updates the functions previously tabulated by O'Hare.[2]

References

[1]JANAF Thermochemical Tables: SF_2(g) and SiF_2(g), 6–30–76; SF_2^+(g), 12–31–76; PF_3(g) and PF_5(g), 12–31–69.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	0.	0.	INFINITE	−11.209	−485.280	−485.280	INFINITE
100	34.623	220.645	299.211	−7.857	−485.722	−488.981	255.417
200	39.685	246.149	266.890	−4.148	−487.206	−491.880	128.466
250	42.344	255.291	263.680	−2.097	−487.749	−492.985	103.004
298.15	44.717	262.957	262.957	0.	−488.256	−493.948	86.538
300	44.803	263.233	262.957	0.083	−488.275	−493.983	86.010
350	46.927	270.304	263.511	2.378	−489.505	−494.823	73.848
400	48.696	276.690	264.766	4.770	−490.060	−495.544	64.711
450	50.142	282.511	266.419	7.242	−490.571	−496.198	57.597
500	51.319	287.858	268.299	9.779	−491.048	−496.797	51.900
600	53.065	297.379	272.372	15.004	−491.929	−497.863	43.343
700	54.253	305.654	276.548	20.374	−492.744	−498.787	37.220
800	55.086	312.956	280.652	25.843	−493.517	−499.597	32.620
900	55.687	319.481	284.610	31.383	−494.263	−500.312	29.037
1000	56.134	325.372	288.397	36.976	−494.994	−500.945	26.167
1100	56.473	330.739	292.006	42.607	−495.715	−501.505	23.814
1200	56.736	335.664	295.441	48.268	−560.005	−500.921	21.805
1300	56.944	340.214	298.713	53.952	−559.947	−496.000	19.930
1400	57.111	344.441	301.830	59.655	−559.898	−491.083	18.323
1500	57.248	348.386	304.804	65.373	−559.857	−486.169	16.930
1600	57.360	352.084	307.644	71.104	−559.825	−481.258	15.711
1700	57.454	355.564	310.362	76.845	−559.803	−476.348	14.636
1800	57.533	358.851	312.965	82.594	−559.790	−471.439	13.681
1900	57.600	361.963	315.463	88.351	−559.784	−466.531	12.826
2000	57.658	364.919	317.862	94.114	−559.783	−461.623	12.056
2100	57.707	367.733	320.171	99.882	−559.786	−456.715	11.360
2200	57.751	370.419	322.394	105.655	−559.787	−451.807	10.727
2300	57.789	372.987	324.538	111.432	−559.786	−446.899	10.149
2400	57.822	375.447	326.609	117.213	−559.778	−441.991	9.620
2500	57.852	377.808	328.610	122.996	−559.760	−437.083	9.132
2600	57.879	380.078	330.546	128.783	−559.728	−432.177	8.683
2700	57.904	382.263	332.421	134.572	−559.679	−427.272	8.266
2800	57.926	384.369	334.239	140.364	−559.611	−422.369	7.879
2900	57.948	386.402	336.003	146.157	−559.520	−417.469	7.519
3000	57.968	388.367	337.716	151.953	−559.405	−412.573	7.184
3100	57.987	390.268	339.381	157.751	−559.262	−407.681	6.869
3200	58.007	392.109	341.000	163.551	−559.089	−402.794	6.575
3300	58.027	393.895	342.576	169.352	−558.886	−397.913	6.298
3400	58.047	395.627	344.111	175.156	−558.651	−393.038	6.038
3500	58.068	397.310	345.607	180.962	−558.383	−388.171	5.793
3600	58.091	398.946	347.066	186.770	−558.080	−383.312	5.562
3700	58.115	400.538	348.490	192.580	−557.743	−378.462	5.343
3800	58.142	402.088	349.880	198.393	−557.370	−373.621	5.136
3900	58.171	403.599	351.238	204.208	−556.962	−368.791	4.939
4000	58.202	405.072	352.565	210.027	−556.518	−363.972	4.753
4100	58.237	406.510	353.864	215.849	−556.037	−359.164	4.576
4200	58.275	407.914	355.134	221.675	−555.521	−354.368	4.407
4300	58.316	409.285	356.377	227.504	−554.969	−349.586	4.247
4400	58.361	410.626	357.595	233.338	−554.381	−344.816	4.093
4500	58.410	411.938	358.788	239.176	−553.757	−340.060	3.947
4600	58.462	413.223	359.958	245.020	−553.098	−335.318	3.808
4700	58.519	414.481	361.104	250.869	−552.404	−330.591	3.674
4800	58.580	415.713	362.229	256.724	−551.675	−325.879	3.546
4900	58.646	416.922	363.333	262.585	−550.911	−321.183	3.424
5000	58.716	418.107	364.417	268.453	−550.114	−316.503	3.306
5100	58.790	419.271	365.481	274.329	−549.282	−311.839	3.194
5200	58.869	420.413	366.526	280.211	−548.417	−307.191	3.086
5300	58.952	421.535	367.554	286.102	−547.519	−302.561	2.982
5400	59.039	422.638	368.564	292.002	−546.588	−297.948	2.882
5500	59.131	423.722	369.557	297.910	−545.624	−293.353	2.786
5600	59.226	424.789	370.534	303.828	−544.628	−288.774	2.694
5700	59.326	425.838	371.495	309.756	−543.600	−284.215	2.605
5800	59.430	426.870	372.440	315.694	−542.540	−279.674	2.519
5900	59.537	427.887	373.372	321.642	−541.449	−275.150	2.436
6000	59.649	428.889	374.289	327.601	−540.327	−270.647	2.356

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = [257.358 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 469.054 \pm 33.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 472.273 \pm 33.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[1]
[25000]	[3]
[40000]	[1]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[840](1)
[350](1)
[860](1)

Point Group: C_{2v} σ = [2]
Bond Distance: P–F = [1.59] Å
Bond Angle: F–P–F = [101]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.412079 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

A summary of the information available on the appearance potential of PF_2^+ from PF_3 is presented below. We analyze these electron–impact results using the expression $\Delta_f H°(0\ K) = AP - E^*$ by assuming that the dissociative ionization process is $PF_3(g) + e^- = PF_2^+(g) + F(g) + 2\ e^-$. Values of $\Delta_f H°$ and the ionization potential are derived by setting E* in the above expression equal to zero. As a result, the values are listed in the table as inequalities to emphasize that they are limiting (upper) values.

Source	AP(PF_2^+/PF) eV	$\Delta_f H°(PF_2^+, g, 0\ K)$ kcal·mol^{-1}	IP(PF_2) eV
[1]	15.4 ± 0.2	<112.78	<9.76
[2]	15.7 ± 0.5	<119.70	<10.06
[3]	15.5 ± 0.2	<115.09	<9.86
[4]	13.5	<68.97	<7.86

The results derived from the first three studies[1–3] are in excellent accord, and we adopt the mean values of $\Delta_f H° = 115.861 \pm 8.0$ kcal·mol^{-1} and IP = 9.89 eV. Dean *et al.*[4] were unable to offer an explanation as to why their results were significantly lower than the other literature data. This study[4] indicates that $IP(PF_2) < IP(PCl_2)$ [3] which we believe is very unlikely. Harland *et al.* [1] have reported the AP for PF_2^+ from PF_2CN as 13.4 ± 0.2 eV, suggesting the possibility that the precursor responsible for the PF_2^+ ion in the measurements of Dean *et al.*[4] was PF_2CN rather than PF_3. A MO study[5] gave $IP(PF_2) = 9.88$ eV based on IP(P) – 10.98 eV. Recalculation of their results using a more recent value of IP(P) = 10.486 eV[6] gives $IP(PF_2) = 9.88$ eV. Our adopted value of IP (9.89 eV) is close to that for atomic phosphorus (10.49 eV). This is consistent with the results of electron spin resonance experiments[7,8] and MO calculations [5,7,9,10] which show that the ionizing orbital is slightly antibonding and located primarily on the phosphorus atom.

The mean bond energy (products $P^+(g)+2F(g)$) is 120.9 kcal·mol^{-1} which when compared with that for PF_2(114.1 kcal·mol^{-1}),[11] suggests that the bonding is somewhat stronger in the positive ion. This predicted increase in bond strength upon ionization is also consistent with the antibonding nature of the ionizing orbital. $\Delta_f H°$ (298.15 K) is calculated to be 117.049 kcal·mol^{-1}.

Heat Capacity and Entropy

The molecular parameters and vibrational frequencies are assumed to lie between those for PF_2 and SiF_2.[11] The electronic levels and quantum weights are estimated by analogy with those for the isoelectronic molecule SiF_2.[11] The principal moments of inertia are: $I_A = 2.8983 \times 10^{-39}$, $I_B = 9.4974 \times 10^{-39}$, and $I_C = 12.3957 \times 10^{-39}$ g·cm^2.

References

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Continued on page 1215

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.207	469.054		
100	34.659	215.050	293.584	−7.853			
200	39.667	240.571	261.285	−4.143			
250	42.285	249.705	258.080	−2.094			
298.15	44.635	257.358	257.358	0.	472.273	461.996	−80.940
300	44.720	257.634	257.359	0.083	472.292	461.932	−80.430
350	46.835	264.691	257.911	2.373	472.097	460.235	−68.686
400	48.602	271.064	259.163	4.760	472.577	458.509	−59.875
450	50.053	276.875	260.813	7.228	473.101	456.719	−53.015
500	51.236	282.212	262.690	9.761	473.658	454.869	−47.520
600	52.996	291.720	266.755	14.979	474.848	451.001	−39.263
700	54.196	299.985	270.925	20.342	476.106	446.928	−33.350
800	55.039	307.280	275.022	25.806	477.407	442.671	−28.903
900	55.648	313.800	278.975	31.342	478.735	438.250	−25.435
1000	56.101	319.687	282.757	36.930	480.079	433.680	−22.653
1100	56.445	325.051	286.362	42.558	481.433	428.974	−20.370
1200	56.712	329.974	289.794	48.217	419.220	425.224	−18.510
1300	56.924	334.523	293.062	53.899	421.353	425.637	−17.102
1400	57.093	338.747	296.176	59.600	423.480	425.887	−15.890
1500	57.232	342.691	299.147	65.317	425.598	425.985	−14.834
1600	57.346	346.389	301.985	71.046	427.706	425.942	−13.906
1700	57.441	349.868	304.700	76.785	429.806	425.767	−13.082
1800	57.522	353.154	307.302	82.534	431.896	425.470	−12.347
1900	57.590	356.266	309.798	88.289	433.980	425.056	−11.686
2000	57.649	359.221	312.196	94.051	436.058	424.532	−11.088
2100	57.699	362.035	314.503	99.819	438.134	423.905	−10.544
2200	57.743	364.720	316.725	105.591	440.209	423.178	−10.048
2300	57.782	367.288	318.868	111.367	442.289	422.358	−9.592
2400	57.817	369.748	320.937	117.147	444.375	421.447	−9.173
2500	57.848	372.109	322.937	122.930	446.471	420.448	−8.785
2600	57.876	374.378	324.872	128.717	448.581	419.366	−8.425
2700	57.903	376.563	326.746	134.506	450.708	418.202	−8.091
2800	57.927	378.669	328.563	140.297	452.855	416.959	−7.778
2900	57.951	380.703	330.326	146.091	455.025	415.638	−7.486
3000	57.975	382.668	332.038	151.887	457.220	414.243	−7.213
3100	57.999	384.569	333.702	157.686	459.442	412.774	−6.955
3200	58.024	386.411	335.321	163.487	461.695	411.232	−6.713
3300	58.050	388.197	336.896	169.291	463.978	409.620	−6.484
3400	58.079	389.930	338.431	175.097	466.295	407.938	−6.267
3500	58.109	391.614	339.926	180.907	468.645	406.188	−6.062
3600	58.143	393.251	341.385	186.719	471.031	404.370	−5.867
3700	58.179	394.845	342.808	192.535	473.453	402.485	−5.682
3800	58.219	396.397	344.198	198.355	475.911	400.534	−5.506
3900	58.264	397.910	345.556	204.179	478.406	398.518	−5.338
4000	58.313	399.386	346.884	210.008	480.939	396.437	−5.177
4100	58.366	400.826	348.182	215.842	483.510	394.293	−5.023
4200	58.424	402.233	349.452	221.682	486.119	392.086	−4.876
4300	58.488	403.609	350.696	227.527	488.766	389.815	−4.735
4400	58.557	404.954	351.913	233.379	491.451	387.483	−4.600
4500	58.631	406.271	353.107	239.239	494.174	385.090	−4.470
4600	58.711	407.560	354.277	245.106	496.935	382.635	−4.345
4700	58.797	408.824	355.424	250.981	499.734	380.120	−4.225
4800	58.888	410.063	356.549	256.865	502.571	377.546	−4.109
4900	58.985	411.278	357.654	262.759	505.446	374.911	−3.997
5000	59.087	412.471	358.738	268.663	508.357	372.218	−3.889
5100	59.195	413.642	359.803	274.577	511.306	369.466	−3.784
5200	59.309	414.792	360.850	280.502	514.292	366.656	−3.683
5300	59.428	415.923	361.878	286.439	517.315	363.788	−3.585
5400	59.551	417.035	362.889	292.387	520.374	360.862	−3.491
5500	59.680	418.129	363.884	298.349	523.470	357.880	−3.399
5600	59.814	419.206	364.862	304.324	526.601	354.841	−3.310
5700	59.952	420.266	365.825	310.312	529.769	351.745	−3.223
5800	60.094	421.309	366.773	316.314	532.971	348.594	−3.139
5900	60.240	422.338	367.706	322.331	536.209	345.388	−3.058
6000	60.390	423.352	368.625	328.362	539.482	342.126	−2.978

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = [257.364 \pm 0.8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-630.010 \pm 69.0]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-639.177 \pm 69.0]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[820](1)
[355](1)
[845](1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: C_{2v}
Bond Distance: P–F = [1.59]Å
Bond Angle: F–P–F = [98]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.409086 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The PF_2^- anion has been observed in the negative ion mass spectra of PF_3[1] and PF_2CN.[2] Both studies included thermochemical calculations on plausible ion formation processes, showing that the measured appearance potentials contained large excess energy contributions. At present, definite values cannot be assigned to these contributions; thus, their studies are of little value in defining $\Delta_f H°$.

Two estimates of the electron affinity of PF_2 have been reported.[2,3] Harland *et al.*[2] considered differences in bond energies for diatomic and triatomic species to obtain a value of EA(PF_2) = 1.4 eV. Rescaled CNDO calculations[3] have led to an EA = 1.71 eV. JANAF data[4] on the S–F system indicate that the EA values alternate between the even − and odd − electron molecules, with the odd–electron molecules having the higher EA values. Assuming the same trend is followed in the P–F system, we predict that EA(PF_2) > EA(PF) which is equal to 1.1 ± 0.5 eV.[4] We adopt an EA of 1.5 ± 0.5 eV for the reaction $PF_2^-(g) = PF_2(g) + e^-$ at 0 K which leads to $\Delta_f H°(PF_2^-, g, 0\ K) = -146.822 \pm 16.5\ kcal \cdot mol^{-1}$ with $\Delta_f H°(PF_2, g, 0\ K) = -112.23 \pm 5.0\ kcal \cdot mol^{-1}$.[4] The adopted value of EA is close to that for atomic phosphorus (0.77 ± 0.05 eV).[5] This is in agreement with results of MO calculations[3,6] and electron spin resonance experiments[6,7] which show that the electron captured by PF_2 goes into an antibonding orbital which is located primarily on the phosphorus atom.

$\Delta_f H°$ at 298.15 K and the fluoride–ion affinity (IA) are calculated to be $-148.594\ kcal \cdot mol^{-1}$ and $78.2\ kcal \cdot mol^{-1}$, respectively. The mean bond energy $\Delta_{at}H°/2$(products P(g) + F(g) + F^-(g)) is 92.2 $kcal \cdot mol^{-1}$ which is 21.9 $kcal \cdot mol^{-1}$ less than that for PF_2(114.1 $kcal \cdot mol^{-1}$).[4] The predicted decrease in the bond strength for the anion is also consistent with the antibonding nature of the electron orbital.

Heat Capacity and Entropy

The molecular parameters and vibrational frequencies are assumed to lie between those for PF_2 and SF_2.[4] The ground state is assumed to be a singlet since PF_2^- has no unpaired electrons. Also, we neglect excited states since these probably lie at energies which would not contribute to the partition function (refer to the table for the isoelectronic species SF_2). The principal moments of inertia are: $I_A = 3.0833 \times 10^{-39}$, $I_B = 9.0858 \times 10^{-39}$, and $I_C = 12.1691 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.215	−630.010		
100	34.601	215.028	293.664	−7.864			
200	39.722	240.527	261.304	−4.155			
250	42.421	249.683	258.088	−2.101			
298.15	44.817	257.364	257.364	0.	−639.177	−636.946	111.590
300	44.903	257.641	257.365	0.083	−639.235	−636.932	110.900
350	47.035	264.728	257.919	2.383	−641.499	−636.355	94.971
400	48.802	271.128	259.177	4.780	−643.087	−635.512	82.989
450	50.242	276.962	260.834	7.258	−644.632	−634.471	73.648
500	51.412	282.318	262.718	9.800	−646.144	−633.261	66.156
600	53.142	291.855	266.799	15.034	−649.096	−630.406	54.882
700	54.315	300.141	270.983	20.410	−651.982	−627.062	46.792
800	55.137	307.450	275.094	25.885	−654.828	−623.308	40.698
900	55.729	313.980	279.058	31.430	−657.648	−619.198	35.937
1000	56.169	319.876	282.850	37.026	−660.453	−614.775	32.113
1100	56.503	325.246	286.464	42.660	−663.250	−610.072	28.970
1200	56.762	330.174	289.904	48.324	−729.615	−604.036	26.293
1300	56.966	334.725	293.179	54.011	−731.634	−593.489	23.847
1400	57.131	338.953	296.299	59.716	−733.661	−582.787	21.744
1500	57.265	342.900	299.276	65.436	−735.697	−571.939	19.917
1600	57.375	346.599	302.119	71.168	−737.742	−560.955	18.313
1700	57.467	350.080	304.839	76.910	−739.798	−549.843	16.895
1800	57.545	353.367	307.444	82.661	−741.862	−538.610	15.630
1900	57.611	356.480	309.944	88.419	−743.933	−527.262	14.495
2000	57.667	359.437	312.345	94.183	−746.010	−515.804	13.471
2100	57.716	362.252	314.655	99.952	−748.090	−504.243	12.542
2200	57.759	364.938	316.880	105.726	−750.170	−492.582	11.695
2300	57.796	367.506	319.026	111.504	−752.246	−480.827	10.920
2400	57.829	369.966	321.098	117.285	−754.316	−468.982	10.207
2500	57.857	372.328	323.100	123.069	−756.376	−457.050	9.550
2600	57.883	374.597	325.037	128.856	−758.422	−445.037	8.941
2700	57.906	376.782	326.914	134.646	−760.452	−432.945	8.376
2800	57.927	378.889	328.732	140.437	−762.462	−420.778	7.850
2900	57.945	380.922	330.497	146.231	−764.450	−408.540	7.359
3000	57.962	382.886	332.211	152.026	−766.413	−396.234	6.899
3100	57.977	384.787	333.877	157.823	−768.350	−383.863	6.468
3200	57.990	386.628	335.496	163.622	−770.257	−371.429	6.063
3300	58.003	388.413	337.073	169.421	−772.135	−358.937	5.681
3400	58.014	390.145	338.609	175.222	−773.981	−346.388	5.322
3500	58.025	391.826	340.105	181.024	−775.795	−333.785	4.981
3600	58.034	393.461	341.565	186.827	−777.576	−321.131	4.659
3700	58.043	395.051	342.989	192.631	−779.324	−308.428	4.354
3800	58.051	396.599	344.379	198.436	−781.038	−295.678	4.064
3900	58.059	398.107	345.738	204.241	−782.718	−282.883	3.789
4000	58.066	399.577	347.066	210.047	−784.365	−270.046	3.526
4100	58.072	401.011	348.364	215.854	−785.978	−257.168	3.276
4200	58.078	402.411	349.634	221.662	−787.559	−244.251	3.038
4300	58.084	403.777	350.877	227.470	−789.107	−231.297	2.810
4400	58.089	405.113	352.095	233.279	−790.622	−218.307	2.592
4500	58.094	406.418	353.288	239.088	−792.106	−205.283	2.383
4600	58.099	407.695	354.457	244.897	−793.560	−192.226	2.183
4700	58.103	408.945	355.603	250.708	−794.983	−179.138	1.991
4800	58.107	410.168	356.727	256.518	−796.377	−166.020	1.807
4900	58.111	411.366	357.830	262.329	−797.743	−152.874	1.630
5000	58.114	412.540	358.912	268.140	−799.081	−139.700	1.459
5100	58.118	413.691	359.975	273.952	−800.391	−126.499	1.296
5200	58.121	414.820	361.019	279.764	−801.676	−113.272	1.138
5300	58.124	415.927	362.044	285.576	−802.935	−100.022	0.986
5400	58.127	417.013	363.052	291.389	−804.169	−86.748	0.839
5500	58.129	418.080	364.043	297.201	−805.380	−73.451	0.698
5600	58.132	419.127	365.018	303.014	−806.567	−60.133	0.561
5700	58.134	420.156	365.976	308.828	−807.732	−46.793	0.429
5800	58.137	421.167	366.919	314.641	−808.875	−33.434	0.301
5900	58.139	422.161	367.847	320.455	−809.998	−20.054	0.178
6000	58.141	423.138	368.760	326.269	−811.100	−6.656	0.058

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = [112.968 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 583 \pm 1\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-676.971 \pm 4.2]\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.463\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Enthalpies of formation derived from the enthalpy changes of different chemical reactions are tabulated below. Due to a lack of sample characterization we can only assume from sample preparation that the following reactions involve α-PbF_2(cr).

Source	Reaction	Method	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
[1]	$Pb(cr) + F_2(g) = PbF_2(\alpha)$	emf	-159.7 ± 0.5	-159.7 ± 0.5
[2]	$PbO(cr) + 2\ HF(40\%\ aq) = PbF_2(\alpha) + H_2O(l)$	calor.	-22.9 ± 0.3	-159.4 ± 0.5
[3]	$PbF_2(\alpha) + 2\ Na(cr) = Pb(cr) + 2\ NaF(aq)$	emf	-112.2 ± 0.2	-162.2 ± 0.4
[4]	$PbF_2(\alpha) + Mg(cr) = Pb(cr) + MgF_2(cr)$	calor.	-109.5 ± 1.5	-159.2 ± 2.0
[5]	$3/2\ PbF_2(cr) + Al(cr) = 3/2\ Pb(cr) + AlF_3(cr)$	calor.	-118.5 ± 0.1	-161.6 ± 1.0
[6]	$3/2\ PbF_2(cr) + Al(cr) = 3/2\ Pb(cr) + AlF_3(cr)$	calor.	-117.7 ± 0.6	-162.2 ± 1.0

The samples used by Gross *et al.*[4, 5] could easily be β-PbF_2 rather than α-PbF_2. Other reactions[7, 8, 9] have led to values near $\Delta_f H°(298.15\ K) = -161.8\ kcal \cdot mol^{-1}$ [10] this value is adopted and is assigned an uncertainty of $\pm 2\ kcal \cdot mol^{-1}$.

The adopted enthalpy of formation is supported by measurements[11] of the reaction $PbF_2(cr) + Be(cr) = BeF_2(cr) + Pb(cr)$ from which the enthalpy of formation of BeF_2(cr) agrees with that from the direct fluorination of beryllium metal if the adopted value for $\Delta_f H°(PbF_2, \alpha, 298.15\ K)$ is used.

Heat Capacity and Entropy

The enthalpy of α-PbF_2(cr) was measured by Linsey.[12] Twenty data points (320–728 K) were obtained using a sample encapsulated in gold while fifteen were obtained (370–595 K) using a sample encapsulated in Nichrome V. We adopt the heat capacity values calculated by Linsey[12] and extrapolate linearly to 1000 K. It should be noted, however, that Linsey[12] adjusted his experimental enthalpy for α-PbF_2(cr) so that when the orthorhombic sample was heated above T_{trs}, the resulting enthalpy was consistent with the cubic PbF_2 enthalpy.

There is no low temperature heat capacity data for α-PbF_2(cr). We estimate $S°(298.15\ K) = 27.0 \pm 2.0\ cal\ K^{-1} \cdot mol^{-1}$.

Transition Data

The transition temperature is that obtained by Linsey[12] via enthalpy measurements on orthorhombic PbF_2. When heated above T_{trs}, orthorhombic PbF_2 changes quickly to the cubic form. Upon cooling the transformation is very sluggish.

The enthalpy of transition at room temperature, $240 \pm 9\ kcal \cdot mol^{-1}$, was determined by Linsey[12] by the differences in the heat of solution of the orthorhombic and cubic modifications in 1.0 M $Fe(NO_3)_3$. $\Delta_{trs}H°$ is calculated from this value using the enthalpy differences $H°(583\ K) - H°(298.15\ K)$ for the cubic and orthorhombic modifications.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	72.258	112.968	112.968	0.	−676.971	−630.875	110.527
300	72.383	113.415	112.969	0.134	−676.945	−630.589	109.795
400	76.065	134.642	115.838	7.522	−675.505	−615.351	80.357
500	79.705	152.035	121.389	15.323	−673.883	−600.497	62.733
583.000	81.965	164.425	126.653	22.021	---- ALPHA <--> BETA ----		
600	82.488	166.788	127.757	23.419	−672.150	−585.980	51.014
700	85.772	179.751	134.276	31.832	−675.110	−570.968	42.606
800	89.056	191.418	140.701	40.574	−672.996	−556.231	36.318
900	92.341	202.097	146.938	49.643	−670.565	−541.778	31.444
1000	95.625	211.996	152.955	59.042	−667.812	−527.613	27.560

PREVIOUS: June 1969 CURRENT: December 1973

$S°(298.15\ K) = [114.398]\ J·K^{-1}·mol^{-1}$
$T_{trs} = 583 \pm 1\ K$
$T_{fus} = 1103 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-675.990]\ kJ·mol^{-1}$
$\Delta_{trs} H° = 1.463\ kJ·mol^{-1}$
$\Delta_{fus} H° = 14.728 \pm 1.3\ kJ·mol^{-1}$

Enthalpy of Formation

Linsey[1] determined the heat of transition at room temperature to be 240 ± 9 $kcal·mol^{-1}$ from heat of solution measurements of the orthorhombic and cubic modifications in 1 M $Fe(NO_3)_3$. We calculate and adopt $\Delta_f H°(PbF_2, \beta, 298.15\ K)$ by adding this heat of transition value to the $\Delta_f H°(298.15\ K)$ value for PbF_2(cr, α).

Other enthalpy of formation values derived from the enthalpy changes of different chemical reactions are tabulated below. Due to a lack of sample characterization we can only assume from the sample preparation and experimental conditions that the following reactions involve β–PbF_2(cr).

Source	Reaction	Method	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$	$\Delta_f H°(298.15K)$ $kcal·mol^{-1}$
[2]	$PbF_2(\beta) + H_2(g) = Pb(l) + 2\ HF(g)$	Press	32.0	−161.3
[3]	$PbF_2(\beta) + H_2O(g) = PbO(cr) + 2\ HF(g)$	Press	30.06	−154.6
[4]	$1/2\ PbF_2(\beta) + 1/3\ Al(cr) = 1/2\ Pb(l) + 1/3\ AlF_3(cr)$	emf	−116.39	−162.0

The two studies by Gross *et al.*[5,6] may well involve β-PbF_2. Kolesov *et al.*[7] used two PbF_2 samples which had been fused. These samples should then be in the β-modification. The results are considerably different from those given in the α–PbF_2 table[8] for α–PbF_2.

Heat Capacity and Entropy

Linsey[1] measured the enthalpy of cubic PbF_2. The enthalpy data (61 data points, 321–1164 K) revealed an anomaly in the enthalpy and heat capacity in the range 573–823 K. Linsey[1] interpreted the results in terms of a lambda-type (cooperative) transition in the heat capacity with a maximum at 716 K. We adopt the heat capacity values calculated and reported by Linsey.[1]

Banashek *et al.*[8] measured the high temperature enthalpies in the range 670–1165 K. Their data is consistent with the interpretation of Linsey.[1]

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ ($J·K^{-1}mol^{-1}$)	$S°$ ($J·K^{-1}mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J·K^{-1}mol^{-1}$)	$H°-H°(T_r)$ ($kJ·mol^{-1}$)	$\Delta_f H°$ ($kJ·mol^{-1}$)	$\Delta_f G°$ ($kJ·mol^{-1}$)	log K_f
0							
100							
200							
298.15	74.266	114.398	114.398	0.	−675.990	−630.320	110.429
300	74.392	114.857	114.399	0.138	−675.960	−630.037	109.699
400	76.776	136.571	117.344	7.691	−674.354	−614.971	80.307
500	80.584	154.051	122.988	15.531	−672.694	−600.315	62.714
583.000	88.868	166.934	128.336	22.502	---- ALPHA <--> BETA ----		
600	91.128	169.518	129.466	24.031	−670.557	−586.025	51.018
700	147.486	186.826	136.333	35.345	−670.616	−571.426	42.640
800	105.939	203.976	143.801	48.140	−664.448	−557.729	36.416
900	94.433	215.393	151.145	57.823	−661.404	−544.583	31.607
1000	94.433	225.342	158.076	67.266	−658.606	−531.753	27.776
1100	94.433	234.342	164.607	76.709	−655.807	−519.203	24.655
1103.000	94.433	234.600	164.797	76.993	---- BETA <--> LIQUID ----		
1200	94.433	242.559	170.765	86.153	−653.003	−506.908	22.065
1300	94.433	250.118	176.583	95.596	−650.200	−494.847	19.883
1400	94.433	257.116	182.088	105.039	−647.410	−483.002	18.021
1500	94.433	263.631	187.310	114.482	−644.642	−471.355	16.414

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [130.927]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-660.320]\ kJ·mol^{-1}$

$T_{fus} = 1103 \pm 4\ K$ $\Delta_{fus}H° = 14.728 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(PbF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(PbF_2, cr, \beta, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1103\ K)-H°(298.25\ K)$, between the β–crystal and liquid.

Heat Capacity and Entropy

The enthalpies of PbF_2(l) in the temperature range 1104–1165 K were determined by Banashek *et al.*[1] Based on their reported results, the heat capacity of PbF_2(l) is evaluated to be 24 ± 2 cal $K^{-1}·mol^{-1}$ by the least square method. Linsey[13] measured the enthalpy of PbF_2(l) in the range 1105–1164 K (8 data points) and reported a constant heat capacity value of 26.10 cal $K^{-1}·mol^{-1}$. We adopt this value and extrapolate to 700 K and 1500 K. A glass transition is assumed at 700 K below which the heat capacity values of cubic PbF_2 are used.

$S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ are taken from the enthalpy data of Linsey.[13] Our analysis of the enthalpy data of Banashek *et al.*[1] yields a heat of melting value of 2.98 kcal·mol^{-1}.

Other values of T_{fus}(K) reported are 1091,[2, 11] 1097,[3, 4, 5] and 1128.[6] Using the freezing point data of binary systems PbF_2–$PbBr_2$,[5] PbF_2–$PbCl_2$,[5, 7] PbF_2–PbI_2,[5, 8] PbF_2–PbO,[9] and PbF_2–NaF.[10] Kelley[3] evaluated the corresponding values of $\Delta_{fus}H°$ kcal·mol^{-1} as 1.70, 1.70, 1.96, 3.87, and 2.47. Other reported values of $\Delta_{fus}H°$ are 3.00[1] and 4.16[2] kcal·mol^{-1}.

Vaporization Data

From mass spectroscopic study on the vapor species in PbF_2, Zmbov *et al.*[4] have shown that molten PbF_2 vaporizes partly as molecular PbF_2. There is considerable disproportionation, and at 988 K the vapor composition is approximately 66% PbF_4, 25% PbF_2, 2% PbF, and 7% Pb.[4, 12] T_{vap} has been reported as 1565 K[11] where the vapor is expected to be a mixture of the above species.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.266	130.927	130.927	0.	−660.320	−619.579	108.548
300	74.392	131.386	130.928	0.138	−660.290	−619.326	107.834
400	76.776	153.101	133.873	7.691	−658.685	−605.914	79.124
500	79.705	170.548	139.517	15.515	−657.040	−592.909	61.941
600	82.634	185.339	145.951	23.632	−655.286	−580.246	50.515
700	85.563	198.297	152.522	32.042	−658.249	−567.089	42.317
700.000	85.563	198.297	152.522	32.042	GLASS <--> LIQUID		
700.000	109 .202	198.297	152.522	32.042	TRANSITION		
800	109.202	212.879	159.176	42.962	−653.956	−554.359	36.196
900	109.202	225.741	165.871	53.883	−649.675	−542.167	31.467
1000	109.202	237.247	172.444	64.803	−645.399	−530.451	27.708
1100	109.202	247.655	178.815	75.723	−641.123	−519.163	24.653
1103.000	109.202	247.952	179.003	76.051	---- BETA <--> LIQUID ----		
1200	109.202	257.157	184.954	86.643	−636.843	−508.265	22.124
1300	109.202	265.897	190.848	97.564	−632.563	−497.723	19.999
1400	109.202	273.990	196.502	108.484	−628.296	−487.511	18.189
1500	109.202	281.524	201.922	119.404	−624.050	−477.604	16.632

PREVIOUS: June 1969 CURRENT: December 1973

0	to	583	K crystal, alpha
583	to	1103	K crystal, beta
above		1103	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	72.258	112.968	112.968	0.	−676.971	−630.875	110.527
300	72.383	113.415	112.969	0.134	−676.945	−630.589	109.795
400	76.065	134.642	115.838	7.522	−675.505	−615.351	80.357
500	79.705	152.035	121.389	15.323	−673.883	−600.497	62.733
583.000	81.965	164.425	126.653	22.021	ALPHA <--> BETA		
583.000	88.868	166.934	126.653	23.484	TRANSITION		
600	91.128	169.518	127.831	25.012	−670.557	−586.025	51.018
700	147.486	186.826	134.931	36.327	−670.616	−571.426	42.640
800	105.939	203.976	142.574	49.121	−664.448	−557.729	36.416
900	94.433	215.393	150.055	58.804	−661.404	−544.583	31.607
1000	94.433	225.342	157.095	68.248	−658.606	−531.753	27.776
1100	94.433	234.343	163.714	77.691	−655.807	−519.203	24.655
1103.000	94.433	234.600	163.907	77.974	BETA <--> LIQUID		
1103.000	109 .202	247.952	163.907	92.702	TRANSITION		
1200	109.202	257.157	171.078	103.294	−636.843	−508.265	22.124
1300	109.202	265.897	178.040	114.215	−632.563	−497.723	19.999
1400	109.202	273.990	184.608	125.135	−628.296	−487.511	18.189
1500	109.202	281.524	190.821	136.055	−624.050	−477.604	16.632

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 292.692\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -431.999 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -435.136 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
545.7(1)
170 (1)
522.5(1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Pb–F = 2.13 ± 0.02 Å

Bond Angle: F–Pb–F = [90]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.571688 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

Vapor pressure data for PbF_2 have previously been interpreted on the assumption that PbF_2 was the only species present in the gas phase.[1,2] Zmbov *et al.*[3] have studied the vapor species over PbF_2(cr, l) mass spectrometrically and shown that PbF_2vaporizes only partly as molecular PbF_2 and there is considerable disproportionation. The vapor composition at 988 K is approximately 66% PbF_4, 25% PbF_2, 2% PbF, and 7% Pb.[3,4] From extrapolation of the ion intensity data from 1043 to 988 K to the temperature region in which Nesmeyanov and Iofa[2] measured the saturated vapor pressures of PbF_2(cr), 792–988 K, by Knudsen effusion method, the partial pressure of PbF_2(g), at 988 K was calculated to be 0.0435 ± 0.005 torr. Based on this calculated vapor pressure, the enthalpy of sublimation $\Delta_{sub}H°(298.15\ K)$ of PbF_2(cr, β) is derived as 57.53 $kcal·mol^{-1}$ by the 3rd law method, yielding $\Delta_f H°(PbF_2, g, 298.15\ K) = -104.0 \pm 2\ kcal·mol^{-1}$.

Due to lack of data on vapor compositions over PbF_2 at various temperatures, the total pressure measurements reported by Wartenberg and Bosse,[1] using boiling point method, and those of Nesmeyanov and Iofa[2] are not used for evaluation.

The adopted $\Delta_f H°(298.15\ K)$ leads to an atomization energy $\Delta_{at}H°(0\ K) = 8.10$ eV for the process $PbF_2(g) = Pb(g) + 2F(g)$, using auxiliary data.[5]

Heat Capacity and Entropy

The bond distance was determined by Akishin *et al.*[6] The bond angle was estimated by Hauge *et al.*[7] from a Group IV A difluoride comparison. Hauge *et al.*[7] determined the vibrational frequencies from the infrared spectra of neon matrix isolated PbF_2(g).

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[4] R. H. Hauge, J. W. Hastie, and J. L. Margrave, J. Phys. Chem. **72**, 3510 (1968).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.567	−431.999	−431.999	INFINITE
100	38.879	244.078	334.499	−9.042	−433.148	−436.836	228.180
200	46.110	273.286	297.217	−4.786	−434.346	−440.018	114.921
250	48.928	283.892	293.521	−2.407	−434.774	−441.385	92.222
298.15	50.950	292.692	292.692	0.	−435.136	−442.625	77.546
300	51.016	293.008	292.693	0.094	−435.149	−442.671	77.076
350	52.537	300.992	293.320	2.685	−435.501	−443.897	66.248
400	53.653	308.084	294.731	5.341	−435.850	−445.073	58.121
450	54.485	314.454	296.575	8.046	−436.210	−446.204	51.794
500	55.116	320.229	298.656	10.786	−436.585	−447.295	46.729
600	55.988	330.361	303.119	16.345	−437.389	−449.362	39.120
700	56.542	339.036	307.645	21.974	−443.134	−450.491	33.616
800	56.914	346.612	312.053	27.648	−444.086	−451.477	29.478
900	57.175	353.332	316.273	33.353	−445.021	−452.344	26.253
1000	57.365	359.366	320.286	39.080	−445.938	−453.109	23.668
1100	57.506	364.840	324.091	44.824	−446.838	−453.782	21.548
1200	57.615	369.849	327.699	50.580	−447.722	−454.374	19.778
1300	57.700	374.464	331.121	56.346	−448.596	−454.893	18.278
1400	57.768	378.743	334.371	62.120	−449.476	−455.345	16.989
1500	57.823	382.730	337.464	67.900	−450.371	−455.733	15.870
1600	57.869	386.464	340.411	73.684	−451.287	−456.060	14.889
1700	57.906	389.973	343.224	79.473	−452.229	−456.330	14.021
1800	57.938	393.284	345.914	85.265	−453.199	−456.543	13.249
1900	57.964	396.417	348.490	91.060	−454.195	−456.702	12.556
2000	57.987	399.391	350.962	96.858	−455.219	−456.808	11.931
2100	58.007	402.220	353.336	102.658	−633.488	−449.747	11.187
2200	58.024	404.919	355.620	108.459	−634.169	−440.981	10.470
2300	58.039	407.499	357.820	114.263	−634.935	−432.183	9.815
2400	58.052	409.969	359.941	120.067	−635.785	−423.350	9.214
2500	58.064	412.339	361.990	125.873	−636.717	−414.480	8.660
2600	58.074	414.617	363.971	131.680	−637.725	−405.570	8.148
2700	58.083	416.809	365.887	137.488	−638.805	−396.621	7.673
2800	58.092	418.921	367.744	143.297	−639.950	−387.631	7.231
2900	58.099	420.960	369.544	149.106	−641.153	−378.598	6.819
3000	58.106	422.930	371.291	154.916	−642.404	−369.523	6.434
3100	58.112	424.835	372.988	160.727	−643.697	−360.406	6.073
3200	58.117	426.680	374.637	166.539	−645.023	−351.247	5.734
3300	58.122	428.469	376.241	172.351	−646.373	−342.045	5.414
3400	58.127	430.204	377.803	178.163	−647.739	−332.803	5.113
3500	58.131	431.889	379.324	183.976	−649.113	−323.520	4.828
3600	58.135	433.526	380.807	189.789	−650.488	−314.198	4.559
3700	58.138	435.119	382.254	195.603	−651.857	−304.837	4.304
3800	58.141	436.670	383.665	201.417	−653.213	−295.441	4.061
3900	58.144	438.180	385.044	207.231	−654.551	−286.008	3.831
4000	58.147	439.652	386.391	213.046	−655.865	−276.541	3.611
4100	58.150	441.088	387.707	218.860	−657.151	−267.042	3.402
4200	58.152	442.489	388.995	224.676	−658.404	−257.512	3.203
4300	58.154	443.858	390.255	230.491	−659.622	−247.953	3.012
4400	58.157	445.195	391.489	236.306	−660.800	−238.365	2.830
4500	58.158	446.502	392.697	242.122	−661.938	−228.751	2.655
4600	58.160	447.780	393.880	247.938	−663.033	−219.113	2.488
4700	58.162	449.031	395.041	253.754	−664.084	−209.451	2.328
4800	58.164	450.255	396.178	259.571	−665.089	−199.767	2.174
4900	58.165	451.455	397.294	265.387	−666.048	−190.063	2.026
5000	58.166	452.630	398.389	271.204	−666.961	−180.340	1.884
5100	58.168	453.782	399.464	277.020	−667.827	−170.599	1.747
5200	58.169	454.911	400.519	282.837	−668.648	−160.841	1.616
5300	58.170	456.019	401.556	288.654	−669.423	−151.068	1.489
5400	58.171	457.106	402.575	294.471	−670.153	−141.281	1.367
5500	58.172	458.174	403.576	300.288	−670.839	−131.481	1.249
5600	58.173	459.222	404.560	306.106	−671.483	−121.668	1.135
5700	58.174	460.252	405.528	311.923	−672.085	−111.845	1.025
5800	58.175	461.263	406.481	317.741	−672.647	−102.011	0.919
5900	58.176	462.258	407.418	323.558	−673.169	−92.168	0.816
6000	58.177	463.236	408.340	329.376	−673.654	−82.317	0.717

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [257.703 \pm 0.084]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -294.629 \pm 16.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -296.646 \pm 16.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[840 ± 20] (1)
[357 ± 2] (1)
[809 ± 10] (1)

Ground State Quantum Weight = [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distance: S–F = 1.59208 ± 0.00008 Å

Bond Angle: F–S–F = 98.197 ± 0.011°

Product of the Moments of Inertia: $I_A I_B I_C = 3.518837 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

We calculate $\Delta_f H°$ from a 3rd law analysis of two sets of equilibrium data for the gaseous isomolecular reaction $S + SF_2 = 2\ SF$. The equilibrium data are obtained from ion currents reported in a mass spectrometric study[1] of the molecular species formed from the reaction of gaseous SF_6 with graphite. We do not include in the equilibrium constants a proportionality constant involving ion multiplier gain and ionization cross sections since Hildenbrand[1] has recently demonstrated that these factors tend to cancel for isomolecular reactions. Results of our analyses are presented below.

Series	Cell Configuration	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[2]	C cell/wound Pt wire	4	1436–1564	3.1	10.68 ± 0.7	5.0 ± 2.3	70.77 ± 4.0
[3]	C cell/Pt partition/packed with cloth and Pt wire	7	1478–1588	7.7	10.87 ± 0.9	2.1 ± 5.0	70.96 ± 4.0

The two cell configurations used by Hildenbrand[1] yield nearly identical 3rd law $\Delta_f H°$ values; thus, we adopt the rounded average of −70.9 ± 4.0 kcal·mol^{-1}. Our adopted $\Delta_f H°$ value corresponds to a enthalpy of atomization and average bond dissociation energy of 172.9 kcal·mol^{-1} and 86.4 kcal·mol^{-1}, respectively. In addition, the primary bond dissociation energy of SF_2 is calculated to be $D_0°$(SF–F) = 91.7 kcal·mol^{-1}, suggesting that the individual S–F bonds are somewhat stronger than that in the SF (81.2 kcal·mol^{-1})[2] radical. This increase in bond strength is predicted by MO calculations[3] and has been qualitatively accounted for in terms of the valence-state model[1] of covalent bonding.

Two additional pieces of information exist which provide some support for our selected $\Delta_f H°$ value. Kinetic studies[4] on the dissociation of SF_3 indicate that $D_0°(SF_2–F)$–72 kcal·mol^{-1}. We calculate $D_0°(SF_2–F)$ = 67.3 kcal·mol^{-1} from JANAF data,[2] indicating that our heats of formation for SF_3 and SF_2 are consistent with these kinetic results. Di Lonardo and Trombetti[5] obtained $D_0°$(SF–F) = 92.2 ± 12 kcal·mol^{-1} from electron–impact threshold measurements on the COS/F and SF_6 systems. This value is to be compared with our calculated value of 91.7 kcal·mol^{-1}.

Heat Capacity and Entropy

We adopt molecular data which refer to an average ground state structure for SF_2. These results are based on microwave measurements and force field calculations performed by Kirchhoff *et al.*[6] Earlier microwave spectroscopic observations[7] on the isotopic $^{34}SF_2$ species support the assignment of the spectrum to the difluoride and confirm its angular structure. The individual moments of inertia are: $I_A = 3.1377 \times 10^{-39}$, $I_B = 9.1367 \times 10^{-39}$, and $I_C = 12.2744 \times 10^{-39}\ g·cm^2$.

A recent review on the chemistry of the lower sulfur fluorides includes a discussion on the vibrational spectrum of SF_2.[8] The only observed vibrational frequency (830 cm^{-1}) which has so far been attributed to the difluoride appeared as a shoulder to a band at 810 cm^{-1} in the infrared spectra of a mixture of S–F compounds. The band at 810 cm^{-1} has been assigned[8] to the S–F equatorial stretching frequency of F_3SSF. We prefer not to adopt the 830 cm^{-1} frequency as a fundamental since the band cannot be positively identified as due to SF_2. Four sets[6,9–11] of estimated frequencies have been reported. We believe that the best estimates are those of Kirchhoff *et al.*[6] which we adopt. These frequencies were obtained from force field calculations and include corrections which were made to account for the differences found between predicted and observed fundamentals for the related molecules of OF_2, SO_2, SiF_2, and CF_2. By analogy with other even electron S–F species,[2] we predict that the ground state is singlet and that there are no low-lying electronic levels which would contribute to the partition function.

Our thermal functions essentially update those reported by Wilkins.[10] Another set of functions which cover a rather short (0–2000 K) temperature interval has been reported by O'Hare.[11] We believe, however, that his estimate (ν_2 = 523 cm^{-1})[11] of the bending frequency is too high based on that observed for SO_2(ν_2 = 517 cm^{-1})[2] indicating that his entropies are probably too low by as much as 0.6–0.8 cal K^{-1}·mol^{-1}.

Continued on page 1215

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−11.221	−294.629	−294.629	INFINITE
100	34.579	215.347	294.044	−7.870	−294.875	−298.121	155.722
200	39.755	240.841	261.651	−4.162	−295.738	−301.049	78.626
250	42.491	250.008	258.429	−2.105	−296.204	−302.322	63.167
298.15	44.906	257.703	257.703	0.	−296.646	−303.461	53.165
300	44.992	257.981	257.704	0.083	−296.662	−303.503	52.845
350	47.131	265.082	258.260	2.388	−297.113	−304.607	45.460
400	48.896	271.495	259.520	4.790	−299.772	−305.560	39.902
450	50.331	277.340	261.180	7.272	−300.882	−306.225	35.546
500	51.493	282.705	263.068	9.818	−302.037	−306.755	32.046
600	53.208	292.256	267.157	15.059	−303.855	−307.520	26.772
700	54.370	300.550	271.348	20.442	−305.370	−308.008	22.984
800	55.181	307.867	275.464	25.922	−306.711	−308.292	20.129
900	55.766	314.402	279.434	31.471	−361.073	−307.334	17.837
1000	56.200	320.301	283.231	37.070	−361.020	−301.365	15.742
1100	56.529	325.673	286.849	42.707	−360.974	−295.402	14.027
1200	56.784	330.603	290.292	48.373	−360.941	−289.443	12.599
1300	56.986	335.157	293.570	54.062	−360.924	−283.485	11.391
1400	57.148	339.386	296.694	59.769	−360.925	−277.529	10.355
1500	57.280	343.333	299.673	65.491	−360.948	−271.571	9.457
1600	57.388	347.034	302.519	71.224	−360.991	−265.611	8.671
1700	57.479	350.516	305.240	76.968	−361.056	−259.648	7.978
1800	57.555	353.803	307.848	82.720	−361.140	−253.681	7.362
1900	57.620	356.917	310.349	88.478	−361.243	−247.708	6.810
2000	57.676	359.874	312.752	94.243	−361.360	−241.729	6.313
2100	57.724	362.689	315.064	100.013	−361.490	−235.745	5.864
2200	57.766	365.375	317.290	105.788	−361.627	−229.754	5.455
2300	57.802	367.944	319.437	111.566	−361.769	−223.756	5.082
2400	57.835	370.405	321.510	117.348	−361.911	−217.753	4.739
2500	57.863	372.766	323.513	123.133	−362.049	−211.743	4.424
2600	57.888	375.036	325.451	128.921	−362.180	−205.728	4.133
2700	57.911	377.221	327.329	134.711	−362.298	−199.709	3.864
2800	57.931	379.328	329.148	140.503	−362.402	−193.685	3.613
2900	57.949	381.361	330.914	146.297	−362.487	−187.658	3.380
3000	57.966	383.326	332.628	152.093	−362.551	−181.628	3.162
3100	57.980	385.227	334.295	157.890	−362.592	−175.597	2.959
3200	57.994	387.068	335.915	163.689	−362.607	−169.564	2.768
3300	58.006	388.853	337.492	169.489	−362.594	−163.532	2.588
3400	58.017	390.584	339.029	175.290	−362.554	−157.500	2.420
3500	58.028	392.266	340.526	181.092	−362.483	−151.470	2.261
3600	58.037	393.901	341.986	186.895	−362.383	−145.442	2.110
3700	58.046	395.491	343.410	192.700	−362.252	−139.418	1.968
3800	58.054	397.040	344.802	198.505	−362.091	−133.398	1.834
3900	58.061	398.548	346.160	204.310	−361.899	−127.382	1.706
4000	58.068	400.018	347.488	210.117	−361.676	−121.371	1.585
4100	58.074	401.452	348.787	215.924	−361.424	−115.367	1.470
4200	58.080	402.851	350.058	221.732	−361.142	−109.369	1.360
4300	58.086	404.218	351.302	227.540	−360.831	−103.378	1.256
4400	58.091	405.553	352.519	233.349	−360.493	−97.394	1.156
4500	58.096	406.859	353.713	239.158	−360.127	−91.419	1.061
4600	58.100	408.136	354.882	244.968	−359.735	−85.452	0.970
4700	58.105	409.385	356.028	250.778	−359.318	−79.494	0.883
4800	58.109	410.609	357.153	256.589	−358.876	−73.544	0.800
4900	58.112	411.807	358.256	262.400	−358.411	−67.605	0.721
5000	58.116	412.981	359.339	268.211	−357.923	−61.675	0.644
5100	58.119	414.132	360.402	274.023	−357.414	−55.755	0.571
5200	58.122	415.260	361.446	279.835	−356.885	−49.845	0.501
5300	58.125	416.368	362.472	285.647	−356.336	−43.946	0.433
5400	58.128	417.454	363.480	291.460	−355.768	−38.057	0.368
5500	58.130	418.521	364.471	297.273	−355.182	−32.179	0.306
5600	58.133	419.568	365.446	303.086	−354.579	−26.311	0.245
5700	58.135	420.597	366.404	308.900	−353.960	−20.455	0.187
5800	58.138	421.608	367.347	314.713	−353.326	−14.610	0.132
5900	58.140	422.602	368.275	320.527	−352.677	−8.775	0.078
6000	58.142	423.579	369.189	326.341	−352.014	−2.952	0.026

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

Sulfur Fluoride, Ion (SF_2^+) IDEAL GAS $M_r = 70.056257$ Sulfur Fluoride, Ion (SF_2^+) $F_2S_1^+(g)$

$S°(298.15\ K) = [263.525 \pm 0.42]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 698.195 \pm 46.0\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 702.389 \pm 46.0\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2B_1]$	[0]	[2]
$[^2A_1]$	[25000]	[2]
$[^2A_1]$	[28000]	[2]
$[^2A_2]$	[30000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[807] (1)
[352] (1)
[844] (1)

Point Group: $[C_{2v}]$ $\sigma = [2]$

Bond Distance: S–F = [1.59] Å

Bond Angle: F–S–F = [100]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.4931 \times 10^{-115}]\ g^3\cdot cm^6$

Enthalpy of Formation

$H°(0\ K) = 166.9 \pm 11.0\ kcal\cdot mol^{-1}$ is calculated as the sum of $\Delta_f H°(SF_3, g, 0\ K) = -70.42 \pm 4\ kcal\cdot mol^{-1}$ [1] and $IP(SF_2) = 10.29 \pm 0.3$ eV (237.29 $kcal\cdot mol^{-1}$). IP is the electron–impact appearance potential of SF_2^+ which was measured by Hildenbrand[2] in a mass spectral study of the products formed from the reaction of SF_6 with C at about 1500 K. We increase the uncertainty in IP to ±0.3 eV from the value (±0.1 eV) assigned by Hildenbrand[2] since recent photoelectron (PE) spectrometric studies on the related dihalides SCl_2[3] and SiF_2[4] show that their adiabatic ionization potentials lie 0.22 and 0.40 eV, respectively, below the corresponding vertical values. The adopted value of IP is bracketed by the accurately known adiabatic values for SCl_2(9.45 ± 0.05 eV),[3] and SiF_2(10.78 ± 0.05 eV),[4] and is close to the IP for atomic sulfur (10.36 eV).[5] MO calculations[6] predict $IP(SF_2) = 9.6$ eV.

Several fragmentation appearnce potentials for the ion–molecule systems SF_2^+/SF_6)[2,7] SF_2^+/SF_4,[2] and SF_2^+/NSF_3[8] have been reported and provide alternate paths leading to $\Delta_f H°$ once the ion formation processes are assigned. We use plausible reactions for the formation of SF_2^+ to calculate $\Delta_f H°$ values which cover the range 146–342 $kcal\cdot mol^{-1}$. The scatter in these values indicate that either the dissociative ionization processes have been incorrectly assigned, or perhaps more likely, the processes involve excess kinetic and/or excitation energies.

We find that the primary bond dissociation energy $D_0°$ (SF^+–F) is 87.1 $kcal\cdot mol^{-1}$ which when compared with $D_0°$ values [1] for SF_2(91.7 $kcal\cdot mol^{-1}$) and SF_2^-(68.7 $kcal\cdot mol^{-1}$) indicates that the trend is $D_0°(SF_2^+)$–$D_0°(SF_2) > D_0°(SF_2^-)$. Similar trends in bond dissociation energies have been reported[9] for the ions and neutrals of phosphorus and nitrogen difluorides.

Heat Capacity and Entropy

According to the Walsh correlation diagram[10] for non–hydride AB_2 molecules, the most loosely bound pair of electrons in SF_2 is in a b_1'' orbital. The Walsh prediction is supported by the results of theoretical studies[3, 11, 12] and assignments of the bands in the PE spectra[3, 12] for the isoelectronic molecules SCl_2, OF_2, and OCl_2. The b_1'' orbital is S–F antibonding and F–F bonding, but its binding energy[10] shows only a small positive angular dependence. We would expect then that removal of an electron from this orbital should be accompanied by a small increase in the bond angle. We adopt a bond angle of 100° which corresponds to roughly a 2° increase from that for SF_2.[1] The antibonding nature of the b_1'' orbital is also expected to produce upon ionization a decrease in the S–F bond length. However, a comparison of the S–F bond strengths in $SF_2^+(D_0° = 87.1\ kcal\cdot mol^{-1})$ and $SF_2(D_0° = 91.7\ kcal\cdot mol^{-1})$ would seem to indicate that any changes in molecular parameters are relatively small. We adopt $r_e(SF_2^+) = 1.59$ Å which amounts to only a 0.002 Å reduction from that for SF_2.[1] Our estimated molecular parameters appear reasonable in comparison with those for SiF_2.[1] The individual moments of inertia are: $I_A = 1.2375 \times 10^{-39}$, $I_B = 9.3597 \times 10^{-39}$, and $I_C = 3.0157 \times 10^{-39}\ g\cdot cm^2$.

We calculate the vibrational frequencies from the force constants $f_r = 4.7$ and $f_\omega/r^2 = 0.49$ mdyn/Å. The stretching force constant (f_r) is estimated from that for SiF_2[1] and PF_2.[13] We obtain the bending force constant from the ratio $f_r/(f_\omega/r^2) = 9.59$ which is the value calculated for SiF_2.[13] The changes in our frequencies on going from SF_2 to SF_2^+ are insignficant, in agreement with the view that the bonding in the two molecules is very similar.

The electronic configurations of the ground and excited states are predicted from the Walsh correlation diagram.[10] We also predict from this diagram that the two $^2A_1 \propto {}^2B_1$ spacings will strongly depend on the bond angle. This is supported at least for the first spacing by PE studies[3, 12] on SCl_2, OCl_2 and OF_2. Based on the similarity in the bond angles for OF_2[3] and SF_2,[1] we estimate the first $^2A_1 \leftarrow {}^2B_1$ spacing to be somewhat greater than that for OF_2^+(23471 cm^{-1}).[12] The PE spectra for SCl_2[3] and OF_2[12] do not provide support for the existence of a second $^2A_1$ state. This state has been observed, however, in the PE spectrum of OCl_2.[12] These results show for OCl_2^+ that the second $^2A_1$ state lies 2258 cm^{-1} above the first $^2A_1$ state. We include a second $^2A_1$–$^2A_1$ spacing of 3000 cm^{-1}. We estimate a somewhat larger spacing for SF_2^+ based on the fact that the bond angle in SF_2^+ is predicted to be smaller than that for OCl_2^+. The relative term value for the upper most state ($^2A_2$) is estimated from that for OF_2^+.[12]

References

[1]JANAF Thermochemical Tables: SF_2(g) and SiF_2(g), 6–30–76; SF_2(g), 12–31–76.

[2]D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).

Continued on page 1215

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.234	698.195		
100	34.639	221.100	299.913	−7.881			
200	39.818	246.644	267.476	−4.166			
250	42.536	255.823	264.251	−2.107			
298.15	44.937	263.525	263.525	0.	702.389	687.583	−120.462
300	45.023	263.803	263.525	0.083	702.411	687.492	−119.703
350	47.151	270.908	264.082	2.389	703.001	684.958	−102.224
400	48.910	277.323	265.342	4.792	701.382	682.428	−89.116
450	50.341	283.169	267.003	7.275	701.311	680.055	−78.939
500	51.500	288.535	268.892	9.822	701.196	677.701	−70.799
600	53.212	298.087	272.981	15.063	701.458	672.985	−58.589
700	54.372	306.382	277.173	20.446	702.021	668.198	−49.862
800	55.183	313.698	281.291	25.926	702.759	663.317	−43.310
900	55.767	320.233	285.261	31.475	650.476	659.418	−38.272
1000	56.200	326.133	289.058	37.074	652.608	660.297	−34.490
1100	56.529	331.505	292.676	42.712	654.732	660.963	−31.387
1200	56.785	336.435	296.120	48.378	656.844	661.437	−28.792
1300	56.986	340.989	299.399	54.067	658.940	661.734	−26.589
1400	57.148	345.218	302.522	59.774	661.017	661.871	−24.695
1500	57.280	349.165	305.502	65.495	663.073	661.860	−23.048
1600	57.388	352.866	308.348	71.229	665.108	661.713	−21.603
1700	57.479	356.348	311.070	76.972	667.122	661.439	−20.324
1800	57.556	359.635	313.677	82.724	669.117	661.047	−19.183
1900	57.621	362.749	316.179	88.483	671.093	660.545	−18.160
2000	57.676	365.706	318.582	94.248	673.054	659.939	−17.236
2100	57.724	368.521	320.894	100.018	675.003	659.235	−16.398
2200	57.766	371.208	323.120	105.793	676.944	658.439	−15.633
2300	57.803	373.776	325.267	111.571	678.881	657.554	−14.934
2400	57.835	376.237	327.340	117.353	680.818	656.585	−14.290
2500	57.864	378.599	329.343	123.138	682.758	655.536	−13.697
2600	57.890	380.869	331.282	128.926	684.706	654.409	−13.147
2700	57.914	383.054	333.159	134.716	686.667	653.206	−12.637
2800	57.936	385.160	334.979	140.509	688.642	651.931	−12.162
2900	57.957	387.194	336.744	146.303	690.636	650.584	−11.718
3000	57.976	389.159	338.459	152.100	692.652	649.169	−11.303
3100	57.995	391.060	340.125	157.899	694.691	647.686	−10.913
3200	58.014	392.902	341.746	163.699	696.756	646.137	−10.547
3300	58.034	394.687	343.323	169.501	698.849	644.523	−10.202
3400	58.053	396.420	344.860	175.306	700.972	642.845	−9.876
3500	58.074	398.103	346.357	181.112	703.125	641.104	−9.568
3600	58.097	399.740	347.817	186.921	705.309	639.301	−9.276
3700	58.121	401.332	349.242	192.732	707.525	637.437	−8.999
3800	58.147	402.882	350.633	198.545	709.774	635.512	−8.736
3900	58.176	404.393	351.992	204.361	712.055	633.529	−8.485
4000	58.207	405.866	353.321	210.180	714.369	631.486	−8.246
4100	58.242	407.304	354.620	216.003	716.715	629.385	−8.018
4200	58.279	408.708	355.891	221.829	719.094	627.226	−7.801
4300	58.320	410.079	357.136	227.659	721.505	625.010	−7.592
4400	58.365	411.421	358.354	233.493	723.947	622.738	−7.393
4500	58.413	412.733	359.548	239.332	726.421	620.410	−7.202
4600	58.466	414.017	360.718	245.176	728.926	618.027	−7.018
4700	58.523	415.275	361.866	251.025	731.461	615.589	−6.842
4800	58.584	416.508	362.991	256.880	734.026	613.096	−6.672
4900	58.649	417.717	364.096	262.742	736.620	610.550	−6.509
5000	58.719	418.902	365.180	268.610	739.243	607.951	−6.351
5100	58.793	420.066	366.245	274.486	741.894	605.299	−6.200
5200	58.872	421.208	367.291	280.369	744.574	602.594	−6.053
5300	58.954	422.330	368.319	286.260	747.280	599.838	−5.912
5400	59.042	423.433	369.329	292.160	750.014	597.031	−5.775
5500	59.133	424.517	370.323	298.069	752.774	594.172	−5.643
5600	59.229	425.584	371.300	303.987	755.560	591.263	−5.515
5700	59.329	426.633	372.262	309.915	758.373	588.304	−5.391
5800	59.432	427.666	373.208	315.853	761.210	585.296	−5.271
5900	59.540	428.682	374.140	321.801	764.072	582.239	−5.155
6000	59.651	429.684	375.057	327.761	766.959	579.132	−5.042

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K)$ = [267.445 ± 0.8] J·K^{-1}·mol^{-1}

$\Delta_f H°(0\ K)$ = [−391.116 ± 64.9] kJ·mol^{-1}
$\Delta_f H°(298.15\ K)$ = [−398.426 ± 64.9] kJ·mol^{-1}

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[479](1)
[286](1)
[594](1)

Ground State Quantum Weight: [2] σ = [2]
Point Group: [C_{2v}]
Bond Distance: S–F = [1.63] Å
Bond Angle: F–S–F = [130]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.856674 × 10^{-115}] g^3·cm^6

Enthalpy of Formation

We calculate the adopted value of $\Delta_f H°(0\ K)$ = −93.5 ± 15.5 kcal·mol^{-1} as the difference between $\Delta_f H°(SF_2,g,0\ K)$ = −70.42 ± 4.0 kcal·mol^{-1} [1] and an estimate EA(SF_2) = 1.0 ± 0.5 eV (23.06 kcal·mol^{-1}). The value of EA is estimated from a consideration of trends in the electron affinities for other S–F species.[1] These data follow a regular pattern among the even–and odd–electron molecules, with the odd–electron molecules having, as expected, the higher electron affinities. Within each even– and odd– electron series, the EA values progressively increase as the number of fluorine atoms are increased in the ions. The only other estimate available to compare with our result is EA = 1.2 ± 0.5 eV. This estimate was made by Hildenbrand[2] who used a method similar to ours. Our $\Delta_f H°$ value corresponds to a fluoride–ion affinity for SF of IA = 36.4 ± 17.0 kcal·mol^{-1}, and $\Delta_f H°$ at 298.15 K is −95.2 kcal·mol^{-1}. In addition, we find that the primary bond dissociation energy $D_0°(SF^-–F)$ is 68.7 kcal·mol^{-1} which when compared with the values for SF_2(91.7 kcal·mol^{-1}) and SF_2^+(87.1 kcal·mol^{-1}) indicates that the trend is $D_0°(SF_2^+)$–$D_0°(SF_2) > D_0°(SF_2^-)$. Similar trends in bond dissociation energies have been reported[3] for the ions and neutrals of phosphorus and nitrogen difluorides.

JANAF data[1] predict that SF_2^- should be reasonably stable at moderate temperatures, with dissociative ionization ($SF + F^-$) becoming thermodynamically favorable above 1500 K. These predictions are qualitatively supported by the observations of Harland and Thynne[4,5] who have observed SF_2^- in the negative ion mass spectra of SF_6, SF_4, and SF_5Cl. The temperature of the ion source was reported as around 325 K.

Heat Capacity and Entropy

According to the Walsh correlation diagram[6] for non–hydride AB_2 molecules, the most loosely bound electron in SF_2^- is in an $\bar{a}_1'$ orbital whose binding energy falls markedly with an increase in bond angle. We predict then that electron capture by SF_2 should be accompanied by a large increase in bond angle. Based on the bond angle reported for the isoelectronic valence (21 electrons) molecule ClF_2(136 ± 15°),[7] we estimate an angle for SF_2^- of 130° which represents a 32° increase from that for SF_2.[1] The addition of an antibonding electron to SF_2 should also produce an increase in the S–F bond length. We estimate $r_e(SF_2^-) = r_e(Cl–F)$ = 1.63 Å[1] which corresponds to $r_e(SF_2^-)–r_e(SF_2)$ = 0.038 Å. The individual moments of inertia are: I_A = 1.3702 × 10^{-39}, I_B = 13.7701 × 10^{-39}, and I_C = 15.1403 × 10^{-39} g·cm^2.

We calculate vibrational frequencies from the force constants f_r = 2.0 and f_α/r^2 = 0.27 mdyn/Å. These force constants are estimated from those for ClF_2(f_r = 1.94 and f_α/r^2 = 0.26 mdyn/Å) which are obtained from the bond angle and vibrational frequencies reported by Mamantov *et al.*[7] Our frequencies on going from SF_2 to SF_2^- show a large decrease, in agreement with the view that the additional antibonding electron weakens the bonding in the radical anion relative to the neutral molecule.

The Walsh correlation diagram[6] predicts a ground state electronic configuration of $^2A_1$ for a 21 valence electron molecule. In addition, the existence of two doublet excited states is highly probable. We omit these excited states since no spectroscopic information is available on these states for isoelectronic molecules which would allow us to estimate the relative term values. We speculate that these levels lie above 20000 cm^{-1}, and thus, their contributions to the thermal functions are probably small below 3000 K.

References

[1]JANAF Thermochemical Tables: SF_2(g), 6–30–76; SF^-(g), SF_3^-(g), SF_4^-(g), SF_5^-(g), and SF_2^+(g), 12–31–76; ClF(g), 9–30–65.
[2]D. L. Hildenbrand, J. Phys. Chem. **77**, 897 (1973).
[3]P. W. Harland, D. W. H. Rankin, and J. C. J. Thynne, Int. J. Mass Spec. and Ion Phys. **13**, 395 (1974).
[4]P. Harland and J. C. J. Thynne, J. Phys. Chem. **73**, 4031 (1969).
[5]P. W. Harland and J. C. J. Thynne, J. Phys. Chem. **75**, 3517 (1971).
[6]A. D. Walsh, J. Chem. Soc. **1953**, 2266 (1953).
[7]G. Mamantov, E. J. Vasini, M. C. Moulton, D. G. Vickroy, and T. Maekawa, J. Chem. Phys. **54**, 3419 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.125	−391.116		
100	36.153	220.728	308.077	−8.735			
200	44.703	248.468	271.882	−4.683			
250	47.901	258.804	268.259	−2.364			
298.15	50.164	267.445	267.445	0.	−398.426	−401.890	70.410
300	50.238	267.756	267.446	0.093	−398.471	−401.912	69.979
350	51.930	275.634	268.064	2.649	−399.709	−402.388	60.053
400	53.167	282.653	269.457	5.278	−403.181	−402.597	52.574
450	54.088	288.971	271.280	7.961	−405.130	−402.416	46.711
500	54.787	294.707	273.341	10.683	−407.148	−402.004	41.997
600	55.752	304.789	277.765	16.214	−410.754	−400.630	34.878
700	56.365	313.432	282.258	21.822	−414.123	−398.674	29.749
800	56.777	320.987	286.636	27.481	−417.364	−396.245	25.872
900	57.065	327.692	290.833	33.174	−473.660	−392.334	22.770
1000	57.275	333.716	294.825	38.891	−475.568	−383.195	20.016
1100	57.432	339.183	298.613	44.627	−477.502	−373.865	17.753
1200	57.552	344.185	302.205	50.376	−479.464	−364.357	15.860
1300	57.647	348.796	305.614	56.136	−481.454	−354.684	14.251
1400	57.722	353.071	308.853	61.905	−483.473	−344.857	12.867
1500	57.783	357.055	311.935	67.680	−485.520	−334.885	11.662
1600	57.833	360.786	314.873	73.461	−487.595	−324.775	10.603
1700	57.875	364.294	317.678	79.247	−489.696	−314.534	9.664
1800	57.909	367.603	320.360	85.036	−491.821	−304.169	8.827
1900	57.939	370.734	322.930	90.828	−493.969	−293.686	8.074
2000	57.964	373.707	325.395	96.624	−496.135	−283.088	7.394
2100	57.986	376.536	327.764	102.421	−498.315	−272.383	6.775
2200	58.005	379.234	330.042	108.221	−500.506	−261.573	6.211
2300	58.022	381.812	332.238	114.022	−502.704	−250.663	5.693
2400	58.036	384.282	334.355	119.825	−504.903	−239.657	5.216
2500	58.049	386.651	336.400	125.629	−507.101	−228.560	4.776
2600	58.061	388.928	338.377	131.435	−509.292	−217.375	4.367
2700	58.071	391.120	340.290	137.241	−511.473	−206.106	3.987
2800	58.080	393.232	342.143	143.049	−513.639	−194.757	3.633
2900	58.088	395.270	343.940	148.857	−515.789	−183.330	3.302
3000	58.095	397.240	345.684	154.666	−517.918	−171.830	2.992
3100	58.102	399.145	347.378	160.476	−520.025	−160.259	2.700
3200	58.108	400.989	349.025	166.287	−522.106	−148.620	2.426
3300	58.114	402.778	350.627	172.098	−524.162	−136.917	2.167
3400	58.119	404.512	352.186	177.910	−526.189	−125.152	1.923
3500	58.123	406.197	353.705	183.722	−528.188	−113.327	1.691
3600	58.128	407.835	355.186	189.534	−530.157	−101.446	1.472
3700	58.131	409.427	356.631	195.347	−532.096	−89.510	1.264
3800	58.135	410.978	358.041	201.160	−534.004	−77.523	1.066
3900	58.138	412.488	359.418	206.974	−535.883	−65.486	0.877
4000	58.141	413.960	360.763	212.788	−537.731	−53.401	0.697
4100	58.144	415.396	362.078	218.602	−539.550	−41.270	0.526
4200	58.147	416.797	363.364	224.417	−541.340	−29.095	0.362
4300	58.149	418.165	364.623	230.232	−543.102	−16.878	0.205
4400	58.152	419.502	365.855	236.047	−544.836	−4.620	0.055
4500	58.154	420.809	367.061	241.862	−546.543	7.677	−0.089
4600	58.156	422.087	368.244	247.678	−548.224	20.011	−0.227
4700	58.158	423.338	369.403	253.493	−549.879	32.382	−0.360
4800	58.160	424.562	370.539	259.309	−551.511	44.788	−0.487
4900	58.161	425.761	371.654	265.125	−553.120	57.228	−0.610
5000	58.163	426.936	372.748	270.941	−554.706	69.700	−0.728
5100	58.164	428.088	373.822	276.758	−556.271	82.203	−0.842
5200	58.166	429.217	374.876	282.574	−557.815	94.738	−0.952
5300	58.167	430.325	375.912	288.391	−559.341	107.302	−1.058
5400	58.168	431.413	376.930	294.208	−560.847	119.894	−1.160
5500	58.169	432.480	377.930	300.025	−562.336	132.514	−1.259
5600	58.171	433.528	378.914	305.842	−563.808	145.161	−1.354
5700	58.172	434.558	379.881	311.659	−565.264	157.834	−1.446
5800	58.173	435.570	380.832	317.476	−566.705	170.532	−1.536
5900	58.174	436.564	381.769	323.293	−568.131	183.256	−1.622
6000	58.174	437.542	382.690	329.111	−569.543	196.003	−1.706

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [294.082 \pm 0.08]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-333.382 \pm 41.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [336.435 \pm 41.8]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
717.0(1)	182.5(1)
614.6(1)	680.8(1)
319.8(1)	301.0(1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_2

Bond Distances: S–F = 1.635 ± 0.01 Å; S–S = 1.888 ± 0.01 Å

Bond Angles: F–S–S = 108.3 ± 0.5°; Dihedral = 87.9 ± 1.5°

Product of Moments of Inertia: $I_A I_B I_C = 7.332228 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

No direct experimental measurement of $\Delta_f H°$ is available. We estimate a value from bond energy considerations. From a comparison of bond lengths and force constants for FSSF[1] and SF_4,[2] we expect that the S–F bond energies in FSSF would be quite similar to those for the axial S–F bonds in SF_4. We assume $D_0°(FSS–F) = D_0°(SF_3–F)_{axial}$ = 73.6 kcal·mol^{-1} which leads to the adopted value of $\Delta_f H°(S_2F_2, g, 0\ K) = -79.7$ kcal·mol^{-1}. We use auxiliary heat of formation data from JANAF[3] and estimate the uncertainty in $\Delta_f H°$ as ±10.0 kcal·mol^{-1}. A previous estimate (−83.5 kcal·mol^{-1}) has been reported by O'Hare[4] who derived this value by a procedure identical with that used here. $\Delta_f H°(298.15\ K)$ corresponds to −80.4 kcal·mol^{-1}, and the atomization energy is calculated from $\Delta_f H°$ to be 247.9 kcal·mol^{-1}.

FSSF is isomeric with SSF_2.[3] Qualitative evidence has been presented[1] which indicates that SSF_2 is the more stable isomer. From our estimated free energy data, we predict a Gibbs energy change for the isomerization reaction FSSF(g) = SSF_2(g) of −15.4 kcal·mol^{-1} at 298.15 K, indicating that SSF_2 is substantially more stable than FSSF. This conflicts with relative stability predictions based on results from two independent MO studies.[5,6] These semiempirical (CNDO/2) calculations indicate that the instability of FSSF relative to SSF_2 amounts to only about 2.0 kcal·mol^{-1}. If we assume that these MO calculations are correct, we calculate that $D_0°(FS–SF) > D_0°(S=SF_2)$ by roughly 7.0 kcal·mol^{-1}. This seems very unlikely in view of what is known[1] about the S–S linkages in the two isomers. Our adopted results give $D_0°(FS–SF)$ = 85.6 kcal·mol^{-1} which lies between that for SSF_2(90.4 kcal·mol^{-1}) and S_2O(79.9 kcal·mol^{-1}).[3]

Heat Capacity and Entropy

The structural data and vibrational frequencies are taken from the recent review of Seel[1] and are based on reliable experimental measurements. We note that the molecular characteristics of FSSF are unusual in that the S–S bond length (1.888 Å) is much shorter than that in HSSH(2.05 Å),[1] and nearly equal to those in S_2(1.889 Å), SSF_2(1.860 Å), and S_2O(1.884 Å).[3] In contrast, the S–F bonds are longer than those in most S–F species (~1.58 Å),[3] and nearly as long as the axial S–F bonds (1.646 Å),[3] in SF_4. Rationale[1] has been presented to explain these unique molecular features in terms of double bond ($F^-S{=}S^+–F$) formation. The individual moments of inertia are: $I_A = 7.3579 \times 10^{-39}$, $I_B = 30.4921 \times 10^{-39}$, and $I_C = 32.6808 \times 10^{-39}\ g \cdot cm^2$.

We assume that there is no free internal rotation in the molecule, and the contribution from the torsional oscillation (ν_4 = 182.5 cm^{-1}) is included in the vibrational partition function. Extended Huckel calculations[7] show that the potential barrier to internal rotation is high (~40 kcal·mol^{-1}), providing some justification for our treatment. We estimate that the uncertainty in our entropies above 2000 K should not exceed 1.0 cal K^{-1}·mol^{-1}. The UV spectra[1] of FSSF reveal no excited states which would be significant in our calculations. Since S_2F_2 has no unpaired electrons, we predict that the ground state is singlet.

Our thermal functions essentially extend those reported by Brown and Pez.[8] Other published functions[4,9] are based on estimated vibrational frequencies and are considered less reliable.

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[3] JANAF Thermochemical Tables: S_2(g), 12–31–65, F(g), 9–30–65, SSF_2(g) and SF_4(g), 6–30–76, S_2O(g), 9–30–65.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.595	−333.382	−333.382	INFINITE
100	42.158	235.778	345.882	−11.010	−334.084	−338.120	176.616
200	56.425	269.610	299.845	−6.047	−335.333	−341.670	89.235
250	61.892	282.811	295.147	−3.084	−335.912	−343.186	71.705
298.15	66.041	294.082	294.082	0.	−336.435	−344.539	60.362
300	66.180	294.491	294.083	0.122	−336.455	−344.590	59.998
350	69.466	304.951	294.902	3.517	−336.981	−345.904	51.623
400	71.974	314.398	296.758	7.056	−341.935	−346.967	45.309
450	73.899	322.991	299.203	10.705	−343.804	−347.501	40.337
500	75.395	330.858	301.980	14.439	−345.774	−347.801	36.335
600	77.509	344.805	307.985	22.092	−348.764	−347.912	30.288
700	78.883	356.864	314.126	29.916	−351.185	−347.573	25.936
800	79.819	367.462	320.144	37.854	−353.279	−346.912	22.651
900	80.482	376.904	325.936	45.871	−461.429	−343.838	19.956
1000	80.968	385.410	331.465	53.945	−460.758	−330.809	17.280
1100	81.333	393.145	336.726	62.061	−460.105	−317.846	15.093
1200	81.614	400.234	341.727	70.208	−459.477	−304.941	13.274
1300	81.835	406.776	346.483	78.381	−458.878	−292.088	11.736
1400	82.011	412.847	351.009	86.574	−458.312	−279.279	10.420
1500	82.154	418.510	355.322	94.782	−457.781	−266.510	9.281
1600	82.272	423.816	359.439	103.004	−457.285	−253.775	8.285
1700	82.370	428.807	363.374	111.236	−456.823	−241.070	7.407
1800	82.453	433.518	367.141	119.477	−456.395	−228.391	6.628
1900	82.523	437.978	370.753	127.726	−455.996	−215.735	5.931
2000	82.583	442.212	374.221	135.982	−455.625	−203.099	5.304
2100	82.635	446.243	377.556	144.243	−455.276	−190.482	4.738
2200	82.679	450.088	380.766	152.508	−454.945	−177.880	4.223
2300	82.719	453.764	383.860	160.778	−454.627	−165.293	3.754
2400	82.753	457.285	386.847	169.052	−454.318	−152.720	3.324
2500	82.784	460.664	389.732	177.329	−454.013	−140.160	2.928
2600	82.811	463.911	392.523	185.609	−453.708	−127.612	2.564
2700	82.835	467.037	395.226	193.891	−453.396	−115.076	2.226
2800	82.856	470.050	397.844	202.175	−453.074	−102.551	1.913
2900	82.876	472.958	400.385	210.462	−452.740	−90.038	1.622
3000	82.893	475.768	402.851	218.751	−452.391	−77.537	1.350
3100	82.909	478.486	405.247	227.041	−452.022	−65.048	1.096
3200	82.923	481.119	407.577	235.332	−451.632	−52.571	0.858
3300	82.937	483.670	409.845	243.625	−451.218	−40.107	0.635
3400	82.949	486.147	412.053	251.920	−450.780	−27.656	0.425
3500	82.960	488.551	414.204	260.215	−450.318	−15.218	0.227
3600	82.970	490.888	416.302	268.511	−449.829	−2.793	0.041
3700	82.979	493.162	418.349	276.809	−449.313	9.618	−0.136
3800	82.987	495.375	420.347	285.107	−448.771	22.014	−0.303
3900	82.995	497.531	422.298	293.406	−448.202	34.396	−0.461
4000	83.003	499.632	424.205	301.706	−447.608	46.763	−0.611
4100	83.009	501.682	426.070	310.007	−446.989	59.114	−0.753
4200	83.016	503.682	427.894	318.308	−446.344	71.451	−0.889
4300	83.022	505.635	429.680	326.610	−445.677	83.771	−1.018
4400	83.027	507.544	431.428	334.913	−444.986	96.076	−1.141
4500	83.032	509.410	433.140	343.215	−444.274	108.365	−1.258
4600	83.037	511.235	434.818	351.519	−443.541	120.637	−1.370
4700	83.042	513.021	436.463	359.823	−442.789	132.894	−1.477
4800	83.046	514.769	438.076	368.127	−442.018	145.135	−1.579
4900	83.050	516.482	439.659	376.432	−441.231	157.359	−1.677
5000	83.054	518.159	441.212	384.737	−440.427	169.567	−1.771
5100	83.057	519.804	442.737	393.043	−439.609	181.759	−1.862
5200	83.060	521.417	444.235	401.349	−438.776	193.935	−1.948
5300	83.063	522.999	445.706	409.655	−437.932	206.094	−2.031
5400	83.066	524.552	447.152	417.961	−437.076	218.237	−2.111
5500	83.069	526.076	448.573	426.268	−436.209	230.364	−2.188
5600	83.072	527.573	449.970	434.575	−435.332	242.476	−2.262
5700	83.074	529.043	451.345	442.882	−434.446	254.572	−2.333
5800	83.077	530.488	452.697	451.190	−433.553	266.652	−2.401
5900	83.079	531.908	454.027	459.498	−432.652	278.717	−2.468
6000	83.081	533.305	455.337	467.806	−431.745	290.766	−2.531

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 292.827 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-397.482 \pm 41.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-401.413 \pm 41.8]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[1]
34000	[1]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[760.5(1)	330.0(1)
718.5(1)	692.3(1)
411.2(1)	274.0(1)

Point Group C_s $\sigma = 1$

Bond Distances: S–S = 1.860 ± 0.015 Å; S–F = 1.598 ± 0.012 Å

Bond Angles: S–S–F = 107.5 ± 1.0°; F–S–F = 92.5 ± 1.0°

Product of the Moments of Inertia: $I_A I_B I_C = 5.957541 \times 10^{-114}\ g^3 \cdot cm^6$

Heat of Formation

No direct experimental measurement of $\Delta_f H°$ is available. We estimate two values from bond energy considerations. Seel[1] has presented a detailed discussion on the bonding in S_2, S_2O, and SSF_2 and has shown from bond length and force constant correlations that the S = S linkages in these molecules are very similar. We assume that $D_0°(S=SF_2) = (D_0°(S_2) + D_0°(S_2O))/2 = 90 \pm 10$ kcal·mol^{-1} which gives $\Delta_f H°(SSF_2, g, 0\ K) = -94.7 \pm 14$ kcal·mol^{-1} when the value of $D_0°$ is combined with $\Delta_f H°(SF_2, g, 0\ K) = -70.4 \pm 4$ kcal·mol^{-1} and $\Delta_f H°(S, g, 0\ K) = 65.75 \pm .01$ kcal·mol^{-1}.[2] From a comparison of bond lengths and force constants[1,3] for the S–F bonds in SSF_2, and SF_4, we would expect that the mean S–F bond energies for these molecules are probably not too different. Values[2] for OSF_2 and SF_4 are 83.4 kcal·mol^{-1} and 80.0 kcal·mol^{-1}, respectively. Using $D_0°(S_2F–F) = 81.5 \pm 2.5$ kcal·mol^{-1}, we calculate $\Delta_r H°(0\ K) = 163.0$ kcal·mol^{-1} for the dissociation process $S_2F_2 = S_2 + 2F$ which leads to $\Delta_f H°(SSF_2, g, 0\ K) = -95.5 \pm 5.0$ kcal·mol^{-1}. These two estimates are in reasonable agreement and we choose to adopt the value of -95.0 ± 10.0 kcal·mol^{-1}.

The heat of atomization $\Delta_{at}H°(0\ K)$ is calculated from our adopted $\Delta_f H°$ value to be 263.2 kcal·mol^{-1} which is close to the value of 262.0 kcal·mol^{-1} predicted by CNDO/2 MO calculations and energy partitioning methods.[4]

Published estimates[1,5,6] of $\Delta_f H°$ based on bond energy schemes similar to those used here include in kcal·mol^{-1} -92 ± 7, -80.2, and -86.4. Wilkins[6] assumed that the mean S–F bond energy for SSF_2 was 80.0 kcal·mol^{-1} and obtained $\Delta_f H° = -86.4$ kcal·mol^{-1}. We believe that this estimate is in error. Recalculation of his data gives $\Delta_f H° = -91.6$ kcal·mol^{-1} which is in much better agreement with our results.

Heat Capacity and Entropy

The structural data and vibrational frequencies are taken from the recent review by Seel[1] and are based on reliable experimental measurements. Since SSF_2 has no unpaired electrons, we predict that the ground state is singlet. The ultra violet spectra[1] show absorption peaks at roughly 34000 cm^{-1} and 42000 cm^{-1}, suggesting the existence of at least two excited states. We do not include the level near 42000 cm^{-1} since its effect is negligible. The individual moments of inertia are: $I_A = 10.2965 \times 10^{-39}$, $I_B = 21.0146 \times 10^{-39}$, and $I_C = 27.5332 \times 10^{-39}$ g·cm^2.

Our thermal functions essentially extend those reported by Brown and Pez.[7] Other published functions[5,6] are based on an older set of vibrational frequencies[8] and include a bias due to incorrect analysis of the SSF_2 structure. O'Hare's analysis[5] of the structural data resulted in a value for the product of the moments of inertia which is about 7% lower than our results. In addition, he assigned SSF_2 to point group C_{2V} and used a symmetry number of two rather than the correct value of one. The moments of inertia used by Wilkins[6] are in units of amu ucang,[2] not g cm^2 as assumed.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−13.718	−397.482	−397.482	INFINITE
100	38.393	238.662	341.446	−10.278	−398.329	−402.654	210.325
200	52.610	269.714	298.294	−5.716	−399.980	−406.337	106.124
250	58.524	282.110	293.842	−2.933	−400.738	−407.837	85.213
298.15	63.127	292.827	292.827	0.	−401.413	−409.143	71.680
300	63.284	293.218	292.828	0.117	−401.438	−409.191	71.246
350	67.002	303.264	293.613	3.378	−402.098	−410.430	61.253
400	69.882	312.408	295.400	6.803	−407.165	−411.401	53.723
450	72.118	320.773	297.761	10.356	−409.131	−411.830	47.804
500	73.869	328.466	300.452	14.007	−411.183	−412.015	43.043
600	76.365	342.171	306.291	21.528	−414.305	−411.873	35.857
700	78.003	354.074	312.286	29.252	−416.827	−411.263	30.689
800	79.124	364.568	318.178	37.111	−418.999	−410.316	26.791
900	79.921	373.936	323.863	45.066	−527.212	−406.950	23.619
1000	80.505	382.388	329.299	53.088	−526.592	−393.621	20.561
1100	80.946	390.082	334.481	61.162	−525.981	−380.353	18.061
1200	81.286	397.141	339.412	69.274	−525.389	−367.141	15.981
1300	81.553	403.658	344.107	77.417	−524.820	−353.977	14.223
1400	81.767	409.710	348.579	85.583	−524.281	−340.855	12.717
1500	81.941	415.357	352.845	93.769	−523.772	−327.771	11.414
1600	82.084	420.650	356.919	101.970	−523.296	−314.720	10.275
1700	82.203	425.630	360.816	110.185	−522.852	−301.698	9.270
1800	82.303	430.332	364.548	118.410	−522.439	−288.701	8.378
1900	82.388	434.784	368.129	126.645	−522.055	−275.726	7.580
2000	82.461	439.012	371.568	134.888	−521.697	−262.771	6.863
2100	82.524	443.037	374.877	143.137	−521.359	−249.833	6.214
2200	82.579	446.877	378.063	151.392	−521.039	−236.911	5.625
2300	82.626	450.549	381.135	159.652	−520.731	−224.003	5.087
2400	82.668	454.067	384.101	167.917	−520.431	−211.108	4.595
2500	82.705	457.442	386.968	176.186	−520.134	−198.226	4.142
2600	82.738	460.686	389.741	184.458	−519.836	−185.355	3.724
2700	82.767	463.810	392.427	192.733	−519.531	−172.496	3.337
2800	82.794	466.820	395.030	201.011	−519.216	−159.649	2.978
2900	82.817	469.726	397.556	209.292	−518.888	−146.813	2.644
3000	82.839	472.534	400.009	217.575	−518.544	−133.989	2.333
3100	82.858	475.250	402.392	225.860	−518.180	−121.176	2.042
3200	82.876	477.881	404.711	234.146	−517.795	−108.376	1.769
3300	82.892	480.432	406.967	242.435	−517.386	−95.588	1.513
3400	82.907	482.907	409.164	250.725	−516.953	−82.812	1.272
3500	82.921	485.310	411.305	259.016	−516.494	−70.050	1.045
3600	82.934	487.646	413.394	267.309	−516.009	−57.301	0.831
3700	82.946	489.919	415.431	275.603	−515.497	−44.566	0.629
3800	82.957	492.131	417.421	283.898	−514.958	−31.846	0.438
3900	82.968	494.286	419.364	292.194	−514.392	−19.139	0.256
4000	82.978	496.387	421.264	300.491	−513.800	−6.448	0.084
4100	82.988	498.436	423.121	308.790	−513.183	6.228	−0.079
4200	82.998	500.436	424.938	317.089	−512.541	18.889	−0.235
4300	83.007	502.389	426.717	325.389	−511.875	31.534	−0.383
4400	83.017	504.297	428.458	333.691	−511.185	44.164	−0.524
4500	83.027	506.163	430.164	341.993	−510.474	56.777	−0.659
4600	83.036	507.988	431.836	350.296	−509.742	69.375	−0.788
4700	83.046	509.774	433.476	358.600	−508.989	81.956	−0.911
4800	83.057	511.522	435.084	366.905	−508.218	94.521	−1.029
4900	83.067	513.235	436.661	375.211	−507.429	107.070	−1.141
5000	83.079	514.913	438.209	383.519	−506.623	119.603	−1.249
5100	83.090	516.558	439.730	391.827	−505.802	132.119	−1.353
5200	83.102	518.172	441.223	400.137	−504.966	144.620	−1.453
5300	83.115	519.755	442.689	408.448	−504.117	157.104	−1.548
5400	83.129	521.309	444.131	416.760	−503.255	169.571	−1.640
5500	83.143	522.834	445.548	425.073	−502.381	182.023	−1.729
5600	83.158	524.332	446.942	433.388	−501.496	194.459	−1.814
5700	83.174	525.804	448.312	441.705	−500.601	206.878	−1.896
5800	83.191	527.251	449.661	450.023	−499.697	219.282	−1.975
5900	83.208	528.673	450.988	458.343	−498.784	231.671	−2.051
6000	83.226	530.072	452.295	466.665	−497.864	244.043	−2.125

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 256.579 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -587.013 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -587.852 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
State	ϵ_i, cm^{-1}	g_i
$^1A_1$	0	1
$^3B_1$	26310	3
$^1B_1$	44109	1
$^1B_2$	62280	1

Electronic Levels and Quantum Weights
ν, cm^{-1}
855 (1)
345 (1)
872 (1)

Point Group: C_{2v} $\sigma = 2$

Bond Distance: Si–F = 1.591 Å

Bond Angle: F–Si–F = 100° 59'

Product of the Moments of Inertia: $I_A I_B I_C = 3.200830 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

Margrave *et al.*[1] have reported some approximate equilibrium constants for the reaction Si(cr) + SiF_4(g) = 2 SiF_2(g). These were calculated from yields of polymerized products and a knowledge of the total system pressure given in U.S. Patent No. 2, 840,588 (1958). The data are subjected to a 3rd law analysis using the present JANAF functions[2] and yield $\Delta_f H°(298.15\ K) = 92 \pm 11\ kcal \cdot mol^{-1}$, which gives $\Delta_f H°(SiF_2, g, 298.15\ K) = -147 \pm 5\ kcal \cdot mol^{-1}$.

Ehlert and Margrave[3] and Farber[13] have determined equilibrium constants mass spectrometrically. A 2nd and 3rd law analysis of the data is shown below. We adopt $\Delta_f H°(SiF_2, g, 298.15\ K) = -140.5 \pm 3\ kcal \cdot mol^{-1}$ ($-587.852 \pm 12.6\ kJ \cdot mol^{-1}$).

Source	Reaction	T/K	Data Points	$\Delta_r H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	Drift cal $K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
[3]	CaF_2(cr) + Si(g) = Ca(g) + SiF_2(g)	1395–1543	12	80.2 ± 14.1	88.0 ± 3.0	4.6 ± 9.7	−140.1
[3]	CaF_2(g) + Si(g) = Ca(g) + SiF_2(g)	1395–1543	12	−8.3 ± 14.1	−18.0 ± 3.0	−6.6 ± 9.6	−140.7
[3]	2 CaF(g) + Si(g) = 2Ca(g) + SiF_2(g)	1395–1543	12	−18.6 ± 7.5	−33.4 ± 1.8	−10.0 ± 5.1	−141.0
[13]	SiF_4(g) + Si(g) = 2SiF_2(g)	1590–1782	10	−2.0 ± 0.3	−3.2 ± 0.3	0.7 ± 0.8	−140.7

Using JANAF values,[2] we calculate $\Delta_{at} H°(0\ K) = 283.7 \pm 5\ kcal \cdot mol^{-1}$ for the process $SiF_2(g) = Si(g) + 2\ F(g)$. Within 2 $kcal \cdot mol^{-1}$ the average bond energies in SiF_2(g), SiF_3(g), and SiF_4(g) are the same.

Heat Capacity and Entropy

The electronic levels are adopted from the ultraviolet spectral work of Khanna *et al.*,[4] Rao[5] and Gole *et al.*[6] The vibrational assignments of $\nu_1 = 855\ cm^{-1}$ (symmetric stretch) and $\nu_3 = 872\ cm^{-1}$ (asymmetric stretch) of Khanna *et al.*[7] are adopted. These assignments are supported by the argon matrix studies of Milligan and Jacox,[8] the neon matrix and the argon matrix measurements of Hastie *et al.*[9] and the excited state microwave work of Shoji *et al.*[10] The bending frequency assignment, $\nu_2 = 345\ cm^{-1}$, is adopted from the ultraviolet and microwave study of Rao and Curl.[11] This assignment is also confirmed by Milligan and Jacox.[8]

The gas phase geometry was established by Rao *et al.*[12] from microwave spectra. The principal moments of inertia are: $I_A = 2.7474 \times 10^{-39}$, $I_B = 9.5072 \times 10^{-39}$, and $I_C = 12.2545 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.204	−587.013	−587.013	INFINITE
100	34.719	214.272	292.766	−7.849	−586.832	−590.839	308.622
200	39.648	239.824	260.498	−4.135	−587.225	−594.726	155.327
250	42.199	248.946	257.299	−2.088	−587.531	−596.567	124.646
298.15	44.509	256.579	256.579	0.	−587.852	−598.278	104.816
300	44.593	256.855	256.580	0.082	−587.865	−598.343	104.181
350	46.691	263.891	257.131	2.366	−588.205	−600.063	89.554
400	48.456	270.244	258.379	4.746	−588.542	−601.733	78.578
450	49.912	276.038	260.024	7.206	−588.873	−603.362	70.036
500	51.105	281.361	261.896	9.733	−589.199	−604.955	63.199
600	52.886	290.847	265.950	14.938	−589.843	−608.046	52.935
700	54.106	299.096	270.109	20.291	−590.489	−611.029	45.596
800	54.964	306.380	274.196	25.747	−591.151	−613.918	40.085
900	55.586	312.892	278.140	31.276	−591.839	−616.723	35.794
1000	56.049	318.774	281.914	36.859	−592.556	−619.449	32.357
1100	56.401	324.133	285.513	42.483	−593.309	−622.103	29.541
1200	56.674	329.053	288.939	48.137	−594.099	−624.685	27.192
1300	56.891	333.598	292.201	53.815	−594.930	−627.201	25.201
1400	57.065	337.821	295.311	59.514	−595.805	−629.651	23.493
1500	57.206	341.763	298.278	65.227	−596.726	−632.036	22.009
1600	57.324	345.459	301.112	70.954	−597.694	−634.359	20.710
1700	57.421	348.937	303.824	76.691	−648.887	−636.173	19.547
1800	57.504	352.221	306.423	82.438	−649.720	−635.401	18.439
1900	57.574	355.332	308.916	88.192	−650.558	−634.583	17.446
2000	57.634	358.287	311.311	93.952	−651.398	−633.720	16.551
2100	57.686	361.100	313.615	99.718	−652.239	−632.816	15.740
2200	57.731	363.785	315.835	105.489	−653.077	−631.871	15.003
2300	57.771	366.352	317.976	111.264	−653.910	−630.888	14.328
2400	57.806	368.811	320.043	117.043	−654.734	−629.870	13.709
2500	57.837	371.172	322.042	122.825	−655.546	−628.817	13.138
2600	57.865	373.441	323.975	128.610	−656.343	−627.732	12.611
2700	57.891	375.625	325.848	134.398	−657.121	−626.617	12.123
2800	57.915	377.731	327.664	140.188	−657.878	−625.473	11.668
2900	57.938	379.764	329.425	145.981	−658.610	−624.303	11.245
3000	57.959	381.728	331.136	151.776	−659.316	−623.108	10.849
3100	57.981	383.629	332.799	157.573	−659.993	−621.890	10.479
3200	58.002	385.470	334.416	163.372	−660.640	−620.650	10.131
3300	58.024	387.255	335.991	169.174	−661.254	−619.391	9.804
3400	58.047	388.988	337.524	174.977	−661.834	−618.113	9.496
3500	58.072	390.671	339.019	180.783	−662.380	−616.819	9.206
3600	58.098	392.307	340.476	186.592	−1047.041	−605.049	8.779
3700	58.127	393.899	341.899	192.403	−1047.100	−592.771	8.368
3800	58.159	395.450	343.288	198.217	−1047.124	−580.492	7.979
3900	58.193	396.961	344.645	204.035	−1047.111	−568.212	7.610
4000	58.231	398.435	345.971	209.856	−1047.062	−555.933	7.260
4100	58.272	399.873	347.268	215.681	−1046.976	−543.656	6.926
4200	58.318	401.278	348.537	221.510	−1046.852	−531.381	6.609
4300	58.367	402.651	349.780	227.345	−1046.691	−519.110	6.306
4400	58.421	403.993	350.997	233.184	−1046.491	−506.843	6.017
4500	58.480	405.307	352.189	239.029	−1046.254	−494.580	5.741
4600	58.544	406.593	353.358	244.880	−1045.979	−482.324	5.477
4700	58.612	407.853	354.504	250.738	−1045.666	−470.074	5.224
4800	58.685	409.087	355.628	256.603	−1045.315	−457.831	4.982
4900	58.764	410.298	356.732	262.475	−1044.927	−445.596	4.750
5000	58.847	411.486	357.815	268.356	−1044.502	−433.369	4.527
5100	58.936	412.652	358.879	274.245	−1044.041	−421.151	4.313
5200	59.029	413.798	359.924	280.143	−1043.542	−408.942	4.108
5300	59.128	414.923	360.951	286.051	−1043.008	−396.743	3.910
5400	59.232	416.029	361.961	291.969	−1042.438	−384.555	3.720
5500	59.340	417.117	362.954	297.897	−1041.832	−372.377	3.537
5600	59.453	418.187	363.931	303.837	−1041.192	−360.211	3.360
5700	59.570	419.241	364.892	309.788	−1040.517	−348.057	3.190
5800	59.692	420.278	365.838	315.751	−1039.809	−335.915	3.025
5900	59.818	421.299	366.769	321.726	−1039.067	−323.784	2.867
6000	59.948	422.306	367.686	327.715	−1038.292	−311.668	2.713

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 82.123 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = [1421]\ K$
$T_{trs} = [1484]\ K$
$T_{fus} = 1750 \pm 2\ K$

$\Delta_f H°(0\ K) = -1214.807 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1217.126 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = [0.0]\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = [0.0]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 29.673 \pm 0.628\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Guntz[1] measured the enthalpy of neutralization of $Sr(OH)_2$ (aq) with HF(aq) as $\Delta H = -35.8$ kcal·mol^{-1} at 284 K. We estimate a $\Delta C_p° = 105$ cal K^{-1}·mol^{-1} for $Sr(OH)_2 \cdot 555\ H_2O + 2(HF \cdot 110\ H_2O) \rightarrow SrF_2$(cr) + 2 H_2O(l) which gives $\Delta H(298.15\ K) = -34.1$ kcal·mol^{-1}. This value leads to $\Delta_f H°(SrF_2, cr, 298.15\ K) = -291.3$ kcal·mol^{-1} when combined with the following enthalpies of formation: $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315$[2] $\Delta_f H°(Sr(OH)_2 \cdot 555\ H_2O, 298.15\ K) = -240.1$[3] and $\Delta_f H°(HF \cdot 110\ H_2O, 298.15\ K) = -76.78$ kcal·mol^{-1}.[4]

Petersen[5] measured the enthalpy of precipitation of SrF_2 from an aqueous $SrCl_2$ solution with AgF(aq) as $\Delta H - 34.5$ kcal·mol^{-1} at 293 K. We estimate a $\Delta C_p° = 108$ cal K^{-1}·mol^{-1} for $2(AgF \cdot 200\ H_2O) + SrCl_2 \cdot 400\ H_2O + SrF_2$(cr) + 2 AgCl(cr) which gives $\Delta H(298.15\ K) = -34.0$ kcal·mol^{-1}. This value leads to $\Delta_f H°(SrF_2, cr, 298.15\ K) = -290.9$ kcal·mol^{-1} when combined with the following enthalpies of formation: $\Delta_f H°(AgCl, cr, 298.15\ K) = -30.37$[6] $\Delta_f H°(AgF \cdot 200\ H_2O, 298.15\ K) = -53.398$[6] and $\Delta_f H°(SrCl_2 \cdot 400\ H_2O, 298.15\ K) = -209.871$ kcal·mol^{-1}.[3]

Stephen and Stephen[7] have selected as a "best" value for the solubility of SrF_2 0.119 g/l at 298.15 K which corresponds to $K_{sp} = 3.397 \times 10^{-9}$. Using $\Delta_f G°(Sr^{+2}, aq\ \infty, 298.15\ K) = -133.71$[3] and $\Delta_f G°(F^-, aq\ \infty, 298.15\ K) = -66.96$ kcal·mol^{-1},[4] we calculate $\Delta_f G°(SrF_2, cr, 298.15\ K) = -279.18$ kcal·mol^{-1}. Based on the adopted functions for SrF_2, this value gives $\Delta_f H°(SrF_2, cr, 298.15\ K) = -291.5$ kcal·mol^{-1}.

Very recently, Finch *et al.*[9] measured the enthalpy of precipitation of SrF_2 from an aqueous $SrCl_2$ solution by addition of a slight excess of NaF. X-ray diffraction patterns showed the precipitate to be crystalline SrF_2. Reduction of their data gives $\Delta_{sln} H° = 0.42$ kcal·mol^{-1} for SrF_2(cr) $\rightarrow Sr^{+2}$(aq ∞) + 2 F^-(aq ∞) from which we obtain $\Delta_f H°(SrF_2, cr, 298.15\ K) = -290.5 \pm 0.5$ kcal·mol^{-1} with $\Delta_f H°(Sr^{+2}, aq\ \infty, 298.15\ K) = -130.45$[3] and $\Delta_f H°(F^-, aq\ \infty, 298.15\ K) = -79.82$ kcal·mol^{-1}.

The adopted enthalpy of formation, $\Delta_f H°(SrF_2, cr, 298.15\ K) = -290.9 \pm 0.7$ kcal·mol^{-1}, is a weighted value of these four results. Barany *et al.*[8] determined the enthalpy of solution of SrO(cr) in 20.1 wt % aqueous HF, which contained some dissolved silica, as -65.41 ± 0.30 kcal·mol^{-1}. We assume this value refers to the process SrO(cr) + 2 HF ∞ 4.41 $H_2O \rightarrow SrF_2$(cr) + 2 H_2O(l) at 298.15 K, and we calculate $\Delta_f H°(SrF_2, cr, 298.15\ K) = -291.8 \pm 2.0$ kcal·mol^{-1} with $\Delta_f H°(SrO, cr, 298.15\ K) = -141.5$ kcal mol^{-1}).[4] These results substantiate our adopted $\Delta_f H°$ value.

Heat Capacity and Entropy

$C_p°$ below 300 K is based on the low-temperature (11–300 K) heat capacities for SrF_2 reported by Smith *et al.*[10] The sample purity was 99.9% by petrographic examination. We have fitted a smooth polynomial curve through their data and obtained $S°(298.15\ K) = 19.63 \pm 0.05$ cal K^{-1}·mol^{-1} based on S(10.9) = 0.021 cal K^{-1}·mol^{-1}.

The only high temperature enthalpy data is that recently reported by Efremova and Matizen[11] in the temperature range 813–2126 K. Spectroscopic analysis showed the SrF_2 sample contained less than 0.04% of foreign metals. A second order transition was observed between the temperatures of 1421 and 1484 K. We adopt their smoothed $C_p°$ data in the temperature range 900–1750 K; $C_p°$'s above the melting point are obtained by graphical extrapolation. $C_p°$ is assumed constant at 39.5 cal K^{-1}·mol^{-1} over the temperature interval (1421–1484 K) of the transition (see further discussion in Transition Data). The observed enthalpies of Efremova and Matizen[11] deviate from our adopted ones by 1.4% at the lowest temperature (813 K) of their measurements and by only a few tenths of one percent at the higher temperatures.

Transition Data

Efremova and Matizen[11] reported that the phase transition for SrF_2 occurs over a short temperature interval (1421–1484 K). There are no discontinuities in their enthalpy data in this temperature range. Other alkaline earth dihalides[12] which have the calcium fluoride structure, are known to exhibit similar behavior, and this fact would seem to rule out the possibility that the observed transition resulted wholly from impurities. We speculate that the two crystalline forms, α and β, of SrF_2 are practically of the same energy content and can therefore, coexist over this temperature interval.

We choose to tentatively adopt two transitions with zero enthalpies, pending resolution of the phases present at these temperatures by X-ray diffraction measurements. The adopted values are placed in brackets above to emphasize that there is no confirmatory evidence for their existence.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

References

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Continued on page 1216

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.075	−1214.807	−1214.807	INFINITE
100	36.671	21.017	137.682	−11.666	−1217.805	−1200.065	626.850
200	61.636	55.736	88.303	−6.513	−1218.070	−1182.045	308.718
298.15	69.985	82.123	82.123	0.	−1217.126	−1164.544	204.023
300	70.103	82.556	82.125	0.130	−1217.104	−1164.218	202.708
400	74.726	103.406	84.936	7.388	−1215.793	−1146.781	149.754
500	77.320	120.379	90.380	14.999	−1214.376	−1129.691	118.018
600	78.827	134.616	96.599	22.810	−1212.968	−1112.887	96.885
700	79.914	146.849	102.924	30.748	−1211.616	−1096.315	81.808
800	80.960	157.585	109.099	38.789	−1210.324	−1079.932	70.512
900	82.341	167.180	115.028	46.937	−1209.705	−1063.636	61.732
1000	85.772	176.024	120.691	55.334	−1208.031	−1047.493	54.715
1100	90.207	184.388	126.104	64.113	−1213.908	−1031.169	48.966
1200	97.069	192.513	131.300	73.455	−1212.258	−1014.624	44.165
1300	108.784	200.659	136.321	83.640	−1209.788	−998.246	40.110
1400	143.930	209.735	141.230	95.907	−1205.258	−982.123	36.643
1421.000	165 .687	212.027	142.259	99.141	ALPHA <--> BETA TRANSITION		
1421.000	165 .268	212.027	142.259	99.141			
1484.000	165.268	219.197	145.374	109.553	UNDEFINED TRANSITION		
1484.000	165.268	219.197	145.374	109.553			
1500	154.808	220.911	146.171	112.110	−1196.812	−966.475	33.656
1600	125.938	229.799	151.132	125.867	−1190.831	−951.330	31.058
1700	113.805	237.012	155.978	137.758	−1323.645	−935.314	28.739
1750.000	109 .441	240.249	158.340	143.342	---- BETA <--> LIQUID ----		
1800	107.320	243.303	160.658	148.762	−1318.587	−912.620	26.484
1900	102.717	248.976	165.159	159.251	−1314.061	−890.192	24.473
2000	99.579	254.159	169.481	169.356	−1309.937	−867.991	22.670
2100	97.696	258.969	173.629	179.213	−1306.079	−845.990	21.043
2200	96.650	263.487	177.612	188.925	−1302.384	−824.168	19.568
2300	96.232	267.772	181.440	198.565	−1298.783	−802.511	18.226
2400	96.232	271.868	185.123	208.189	−1295.222	−781.011	16.998
2500	96.232	275.796	188.672	217.812	−1291.689	−759.658	15.872

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = [109.445]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1750 \pm 2\ K$

$\Delta_f H°(298.15\ K) = [-1172.043]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 29.673 \pm 0.628\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(SrF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(SrF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1750\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for liquid SrF_2 is obtained from the enthalpy measurements of Efremova and Matizen[1]. $C_p°$ is assumed to be constant in the temperature range 1200–3500 K. At 1200 K a glass transition is assumed below which $C_p°$ follows that of the crystal. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Kojima *et al.*[2] determined the melting point of a SrF_2 sample, which had been purified by passing anhydrous HF through the melt, as 1746 ± 1 K. Porter and Brown[3] found a melting point of 1736 ± 5 K for a sample of 99.8 + % purity, while Petit and Delbove[4] reported 1735 K. The adopted melting point, 1750 ± 2 K, is that determined by Efremova and Matizen[1] in their calorimetric studies of a high purity SrF_2 sample. The enthalpy of melting, 7.092 ± 0.150 $kcal·mol^{-1}$, is calculated as the difference between the adopted enthalpies of the liquid and crystal at T_{fus}.

Vaporization Data

The boiling point is calculated as the temperature at which the fugacity is one atmosphere for the vaporization process. The enthalpy of vaporization is the difference in $\Delta_f H°(T_{vap})$ for the liquid and gas.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$		
0							
100							
200							
298.15	69.977	109.445	109.445	0.	−1172.043	−1127.607	197.552
300	70.103	109.878	109.446	0.130	−1172.021	−1127.331	196.286
400	74.726	130.727	112.257	7.388	−1170.711	−1112.627	145.294
500	77.320	147.701	117.702	14.999	−1169.293	−1098.269	114.735
600	78.827	161.937	123.920	22.810	−1167.885	−1084.197	94.388
700	79.914	174.171	130.246	30.748	−1166.533	−1070.357	79.871
800	80.960	184.906	136.421	38.789	−1165.242	−1056.706	68.996
900	82.341	194.502	142.350	46.937	−1164.622	−1043.142	60.542
1000	85.772	203.346	148.012	55.334	−1162.948	−1029.732	53.788
1100	90.207	211.710	153.425	64.113	−1168.825	−1016.139	48.252
1200	97.069	219.835	158.622	73.456	−1167.174	−1002.327	43.630
1200.000	97.069	219.835	158.622	73.456	GLASS <--> LIQUID		
1200.000	99.048	219.835	158.622	73.456	TRANSITION		
1300	99.048	227.763	163.640	83.361	−1164.985	−988.678	39.726
1400	99.048	235.104	168.485	93.266	−1162.817	−975.198	36.385
1500	99.048	241.937	173.157	103.170	−1160.669	−961.872	33.495
1600	99.048	248.330	177.658	113.075	−1158.539	−948.688	30.971
1700	99.048	254.334	181.993	122.980	−1293.340	−934.457	28.712
1750.000	99.048	257.205	184.101	127.932	---- BETA <--> LIQUID ----		
1800	99.048	259.996	186.171	132.885	−1289.381	−913.461	26.508
1900	99.048	265.351	190.199	142.790	−1285.440	−892.684	24.542
2000	99.048	270.431	194.084	152.694	−1281.516	−872.114	22.777
2100	99.048	275.264	197.836	162.599	−1277.610	−851.740	21.186
2200	99.048	279.872	201.461	172.504	−1273.722	−831.552	19.744
2300	99.048	284.275	204.966	182.409	−1269.856	−811.540	18.431
2400	99.048	288.490	208.359	192.313	−1266.014	−791.696	17.231
2500	99.048	292.533	211.646	202.218	−1262.199	−772.011	16.130
2600	99.048	296.418	214.832	212.123	−1258.416	−752.478	15.117
2700	99.048	300.156	217.924	222.028	−1254.671	−733.090	14.182
2800	99.048	303.758	220.925	231.933	−1250.970	−713.840	13.317
2900	99.048	307.234	223.842	241.837	−1247.320	−694.721	12.513
3000	99.048	310.592	226.678	251.742	−1243.729	−675.728	11.765
3100	99.048	313.840	229.437	261.647	−1240.204	−656.853	11.068
3200	99.048	316.984	232.124	271.552	−1236.754	−638.090	10.416
3300	99.048	320.032	234.742	281.457	−1233.386	−619.434	9.805
3400	99.048	322.989	237.294	291.361	−1230.108	−600.879	9.231
3500	99.048	325.860	239.784	301.266	−1226.929	−582.419	8.692

PREVIOUS: CURRENT: December 1972

0	to	1421	K crystal
1421	to	1484	K crystal
1484	to	1750	K crystal
above		1750	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.075	−1214.807	−1214.807	INFINITE
100	36.671	21.017	137.682	−11.666	−1217.805	−1200.065	626.850
200	61.636	55.736	88.303	−6.513	−1218.070	−1182.045	308.718
298.15	69.985	82.123	82.123	0.	−1217.126	−1164.544	204.023
300	70.103	82.556	82.125	0.130	−1217.104	−1164.218	202.708
400	74.726	103.406	84.936	7.388	−1215.793	−1146.781	149.754
500	77.320	120.379	90.380	14.999	−1214.376	−1129.691	118.018
600	78.827	134.616	96.599	22.810	−1212.968	−1112.887	96.885
700	79.914	146.849	102.924	30.748	−1211.616	−1096.315	81.808
800	80.960	157.585	109.099	38.789	−1210.324	−1079.932	70.512
900	82.341	167.180	115.028	46.937	−1209.705	−1063.636	61.732
1000	85.772	176.024	120.691	55.334	−1208.031	−1047.493	54.715
1100	90.207	184.388	126.104	64.113	−1213.908	−1031.169	48.966
1200	97.069	192.513	131.300	73.455	−1212.258	−1014.624	44.165
1300	108.784	200.659	136.321	83.640	−1209.788	−998.246	40.110
1400	143.930	209.735	141.230	95.907	−1205.258	−982.123	36.643
1421.000	165.687	212.027	142.259	99.141	ALPHA <--> BETA		
1421.000	165.268	212.027	142.259	99.141	TRANSITION		
1484.000	165.268	219.197	145.374	109.553	UNDEFINED		
1484.000	165.268	219.197	145.374	109.553	TRANSITION		
1500	154.808	220.911	146.171	112.110	−1196.812	−966.475	33.656
1600	125.938	229.799	151.132	125.867	−1190.831	−951.330	31.058
1700	113.805	237.012	155.978	137.758	−1323.645	−935.314	28.739
1750.000	109.441	240.249	158.340	143.342	BETA <--> LIQUID		
1750.000	99.048	257.205	158.340	173.015	TRANSITION		
1800	99.048	259.996	161.125	177.968	−1289.381	−913.461	26.508
1900	99.048	265.351	166.471	187.872	−1285.440	−892.684	24.542
2000	99.048	270.431	171.543	197.777	−1281.516	−872.114	22.777
2100	99.048	275.264	176.368	207.682	−1277.610	−851.740	21.186
2200	99.048	279.872	180.969	217.587	−1273.722	−831.552	19.744
2300	99.048	284.275	185.365	227.492	−1269.856	−811.540	18.431
2400	99.048	288.490	189.575	237.396	−1266.014	−791.695	17.231
2500	99.048	292.533	193.613	247.301	−1262.199	−772.011	16.130
2600	99.048	296.418	197.493	257.206	−1258.416	−752.478	15.117
2700	99.048	300.156	201.226	267.111	−1254.671	−733.090	14.182
2800	99.048	303.758	204.824	277.015	−1250.970	−713.840	13.317
2900	99.048	307.234	208.296	286.920	−1247.320	−694.721	12.513
3000	99.048	310.592	211.650	296.825	−1243.729	−675.728	11.765
3100	99.048	313.840	214.895	306.730	−1240.204	−656.853	11.068
3200	99.048	316.984	218.036	316.635	−1236.754	−638.090	10.416
3300	99.048	320.032	221.081	326.539	−1233.386	−619.434	9.805
3400	99.048	322.989	224.035	336.444	−1230.108	−600.879	9.231
3500	99.048	325.860	226.903	346.349	−1226.929	−582.419	8.692

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = 291.715 \pm 2.1\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -764.053 \pm 4.2\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -766.090 \pm 4.2\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
442 (1)
82 (1)
443 (1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Sr–F = 2.20 ± 0.03Å

Bond Angle: F–Sr–F = 108°

Product of the Moments of Inertia: $I_A I_B I_C = 4.022689 \times 10^{-114}\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H°$ is obtained from that of the crystal by addition of the adopted $\Delta_{sub}H° = 107.8 \pm 0.3\ kcal\cdot mol^{-1}$. 2nd and 3rd law analyses of four sets of vapor pressure data for SrF_2(cr, l) are listed below.

Source	Method	T/K	$\Delta_{sub}H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal $K^{-1}\cdot mol^{-1}$	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Ruff and Le Boucher[1]	Dynamic B.P.	2095–2232	106.4[a]	96.1 ± 0.8	−4.8 ± 3.1	−184.0 ± 1.5
Bautista and Margrave[2]	Langmuir	1235–1319	104.5	108.0 ± 0.5	2.8 ± 2.9	−182.9 ± 1.2
Green *et al.*[3]	Knudsen	1207–1563[b]	107.9	107.8 ± 0.3	−0.07 ± 0.38	−183.1 ± 1.0
Hildenbrand[4]	Torsion–Effusion	1420–1710	103.8	106.5 ± 0.4	1.7	−184.4 ± 1.1

[a] $\Delta_{vap}H°(298.15\ K)$

[b] Six of the 30 experimental points were rejected due to failure of a statistical test.

Note that the drifts are both positive and negative indicating the correctness of the functions used in the analysis. A weighted value of these four results is adopted.

Heat Capacity and Entropy

The bond length is that measured by Akishin and Spiridonov [5] in their high–temperature electron diffraction studies of the alkaline earth dihalide vapors. Although it was inferred from these measurements that all the dihalides are linear, recent results of electric–deflection experiments [6] and matrix isolation infrared spectra[1,8] for SrF_2 can only be satisfactorily interpreted in terms of a molecule with a bent configuration. We adopt the vibrational frequencies and bond angle determined by Calder *et al.*[8] in their thorough investigation of the infrared spectra of isotopically enriched samples of SrF_2 trapped in krypton matrices. The uncertainty assigned to the entropy reflects possible errors due to matrix–shift effects in these frequencies. The adopted symmetric (ν_1) and antisymmetric (ν_3) stretching frequencies are in reasonable agreement with those determined by Snelson[7] for SrF_2 trapped in neon, argon, and krypton matrices. Also, the antisymmetric frequency is quite consistent with the value 445 ± 7 cm^{-1} observed by Baikov[9] in the infrared spectra of SrF_2 vapor at 2050 K. In an earlier paper, Baikov[10] reported observing under similar conditions a broad absorption band at 105 cm^{-1} which he assigned to the symmetric bending (ν_2) mode of SrF_2. We prefer the matrix value (82 cm^{-1}, since Baikov[10] recorded only the high–frequency (>90 cm^{-1}) portion of this band. Furthermore, Hastie *et al.*[11] have pointed out that, in general, bending frequencies are less influenced by matrix effects and in some cases may be shifted slightly upwards from the gas phase values.

The individual moments of inertia are: $I_A = 7.3594 \times 10^{-39}$, $I_B = 19.9877 \times 10^{-39}$, and $I_C = 27.3471 \times 10^{-39}\ g\cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.356	−764.053	−764.053	INFINITE
100	41.833	240.072	335.836	−9.576	−764.680	−768.845	401.604
200	48.936	271.323	296.453	−5.026	−765.547	−772.639	201.793
250	51.366	282.520	292.579	−2.515	−765.841	−774.382	161.798
298.15	52.991	291.715	291.715	0.	−766.090	−775.998	135.952
300	53.042	292.043	291.716	0.098	−766.100	−776.060	135.124
350	54.207	300.312	292.366	2.781	−766.358	−777.700	116.065
400	55.034	307.607	293.825	5.513	−766.633	−779.301	101.766
450	55.637	314.126	295.725	8.281	−766.934	−780.867	90.641
500	56.087	320.012	297.864	11.074	−767.266	−782.398	81.737
600	56.698	330.297	302.437	16.716	−768.027	−785.355	68.371
700	57.081	339.068	307.059	22.406	−768.922	−788.174	58.814
800	57.335	346.708	311.548	28.128	−769.950	−790.856	51.638
900	57.513	353.472	315.837	33.871	−771.735	−793.329	46.044
1000	57.641	359.538	319.909	39.629	−772.701	−795.677	41.562
1100	57.736	365.037	323.766	45.398	−781.588	−797.561	37.873
1200	57.810	370.064	327.417	51.175	−783.502	−798.929	34.776
1300	57.867	374.693	330.878	56.959	−785.434	−800.136	32.150
1400	57.912	378.983	334.163	62.748	−787.382	−801.194	29.893
1500	57.949	382.980	337.286	68.542	−789.345	−802.112	27.932
1600	57.979	386.721	340.260	74.338	−791.324	−802.899	26.212
1700	58.005	390.237	343.097	80.137	−930.231	−802.382	24.654
1800	58.026	393.553	345.809	85.939	−930.375	−794.857	23.066
1900	58.043	396.691	348.405	91.742	−930.535	−787.324	21.645
2000	58.059	399.668	350.895	97.547	−930.710	−779.782	20.366
2100	58.072	402.501	353.285	103.354	−930.902	−772.231	19.208
2200	58.083	405.203	355.584	109.162	−931.112	−764.671	18.156
2300	58.093	407.785	357.798	114.971	−931.342	−757.100	17.194
2400	58.102	410.258	359.933	120.780	−931.595	−749.519	16.313
2500	58.110	412.630	361.993	126.591	−931.874	−741.927	15.502
2600	58.117	414.909	363.985	132.402	−932.185	−734.323	14.753
2700	58.123	417.102	365.912	138.214	−932.533	−726.706	14.059
2800	58.128	419.216	367.778	144.027	−932.924	−719.076	13.415
2900	58.133	421.256	369.587	149.840	−933.365	−711.431	12.814
3000	58.138	423.227	371.343	155.653	−933.865	−703.770	12.254
3100	58.142	425.134	373.047	161.467	−934.431	−696.091	11.729
3200	58.145	426.979	374.704	167.282	−935.071	−688.393	11.237
3300	58.148	428.769	376.315	173.096	−935.794	−680.673	10.774
3400	58.152	430.505	377.884	178.911	−936.606	−672.930	10.338
3500	58.154	432.190	379.411	184.727	−937.516	−665.162	9.927
3600	58.157	433.829	380.900	190.542	−938.530	−657.366	9.538
3700	58.159	435.422	382.352	196.358	−939.654	−649.541	9.170
3800	58.161	436.973	383.770	202.174	−940.893	−641.684	8.821
3900	58.163	438.484	385.153	207.990	−942.252	−633.792	8.489
4000	58.165	439.957	386.505	213.807	−943.733	−625.864	8.173
4100	58.167	441.393	387.826	219.623	−945.338	−617.898	7.872
4200	58.169	442.795	389.118	225.440	−947.065	−609.891	7.585
4300	58.170	444.163	390.383	231.257	−948.918	−601.842	7.311
4400	58.171	445.501	391.620	237.074	−950.895	−593.748	7.049
4500	58.173	446.808	392.832	242.891	−952.992	−585.607	6.798
4600	58.174	448.087	394.019	248.709	−955.140	−577.424	6.557
4700	58.175	449.338	395.183	254.526	−957.448	−569.188	6.326
4800	58.176	450.562	396.324	260.344	−959.857	−560.902	6.104
4900	58.177	451.762	397.443	266.161	−962.365	−552.565	5.890
5000	58.178	452.937	398.542	271.979	−964.957	−544.176	5.685
5100	58.179	454.089	399.619	277.797	−967.614	−535.736	5.487
5200	58.180	455.219	400.678	283.615	−970.364	−527.241	5.296
5300	58.181	456.327	401.717	289.433	−973.181	−518.693	5.112
5400	58.181	457.415	402.739	295.251	−976.057	−510.091	4.934
5500	58.182	458.482	403.743	301.069	−978.984	−501.435	4.762
5600	58.183	459.531	404.730	306.887	−981.955	−492.725	4.596
5700	58.183	460.561	405.700	312.706	−984.962	−483.963	4.435
5800	58.184	461.573	406.655	318.524	−987.997	−475.147	4.279
5900	58.184	462.567	407.594	324.342	−990.843	−466.302	4.128
6000	58.185	463.545	408.518	330.161	−993.883	−457.386	3.982

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 255.690 \pm 6.3\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -686.627 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -688.268 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[473](1)
[283](2)
[633](1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Ti–F = [1.95]Å
Bond Angle: F–Ti–F = [180]°
Rotational Constant: B_0 = [0.116676] cm^{-1}

Enthalpy of Formation

Zmbov and Margrave[1] have reported ion intensities and the corresponding equilibrium constants for the reaction $Ca(g) + TiF_3(g) = CaF(g) + TiF_2(g)$. 2nd and 3rd law analyses of their data give a 2nd law $\Delta_r H°(298.15\ K)$ of 7.0 $kcal \cdot mol^{-1}$, a 3rd law $\Delta_r H°(298.15\ K)$ of 11.76 $kcal \cdot mol^{-1}$, and a 3rd law drift of 3.1 ± 3.8 $cal\ K^{-1} \cdot mol^{-1}$. The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of $TiF_2(g)$ is calculated from the 3rd law $\Delta_r H°(298.15\ K)$, above, and the JANAF enthalpies of formation of $TiF_3(g)$, CaF(g) and Ca(g).

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2$, $TiCl_4$, and TiF_4. The vibrational frequencies are estimated from a valence force field model.

The electronic levels are assumed to be the same as $TiCl_2(g)$. The levels of $TiCl_2(g)$ are estimated by assuming they correspond to the inverted states of $NiCl_2(g)$.[2] The linear configuration is assumed because experimental evidence[3] indicates that other transition metal difluorides, viz those of Mn, Co, Ni, Cu, and Zn, are linear.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.013	−686.627	−686.627	INFINITE
100	34.469	208.036	297.829	−8.979	−687.060	−690.000	360.419
200	46.288	235.823	260.331	−4.902	−687.828	−692.617	180.893
250	50.179	246.593	256.532	−2.485	−688.077	−693.784	144.958
298.15	52.878	255.675	255.675	.000	−688.268	−694.865	121.737
300	52.965	256.002	255.676	.098	−688.275	−694.906	120.994
350	54.966	264.326	256.329	2.799	−688.450	−695.997	103.872
400	56.425	271.765	257.802	5.586	−688.620	−697.064	91.027
450	57.510	278.477	259.732	8.435	−688.795	−698.109	81.034
500	58.333	284.581	261.917	11.332	−688.979	−699.134	73.038
600	59.470	295.325	266.614	17.227	−689.383	−701.128	61.039
700	60.194	304.551	271.390	23.213	−689.837	−703.050	52.462
800	60.686	312.622	276.050	29.258	−690.326	−704.904	46.026
900	61.046	319.792	280.519	35.345	−690.884	−706.694	41.015
1000	61.336	326.239	284.774	41.465	−691.576	−708.415	37.004
1100	61.597	332.098	288.814	47.612	−692.464	−710.058	33.718
1200	61.857	337.468	292.648	53.784	−697.532	−711.491	30.970
1300	62.134	342.430	296.289	59.984	−698.082	−712.633	28.634
1400	62.437	347.046	299.752	66.212	−698.703	−713.729	26.630
1500	62.770	351.365	303.050	72.472	−699.404	−714.778	24.891
1600	63.132	355.427	306.198	78.767	−700.192	−715.778	23.368
1700	63.518	359.266	309.208	85.099	−701.078	−716.726	22.022
1800	63.924	362.908	312.091	91.471	−702.069	−717.618	20.825
1900	64.341	366.375	314.857	97.885	−703.176	−718.452	19.752
2000	64.764	369.686	317.517	104.340	−719.094	−718.771	18.772
2100	65.185	372.857	320.077	110.837	−721.207	−718.703	17.877
2200	65.599	375.899	322.546	117.377	−723.281	−718.535	17.060
2300	66.002	378.823	324.929	123.957	−725.313	−718.274	16.313
2400	66.391	381.641	327.234	130.577	−727.300	−717.925	15.625
2500	66.762	384.359	329.465	137.234	−729.241	−717.494	14.991
2600	67.113	386.984	331.627	143.928	−731.133	−716.987	14.404
2700	67.445	389.523	333.724	150.656	−732.975	−716.408	13.860
2800	67.758	391.982	335.761	157.417	−734.766	−715.761	13.353
2900	68.051	394.364	337.741	164.207	−736.505	−715.051	12.879
3000	68.325	396.676	339.667	171.026	−738.191	−714.283	12.437
3100	68.582	398.921	341.543	177.872	−739.824	−713.459	12.022
3200	68.823	401.102	343.370	184.742	−741.403	−712.583	11.632
3300	69.050	403.223	345.152	191.636	−742.929	−711.659	11.265
3400	69.263	405.288	346.890	198.552	−744.401	−710.689	10.918
3500	69.465	407.299	348.588	205.488	−745.820	−709.676	10.591
3600	69.656	409.258	350.246	212.444	−747.186	−708.624	10.282
3700	69.838	411.169	351.867	219.419	−1157.598	−699.746	9.879
3800	70.012	413.034	353.452	226.412	−1157.626	−687.372	9.449
3900	70.179	414.855	355.003	233.421	−1157.657	−674.996	9.041
4000	70.339	416.634	356.522	240.447	−1157.692	−662.620	8.653
4100	70.494	418.372	358.009	247.489	−1157.730	−650.243	8.284
4200	70.643	420.073	359.467	254.546	−1157.771	−637.864	7.933
4300	70.788	421.737	360.896	261.618	−1157.812	−625.486	7.598
4400	70.928	423.366	362.297	268.703	−1157.854	−613.105	7.278
4500	71.063	424.961	363.672	275.803	−1157.896	−600.724	6.973
4600	71.195	426.525	365.021	282.916	−1157.937	−588.342	6.681
4700	71.322	428.057	366.346	290.042	−1157.975	−575.959	6.401
4800	71.445	429.560	367.648	297.180	−1158.011	−563.575	6.133
4900	71.564	431.034	368.926	304.331	−1158.043	−551.191	5.876
5000	71.678	432.481	370.183	311.493	−1158.071	−538.806	5.629
5100	71.788	433.902	371.418	318.666	−1158.093	−526.420	5.392
5200	71.893	435.297	372.633	325.850	−1158.109	−514.034	5.164
5300	71.994	436.667	373.829	333.044	−1158.118	−501.648	4.944
5400	72.089	438.014	375.005	340.249	−1158.119	−489.262	4.733
5500	72.180	439.337	376.163	347.462	−1158.112	−476.876	4.529
5600	72.266	440.639	377.302	354.685	−1158.097	−464.490	4.333
5700	72.346	441.919	378.425	361.915	−1158.072	−452.104	4.143
5800	72.421	443.178	379.530	369.154	−1158.037	−439.719	3.960
5900	72.490	444.416	380.620	376.399	−1157.992	−427.335	3.783
6000	72.554	445.635	381.693	383.651	−1157.936	−414.951	3.612

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [75.312 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [1175 \pm 150]\ K$

$\Delta_f H°(298.15\ K) = [-962.320 \pm 63]\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [38 \pm 8]\ kJ \cdot mol^{-1}$
$\Delta_{sub} H°(298.15\ K) = [404.174]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(ZrF_2, cr, 298.15\ K)$ value is taken from NBS[1] which was estimated by Brewer.[2] More recent thermal data related to the enthalpy of formation of ZrF_2(cr) is unavailable.

Heat Capacity and Entropy

The heat capacities in the temperature range 298–2000 K are estimated by comparison with those of ZrF_4(cr) and Zr(cr). The $S°(298.15\ K)$ is calculated as 17.2 and 17.0 cal $K^{-1} \cdot mol^{-1}$ based on the assumptions that $S(ZrF_2) = 1/2[S(ZrF_4) + S(Zr)]$ and $S(ZrF_2) = S(ZnF_2) - S(Zn) + S(Zr)$. Using the additive entropy constants $S°(298.15\ K) = 12.1$ and 4.7 cal $K^{-1} \cdot mol^{-1}$ for Zr and F suggested by Kubaschewski and Evans[3] we obtain $S°(ZrF_2, cr, 298.15\ K) = 12.1 + 2\ (4.7) = 21.5$ cal $K^{-1} \cdot mol^{-1}$. Based on $S°(298.15\ K) = 11.5$ and 3.9 cal $K^{-1} \cdot mol^{-1}$ for Zr^{4+} and F^- recommended by Kelley,[4] the value $S°(ZrF_2, cr, 298.15\ K)$ is derived as 19.3 cal $K^{-1} \cdot mol^{-1}$. The entropy at 298 K for ZrF_2(cr) is tentatively adopted as 18 ± 2 cal $K^{-1} \cdot mol^{-1}$.

Sublimation Data

The difference between $\Delta_f H°(298.15\ K)$ for ZrF(g) and ZrF_2(cr) is $\Delta_{sub} H°(298.15\ K)$.

References

[1]U. S. Nat. Bur. Stand. Circ. 500, (1952).
[2]L. Brewer, University of California, Berkeley, California, unpublished data.
[3]O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[4]K. K. Kelley, U.S. Bur. Mines, personal communication, June, (1960).
[5]R. A. McDonald, G. C. Sinke, and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K; Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	65.940	75.312	75.312	0.	−962.320	−912.724	159.905
300	66.024	75.720	75.313	0.122	−962.303	−912.416	158.866
400	69.873	95.253	77.950	6.921	−961.282	−895.937	116.997
500	73.220	111.212	83.054	14.079	−960.115	−879.733	91.905
600	76.149	124.827	88.908	21.551	−958.807	−863.777	75.198
700	78.659	136.761	94.909	29.296	−957.380	−848.050	63.282
800	80.626	147.395	100.817	37.262	−955.874	−832.533	54.359
900	82.425	156.997	106.535	45.416	−954.322	−817.209	47.430
1000	84.015	165.766	112.026	53.741	−952.743	−802.058	41.895
1100	85.270	173.834	117.283	62.206	−951.168	−787.066	37.375
1175.000	86.107	179.486	121.074	68.633	--- CRYSTAL <--> LIQUID ---		
1200	86.400	181.302	122.310	70.790	−953.333	−771.995	33.604
1300	87.404	188.258	127.119	79.481	−951.279	−756.966	30.415
1400	88.282	194.770	131.721	88.268	−949.193	−742.097	27.688
1500	88.826	200.879	136.130	97.124	−947.112	−727.377	25.330
1600	89.328	206.629	140.358	106.033	−945.058	−712.796	23.270
1700	89.621	212.053	144.418	114.981	−943.056	−698.341	21.457
1800	89.914	217.185	148.319	123.960	−941.123	−684.002	19.849
1900	89.956	222.048	152.073	132.954	−939.282	−669.768	18.413
2000	89.956	226.663	155.688	141.950	−937.554	−655.628	17.123

PREVIOUS: June 1961 CURRENT: June 1969

$S°(298.15\ K) = [100.846]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1175 \pm 150]\ K$

$\Delta_f H°(298.15\ K) = [-936.951]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [38 \pm 8]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrF_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(ZrF_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1175\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is estimated from those of $ZrF_4(l)$, $CaF_2(l)$, Zr(l) and Ca(l) and is assumed to be constant in the temperature range 800–3000 KA glass transition temperature is assumed at 800 K. The $C_p°$ values below 800 K are adopted from the ZrF_2(cr) table. The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Both T_{fus} and $\Delta_{fus}H°$ are estimated. The derived entorpy of melting, 2.55 cal $K^{-1}·mol^{-1}$/atom, is the same as that of ZrF_4(cr) which was obtained from experimental measurements.[1] Therefore these estimated values are tentatively adopted.

Vaporization Data

The boiling point, T_{vap}, is calculated as the temperature at which the fugacity is one atmosphere for the process $ZrF_2(l) = ZrF_2(g)$.

Reference

[1]R. A. McDonald, G. C. Sinke and D. R. Stull, J. Chem. Eng. Data 7, 83 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	65.940	100.846	100.846	0.	−936.951	−894.968	156.795
300	66.024	101.254	100.847	0.122	−936.934	−894.708	155.782
400	69.873	120.787	103.484	6.921	−935.914	−880.782	115.018
500	73.220	136.746	108.588	14.079	−934.746	−867.131	90.589
600	76.149	150.361	114.442	21.551	−933.439	−853.729	74.324
700	78.659	162.295	120.443	29.296	−932.012	−840.555	62.723
800	80.626	172.933	126.351	37.265	−930.502	−827.592	54.036
800.000	80.626	172.933	126.351	37.265	____ GLASS <--> LIQUID ____		
800.000	100.416	172.933	126.351	37.265	TRANSITION		
900	100.416	184.760	132.197	47.306	−927.063	−814.936	47.298
1000	100.416	195.340	137.992	57.348	−923.767	−802.656	41.926
1100	100.416	204.910	143.647	67.390	−920.616	−790.698	37.547
1175.000	100.416	211.534	147.771	74.921	--- CRYSTAL <--> LIQUID ---		
1200	100.416	213.648	149.122	77.431	−921.322	−778.800	33.900
1300	100.416	221.685	154.398	87.473	−917.919	−767.061	30.821
1400	100.416	229.127	159.474	97.514	−914.578	−755.583	28.191
1500	100.416	236.055	164.351	107.556	−911.311	−744.340	25.920
1600	100.416	242.536	169.037	117.598	−908.125	−733.313	23.940
1700	100.416	248.623	173.541	127.639	−905.029	−722.483	22.199
1800	100.416	254.363	177.874	137.681	−902.033	−711.832	20.657
1900	100.416	259.792	182.043	147.722	−899.144	−701.344	19.281
2000	100.416	264.943	186.061	157.764	−896.371	−691.006	18.047
2100	100.416	269.842	189.935	167.806	−893.719	−680.804	16.934
2200	100.416	274.513	193.674	177.847	−912.521	−669.979	15.907
2300	100.416	278.977	197.286	187.889	−910.551	−658.998	14.966
2400	100.416	283.251	200.780	197.930	−908.577	−648.103	14.106
2500	100.416	287.350	204.161	207.972	−906.594	−637.291	13.315
2600	100.416	291.288	207.437	218.014	−904.599	−626.558	12.588
2700	100.416	295.078	210.613	228.055	−902.587	−615.902	11.915
2800	100.416	298.730	213.695	238.097	−900.557	−605.321	11.292
2900	100.416	302.254	216.689	248.138	−898.505	−594.813	10.714
3000	100.416	305.658	219.598	258.180	−896.429	−584.377	10.175

PREVIOUS: June 1961 CURRENT: June 1969

0	to	1175	K crystal
above		1175	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0							
100							
200							
298.15	65.940	75.312	75.312	0.	−962.320	−912.724	159.905
300	66.024	75.720	75.313	0.122	−962.303	−912.416	158.866
400	69.873	95.253	77.950	6.921	−961.282	−895.937	116.997
500	73.220	111.212	83.054	14.079	−960.115	−879.733	91.905
600	76.149	124.827	88.908	21.551	−958.807	−863.777	75.198
700	78.659	136.761	94.909	29.296	−957.380	−848.050	63.282
800	80.626	147.395	100.817	37.262	−955.874	−832.533	54.359
900	82.425	156.997	106.535	45.416	−954.322	−817.209	47.430
1000	84.015	165.766	112.026	53.741	−952.743	−802.058	41.895
1100	85.270	173.834	117.283	62.206	−951.168	−787.066	37.375
1175.000	86.107	179.486	121.074	68.633	____ CRYSTAL <-- --> LIQUID ____		
1175.000	100.416	211.534	121.074	106.289	TRANSITION		
1200	100.416	213.648	122.981	108.800	−915.322	−772.800	33.639
1300	100.416	221.685	130.269	118.841	−911.919	−761.061	30.580
1400	100.416	229.127	137.068	128.883	−908.578	−749.583	27.967
1500	100.416	236.055	143.438	138.925	−905.311	−738.340	25.711
1600	100.416	242.536	149.432	148.966	−902.125	−727.313	23.744
1700	100.416	248.623	155.089	159.008	−899.029	−716.483	22.015
1800	100.416	254.363	160.447	169.049	−896.033	−705.832	20.483
1900	100.416	259.792	165.534	179.091	−893.144	−695.344	19.116
2000	100.416	264.943	170.376	189.133	−890.371	−685.006	17.891
2100	100.416	269.842	174.997	199.174	−887.719	−674.803	16.785
2200	100.416	274.513	179.415	209.216	−906.521	−663.979	15.765
2300	100.416	278.977	183.648	219.257	−904.551	−652.998	14.830
2400	100.416	283.251	187.709	229.299	−902.577	−642.103	13.975
2500	100.416	287.350	191.614	239.341	−900.594	−631.291	13.190
2600	100.416	291.288	195.372	249.382	−898.599	−620.558	12.467
2700	100.416	295.078	198.995	259.424	−896.587	−609.902	11.799
2800	100.416	298.730	202.492	269.465	−894.557	−599.321	11.180
2900	100.416	302.254	205.872	279.507	−892.505	−588.813	10.606
3000	100.416	305.658	209.142	289.549	−890.429	−578.377	10.070

PREVIOUS: CURRENT: June 1969

$S°(298.15\ K) = [283.434 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -555.653 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -558.146 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[560](1)
[300](1)
[670](1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: C_{2v}
Bond Distance: Zr–F = [1.92] Å
Bond Angle: F–Zr–F = [125]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.396810 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

Murad and Hildenbrand[1] studied the gaseous equilibria involving ZrF_4, ZrF_3, ZrF_2, Ca, and CaF, mass-spectrometrically. Ion intensities were measured 3 cal $K^{-1}·mol^{-1}$ above threshold over the temperature range 1665–1747 K, and the equilibrium constants for the reaction 2 Ca(g) + ZrF_4(g) = 2 CaF(g) + ZrF_2(g) were calculated. Using the reported equilibrium constants, the enthalpy changes $\Delta_r H°(298.15\ K)$ of this reaction are evaluated by the 2nd and 3rd law methods to be 15.4 and 50.9 kcal·mol^{-1}, respectively. The drift in 3rd law values is 20.4 ± 17.6 cal $K^{-1}·mol^{-1}$. Based on the 3rd law $\Delta_r H°(298.15\ K)$ value and $\Delta_f H°(298.15\ K) = 42.85 \pm 0.3$, -65.0 ± 2, and -400.0 ± 0.5 kcal·mol^{-1} for Ca(g), CaF(g), and ZrF_4, respectively, we obtain $\Delta_f H°(ZrF_2, g, 298.15\ K) = -133.4 \pm 5$ kcal·mol^{-1}(-558.146 ± 20.9 kJ·mol^{-1}) which is adopted.

Using Gibbs energy functions derived from different molecular constants for the reactants and products, Murad and Hildenbrand[1] derived a 3rd law $\Delta_r H°(298.15\ K) = 42.6 \pm 5$ and $\Delta_f H°(ZrF_2, g, 298.15\ K) = -141 \pm 5$ kcal·mol^{-1}, which are in fair agreement with the adopted values.

Heat Capacity and Entropy

According to the correlations of Charkin and Dyatkina,[2] the ZrF_2(g) molecule has an angular configuration. The F–Zr–F angle is estimated at 125°, which is similar to the value reported by Hastie *et al.*[4] for TiF_2(g). The F–Zr bond distance is estimated from that of ZrF_4(g). The vibrational frequencies are calculated based on the method suggested by Herzberg.[3] The value ν_1 is calculated from the vibrational frequency (ν) of ZrF(g) by use of the relation $\nu_1 = \nu[Zr/(Zr+F)]^{1/2}$ where Zr and F are gram atomic weights of zirconium and fluorine. ν_3 is derived from ν_1 using the formula $\nu_3 = \nu_1[(Zr_1+2F)/Zr]^{1/2}$ and ν_2 is calculated as 0.44 ν_3 where the value 0.44 is estimated by comparison with the ratios of ν_2/ν_3 or other related compounds. Ground state quantum weight is taken to be the same as that of TiF_2(g). The three principal moments of inertia are: $I_A = 3.5010 \times 10^{-39}$, $I_B = 18.3005 \times 10^{-39}$, and $I_C = 21.8015 \times 10^{-39}$ g·cm^2. The electronic levels and quantum weights are estimated to be the same as those of TiF_2(g).

References

[1] E. Murad and D. L. Hildenbrand, J. Chem. Phys. **45**, 4751 (1966).
[2] O. P. Charkin and M. E. Dyatkina, Russ. J. Struct. Chem. **6**, 550 (1965).
[3] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, (1945).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.829	−555.653	−555.653	INFINITE
100	35.603	238.172	322.695	−8.452	−556.069	−561.444	293.268
200	43.051	265.112	287.723	−4.522	−557.261	−566.343	147.914
250	46.243	275.074	284.222	−2.287	−557.744	−568.556	118.793
298.15	48.652	283.434	283.434	0.	−558.146	−570.601	99.967
300	48.732	283.735	283.435	0.090	−558.160	−570.678	99.364
350	50.617	291.396	284.036	2.576	−558.534	−572.735	85.476
400	52.039	298.252	285.392	5.144	−558.885	−574.739	75.053
450	53.121	304.447	287.170	7.774	−559.226	−576.700	66.942
500	53.956	310.089	289.184	10.452	−559.567	−578.624	60.448
600	55.128	320.038	293.520	15.911	−560.273	−582.369	50.700
700	55.886	328.597	297.934	21.464	−561.038	−585.992	43.727
800	56.405	336.095	302.245	27.080	−561.881	−589.501	38.490
900	56.787	342.762	306.383	32.741	−562.823	−592.898	34.411
1000	57.094	348.761	310.326	38.435	−563.874	−596.184	31.141
1100	57.368	354.216	314.072	44.158	−565.042	−599.360	28.461
1200	57.638	359.219	317.628	49.908	−570.039	−602.202	26.213
1300	57.923	363.844	321.008	55.686	−570.899	−604.848	24.303
1400	58.233	368.147	324.223	61.494	−571.793	−607.426	22.663
1500	58.572	372.176	327.287	67.334	−572.727	−609.939	21.240
1600	58.938	375.968	330.212	73.209	−573.707	−612.388	19.992
1700	59.329	379.553	333.010	79.123	−574.740	−614.774	18.890
1800	59.738	382.955	335.691	85.076	−575.833	−617.097	17.908
1900	60.158	386.197	338.265	91.070	−576.991	−619.359	17.027
2000	60.583	389.293	340.739	97.107	−578.221	−621.557	16.233
2100	61.006	392.259	343.122	103.187	−579.532	−623.692	15.513
2200	61.423	395.107	345.421	109.308	−602.253	−625.017	14.840
2300	61.827	397.846	347.641	115.471	−604.163	−626.009	14.217
2400	62.217	400.486	349.788	121.673	−606.028	−626.918	13.645
2500	62.589	403.033	351.868	127.914	−607.846	−627.751	13.116
2600	62.942	405.495	353.883	134.191	−609.616	−628.512	12.627
2700	63.275	407.877	355.839	140.502	−611.335	−629.206	12.173
2800	63.588	410.184	357.739	146.845	−613.003	−629.838	11.750
2900	63.882	412.420	359.586	153.219	−614.619	−630.410	11.355
3000	64.157	414.591	361.384	159.621	−616.183	−630.928	10.985
3100	64.415	416.698	363.134	166.050	−617.692	−631.394	10.639
3200	64.657	418.747	364.840	172.503	−619.149	−631.813	10.313
3300	64.884	420.741	366.504	178.980	−620.551	−632.187	10.007
3400	65.098	422.681	368.128	185.480	−621.900	−632.519	9.717
3500	65.300	424.571	369.714	192.000	−623.196	−632.812	9.444
3600	65.492	426.413	371.263	198.539	−624.439	−633.069	9.186
3700	65.674	428.210	372.778	205.098	−625.629	−633.293	8.940
3800	65.848	429.964	374.260	211.674	−626.768	−633.485	8.708
3900	66.016	431.676	375.710	218.267	−627.855	−633.647	8.487
4000	66.176	433.350	377.130	224.877	−628.891	−633.782	8.276
4100	66.331	434.986	378.522	231.502	−629.878	−633.892	8.076
4200	66.481	436.586	379.885	238.143	−630.816	−633.978	7.885
4300	66.625	438.152	381.222	244.798	−631.707	−634.043	7.702
4400	66.765	439.685	382.533	251.468	−632.550	−634.088	7.528
4500	66.901	441.187	383.820	258.151	−633.347	−634.113	7.361
4600	67.033	442.659	385.083	264.848	−634.099	−634.122	7.201
4700	67.160	444.102	386.324	271.557	−634.808	−634.115	7.047
4800	67.283	445.517	387.542	278.280	−1196.410	−622.476	6.774
4900	67.402	446.906	388.740	285.014	−1196.686	−610.516	6.508
5000	67.517	448.269	389.917	291.760	−1196.939	−598.551	6.253
5100	67.627	449.607	391.074	298.517	−1197.169	−586.581	6.008
5200	67.732	450.921	392.212	305.285	−1197.375	−574.606	5.772
5300	67.833	452.212	393.332	312.064	−1197.557	−562.628	5.545
5400	67.929	453.481	394.434	318.852	−1197.715	−550.647	5.326
5500	68.020	454.728	395.519	325.649	−1197.850	−538.663	5.116
5600	68.105	455.955	396.588	332.455	−1197.960	−526.677	4.913
5700	68.186	457.161	397.640	339.270	−1198.047	−514.689	4.717
5800	68.261	458.347	398.676	346.092	−1198.110	−502.700	4.527
5900	68.330	459.515	399.698	352.922	−1198.150	−490.709	4.344
6000	68.394	460.664	400.704	359.758	−1198.165	−478.719	4.168

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K)$ = [98.324 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K)$ = −1041.816 ± 12.6 $kJ·mol^{-1}$

Enthalpy of Formation

The equilibrium pressures for the reaction 2 FeF_3(cr) + H_2(g) = 2 FeF_2(cr) + 2 HF(g) have been measured at temperatures 623, 723, and 823 K by Jellinek and Rudat.[1] Using the reported data, the enthalpy change of the reaction was evaluated as 37.9 and 31.3 $kcal·mol^{-1}$ by the 3rd and 2nd law, respectively. The corresponding $\Delta_f H°$(FeF_3, cr, 298.15 K) values are calculated to be −252.4 and −249.2 $kcal·mol^{-1}$. The equilibrium constants for the reaction 2 FeF_3(cr) + 3 H_2O(g) = Fe_2O_3(cr) + 6 HF(g) were determined by Domange.[2] Based on the 3rd law value of $\Delta_r H°$(298.15 K), 62.0 $kcal·mol^{-1}$, the $\Delta_f H°$(FeF_3, cr, 298.15 K) was calculated as −237.4 $kcal·mol^{-1}$. The value of $\Delta_f H°$(298.15 K) for FeF_3(cr) is selected to be −249 ± 3 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The heat capacities of FeF_3(cr) at temperatures 100–450 K were determined by Bizette *et al.*[3] The results were presented graphically by plotting $C_p°$ vs T. The $C_p°$ curve shows a peak at 367 K. An antiferromagnetic transition at about 394 K was reported by Wollan *et al.*[4] The heat capacities above 450 K and $S°$(298.15 K) were estimated by comparison with those for $FeCl_3$(cr), $AlCl_3$(cr) and AlF_3(cr).

Sublimation Data

The phenomenon that FeF_3(cr) sublimes without fusion at temperatures near 1000°C has been observed and reported by Poulenc.[5] Based on this data, the value of T_{sub} was estimated. The value of heat of sublimation, $\Delta_{sub}H°$(298.15 K), is calculated using an estimated entropy of sublimation, $\Delta_{sub}S°$ = 40 cal $K^{-1}·mol^{-1}$ in order to have $\Delta_r G°$(1200 K) = 0 for the reaction FeF_3(cr) = FeF_3(g).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.002	98.324	98.324	0.	−1041.816	−972.293	170.342
300	91.630	98.889	98.326	0.169	−1041.780	−971.862	169.216
367.000	113.047	119.010	100.268	6.878	____ C_p LAMBDA MAXIMUM ____		
367.000	113.408	119.021	100.268	6.882	TRANSITION		
400	96.371	127.516	102.176	10.136	−1039.270	−948.929	123.917
500	95.667	148.882	109.462	19.710	−1037.598	−926.547	96.796
600	96.818	166.429	117.536	29.336	−1036.268	−904.466	78.741
700	98.073	181.448	125.619	39.080	−1035.177	−882.588	65.860
800	99.328	194.626	133.438	48.950	−1034.335	−860.851	56.208
900	100.583	206.397	140.902	58.946	−1033.850	−839.199	48.706
1000	101.839	217.060	147.993	69.067	−1034.011	−817.571	42.706
1100	103.094	226.825	154.722	79.314	−1034.986	−795.865	37.792
1200	104.349	235.849	161.111	89.686	−1035.323	−774.130	33.697
1300	105.604	244.251	167.187	100.183	−1033.923	−752.421	30.233
1400	106.859	252.123	172.976	110.807	−1032.513	−730.820	27.267
1500	108.115	259.539	178.502	121.555	−1031.091	−709.320	24.701
1600	109.370	266.556	183.788	132.429	−1029.654	−687.915	22.458
1700	110.625	273.224	188.854	143.429	−1029.151	−666.582	20.482
1800	111.880	279.583	193.719	154.554	−1028.012	−645.288	18.726
1900	113.135	285.666	198.400	165.805	−1040.947	−623.355	17.137
2000	114.391	291.501	202.910	177.182	−1039.994	−601.400	15.707

PREVIOUS: CURRENT: September 1965

$S°(298.15\ K)$ = [304.236] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−817.965 ± 20.9] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−820.901 ± 20.9] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[600](1)	[800](2)
[250](1)	[220](2)

Ground State Quantum Weight: [1] σ = [6]
Point Group: [D_{3h}]
Bond Distance: Fe–F = [1.9] Å
Bond Angle: F–Fe–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [9.971132 × 10^{-114}] $g^3·cm^6$

Enthalpy of Formation

The value of $\Delta_f H°(FeF_3, g, 298.15\ K)$ is calculated from $\Delta_{sub}H°(298.15\ K)$ and $\Delta_f H°(298.15\ K)$ for FeF_3(cr). The value $\Delta_{sub}H°(298.15\ K)$ = 65.5 $kcal·mol^{-1}$ is derived from $\Delta_{sub}H°(1200\ K)$. Refer to the crystal table for details.

Heat Capacity and Entropy

The molecular structure, bond distance and angle are estimated by comparison with those for AlF_3(g). The vibrational frequencies are estimated by comparison with those for AlF_3(g), TiF_3(g) and ZrF_3(g). The three principal moments of inertia are: $I_A = I_B$ = 17.0833 × 10^{-39} and I_C = 34.1666 × 10^{-39} $g·cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.808	−817.965	−817.965	INFINITE
100	44.171	244.781	356.426	−11.164	−819.104	−817.420	426.977
200	57.084	279.760	309.982	−6.044	−820.147	−815.313	212.938
250	61.796	293.020	305.295	−3.069	−820.563	−814.055	170.088
298.15	65.546	304.236	304.236	0.	−820.901	−812.771	142.394
300	65.676	304.642	304.238	0.121	−820.913	−812.720	141.507
350	68.783	315.009	305.049	3.486	−821.218	−811.330	121.084
400	71.241	324.360	306.888	6.989	−821.502	−809.898	105.762
450	73.180	332.868	309.309	10.601	−821.788	−808.431	93.840
500	74.717	340.661	312.060	14.300	−822.092	−806.930	84.299
600	76.939	354.494	318.009	21.891	−822.797	−803.834	69.980
700	78.415	366.472	324.096	29.663	−823.678	−800.607	59.742
800	79.434	377.014	330.065	37.559	−824.812	−797.237	52.054
900	80.162	386.414	335.813	45.541	−826.340	−793.704	46.065
1000	80.699	394.889	341.304	53.585	−828.578	−789.968	41.264
1100	81.105	402.600	346.531	61.676	−831.709	−785.941	37.321
1200	81.418	409.672	351.503	69.803	−834.291	−781.685	34.026
1300	81.665	416.199	356.231	77.957	−835.234	−777.264	31.231
1400	81.863	422.258	360.734	86.134	−836.270	−772.766	28.832
1500	82.025	427.912	365.026	94.329	−837.402	−768.191	26.751
1600	82.157	433.210	369.124	102.538	−838.630	−763.538	24.927
1700	82.268	438.194	373.041	110.760	−840.905	−758.785	23.315
1800	82.361	442.899	376.793	118.991	−842.660	−753.905	21.878
1900	82.440	447.354	380.390	127.231	−858.605	−748.222	20.570
2000	82.508	451.585	383.845	135.479	−860.782	−742.356	19.388
2100	82.566	455.612	387.168	143.733	−862.961	−736.381	18.316
2200	82.617	459.454	390.367	151.992	−865.139	−730.303	17.340
2300	82.661	463.127	393.451	160.256	−867.309	−724.125	16.445
2400	82.700	466.646	396.428	168.524	−869.469	−717.853	15.624
2500	82.735	470.023	399.305	176.796	−871.611	−711.492	14.866
2600	82.765	473.268	402.087	185.071	−873.732	−705.045	14.165
2700	82.793	476.393	404.782	193.349	−875.826	−698.517	13.514
2800	82.817	479.404	407.394	201.629	−877.889	−691.912	12.908
2900	82.839	482.311	409.927	209.912	−879.917	−685.234	12.342
3000	82.859	485.119	412.387	218.197	−881.907	−678.487	11.814
3100	82.877	487.837	414.777	226.484	−883.854	−671.675	11.318
3200	82.893	490.468	417.102	234.772	−1234.057	−657.376	10.731
3300	82.908	493.019	419.364	243.062	−1234.012	−639.355	10.120
3400	82.922	495.494	421.567	251.354	−1233.952	−621.336	9.546
3500	82.934	497.898	423.713	259.647	−1233.874	−603.319	9.004
3600	82.946	500.235	425.807	267.941	−1233.780	−585.304	8.493
3700	82.956	502.507	427.849	276.236	−1233.669	−567.292	8.009
3800	82.966	504.720	429.843	284.532	−1233.541	−549.284	7.550
3900	82.975	506.875	431.791	292.829	−1233.397	−531.279	7.116
4000	82.983	508.976	433.694	301.127	−1233.239	−513.278	6.703
4100	82.991	511.025	435.555	309.426	−1233.068	−495.281	6.310
4200	82.998	513.025	437.376	317.725	−1232.884	−477.288	5.936
4300	83.005	514.978	439.158	326.025	−1232.691	−459.301	5.579
4400	83.011	516.886	440.903	334.326	−1232.489	−441.317	5.239
4500	83.017	518.752	442.613	342.627	−1232.281	−423.338	4.914
4600	83.022	520.577	444.288	350.929	−1232.069	−405.364	4.603
4700	83.028	522.362	445.930	359.232	−1231.854	−387.394	4.305
4800	83.032	524.110	447.541	367.535	−1231.640	−369.429	4.020
4900	83.037	525.822	449.121	375.838	−1231.428	−351.469	3.747
5000	83.041	527.500	450.672	384.142	−1231.221	−333.512	3.484
5100	83.045	529.145	452.194	392.447	−1231.021	−315.560	3.232
5200	83.049	530.757	453.690	400.751	−1230.831	−297.612	2.990
5300	83.052	532.339	455.159	409.056	−1230.654	−279.667	2.756
5400	83.056	533.892	456.602	417.362	−1230.492	−261.725	2.532
5500	83.059	535.416	458.021	425.668	−1230.348	−243.787	2.315
5600	83.062	536.912	459.417	433.974	−1230.225	−225.850	2.107
5700	83.065	538.382	460.789	442.280	−1230.127	−207.916	1.905
5800	83.068	539.827	462.140	450.587	−1230.057	−189.984	1.711
5900	83.070	541.247	463.469	458.893	−1230.018	−172.051	1.523
6000	83.073	542.643	464.776	467.201	−1230.014	−154.120	1.342

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 277.268 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1193.663 \pm 20.9]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-1200.808 \pm 20.9]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2316(1)	998(2)
858(1)	844(2)
425(1)	306(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.4468 Å; Si–F = 1.5624 Å
Bond Angles: H–Si–F = 110.64°; F–Si–F = 108.28°
Product of the Moments of Inertia: $I_A I_B I_C = 2.726959 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

There are no reported experimental studies leading to the enthalpy of formation of $SiHF_3(g)$. We estimate this value via a linear interpolation between the established $\Delta_f H°(298.15\ K)$ values of $SiH_4(g)$ and $SiF_4(g)$.[1] The reasonableness of this approach has been demonstrated by Lapidus *et al.*,[2] Hunt and Sirtl,[3] and Seiter and Sirtl.[4] Lapidus *et al.*[2] comparatively examined the thermodynamic properties of halogenated silanes and methanes. Hunt and Sirtl[3] and Seiter and Sirtl[4] studied the chlorinated silanes and proposed a linear $\Delta_f H°$ relationship within the sequence $SiH_4(g)$ to $SiCl_4(g)$.

Heat Capacity and Entropy

The adopted vibrational frequencies are from the infrared gas phase studies of Buerger *et al.*[5,6] These values are all within $\pm 1\ cm^{-1}$ of the suggested values in the compilation by Shimanouchi,[7] as derived from Newman *et al.*[8]

The adopted bond angles and bond distances are obtained from the microwave spectrum study of six isotopic species of $HSiF_3$.[9] Earlier work by Sheridan and Gordy[11] and Heath *et al.*[11] is in good agreement with these values. The moments of inertia are calculated to be $I_A = I_B = 11.6094 \times 10^{-39}\ g\ cm^2$ and $I_C = 20.2329 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.544	−1193.663	−1193.663	INFINITE
100	38.013	224.001	325.165	−10.116	−1196.362	−1187.787	620.436
200	51.293	254.467	282.691	−5.645	−1198.809	−1178.233	307.723
250	57.690	266.604	278.281	−2.919	−1199.886	−1172.962	245.077
298.15	63.485	277.268	277.268	0.	−1200.808	−1167.691	204.575
300	63.696	277.662	277.269	0.118	−1200.841	−1167.485	203.277
350	69.048	287.892	278.065	3.439	−1201.662	−1161.859	173.398
400	73.663	297.421	279.896	7.010	−1202.352	−1156.125	150.974
450	77.588	306.330	282.343	10.794	−1202.923	−1150.311	133.525
500	80.918	314.682	285.164	14.759	−1203.391	−1144.439	119.559
600	86.189	329.926	291.379	23.128	−1204.073	−1132.579	98.600
700	90.118	343.521	297.875	31.952	−1204.492	−1120.628	83.622
800	93.123	355.759	304.358	41.121	−1204.724	−1108.629	72.386
900	95.469	366.868	310.696	50.555	−1204.820	−1096.610	63.646
1000	97.332	377.027	316.829	60.198	−1204.824	−1084.586	56.653
1100	98.831	386.377	322.732	70.009	−1204.769	−1072.565	50.932
1200	100.052	395.030	328.401	79.955	−1204.679	−1060.550	46.165
1300	101.057	403.080	333.839	90.012	−1204.577	−1048.543	42.131
1400	101.891	410.600	339.056	100.161	−1204.478	−1036.545	38.674
1500	102.591	417.655	344.064	110.386	−1204.397	−1024.552	35.678
1600	103.183	424.295	348.873	120.676	−1204.343	−1012.565	33.057
1700	103.687	430.566	353.495	131.020	−1254.498	−1000.133	30.730
1800	104.119	436.505	357.944	141.411	−1254.284	−985.176	28.589
1900	104.492	442.145	362.228	151.842	−1254.066	−970.232	26.674
2000	104.816	447.513	366.359	162.307	−1253.847	−955.298	24.950
2100	105.099	452.634	370.346	172.804	−1253.624	−940.377	23.391
2200	105.347	457.529	374.199	183.326	−1253.394	−925.466	21.973
2300	105.567	462.217	377.925	193.872	−1253.156	−910.565	20.680
2400	105.761	466.714	381.531	204.439	−1252.905	−895.675	19.494
2500	105.934	471.035	385.025	215.024	−1252.636	−880.796	18.403
2600	106.089	475.193	388.414	225.625	−1252.347	−865.928	17.397
2700	106.228	479.199	391.702	236.241	−1252.032	−851.072	16.465
2800	106.353	483.065	394.897	246.870	−1251.688	−836.227	15.600
2900	106.466	486.799	398.002	257.511	−1251.312	−821.396	14.795
3000	106.569	490.410	401.022	268.163	−1250.901	−806.578	14.044
3100	106.662	493.906	403.962	278.825	−1250.450	−791.775	13.341
3200	106.747	497.294	406.826	289.495	−1249.960	−776.987	12.683
3300	106.825	500.580	409.618	300.174	−1249.426	−762.214	12.065
3400	106.896	503.770	412.340	310.860	−1248.848	−747.459	11.483
3500	106.961	506.869	414.997	321.553	−1248.225	−732.721	10.935
3600	107.021	509.883	417.591	332.252	−1631.707	−707.541	10.266
3700	107.077	512.816	420.125	342.957	−1630.577	−681.885	9.626
3800	107.128	515.673	422.602	353.667	−1629.402	−656.261	9.021
3900	107.175	518.456	425.025	364.382	−1628.182	−630.667	8.447
4000	107.220	521.170	427.394	375.102	−1626.917	−605.106	7.902
4100	107.261	523.818	429.714	385.826	−1625.606	−579.577	7.384
4200	107.299	526.403	431.986	396.554	−1624.251	−554.080	6.891
4300	107.334	528.928	434.211	407.286	−1622.851	−528.617	6.421
4400	107.368	531.396	436.392	418.021	−1621.408	−503.186	5.974
4500	107.399	533.810	438.530	428.759	−1619.922	−477.788	5.546
4600	107.428	536.170	440.627	439.501	−1618.395	−452.424	5.137
4700	107.455	538.481	442.684	450.245	−1616.826	−427.094	4.747
4800	107.481	540.744	444.704	460.992	−1615.217	−401.797	4.372
4900	107.505	542.960	446.686	471.741	−1613.570	−376.535	4.014
5000	107.528	545.132	448.634	482.492	−1611.885	−351.306	3.670
5100	107.549	547.262	450.547	493.246	−1610.162	−326.112	3.340
5200	107.569	549.350	452.427	504.002	−1608.404	−300.951	3.023
5300	107.589	551.399	454.275	514.760	−1606.611	−275.824	2.718
5400	107.607	553.411	456.092	525.520	−1604.785	−250.732	2.425
5500	107.624	555.385	457.880	536.282	−1602.925	−225.675	2.143
5600	107.640	557.325	459.638	547.045	−1601.034	−200.651	1.872
5700	107.655	559.230	461.369	557.809	−1599.113	−175.661	1.610
5800	107.670	561.102	463.072	568.576	−1597.161	−150.705	1.357
5900	107.684	562.943	464.749	579.343	−1595.181	−125.783	1.114
6000	107.697	564.753	466.401	590.113	−1593.173	−100.896	0.878

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [288.458 \pm 12.6]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -869.289 \pm 12.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -879.100 \pm 12.6\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[202](3)
[962](3)
[552](3)
[3060](3)

Ground State Quantum Weight: 1 σ = [3]
Point Group: C_3
Interatomic Distance: F–F = [2.5] Å
Product of the Moments of Inertia: $I_A I_B I_C = [2.237956 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of 3 HF(g) → H_3F_3(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluted K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta_r H°$ and $\Delta_r S°$. At $n = 3$, their 2nd law values differed by 2.7 $kcal·mol^{-1}$ which was taken as an estimate of error, while the 3rd law values differed by 0.20 $kcal·mol^{-1}$. Using $\Delta_r H°(298.15\ K) = -14.69\ kcal·mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of H_3F_3(g).

Heat Capacity and Entropy

The molecular structure of H_3F_3 was assumed as planar with the F atoms forming the vertices of a regular triangle and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular-orbital studies on HF polymers. The length of side (F-F axis) was taken from Atoji and Lipscomb's[5] X-studies of solid HF (F−F = 2.49 Å) and agrees with 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. Vibrational frequencies were taken from Kittelberger and Hornig's[7] work on crystalline HF. Huong and Couzi[8] and Smith[9] have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table[10] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[10] we recalculate the table in terms of 1973 fundamental constants,[11] 1975 atomic weights,[12] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.127	−869.289	−869.289	INFINITE
100	46.713	223.110	346.863	−12.375	−874.397	−856.043	447.151
200	63.124	260.767	295.010	−6.849	−877.304	−836.438	218.455
250	70.045	275.612	289.675	−3.516	−878.320	−826.100	172.604
298.15	75.849	288.458	288.458	0.	−879.100	−815.968	142.954
300	76.055	288.928	288.460	0.141	−879.127	−815.577	142.005
350	81.120	301.044	289.405	4.074	−879.750	−804.933	120.130
400	85.327	312.160	291.564	8.238	−880.217	−794.212	103.713
450	88.821	322.418	294.430	12.595	−880.552	−783.440	90.939
500	91.760	331.932	297.710	17.111	−880.776	−772.636	80.717
600	96.495	349.099	304.876	26.534	−880.957	−750.986	65.379
700	100.303	364.269	312.298	36.380	−880.846	−729.329	54.423
800	103.575	377.881	319.659	46.577	−880.492	−707.705	46.208
900	106.478	390.251	326.826	57.082	−879.930	−686.139	39.822
1000	109.082	401.607	333.744	67.863	−879.190	−664.645	34.717
1100	111.416	412.115	340.397	78.890	−878.301	−643.232	30.545
1200	113.502	421.900	346.786	90.138	−877.290	−621.906	27.071
1300	115.359	431.060	352.920	101.582	−876.180	−600.668	24.135
1400	117.008	439.671	358.812	113.202	−874.992	−579.519	21.622
1500	118.470	447.794	364.476	124.978	−873.744	−558.457	19.447
1600	119.767	455.482	369.925	136.891	−872.451	−537.480	17.547
1700	120.917	462.778	375.175	148.926	−871.124	−516.585	15.873
1800	121.938	469.719	380.236	161.070	−869.771	−495.769	14.387
1900	122.847	476.337	385.121	173.310	−868.398	−475.028	13.059
2000	123.657	482.659	389.841	185.636	−867.008	−454.360	11.867
2100	124.380	488.710	394.406	198.039	−865.604	−433.763	10.789
2200	125.029	494.512	398.825	210.510	−864.186	−413.232	9.811
2300	125.611	500.082	403.108	223.042	−862.752	−392.766	8.920
2400	126.135	505.440	407.260	235.630	−861.301	−372.363	8.104
2500	126.608	510.598	411.291	248.267	−859.831	−352.020	7.355
2600	127.037	515.573	415.207	260.950	−858.338	−331.737	6.665
2700	127.425	520.374	419.014	273.673	−856.821	−311.512	6.027
2800	127.779	525.015	422.717	286.434	−855.276	−291.344	5.435
2900	128.101	529.505	426.323	299.228	−853.701	−271.231	4.885
3000	128.395	533.853	429.835	312.053	−852.093	−251.173	4.373
3100	128.665	538.067	433.259	324.906	−850.452	−231.170	3.895
3200	128.912	542.156	436.598	337.785	−848.775	−211.220	3.448
3300	129.139	546.126	439.857	350.688	−847.061	−191.322	3.028
3400	129.349	549.985	443.040	363.613	−845.309	−171.478	2.634
3500	129.543	553.737	446.149	376.557	−843.520	−151.685	2.264
3600	129.722	557.389	449.189	389.521	−841.691	−131.944	1.914
3700	129.887	560.945	452.161	402.501	−839.825	−112.254	1.585
3800	130.041	564.411	455.070	415.498	−837.920	−92.616	1.273
3900	130.184	567.791	457.917	428.509	−835.979	−73.027	0.978
4000	130.318	571.089	460.705	441.534	−834.000	−53.490	0.699
4100	130.442	574.308	463.437	454.572	−831.986	−34.002	0.433
4200	130.558	577.453	466.114	467.622	−829.937	−14.563	0.181
4300	130.667	580.526	468.739	480.684	−827.854	4.825	−0.059
4400	130.768	583.531	471.314	493.756	−825.738	24.166	−0.287
4500	130.864	586.471	473.841	506.837	−823.591	43.458	−0.504
4600	130.953	589.349	476.321	519.928	−821.413	62.701	−0.712
4700	131.037	592.166	478.756	533.028	−819.206	81.897	−0.910
4800	131.116	594.925	481.147	546.135	−816.970	101.047	−1.100
4900	131.191	597.630	483.497	559.251	−814.706	120.148	−1.281
5000	131.261	600.281	485.806	572.373	−812.415	139.204	−1.454
5100	131.328	602.881	488.076	585.503	−810.099	158.213	−1.620
5200	131.391	605.432	490.309	598.639	−807.757	177.177	−1.780
5300	131.450	607.935	492.504	611.781	−805.390	196.096	−1.933
5400	131.507	610.392	494.665	624.929	−802.998	214.969	−2.079
5500	131.560	612.806	496.791	638.082	−800.582	233.797	−2.220
5600	131.611	615.177	498.884	651.241	−798.143	252.583	−2.356
5700	131.659	617.507	500.945	664.404	−795.679	271.324	−2.486
5800	131.704	619.797	502.974	677.572	−793.192	290.022	−2.612
5900	131.748	622.049	504.973	690.745	−790.681	308.676	−2.733
6000	131.789	624.263	506.943	703.922	−788.145	327.287	−2.849

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = [318.087 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1510.529 \pm 25.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1517.202 \pm 25.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
280 (1)	530 (2)
[430](1)	755 (2)
[640](1)	245 (2)
[480](1)	[140](2)

Ground State Quantum Weight: [1] $\sigma = 6$
Point Group: [D_{3h}]
Bond Distance: Li–F = [1.68] Å
Bond Angles: F–Li–F = [120]°; Li–F–Li = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.212852 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(Li_3F_3, g, 298.15\ K)$ is derived based on the adopted value $\Delta_r H°(298.15\ K) = 79.73\ kcal \cdot mol^{-1}$ for the reaction $3LiF(cr) = Li_3F_3(g)$, using $\Delta_f H(LiF, cr, 298.15\ K) = -147.45\ kcal \cdot mol^{-1}$. The $\Delta_r H°(298.15\ K)$ value is calculated to be 73.9 $kcal \cdot mol^{-1}$ at 1000 K, which is consistent with the values $\Delta_s H°(1000\ K) = 73.9 \pm 3$ and $74.9 \pm 1\ kcal \cdot mol^{-1}$ reported by Buchler and Stauffer[1] and Akishin *et al.*,[2] respectively. Using the adopted $\Delta_f H°(298.15\ K)$ values for monomer, dimer, and trimer, we also evaluate the value $\Delta_r H°(1073\ K) = 53.8\ kcal \cdot mol^{-1}$ for the reaction $Li_3F_3(g) = Li_2F_2(g) + LiF(g)$ which is in agreement with the value $50 < \Delta_r H°(1073\ K) < 65\ kcal \cdot mol^{-1}$ reported by Porter and Schoonmaker.[3] Rothberg *et al.*[4] have determined the partial pressures of LiF monomer, dimer, and trimer in the temperature range 980–1070 K, using the molecular-beam velocity-selector method.[5] However, the total pressures derived from these data are too low in comparison with the other reported vapor pressures. Thus their data are not adopted for evaluation.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of the BeO trimer. The Li–F bond distance is taken from that of the Li_2F_2 molecule determined by Akishin and Rambidi.[6] Four vibrational frequencies, A_2'' and three E', are reported by Snelson[7] from analysis of the infrared spectra of LiF Using the matrix isolation technique. The reported frequencies are corrected to the average isotopic species. The other four frequencies, E_2'' and three A', are estimated by comparison with those for the isoelectronic molecule Be_3O_3. The three principal moments of inertia are: $I_A = I_B = 18.2358 \times 10^{-39}$ and $I_C = 36.4717 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.431	−1510.529	−1510.529	INFINITE
100	55.829	232.778	396.049	−16.327	−1512.271	−1507.790	787.589
200	84.315	280.714	326.946	−9.247	−1515.108	−1502.160	392.324
250	94.780	300.702	319.734	−4.758	−1516.258	−1498.785	313.154
298.15	102.501	318.087	318.087	0.	−1517.202	−1495.332	261.976
300	102.757	318.722	318.089	0.190	−1517.236	−1495.197	260.337
350	108.755	335.035	319.364	5.485	−1518.113	−1491.453	222.587
400	113.278	349.866	322.264	11.041	−1519.015	−1487.584	194.259
450	116.724	363.416	326.095	16.795	−1520.032	−1483.596	172.211
500	119.386	375.858	330.457	22.700	−1530.203	−1478.565	154.465
600	123.131	397.982	339.914	34.840	−1532.223	−1468.041	127.804
700	125.556	417.157	349.610	47.283	−1533.883	−1457.208	108.738
800	127.203	434.037	359.130	59.926	−1535.343	−1446.154	94.424
900	128.368	449.091	368.304	72.708	−1536.716	−1434.922	83.281
1000	129.220	462.662	377.073	85.589	−1538.028	−1423.541	74.358
1100	129.860	475.009	385.423	98.545	−1539.296	−1412.030	67.052
1200	130.352	486.330	393.367	111.556	−1540.531	−1400.406	60.958
1300	130.739	496.780	400.925	124.612	−1541.746	−1388.680	55.798
1400	131.048	506.481	408.122	137.702	−1542.940	−1376.860	51.371
1500	131.299	515.531	414.985	150.819	−1544.111	−1364.957	47.532
1600	131.506	524.012	421.537	163.960	−1545.262	−1352.975	44.170
1700	131.677	531.989	427.801	177.119	−1982.103	−1319.394	40.540
1800	131.822	539.520	433.801	190.294	−1980.958	−1280.444	37.158
1900	131.944	546.651	439.554	203.483	−1979.823	−1241.558	34.133
2000	132.049	553.421	445.080	216.683	−1978.696	−1202.731	31.412
2100	132.140	559.866	450.394	229.892	−1977.576	−1163.961	28.952
2200	132.218	566.015	455.510	243.110	−1976.463	−1125.243	26.717
2300	132.287	571.894	460.444	256.336	−1975.356	−1086.576	24.677
2400	132.347	577.525	465.206	269.567	−1974.253	−1047.957	22.808
2500	132.400	582.929	469.807	282.805	−1973.154	−1009.384	21.090
2600	132.447	588.123	474.259	296.047	−1972.059	−970.855	19.505
2700	132.490	593.122	478.569	309.294	−1970.968	−932.368	18.038
2800	132.527	597.941	482.747	322.545	−1969.882	−893.921	16.676
2900	132.561	602.593	486.800	335.799	−1968.801	−855.513	15.409
3000	132.592	607.087	490.735	349.057	−1967.728	−817.142	14.228
3100	132.620	611.435	494.559	362.318	−1966.665	−778.807	13.123
3200	132.645	615.646	498.277	375.581	−1965.613	−740.506	12.088
3300	132.668	619.728	501.896	388.847	−1964.575	−702.237	11.115
3400	132.689	623.689	505.420	402.114	−1963.555	−664.000	10.201
3500	132.708	627.536	508.854	415.384	−1962.556	−625.792	9.339
3600	132.726	631.274	512.203	428.656	−1961.582	−587.612	8.526
3700	132.742	634.911	515.471	441.929	−1960.635	−549.460	7.757
3800	132.757	638.451	518.661	455.204	−1959.721	−511.333	7.029
3900	132.771	641.900	521.777	468.481	−1958.844	−473.228	6.338
4000	132.783	645.262	524.822	481.758	−1958.008	−435.146	5.682
4100	132.795	648.540	527.800	495.037	−1957.218	−397.085	5.059
4200	132.806	651.741	530.713	508.317	−1956.480	−359.042	4.465
4300	132.817	654.866	533.564	521.599	−1955.798	−321.016	3.900
4400	132.826	657.919	536.355	534.881	−1955.115	−283.010	3.360
4500	132.835	660.904	539.090	548.164	−1954.533	−245.015	2.844
4600	132.844	663.824	541.770	561.448	−1954.026	−207.031	2.351
4700	132.851	666.681	544.398	574.733	−1953.593	−169.058	1.879
4800	132.859	669.478	546.974	588.018	−1953.238	−131.093	1.427
4900	132.866	672.218	549.503	601.304	−1952.969	−93.134	0.993
5000	132.872	674.902	551.984	614.591	−1952.790	−55.181	0.576
5100	132.878	677.533	554.420	627.879	−1952.690	−17.231	0.176
5200	132.884	680.114	556.812	641.167	−1952.706	20.720	−0.208
5300	132.890	682.645	559.163	654.455	−1952.830	58.671	−0.578
5400	132.895	685.129	561.472	667.745	−1953.067	96.626	−0.935
5500	132.900	687.567	563.743	681.034	−1953.424	134.586	−1.278
5600	132.904	689.962	565.976	694.325	−1953.907	172.554	−1.610
5700	132.909	692.314	568.171	707.615	−1954.521	210.531	−1.929
5800	132.913	694.626	570.332	720.906	−1955.273	248.521	−2.238
5900	132.917	696.898	572.458	734.198	−1956.167	286.526	−2.537
6000	132.921	699.132	574.550	747.490	−1957.210	324.546	−2.825

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [295.968 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-603.975 \pm 16.7]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -607.098 \pm 16.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[3505]	[2]
[10861]	[4]
[11062]	[4]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[600](1)	[650](2)
[300](1)	[250](2)

Ground State Quantum Weight: [2] σ = [6]
Point Group: D_{3h}
Bond Distance: Mo–F = [1.82] Å
Bond Angle: F–Mo–F = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.702846 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted enthalpy of formation at 298.15 K is that derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous molybdenum fluorides by Hildenbrand [1664 and 2146 K][2] and among gaseous and hetrogeneous phases by Alikhanyan *et al.* [911 and 964 K].[3] The value of $\Delta_f H°(0\ K)$ combined with JANAF data[4] for Mo(g) and F(g) gives $\Delta_{at} H°(0\ K) = 356.5 \pm 6$ kcal·mol^{-1} and an average Mo–F bond energy of $\Delta_{at} H°(0\ K)/3 = 118.8 \pm 2$ kcal·mol^{-1}.

Heat Capacity and Entropy

We use the vibrational frequencies and degeneracies estimated by Hildenbrand[2] and adopted by Brewer.[1] The correlation of Drake and Rosenblatt[5] leads to a planar configuration for MoF_3(g). The Mo–F distances of 1.82 Å from MoF_6(g) is used. The observed electronic levels[4] of the isoelectronic TaO(g) are assumed, as suggested by Brewer,[1] up through 11062 cm^{-1}. The principal moments of inertia are: $I_A = I_B = 15.6750 \times 10^{-39}$ and $I_C = 31.3500 \times 10^{-39}$ g·cm^2.

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

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[4] JANAF Thermochemical Tables: Mo(g), 3-31-78; F(g), 9-30-65; TaO(g), 9-31-73.

[5] M. C. Drake and G. M. Rosenblatt in Proc. Symp. on High Temperature Metal Halide Chemistry, D. L. Hildenbrand and D. D. Cubicciotti, Eds., The Electrochem. Soc., Vol. 78-1, pp. 199-209, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	-14.699	-603.975	-603.975	INFINITE
100	41.852	237.013	348.551	-11.154	-605.282	-602.725	314.831
200	57.340	271.083	301.828	-6.149	-606.513	-599.638	156.609
250	62.957	284.508	297.050	-3.135	-606.871	-597.875	124.919
298.15	67.093	295.968	295.968	0.	-607.098	-596.120	104.438
300	67.230	296.383	295.969	0.124	-607.105	-596.052	103.782
350	70.430	306.999	296.800	3.570	-607.257	-594.197	88.679
400	72.834	316.568	298.683	7.154	-607.360	-592.324	77.350
450	74.665	325.257	301.160	10.844	-607.436	-590.439	68.536
500	76.087	333.200	303.973	14.614	-607.498	-588.547	61.485
600	78.145	347.267	310.047	22.332	-607.606	-584.747	50.907
700	79.599	359.428	316.252	30.223	-607.715	-580.929	43.349
800	80.737	370.134	322.332	38.242	-607.832	-577.094	37.680
900	81.694	379.700	328.184	46.364	-607.957	-573.244	33.270
1000	82.528	388.351	333.775	54.576	-608.092	-569.380	29.741
1100	83.262	396.252	339.101	62.867	-608.245	-565.502	26.853
1200	83.908	403.525	344.170	71.226	-608.423	-561.609	24.446
1300	84.472	410.264	348.998	79.645	-608.638	-557.699	22.409
1400	84.963	416.543	353.601	88.118	-608.902	-553.771	20.661
1500	85.391	422.419	357.995	96.636	-609.224	-549.822	19.147
1600	85.766	427.943	362.196	105.194	-609.616	-545.850	17.820
1700	86.101	433.152	366.218	113.788	-610.086	-541.850	16.649
1800	86.405	438.082	370.075	122.413	-610.642	-537.821	15.607
1900	86.689	442.762	373.779	131.068	-611.289	-533.758	14.674
2000	86.958	447.215	377.340	139.751	-612.035	-529.659	13.833
2100	87.220	451.464	380.769	148.460	-612.883	-525.520	13.072
2200	87.479	455.528	384.076	157.195	-613.838	-521.338	12.378
2300	87.736	459.422	387.268	165.955	-614.904	-517.109	11.744
2400	87.993	463.161	390.352	174.742	-616.086	-512.833	11.162
2500	88.250	466.759	393.337	183.554	-617.389	-508.504	10.625
2600	88.506	470.225	396.228	192.392	-618.830	-504.121	10.128
2700	88.760	473.570	399.031	201.255	-620.444	-499.679	9.667
2800	89.011	476.803	401.751	210.144	-622.287	-495.173	9.238
2900	89.256	479.930	404.393	219.057	-660.323	-490.547	8.836
3000	89.493	482.960	406.962	227.995	-660.823	-484.684	8.439
3100	89.721	485.898	409.461	236.955	-661.260	-478.806	8.068
3200	89.938	488.750	411.895	245.938	-661.631	-472.914	7.720
3300	90.144	491.521	414.266	254.943	-661.936	-467.011	7.392
3400	90.335	494.215	416.578	263.967	-662.174	-461.101	7.084
3500	90.512	496.836	418.834	273.009	-662.345	-455.184	6.793
3600	90.674	499.388	421.036	282.069	-662.449	-449.263	6.519
3700	90.820	501.875	423.187	291.144	-662.487	-443.341	6.259
3800	90.950	504.299	425.290	300.232	-662.460	-437.419	6.013
3900	91.064	506.663	427.346	309.333	-662.369	-431.497	5.779
4000	91.162	508.969	429.358	318.445	-662.216	-425.579	5.557
4100	91.245	511.221	431.328	327.565	-662.004	-419.666	5.347
4200	91.312	513.421	433.256	336.693	-661.734	-413.758	5.146
4300	91.364	515.570	435.145	345.827	-661.408	-407.858	4.954
4400	91.402	517.671	436.997	354.965	-661.028	-401.966	4.772
4500	91.426	519.726	438.813	364.107	-660.597	-396.083	4.598
4600	91.438	521.735	440.594	373.250	-660.117	-390.210	4.431
4700	91.437	523.702	442.341	382.394	-659.590	-384.348	4.272
4800	91.425	525.627	444.056	391.537	-659.018	-378.498	4.119
4900	91.403	527.512	445.740	400.679	-658.405	-372.660	3.973
5000	91.371	529.358	447.394	409.817	-1249.136	-361.104	3.772
5100	91.329	531.167	449.019	418.953	-1250.123	-343.333	3.516
5200	91.280	532.940	450.616	428.083	-1251.221	-325.542	3.270
5300	91.223	534.678	452.186	437.208	-1252.428	-307.730	3.033
5400	91.159	536.383	453.729	446.327	-1253.745	-289.893	2.804
5500	91.089	538.055	455.247	455.440	-1255.172	-272.031	2.584
5600	91.013	539.695	456.741	464.545	-1256.709	-254.142	2.371
5700	90.933	541.305	458.210	473.642	-1258.352	-236.225	2.165
5800	90.848	542.886	459.657	482.731	-1260.102	-218.278	1.966
5900	90.759	544.438	461.080	491.812	-1261.955	-200.300	1.773
6000	90.667	545.963	462.483	500.883	-1263.914	-182.290	1.587

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

$S°(298.15\ K) = 260.773 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -126.366 \pm 1.13\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -132.089 \pm 1.13\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1032(1)
642(1)
906(2)
492(2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distance: N–F = 1.371 Å
Bond Angle: F–N–F = 102°9'
Product of the Moments of Inertia: $I_A I_B I_C = 8.858632 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted enthalpy of formation is the mean of values calculated from the reaction processes listed below and weighted inversely as the squares of the standard deviations. Auxiliary enthalpies of formation were taken from NBS [1] or from simultaneous adjustment of several interconnecting pieces of data.[2] Also given below are the references, individual and averaged measured values of enthalpies of reaction and their uncertainties, the value of enthalpy of formation calculated from each process and its uncertainty, and the weighted mean.

Source	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}		$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
	$NF_3(g)+3/2\ H_2(g)=3\ HF(aq,\ 50\ H_2O)+1/2\ N_2(g)$	-199.42 ± 0.22		-30.92 ± 1.72
[3]	196.3 ± 64			
[4]	-199.49 ± 0.22			
[5]	We derive -196.23 ± 0.77			
[6]	$S(cr, rh)+2\ NF_3(g)=SF_6(g)+N_2(g)$	-228.26 ± 0.2		-31.77 ± 0.33
[7]	$NF_3(g) \rightarrow 1/2\ N_2(g)+3/2\ F_2(g)$	31.44 ± 0.3		-31.44 ± 0.3
[8]	$NF_3(g)+3\ C_2N_2(g)=6\ CF_4(g)+7\ N_2(g)$	-1308.8 ± 1.3		-31.4 ± 4.4
[9]	$B(cr)+NF_3(g)=BF_3(g)+1/2\ N_2(g)$	-239.7 ± 1.2		-31.7 ± 1.6
[3]	$NF_3(g)+4\ NH_3(g)=3\ NH_4F(cr)+N_2(g)$	-259.5 ± 1.0		-29.0 ± 3.0
			Weighted Mean	-31.57 ± 0.27

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Schatz and Levin [10] and are in good agreement with those of Pace and Pierce,[11] and Wilson and Polo.[12] The adopted values are also in agreement with the Raman studies of Kotov and Tatevskii.[13] The bond length and angle are from the microwave studies of Sheridan and Gordy,[14] whose values are in substantial agreement with the electron diffraction results of Schomaker and Lu.[15]

The principal moments of inertia are $I_A = I_B = 7.8554 \times 10^{-39}$ g cm^2 and $I_C = 14.3560 \times 10^{-39}$ g·cm^2.

Pierce and Pace [16] have obtained the entropy of the gas at 144.15 K from solid heat capacity measurements and the heats of melting and vaporization. Their reported value of 54.50 cal $K^{-1} \cdot mol^{-1}$ is in good agreement with our calculated value of 54.56 cal $K^{-1} \cdot mol^{-1}$.

The National Bureau of Standards prepared this table [17] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[17] we recalculate the table in terms of 1973 fundamental constants,[18] 1975 atomic weights,[19] and current JANAF reference states for the elements.

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Continued on page 1216

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.850	−126.366	−126.366	INFINITE
100	34.037	215.800	300.931	−8.513	−128.841	−116.875	61.049
200	42.777	241.672	265.323	−4.730	−130.907	−104.047	27.174
250	48.357	251.819	261.624	−2.451	−131.609	−97.246	20.319
298.15	53.370	260.773	260.773	0.	−132.089	−90.582	15.870
300	53.551	261.104	260.774	0.099	−132.104	−90.324	15.727
350	58.068	269.707	261.443	2.892	−132.422	−83.334	12.437
400	61.860	277.717	262.983	5.894	−132.597	−76.307	9.965
450	64.994	285.190	265.040	9.067	−132.656	−69.267	8.040
500	67.568	292.175	267.408	12.384	−132.625	−62.224	6.501
600	71.430	304.858	272.615	19.346	−132.365	−48.165	4.193
700	74.090	316.081	278.039	26.630	−131.929	−34.164	2.549
800	75.971	326.104	283.432	34.138	−131.390	−20.234	1.321
900	77.340	335.135	288.683	41.807	−130.791	−6.375	0.370
1000	78.360	343.339	293.745	49.594	−130.158	7.416	−0.387
1100	79.138	350.846	298.599	57.471	−129.510	21.142	−1.004
1200	79.744	357.759	303.245	65.416	−128.858	34.809	−1.515
1300	80.224	364.161	307.688	73.416	−128.210	48.421	−1.946
1400	80.611	370.121	311.937	81.458	−127.570	61.984	−2.313
1500	80.926	375.694	316.004	89.535	−126.942	75.501	−2.629
1600	81.186	380.925	319.899	97.641	−126.329	88.978	−2.905
1700	81.404	385.854	323.636	105.771	−125.730	102.416	−3.147
1800	81.587	390.512	327.223	113.921	−125.144	115.819	−3.361
1900	81.744	394.928	330.671	122.088	−124.570	129.190	−3.552
2000	81.877	399.124	333.990	130.269	−124.005	142.532	−3.723
2100	81.993	403.122	337.187	138.463	−123.444	155.845	−3.876
2200	82.094	406.939	340.272	146.667	−122.884	169.131	−4.016
2300	82.182	410.590	343.250	154.881	−122.319	182.392	−4.142
2400	82.259	414.089	346.129	163.103	−121.745	195.628	−4.258
2500	82.328	417.448	348.915	171.333	−121.156	208.840	−4.363
2600	82.389	420.679	351.614	179.568	−120.546	222.028	−4.461
2700	82.443	423.789	354.230	187.810	−119.912	235.192	−4.550
2800	82.492	426.788	356.768	196.057	−119.249	248.332	−4.633
2900	82.535	429.684	359.233	204.308	−118.552	261.447	−4.709
3000	82.575	432.482	361.628	212.564	−117.818	274.538	−4.780
3100	82.611	435.191	363.957	220.823	−117.044	287.604	−4.846
3200	82.643	437.814	366.225	229.086	−116.226	300.644	−4.908
3300	82.673	440.357	368.433	237.352	−115.364	313.658	−4.965
3400	82.700	442.826	370.585	245.620	−114.454	326.645	−5.018
3500	82.725	445.224	372.683	253.892	−113.495	339.605	−5.068
3600	82.748	447.554	374.731	262.165	−112.486	352.537	−5.115
3700	82.769	449.822	376.730	270.441	−111.427	365.440	−5.159
3800	82.788	452.029	378.682	278.719	−110.318	378.313	−5.200
3900	82.806	454.180	380.591	286.999	−109.157	391.157	−5.239
4000	82.823	456.277	382.457	295.280	−107.945	403.970	−5.275
4100	82.838	458.322	384.282	303.563	−106.683	416.752	−5.309
4200	82.852	460.318	386.069	311.848	−105.371	429.504	−5.342
4300	82.866	462.268	387.818	320.134	−104.010	442.222	−5.372
4400	82.878	464.173	389.532	328.421	−102.600	454.909	−5.400
4500	82.890	466.036	391.212	336.709	−101.142	467.564	−5.427
4600	82.901	467.858	392.858	344.999	−99.638	480.185	−5.453
4700	82.911	469.641	394.473	353.289	−98.088	492.774	−5.477
4800	82.921	471.387	396.057	361.581	−96.494	505.328	−5.499
4900	82.930	473.096	397.612	369.873	−94.857	517.849	−5.520
5000	82.938	474.772	399.139	378.167	−93.177	530.337	−5.540
5100	82.946	476.414	400.638	386.461	−91.457	542.790	−5.559
5200	82.954	478.025	402.110	394.756	−89.697	555.209	−5.577
5300	82.961	479.605	403.558	403.052	−87.898	567.594	−5.594
5400	82.967	481.156	404.980	411.348	−86.062	579.945	−5.610
5500	82.974	482.678	406.379	419.645	−84.190	592.261	−5.625
5600	82.980	484.174	407.755	427.943	−82.283	604.543	−5.639
5700	82.985	485.642	409.109	436.241	−80.342	616.790	−5.652
5800	82.991	487.086	410.441	444.540	−78.369	629.003	−5.665
5900	82.996	488.504	411.752	452.839	−76.364	641.183	−5.677
6000	83.001	489.899	413.043	461.139	−74.329	653.327	−5.688

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 278.490 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -154.926 \pm 20.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -163.176 \pm 20.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1687(1)	887(2)
743(1)	528(2)
558(1)	398(2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distances: N–O = [1.15]Å; N–F = 1.48 ± 0.1Å
Bond Angles: O–N–F = [109° 28']; F–N–F = [109° 28']
Product of the Moments of Inertia: $I_A I_B I_C$ = [4.064027 × 10^{-114}] $g^3 \cdot cm^6$

Enthalpy of Formation

Bougon *et al.*[1] determined equilibrium constants for the reaction NOF(g) + F_2(g)⇆NOF_3(g) as a function of temperature and total pressure. 2nd and 3rd law analyses of these equilibrium data are given below:

	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal $K^{-1} \cdot mol^{-1}$
Set I	7	533–643	−17.1	−18.7	−2.4 ± 2.1
Set II	1	533.2		−18.2	

Set I contains their equilibrium data as a function of temperature, while Set II is their adopted equilibrium constant, $K_p°$ (553.2 K) = 0.015 ± 0.005 atm^{-1}, corresponding to the lowest pressure (103 atm.) that was studied. Estimated corrections for nonideality are small and neglected. Adopting $\Delta_f H°(298.15\ K) = -18.7 \pm 1.0\ kcal \cdot mol^{-1}$, we derive $\Delta_f H°(NOF_3, g, 298.15\ K) = -34.4 \pm 1.4\ kcal \cdot mol^{-1}$ with $\Delta_f H°(NOF, g, 298.15\ K) = -15.7 \pm 0.4\ kcal \cdot mol^{-1}$.[2]

Armstrong and King [3] determined $\Delta_r H°(304\ K) = -253.7 \pm 0.6\ kcal \cdot mol^{-1}$ for the reaction $NOF_3(g) + 5/2\ H_2(g) + 122\ H_2O(l) \rightarrow 1/2\ N_2(g) + [3\ HF123 \cdot H_2O](l)$ in a constant pressure flame calorimeter. Combining this result with their earlier enthalpy data for reduction reactions involving F_2(g) and O_2(g) with H_2(g), they obtained $\Delta_f H°(NOF_3, g, 304\ K) = -44.7 \pm 1.5\ kcal \cdot mol^{-1}$.

Very recently, Dibeler and Walker[4] investigated the photoionization of NOF_3 by mass spectrometry. From their ionization threshold data, they determined $\Delta_f H°(NOF_3, g, 0\ K) = -69.6 \pm 1.2\ kcal \cdot mol^{-1}$.

The value for the enthalpy of formation of gaseous NOF_3 is tentatively selected as $-39.0 \pm 5.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Several recent infrared[5,6,7] and Raman[8] studies of NOF_3 have been reported in the literature. The fundamental vibrational frequencies observed in the infrared spectrum of the molecule by the various investigators are in good agreement, although the assignment of the ν_3 and ν_5 bending modes has varied. Fox *et al.*[6] assigned $\nu_3 = 558\ cm^{-1}$ and $\nu_5 = 528\ cm^{-1}$, while Curtis *et al.*[7] reversed the assignments. Very recently, Abramowitz and Levin[8] investigated the Raman spectrum of polycrystalline film of NOF_3 at 78 K and assigned $\nu_3 = 535\ cm^{-1}$ and $\nu_5 = 522\ cm^{-1}$ consistent with the infrared work of Fox *et al.*[6] The fundamental vibrational frequencies and assignments given by Fox *et al.*[6] are adopted here.

Fox *et al.*[9] also investigated the nuclear magnetic resonance spectrum of NOF_3 which indicated that the molecule contained three equivalent fluorine atoms. This result, along with the general appearance of the infrared spectrum, clearly establishes that the molecule has C_{3v} symmetry. The N–O bond distance and bond angles are estimated quantities from the work of Curtis *et al.*[7] These estimated data have been used in calculating the N–F bond distance from the rotational constants given by Curtis *et al.*[7] Individual moments of inertia calculated from the structural data given above are: $I_A = I_B = 14.8502 \times 10^{-39}$ and $I_C = 18.4285 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.664	−154.926	−154.926	INFINITE
100	35.733	225.011	327.998	−10.299	−158.825	−139.114	72.666
200	52.446	254.510	284.237	−5.945	−161.776	−118.135	30.854
250	60.935	267.147	279.570	−3.106	−162.646	−107.116	22.381
298.15	67.862	278.490	278.490	0.	−163.176	−96.369	16.883
300	68.103	278.911	278.492	0.126	−163.191	−95.954	16.707
350	73.975	289.865	279.343	3.683	−163.484	−84.722	12.644
400	78.762	300.067	281.304	7.505	−163.585	−73.461	9.593
450	82.682	309.577	283.923	11.545	−163.538	−62.197	7.220
500	85.920	318.462	286.937	15.762	−163.376	−50.945	5.322
600	90.882	334.592	293.564	24.617	−162.803	−28.508	2.482
700	94.429	348.882	300.465	33.892	−162.004	−6.186	0.462
800	97.033	361.670	307.331	43.471	−161.062	16.010	−1.045
900	98.988	373.217	314.021	53.277	−160.029	38.083	−2.210
1000	100.486	383.727	320.474	63.254	−158.937	60.037	−3.136
1100	101.654	393.362	326.668	73.363	−157.811	81.880	−3.888
1200	102.579	402.248	332.601	83.576	−156.666	103.620	−4.510
1300	103.324	410.489	338.279	93.873	−155.511	125.264	−5.033
1400	103.930	418.169	343.714	104.236	−154.357	146.819	−5.478
1500	104.430	425.357	348.920	114.655	−153.209	168.291	−5.860
1600	104.846	432.110	353.911	125.120	−152.071	189.687	−6.193
1700	105.197	438.478	358.700	135.622	−150.945	211.013	−6.484
1800	105.494	444.499	363.301	146.157	−149.832	232.272	−6.740
1900	105.748	450.210	367.726	156.720	−148.732	253.470	−6.968
2000	105.967	455.640	371.987	167.306	−147.643	274.610	−7.172
2100	106.157	460.815	376.095	177.912	−146.563	295.696	−7.355
2200	106.323	465.757	380.059	188.536	−145.487	316.731	−7.520
2300	106.469	470.486	383.888	199.176	−144.411	337.717	−7.670
2400	106.597	475.021	387.592	209.830	−143.332	358.656	−7.806
2500	106.711	479.374	391.176	220.495	−142.244	379.550	−7.930
2600	106.812	483.562	394.650	231.171	−141.142	400.400	−8.044
2700	106.903	487.595	398.018	241.857	−140.023	421.207	−8.149
2800	106.984	491.484	401.287	252.552	−138.881	441.973	−8.245
2900	107.058	495.239	404.462	263.254	−137.712	462.697	−8.334
3000	107.124	498.870	407.549	273.963	−136.513	483.380	−8.416
3100	107.184	502.383	410.552	284.678	−135.280	504.023	−8.493
3200	107.239	505.787	413.475	295.399	−134.011	524.625	−8.564
3300	107.289	509.088	416.323	306.126	−132.703	545.188	−8.630
3400	107.334	512.292	419.098	316.857	−131.355	565.710	−8.691
3500	107.376	515.404	421.806	327.593	−129.964	586.191	−8.748
3600	107.415	518.429	424.448	338.332	−128.529	606.633	−8.802
3700	107.450	521.372	427.028	349.075	−127.050	627.034	−8.852
3800	107.483	524.238	429.548	359.822	−125.525	647.394	−8.899
3900	107.513	527.031	432.012	370.572	−123.955	667.714	−8.943
4000	107.541	529.753	434.422	381.325	−122.340	687.993	−8.984
4100	107.567	532.409	436.780	392.080	−120.680	708.230	−9.023
4200	107.591	535.001	439.087	402.838	−118.975	728.427	−9.059
4300	107.614	537.533	441.348	413.598	−117.226	748.583	−9.093
4400	107.635	540.007	443.562	424.361	−115.434	768.697	−9.126
4500	107.655	542.427	445.732	435.125	−113.600	788.771	−9.156
4600	107.673	544.793	447.860	445.892	−111.724	808.802	−9.184
4700	107.691	547.109	449.947	456.660	−109.808	828.794	−9.211
4800	107.707	549.376	451.995	467.430	−107.853	848.743	−9.236
4900	107.722	551.597	454.005	478.201	−105.860	868.652	−9.260
5000	107.736	553.774	455.979	488.974	−103.832	888.520	−9.282
5100	107.750	555.907	457.917	499.748	−101.769	908.346	−9.303
5200	107.763	558.000	459.822	510.524	−99.672	928.132	−9.323
5300	107.775	560.052	461.694	521.301	−97.544	947.877	−9.342
5400	107.786	562.067	463.534	532.079	−95.385	967.582	−9.359
5500	107.797	564.045	465.343	542.858	−93.198	987.246	−9.376
5600	107.807	565.987	467.123	553.638	−90.984	1006.871	−9.392
5700	107.817	567.896	468.875	564.420	−88.745	1026.455	−9.406
5800	107.826	569.771	470.598	575.202	−86.482	1046.000	−9.420
5900	107.835	571.614	472.295	585.985	−84.197	1065.506	−9.433
6000	107.843	573.427	473.965	596.769	−81.892	1084.973	−9.446

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 285.413 \pm 0.30\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1245.468 \pm 8.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1254.250 \pm 8.0\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1417.7(1)	994 (2)
872.8(1)	488.2(2)
473.2(1)	335.6(2)

Ground State Quantum Weight: [1] $\sigma = 3$

Point Group: C_{3v}

Bond Distances: P–O = 1.45 ± 0.03 Å; P–F = 1.52 ± 0.02 Å

Bond Angles: F–P–F = 102.5 ± 2°; F–P–O = 115.8 ± 2°

Product of the Moments of Inertia: $I_A I_B I_C = 5.907318 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Ebel and Bretscher[1] measured the enthalpy change for the following reaction: $PF_3(g) + 1/2\ O_2(g) \rightarrow POF_3(g)$. They reported a heat of reaction of $-70.6 \pm 1\ kcal \cdot mol^{-1}$. Combining this result with the enthalpy of formation of PF_3, $\Delta_f H°(298.15\ K) = -224.9 \pm 0.9\ kcal \cdot mol^{-1}$,[2] we derive, $\Delta_f H°(POF_3, g, 298.15\ K) = -295.6 \pm 1.9\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies are from the infrared studies of Selig and Claasen[3] and are in good agreement with the Raman and infrared studies of Gutowsky and Liehr.[4] Several microwave studies[5,6,7,8] of POF_3 have been reported. As pointed out by Williams *et al.*,[7] the rotational constant calculated from their microwave studies leads to a moment of inertia, I_B, which is in disagreement with the moment of inertia calculated from the molecular constants obtained from electron-diffraction studies by Brockway and Beach.[9] Since insufficient microwave data were available for an independent determination, Williams *et al.*[7] sought to find parameters which were consistent with both measurements. Their molecular constants are adopted for this tabulation. Individual moments of inertia are $I_A = 17.7329 \times 10^{-39}$, $I_B = I_C = 18.2518 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.157	−1245.468	−1245.468	INFINITE
100	37.612	229.302	336.796	−10.749	−1248.761	−1235.701	645.464
200	55.073	260.721	291.294	−6.115	−1252.238	−1221.413	319.000
250	62.605	273.841	286.512	−3.168	−1253.366	−1213.571	253.562
298.15	68.815	285.413	285.413	0.	−1254.250	−1205.824	211.255
300	69.034	285.839	285.414	0.128	−1254.281	−1205.523	209.900
350	74.490	296.902	286.275	3.719	−1255.746	−1197.265	178.682
400	79.094	307.158	288.252	7.562	−1256.413	−1188.863	155.250
450	82.962	316.704	290.890	11.617	−1256.934	−1180.387	137.016
500	86.209	325.618	293.922	15.848	−1257.337	−1171.859	122.423
600	91.231	341.806	300.582	24.735	−1257.873	−1154.708	100.526
700	94.821	356.154	307.516	34.047	−1258.148	−1137.489	84.880
800	97.435	368.995	314.412	43.666	−1258.244	−1120.243	73.144
900	99.378	380.589	321.132	53.512	−1258.215	−1102.994	64.016
1000	100.853	391.139	327.613	63.527	−1258.099	−1085.753	56.714
1100	101.993	400.807	333.834	73.671	−1257.921	−1068.526	50.740
1200	102.890	409.722	339.791	83.917	−1321.273	−1050.239	45.716
1300	103.607	417.987	345.492	94.243	−1320.251	−1027.695	41.293
1400	104.188	425.687	350.948	104.634	−1319.215	−1005.229	37.506
1500	104.664	432.892	356.174	115.077	−1318.175	−982.838	34.225
1600	105.060	439.660	361.182	125.564	−1317.135	−960.516	31.358
1700	105.391	446.039	365.988	136.087	−1316.100	−938.259	28.829
1800	105.672	452.071	370.604	146.641	−1315.070	−916.063	26.583
1900	105.911	457.791	375.044	157.220	−1314.047	−893.924	24.576
2000	106.117	463.229	379.318	167.822	−1313.030	−871.838	22.770
2100	106.295	468.411	383.438	178.443	−1312.015	−849.804	21.138
2200	106.451	473.360	387.414	189.080	−1311.002	−827.817	19.655
2300	106.587	478.095	391.255	199.732	−1309.985	−805.877	18.302
2400	106.707	482.633	394.968	210.397	−1308.961	−783.981	17.063
2500	106.813	486.992	398.562	221.073	−1307.925	−762.128	15.924
2600	106.907	491.183	402.045	231.759	−1306.873	−740.317	14.873
2700	106.992	495.219	405.421	242.454	−1305.800	−718.547	13.901
2800	107.067	499.112	408.698	253.157	−1304.703	−696.817	12.999
2900	107.135	502.870	411.881	263.867	−1303.578	−675.126	12.160
3000	107.197	506.503	414.975	274.584	−1302.420	−653.475	11.378
3100	107.253	510.019	417.985	285.306	−1301.227	−631.863	10.647
3200	107.303	513.425	420.914	296.034	−1299.997	−610.291	9.962
3300	107.350	516.727	423.768	306.767	−1298.726	−588.757	9.319
3400	107.392	519.933	426.549	317.504	−1297.414	−567.262	8.715
3500	107.431	523.046	429.262	328.245	−1296.058	−545.807	8.146
3600	107.466	526.073	431.909	338.990	−1294.657	−524.390	7.609
3700	107.499	529.018	434.494	349.738	−1293.211	−503.014	7.101
3800	107.530	531.885	437.020	360.490	−1291.720	−481.677	6.621
3900	107.558	534.679	439.488	371.244	−1290.182	−460.380	6.166
4000	107.583	537.402	441.902	382.001	−1288.598	−439.123	5.734
4100	107.608	540.059	444.264	392.761	−1286.968	−417.907	5.324
4200	107.630	542.653	446.576	403.523	−1285.294	−396.730	4.934
4300	107.651	545.185	448.840	414.287	−1283.574	−375.594	4.563
4400	107.670	547.660	451.058	425.053	−1281.811	−354.499	4.208
4500	107.689	550.080	453.231	435.821	−1280.006	−333.444	3.871
4600	107.706	552.447	455.362	446.591	−1278.158	−312.430	3.548
4700	107.722	554.764	457.453	457.362	−1276.270	−291.455	3.239
4800	107.737	557.032	459.504	468.135	−1274.343	−270.522	2.944
4900	107.751	559.254	461.517	478.909	−1272.377	−249.629	2.661
5000	107.764	561.431	463.494	489.685	−1270.375	−228.777	2.390
5100	107.776	563.565	465.435	500.462	−1268.338	−207.965	2.130
5200	107.788	565.658	467.342	511.240	−1266.268	−187.194	1.880
5300	107.799	567.711	469.217	522.020	−1264.165	−166.462	1.641
5400	107.810	569.726	471.059	532.800	−1262.032	−145.771	1.410
5500	107.820	571.704	472.871	543.582	−1259.869	−125.120	1.188
5600	107.829	573.647	474.654	554.364	−1257.679	−104.507	0.975
5700	107.838	575.556	476.407	565.147	−1255.464	−83.935	0.769
5800	107.847	577.431	478.133	575.932	−1253.223	−63.401	0.571
5900	107.855	579.275	479.831	586.717	−1250.961	−42.907	0.380
6000	107.862	581.088	481.504	597.503	−1248.677	−22.450	0.195

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 273.064 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -952.782 \pm 3.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -958.441 \pm 3.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
892 (1)	860 (2)
487 (1)	344 (2)

Ground State Quantum Weight: [1] $\sigma = 3$

Point Group: C_{3v}

Bond Distances: P–F = 1.5700 ± 0.0012 Å; F....F = 2.3643 ± 0.0028 Å

Bond Angle: F–P–F = 97.8 ± 0.2°

Product of the Moments of Inertia: $I_A I_B I_C = 2.070369 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Berthelot[1] measured the enthalpy of hydrolysis of PF_3(g) and PCl_3(l). These results can be combined to give, $\Delta_r H° = 24.5\ kcal \cdot mol^{-1}$ for the reaction

$$PF_3(g) + 3\ KCl \cdot 157\ H_2O \rightarrow PCl_3(l) + 3\ KF \cdot 112\ H_2O.$$

Combining this result with the following enthalpy of formation data,

$\Delta_f H°(PCL_3, l, 298.15\ K) = -72.2\ kcal \cdot mol^{-1}$ [2]

$\Delta_f H°(KCl \cdot 157\ H_2O, 298.15\ K) = -100.0\ kcal \cdot mol^{-1}$ [3]

$\Delta_f H°(KF \cdot 112\ H_2O, 298.15\ K) = -138.5\ kcal \cdot mol^{-1}$ [3]

we derive, $\Delta_f H°(PF_3, g, 298.15\ K) = -212.2\ kcal \cdot mol^{-1}$.

Duus and Mykytink [4] reported an enthalpy of reaction of −2.361 $kcal \cdot mol^{-1}$ (corrected to 25°C) for the following reaction

$$PCl_3(g) + 3/2\ CaF_2(cr) \rightarrow PF_3(g) + 3/2\ CaCl_2(cr).$$

Combining this result with the following enthalpy of formation data,

$\Delta_f H°(PCl_3, g, 298.15\ K) = -64.4\ kcal \cdot mol^{-1}$ [2]

$\Delta_f H°(CaF_2, cr, 298.15\ K) = 293.0 \pm 1.5\ kcal \cdot mol^{-1}$ [5]

$\Delta_f H°(CaCl_2, cr, 298.15\ K) = -190.0\ kcal \cdot mol^{-1}$ [3]

we derive, $\Delta_f H°(PF_3, g, 298.15\ K) = -221.9\ kcal \cdot mol^{-1}$.

Recently, Rudzitis *et al.* [6] measured the enthalpy of combustion of PF_3 in fluorine in a two-chambered bomb calorimeter at 25°C. They reported an enthalpy of combustion of $-152.0 \pm 0.2\ kcal \cdot mol^{-1}$ for the reaction

$$PF_3(g) + F_2(g) \rightarrow PF_5(g).$$

Combining this result with $\Delta_f H°(PF_5, g, 298.15\ K) = -376.9 \pm 0.7\ kcal \cdot mol^{-1}$,[5] we derive $\Delta_f H°(PF_3, g, 298.15\ K) = -224.9 \pm 0.9\ kcal \cdot mol^{-1}$. This result is adopted for this tabulation.

Heat Capacity and Entropy

The vibrational frequencies are those reported by Wilson and Palo.[8] Several different values for the P–F bond length and F–P–F bond angle have been reported in the literature. This problem was recently discussed by Morino *et al.*[9] who also reported new data obtained from electron–diffraction studies. Their results are adopted for this tabulation. Individual moments of inertia calculated according to their structure are: $I_A = I_B = 10.8265 \times 10^{-39}$ and $I_C = 17.6633 \times 10^{-39}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.938	−952.782	−952.782	INFINITE
100	36.571	222.647	318.125	−9.548	−954.640	−949.580	496.010
200	48.620	251.683	278.127	−5.289	−957.038	−943.753	246.483
250	54.098	263.132	274.006	−2.718	−957.812	−940.340	196.473
298.15	58.691	273.064	273.064	0.	−958.441	−936.916	164.144
300	58.853	273.428	273.065	0.109	−958.464	−936.782	163.108
350	62.825	282.808	273.797	3.154	−959.738	−933.052	139.250
400	66.071	291.417	275.469	6.379	−960.274	−929.202	121.341
450	68.700	299.356	277.688	9.751	−960.720	−925.291	107.405
500	70.827	306.708	280.227	13.241	−961.094	−921.334	96.251
600	73.966	319.918	285.767	20.491	−961.686	−913.323	79.512
700	76.094	331.490	291.489	28.001	−962.137	−905.225	67.549
800	77.584	341.754	297.143	35.689	−962.495	−897.070	58.573
900	78.658	350.957	302.620	43.504	−962.794	−888.873	51.589
1000	79.455	359.288	307.877	51.411	−963.054	−880.646	46.000
1100	80.061	366.891	312.901	59.388	−963.290	−872.393	41.427
1200	80.531	373.878	317.695	67.419	−1027.083	−863.042	37.567
1300	80.902	380.339	322.269	75.491	−1026.522	−849.394	34.129
1400	81.201	386.346	326.634	83.597	−1025.965	−835.790	31.184
1500	81.444	391.957	330.804	91.729	−1025.415	−822.225	28.632
1600	81.644	397.219	334.792	99.884	−1024.874	−808.697	26.401
1700	81.811	402.174	338.611	108.057	−1024.342	−795.202	24.434
1800	81.952	406.855	342.274	116.245	−1023.820	−781.739	22.685
1900	82.072	411.289	345.790	124.447	−1023.305	−768.304	21.122
2000	82.175	415.501	349.171	132.659	−1022.795	−754.896	19.716
2100	82.264	419.513	352.426	140.881	−1022.287	−741.514	18.444
2200	82.341	423.341	355.563	149.112	−1021.777	−728.155	17.289
2300	82.408	427.003	358.590	157.349	−1021.259	−714.820	16.234
2400	82.468	430.512	361.515	165.593	−1020.729	−701.508	15.268
2500	82.520	433.879	364.342	173.843	−1020.183	−688.218	14.380
2600	82.567	437.117	367.079	182.097	−1019.614	−674.951	13.560
2700	82.608	440.234	369.731	190.356	−1019.019	−661.706	12.801
2800	82.646	443.239	372.303	198.618	−1018.394	−648.483	12.098
2900	82.679	446.139	374.800	206.885	−1017.733	−635.284	11.443
3000	82.709	448.943	377.225	215.154	−1017.034	−622.108	10.832
3100	82.737	451.655	379.582	223.426	−1016.294	−608.956	10.261
3200	82.762	454.282	381.876	231.701	−1015.509	−595.828	9.726
3300	82.784	456.829	384.109	239.979	−1014.679	−582.726	9.224
3400	82.805	459.301	386.284	248.258	−1013.800	−569.650	8.752
3500	82.824	461.702	388.405	256.540	−1012.872	−556.600	8.307
3600	82.841	464.035	390.473	264.823	−1011.893	−543.577	7.887
3700	82.858	466.305	392.492	273.108	−1010.864	−530.582	7.490
3800	82.872	468.515	394.464	281.394	−1009.782	−517.616	7.115
3900	82.886	470.668	396.390	289.682	−1008.650	−504.679	6.759
4000	82.899	472.767	398.274	297.972	−1007.466	−491.771	6.422
4100	82.911	474.814	400.116	306.262	−1006.232	−478.895	6.101
4200	82.921	476.812	401.918	314.554	−1004.947	−466.048	5.796
4300	82.932	478.763	403.683	322.846	−1003.612	−453.233	5.506
4400	82.941	480.670	405.411	331.140	−1002.228	−440.449	5.229
4500	82.950	482.534	407.104	339.435	−1000.797	−427.697	4.965
4600	82.958	484.357	408.764	347.730	−999.318	−414.978	4.712
4700	82.966	486.141	410.391	356.026	−997.794	−402.291	4.471
4800	82.973	487.888	411.987	364.323	−996.225	−389.637	4.240
4900	82.980	489.599	413.554	372.621	−994.613	−377.017	4.019
5000	82.987	491.275	415.092	380.919	−992.958	−364.430	3.807
5100	82.993	492.919	416.602	389.218	−991.262	−351.876	3.604
5200	82.999	494.530	418.085	397.518	−989.526	−339.356	3.409
5300	83.004	496.112	419.542	405.818	−987.750	−326.869	3.221
5400	83.009	497.663	420.974	414.119	−985.938	−314.417	3.041
5500	83.014	499.186	422.383	422.420	−984.088	−301.999	2.868
5600	83.019	500.682	423.768	430.721	−982.204	−289.613	2.701
5700	83.023	502.152	425.130	439.024	−980.285	−277.263	2.541
5800	83.027	503.595	426.470	447.326	−978.333	−264.947	2.386
5900	83.031	505.015	427.790	455.629	−976.349	−252.663	2.237
6000	83.035	506.410	429.088	463.932	−974.334	−240.415	2.093

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 298.139 \pm 0.21\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1001.318 \pm 62.8]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1009.068 \pm 62.8]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
981(1)	945(2)
442(1)	275(2)
695(1)	402(2)

Ground Quantum Weight: [1] $\sigma = 3$

Point Group: C_{3v}

Bond Distances: P–S = 1.87 ± 0.03 Å; P–F = 1.53 ± 0.02 Å

Bond Angles: F–P–F = 100.3 ± 2°; F–P–S = 117.6 ± 2°

Product of the Moments of Inertia: $I_A I_B I_C = 1.731454 \times 10^{-113}\ g^3\cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of PSF_3 is calculated from the enthalpy of formation of POF_3 and estimated P=O and P=S bond strengths. Mortimer[1] calculated several P=O and P=S bond dissociation energies from enthalpy of reaction data reported in the literature. Some of these data are given below.

Reaction	D(P=O)	D(P=S)
	kcal·mol^{-1}	
ΔH oxidation PF_3 to POF_3	130.3	
ΔH oxidation $P(OEt)_3$ to $PS(OEt)_3$		81.6
ΔH oxidation PPr_3 to $PSPr_3$		82.6

Mole and McCoubrey[2] reported the following enthalpy of reaction:

$$PCl_3(l) + Si(cr) \rightarrow PSCl_3(l).\ \Delta_r H = -5.6\ kcal\cdot mol^{-1}.$$

Combining this result with enthalpy of vaporization data for PCl_3[3] and $PSCl_3$,[4] along with the enthalpy of sublimation of S,[3] we derive $D(P=S) = 71\ kcal\cdot mol^{-1}$. Averaging this result with the two values given above, we obtain $D(P=S) = 78.4\ kcal\cdot mol^{-1}$. We assume that this result represents the enthalpy change for reaction $PSF_3(g) \rightarrow PF_3(g) + S(g)$. Combining this result with similar data for POF_3, namely $D(P=O) = 130.3\ kcal\cdot mol^{-1}$ and $\Delta_f H°(POF_3, g, 298.15\ K) = -295.6 \pm 1.9\ kcal\cdot mol^{-1}$,[3] we derive $\infty_f H°(PSF_3, g, 298.15\ K) = -237 \pm 15\ kcal\cdot mol^{-1}$, from the relationship $\infty_f H°(PSF_3, g, 298.15\ K) = \infty_f H°(POF_3, g, 298.15\ K) + \infty_f H°(S, g, 298.15\ K) - \infty_f H°(O, g, 298.15\ K) - D(P=O) + D(P=S)$.

Heat Capacity and Entropy

Several recent infrared and Raman studies[7, 8, 9, 10] of PSF_3 have been reported. These data are in good agreement, except for the τ_1 fundamental. Dewaulle and Francois[11] assigned this fundamental to the 869 cm^{-1} band observed in their spectra. The recent work indicates that this fundamental should be assigned to the 981 cm^{-1} band. Average values of the vibrational frequencies reported by[8, 9, 10] are adopted for this tabulation. The molecular structure of this molecule was determined by Williams *et al.*[12] and Hawkins and Cohen[13] from microwave studies. The individual moments of inertia calculated from the constants given by Williams *et al.*[12] are $I_A = 1.74111 \times 10^{-39}$, $I_B = I_C = 31.5349 \times 10^{-39}\ g\cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.260	−1001.318	−1001.318	INFINITE
100	40.782	236.647	354.315	−11.767	−1003.763	−998.851	521.746
200	60.470	271.207	304.539	−6.666	−1006.961	−992.854	259.307
250	68.259	285.562	299.333	−3.443	−1008.103	−989.192	206.680
298.15	74.551	298.139	298.139	0.	−1009.068	−985.461	172.649
300	74.771	298.601	298.140	0.138	−1009.103	−985.314	171.558
350	80.142	310.544	299.071	4.015	−1010.711	−981.207	146.437
400	84.525	321.542	301.202	8.136	−1013.783	−976.844	127.563
450	88.085	331.710	304.034	12.454	−1015.207	−972.149	112.844
500	90.978	341.146	307.279	16.933	−1016.595	−967.287	101.052
600	95.275	358.139	314.372	26.260	−1018.696	−957.218	83.333
700	98.210	373.059	321.712	35.943	−1020.319	−946.838	70.654
800	100.276	386.316	328.975	45.873	−1021.647	−936.247	61.131
900	101.774	398.218	336.018	55.980	−1075.911	−924.422	53.652
1000	102.888	409.001	342.786	66.215	−1075.699	−907.600	47.408
1100	103.737	418.849	349.260	76.548	−1075.450	−890.802	42.301
1200	104.396	427.905	355.441	86.956	−1138.753	−872.950	37.999
1300	104.919	436.282	361.342	97.423	−1137.700	−850.842	34.187
1400	105.339	444.074	366.976	107.937	−1136.653	−828.815	30.923
1500	105.682	451.353	372.361	118.488	−1135.617	−806.863	28.097
1600	105.965	458.183	377.514	129.071	−1134.596	−784.980	25.627
1700	106.201	464.615	382.450	139.680	−1133.592	−763.159	23.449
1800	106.400	470.691	387.185	150.310	−1132.604	−741.398	21.515
1900	106.569	476.448	391.733	160.959	−1131.632	−719.691	19.786
2000	106.714	481.918	396.107	171.623	−1130.672	−698.034	18.231
2100	106.840	487.128	400.318	182.301	−1129.720	−676.426	16.825
2200	106.949	492.101	404.378	192.990	−1128.773	−654.863	15.548
2300	107.045	496.857	408.296	203.690	−1127.825	−633.343	14.384
2400	107.128	501.414	412.082	214.399	−1126.871	−611.864	13.317
2500	107.203	505.789	415.743	225.116	−1125.906	−590.425	12.336
2600	107.269	509.995	419.288	235.839	−1124.924	−569.025	11.432
2700	107.328	514.045	422.723	246.569	−1123.920	−547.663	10.595
2800	107.380	517.949	426.054	257.305	−1122.889	−526.339	9.819
2900	107.428	521.718	429.288	268.045	−1121.828	−505.053	9.097
3000	107.471	525.360	432.430	278.790	−1120.732	−483.803	8.424
3100	107.510	528.885	435.485	289.539	−1119.599	−462.591	7.795
3200	107.545	532.299	438.458	300.292	−1118.424	−441.416	7.205
3300	107.577	535.609	441.352	311.048	−1117.207	−420.278	6.652
3400	107.606	538.821	444.172	321.807	−1115.944	−399.178	6.133
3500	107.633	541.940	446.921	332.569	−1114.636	−378.115	5.643
3600	107.658	544.973	449.602	343.334	−1113.281	−357.091	5.181
3700	107.681	547.923	452.220	354.101	−1111.877	−336.105	4.745
3800	107.702	550.795	454.776	364.870	−1110.426	−315.157	4.332
3900	107.721	553.593	457.274	375.641	−1108.928	−294.248	3.941
4000	107.739	556.320	459.717	386.414	−1107.382	−273.379	3.570
4100	107.756	558.981	462.105	397.189	−1105.789	−252.549	3.218
4200	107.771	561.578	464.443	407.965	−1104.151	−231.757	2.882
4300	107.786	564.114	466.732	418.743	−1102.467	−211.006	2.563
4400	107.799	566.592	468.973	429.522	−1100.740	−190.294	2.259
4500	107.812	569.014	471.169	440.303	−1098.969	−169.622	1.969
4600	107.824	571.384	473.322	451.085	−1097.157	−148.990	1.692
4700	107.835	573.703	475.433	461.868	−1095.305	−128.397	1.427
4800	107.845	575.974	477.504	472.652	−1093.414	−107.845	1.174
4900	107.855	578.197	479.537	483.437	−1091.485	−87.332	0.931
5000	107.864	580.376	481.532	494.223	−1089.521	−66.859	0.698
5100	107.873	582.512	483.491	505.010	−1087.521	−46.425	0.475
5200	107.881	584.607	485.415	515.797	−1085.488	−26.031	0.261
5300	107.889	586.662	487.306	526.586	−1083.423	−5.677	0.056
5400	107.896	588.679	489.165	537.375	−1081.327	14.638	−0.142
5500	107.903	590.659	490.993	548.165	−1079.202	34.914	−0.332
5600	107.909	592.603	492.790	558.955	−1077.048	55.152	−0.514
5700	107.916	594.513	494.558	569.747	−1074.867	75.350	−0.691
5800	107.921	596.390	496.297	580.539	−1072.661	95.510	−0.860
5900	107.927	598.235	498.009	591.331	−1070.429	115.632	−1.024
6000	107.932	600.049	499.695	602.124	−1068.174	135.715	−1.182

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°$(298.15 K) = [286.174 ± 4.2] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −498.980 ± 33.5 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −503.030 ± 33.5 kJ·mol^{-1}

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[25000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
{850](1)	[725](1)
[550](1)	[450](1)
[300]	[350](1)

Point Group: C_{2v} σ = 2
Bond Distances: S–F* = [1.545] Å; S–F** = [1.646] Å
Bond Angles: F*–S–F** = [89]°; F**–S–F** = [178]°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.272514 × 10^{-114}] g^3·cm^6

Enthalpy of Formation

$\Delta_f H°$(0 K) = −119.26 ± 8.0 kcal·mol^{-1} is calculated from the primary bond dissociation energy for SF_4 of $D_0°$ (SF_3−F) = 80.0 ± 3.0 kcal·mol^{-1} with JANAF[1] $\Delta_f H°$ data for F(g) and SF_4(g). The value of $D_0°$ is taken to be equal to one-fourth the enthalpy of atomization of SF_4.[1] We calculate the heat of atomization, $\Delta_{at}H°$(0 K), and mean bond dissocation energy ($D_0°$) for SF_3 to be 240.1 kcal·mol^{-1} and 80.0 kcal·mol^{-1}, respectively. $\Delta_f H°$ is −120.227 kcal·mol^{-1} at 298.15 K.

Several pieces of information are available which are relatively imprecise but do support our assumption that $D_0°$ (SF_3−F) = $\Delta_{at}H°$(SF_4)/4. Bott[2] has reported the results of shock-tube experiments on the dissociation of SF_4 over the temperature range 1650–1950 K. Rate constants based on spectroscopic measurements were correlated with the Rice–Ramsperger–Kassel (RRK) theory. This study strongly suggests that $D_0°$ (SF_3−F) = 79.0 ± 3.0 kcal·mol^{-1}.

Electron–impact threshold measurements for SF_3^+ from SF_4 have been reported by Hildenbrand[3] and Glemser *et al.*[4] The measured appearance potentials (AP) are in good agreement and indicate AP(SF_3^+/SF_4) = 12.67 ± 0.1 eV. Combining this value with an upper limit for the ionization potential of SF_3(IP≤9.25 eV, *5*), we obtain a lower limit for $D_0°$ (SF_3−F) of 78.9 kcal·mol^{-1}.

Two upper limit values for $D_0°$ (SF_3−F) can be obtained from threshold measurements by Harland and Thynne[6] on dissociative attachment in SF_6 and SF_4. We combine their AP(F^-/SF_4) = 0.20 ± 0.05 eV with the electron affinity of F(EA = 3.399 eV,)[1] to obtain $D_0°$ (SF_3−F) ≤ 83.0 kcal·mol^{-1}. In addition, their appearance potentials[6] for the formation of F^- from SF_6 by two distinct processes are combined directly to give $D_0°$ (SF_3−F) ≤ 80.7 kcal·mol^{-1}.

The AP of SF_3^+ from SF_6 has been measured by electron–impact[3,7] and photoelectron spectroscopy.[8] These three threshold values are in agreement with AP(SF_3^+/SF_6) = 19.97 ± 0.1 eV. Assuming the ionization process to be SF_6(g) + e^- = SF_3^+(g) + 3 F(g) + 2 e^-, we combine the mean AP value with IP(SF_3) ≤ 9.25 eV[5] to obtain $\Delta_f H°$(SF_3, g, 0 K) < − 96.3 kcal·mol^{-1}. This result conflicts with all of the other available information; thus, we are led to conclude that the formation of SF_3^+ from SF_6 probably involves significant kinetic and/or excitation energies.

Heat Capacity and Entropy

We assume a molecular structure in which the four atoms form a slightly distorted T–shaped molecule having bond angles similar to those for ClF_3.[1] We eliminate a nonplanar pyramid (C_{3v} symmetry) as a plausible structure since recent ESR studies[9] show that the radical has only two equivalent fluorine nuclei. The equatorial and axial S–F bond lengths are assumed to be equal to those for SF_4.[1] The principal moments of inertia are: I_A = 5.8076 × 10^{-39}, I_B = 17.0895 × 10^{-39}, and I_C = 22.8971 × 10^{-39} g·cm^2.

The vibrational representation for the adopted structure is $3A_1 + 2B_1 + B_2$. We estimate the six fundamentals according to symmetry species by analogy with the frequencies and assignments for ClF_3 and SF_4.[1,10] Since several of the assignments for SF_4[11] are uncertain, more weight is given to the results for ClF_3. Bott[2] detected IR radiation in emission at 11.0–12.6 μ in SF_4/Ar mixtures which were shock–heated to temperatures above 2050 K. He attributed this radiation to SF_3, indicating that at least one fundamental lies in the region 794–909 cm^{-1}. We assume that the unpaired electron will form all doublet states, and we include an excited level at 25000 cm^{-1} by analogy with that which has been observed for SF_4^+.[8]

Wilkins[12] has previously reported thermal functions for SF_3 which cover an extended temperature range (0–6000 K). These functions are based on a pyramidal structure and vibrational frequencies obtained from estimated force constants. Since this structure now appears to be incorrect, our functions are believed to be more reliable.

References

[1]JANAF Thermochemical Tables: F(g), 9–30–65; SF_4(g) and SF_6(g), 6–30–76; F^-(g), 12–31–71; ClF_3(g), 9–30–65.
[2]J. F. Bott, J. Chem. Phys. **54**, 181 (1971).
[3]D. L. Hildenbrand, J. Phys. Chem. **77**, 897 (1973).
[4]O. Glemser, A. Muller, D. Bohler and B. Krebs, Z. Anorg. Allg. Chem. **357**, 184 (1968).
[5]F. C. Fehsenfeld, J. Chem. Phys. **54**, 438 (1971).

Continued from page 1216

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.599	−498.980	−498.980	INFINITE
100	37.533	232.606	334.474	−10.187	−500.617	−497.070	259.643
200	52.232	263.155	291.624	−5.694	−502.160	−492.868	128.724
250	58.316	275.488	287.187	−2.925	−502.664	−490.483	102.481
298.15	62.978	286.174	286.174	0.	−503.030	−488.103	85.514
300	63.136	286.564	286.176	0.117	−503.042	−488.010	84.970
350	66.875	296.590	286.959	3.371	−503.337	−485.480	72.454
400	69.763	305.717	288.742	6.790	−505.795	−482.825	63.050
450	72.006	314.069	291.099	10.336	−506.674	−479.909	55.706
500	73.764	321.750	293.785	13.982	−507.579	−476.884	49.820
600	76.276	335.437	299.615	21.494	−508.863	−470.617	40.971
700	77.927	347.328	305.600	29.209	−509.821	−464.163	34.636
800	79.060	357.812	311.484	37.062	−510.594	−457.586	29.877
900	79.867	367.173	317.161	45.010	−564.383	−449.839	26.108
1000	80.460	375.620	322.592	53.028	−563.757	−437.145	22.834
1100	80.907	383.311	327.767	61.098	−563.139	−424.514	20.159
1200	81.252	390.366	332.694	69.206	−562.536	−411.939	17.931
1300	81.524	396.881	337.384	77.346	−561.953	−399.413	16.049
1400	81.742	402.930	341.852	85.509	−561.393	−386.931	14.437
1500	81.918	408.576	346.115	93.693	−560.859	−374.488	13.041
1600	82.064	413.868	350.185	101.892	−560.351	−362.080	11.821
1700	82.185	418.847	354.079	110.105	−559.869	−349.703	10.745
1800	82.287	423.547	357.809	118.328	−559.411	−337.354	9.790
1900	82.374	427.999	361.387	126.562	−558.975	−325.029	8.936
2000	82.448	432.226	364.825	134.803	−558.557	−312.727	8.168
2100	82.512	436.250	368.131	143.051	−558.152	−300.446	7.473
2200	82.568	440.090	371.315	151.305	−557.755	−288.183	6.842
2300	82.616	443.761	374.386	159.564	−557.360	−275.939	6.267
2400	82.659	447.278	377.350	167.828	−556.962	−263.712	5.740
2500	82.698	450.654	380.215	176.096	−556.555	−251.501	5.255
2600	82.732	453.898	382.987	184.367	−556.132	−239.307	4.808
2700	82.762	457.021	385.672	192.642	−555.689	−227.130	4.394
2800	82.790	460.031	388.274	200.920	−555.221	−214.970	4.010
2900	82.816	462.937	390.799	209.200	−554.722	−202.826	3.653
3000	82.840	465.745	393.250	217.483	−554.190	−190.701	3.320
3100	82.862	468.461	395.633	225.768	−553.620	−178.594	3.009
3200	82.884	471.092	397.950	234.055	−553.010	−166.506	2.718
3300	82.905	473.643	400.205	242.345	−552.356	−154.438	2.445
3400	82.925	476.118	402.402	250.636	−551.657	−142.390	2.188
3500	82.945	478.523	404.543	258.930	−550.911	−130.364	1.946
3600	82.965	480.859	406.630	267.225	−550.118	−118.359	1.717
3700	82.986	483.133	408.667	275.523	−549.276	−106.377	1.502
3800	83.007	485.346	410.656	283.823	−548.385	−94.419	1.298
3900	83.029	487.503	412.599	292.124	−547.445	−82.484	1.105
4000	83.052	489.605	414.498	300.428	−546.456	−70.575	0.922
4100	83.076	491.656	416.355	308.735	−545.419	−58.691	0.748
4200	83.101	493.658	418.172	317.044	−544.333	−46.832	0.582
4300	83.127	495.614	419.950	325.355	−543.200	−35.001	0.425
4400	83.155	497.526	421.692	333.669	−542.021	−23.195	0.275
4500	83.185	499.395	423.398	341.986	−540.796	−11.417	0.133
4600	83.215	501.223	425.070	350.306	−539.526	0.332	−0.004
4700	83.248	503.013	426.709	358.629	−538.213	12.055	−0.134
4800	83.282	504.766	428.317	366.956	−536.858	23.748	−0.258
4900	83.317	506.484	429.895	375.286	−535.461	35.413	−0.378
5000	83.354	508.167	431.444	383.619	−534.024	47.049	−0.492
5100	83.393	509.818	432.964	391.957	−532.549	58.656	−0.601
5200	83.433	511.438	434.458	400.298	−531.036	70.234	−0.706
5300	83.475	513.028	435.925	408.643	−529.486	81.782	−0.806
5400	83.518	514.588	437.368	416.993	−527.901	93.300	−0.903
5500	83.563	516.121	438.786	425.347	−526.281	104.789	−0.995
5600	83.609	517.627	440.180	433.706	−524.628	116.248	−1.084
5700	83.657	519.108	441.552	442.069	−522.942	127.677	−1.170
5800	83.706	520.563	442.902	450.437	−521.226	139.076	−1.253
5900	83.756	521.994	444.230	458.810	−519.479	150.447	−1.332
6000	83.807	523.403	445.538	467.188	−517.703	161.786	−1.408

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 268.972 \pm 2.1\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 392.632 \pm 33.5\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 393.589 \pm 33.5\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	1
21777	1

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
938 (1)	914 (2)
530 (1)	411 (2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: S–F = 1.497 ± 0.03Å
Bond Angle: F–S–F = 97.51 ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 1.5584 \times 10^{-114}\ g^3\cdot cm^6$

Enthalpy of Formation

Glemser *et al.*[1] determined AP(SF_3^+) = 12.70 ± 0.03 eV from electron–impact measurements on SF_4. Their results[1] are confirmed by the subsequent measurements of Hildenbrand[2] who reported AP values of 12.63 ± 0.1 eV (from SF_4) and 12.8 eV (from SF_4 formed as a reaction product in $SF_6 + C$). From these results we arrive at a $\Delta_f H°(0\ K) = 293.1 \pm 2.3$ kcal·mol^{-1} (mean AP value) for the process $SF_4(g) + e^- = SF_3^+(g) + F(g) + 2\,e^-$. Assuming that the products are formed with no excess energies, we combine the value of $\Delta_f H°(0\ K)$ with JANAF enthalpy of formation[3] for SF_4 and F to obtain the result, $\Delta_f H°(SF_3^+, g, 0\ K) = 93.84 \pm 8.0$ kcal·mol^{-1} which is adopted. Our $\Delta_f H°$ value corresponds to $IP(SF_3) = 213.1 \pm 16.0$ kcal·mol^{-1} (9.24 ± 0.7 eV). This value is consistent with the observations of Fehsenfeld[4] who found no charge transfer reaction between NO and SF_3^+, suggesting that $IP(SF_3) < 9.25$ eV. In addition, we predict that $IP(SF_3) << IP(SF_2)$ due to a stabilization of the positive charge in the even–electron SF_3^+ cation by resonance structures such as $F_2S{=}F^+$. JANAF data[3] gives $IP(SF_2)–IP(SF_3) = 1.05$ eV which compares favorably with the 1–2 eV lowerings[5] observed in other di– and tri–fluoride molecules and radicals.

Paulett and Lustig [6] reported appearance potentials for SF_3^+ and SF_4+ from SF_5NF_2. We combine their results to arrive at $\Delta_f H°(0\ K) = 2.31 \pm 4.6$ kcal·mol^{-1} for the process $SF_4^+(g) + NF_3(g) = SF_3^+(g) + NF_2(g) + F_2(g)$ which leads to $\Delta_f H°(SF_3^+, g, 0\ K) = 61.5$ kcal·mol^{-1}. This value is in poor agreement with the adopted result, suggesting that the fragmentation processes involving SF_5NF_2 probably include unknown excess energy terms. Other reported fragment–ion appearance potentials for SF^+ have been previously analyzed (refer to $SF_3(g)$ and $SF_4(g)$ tables) and were shown to be seriously in error.

$\Delta_f H°(298.15\ K)$ is calculated to be 94.07 kcal·mol^{-1}. Using JANAF data.[3] we find that the primary bond dissociation energy $D_0°(SF_2^+–F)$ is 91.4 kcal·mol^{-1} which when compared with $D_0°$ values for SF_3 (67.3 kcal·mol^{-1}) and SF_3^- (106.4 kcal·mol^{-1}) indicates that the trend is $D_0°(SF_3^-) > D_0°(SF_3^+) >> D_0°(SF_3)$. The observed increased bond strengths in both ions relative to the SF_3 radical provide additional support to the view that the positive and negative charges are delocalized in the even–electron ions. Furthermore, available structural information shows that the bond length in SF_3^+ is the shortest S–F bond that has so far been reported. The heat of atomization, $\Delta_{at} H°(0\ K)$, and average bond dissociation energy are 265.9 kcal·mol^{-1} and 88.6 kcal·mol^{-1}, respectively.

Heat Capacity and Entropy

The molecular structure and vibrational frequencies are those measured by Gibler *et al.*[7] for the SF_3^+ ion in the solid SF_4BF_3 adduct. We adopt average values of the bond lengths and angles reported by Gibler *et al.*[7] since spectroscopic evidence[8] indicates that in crystal adducts the SF_3^+ symmetry is lowered somewhat as a result of flourine bridging with the anion. The adopted bond length is estimated to be within ±2.0% of the true gas–phase value, based on a comparison of structural data for gaseous and crystalline ClF_3.[9] The adopted bond angle (97.51°) is close to the gas–phase value (97.8 ± 0.2°) found for the isoelectronic molecule PF_3,[3] suggesting that the gas–phase bond angle for SF_3^+ is probably within ±0.5° of the adopted solid–state value. Our frequencies show good agreement with those determined by Azeem *et al.*[8] in their infrared and Raman studies of solid adducts of SF_4 with several fluoride acceptors. Their results[8] indicate that the SF_3^+ frequencies are relatively independent of the anion and are not significantly different when measured in the liquid state. Thus, we believe that the error introduced in the SF_3^+ thermal functions by use of solid–state frequencies is probably small. The individual moments of inertia are: $I_A = 1.5987 \times 10^{-38}$, $I_B = 9.8733 \times 10^{-39}$, and $I_C = 9.8733 \times 10^{-39}$ g·cm^2.

Delwiche[10] has reported an ionization efficiency curve for SF_3^+ which was obtained by retarded potential difference (RPD) measurements. This curve reveals the existence of an excited state, lying 2177 cm^{-1} above the ground state. We include this level and assume that the ground and excited states are both singlets since SF_3^+ has no unpaired electrons.

References

[1]O. Glemser, A. Muller, D. Bohler, and B. Krebs, Z. anorg. allg. Chem. **357**, 184 (1968).
[2]D. L. Hildenbrand, J. Phys. Chem. **77**, 897 (1973).
[3]JANAF Thermochemical Tables: $SF_4(g)$ and $SF_3(g)$, 6–30–76, F(g), 9–30–65; $SF_2^+(g)$, 12–31–76; $PF_3(g)$, 12–31–69.
[4]F. C. Fehsenfeld, J. Chem. Phys. **54**, 438 (1971).

Continued on page 1216

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.409	392.632		
100	35.082	221.200	311.734	−9.053			
200	45.909	248.643	273.799	−5.031			
250	51.457	259.492	269.872	−2.595			
298.15	56.223	268.972	268.972	0.	393.589	407.390	−71.373
300	56.393	269.321	268.974	0.104	393.603	407.476	−70.948
350	60.593	278.339	269.676	3.032	394.020	409.756	−61.153
400	64.076	286.665	271.286	6.151	392.303	412.059	−53.809
450	66.931	294.382	273.429	9.429	392.193	414.526	−48.117
500	69.262	301.559	275.887	12.836	392.089	417.016	−43.565
600	72.739	314.515	281.270	19.947	392.484	421.974	−36.736
700	75.120	325.917	286.850	27.347	393.288	426.830	−31.850
800	76.797	336.064	292.379	34.948	394.342	431.552	−28.177
900	78.014	345.183	297.748	42.691	342.426	437.213	−25.375
1000	78.919	353.452	302.912	50.540	344.963	447.609	−23.381
1100	79.609	361.008	307.855	58.468	347.518	457.750	−21.737
1200	80.145	367.958	312.578	66.457	350.079	467.658	−20.357
1300	80.570	374.391	317.088	74.493	352.638	477.352	−19.180
1400	80.911	380.375	321.397	82.568	355.187	486.850	−18.165
1500	81.189	385.967	325.518	90.673	357.722	496.166	−17.278
1600	81.419	391.214	329.461	98.804	360.240	505.313	−16.497
1700	81.611	396.156	333.241	106.956	362.740	514.304	−15.803
1800	81.773	400.825	336.867	115.125	365.222	523.148	−15.181
1900	81.911	405.250	340.351	123.310	367.688	531.854	−14.622
2000	82.029	409.455	343.702	131.507	370.140	540.431	−14.115
2100	82.131	413.460	346.929	139.715	372.584	548.885	−13.653
2200	82.220	417.283	350.040	147.933	375.023	557.223	−13.230
2300	82.299	420.939	353.044	156.159	377.464	565.451	−12.842
2400	82.368	424.443	355.947	164.392	379.910	573.571	−12.483
2500	82.430	427.807	358.754	172.632	382.368	581.590	−12.152
2600	82.486	431.041	361.473	180.878	384.843	589.510	−11.843
2700	82.537	434.155	364.107	189.129	387.341	597.335	−11.556
2800	82.584	437.158	366.663	197.385	389.867	605.066	−11.288
2900	82.628	440.056	369.144	205.646	392.424	612.707	−11.036
3000	82.670	442.858	371.555	213.911	395.017	620.259	−10.800
3100	82.709	445.570	373.899	222.180	397.649	627.723	−10.577
3200	82.748	448.196	376.180	230.453	400.324	635.102	−10.367
3300	82.786	450.743	378.401	238.729	403.044	642.397	−10.168
3400	82.824	453.215	380.565	247.010	405.810	649.609	−9.980
3500	82.862	455.616	382.675	255.294	408.625	656.739	−9.801
3600	82.900	457.951	384.734	263.582	411.490	663.788	−9.631
3700	82.939	460.223	386.744	271.874	414.405	670.756	−9.469
3800	82.979	462.436	388.707	280.170	417.370	677.644	−9.315
3900	83.021	464.592	390.625	288.470	420.387	684.455	−9.167
4000	83.063	466.694	392.500	296.774	423.455	691.187	−9.026
4100	83.108	468.746	394.335	305.083	426.573	697.841	−8.891
4200	83.154	470.749	396.131	313.396	429.742	704.420	−8.761
4300	83.201	472.706	397.889	321.714	432.960	710.921	−8.636
4400	83.250	474.619	399.611	330.036	436.226	717.348	−8.516
4500	83.301	476.491	401.299	338.364	439.540	723.700	−8.400
4600	83.354	478.322	402.953	346.696	442.901	729.978	−8.289
4700	83.408	480.115	404.576	355.034	446.308	736.182	−8.182
4800	83.464	481.872	406.168	363.378	449.759	742.313	−8.078
4900	83.522	483.594	407.731	371.727	453.253	748.372	−7.978
5000	83.580	485.282	409.265	380.082	456.790	754.359	−7.881
5100	83.641	486.937	410.772	388.443	460.368	760.275	−7.787
5200	83.702	488.562	412.252	396.811	463.986	766.120	−7.696
5300	83.765	490.157	413.707	405.184	467.642	771.896	−7.607
5400	83.829	491.723	415.137	413.564	471.336	777.602	−7.522
5500	83.894	493.262	416.544	421.950	475.066	783.239	−7.439
5600	83.960	494.774	417.927	430.343	478.832	788.808	−7.358
5700	84.026	496.261	419.289	438.742	482.632	794.309	−7.279
5800	84.093	497.723	420.628	447.148	486.465	799.744	−7.202
5900	84.161	499.161	421.947	455.560	490.330	805.113	−7.128
6000	84.228	500.576	423.246	463.980	494.226	810.415	−7.055

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K)$ = [280.198 ± 4.2] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -766.148 \pm 29.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -776.396 \pm 29.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[850](1)	[300](1)	[450](1)
[550](1)	[725](1)	[350](1)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: S–F* = [1.545] Å; S–F** = [1.646] Å
Bond Angles: F*–S–F** = [87]°; F**–S–F** = [174]°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.158616 × 10^{-114}] $g^3·cm^6$

Enthalpy of Formation

Using time–of–flight measurements, Harland and Thynne[1,2] have identified SF_3^- in the negative ion mass spectra of SF_4, SF_6, and SF_5Cl. Ionization efficiency curves obtained for a dissociative resonance capture process involving SF_4 were analyzed by a deconvolution procedure to give an appearance potential (AP) for SF_3^- of 0.70 ± 0.05 eV. Harland and Thynne[1] suggested that the process responsible for ion formation was $SF_4(g) + e^- = SF_3^-(g) + F(g)$. Assuming that the products are formed with no excess energies, we assign the measured value of AP to $\Delta_f H°$ of the proposed ion–formation process, and we obtain the adopted value, $\Delta_f H°(SF_3^-, g, 0\ K) = -183.1 \pm 7.0$ $kcal·mol^{-1}$ by combining $\Delta_f H°(0\ K)$ with JANAF enthalpies of formation[3] for SF_4 and F. Using this $\Delta_f H°$ value, we calculate $EA(SF_3) = 2.72 \pm 0.65$ eV and a fluoride–ion affinity (IA) of $IA(SF_2) = 52.7$ $kcal·mol^{-1}$. This value of EA is in excellent agreement with the result (EA = 2.71 eV) obtained by a magnetron technique,[4] suggesting that the electron–impact data are reliable and that the interpretation is correct.

The electron–impact AP for SF_3^- from SF_5Cl has been reported[2] as 7.0 ± 0.2 eV. Harland and Thynne[1,2] have suggested two ion formation processes; namely, (A) $SF_5Cl(g) + e^- = SF_3^-(g) + F(g) + FCl(g)$ and (B) $SF_5Cl(g) + e^- = SF_3^-(g) + 2\ F(g) + Cl(g)$. We eliminate (A) as a plausible process since it leads to $EA(SF_3) = -2.1$ eV. We are unable to reproduce the result (EA = 2.9 ± 0.1 eV) obtained for process (A) by Harland and Thynne[1] and believe their calculations to be in error. Process (B) leads to $EA(SF_3) = 0.5$ eV which suggests that $EA(SF_3) < EA(SF_4)$. We believe that this is very unlikely based on trends in the electron affinities for S–F species.[3] We conclude that process (B) very likely involves excess energy terms, amounting to about 2.2 eV.

$\Delta_f H°(298.15\ K)$ is calculated to be -185.6 $kcal·mol^{-1}$ at 298.15 K. In addition, we find that the primary bond dissociation energy $D_0°(SF_2-F)$ is 108.0 $kcal·mol^{-1}$ which when compared with JANAF $D_0°$ values for SF_3^+(91.4 $kcal·mol^{-1}$) and SF_3(67.3 $kcal·mol^{-1}$) indicates that the trend is $D_0°(SF_3^-) > D_0°(SF_3^+) >> D_0°(SF_3)$. The observed increased bond strengths in both ions relative to the SF_3 radical suggest that the positive and negative charges are delocalized in the even–electron ions. Further evidence supporting this view is presented on the SF_3^+ (g) table.[3] The enthalpy of atomization and average bond dissociation energy are 225.6 $kcal·mol^{-1}$ and 75.2 $kcal·mol^{-1}$, respectively.

Heat Capacity and Entropy

SF_3^- has 28 valence electrons, and according to the Walsh correlation diagram,[5] the ion should have a planar structure. We predict that this planar structure will have a slightly distorted T–shape (C_{2v} symmetry) by analogy with that for the isoelectronic molecule ClF_3.[3] As pointed out by Frey *et al.*,[6] the slightly distorted T–shaped structure of ClF_3 is closely related to the trigonal bipyramidal structure of SF_4. We estimate structural data for SF_3^- from that for SF_4[3] by considering the effects of removing one of its equatorial fluorine atoms. We assume that this removal process would produce no change in the S–F bond lengths and only minor changes in the bond angles. The structural data obtained in this way appear reasonable in comparison with that for ClF_3.[3] The individual moments of inertia are: $I_A = 5.5926 \times 10^{-39}$, $I_B = 17.0479 \times 10^{-39}$, and $I_C = 22.6406 \times 10^{-39}$ $g·cm^2$.

The vibrational representation for the adopted structure of SF_3^- is $3A_1 + 2B_1 + B_2$. We estimate the fundamentals according to symmetry species by analogy with the frequencies and assignments for ClF_3 and SF_4.[3,6] Since several of the assignments for SF_4[7] are uncertain, more weight is given to the results for ClF_3. We assume a singlet ground state (no unpaired electrons) and neglect excited states.

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[3]JANAF Thermochemical Tables: SF_4(g) and SF_3(g), 6–30–76; F(g) and ClF_3(g), 9–30–65; SF_3^+(g), SF^-(g), SF_2^-, SF_4^-(g), SF_5^-(g), 12–31–76; SF_6^-(g), 6–30–77.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.599	−766.148		
100	37.533	226.630	328.497	−10.187			
200	52.232	257.178	285.647	−5.694			
250	58.316	269.511	281.210	−2.925			
298.15	62.978	280.198	280.198	0.	−776.396	−753.432	131.998
300	63.136	280.588	280.199	0.117	−776.446	−753.289	131.159
350	66.875	290.613	280.982	3.371	−777.781	−749.323	111.830
400	69.763	299.740	282.765	6.790	−781.277	−745.082	97.298
450	72.006	308.092	285.122	10.336	−783.196	−740.451	85.949
500	73.764	315.773	287.808	13.982	−785.140	−735.594	76.847
600	76.276	329.461	293.638	21.494	−788.503	−725.362	63.148
700	77.927	341.351	299.623	29.209	−791.540	−714.595	53.324
800	79.060	351.835	305.508	37.062	−794.391	−703.406	45.928
900	79.867	361.196	311.184	45.010	−850.259	−690.787	40.092
1000	80.460	369.643	316.615	53.028	−851.711	−672.990	35.153
1100	80.907	377.334	321.790	61.098	−853.172	−655.047	31.106
1200	81.252	384.389	326.717	69.206	−854.647	−636.971	27.727
1300	81.524	390.904	331.407	77.346	−856.143	−618.771	24.863
1400	81.742	396.954	335.876	85.509	−857.662	−600.455	22.403
1500	81.918	402.599	340.138	93.693	−859.206	−582.029	20.268
1600	82.064	407.891	344.209	101.892	−860.777	−563.499	18.396
1700	82.185	412.870	348.103	110.105	−862.374	−544.871	16.742
1800	82.287	417.571	351.833	118.328	−863.995	−526.147	15.268
1900	82.374	422.022	355.411	126.562	−865.637	−507.334	13.948
2000	82.448	426.249	358.848	134.803	−867.298	−488.432	12.757
2100	82.512	430.273	362.154	143.051	−868.971	−469.448	11.677
2200	82.568	434.113	365.338	151.305	−870.653	−450.384	10.693
2300	82.616	437.785	368.409	159.564	−872.336	−431.243	9.794
2400	82.659	441.302	371.373	167.828	−874.017	−412.029	8.968
2500	82.697	444.677	374.238	176.096	−875.688	−392.745	8.206
2600	82.730	447.921	377.010	184.367	−877.345	−373.395	7.502
2700	82.760	451.044	379.695	192.642	−878.980	−353.981	6.848
2800	82.787	454.054	382.297	200.919	−880.591	−334.507	6.240
2900	82.811	456.959	384.822	209.199	−882.172	−314.976	5.673
3000	82.833	459.767	387.273	217.481	−883.719	−295.391	5.143
3100	82.852	462.484	389.656	225.765	−885.228	−275.755	4.646
3200	82.870	465.114	391.973	234.051	−886.697	−256.071	4.180
3300	82.886	467.665	394.228	242.339	−888.124	−236.342	3.741
3400	82.901	470.139	396.425	250.629	−889.505	−216.570	3.327
3500	82.915	472.543	398.566	258.920	−890.841	−196.758	2.936
3600	82.927	474.878	400.653	267.212	−892.130	−176.909	2.567
3700	82.939	477.151	402.690	275.505	−893.371	−157.024	2.217
3800	82.950	479.363	404.679	283.799	−894.564	−137.107	1.885
3900	82.959	481.518	406.621	292.095	−895.709	−117.159	1.569
4000	82.968	483.618	408.520	300.391	−896.806	−97.182	1.269
4100	82.977	485.667	410.377	308.689	−897.856	−77.178	0.983
4200	82.985	487.666	412.193	316.987	−898.860	−57.149	0.711
4300	82.992	489.619	413.971	325.285	−899.818	−37.098	0.451
4400	82.999	491.527	415.712	333.585	−900.732	−17.024	0.202
4500	83.005	493.393	417.418	341.885	−901.602	3.071	−0.036
4600	83.011	495.217	419.090	350.186	−902.430	23.184	−0.263
4700	83.017	497.002	420.728	358.487	−903.218	43.315	−0.481
4800	83.022	498.750	422.336	366.789	−903.965	63.462	−0.691
4900	83.027	500.462	423.913	375.092	−904.675	83.624	−0.891
5000	83.032	502.139	425.460	383.395	−905.347	103.800	−1.084
5100	83.036	503.784	426.980	391.698	−905.984	123.989	−1.270
5200	83.040	505.396	428.473	400.002	−906.587	144.191	−1.448
5300	83.044	506.978	429.939	408.306	−907.157	164.404	−1.620
5400	83.048	508.530	431.380	416.611	−907.696	184.627	−1.786
5500	83.051	510.054	432.797	424.916	−908.204	204.859	−1.946
5600	83.054	511.551	434.190	433.221	−908.683	225.102	−2.100
5700	83.057	513.021	435.560	441.526	−909.134	245.351	−2.248
5800	83.060	514.465	436.908	449.832	−909.558	265.609	−2.392
5900	83.063	515.885	438.235	458.139	−909.957	285.875	−2.531
6000	83.066	517.281	439.540	466.445	−910.331	306.146	−2.665

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$\Delta_a H°(0\ K) = 1758.954 \pm 16.7\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = [282.381 \pm 0.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1082.273 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1085.330 \pm 16.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X[^2A_1]$	0	[2]
$[^2E]$	44120	[2]

Vibratonal Frequencies and Degeneracies
ν, cm^{-1}
832 (1)
406 (1)
954 (2)
290 (2)

Point Group: C_{3v} $\sigma = 3$
Bond Distance: Si–F = [1.5624] Å
Bond Angle: F–Si–F = 109.4712°
Product of the Moments of Inertia: $I_A I_B I_C = [2.537436 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(SiF_3, g, 298.15\ K) = -259.4 \pm 2\ kcal \cdot mol^{-1}$ is derived from the mass spectrometric equilibrium constants determined by Farber[9] for the reaction $SiF_4(g) + SiF_2(g) = 2SiF_3(g)$. Our 2nd and 3rd law analysis of the ten points in the 1590 to 1782 K range, using auxiliary data,[1] gives $\Delta_r H°(298.15\ K) = 7.47 \pm 0.19\ kcal \cdot mol^{-1}$ (2nd law) and $\Delta_r H°(298.15\ K) = 7.61 \pm 0.04\ kcal \cdot mol^{-1}$ (3rd law) with a drift of 0.09 ± 0.11 cal $K^{-1} \cdot mol^{-1}$ (3rd law). The 3rd law heat of reaction leads to the adopted enthalpy of formation. The adopted value is consistent with the total pressure data above the silicon–magnesium fluoride system observed by Layne.[2] The value of $\Delta_f H° = -235 \pm 20\ kcal \cdot mol^{-1}$, derived by McDonald *et al.*[3] from appearance and ionization potentials and by Wang *et al.*[4] from appearance potentials and translational energies, appears to be too positive. A later paper by Franklin[10] suggests that the assumption of the fraction of active vibrations as a constant may have caused a bias of 15 $kcal \cdot mol^{-1}$ or more in the derived enthalpy of formation.

$\Delta_f H°(0\ K) = -258.7\ kcal \cdot mol^{-1}$ corresponds to $\Delta_a H°(0\ K) = 420.4\ kcal \cdot mol^{-1}$, using auxiliary data.[1] The average bond energies in $SiF_2(g)$, $SiF_3(g)$, and $SiF_4(g)$ are all within ~2 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The electronic levels are those tentatively assigned by Wang *et al.*[5] from emission spectral observations. The first excited state is designated as ^2E, rather than ^2B, as stated by So[11] based on ab initio Hartree–Fock calculations and group theory arguments. The vibrational frequencies are derived from matrix–isolation UV and IR spectra of Milligan *et al.*[6] They also determined the angle between the Si–F bonds and the three–fold axis to be $71 \pm 2°$ which is consistent with the adopted tetrahedral F–Si–F bond angle. Theoretical calculations[7,8,11] indicate that this angle should be somewhat less than the tetrahedral angle. Calculations based on a bond angle of 108° decrease $S°(298.15\ K)$ by 0.029 cal $K^{-1} \cdot mol^{-1}$. As suggested by Milligan *et al.*,[6] the Si–F bond length is assumed to be that in $SiHF_3$.[1] The C_{3v} structure is well established by ESR studies.[12,13] The principal moments of inertia are $I_A = I_B = 11.1156 \times 10^{-39}$ and $I_C = 20.5365 \times 10^{-39}\ g \cdot cm^2$.

References

[1]JANAF Thermochemical Tables: $SiHF_3(g)$ and $SiF_4(g)$, 6–30–76; F(g), 9–30–65; Si(g), 3–31–67; $SiF_2(g)$, 12–31–77.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.399	−1082.273	−1082.273	INFINITE
100	38.701	229.583	329.089	−9.951	−1083.451	−1080.471	564.380
200	50.816	260.374	287.566	−5.438	−1084.512	−1077.058	281.299
250	55.586	272.237	283.340	−2.776	−1084.953	−1075.143	224.639
298.15	59.625	282.381	282.381	0.	−1085.330	−1073.218	188.023
300	59.769	282.750	282.382	0.110	−1085.343	−1073.143	186.851
350	63.348	292.240	283.123	3.191	−1085.681	−1071.082	159.850
400	66.341	300.901	284.812	6.435	−1085.968	−1068.976	139.594
450	68.812	308.862	287.048	9.816	−1086.212	−1066.837	123.835
500	70.843	316.221	289.602	13.309	−1086.421	−1064.673	111.226
600	73.891	329.424	295.164	20.556	−1086.761	−1060.290	92.306
700	75.992	340.982	300.901	28.056	−1087.036	−1055.855	78.789
800	77.478	351.231	306.564	35.734	−1087.281	−1051.384	68.648
900	78.559	360.423	312.047	43.538	−1087.520	−1046.883	60.759
1000	79.365	368.743	317.307	51.436	−1087.768	−1042.354	54.447
1100	79.980	376.338	322.333	59.405	−1088.035	−1037.800	49.281
1200	80.458	383.318	327.128	67.428	−1088.330	−1033.221	44.975
1300	80.838	389.774	331.702	75.493	−1088.659	−1028.615	41.330
1400	81.143	395.776	336.067	83.593	−1089.027	−1023.983	38.205
1500	81.392	401.383	340.237	91.720	−1089.440	−1019.323	35.496
1600	81.598	406.643	344.224	99.870	−1089.899	−1014.634	33.124
1700	81.770	411.595	348.043	108.039	−1140.584	−1009.467	31.017
1800	81.915	416.273	351.705	116.223	−1140.909	−1001.745	29.070
1900	82.038	420.705	355.221	124.421	−1141.238	−994.005	27.327
2000	82.144	424.916	358.601	132.630	−1141.570	−986.247	25.758
2100	82.235	428.926	361.855	140.849	−1141.901	−978.473	24.338
2200	82.314	432.754	364.992	149.077	−1142.228	−970.683	23.047
2300	82.384	436.414	368.018	157.312	−1142.545	−962.878	21.868
2400	82.445	439.922	370.941	165.553	−1142.848	−955.060	20.786
2500	82.499	443.289	373.768	173.800	−1143.132	−947.230	19.791
2600	82.547	446.525	376.505	182.053	−1143.393	−939.388	18.873
2700	82.590	449.641	379.156	190.310	−1143.625	−931.538	18.022
2800	82.629	452.646	381.728	198.571	−1143.825	−923.679	17.231
2900	82.663	455.546	384.223	206.835	−1143.988	−915.813	16.496
3000	82.695	458.349	386.648	215.103	−1144.112	−907.943	15.809
3100	82.723	461.061	389.005	223.374	−1144.193	−900.070	15.166
3200	82.749	463.688	391.298	231.648	−1144.227	−892.194	14.564
3300	82.772	466.234	393.530	239.924	−1144.215	−884.318	13.998
3400	82.793	468.706	395.705	248.202	−1144.152	−876.443	13.465
3500	82.813	471.106	397.825	256.482	−1144.039	−868.571	12.963
3600	82.831	473.439	399.893	264.765	−1528.026	−850.241	12.337
3700	82.848	475.709	401.912	273.049	−1527.395	−831.423	11.738
3800	82.863	477.918	403.883	281.334	−1526.713	−812.622	11.170
3900	82.877	480.071	405.809	289.621	−1525.979	−793.839	10.632
4000	82.891	482.169	407.692	297.910	−1525.194	−775.076	10.121
4100	82.903	484.216	409.534	306.199	−1524.357	−756.334	9.636
4200	82.914	486.214	411.336	314.490	−1523.469	−737.612	9.174
4300	82.925	488.165	413.100	322.782	−1522.531	−718.912	8.733
4400	82.935	490.072	414.828	331.075	−1521.542	−700.235	8.313
4500	82.945	491.936	416.520	339.369	−1520.504	−681.580	7.912
4600	82.954	493.759	418.180	347.664	−1519.418	−662.949	7.528
4700	82.962	495.543	419.807	355.960	−1518.284	−644.342	7.161
4800	82.970	497.290	421.403	364.256	−1517.104	−625.760	6.810
4900	82.978	499.001	422.969	372.554	−1515.878	−607.203	6.473
5000	82.985	500.677	424.507	380.852	−1514.608	−588.672	6.150
5100	82.993	502.320	426.016	389.151	−1513.296	−570.166	5.840
5200	83.000	503.932	427.499	397.450	−1511.942	−551.686	5.542
5300	83.007	505.513	428.956	405.751	−1510.547	−533.233	5.255
5400	83.014	507.065	430.389	414.052	−1509.114	−514.807	4.980
5500	83.020	508.588	431.797	422.353	−1507.642	−496.407	4.714
5600	83.027	510.084	433.181	430.656	−1506.134	−478.034	4.459
5700	83.034	511.554	434.543	438.959	−1504.591	−459.690	4.213
5800	83.041	512.998	435.884	447.263	−1503.015	−441.372	3.975
5900	83.048	514.417	437.203	455.567	−1501.405	−423.081	3.746
6000	83.055	515.813	438.501	463.872	−1499.764	−404.818	3.524

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$\Delta_f H°$(0 K) = Unknown

$S°$(298.15 K) = [87.864 ± 12.6] J·K^{-1}·mol^{-1} $\Delta_f H°$(298.15 K) = −1435.530 ± 41.8 kJ·mol^{-1}

Enthalpy of Formation

Blocher and Hall[1] have reported vapor pressure data for the process 1/2 Hg_2F_2 + TiF_3(cr) = TiF_4(g) + Hg(l). 2nd and 3rd law analyses of their data give a 2nd law $\Delta_r H°$(298.15 K) of 23.7 kcal·mol^{-1}, a 3rd law $\Delta_r H°$(298.15 K) of 29.864, and a 3rd law drift of 11.9 ± 1.0 cal K^{-1}·mol^{-1}. The 3rd law value is combined with the JANAF values for the enthalpy of formation of Hg_2F_2(cr) and TiF_4(g) to give a $\Delta_f H°$(298.15 K) of −343.1 ± 10.0 kcal·mol^{-1}. The large uncertainty on $\Delta_f H°$(298.15 K) is assigned because Blocher and Hall were not able to identify TiF_3(cr) as the reaction product in the above process. They reported that the X-ray pattern of the products contained lines corresponding to Hg_2F_2(cr) plus others that did not correspond to TiF_3(cr).

Heat Capacity and Entropy

The heat capacity of TiF_3(cr) is estimated from the heat capacities of ZrF_4 and TiF_4. The entropy, $S°$(298.15 K), is estimated from CrF_3 and from ionic entropy contributions. Both methods give values which are within ±0.5 cal K^{-1}·mol^{-1} of the chosen value of 21 ± 3 cal K^{-1}·mol^{-1}.

Sublimation Data

The heat of sublimation is calculated from the vapor pressure data of Zmbov and Margrave.[2] Refer to TiF_3(g) table for details. The sublimation temperature is taken as temperature at which the fugacity is one atmosphere for the process TiF_3(cr) = TiF_3(g).

References

[1]J. N. Blocher, Jr. and E. N. Hall, J. Phys. Chem. **63**, 127 (1959).
[2]K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	92.023	87.864	87.864	0.	−1435.530	−1361.864	238.593
300	92.048	88.433	87.866	0.170	−1435.494	−1361.407	237.042
400	93.303	115.049	91.486	9.425	−1433.682	−1336.992	174.593
500	96.106	136.170	98.379	18.895	−1432.000	−1313.014	137.170
600	98.475	153.900	106.194	28.624	−1430.307	−1289.376	112.250
700	100.952	169.264	114.130	38.594	−1428.552	−1266.025	94.472
800	103.537	182.912	121.890	48.817	−1426.668	−1242.933	81.155
900	106.232	195.262	129.367	59.305	−1424.653	−1220.086	70.812
1000	109.035	206.598	136.531	70.067	−1422.546	−1197.469	62.549
1100	111.947	217.126	143.385	81.116	−1420.393	−1175.066	55.799
1200	114.968	226.996	149.945	92.461	−1422.162	−1152.740	50.177
1300	118.098	236.321	156.234	104.113	−1419.144	−1130.409	45.420
1400	121.336	245.191	162.274	116.084	−1415.918	−1108.319	41.352
1500	124.683	253.691	168.087	128.406	−1412.462	−1086.467	37.834
1600	125.520	261.764	173.692	140.916	−1408.949	−1064.849	34.764
1700	126.357	269.399	179.099	153.510	−1405.496	−1043.448	32.061
1800	127.194	276.645	184.319	166.187	−1402.112	−1022.249	29.665
1900	128.030	283.544	189.361	178.948	−1398.807	−1001.237	27.526
2000	128.867	290.133	194.236	191.793	−1410.275	−979.942	25.593

PREVIOUS: December 1967 CURRENT: June 1968

$S°(298.15\ K) = [291.440 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1184.510 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1188.674 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm-1	g_i
0	[2]
[600]	[2]
[1500]	[2]
[4000]	[2]
[10000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[800](1)
[450](1)
[750](2)
[300](2)

Ground State Quantum Weight: [2] $\sigma = 3$
Point Group: C_{3v}
Bond Distance: Ti–F = [1.9]Å
Bond Angle: F–Ti–F = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.509460 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiF_3(g)$ is calculated from that of $TiF_3(cr)$ and the enthalpy of sublimation determined from the mass spectrometric vapor pressure data of Zmbov and Margrave.[1] Their data give nine points over the temperature range 759–865 K.

2nd and 3rd law analyses of their data give a 2nd law $\Delta_{sub}H°(298.15\ K)$ of 61.2 ± 0.4 kcal·mol^{-1} and a 3rd law $\Delta_{sub}H°(298.15\ K)$ of 59.0 kcal·mol^{-1} with an entropy drift of −2.7 ± 0.5 units. The 3rd law value is used to calculate $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

The interatomic distance is estimated from those of $TiF_4(g)$, and $TiCl_4(g)$, and $TiCl_3(g)$. The pyramidal bond angle is estimated assuming $TiF_3(g)$ similar to the group V trihalides. The principal moments of inertia are $I_A = I_B = 16.7602 \times 10^{-39}$ and $I_C = 26.7330 \times 10^{-39}\ g \cdot cm^2$. The vibrational frequencies are estimated from those of PF_3 and AsF_3. The electronic levels are estimated from the levels of Ti^{+3}.[2]

References

[1]K. F. Zmbov and J. L. Margrave, J. Phys. Chem. **71**, 2893 (1967).
[2]C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, (1949).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.903	−1184.510	−1184.510	INFINITE
100	38.206	236.501	341.197	−10.470	−1185.998	−1183.266	618.075
200	53.531	267.655	297.086	−5.886	−1187.725	−1179.815	308.136
250	60.296	280.349	292.491	−3.035	−1188.291	−1177.768	246.081
298.15	65.585	291.440	291.440	0.	−1188.674	−1175.704	205.978
300	65.764	291.846	291.441	0.121	−1188.687	−1175.623	204.694
350	70.016	302.317	292.258	3.521	−1188.958	−1173.423	175.124
400	73.278	311.889	294.123	7.107	−1189.144	−1171.191	152.942
450	75.772	320.671	296.591	10.836	−1189.273	−1168.938	135.687
500	77.684	328.757	299.409	14.674	−1189.365	−1166.673	121.882
600	80.293	343.172	305.531	22.584	−1189.491	−1162.122	101.172
700	81.878	355.678	311.822	30.699	−1189.591	−1157.553	86.378
800	82.877	366.681	318.006	38.940	−1189.689	−1152.970	75.281
900	83.536	376.483	323.968	47.263	−1189.839	−1148.372	66.650
1000	83.989	385.309	329.669	55.641	−1190.117	−1143.751	59.743
1100	84.314	393.330	335.097	64.057	−1190.596	−1139.093	54.091
1200	84.554	400.678	340.260	72.501	−1195.265	−1134.262	49.373
1300	84.733	407.453	345.172	80.966	−1195.435	−1129.172	45.371
1400	84.869	413.738	349.847	89.446	−1195.699	−1124.066	41.939
1500	84.973	419.597	354.304	97.938	−1196.073	−1118.937	38.965
1600	85.052	425.083	358.558	106.440	−1196.569	−1113.779	36.361
1700	85.112	430.241	362.625	114.948	−1197.202	−1108.586	34.063
1800	85.157	435.108	366.518	123.462	−1197.981	−1103.351	32.018
1900	85.192	439.713	370.250	131.979	−1198.920	−1098.070	30.188
2000	85.218	444.083	373.833	140.500	−1214.713	−1092.280	28.527
2100	85.238	448.241	377.278	149.023	−1216.744	−1086.109	27.015
2200	85.253	452.207	380.595	157.547	−1218.778	−1079.840	25.639
2300	85.265	455.997	383.791	166.073	−1220.808	−1073.479	24.379
2400	85.273	459.626	386.876	174.600	−1222.830	−1067.030	23.223
2500	85.280	463.107	389.856	183.128	−1224.838	−1060.497	22.158
2600	85.285	466.452	392.738	191.656	−1226.827	−1053.884	21.173
2700	85.288	469.671	395.528	200.184	−1228.791	−1047.195	20.259
2800	85.290	472.773	398.232	208.713	−1230.728	−1040.434	19.410
2900	85.291	475.765	400.854	217.242	−1232.631	−1033.604	18.617
3000	85.290	478.657	403.400	225.771	−1234.497	−1026.709	17.877
3100	85.289	481.454	405.873	234.300	−1236.324	−1019.753	17.183
3200	85.287	484.161	408.277	242.829	−1238.108	−1012.738	16.531
3300	85.283	486.786	410.617	251.358	−1239.847	−1005.668	15.918
3400	85.279	489.332	412.895	259.886	−1241.539	−998.546	15.341
3500	85.274	491.804	415.114	268.413	−1243.183	−991.376	14.795
3600	85.268	494.206	417.278	276.941	−1244.777	−984.158	14.280
3700	85.260	496.542	419.389	285.467	−1655.420	−969.109	13.681
3800	85.252	498.816	421.449	293.993	−1655.680	−950.557	13.066
3900	85.243	501.030	423.461	302.517	−1655.944	−931.997	12.483
4000	85.234	503.188	425.428	311.041	−1656.213	−913.431	11.928
4100	85.223	505.292	427.350	319.564	−1656.484	−894.859	11.401
4200	85.212	507.346	429.230	328.086	−1656.756	−876.279	10.898
4300	85.199	509.351	431.070	336.606	−1657.030	−857.693	10.419
4400	85.187	511.309	432.872	345.126	−1657.302	−839.101	9.961
4500	85.173	513.224	434.636	353.644	−1657.574	−820.502	9.524
4600	85.159	515.096	436.365	362.160	−1657.844	−801.897	9.106
4700	85.144	516.927	438.060	370.675	−1658.110	−783.287	8.705
4800	85.129	518.719	439.722	379.189	−1658.373	−764.671	8.321
4900	85.113	520.474	441.352	387.701	−1658.630	−746.049	7.953
5000	85.097	522.194	442.951	396.212	−1658.883	−727.423	7.599
5100	85.080	523.879	444.522	404.721	−1659.128	−708.791	7.260
5200	85.063	525.531	446.064	413.228	−1659.367	−690.154	6.933
5300	85.046	527.151	447.579	421.733	−1659.597	−671.513	6.618
5400	85.028	528.740	449.067	430.237	−1659.819	−652.869	6.315
5500	85.010	530.300	450.530	438.739	−1660.031	−634.220	6.023
5600	84.992	531.832	451.968	447.239	−1660.233	−615.566	5.742
5700	84.974	533.336	453.382	455.737	−1660.424	−596.910	5.470
5800	84.955	534.814	454.774	464.234	−1660.603	−578.251	5.208
5900	84.937	536.266	456.142	472.728	−1660.770	−559.587	4.954
6000	84.918	537.693	457.490	481.221	−1660.924	−540.922	4.709

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [87.864 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = [-1401.640 \pm 83.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation at 298.15 K for ZrF_3(cr) was reported as $-350\ kcal \cdot mol^{-1}$ [1] which was estimated by Brewer.[2] Based on this $\Delta_f H°(298.15\ K)$ value, the crystal lattice energy (U) of ZrF_3(cr) is calculated to be 1371 $kcal \cdot mol^{-1}$ by the Born–Haber cycle method.[3] For the evaluation of U from the relation: $\Delta_f H°(ZrF_3, cr, 298.15\ K) = \Sigma I_i + L - 3(E - D/2) - U$, the following values ($kcal \cdot mol^{-1}$) are used: ΣI_i (the sum of the successive three ionization potentials of Zr metal) = 1055[4] L (the enthalpy of sublimation of Zr metal) = 148.3[5] E (the electron affinity of fluorine) = 79.5[6] and D (the enthalpy of dissociation of fluorine) = 37.7).[5] The derived value of $U(ZrF_3, cr)$ is of the same order of magnitude of the value, $U(TiF_3, cr)$ = 1376 $kcal \cdot mol^{-1}$, calculated by Cavell and Clark[3] using the same method.

From $\Delta_f H°(ZrF_3, cr, 298.15\ K) = -350\ kcal \cdot mol^{-1}$, the derived $\Delta_f G(ZrF_3, cr)$ values indicate that ZrF_3(cr) is thermodynamically more stable than the system ZrF_4(cr) + Zr(cr). For example, in the temperature range 298–1200 K, the Gibbs energy changes for the reaction 3 ZrF_4(cr) + Zr(cr) = 4 ZrF_3(cr) are about $-29 \pm 1\ kcal \cdot mol^{-1}$. However, this product ZrF_3(cr) has never been prepared successfully from this reaction in many laboratories.[7] In order to make the $\Delta_f G°(ZrF_3, cr, 298.15\ K)$ values consistent with the experimental observations, the enthalpy of formation of ZrF_3(cr) is arbitrarily adjusted to be 15 $kcal \cdot mol^{-1}$ less negative, or $\Delta_f H°(ZrF_3, cr, 298.15\ K) = -335\ kcal \cdot mol^{-1}$ with uncertainty as high as $\pm 20\ kcal \cdot mol^{-1}$. This value is tentatively adopted.

The Gibbs energy changes for the reaction 3 $ZrF_4(g)$ + Zr(cr) = 4 ZrF_3(cr) are evaluated to be very favorable at temperatures below 900 K, e.g., $\Delta_r G° = -93.9$ and $-6.7\ kcal \cdot mol^{-1}$ at 298 and 900 K, respectively. But according to Larsen and Leddy[8] this reaction does not occur in the temperature range 473–973 K, and pressure range 5–15 atm. One possible explanation is that these heterogeneous reactants may require very high activation energy to initiate the reaction. In other words, this reaction is unfavorable at these temperatures probably due to kinetic rather than thermodynamic reasons.

Heat Capacity and Entropy

The heat capacities of ZrF_3(cr) are not available in the literature. They are estimated from the $C_p°$ values of ZrF_4(cr) by deduction of one F atom $C_p°$ contributions which are calculated as $1/4[C_p°(ZrF_4, cr) - C_p°(Zr, cr)]$. The $S°(298.15\ K)$ is taken to be $1/2[S°(ZrF_4, cr, 298.15\ K) + S°(ZrF_2, cr, 298.15\ K)]$ of which the value $S°(ZrF_2, cr, 298.15\ K)$ is estimated; refer to ZrF_2(cr) table for details.

Sublimation Data

The difference between $\Delta_f H°(298.15\ K)$ for $ZrF_3(g)$ and ZrF_3(cr) is $\Delta_{sub} H°(298.15\ K)$. Actually ZrF_3(cr) is thermodynamically unstable, e.g., the Gibbs energy changes for the reaction 4 ZrF_3(cr) = 3 ZrF_4(cr) + Zr(cr) are about $-30\ kcal \cdot mol^{-1}$ in the temperature range 298–1400 K. In other words, ZrF_3(cr) decomposes into ZrF_4(cr) + Zr(cr) before sublimation occurs.

References

[1] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[2] L. Brewer, University of California, Berkeley, California, personal communication; cited in reference 1.
[3] R. G. Cavell and H. C. Clark, J. Chem. Soc. **1965**, 444 (1965).
[4] C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, Vol. III, (1958).
[5] JANAF Thermochemical Tables: Zr(cr), 12–31–67; F(g), 9–30–65.
[6] U. S. Nat. Bur. Stand. Report 8628, (1965).
[7] T. B. Douglas, U. S. Nat. Bur. Stand., personal communication, (July 10, 1961).
[8] E. M. Larsen and J. J. Leddy, J. Amer. Chem. Soc. **78**, 5983 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	83.680	87.864	87.864	0.	−1401.640	−1325.555	232.232
300	84.308	88.384	87.866	0.155	−1401.618	−1325.083	230.718
400	91.839	113.729	91.270	8.984	−1400.178	−1299.777	169.733
500	96.860	134.789	97.927	18.431	−1398.404	−1274.876	133.185
600	100.416	152.778	105.606	28.303	−1396.433	−1250.353	108.853
700	102.926	168.451	113.489	38.474	−1394.357	−1226.170	91.498
800	105.018	182.339	121.244	48.876	−1392.218	−1202.289	78.501
900	106.483	194.795	128.736	59.453	−1390.070	−1178.677	68.409
1000	107.738	206.083	135.915	70.168	−1387.946	−1155.303	60.347
1100	108.491	216.390	142.769	80.983	−1385.882	−1132.139	53.761
1200	108.868	225.847	149.304	91.851	−1387.635	−1108.937	48.271
1300	109.202	234.574	155.532	102.755	−1385.253	−1085.809	43.628
1400	109.495	242.678	161.471	113.690	−1382.915	−1062.863	39.656
1500	109.746	250.241	167.139	124.653	−1380.632	−1040.082	36.219

PREVIOUS: June 1968 (1 atm) CURRENT: June 1968 (1 bar)

$S°(298.15\ K) = [305.742 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1101.784 \pm 20.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1105.413 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[1800]	[2]
[4500]	[2]
[12000]	[2]
[30000]	[2]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[611](1)	[655](2)
[203](1)	[240](2)

Ground State Quantum Weight: [2] σ = [3]
Point Group: C_{3v}
Bond Distance: Zr–F = [1.93]Å
Bond Angle: F–Zr–F = [105]°
Product of the Moments of Inertia: $I_A I_B I_C = [9.87893 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Murad and Hildenbrand[1] studied the gaseous equilibria involving ZrF_4, ZrF_3, ZrF_2, Ca and CaF. These species were generated at high temperatures in a graphite Knudsen cell containing powdered calcium fluoride and elemental zirconium. Ion intensities were measured 3 eV above threshold over the temperature range 1665–1747 K and the equilibrium constants were calculated for the following isomolecular reaction: $Ca(g) + ZrF_4(g) = CaF(g) + ZrF_3(g)$. Based on the reported equilibrum constants the enthalpy change of this reaction is evaluated by the 2nd and 3rd law methods to be -8.0 ± 25 and 28.0 ± 2 kcal·mol^{-1}, respectively. The 3rd law entropy drift is 20 ± 15 cal K^{-1}·mol^{-1}. Using the 3rd law value and $\Delta_f H°(298.15\ K) = 42.85 \pm 0.3$, -400.0 ± 0.5, and -65.0 ± 2 kcal·mol^{-1} for Ca(g), ZrF_4(g), and CaF(g) we obtain $\Delta_f H°(ZrF_3, g, 298.15\ K) = -264.2 \pm 5$ kcal·mol^{-1} which is adopted. Employing slightly different Gibbs energy functions and $\Delta_f H°(298.15\ K)$ values for the products and reactants, Murad and Hildenbrand[1] evaluated the 3rd law enthalpy change of the above reaction as 29.4 ± 5 and $\Delta_f H°(ZrF_3, g, 298.15\ K) = -262 \pm 5$ kcal·mol^{-1} which are in reasonable agreement with the values adopted here.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that of TiF_3(g). The Zr–F bond distance is estimated by comparison with those for ZrF_4(g) and ZrF_2(g). The F–Zr–F bond angle is taken to be slightly bigger than the F–Ti–F bond angle in TiF_3(g) molecule. The vibrational frequencies are calculated by the valence force method[2] using force constants transferred from those for the ZrF_2(g) molecule. The three principal moments of inertia are: $I_A = I_B = 18.2815 \times 10^{-39}$ and $I_C = 29.5856 \times 10^{-39}$ g·cm^2. The electronic levels are estimated to be three times higher than those of TiF_3(g), based on the ratio of the first splitting interval between Ti(IV) and Zr(IV), given by Moore.[3] The quantum weights are assumed to be the same as those of TiF_3(g).

References

[1]E. Murad and D. L. Hildenbrand, J. Chem. Phys. **45**, 4751 (1966).
[2]G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, (1945).
[3]C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, Vol. III, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.106	−1101.784	−1101.784	INFINITE
100	44.437	244.931	359.453	−11.452	−1103.377	−1100.909	575.056
200	58.700	280.460	311.683	−6.245	−1104.756	−1097.842	286.727
250	63.889	294.138	306.838	−3.175	−1105.156	−1096.064	229.010
298.15	67.832	305.742	305.742	0.	−1105.413	−1094.288	191.715
300	67.965	306.162	305.743	0.126	−1105.421	−1094.219	190.521
350	71.158	316.888	306.583	3.607	−1105.594	−1092.338	163.022
400	73.704	326.562	308.486	7.231	−1105.704	−1090.436	142.396
450	75.781	335.367	310.991	10.969	−1105.770	−1088.523	126.352
500	77.506	343.444	313.838	14.803	−1105.805	−1086.604	113.517
600	80.188	357.825	320.000	22.695	−1105.814	−1082.762	94.263
700	82.126	370.340	326.317	30.816	−1105.787	−1078.922	80.510
800	83.534	381.403	332.525	39.103	−1105.765	−1075.086	70.196
900	84.561	391.304	338.515	47.510	−1105.786	−1071.251	62.174
1000	85.314	400.255	344.249	56.006	−1105.881	−1067.409	55.756
1100	85.869	408.413	349.717	64.566	−1106.072	−1063.554	50.504
1200	86.277	415.903	354.924	73.175	−1110.084	−1059.454	46.117
1300	86.576	422.822	359.885	81.818	−1109.963	−1055.240	42.400
1400	86.791	429.246	364.612	90.487	−1109.891	−1051.034	39.215
1500	86.941	435.239	369.123	99.174	−1109.883	−1046.831	36.454
1600	87.040	440.854	373.433	107.873	−1109.954	−1042.625	34.038
1700	87.100	446.132	377.556	116.581	−1110.115	−1038.413	31.907
1800	87.129	451.112	381.505	125.292	−1110.379	−1034.188	30.011
1900	87.134	455.823	385.294	134.006	−1110.754	−1029.946	28.315
2000	87.122	460.292	388.933	142.719	−1111.250	−1025.680	26.788
2100	87.097	464.542	392.433	151.430	−1111.873	−1021.387	25.406
2200	87.062	468.593	395.803	160.138	−1133.952	−1016.315	24.130
2300	87.021	472.462	399.053	168.842	−1135.264	−1010.938	22.959
2400	86.976	476.165	402.189	177.542	−1136.573	−1005.505	21.884
2500	86.928	479.715	405.220	186.237	−1137.874	−1000.017	20.894
2600	86.880	483.123	408.151	194.927	−1139.161	−994.477	19.979
2700	86.832	486.401	410.989	203.613	−1140.429	−988.888	19.131
2800	86.784	489.558	413.739	212.294	−1141.674	−983.253	18.343
2900	86.738	492.602	416.406	220.970	−1142.890	−977.573	17.608
3000	86.693	495.542	418.995	229.641	−1144.074	−971.853	16.921
3100	86.651	498.384	421.511	238.309	−1145.223	−966.093	16.279
3200	86.610	501.135	423.956	246.972	−1146.333	−960.297	15.675
3300	86.570	503.799	426.335	255.631	−1147.402	−954.467	15.108
3400	86.533	506.383	428.652	264.286	−1148.427	−948.605	14.574
3500	86.497	508.891	430.909	272.937	−1149.407	−942.713	14.069
3600	86.463	511.327	433.109	281.585	−1150.341	−936.794	13.593
3700	86.431	513.696	435.255	290.230	−1151.227	−930.850	13.141
3800	86.400	516.000	437.350	298.871	−1152.066	−924.883	12.713
3900	86.370	518.244	439.395	307.510	−1152.856	−918.893	12.307
4000	86.341	520.430	441.394	316.145	−1153.598	−912.885	11.921
4100	86.313	522.562	443.348	324.778	−1154.291	−906.859	11.554
4200	86.287	524.642	445.259	333.408	−1154.937	−900.815	11.203
4300	86.261	526.672	447.129	342.036	−1155.536	−894.758	10.869
4400	86.236	528.655	448.959	350.660	−1156.088	−888.687	10.550
4500	86.212	530.592	450.752	359.283	−1156.595	−882.603	10.245
4600	86.189	532.487	452.508	367.903	−1157.056	−876.510	9.953
4700	86.166	534.340	454.229	376.521	−1157.474	−870.406	9.673
4800	86.144	536.154	455.917	385.136	−1718.785	−852.677	9.279
4900	86.123	537.930	457.573	393.749	−1718.770	−834.633	8.897
5000	86.102	539.670	459.198	402.361	−1718.730	−816.590	8.531
5100	86.082	541.375	460.792	410.970	−1718.667	−798.548	8.179
5200	86.062	543.046	462.358	419.577	−1718.579	−780.507	7.840
5300	86.043	544.685	463.896	428.182	−1718.467	−762.468	7.515
5400	86.024	546.293	465.407	436.786	−1718.330	−744.432	7.201
5500	86.006	547.872	466.892	445.387	−1718.168	−726.399	6.899
5600	85.989	549.421	468.352	453.987	−1717.980	−708.368	6.607
5700	85.971	550.943	469.788	462.585	−1717.767	−690.341	6.326
5800	85.955	552.438	471.200	471.181	−1717.528	−672.318	6.055
5900	85.938	553.907	472.589	479.776	−1717.264	−654.299	5.793
6000	85.923	555.351	473.957	488.369	−1716.974	−636.286	5.539

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = [349.210 \pm 16.7]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1171.786 \pm -20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1183.821 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[202](4)
[53](2)
[962](4)
[552](4)
[3060](4)

Ground State Quantum Weight: 1 σ = [4]
Point Group: C_4
Bond Distance: F–F = [2.5] Å
Product of the Moments of Inertia: $I_A I_B I_C = [1.790364 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of 4 HF(g) → H_4F_4(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p^°$ between −20 and 100 °C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3,4, ... for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta H°$ and $\Delta S°$. At n = 4 their 2nd law values differed by 4.2 $kcal·mol^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 1.5 $kcal·mol^{-1}$. Using $\Delta_f H°(298.15\ K) = -22.38\ kcal·mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of H_4F_4(g).

Heat Capacity and Entropy

The molecular structure of H_4F_4 was assumed as planar with the F atoms forming the vertices of a square and with the H atoms also lying in the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular-orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X-ray studies of solid HF (F–F = 2.49 Å) and agrees with the 2.52Å which Janzen and Bartell[6] determined for the gaseous polymers by electron diffraction. The low F–bending frequency (53 cm^{-1}) was taken from Boutin *et al.*[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights,[13] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−22.549	−1171.786	−1171.786	INFINITE
100	67.044	256.376	431.836	−17.546	−1178.595	−1150.013	600.705
200	89.508	310.130	358.442	−9.662	−1181.957	−1119.957	292.503
250	98.807	331.124	350.923	−4.950	−1183.042	−1104.326	230.736
298.15	106.585	349.210	349.210	0.	−1183.821	−1089.090	190.804
300	106.860	349.870	349.212	0.197	−1183.846	−1088.502	189.525
350	113.638	366.868	350.539	5.715	−1184.404	−1072.565	160.072
400	119.262	382.421	353.566	11.542	−1184.752	−1056.562	137.973
450	123.931	396.746	357.578	17.625	−1184.923	−1040.526	120.781
500	127.857	410.012	362.167	23.923	−1184.948	−1024.479	107.027
600	134.181	433.907	372.177	37.038	−1184.637	−992.407	86.397
700	139.264	454.985	382.530	50.718	−1183.937	−960.419	71.667
800	143.630	473.872	392.788	64.868	−1182.911	−928.555	60.628
900	147.504	491.017	402.764	79.428	−1181.609	−896.835	52.051
1000	150.977	506.741	412.386	94.355	−1180.069	−865.275	45.197
1100	154.091	521.280	421.633	109.611	−1178.330	−833.878	39.598
1200	156.873	534.809	430.507	125.162	−1176.428	−802.647	34.938
1300	159.350	547.465	439.022	140.976	−1174.394	−771.580	31.002
1400	161.549	559.356	447.197	157.023	−1172.257	−740.674	27.635
1500	163.500	570.570	455.052	173.277	−1170.039	−709.924	24.722
1600	165.229	581.178	462.606	189.715	−1167.761	−679.323	22.178
1700	166.762	591.242	469.880	206.316	−1165.437	−648.867	19.937
1800	168.124	600.813	476.890	223.062	−1163.079	−618.548	17.950
1900	169.336	609.937	483.654	239.936	−1160.695	−588.362	16.175
2000	170.416	618.650	490.188	256.925	−1158.288	−558.300	14.581
2100	171.382	626.989	496.505	274.016	−1155.862	−528.361	13.142
2200	172.246	634.982	502.619	291.198	−1153.417	−498.537	11.837
2300	173.023	642.656	508.542	308.462	−1150.951	−468.825	10.647
2400	173.722	650.035	514.285	325.800	−1148.462	−439.221	9.559
2500	174.353	657.139	519.858	343.204	−1145.947	−409.720	8.561
2600	174.924	663.989	525.270	360.669	−1143.403	−380.322	7.641
2700	175.442	670.600	530.531	378.187	−1140.826	−351.021	6.791
2800	175.913	676.990	535.648	395.755	−1138.211	−321.817	6.004
2900	176.343	683.170	540.629	413.369	−1135.557	−292.706	5.272
3000	176.736	689.155	545.481	431.023	−1132.860	−263.689	4.591
3100	177.095	694.956	550.210	448.715	−1130.117	−234.762	3.956
3200	177.425	700.584	554.821	466.441	−1127.327	−205.924	3.361
3300	177.728	706.048	559.322	484.199	−1124.487	−177.173	2.804
3400	178.008	711.358	563.716	501.986	−1121.598	−148.510	2.282
3500	178.266	716.522	568.008	519.799	−1118.657	−119.933	1.790
3600	178.504	721.547	572.204	537.638	−1115.665	−91.439	1.327
3700	178.726	726.441	576.306	555.500	−1112.622	−63.031	0.890
3800	178.931	731.210	580.320	573.383	−1109.529	−34.705	0.477
3900	179.122	735.861	584.249	591.285	−1106.386	−6.460	0.087
4000	179.299	740.398	588.096	609.207	−1103.193	21.702	−0.283
4100	179.465	744.827	591.865	627.145	−1099.953	49.784	−0.634
4200	179.620	749.154	595.559	645.099	−1096.667	77.788	−0.967
4300	179.765	753.382	599.180	663.069	−1093.336	105.711	−1.284
4400	179.900	757.516	602.732	681.052	−1089.961	133.557	−1.586
4500	180.027	761.561	606.217	699.048	−1086.543	161.326	−1.873
4600	180.147	765.519	609.637	717.057	−1083.085	189.018	−2.146
4700	180.259	769.394	612.995	735.077	−1079.588	216.635	−2.408
4800	180.364	773.191	616.293	753.109	−1076.052	244.178	−2.657
4900	180.464	776.911	619.533	771.150	−1072.480	271.644	−2.896
5000	180.558	780.557	622.717	789.201	−1068.871	299.040	−3.124
5100	180.647	784.134	625.847	807.262	−1065.228	326.361	−3.343
5200	180.730	787.642	628.925	825.330	−1061.551	353.612	−3.552
5300	180.810	791.086	631.952	843.407	−1057.841	380.791	−3.753
5400	180.885	794.466	634.931	861.492	−1054.098	407.900	−3.946
5500	180.956	797.786	637.862	879.584	−1050.323	434.938	−4.131
5600	181.023	801.047	640.747	897.683	−1046.515	461.910	−4.309
5700	181.088	804.252	643.587	915.789	−1042.676	488.812	−4.479
5800	181.149	807.402	646.384	933.901	−1038.806	515.646	−4.644
5900	181.207	810.499	649.140	952.018	−1034.903	542.414	−4.802
6000	181.262	813.545	651.855	970.142	−1030.968	569.114	−4.955

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = [337.014 \pm 20.9]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1711.866 \pm 20.9$ (or ± 37.7) $kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1718.369 \pm 20.9$ (or ± 37.7) $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
585(1)	[235](1)	487(1)
353(1)	[220](1)	[220](1)
[400](1)	[240](1)	747(1)
[508](1)	[200](1)	450(1)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: $[D_{2h}]$

Bond Distances: Mg–F = [1.77] Å; Mg–F' = [1.96] Å

Bond Angles: Mg–F'–Mg = [90]°; F'–Mg–F' = [90]°; F–Mg–F' = [135]°

(F' = Ring Fluorine)

Product of Moments of Inertia: $I_A I_B I_C = [8.5873 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Berkowitz and Marquart[1] have found approximately 1% dimer in the equilibrium vapor over MgF_2(cr) at about 1400 K by mass spectrometry. Independent measurements which are discussed elsewhere (See MgF_2(g) table) support their results. Berkowitz and Marquart[1] reported a 2nd law $\Delta_f H°$(1440 K) of 30 kcal·mol^{-1} for the reaction MgF_2(cr) + MgF_2(g) = Mg_2F_2(g). This value corrected to 298.15 K gives $\Delta_f H° = 31.7$ kcal·mol^{-1} which leads to $\Delta_f H°(Mg_2F_4, g, 298.15\ K) = -410.7$ kcal·mol^{-1}. The corresponding heat of dimerization at 298.15 K is −63.3 kcal·mol^{-1}. Berkowitz and Marquart[1] also reported approximate absolute pressures for MgF_2(g) and Mg_2F_4(g) at 1429 K. A 3rd law analysis of these reported pressures gives $\Delta_r H°(298.15\ K)$ of −69.5 kcal·mol^{-1} for the process $2MgF_2(g) = Mg_2F_4(g)$, or $\Delta_f H°(Mg_2F_4, g, 298.15\ K) = -416.9$ kcal·mol^{-1}. We prefer the 2nd law result $\Delta_f H° = 410.7$ kcal·mol^{-1} since the else negative (−63.3 kcal·mol^{-1}) heat of dimerization is more consistent with the dimerization energies for the alkali metal fluorides.[2] The uncertainty in $\Delta_f H°$ is estimated as ±5.0 kcal·mol^{-1}, however, we also include an alternate uncertainty (±9 kcal·mol^{-1}) to cover the possibility that M_gF_2(g) is linear.[2]

Heat Capacity and Entropy

The dimer is assumed to have a bridge–bond structure of D_{2h} symmetry similar to that suggested by Thompson and Carlson[3] for the dimers of several transition metal dichlorides. The two outer Mg–F bond lengths are assumed to be the same as that for MgF_2.[2] The four ring Mg–F' bond lengths are assumed to be 10% longer. The four atoms which lie in the ring form a square. The F'–MgF' bond angle is estimated as 135°. The individual moments of inertia are: $I_A = 9.0458 \times 10^{-38}$, $I_B = 7.8340 \times 10^{-38}$ and $I_C = 1.2118 \times 10^{-38}$ g·cm^2.

This planar bridge–bond structure will have six Raman ($3A_g + 2B_{1g} + 2B_{2g}$) and six infrared ($2B_{1u} + 2B_{2u} + 2B_{3u}$) active fundamentals. The Raman spectra of MgF_2 isolated in an argon matrix has been recorded by Lesiecki and Nibler.[4] They assigned two bands observed at 585 and 353 cm^{-1} to ν_1 and ν_2, respectively, of Mg_2F_4. Lesiecki and Nibler,[4] using a standard high–low frequency separation method and a diagonal force field, calculated ν_4 as 508 cm^{-1}. The other three Raman active frequencies (ν_3, ν_5, ν_6) are estimated by analogy with those for MgF_2 and Na_2F_2.[2] Four of the six infrared active fundamentals have been osbserved and assigned by Lesiecki and Nibler.[4] These frequencies were recorded in an argon matrix. Results of three independent infrared studies.[5–7] conducted with various matrices support these assignments. The other two infrared active fundamentals (ν_8 and ν_{10}) are estimated from the bending frequency ($\nu_2 = 215$ cm^{-1}) for MgF_2.[2] Following the observations made by Thompson and Carlson,[3] all the estimated frequencies are taken to lie above the bending frequency of the monomer.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.143	−1711.866	−1711.866	INFINITE
100	55.670	247.462	419.349	−17.189	−1715.010	−1703.781	889.964
200	89.656	297.494	346.359	−9.773	−1717.466	−1691.447	441.761
250	100.233	318.704	338.746	−5.011	−1718.051	−1684.868	352.034
298.15	107.501	337.014	337.014	0.	−1718.369	−1678.445	294.057
300	107.735	337.680	337.016	0.199	−1718.378	−1678.197	292.200
350	113.108	354.713	338.349	5.727	−1718.551	−1671.485	249.455
400	117.026	370.086	341.372	11.486	−1718.640	−1664.754	217.395
450	119.941	384.046	345.350	17.413	−1718.687	−1658.015	192.457
500	122.154	396.803	349.866	23.468	−1718.722	−1651.272	172.507
600	125.214	419.367	359.619	35.849	−1718.823	−1637.774	142.581
700	127.164	438.825	369.576	48.474	−1719.045	−1624.251	121.203
800	128.475	455.897	379.321	61.260	−1719.454	−1610.683	105.167
900	129.395	471.085	388.689	74.157	−1720.103	−1597.051	92.690
1000	130.065	484.755	397.624	87.131	−1738.221	−1581.906	82.630
1100	130.567	497.176	406.118	100.164	−1739.490	−1566.213	74.373
1200	130.952	508.554	414.187	113.241	−1740.767	−1550.404	67.487
1300	131.254	519.048	421.855	126.352	−1742.056	−1534.489	61.657
1400	131.495	528.784	429.149	139.489	−1998.180	−1512.139	56.419
1500	131.690	537.863	436.097	152.649	−1996.798	−1477.470	51.450
1600	131.850	546.368	442.726	165.826	−1995.436	−1442.893	47.106
1700	131.984	554.365	449.060	179.018	−1994.092	−1408.400	43.275
1800	132.096	561.912	455.122	192.222	−1992.765	−1373.986	39.872
1900	132.191	569.057	460.932	205.437	−1991.451	−1339.645	36.829
2000	132.272	575.840	466.510	218.660	−1990.148	−1305.373	34.093
2100	132.342	582.295	471.871	231.891	−1988.849	−1271.167	31.619
2200	132.403	588.453	477.031	245.128	−1987.549	−1237.022	29.371
2300	132.456	594.340	482.004	258.371	−1986.243	−1202.936	27.320
2400	132.502	599.978	486.803	271.619	−1984.923	−1168.907	25.441
2500	132.544	605.388	491.439	284.871	−1983.583	−1134.934	23.713
2600	132.580	610.587	495.923	298.128	−1982.218	−1101.015	22.120
2700	132.613	615.591	500.263	311.387	−1980.824	−1067.149	20.645
2800	132.642	620.415	504.468	324.650	−1979.394	−1033.335	19.277
2900	132.668	625.070	508.547	337.916	−1977.926	−999.573	18.004
3000	132.692	629.568	512.507	351.184	−1976.417	−965.863	16.817
3100	132.713	633.919	516.353	364.454	−1974.866	−932.203	15.708
3200	132.733	638.133	520.093	377.726	−1973.271	−898.594	14.668
3300	132.751	642.218	523.733	391.000	−1971.633	−865.035	13.692
3400	132.767	646.181	527.276	404.276	−1969.952	−831.527	12.775
3500	132.782	650.030	530.728	417.554	−1968.231	−798.069	11.911
3600	132.795	653.770	534.095	430.833	−1966.473	−764.661	11.095
3700	132.808	657.409	537.378	444.113	−1964.679	−731.302	10.324
3800	132.819	660.951	540.584	457.394	−1962.855	−697.992	9.595
3900	132.830	664.401	543.715	470.677	−1961.004	−664.730	8.903
4000	132.840	667.764	546.774	483.960	−1959.132	−631.516	8.247
4100	132.849	671.044	549.765	497.245	−1957.242	−598.349	7.623
4200	132.857	674.246	552.691	510.530	−1955.342	−565.228	7.030
4300	132.865	677.372	555.554	523.816	−1953.436	−532.153	6.464
4400	132.873	680.427	558.358	537.103	−1951.529	−499.122	5.925
4500	132.880	683.413	561.104	550.391	−1949.628	−466.133	5.411
4600	132.886	686.333	563.795	563.679	−1947.738	−433.188	4.919
4700	132.892	689.191	566.432	576.968	−1945.865	−400.283	4.449
4800	132.898	691.989	569.019	590.257	−1944.015	−367.418	3.998
4900	132.903	694.730	571.557	603.547	−1942.194	−334.591	3.567
5000	132.908	697.415	574.047	616.838	−1940.406	−301.801	3.153
5100	132.913	700.047	576.492	630.129	−1938.657	−269.047	2.756
5200	132.918	702.628	578.893	643.421	−1936.952	−236.325	2.374
5300	132.922	705.160	581.251	656.713	−1935.296	−203.637	2.007
5400	132.926	707.644	583.569	670.005	−1933.694	−170.980	1.654
5500	132.930	710.083	585.847	683.298	−1932.150	−138.352	1.314
5600	132.933	712.478	588.087	696.591	−1930.669	−105.750	0.986
5700	132.937	714.831	590.290	709.884	−1929.256	−73.176	0.671
5800	132.940	717.143	592.457	723.178	−1927.914	−40.625	0.366
5900	132.943	719.416	594.590	736.472	−1926.647	−8.095	0.072
6000	132.946	721.650	596.689	749.767	−1925.459	24.412	−0.213

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K)$ = [328.940 ± 8.4] J K^{-1}·mol^{-1}

$\Delta_f H°(0\ K) = -944.351 \pm 16.7$ kJ·mol^{-1}

$\Delta_f H°(298.15\ K) = -947.676 \pm 16.7$ kJ·mol^{-1}

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[15000]	[11]
[20000]	[9]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[700](1)	[750](3)
[160](2)	[180](2)

Point Group: [T_d] σ = [12]
Bond Distance: Mo–F = [1.82] Å
Bond Angle: F–Mo–F = [109.47]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.163977 × 10^{-113}] g^3·cm^6

Enthalpy of Formation

We adopt the weighted average value derived by Brewer[1] from several divergent equilibria measurements. Weaver *et al.*[2] reported a partial pressure of 4.6 × 10^{-6} atm MoF_4(g) in equilibrium with Mo and MoF_3 solids at 973 K. Hildenbrand[3] has measured several gaseous equilibria for reactions involving MoF_4(g) [1143–2146 K]; and Alikhanyan[4] has measured partial pressures for the reaction $MoF_5(g) + MoF_3(g) = 2\ MoF_4(g)$ [911 and 964 K]. Our 3rd law analyses of the equilibrium reactions, using auxiliary data from Brewer[1] for the MoF_x compounds other than MoF_4(g) and other auxiliary data from the JANAF Thermochemical Tables,[5] leads to $\Delta_f H°(MoF_4, g, 298.15\ K)$ values ranging from −216.0 to −226.6 kcal·mol^{-1}. The value of $\Delta_f H°(0\ K)$ combined with JANAF data[5] for Mo(g) and F(g) gives $\Delta_{at} H°(0\ K)$ = 456.357 kcal·mol^{-1} and an average Mo–F bond energy of $\Delta_{at} H°(0\ K)/4$ = 114.1 ± 2 kcal·mol^{-1}.

Heat Capacity and Entropy

We use the vibrational frequencies and degeneracies estimated by Hildenbrand[3] and adopted by Brewer.[1] These are in reasonable agreement with the estimates of Tumanov and Galkin.[6] The structure is assumed to be tetrahedral and a Mo–F distance of 1.82 Å from MoF_6(g) is used. The electronic contributions are those estimated by Brewer[1] based on crystal field theory. The principal moments of inertia are: $I_A = I_B = I_C = 27.8666 \times 10^{39}$ g·cm^2.

This table is based on the critical analysis of data existing in 1978 by Brewer.[1]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−18.909	−944.351	−944.351	INFINITE
100	58.912	250.806	397.136	−14.633	−946.380	−936.684	489.273
200	74.611	297.057	336.418	−7.872	−947.319	−926.574	241.996
250	80.449	314.348	330.317	−3.992	−947.562	−921.357	192.507
298.15	85.232	328.940	328.940	0.	−947.676	−916.298	160.532
300	85.398	329.468	328.942	0.158	−947.678	−916.103	159.508
350	89.417	342.945	329.997	4.532	−947.696	−910.838	135.935
400	92.611	355.102	332.388	9.086	−947.645	−905.575	118.256
450	95.137	366.162	335.535	13.782	−947.547	−900.322	104.507
500	97.141	376.293	339.111	18.591	−947.420	−895.081	93.508
600	100.035	394.278	346.845	28.460	−947.114	−884.641	77.015
700	101.955	409.853	354.759	38.565	−946.784	−874.255	65.238
800	103.279	423.558	362.520	48.831	−946.459	−863.916	56.408
900	104.225	435.780	369.993	59.209	−946.156	−853.617	49.543
1000	104.921	446.799	377.132	69.668	−945.889	−843.350	44.052
1100	105.447	456.825	383.928	80.187	−945.672	−833.107	39.561
1200	105.854	466.018	390.391	90.753	−945.517	−822.881	35.819
1300	106.174	474.504	396.539	101.355	−945.434	−812.665	32.653
1400	106.432	482.383	402.393	111.986	−945.435	−802.453	29.940
1500	106.643	489.733	407.973	122.640	−945.527	−792.237	27.588
1600	106.819	496.621	413.301	133.313	−945.718	−782.012	25.530
1700	106.969	503.102	418.394	144.003	−946.015	−771.772	23.714
1800	107.102	509.220	423.272	154.707	−946.422	−761.511	22.098
1900	107.224	515.014	427.949	165.423	−946.944	−751.225	20.653
2000	107.340	520.517	432.441	176.151	−947.584	−740.907	19.351
2100	107.456	525.757	436.761	186.891	−948.345	−730.556	18.172
2200	107.575	530.758	440.921	197.642	−949.228	−720.165	17.099
2300	107.703	535.543	444.931	208.406	−950.235	−709.730	16.118
2400	107.842	540.130	448.803	219.183	−951.368	−699.250	15.219
2500	107.995	544.535	452.545	229.975	−952.629	−688.719	14.390
2600	108.166	548.774	456.165	240.783	−954.031	−678.136	13.624
2700	108.356	552.860	459.671	251.609	−955.605	−667.495	12.913
2800	108.566	556.804	463.070	262.455	−957.406	−656.792	12.253
2900	108.798	560.618	466.368	273.323	−995.389	−645.971	11.635
3000	109.053	564.310	469.572	284.215	−995.825	−633.914	11.037
3100	109.330	567.891	472.686	295.134	−996.181	−621.845	10.478
3200	109.629	571.366	475.716	306.082	−996.451	−609.765	9.953
3300	109.951	574.745	478.666	317.061	−996.629	−597.678	9.460
3400	110.293	578.032	481.540	328.073	−996.711	−585.587	8.996
3500	110.654	581.234	484.343	339.120	−996.693	−573.495	8.559
3600	111.034	584.357	487.078	350.204	−996.572	−561.405	8.146
3700	111.429	587.404	489.748	361.327	−996.344	−549.320	7.755
3800	111.839	590.382	492.358	372.491	−996.007	−537.243	7.385
3900	112.261	593.292	494.909	383.696	−995.561	−525.175	7.034
4000	112.693	596.140	497.404	394.943	−995.003	−513.121	6.701
4100	113.133	598.928	499.846	406.235	−994.334	−501.082	6.384
4200	113.578	601.659	502.238	417.570	−993.553	−489.060	6.082
4300	114.026	604.337	504.581	428.950	−992.662	−477.059	5.795
4400	114.474	606.964	506.878	440.375	−991.660	−465.080	5.521
4500	114.921	609.541	509.131	451.845	−990.549	−453.124	5.260
4600	115.365	612.072	511.342	463.359	−989.330	−441.195	5.010
4700	115.803	614.558	513.511	474.918	−988.006	−429.293	4.771
4800	116.233	617.000	515.642	486.520	−986.578	−417.420	4.542
4900	116.654	619.401	517.735	498.164	−985.048	−405.578	4.324
5000	117.064	621.762	519.792	509.850	−1574.805	−388.038	4.054
5100	117.461	624.084	521.814	521.576	−1574.760	−364.303	3.731
5200	117.845	626.369	523.803	533.342	−1574.769	−340.568	3.421
5300	118.213	628.617	525.760	545.145	−1574.830	−316.833	3.123
5400	118.565	630.830	527.685	556.984	−1574.948	−293.096	2.835
5500	118.900	633.009	529.580	568.857	−1575.121	−269.357	2.558
5600	119.217	635.154	531.446	580.763	−1575.352	−245.613	2.291
5700	119.516	637.267	533.284	592.700	−1575.639	−221.867	2.033
5800	119.796	639.348	535.095	604.666	−1575.985	−198.113	1.784
5900	120.057	641.398	536.879	616.659	−1576.387	−174.353	1.544
6000	120.299	643.418	538.638	628.677	−1576.849	−150.587	1.311

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

$S°(298.15\ K) = [330.617 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1248.030 \pm 126]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1255.200 \pm 126]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1045 (1)	[600](1)	720 (2)
[300](1)	[300](1)	530 (2)
680 (1)	[200](1)	[150](2)

Ground State Quantum Weight: [1] σ = [4]
Point Group: [C_{4v}]
Bond Distance: Mo–O = [1.64] Å; Mo–F = [1.82] Å
Bond Angles: O–Mo–F = [90]°; F–Mo–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.1468 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Zmbov *et al.*[1] investigated the stabilities of some molybdenum and tungsten oxyfluorides by means of mass spectrometry. These studies led to enthalpies of formation for MoO_2F_2(g), WO_2F_2(g), and WOF_4(g) which were used by the authors to develop a correlation among the enthalpies of formation of the oxides, oxyfluorides, and fluorides of Mo and W. $\Delta_f H°(298.15\ K)$ varies almost linearly with the number of oxygen atoms[1] for the series WF_6, WOF_4 and WO_2F_2. Assuming a similar variation for MoF_6, $MoOF_4$ and MoO_2F_2, we estimate $\Delta_f H°(MoOF_4, g) = -320\ kcal \cdot mol^{-1}$.

$\Delta_f H$ data[2] for MoF_6(g), MoO(g), MoO_2(g), and MoO_3(g) have been used to derive the following average bond dissociation energies:

$$\Delta H°(MoF, g)/6 = 107\ kcal \cdot mol^{-1}$$
$$\Delta H°(MoO_n, g)/n = 135\ kcal \cdot mol^{-1}$$

From these data we derive $\Delta_f H°(MoOF_4, g) = -271\ kcal \cdot mol^{-1}$.

The enthalpy of formation for $MoOF_4$ is tentatively selected as $-300 \pm 30\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Blanchard[3] suggested that $MoOF_4$(g) possessed C_{4v} symmetry by reason of the similarity of its infrared spectra with that of $XeOF_4$(g). X-ray diffraction studies of crystalline $MoOF_4$ by Edwards *et al.*[4,5] support this view. The structure of the molecule is assumed to be square-pyramidal. The bond lengths are from the crystallographic studies of $MoOF_4$ by Edwards *et al.*[4,5] Individual moments of inertia are $I_A = I_B = 27.437 \times 10^{-39}$, $I_C = 41.8010 \times 10^{-39}\ g \cdot cm^2$.

Blanchard[3] reported the following vibrational frequencies and assignments:

$$\nu_1 = 1045,\ \nu_7 = 720,\ \nu_3 = 680,\ \text{and}\ \nu_8 = 530\ cm^{-1}.$$

Similar frequencies have been reported by Edwards *et al.*[4] from their study of the infrared spectra of gaseous $MoOF_4$. The rest of the frequencies and assignments are estimated by comparison with data for $XeOF_4$.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−19.407	−1248.030	−1248.030	INFINITE
100	53.979	250.195	403.835	−15.364	−1251.745	−1233.323	644.222
200	78.838	295.560	338.941	−8.676	−1254.213	−1213.820	317.017
250	88.874	314.265	332.167	−4.476	−1254.864	−1203.639	251.487
298.15	96.740	330.617	330.617	0.	−1255.200	−1193.739	209.138
300	97.009	331.216	330.618	0.179	−1255.208	−1193.358	207.782
350	103.440	346.673	331.824	5.197	−1255.320	−1183.038	176.559
400	108.488	360.828	334.578	10.500	−1255.267	−1172.714	153.141
450	112.460	373.845	338.228	16.028	−1255.097	−1162.404	134.928
500	115.608	385.863	342.398	21.732	−1254.844	−1152.117	120.361
600	120.165	407.373	351.478	33.537	−1254.183	−1131.631	98.517
700	123.201	426.139	360.832	45.715	−1253.408	−1111.267	82.924
800	125.304	442.736	370.053	58.147	−1252.585	−1091.017	71.236
900	126.812	457.587	378.968	70.756	−1251.753	−1070.871	62.152
1000	127.925	471.008	387.512	83.496	−1250.937	−1050.817	54.889
1100	128.769	483.242	395.667	96.333	−1250.157	−1030.843	48.951
1200	129.422	494.476	403.439	109.243	−1249.431	−1010.937	44.005
1300	129.937	504.856	410.846	122.212	−1248.773	−991.090	39.822
1400	130.350	514.501	417.910	135.227	−1248.196	−971.291	36.239
1500	130.686	523.506	424.653	148.280	−1247.710	−951.529	33.135
1600	130.964	531.949	431.098	161.363	−1247.326	−931.797	30.420
1700	131.195	539.896	437.266	174.471	−1247.049	−912.085	28.025
1800	131.389	547.401	443.178	187.600	−1246.889	−892.387	25.896
1900	131.555	554.509	448.852	200.748	−1246.849	−872.694	23.992
2000	131.696	561.261	454.305	213.911	−1246.936	−853.000	22.278
2100	131.819	567.689	459.553	227.087	−1247.154	−833.299	20.727
2200	131.925	573.824	464.609	240.274	−1247.505	−813.583	19.317
2300	132.018	579.690	469.485	253.471	−1247.995	−793.849	18.029
2400	132.100	585.311	474.195	266.677	−1248.625	−774.091	16.848
2500	132.172	590.705	478.748	279.891	−1249.401	−754.303	15.760
2600	132.236	595.890	483.155	293.111	−1250.339	−734.481	14.756
2700	132.293	600.882	487.423	306.338	−1251.471	−714.619	13.825
2800	132.345	605.694	491.562	319.570	−1252.854	−694.712	12.960
2900	132.391	610.339	495.578	332.806	−1290.448	−674.700	12.153
3000	132.433	614.828	499.479	346.048	−1290.524	−653.466	11.378
3100	132.470	619.171	503.270	359.293	−1290.551	−632.230	10.653
3200	132.505	623.377	506.958	372.542	−1290.527	−610.994	9.973
3300	132.536	627.455	510.548	385.794	−1290.447	−589.760	9.335
3400	132.564	631.412	514.045	399.049	−1290.310	−568.529	8.734
3500	132.590	635.255	517.453	412.306	−1290.114	−547.302	8.168
3600	132.614	638.991	520.778	425.567	−1289.856	−526.082	7.633
3700	132.637	642.624	524.022	438.829	−1289.535	−504.871	7.128
3800	132.657	646.162	527.190	452.094	−1289.151	−483.669	6.648
3900	132.676	649.608	530.285	465.361	−1288.704	−462.477	6.194
4000	132.693	652.967	533.310	478.629	−1288.194	−441.298	5.763
4100	132.709	656.244	536.269	491.899	−1287.620	−420.133	5.353
4200	132.724	659.442	539.163	505.171	−1286.984	−398.982	4.962
4300	132.738	662.565	541.997	518.444	−1286.286	−377.848	4.590
4400	132.752	665.617	544.772	531.719	−1285.528	−356.730	4.235
4500	132.764	668.601	547.491	544.994	−1284.710	−335.630	3.896
4600	132.775	671.519	550.155	558.271	−1283.833	−314.549	3.572
4700	132.786	674.374	552.768	571.549	−1282.901	−293.488	3.262
4800	132.796	677.170	555.331	584.828	−1281.913	−272.446	2.965
4900	132.805	679.908	557.845	598.109	−1280.872	−251.426	2.680
5000	132.814	682.591	560.313	611.390	−1871.164	−224.697	2.347
5100	132.823	685.222	562.737	624.671	−1871.701	−191.763	1.964
5200	132.831	687.801	565.117	637.954	−1872.336	−158.817	1.595
5300	132.838	690.331	567.456	651.237	−1873.069	−125.857	1.240
5400	132.845	692.814	569.755	664.522	−1873.901	−92.884	0.898
5500	132.852	695.252	572.014	677.807	−1874.829	−59.894	0.569
5600	132.858	697.646	574.236	691.092	−1875.856	−26.885	0.251
5700	132.864	699.997	576.422	704.378	−1876.979	6.141	−0.056
5800	132.870	702.308	578.573	717.665	−1878.197	39.189	−0.353
5900	132.875	704.579	580.689	730.952	−1879.508	72.258	−0.640
6000	132.880	706.813	582.773	744.240	−1880.915	105.350	−0.917

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 301.191\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 2.430 \pm 10.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -8.368 \pm 10.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1010 (1)	549 (1)	946 (1)
998 (1)	390 (1)	737 (1)
933 (1)	122 (1)	519 (1)
591 (1)	959 (1)	467 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_2
Bond Distances: N–N = [1.47] Å; N–F = [1.37] Å
Bond Angles: F–N–F = [108]°; N–N–F = [104]°; Dihedral Angle = [65]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.1817 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

Armstrong *et al.*[1] studied the reaction $N_2F_4(g) + 16/3\ NH_3(g) = 4\ NH_4F(s) + 5/3\ N_2(g)$. From this reaction, they calculate the enthalpy of formation of N_2F_4 to be $-2.0 \pm 2.5\ kcal·mol^{-1}$. The recalculated enthalpy of formation of $NH_4F(s)$ (refer to NF_2 table) differs from the value quoted in Circular 500 by 0.06 $kcal·mol^{-1}$. This correction would make the enthalpy of formation of tetrafluorohydrazine more negative by 0.24 $kcal·mol^{-1}$. In view of the large uncertainty in the enthalpy of formation, however, this correction was not applied.

Heat Capacity and Entropy – N_2F_4(g)

The fundamental frequencies were taken from the vapor phase infrared work of Durig and Lord.[2] The principal moments of inertia were calculated from the rotational constants reported by Lide and Mann.[3] Lide and Mann calculated the bond angles for assumed values of the NN and NF distance.

The principal moments of inertia are: $I_A = 1.5051 \times 10^{-38}$, $I_B = 2.6315 \times 10^{-38}$, and $I_C = 2.9836 \times 10^{-38}\ g·cm^2$.

Heat Capacity and Entropy – NF_2(g)

Harmony *et al.*[4] investigated the infrared spectrum of NF_2. They were able to assign the band center at 1074 cm^{-1} to the symmetric stretching mode ν_1. The absorption in the 930–940 cm^{-1} region was assigned to ν_3.

Harmony and Myers [5] performed matrix isolation experiments on NF_2. They arrived at the assignment $\nu_1 = 1070\ cm^{-1}$, $\nu_2 = 573\ cm^{-1}$ and $\nu_3 = 931\ cm^{-1}$. The stretching frequencies for similar molecules in an N_2 matrix are about 5 cm^{-1} below the gas phase values. A comparison of the gas phase and matrix values of ν_1 show excellent agreement.

Johnson and Colburn[6] report infrared studies on NF_2 but they draw no definite conclusions.

The gas phase value for ν_1 and the matrix values of ν_2 and ν_3 were taken to represent the fundamental vibrational frequencies of NF_2.

Harmony *et al.*[4] estimated the N–F distance as 1.37 and used this with their data to calculate an F–N–F angle of 104.2°. Using these data the moments of inertia are: $I_A = 7.3728 \times 10^{-39}$, $I_B = 1.2035 \times 10^{-39}$, and $I_C = 8.5763 \times 10^{-39}\ g·cm^2$.

References

[1]G. T. Armstrong, S. Marantz, and C. F. Coyle, U. S. Nat. Bur. Stand. Report 6584, (1959).
[2]J. R. Durig and R. C. Lord, Spectrochim. Acta **19**, 1877 (1963).
[3]D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. **31**, 1129 (1959).
[4]M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, J. Chem. Phys. **35**, 1129 (1961).
[5]M. D. Harmony and R. J. Myers, J. Chem. Phys. **37**, 636 (1962).
[6]F. A. Johnson and C. B. Colburn, Inorg. Chem. **1**, 431 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−15.522	2.430	2.430	INFINITE
100	41.759	239.576	358.172	−11.860	−2.624	23.474	−12.261
200	59.845	273.592	307.831	−6.848	−6.381	51.159	−13.361
250	70.089	288.055	302.445	−3.598	−7.591	65.693	−13.726
298.15	79.169	301.191	301.191	0.	−8.368	79.883	−13.995
300	79.496	301.682	301.193	0.147	−8.391	80.431	−14.004
350	87.647	314.566	302.192	4.331	−8.842	95.275	−14.219
400	94.490	326.730	304.506	8.890	−9.004	110.163	−14.386
450	100.146	338.197	307.619	13.760	−8.933	125.056	−14.516
500	104.796	348.997	311.222	18.887	−8.677	139.932	−14.619
600	111.781	368.762	319.197	29.739	−7.756	169.575	−14.763
700	116.598	386.377	327.560	41.172	−6.469	199.032	−14.852
800	120.009	402.181	335.917	53.012	−4.957	228.288	−14.906
900	122.490	416.467	344.086	65.143	−3.311	257.346	−14.936
1000	124.341	429.473	351.984	77.489	−1.585	286.216	−14.950
1100	125.754	441.393	359.578	89.996	0.186	314.911	−14.954
1200	126.854	452.384	366.860	102.629	1.978	343.443	−14.950
1300	127.726	462.574	373.835	115.360	3.776	371.826	−14.940
1400	128.427	472.066	380.517	128.169	5.570	400.070	−14.927
1500	129.000	480.946	386.919	141.041	7.353	428.186	−14.911
1600	129.473	489.287	393.059	153.965	9.121	456.184	−14.893
1700	129.868	497.149	398.953	166.933	10.872	484.072	−14.874
1800	130.202	504.582	404.617	179.937	12.607	511.857	−14.854
1900	130.485	511.629	410.065	192.972	14.328	539.546	−14.833
2000	130.728	518.328	415.312	206.033	16.039	567.145	−14.812
2100	130.939	524.712	420.371	219.116	17.743	594.658	−14.791
2200	131.121	530.807	425.253	232.219	19.448	622.090	−14.770
2300	131.281	536.640	429.970	245.340	21.158	649.445	−14.749
2400	131.422	542.230	434.532	258.475	22.881	676.725	−14.729
2500	131.547	547.597	438.948	271.624	24.625	703.933	−14.708
2600	131.657	552.759	443.227	284.784	26.394	731.070	−14.687
2700	131.756	557.730	447.376	297.955	28.196	758.139	−14.667
2800	131.845	562.523	451.403	311.135	30.037	785.141	−14.647
2900	131.924	567.151	455.315	324.323	31.922	812.075	−14.627
3000	131.996	571.625	459.118	337.519	33.856	838.944	−14.607
3100	132.061	575.954	462.818	350.722	35.843	865.748	−14.588
3200	132.120	580.148	466.419	363.931	37.888	892.487	−14.568
3300	132.174	584.214	469.927	377.146	39.992	919.160	−14.549
3400	132.224	588.161	473.347	390.366	42.159	945.769	−14.530
3500	132.269	591.994	476.682	403.591	44.390	972.314	−14.511
3600	132.310	595.721	479.938	416.820	46.688	998.794	−14.492
3700	132.348	599.346	483.116	430.053	49.051	1025.209	−14.473
3800	132.384	602.876	486.221	443.289	51.483	1051.559	−14.455
3900	132.416	606.316	489.257	456.529	53.981	1077.845	−14.436
4000	132.446	609.668	492.225	469.772	56.547	1104.065	−14.418
4100	132.474	612.939	495.130	483.018	59.179	1130.220	−14.399
4200	132.500	616.132	497.973	496.267	61.878	1156.311	−14.381
4300	132.525	619.250	500.757	509.518	64.641	1182.336	−14.363
4400	132.547	622.297	503.485	522.772	67.469	1208.296	−14.344
4500	132.568	625.276	506.159	536.028	70.360	1234.192	−14.326
4600	132.588	628.190	508.780	549.286	73.312	1260.022	−14.308
4700	132.607	631.041	511.351	562.545	76.324	1285.788	−14.290
4800	132.624	633.833	513.874	575.807	79.395	1311.489	−14.272
4900	132.641	636.568	516.350	589.070	82.523	1337.126	−14.254
5000	132.656	639.248	518.781	602.335	85.706	1362.697	−14.236
5100	132.671	641.875	521.169	615.601	88.943	1388.205	−14.218
5200	132.684	644.452	523.515	628.869	92.232	1413.649	−14.200
5300	132.697	646.979	525.821	642.138	95.571	1439.029	−14.182
5400	132.709	649.460	528.088	655.409	98.960	1464.346	−14.165
5500	132.721	651.895	530.317	668.680	102.396	1489.599	−14.147
5600	132.732	654.286	532.509	681.953	105.878	1514.790	−14.129
5700	132.742	656.636	534.666	695.226	109.404	1539.917	−14.112
5800	132.752	658.944	536.789	708.501	112.972	1564.982	−14.094
5900	132.761	661.214	538.879	721.777	116.581	1589.987	−14.077
6000	132.770	663.445	540.936	735.053	120.230	1614.929	−14.059

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

Tungsten Fluoride Oxide (WF_4O) CRYSTAL M_r = 275.843012

$S°(298.15\ K) = 175.728 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 379\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -1406.908 \pm 62.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 5.021 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WOF_4, cr, 298.15\ K) = -333.26\ kcal \cdot mol^{-1}$, is calculated from the enthalpy of formation of $WOF_4(g)$ less the enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K) = 16.80\ kcal \cdot mol^{-1}$. This latter quantity is calculated by the 3rd law method from the vapor pressure equation determined by Cady and Hargreaves.[1] The 2nd law value is $\Delta_{sub} H°(298.15\ K) = 16.94\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacities are estimated from those of $WOCl_4(cr)$, $WO_3(cr)$, $WO_2(cr)$, $WCl_6(cr)$, and $WF_6(cr, l)$.[3]

The entropy, $S°(298.15\ K) = 42.0\ cal\ K^{-1} \cdot mol^{-1}$ is calculated from the vapor pressure equaiton of Cady and Hargreaves[1] using a 2nd law analysis.

This entropy is larger than the corresponding value for $WOCl_4(cr)$.[2] In both cases the entropies of the condensed phases are derived from gas phase values using 2nd law analysis of sublimation and vaporization data. The entropy of melting for $WOCl_4$ is an order of magnitude larger than that of WOF_4. This suggests some inconsistency in the data for $WOCl_4$ since all values for $WOF_4(cr, l, g)$ appear internally reasonable.

Fusion Data

T_{fus} is calculated as the temperature at which the Gibbs energy of reaction $WOF_4(cr) \rightarrow WOF_4(l)$ approaches zero. The difference between the enthalpies of formation for the crystal and liquid at the melting point is $\Delta_{fus} H°$.

Ruff *et al.*[3] reported the melting point as 383 K. Cady and Hargreaves[1] calculated the melting point as 378 K, and the heat of fusion as $2.26\ kcal \cdot mol^{-1}$ from vapor pressure equations for the crystal and liquid. This 2nd law value of $\Delta_{fus} H°$, when corrected for $\Delta C_p°$ of vaporization and sublimation, is in good agreement with the value adopted in this table.

References

[1] G. H. Cady and G. B. Hargreaves, J. Chem. Soc. (London) **1961**, 1563.
[2] JANAF Thermochemical Tables: $WOCl_4(cr)$, 3-31-67, $WCl_6(cr)$, 12-31-66; $WF_6(cr)$, 3-31-67; $WO_2(cr)$, 9-30-66; $WO_3(cr)$, 9-30-66.
[3] O. Ruff, F. Eisner, and W. Heller, Z. Anorg. Chem. **52**; 256 (1907).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	133.578	175.728	175.728	0.	−1406.908	−1298.058	227.414
300	133.888	176.555	175.731	0.247	−1406.848	−1297.383	225.894
379.000	147.109	209.337	179.398	11.347	--- CRYSTAL <--> LIQUID ---		
400	150.624	217.357	181.182	14.470	−1403.013	−1261.438	164.727
500	166.523	252.746	192.028	30.359	−1397.900	−1226.610	128.143
600	178.657	284.242	204.821	47.653	−1391.690	−1192.920	103.853
700	186.606	312.412	218.216	65.937	−1384.737	−1160.334	86.585
800	192.046	337.703	231.599	84.883	−1377.323	−1128.778	73.702
900	195.811	360.557	244.679	104.290	−1369.616	−1098.170	63.736
1000	197.903	381.310	257.321	123.990	−1361.761	−1068.430	55.809

PREVIOUS: March 1967 CURRENT: December 1971

$S°(298.15\ K) = 178.915 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 379\ K$

$\Delta_f H°(298.15\ K) = -1405.255 \pm 62.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 5.021 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WOF_4, l, 298.15\ K) = -335.84\ kcal \cdot mol^{-1}$ is calculated from that of the gas less the enthalpy eat of vaporization, $\Delta_{vap} H°(298.15\ K) = 16.38\ kcal \cdot mol^{-1}$. This latter value is calculated by the 3rd law method from the vapor pressure equation determined by Cady and Hargreaves.[1] The 2nd law value is $\Delta_{vap} H°(298.15\ K) = 16.50\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 7.25 cal K^{-1} g-atom^{-1} as suggested by Kubaschewski and Evans.[2] The entropy, $S°(298.15\ K) = 42.8\ cal\ K^{-1} \cdot mol^{-1}$ is calculated by a 2nd law analysis of the vapor pressure equation given by Cady and Hargreaves[1] for the system $WOF_4(l) \rightarrow WOF_4(g)$.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is calculated as the temperature at which the fugacity is one atmosphere for the process $WOF_4(l) \rightarrow WOF_4(g)$. The difference between the enthalpies of formation for the liquid and gas at T_{vap} is $\Delta_{vap} H°$.

Ruff *et al.*[3] reported the boiling point of WOF_4(l) as 459 K. Cady and Hargreaves[1] calculated the boiling point as 459 K, and the enthalpy eat of vaporization as 14.23 $kcal \cdot mol^{-1}$ from the vapor pressure equation for the liquid. This 2nd law value of $\Delta_{vap} H°$, when corrected for $\Delta C_p°$ of vaporization, is in good agreement with the value adopted in the tabulation.

References

[1] G. H. Cady and G. B. Hargreaves, J. Chem. Soc. (London) **1961**, 1563.
[2] O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York, (1958).
[3] O. Ruff, F. Eisner, and W. Zeller, Z. Anorg. Chem. **52**, 256 (1907).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	182.004	178.915	178.915	0.	−1405.255	−1297.355	227.291
300	182.004	180.041	178.918	0.337	−1405.106	−1296.686	225.773
379.000	182.004	222.585	183.759	14.715	--- CRYSTAL <--> LIQUID ---		
400	182.004	232.400	186.057	18.537	−1397.294	−1261.736	164.766
500	182.004	273.013	199.538	36.738	−1389.868	−1228.713	128.363
600	182.004	306.196	214.633	54.938	−1382.752	−1197.155	104.222
700	182.004	334.252	229.769	73.138	−1375.883	−1166.768	87.065
800	182.004	358.555	244.382	91.339	−1369.215	−1137.351	74.261
900	182.004	379.992	258.282	109.539	−1362.715	−1108.760	64.351
1000	182.004	399.168	271.429	127.740	−1356.359	−1080.885	56.460

PREVIOUS: March 1967 CURRENT: December 1971

0 to 379 K crystal
above 379 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	133.578	175.728	175.728	0.	−1406.908	−1298.058	227.414
300	133.888	176.555	175.731	0.247	−1406.848	−1297.383	225.894
379.000	147.109	209.337	179.398	11.347	____ CRYSTAL <--> LIQUID ____		
379.000	182.004	222.585	179.398	16.368	TRANSITION		
400	182.004	232.400	181.926	20.190	−1397.294	−1261.736	164.766
500	182.004	273.013	196.233	38.390	−1389.868	−1228.713	128.363
600	182.004	306.196	211.879	56.590	−1382.752	−1197.155	104.222
700	182.004	334.252	227.408	74.791	−1375.883	−1166.768	87.065
800	182.004	358.555	242.316	92.991	−1369.215	−1137.351	74.261
900	182.004	379.992	256.446	111.192	−1362.715	−1108.760	64.351
1000	182.004	399.168	269.776	129.392	−1356.359	−1080.885	56.460

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K)$ = [335.705 ± 4.2] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1328.914 \pm 62.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1336.621 \pm 62.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm-1
1055 (1)	620 (1)	700 (2)
[300](1)	[300](1)	560 (2)
735 (1)	[200](1)	[150](2)

Ground State Quantum Weight: [1] σ = [4]
Point Group: [C_{4v}]
Bond Distances: W–O = [1.64]Å; W–F = [1.82] Å
Bond Angles: O–W–F = [90]°; F–W–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.1909×10^{-113}] $g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(WOF_4, g, 298.15\ K) = -319.46\ kcal·mol^{-1}$, is calculated from the enthalpy of reaction data of Zmbov *et al.*[1] This data came from a mass spectrometric study of the equilibrium in the reaction:

$$2\ TaF_5(g) + WO_3(cr) = 2\ TaOF_3(g) + WOF_4(g).$$

Heat Capacity and Entropy

The infrared spectra of WOF_4 and $MoOF_4$ in the vapor state are very similar[2, 3, 4] and have been interpreted on the basis of a monomeric unit with C_{4v} symmetry[5] by comparison with the spectrum of $XeOF_4$.[6] Thus, as with $XeOF_4$ and $MoOF_4$, gaseous WOF_4 is assumed to be C_{4v} symmetry with a square–pyamidal structure.

Blanchard[5] and Reynes[10] reported the following vibrational assignments and frequencies, the Q frequency being adopted in this tabulation:

ν_1 = 1064(R), 1055(Q), 1047(P); ν_7 = 705(R), 700(Q), 690(P); ν_3 = 745(R), 735(Q), 720(P); ν_8 = 560 cm^{-1}

Similar frequencies, as well as additional frequencies, have been reported by Ward and Stafford,[4] Edwards *et al.*,[3] and Edwards and Jones.[2] The remaining frequencies and assignments are estimated with regard to the preceding references, the data for X_3OF_4,[6] and results for $MoOF_4$.[7] There exists some controversy as the crystallographic structure of WOF_4. Beattie *et al.*[8] suggest fluorine–bridged tetramers as in $MoOF_4$[9] rather than an oxygen–bridged structure as suggested by Edwards and Jones.[2] This leads to significantly different bond lengths for W–F and W–O. Due to the similarities in the melt, solid, and vapor phase infrared spectra of $MoOF_4$ and WOF_4, one would suspect similar structures.[4, 8] The assumption is made that the structures are similar and thus the bond lengths are taken to be the same as those of $MoOF_4$. Further support for the bond length assumption is the similarity of bond lengths in MoO_3 and WO_3 and in MoF_6 and WF_6.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.257	−1328.914	−1328.914	INFINITE
100	53.821	255.014	407.184	−15.217	−1332.792	−1314.592	686.673
200	77.962	300.014	342.945	−8.586	−1335.482	−1295.221	338.277
250	87.938	318.515	336.240	−4.431	−1336.218	−1285.063	268.499
298.15	95.853	334.705	334.705	0.	−1336.621	−1275.170	223.404
300	96.125	335.298	334.706	0.178	−1336.631	−1274.788	221.960
350	102.646	350.626	335.902	5.153	−1336.795	−1264.465	188.711
400	107.789	364.681	338.633	10.419	−1336.777	−1254.132	163.773
450	111.850	377.621	342.256	15.914	−1336.627	−1243.809	144.378
500	115.076	389.579	346.398	21.590	−1336.381	−1233.508	128.864
600	119.756	411.003	355.423	33.348	−1335.707	−1212.994	105.601
700	122.882	429.714	364.728	45.490	−1334.897	−1192.605	88.993
800	125.049	446.272	373.906	57.893	−1334.026	−1172.336	76.546
900	126.604	461.096	382.785	70.480	−1333.140	−1152.178	66.871
1000	127.753	474.497	391.297	83.200	−1332.264	−1132.119	59.136
1100	128.624	486.716	399.424	96.021	−1331.416	−1112.145	52.811
1200	129.299	497.938	407.172	108.919	−1330.609	−1092.247	47.544
1300	129.831	508.309	414.558	121.876	−1329.852	−1072.415	43.090
1400	130.258	517.947	421.603	134.882	−1329.151	−1052.639	39.274
1500	130.606	526.946	428.329	147.925	−1328.511	−1032.911	35.969
1600	130.892	535.385	434.759	161.001	−1327.937	−1013.223	33.078
1700	131.131	543.327	440.914	174.102	−1327.429	−993.569	30.529
1800	131.333	550.828	446.814	187.226	−1326.988	−973.944	28.263
1900	131.504	557.934	452.477	200.368	−1326.611	−954.341	26.237
2000	131.650	564.683	457.920	213.526	−1326.298	−934.756	24.413
2100	131.777	571.109	463.158	226.697	−1326.043	−915.186	22.764
2200	131.887	577.242	468.206	239.880	−1325.842	−895.626	21.265
2300	131.983	583.107	473.075	253.074	−1325.689	−876.074	19.896
2400	132.067	588.726	477.777	266.277	−1325.578	−856.528	18.642
2500	132.142	594.119	482.324	279.487	−1325.502	−836.986	17.488
2600	132.209	599.303	486.724	292.705	−1325.453	−817.446	16.423
2700	132.268	604.293	490.986	305.929	−1325.450	−797.908	15.436
2800	132.321	609.105	495.120	319.158	−1325.523	−778.368	14.521
2900	132.369	613.749	499.131	332.393	−1325.705	−758.824	13.668
3000	132.412	618.237	503.026	345.632	−1326.018	−739.272	12.872
3100	132.451	622.579	506.813	358.875	−1326.502	−719.706	12.127
3200	132.486	626.785	510.497	372.122	−1327.184	−700.122	11.428
3300	132.519	630.863	514.083	385.372	−1328.087	−680.513	10.772
3400	132.548	634.819	517.576	398.625	−1329.241	−660.872	10.153
3500	132.575	638.662	520.981	411.882	−1330.711	−641.194	9.569
3600	132.600	642.397	524.302	425.140	−1332.590	−621.468	9.017
3700	132.623	646.030	527.543	438.401	−1369.743	−601.492	8.492
3800	132.644	649.567	530.708	451.665	−1369.152	−580.737	7.983
3900	132.663	653.013	533.800	464.930	−1368.497	−559.997	7.500
4000	132.681	656.372	536.823	478.197	−1367.778	−539.275	7.042
4100	132.698	659.648	539.779	491.466	−1366.997	−518.572	6.607
4200	132.714	662.846	542.671	504.737	−1366.152	−497.889	6.192
4300	132.728	665.969	545.502	518.009	−1365.246	−477.227	5.797
4400	132.742	669.021	548.275	531.283	−1364.280	−456.586	5.420
4500	132.754	672.004	550.991	544.558	−1363.253	−435.968	5.061
4600	132.766	674.922	553.654	557.834	−1362.169	−415.374	4.717
4700	132.777	677.777	556.265	571.111	−1361.028	−394.804	4.388
4800	132.788	680.573	558.825	584.389	−1359.832	−374.258	4.073
4900	132.798	683.311	561.338	597.668	−1358.582	−353.738	3.771
5000	132.807	685.994	563.804	610.949	−1357.281	−333.244	3.481
5100	132.815	688.624	566.226	624.230	−1355.930	−312.777	3.203
5200	132.824	691.203	568.605	637.512	−1354.531	−292.336	2.937
5300	132.831	693.733	570.942	650.794	−1353.086	−271.923	2.680
5400	132.839	696.216	573.239	664.078	−1351.597	−251.538	2.433
5500	132.846	698.654	575.497	677.362	−1350.065	−231.181	2.196
5600	132.852	701.048	577.718	690.647	−1348.493	−210.851	1.967
5700	132.858	703.399	579.902	703.932	−1346.883	−190.551	1.746
5800	132.864	705.710	582.051	717.219	−1345.236	−170.278	1.534
5900	132.870	707.981	584.167	730.505	−1343.554	−150.035	1.328
6000	132.875	710.214	586.249	743.793	−1341.841	−129.820	1.130

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = [333.602 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1128.678 \pm 20.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1133.446 \pm 20.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[564](1)
[158](2)
[570](3)
[180](3)

Ground State Quantum Weight: [1] σ = [12]
Point Group: [T_d]
Bond Distance: Pb–F = [2.08] Å
Bond Angle: F–Pb–F = [109° 28']
Product of the Moments of Inertia: $I_A I_B I_C = [4.821770 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

A 3rd law analysis of the partial pressure data at 988 K reported by Zmbov *et al.*[1] for the equilibrium 2 $PbF_2(g) = PbF_4(g) + Pb(g)$ gives $\Delta_f H°(298.15\ K) = -16.15\ kcal \cdot mol^{-1}$. There are inconsistencies in the published results but the partial pressure data are correctly given.[2] The 2nd law enthalpy of reaction derived by Zmbov *et al.*[1] from a graphical plot of six ion current quotient values vs. reciprocal temperature (approximately 1020 to 1110 K), when corrected to 298.15 K, is in agreement with the 3rd law value of $-16.15\ kcal \cdot mol^{-1}$. Combining this enthalpy of reaction with $\Delta_f H°(PbF_2, g, 298.15\ K) = -104.0 \pm 1\ kcal \cdot mol^{-1}$ [3] and $\Delta_f H°(Pb, g, 298.15\ K) = 46.75 \pm 0.13\ kcal \cdot mol^{-1}$ [3] gives the adopted $\Delta_f H°(PbF_4, g, 298.15\ K) = -270.9 \pm 5\ kcal \cdot mol^{-1}$. The adopted enthalpy of formation leads to a dissociation energy $\Delta_{at} H° = 16.96$ eV for the process $PbF_4(g) = Pb(g) + 4\,F(g)$. This is consistent with $\Delta_{at} H° = 8.10$ eV for $PbF_2(g)$ [3] and $D_0° = 3.64$ eV for PbF(g).[3]

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya *et al.*[4] Later works[5,6,7] mistakenly cite this work as observed data. A band at 663 cm^{-1} was recently observed in an infrared study by Hauge *et al.*[8] and was assigned to matrix isolated PbF_4. Calculation with infrared active $\nu_3 = 663\ cm^{-1}$ decreases $S°(298.15\ K)$ by 0.45 cal $K^{-1} \cdot mol^{-1}$. Only the calculated frequencies are used for the present table pending more complete observation.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−19.761	−1128.678	−1128.678	INFINITE
100	59.551	251.440	406.137	−15.470	−1131.968	−1119.354	584.691
200	79.572	299.488	341.603	−8.423	−1133.303	−1106.086	288.880
250	86.207	317.993	335.075	−4.270	−1133.461	−1099.258	229.677
298.15	90.935	333.602	333.602	0.	−1133.446	−1092.670	191.431
300	91.090	334.165	333.604	0.168	−1133.443	−1092.417	190.207
350	94.654	348.489	334.727	4.817	−1133.326	−1085.588	162.015
400	97.277	361.308	337.263	9.618	−1133.160	−1078.779	140.874
450	99.239	372.884	340.588	14.533	−1132.976	−1071.992	124.434
500	100.733	383.421	344.352	19.534	−1132.789	−1065.226	111.283
600	102.801	401.984	352.453	29.719	−1132.441	−1051.747	91.563
700	104.120	417.937	360.695	40.070	−1137.015	−1037.524	77.421
800	105.007	431.902	368.741	50.529	−1136.792	−1023.326	66.816
900	105.630	444.308	376.461	61.063	−1136.552	−1009.157	58.570
1000	106.083	455.462	383.813	71.649	−1136.300	−995.015	51.974
1100	106.422	465.590	390.794	82.275	−1136.038	−980.900	46.579
1200	106.683	474.861	397.419	92.931	−1135.768	−966.808	42.084
1300	106.887	483.409	403.709	103.610	−1135.498	−952.739	38.282
1400	107.050	491.336	409.688	114.307	−1135.245	−938.690	35.023
1500	107.182	498.727	415.381	125.019	−1135.019	−924.659	32.199
1600	107.290	505.648	420.808	135.743	−1134.825	−910.641	29.729
1700	107.380	512.155	425.992	146.476	−1134.668	−896.634	27.550
1800	107.456	518.295	430.951	157.218	−1134.547	−882.636	25.613
1900	107.520	524.106	435.702	167.967	−1134.462	−868.644	23.881
2000	107.575	529.623	440.262	178.722	−1134.409	−854.655	22.321
2100	107.622	534.872	444.643	189.482	−1311.605	−833.553	20.733
2200	107.663	539.880	448.859	200.246	−1311.212	−810.798	19.251
2300	107.699	544.667	452.921	211.014	−1310.902	−788.059	17.897
2400	107.731	549.251	456.840	221.786	−1310.669	−765.332	16.657
2500	107.758	553.649	460.625	232.560	−1310.506	−742.613	15.516
2600	107.783	557.876	464.285	243.338	−1310.407	−719.899	14.463
2700	107.805	561.944	467.827	254.117	−1310.362	−697.189	13.488
2800	107.825	565.865	471.259	264.898	−1310.362	−674.479	12.583
2900	107.843	569.649	474.587	275.682	−1310.396	−651.768	11.740
3000	107.859	573.306	477.817	286.467	−1310.454	−629.056	10.953
3100	107.873	576.843	480.954	297.254	−1310.525	−606.342	10.217
3200	107.886	580.268	484.005	308.042	−1310.601	−583.625	9.527
3300	107.898	583.588	486.972	318.831	−1310.669	−560.906	8.878
3400	107.909	586.809	489.862	329.621	−1310.721	−538.185	8.268
3500	107.919	589.937	492.676	340.413	−1310.749	−515.463	7.693
3600	107.928	592.977	495.420	351.205	−1310.743	−492.740	7.149
3700	107.937	595.935	498.097	361.998	−1310.697	−470.018	6.635
3800	107.945	598.813	500.710	372.792	−1310.604	−447.299	6.149
3900	107.952	601.617	503.262	383.587	−1310.458	−424.581	5.687
4000	107.958	604.350	505.755	394.383	−1310.253	−401.869	5.248
4100	107.965	607.016	508.192	405.179	−1309.986	−379.163	4.831
4200	107.970	609.618	510.576	415.976	−1309.652	−356.463	4.433
4300	107.976	612.159	512.909	426.773	−1309.249	−333.774	4.055
4400	107.981	614.641	515.193	437.571	−1308.774	−311.093	3.693
4500	107.985	617.068	517.430	448.369	−1308.226	−288.424	3.348
4600	107.990	619.441	519.622	459.168	−1307.603	−265.769	3.018
4700	107.994	621.764	521.771	469.967	−1306.905	−243.128	2.702
4800	107.998	624.037	523.878	480.767	−1306.131	−220.502	2.400
4900	108.001	626.264	525.945	491.567	−1305.281	−197.894	2.110
5000	108.005	628.446	527.973	502.367	−1304.357	−175.303	1.831
5100	108.008	630.585	529.964	513.167	−1303.357	−152.732	1.564
5200	108.011	632.682	531.919	523.968	−1302.285	−130.181	1.308
5300	108.014	634.740	533.840	534.770	−1301.141	−107.651	1.061
5400	108.017	636.759	535.727	545.571	−1299.926	−85.144	0.824
5500	108.019	638.741	537.582	556.373	−1298.642	−62.660	0.595
5600	108.022	640.687	539.406	567.175	−1297.291	−40.199	0.375
5700	108.024	642.599	541.200	577.977	−1295.875	−17.764	0.163
5800	108.026	644.478	542.964	588.780	−1294.397	4.646	−0.042
5900	108.028	646.325	544.700	599.582	−1292.856	27.031	−0.239
6000	108.030	648.140	546.409	610.385	−1291.258	49.387	−0.430

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 299.644 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -756.882 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -763.162 \pm 20.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
891.5(1)	228.0(1)	532.5(1)
558.4(1)	475.0(1)	867.0(1)
353.0(1)	728.0(1)	233.0(1)

Ground State Quantum Weight: 1; Point Group: C_{2v} $\sigma = 2$
Bond Distances: S–F* = 1.545 ± 0.003 S–F** = 1.646 ± 0.003 Å
Bond Angles: F*–S–F* = 101.55 ± 0.5°; F*–S–F** = 87.81 ± 0.5°
F**–S–F** = 173.07 ± 0.5° (*–equatorial **–axial)
Product of Moments of Inertia: $I_A I_B I_C = 6.723859 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Data on $\Delta_f H°$ published prior to 1970 have been reviewed by O'Hare *et al.*[1] We reanalyze this earlier work together with more recent studies. Unless otherwise indicated, all auxiliary data are taken from JANAF tables.[2] We also include, for those reactions involving the formation of HF, $\Delta_f H°$ values which have been derived in previous analyses.[11, 12, 13]

Source	Method	Reaction	$\Delta_f H°(T/K)$ kcal·mol^{-1}	$\Delta_f H°(SF_4, g, 298.15\ K)$, From (Ref.)	kcal·mol^{-1} This Work
3	Calorimetric	$SF_4(g) + 2\ H_2(g) = 4\ HF(l) + S(cr)$	104.8(298)[b] ± 4.0	185.2[11, 12] 188.5[13]	184.7[a] ± 6.0
4	Calorimetric	$SF_4(g) + 3\ H_2O(l) = 4\ HF(aq) + H_2SO_3(aq)$	[c]	179.0[11]	180.8
5-8	Appearance Potentials[d]	$SF_6(g) = SF_4(g) + 2\ F(g)$	145.0 ± 4.6(0)	181.6 ± 5.0	
8	Appearance Potentials[e]	$NSF_3(g) + F(g) = SF_4(g) + N(g)$	17.5(0)	161.8	
9	Appearance Potentials[f]	$SF_6(g) = SF_4(g) + 2\ F(g)$	116.2(0)	210.4	

[a]Auxiliary $\Delta_f H°(298.15\ K)$ data in kcal·mol^{-1}: $NSF_3(g)$, −85.2 ± 0.5;[1] HF(l), −72.37.[2, 10]
[b]Results reduced with HF PVT and calorimetric data from.[10]
[c]Hydrolysis data unavailable; $\Delta_f H°$ value from[11] adjusted for changes in $\Delta_f H°$ of HF(aq).
[d]Ion Processes: $SF_6(g) + e^- = SF_4^+(g) + 2\ F(g) + 2\ e^-$ $SF_4(g) + e^- = SF_4^+(g) + 2\ e^-$
[e]Ion Processes: $SF_4(g) + e^- = SF_3^+(g) + F(g) + 2\ e^-$ $NSF_3(g) + e^- = SF_3^+(g) + N(g) + 2\ e^-$
[f]Ion Processes: $SF_5(g) + e^- = SF_4(g) + F\ (g)$ $SF_5(g) + e^- = SF_5\ (g)$ $SF_6(g) + e^- = SF_5\ (g) + F(g)$

All of these studies are relatively imprecise, suggesting the need for an unequivocal redetermination of $\Delta_f H°$. Both calorimetric results[3, 4] are based on measurements made with impure samples (−98% SF_4) and suffer from the additional uncertainties introduced by the formation of HF. The ionization processes involve unknown kinetic and excitation energies, as evidenced by the widely scattered results. The first three $\Delta_f H°$ values listed above are reasonably consistent; thus, we are led to adopt their mean value of $\Delta_f H°(SF_4, g, 298.15\ K) = -182.4$ kcal·mol^{-1}. The estimated uncertainty is ± 5.0 kcal·mol^{-1}. Our $\Delta_f H°$ value corresponds to a enthalpy of atomization and average bond dissociation energy of 320.1 and 80.0 kcal·mol^{-1}, respectively.

Heat Capacity and Entropy

Detailed structural data determined by electron diffraction[14] and microwave spectroscopy[15] show good agreement. We arbitrarily adopt the microwave data which indicate a trigonal bipyramid structure with two inequivalent sets of fluorine atoms. The inequivalence of the fluorines is also supported by nuclear resonance[16, 17] and x-ray photoelectron spectroscopic[18, 19] studies. The principal moments of inertia are: $I_A = 12.5525 \times 10^{-39}$, $I_B = 20.5464 \times 10^{-39}$ and $I_C = 26.0707 \times 10^{-39}\ g \cdot cm^2$.

Various spectroscopic methods have been used to study the vibrational spectrum of SF_4. These studies include crystal,[20] liquid[21] and gas[22] phase Raman and gas[21-23] phase and argon matrix isolation[24] infrared spectra. The measured frequencies show good agreement but various interpretations of the observed spectra have been presented. We choose to adopt the results of the latest interpretation by Levin.[20] It should be noted that the vibrational assignments are immaterial for the purpose of evaluating the thermal functions since none of the fundamentals are degenerate. MO calculations[25] predict a singlet ground state with no excited states lying at energies which would be significant in the statistical calculations.

Our thermal functions essentially extend and update those reported by O'Hare[11] but are in disagreement with other literature data.[26, 27] The functions reported by Radhakrishnan[26] are based on an incorrect structure and older vibrational frequencies.[21] The set of frequencies used by Wilkins[27] are very similar to ours but his moments of inertia appear unrealistic. We conclude that his thermal functions[27] are erroneous.

References

[1]P. A. O'Hare, W. N. Hubbard, O. Glemser, and J. Wegener, J. Chem. Thermodyn. 2, 71 (1970).
[2]JANAF Thermochemical Tables: HF(g), 12–31–68; F(g), 9–30–65; SF_6(g), 6–30–76; F (g), 12–31–71; N(g), 3–31–61.

Continued on page 1216

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−15.782	−756.882	−756.882	INFINITE
100	42.613	235.853	357.961	−12.211	−759.814	−748.073	390.754
200	62.633	271.650	306.302	−6.931	−762.034	−735.376	192.060
250	71.003	286.554	300.887	−3.583	−762.711	−728.628	152.238
298.15	77.598	299.644	299.644	0.	−763.162	−722.020	126.495
300	77.824	300.125	299.646	0.144	−763.176	−721.764	125.670
350	83.238	312.545	300.614	4.176	−763.488	−714.836	106.683
400	87.497	323.949	302.828	8.448	−765.907	−707.783	92.427
450	90.849	334.456	305.766	12.910	−766.704	−700.478	81.309
500	93.504	344.171	309.127	17.522	−767.493	−693.074	72.405
600	97.341	361.583	316.453	27.078	−768.469	−678.089	59.033
700	99.891	376.792	324.010	36.947	−769.049	−662.976	49.472
800	101.653	390.252	331.465	47.030	−769.397	−647.797	42.297
900	102.914	402.302	338.678	57.261	−822.730	−631.503	36.651
1000	103.844	413.196	345.594	67.602	−821.626	−610.315	31.880
1100	104.547	423.128	352.198	78.023	−820.516	−589.237	27.981
1200	105.091	432.249	358.494	88.506	−819.412	−568.260	24.736
1300	105.519	440.678	364.496	99.037	−818.322	−547.376	21.994
1400	105.863	448.511	370.220	109.607	−817.251	−526.574	19.647
1500	106.143	455.824	375.686	120.207	−816.205	−505.848	17.615
1600	106.373	462.682	380.911	130.834	−815.184	−485.191	15.840
1700	106.565	469.137	385.913	141.481	−814.191	−464.597	14.275
1800	106.726	475.233	390.708	152.146	−813.222	−444.060	12.886
1900	106.864	481.007	395.310	162.825	−812.275	−423.578	11.645
2000	106.981	486.491	399.733	173.518	−811.347	−403.144	10.529
2100	107.083	491.714	403.989	184.221	−810.430	−382.757	9.521
2200	107.171	496.697	408.091	194.934	−809.519	−362.412	8.605
2300	107.248	501.463	412.048	205.655	−808.606	−342.109	7.770
2400	107.316	506.029	415.869	216.383	−807.685	−321.847	7.005
2500	107.376	510.411	419.564	227.118	−806.748	−301.623	6.302
2600	107.429	514.623	423.139	237.858	−805.788	−281.437	5.654
2700	107.477	518.679	426.603	248.603	−804.798	−261.288	5.055
2800	107.519	522.588	429.962	259.353	−803.771	−241.177	4.499
2900	107.557	526.362	433.221	270.107	−802.702	−221.103	3.982
3000	107.592	530.009	436.387	280.865	−801.586	−201.067	3.501
3100	107.623	533.537	439.464	291.625	−800.417	−181.069	3.051
3200	107.652	536.954	442.458	302.389	−799.193	−161.109	2.630
3300	107.677	540.267	445.372	313.156	−797.910	−141.188	2.235
3400	107.701	543.482	448.210	323.925	−796.566	−121.308	1.864
3500	107.723	546.605	450.977	334.696	−795.159	−101.467	1.514
3600	107.743	549.640	453.676	345.469	−793.687	−81.668	1.185
3700	107.761	552.592	456.310	356.244	−792.150	−61.911	0.874
3800	107.778	555.466	458.881	367.021	−790.547	−42.196	0.580
3900	107.793	558.266	461.394	377.800	−788.878	−22.524	0.302
4000	107.808	560.995	463.850	388.580	−787.144	−2.896	0.038
4100	107.821	563.657	466.252	399.361	−785.346	16.688	−0.213
4200	107.834	566.256	468.602	410.144	−783.484	36.228	−0.451
4300	107.845	568.793	470.903	420.928	−781.559	55.721	−0.677
4400	107.856	571.273	473.156	431.713	−779.573	75.170	−0.892
4500	107.866	573.696	475.363	442.499	−777.527	94.574	−1.098
4600	107.876	576.067	477.527	453.286	−775.423	113.930	−1.294
4700	107.885	578.387	479.648	464.074	−773.262	133.241	−1.481
4800	107.893	580.659	481.729	474.863	−771.046	152.505	−1.660
4900	107.901	582.884	483.771	485.653	−768.777	171.722	−1.831
5000	107.908	585.064	485.775	496.443	−766.457	190.893	−1.994
5100	107.915	587.201	487.743	507.235	−764.086	210.016	−2.151
5200	107.922	589.296	489.676	518.026	−761.668	229.093	−2.301
5300	107.928	591.352	491.575	528.819	−759.204	248.123	−2.445
5400	107.934	593.369	493.441	539.612	−756.695	267.105	−2.584
5500	107.939	595.350	495.276	550.406	−754.143	286.041	−2.717
5600	107.945	597.295	497.081	561.200	−751.549	304.930	−2.844
5700	107.949	599.205	498.856	571.995	−748.916	323.772	−2.967
5800	107.954	601.083	500.602	582.790	−746.245	342.568	−3.085
5900	107.959	602.928	502.321	593.585	−743.537	361.318	−3.199
6000	107.963	604.743	504.013	604.382	−740.794	380.021	−3.308

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [311.7 \pm 8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 415.4 \pm 50\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 416.0 \pm 50\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
26213	[2]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[850](1)	[200](1)	[500](1)
[500](1)	[450](1)	[800](1)
[300](1)	[700](1)	[200](1)

Point Group: $[C_{2v}]$ σ = [2]
Bond Distance: S–F* = [1.62] Å; S–F** = [1.73] Å
Bond Angles: F*–S–F* = [109]°; F*–S–F** = [88.3]°; F**–S–F** = [174]°
(* – equatorial ** – axial)
Product of Moments of Inertia: $I_A I_B I_C = [9.391199 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The electron–impact AP of SF_4^+ from SF_4 has been reported as 12.28 ± 0.03 eV,[1] 12.08 ± 0.1 eV,[2] and 12.1 ± 0.5 eV.[2] Using the mean value (12.15 eV) of these three measured AP as $\Delta_r H°(0\ K)$ for the direct ionization process $SF_4(g) + e^- \rightarrow SF_4^+ + 2\,e^-$, we obtain the adopted value $\Delta_f H°(SF_4^+, g, 0\ K) = 99.3\ kcal \cdot mol^{-1}$, by combining $\Delta_f H°(0\ K)$ with $\Delta_f H°(SF_4, g, 0\ K) = -180.9 \pm 5.0\ kcal \cdot mol^{-1}$.[3] We estimate that the adiabatic AP (or IP) could be as much as 0.3 eV lower than the measured vertical values,[1,2] suggesting uncertainties in $\Delta_r H°(0\ K)$ and $\Delta_f H°(0\ K)$ of ±7.0 $kcal \cdot mol^{-1}$ and ±12.0 $kcal \cdot mol^{-1}$, respectively. Our predictions are based on the fact that photoelectron studies[4] on the species ClF_3 show that the first adiabatic ionization potential is 0.23 eV lower than the vertical value and 0.35 eV lower than the results obtained by the electron–impact method. The similarity in the structures of SF_4 and ClF_3 has been noted,[5] and we predict that the geometry changes produced by ionization should also be very similar for the two fluorides.

Additional information is available which tends to provide some support for our adopted value of $IP(SF_4) = 12.15 \pm 0.3$ eV. Fehsenfeld[6] has observed a charge–transfer reaction between SF_4^+ and NO which sets the lower limit of IP at 9.25 eV. Binding energies[7] for SF_4 and SF_4^+, computed by CNDO/2 calculations and rescaled according to energy partitioning concepts, have been combined to give IP values of 11.1 eV and 10.6 eV. Three independent measurements[2,8,9] of the fragment–ion AP for SF_4^+ from SF_6 are in agreement with the result AP = 18.61 eV. We combine this $AP(SF_4^+/SF_6)$ with our adopted IP value and obtain $\Delta_r H°(0\ K) = 149.0\ kcal \cdot mol^{-1}$ for the process $SF_6(g) = SF_4(g) + 2F(g)$. This leads to a $\Delta_f H°$ of $-176.2\ kcal \cdot mol^{-1}$ for SF_4 which compares favorably with JANAF data.[3]

$\Delta_f H°$ is calculated to be 99.4 $kcal \cdot mol^{-1}$ at 298.15 K. Also, we find that the primary bond dissociation energy $D_0°(SF_3^+–F)$ is 12.9 $kcal \cdot mol^{-1}$ which when compared with $D_0°$ values[3] for SF_4 (80.0 $kcal \cdot mol^{-1}$) and SF_4^- (46.6 $kcal \cdot mol^{-1}$) indicates that the trend is $D_0°(SF_4) >> D_0°(SF_4^-) >> D_0°(SF_4^+)$. The observed instability of the radical cation towards dissociation to SF_3^+ and F is consistent with ion abundances[9,10] obtained for SF_4^+ and SF_3^+ in the mass spectra of SF_5Cl and SF_6. Values of the ratio $I(SF_3^+)/I(SF_4^+)$ lie in the range 3.1–7.0. (See the $SF_3^+(g)$ table for a discussion on its stability.) The enthalpy of atomization and mean bond dissociation energy are 278.8 $kcal \cdot mol^{-1}$ and 69.7 $kcal \cdot mol^{-1}$, respectively.

Heat Capacity and Entropy

Delwiche[8] has reported an ionization efficiency curve for SF_4^+ which was obtained from retarded potential difference (RPD) measurements on SF_6. This curve shows the existence of two excited states, lying 26213 cm^{-1} and 45167 cm^{-1} above the ground state. The level at 45167 cm^{-1} is not included here since it has a negligible effect on the thermal functions. We assume that the one unpaired electron forms two doublet states which are non–degenerate.

The ESR spectrum[11] of SF_4^+, recorded during the radiolysis of SF_6 with 2.8 MeV electrons, suggests that the four fluorine nuclei are equivalent. However, the assignment of this spectrum to SF_4^+ has been questioned by Morton and Preston[12] who presented evidence which indicates that the radical responsible is more likely be be SF_5. Their re–assignment[12] is substantiated by the results of SCF MO calculations[13] on SF_5. By analogy with the isoelectronic radical PF_4,[14,15] we predict that the SF_4^+ structure is trigonal bipyramid with the unpaired electron occupying one of the equatorial positions. We use bond angles from PF_4[14] and assume that the loss of an electron from SF_4 increases both the equatorial and axial bond lengths by 5%. Our view that the bonding in SF_4^+ is weaker than that in SF_4 follows the predictions[14] made for PF_4 and is further confirmed by the fact that the mean bond dissociation energy in SF_4 (80.0 $kcal \cdot mol^{-1}$) is roughly 10 $kcal \cdot mol^{-1}$ greater than in SF_4^+ (69.7 $kcal \cdot mol^{-1}$). The individual moments of inertia are: $I_A = 14.2509 \times 10^{-39}$, $I_B = 22.1083 \times 10^{-39}$, and $I_C = 29.8073 \times 10^{-39}\ g \cdot cm^2$.

We estimate vibrational frequencies from those for SF_4[3] by considering the effect of the structural changes brought about by ionization. On going from SF_4 to SF_4^+, we expect a decrease in all frequencies to reflect the weaker bonding in the cation.

References

[1] O. Glemser, A. Muller, D. Bohler, and B. Krebs, Z. anorg. allgem. Chem. 357, 184 (1968).
[2] D. L. Hildenbrand, J. Phys. Chem. 77, 897 (1973).

Continued from page 1216

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.505	415.404		
100	45.321	244.482	372.760	−12.828			
200	65.909	282.444	318.604	−7.232			
250	74.087	298.061	312.961	−3.725			
298.15	80.395	311.671	311.671	0.	416.044	447.346	−78.373
300	80.609	312.169	311.672	0.149	416.074	447.540	−77.924
350	85.696	324.993	312.674	4.312	416.932	452.718	−67.564
400	89.643	336.705	314.956	8.700	415.668	457.854	−59.790
450	92.718	347.449	317.978	13.262	416.010	463.099	−53.755
500	95.133	357.347	321.427	17.960	416.348	468.315	−48.925
600	98.591	375.021	328.922	27.659	417.593	478.601	−41.666
700	100.869	390.401	336.630	37.640	419.202	488.645	−36.463
800	102.435	403.979	344.217	47.809	421.021	498.443	−32.545
900	103.550	416.112	351.543	58.112	369.836	509.086	−29.547
1000	104.370	427.066	358.557	68.510	373.077	524.384	−27.391
1100	104.989	437.044	365.245	78.979	376.314	539.358	−25.612
1200	105.467	446.201	371.615	89.503	379.537	554.038	−24.117
1300	105.843	454.658	377.682	100.069	382.741	568.450	−22.841
1400	106.144	462.513	383.464	110.669	385.920	582.616	−21.738
1500	106.389	469.845	388.981	121.296	389.071	596.555	−20.774
1600	106.591	476.718	394.252	131.945	392.193	610.286	−19.924
1700	106.758	483.185	399.295	142.613	395.286	623.822	−19.168
1800	106.900	489.291	404.127	153.296	398.352	637.177	−18.490
1900	107.020	495.075	408.763	163.992	401.394	650.361	−17.880
2000	107.123	500.567	413.217	174.699	404.416	663.387	−17.326
2100	107.211	505.795	417.502	185.416	407.425	676.261	−16.821
2200	107.288	510.785	421.630	196.141	410.427	688.992	−16.359
2300	107.356	515.555	425.610	206.874	413.429	701.588	−15.934
2400	107.415	520.126	429.454	217.612	416.439	714.052	−15.541
2500	107.468	524.512	433.169	228.356	419.464	726.390	−15.177
2600	107.514	528.727	436.764	239.105	422.511	738.607	−14.839
2700	107.556	532.786	440.246	249.859	425.589	750.706	−14.523
2800	107.594	536.698	443.621	260.617	428.702	762.691	−14.228
2900	107.629	540.474	446.896	271.378	431.857	774.563	−13.951
3000	107.660	544.124	450.076	282.142	435.059	786.326	−13.691
3100	107.689	547.654	453.167	292.910	438.312	797.982	−13.446
3200	107.716	551.074	456.174	303.680	441.621	809.531	−13.214
3300	107.742	554.389	459.100	314.453	444.989	820.977	−12.995
3400	107.766	557.606	461.950	325.228	448.419	832.319	−12.787
3500	107.790	560.730	464.728	336.006	451.911	843.559	−12.589
3600	107.813	563.767	467.437	346.786	455.469	854.700	−12.401
3700	107.835	566.721	470.081	357.569	459.092	865.739	−12.222
3800	107.858	569.597	472.662	368.353	462.781	876.680	−12.051
3900	107.880	572.399	475.183	379.140	466.536	887.524	−11.887
4000	107.903	575.131	477.648	389.929	470.358	898.270	−11.730
4100	107.927	577.795	480.058	400.721	474.245	908.919	−11.580
4200	107.951	580.396	482.417	411.515	478.197	919.474	−11.435
4300	107.976	582.937	484.725	422.311	482.213	929.933	−11.296
4400	108.002	585.419	486.985	433.110	486.291	940.298	−11.163
4500	108.029	587.847	489.200	443.911	490.431	950.570	−11.034
4600	108.057	590.221	491.370	454.716	494.631	960.749	−10.910
4700	108.086	592.546	493.498	465.523	498.889	970.836	−10.790
4800	108.117	594.821	495.585	476.333	503.205	980.832	−10.674
4900	108.148	597.051	497.633	487.146	507.576	990.738	−10.561
5000	108.182	599.236	499.644	497.963	512.001	1000.553	−10.453
5100	108.216	601.379	501.618	508.783	516.479	1010.280	−10.347
5200	108.252	603.481	503.556	519.606	521.007	1019.919	−10.245
5300	108.290	605.543	505.461	530.433	525.585	1029.469	−10.146
5400	108.329	607.567	507.333	541.264	530.210	1038.933	−10.050
5500	108.369	609.556	509.174	552.099	534.882	1048.311	−9.956
5600	108.410	611.509	510.984	562.938	539.599	1057.604	−9.865
5700	108.453	613.428	512.764	573.781	544.359	1066.811	−9.776
5800	108.497	615.314	514.516	584.628	549.161	1075.935	−9.690
5900	108.542	617.169	516.241	595.480	554.004	1084.976	−9.606
6000	108.589	618.994	517.938	606.337	558.887	1093.934	−9.524

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [312.962 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -877.685 \pm 33.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -887.464 \pm 33.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^2A_1]$	0	[2]
$[^2B_1]$	[15000]	[2]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[500](1)	[375](1)	[150](2)
[430](1)	[325](1)	
[300](1)	[595](2)	

Point Group: $[D_{4h}]$ σ = [8]
Bond Distance: S–F = [1.63 ± 0.1] Å
Bond Angle: F–S–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [9.4210 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(SF_4^-, g, 0\ K) = -209.8 \pm 8.0$ kcal mol^{-1} and $EA(SF_4) = 1.25 \pm 0.56$ eV. The value of $\Delta_f H°(0\ K)$ is obtained from the electron–impact appearance potential for SF_4^- from SF_6, reported by Harland and Thynne[1] as AP = 5.0 ± 0.1 eV. This value has been verified in an independent study.[9] We assume that the negative ion is formed by the process $SF_6(g) + e^- = SF_4^-(g) + 2\ F(g)$ with no excess energies. We estimate the error in the electron–impact experiments to be ±0.3 eV (7.0 kcal mol^{-1}) which when combined with the uncertainties in the auxiliary data[2] gives an overall uncertainty in $\Delta_f H°(0\ K)$ of ±8.0 kcal mol^{-1}. Our adopted value of EA = 1.25 eV is supported by EA = 1.5 eV[3] and EA = 1.26 eV[10] which were predicted by theoretical calculations.

In the same paper, Harland and Thynne[1] also reported the $AP(SF_4^-/SF_5Cl)$ as 4.1 ± 0.1 eV. This leads to $\Delta_f H°(SF_4^-, g, 0\ K) = -199.9 \pm 5.0$ kcal mol^{-1} and $EA(SF_4) = 0.82 \pm 0.4$ eV. They[1] also reported appearance potentials for SF_3^- and SF_5^- from SF_5Cl which give EA values that are several tenths of an electron volt below JANAF data.[2] Thus, we are led to conclude that dissociative ionization of SF_5Cl probably involves excess energies and that the derived electron affinities are lower limit values.

Our adopted results give $\Delta_f H°(298.15\ K) = -212.1$ kcal·mol^{-1} and a fluoride-ion affinity (IA) of $IA(SF_3) = 30.5$ kcal·mol^{-1}. Also, we find that the primary bond dissociation energy $D_0°(SF_3^- – F)$ is 46.6 kcal·mol^{-1} which when compared with $D_0°$ values[2] for SF_4 (80.0 kcal·mol^{-1}) and SF_4^+ (12.9 kcal·mol^{-1}) indicates that the trend is $D_0°(SF_4) >> D_0°(SF_4^-) >> D_0°(SF_4^+)$. These thermochemical predictions of the SF_4^- stability are consistent with an autodetachment lifetime of 16.3 μsec, as measured by Harland and Thynne[4] using time–of–flight techniques. The enthalpy of atomization ($\Delta_{at}H°$) for the products S(g) + F^-(g) + 3 F(g) and mean bond dissociation energy are 270.5 kcal·mol^{-1} and 67.7 kcal·mol^{-1}, respectively.

Heat Capacity and Entropy

We assume a square–planar configuration (D_{4h} symmetry) similar to that found for the isoelectronic radical ClF_4.[5-7] We estimate the bond length to be slightly greater (0.03Å) than the mean (1.60Å) of the equatorial and axial S–F bonds in SF_4.[2] An upper limit of 1.70Å can be established from results of MO calculations on ClF_4.[7] The individual moments of inertia are: $I_A = 3.3526 \times 10^{-38}$ and $I_B = I_C = 1.6763 \times 10^{-38}$ g·cm^2.

The square–planar structure follows the vibrational representation $A_1 + A_2 + 2B_1 + B_2 + 2E$. We estimate the seven fundamentals by comparison with the observed frequencies for the approximately square–planar SF_4 part of SF_5^-.[2] Comparison of the experimentally measured frequencies for the related species ClF_5[2] and ClF_4^- [8] suggests that this procedure should give reliable estimates.

The electronic states and levels are based on those for ClF_4 which were predicted by Ungemach and Schaefer[7] from MO calculations. An independent MO study of ClF_4 by Gregory[6] indicates that the upper level is an $^2A_2$ state. This, however, would not alter our functions since both configurations have the same degeneracy.

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Continued on page 1216

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K							
0	0.	0.	INFINITE	−18.480	−877.685		
100	50.869	236.570	382.190	−14.562			
200	75.553	279.949	320.747	−8.160			
250	83.644	297.728	314.402	−4.168			
298.15	89.187	312.962	312.962	0.	−887.464	−844.038	147.872
300	89.365	313.514	312.964	0.165	−887.495	−843.769	146.913
350	93.431	327.613	314.068	4.741	−888.303	−836.416	124.828
400	96.371	340.291	316.567	9.490	−891.285	−828.863	108.238
450	98.542	351.773	319.851	14.365	−892.708	−820.984	95.297
500	100.180	362.244	323.574	19.335	−894.178	−812.933	84.927
600	102.430	380.725	331.601	29.475	−896.648	−796.445	69.337
700	103.854	396.629	339.781	39.794	−898.858	−779.568	58.172
800	104.807	410.563	347.776	50.230	−900.931	−762.384	49.779
900	105.473	422.948	355.453	60.746	−956.058	−743.864	43.173
1000	105.957	434.087	362.769	71.318	−956.800	−720.248	37.622
1100	106.319	444.204	369.719	81.933	−957.575	−696.555	33.077
1200	106.596	453.467	376.318	92.579	−958.386	−672.790	29.286
1300	106.814	462.009	382.585	103.250	−959.235	−648.956	26.075
1400	106.987	469.931	388.545	113.941	−960.123	−625.056	23.321
1500	107.128	477.317	394.219	124.647	−961.050	−601.090	20.932
1600	107.244	484.235	399.631	135.366	−962.015	−577.062	18.839
1700	107.342	490.740	404.801	146.095	−963.018	−552.972	16.991
1800	107.425	496.877	409.748	156.833	−964.054	−528.821	15.346
1900	107.499	502.688	414.488	167.580	−965.119	−504.613	13.873
2000	107.564	508.203	419.037	178.333	−966.208	−480.348	12.545
2100	107.625	513.453	423.409	189.092	−967.314	−456.028	11.343
2200	107.682	518.461	427.616	199.858	−968.429	−431.655	10.249
2300	107.738	523.249	431.671	210.629	−969.545	−407.231	9.248
2400	107.793	527.835	435.583	221.405	−970.654	−382.758	8.331
2500	107.849	532.237	439.362	232.187	−971.749	−358.240	7.485
2600	107.907	536.468	443.016	242.975	−972.820	−333.679	6.704
2700	107.968	540.541	446.553	253.769	−973.860	−309.076	5.979
2800	108.031	544.469	449.980	264.569	−974.861	−284.436	5.306
2900	108.098	548.261	453.304	275.375	−975.818	−259.761	4.679
3000	108.168	551.927	456.531	286.189	−976.725	−235.054	4.093
3100	108.241	555.475	459.666	297.009	−977.576	−210.318	3.544
3200	108.319	558.913	462.714	307.837	−978.366	−185.555	3.029
3300	108.399	562.247	465.680	318.673	−979.092	−160.768	2.545
3400	108.483	565.484	468.568	329.517	−979.751	−135.960	2.089
3500	108.570	568.630	471.382	340.370	−980.341	−111.134	1.659
3600	108.660	571.690	474.126	351.231	−980.860	−86.292	1.252
3700	108.752	574.668	476.803	362.102	−981.306	−61.436	0.867
3800	108.846	577.570	479.417	372.981	−981.679	−36.570	0.503
3900	108.942	580.398	481.970	383.871	−981.978	−11.694	0.157
4000	109.039	583.158	484.465	394.770	−982.203	13.188	−0.172
4100	109.138	585.852	486.905	405.679	−982.356	38.074	−0.485
4200	109.236	588.483	489.293	416.597	−982.437	62.964	−0.783
4300	109.336	591.054	491.630	427.526	−982.446	87.854	−1.067
4400	109.435	593.569	493.918	438.465	−982.385	112.745	−1.338
4500	109.534	596.029	496.160	449.413	−982.255	137.633	−1.598
4600	109.632	598.438	498.357	460.371	−982.059	162.517	−1.845
4700	109.730	600.797	500.512	471.339	−981.796	187.397	−2.083
4800	109.826	603.108	502.625	482.317	−981.470	212.270	−2.310
4900	109.921	605.373	504.699	493.305	−981.082	237.135	−2.528
5000	110.014	607.595	506.735	504.301	−980.634	261.992	−2.737
5100	110.105	609.774	508.734	515.307	−980.128	286.840	−2.938
5200	110.194	611.913	510.698	526.322	−979.565	311.678	−3.131
5300	110.281	614.013	512.627	537.346	−978.948	336.503	−3.316
5400	110.366	616.075	514.524	548.378	−978.278	361.317	−3.495
5500	110.448	618.101	516.389	559.419	−977.558	386.117	−3.667
5600	110.528	620.092	518.223	570.468	−976.788	410.905	−3.833
5700	110.605	622.049	520.027	581.524	−975.972	435.677	−3.993
5800	110.679	623.973	521.803	592.589	−975.110	460.435	−4.147
5900	110.751	625.866	523.551	603.660	−974.205	485.179	−4.295
6000	110.820	627.728	525.271	614.739	−973.257	509.906	−4.439

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 282.760 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1609.428 \pm 0.84\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1614.940 \pm 0.84\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
800.8(1)	1029.6(3)
264.2(2)	388.7(3)

Ground State Quantum Weight: [1] $\sigma = 12$

Point Group: T_d

Bond Distance: Si–F = 1.552 ± 0.002 Å

Bond Angle: F–Si–F = 109° 28'

Product of the Moments of Inertia: $I_A I_B I_C = 8.321027 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(SiF_4, g, 298.15\ K) = -385.98 \pm 0.20\ kcal \cdot mol^{-1}$ is the result of measurement of the direct combination of the elements in a bomb calorimeter by Wise *et al.*[1] and is the value recommended by CODATA.[2] Bousquet *et al.*[3] determined $\Delta_f H°(298.15\ K) = -385 \pm 4\ kcal \cdot mol^{-1}$, also by fluorine combustion calorimetry, which is less precise but is in agreement with the adopted value. An average result, $\Delta_f H°(298.15\ K) = -372.4 \pm 0.4\ kcal \cdot mol^{-1}$ by Vorob'ev *et al.*[4] from the reaction of $SiF_4(g)$ and Na(cr) and from two rather involved enthalpy of solution schemes, is not used.

Using JANAF auxiliary values,[5] $\Delta_{at} H°(0\ K) = 564.76 \pm 3\ kcal \cdot mol^{-1}$ is calculated for the process $SiF_4(g) = Si(g) + 4\ F(g)$.

Heat Capacity and Entropy

The four fundamental vibrational frequencies are adopted from the vapor–phase Raman spectral investigation of Clark and Rippon.[6] Jones *et al.*[7] photographed the Raman spectrum of the liquid and assigned values of 800, 268, 1010, and 390 cm^{-1} to the four fundamental vibrational frequencies. Yost *et al.*[8] determined only ν_1 at 800 cm^{-1} Shimanouchi[9] references four articles including that of Jones *et al.*[7] and has selected 800, 268, 1032, and 389 cm^{-1}. All of these assignments are in good agreement.

The interatomic distances from electron diffraction studies were found to be 1.555 ± 0.002 and 2.534 ± 0.003 Å for Si–F and F...F, respectively, by Beagley *et al.*[10] and 1.552 ± 0.002 and 2.534 ± 0.003 Å by Hagen and Hedberg.[11] The value of Si–F = 1.552 ± 0.002 Å is adopted because it is in agreement with the F...F distance and the tetrahedral bond angle. The three principal moments of inertia are: $I_A = I_B = I_C = 20.2640 \times 10^{-39}\ g \cdot cm^2$.

Our calculation of $S°(298.15\ K) = 67.55 \pm 0.10\ cal\ K^{-1} \cdot mol^{-1}$ agrees with the value recommended by CODATA.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.356	−1609.428	−1609.428	INFINITE
100	41.815	220.670	339.001	−11.833	−1611.986	−1599.596	835.543
200	60.878	255.943	289.111	−6.634	−1613.823	−1586.418	414.330
250	67.873	270.301	283.941	−3.410	−1614.454	−1579.491	330.017
298.15	73.621	282.760	282.760	0.	−1614.940	−1572.711	275.532
300	73.825	283.216	282.761	0.136	−1614.957	−1572.449	273.788
350	78.887	294.987	283.679	3.958	−1615.348	−1565.332	233.613
400	83.143	305.807	285.778	8.012	−1615.642	−1558.165	203.476
450	86.687	315.811	288.566	12.260	−1615.851	−1550.967	180.032
500	89.626	325.102	291.761	16.670	−1615.992	−1543.750	161.274
600	94.090	341.862	298.746	25.870	−1616.116	−1529.287	133.136
700	97.207	356.614	305.980	35.444	−1616.093	−1514.816	113.037
800	99.433	369.747	313.145	45.282	−1615.983	−1500.354	97.963
900	101.063	381.558	320.102	55.311	−1615.824	−1485.910	86.240
1000	102.285	392.272	326.791	65.481	−1615.645	−1471.484	76.862
1100	103.221	402.067	333.196	75.758	−1615.463	−1457.077	69.191
1200	103.952	411.081	339.316	86.118	−1615.294	−1442.686	62.798
1300	104.532	419.425	345.161	96.543	−1615.147	−1428.308	57.390
1400	105.000	427.190	350.746	107.021	−1615.034	−1413.941	52.755
1500	105.383	434.447	356.087	117.541	−1614.959	−1399.580	48.738
1600	105.699	441.259	361.199	128.095	−1614.928	−1385.222	45.223
1700	105.963	447.675	366.099	138.679	−1665.120	−1370.418	42.108
1800	106.186	453.738	370.801	149.286	−1664.952	−1353.088	39.266
1900	106.376	459.485	375.319	159.915	−1664.787	−1335.767	36.723
2000	106.540	464.945	379.665	170.561	−1664.622	−1318.454	34.434
2100	106.681	470.147	383.851	181.222	−1664.455	−1301.150	32.364
2200	106.803	475.113	387.887	191.896	−1664.279	−1283.854	30.483
2300	106.911	479.863	391.783	202.582	−1664.090	−1266.565	28.765
2400	107.005	484.415	395.549	213.278	−1663.880	−1249.286	27.190
2500	107.089	488.785	399.191	223.983	−1663.644	−1232.016	25.742
2600	107.163	492.986	402.719	234.696	−1663.375	−1214.756	24.405
2700	107.229	497.032	406.137	245.415	−1663.068	−1197.508	23.167
2800	107.289	500.933	409.454	256.141	−1662.717	−1180.271	22.018
2900	107.342	504.698	412.673	266.873	−1662.316	−1163.047	20.949
3000	107.391	508.338	415.802	277.610	−1661.862	−1145.839	19.951
3100	107.435	511.860	418.844	288.351	−1661.349	−1128.647	19.018
3200	107.474	515.272	421.804	299.096	−1660.775	−1111.472	18.143
3300	107.511	518.580	424.687	309.846	−1660.137	−1094.316	17.322
3400	107.544	521.790	427.496	320.598	−1659.432	−1077.180	16.549
3500	107.574	524.908	430.235	331.354	−1658.660	−1060.066	15.821
3600	107.602	527.938	432.907	342.113	−2041.969	−1032.514	14.981
3700	107.628	530.887	435.515	352.875	−2040.643	−1004.492	14.181
3800	107.652	533.758	438.063	363.639	−2039.247	−976.507	13.423
3900	107.674	536.554	440.553	374.405	−2037.783	−948.558	12.705
4000	107.694	539.280	442.987	385.173	−2036.248	−920.649	12.022
4100	107.713	541.940	445.368	395.944	−2034.645	−892.779	11.374
4200	107.730	544.536	447.699	406.716	−2032.973	−864.948	10.757
4300	107.747	547.071	449.980	417.490	−2031.234	−837.159	10.169
4400	107.762	549.548	452.215	428.265	−2029.427	−809.410	9.609
4500	107.776	551.970	454.405	439.042	−2027.554	−781.703	9.074
4600	107.789	554.339	456.552	449.820	−2025.617	−754.039	8.562
4700	107.802	556.657	458.657	460.600	−2023.617	−726.417	8.073
4800	107.814	558.927	460.723	471.381	−2021.554	−698.839	7.605
4900	107.825	561.150	462.750	482.162	−2019.432	−671.305	7.156
5000	107.835	563.329	464.739	492.945	−2017.250	−643.814	6.726
5100	107.845	565.464	466.694	503.729	−2015.012	−616.367	6.313
5200	107.854	567.558	468.613	514.514	−2012.718	−588.965	5.916
5300	107.863	569.613	470.500	525.300	−2010.371	−561.607	5.535
5400	107.871	571.629	472.354	536.087	−2007.971	−534.295	5.168
5500	107.879	573.608	474.177	546.874	−2005.521	−507.027	4.815
5600	107.886	575.552	475.970	557.663	−2003.022	−479.804	4.475
5700	107.893	577.462	477.734	568.452	−2000.477	−452.627	4.148
5800	107.900	579.338	479.469	579.241	−1997.886	−425.494	3.832
5900	107.906	581.183	481.178	590.031	−1995.253	−398.406	3.527
6000	107.912	582.997	482.860	600.822	−1992.577	−371.364	3.233

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 133.955\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 558.6\ K$

$\Delta_f H°(0\ K) = -1647.108 \pm 3.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1649.333 \pm 3.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of TiF_4(cr) was measured using a fluorine bomb calorimeter by Greenberg *et al.*[1] Gross *et al.*[2] reported a value of $-393.4\ kcal \cdot mol^{-1}$ for $\Delta_f H°(298.15\ K)$. The latter measurements were not corrected for impurities in the titanium sample, thus the value reported by Greenberg *et al.*[1] is adopted.

Heat Capacity and Entropy

The heat capacity of TiF_4(cr) has been measured over the temperature range 6 to 304 K by Euler and Westrum.[3] They obtained the value of $S°(298.15\ K)$ based on $S°(10\ K) = 0.11\ cal\ K^{-1} \cdot mol^{-1}$. Heat capacities above 300 K are estimated from those of ZrF_4(cr).[4]

Sublimation Data

The sublimation point is calculated as the temperature at which the fugacity is one atmosphere for the process $TiF_4(cr) = TiF_4(g)$. The enthalpy of sublimation is obtained from the data of Hall *et al.*[5]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.255	−1647.108	−1647.108	INFINITE
100	54.518	41.970	219.476	−17.751	−1650.978	−1620.275	846.345
200	92.383	92.772	143.789	−10.204	−1651.206	−1589.254	415.071
298.15	114.265	133.955	133.955	0.	−1649.333	−1559.177	273.161
300	114.600	134.663	133.957	0.212	−1649.284	−1558.618	271.380
400	126.650	169.380	138.609	12.309	−1646.239	−1528.835	199.645
500	134.557	198.535	147.757	25.389	−1642.630	−1499.893	156.693
600	140.080	223.578	158.357	39.133	−1638.659	−1471.714	128.124
700	144.139	245.489	169.272	53.352	−1634.431	−1444.221	107.769
800	147.235	264.946	180.038	67.926	−1630.000	−1417.348	92.543
900	149.662	282.432	190.460	82.775	−1625.451	−1391.039	80.734
1000	151.670	298.307	200.463	97.844	−1620.883	−1365.239	71.313
1100	153.302	312.842	210.028	113.095	−1616.386	−1339.893	63.626
1200	154.641	326.239	219.161	128.494	−1615.974	−1314.832	57.233
1300	155.812	338.665	227.882	144.018	−1610.969	−1289.939	51.830
1400	156.816	350.249	236.213	159.650	−1605.977	−1265.432	47.214
1500	157.695	361.099	244.181	175.377	−1601.022	−1241.281	43.225

PREVIOUS: June 1964 CURRENT: September 1967

$S°(298.15\ K)$ = [314.928 ± 2.1] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1547.811 \pm 4.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1551.427 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[701](1)	[750](3)
[168](2)	[178](3)

Ground State Quantum Weight: [1] σ = [12]
Point Group: [T_d]
Bond Distance: Ti-F = [1.80]Å
Bond Angle: F-Ti-F = [109°28']
Product of the Moments of Inertia: $I_A I_B I_C$ = [2.025160 × 10^{-113}] $g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiF_4(g)$ is calculated from that of the crystal and the enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, obtained from vapor pressure measurements. Hall *et al.*[1] have reported extensive vapor pressure data for the reaction $TiF_4(cr) = TiF_4(g)$. 2nd and 3rd law analyses of their data yielded the following results.

Method	Data Points	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift cal $K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$* $kcal·mol^{-1}$
1. Spoon Gauge	25**	441-552	23.5 ± 0.1	23.37	−0.3 ± 0.1	−370.8
2. Ruff-Fischer	6	435-498	23.0 ± 0.4	23.40	+0.9 ± 0.9	−370.8
3. Transpiration	3	426-512	25.8 ± 2.0	23.72	−4.5 ± 4.3	−370.5
4. Rodebush	6	473-537	23.7 ± 0.6	23.39	−0.5 ± 1.2	−370.8
5. 1, 2, and 4	36***	435-552	23.4 ± 0.1	23.37	−0.1 ± 0.1	−370.8

* Calculation based on 3rd law $\Delta_r H°$.
** Four points rejected due to failure of a statistical test.
*** Eight points rejected due to failure of a statistical test.

Heat Capacity and Entropy

The interatomic distance is obtained from a correlation of the measured values for $TiCl_4(g)$, $TiBr_4(g)$, $TiCl_6$,[-2] and TiF_6.[-2] The principal moments of inertia are $I_A = I_B = I_C = 27.2575 \times 10^{-39}\ g·cm^2$.

The vibrational frequencies are estimated by a valence force field treatment of estimated force constants. The force constants are estimated from a correlation with the constants of CF_4, SiF_4, CCl_4, $SiCl_4$, CBr_4, $SiBr_4$, $TiCl_4$, and $TiBr_4$. The resulting frequencies are adjusted so that calculations of $\Delta_{sub}H°(298.15\ K)$ by both 2nd and 3rd law methods are in agreement.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−18.863	−1547.811	−1547.811	INFINITE
100	58.633	236.952	383.035	−14.608	−1549.930	−1538.725	803.748
200	74.506	283.076	322.400	−7.865	−1550.962	−1527.071	398.830
250	80.375	300.348	316.305	−3.989	−1551.255	−1521.061	317.808
298.15	85.177	314.928	314.928	0.	−1551.427	−1515.229	265.462
300	85.344	315.455	314.930	0.158	−1551.432	−1515.004	263.786
350	89.374	328.925	315.984	4.529	−1551.525	−1508.925	225.195
400	92.577	341.077	318.374	9.081	−1551.561	−1502.836	196.250
450	95.109	352.133	321.520	13.776	−1551.558	−1496.745	173.738
500	97.118	362.262	325.095	18.584	−1551.530	−1490.656	155.728
600	100.018	380.244	332.826	28.451	−1551.435	−1478.490	128.714
700	101.942	395.816	340.737	38.555	−1551.322	−1466.341	109.420
800	103.269	409.520	348.496	48.819	−1551.202	−1454.209	94.950
900	104.217	421.741	355.968	59.196	−1551.124	−1442.090	83.697
1000	104.915	432.759	363.105	69.655	−1551.167	−1429.975	74.694
1100	105.442	442.785	369.900	80.174	−1551.403	−1417.846	67.328
1200	105.849	451.977	376.362	90.739	−1555.824	−1405.567	61.183
1300	106.170	460.463	382.509	101.340	−1555.741	−1393.049	55.973
1400	106.427	468.341	388.362	111.971	−1555.751	−1380.535	51.508
1500	106.636	475.691	393.941	122.624	−1555.869	−1368.016	47.639
1600	106.808	482.579	399.268	133.297	−1556.108	−1355.485	44.252
1700	106.952	489.058	404.361	143.985	−1556.483	−1342.935	41.263
1800	107.072	495.175	409.238	154.686	−1557.005	−1330.359	38.606
1900	107.175	500.967	413.915	165.399	−1557.684	−1317.751	36.227
2000	107.263	506.467	418.406	176.121	−1573.217	−1304.647	34.074
2100	107.338	511.702	422.725	186.851	−1574.985	−1291.176	32.116
2200	107.404	516.697	426.884	197.588	−1576.750	−1277.620	30.335
2300	107.462	521.472	430.894	208.332	−1578.507	−1263.983	28.706
2400	107.512	526.047	434.764	219.080	−1580.249	−1250.271	27.211
2500	107.557	530.437	438.503	229.834	−1581.968	−1236.486	25.835
2600	107.597	534.656	442.121	240.592	−1583.658	−1222.634	24.563
2700	107.632	538.718	445.624	251.353	−1585.314	−1208.716	23.384
2800	107.664	542.632	449.019	262.118	−1586.928	−1194.739	22.288
2900	107.692	546.411	452.313	272.886	−1588.495	−1180.704	21.267
3000	107.718	550.062	455.510	283.656	−1590.011	−1166.617	20.313
3100	107.741	553.595	458.618	294.429	−1591.470	−1152.479	19.419
3200	107.763	557.016	461.639	305.204	−1592.871	−1138.296	18.581
3300	107.782	560.332	464.580	315.982	−1594.209	−1124.069	17.793
3400	107.800	563.550	467.444	326.761	−1595.482	−1109.804	17.050
3500	107.816	566.675	470.235	337.542	−1596.689	−1095.501	16.349
3600	107.830	569.713	472.956	348.324	−1597.827	−1081.165	15.687
3700	107.844	572.667	475.611	359.108	−2007.995	−1059.010	14.951
3800	107.857	575.543	478.203	369.893	−2007.761	−1033.365	14.205
3900	107.868	578.345	480.735	380.679	−2007.512	−1007.726	13.497
4000	107.879	581.076	483.210	391.466	−2007.248	−982.094	12.825
4100	107.889	583.740	485.629	402.255	−2006.968	−956.469	12.186
4200	107.898	586.340	487.996	413.044	−2006.670	−930.850	11.577
4300	107.907	588.879	490.313	423.834	−2006.354	−905.240	10.996
4400	107.915	591.360	492.582	434.625	−2006.020	−879.636	10.443
4500	107.923	593.785	494.804	445.417	−2005.666	−854.040	9.913
4600	107.930	596.157	496.981	456.210	−2005.292	−828.452	9.407
4700	107.936	598.479	499.116	467.003	−2004.897	−802.873	8.923
4800	107.943	600.751	501.210	477.797	−2004.482	−777.302	8.459
4900	107.948	602.977	503.264	488.592	−2004.044	−751.741	8.014
5000	107.954	605.158	505.280	499.387	−2003.585	−726.188	7.586
5100	107.959	607.296	507.260	510.183	−2003.103	−700.645	7.176
5200	107.964	609.392	509.204	520.979	−2002.598	−675.111	6.782
5300	107.969	611.449	511.114	531.775	−2002.070	−649.587	6.402
5400	107.973	613.467	512.990	542.572	−2001.517	−624.074	6.037
5500	107.977	615.448	514.835	553.370	−2000.941	−598.572	5.685
5600	107.981	617.394	516.649	564.168	−2000.340	−573.079	5.345
5700	107.985	619.305	518.434	574.966	−1999.715	−547.598	5.018
5800	107.988	621.183	520.189	585.765	−1999.064	−522.128	4.702
5900	107.991	623.029	521.917	596.564	−1998.388	−496.669	4.397
6000	107.995	624.844	523.617	607.363	−1997.687	−471.223	4.102

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 104.700 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}\ (\alpha \rightarrow \beta) = 723\ K$
$T_{fus} = 1205 \pm 2\ K$

$\Delta_f H°(0\ K) = -1905.601 \pm 0.11\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1911.251 \pm 0.11\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° =$ Unknown
$\Delta_{fus} H° = 64.224 \pm 0.42\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of zirconium tetrafluoride was measured by direct combination of the elements in a bomb calorimeter by Greenberg *et al.*[1] The reported value, $\Delta_f H°(ZrF_4, cr, 298.15\ K) = -456.80 \pm 0.25\ kcal \cdot mol^{-1}$, is adopted.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range 5 to 307 K were determined by adiabatic calorimetry by Westrum.[2] Using these low temperature $C_p°$ data the value of $S°(298.15\ K)$ is derived as 25.024 ± 0.05 cal $K^{-1} \cdot mol^{-1}$ based on $S°(10\ K) = 0.0074$ cal $K^{-1} \cdot mol^{-1}$.

McDonald *et al.*[3] measured the high temperature enthalpies of ZrF_4(cr) at temperatures 283.9–1225.8 K in a copper block drop calorimeter. Smith *et al.*[4] used a Bunsen ice calorimeter for the enthalpy measurements in the temperature range 273–1150 K. These two sets of enthalpy data are not in good agreement. It is possible that the discrepancies are due to the difference in crystal structure of the samples used (see "Transition Data" for more information). In order to join smoothly with the low temperature heat capacities at 298.15 K, the high temperature heat capacities derived from the enthalpy data of McDonald *et al.*[3] are adopted. The $C_p°$ values above 1200 K are obtained by smooth extrapolation.

Fontana and Winand[8] also measured the enthalpy of ZrF_4 in the range 773–1350 K. Their reported average heat capacity in this range and their reported enthalpies are considerably lower than those adopted.

Transition Data

Gaudreau[5] presented evidence that ZrF_4 has three crystal structures (α, β, and) and one amorphous form. Chretien and Gaudreau[6] found that ZrF_4(cr) has an α (tetragonal) and β (monoclinic) form with a transition temperature of $T_{trs} = 723$ K. The crystal data compilation of Donnay and Ondik[7] tabulated two monoclinic structures for ZrF_4; one of which was specified as the β form while no mention was made of a tetragonal form.

The ZrF_4 sample employed by McDonald *et al.*[3] for enthalpy measurement was prepared by dissolving hafnium–free zirconium metal in 48% aqueous HF, and the resulting solution was evaporated to dryness. The crystalline product was heated slowly to 773 K in a platinum boat in a slow current of anhydrous HF. X–ray diffraction showed only crysalline ZrF_4. Wet analysis indicated 54.6% Zr (theory 54.55) and 44.9% F (theory 45.45). Due to the above facts we are uncertain whether the sample prepared is a mixture of α and β forms of a pure $ZrF_4(\beta)$. Smith *et al.*[4] obtained their ZrF_4 sample from the Oak Ridge National Laboratories, Oak Ridge, Tenn. Since the method of preparation of the compound is unavailable from the report, we do not know what kind of sample they used for measurement.

Because of the above unresolved situation, we emphasize that this ZrF_4(cr) table is not strictly a α, β-combined phase table. However, the differences in the calculated functions are probably not significant.

Fusion Data

T_{fus} and $\Delta_{fus}H°$ are taken from McDonald *et al*[3]. The values were obtained under conditions greater than one atmosphere. Fontana and Winand[8] reported a heat of melting of 11.81 ± 2.40 kcal $\cdot mol^{-1}$ (under pressure).

Sublimation Data

The sublimation temperature ($T_{sub} = 1179$) is calculated as the temperature at which the fugacity is one atmosphere for the process $ZrF_4(cr) = ZrF_4(g)$. Since the sublimation temperature is lower than the melting point, the ZrF_4 sublimes before it melts.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−17.497	−1905.601	−1905.601	INFINITE
100	42.091	22.932	182.385	−15.945	−1910.750	−1877.563	980.738
200	84.559	66.906	113.663	−9.351	−1912.207	−1843.517	481.477
298.15	103.596	104.700	104.700	0.	−1911.251	−1809.955	317.097
300	103.805	105.342	104.702	0.192	−1911.222	−1809.327	315.032
400	113.470	136.661	108.907	11.101	−1909.310	−1775.635	231.874
500	119.704	162.685	117.134	22.776	−1906.992	−1742.478	182.035
600	123.972	184.911	126.623	34.973	−1904.433	−1709.812	148.852
700	126.984	204.264	136.362	47.531	−1901.745	−1677.587	125.183
800	129.411	221.379	145.940	60.351	−1898.994	−1645.751	107.457
900	131.838	236.761	155.191	73.413	−1896.187	−1614.264	93.689
1000	134.097	250.772	164.059	86.713	−1893.323	−1583.092	82.692
1100	136.231	263.652	172.535	100.228	−1890.419	−1552.210	73.708
1200	138.281	275.592	180.632	113.953	−1891.188	−1521.371	66.224
1300	140.373	286.743	188.370	127.885	−1887.663	−1490.695	59.897
1400	142.507	297.225	195.774	142.031	−1884.009	−1460.296	54.484

PREVIOUS: June 1969 CURRENT: June 1975

$S°(298.15\ K) = [319.516 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1669.395 \pm 3.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1673.600 \pm 3.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[630](1)	668(3)
[180](2)	190(3)

Ground State Quantum Weight: [1] $\sigma = 12$
Point Group: T_d
Bond Distance: Zr–F = 1.94 ± 0.02 Å
Bond Angle: F–Zr–F = 109° 28'
Products of the Moments of Inertia: $I_A I_B I_C = 3.174220 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The vapor pressures of ZrF_4(cr) in the temperature range 617–1150 K were determined by many investigators using various methods. Based on the reported vapor pressure data, the corresponding enthalpies of sublimation are evaluated by the 2nd and 3rd law methods. Using the 3rd law $\Delta_{sub}H(298.15\ K)$ and $\Delta_f H°(ZrF_4, cr, 298.15\ K) = -456.8\ kcal \cdot mol^{-1}$, the enthalpies of formation at 298.15 K for ZrF_4(g) are evaluated. The results are presented in the table below. The values of $\Delta_f H°(ZrF_4, g, 298.15\ K)$, listed in the last column of this table are in excellent agreement which indicate that the estimated missing vibrational frequencies ν_1 and ν_2 are reasonable. The enthalpy of formation at 298.15 K for ZrF_4 (g) is adopted as $-400.0\ kcal \cdot mol^{-1}$.

Source	Method	T/K	Points	$\Delta_{sub}H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	Drift J $K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ kcal·mol⁻¹
[1]	unavailable	950–1150	eqn	56.49 ± 0.12	56.83	0.3	−399.97
[2]	transpiration	617–881	14	60.67 ± 0.09	57.13	−3.4 ± 0.1	−399.67
[3]	transpiration	900–1150	6	60.64 ± 0.13	57.24	−3.3 ± 0.1	−399.56
[4]	quasistatic	710–808	29	56.11 ± 0.62	56.65	0.5 ± 0.6	−400.15
[5]	torsion/effusion	748–849	15	55.81 ± 1.44	57.05	1.5 ± 1.8	−399.75
[6]	torsion/effusion	735–825	10	52.59 ± 0.39	57.09	5.7 ± 0.5	−399.71
[7]	Knudsen–effusion	720–825	5	51.53 ± 0.05	54.79	4.1 ± 0.1	−402.01
[8]	mass spectrometry	700–900	5	59.25 ± 2.34	57.30	−2.4 ± 2.9	−399.50
[9]	"bell method"	1000–1150	eqn	57.38 ± 0.12	56.89	−0.5	−399.91
[10]	mass spectrometry	769	1	—	57.58	—	−399.22

Heat Capacity and Entropy

The molecular structure of ZrF_4(g) has been studied by electron diffraction by Spiridonov.[11] The configuration was found to be a regular tetrahedron with interatomic distance Zr–F = 1.94 ± 0.02 Å and F–Zr–F bond angle = 109.47° which are adopted.

Employing the estimated interaction coefficients and interatomic distance Zr–F = 1.85 Å, Godnev *et al.*[12] calculated three vibrational frequencies for ZrF_4(g) as ν_2 = 150–200, and $\nu_4 = 180 \pm 230\ cm^{-1}$. Bucher *et al.*[13] observed the infrared spectra of some group IV halides and assigned $\nu_3 = 668$ and $\nu_4 = 190 \pm 20\ cm^{-1}$ for ZrF_4 (g). The frequency ν_3 has also been reported as $670\ cm^{-1}$.[14] In studying matrix isolated ZrF_4, Hauge *et al.*[15] found a strong infrared band at 668.0 cm^{-1} in an argon matrix and 677.0 cm^{-1} in a neon matrix; both of which were attributed to the ν_3 stretch frequency. The values of ν_3 and ν_4 adopted here are those reported by Buchler *et al.*[13] The adopted ν_1 is obtained by correlating the corresponding frequencies of the tetrafluorides of C, Pb, Si, Ti and Ge with their respective interatomic distances. ν_2 is calculated from ν_1, ν_3 and ν_4 usng the relationship[15] $\nu_3\nu_4/\nu_1\nu_2 = 2/3 + 4$ F/Zr where F and Zr are gram atomic weights of fluorine and zirconium, respectively. Vibrational frequencies (635, 178, 668, and 190 cm^{-1}) were suggested by Godnev *et al.*[12] who also critically examined the sublimation data in order to achieve internal consistency. These values are in good agreement with our adopted values. The three principal moments of inertia are $I_A = I_B = I_C = 31.6625 \times 10^{-39}\ g \cdot cm^2$.

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Continued on page 1216

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹·mol⁻¹)	$S°$ (J·K⁻¹·mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹·mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−18.942	−1669.395	−1669.395	INFINITE
100	57.127	240.945	388.852	−14.791	−1671.944	−1660.559	867.387
200	75.813	286.909	327.175	−8.053	−1673.258	−1648.568	430.562
250	82.385	304.559	320.928	−4.092	−1673.517	−1642.362	343.153
298.15	87.393	319.516	319.516	0.	−1673.600	−1636.352	286.682
300	87.561	320.057	319.518	0.162	−1673.601	−1636.120	284.874
350	91.536	333.867	320.599	4.644	−1673.567	−1629.875	243.246
400	94.573	346.297	323.048	9.300	−1673.461	−1623.640	212.026
450	96.905	357.577	326.267	14.089	−1673.310	−1617.421	187.745
500	98.716	367.885	329.921	18.982	−1673.135	−1611.220	168.323
600	101.275	386.127	337.808	28.991	−1672.764	−1598.872	139.194
700	102.939	401.872	345.861	39.207	−1672.417	−1586.585	118.392
800	104.071	415.696	353.744	49.561	−1672.132	−1574.344	102.794
900	104.872	428.002	361.324	60.011	−1671.939	−1562.133	90.664
1000	105.459	439.084	368.555	70.529	−1671.856	−1549.938	80.960
1100	105.900	449.157	375.432	81.097	−1671.899	−1537.745	73.021
1200	106.239	458.386	381.965	91.705	−1675.785	−1525.320	66.395
1300	106.506	466.901	388.176	102.343	−1675.554	−1512.791	60.785
1400	106.719	474.802	394.084	113.005	−1675.384	−1500.278	55.976
1500	106.893	482.171	399.714	123.685	−1675.288	−1487.775	51.809
1600	107.035	489.074	405.086	134.382	−1675.276	−1475.275	48.163
1700	107.153	495.567	410.219	145.092	−1675.357	−1462.772	44.946
1800	107.253	501.695	415.132	155.812	−1675.542	−1450.262	42.086
1900	107.338	507.496	419.842	166.542	−1675.837	−1437.740	39.526
2000	107.410	513.003	424.364	177.279	−1676.249	−1425.198	37.222
2100	107.472	518.245	428.710	188.023	−1676.782	−1412.633	35.137
2200	107.526	523.246	432.895	198.773	−1698.764	−1399.294	33.223
2300	107.574	528.027	436.928	209.528	−1699.970	−1385.654	31.469
2400	107.615	532.606	440.820	220.288	−1701.161	−1371.963	29.860
2500	107.652	537.000	444.580	231.051	−1702.330	−1358.222	28.379
2600	107.685	541.223	448.216	241.818	−1703.472	−1344.435	27.010
2700	107.714	545.288	451.736	252.588	−1704.579	−1330.605	25.742
2800	107.740	549.205	455.148	263.361	−1705.645	−1316.735	24.564
2900	107.763	552.987	458.457	274.136	−1706.666	−1302.827	23.466
3000	107.785	556.640	461.669	284.914	−1707.635	−1288.885	22.441
3100	107.804	560.175	464.790	295.693	−1708.548	−1274.911	21.482
3200	107.821	563.598	467.825	306.474	−1709.403	−1260.909	20.582
3300	107.837	566.916	470.777	317.257	−1710.196	−1246.881	19.736
3400	107.851	570.135	473.652	328.042	−1710.924	−1232.830	18.940
3500	107.865	573.262	476.454	338.827	−1711.586	−1218.759	18.189
3600	107.877	576.301	479.186	349.614	−1712.180	−1204.669	17.479
3700	107.888	579.257	481.850	360.403	−1712.705	−1190.564	16.808
3800	107.898	582.134	484.452	371.192	−1713.161	−1176.447	16.171
3900	107.908	584.937	486.992	381.982	−1713.547	−1162.317	15.567
4000	107.917	587.669	489.475	392.774	−1713.864	−1148.179	14.994
4100	107.925	590.334	491.903	403.566	−1714.113	−1134.034	14.448
4200	107.932	592.934	494.278	414.359	−1714.293	−1119.883	13.928
4300	107.940	595.474	496.602	425.152	−1714.407	−1105.729	13.432
4400	107.946	597.956	498.877	435.946	−1714.454	−1091.573	12.959
4500	107.952	600.382	501.106	446.741	−1714.436	−1077.416	12.506
4600	107.958	602.754	503.290	457.537	−1714.355	−1063.261	12.074
4700	107.964	605.076	505.431	468.333	−1714.211	−1049.108	11.660
4800	107.969	607.349	507.531	479.130	−2274.943	−1023.342	11.136
4900	107.974	609.576	509.591	489.927	−2274.331	−997.273	10.631
5000	107.978	611.757	511.612	500.724	−2273.679	−971.218	10.146
5100	107.982	613.895	513.597	511.522	−2272.986	−945.175	9.681
5200	107.986	615.992	515.546	522.321	−2272.252	−919.146	9.233
5300	107.990	618.049	517.461	533.120	−2271.479	−893.132	8.802
5400	107.994	620.068	519.342	543.919	−2270.665	−867.134	8.388
5500	107.997	622.049	521.191	554.718	−2269.812	−841.151	7.989
5600	108.000	623.995	523.010	565.518	−2268.920	−815.182	7.604
5700	108.003	625.907	524.798	576.318	−2267.988	−789.232	7.232
5800	108.006	627.785	526.558	587.119	−2267.018	−763.297	6.874
5900	108.009	629.632	528.289	597.920	−2266.009	−737.379	6.528
6000	108.011	631.447	529.994	608.721	−2264.961	−711.479	6.194

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

$S°(298.15\ K) = [408.442 \pm 20.9]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1475.453 \pm 25.1]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1489.713 \pm 25.1]\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[202](5)
[53](4)
[962](5)
[552](5)
[3060](5)

Ground State Quantum Weight: 1 σ = [5]

Point Group: [C_5]

Bond Distance: F–F = [2.5] Å

Product of the Moments of Inertia: $I_A I_B I_C = [1.059909 \times 10^{-112}]\ g^3\cdot cm^6$

Enthalpy of Formation

The enthalpy of 5 HF(g) → H_5F_5(g) was taken as the mean of the 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta_f H$ and $\Delta_f S$. At n = 5 their 2nd law values differed by 5.2 $kcal\cdot mol^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 3.1 $kcal\cdot mol^{-1}$. Using $\Delta_f H°(298.15\ K) = -30.35\ kcal\cdot mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of H_5F_5(g).

Heat Capacity and Entropy

The molecular structure of H_5F_5 was assumed as planar with the F atoms forming the vertices of a regular pentagon and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular-orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X-ray studies of solid HF (F–F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. The low F–bending frequency (53 cm^{-1}) was taken from Boutin *et al.*)[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights,[13] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−28.970	−1475.453	−1475.453	INFINITE
100	87.374	288.122	515.288	−22.717	−1483.965	−1445.003	754.792
200	115.893	357.974	420.354	−12.476	−1487.781	−1404.344	366.777
250	127.570	385.117	410.650	−6.383	−1488.935	−1383.343	289.034
298.15	137.321	408.442	408.442	0.	−1489.713	−1362.931	238.780
300	137.665	409.293	408.445	0.254	−1489.737	−1362.144	237.170
350	146.155	431.171	410.153	7.356	−1490.230	−1340.836	200.109
400	153.197	451.162	414.048	14.846	−1490.459	−1319.475	172.306
450	159.042	469.554	419.207	22.656	−1490.467	−1298.100	150.679
500	163.954	486.572	425.103	30.734	−1490.291	−1276.733	133.379
600	171.866	517.195	437.958	47.543	−1489.489	−1234.088	107.437
700	178.225	544.180	451.243	65.057	−1488.199	−1191.617	88.920
800	183.685	568.343	464.396	83.158	−1486.503	−1149.359	75.045
900	188.530	590.263	477.182	101.773	−1484.459	−1107.336	64.268
1000	192.872	610.356	489.509	120.847	−1482.120	−1065.556	55.659
1100	196.766	628.925	501.349	140.333	−1479.531	−1024.023	48.627
1200	200.244	646.198	512.709	160.187	−1476.738	−982.735	42.777
1300	203.341	662.350	523.605	180.369	−1473.781	−941.687	37.837
1400	206.091	677.522	534.063	200.843	−1470.693	−900.872	33.612
1500	208.529	691.826	544.108	221.577	−1467.506	−860.281	29.958
1600	210.691	705.354	553.767	242.540	−1464.243	−819.906	26.767
1700	212.608	718.186	563.065	263.707	−1460.923	−779.736	23.958
1800	214.311	730.388	572.024	285.054	−1457.560	−739.763	21.467
1900	215.826	742.016	580.667	306.563	−1454.163	−699.978	19.244
2000	217.176	753.122	589.015	328.214	−1450.740	−660.372	17.247
2100	218.383	763.747	597.084	349.993	−1447.291	−620.939	15.445
2200	219.464	773.932	604.893	371.886	−1443.819	−581.670	13.811
2300	220.435	783.709	612.456	393.882	−1440.321	−542.560	12.322
2400	221.309	793.110	619.789	415.970	−1436.795	−503.602	10.961
2500	222.097	802.160	626.904	438.141	−1433.236	−464.792	9.711
2600	222.811	810.885	633.813	460.387	−1429.640	−426.125	8.561
2700	223.459	819.307	640.528	482.701	−1426.002	−387.598	7.499
2800	224.048	827.444	647.059	505.077	−1422.319	−349.205	6.515
2900	224.585	835.316	653.416	527.509	−1418.585	−310.945	5.601
3000	225.076	842.938	659.607	549.992	−1414.798	−272.815	4.750
3100	225.525	850.325	665.641	572.523	−1410.954	−234.813	3.957
3200	225.938	857.492	671.525	595.096	−1407.050	−196.935	3.215
3300	226.317	864.451	677.266	617.709	−1403.085	−159.180	2.520
3400	226.666	871.212	682.871	640.359	−1399.058	−121.546	1.867
3500	226.989	877.787	688.347	663.042	−1394.966	−84.032	1.254
3600	227.287	884.186	693.698	685.756	−1390.811	−46.635	0.677
3700	227.564	890.417	698.931	708.498	−1386.591	−9.354	0.132
3800	227.820	896.489	704.051	731.268	−1382.309	27.811	−0.382
3900	228.059	902.410	709.061	754.062	−1377.964	64.863	−0.869
4000	228.281	908.187	713.967	776.879	−1373.558	101.803	−1.329
4100	228.488	913.827	718.773	799.717	−1369.092	138.631	−1.766
4200	228.682	919.335	723.483	822.576	−1364.569	175.351	−2.181
4300	228.863	924.718	728.101	845.453	−1359.989	211.961	−2.575
4400	229.032	929.981	732.630	868.348	−1355.354	248.465	−2.950
4500	229.191	935.130	737.073	891.259	−1350.667	284.863	−3.307
4600	229.340	940.169	741.433	914.186	−1345.929	321.155	−3.647
4700	229.481	945.103	745.714	937.127	−1341.141	357.345	−3.971
4800	229.613	949.936	749.919	960.082	−1336.306	393.433	−4.281
4900	229.737	954.671	754.049	983.050	−1331.425	429.417	−4.578
5000	229.854	959.314	758.108	1006.029	−1326.499	465.304	−4.861
5100	229.965	963.867	762.098	1029.020	−1321.529	501.090	−5.132
5200	230.070	968.333	766.021	1052.022	−1316.517	536.780	−5.392
5300	230.169	972.717	769.880	1075.034	−1311.463	572.372	−5.641
5400	230.263	977.020	773.676	1098.056	−1306.369	607.868	−5.880
5500	230.352	981.246	777.412	1121.086	−1301.234	643.268	−6.109
5600	230.436	985.397	781.089	1144.126	−1296.059	678.578	−6.330
5700	230.516	989.477	784.709	1167.173	−1290.845	713.792	−6.541
5800	230.593	993.486	788.274	1190.229	−1285.591	748.915	−6.745
5900	230.665	997.429	791.786	1213.292	−1280.297	783.948	−6.941
6000	230.734	1001.306	795.246	1236.362	−1274.963	818.889	−7.129

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 334.663 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -831.702 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -840.315 \pm 1.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
710(1)	604(1)	631(2)
616(1)	[257](1)	372(2)
318(1)	276(1)	190(2)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: C_{4v}
Bond Distances: I–F(equatorial) = [1.86] Å; I–F(axial) = [1.75] Å
Bond Angle: F–I–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [4.104805 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value is derived from calorimetric data of Settle *et al.*[1] for the combustion of iodine in fluorine. Although the combustions gave various mixtures of IF_5 and IF_7, the proportions ranged up to almost pure pentafluoride. Reduction of the data gave $\Delta_f H° = -210.80 \pm 0.32$ kcal·mol^{-1} for IF_5(l) at 298.15 K. The result is essentially independent of the heptafluoride.

Comparison values of $-208.9 \pm [>1]$ and $-208.8 \pm [>1.7]$ kcal·mol^{-1} may be obtained from calorimetric data of Woolf[2] for hydrolysis in water and in aqueous KOH. Uncertainties for these values include large contributions due to auxiliary data.[3] In particular, we estimate lower limits of ±0.8 kcal·mol^{-1} for $\Delta_f H°$ of HIO_3(1250 H_2O) and KIO_3(1250 H_2O) by comparison with recent data.[4]

$\Delta_f H°$ for the ideal gas is derived from that of the liquid by use of $\Delta_{vap} H° = 9.96$ kcal·mol^{-1} at 298.15 K. $\Delta_{vap} H°$ was derived by Osborne *et al.*[5] from measurements of vapor pressure and the second virial coefficient.

Heat Capacity and Entropy

There is no published structural determination for gaseous IF_5, but spectral data are consistent with C_{4v} symmetry and a configuration which is approximately a square pyramid. It is uncertain whether the iodine is located above, in, or below the base of the pyramid and whether or not the axial and equatorial I–F distances are equal. We adopt the structure used by Begun *et al.*[7] in correlation of infrared and Raman spectra of BrF_5, IF_5, ClF_5, and $XeOF_4$ by normal coordinate analysis. In this structure the axial bond length is shorter than the equatorial length and the values are close to those observed experimentally for IF_7. The iodine is presumed to be in the base of the pyramid. Simplified Huckel–molecular–orbital calculations[8] predict that C_{4v} is the most stable symmetry, that the axial bond is shorter, and that the equatorial flourines are distorted toward the axial fluorine. It is not clear to what extent these predictions depend on the simplified HMO model used in the calculations. Begun *et al.*[7] note that the normal coordinate calculations are insensitive to changes in the bond angles. Principal moments are $I_A = 43.6575 \times 10^{-39}$, $I_B = I_C = 30.6631 \times 10^{-39}$ g·cm^2.

Vibrational frequencies are based on the assignments of Begun *et al.*[7] as modified by the vapor–phase Raman spectra observed by Selig.[6] Location of the band center of ν_9(~200 cm^{-1}) is difficult, so we substitute the liquid value of 190 cm^{-1}. The Raman–active fundamental ν_5 is not observed for IF_5 or any of the similar molecules, so its value is taken from the calculations.[7] Osborne *et al.*[5] used calorimetric data at low temperatures to derive $S° = 57.96 \pm 0.06$ cal $K^{-1} \cdot mol^{-1}$ for the liquid at 330 K. Combining this with $\Delta_{vap} S°$ based on their vapor pressure equation, the authors obtained $S° = 83.06 \pm 0.20$ cal $K^{-1} \cdot mol^{-1}$ for the ideal gas at 330 K. The corresponding value from this table (82.50) is lower by 0.56 cal $K^{-1} \cdot mol^{-1}$. Part of this difference arises from uncertainties in ν_5 and ν_9 the product of the moments of inertia. We estimate this uncertainty at about 0.5 cal K·mol^{-1}. Another source of minor uncertainty is the neglect of anharmonicity in the calculations.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$	$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	0.	0.	INFINITE	−20.049	−831.702	−831.702	INFINITE
100	52.519	250.536	412.327	−16.179	−836.625	−816.036	426.254
200	83.943	297.260	343.540	−9.256	−839.491	−794.121	207.403
250	94.929	317.229	336.315	−4.771	−840.076	−782.702	163.537
298.15	102.878	334.663	334.663	0.	−840.315	−771.626	135.186
300	103.139	335.300	334.664	0.191	−840.319	−771.200	134.278
350	109.222	351.679	335.944	5.507	−840.381	−759.674	113.375
400	113.756	366.574	338.856	11.087	−848.290	−747.874	97.662
450	117.181	380.179	342.703	16.864	−848.697	−735.297	85.351
500	119.808	392.667	347.084	22.792	−869.098	−720.779	75.299
600	123.478	414.861	356.577	34.970	−867.480	−691.265	60.180
700	125.838	434.085	366.308	47.444	−865.769	−662.030	49.401
800	127.434	450.999	375.858	60.113	−864.013	−633.044	41.334
900	128.559	466.078	385.060	72.916	−862.241	−604.279	35.071
1000	129.379	479.667	393.853	85.815	−860.468	−575.712	30.072
1100	129.994	492.029	402.224	98.785	−858.705	−547.322	25.990
1200	130.468	503.361	410.187	111.809	−856.962	−519.091	22.595
1300	130.839	513.819	417.761	124.875	−855.247	−491.005	19.729
1400	131.135	523.526	424.974	137.974	−853.568	−463.050	17.277
1500	131.376	532.582	431.849	151.100	−851.932	−435.213	15.155
1600	131.573	541.068	438.413	164.248	−850.345	−407.484	13.303
1700	131.738	549.049	444.688	177.414	−848.810	−379.852	11.671
1800	131.876	556.583	450.697	190.594	−847.329	−352.309	10.224
1900	131.993	563.717	456.460	203.788	−845.901	−324.848	8.931
2000	132.093	570.490	461.993	216.993	−844.519	−297.460	7.769
2100	132.180	576.937	467.315	230.206	−843.177	−270.140	6.719
2200	132.255	583.087	472.438	243.428	−841.864	−242.884	5.767
2300	132.320	588.968	477.378	256.657	−840.569	−215.686	4.898
2400	132.378	594.601	482.146	269.892	−839.277	−188.545	4.104
2500	132.429	600.006	486.753	283.132	−837.975	−161.458	3.373
2600	132.474	605.200	491.209	296.378	−836.649	−134.423	2.701
2700	132.514	610.201	495.524	309.627	−835.284	−107.440	2.079
2800	132.550	615.021	499.706	322.880	−833.867	−80.509	1.502
2900	132.583	619.673	503.763	336.137	−832.387	−53.629	0.966
3000	132.612	624.168	507.702	349.397	−830.832	−26.802	0.467
3100	132.638	628.517	511.530	362.659	−829.193	−0.028	0.
3200	132.662	632.728	515.252	375.924	−827.461	26.692	−0.436
3300	132.684	636.811	518.874	389.192	−825.629	53.357	−0.845
3400	132.704	640.772	522.401	402.461	−823.693	79.964	−1.228
3500	132.723	644.619	525.838	415.732	−821.647	106.512	−1.590
3600	132.740	648.358	529.190	429.006	−819.489	133.001	−1.930
3700	132.755	651.995	532.460	442.280	−817.216	159.428	−2.251
3800	132.769	655.536	535.653	455.557	−814.827	185.792	−2.554
3900	132.782	658.985	538.771	468.834	−812.322	212.092	−2.841
4000	132.795	662.347	541.818	482.113	−809.700	238.326	−3.112
4100	132.806	665.626	544.798	495.393	−806.963	264.492	−3.370
4200	132.817	668.826	547.713	508.674	−804.111	290.592	−3.614
4300	132.826	671.952	550.567	521.956	−801.146	316.621	−3.846
4400	132.836	675.005	553.360	535.239	−798.071	342.580	−4.067
4500	132.844	677.991	556.097	548.523	−794.887	368.469	−4.277
4600	132.852	680.911	558.778	561.808	−791.596	394.285	−4.477
4700	132.860	683.768	561.407	575.094	−788.202	420.029	−4.668
4800	132.867	686.565	563.986	588.380	−784.707	445.699	−4.850
4900	132.873	689.305	566.515	601.667	−781.114	471.295	−5.024
5000	132.879	691.989	568.998	614.955	−777.425	496.817	−5.190
5100	132.885	694.621	571.436	628.243	−773.644	522.265	−5.349
5200	132.891	697.201	573.830	641.532	−769.772	547.638	−5.501
5300	132.896	699.732	576.181	654.821	−765.814	572.935	−5.647
5400	132.901	702.217	578.492	668.111	−761.771	598.156	−5.786
5500	132.906	704.655	580.764	681.401	−757.647	623.301	−5.920
5600	132.910	707.050	582.998	694.692	−753.444	648.373	−6.048
5700	132.914	709.403	585.195	707.983	−749.164	673.366	−6.171
5800	132.918	711.714	587.356	721.275	−744.811	698.285	−6.289
5900	132.922	713.986	589.483	734.567	−740.386	723.129	−6.402
6000	132.926	716.220	591.577	747.859	−735.893	747.896	−6.511

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = 347.655 \pm 8.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1235.878 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1241.393 \pm 4.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[1000]	[2]
[7500]	[2]
[25000]	[4]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
759 (1)	713 (2)
738 (1)	261 (2)
683 (1)	112 (2)
[500](1)	[200](2)

Point Group: [D_{3h}] σ = [6]
Bond Distance: Mo–F = [1.78] Å
Bond Angle: F–Mo–F = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.670258 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

We adopt the enthalpy of formation at 298.15 K derived by Brewer[1] from the high temperature mass spectrometric measurements of equilibria among gaseous molybdenum fluorides by Hildenbrand [1143–1664 K][2] and by Kleinschmidt *et al.* [460–525 K].[8] The value of $\Delta_f H°(0\ K)$ combined with JANAF data[3] for Mo(g) and F(g) gives $\Delta_{at} H°(0\ K) = 544.3 \pm 4\ kcal·mol^{-1}$ and an average Mo–F bond energy of $\Delta_{at} H°(0\ K)/5 = 108.9 \pm 1\ kcal·mol^{-1}$.

Heat Capacity and Entropy

Hildenbrand,[4] Douglas,[5] and Krause[6] have calculated somewhat different thermodynamic properties of $MoF_5(g)$ monomer. All have used the vibrational frequencies, cm^{-1}, and degeneracies determined by Acquista and Abramowitz[7] —759,[1] 738,[1] 683,[1] 713,[2] 261,[2] and 112[2] — and an estimated frequency of 500.[1] For the remaining doubly degenerate frequency, Hildenbrand[4] estimated 200 cm^{-1} and both Douglas[5] and Drause[6] estimated 400 cm^{-1}. We follow Brewer[1] who has used the determined vibrational frequencies and the estimated frequencies [500][1] and [200],[2] as had Hildenbrand.[4]

From the following analysis, Brewer[1] has attempted to define the electronic contribution more accurately then just a ground state degeneracy of 2.[4,5] or 4.[6] Mo^{5+} has only the low-lying electronic state ^2D with a spin orbit splitting of 2578 cm^{-1} and a total degeneracy of 10. From the liquid field treatment of ReF_6 by Moffitt *et al.*,[9] one might expect an intermediate coupling case with a $t_{3/2}$ quartet ground state and a low-lying $t_{1/2}$ state, with the next quartet state well above 20000 cm^{-1}. Peacock and Sleight[10] observed an absorption in liquid MoF_5 at 7500 cm^{-1}. For MoF_5 monomer, the actual levels would be split more. On this basis, the following electronic energy levels, cm^{-1}, and quantum weights were assigned:[1] 0,[2] [1000],[2] [7500],[2] and [25000].[4]

The trigonal bipyramid symmetry tentatively assigned by Acquista and Abramowitz[7] is used with the Mo–F distance of 1.78 Å adopted by Brewer.[1] The principal moments of inertia are: $I_A = 29.9871 \times 10^{-39}\ g\ cm^2$, $I_B = I_C = 34.9849 \times 10^{-39}\ g·cm^2$.

This table is based on the critical analysis of data existing in 1978 by Brewer [1].

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.132	−1235.878	−1235.878	INFINITE
100	61.633	259.654	426.629	−16.697	−1239.202	−1221.872	638.241
200	85.339	310.140	356.534	−9.279	−1240.948	−1203.754	314.388
250	94.948	330.241	349.304	−4.766	−1241.309	−1194.408	249.558
298.15	102.763	347.655	347.655	0.	−1241.393	−1185.363	207.671
300	103.034	348.291	347.657	0.190	−1241.392	−1185.016	206.330
350	109.545	364.682	348.936	5.511	−1241.257	−1175.628	175.453
400	114.655	379.658	351.854	11.121	−1240.964	−1166.271	152.299
450	118.614	393.401	355.718	16.957	−1240.561	−1156.957	134.296
500	121.664	406.063	360.127	22.968	−1240.081	−1147.693	119.899
600	125.825	428.645	369.712	35.360	−1238.989	−1129.316	98.316
700	128.324	448.245	379.562	48.078	−1237.823	−1111.129	82.913
800	129.862	465.489	389.247	60.993	−1236.652	−1093.110	71.373
900	130.837	480.845	398.587	74.032	−1235.516	−1075.236	62.405
1000	131.478	494.665	407.516	87.150	−1234.435	−1057.485	55.237
1100	131.918	507.218	416.018	100.321	−1233.426	−1039.840	49.378
1200	132.235	518.711	424.103	113.529	−1232.501	−1022.282	44.499
1300	132.478	529.305	431.794	126.765	−1231.669	−1004.799	40.373
1400	132.676	539.130	439.114	140.023	−1230.938	−987.375	36.839
1500	132.847	548.290	446.090	153.300	−1230.313	−970.001	33.778
1600	133.001	556.869	452.749	166.592	−1229.799	−952.664	31.101
1700	133.147	564.936	459.113	179.899	−1229.401	−935.355	28.740
1800	133.285	572.551	465.206	193.221	−1229.120	−918.067	26.642
1900	133.420	579.761	471.047	206.556	−1228.959	−900.792	24.764
2000	133.550	586.608	476.655	219.905	−1228.919	−883.521	23.075
2100	133.676	593.127	482.047	233.266	−1229.002	−866.250	21.547
2200	133.799	599.348	487.239	246.640	−1229.208	−848.972	20.157
2300	133.916	605.298	492.244	260.026	−1229.537	−831.681	18.888
2400	134.028	611.000	497.074	273.423	−1229.992	−814.374	17.724
2500	134.135	616.474	501.741	286.831	−1230.573	−797.045	16.653
2600	134.236	621.736	506.256	300.250	−1231.296	−779.690	15.664
2700	134.331	626.804	510.627	313.678	−1232.191	−762.304	14.748
2800	134.419	631.691	514.864	327.116	−1233.313	−744.881	13.896
2900	134.502	636.410	518.974	340.562	−1270.622	−727.363	13.101
3000	134.579	640.971	522.965	354.016	−1270.386	−708.634	12.338
3100	134.649	645.385	526.844	367.478	−1270.077	−689.915	11.625
3200	134.714	649.661	530.615	380.946	−1269.689	−671.205	10.956
3300	134.774	653.807	534.286	394.420	−1269.220	−652.510	10.328
3400	134.829	657.831	537.861	407.901	−1268.666	−633.830	9.738
3500	134.880	661.740	541.344	421.386	−1268.026	−615.167	9.181
3600	134.926	665.541	544.742	434.876	−1267.297	−596.524	8.655
3700	134.969	669.238	548.057	448.371	−1266.480	−577.902	8.159
3800	135.008	672.838	551.293	461.870	−1265.573	−559.305	7.688
3900	135.044	676.345	554.455	475.373	−1264.577	−540.731	7.242
4000	135.078	679.765	557.545	488.879	−1263.492	−522.184	6.819
4100	135.109	683.101	560.567	502.388	−1262.319	−503.666	6.417
4200	135.138	686.357	563.523	515.900	−1261.059	−485.177	6.034
4300	135.166	689.537	566.417	529.416	−1259.713	−466.720	5.670
4400	135.192	692.645	569.251	542.934	−1258.282	−448.295	5.322
4500	135.217	695.683	572.027	556.454	−1256.769	−429.902	4.990
4600	135.241	698.655	574.747	569.977	−1255.174	−411.545	4.673
4700	135.265	701.564	577.415	583.502	−1253.500	−393.223	4.370
4800	135.288	704.412	580.031	597.030	−1251.748	−374.938	4.080
4900	135.310	707.202	582.598	610.560	−1249.921	−356.690	3.802
5000	135.332	709.936	585.117	624.092	−1839.405	−332.748	3.476
5100	135.354	712.616	587.591	637.626	−1839.111	−302.618	3.099
5200	135.376	715.245	590.021	651.163	−1838.894	−272.493	2.737
5300	135.398	717.823	592.408	664.702	−1838.752	−242.371	2.389
5400	135.420	720.355	594.754	678.243	−1838.688	−212.252	2.053
5500	135.443	722.840	597.060	691.786	−1838.698	−182.133	1.730
5600	135.465	725.280	599.328	705.331	−1838.785	−152.012	1.418
5700	135.488	727.678	601.559	718.879	−1838.945	−121.891	1.117
5800	135.510	730.035	603.754	732.429	−1839.179	−91.766	0.826
5900	135.533	732.351	605.914	745.981	−1839.483	−61.635	0.546
6000	135.556	734.629	608.040	759.535	−1839.859	−31.500	0.274

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

$S°(298.15\ K) = 300.810 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1583.514 \pm 2.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1594.409 \pm 2.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
817 (1)	1025 (2)
640 (1)	532.5(2)
946.6(1)	179 (2)
575.1(1)	514 (2)

Ground State Quantum Weight: [1] $\sigma = 6$

Point Group: D_{3h}

Bond Distances: $P–F_{eq} = 1.534 \pm 0.004$ Å; $P–F_{ax} = 1.577 \pm 0.005$ Å

Bond Angles: $F_{eq}–P–F_{eq} = 120 \pm 0.4°$; $F_{eq}–P–F_{ax} = 74.3 \pm 0.4°$

Product of the Moments of Inertia: $I_A I_B I_C = 1.614 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

Gross *et al.*[1] measured the heat of combustion of α–white phosphorus in fluorine at 25 °C. They reported an enthalpy of formation of -381.4 ± 0.8 kcal·mol^{-1} (based on α–white phosphorus standard state) calculated from their combustion studies. Similar combustion studies were performed by O'Hare and Hubbard.[2] They reported a enthalpy of formation of -380.8 ± 0.3 kcal·mol^{-1} (α– white phosphorus standard state), which is in excellent agreement with the work of Gross *et al.*[1] An average value of -381.1 ± 0.5 kcal·mol^{-1} is adopted for this tabulation. Converting to the P(red,V) standard state with a $\Delta_f H$ trans = 4.2 ± 0.2 kcal·mol^{-1},[3] we derive, $\Delta_f H°(PF_5, g, 298.15\ K) = -376.9 \pm 0.7$ kcal·mol^{-1} (-1576.950 ± 2.9 kJ·mol^{-1}).

Heat Capacity and Entropy

The molecular structure and bond lengths given above for PF_5 were recently determined by Hansen and Bartell[4] from electron–diffraction studies. These results indicate that PF_5 has a trigonal bipyramid structure with nonequivalent axial and equatorial bonds. Wyatt *et al.*[5] determined rotational constants for PF_5 from a study of the infrared vibration–rotation band contour of the ν_4(575 cm^{-1}) fundamental. Their analysis led to the following P–F bond lengths which are in excellent agreement with the electron–diffraction results: $r_{eq.} = 1.534 \pm 0.024$Å and $r_{ax.} = 1.581 \pm 0.025$Å. Individual moments of inertia, calculated from the rotational constants given by Wyatt *et al.*[5] and adopted for this table, are $I_A = 2.230 \times 10^{-38}$ g cm^2 and $I_B = I_C = 2.690 \times 10^{-38}$ g cm^2. The electron diffraction data lead to a product of moments of inertia of $1.604 \times 10^{-113}\ g^3 \cdot cm^6$.

Several recent infrared and Raman studies[6,7,8] have been reported for PF_5. These data are in good agreement except for the ν_7 fundamental. Griffiths *et al.*[6] originally assigned this fundamental to the 126 cm^{-1} band observed in their infrared spectra. Hoskins[9] later attributed this band to one of the pure rotational lines of hydrogen fluoride, which he felt was present in the sample as an impurity. Further work by Griffiths[10] on the pressure dependence of the infrared spectra of PF_5 indicated that the missing fundamental should be assigned to the weak band at 301 cm^{-1}. Deiters and Holmes[11] recently showed that this band is not a fundamental of PF_5 but a difference band (ν_3–ν_2). Very recently, Levin[8] investigated the Raman spectra of solid phosphorus pentafluoride and assigned the ν_7 fundamental to the 179 cm^{-1} band. Also, Beattie *et al.*[12] investigated the Raman spectra of PF_5 in the gas phase at 25°C and 125°C and assigned the ν_7 fundamental to 175 cm^{-1} band which is in excellent agreement with Levin's assignment.[8] The fundamental vibrational frequencies of Holmes and Lord[7] are adopted along with Levin's assignment[8] of the ν_7 fundamental (179 cm^{-1}).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.527	−1583.514	−1583.514	INFINITE
100	44.341	234.160	362.483	−12.832	−1587.974	−1567.029	818.532
200	65.173	270.951	307.973	−7.404	−1592.132	−1544.571	403.401
250	75.849	286.661	302.158	−3.874	−1593.450	−1532.521	320.203
298.15	84.836	300.810	300.810	0.	−1594.409	−1520.695	266.419
300	85.152	301.336	300.811	0.157	−1594.441	−1520.237	264.697
350	92.905	315.064	301.878	4.615	−1595.891	−1507.738	225.018
400	99.238	327.897	304.337	9.424	−1596.474	−1495.102	195.240
450	104.373	339.893	307.629	14.519	−1596.864	−1482.405	172.073
500	108.537	351.113	311.423	19.845	−1597.100	−1469.673	153.536
600	114.710	371.484	319.771	31.028	−1597.234	−1444.169	125.726
700	118.917	389.503	328.471	42.722	−1597.051	−1418.669	105.862
800	121.874	405.586	337.124	54.770	−1596.660	−1393.211	90.967
900	124.015	420.071	345.549	67.070	−1596.127	−1367.811	79.386
1000	125.608	433.224	353.669	79.555	−1595.500	−1342.475	70.124
1100	126.821	445.255	361.456	92.179	−1594.808	−1317.206	62.549
1200	127.763	456.332	368.906	104.910	−1657.647	−1290.923	56.192
1300	128.509	466.589	376.031	117.725	−1656.113	−1260.424	50.644
1400	129.109	476.135	382.844	130.607	−1654.570	−1230.045	45.894
1500	129.598	485.060	389.364	143.543	−1653.027	−1199.776	41.780
1600	130.002	493.437	395.610	156.524	−1651.488	−1169.609	38.184
1700	130.339	501.329	401.599	169.541	−1649.958	−1139.538	35.014
1800	130.623	508.787	407.348	182.590	−1648.435	−1109.557	32.199
1900	130.865	515.856	412.875	195.664	−1646.919	−1079.662	29.682
2000	131.072	522.574	418.193	208.762	−1645.406	−1049.845	27.419
2100	131.251	528.973	423.317	221.878	−1643.891	−1020.104	25.374
2200	131.407	535.083	428.260	235.011	−1642.367	−990.436	23.516
2300	131.543	540.927	433.032	248.159	−1640.827	−960.836	21.821
2400	131.663	546.528	437.645	261.319	−1639.264	−931.305	20.269
2500	131.769	551.905	442.109	274.491	−1637.670	−901.840	18.843
2600	131.863	557.075	446.432	287.672	−1636.036	−872.439	17.528
2700	131.947	562.053	450.623	300.863	−1634.356	−843.101	16.311
2800	132.022	566.853	454.688	314.061	−1632.622	−813.827	15.182
2900	132.090	571.487	458.637	327.267	−1630.828	−784.616	14.132
3000	132.151	575.966	462.473	340.479	−1628.968	−755.468	13.154
3100	132.206	580.300	466.205	353.697	−1627.036	−726.383	12.239
3200	132.257	584.499	469.836	366.920	−1625.030	−697.361	11.383
3300	132.303	588.569	473.373	380.148	−1622.944	−668.403	10.580
3400	132.345	592.519	476.819	393.381	−1620.777	−639.510	9.825
3500	132.383	596.356	480.180	406.617	−1618.525	−610.682	9.114
3600	132.418	600.086	483.459	419.857	−1616.188	−581.919	8.443
3700	132.451	603.715	486.660	433.101	−1613.765	−553.223	7.810
3800	132.481	607.247	489.788	446.347	−1611.254	−524.593	7.211
3900	132.508	610.689	492.844	459.597	−1608.657	−496.030	6.644
4000	132.534	614.044	495.832	472.849	−1605.972	−467.535	6.105
4100	132.558	617.317	498.755	486.103	−1603.202	−439.109	5.594
4200	132.580	620.512	501.616	499.360	−1600.346	−410.750	5.108
4300	132.601	623.632	504.418	512.619	−1597.407	−382.462	4.646
4400	132.620	626.680	507.162	525.880	−1594.384	−354.242	4.205
4500	132.638	629.661	509.851	539.143	−1591.281	−326.091	3.785
4600	132.655	632.576	512.487	552.408	−1588.099	−298.011	3.384
4700	132.670	635.429	515.073	565.674	−1584.839	−270.000	3.001
4800	132.685	638.223	517.610	578.942	−1581.503	−242.060	2.634
4900	132.699	640.959	520.099	592.211	−1578.094	−214.190	2.283
5000	132.712	643.640	522.543	605.482	−1574.613	−186.391	1.947
5100	132.725	646.268	524.943	618.754	−1571.062	−158.661	1.625
5200	132.736	648.845	527.301	632.027	−1567.443	−131.002	1.316
5300	132.747	651.374	529.619	645.301	−1563.759	−103.413	1.019
5400	132.758	653.855	531.896	658.576	−1560.011	−75.895	0.734
5500	132.767	656.291	534.136	671.852	−1556.201	−48.447	0.460
5600	132.777	658.683	536.339	685.130	−1552.332	−21.067	0.197
5700	132.785	661.034	538.506	698.408	−1548.404	6.241	−0.057
5800	132.794	663.343	540.638	711.687	−1544.420	33.481	−0.302
5900	132.802	665.613	542.737	724.966	−1540.382	60.653	−0.537
6000	132.809	667.845	544.804	738.247	−1536.291	87.754	−0.764

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = [304.752 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -898.295 \pm 15.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -908.447 \pm 15.1\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	[25000]	[2]
[10000]	[2]	[30000]	[2]
[20000]	[2]		

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[800](1)	[550](1)	812 (2)
[600](1)	[400](1)	552 (2)
[550](1)	[450](1)	[350](2)

Point Group: C_{4v} $\sigma = 4$

Bond Distances: S–F* = [1.58]Å; S–F** = [1.51]Å

Bond Angles: F*–S–F* = [90]°; F**–S–F* = [90]°

(* = equatorial, ** = axial)

Product of the Moments of Inertia: $I_A I_B I_C = [1.415983 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(0\ K)$ is calculated from the bond dissociation process $SF_6(g) = SF_5(g) + F(g)$ with $D_0° = 92.0 \pm 3.0$ kcal·mol^{-1} and JANAF auxiliary enthapies of formation.[1] The information which was considered in arriving at the selected $D_0°$ value is reviewed below. Another recent review[2] of the thermodynamics of SF_5 led to selected values of $D_0°(SF_5–F) = 92.6 \pm 3.0$ kcal·mol^{-1} and $\Delta_f H°(298.15\ K) = -218 \pm 3$ kcal·mol^{-1} which agree with the results adopted here.

The electron–impact appearance potential of F^- from SF_6 has been reported as approximately zero by Harland and Thynne[3] and Curran.[4] In addition, Curran[4] measured the kinetic energy of the negative ion and found K.E. (Total) = 0.23 ± 0.05 eV. Combining these results with EA(F) = 3.399 eV,[1] we obtain an upper limit value for $D_0°$ of <3.2 eV (73.1 kcal·mol^{-1}).

Modica[5] performed shock tube measurements on mixtures of SF_6/Ar, SF_5Cl/Ar, and SF_6/H_2 and analyzed the equilibrium data with a thermochemical equilibrium computer program. With $\Delta_f H°(SF_4, g, 0\ K) = -172.2$ kcal·mol^{-1}, Modica [5] adjusted the value of $\Delta_f H°$ for SF_5 to bring the calculated and experimental SF_4/HF concentrations into good agreement. These results suggest $\Delta_f H°(SF_5, g, 0\ K) = -241.7$ kcal·mol^{-1} or $D_0°(SF_5–F) = 65.2$ kcal·mol^{-1}. We are unable to reanalyze these shock tube equilibrium data but presumably the $\Delta_f H°$ and $D_0°$ values should be adjusted for the changes in $\Delta_f H°$ of SF_4.[1]

Bott and Jacobs[6] used infrared and ultraviolet absorption techniques to study the thermal (1650–2050 K) dissociation of SF_6 in a shock tube. They interpreted their rate data in terms of the RRK theory and showed that the results were consistent with $D_0°(SF–F) = 75.9 \pm 4.0$ kcal mol^{-1}. Lyman[7] has re-evaluated the SF_6 dissociation data in terms of the more complete RRKM unimolecular reaction rate theory and presented evidence which indicates that the $D_0°(SF_5–F)$ is considerably higher than previously reported. His analysis of the rate data yielded a $D_0°$ value of 92 kcal·mol^{-1} which we adopt.

The enthalpy of atomization and mean bond dissociation energy are calculated to be 372.2 kcal·mol^{-1} and 74.4 kcal·mol^{-1}, respectively. $\Delta_f H°(0\ K)$ combined with that for SF_5^+ [1] gives IP = 11.14 eV which appears reasonable in comparison with IP values for the other sulfur fluorides.[1]

Heat Capacity and Entropy

We assume that the five fluorine atoms form a tetragonal pyramid around the central sulfur atom based on evidence from an EPR study[8] which shows that four of the fluorine atoms are equivalent. This structure is further supported by recent SCF MO calculations[9] which predict that the F**–S–F* bond angle is near 90°. The geometry optimized bond lengths[9] appear to be about 0.2Å too large in comparison with experimentally measured S–F bond lengths for other sulfur–fluorine species.[1] We assume that the S–F* bond length is the same as that reported for SF_6 and S_2F_{10}.[1] The axial bond length is taken to be slightly shorter than the equatorial bonds, in accordance with the pattern followed in the related molecules ClF_5[12] and TeF_5^-.[10] The principal moments of inertia are: $I_A = 30.7102 \times 10^{-39}$ and $I_B = I_C = 21.4728 \times 10^{-39}$ g·cm^2.

Smardzewski and Fox[11] reported the matrix infrared spectra of SF_5 formed during the vacuum ultraviolet photolysis of SF_6 and its derivatives, SF_5X (X=F, Cl, Br, SF_5), in argon matrices at 8 K. Values of ν_7 and ν_8 are taken from this study. The other seven fundamentals are estimated by analogy with those for SF_5^- [1] and ClF_5.[12] Double (ν_1 and ν_7) and triple (ν_3, ν_4 and ν_8) coincidences are predicted at about 800 cm^{-1} and 550 cm^{-1}, respectively, based on the infrared spectra of ClF_5.[12] The four upper electronic levels are estimated from those observed for SF_6^+ [13] and are assummed to be doublets.

Our thermal functions essentially update and extend those previously reported by O'Hare.[14] Wilkins[15] has also calculated functions covering the temperature range 50–6000 K. He assumed that the structure of the radical was a trigonal bipyramid (D_{3h} symmetry). We cannot completely rule out this structure but consider it to be unlikely.

References

[1]JANAF Thermochemical Tables: SF_6(g), SF_4(g), SF_3(g), SF_2(g) and SF(g), 6–30–76; F(g), 9–30–65; F^-(g), 12–31–71; S_2F_{10}(g), S_2F_{10}(g), SF_5^+(g) and SF_5^-(g), 12–31–77; ClF_5(g), 6–30–66.

[2]S. W. Benson, Chem. Rev. (to be published).

[3]P. Harland and J. C. J. Thynne, J. Phys. Chem. **73**, 4031 (1969).

[4]R. K. Curran, J. Chem. Phys. **34**, 1069 (1961).

Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}		kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.323	−898.295	−898.295	INFINITE
100	38.347	238.884	367.958	−12.907	−902.837	−882.881	461.170
200	66.342	273.589	312.273	−7.737	−906.631	−861.295	224.947
250	79.469	289.850	306.174	−4.081	−907.751	−849.822	177.561
298.15	89.642	304.752	304.752	0.	−908.447	−838.597	146.919
300	89.986	305.308	304.754	0.166	−908.468	−838.163	145.937
350	98.138	319.818	305.881	4.878	−908.894	−826.409	123.335
400	104.412	333.351	308.479	9.949	−911.330	−814.521	106.365
450	109.265	345.941	311.950	15.296	−912.076	−802.382	93.138
500	113.054	357.657	315.942	20.857	−912.764	−790.154	82.547
600	118.445	378.782	324.695	32.452	−913.437	−765.557	66.648
700	121.973	397.324	333.774	44.485	−913.630	−740.890	55.286
800	124.386	413.778	342.765	56.810	−913.540	−716.217	46.764
900	126.101	428.533	351.490	69.339	−966.403	−690.485	40.075
1000	127.359	441.888	359.872	82.015	−964.808	−659.913	34.470
1100	128.309	454.073	367.890	94.801	−963.194	−629.501	29.893
1200	129.044	465.270	375.545	107.670	−961.577	−599.237	26.084
1300	129.627	475.623	382.850	120.604	−959.968	−569.107	22.867
1400	130.102	485.247	389.824	133.592	−958.375	−539.101	20.114
1500	130.497	494.237	396.489	146.622	−956.804	−509.208	17.732
1600	130.836	502.670	402.864	159.689	−955.257	−479.419	15.651
1700	131.134	510.611	408.971	172.788	−953.735	−449.725	13.818
1800	131.403	518.114	414.828	185.915	−952.233	−420.121	12.192
1900	131.652	525.226	420.453	199.068	−950.750	−390.600	10.738
2000	131.887	531.985	425.862	212.245	−949.277	−361.156	9.432
2100	132.112	538.425	431.070	225.445	−947.807	−331.787	8.253
2200	132.331	544.576	436.091	238.667	−946.331	−302.487	7.182
2300	132.545	550.463	440.936	251.911	−944.840	−273.255	6.206
2400	132.757	556.108	445.618	265.176	−943.324	−244.088	5.312
2500	132.966	561.532	450.147	278.462	−941.773	−214.985	4.492
2600	133.174	566.751	454.532	291.769	−940.177	−185.945	3.736
2700	133.380	571.781	458.782	305.097	−938.528	−156.967	3.037
2800	133.584	576.635	462.905	318.445	−936.816	−128.051	2.389
2900	133.787	581.327	466.908	331.814	−935.035	−99.198	1.787
3000	133.988	585.866	470.798	345.202	−933.178	−70.407	1.226
3100	134.187	590.262	474.581	358.611	−931.239	−41.680	0.702
3200	134.384	594.526	478.263	372.040	−929.213	−13.017	0.212
3300	134.578	598.664	481.849	385.488	−927.097	15.582	−0.247
3400	134.769	602.684	485.344	398.955	−924.886	44.115	−0.678
3500	134.958	606.594	488.753	412.442	−922.580	72.582	−1.083
3600	135.143	610.398	492.079	425.947	−920.175	100.982	−1.465
3700	135.326	614.103	495.328	439.470	−917.672	129.313	−1.826
3800	135.505	617.715	498.501	453.012	−915.070	157.574	−2.166
3900	135.682	621.237	501.603	466.571	−912.369	185.767	−2.488
4000	135.855	624.674	504.637	480.148	−909.569	213.889	−2.793
4100	136.026	628.031	507.606	493.742	−906.672	241.940	−3.082
4200	136.193	631.311	510.512	507.353	−903.679	269.919	−3.357
4300	136.357	634.517	513.359	520.981	−900.592	297.825	−3.618
4400	136.518	637.654	516.148	534.624	−897.411	325.659	−3.866
4500	136.675	640.724	518.883	548.284	−894.140	353.420	−4.102
4600	136.830	643.729	521.564	561.959	−890.780	381.106	−4.328
4700	136.982	646.674	524.195	575.650	−887.334	408.719	−4.542
4800	137.131	649.559	526.777	589.356	−883.803	436.257	−4.747
4900	137.277	652.388	529.311	603.076	−880.191	463.721	−4.943
5000	137.419	655.163	531.801	616.811	−876.499	491.111	−5.131
5100	137.559	657.886	534.246	630.560	−872.730	518.425	−5.310
5200	137.696	660.558	536.650	644.323	−868.887	545.666	−5.481
5300	137.830	663.182	539.013	658.099	−864.971	572.832	−5.646
5400	137.961	665.760	541.336	671.888	−860.985	599.923	−5.803
5500	138.088	668.292	543.621	685.691	−856.931	626.939	−5.954
5600	138.213	670.782	545.870	699.506	−852.812	653.882	−6.099
5700	138.335	673.229	548.083	713.333	−848.630	680.749	−6.238
5800	138.454	675.636	550.261	727.173	−844.387	707.543	−6.372
5900	138.569	678.004	552.406	741.024	−840.085	734.265	−6.501
6000	138.681	680.334	554.519	754.887	−835.726	760.911	−6.624

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = [298.151 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 176.574 \pm 20.9\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [172.644]\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[1]	29036	[1]
9275	[1]	37101	[1]
17341	[1]		

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[800](1)	[550](1)	[800](2)
[600](1)	[400](1)	[550](2)
[550](1)	[450](1)	[350](2)

Point Group: $[C_{4v}]$ $\sigma = [4]$
Bond Distances: S–F* = [1.50] Å; S–F** = [1.46] Å
Bond Angles: F**–S–F* = [90]°; F*–S–F* = [90]°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_A I_B I_C = [1.126194 \times 10^{-113}]\ g^3\cdot cm^6$

Enthalpy of Formation

The threshold energy for the formation of SF_5^+ from SF_6 has been measured by photoionization,[1] electron–impact,[2-5] and photoelectron spectroscopy.[4,6-8] Presented below is a summary of the reported appearance potentials (AP) along with results arrived at from an analysis of the data. Also included in the summary are results derived from an electron–impact study[9] on the formation of SF_5^+ from SF_5Cl. All auxiliary data are from the most recent JANAF tables[10] with the exception of the value for $\Delta_f H°(0\ K)$ of SF_5Cl. We use $\Delta_f H°(SF_5Cl, g, 0\ K) = -247.4\ kcal\cdot mol^{-1}$.

Source	Method	AP[a], eV	$\Delta_f H°(0K)$ $kcal\cdot mol^{-1}$	IP, eV
1	Photoionization	<15.29	<45.88	<11.3
2	Electron–Impact	15.9 ± 0.2	<59.94	<11.9
3	Electron–Impact	15.85 ± 0.15	<59.79	<11.9
4	RPD	15.75 ± 0.05	<56.48	<11.8
	Photoelectron Spectroscopy	15.30	46.11	11.31
5	Electron–Impact	15.50 ± 0.1	<50.72	<11.5
6	Photoelectron Spectroscopy	15.35 ± 0.2	47.26	11.36
7	Photoelectron Spectroscopy	15.15	42.65	11.16
8	Photoelectron Spectroscopy	14.72	32.73	10.73
9	Electron–Impact	13.2 ± 0.2[b]	<28.33	<10.5

[a] $SF_6(g) + e^- = SF_5^+(g) + F(g) + 2\ e^-$ [b] $SF_5Cl(g) + e^- = SF_5^+(g) + Cl(g) + 2\ e^-$

No study has been made of the kinetic energies of the fragments produced by photoionization or electron–impact of SF_6 and SF_5Cl. As a result, the ionization potentials (IP) derived from these studies[1-5,9] represent upper limits to the true value. SF_5^+ is produced in the photoionization of SF_6 by rapid dissociation of SF_6^+ whose ground state is expected to exhibit Jahn–Teller instability.[1] As a result of this, an accurate determination of the threshold energy for the dissociation process is difficult. We choose to adopt a mean $\Delta_f H°(0\ K)$ value of 42.2 ± 5.0 $kcal\cdot mol^{-1}$ based on the results measured in four photoelectron spectroscopic studies[4,6-8] of the SF_6/SF_5^+ dissociation. Our adopted enthalpies of formation correspond to $IF(SF_5) = 11.14 \pm 0.37$ eV which is in agreement with the limiting values of 9.25<IP<12.05 eV.[13]

$\Delta_f H°$ is calculated to be 41.263 $kcal\cdot mol^{-1}$ at 298.15 K. Using JANAF data,[10] we find that the primary bond dissociation energy, $D_0°(SF_4^+-F)$, is 75.4 $kcal\cdot mol^{-1}$. This value appears reasonable in comparison with $D_0°$ values for other even–electron positive and negative S–F species,[10] providing some additional support for our adopted results.

Heat Capacity and Entropy

By anolog with SF_5[14,15] and SF_5^-,[10] we adopt a tetragonal pyramidal structure (C_{4v} symmetry). The SF_4 part of this configuration is predicted to be planar as a result of a reduction in the repulsive forces[16] upon ionization. The four equatorial S–F bond lengths are assumed equal to that for SF_3^+.[10] The axial bond length is assumed to be slightly shorter than the equatorial bonds, in accordance with the pattern followed in the related molecules ClF_5[10] and TeF_5^-.[17] The individual moments of inertia are: $I_A = 28.3933 \times 10^{-39}$ and $I_B = I_C = 19.9158 \times 10^{-39}\ g\cdot cm^2$. We estimate vibrational frequencies from those for SF_5,[10] SF_5^- [10] and ClF_5.[18] Double (ν_1 and ν_7) and triple (ν_3, ν_4, and ν_8) coincidences are predicted at 800 cm^{-1} and 550 cm^{-1}, respectively, based on the infrared spectra of ClF_5.[18] The electronic levels are calculated from the RPD measurements of Delwiche.[4] We do not include levels predicted to lie above 40,000 cm^{-1} since these have a negligible effect on the thermal functions. The existence of the first two excited states is verified by an independent RPD study.[3]

Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.347	176.574		
100	38.358	232.170	361.488	−12.932			
200	66.479	266.918	305.689	−7.754			
250	79.653	283.215	299.576	−4.090			
298.15	89.842	298.151	298.151	0.	172.644	238.207	−41.733
300	90.187	298.708	298.153	0.167	172.662	238.614	−41.546
350	98.336	313.250	299.283	4.889	173.286	249.560	−37.245
400	104.598	326.808	301.886	9.969	171.898	260.490	−34.017
450	109.434	339.419	305.364	15.325	172.200	271.538	−31.519
500	113.207	351.152	309.363	20.894	172.560	282.560	−29.519
600	118.567	372.303	318.131	32.503	173.979	304.438	−26.504
700	122.071	390.861	327.223	44.547	175.875	326.036	−24.329
800	124.466	407.327	336.226	56.881	178.053	347.341	−22.679
900	126.167	422.091	344.961	69.417	127.276	369.443	−21.442
1000	127.415	435.451	353.352	82.099	130.955	396.154	−20.693
1100	128.358	447.642	361.378	94.890	134.653	422.495	−20.063
1200	129.091	458.843	369.040	107.764	138.354	448.499	−19.523
1300	129.676	469.200	376.351	120.703	142.047	474.195	−19.053
1400	130.156	478.828	383.331	133.695	145.723	499.606	−18.641
1500	130.561	487.822	390.001	146.732	149.378	524.756	−18.274
1600	130.914	496.259	396.381	159.806	153.011	549.662	−17.945
1700	131.229	504.206	402.492	172.913	156.621	574.343	−17.647
1800	131.519	511.715	408.353	186.051	160.211	598.811	−17.377
1900	131.791	518.833	413.982	199.216	163.786	623.080	−17.130
2000	132.050	525.600	419.395	212.408	167.353	647.161	−16.902
2100	132.301	532.049	424.608	225.626	170.919	671.063	−16.692
2200	132.547	538.209	429.632	238.869	174.494	694.796	−16.497
2300	132.789	544.106	434.482	252.135	178.086	718.366	−16.315
2400	133.027	549.763	439.168	265.426	181.707	741.779	−16.144
2500	133.263	555.198	443.702	278.741	185.365	765.041	−15.985
2600	133.496	560.429	448.091	292.079	189.070	788.154	−15.834
2700	133.727	565.472	452.346	305.440	192.831	811.125	−15.692
2800	133.954	570.339	456.473	318.824	196.657	833.955	−15.558
2900	134.179	575.044	460.481	332.231	200.555	856.647	−15.430
3000	134.399	579.596	464.376	345.660	204.531	879.203	−15.308
3100	134.616	584.007	468.165	359.110	208.590	901.625	−15.192
3200	134.829	588.284	471.852	372.583	212.739	923.916	−15.081
3300	135.037	592.436	475.443	386.076	216.979	946.075	−14.975
3400	135.240	596.470	478.944	399.590	221.315	968.103	−14.873
3500	135.437	600.393	482.358	413.124	225.747	990.004	−14.775
3600	135.630	604.212	485.690	426.677	230.279	1011.776	−14.680
3700	135.816	607.930	488.944	440.249	234.909	1033.421	−14.589
3800	135.997	611.555	492.123	453.840	239.639	1054.938	−14.501
3900	136.172	615.089	495.231	467.449	244.468	1076.331	−14.416
4000	136.341	618.539	498.271	481.074	249.395	1097.599	−14.333
4100	136.504	621.908	501.245	494.717	254.419	1118.741	−14.253
4200	136.662	625.199	504.157	508.375	259.538	1139.761	−14.175
4300	136.813	628.417	507.010	522.049	264.751	1160.657	−14.099
4400	136.959	631.564	509.805	535.738	270.054	1181.431	−14.025
4500	137.099	634.643	512.545	549.440	275.447	1202.084	−13.953
4600	137.233	637.658	515.232	563.157	280.927	1222.615	−13.883
4700	137.361	640.611	517.869	576.887	286.491	1243.027	−13.815
4800	137.485	643.504	520.456	590.629	292.137	1263.320	−13.748
4900	137.603	646.340	522.996	604.384	297.862	1283.493	−13.682
5000	137.715	649.121	525.491	618.150	303.663	1303.549	−13.618
5100	137.823	651.849	527.942	631.926	309.539	1323.489	−13.555
5200	137.926	654.526	530.351	645.714	315.486	1343.313	−13.494
5300	138.024	657.155	532.718	659.512	321.502	1363.021	−13.433
5400	138.118	659.735	535.047	673.319	327.584	1382.616	−13.374
5500	138.208	662.271	537.337	687.135	333.730	1402.096	−13.316
5600	138.293	664.762	539.590	700.960	339.937	1421.466	−13.259
5700	138.374	667.210	541.808	714.793	346.204	1440.722	−13.203
5800	138.451	669.617	543.991	728.635	352.528	1459.869	−13.148
5900	138.524	671.985	546.140	742.484	358.906	1478.908	−13.093
6000	138.594	674.313	548.257	756.339	365.337	1497.836	−13.040

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$\Delta_a H°(0\ K) = 1586.154 \pm 41.8\ kJ·mol^{-1}$
$S°(298.15\ K) = [315.571 \pm 2.1]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1255.192 \pm 33.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-1268.706]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
796(1)	435(1)	595 (2)
522(1)	269(1)	[435](2)
470(1)	342(1)	241 (2)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: C_{4v}
Bond Distances: S–F* = [1.56] Å; S–F** = [1.46] Å
Bond Angles: F**–S–F* = [85]°; F*–S–F* = 90°
(* – equatorial ** – axial)
Product of the Moments of Inertia: $I_A I_B I_C = [1.256203 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The threshold energy for the dissociative electron attachment process $e^- + SF_6(g) = SF_5^-(g) + F(g)$ has been measured directly by means of mass spectrometry.[1-4] In addition, mass spectrometric studies[5] have been reported on various electron transfer reactions which provide independent estimates of the enthalpy for the above process. Presented below is a summary of the results derived from these measurements. Also included in the summary are results obtained from an electron–impact study[1] of the process $e^- + SF_5Cl(g) = SF_5^-(g) + Cl(g)$. We assume that the fragment–ions are formed in each process with no excess or kinetic energies. As a result, the derived electron affinities represent lower limits to the true value. Other reported values of $EA(SF_5)$ include >1.465 eV,[9] 3.2 eV[5] and 3.66 ± 0.04 eV.[10] The first two results are based on charge–transfer studies[5-9] while the latter value represents a direct measurement of EA using the magnetron technique.[10]

Source	Reaction	Method	AP or $\Delta_r H°(0\ K)$ kcal·mol^{-1}	$\Delta_f H°(SF_5^-, g, 0\ K)$[a] kcal·mol^{-1}	$EA(SF_5)$[a] eV
1	A	Electron–impact	2.31	−304.41	>3.89
2	A	RPD	1.15	−305.56	>3.94
3	A	RPD	5.77	−300.95	>3.74
4	A	Electron–impact	~0	−308.72	>3.99
5	A	Electron transfer	11.53	−295.19	>3.49
6	A	Collisional ionization	11.45	−295.07	>3.49
1	B	Electron–impact	4.61	−271.45	>2.46

Reactions: (A) $e^- + SF_6(g) = SF_5^-(g) + F(g)$ [a]Auxiliary $\Delta_f H°(0\ K)$ data (in kcal·mol^{-1}): SF_6,[7] − 288.36 ± 0.2; F,[7]
(B) $e^- + SF_5(g) = SF_5^-(g) + Cl(g)$ 18.36 ± 0.4; Cl,[7] 28.587; SF_5Cl,[8] −247.48; SF_5,[7] −214.7 ± 3.6.

We reject the electron–impact results on the dissociative electron attachment process for SF_5Cl since Harland and Thynne[1] also reported results for SF_5^- and SF_4^- which lead to EA that are too low.[7] The other results are reasonably consistent with the mean EA value of 3.7 ± 0.2 eV. This value corresponds to $\Delta_f H°(SF_5, g, 0\ K) = -300.0 \pm 8.0\ kcal·mol^{-1}$ which we adopt.

$\Delta_f H°$ (298.15 K) is −303.228 kcal·mol^{-1} and the fluoride–ion affinity is $IA(SF_4) = 59.1\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The infrared and Raman spectra[11,12] of the solid adduct $CsFSF_4$ are consistent with a slightly distorted tetragonal pyramidal structure for the SF_5^- anion. We adopt this configuration assuming the length of the four equivalent bonds is the same as that in SF_6.[7] The axial bond length is taken to be slightly shorter (0.1–) than the equatorial bonds, in accordance with the pattern followed in the related molecules ClF_5[7] and TeF_5^-.[13] The F**–S–F* bond angle has been estimated by Drullinger and Griffiths.[11] The principal moments of inertia are: $I_A = 30.4769 \times 10^{-39}$ and $I_B = I_C = 20.3023 \times 10^{-39}\ g·cm^2$.

Smardzewski and Fox[14] reported the matrix infrared spectra of SF_5^- formed during the vacuum ultraviolet photolysis of $SF_6$and SD_2F_{10} in argon matrices at 8 K. Values of ν_1, ν_3 and ν_7 are taken from this recent study. The other six fundamentals are those measured by Christe *et al.*[12] for the SF_5^- anion observed in the Raman spectra of the solid adduct $CsFSF_4$. An independent set[11] of vibrational frequencies for the SF_5^- anion show good agreement with those adopted here except for ν_8. Drullinger and Griffiths[11] observed a weak band at 388 cm^{-1} in the infrared spectra of solid $Cs^+SF_5^-$ which they assigned to ν_8. This band does not appear in the spectrum reported by Christe *et al.*[12] who assumed a double coincidence between ν_4 and ν_8 as observed for the related molecule ClF_5.[12] We adopt this latter assignment.

Drullinger and Griffiths[11] have previously evaluated thermal functions for SF_5^- at selected temperatures in the range 200–2000 K. Using the bond lengths estimated by Drullinger and Griffiths[11] and their vibrational frequencies, we calculate entropies which are about 0.8 cal $K^{-1}·mol^{-1}$ lower than those reported. The reason for this discrepancy is not apparent.

Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.158	−1255.192		
100	46.921	235.666	390.718	−15.505			
200	80.815	279.023	324.282	−9.052			
250	92.943	298.427	317.198	−4.693			
298.15	101.535	315.571	315.571	0.	−1268.706	−1195.827	209.504
300	101.815	316.200	315.573	0.188	−1268.743	−1195.375	208.133
350	108.286	332.407	316.838	5.449	−1269.660	−1183.072	176.564
400	113.061	347.194	319.722	10.989	−1272.666	−1170.559	152.859
450	116.644	360.727	323.537	16.735	−1274.052	−1157.721	134.385
500	119.381	373.165	327.887	22.639	−1275.437	−1144.718	119.58
600	123.187	395.294	337.324	34.782	−1277.641	−1118.359	97.362
700	125.627	414.480	347.006	47.231	−1279.496	−1091.662	81.461
800	127.273	431.369	356.517	59.881	−1281.160	−1064.713	69.519
900	128.432	446.430	365.686	72.670	−1335.842	−1036.482	60.156
1000	129.276	460.008	374.450	85.557	−1336.114	−1003.206	52.402
1100	129.910	472.360	382.798	98.518	−1336.403	−969.901	46.057
1200	130.396	483.686	390.740	111.534	−1336.717	−936.569	40.768
1300	130.778	494.139	398.297	124.594	−1337.062	−903.209	36.291
1400	131.083	503.842	405.494	137.688	−1337.441	−869.822	32.453
1500	131.330	512.894	412.355	150.809	−1337.858	−836.407	29.126
1600	131.533	521.377	418.907	163.952	−1338.314	−802.962	26.214
1700	131.702	529.356	425.171	177.114	−1338.806	−769.487	23.643
1800	131.844	536.888	431.171	190.292	−1339.333	−735.983	21.358
1900	131.965	544.020	436.924	203.482	−1339.890	−702.449	19.312
2000	132.068	550.792	442.450	216.684	−1340.471	−668.884	17.469
2100	132.157	557.238	447.763	229.895	−1341.069	−635.290	15.802
2200	132.234	563.387	452.880	243.115	−1341.674	−601.668	14.285
2300	132.301	569.267	457.814	256.342	−1342.279	−568.017	12.900
2400	132.360	574.899	462.576	269.575	−1342.873	−534.341	11.630
2500	132.412	580.303	467.178	282.814	−1343.448	−500.640	10.460
2600	132.459	585.497	471.629	296.057	−1343.994	−466.917	9.380
2700	132.500	590.497	475.940	309.305	−1344.503	−433.173	8.380
2800	132.537	595.317	480.118	322.557	−1344.967	−399.412	7.451
2900	132.571	599.968	484.171	335.813	−1345.377	−365.634	6.586
3000	132.601	604.463	488.106	349.071	−1345.729	−331.844	5.778
3100	132.628	608.811	491.930	362.333	−1346.016	−298.043	5.022
3200	132.652	613.022	495.648	375.597	−1346.234	−264.234	4.313
3300	132.675	617.105	499.267	388.863	−1346.377	−230.419	3.647
3400	132.696	621.066	502.792	402.132	−1346.444	−196.601	3.020
3500	132.714	624.913	506.226	415.402	−1346.432	−162.782	2.429
3600	132.732	628.651	509.575	428.674	−1346.339	−128.964	1.871
3700	132.748	632.288	512.843	441.948	−1346.164	−95.150	1.343
3800	132.762	635.829	516.033	455.224	−1345.906	−61.343	0.843
3900	132.776	639.278	519.149	468.501	−1345.566	−27.542	0.369
4000	132.788	642.639	522.194	481.779	−1345.144	6.248	−0.082
4100	132.800	645.918	525.172	495.058	−1344.640	40.026	−0.510
4200	132.811	649.119	528.085	508.339	−1344.056	73.792	−0.918
4300	132.821	652.244	530.937	521.621	−1343.393	107.542	−1.306
4400	132.830	655.297	533.728	534.903	−1342.653	141.277	−1.677
4500	132.839	658.283	536.463	548.187	−1341.836	174.994	−2.031
4600	132.847	661.202	539.143	561.471	−1340.946	208.691	−2.370
4700	132.855	664.059	541.771	574.756	−1339.984	242.369	−2.694
4800	132.862	666.857	544.348	588.042	−1338.952	276.025	−3.004
4900	132.869	669.596	546.876	601.329	−1337.852	309.659	−3.301
5000	132.875	672.281	549.357	614.616	−1336.686	343.270	−3.586
5100	132.881	674.912	551.794	627.904	−1335.457	376.857	−3.860
5200	132.887	677.492	554.186	641.192	−1334.166	410.420	−4.123
5300	132.892	680.024	556.537	654.481	−1332.816	443.957	−4.375
5400	132.898	682.508	558.846	667.770	−1331.409	477.467	−4.619
5500	132.902	684.946	561.117	681.060	−1329.947	510.951	−4.853
5600	132.907	687.341	563.350	694.351	−1328.431	544.409	−5.078
5700	132.911	689.693	565.546	707.642	−1326.864	577.838	−5.295
5800	132.915	692.005	567.706	720.933	−1325.247	611.239	−5.505
5900	132.919	694.277	569.832	734.225	−1323.583	644.614	−5.707
6000	132.923	696.511	571.925	747.517	−1321.873	677.958	−5.902

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = [466.420 \pm 25.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1791.171 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1807.655 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[202](5)
[53](4)
[962](5)
[552](5)
[3060](5)

Ground State Quantum Weight: 1 σ = [6]

Point Group: [C_6]

Bond Distance: F–F = [2.5] Å

Product of the Moments of Inertia: $I_A I_B I_C = [4.833984 \times 10^{-112}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of 6 HF(g) → H_6F_6(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Storhmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → $(HF)_n$ and reported 2nd law values of $\Delta_f H$ and $\Delta_f S$. At n = 6 their 2nd and 3rd law values differed by 0.8 kcal mol^{-1}, which was taken as an estimate of error, while the calculated 3rd law values differed by 0.6 kcal mol^{-1}. Using $\Delta_f H°(298.15\ K) = -41.20$ $kcal \cdot mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of H_6F_6(g).

Heat Capacity and Entropy

The molecular structure of H_6F_6 was assumed as planar with the F atoms forming the vertices of a regular hexagon and with the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular–orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X–ray studies of solid HF(F–F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. The low F–bending frequency (53 cm^{-1}) was taken from Boutin *et al.*[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights,[13] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−35.392	−1791.171	−1791.171	INFINITE
100	107.705	318.614	597.486	−27.887	−1801.385	−1751.917	915.107
200	142.277	404.563	481.012	−15.290	−1805.656	−1700.530	444.133
250	156.333	437.855	469.123	−7.817	−1806.879	−1674.097	349.783
298.15	168.056	466.420	466.420	0.	−1807.655	−1648.447	288.801
300	168.470	467.461	466.423	0.311	−1807.678	−1647.459	286.848
350	178.673	494.221	468.513	8.998	−1808.105	−1620.717	241.879
400	187.132	518.649	473.276	18.149	−1808.215	−1593.937	208.147
450	194.152	541.108	479.582	27.687	−1808.060	−1567.159	181.911
500	200.051	561.878	486.786	37.546	−1807.684	−1540.410	160.926
600	209.552	599.229	502.484	58.047	−1806.391	−1487.066	129.461
700	217.186	632.122	518.701	79.395	−1804.511	−1433.987	107.005
800	223.740	661.561	534.750	101.448	−1802.144	−1381.211	90.184
900	229.555	688.256	550.346	124.119	−1799.360	−1328.757	77.119
1000	234.768	712.716	565.377	147.340	−1796.220	−1276.633	66.684
1100	239.440	735.316	579.812	171.054	−1792.782	−1224.839	58.163
1200	243.615	756.332	593.656	195.211	−1789.098	−1173.368	51.075
1300	247.332	775.981	606.934	219.762	−1785.217	−1122.214	45.091
1400	250.632	794.434	619.674	244.664	−1781.180	−1071.365	39.973
1500	253.559	811.827	631.910	269.876	−1777.023	−1020.808	35.548
1600	256.153	828.276	643.674	295.364	−1772.775	−970.532	31.685
1700	258.454	843.876	654.995	321.097	−1768.458	−920.523	28.284
1800	260.497	858.708	665.904	347.046	−1764.090	−870.770	25.269
1900	262.315	872.842	676.427	373.189	−1759.682	−821.262	22.578
2000	263.936	886.339	686.587	399.503	−1755.241	−771.986	20.162
2100	265.384	899.252	696.409	425.970	−1750.771	−722.933	17.982
2200	266.681	911.628	705.912	452.575	−1746.271	−674.094	16.005
2300	267.846	923.509	715.116	479.302	−1741.741	−625.460	14.205
2400	268.895	934.931	724.039	506.140	−1737.177	−577.023	12.559
2500	269.842	945.927	732.696	533.078	−1732.574	−528.778	11.048
2600	270.699	956.527	741.102	560.105	−1727.926	−480.718	9.658
2700	271.476	966.758	749.271	587.215	−1723.228	−432.838	8.374
2800	272.183	976.644	757.216	614.398	−1718.476	−385.132	7.185
2900	272.828	986.207	764.949	641.649	−1713.663	−337.597	6.081
3000	273.416	995.466	772.479	668.962	−1708.786	−290.230	5.053
3100	273.956	1004.441	779.818	696.331	−1703.841	−243.027	4.095
3200	274.451	1013.146	786.974	723.752	−1698.824	−195.983	3.199
3300	274.906	1021.599	793.956	751.220	−1693.733	−149.097	2.360
3400	275.325	1029.812	800.773	778.732	−1688.567	−102.368	1.573
3500	275.712	1037.798	807.432	806.284	−1683.325	−55.791	0.833
3600	276.070	1045.570	813.939	833.873	−1678.006	−9.365	0.136
3700	276.402	1053.139	820.302	861.497	−1672.610	36.912	−0.521
3800	276.710	1060.514	826.527	889.153	−1667.139	83.042	−1.141
3900	276.996	1067.706	832.619	916.838	−1661.592	129.028	−1.728
4000	277.263	1074.722	838.584	944.551	−1655.973	174.870	−2.284
4100	277.511	1081.572	844.428	972.290	−1650.281	220.570	−2.810
4200	277.744	1088.262	850.154	1000.053	−1644.521	266.132	−3.310
4300	277.961	1094.800	855.768	1027.838	−1638.692	311.554	−3.785
4400	278.164	1101.192	861.273	1055.645	−1632.798	356.841	−4.236
4500	278.355	1107.446	866.674	1083.471	−1626.841	401.993	−4.666
4600	278.534	1113.565	871.975	1111.315	−1620.822	447.011	−5.076
4700	278.702	1119.557	877.179	1139.177	−1614.745	491.899	−5.467
4800	278.861	1125.427	882.290	1167.055	−1608.610	536.658	−5.840
4900	279.010	1131.178	887.311	1194.949	−1602.420	581.286	−6.197
5000	279.151	1136.816	892.245	1222.857	−1596.176	625.789	−6.538
5100	279.284	1142.346	897.095	1250.779	−1589.880	670.164	−6.864
5200	279.409	1147.770	901.864	1278.713	−1583.533	714.419	−7.176
5300	279.528	1153.093	906.554	1306.660	−1577.136	758.549	−7.476
5400	279.641	1158.319	911.168	1334.619	−1570.690	802.558	−7.763
5500	279.748	1163.452	915.708	1362.588	−1564.196	846.446	−8.039
5600	279.849	1168.493	920.177	1390.568	−1557.654	890.218	−8.304
5700	279.945	1173.447	924.577	1418.558	−1551.064	933.871	−8.558
5800	280.037	1178.317	928.910	1446.557	−1544.426	977.409	−8.803
5900	280.124	1183.105	933.178	1474.565	−1537.741	1020.831	−9.038
6000	280.207	1187.813	937.383	1502.582	−1531.007	1064.139	−9.264

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 259.693 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 263.5 \pm 0.02\ K$
$T_{fus} = 290.76 \pm 0.02\ K$

$\Delta_f H°(298.15\ K) = -1585.656 \pm 0.11\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 8.171 \pm 0.008\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 4.326 \pm 0.004\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(MoF_6, l, 298.15\ K) = -378.98 \pm 0.25\ kcal \cdot mol^{-1} (-1585.657 \pm 0.11\ kJ \cdot mol^{-1})$ is calculated from $\Delta_f H°(MoF_6, g, 298.15\ K) = -372.29 \pm 0.22\ kcal \cdot mol^{-1}$ minus $\Delta_{vap} H°(298.15\ K) = 6.69 \pm 0.03\ kcal \cdot mol^{-1}$ from our 3rd law analysis of vapor pressure data.

The enthalpy of reaction of MoF_6(l) with excess of OH^-(aq) has been measured by Myers and Brady[2] and by Nuttall *et al.*;[3] the derived $\Delta_f H°(MoF_6, l, 298.15\ K)$ is −393.2 and −380.81 ± 1.3-1.0 kcal·mol^{-1}, respectively. The agreement of the latter value with the adopted value is not quite within the assigned uncertainties.

Heat Capacity and Entropy

The heat capacity of MoF_6 has been measured by Brady *et al.* (50–300 K, 4) and by Osborne et al. (4–350 K, 5).

We adopt the more extensive data of Osborne *et al.*[5] extrapolating $C_p°$ linearly with temperature outside the observed range. $S°(298.15\ K) = 62.07 \pm 0.06\ cal\ K^{-1} \cdot mol^{-1}$ is derived from heat capacity, heat of transition, and heat of melting data and $S°(5\ K) = 0.024\ cal\ K^{-1} \cdot mol^{-1}$ from the T^3 extrapolation of Osborne *et al.*[5]

Transition Data

Osborne *et al.*[5] confirmed the solid state transition (263.5 ± 0.02 K, $\Delta_{trs} H° = 1.953 \pm 0.002\ kcal \cdot mol^{-1}$ found by Brady *et al.* (263.6 K, $\Delta_{trs} H° = 1.957 \pm 0.010\ kcal \cdot mol^{-1}$)[4].

Fusion Data

Melting point and enthalpy of fusion data have been reported by several investigators. These results are summarized below:

Source	Method	T_{fus}/K	$\Delta_{fus} H°$, kcal·mol^{-1}
4	Calorimetric	290.7	1.059 ± 0.010
5	Calorimetric	290.76 ± 0.02	1.034 ± 0.001
6	Vap Pressure	290.65	0.858*
7	Vap Pressure	290.55	0.902*
8	Vap Pressure	290.95	0.987*

*Calculated as the difference between the 2nd law heat of sublimation at 291 K and the adopted 3rd law $\Delta_{vap} H°(298.15\ K)$ corrected to 291 K.

We adopt the calorimetric values of Osborne *et al.*[5]

Vaporization Data

Our 2nd and 3rd law analysis of four sets of vapor pressure data produces the following results. The second virial coefficient determined by Osborne *et al.*[5] is used to convert all four vapor pressure data sets to ideal gas fugacity.

Source	T/K	Data Points	$\Delta_{vap} H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}
6	291-295	4	5.981 ± 0.467	6.691 ± 0.012	2.42 ± 1.59
7	291-307	Eqn	6.737	6.692 ± 0.002	−0.15
5	291-320	21	6.691 ± 0.002	6.691 ± 0.000	0.00 ± 0.01
8	291-335	Eqn	6.696	6.691 ± 0.001	−0.02

The agreement in 3rd law values is excellent and we adopt $\Delta_{vap} H°(298.15\ K) = 6.69 \pm 0.03\ kcal \cdot mol^{-1}$. $T_{vap} = 308.0\ K$ and $\Delta_{vap} H°(308\ K) = 6.57\ kcal \cdot mol^{-1}$ are calculated for a fugacity of one atmosphere for the process $MoF_6(l) = MoF_6(g)$. For vaporization to the real gas, $T_{vap} = 307.04\ K$ and $\Delta_{vap} H°(307\ K) = 6.51\ kcal \cdot mol^{-1}$.

This table is based on the critical analysis of data existing in 1978 by Brewer.[9]

References

[1]JANAF Thermochemical Tables: MoF_6(g), 9-30-78.
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[3]R. L. Nuttall, K. L. Churney and M. V. Kilday, J. Res. Nat. Bur. Stand. 83, 335 (1978).

Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200	152.720	195.532	274.669	−15.827	−1590.266	−1511.085	394.655
298.15	169.795	259.693	259.693	0.	−1585.656	−1473.170	258.093
300	170.117	260.744	259.696	0.314	−1585.560	−1472.473	256.380
400	187.512	312.066	266.576	18.196	−1579.792	−1435.615	187.472
500	204.907	355.777	280.143	37.817	−1572.817	−1400.351	146.294
600	222.302	394.673	296.044	59.177	−1564.493	−1366.617	118.975
700	239.697	430.247	312.709	82.277	−1554.721	−1334.389	99.573
800	257.092	463.390	329.494	107.117	−1543.431	−1303.665	85.121
900	274.487	494.675	346.125	133.696	−1530.581	−1274.450	73.967
1000	291.882	524.496	362.482	162.014	−1516.145	−1246.750	65.124

PREVIOUS: June 1970 CURRENT: September 1978

$S°(298.15\ K) = 350.710 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1550.595 \pm 0.92\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1557.661 \pm 0.92\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
741.8(1)	264(3)
652.0(2)	317(3)
742 (3)	117(3)

Ground State Quantum Weight: 1 $\sigma = 24$

Point Group: O_h

Bond Distance: Mo–F = 1.82 ± 0.01 Å

Bond Angle: F–Mo–F = 90°

Product of the Moments of Inertia: $I_A I_B I_C = 7.303442 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(MoF_6, g, 298.15\ K) = -372.29 \pm 0.22\ kcal \cdot mol^{-1}$ is from the measurements of the direct combination of the elements by Settle *et al.*[1] with the minor corrections[2] for a change in atomic weights and new values for the enthalpy of formation of MoF_5(cr) and NiF_2(cr).

Burgess *et al.*[3] reacted MoF_6(g) with excess NaOH solution and derived $\Delta_f H°(MoF_6, g, 298.15\ K) = -373.8\ kcal \cdot mol^{-1}$. The result of the direct measurement of Settle *et al.*[1] is preferred. The value of $\Delta_f H°(0\ K)$ combined with JANAF data[15] for Mo(g) and F(g) gives $\Delta_{at} H°(0\ K) = 637.9 \pm 1.5\ kcal \cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_{at} H°(0\ K)/6 = 106.3 \pm 0.3\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

From the Raman spectra of liquid MoF_6, Tanner and Duncan[4] concluded that the structure of the molecule was a regular octahedron with O_h symmetry rather than the unsymmetrical structure deduced by Braune and Pinnow[5] from electron diffraction studies. This discrepancy was explained by Glauber and Schomaker.[6]

Values of the Mo–F bond distance vary from 1.84 Å from electron diffraction[7] to 1.80 Å from x-ray diffraction of the cubic solid.[8] Seip and Seip[9] calculated a bond distance of 1.82 Å from electron diffraction measurements. We adopt this value with an uncertainty of ±0.01 Å.[10] The individual moments of inertia are $I_A = I_B = I_C = 41.8000 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies are those adopted by Brewer[10] from the assignment by Weinstock and Goodman[11] and the more recent studies of Claasen *et al.*[12] and McDowell *et al.*[13]

$S°(MoF_6, g, 298.15\ K) = 83.796\ cal\ K^{-1} \cdot mol^{-1}$ calculated from the molecular data is in excellent agreement with $S°(MoF_6, l, 298.15\ K) = 62.068\ cal\ K^{-1} \cdot mol^{-1}$ plus $\Delta_{vap} S°(298.15\ K) = 21.727\ cal\ K^{-1} \cdot mol^{-1}$ to give $S°(MoF_6, g, 298.15\ K) = 83.795 \pm 0.10\ cal\ K^{-1} \cdot mol^{-1}$ based on our analysis of the data of Osborne *et al.*[14]

This table is based on the critical analysis of data existing in 1978 by Brewer.[10]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.993	−1550.595	−1550.595	INFINITE
100	67.247	249.179	442.877	−19.370	−1555.184	−1528.288	798.296
200	99.881	306.715	361.123	−10.882	−1557.325	−1500.381	391.859
250	111.452	330.294	352.644	−5.587	−1557.656	−1486.099	310.503
298.15	120.276	350.710	350.710	0.	−1557.661	−1472.312	257.943
300	120.574	351.455	350.713	0.223	−1557.657	−1471.782	256.260
350	127.635	370.596	352.208	6.436	−1557.424	−1457.486	217.518
400	133.077	388.010	355.611	12.959	−1557.033	−1443.234	188.467
450	137.291	403.938	360.109	19.723	−1556.536	−1429.038	165.878
500	140.585	418.580	365.234	26.673	−1555.965	−1414.902	147.814
600	145.275	444.658	376.352	40.984	−1554.692	−1386.806	120.732
700	148.347	467.299	387.763	55.675	−1553.328	−1358.932	101.405
800	150.448	487.253	398.977	70.621	−1551.932	−1331.257	86.922
900	151.941	505.064	409.793	85.744	−1550.537	−1303.756	75.668
1000	153.036	521.132	420.137	100.996	−1549.168	−1276.410	66.673
1100	153.861	535.759	429.993	116.342	−1547.844	−1249.199	59.320
1200	154.497	549.175	439.373	131.762	−1546.581	−1222.105	53.197
1300	154.997	561.562	448.302	147.237	−1545.394	−1195.114	48.020
1400	155.398	573.063	456.808	162.758	−1544.295	−1168.212	43.587
1500	155.723	583.796	464.920	178.314	−1543.295	−1141.384	39.747
1600	155.991	593.855	472.667	193.901	−1542.403	−1114.620	36.389
1700	156.214	603.319	480.077	209.511	−1541.624	−1087.907	33.427
1800	156.401	612.253	487.174	225.142	−1540.963	−1061.238	30.796
1900	156.560	620.714	493.982	240.790	−1540.425	−1034.602	28.443
2000	156.696	628.748	500.521	256.453	−1540.012	−1007.991	26.326
2100	156.814	636.396	506.811	272.129	−1539.724	−981.398	24.411
2200	156.916	643.693	512.868	287.816	−1539.562	−954.815	22.670
2300	157.005	650.671	518.709	303.512	−1539.525	−928.236	21.081
2400	157.084	657.354	524.348	319.216	−1539.613	−901.657	19.624
2500	157.153	663.768	529.797	334.928	−1539.829	−875.072	18.284
2600	157.214	669.933	535.069	350.647	−1540.182	−848.475	17.046
2700	157.269	675.868	540.175	366.371	−1540.705	−821.862	15.900
2800	157.318	681.588	545.124	382.100	−1541.449	−795.225	14.835
2900	157.363	687.109	549.925	397.834	−1578.373	−768.507	13.842
3000	157.402	692.445	554.587	413.573	−1577.744	−740.592	12.895
3100	157.439	697.607	559.118	429.315	−1577.031	−712.698	12.009
3200	157.471	702.606	563.524	445.060	−1576.229	−684.829	11.179
3300	157.501	707.452	567.813	460.809	−1575.333	−656.986	10.399
3400	157.528	712.154	571.989	476.560	−1574.340	−629.172	9.666
3500	157.553	716.721	576.059	492.314	−1573.247	−601.389	8.975
3600	157.576	721.159	580.029	508.071	−1572.052	−573.638	8.323
3700	157.597	725.477	583.902	523.830	−1570.753	−545.922	7.707
3800	157.617	729.680	587.683	539.590	−1569.349	−518.243	7.124
3900	157.635	733.775	591.377	555.353	−1567.842	−490.601	6.571
4000	157.652	737.766	594.987	571.117	−1566.230	−462.999	6.046
4100	157.667	741.659	598.517	586.883	−1564.514	−435.440	5.548
4200	157.682	745.459	601.970	602.651	−1562.696	−407.923	5.073
4300	157.695	749.169	605.350	618.420	−1560.778	−380.452	4.622
4400	157.707	752.794	608.660	634.190	−1558.759	−353.025	4.191
4500	157.719	756.339	611.903	649.961	−1556.643	−325.645	3.780
4600	157.730	759.805	615.081	665.734	−1554.431	−298.314	3.387
4700	157.740	763.198	618.196	681.507	−1552.126	−271.032	3.012
4800	157.750	766.519	621.252	697.282	−1549.730	−243.799	2.653
4900	157.759	769.771	624.250	713.057	−1547.244	−216.618	2.309
5000	157.767	772.959	627.192	728.833	−2136.057	−183.758	1.920
5100	157.775	776.083	630.081	744.610	−2135.079	−144.722	1.482
5200	157.783	779.147	632.918	760.388	−2134.166	−105.703	1.062
5300	157.790	782.152	635.706	776.167	−2133.317	−66.703	0.657
5400	157.797	785.102	638.445	791.946	−2132.534	−27.718	0.268
5500	157.803	787.997	641.138	807.726	−2131.815	11.253	−0.107
5600	157.809	790.841	643.786	823.507	−2131.161	50.213	−0.468
5700	157.815	793.634	646.390	839.288	−2130.571	89.159	−0.817
5800	157.820	796.379	648.953	855.070	−2130.046	128.097	−1.154
5900	157.825	799.077	651.475	870.852	−2129.581	167.027	−1.479
6000	157.830	801.729	653.957	886.635	−2129.180	205.948	−1.793

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = 291.535 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1206.501 \pm 0.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1220.473 \pm 0.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
773.5(1)	947.5(3)	525.0(3)
641.7(2)	615.5(3)	347.0(3)

Ground State Quantum Weight: 1 $\sigma = 24$

Point Group: O_h

Bond Distance: S–F = 1.564 ± 0.01 A

Bond Angle: F–S–F = 90°

Product of the Moments of Inertia: $I_A I_B I_C = 2.941168 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The calorimetric measurement of $\Delta_f H°$ by direct combination of the elements has been the subject of numerous investigations.[1–6] O'Hare *et al.*[1] performed six combustion experiments on a sample of rhombic sulfur which contained 60 ppm oxygen as the major impurity. The sulfur (−0.5 gram) was burned in 5–6 atmospheres of fluorine which had a purity of 99.97%. Spectrometric and gas chromatographic analyses of the product gases indicated that the sole combustion product was SF_6. We adjust their result $\Delta_f H°(298.15\ k) = -271.7 \pm 0.24\ kcal \cdot mol^{-1}$ to correspond to an atomic weight of sulfur equal to 32.06, and we obtain $\Delta_f H°(SF_6, g, 298.15\ k) = -291.7_3 \pm 0.2\ kcal \cdot mol^{-1}$. The rounded value of $-291.7 \pm 0.2\ kcal \cdot mol^{-1}$ is adopted in this tabulation. Less extensive measurements (3 determinations) by Schroder and Sieben[2] on a portion of the same sample used by O'Hare *et al.*[1] gave $\Delta_f H°(SF_6, g, 298.15\ K) = -291.4\ kcal \cdot mol^{-1}$ which provides confirmation for our selected value.

Other reported $\Delta_f H°$ values which are consistently less negative than the value selected here include (in $kcal \cdot mol^{-1}$) -291.0 ± 0.3,[3] -288.9 ± 0.7,[4] -288.5 ± 0.7[5] and -262.0.[6] The fluorine used by Leonidov *et al.*[3] contained 0.13 wt. % oxygen, and this impurity may be responsible for their low results. Gross *et al.*[4] studied the sulfur fluorination reaction in a glass apparatus and also applied their technique to titanium. Their reported $\Delta_f H°$ value for TiF_4 is in satisfactory agreement ($\pm 0.8\ kcal \cdot mol^{-1}$) with JANAF data.[7] Insufficient information has been reported[4] to resolve the discrepancy for SF_6.

Our adopted $\Delta_f H°$ value is essentially the same as that recently selected by NBS.[8] The earlier NBS selection[9] of $-289.0\ kcal \cdot mol^{-1}$ based on the work of Gross *et al.*,[4,5] is unreliable.

Heat Capacity and Entropy

The product of the moments of inertia is calculated for a structure in which the fluorine atoms lie at the corners of a regular octahedran. This structure belongs to the highest symmetry point group O_h ($\sigma = 24$) and is consistent with observations made from electron diffraction,[10–12] Raman[13–15] and infrared[16–18] studies. The bond length and angle are from the electron diffraction work of Ewing and Sutton.[10] Earlier and less precise work[11–12] led to r_e(S–F) values which are only slightly different from the adopted value. The individual moments of inertia are: $I_A = I_B = I_C = 30.8679 \times 10^{-39}\ g \cdot cm^2$.

The SF_6 molecule has been extensively characterized by vibrational spectroscopy. Weinstock and Goodman[19] reviewed work prior to 1965. Recent studies include gas–phase Raman,[13–14] matrix–isolation Raman,[15] and gas–phase infrared.[16–18] These spectrometric results are in good agreement; the largest deviation arising in the Raman and infrared inactive fundamental ν_6. Weinstock and Goodman[19] obtained $\nu_6 = 349\ cm^{-1}$ from the combination (2 + 6) band. Claassen *et al.*[13] reported $\nu_6 = 347\ cm^{-1}$ from the overtone $2\nu_6$ band, and Holzer and Ouillon[14] have directly observed this forbidden fundamental in the collision–induced Raman spectra at 336 cm^{-1}. Rosenberg and Birnbaum[20] recorded the far–infrared absorption spectrum of gaseous SF_6 and assigned a band centered at 173 cm^{-1} to $\nu_5 - \nu_6$. The difference band gives $\nu_6 = 352\ cm^{-1}$ with $\nu_5 = 525\ cm^{-1}$ [13] and supports the higher value for ν_6. All frequencies used in this tabulation except for the two infrared active (ν_3 and ν_4) fundamentals are taken from the work of Claassen *et al.*[13] Values for the infrared active frequencies are from Abramowitz and Levin.[16] Recent MO calculations[21] predict a singlet ground state with no low–lying electronic levels, and are supported by the x–ray emission[22] and absorption[22,23] spectra of gaseous SF_6. Gianturco[28] has presented a description of the electronic properties.

Kelley and King[24] analyzed $C_p°$ data (13–230 K) reported by Eucken and Schroder[25] and obtained $S°(298.15\ K) = 70.3 \pm 0.7\ cal\ K^{-1} \cdot mol^{-1}$ for the gas phase. This value is in reasonable agreement with the spectroscopic result ($69.7 \pm 0.1\ cal\ K^{-1} \cdot mol^{-1}$). Our thermal functions essentially extend and update those reported in the literature.[1,26,27]

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Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.915	−1206.501	−1206.501	INFINITE
100	38.721	223.132	358.027	−13.490	−1212.486	−1182.436	617.641
200	68.822	258.508	299.562	−8.211	−1217.637	−1150.220	300.407
250	84.315	275.568	293.063	−4.374	−1219.327	−1133.158	236.760
298.15	96.960	291.535	291.535	0.	−1220.473	−1116.451	195.598
300	97.398	292.136	291.537	0.180	−1220.509	−1115.806	194.279
350	107.968	307.974	292.763	5.324	−1221.297	−1098.288	163.911
400	116.373	322.962	295.610	10.940	−1224.003	−1080.591	141.111
450	123.040	337.068	299.441	16.932	−1224.938	−1062.615	123.345
500	128.351	350.317	303.873	23.222	−1225.747	−1044.532	109.122
600	136.069	374.450	313.667	36.470	−1226.504	−1008.204	87.772
700	141.228	395.838	323.907	50.351	−1226.624	−971.804	72.517
800	144.808	414.944	334.114	64.663	−1226.352	−935.416	61.076
900	147.375	432.156	344.068	79.279	−1278.955	−897.998	52.118
1000	149.272	447.786	353.670	94.116	−1277.044	−855.771	44.701
1100	150.709	462.084	362.885	109.118	−1275.073	−813.739	38.641
1200	151.822	475.247	371.707	124.247	−1273.069	−771.888	33.599
1300	152.700	487.435	380.147	139.475	−1271.051	−730.204	29.340
1400	153.404	498.778	388.220	154.782	−1269.035	−688.677	25.695
1500	153.978	509.382	395.948	170.152	−1267.030	−647.293	22.541
1600	154.450	519.335	403.352	185.574	−1265.042	−606.042	19.785
1700	154.844	528.711	410.453	201.039	−1263.075	−564.914	17.358
1800	155.176	537.571	417.271	216.540	−1261.130	−523.902	15.203
1900	155.458	545.969	423.825	232.073	−1259.203	−482.998	13.279
2000	155.700	553.949	430.134	247.631	−1257.289	−442.195	11.549
2100	155.908	561.551	436.212	263.211	−1255.382	−401.487	9.986
2200	156.089	568.808	442.076	278.811	−1253.473	−360.870	8.568
2300	156.248	575.750	447.738	294.428	−1251.553	−320.340	7.275
2400	156.387	582.403	453.211	310.060	−1249.612	−279.894	6.092
2500	156.510	588.789	458.507	325.705	−1247.639	−239.529	5.005
2600	156.620	594.930	463.637	341.362	−1245.625	−199.245	4.003
2700	156.717	600.843	468.610	357.029	−1243.560	−159.038	3.077
2800	156.805	606.544	473.435	372.705	−1241.434	−118.910	2.218
2900	156.883	612.048	478.120	388.390	−1239.240	−78.858	1.420
3000	156.954	617.368	482.674	404.082	−1236.970	−38.883	0.677
3100	157.019	622.515	487.102	419.780	−1234.619	1.014	−0.017
3200	157.077	627.501	491.412	435.485	−1232.180	40.835	−0.667
3300	157.130	632.336	495.610	451.195	−1229.649	80.578	−1.275
3400	157.179	637.027	499.700	466.911	−1227.022	120.242	−1.847
3500	157.224	641.584	503.689	482.631	−1224.298	159.828	−2.385
3600	157.264	646.014	507.582	498.356	−1221.473	199.336	−2.892
3700	157.302	650.323	511.381	514.084	−1218.547	238.762	−3.371
3800	157.337	654.519	515.093	529.816	−1215.520	278.108	−3.823
3900	157.369	658.606	518.721	545.551	−1212.391	317.374	−4.251
4000	157.399	662.590	522.268	561.290	−1209.161	356.558	−4.656
4100	157.426	666.477	525.738	577.031	−1205.831	395.659	−5.041
4200	157.452	670.271	529.134	592.775	−1202.403	434.680	−5.406
4300	157.476	673.976	532.460	608.521	−1198.877	473.615	−5.753
4400	157.498	677.597	535.718	624.270	−1195.256	512.469	−6.084
4500	157.519	681.137	538.910	640.021	−1191.542	551.240	−6.399
4600	157.539	684.599	542.040	655.774	−1187.737	589.926	−6.699
4700	157.557	687.987	545.109	671.528	−1183.843	628.530	−6.985
4800	157.574	691.305	548.120	687.285	−1179.864	667.049	−7.259
4900	157.590	694.554	551.076	703.043	−1175.801	705.484	−7.521
5000	157.605	697.738	553.977	718.803	−1171.658	743.836	−7.771
5100	157.620	700.859	556.827	734.564	−1167.436	782.104	−8.010
5200	157.633	703.920	559.626	750.327	−1163.138	820.289	−8.240
5300	157.646	706.922	562.377	766.091	−1158.767	858.390	−8.460
5400	157.658	709.869	565.081	781.856	−1154.325	896.408	−8.671
5500	157.669	712.762	567.740	797.622	−1149.815	934.342	−8.874
5600	157.680	715.603	570.355	813.390	−1145.239	972.196	−9.068
5700	157.690	718.394	572.928	829.158	−1140.599	1009.965	−9.255
5800	157.700	721.137	575.460	844.928	−1135.898	1047.653	−9.435
5900	157.709	723.833	577.952	860.698	−1131.137	1085.261	−9.608
6000	157.718	726.483	580.405	876.470	−1126.320	1122.785	−9.775

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = [302.860 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1322.282 \pm 29.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1341.876 \pm 29.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[700](1)	[925](3)	[500](3)
[625](2)	594(3)	[325](3)

Ground State Quantum Weight: 2 $\sigma = 24$

Point Group: O_h

Bond Distance: S–F = [1.72] Å

Bond Angle: F–S–F = 90°

Product of the Moments of Inertia: $I_A I_B I_C = [5.203193 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We calculate the enthalpy of formation at 0 K as the difference between $\Delta_f H°(SF_6, g) = -288.36 \pm 0.2$ kcal·mol^{-1} [1] and the selected value of the electron affinity (EA) equal to 1.2 ± 0.3 eV (27.67 kcal·mol^{-1}). There have been numerous values proposed for EA(SF_6). Franklin and Harland[2] have recently reviewed several of the published values; other values of EA not included in the review are tabulated below. The only direct measurement of EA = 1.49 eV by the magnetron technique[3] is suspect since mass spectral studies[4] have shown that SF_5 rather than SF_6 is the predominant ion formed under conditions used in the magnetron experiments. An EA = 1.2 eV is consistent with most of the available information and is adopted here as the best current value.

Source	Method	EA(SF_6), eV
[5]	Electron Transfer	<1.18
[6]	Collisional Ionization Cs/SF_6	>0.54
[7]	Rate Measurements	>0.7
[8]	Electron Transfer	>0.43
		<1.47
[9]	Solution Electron Transfer	0.6
[10]	MO Calculation	1.7

From the adopted results, we calculate the primary bond dissociation energy $D_0°(SF_6^- - F)$ to be 34.4 kcal·mol^{-1} which agrees with the value of 24.2 kcal·mol^{-1} obtained from threshold energies for SF_6^- and SF_5^- measured in collisional ionization studies[6] on the Cs/SF_6 system. $\Delta_f H°(298.15\ K)$ is −320.7 kcal·mol^{-1}, and the fluoride ion affinity (IA) is IA = 41.3 kcal·mol^{-1}.

Heat Capacity and Entropy

The six fluorine atoms are assumed to form a regular octahedron around the central sulfur atom, in accordance with observations[11] on the ESR spectrum of SF_6^-. The value of the bond length is taken from theoretical calculations.[11] This value (1.72 Å) is intermediate between the bond lengths for SF_6[1] and XeF_6[12] and therefore appears to be a reasonable estimate. The principal moments of inertia are: $I_A = I_B = I_C = 37.3328 \times 10^{-39}\ g \cdot cm^2$.

MO calculations[11] in the INDO approximation indicate that the unpaired electron occupies a totally symmetric antibonding orbital (A_{1g}). Thus, we predict that the bonding in SF_6^- is somewhat weaker than that in the neutral molecule. Additional support for this is provided by the fact that the mean S–F bond energy (products S(g)+F (g) + 5F(g)) in SF_6^- is 8.5 kcal·mol^{-1} less than that in SF_6.[1] Due to the weaker bonding in SF_6^-, all vibrational frequencies are expected to show a lowering relative to those for SF_6.[1] Very recently, Barefield and Guillory[13] have assigned an absorption band at 594 cm^{-1} observed in the matrix isolated infrared spectra of NO, Na, and K photoionized in the presence of SF_6 as the ν_4 fundamental of SF_6^-. This represents a lowering of 21.3 cm^{-1} from the gas phase frequency for SF_6.[1] The other infrared active mode (ν_3) for SF_6^- expected to lie near 925 cm^{-1} was not observed but was believed to be hidden beneath the matrix isolated ν_3 band (937 cm^{-1}) of SF_6. We estimate the eight unobserved fundamental from the gas phase values for SF_6.[1]

MO calculations[11] indicate that the ground state electronic configuration is A_{1g}. There is, however, little information available on the excited states for SF_6^- or for isoelectronic molecules such as $ClF_6$6 and BrF_6. Indirect experimental evidence for the existence of an excited state at 0.5 eV (4033 cm^{-1}) has been reported by Lifshitz *et al.*[14] from mass spectral studies of charge–transfer reactions. As shown by Fehsenfeld,[15] stable excited states are expected to exist only if $D_0°(SF_5 - F) > EA(SF_6)$. Our adopted results give a difference in $D_0°(SF_5 - F)$ and EA(SF_6) of only 0.053 eV, suggesting that perhaps the SF_6^- ion observed by Lifshitz *et al.*[14] was vibrationally rather than electronically excited. We prefer not to include this level, but if it does exist, our entropies should be increased by 0.41 and 1.0 cal $K^{-1} \cdot mol^{-1}$ at 2000 K and 4500 K.

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Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−17.490	−1322.282		
100	39.970	231.635	371.985	−14.035			
200	71.908	268.576	311.174	−8.520			
250	87.504	286.343	304.439	−4.524			
298.15	99.984	302.860	302.860	0.	−1341.876	−1234.976	216.363
300	100.413	303.480	302.862	0.185	−1341.945	−1234.313	214.913
350	110.698	319.762	304.124	5.473	−1343.629	−1216.236	181.513
400	118.794	335.094	307.047	11.219	−1347.245	−1197.851	156.423
450	125.168	349.469	310.971	17.324	−1349.105	−1179.072	136.863
500	130.218	362.928	315.501	23.713	−1350.854	−1160.082	121.193
600	137.516	387.362	325.485	37.126	−1353.525	−1121.663	97.649
700	142.367	408.948	335.897	51.136	−1355.595	−1082.850	80.803
800	145.720	428.191	346.253	65.550	−1357.300	−1043.766	68.151
900	148.119	445.500	356.335	80.248	−1411.899	−1003.403	58.236
1000	149.889	461.202	366.049	95.153	−1411.999	−958.009	50.041
1100	151.228	475.554	375.361	110.212	−1412.050	−912.607	43.336
1200	152.264	488.758	384.268	125.388	−1412.076	−867.202	37.748
1300	153.080	500.980	392.782	140.657	−1412.097	−821.795	33.020
1400	153.735	512.349	400.921	155.999	−1412.123	−776.387	28.967
1500	154.268	522.974	408.707	171.400	−1412.166	−730.975	25.455
1600	154.707	532.945	416.164	186.850	−1412.229	−685.561	22.381
1700	155.072	542.335	423.312	202.339	−1412.317	−640.141	19.669
1800	155.380	551.208	430.173	217.862	−1412.429	−594.716	17.258
1900	155.642	559.616	436.767	233.414	−1412.561	−549.284	15.101
2000	155.866	567.605	443.111	248.989	−1412.708	−503.844	13.159
2100	156.059	575.215	449.222	264.586	−1412.864	−458.398	11.402
2200	156.227	582.479	455.115	280.200	−1413.019	−412.943	9.805
2300	156.374	589.427	460.805	295.830	−1413.164	−367.482	8.346
2400	156.504	596.085	466.303	311.475	−1413.290	−322.015	7.008
2500	156.618	602.476	471.623	327.131	−1413.385	−276.543	5.778
2600	156.719	608.620	476.775	342.798	−1413.439	−231.068	4.642
2700	156.810	614.537	481.768	358.474	−1413.442	−185.592	3.590
2800	156.891	620.241	486.613	374.159	−1413.386	−140.117	2.614
2900	156.964	625.748	491.316	389.852	−1413.262	−94.645	1.705
3000	157.029	631.070	495.886	405.552	−1413.064	−49.178	0.856
3100	157.089	636.220	500.331	421.258	−1412.784	−3.720	0.063
3200	157.143	641.208	504.656	436.969	−1412.416	41.728	−0.681
3300	157.192	646.045	508.867	452.686	−1411.957	87.163	−1.380
3400	157.238	650.738	512.971	468.408	−1411.403	132.583	−2.037
3500	157.279	655.297	516.973	484.134	−1410.752	177.985	−2.656
3600	157.317	659.728	520.877	499.863	−1410.001	223.368	−3.241
3700	157.352	664.039	524.688	515.597	−1409.148	268.727	−3.794
3800	157.384	668.235	528.411	531.334	−1408.195	314.062	−4.317
3900	157.414	672.324	532.049	547.074	−1407.140	359.372	−4.813
4000	157.441	676.310	535.606	562.816	−1405.984	404.653	−5.284
4100	157.467	680.198	539.085	578.562	−1404.729	449.903	−5.732
4200	157.490	683.992	542.490	594.310	−1403.375	495.122	−6.158
4300	157.513	687.699	545.824	610.060	−1401.924	540.306	−6.563
4400	157.533	691.320	549.090	625.812	−1400.378	585.457	−6.950
4500	157.553	694.860	552.290	641.566	−1398.739	630.572	−7.319
4600	157.571	698.323	555.427	657.323	−1397.009	675.649	−7.672
4700	157.588	701.712	558.504	673.080	−1395.191	720.687	−8.010
4800	157.603	705.030	561.522	688.840	−1393.288	765.686	−8.332
4900	157.618	708.280	564.484	704.601	−1391.301	810.644	−8.642
5000	157.632	711.465	567.392	720.364	−1389.233	855.561	−8.938
5100	157.646	714.586	570.247	736.128	−1387.087	900.435	−9.222
5200	157.658	717.647	573.053	751.893	−1384.865	945.268	−9.495
5300	157.670	720.651	575.809	767.659	−1382.570	990.056	−9.758
5400	157.681	723.598	578.519	783.427	−1380.204	1034.800	−10.010
5500	157.692	726.491	581.183	799.195	−1377.770	1079.500	−10.252
5600	157.702	729.333	583.803	814.965	−1375.271	1124.156	−10.486
5700	157.711	732.124	586.381	830.736	−1372.707	1168.765	−10.711
5800	157.720	734.867	588.918	846.507	−1370.083	1213.329	−10.927
5900	157.728	737.563	591.414	862.280	−1367.399	1257.849	−11.136
6000	157.737	740.214	593.872	878.053	−1364.659	1302.321	−11.338

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 249.216 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 275.2\ K$

$\Delta_f H°(298.15\ K) = -1748.368 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 4.100\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $-417.87\ kcal \cdot mol^{-1}$, is calculated from the chosen $\Delta_{vap}H°(290.3\ K) = 6.465 \pm 0.08\ kcal \cdot mol^{-1}$ with $\Delta_f H°(WF_6, g, 298.15\ K) = -411.5 \pm 0.4\ kcal \cdot mol^{-1}$. The value of $\Delta_{vap}H°(290.3\ K)$ is obtained by corrected 2nd law analysis of vapor pressure data[6,7,8] which are given in the vaporization section of this table.

Myers and Brady[1] measured calorimetrically $\Delta_r H°(298.15\ K) = -150.1\ kcal \cdot mol^{-1}$ for the reaction $WF_6(l) + 8\ NaOH(aq, 500\ H_2O) \rightarrow Na_2WO_4(aq, 4900\ H_2O) + 4\ H_2O(l) + 6\ NaF(aq, 800\ H_2O)$. Spitsyn and Patsukova[2] measurd calorimetrically $\Delta_r H°(298.15\ K) = -13.8\ kcal \cdot mol^{-1}$ for the reaction $WO_3(cr) + 2\ NaOH_4(aq, 66\ H_2O) \rightarrow Na_2WO_4(aq, 4200\ H_2O) + H_2O(l)$. Based on these data and auxiliary data for NaOH(aq),[3,9] NaF(aq)[3,10] and $Na_2WO_4(aq)$[4] we obtain $\Delta_r H°(298.15\ K) = -136.2\ kcal \cdot mol^{-1}$ for $WF_6(l) + 6\ NaOH(aq, \infty) \rightarrow WO_3(cr) + 3\ H_2O(l) + 6\ NaF(aq, \infty)$. This leads to $\Delta_f H°(WF_6, l, 298.15\ K) = -416.9 \pm 1\ kcal \cdot mol^{-1}$ which is in good agreement with the value adopted.

Heat Capacity and Entropy

The heat capacity, $40.5\ cal\ K^{-1} \cdot mol^{-1}$, is obtained from a graph of the $C_p°$ versus temperature curve determined calorimetrically by Westrum.[5]

The entropy, $S°(298.15\ K) = 59.564\ cal\ K^{-1} \cdot mol^{-1}$, is calculated from the chosen $\Delta_{vap}H°(290.3) = 6.465\ kcal \cdot mol^{-1}$ with $S°(WF_6, g, 298.15\ K) = 81.50\ cal\ K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and heat of melting have been reported by the following investigators, and their results are summarized below. Ruff and Ascher's value, $2.40\ kcal \cdot mol^{-1}$, is too high because they did not know of the existence of a solid–solid transition[5] at 264.7 K with $\Delta_{trs}H° = 2.067\ kcal \cdot mol^{-1}$. Westrum's data are adopted in the tabulation.

Source	Method	T_{fus}/K	$\Delta_{fus}H°\ kcal \cdot mol^{-1}$
5	Calorimetric	275.2	0.980
7	Vapor pressure	275.4	2.400*
8	Warming curve	275.1	0.500
6	Vapor pressure	275.2	0.420*

*This value is the difference between the 2nd law heats of sublimation and vaporization without correction for $\Delta C_p°$ for both processes.

Vaporization Data

2nd law analyses of the data,[6,7,8] neglecting corrections for nonideality of the vapor, are summarized below. The value of $\Delta_{vap}H°(298.15\ K) = 6.37\ kcal \cdot mol^{-1}$ ($\Delta_{vap}H°(290.3\ K) = 6.465\ kcal \cdot mol^{-1}$ is selected in the tabulation.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	169.452	249.216	249.216	0.	−1748.368	−1631.549	285.841
300	169.452	250.264	249.219	0.313	−1748.273	−1630.825	283.952
400	169.452	299.012	255.866	17.259	−1743.449	−1592.418	207.948
500	169.452	336.824	268.417	34.204	−1739.116	−1555.170	162.468
600	169.452	367.719	282.471	51.149	−1735.148	−1518.759	132.220
700	169.452	393.840	296.563	68.094	−1731.459	−1482.989	110.662
800	169.452	416.467	310.168	85.039	−1727.987	−1447.733	94.527
900	169.452	436.426	323.110	101.985	−1724.693	−1412.900	82.003
1000	169.452	454.280	335.350	118.930	−1721.552	−1378.426	72.002

PREVIOUS: December 1963 CURRENT: March 1967

$S°(298.15\ K) = 341.127\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1713.009 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1721.716 \pm 1.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
769 (1)	256 (3)
670 (2)	322 (3)
712 (3)	216 (3)

Ground State Quantum Weight: 1 $\sigma = 24$
Point Group: O_h
Bond Distance: W–F = 1.83 Å
Bond Angle: F–W–F = 90°
Product of the Moments of Inertia: $I_A I_B I_C = 7.547547 \times 10^{-113}\ g^3·cm^6$

Enthalpy of Formation

O'Hare and Hubbard[7] determined the enthalpy of formation, $\Delta_f H°(WF_6, g, 298.15\ K) = -411.5 \pm 0.4\ kcal·mol^{-1}$, by combustion of tungsten in fluorine in a bomb calorimeter. This value is adopted in the tabulation.

Heat Capacity and Entropy

The molecular configuration and vibrational frequencies were obtained from the infrared and Raman spectroscopic studies by Gaunt,[1] Burke *et al.*[2] and Tanner and Duncan.[3]

The bond distance was reported by Claasen,[4] based on the preliminary result of Schomaker *et al.*[5] who determined the bond distance by electron diffraction. Gaunt[6] derived W–F = 1.89 Å from correlations with other hexafluorides and a valence force constant calculation. The three principal moments of inertia are $I_A = I_B = I_C = 42.2606 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.741	−1713.009	−1713.009	INFINITE
100	59.529	243.924	430.923	−18.700	−1718.341	−1690.661	883.111
200	97.058	297.911	351.387	−10.695	−1721.131	−1661.668	433.983
250	109.635	320.979	343.037	−5.515	−1721.615	−1646.736	344.067
298.15	119.029	341.127	341.127	0.	−1721.716	−1632.301	285.972
300	119.343	341.865	341.130	0.220	−1721.714	−1631.746	284.112
350	126.763	360.844	342.612	6.382	−1721.544	−1616.762	241.288
400	132.434	378.158	345.989	12.868	−1721.188	−1601.815	209.176
450	136.800	394.020	350.457	19.603	−1720.706	−1586.921	184.205
500	140.200	408.616	355.553	26.532	−1720.136	−1572.086	164.235
600	145.020	434.637	366.619	40.811	−1718.835	−1542.596	134.295
700	148.166	457.244	377.986	55.481	−1717.421	−1513.333	112.926
800	150.313	477.178	389.164	70.411	−1715.964	−1484.277	96.913
900	151.836	494.975	399.950	85.523	−1714.503	−1455.404	84.469
1000	152.952	511.033	410.268	100.765	−1713.065	−1426.693	74.523
1100	153.793	525.652	420.103	116.104	−1711.664	−1398.124	66.391
1200	154.440	539.063	429.466	131.517	−1710.314	−1369.680	59.621
1300	154.950	551.446	438.378	146.987	−1709.021	−1341.347	53.896
1400	155.357	562.944	446.870	162.503	−1707.793	−1313.111	48.993
1500	155.688	573.674	454.970	178.056	−1706.634	−1284.960	44.746
1600	155.960	583.731	462.707	193.639	−1705.548	−1256.885	41.033
1700	156.186	593.193	470.107	209.247	−1704.533	−1228.874	37.759
1800	156.377	602.126	477.195	224.875	−1703.589	−1200.922	34.850
1900	156.538	610.585	483.995	240.521	−1702.711	−1173.021	32.249
2000	156.677	618.618	490.527	256.182	−1701.894	−1145.163	29.909
2100	156.796	626.265	496.810	271.856	−1701.131	−1117.346	27.792
2200	156.900	633.562	502.862	287.541	−1700.414	−1089.564	25.870
2300	156.990	640.539	508.697	303.235	−1699.733	−1061.813	24.115
2400	157.070	647.222	514.331	318.938	−1699.078	−1034.091	22.506
2500	157.140	653.635	519.776	334.649	−1698.439	−1006.397	21.028
2600	157.203	659.800	525.043	350.366	−1697.804	−978.728	19.663
2700	157.259	665.733	530.145	366.089	−1697.190	−951.083	18.400
2800	157.308	671.454	535.090	381.818	−1696.623	−923.460	17.227
2900	157.353	676.974	539.888	397.551	−1696.133	−895.855	16.136
3000	157.394	682.310	544.547	413.288	−1695.741	−868.267	15.118
3100	157.430	687.471	549.075	429.029	−1695.484	−840.689	14.166
3200	157.464	692.470	553.478	444.774	−1695.387	−813.117	13.273
3300	157.494	697.316	557.764	460.522	−1695.472	−785.545	12.434
3400	157.522	702.018	561.938	476.273	−1695.770	−757.968	11.645
3500	157.547	706.584	566.006	492.026	−1696.342	−730.378	10.900
3600	157.570	711.023	569.972	507.782	−1697.283	−702.766	10.197
3700	157.592	715.341	573.843	523.540	−1733.457	−674.932	9.528
3800	157.612	719.544	577.622	539.300	−1731.845	−646.345	8.885
3900	157.630	723.638	581.314	555.063	−1730.128	−617.801	8.275
4000	157.647	727.629	584.922	570.826	−1728.308	−589.302	7.696
4100	157.663	731.522	588.451	586.592	−1726.384	−560.852	7.145
4200	157.677	735.321	591.903	602.359	−1724.357	−532.448	6.622
4300	157.691	739.032	595.281	618.127	−1722.229	−504.095	6.124
4400	157.703	742.657	598.590	633.897	−1720.002	−475.791	5.648
4500	157.715	746.201	601.831	649.668	−1717.677	−447.539	5.195
4600	157.726	749.668	605.007	665.440	−1715.257	−419.341	4.762
4700	157.737	753.060	608.121	681.213	−1712.743	−391.195	4.348
4800	157.747	756.381	611.175	696.987	−1710.137	−363.104	3.951
4900	157.756	759.634	614.172	712.762	−1707.443	−335.069	3.572
5000	157.764	762.821	617.113	728.538	−1704.662	−307.090	3.208
5100	157.772	765.945	620.001	744.315	−1701.796	−279.167	2.859
5200	157.780	769.009	622.837	760.093	−1698.848	−251.300	2.524
5300	157.787	772.014	625.623	775.871	−1695.821	−223.491	2.203
5400	157.794	774.964	628.362	791.650	−1692.716	−195.741	1.893
5500	157.801	777.859	631.054	807.430	−1689.536	−168.049	1.596
5600	157.807	780.703	633.701	823.210	−1686.284	−140.414	1.310
5700	157.813	783.496	636.304	838.991	−1682.960	−112.840	1.034
5800	157.818	786.240	638.866	854.773	−1679.569	−85.324	0.768
5900	157.823	788.938	641.387	870.555	−1676.111	−57.865	0.512
6000	157.828	791.591	643.868	886.338	−1672.589	−30.467	0.265

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K)$ = [523.432 ± 29.3] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2083.834 \pm 37.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -2102.544 \pm 37.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[202](7)
[53](8)
[962](7)
[552](7)
[3060](7)

Ground State Quantum Weight: 1 σ = [7]
Point Group: [C_7]
Interatomic Distance: F–F = [2.5]Å
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.797733 × 10^{-111}] $g^3·cm^6$

Enthalpy of Formation

The enthalpy of 7 HF(g) → H_7F_7(g) was taken as the mean of 3rd law values which were determined from the equilibrium data of two investigations. Briegleb and Strohmeier[1] measured the vapor density of associated HF between 20 and 60°C and between 50 and 650 torr. Franck and Meyer[2] measured $C_p°$ between −20 and 100°C and between 100 and 700 torr. Each investigation evaluated K_p at n = 2, 3, 4, ... for the reactions n(HF) → (HF) and reported 2nd law values of ΔH and ΔS. At n = 7 their 2nd law values differed by 7.3 $kcal·mol^{-1}$, which was taken as an estimate of error, while the calculated 3rd law values differed by 6.4 $kcal·mol^{-1}$. Using $\Delta_f H°(298.15\ K)$ = 046.54 $kcal·mol^{-1}$ and auxiliary JANAF data[3] gives the enthalpy of formation of H_7F_7(g).

Heat Capacity and Entropy

The molecular structure of H_7F_7 was assumed as planar with the F atoms forming the vertices of a regular heptagon and the H atoms also lying on the circumscribed circle. That rings are more stable than open chains was confirmed by Del Bene and Pople's[4] theoretical molecular orbital studies on HF polymers. The length of side (F–F axis) was taken from Atoji and Lipscomb's[5] X-ray studies of solid HF (F–F = 2.49 Å) and agrees with the 2.52 Å which Janzen and Bartell[6] determined for HF gaseous polymers by electron diffraction. The low F bending frequency (53 cm^{-1}) was taken from Boutin *et al.*[7] The other vibrational frequencies were taken from Kittelberger and Hornig's[8] work on crystalline HF. Huong and Couzi[9] and Smith[10] have made spectral studies of the gas phase in the range from 350 to 4000 cm^{-1}.

The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights[13] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−41.813	−2083.834	−2083.834	INFINITE
100	128.036	348.140	678.718	−33.058	−2095.751	−2035.680	1063.330
200	168.661	450.187	540.705	−18.104	−2100.476	−1973.468	515.417
250	185.096	489.628	526.631	−9.251	−2101.769	−1941.556	405.666
298.15	198.792	523.432	523.432	0.	−2102.544	−1910.622	334.733
300	199.275	524.663	523.436	0.368	−2102.565	−1909.431	332.461
350	211.190	556.305	525.908	10.639	−2102.927	−1877.208	280.158
400	221.067	585.171	531.538	21.453	−2102.918	−1844.959	240.927
450	229.262	611.697	538.991	32.718	−2102.600	−1812.730	210.416
500	236.149	636.218	547.503	44.358	−2102.023	−1780.551	186.013
600	247.237	680.297	566.046	68.551	−2100.239	−1716.411	149.427
700	256.147	719.099	585.194	93.733	−2097.769	−1652.627	123.321
800	263.796	753.813	604.139	119.739	−2094.731	−1589.236	103.766
900	270.581	785.283	622.545	146.464	−2091.207	−1526.256	88.582
1000	276.663	814.112	640.280	173.832	−2087.267	−1463.692	76.455
1100	282.115	840.741	657.308	201.776	−2082.979	−1401.539	66.554
1200	286.986	865.501	673.638	230.236	−2078.404	−1339.789	58.320
1300	291.323	888.647	689.297	259.155	−2073.599	−1278.432	51.368
1400	295.174	910.380	704.320	288.484	−2068.612	−1217.451	45.424
1500	298.588	930.864	718.747	318.175	−2063.486	−1156.832	40.284
1600	301.615	950.233	732.615	348.189	−2058.252	−1096.559	35.799
1700	304.300	968.600	745.961	378.487	−2052.939	−1036.615	31.851
1800	306.684	986.062	758.819	409.038	−2047.566	−976.986	28.351
1900	308.805	1002.702	771.220	439.815	−2042.146	−917.658	25.228
2000	310.696	1018.590	783.194	470.792	−2036.688	−858.614	22.425
2100	312.385	1033.791	794.768	501.947	−2031.196	−799.846	19.895
2200	313.899	1048.359	805.966	533.263	−2025.670	−741.340	17.602
2300	315.258	1062.343	816.811	564.722	−2020.108	−683.085	15.513
2400	316.482	1075.786	827.324	596.310	−2014.506	−625.074	13.604
2500	317.586	1088.728	837.523	628.014	−2008.858	−567.297	11.853
2600	318.586	1101.204	847.426	659.824	−2003.158	−509.747	10.241
2700	319.493	1113.245	857.049	691.729	−1997.401	−452.417	8.753
2800	320.318	1124.879	866.408	723.720	−1991.579	−395.302	7.374
2900	321.070	1136.133	875.516	755.790	−1985.687	−338.395	6.095
3000	321.757	1147.029	884.386	787.932	−1979.720	−281.694	4.905
3100	322.386	1157.590	893.029	820.139	−1973.673	−225.193	3.794
3200	322.963	1167.835	901.458	852.407	−1967.543	−168.888	2.757
3300	323.494	1177.781	909.681	884.730	−1961.327	−112.775	1.785
3400	323.984	1187.446	917.709	917.105	−1955.023	−56.853	0.873
3500	324.435	1196.844	925.551	949.526	−1948.630	−1.118	0.017
3600	324.853	1205.989	933.214	981.990	−1942.147	54.435	−0.790
3700	325.240	1214.895	940.707	1014.495	−1935.575	109.805	−1.550
3800	325.599	1223.574	948.038	1047.038	−1928.915	164.996	−2.268
3900	325.933	1232.036	955.212	1079.614	−1922.167	220.012	−2.947
4000	326.244	1240.292	962.236	1112.223	−1915.334	274.852	−3.589
4100	326.534	1248.351	969.116	1144.863	−1908.417	329.521	−4.198
4200	326.805	1256.223	975.859	1177.530	−1901.418	384.022	−4.776
4300	327.059	1263.916	982.469	1210.223	−1894.341	438.352	−5.325
4400	327.296	1271.438	988.951	1242.941	−1887.188	492.519	−5.847
4500	327.519	1278.795	995.311	1275.682	−1879.961	546.522	−6.344
4600	327.727	1285.996	1001.552	1308.444	−1872.662	600.362	−6.817
4700	327.924	1293.047	1007.679	1341.227	−1865.294	654.045	−7.269
4800	328.109	1299.952	1013.696	1374.029	−1857.860	707.571	−7.700
4900	328.283	1306.720	1019.608	1406.848	−1850.361	760.938	−8.112
5000	328.447	1313.353	1025.417	1439.685	−1842.799	814.155	−8.505
5100	328.602	1319.859	1031.126	1472.537	−1835.177	867.217	−8.882
5200	328.749	1326.241	1036.740	1505.405	−1827.495	920.132	−9.243
5300	328.888	1332.505	1042.262	1538.287	−1819.754	972.897	−9.588
5400	329.019	1338.654	1047.694	1571.182	−1811.957	1025.515	−9.920
5500	329.144	1344.692	1053.039	1604.091	−1804.103	1077.987	−10.238
5600	329.262	1350.624	1058.300	1637.011	−1796.194	1130.319	−10.543
5700	329.374	1356.453	1063.480	1669.943	−1788.228	1182.506	−10.836
5800	329.481	1362.182	1068.581	1702.886	−1780.207	1234.555	−11.118
5900	329.583	1367.815	1073.605	1735.839	−1772.131	1286.464	−11.389
6000	329.679	1373.355	1078.555	1768.802	−1763.998	1338.235	−11.650

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 347.740 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -947.050 \pm 2.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -961.065 \pm 2.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
676(1)	746(2)	510(2)
635(1)	425(2)	352(2)
670(1)	257(2)	310(2)
365(1)		[340](2)

Ground State Quantum Weight: [1] $\sigma = 10$

Point Group: D_{5h}

Bond Distances: I–F(equatorial) = 1.86 Å; I–F(axial) = 1.76 Å

Bond Angles: F(eq)–I–F(ax) = 90°; F(eq)–I–F(eq) = 72°

Product of the Moments of Inertia: $I_A I_B I_C = 1.196821 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

Settle *et al.*[1] derived $\Delta_f H° = 229.7 \pm 0.6$ kcal·mol^{-1} for IF_7(g) at 298.15 K from treatment of their calorimetric data on combustion of iodine in fluorine. The combustion products, consisting of mixtures of IF_5 and IF_7, were expanded, treated to remove excess fluorine, and then hydrolyzed. The solutions were analyzed for iodate and the sum of iodate plus periodate. Since the recovery of iodine was not complete (about 70 to 99%), it was necessary to try various assumptions about the form of the unrecovered iodine. Consistent results were obtained only by assigning the unrecovered iodine to IF_7, the less volatile product. This treatment indicated that IF_7 was formed in yields ranging from about 1 to 70%.

$\Delta_r H°$ for the reaction $IF_7(g) \rightarrow IF_5(g) + F_2(g)$ may be checked via equilibrium data.[2] Using six points read from Figure 2 of Bernstein and Katz, we obtain $\Delta_r H°$(3rd law) = 29.36 ± 0.2 kcal·mol^{-1} and $\Delta_r H°$(2nd law) = 29.53 ± 0.7 kcal·mol^{-1}, both at 298.15 K. The entopy test, $\Delta_r S°$(2nd law) $\Delta_r S°$(JANAF Functions) = 0.3 ± 1.4 cal K^{-1}·mol^{-1}, indicates consistency with the JANAF functions. Combination of $\Delta_r H°$(3rd law) with $\Delta_f H°$ for IF_5(g) yields $\Delta_f H°(IF_7, g) = -230.2 \pm 0.6$ kcal·mol^{-1}. In deriving the uncertainty, we assume that $\Delta_r H°$(3rd law) is uncertain by ±0.5 kcal·mol^{-1} due to an estimated uncertainty of about 1.0 cal K^{-1}·mol^{-1} in the JANAF value of $\Delta_r S°$ at 500 K.

Heat Capacity and Entropy

Recent evidence favors D_{5h} symmetry and a pentagonal bipyramidal structure for the heptafluoride. Claassen *et al.*[3] review the earlier debate about structure of lower symmetry. They provide convincing evidence of D_{5h} symmetry from the first observation of Raman spectra of the vapor state and re examination of the infrared spectra. Their data including five fundamentals in Raman (two polarized), five fundamentals in infrared, no coincidences between Raman and infrared, and one fundamental inactive are consistent only with D_{5h} symmetry. This is confirmed by Falconer *et al.*[4] who interpret their electric deflection experiments as indicating a symmetry forbidden dipole moment. Extended Huckel molecular orbital calculations[5] also predict D_{5h} symmetry. The adopted structural parameters are from our approximate analysis of the electron diffraction data of Thompson and Bartell.[6] The authors gave a radial distribution curve and suggested only a gross (unrefined) structure because of the probable presence of a fluorocarbon impurity in their sample. Principal moments of inertia are $I_A = I_B = 46.8306 \times 10^{-39}$ and $I_C = 54.5719 \times 10^{-39}$ g·cm^2.

Observed vibrational fundamentals are from Claassen *et al.*[3] The inactive fundamental is estimated from the calculations of Khanna.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.471	−947.050	−947.050	INFINITE
100	52.248	247.318	444.637	−19.732	−955.010	−917.063	479.024
200	103.461	300.045	359.173	−11.826	−959.821	−876.878	229.017
250	121.537	325.173	349.886	−6.178	−960.746	−856.020	178.856
298.15	134.451	347.740	347.740	0.	−961.065	−835.814	146.431
300	134.875	348.573	347.743	0.249	−961.069	−835.037	145.393
350	144.688	370.140	349.424	7.251	−961.034	−814.031	121.487
400	151.979	389.959	353.269	14.676	−968.728	−792.774	103.526
450	157.478	408.192	358.373	22.419	−968.837	−770.771	89.469
500	161.694	425.012	364.207	30.403	−988.880	−746.865	78.024
600	167.580	455.054	376.906	46.889	−986.428	−698.688	60.826
700	171.367	481.191	389.978	63.850	−983.782	−650.938	48.574
800	173.928	504.252	402.849	81.122	−981.032	−603.576	39.409
900	175.733	524.848	415.281	98.610	−978.229	−556.562	32.302
1000	177.050	543.434	427.182	116.252	−975.402	−509.861	26.632
1100	178.038	560.358	438.531	134.009	−972.573	−463.444	22.007
1200	178.798	575.883	449.339	151.853	−969.756	−417.284	18.164
1300	179.395	590.219	459.632	169.763	−966.966	−371.358	14.921
1400	179.871	603.531	469.440	187.727	−964.212	−325.646	12.150
1500	180.257	615.955	478.799	205.734	−961.506	−280.129	9.755
1600	180.575	627.599	487.739	223.777	−958.853	−234.791	7.665
1700	180.839	638.554	496.291	241.848	−956.258	−189.616	5.826
1800	181.061	648.897	504.485	259.943	−953.723	−144.593	4.196
1900	181.249	658.692	512.345	278.059	−951.244	−99.710	2.741
2000	181.410	667.993	519.897	296.192	−948.815	−54.955	1.435
2100	181.549	676.847	527.162	314.340	−946.425	−10.321	0.257
2200	181.670	685.296	534.159	332.501	−944.062	34.200	−0.812
2300	181.775	693.374	540.907	350.674	−941.712	78.614	−1.785
2400	181.868	701.112	547.422	368.856	−939.356	122.925	−2.675
2500	181.950	708.538	553.719	387.047	−936.978	167.138	−3.492
2600	182.022	715.676	559.812	405.245	−934.560	211.256	−4.244
2700	182.087	722.547	565.713	423.451	−932.086	255.279	−4.939
2800	182.145	729.170	571.433	441.663	−929.539	299.209	−5.582
2900	182.197	735.562	576.983	459.880	−926.904	343.046	−6.179
3000	182.244	741.740	582.373	478.102	−924.168	386.791	−6.735
3100	182.287	747.716	587.610	496.328	−921.319	430.443	−7.253
3200	182.325	753.504	592.705	514.559	−918.347	474.001	−7.737
3300	182.360	759.115	597.663	532.793	−915.245	517.465	−8.191
3400	182.393	764.560	602.492	551.031	−912.005	560.832	−8.616
3500	182.422	769.847	607.198	569.272	−908.621	604.102	−9.016
3600	182.449	774.987	611.788	587.515	−905.091	647.273	−9.392
3700	182.474	779.986	616.267	605.761	−901.412	690.344	−9.746
3800	182.497	784.853	620.639	624.010	−897.581	733.313	−10.080
3900	182.518	789.593	624.911	642.261	−893.599	776.180	−10.396
4000	182.538	794.214	629.086	660.514	−889.465	818.943	−10.694
4100	182.556	798.722	633.169	678.768	−885.181	861.599	−10.977
4200	182.573	803.121	637.163	697.025	−880.749	904.151	−11.245
4300	182.589	807.418	641.073	715.283	−876.170	946.594	−11.499
4400	182.603	811.615	644.901	733.542	−871.446	988.930	−11.740
4500	182.617	815.719	648.652	751.804	−866.582	1031.158	−11.969
4600	182.630	819.733	652.327	770.066	−861.579	1073.274	−12.187
4700	182.642	823.661	655.931	788.330	−856.441	1115.281	−12.395
4800	182.653	827.506	659.466	806.594	−851.172	1157.178	−12.593
4900	182.664	831.273	662.934	824.860	−845.774	1198.962	−12.781
5000	182.674	834.963	666.338	843.127	−840.252	1240.635	−12.961
5100	182.684	838.580	669.679	861.395	−834.609	1282.197	−13.132
5200	182.692	842.128	672.962	879.664	−828.849	1323.648	−13.296
5300	182.701	845.608	676.187	897.933	−822.976	1364.986	−13.453
5400	182.709	849.023	679.356	916.204	−816.992	1406.212	−13.602
5500	182.716	852.376	682.471	934.475	−810.901	1447.326	−13.746
5600	182.723	855.668	685.535	952.747	−804.707	1488.330	−13.883
5700	182.730	858.902	688.548	971.020	−798.413	1529.220	−14.014
5800	182.736	862.080	691.513	989.293	−792.023	1570.000	−14.139
5900	182.742	865.204	694.430	1007.567	−785.539	1610.671	−14.260
6000	182.748	868.276	697.302	1025.842	−778.964	1651.228	−14.375

PREVIOUS: December 1969 (1 atm) CURRENT: December 1969 (1 bar)

$S°(298.15\ K) = [531.554 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2686.418 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 2697.843 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
759 (2)	261 (4)
738 (2)	112 (4)
683 (2)	[400](4)
[500](2)	[90](3)
713 (4)	[60](3)

Ground State Quantum Weight: [3] σ = [4]
Point Group: $[D_{2h}]$
Bond Distances: Mo–F = [1.78] Å; $Mo–F_{bridge}$ = [2.06] Å
Bond Angles: F–Mo–F = [90° or 180°]; $F_{bridge}–Mo–F_{bridge}$ = [90]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.683573 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(298.15\ K) = -644.8 \pm 2\ kcal \cdot mol^{-1}$ in agreement with Brewer.[1] This is derived by proceeding from $\Delta_f H°(MoF_5, cr, 298.15\ K)$ to $\Delta_f H°(MoF_5, l, 298.15\ K)$ to $\Delta_f H°$(dimer, g, 298.15 K). Brewer[1] adopted $\Delta_f H°(MoF_5, cr, 298.15\ K) = -331.9 \pm 1\ kcal \cdot mol^{-1}$ from the measurements of Burgess *et al.*[2a]nd Nuttall *et al.*[3] Krause and Douglas[4] measured $\Delta_{fus}H°(318.82\ K) = 1.46 \pm 0.07\ kcal \cdot mol^{-1}$ and the $\Delta C_p°$ correction to 298.15 K is only $-4\ cal\ K^{-1} \cdot mol^{-1}$. The heat of vaporization to the dimer $\Delta_{vap}H°(298.15\ K) = 15.99\ kcal \cdot mol^{-1}$ was derived by Krause[5] from vapor density data.

The value of $\Delta_f H°(0\ K)$ combined with JANAF data[11] for Mo(g) and F(g) gives $\Delta_{at}H°(0\ K) = 1139.9 \pm 8\ kcal \cdot mol^{-1}$ and an average bond energy of $\Delta_{at}H°(0\ K)/10 = 114.0 \pm 1\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

For Mo_2F_{10}(g), the dimer of MoF_5(g), Douglas,[6] Krause,[5] and Brewer[1] have used the MoF_5(g) frequencies with doubled degeneracy along with estimates of two triply degenerate frequencies. The frequencies, cm^{-1}, and degeneracies for MoF_5(g) were assigned from the spectroscopic data of Acquista and Abramowitz[7] and two fundamentals were estimated[8] -- 759(1), 738(1), 683(1), [500](1), 713(2), 261(2), ll2(2), and [200](2). Douglas[6] and Krause[5] elected to use an estimate of [400](2) rather than [200](2) while, for MoF_5, Brewer[1a]nd Hildenbrand[9] retained the [200](2) estimate. The derived functions for Mo_2F_{10}(g) presented here and by Brewer[1] use the [400](4) estimate. For the six remaining frequencies, Douglas[6] has chosen the estimates [121](3) and [90](3) and Krause[5] has chosen [60](6); Brewer[1] has used [90](3) and [60](3), one of the alternative estimates of Douglas,[6] in order to match the selected entropy of the liquid and the entropy of vaporization to the dimer.[5] We adopt Brewer's[1] evaluation of the vibrational assignment and the estimate of an electronic ground state quantum weight of [3].[1-6]

By analogy with the MoF_5(cr) structure,[10] the dimer(g) molecule was assumed to have the structure of two octahedra sharing a common edge.[5, 6] The two Mo atoms at the centers of the octahedra and the two bridging F atoms at the ends of the common edge form Mo–F–Mo angles of 90°. The bridging Mo–F bond distance of 2.06 Å and the non bridging Mo–F distance of 1.78 Å from MoF_5(cr),[10] were assumed for the gaseous dimer. All adjacent F–Mo–F angles are 90°.

The principal moments of inertia are: $I_A = 73.3619 \times 10^{-39}$, $I_B = 220.8005 \times 10^{-39}$, $I_C = 227.4042 \times 10^{-39}\ g \cdot cm^2$.

This table is in good agreement with the critical evaluation by Brewer[1] on which it is based.

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[10] A. J. Edwards, R. D. Peacock, and R. W. H. Small, J. Chem. Soc. 4486 (1962).
[11] JANAF Thermochemical Tables: Mo(g), 3-31-78; F(g), 9-30-65.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−41.869	−2686.418	−2686.418	INFINITE
100	121.299	352.980	693.437	−34.046	−2694.112	−2642.820	1380.468
200	174.754	454.231	549.884	−19.131	−2697.527	−2589.929	676.420
250	195.952	495.583	534.963	−9.845	−2697.989	−2562.962	535.502
298.15	212.349	531.554	531.554	0.	−2697.843	−2536.961	444.465
300	212.904	532.870	531.558	0.393	−2697.828	−2535.962	441.550
350	226.083	566.722	534.202	11.382	−2697.211	−2509.028	374.452
400	236.249	597.604	540.226	22.951	−2696.277	−2482.206	324.143
450	244.122	625.905	548.196	34.969	−2695.125	−2455.514	285.029
500	250.274	651.957	557.287	47.335	−2693.820	−2428.959	253.752
600	259.028	698.420	577.032	72.833	−2690.923	−2376.255	206.871
700	264.757	738.809	597.322	99.041	−2687.818	−2324.053	173.423
800	268.674	774.434	617.279	125.724	−2684.624	−2272.304	148.366
900	271.456	806.248	636.539	152.738	−2681.414	−2220.957	128.901
1000	273.496	834.960	654.969	179.991	−2678.236	−2169.967	113.347
1100	275.033	861.102	672.538	207.421	−2675.131	−2119.291	100.637
1200	276.218	885.086	689.265	234.986	−2672.133	−2068.893	90.057
1300	277.150	907.234	705.191	262.656	−2669.271	−2018.740	81.114
1400	277.895	927.801	720.366	290.409	−2666.570	−1968.802	73.457
1500	278.501	946.995	734.842	318.230	−2664.052	−1919.050	66.827
1600	278.999	964.986	748.669	346.106	−2661.735	−1869.460	61.032
1700	279.414	981.913	761.897	374.027	−2659.631	−1820.008	55.922
1800	279.763	997.894	774.568	401.987	−2657.753	−1770.673	51.384
1900	280.059	1013.028	786.724	429.978	−2656.110	−1721.438	47.326
2000	280.313	1027.400	798.401	457.997	−2654.709	−1672.281	43.676
2100	280.531	1041.082	809.634	486.040	−2653.555	−1623.190	40.375
2200	280.721	1054.136	820.453	514.102	−2652.651	−1574.147	37.375
2300	280.887	1066.619	830.887	542.183	−2652.001	−1525.139	34.637
2400	281.033	1078.576	840.960	570.279	−2651.608	−1476.155	32.128
2500	281.162	1090.051	850.696	598.389	−2651.478	−1427.181	29.819
2600	281.277	1101.081	860.115	626.511	−2651.638	−1378.207	27.689
2700	281.379	1111.698	869.238	654.644	−2652.152	−1329.220	25.715
2800	281.470	1121.933	878.081	682.787	−2653.129	−1280.207	23.883
2900	281.553	1131.812	886.661	710.938	−2726.487	−1231.049	22.174
3000	281.627	1141.358	894.992	739.097	−2724.766	−1179.511	20.537
3100	281.694	1150.594	903.090	767.263	−2722.904	−1128.034	19.007
3200	281.755	1159.538	910.965	795.435	−2720.893	−1076.618	17.574
3300	281.810	1168.209	918.629	823.614	−2718.724	−1025.267	16.229
3400	281.861	1176.623	926.094	851.797	−2716.393	−973.985	14.963
3500	281.908	1184.794	933.369	879.986	−2713.895	−922.773	13.772
3600	281.950	1192.736	940.464	908.179	−2711.226	−871.635	12.647
3700	281.990	1200.462	947.387	936.376	−2708.383	−820.574	11.584
3800	282.026	1207.982	954.146	964.577	−2705.367	−769.594	10.579
3900	282.059	1215.309	960.749	992.781	−2702.176	−718.692	9.626
4000	282.091	1222.450	967.203	1020.988	−2698.811	−667.876	8.722
4100	282.119	1229.416	973.514	1049.199	−2695.273	−617.147	7.863
4200	282.146	1236.215	979.688	1077.412	−2691.564	−566.505	7.046
4300	282.171	1242.854	985.731	1105.628	−2687.687	−515.955	6.268
4400	282.194	1249.341	991.649	1133.846	−2683.643	−465.495	5.526
4500	282.216	1255.683	997.446	1162.067	−2679.437	−415.129	4.819
4600	282.236	1261.886	1003.128	1190.290	−2675.071	−364.860	4.143
4700	282.255	1267.956	1008.698	1218.514	−2670.549	−314.686	3.497
4800	282.273	1273.899	1014.161	1246.741	−2665.874	−264.610	2.880
4900	282.290	1279.719	1019.522	1274.969	−2661.051	−214.633	2.288
5000	282.306	1285.423	1024.783	1303.199	−3838.853	−153.294	1.601
5100	282.321	1291.013	1029.948	1331.430	−3837.103	−79.601	0.815
5200	282.335	1296.495	1035.022	1359.663	−3835.509	−5.939	0.060
5300	282.348	1301.873	1040.006	1387.897	−3834.068	67.692	−0.667
5400	282.361	1307.151	1044.905	1416.132	−3832.786	141.298	−1.367
5500	282.372	1312.332	1049.720	1444.369	−3831.657	214.880	−2.041
5600	282.384	1317.421	1054.455	1472.607	−3830.683	288.446	−2.691
5700	282.394	1322.419	1059.112	1500.846	−3829.859	361.992	−3.317
5800	282.404	1327.330	1063.695	1529.086	−3829.186	435.526	−3.922
5900	282.414	1332.158	1068.204	1557.327	−3828.658	509.053	−4.507
6000	282.423	1336.904	1072.643	1585.568	−3828.279	582.568	−5.072

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$S°(298.15\ K) = [396.943 \pm 8.4]\ kJ \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2040.744 \pm 29.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -2064.386 \pm 29.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
913 (1)	938 (1)	410 (2)	860 (2)
690 (1)	684 (1)	[150](2)	634 (2)
[642](1)	571 (1)	728 (2)	425 (2)
247 (1)	826 (2)	624 (2)	188 (2)
Torsion	544 (2)	509 (2)	

Ground State Quantum Weight: [1] $\sigma = 8$

Point Group: [D_{4h}]

Bond Distances: S–F = 1.56 ± 0.02 Å; S–S = 2.21 ± 0.03 Å

Bond Angles: F*–S–F* = 90°; F*–S–S = 90°

F**–S–S* = 180°; (*–equatorial **–axial)

Product of the Moments of Inertia: $I_A I_B I_C = 8.747547 \times 10^{-112}\ g^3 \cdot cm^6$

Reduced Moment of Inertia: $I_{red} = 1.5354 \times 10^{-38}\ g \cdot cm^2$

Barrier to Internal Rotation: V = [8.0] $kcal \cdot mol^{-1}$

Enthalpy of Formation

The kinetics of the decomposition of gaseous S_2F_{10} have been studied by Trost and McIntosh[1] from 434 455 K. Benson and Bott[2] have reevaluated these kinetic data and have reported two values for the equilibrium constant of the dissociation process $S_2F_{10}(g) = SF_4(g) + SF_6(g)$. Both values refer to a temperature of 444 K. We analyze these two K_p values by the 3rd law method, and we obtain the result $\Delta_r H°(298.15\ K) = 19.26 \pm 1.4\ kcal \cdot mol^{-1}$. The adopted value of $\Delta_f H°(S_2F_{10}, g, 298.15\ K) = -493.4 \pm 7\ kcal \cdot mol^{-1}$ is obtained by combining the value of $\Delta_r H°$ with JANAF enthalpies of formation[3] for SF_4 and SF_6.

The heat of atomization, $\Delta_{at} H°(0\ K)$, and bond dissocation energy $D_0°(F_5S–SF_5)$ are calculated to be $802.8 \pm 11.0\ kcal \cdot mol^{-1}$ and $58.4 \pm 14.0\ kcal \cdot mol^{-1}$, respectively. The latter value agrees with an upper limit value of $62.6\ kcal \cdot mol^{-1}$ for the bond energy of a covalent S–S linkage established from thermochemical data[3] for the S_8 ring.

Heat Capacity and Entropy

The results of electron diffraction experiments[4] show that the S_2F_{10} molecule consists of two SF_5 octahedral groups sharing a common S–S bond. The adopted bond lengths and angles are taken from this study.[4] The relative orientation of the two SF_5 groups has not been experimentally established,[5–7] but the staggered configuration of D_{4d} symmetry has been predicted to be more stable[8] than the eclipsed form (D_{4h} symmetry). We assume that the point group is D_{4d}. The principal moments of inertia are: $I_A = 61.4204 \times 10^{-39}$ and $I_B = I_C = 119.3402 \times 10^{-39}\ g \cdot cm^2$.

The vibrational spectra of S_2F_{10} have been studied in detail in three independent investigations.[5–7] The reported fundamental frequencies show reasonable agreement but the assignments of the observed fundamentals made by Wilmshurst and Bernstein[5] differ somewhat from those made by Dodd *et al.*[6] The adopted frequencies and assignments except for the torsion (ν_5) and SF_5 rocking frequency (ν_{12}) are taken from Dodd *et al.*[6] We estimate the unobserved ν_{12} fundamental at 150 cm^{-1}. Other estimated values that have been reported include 200 cm^{-1} [2] and 37 cm^{-1}.[5] The inactive torsional frequency is treated as a hindered internal rotation. We use an estimated potential barrier of 8.0 $kcal \cdot mol^{-1}$ [5] to calculate heat capacity contributions for hindered rotation from the table of Pitzer and Brewer.[9] Contributions below 201 K could not be obtained by this procedure since the values of the ratio V/RT were outside the range of the table. $C_p°$ value between 150 200 K are estimated by graphical interpolation of the hindered rotor $C_p°$ data above 210 K and the corresponding data for a harmonic oscillator ($\nu_5 = 89$ cm^{-1})[5] below 150 K. This treatment assumes that the internal rotation approaches harmonic oscillation as V/RT >> 1. The uncertainty (±2 cal $K^{-1} \cdot mol^{-1}$) in the value of $S°(298.15\ K)$ includes the possibility that the potential barrier is as low as 4.0 $kcal \cdot mol^{-1}$ [8] and contains a contribution from the uncertainty due to the two estimated vibrational frequencies.

Previously published thermodynamic functions[10,11] for S_2F_{10} are based on the assumption that free internal rotation exists in the molecule and on different estimates[5] for the SF_5 rocking fundamentals. Benson and Bott[2] have shown that these earlier frequencies[5] give values for $S°(S_2F_{10}, g)$ which are too high by several units. Our treatment of internal rotation is consistent with the interpretation of electron diffraction data[4] which indicates that the rotation is not completely restricted. It should also be noted that the $C_p°$ data reported by Pass[11] are erroneous above 400 K.

References

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Continued on page 1217

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−29.307	−2040.744	−2040.744	INFINITE
100	69.170	271.813	518.037	−24.622	−2051.974	−1991.466	1040.235
200	124.892	336.657	411.591	−14.987	−2060.267	−1927.492	503.409
298.15	176.682	396.943	396.943	0.	−2064.386	−1861.311	326.094
300	177.473	398.038	396.946	0.328	−2064.432	−1860.051	323.864
400	211.418	454.110	404.360	19.900	−2070.149	−1791.494	233.945
500	232.735	503.752	419.380	42.186	−2072.548	−1721.547	179.849
600	246.438	547.482	437.162	66.192	−2073.079	−1651.270	143.756
700	255.525	586.198	455.742	91.319	−2072.404	−1581.009	117.976
800	261.768	620.750	474.248	117.202	−2070.991	−1510.899	98.652
900	266.123	651.847	492.282	143.608	−2175.369	−1438.835	83.508
1000	269.228	680.054	509.671	170.383	−2170.756	−1357.244	70.895
1100	271.377	705.819	526.349	197.417	−2166.065	−1276.120	60.598
1200	273.094	729.508	542.305	224.644	−2161.341	−1195.424	52.035
1300	274.275	751.416	557.558	252.014	−2156.622	−1115.122	44.806
1400	275.232	771.778	572.141	279.492	−2151.934	−1035.184	38.623
1500	275.907	790.791	586.091	307.049	−2147.295	−955.578	33.276
1600	276.470	808.616	599.448	334.669	−2142.716	−876.279	28.608
1700	276.813	825.387	612.250	362.334	−2138.203	−797.265	24.497
1800	277.117	841.218	624.535	390.030	−2133.759	−718.515	20.851
1900	277.384	856.208	636.337	417.756	−2129.371	−640.011	17.595
2000	277.613	870.442	647.689	445.506	−2125.029	−561.735	14.671
2100	277.754	883.991	658.622	473.274	−2120.721	−483.678	12.031
2200	277.883	896.915	669.162	501.056	−2116.432	−405.824	9.635
2300	277.997	909.270	679.335	528.851	−2112.143	−328.164	7.453
2400	278.098	921.103	689.164	556.655	−2107.836	−250.692	5.456
2500	278.186	932.458	698.670	584.470	−2103.492	−173.400	3.623
2600	278.245	943.370	707.873	612.291	−2099.093	−96.283	1.934
2700	278.298	953.872	716.791	640.119	−2094.622	−19.337	0.374
2800	278.345	963.994	725.440	667.951	−2090.064	57.443	−1.072
2900	278.386	973.762	733.835	695.787	−2085.402	134.057	−2.415
3000	278.420	983.200	741.991	723.628	−2080.626	210.509	−3.665
3100	278.441	992.330	749.920	751.471	−2075.722	286.799	−4.833
3200	278.459	1001.170	757.634	779.316	−2070.683	362.930	−5.924
3300	278.475	1009.739	765.144	807.162	−2065.499	438.901	−6.947
3400	278.488	1018.053	772.461	835.011	−2060.164	514.712	−7.908
3500	278.500	1026.125	779.594	862.860	−2054.674	590.364	−8.811
3600	278.504	1033.971	786.552	890.710	−2049.026	665.858	−9.661
3700	278.508	1041.602	793.342	918.561	−2043.216	741.191	−10.464
3800	278.512	1049.029	799.973	946.412	−2037.243	816.365	−11.222
3900	278.516	1056.264	806.453	974.263	−2031.108	891.381	−11.939
4000	278.521	1063.315	812.786	1002.115	−2024.811	966.238	−12.618
4100	278.526	1070.193	818.981	1029.967	−2018.353	1040.933	−13.262
4200	278.531	1076.905	825.043	1057.820	−2011.736	1115.471	−13.873
4300	278.535	1083.459	830.976	1085.674	−2004.963	1189.847	−14.454
4400	278.539	1089.862	836.788	1113.527	−1998.036	1264.066	−15.006
4500	278.541	1096.122	842.481	1141.381	−1990.959	1338.126	−15.533
4600	278.542	1102.244	848.062	1169.235	−1983.735	1412.025	−16.034
4700	278.543	1108.234	853.534	1197.090	−1976.370	1485.768	−16.512
4800	278.543	1114.098	858.902	1224.944	−1968.866	1559.351	−16.969
4900	278.544	1119.842	864.169	1252.798	−1961.228	1632.777	−17.406
5000	278.546	1125.469	869.338	1280.653	−1953.459	1706.045	−17.823
5100	278.548	1130.985	874.415	1308.507	−1945.565	1779.157	−18.222
5200	278.549	1136.394	879.401	1336.362	−1937.548	1852.114	−18.605
5300	278.551	1141.700	884.300	1364.217	−1929.414	1924.914	−18.971
5400	278.553	1146.906	889.115	1392.073	−1921.166	1997.560	−19.323
5500	278.554	1152.018	893.849	1419.928	−1912.809	2070.051	−19.660
5600	278.555	1157.037	898.504	1447.783	−1904.345	2142.392	−19.983
5700	278.556	1161.967	903.083	1475.639	−1895.780	2214.577	−20.294
5800	278.557	1166.812	907.589	1503.495	−1887.117	2286.613	−20.593
5900	278.558	1171.574	912.023	1531.350	−1878.359	2358.501	−20.881
6000	278.558	1176.255	916.388	1559.206	−1869.510	2430.236	−21.157

PREVIOUS: CURRENT: December 1977

$S°(298.15\ K) = [706.844 \pm 29.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -4049.417 \pm 20.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -4065.593 \pm 20.9\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
759 (3)	261 (6)
738 (3)	112 (6)
683 (3)	[400](6)
[500](3)	[106](6)
713 (6)	[53](6)

Ground State Quantum Weight: [4] σ = [6]

Point Group: $[D_{3h}]$

Bond Distances: Mo–F = [1.78] Å; $Mo–F_{bridge}$ = [2.06] Å

Bond Angles: F–Mo–F = [90° or 180°]; $F_{bridge}–Mo–F_{bridge}$ = [90°]

Product of the Moments of Inertia: $I_A I_B I_C = [9.5696 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

We adopt $\Delta_f H°(Mo_3F_{15}, g, 298.15\ K) = -971.7 \pm 5\ kcal \cdot mol^{-1}$ to agree with Brewer.[1] This is based on 1) the $\Delta_f H°(MoF_5, cr, 298.15\ K) = -331.9 \pm 1\ kcal \cdot mol^{-1}$ adopted by Brewer from the measurements of Burgess *et al.*[2] and Nuttall *et al.*[3] 2) the heat of fusion $\Delta_{fus}H°(318.82\ K) = 1.46 \pm 0.07\ kcal \cdot mol^{-1}$ measured by Krause and Douglas,[4] and 3) a heat of vaporization to the trimer $\Delta_{vap}H°(298.15\ K) = 18.9\ kcal \cdot mol^{-1}$. This heat of vaporization was derived by Brewer[1] from a re-evaluation of the vapor density data of Douglas[5] — the proportion of $Mo_3F_{15}(g)$ in the saturated vapor was reduced to be consistent with no appreciable monomer and a vapor density corresponding to $Mo_2F_{10}(g)$. Douglas[5] had chosen $\Delta_{vap}H°(298.15\ K)$ of $MoF_5(l)$ to $Mo_3F_{15}(g)$ equal to 17.7 $kcal \cdot mol^{-1}$ from a possible range of 16 to 21 $kcal \cdot mol^{-1}$. The value of $\Delta_f H°(0\ K)$ combined with JANAF data[6] for Mo(g) and F(g) gives $\Delta_{at}H°(0\ K) = 1714.5 \pm 14\ kcal \cdot mol^{-1}$ and an average Mo–F bond energy of $\Delta_{at}H°(0\ K)/15 = 114.3 \pm 1\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Brewer[1] has followed Douglas's[5] choice of [4] for the electronic ground state quantum weight, 2) of vibrational frequencies and 3) of molecular configuration.

The $MoF_5(g)$ monomer vibrational frequencies were used, with triple the degeneracy, for the trimer, Mo_3F_{15}, and the 12 remaining frequencies were estimated as [106](6) and [53](6).[5] The vibrational frequencies for $MoF_5(g)$ had been assigned from the spectroscopic data of Aquista and Abramowitz[7] and two fundamentals had been estimated;[8] these frequencies, cm^{-1}, and degeneracies are 759(1), 738(1), 683(1), [500](1), 713(2), 261(2), and [200](2). Douglas[5] used [400](2) rather than [200](2).

The structure assumed by Douglas[5] consists of three tetragonal bipyramids joined by three bridging F atoms such that the three Mo atoms and the three bridging F atoms form a planar, irregular hexagon. The $F_{bridge}–Mo–F_{bridge}$ angles are 90°, the Mo– F_{bridge}–Mo angles are 150°; the remaining F–Mo–F angles are either 90° or 180°. The Mo–F_{bridge} bond distance, 2.06 Å, and the Mo–F bond distance, 1.78 Å, are taken from the x-ray study of MoF_5(cr) by Edwards *et al.*[9]

The principal moments of inertia are $I_A = I_B = 3.8417 \times 10^{-37}$, $I_C = 6.4840 \times 10^{-37}\ g \cdot cm^2$.

This table is in good agreement with the critical evaluation of Brewer[1] on which it is based.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$	$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$		$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−63.765	−4049.417	−4049.417	INFINITE
100	186.331	431.758	956.105	−52.435	−4061.363	−3974.653	2076.146
200	269.353	587.843	735.038	−29.439	−4065.861	−3885.765	1014.858
250	301.534	651.527	712.085	−15.139	−4066.184	−3840.681	802.466
298.15	326.335	706.844	706.844	0.	−4065.593	−3797.290	665.269
300	327.175	708.865	706.850	0.604	−4065.556	−3795.625	660.877
350	347.072	760.860	710.911	17.482	−4064.236	−3750.733	559.766
400	362.408	808.250	720.161	35.236	−4062.436	−3706.066	483.963
450	374.275	851.650	732.394	53.665	−4060.304	−3661.644	425.033
500	383.545	891.583	746.343	72.620	−4057.940	−3617.474	377.915
600	396.731	962.767	776.629	111.683	−4052.778	−3529.858	307.301
700	405.357	1024.615	807.735	151.816	−4047.300	−3443.135	256.930
800	411.255	1079.152	838.321	192.664	−4041.687	−3357.208	219.203
900	415.443	1127.846	867.834	234.010	−4036.046	−3271.987	189.901
1000	418.513	1171.784	896.068	275.716	−4030.453	−3187.392	166.492
1100	420.826	1211.786	922.979	317.688	−4024.968	−3103.353	147.366
1200	422.610	1248.482	948.596	359.863	−4019.642	−3019.805	131.449
1300	424.012	1282.366	972.984	402.197	−4014.521	−2936.695	117.998
1400	425.134	1313.832	996.220	444.656	−4009.641	−2853.971	106.483
1500	426.046	1343.195	1018.384	487.217	−4005.035	−2771.585	96.515
1600	426.795	1370.716	1039.553	529.860	−4000.729	−2689.497	87.803
1700	427.420	1396.610	1059.803	572.572	−3996.743	−2607.668	80.124
1800	427.945	1421.056	1079.200	615.341	−3993.097	−2526.064	73.304
1900	428.391	1444.206	1097.807	658.158	−3989.802	−2444.656	67.208
2000	428.772	1466.189	1115.681	701.017	−3986.871	−2363.408	61.726
2100	429.101	1487.117	1132.874	743.911	−3984.309	−2282.301	56.769
2200	429.387	1507.086	1149.433	786.836	−3982.123	−2201.306	52.266
2300	429.637	1526.178	1165.401	829.787	−3980.317	−2120.400	48.156
2400	429.857	1544.468	1180.817	872.762	−3978.897	−2039.566	44.390
2500	430.051	1562.020	1195.717	915.758	−3977.871	−1958.783	40.927
2600	430.223	1578.890	1210.132	958.771	−3977.280	−1878.033	37.730
2700	430.376	1595.130	1224.092	1001.802	−3977.221	−1797.296	34.771
2800	430.514	1610.784	1237.625	1044.846	−3977.856	−1716.549	32.023
2900	430.638	1625.894	1250.754	1087.904	−4087.062	−1635.615	29.461
3000	430.749	1640.495	1263.504	1130.973	−4083.649	−1551.140	27.008
3100	430.850	1654.621	1275.894	1174.053	−4080.025	−1466.784	24.715
3200	430.942	1668.301	1287.944	1217.143	−4076.177	−1382.546	22.568
3300	431.026	1681.563	1299.672	1260.242	−4072.094	−1298.432	20.552
3400	431.102	1694.432	1311.094	1303.348	−4067.766	−1214.446	18.658
3500	431.172	1706.929	1322.226	1346.462	−4063.187	−1130.591	16.873
3600	431.237	1719.077	1333.082	1389.582	−4058.352	−1046.869	15.190
3700	431.296	1730.893	1343.674	1432.709	−4053.258	−963.286	13.599
3800	431.350	1742.396	1354.016	1475.841	−4047.902	−879.847	12.094
3900	431.401	1753.601	1364.119	1518.979	−4042.284	−796.548	10.669
4000	431.447	1764.524	1373.993	1562.121	−4036.406	−713.397	9.316
4100	431.491	1775.178	1383.649	1605.268	−4030.268	−630.399	8.031
4200	431.531	1785.576	1393.095	1648.419	−4023.873	−547.551	6.810
4300	431.569	1795.731	1402.341	1691.574	−4017.226	−464.862	5.647
4400	431.604	1805.653	1411.395	1734.733	−4010.330	−382.327	4.539
4500	431.636	1815.352	1420.265	1777.895	−4003.189	−299.951	3.482
4600	431.667	1824.840	1428.957	1821.060	−3995.808	−217.739	2.473
4700	431.696	1834.123	1437.479	1864.228	−3988.194	−135.688	1.508
4800	431.722	1843.212	1445.838	1907.399	−3980.351	−53.801	0.585
4900	431.748	1852.114	1454.038	1950.573	−3972.285	27.918	−0.298
5000	431.771	1860.837	1462.087	1993.749	−3738.157	126.664	−1.323
5100	431.794	1869.388	1469.990	2036.927	−5734.700	243.926	−2.498
5200	431.815	1877.772	1477.752	2080.108	−5731.478	361.124	−3.628
5300	431.835	1885.998	1485.377	2123.290	−5728.486	478.260	−4.714
5400	431.854	1894.070	1492.871	2166.474	−5725.731	595.341	−5.759
5500	431.872	1901.994	1500.238	2209.661	−5723.206	712.373	−6.766
5600	431.888	1909.776	1507.482	2252.849	−5720.914	829.365	−7.736
5700	431.905	1917.421	1514.607	2296.038	−5718.847	946.312	−8.672
5800	431.920	1924.932	1521.617	2339.230	−5717.007	1063.227	−9.575
5900	431.934	1932.316	1528.515	2382.422	−5715.382	1180.116	−10.448
6000	431.948	1939.576	1535.306	2425.616	−5713.982	1296.974	−11.291

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

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However, thermodynamic functions calculated with the alternate set of vibrational constants are not significantly different from those adopted here. The uncertainty in the $\omega_e x_e$ values is large, probably near ± 1 cm^{-1}. The partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-C_2\epsilon_i/T)$ is used to calculate the thermodynamic functions with first-order anharmonic corrections included for Q_r and Q_v.

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is 158°. An energy minimum has been reported at 140° with a CNDO approximation.[19] Unfortunately, the vapor pressure data are not sufficiently precise to be of use in the selection of a structure. The entropies of these two forms differ by only about 1.5 cal $K^{-1}\cdot mol^{-1}$ at temperatures in the range of the vapor pressure data. We tentatively adopt a bond angle of 158° but assign an alternate uncertainty (± 3 cal $K^{-1}\cdot mol^{-1}$) to $S°(298.15\ K)$ to include the possibility that the angle is 180°. The Mg–F bond length is taken from the electron diffraction studies of Akishin *et al.*[11] The individual moments of inertia are: $I_A = 0.2808 \times 10^{-39}$, $I_B = 19.0477 \times 10^{-39}$, and $I_C = 9.3285\ 10^{-39}$ g·cm^2.

The symmetric stretching frequency is a compromise between the Krypton matrix infrared ($\nu_1 = 478$ cm^{-1})[17] and Raman ($\nu_1 = 545$ cm^{-1})[23] values. Also, an intermediate value ($\nu_2 = 215$ cm^{-1}) is selected for the bending frequency from the estimated gas–phase value (270 cm^{-1}) of Snelson[13] and that (165 cm^{-1}) which was observed in the high temperature (~2000 K) infrared spectrum[20] of the vapor. ν_3 is the gas phase value that was estimated by Snelson[13] from frequencies measured in three matrices. The Krypton frequencies for ν_2 and ν_3 reported by Mann *et al.*[17] and Lesiecki and Nibler[23] agree quite well with those of Snelson.[13] Also, the results of Hauge *et al.*[22] provide further support for the adopted ν_3 value. If MgF_2 is assumed to be linear and ν_2 is reduced to 165 cm^{-1}, then our free energy functions are decreased by 2.1 cal $K^{-1}\cdot mol^{-1}$ at 298.15 K, 1.6 cal $K^{-1}\cdot mol^{-1}$ at 1000 K and 1.0 cal $K^{-1}\cdot mol^{-1}$ at 2000 K. These alternate functions are also reasonably consistent with the reported vapor pressure data. Previously published free energy functions[21] for MgF_2(g) which were based on a linear structure are several units (2 5 cal $K^{-1}\cdot mol^{-1}$) too low due to the use of an incorrect bending frequency (470 cm^{-1}).

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$S°$(298.15 K) = 57.588 ± 0.42 J·K^{-1}·mol^{-1}
T_{fus} = 1650 K

$\Delta_f H°$(0 K) = −267.123 ± 0.84 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −266.270 ± 0.84 kJ·mol^{-1}
$\Delta_{fus} H°$ = 31.338 kJ·mol^{-1}

Enthalpy of Formation

The chemical equilibria in the Fe–C–O and Fe–H–O system have been studied by many investigators. Using the reported equilibrium constants for the following two reactions (A) $Fe_{0.947}O$(cr) + CO(g) = 0.947Fe(cr) + CO_2(g) and (B) $Fe_{0.947}O$(cr, l) + H_2(g) = 0.947Fe(cr) + H_2O(g), the corresponding enthalpy changes $\Delta_r H°$ were evaluated by both the 2nd and 3rd law methods. Based on the 3rd law values for $\Delta_r H°$, the $\Delta_f H°$(Wustite, cr, 298.15 K) values were also calculated. The results obtained are presented as follows.

Source	Reaction	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Eastman[1]	A	873.2–1273.2	−3.80 ± 0.01	−4.01	−63.63
Eastman–Evans[2]	A	973.2–1273.2	−4.02 ± 0.01	−4.03	−63.61
Eastman[1]	B	873.2–1273.2	6.50 ± 0.12	5.90	−63.70
Eastman–Evans[2]	B	973.2–1273.2	5.81 ± 0.01	5.07	−62.86
Emmett–Schultz[3]	B	873.2–1273.2	5.95 ± 0.07	5.82	−63.62
Britzke *et al.*[4]	B	1123.2–1498.2	−2.25 ± 0.03	4.26	−62.06
Jominy–Murphy[5]	B	1360.0–1646.0	5.01 ± 0.61	6.01	−63.81
Chipman–Marshall[6]	B	1438.2–1633.2	5.03 ± 0.34	5.85	−62.83
Chipman–Marshall[6]	B	1653.2–1787.2	−2.61 ± 0.77	−0.02	−61.87
Jominy–Murphy[5]	B	1698.0–1700.0	−0.87	−62.72	
Britzke *et al.*[4]	C	1123.0 1473.0	−129.08 ± 0.18	−126.28	−63.14

Britzke *et al.*[4] also determined the equilibrium pressures for the reaction (C) 1.894 Fe(cr) + O_2(g) = 2$Fe_{0.947}O$(cr). The corresponding $\Delta_f H°$(298.15 K) for Wustite was evaluated based on the 3rd law value for $\Delta_r H°$(298.15 K). The adopted value of $\Delta_f H°$(Wustite, cr, 298.15 K) is the weighted average of the $\Delta_f H°$(298.15 K) listed in the above table.

Heat Capacity and Entropy

The low temperature (54.37–298.16 K) heat capacities were measured by Todd and Bonnickson.[7] The high temperture (298–1650 K) heat capacities were determined by Coughlin *et al.*[8] The two sets of $C_p°$ data were plotted and joined smoothly at 298.15 K. The $C_p°$ values above 1650 K were obtained by graphical extrapolation. The low temperature (70.7–279.8 K) $C_p°$'s were also reported by Millar.[9] $S°$(298.15 K) was derived from the low-temperature heat capacities, based on $S°$(52 K) = 0.696 cal·K^{-1}·mol^{-1}. Todd and Bonnickson[7] added 0.41 cal·K^{-1}·mol^{-1}, the amount calculated for completely random distribution of the vacant Fe spaces in the Wustite lattice. However, the Gibbs energy functions derived from $S°$(52 K) = 0.696 cal·K^{-1}·mol^{-1} give better agreement between 2nd and 3rd law values for $\Delta_r H°$ than those derived from $S°$(52 K) = 1.11 cal·K^{-1}·mol^{-1}. Therefore, the value 0.41 cal·K^{-1}·mol^{-1} was not added here.

Fusion Data

T_{fus} and $\Delta_{fus} H°$ were taken from Coughlin *et al.*[8] T_{fus} was reported as 1372°C (1645 K) by Darken and Gurry[9] and as 1369°C (1642 K) by Chipman and Marshall.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.462	−267.123	−267.123	INFINITE
100	23.336	12.294	98.526	−8.623	−268.136	−260.126	135.876
187.670	58.206	35.752	63.498	−5.207	___ C_p LAMBDA MAXIMUM ___		
187.670	58.196	35.754	63.498	−5.207	TRANSITION		
200	45.966	38.989	61.893	−4.581	−267.224	−252.274	65.887
298.15	48.116	57.588	57.588	0.	−266.270	−245.143	42.948
300	48.183	57.886	57.589	0.089	−266.252	−245.012	42.660
400	50.380	72.065	59.507	5.023	−265.292	−238.078	31.090
500	51.848	83.470	63.196	10.137	−264.409	−231.379	24.172
600	53.028	93.030	67.393	15.382	−263.666	−224.845	19.575
700	54.070	101.283	71.658	20.737	−263.088	−218.423	16.299
800	55.041	108.567	75.825	26.193	−262.723	−212.071	13.847
900	55.969	115.104	79.833	31.744	−262.690	−205.745	11.941
1000	56.873	121.048	83.661	37.386	−263.275	−199.395	10.415
1100	57.760	126.510	87.312	43.118	−264.641	−192.927	9.161
1200	58.630	131.573	90.792	48.938	−265.416	−186.391	8.113
1300	59.496	136.300	94.112	54.844	−264.562	−179.840	7.226
1400	60.358	140.741	97.286	60.837	−263.716	−173.355	6.468
1500	61.212	144.934	100.324	66.915	−262.878	−166.930	5.813
1600	62.065	148.912	103.238	73.079	−262.046	−160.561	5.242
1700	62.787	152.699	106.037	79.325	−262.124	−154.225	4.739
1800	63.304	156.303	108.730	85.631	−261.650	−147.892	4.292
1900	63.696	159.736	111.325	91.982	−274.573	−140.919	3.874
2000	64.015	163.012	113.828	98.368	−274.427	−133.889	3.497
2100	64.238	166.141	116.245	104.781	−274.265	−126.866	3.156
2200	64.434	169.134	118.582	111.214	−274.094	−119.850	2.846
2300	64.601	172.002	120.842	117.666	−273.916	−112.844	2.563
2400	64.740	174.754	123.032	124.134	−273.733	−105.844	2.304
2500	64.852	177.399	125.154	130.614	−273.549	−98.853	2.065

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 60.799 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs2} = 598 \pm 3\ K$

$\Delta_f H°(0\ K) = -106.31 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -105.44 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 0.398 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K)$ is based on the calorimetric determination of Stolyarova and Bezmen[1] assuming that their reported value refers to 298.15 K. This value came from an average of eight determinations of $\Delta_r H°$ for $Fe_{0.877}S(cr) + Zn(cr) \rightarrow ZnS(cr) + 0.877\ Fe(cr)$.

In the composition range $y = 0.095$ to 0.145, Bugli *et al.*[2] determined $\Delta_r H°(433\ K) = -14.4(y\ 0.025)\ kcal \cdot mol^{-1}$ for $Fe S(cr) + yS(l) \rightarrow (1+y)Fe_{1/(1+y)}S(cr)$. Using $y = x/(1-x)$ we calculate that $\Delta_r H°(433\ K) = -14.76x + 0.36\ kcal \cdot mol^{-1}$ for $(1-x)FeS(cr) + xS(l) \rightarrow Fe_{1-x}S(cr)$ in this same composition range. Using $x = 0.123$ and auxiliary JANAF data[3] we can then calculate $\Delta_f H°(Fe_{0.877}S, cr) = -22.1\ kcal \cdot mol^{-1}$ based on Bugli's data. The difference between this value of $\Delta_f H°(298.15\ K)$ and that of Stolyarova and Bezmen is probably due to different morphology of the products; Bugli *et al.* state they are uncertain as to the exact nature of their product. Due to the complicated and kinetically slow phase behavior of $Fe_{0.877}S$, it appears they may not have obtained the pure monoclinic product.

Heat Capacity and Entropy

The adopted heat capacities from 6–350 K are based on our analysis of the $C_p°$ data of Gronvold *et al.*[4] Two small anomalies in the $C_p°$ curve, for which there is no obvious explanation, were observed near 8 and 30 K.[4] These lead to entropy increments of 0.003 and 0.03 cal $K^{-1} \cdot mol^{-1}$, respectively. Since there are no measured $C_p°$ or enthalpy data above 350 K, the $C_p°$ is estimated via the following procedure. Above Tβ, $C_p°$ is estimated as $C_p°(Fe_{0.877}S, cr) - C_p°(FeS, cr) = 0.123\ C_p°(Fe, cr)$ using auxiliary JANAF data.[3] Since the $T\alpha$ transition present in FeS(cr, troilite) is not present in pyrrhotite of composition $Fe_{0.877}S$[3] the heat capacity is assumed to be linear between 350 and 598 K where $C_p°(598\ K)$ is estimated via the procedure outlined above. Hirone *et al.*[5] observed non–linear behavior for $C_p°$ of $Fe_{0.90}S$ from 513 to 593 K.

The value of $S°(298.15\ K)$ is derived from the appropriate integration of $C_p°$ data assuming $S°(6\ K) = 0.0007\ cal \cdot K^{-1} \cdot mol^{-1}$.

Phase Data

The mineral pyrrhotite has a composition range extending from FeS to $Fe_{0.877}S$ ($\sim Fe_7S_8$); the name troilite is reserved for the stoichiometric FeS composition. The data presented in this table refer to the iron poor composition limit which is found to be $Fe_{0.877}S$ below T_{trs2}[6]. For stoichiometric FeS there are 3 crystalline polymorphs designated α, β, γ from low to high temperature, where the α β transition is designated T_{trs1} and the β–γ transition is designated T_{trs2}. We retain this nomenclature for $Fe_{0.877}S$ while recognizing that the α phase does not exist for this composition. Hirone *et al.*[5] found Tβ and ΔHβ° to be independent of composition so we adopt the same values as for FeS(cr, troilite).[3] The transition at 411 K (T_{trs1}) in FeS was found to be non–existent i compositions containing less iron than $Fe_{0.95}S$[2] so it will not be present in $Fe_{0.877}S$. The crystal structure of $Fe_{0.877}S$ is hexagonal above T_{trs2} while the stable form below T_{trs2} is monoclinic.[6,7] The conversion from hexagonal to monoclinic when cooling through T_{trs2} is kinetically slow and even annealing for several months may not be sufficient for complete conversion.[6,7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.241	−106.313	−106.313	INFINITE
100	25.899	18.565	99.374	−8.081	−106.214	−106.286	55.518
200	42.257	42.394	65.139	−4.549	−105.875	−106.478	27.809
298.15	49.883	60.799	60.799	0.	−105.437	−106.863	18.722
300	50.000	61.108	60.800	0.092	−105.427	−106.872	18.608
400	56.149	76.334	62.835	5.399	−107.022	−107.353	14.019
500	62.383	89.531	66.880	11.325	−107.526	−107.381	11.218
598.000	68.563	101.232	71.565	17.741	BETA <--> GAMMA		
598.000	58.175	101.897	71.565	18.139	TRANSITION		
600	58.116	102.091	71.666	18.255	−106.887	−107.365	9.347
700	55.564	110.847	76.659	23.932	−107.474	−107.403	8.015
800	53.848	118.146	81.401	29.396	−108.391	−107.335	7.008
900	52.886	124.432	85.841	34.732	−162.845	−106.047	6.155
1000	52.007	129.922	89.980	39.941	−163.655	−99.702	5.208
1100	55.396	135.035	93.845	45.309	−165.108	−93.221	4.427
1200	59.120	140.016	97.486	51.036	−165.731	−86.673	3.773
1300	62.676	144.882	100.945	57.118	−164.572	−80.130	3.220
1400	67.195	149.686	104.255	63.603	−163.098	−73.687	2.749
1500	72.676	154.503	107.444	70.589	−161.213	−67.364	2.346
1600	79.161	159.398	110.538	78.177	−158.813	−61.182	1.997
1700	86.107	164.398	113.558	86.428	−156.671	−55.152	1.695
1800	94.517	169.551	116.525	95.447	−153.309	−49.274	1.430

PREVIOUS: CURRENT: September 1977

REFERENCE STATE

0	to	1184	K crystal, alpha
1184	to	1665	K crystal, gamma
1665	to	1809	K crystal, delta
1809	to	3133.345	K liquid
above		3133.345	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.507	0.	0.	0.
100	12.101	6.065	46.905	−4.084	0.	0.	0.
200	21.588	17.949	29.524	−2.315	0.	0.	0.
298.15	25.094	27.321	27.321	0.	0.	0.	0.
300	25.140	27.476	27.321	0.046	0.	0.	0.
400	27.386	35.021	28.335	2.674	0.	0.	0.
500	29.702	41.377	30.323	5.527	0.	0.	0.
600	32.049	46.997	32.642	8.613	0.	0.	0.
700	34.602	52.119	35.063	11.939	0.	0.	0.
800	37.949	56.940	37.498	15.553	0.	0.	0.
900	43.095	61.679	39.922	19.582	0.	0.	0.
1000	54.434	66.672	42.342	24.329	0.	0.	0.
1042.000	83.680	69.245	43.372	26.960	____ C_p LAMBDA MAXIMUM ____		
1042.000	83.681	69.245	43.372	26.960	TRANSITION		
1100	46.401	72.062	44.815	29.972	0.	0.	0.
1184.000	41.422	75.260	46.865	33.619	____ ALPHA <--> GAMMA ____		
1184.000	33.882	76.020	46.865	34.519	TRANSITION		
1200	34.016	76.476	47.257	35.062	0.	0.	0.
1300	34.853	79.231	49.612	38.505	0.	0.	0.
1400	35.690	81.845	51.822	42.033	0.	0.	0.
1500	36.526	84.336	53.907	45.643	0.	0.	0.
1600	37.363	86.720	55.884	49.338	0.	0.	0.
1665.000	37.907	88.218	57.117	51.784	____ GAMMA <--> DELTA ____		
1665.000	41.112	88.721	57.117	52.621	TRANSITION		
1700	41.463	89.580	57.776	54.066	0.	0.	0.
1800	42.468	91.978	59.610	58.263	0.	0.	0.
1809.000	42.558	92.190	59.772	58.645	____ DELTA <--> LIQUID ____		
1809.000	46.024	99.823	59.772	72.452	TRANSITION		
1900	46.024	102.082	61.744	76.641	0.	0.	0.
2000	46.024	104.442	63.821	81.243	0.	0.	0.
2100	46.024	106.688	65.809	85.845	0.	0.	0.
2200	46.024	108.829	67.716	90.448	0.	0.	0.
2300	46.024	110.875	69.549	95.050	0.	0.	0.
2400	46.024	112.833	71.312	99.653	0.	0.	0.
2500	46.024	114.712	73.010	104.255	0.	0.	0.
2600	46.024	116.517	74.649	108.857	0.	0.	0.
2700	46.024	118.254	76.232	113.460	0.	0.	0.
2800	46.024	119.928	77.763	118.062	0.	0.	0.
2900	46.024	121.543	79.245	122.665	0.	0.	0.
3000	46.024	123.103	80.681	127.267	0.	0.	0.
3133.345	46.024	125.105	82.529	133.404	____ LIQUID <--> IDEAL GAS ____		
3133.345	26.642	236.674	82.530	482.989	FUGACITY = 1 bar		
3200	26.856	237.237	85.746	484.772	0.	0.	0.
3400	27.511	238.885	94.706	490.208	0.	0.	0.
3600	28.192	240.477	102.761	495.778	0.	0.	0.
3800	28.905	242.020	110.050	501.487	0.	0.	0.
4000	29.654	243.521	116.686	507.342	0.	0.	0.
4200	30.442	244.987	122.761	513.351	0.	0.	0.
4400	31.270	246.422	128.349	519.521	0.	0.	0.
4600	32.142	247.831	133.514	525.862	0.	0.	0.
4800	33.058	249.219	138.306	532.381	0.	0.	0.
5000	34.022	250.587	142.770	539.088	0.	0.	0.
5200	35.040	251.941	146.943	545.993	0.	0.	0.
5400	36.120	253.284	150.856	553.108	0.	0.	0.
5600	37.274	254.618	154.538	560.446	0.	0.	0.
5800	38.513	255.947	158.012	568.024	0.	0.	0.
6000	39.853	257.275	161.299	575.858	0.	0.	0.

PREVIOUS: March 1978 (1 atm) CURRENT: March 1978 (1 bar)

$S°(298.15\ K) = 27.32 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1} = 1042 \pm 1\ K$ (Curie temp)
$T_{trs2} = 1184 \pm 3\ K$ (α–γ)
$T_{trs3} = 1665 \pm 3\ K$ (γ–δ)
$T_{fus} = 1809 \pm 5\ K$ (δ –l)

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 0.900 \pm 0.042\ kJ \cdot mol^{-1}$
$\Delta_{trs3} H° = 0.837 \pm 0.084\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 13.807 \pm 0.837\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The current literature was surveyed by Hultgren.[1] Smoothed low temperature heat capacity values are obtained by fitting the data[2-7] graphically and with orthogonal polynomials over selected overlapping temperature intervals. Using $S°(20\ K) = 0.0364\ cal\ K^{-1} \cdot mol^{-1}$, we integrate over the adopted smoothed heat capacity values to obtain $S°(298.15\ K) = 6.529\ cal\ K^{-1} \cdot mol^{-1}$. An uncertainty of 0.015 $cal\ K^{-1} \cdot mol^{-1}$ arises due to the choice of heat capacity values in the region 20–55 K. In this region there is considerable disagreement between the reported heat capacity values of Eucken and Werth,[2] Simon and Swain,[3] and those of Duyckaerts[4] and Keesom and Kurrelmeyer.[5] An additional uncertainty of 0.01 $cal\ K^{-1} \cdot mol^{-1}$ results from the differences in the range 50–298 K in the heat capacity data of Kelley[6] and Stepakoff and Kaufman.[7]

The heat capacity and enthalpy studies above room temperature and numerous. A bibliography of all known studies (including low temperature studies) is available on request. The adopted heat capacity values above 400 K are those selected by Hultgren[8] and Orr and Chipman.[9] The method of orthogonal polynomials is used to join smoothly the low and high temperature heat capacity values. The smooth heat capacity values for metastable α–Fe in the range 1184–1665 K are adjusted from those of Hultgren[8] so as to yield the proper entropy values for γ–Fe. The available heat capacity/enthalpy data show differences up to 10% in $C_p°$ for δ–Fe with the major discrepancies being different slopes in $dC_p°/dT$.

Transition Data

The enthalpies of the α–γ transition at 1184 K and the γ–δ transition at 1665 K are those selected by Hultgren[8] and Orr and Chipman.[9] The α and δ phase has a bcc structure whereas the γ phase has a fcc structure.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The value adopted for the enthalpy of sublimation is that selected by Hultgren[8] and is based on a 2nd and 3rd law analysis of sublimation data over γ–Fe. Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.507	0.	0.	0.
100	12.101	6.065	46.905	−4.084	0.	0.	0.
200	21.588	17.949	29.524	−2.315	0.	0.	0.
250	23.742	23.018	27.727	−1.177	0.	0.	0.
298.15	25.094	27.321	27.321	0.	0.	0.	0.
300	25.140	27.476	27.321	0.046	0.	0.	0.
350	26.287	31.439	27.632	1.333	0.	0.	0.
400	27.386	35.021	28.335	2.674	0.	0.	0.
450	28.518	38.312	29.263	4.072	0.	0.	0.
500	29.702	41.377	30.323	5.527	0.	0.	0.
600	32.049	46.997	32.642	8.613	0.	0.	0.
700	34.602	52.119	35.063	11.939	0.	0.	0.
800	37.949	56.940	37.498	15.553	0.	0.	0.
900	43.095	61.679	39.922	19.582	0.	0.	0.
1000	54.434	66.672	42.342	24.329	0.	0.	0.
1042.000	83.680	69.245	43.372	26.960	C_p LAMBDA MAXIMUM		
1042.000	83.681	69.245	43.372	26.960	TRANSITION		
1100	46.401	72.062	44.815	29.972	0.	0.	0.
1184.000	41.422	75.260	46.865	33.619	--- ALPHA <--> GAMMA ---		
1200	40.794	75.830	47.249	34.298	−0.764	0.010	0.001
1300	38.493	78.985	49.571	38.238	−0.267	0.052	−0.002
1400	38.535	81.830	51.775	42.077	0.044	0.065	−0.002
1500	39.455	84.518	53.869	45.974	0.330	0.056	−0.002
1600	40.459	87.097	55.866	49.969	0.631	0.029	−0.001
1665.000	41.112	88.721	57.117	52.620	--- GAMMA <--> DELTA ---		
1700	41.463	89.580	57.776	54.065	−0.001	0.	0.
1800	42.468	91.978	59.610	58.262	−0.001	0.	0.
1809.000	42.558	92.190	59.772	58.645	--- DELTA <--> LIQUID ---		
1900	43.472	94.301	61.375	62.559	−14.082	0.702	−0.019
2000	44.476	96.556	63.078	66.956	−14.287	1.486	−0.039
2100	45.480	98.751	64.725	71.454	−14.391	2.277	−0.057
2200	46.484	100.889	66.320	76.052	−14.395	3.071	−0.073

PREVIOUS: March 1965 CURRENT: March 1978

$S°(298.15\ K) = 35.545\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 1184 \pm 3\ K\ (\alpha–\gamma)$
$T_{trs2} = 1665 \pm 3\ K\ (\gamma–\delta)$

$\Delta_f H°(298.15\ K) = 7.788\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 0.900 \pm 0.042\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 0.837 \pm 0.084\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation at 298.15 K is obtained from that of Fe(α) by adding $\Delta_{trs1}H°$ and the difference between $H°(1184)–H°(298.15\ K)$ of Fe(α] and Fe(γ).

Heat Capacity and Entropy

A current literature survey by Hultgren[1] yielded approximately twenty heat capacity/enthalpy studies which gave information as to the heat capacity of γ–Fe in the stable and metastable region. A listing of these studies is available on request. We adopt the heat capacity values chosen by Hultgren[2] and Orr and Chipman.[3] These values are based primarily on the studies by Dench and Kubaschewski,[4] Braun and Kohlhaas,[5] and Wallace *et al.*[6] However, all the available heat capacity/enthalpy data show discrepancies up to 5% (in $C_p°$); with the major discrepancies appearing as different slopes in $C_p°$ vs T plots. Values are not extended below 298.15 K due to the lack of substantial data in this metastable region. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

Refer to the Fe(α, δ) table.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	26.469	35.545	35.545	0.	7.788	5.336	−0.935
300	26.485	35.709	35.546	0.049	7.790	5.321	−0.926
350	26.903	39.823	35.870	1.384	7.839	4.905	−0.732
400	27.322	43.443	36.594	2.739	7.853	4.484	−0.586
450	27.740	46.685	37.539	4.116	7.832	4.064	−0.472
500	28.158	49.629	38.603	5.513	7.774	3.648	−0.381
600	28.995	54.837	40.885	8.371	7.546	2.842	−0.247
700	29.832	59.369	43.209	11.312	7.161	2.086	−0.156
800	30.669	63.408	45.486	14.337	6.572	1.398	−0.091
900	31.506	67.068	47.684	17.446	5.652	0.802	−0.047
1000	32.342	70.431	49.792	20.638	4.097	0.338	−0.018
1100	33.179	73.553	51.812	23.915	1.730	0.091	−0.004
1184.000	33.882	76.020	53.443	26.731	--- ALPHA <--> GAMMA ---		
1200	34.016	76.476	53.747	27.274	0.	0.	0.
1300	34.853	79.231	55.602	30.718	0.	0.	0.
1400	35.690	81.845	57.384	34.245	0.	0.	0.
1500	36.526	84.336	59.099	37.856	0.	0.	0.
1600	37.363	86.720	60.751	41.550	0.	0.	0.
1665.000	37.907	88.218	61.794	43.996	--- GAMMA <--> DELTA ---		
1700	38.200	89.010	62.346	45.328	−0.950	0.019	−0.001
1800	39.037	91.217	63.889	49.190	−1.285	0.085	−0.002
1900	39.874	93.350	65.384	53.136	−15.717	0.873	−0.024
2000	40.710	95.417	66.834	57.165	−16.290	1.761	−0.046
2100	41.547	97.423	68.243	61.278	−16.780	2.676	−0.067
2200	42.384	99.375	69.614	65.474	−17.186	3.612	−0.086

PREVIOUS: CURRENT: March 1978

$S°(298.15\ K) = [34.763]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1809 \pm 5\ K$ (δ–l)

$\Delta_f H°(298.15\ K) = [12.395]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 13.807 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation at 298.15 K is calculated from that of the combined phase crystal (α–γ–δ) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1809\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is taken to be 11.0 cal $K^{-1}·mol^{-1}$ as in Hultgren[1] and Orr and Chipman.[2] We adopt this value in the real liquid region as well as in the extrapolated region to 1200 K and to 3500 K. Below 1200 K, heat capacity values are chosen so as to form a curve which joins smoothly the α–Fe heat capacity values in the range 298–500 K. The entropy is calculated in a manner analogous to that used for the enthalpy of formation. A current literature survey[3] revealed numerous heat capacity and enthalpy studies in the liquid region which yielded heat capacity values in the range 8.0 to 12.4 cal $K^{-1}·mol^{-1}$ as given in the table below. The more recent studies by Braun *et al.*,[10] using a quasi–adiabatic calorimeter suggest $C_p° = 10.938$ cal $K^{-1}·mol^{-1}$ whereas the levitation calorimetric enthalpy measurements of Margrave *et al.*[12,14] suggest 10.29 ± 0.29 and 11.138 ± 0.43 cal $K^{-1}·mol^{-1}$ respectively.

Fusion Data

The adopted T_{fus} and $\Delta_{fus}H°$ values are those selected by Hultgren[1] and Orr and Chipman;[2] 1809 ± 5 K and 3300 ± 100 cal·mol^{-1}, respectively. Reported values for $\Delta_{fus}H°$ vary from a low of 2760 to a high of 3865 cal·mol^{-1}, as given in the table below.

Vaporization Data

The boiling point is calculated from the adopted thermodynamic functions and the chosen enthalpy of sublimation so that the Gibbs energy functions calculated by integration of the crystal–liquid data and by statistical methods for the gas phase are equal at T_{vap}.

Reference	Year	Calorimetric Method	T_{fus}, K	$\Delta_{fus}H°$ kcal·mol^{-1}	$C_p°(l)$ cal $K^{-1}·mol^{-1}$	T/K
4	1918	drop	1801	2760	11.96	373 – 1873
5	1926, 1929	mixture	1800	3865	12.398	373 – 1906
6	1927	drop	1801	3595	11.2	370 – 1860
7	1956	mixture	1806	3658	8.0	1273 – 1923
8	1962	drop	1809 ± 1	3292 ± 80	11.226	1665 – 2210
9	1966	drop	1808	3298 ± 100	9.766	1720 – 1875
10	1965 – 1968	quasi adiab.	1809	3442 ± 50	10.038	300 – 1900
11	1971	exploding wire	3256			
12	1971	levitation	3307 ± 70	10.29 ± 0.29	1804 – 2142	
13	1974	pulse	1808 ± 5			
14	1975	levitation	1811	3370 ± 90	11.138 ± 0.43	

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K^{-1}·mol^{-1}		kJ·mol^{-1}			
0							
100							
200							
250							
298.15	25.096	34.763	34.763	0.	12.395	10.177	−1.783
300	25.142	34.918	34.764	0.046	12.395	10.163	−1.769
350	26.254	38.877	35.074	1.331	12.394	9.791	−1.461
400	27.384	42.457	35.776	2.672	12.393	9.419	−1.230
450	28.542	45.749	36.704	4.070	12.394	9.047	−1.050
500	29.702	48.816	37.763	5.526	12.395	8.675	−0.906
600	32.033	54.437	40.082	8.613	12.396	7.931	−0.690
700	34.363	59.550	42.503	11.933	12.389	7.187	−0.536
800	36.694	64.291	44.934	15.486	12.328	6.447	−0.421
900	39.024	68.747	47.334	19.272	12.085	5.724	−0.332
1000	41.355	72.980	49.689	23.291	11.356	5.049	−0.264
1100	43.689	77.031	51.992	27.543	9.966	4.501	−0.214
1200	46.024	80.932	54.242	32.028	9.362	4.014	−0.175
1200.000	46.024	80.932	54.242	32.028	____ GLASS <--> LIQUID ____		
1200.000	46.024	80.932	54.242	32.028	TRANSITION		
1300	46.024	84.616	56.438	36.631	10.521	3.521	−0.141
1400	46.024	88.027	58.574	41.233	11.596	2.941	−0.110
1500	46.024	91.202	60.645	45.836	12.588	2.288	−0.080
1600	46.024	94.172	62.649	50.438	13.495	1.571	−0.051
1700	46.024	96.963	64.586	55.040	13.370	0.819	−0.025
1800	46.024	99.593	66.458	59.643	13.776	0.069	−0.002
1809.000	46.024	99.823	66.624	60.057	---- DELTA <--> LIQUID ----		
1900	46.024	102.082	68.268	64.245	0.	0.	0.
2000	46.024	104.442	70.019	68.848	0.	0.	0.
2100	46.024	106.688	71.712	73.450	0.	0.	0.
2200	46.024	108.829	73.351	78.052	0.	0.	0.
2300	46.024	110.875	74.938	82.655	0.	0.	0.
2400	46.024	112.834	76.476	87.257	0.	0.	0.
2500	46.024	114.712	77.968	91.860	0.	0.	0.
2600	46.024	116.517	79.417	96.462	0.	0.	0.
2700	46.024	118.254	80.823	101.064	0.	0.	0.
2800	46.024	119.928	82.190	105.667	0.	0.	0.
2900	46.024	121.543	83.519	110.269	0.	0.	0.
3000	46.024	123.103	84.813	114.872	0.	0.	0.
3100	46.024	124.613	86.073	119.474	0.	0.	0.
3133.345	46.024	125.105	86.485	121.009	----- FUGACITY = 1 bar -----		
3200	46.024	126.074	87.300	124.076	−348.300	7.424	−0.121
3300	46.024	127.490	88.496	128.679	−346.399	18.511	−0.293
3400	46.024	128.864	89.664	133.281	−344.531	29.541	−0.454
3500	46.024	130.198	90.803	137.884	−342.697	40.516	−0.605
3600	46.024	131.495	91.915	142.486	−340.896	51.439	−0.746
3700	46.024	132.756	93.002	147.088	−339.131	62.313	−0.880
3800	46.024	133.983	94.064	151.691	−337.401	73.140	−1.005
3900	46.024	135.179	95.103	156.293	−335.707	83.921	−1.124
4000	46.024	136.344	96.120	160.896	−334.051	94.660	−1.236

PREVIOUS: March 1965 CURRENT: March 1978

0	to	1184	K alpha
1184	to	1665	K gamma
1665	to	1809	K delta
above		1809	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.507	0.	0.	0.
100	12.101	6.065	46.905	−4.084	0.	0.	0.
200	21.588	17.949	29.524	−2.315	0.	0.	0.
298.15	25.094	27.321	27.321	0.	0.	0.	0.
300	25.140	27.476	27.321	0.046	0.	0.	0.
400	27.386	35.021	28.335	2.674	0.	0.	0.
500	29.702	41.377	30.323	5.527	0.	0.	0.
600	32.049	46.997	32.642	8.613	0.	0.	0.
700	34.602	52.119	35.063	11.939	0.	0.	0.
800	37.949	56.940	37.498	15.553	0.	0.	0.
900	43.095	61.679	39.922	19.582	0.	0.	0.
1000	54.434	66.672	42.342	24.329	0.	0.	0.
1042.000	83.680	69.245	43.372	26.960	____ C_p LAMBDA MAXIMUM ____		
1042.000	83.681	69.245	43.372	26.960	TRANSITION		
1100	46.401	72.062	44.815	29.972	0.	0.	0.
1184.000	41.422	75.260	46.865	33.619	____ ALPHA <--> GAMMA ____		
1184.000	33.882	76.020	46.865	34.519	TRANSITION		
1200	34.016	76.476	47.257	35.062	0.	0.	0.
1300	34.853	79.231	49.612	38.505	0.	0.	0.
1400	35.690	81.845	51.822	42.033	0.	0.	0.
1500	36.526	84.336	53.907	45.643	0.	0.	0.
1600	37.363	86.720	55.884	49.338	0.	0.	0.
1665.000	37.907	88.218	57.117	51.784	____ GAMMA <--> DELTA ____		
1665.000	41.112	88.721	57.117	52.621	TRANSITION		
1700	41.463	89.580	57.776	54.066	0.	0.	0.
1800	42.468	91.978	59.610	58.263	0.	0.	0.
1809.000	42.558	92.190	59.772	58.645	____ DELTA <--> LIQUID ____		
1809.000	46.024	99.823	59.772	72.452	TRANSITION		
1900	46.024	102.082	61.744	76.641	0.	0.	0.
2000	46.024	104.442	63.821	81.243	0.	0.	0.
2100	46.024	106.688	65.809	85.845	0.	0.	0.
2200	46.024	108.829	67.716	90.448	0.	0.	0.
2300	46.024	110.875	69.549	95.050	0.	0.	0.
2400	46.024	112.833	71.312	99.653	0.	0.	0.
2500	46.024	114.712	73.010	104.255	0.	0.	0.
2600	46.024	116.517	74.649	108.857	0.	0.	0.
2700	46.024	118.254	76.232	113.460	0.	0.	0.
2800	46.024	119.928	77.763	118.062	0.	0.	0.
2900	46.024	121.543	79.245	122.665	0.	0.	0.
3000	46.024	123.103	80.681	127.267	0.	0.	0.
3100	46.024	124.613	82.074	131.869	0.	0.	0.
3133.345	46.024	125.105	82.529	133.404	----- FUGACITY = 1 bar -----		
3200	46.024	126.074	83.426	136.472	−348.300	7.424	−0.121
3300	46.024	127.490	84.740	141.074	−346.399	18.511	−0.293
3400	46.024	128.864	86.018	145.677	−344.531	29.541	−0.454
3500	46.024	130.198	87.261	150.279	−342.697	40.516	−0.605
3600	46.024	131.495	88.472	154.881	−340.896	51.439	−0.746
3700	46.024	132.756	89.652	159.484	−339.131	62.313	−0.880
3800	46.024	133.983	90.802	164.086	−337.401	73.140	−1.005
3900	46.024	135.179	91.925	168.689	−335.707	83.921	−1.124
4000	46.024	136.344	93.021	173.291	−334.051	94.660	−1.236

PREVIOUS: CURRENT: March 1978

IP(Fe, g) = 63480 ± 500 cm^{-1}
$S°(298.15\ K) = 180.49 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 413.1 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 415.5 \pm 1.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5D_4$	0.000	9
$^5D_3$	415.932	7
$^5D_2$	704.004	5
$^5D_1$	888.129	3
$^5D_0$	978.072	1
.	.	.
.	.	.
.	.	.
$^3G_2^\circ$	62081.27	5
IP	63480	

Enthalpy of Formation

The sublimation and vaporization studies on iron are too numerous to tabulate. A current literature survey by Hultgren yielded approximately thirty investigations.[1] As in Hultgren,[2] we adopt $\Delta_f H°$(Fe, g, 298.15 K) = 99.3 ± 0.3 kcal·mol^{-1} based on the studies of Morris *et al.*[3] and Myles and Aldred.[4] A complete listing of all vapor pressure studies is available on request. Many of the more recent studies do not provide sufficient information to enable calculation of enthalpy of formation values via the 2nd and 3rd law approach.

Our 2nd and 3rd law analyses of the vaporization data of Morris *et al.*[3] and the sublimation data of Myles and Aldred[4] are given below.

Source	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Fe(l) = Fe(g)	21	1812–1891	96.8 ± 1.1	96.5 ± 0.1	0.1 ± 6	99.5
Fe(γ) = Fe(g)	eqn	1450–1650	98.1	97.1	−0.6	99.0

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Reader and Sugar.[5] Although we have only listed the ground state, the lowest four excited states, the highest observed excited state, and the ionization limit for Fe(g), all levels listed by Reader and Sugar,[5] as well as estimated missing levels, are used in the calculations. The observed levels are too numerous to list completely. Our calculations indicate that for Fe(g) the thermochemical functions are independent of the estimated missing levels (for $n = 4, 5, 6, 7$) and the cutoff procedure up to 3500 K. The Gibbs energy function is essentially unaffected up to 5200 K. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cutoff procedures.[6] In fact, the inclusion of some higher states ($n = 4, 5, 6, 7$) and consideration of various cut–off procedures leads to calculational differences in the Gibbs energy function of roughly 0.1 cal·K^{-1}·mol^{-1} or greater at temperatures in excess of 8000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−6.850	413.127	413.127	INFINITE
100	21.387	154.700	202.317	−4.762	414.794	399.930	−208.902
200	24.362	170.450	182.809	−2.472	415.314	384.814	−100.503
250	25.279	175.995	180.909	−1.228	415.420	377.176	−78.807
298.15	25.675	180.488	180.488	0.	415.471	369.804	−64.788
300	25.682	180.647	180.488	0.048	415.472	369.521	−64.339
350	25.718	184.612	180.801	1.334	415.472	361.862	−54.005
400	25.533	188.036	181.497	2.616	415.412	354.207	−46.255
450	25.233	191.027	182.393	3.885	415.284	346.563	−40.228
500	24.889	193.668	183.391	5.138	415.082	338.937	−35.409
600	24.202	198.144	185.490	7.592	414.451	323.762	−28.186
700	23.610	201.829	187.569	9.982	413.514	308.717	−23.037
800	23.133	204.949	189.551	12.318	412.236	293.829	−19.185
900	22.763	207.651	191.416	14.612	410.501	279.127	−16.200
1000	22.488	210.035	193.161	16.874	408.016	264.653	−13.824
1100	22.297	212.168	194.793	19.113	404.612	250.495	−11.895
1200	22.183	214.103	196.323	21.336	401.745	236.592	−10.299
1300	22.137	215.876	197.760	23.551	400.517	222.879	−8.955
1400	22.156	217.517	199.113	25.766	399.204	209.263	−7.808
1500	22.231	219.048	200.392	27.984	397.812	195.744	−6.816
1600	22.356	220.487	201.603	30.213	396.347	182.320	−5.952
1700	22.523	221.847	202.754	32.457	393.862	169.009	−5.193
1800	22.726	223.140	203.851	34.719	391.928	155.837	−4.522
1900	22.958	224.374	204.899	37.003	375.834	143.477	−3.944
2000	23.213	225.558	205.903	39.312	373.540	131.308	−3.429
2100	23.485	226.698	206.866	41.646	371.272	119.252	−2.966
2200	23.771	227.797	207.793	44.009	369.033	107.303	−2.548
2300	24.065	228.860	208.685	46.401	366.822	95.456	−2.168
2400	24.365	229.890	209.548	48.822	364.641	83.705	−1.822
2500	24.669	230.891	210.381	51.274	362.490	72.043	−1.505
2600	24.976	231.865	211.189	53.756	360.370	60.467	−1.215
2700	25.284	232.813	211.973	56.269	358.280	48.972	−0.947
2800	25.594	233.738	212.733	58.813	356.222	37.554	−0.701
2900	25.905	234.642	213.473	61.388	354.195	26.209	−0.472
3000	26.219	235.525	214.194	63.994	352.198	14.933	−0.260
3100	26.536	236.390	214.896	66.632	350.234	3.724	−0.063
3133.345	26.642	236.674	215.126	67.518	----- FUGACITY = 1 bar -----		
3200	26.856	237.237	215.581	69.301	0.	0.	0.
3300	27.181	238.069	216.250	72.003	0.	0.	0.
3400	27.511	238.885	216.903	74.738	0.	0.	0.
3500	27.848	239.687	217.543	77.506	0.	0.	0.
3600	28.192	240.477	218.169	80.308	0.	0.	0.
3700	28.544	241.254	218.783	83.144	0.	0.	0.
3800	28.905	242.020	219.384	86.017	0.	0.	0.
3900	29.274	242.776	219.974	88.925	0.	0.	0.
4000	29.654	243.521	220.554	91.872	0.	0.	0.
4100	30.043	244.258	221.123	94.856	0.	0.	0.
4200	30.442	244.987	221.682	97.881	0.	0.	0.
4300	30.851	245.708	222.233	100.945	0.	0.	0.
4400	31.270	246.422	222.774	104.051	0.	0.	0.
4500	31.701	247.130	223.308	107.200	0.	0.	0.
4600	32.142	247.831	223.833	110.392	0.	0.	0.
4700	32.594	248.527	224.351	113.628	0.	0.	0.
4800	33.058	249.219	224.862	116.911	0.	0.	0.
4900	33.533	249.905	225.366	120.240	0.	0.	0.
5000	34.022	250.587	225.864	123.618	0.	0.	0.
5100	34.524	251.266	226.355	127.045	0.	0.	0.
5200	35.040	251.941	226.841	130.523	0.	0.	0.
5300	35.572	252.614	227.321	134.054	0.	0.	0.
5400	36.120	253.284	227.795	137.638	0.	0.	0.
5500	36.687	253.952	228.265	141.278	0.	0.	0.
5600	37.274	254.618	228.729	144.976	0.	0.	0.
5700	37.882	255.283	229.189	148.734	0.	0.	0.
5800	38.513	255.947	229.645	152.553	0.	0.	0.
5900	39.170	256.611	230.097	156.437	0.	0.	0.
6000	39.853	257.275	230.544	160.388	0.	0.	0.

PREVIOUS: March 1978 (1 atm) CURRENT: March 1978 (1 bar)

IP(Fe^+, g) = 130563 ± 10 cm^{-1}
$S°$(298.15 K) = 181.86 ± 0.05 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1172.52 ± 7.5 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1181.144] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6D_{9/2}$	0.000	10
$^6D_{7/2}$	384.790	8
$^6D_{5/2}$	667.683	6
$^6D_{3/2}$	862.613	4
$^6D_{1/2}$	977.053	2
.	.	.
.	.	.
.	.	.

Enthalpy of Formation

$\Delta_f H°(Fe^+, g, 0 K)$ is calculated from $\Delta_f H°$(Fe, g, 0 K)[1] using the spectroscopic value of IP(Fe) = 63480 ± 500 cm^{-1} (759.390 ± 5.98 $kJ·mol^{-1}$) from Corliss and Sugar.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Fe^+, g, 298.15 K)$ is calculated from $\Delta_f H°$(Fe, g, 0 K) by using IP(Fe) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Fe(g), Fe^+(g), and e^-(ref). $\Delta_f H°(Fe \rightarrow Fe^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only five levels for Fe^+(g), all levels listed by Corliss and Sugar,[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Fe^+(g), the thermodynamic functions are independent of the estimated missing levels (for n=4), the cut–off procedure, and the inclusion of n=5 levels up to 6000 K; the Gibbs energy function showing no significant variations at this temperature. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>5), and use of different fill and cut–off procedures.[6]

References

[1]JANAF Thermochemical Tables: Fe(g), 3–31–78; e^-(ref), 3–31–82.
[2]C. Corliss and J. Sugar, J. Phys. Chem. Ref. Data **11**, 135 (1982).
[3]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
[4]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
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[6]J. R. Downey, Jr., The Dow Chemical Company, AFOSR–TR–78–0960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.936	1172.517		
100	21.618	155.635	204.058	−4.842			
200	24.813	171.652	184.215	−2.512			
250	25.689	177.294	182.284	−1.248			
298.15	26.068	181.857	181.857	0.	1181.144	1128.814	−197.764
300	26.075	182.018	181.857	0.048	1181.184	1128.489	−196.487
350	26.163	186.047	182.175	1.355	1182.244	1119.622	−167.094
400	26.112	189.538	182.882	2.662	1183.249	1110.607	−145.030
450	26.018	192.608	183.796	3.966	1184.194	1101.470	−127.855
500	25.931	195.345	184.816	5.264	1185.076	1092.230	−114.104
600	25.830	200.062	186.976	7.851	1186.656	1073.508	−93.457
700	25.802	204.041	189.137	10.433	1187.990	1054.541	−78.691
800	25.786	207.485	191.220	13.012	1189.034	1035.402	−67.605
900	25.744	210.521	193.199	15.589	1189.661	1016.155	−58.976
1000	25.661	213.229	195.069	18.160	1189.562	996.872	−52.071
1100	25.539	215.669	196.833	20.720	1188.559	977.666	−46.425
1200	25.390	217.885	198.497	23.266	1188.094	958.495	−41.722
1300	25.225	219.911	200.067	25.797	1189.260	939.314	−37.742
1400	25.054	221.774	201.552	28.311	1190.325	920.047	−34.327
1500	24.885	223.497	202.958	30.808	1191.290	900.707	−31.365
1600	24.726	225.098	204.293	33.289	1192.155	881.306	−28.772
1700	24.579	226.592	205.561	35.754	1191.970	861.872	−26.482
1800	24.447	227.993	206.769	38.205	1192.303	842.445	−24.447
1900	24.330	229.312	207.921	40.644	1178.443	823.703	−22.645
2000	24.229	230.557	209.022	43.071	1178.347	805.035	−21.025
2100	24.144	231.737	210.076	45.490	1178.242	786.372	−19.560
2200	24.074	232.859	211.086	47.901	1178.129	767.714	−18.228
2300	24.018	233.928	212.056	50.305	1178.009	749.062	−17.012
2400	23.975	234.949	212.989	52.705	1177.885	730.415	−15.897
2500	23.945	235.927	213.887	55.101	1177.757	711.773	−14.872
2600	23.927	236.866	214.753	57.494	1177.627	693.136	−13.925
2700	23.920	237.769	215.588	59.886	1177.495	674.504	−13.049
2800	23.925	238.639	216.396	62.278	1177.363	655.877	−12.236
2900	23.940	239.478	217.178	64.672	1177.233	637.255	−11.478
3000	23.966	240.290	217.935	67.067	1177.104	618.637	−10.771
3100	24.002	241.077	218.669	69.465	1176.979	600.024	−10.110
3200	24.049	241.840	219.381	71.868	828.558	588.838	−9.612
3300	24.104	242.580	220.073	74.275	830.342	581.319	−9.202
3400	24.170	243.301	220.745	76.689	832.100	573.747	−8.815
3500	24.245	244.003	221.400	79.110	833.831	566.123	−8.449
3600	24.329	244.687	222.037	81.538	835.536	558.450	−8.103
3700	24.423	245.355	222.658	83.976	837.216	550.730	−7.775
3800	24.525	246.007	223.264	86.423	838.869	542.965	−7.464
3900	24.636	246.646	223.856	88.881	840.497	535.156	−7.168
4000	24.756	247.271	224.433	91.351	842.099	527.307	−6.886
4100	24.883	247.884	224.998	93.833	843.675	519.417	−6.617
4200	25.018	248.485	225.550	96.328	845.224	511.490	−6.361
4300	25.161	249.075	226.090	98.836	846.747	503.526	−6.117
4400	25.310	249.656	226.619	101.360	848.243	495.526	−5.883
4500	25.467	250.226	227.137	103.899	849.712	487.493	−5.659
4600	25.629	250.788	227.646	106.453	851.154	479.428	−5.444
4700	25.797	251.341	228.144	109.025	852.567	471.332	−5.238
4800	25.970	251.885	228.633	111.613	853.951	463.206	−5.041
4900	26.149	252.423	229.113	114.219	855.306	455.051	−4.851
5000	26.331	252.953	229.584	116.843	856.631	446.869	−4.668
5100	26.518	253.476	230.048	119.485	857.925	438.661	−4.493
5200	26.708	253.993	230.503	122.147	859.187	430.428	−4.324
5300	26.901	254.503	230.951	124.827	860.415	422.171	−4.161
5400	27.096	255.008	231.392	127.527	861.609	413.891	−4.004
5500	27.293	255.507	231.826	130.246	862.767	405.589	−3.852
5600	27.493	256.001	232.253	132.985	863.887	397.266	−3.706
5700	27.693	256.489	232.674	135.745	864.967	388.924	−3.564
5800	27.894	256.972	233.089	138.524	866.006	380.564	−3.427
5900	28.095	257.451	233.498	141.324	867.000	372.185	−3.295
6000	28.297	257.925	233.901	144.143	867.947	363.791	−3.167

PREVIOUS: March 1978 (1 atm) CURRENT: June 1984 (1 bar)

EA(Fe, g) = 0.163 ± 0.035 eV
$S°(298.15\ K) = 180.198 \pm 0.005\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 397.400 \pm 4.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [393.338]\ kJ·mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{9/2}$	0	10
$^4F_{7/2}$	540	8
$^4F_{5/2}$	930	6
$^4F_{3/2}$	1200	4

Enthalpy of Formation

$\Delta_f H°(Fe^-, g, 0\ K)$ is calculated from $\Delta_f H°(Fe, g, 0\ K)$[1] using the adopted electron affinity of EA(Fe) = 0.163 ± 0.035 eV (15.727 ± 3.377 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Fe^-(ref) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Fe^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Fe, g, 0\ K)$ by using EA(Fe) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, or Fe^-(ref), Fe(g), and e^-(ref). $\Delta_f H°(Fe^- \rightarrow Fe + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Fe^-(ref) is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] The fine structure separations in the ground state have been calculated by an isoelectronic extropolation of ratios of fine structure separations.[7]

References

[1]JANAF Thermochemical Tables: Fe(g), 3–31–78; e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.642	397.400		
100	20.957	155.485	201.095	−4.561			
200	23.092	170.579	182.433	−2.371			
250	24.226	175.858	180.606	−1.187			
298.15	25.023	180.198	180.198	0.	393.338	354.013	−62.022
300	25.047	180.353	180.198	0.046	393.300	353.769	−61.597
350	25.536	184.254	180.505	1.312	392.240	347.264	−51.826
400	25.748	187.681	181.193	2.595	391.142	340.913	−44.519
450	25.758	190.716	182.085	3.884	389.994	334.703	−38.851
500	25.632	193.424	183.086	5.169	388.784	328.624	−34.331
600	25.172	198.059	185.208	7.710	386.162	316.833	−27.583
700	24.627	201.899	187.327	10.201	383.247	305.505	−22.797
800	24.108	205.153	189.357	12.637	379.990	294.616	−19.236
900	23.652	207.965	191.272	15.024	376.271	284.162	−16.492
1000	23.264	210.437	193.067	17.370	371.790	274.158	−14.321
1100	22.938	212.638	194.748	19.679	366.378	264.671	−12.568
1200	22.666	214.622	196.323	21.959	361.489	255.621	−11.127
1300	22.438	216.427	197.801	24.214	358.222	246.930	−9.922
1400	22.246	218.083	199.191	26.448	354.851	238.495	−8.898
1500	22.084	219.612	200.502	28.664	351.377	230.305	−8.020
1600	21.946	221.033	201.742	30.865	347.806	222.349	−7.259
1700	21.829	222.360	202.916	33.054	343.188	214.639	−6.595
1800	21.727	223.604	204.031	35.232	339.090	207.195	−6.013
1900	21.640	224.777	205.092	37.400	320.802	200.683	−5.517
2000	21.563	225.885	206.105	39.560	316.281	194.478	−5.079
2100	21.496	226.935	207.072	41.713	311.753	188.499	−4.689
2200	21.438	227.934	207.997	43.860	307.218	182.736	−4.339
2300	21.386	228.885	208.885	46.001	302.678	177.179	−4.024
2400	21.340	229.795	209.738	48.137	298.134	171.820	−3.740
2500	21.299	230.665	210.557	50.269	293.585	166.651	−3.482
2600	21.262	231.500	211.347	52.397	289.032	161.663	−3.248
2700	21.229	232.301	212.108	54.521	284.475	156.851	−3.034
2800	21.199	233.073	212.843	56.643	279.916	152.208	−2.839
2900	21.173	233.816	213.554	58.761	275.353	147.727	−2.661
3000	21.148	234.534	214.241	60.877	270.788	143.404	−2.497
3100	21.126	235.227	214.907	62.991	266.221	139.233	−2.346
3200	21.106	235.897	215.553	65.103	−86.649	142.634	−2.328
3300	21.088	236.546	216.179	67.212	−89.319	149.840	−2.372
3400	21.071	237.176	216.787	69.320	−92.024	157.128	−2.414
3500	21.055	237.786	217.379	71.427	−94.765	164.495	−2.455
3600	21.041	238.379	217.954	73.531	−97.540	171.942	−2.495
3700	21.028	238.955	218.514	75.635	−100.352	179.466	−2.534
3800	21.015	239.516	219.059	77.737	−103.201	187.067	−2.571
3900	21.004	240.062	219.590	79.838	−106.088	194.743	−2.608
4000	20.993	240.593	220.109	81.938	−109.013	202.494	−2.644
4100	20.984	241.112	220.615	84.037	−111.977	210.318	−2.679
4200	20.975	241.617	221.109	86.134	−114.982	218.215	−2.714
4300	20.966	242.111	221.592	88.232	−118.028	226.184	−2.748
4400	20.958	242.593	222.063	90.328	−121.116	234.225	−2.781
4500	20.951	243.063	222.525	92.423	−124.248	242.336	−2.813
4600	20.944	243.524	222.976	94.518	−127.424	250.517	−2.845
4700	20.937	243.974	223.418	96.612	−130.645	258.768	−2.876
4800	20.931	244.415	223.851	98.705	−133.913	267.088	−2.907
4900	20.925	244.846	224.275	100.798	−137.228	275.476	−2.937
5000	20.920	245.269	224.691	102.890	−140.592	283.933	−2.966
5100	20.915	245.683	225.099	104.982	−144.006	292.457	−2.995
5200	20.910	246.089	225.498	107.073	−147.472	301.049	−3.024
5300	20.905	246.488	225.891	109.164	−150.990	309.708	−3.052
5400	20.901	246.878	226.276	111.255	−154.563	318.434	−3.080
5500	20.897	247.262	226.654	113.344	−158.191	327.226	−3.108
5600	20.893	247.638	227.025	115.434	−161.878	336.085	−3.135
5700	20.890	248.008	227.390	117.523	−165.626	345.011	−3.162
5800	20.886	248.371	227.749	119.612	−169.435	354.003	−3.188
5900	20.883	248.728	228.101	121.700	−173.309	363.060	−3.214
6000	20.880	249.079	228.448	123.788	−177.250	372.184	−3.240

PREVIOUS: March 1978 (1 atm) CURRENT: June 1984 (1 bar)

$S°(298.15\ K) = [87.864 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = Unknown

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -574.04 \pm 2.9\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy of combustion of $Fe(OH)_2$(cr), according to the chemical reaction $Fe(OH)_2(cr) + 1/4\ O_2(g) = 1/2\ Fe_2O_3(cr) + H_2O(l)$ was determined to be -29.8 ± 0.65 kcal·mol^{-1} by Fricke and Rihl.[1] From these data the adopted enthalpy of formation, $\Delta_f H°(298.15\ K)$, was evaluated to be -137.2 ± 0.7 kcal·mol^{-1}.

The enthalpy changes for the following three reactions were determined by Thomsen.[2]

Reaction	$\Delta_r H°(291\ K)$, kcal·mol^{-1}
$FeCl_2(cr) = FeCl_2\ (400\ H_2O)$	−17.9
$FeCl_2(200\ H_2O) + H_2SO_4(200\ H_2O) = FeSO_4(200\ H_2O) + 2\ HCl(100\ H_2O)$	−3.6
$FeSO_4(aq) + 2\ KOH(aq) = Fe(OH)_2(cr) + K_2SO_4(aq)$	−6.34

Using $\Delta_f H°(298.15\ K) = -81.7$ kcal·mol^{-1} for $FeCl_2$(cr) and those for the other compounds in aqueous solution (assuming aq. = 200 H_2O in Reaction 3) obtained from Wagman *et al.*[3] the enthalpy of formation at 298.15 K for $Fe(OH)_2$(cr) was derived as -135.8 kcal·mol^{-1} which agrees reasonably with the adopted value.

Heat Capacity and Entropy

The heat capacities, 298.15–700 K and $S°(298.15\ K)$ were estimated by comparison with those for $FeCl_2$(cr), $CaCl_2$(cr) and $Ca(OH)_2$(cr). The $C_p°$ values above 700 K were obtained by graphical extrapolation of the $C_p°$ curve plotted using the above $C_p°$ values.

Sublimation Data

The value of $\Delta_{sub} H°(298.15\ K)$ was calculated as the difference between $\Delta_f H°(298.15\ K)$ for $Fe(OH)_2$(g) and $Fe(OH)_2$(cr).

References

[1]R. Fricke and S. Rihl, Z. anorg. allg. Chem. **251**, 414 (1943).
[2]J. Thomsen, "Thermochemische Untersuchungen," Barth, Leipzig, 1882–1886.
[3]U. S. Nat. Bur. Stand. Tech. Note 270–1, (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	97.069	87.864	87.864	0.	−574.045	−491.969	86.191
300	97.152	88.465	87.866	0.180	−574.019	−491.460	85.571
400	102.090	117.096	91.736	10.144	−572.560	−464.155	60.612
500	106.776	140.383	99.206	20.589	−570.950	−437.238	45.678
600	111.294	160.255	107.764	31.495	−569.218	−410.656	35.751
700	115.478	177.734	116.535	42.839	−567.392	−384.373	28.682
800	118.951	193.391	125.181	54.568	−565.567	−358.353	23.398
900	121.545	207.559	133.559	66.599	−563.945	−332.552	19.301
1000	123.386	220.466	141.614	78.852	−562.905	−306.906	16.031
1100	124.516	232.283	149.328	91.251	−562.696	−281.301	13.358
1200	125.102	243.145	156.699	103.735	−561.930	−255.773	11.134
1300	125.353	253.170	163.740	116.259	−559.553	−230.357	9.256
1400	125.436	262.462	170.463	128.799	−557.318	−205.119	7.653
1500	125.520	271.119	176.889	141.346	−555.230	−180.036	6.269

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = [283.088]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-323.09 \pm 2.1]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-330.54 \pm 2.1]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[5]
[700]	[10]
[2500]	[5]
[4000]	[5]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[2300](1)	[450](1)	[800](1)
[750](1)	[320](1)	[700](1)
[400](1)	[2600](1)	[570](1)

Point Group: $[C_{2h}]$ $\sigma = 2$

Bond Distances: Fe–O = [1.8] Å O–H = [0.96] Å

Bond Angles: O–Fe–O = [180]° Fe–O–H = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [9.90391 \times 10^{-116}]\ g^3·cm^6$

Enthalpy of Formation

The equilibrium constants, at temperatures between 1300 and 1460°C, for the chemical reaction $Fe(cr) + 2\ H_2O(g) = Fe(OH)_2(g) + H_2(g)$ were determined by Belton and Richardson.[1] Using these data, the enthalpy change, $\Delta_r H°$ (298.15 K), of the reaction is evaluated to be 35.53 ± 3.0 and $36.57\ kcal·mol^{-1}$ by the 2nd and 3rd law method, respectively. Based on the 3rd law value for $\Delta_f H°(298.15\ K)$, the enthalpy of formation, $\Delta_f H°(Fe[OH]_2, g, 298.15\ K)$, is calculated to be $-79 \pm 0.5\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular structure is assumed to be the same as that for $B(OH)_2(g)$. The Fe–O bond distance is taken from FeO(g). The O–H bond distance and Fe–O–H bond angle are estimated from those for $H_2O(g)$. The vibrational frequencies, and electronic levels and quantum weights are obtained by comparison with those for $B(OH)_2(g)$ and $FeCl_2(g)$, respectively. These values are adjusted to give reasonable 2nd and 3rd law agreements. The principal moments of inertia are: $I_A = 0.2814 \times 10^{-39}$, $I_B = 18.6208\ 10^{-39}$, and $I_C = 18.9022 \times 10^{-39}\ g·cm^2$.

Reference

[1]G. R. Belton and F. D. Richardson, Trans. Faraday Soc. **58**, 1562 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	.000	.000	INFINITE	−14.209	−323.088	−323.088	INFINITE
100	36.766	227.041	335.221	−10.818	−326.023	−320.717	167.526
200	55.199	257.765	289.157	−6.278	−328.857	−314.241	82.071
250	64.437	271.106	284.228	−3.280	−329.851	−310.466	64.868
298.15	71.504	283.088	283.088	.000	−330.536	−306.666	53.727
300	71.738	283.531	283.089	.133	−330.558	−306.518	53.370
350	77.115	295.015	283.984	3.861	−331.041	−302.471	45.141
400	81.011	305.581	286.032	7.819	−331.376	−298.365	38.962
450	83.894	315.297	288.752	11.945	−331.625	−294.223	34.153
500	86.129	324.256	291.860	16.198	−331.831	−290.056	30.302
600	89.528	340.275	298.626	24.989	−332.215	−281.665	24.521
700	92.212	354.284	305.598	34.080	−332.642	−273.207	20.387
800	94.509	366.751	312.477	43.419	−333.207	−264.681	17.282
900	96.515	378.001	319.142	52.973	−334.063	−256.067	14.862
1000	98.263	388.262	325.549	62.714	−335.535	−247.331	12.919
1100	99.773	397.700	331.685	72.617	−337.821	−238.385	11.320
1200	101.068	406.439	337.554	82.661	−339.495	−229.290	9.981
1300	102.172	414.573	343.170	92.825	−339.479	−220.108	8.844
1400	103.108	422.180	348.545	103.090	−339.518	−210.924	7.870
1500	103.901	429.322	353.694	113.441	−339.627	−201.736	7.025
1600	104.571	436.049	358.633	123.866	−339.815	−192.537	6.286
1700	105.137	442.406	363.376	134.352	−341.042	−183.306	5.632
1800	105.614	448.430	367.935	144.890	−341.750	−174.007	5.050
1900	106.018	454.151	372.323	155.473	−356.658	−163.965	4.508
2000	106.360	459.598	376.552	166.092	−357.814	−153.793	4.017
2100	106.650	464.795	380.631	176.743	−358.996	−143.563	3.571
2200	106.895	469.762	384.571	187.420	−360.208	−133.275	3.164
2300	107.104	474.518	388.379	198.121	−361.452	−122.933	2.792
2400	107.281	479.080	392.064	208.840	−362.729	−112.536	2.449
2500	107.432	483.463	395.633	219.576	−364.040	−102.084	2.133
2600	107.561	487.679	399.092	230.326	−365.387	−91.579	1.840
2700	107.671	491.741	402.449	241.088	−366.769	−81.022	1.567
2800	107.765	495.658	405.708	251.860	−368.187	−70.412	1.314
2900	107.845	499.441	408.876	262.640	−369.640	−59.753	1.076
3000	107.914	503.098	411.956	273.428	−371.129	−49.041	.854
3100	107.973	506.638	414.953	284.223	−372.652	−38.280	.645
3200	108.023	510.067	417.872	295.022	−722.510	−20.046	.327
3300	108.066	513.391	420.717	305.827	−722.202	1.901	−.030
3400	108.103	516.618	423.490	316.635	−721.960	23.841	−.366
3500	108.134	519.752	426.196	327.447	−721.785	45.773	−.683
3600	108.161	522.799	428.837	338.262	−721.676	67.702	−.982
3700	108.184	525.763	431.417	349.079	−721.634	89.628	−1.265
3800	108.203	528.648	433.938	359.899	−721.660	111.555	−1.533
3900	108.220	531.459	436.402	370.720	−721.753	133.483	−1.788
4000	108.234	534.199	438.813	381.543	−721.915	155.413	−2.029
4100	108.245	536.872	441.172	392.367	−722.145	177.349	−2.259
4200	108.255	539.480	443.482	403.192	−722.444	199.292	−2.479
4300	108.263	542.028	445.744	414.018	−722.814	221.242	−2.688
4400	108.270	544.517	447.961	424.844	−723.255	243.201	−2.887
4500	108.275	546.950	450.134	435.671	−723.767	265.171	−3.078
4600	108.279	549.330	452.265	446.499	−724.352	287.154	−3.261
4700	108.283	551.658	454.355	457.327	−725.010	309.150	−3.436
4800	108.285	553.938	456.406	468.156	−725.743	331.162	−3.604
4900	108.287	556.171	458.419	478.984	−726.551	353.189	−3.765
5000	108.288	558.358	460.396	489.813	−727.436	375.234	−3.920
5100	108.289	560.503	462.338	500.642	−728.399	397.297	−4.069
5200	108.289	562.606	464.246	511.471	−729.442	419.378	−4.213
5300	108.288	564.668	466.121	522.300	−730.565	441.483	−4.351
5400	108.288	566.692	467.965	533.128	−731.770	463.607	−4.485
5500	108.287	568.679	469.778	543.957	−733.060	485.755	−4.613
5600	108.286	570.631	471.562	554.786	−734.436	507.929	−4.738
5700	108.284	572.547	473.317	565.614	−735.900	530.126	−4.858
5800	108.283	574.430	475.044	576.443	−737.455	552.352	−4.974
5900	108.281	576.281	476.744	587.271	−739.103	574.601	−5.087
6000	108.279	578.101	478.418	598.099	−740.847	596.883	−5.196

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°$(298.15 K) = [104.600 ± 8.4] J·K^{-1}·mol^{-1}
T_{fus} = Unknown

$\Delta_f H°$(0 K) = Unknown
$\Delta_f H°$(298.15 K) = −832.62 ± 12.6 kJ·mol^{-1}
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

Schindler *et al.*[1] investigated the solubility of aged $Fe(OH)_3$ precipitates by determining the Fe^{++} + and H^+ ion concentration of solution in contact with the solid phase. The ion concentration was measured by the EMF–method at the constant ionic strength 3M $NaClO_4$(solution). The precipitates were investigated by X–ray and electron microscope methods. The equilibrium constant was derived as log $[Fe^{+++}][H^+]^3$ = log K = 3.55 ± 0.1 for amorphous inactive hydroxide at 25°C. From these data the quantity log Ks = −39.1 ± 0.2 was evaluated where Ks is the solubility product of $Fe(OH)_3$. The Gibbs energy change, $\Delta_r G°$(298.15 K), of the reaction $Fe(OH)_3$(cr) = Fe^{+++}(aq) + 3 OH^-(aq) was calculated to be 53.34 ± 0.27 kcal·mol^{-1}. Using $S°$(298.15 K) = −70.1 and 2.57 cal·K^{-1}·mol^{-1} for Fe^{+++}(aq) and OH^-(aq), respectively, and an estimated $S°$($Fe(OH)_3$, cr, 298.15 K) = 25 cal·K^{-1}·mol^{-1}, the enthalpy change, $\Delta_r H°$(298.15 K) of the reaction is calculated to be 22.69 kcal·mol^{-1}, according to the relationship $\Delta H = \Delta F + T\Delta S$. The entropy values for Fe^{++} + and OH^- ions, were obtained from[2] and[3] respectively. Based on $\Delta_f H°$(Fe^{+++}, aq, 298.15 K) = −11.4 and $\Delta_f H°$(OH^-, aq, 298.15 K) = −54.97 kcal·mol^{-1}, taken from the same sources, the enthalpy of formation, $\Delta_f H°$(298.15 K), for $Fe(OH)_3$(cr) was evaluated to be −199 ± 3 kcal·mol^{-1}, which was adopted here.

The divergent values for solubility product (SP) of $Fe(OH)_3$ found in the literature may be due, not only to the various forms of precipitate but also to the tendency to form colloidal solutions. The SP values for $Fe(OH)_3$ were also reported by Evans and Pryor[4] Kriukor and Awsejewitsch[5] Ruff and Hirsch[6] Britton[7] and Jellinek and Gorden.[8]

The enthalpy changes, $\Delta_r H°$(291 K), for the reactions: (1) $FeCl_3$(aq) + 3NaOH(aq) = $Fe(OH)_3$(cr) + 3NaCl(aq) and (2) $FeCl_3$(cr) = $FeCl_3$(aq) were determined to be −24.50 and −31.68 kcal·mol^{-1}, respectively by Thomsen.[9] Assuming the aqueous solutions all contain 200 mol of H_2O, the enthalpy of formation, $\Delta_f H°$(298.15 K), for $Fe(OH)_3$ was calculated as −196.9 kcal·mol^{-1} from Reaction (1) and (2). The $\Delta_f H°$(298.15 K) values for NaOH(aq) and NaCl(aq) were obtained from Parker[10] and JANAF $\Delta_f H°$(298.15 K) values for NaOH(cr) and NaCl(cr).

Heat Capacity and Entropy

The heat capacities, 298.15–1000 K, were estimated by comparison with those for B_2O_3(cr), Fe_2O_3(cr) and $B(OH)_3$(cr). The $C_p°$ values above 1000 K were obtained by graphical extrapolation. The $S°$($Fe(OH)_3$, cr, 298.15 K) value was estimated by comparison with that for $B(OH)_3$(cr).

References

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[4]Evans and Pryor, J. Chem. Soc. S157 (1949).
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[6]Ruff and Hirsch, Z. Anorg. Chem. **146**, 338 (1925).
[7]Britton, J. Chem. Soc. 2148 (1925).
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[10]V. B. Parker, NSRDS NBS 2, (1965).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	101.671	104.600	104.600	0.	−832.616	−705.467	123.595
300	102.090	105.230	104.602	0.188	−832.636	−704.678	122.695
400	117.989	136.877	108.809	11.227	−833.040	−661.930	86.439
500	129.704	164.480	117.242	23.619	−832.474	−619.202	64.688
600	140.582	189.140	127.205	37.161	−831.150	−576.661	50.203
700	148.114	211.387	137.669	51.603	−829.323	−534.385	39.876
800	154.808	231.616	148.166	66.759	−827.216	−492.393	32.150
900	160.247	250.172	158.484	82.519	−825.055	−450.671	26.156
1000	164.850	267.303	168.520	98.783	−823.237	−409.177	21.373
1100	168.406	283.188	178.231	115.452	−822.032	−367.813	17.466
1200	171.126	297.962	187.601	132.434	−820.081	−326.624	14.218
1300	173.218	311.747	196.626	149.657	−816.357	−285.654	11.478
1400	174.682	324.640	205.315	167.055	−812.653	−244.970	9.140
1500	175.728	336.729	213.677	184.579	−809.013	−204.549	7.123

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = [167.360 \pm 8.4]\ J·K^{-1}·mol^{-1}$
$T_{trs}H° = 650\ K$
$T_{fus} = 860 \pm 2\ K$

$\Delta_fH°(0\ K)$ = Unknown
$\Delta_fH°(298.15\ K) = -104.60 \pm 8.4\ kJ·mol^{-1}$
$\Delta_{trs}H° = 0.8\ kJ·mol^{-1}$
$\Delta_{fus}H° = [44.769]\ kJ·mol^{-1}$

Enthalpy of Formation

The chemical equilibrium of the decomposition of FeI_2(cr), 771.15–858.15 K, has been studied by Zaugg and Gregory.[1] Using the reported partial pressures for I_2(g), the enthalpy change, $\Delta_rH°(298.15\ K)$, for the reaction $FeI_2(cr) = Fe(cr) + I_2(g)$ was evaluated by both the 2nd and 3rd law methods to be 39.79 ± 1.0 and 39.69 ± 0.3 kcal·mol^{-1}, respectively. Based on the 3rd law $\Delta_rH°(298.15\ K)$ value, the enthalpy of formation, $\Delta_fH°(298.15\ K)$ for FeI_2(cr) was calculated as −25 kcal·mol^{-1} which was adopted here.

The enthalpy change for the reaction $FeI_2(cr) = Fe^{++}(aq) = 2\ I^-(aq)$ was determined to be −19.46 ± 0.03 kcal·mol^{-1} by Paoletti *et al.*[2] using a solution calorimetric method. Adopting $\Delta_fH°(298.15\ K) = -21.3$ and −13.19 kcal·mol^{-1} for Fe^{++}(aq) and I^-(aq), respectively, the value of $\Delta_fH°(FeI_2, cr, 298.15\ K)$ was derived as −28.22 ± 1 kcal·mol^{-1}. The value of $\Delta_fH°(I^-, aq, 298.15\ K)$ was taken from Wagman *et al.*[3] The value of $\Delta_fH°(Fe^{++}, aq, 298.15\ K)$ was derived from enthalpy of solution and formation for $FeCl_2$(cr).

The enthalpies of solution of Fe(cr), I_2(cr) and FeI_2(cr) in aqueous Br_2–KBr solution were measured by Hieber and Woerner[4] using an ice calorimeter. From the results obtained the enthalpy of formation for FeI_2(cr) was reported as −30.1 kcal·mol^{-1}.

Heat Capacity and Entropy

The heat capacities, 343.15–773.15 K, were measured by Oetting and Gregory.[5] The $C_p°$ value at temperatures below 343.15 and above 773.15 K were estimated by graphic extrapolation. The low temperature heat capacities, 11–130 K were determined by Miljutin and Parfenowa.[6] These data appear to be inadequate for the derivation of the entropy at 298.15 K. The value of $S°(298.15\ K)$ adopted was calculated from the entropy change, $\Delta_rS°(298.15\ K) = 28.7\ cal·K^{-1}·mol^{-1}$, for the decomposition reaction $FeI_2(cr) = Fe(cr) + I_2(g)$, obtained by the second law analysis on the equilibrium pressure data reported by Zaugg and Gregory.[1]

Transition Data

A minor transition in the vicinity of 370°C (360–385°C) has been reported by Oetting and Gregory.[5] Subsequent studies by Wydeven[7] have shown the magnitude of the transition to be sensitive to trace amounts of impurities, but the nature of the transition has not been clearly established. A magnetic transition at 10 K was reported by Bizette *et al.*[8] The $\Delta_{trs}H°$ value was evaluated from the heat capacity–temperature plot given by Oetting and Gregory.[5]

Fusion Data

T_{fus} was reported by Fischer and Gewehr.[9] $\Delta_{fus}H°$ was estimated by comparison with that for $FeBr_2$(cr).

Sublimation Data

$\Delta_{sub}H°(cr \rightarrow monomer, 298.15\ K)$ is calculated as the difference between $\Delta_fH°(298.15\ K)$ for FeI_2(g) and FeI_2(cr). $\Delta_{sub}H°(cr \rightarrow dimer, 298.15\ K)$ was calculated as the difference between those for Fe_2I_4(g) and 2 FeI_2(cr).

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	83.680	167.360	167.360	0.	−104.600	−111.725	19.574
300	83.680	167.878	167.362	0.155	−104.592	−111.769	19.461
400	83.931	191.985	170.647	8.535	−120.478	−113.639	14.840
500	84.182	210.741	176.859	16.941	−163.121	−107.843	11.266
600	84.425	226.111	183.825	25.371	−161.531	−96.941	8.439
650.000	84.546	232.873	187.341	29.596	I <--> II		
650.000	87.864	234.160	187.341	30.432	TRANSITION		
700	95.395	240.947	190.927	35.013	−158.983	−86.362	6.444
800	110.876	254.699	198.037	45.330	−156.060	−76.173	4.974
860.000	120 .005	263.045	202.281	52.257	----- II <--> LIQUID -----		
900	126.224	268.644	205.106	57.184	−152.024	−66.419	3.855
1000	136.817	282.555	212.158	70.397	−147.361	−57.157	2.986
1100	141.188	295.834	219.168	84.333	−142.883	−48.336	2.295
1200	142.256	308.176	226.078	98.517	−137.621	−39.991	1.741
1300	142.256	319.562	232.837	112.743	−130.695	−32.137	1.291
1400	142.256	330.105	239.413	126.969	−123.883	−24.812	0.926
1500	142.256	339.919	245.790	141.194	−117.196	−17.970	0.626

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [195.430]\ J·K^{-1}·mol^{-1}$ $\Delta_fH°(298.15\ K) = [-71.046]\ kJ·mol^{-1}$
$T_{fus} = 860 \pm 2\ K$ $\Delta_{fus}H° = 44.769\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(FeI_2, l, 298.15\ K)$ is calculated from $\Delta_fH°(FeI_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(860\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to be constant in the temperature range from 298.15 to 2000 K and is calculated on the assumption that $C_p° = 9.0\ cal·K^{-1}\ g·atom^{-1}$ for FeI_2(l). $S°(FeI_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

T_{vap} is the temperature at which the vapor pressure of FeI_2(g) and Fe_2I_4(g) over FeI_2(l) equals one bar. The value of $\Delta_{vap}H°$ is derived from the vapor composition and the enthalpies of vaporization of FeI_2(l) to monomer and dimer at T_{vap}.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0							
100							
200							
298.15	112.968	195.430	195.430	0.	−71.046	−86.540	15.161
300	112.968	196.129	195.433	0.209	−70.984	−86.636	15.085
400	112.968	228.628	199.864	11.506	−83.953	−91.771	11.984
500	112.968	253.836	208.231	22.803	−123.705	−89.975	9.400
600	112.968	274.433	217.600	34.099	−119.249	−83.652	7.283
700	112.968	291.847	226.995	45.396	−115.045	−78.055	5.825
800	112.968	306.931	236.065	56.693	−111.142	−73.041	4.769
860.000	112 .968	315.101	241.298	63.471	----- II <--> LIQUID -----		
900	112.968	320.237	244.693	67.990	−107.664	−68.493	3.975
1000	112.968	332.140	252.853	79.287	−104.917	−64.297	3.359
1100	112.968	342.907	260.558	90.583	−103.078	−60.310	2.864
1200	112.968	352.736	267.836	101.880	−100.704	−56.546	2.461
1300	112.968	361.778	274.719	113.177	−96.706	−53.029	2.131
1400	112.968	370.150	281.240	124.474	−92.823	−49.816	1.859
1500	112.968	377.944	287.430	135.771	−89.065	−46.876	1.632
1600	112.968	385.235	293.318	147.067	−85.440	−44.183	1.442
1700	112.968	392.084	298.928	158.364	−82.907	−41.693	1.281
1800	112.968	398.541	304.285	169.661	−79.907	−39.356	1.142
1900	112.968	404.649	309.408	180.958	−91.159	−36.479	1.003
2000	112.968	410.443	314.316	192.255	−88.705	−33.665	0.879

PREVIOUS: CURRENT: September 1966

0	to	650	K crystal, I
650	to	860	K crystal, II
above		860	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
298.15	83.680	167.360	167.360	0.	−104.600	−111.725	19.574
300	83.680	167.878	167.362	0.155	−104.592	−111.769	19.461
400	83.931	191.985	170.647	8.535	−120.478	−113.639	14.840
500	84.182	210.741	176.859	16.941	−163.121	−107.843	11.266
600	84.425	226.111	183.825	25.371	−161.531	−96.941	8.439
650.000	84.546	232.873	187.341	29.596	I <--> II		
650.000	87.864	234.160	187.341	30.432	TRANSITION		
700	95.395	240.947	190.927	35.013	−158.983	−86.362	6.444
800	110.876	254.699	198.037	45.330	−156.060	−76.173	4.974
860.000	120 .005	263.045	202.281	52.257	II <--> LIQUID		
860.000	112 .968	315.101	202.281	97.026	TRANSITION		
900	112.968	320.237	207.410	101.544	−107.664	−68.493	3.975
1000	112.968	332.140	219.298	112.841	−104.917	−64.297	3.359
1100	112.968	342.907	230.054	124.138	−103.078	−60.310	2.864
1200	112.968	352.736	239.874	135.435	−100.704	−56.546	2.461
1300	112.968	361.778	248.908	146.731	−96.706	−53.029	2.131
1400	112.968	370.150	257.273	158.028	−92.823	−49.816	1.859
1500	112.968	377.944	265.061	169.325	−89.065	−46.876	1.632
1600	112.968	385.235	272.346	180.622	−85.440	−44.183	1.442
1700	112.968	392.084	279.190	191.919	−82.907	−41.693	1.281
1800	112.968	398.541	285.643	203.215	−79.907	−39.356	1.142
1900	112.968	404.648	291.747	214.512	−91.159	−36.479	1.003
2000	112.968	410.443	297.538	225.809	−88.705	−33.665	0.879

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K)$ = [349.597] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [89.40 ± 12.6] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [87.86 ± 12.6] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[10]
[4200]	[10]
[6800]	[5]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[140] (1)
[32] (2)
[280] (1)

Point Group: [$D_{\infty h}$] σ = 2
Bond Distance: Fe–I = [2.43] Å
Bond Angle: I–Fe–I = [180]°
Rotational Constant: B_0 = [0.011248] cm^{-1}

Enthalpy of Formation

The chemical equilibria for the reactions: (A) FeI_2(cr) = FeI_2(g), (B) FeI_2(l) = FeI_2(g), and (C) Fe(cr) + 2 I(g) = FeI_2(g), have been studied by several investigators. Based on the equilibrium pressures reported, the corresponding enthalpy changes were evaluated by both the 2nd and 3rd law method. The results obtained are presented in the table below. Using the third law $\Delta_f H°(298.15\ K)$ values, the enthalpy of formation for FeI_2(g) were calculated. The adopted value for $\Delta_f H°(FeI_2, g, 298.15\ K)$ is 21.0 ± 3 $kcal·mol^{-1}$. The disagreement between the sets of 2nd and 3rd law $\Delta_f H°(298.15\ K)$ values listed in the table may be due to the presence of dimer, Fe_2I_4(g) which was not accounted for in deriving the partial pressure of FeI_2(g). The data obtained from Schoonmaker *et al.* was corrected for the presence of dimer. However, only one point value was given.

Source	Reaction	T/K	Method	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$
Schafer and Honest*[1]	A	790.15–850.15	Transpiration	41.81	45.58	+5.78	21.58
	B	874.15–959.15	Transpiration	43.56	35.58	−8.75	18.6
Schoonmaker *et al.*[2]	A	714	Mass Spectrometric	–	46.78	–	21.78
Sime and Gregory*[3]	A	670.0–740.0	Torsion–Effusion	45.13	45.70	0.85	20.7
Zaugg and Gregory[4]	C	865.15–1023.15	Transpiration	−32.53	−28.99	3.75	22.1

*The vapor pressure data used for evaluation were those corrected by Zaugg and Gregory.[4]

Heat Capacity and Entropy

The molecular structure was assumed to be linear. The Fe–I bond distance was estimated by Brewer *et al.*[5] The vibrational frequencies were estimated so that the derived Gibbs energy fucntions yielded 2nd and 3rd law $\Delta_r H°(298.15\ K)$ values in reasonable agreements, see the above table. The electronic levels and quantum weights were estimated from those for $FeCl_2$(g) reported by DeKock and Gruen.[6]

References

[1]H. Schafer and W. J. Hones, Z. anorg. allgem. Chem. **288**, 62 (1956).
[2]R. C. Schoonmaker, A. H. Friedman and F. R. Porter, J. Chem. Phys. **31**, 1586 (1959).
[3]R. J. Sime and N. W. Gregory, J. Phys. Chem. **64**, 86 (1960). The vapor pressure equation used for calculation is log P(mmHg) = −(9760)/T + 11.82; In the original paper, the term A = 960 instead of 9760 is in error.
[4]W. E. Zaugg and N. W. Gregory, J. Phys. Chem. **70**, 490 (1966).
[5]L. Brewer, G. R. Somayajulu and E. Brackett, Chem. Rev. **63**, 111 (1963).
[6]C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−16.167	89.402	89.402	INFINITE
100	53.921	286.148	402.435	−11.629	90.467	68.558	−35.811
200	59.295	325.577	355.125	−5.910	89.485	46.951	−12.262
250	60.288	338.925	350.596	−2.918	88.712	36.404	−7.606
298.15	60.859	349.597	349.597	0.	87.864	26.405	−4.626
300	60.876	349.973	349.598	0.113	87.829	26.024	−4.531
350	61.248	359.387	350.341	3.166	86.785	15.802	−2.358
400	61.498	367.583	351.995	6.235	69.686	6.286	−0.821
450	61.675	374.838	354.138	9.315	67.335	−1.499	0.174
500	61.806	381.343	356.538	12.402	24.804	−5.219	0.545
600	62.003	392.630	361.641	18.593	24.154	−11.167	0.972
700	62.180	402.200	366.769	24.802	23.270	−16.987	1.268
800	62.388	410.517	371.729	31.030	22.104	−22.663	1.480
900	62.645	417.879	376.455	37.281	20.537	−28.169	1.635
1000	62.955	424.495	380.934	43.561	18.267	−33.469	1.748
1100	63.308	430.512	385.172	49.874	15.122	−38.476	1.827
1200	63.690	436.036	389.183	56.224	12.549	−43.254	1.883
1300	64.085	441.150	392.987	62.612	11.639	−47.868	1.923
1400	64.479	445.914	396.599	69.041	10.653	−52.409	1.955
1500	64.861	450.375	400.037	75.508	9.582	−56.876	1.981
1600	65.220	454.573	403.315	82.012	8.414	−61.269	2.000
1700	65.551	458.537	406.448	88.551	6.189	−65.567	2.015
1800	65.850	462.292	409.447	95.121	4.462	−69.739	2.024
1900	66.113	465.860	412.323	101.720	−11.487	−73.109	2.010
2000	66.340	469.257	415.086	108.343	−13.707	−76.295	1.993
2100	66.533	472.499	417.743	114.987	−15.974	−79.369	1.974
2200	66.691	475.597	420.303	121.648	−18.285	−82.334	1.955
2300	66.818	478.565	422.772	128.324	−20.637	−85.193	1.935
2400	66.916	481.411	425.156	135.011	−23.023	−87.949	1.914
2500	66.987	484.144	427.462	141.706	−25.434	−90.605	1.893
2600	67.034	486.772	429.693	148.407	−27.861	−93.163	1.872
2700	67.059	489.303	431.854	155.112	−30.296	−95.629	1.850
2800	67.065	491.742	433.949	161.819	−32.728	−98.004	1.828
2900	67.055	494.095	435.983	168.525	−35.148	−100.293	1.806
3000	67.031	496.368	437.958	175.229	−37.549	−102.498	1.785
3100	66.994	498.565	439.878	181.930	−39.924	−104.624	1.763
3200	66.947	500.691	441.745	188.628	−390.566	−99.249	1.620
3300	66.892	502.751	443.563	195.320	−390.968	−90.140	1.427
3400	66.829	504.747	445.333	202.006	−391.362	−81.018	1.245
3500	66.760	506.683	447.059	208.685	−391.743	−71.884	1.073
3600	66.686	508.563	448.741	215.358	−392.110	−62.740	0.910
3700	66.609	510.389	450.383	222.022	−392.462	−53.586	0.756
3800	66.529	512.164	451.985	228.679	−392.799	−44.423	0.611
3900	66.447	513.891	453.551	235.328	−393.121	−35.251	0.472
4000	66.363	515.572	455.080	241.969	−393.430	−26.071	0.340
4100	66.278	517.210	456.576	248.601	−393.726	−16.883	0.215
4200	66.193	518.806	458.038	255.224	−394.012	−7.688	0.096
4300	66.108	520.363	459.470	261.839	−394.289	1.513	−0.018
4400	66.024	521.881	460.871	268.446	−394.560	10.721	−0.127
4500	65.940	523.364	462.243	275.044	−394.827	19.935	−0.231
4600	65.857	524.813	463.588	281.634	−395.093	29.155	−0.331
4700	65.776	526.228	464.906	288.216	−395.360	38.380	−0.427
4800	65.695	527.612	466.198	294.789	−395.631	47.612	−0.518
4900	65.616	528.966	467.465	301.355	−395.908	56.849	−0.606
5000	65.539	530.291	468.708	307.912	−396.195	66.092	−0.690
5100	65.463	531.588	469.928	314.463	−396.495	75.341	−0.772
5200	65.389	532.858	471.126	321.005	−396.809	84.596	−0.850
5300	65.316	534.103	472.303	327.540	−397.142	93.856	−0.925
5400	65.246	535.323	473.459	334.068	−397.497	103.124	−0.998
5500	65.177	536.520	474.594	340.589	−397.875	112.398	−1.067
5600	65.109	537.694	475.711	347.104	−398.282	121.679	−1.135
5700	65.044	538.845	476.808	353.611	−398.719	130.968	−1.200
5800	64.980	539.976	477.888	360.113	−399.192	140.265	−1.263
5900	64.918	541.086	478.950	366.607	−399.702	149.570	−1.324
6000	64.858	542.177	479.994	373.096	−400.254	158.884	−1.383

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = [60.752]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1650]\ K$

$\Delta_f H°(0\ K) = Unknown$
$\Delta_f H°(298.15\ K) = [-272.044]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [24.058]\ kJ·mol^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(298.15\ K)$ for FeO(cr) was derived based on an assumption that at 1650 K, $\Delta_f F°$(FeO, cr) = $\Delta_f F°$(FeO, l). From the value $\Delta_f F°$(FeO, cr, 1650 K) = −39.77 kcal·mol^{-1}, $\Delta_f H°$(FeO, cr, 1650 K) was calculated to be −63.97 kcal·mol^{-1}, yielding $\Delta_f H°$(FeO, cr, 298.15 K) = −65.02 kcal·mol^{-1} (−272.044 kJ·mol^{-1}).

Heat Capacity and Entropy

The $C_p°$ values were estimated assuming $C_p°$ (FeO, cr) = $C_p°$(Wustite, cr) + 0.053 $C_p°$(Fe, cr). The $C_p°$ values obtained were plotted. The adopted $C_p°$ points were taken from the smoothed $C_p°$ curve. $S°(298.15\ K)$ for FeO(cr) was calculated as $S°$(FeO, cr) = $S°$ (Wustite, cr) + 0.053 $S°$(Fe, cr) + $\Delta S°$(mixing) where $\Delta S°$ is the entropy of mixing (0.41 cal K^{-1}·mol^{-1}).

Fusion Data

T_{fus} is assumed to be the same as that for Wustite. The difference between $\Delta_f H°(1650\ K)$ for FeO(l) and FeO(cr) is $\Delta_{fus} H°$.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated as the difference between $\Delta_f H°(298.15\ K)$ for FeO(g) and FeO(cr).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	49.915	60.752	60.752	0.	−272.044	−251.429	44.049
300	49.999	61.061	60.753	0.092	−272.025	−251.301	43.755
400	51.840	75.704	62.737	5.187	−271.044	−244.543	31.934
500	53.388	87.438	66.541	10.449	−270.164	−238.022	24.866
600	54.894	97.309	70.868	15.865	−269.414	−231.666	20.168
700	56.149	105.866	75.270	21.418	−268.814	−225.425	16.821
800	57.321	113.443	79.577	27.093	−268.422	−219.256	14.316
900	58.283	120.249	83.724	32.872	−268.374	−213.118	12.369
1000	59.371	126.447	87.691	38.756	−268.969	−206.955	10.810
1100	60.234	132.146	91.477	44.736	−270.385	−200.670	9.529
1200	61.086	137.424	95.089	50.802	−271.184	−194.316	8.458
1300	61.975	142.349	98.537	56.956	−270.265	−187.947	7.552
1400	62.760	146.971	101.833	63.194	−269.361	−181.649	6.777
1500	63.396	151.323	104.989	69.502	−268.484	−175.415	6.108
1600	64.015	155.435	108.014	75.873	−267.642	−169.238	5.525
1650.000	64.319	157.409	109.481	79.081	− − − CRYSTAL <− −> LIQUID − − −		
1700	64.631	159.334	110.919	82.305	−267.784	−163.094	5.011
1800	65.229	163.045	113.713	88.798	−267.345	−156.949	4.555
1900	65.790	166.587	116.403	95.349	−281.041	−150.125	4.127
2000	66.316	169.975	118.998	101.955	−280.919	−143.237	3.741

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 75.415\ J·K^{-1}·mol^{-1}$
$T_{fus} = [1650]\ K$

$\Delta_f H°(298.15\ K) = [-249.532]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [24.058]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(FeO, l, 298.15 K), is evaluated based on as assumption that the enthalpy of fusion of O_2(g). In other words, during melting the Wustite releases O_2(g) and converts tp FeO(l).

Heat Capacity and Entropy

The enthalpy changes, $H°(T)-H°(298.15\ K)$, for 1650–1800 K of liquid iron oxide were determined by Coughlin *et al.*[1] The $C_p°$ (FeO, l) was derived as 16.3 $cal·K^{-1}$. This value was adopted as the heat capacity for FeO(l) up to 4000 K. A glass transition temperature was assumed at 1100 K. $S°$(FeO, l, 298.15 K) is calculated based on an assumption that the entropy of fusion of Wustite represents also the entropy change of the reaction. $Fe_{0.947}O(cr) = 0.947\ FeO(l) + (0.053/2)\ O_2(g)$. From the entropy of fusion, $\Delta_{fus} H°(1650\ K) = 4.539\ cal·K^{-1}·mol^{-1}$, the value $S°$(FeO), l, 298.15 K) = 18.029 $cal·K^{-1}·mol^{-1}$ was derived.

Fusion Data

The melting point (T_{fus}) for Wustite ($Fe_{0.947}O$, cr) has been reported by many investigators. However, the composition of the liquid state of Wustite was not identified. An assumption was made that during melting the reaction $Fe_{0.947}O(cr) = 0.947\ FeO(l) + (0.053/2)\ O_2(g)$ occurs. Hence the related thermodynamic properties were derived.

Decomposition Data

T_{dcm} is the temperature at which $\Delta_f G°$ equals zero.

Reference

[1] J. P. Coughlin, E. G. King and K. R. Bonnickson, J. Amer. Chem. Soc. **73**, 3891 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	48.116	75.415	75.415	0.	−249.532	−233.289	40.871
300	48.183	75.713	75.416	0.089	−249.517	−233.189	40.602
400	50.380	89.893	77.334	5.023	−248.696	−227.871	29.757
500	51.848	101.298	81.023	10.137	−247.965	−222.752	23.271
600	53.028	110.857	85.220	15.382	−247.385	−217.766	18.958
700	54.070	119.110	89.485	20.737	−246.983	−212.864	15.884
800	55.041	126.394	93.653	26.193	−246.810	−208.005	13.581
900	55.969	132.931	97.660	31.744	−246.991	−203.148	11.790
1000	56.873	138.875	101.489	37.386	−247.827	−198.241	10.355
1100	57.761	144.337	105.139	43.118	−249.492	−193.187	9.174
1100.000	57.761	144.337	105.139	43.118	GLASS <--> LIQUID TRANSITION		
1100.000	68.199	144.337	105.139	43.118			
1200	68.199	150.271	108.656	49.938	−249.537	−188.086	8.187
1300	68.199	155.730	112.070	56.758	−247.952	−183.030	7.354
1400	68.199	160.784	115.371	63.578	−246.466	−178.092	6.645
1500	68.199	165.490	118.558	70.398	−245.077	−173.257	6.033
1600	68.199	169.891	121.630	77.218	−243.785	−168.512	5.501
1650.000	68.199	171.990	123.124	80.628	--- CRYSTAL <--> LIQUID ---		
1700	68.199	174.026	124.592	84.038	−243.540	−163.826	5.034
1800	68.199	177.924	127.447	90.858	−242.774	−159.160	4.619
1900	68.199	181.611	130.202	97.678	−256.202	−153.831	4.229
2000	68.199	185.109	132.861	104.497	−255.866	−148.452	3.877
2100	68.199	188.437	135.428	111.317	−255.541	−143.089	3.559
2200	68.199	191.609	137.911	118.137	−255.227	−137.741	3.270
2300	68.199	194.641	140.312	124.957	−254.925	−132.408	3.007
2400	68.199	197.543	142.636	131.777	−254.634	−127.088	2.766
2500	68.199	200.327	144.889	138.597	−254.354	−121.779	2.544
2600	68.199	203.002	147.073	145.417	−254.085	−116.481	2.340
2700	68.199	205.576	149.192	152.237	−253.826	−111.194	2.151
2800	68.199	208.056	151.250	159.057	−253.577	−105.915	1.976
2900	68.199	210.450	153.251	165.877	−253.338	−100.646	1.813
3000	68.199	212.762	155.196	172.697	−253.109	−95.385	1.661
3100	68.199	214.998	157.089	179.517	−252.890	−90.131	1.519
3200	68.199	217.163	158.933	186.336	−600.979	−77.460	1.264
3300	68.199	219.262	160.729	193.156	−598.876	−61.133	0.968
3400	68.199	221.298	162.481	199.976	−596.815	−44.869	0.689
3500	68.199	223.275	164.190	206.796	−594.795	−28.665	0.428
3600	68.199	225.196	165.858	213.616	−592.816	−12.518	0.182
3700	68.199	227.064	167.487	220.436	−590.880	3.575	−0.050
3800	68.199	228.883	169.079	227.256	−588.987	19.616	−0.270
3900	68.199	230.655	170.635	234.076	−587.137	35.608	−0.477
4000	68.199	232.381	172.157	240.896	−585.331	51.553	−0.673
4100	68.199	234.065	173.647	247.716	−583.570	67.453	−0.859
4200	68.199	235.709	175.105	254.536	−581.855	83.311	−1.036
4300	68.199	237.314	176.533	261.356	−580.186	99.128	−1.204
4400	68.199	238.881	177.932	268.176	−578.566	114.907	−1.364
4500	68.199	240.414	179.304	274.995	−576.993	130.650	−1.517
4600	68.199	241.913	180.649	281.815	−575.470	146.358	−1.662
4700	68.199	243.380	181.968	288.635	−573.998	162.034	−1.801
4800	68.199	244.816	183.262	295.455	−572.578	177.680	−1.934
4900	68.199	246.222	184.533	302.275	−571.212	193.296	−2.061
5000	68.199	247.600	185.781	309.095	−569.900	208.885	−2.182

PREVIOUS: CURRENT: June 1965

0 to 1650 K crystal
above 1650 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	49.915	60.752	60.752	0.	−272.044	−251.429	44.049
300	49.999	61.061	60.753	0.092	−272.025	−251.301	43.755
400	51.840	75.704	62.737	5.187	−271.044	−244.543	31.934
500	53.388	87.438	66.541	10.449	−270.164	−238.022	24.866
600	54.894	97.309	70.868	15.865	−269.414	−231.666	20.168
700	56.149	105.866	75.270	21.418	−268.814	−225.425	16.821
800	57.321	113.443	79.577	27.093	−268.422	−219.256	14.316
900	58.283	120.249	83.724	32.872	−268.374	−213.118	12.369
1000	59.371	126.447	87.691	38.756	−268.969	−206.955	10.810
1100	60.234	132.146	91.477	44.736	−270.385	−200.670	9.529
1200	61.086	137.424	95.089	50.802	−271.184	−194.316	8.458
1300	61.975	142.349	98.537	56.956	−270.265	−187.947	7.552
1400	62.760	146.971	101.833	63.194	−269.361	−181.649	6.777
1500	63.396	151.323	104.989	69.502	−268.484	−175.415	6.108
1600	64.015	155.435	108.014	75.873	−267.642	−169.238	5.525
1650.000	64.319	157.409	109.481	79.081	CRYSTAL <--> LIQUID TRANSITION		
1650.000	68.199	171.990	109.481	103.139			
1700	68.199	174.026	111.350	106.549	−243.540	−163.826	5.034
1800	68.199	177.924	114.941	113.369	−242.774	−159.160	4.619
1900	68.199	181.611	118.354	120.189	−256.202	−153.831	4.229
2000	68.199	185.109	121.605	127.009	−255.866	−148.452	3.877
2100	68.199	188.437	124.709	133.829	−255.541	−143.089	3.559
2200	68.199	191.609	127.678	140.649	−255.227	−137.741	3.270
2300	68.199	194.641	130.524	147.468	−254.925	−132.408	3.007
2400	68.199	197.543	133.257	154.288	−254.634	−127.088	2.766
2500	68.199	200.327	135.884	161.108	−254.354	−121.779	2.544
2600	68.199	203.002	138.415	167.928	−254.085	−116.481	2.340
2700	68.199	205.576	140.855	174.748	−253.826	−111.194	2.151
2800	68.199	208.056	143.211	181.568	−253.577	−105.915	1.976
2900	68.199	210.450	145.488	188.388	−253.338	−100.646	1.813
3000	68.199	212.762	147.692	195.208	−253.109	−95.385	1.661
3100	68.199	214.998	149.828	202.028	−252.890	−90.131	1.519
3200	68.199	217.163	151.898	208.848	−600.979	−77.460	1.264
3300	68.199	219.262	153.908	215.668	−598.876	−61.133	0.968
3400	68.199	221.298	155.860	222.488	−596.815	−44.869	0.689
3500	68.199	223.275	157.758	229.308	−594.795	−28.665	0.428
3600	68.199	225.196	159.605	236.127	−592.816	−12.518	0.182
3700	68.199	227.064	161.403	242.947	−590.880	3.575	−0.050
3800	68.199	228.883	163.155	249.767	−588.987	19.616	−0.270
3900	68.199	230.655	164.863	256.587	−587.137	35.608	−0.477
4000	68.199	232.381	166.530	263.407	−585.331	51.552	−0.673
4100	68.199	234.065	168.156	270.227	−583.570	67.453	−0.859
4200	68.199	235.709	169.745	277.047	−581.855	83.310	−1.036
4300	68.199	237.314	171.298	283.867	−580.186	99.128	−1.204
4400	68.199	238.881	172.816	290.687	−578.566	114.907	−1.364
4500	68.199	240.414	174.301	297.507	−576.993	130.650	−1.517
4600	68.199	241.913	175.755	304.327	−575.470	146.358	−1.662
4700	68.199	243.380	177.178	311.147	−573.998	162.034	−1.801
4800	68.199	244.816	178.573	317.966	−572.578	177.679	−1.934
4900	68.199	246.222	179.939	324.786	−571.212	193.296	−2.061
5000	68.199	247.600	181.278	331.606	−569.900	208.885	−2.182

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = [241.924]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 251.05 \pm 20.9\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 251.04 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^5\Delta]$	0	[10]
	[10000]	[10]
	[16000]	[5]

$\omega_e = 880.0\ cm^{-1}$ $\omega_e x_e = 5.0\ cm^{-1}$ $\sigma = 1$

$B_e = [0.4184]\ cm^{-1}$ $\alpha_e = [0.00293]\ cm^{-1}$ $r_e = [1.8]$ Å

Enthalpy of Formation

The enthalpy of formation for FeO(g) is not well established at the present time. The values of $\Delta_f H°$(FeO, g, 298.15 K) derived from the following reactions: (A) FeO(g) = Fe(g) + O(g) , (B) FeO(g) + 1/2 O_2(g), and (C) FeO(l) = FeO(g), are not in agreement. There are three $D_0°$(Fe–O) values reported for reaction (1). The enthalpy change for reaction (2) was evaluated based on the partial pressure data (PFeO/PFe) = 0.2 at 1600°C, measured by Washburn,[4] using a mass spectrometric method,[6] and $PO_2 = 1.66 \times 10^{-6}$ atm reported by Darken and Gurry.[7] The enthalpy value for reaction (3) was calculated based on the reported value, $\Delta_{vap}H°(2785\ K) = 96.096\ kcal·mol^{-1}$ determined by Burtsev *et al.*[5] The results obtained are presented as follows. The value of $\Delta_f H°(298.15\ K)$ for FeO(g) adopted is 60 ± 5 $kcal·mol^{-1}$.

Source	Reaction	Method	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Herzberg[1]	A	Spectroscopic	111.9	47.2
Gaydon[2]	A	Spectroscopic	93.4 ± 23.1	65.7 ± 23.1
Lagerqvist and Huldt[3]	A	Spectroscopic	99.0 ± 11.6	60.1 ± 11.6
Washburn *et al.*[4]	B	Spectroscopic	99.3 ± 5	59.8 ± 5
Burtsev *et al.*[5]	C	Transpiration	111.8	52.2

Heat Capacity and Entropy

Since the ground state configuration is mainly that due to Fe^{++} in a ligand field, it was assumed to be the same as that for $FeCl_2$(g) reported by DeKock and Gruen.[8] The electronic levels and quantum weights were estimated by comparison with those for $FeCl_2$(g). The values of ω_e and $\omega_e x_e$ were taken from Herzberg.[1] The bond distance was calculated according to the method suggested by Guggenheimer,[9] assuming FeO(g) as a polar molecule. The value of B_e was calculated by use of the relationship: $B_e = (2.799076 \times 10^{-39})/I$ where I is the moment of inertia of FeO(g). The value of α_e was derived from ω_e, $\omega_e x_e$ and B_e by the method suggested by Herzberg.[1]

References

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[9]K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.837	251.051	251.051	INFINITE
100	29.110	209.460	268.743	−5.928	252.085	240.411	−125.578
200	29.741	229.752	244.739	−2.997	251.791	228.779	−59.751
250	30.538	236.471	242.436	−1.491	251.431	223.067	−46.607
298.15	31.406	241.924	241.924	0.	251.040	217.639	−38.129
300	31.439	242.118	241.924	0.058	251.024	217.431	−37.858
350	32.302	247.030	242.310	1.652	250.594	211.866	−31.619
400	33.065	251.394	243.178	3.287	250.139	206.364	−26.948
450	33.715	255.328	244.313	4.957	249.653	200.921	−23.322
500	34.261	258.909	245.596	6.656	249.127	195.534	−20.427
600	35.098	265.234	248.356	10.127	247.932	184.925	−16.099
700	35.689	270.691	251.166	13.668	246.520	174.532	−13.024
800	36.118	275.486	253.912	17.259	244.828	164.360	−10.732
900	36.439	279.760	256.551	20.888	242.725	154.422	−8.962
1000	36.687	283.612	259.068	24.545	239.904	144.752	−7.561
1100	36.884	287.119	261.461	28.223	236.186	135.431	−6.431
1200	37.048	290.335	263.735	31.920	233.018	126.392	−5.502
1300	37.188	293.306	265.897	35.632	231.495	117.568	−4.724
1400	37.315	296.067	267.954	39.357	229.886	108.864	−4.062
1500	37.434	298.645	269.915	43.095	228.192	100.278	−3.492
1600	37.550	301.065	271.787	46.844	226.413	91.808	−2.997
1700	37.669	303.345	273.577	50.605	223.600	83.471	−2.565
1800	37.792	305.502	275.291	54.378	221.319	75.293	−2.185
1900	37.922	307.548	276.936	58.164	204.857	67.947	−1.868
2000	38.060	309.497	278.516	61.963	202.172	60.811	−1.588
2100	38.207	311.357	280.035	65.776	199.490	53.809	−1.338
2200	38.363	313.138	281.500	69.605	196.812	46.934	−1.114
2300	38.527	314.847	282.913	73.449	194.139	40.182	−0.913
2400	38.699	316.491	284.278	77.310	191.471	33.545	−0.730
2500	38.877	318.074	285.598	81.189	188.810	27.019	−0.565
2600	39.063	319.602	286.877	85.086	186.157	20.600	−0.414
2700	39.253	321.080	288.117	89.002	183.511	14.283	−0.276
2800	39.447	322.511	289.319	92.936	180.875	8.063	−0.150
2900	39.644	323.899	290.488	96.891	178.248	1.938	−0.035
3000	39.842	325.246	291.624	100.865	175.632	−4.097	0.071
3100	40.041	326.556	292.730	104.859	173.025	−10.045	0.169
3200	40.240	327.830	293.807	108.873	−177.870	−8.485	0.139
3300	40.437	329.071	294.857	112.907	−178.553	−3.182	0.050
3400	40.633	330.281	295.881	116.961	−179.258	2.143	−0.033
3500	40.825	331.462	296.881	121.034	−179.985	7.489	−0.112
3600	41.014	332.615	297.858	125.126	−180.734	12.856	−0.187
3700	41.198	333.741	298.812	129.236	−181.508	18.244	−0.258
3800	41.378	334.842	299.746	133.365	−182.305	23.654	−0.325
3900	41.553	335.919	300.660	137.512	−183.129	29.084	−0.390
4000	41.722	336.973	301.555	141.676	−183.979	34.536	−0.451
4100	41.885	338.006	302.431	145.856	−184.858	40.010	−0.510
4200	42.042	339.017	303.290	150.052	−185.766	45.505	−0.566
4300	42.193	340.008	304.133	154.264	−186.706	51.023	−0.620
4400	42.338	340.980	304.959	158.491	−187.678	56.563	−0.671
4500	42.476	341.933	305.770	162.732	−188.685	62.125	−0.721
4600	42.608	342.868	306.566	166.986	−189.727	67.709	−0.769
4700	42.734	343.785	307.349	171.253	−190.808	73.318	−0.815
4800	42.853	344.686	308.117	175.532	−191.929	78.949	−0.859
4900	42.966	345.571	308.872	179.823	−193.091	84.605	−0.902
5000	43.072	346.440	309.615	184.125	−194.297	90.284	−0.943
5100	43.173	347.294	310.346	188.438	−195.549	95.988	−0.983
5200	43.267	348.133	311.064	192.760	−196.849	101.717	−1.022
5300	43.356	348.958	311.771	197.091	−198.200	107.472	−1.059
5400	43.440	349.770	312.468	201.431	−199.604	113.252	−1.095
5500	43.518	350.567	313.153	205.779	−201.063	119.059	−1.131
5600	43.590	351.352	313.828	210.134	−202.581	124.893	−1.165
5700	43.658	352.124	314.493	214.497	−204.161	130.755	−1.198
5800	43.721	352.884	315.149	218.866	−205.805	136.645	−1.231
5900	43.779	353.632	315.795	223.241	−207.518	142.563	−1.262
6000	43.833	354.368	316.431	227.621	−209.302	148.512	−1.293

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = 120.957 \pm 1.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -919.33 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -928.85 \pm 8.4\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy change for the reaction $FeSO_4(cr) = FeSO_4(110 \infty H_2O)$ was determined to be $-14.9\ kcal·mol^{-1}$ by Forcrand.[1] Using $\Delta_f H°(298.15\ K) = -345.85\ kcal·mol^{-1}$ for $FeSO_4(110 \infty H_2O)$, the enthalpy of formation (298.15 K) for $FeSO_4$(cr) was calculated as $-221\ kcal·mol^{-1}$. The value of $\Delta_f H°(FeSO_4$, cr, 298.15 K) was estimated based on $\Delta_f H°(298.15\ K) = 235.9\ kcal·mol^{-1}$ for $FeSO_4(200 \infty H_2O) + H_2SO_4(200\ H_2O) = FeSO_4(200\ H_2O) + 2HCl(100 \infty H_2O)$ measured by Thomsen.[2] See the $Fe(OH)_2$(cr) table for details.

The decomposition pressures of $FeSO_4$(cr) at different temperatures were investigated by D'Ans[3] and Greulich.[4] Using their reported partial pressures for SO_3(g) and SO_2(g), the enthalpy change for the reaction $2FeSO_4(cr) = Fe_2O_3(cr) + SO_3(g) + SO_2(g)$ was evaluated by both the 2nd and 3rd law methods. The results obtained are presented in the following table.

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
D'Ans[3](1905)	753.15–908.15	83.2 ± 4.6	82.7 ± 1.1	−222.7
Greulich[4](1927)	887.15–971.15	64.8 ± 8.8	80.1 ± 1.4	−221.5
Neumann and Heintke[5](1937)	633.15–862.15	72.4 ± 5.4	75.3 ± 0.5	−219.1

The decomposition pressures asumed for the same reaction have been determined by Neumann and Heintke.[5] From their data the partial pressures for SO_3(g) and SO_2(g) were evaluated. Using the derived SO_3(g) and SO_2(g) partial pressures, the corresponding enthalpy change for the reaction were calculated by both the 2nd and 3rd law methods. The results obtained are also listed in the same table.

The value of $\Delta_f H°(298.15\ K)$ for $FeSO_4$(cr) is selected as $222 \pm 2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The low temperature heat capacities, 50.12 294.9 K, were determined by Moore and Kelley.[6] Based on $S°(50.12\ K) = 2.10\ cal·K^{-1}·mol^{-1}$, the value of $S°(FeSO_4$, cr, 298.15 K) was reported to be $25.71 \pm 0.2\ cal·K^{-1}·mol^{-1}$. Using the Gibbs energy functions for $FeSO_4$(cr) based on this $S°(298.15\ K)$ value, to evaluate the vapor pressure data for Reaction,[1] the 2nd and 3rd law values of $\Delta_f H°(298.15\ K)$ were derived as 72.36 ± 7.60 and $86.51 \pm 1.26\ kcal·mol^{-1}$, respectively. Since the report by Moore and Kelley[6] did not mention the magnetic entropy contribution, an attempt was made to add 3.20 (=Rln5) $cal·K^{-1}·mol^{-1}$ to $S°(FeSO_4$, cr, 298.15 K) and reevaluate the decomposition pressure data. The results obtained were better than before, see the paragraph on "Enthalpy of Formation," for details. Therefore the value, $S°(298.15\ K) = 25.71 + 3.2 = 28.91\ cal·K^{-1}·mol^{-1}$ for $FeSO_4$(cr), was adopted. The heat capacities above 294.9 K were estimated by comparison with those for $MnSO_4$(cr). The high temperature heat capacities, 870.3–1082.3 K, were determined by Southard and Shomate[7]. The two sets of data were joined smoothly at 298.15 K by use of Shomate–function plot.

Decomposition Data

$T_{dcm} = 944$ K is the temperature at which the vapor pressure of the gaseous decomposition products equals one atmosphere, which was obtained by graphical interpolation of the decomposition pressure data on $FeSO_4$(cr), reported by Greulich.[4]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.769	−919.331	−919.331	INFINITE
100	44.074	42.771	194.810	−15.204	−924.688	−892.445	466.166
200	78.848	85.016	129.562	−8.909	−927.627	−858.919	224.327
298.15	100.583	120.957	120.957	0.	−928.848	−824.879	144.515
300	101.002	121.580	120.959	0.186	−928.859	−824.234	143.512
400	116.650	152.861	125.118	11.097	−931.115	−789.237	103.064
500	128.909	180.266	133.463	23.401	−931.710	−753.695	78.738
600	138.030	204.613	143.331	36.769	−931.332	−718.113	62.517
700	144.641	226.410	153.670	50.918	−930.365	−682.648	50.940
800	149.411	246.052	164.011	65.633	−929.150	−647.342	42.267
900	152.758	263.849	174.131	80.746	−981.132	−611.106	35.468
1000	155.477	280.088	183.927	96.161	−979.245	−570.101	29.779
1100	157.779	295.017	193.356	111.826	−978.112	−529.226	25.131
1200	159.829	308.835	202.411	127.709	−976.304	−488.516	21.265
1300	161.670	321.702	211.098	143.785	−972.740	−448.012	18.001
1400	163.343	333.744	219.433	160.036	−969.161	−407.782	15.215
1500	164.933	345.069	227.435	176.451	−965.573	−367.809	12.808
1600	166.440	355.762	235.124	193.020	−961.981	−328.076	10.711
1700	167.862	365.895	242.521	209.735	−959.340	−288.548	8.866
1800	169.285	375.530	249.645	226.593	−956.087	−249.184	7.231
1900	170.624	384.719	256.514	243.589	−966.938	−209.298	5.754
2000	171.962	393.505	263.146	260.718	−963.937	−169.499	4.427

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 60.321 \pm 0.04\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 411 \pm 3\ K$
$T_{trs2} = 598 \pm 3\ K$
$T_{fus} = 1463 \pm 3\ K$

$\Delta_f H°(0\ K) = -102.17 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -101.67 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 1.665 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 0.397 \pm 0.08\ kJ·mol^{-1}$
$\Delta_{fus} H° = 31.464 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K)$ is $24.30 \pm 0.2\ kcal·mol^{-1}$ and is based on our 3rd law analysis of gas phase H_2S/H_2 equilibrium data of.[1-7] Additional studies of a similar nature are reported by Mills.[8] The gas phase equilibrium results are favored over calorimetric[8] and emf[9-11] results because of greater certainty in the stoichiometry of the iron sulfide. Of the calorimetric studies[8] only those of Adami and King ($\Delta_f H°(298.15\ K) = -23.89 \pm 0.41\ kcal·mol^{-1}$) and the annealed sample of Ariya *et al.* ($\Delta_f H°(298.15\ K) = -24.4\ kcal·mol^{-1}$) are in reasonable agreement with the adopted value. Of the emf results, all refer to less than stoichiometric composition $Fe_{0.95}S$[9] $Fe_{0.98}S$[10] or to impure sample, 97.58%.[11] $\Delta_f H°(298.15\ K)$ has been shown to vary significantly as a function of stoichiometry[12] which is a result of the variation of $\Delta_\alpha H°$ with composition.[12]

Source	Reaction†	Method	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Rosenqvist[1]	C	H_2S/H^2	11	773–1257	17.89 ± 0.41	−19.40 ± 0.53	−1.45 ± 0.40	−24.30 ± 0.6
Blaise[2]	C	"	equation	923–1043	−17.87	−19.41 ± 0.14	−1.57	−24.31 ± 0.2
Turkdogan[3]	C	"	3	943–1173	−17.24 ± 0.39	−19.40 ± 0.48	−2.03 ± 0.36	−24.30 ± 0.5
Alcock[4]	B	"	equation	720–1261	−38.30	−39.68 ± 0.56	−1.38	−24.26 ± 0.6
McCabe[5]	B	"	10	1224–1255	−33.76 ± 2.84	−39.70 ± 0.15	4.81 ± 2.3	−24.28 ± 0.2
Sudo[6]	C	"	4	1048–1145	−17.39 ± 2.19	−19.51 ± 0.29	−1.95 ± 2.01	−24.41 ± 0.4
Rau[7]	C	"	9	820–1257	−19.40 ± 0.23	−19.31 ± 0.20	0.09 ± 0.22	−24.15 ± 0.3
Berner[9]	A	emf	1	298.15		−24.08		−24.08
DeRanter[10]	A	H titration	1	298.15				−20.55
DeRanter[10]	A	emf	1	298.15		−20.56		−20.56
Guldin[11]	B	emf	1	973		36.445		−21.02

†Reactions: (A) Fe(cr) + S(cr) → FeS(cr), (B) Fe(cr) + 1/2 S_2(g) → FeS(cr), (C) Fe(cr) + H_2S(g) → FeS(cr) + H_2(g)

Heat Capacity and Entropy

The adopted heat capacities are obtained by merging the $C_p°$ data (7–345 K) of Gronvold *et al.*[13] and the enthalpy data (356–1488 K) of Coughlin.[14] The data are difficult to merge smoothly because of the proximity of the α β transition at 411 K. Coughlin gives the composition of his sample as $FeS_{1.02}$ and this introduces some uncertainty at the higher temperatures.

The value of $S°(298.15\ K)$ is obtained from the appropriate integration of $C_p°$ values assuming $S°(7\ K) = 0.0028\ cal·K^{-1}·mol^{-1}$.

Phase Data

The mineral pyrrhotite has a composition range extending from FeS to $Fe_{0.875}S$ (Fe_7S_8); the name troilite is reserved for the stoichiometric FeS composition. The phase diagram[15] of this system shows that the iron rich limit of this phase corresponds to stoichiometric FeS below 1370 K; above this temperature only an iron deficient material exists so that stoichiometric FeS will melt incongruently.

There are two solid state phase transitions, both associated with electronic magnetic phenomena. The adopted temperature of the α β transition is $T_{trs1} = 411 \pm 3$ K.[15] Our analysis of the adopted $C_p°$ data yields $\Delta_{trs1} H° = 0.398\ kcal·mol^{-1}$; in view of the uncertainties in these data we adopt an uncertainty of $\pm 0.2\ kcal·mol^{-1}$ in $\Delta_{trs1} H°$. The adopted temperature of the β–γ transition is $T_{trs2} = 598 \pm 3$ K[15] and our analysis of Coughlin's high temperature enthalpy data[14] yields $\Delta_{trs2} H° = 0.095 \pm 0.02\ kcal·mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

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Continued on page 1251

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.413	−102.166	−102.166	INFINITE
100	26.670	17.216	99.528	−8.231	−102.096	−101.959	53.258
200	43.052	41.665	64.714	−4.610	−101.886	−101.901	26.614
298.15	50.517	60.321	60.321	0.	−101.671	−101.953	17.862
300	50.671	60.634	60.322	0.094	−101.666	−101.954	17.752
400	89.203	79.060	62.567	6.597	−102.388	−102.086	13.331
411.000	95.051	81.559	63.042	7.610	ALPHA <--> BETA		
411.000	72.358	85.611	63.042	9.276	TRANSITION		
500	72.358	99.794	68.363	15.715	−100.050	−102.492	10.707
598.000	72.358	112.745	74.607	22.807	BETA <--> GAMMA		
598.000	62.085	113.409	74.607	23.204	TRANSITION		
600	62.030	113.617	74.736	23.328	−99.108	−103.033	8.970
700	59.808	122.999	80.982	29.412	−99.697	−103.645	7.734
800	58.560	130.893	86.740	35.322	−100.612	−104.151	6.800
900	58.286	137.765	92.036	41.156	−155.064	−103.437	6.003
1000	58.986	143.934	96.922	47.012	−155.812	−97.670	5.102
1100	60.662	149.627	101.457	52.986	−157.351	−91.766	4.358
1200	63.311	155.011	105.697	59.177	−158.138	−85.786	3.734
1300	66.935	160.216	109.692	65.681	−156.980	−79.802	3.206
1400	71.533	165.338	113.484	72.596	−155.509	−73.918	2.758
1463.000	74.930	168.560	115.786	77.208	--- GAMMA <--> LIQUID ---		
1500	77.106	170.458	117.111	80.020	−153.630	−68.153	2.373
1600	83.653	175.638	120.607	88.050	−151.243	−62.529	2.041
1700	91.174	180.930	123.999	96.783	−149.200	−57.054	1.753
1800	99.670	186.377	127.312	106.317	−145.839	−51.727	1.501
1900	109.140	192.016	130.568	116.749	−155.774	−45.906	1.262

PREVIOUS: CURRENT: September 1977

Iron Sulfide (FeS) LIQUID M_r = 87.907

$S°(298.15\ K) = [82.811]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-68.811]\ kJ·mol^{-1}$

$T_{fus} = 1463 \pm 3\ K$ $\Delta_{fus}H° = 31.464 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(FeS, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1463\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of liquid FeS above an assumed glass transition temperature of 1050 K is taken from Vaisburd and Zedina.[2] Their constant value of $C_p° = 14.95\ cal·K^{-1}·mol^{-1}$ is lower than $C_p° = 17.8\ cal·K^{-1}·mol^{-1}$ which we derive from the enthalpy data of Coughlin.[3] The latter value is based on two points separated by only 9 K while the results of Vaisburd and Zedina are quoted as covering the range from the mp to 1723 K. The heat capacity below the glass transition is that of the crystal.[1]

$S°$(FeS, l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted melting point of 1463 ± 3 K is taken from the phase diagram of Hansen and Anderko.[4] The adopted enthalpy of fusion, $\Delta_{fus}H° = 7.52 \pm 0.5\ kcal·mol^{-1}$, is from our analysis of the high temperature enthalpy data of Coughlin.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	50.517	82.811	82.811	0.	−68.811	−75.798	13.280
300	50.671	83.124	82.812	0.094	−68.806	−75.842	13.205
400	89.203	101.550	85.057	6.597	−69.528	−78.222	10.215
411.000	95.051	104.049	85.532	7.610	ALPHA <--> BETA		
411.000	72.358	108.100	85.532	9.276	TRANSITION		
500	72.358	122.284	90.853	15.715	−67.190	−80.877	8.449
598.000	72.358	135.235	97.096	22.807	BETA <--> GAMMA		
598.000	62.085	135.899	97.096	23.204	TRANSITION		
600	62.030	136.106	97.226	23.328	−66.248	−83.667	7.284
700	59.808	145.489	103.472	29.412	−66.837	−86.528	6.457
800	58.560	153.383	109.230	35.322	−67.752	−89.283	5.830
900	58.286	160.255	114.526	41.156	−122.204	−90.818	5.271
1000	58.986	166.424	119.412	47.012	−122.952	−87.300	4.560
1050.000	59.702	169.318	121.720	49.978	GLASS <--> LIQUID		
1050.000	62.551	169.318	121.720	49.978	TRANSITION		
1100	62.551	172.228	123.950	53.106	−124.372	−83.648	3.972
1200	62.551	177.670	128.203	59.361	−125.094	−79.933	3.479
1300	62.551	182.677	132.203	65.616	−124.185	−76.207	3.062
1400	62.551	187.313	135.976	71.871	−123.375	−72.548	2.707
1463.000	62.551	190.066	138.247	75.812	--- GAMMA <--> LIQUID ---		
1500	62.551	191.628	139.544	78.126	−122.664	−68.943	2.401
1600	62.551	195.665	142.927	84.381	−122.052	−65.382	2.134
1700	62.551	199.457	146.142	90.636	−122.487	−61.837	1.900
1800	62.551	203.033	149.204	96.891	−122.405	−58.273	1.691
1900	62.551	206.415	152.127	103.146	−136.518	−54.008	1.485
2000	62.551	209.623	154.922	109.401	−136.866	−49.656	1.297
2100	62.551	212.675	157.600	115.656	−137.226	−45.287	1.126
2200	62.551	215.585	160.170	121.911	−137.596	−40.900	0.971
2300	62.551	218.365	162.641	128.167	−137.975	−36.497	0.829
2400	62.551	221.027	165.018	134.422	−138.363	−32.076	0.698
2500	62.551	223.581	167.310	140.677	−138.759	−27.639	0.577
2600	62.551	226.034	169.522	146.932	−139.163	−23.187	0.466
2700	62.551	228.395	171.659	153.187	−139.572	−18.718	0.362
2800	62.551	230.670	173.726	159.442	−139.987	−14.235	0.266
2900	62.551	232.865	175.728	165.697	−140.408	−9.736	0.175
3000	62.551	234.985	177.668	171.952	−140.834	−5.223	0.091
3100	62.551	237.036	179.550	178.207	−141.265	−0.695	0.012
3200	62.551	239.022	181.378	184.462	−490.000	11.270	−0.184
3300	62.551	240.947	183.154	190.717	−488.538	26.912	−0.426
3400	62.551	242.814	184.881	196.972	−487.114	42.510	−0.653
3500	62.551	244.627	186.562	203.228	−485.727	58.067	−0.867
3600	62.551	246.389	188.200	209.483	−484.378	73.585	−1.068
3700	62.551	248.103	189.796	215.738	−483.069	89.066	−1.257
3800	62.551	249.771	191.352	221.993	−481.799	104.512	−1.437

PREVIOUS: CURRENT: September 1977

0	to	41	K	crystal, alpha
411	to	598	K	crystal, beta
598	to	1463	K	crystal, gamma
above		1463	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.413	−102.166	−102.166	INFINITE
100	26.670	17.216	99.528	−8.231	−102.096	−101.959	53.258
200	43.052	41.665	64.714	−4.610	−101.886	−101.901	26.614
298.15	50.517	60.321	60.321	0.	−101.671	−101.953	17.862
300	50.671	60.634	60.322	0.094	−101.666	−101.954	17.752
400	89.203	79.060	62.567	6.597	−102.388	−102.086	13.331
411.000	95.051	81.559	63.042	7.610	ALPHA <--> BETA		
411.000	72.358	85.611	63.042	9.276	TRANSITION		
500	72.358	99.794	68.363	15.715	−100.050	−102.492	10.707
598.000	72.358	112.745	74.607	22.807	BETA <--> GAMMA		
598.000	62.085	113.409	74.607	23.204	TRANSITION		
600	62.030	113.617	74.736	23.328	−99.108	−103.033	8.970
700	59.808	122.999	80.982	29.412	−99.697	−103.645	7.734
800	58.560	130.893	86.740	35.322	−100.612	−104.151	6.800
900	58.286	137.765	92.036	41.156	−155.064	−103.437	6.003
1000	58.986	143.934	96.922	47.012	−155.812	−97.670	5.102
1100	60.662	149.627	101.457	52.986	−157.351	−91.766	4.358
1200	63.311	155.011	105.697	59.177	−158.138	−85.786	3.734
1300	66.935	160.216	109.692	65.681	−156.980	−79.802	3.206
1400	71.533	165.338	113.484	72.596	−155.509	−73.918	2.758
1463.000	74.930	168.560	115.786	77.208	GAMMA <--> LIQUID		
1463.000	62.551	190.066	115.786	108.671	TRANSITION		
1500	62.551	191.628	117.638	110.986	−122.664	−68.943	2.401
1600	62.551	195.665	122.390	117.241	−122.052	−65.382	2.134
1700	62.551	199.457	126.813	123.496	−122.487	−61.837	1.900
1800	62.551	203.033	130.949	129.751	−122.405	−58.273	1.691
1900	62.551	206.415	134.832	136.006	−136.518	−54.008	1.485
2000	62.551	209.623	138.492	142.261	−136.866	−49.656	1.297
2100	62.551	212.675	141.953	148.516	−137.226	−45.287	1.126
2200	62.551	215.585	145.234	154.771	−137.596	−40.900	0.971
2300	62.551	218.365	148.354	161.026	−137.975	−36.496	0.829
2400	62.551	221.027	151.327	167.281	−138.363	−32.076	0.698
2500	62.551	223.581	154.166	173.537	−138.759	−27.639	0.577
2600	62.551	226.034	156.883	179.792	−139.163	−23.187	0.466
2700	62.551	228.395	159.489	186.047	−139.572	−18.718	0.362
2800	62.551	230.670	161.990	192.302	−139.987	−14.235	0.266
2900	62.551	232.865	164.397	198.557	−140.408	−9.736	0.175
3000	62.551	234.985	166.714	204.812	−140.834	−5.223	0.091
3100	62.551	237.036	168.950	211.067	−141.265	−0.695	0.012
3200	62.551	239.022	171.109	217.322	−490.000	11.270	−0.184
3300	62.551	240.947	173.196	223.577	−488.538	26.912	−0.426
3400	62.551	242.814	175.216	229.832	−487.114	42.510	−0.653
3500	62.551	244.627	177.174	236.087	−485.727	58.067	−0.867
3600	62.551	246.389	179.072	242.342	−484.378	73.585	−1.068
3700	62.551	248.103	180.915	248.597	−483.069	89.066	−1.257
3800	62.551	249.771	182.705	254.853	−481.799	104.512	−1.437

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 252.344 \pm 12.6\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 370.49 \pm 16.3\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 370.77 \pm 16.3\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
[0]	[9]	[20481.9]	[9]	[30716.2]	[5]
[436.2]	[7]	[21462.2]	[9]	[30857.8]	[7]
[738.9]	[5]	[21699.9]	[7]	[30886.4]	[9]
[932.4]	[3]	[21857.2]	[5]	[34812.4]	[1]
[1027.3]	[1]	[24558.8]	[11]	[35803.7]	[5]
[19404.8]	[5]	[24940.9]	[9]	[40999.9]	[5]
[20688.4]	[3]	[25142.4]	[7]	[42896.9]	[7]
[21208.5]	[1]	[30088.8]	[7]	[49148.0]	[1]
[20051.1]	[13]	[30356.2]	[13]	[49576.9]	[3]
[20300.8]	[11]	[30725.8]	[3]	[50412.3]	[5]

$\omega_e = 550\ cm^{-1}$ $\omega_e x_e = [2.8]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.198]\ cm^{-1}$ $\alpha_e = [0.0012]\ cm^{-1}$ $r_e = [2.05]$ Å

Enthalpy of Formation

Drowart *et al.*[1] used a modified Knudsen cell and a mass spectrometric technique to study the equilibrium FeS(g) + Mn(g) = MnS(g) + Fe(g). We adopt a value of $D_0° = 76.3 \pm 3.5\ kcal\cdot mol^{-1}$ based on their 3rd law analysis of this equilibrium. With auxiliary JANAF data[2] this yields $\Delta_f H°(298.15\ K) = 88.6 \pm 3.9\ kcal\cdot mol^{-1}$. Trevedi[3] studied the absorption spectrum of FeS and determined $D_0° = 93\ kcal\cdot mol^{-1}$ from the onset of continuous absorption due to photodissociation. This value is likely to be too high in view of the experimental difficulties in determining the exact position of the onset of continuous absorption. Complications arise because of background emission from the furnace. Marquardt and Berkowitz[4] determined an upper limit $D_0° < 77\ kcal\cdot mol^{-1}$ by mass-spectrometric meaurements. These results may be biased since they used $\nu = 412\ cm^{-1}$ for the vibrational frequency of FeS in determining their Gibbs energy functions. A Birge–Sponer extrapolation of the vibrational data to determine $D_0°$ is not meaningful since DeVore and Franzen[5] used the reverse procedure to arrive at the reported value of $\omega_e x_e$.

Heat Capacity and Entropy

With the exception of the observance of one excited state at 17992 cm^{-1} with a vibrational spacing of ~497 cm^{-1} by DeVore and Franzen,[5] there is no information on the electronic spectrum of FeS(g). The identity and quantum weight of this state, as well as the ground state, are unknown. As a result, the electronic states are estimated to be identical to those of the Fe^{2+} ion[6] following the procedure of Brewer and Rosenblatt[7] for the transition metal oxides. As stated by Brewer and Rosenblatt,[7] this procedure usually overestimates the contribution of electronic states. Nevertheless; it appears to be the best method available. The uncertainty assigned to $S°(298.15\ K)$ is based mainly on the uncertainties in this approximation since the presence of the sulfide ion will undoubtedly alter the electronic structure of the iron ion. Levels above 50,000 cm^{-1} are not included since they have a negligible effect on the thermodynamic properties. The vibrational constants are taken from a study of the matrix isolation spectrum by DeVore and Franzen.[5] The rotational constants are estimated based on an oxide–sulfide correlation due to Barrow and Cousins,[8] r(FeS) = 0.237 ± 1.116 r(FeO). The value r(FeO) = 1.626 Å is taken from Suchard.[9] The value of α_e is estimated assuming a Morse potential function using the expression given by Herzberg.[10]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.191	370.494	370.494	INFINITE
100	29.310	218.223	281.010	−6.279	372.294	352.331	−184.039
200	31.780	239.206	255.391	−3.237	371.925	332.401	−86.814
250	33.047	246.438	252.899	−1.615	371.390	322.579	−67.399
298.15	34.002	252.344	252.344	0.	370.767	313.234	−54.877
300	34.033	252.555	252.345	0.063	370.741	312.877	−54.477
350	34.775	257.860	252.762	1.784	370.010	303.289	−45.263
400	35.332	262.541	253.698	3.537	366.991	293.900	−38.379
450	35.756	266.728	254.917	5.315	365.446	284.847	−33.064
500	36.085	270.513	256.291	7.111	363.784	275.982	−28.832
600	36.554	277.137	259.229	10.745	360.747	258.710	−22.523
700	36.870	282.797	262.201	14.417	357.746	241.940	−18.054
800	37.095	287.736	265.091	18.116	354.619	225.607	−14.731
900	37.266	292.115	267.855	21.834	298.052	210.764	−12.232
1000	37.402	296.049	270.481	25.568	295.183	201.209	−10.510
1100	37.516	299.619	272.970	29.314	291.415	192.008	−9.118
1200	37.615	302.888	275.329	33.071	288.194	183.094	−7.970
1300	37.707	305.902	277.566	36.837	286.614	174.399	−7.007
1400	37.796	308.700	279.691	40.612	284.944	165.830	−6.187
1500	37.886	311.310	281.713	44.396	283.184	157.382	−5.481
1600	37.981	313.759	283.640	48.189	281.335	149.055	−4.866
1700	38.083	316.064	285.480	51.992	278.447	140.865	−4.328
1800	38.194	318.244	287.241	55.806	276.088	132.840	−3.855
1900	38.315	320.312	288.927	59.632	259.546	125.650	−3.454
2000	38.448	322.281	290.546	63.470	256.780	118.674	−3.099
2100	38.590	324.160	292.102	67.322	254.017	111.837	−2.782
2200	38.744	325.959	293.601	71.188	251.259	105.131	−2.496
2300	38.908	327.685	295.045	75.071	248.507	98.551	−2.238
2400	39.081	329.344	296.440	78.970	245.763	92.090	−2.004
2500	39.262	330.943	297.788	82.887	243.029	85.743	−1.791
2600	39.451	332.487	299.093	86.823	240.307	79.505	−1.597
2700	39.645	333.979	300.358	90.778	237.597	73.372	−1.419
2800	39.844	335.425	301.585	94.752	234.901	67.339	−1.256
2900	40.046	336.826	302.776	98.746	232.220	61.402	−1.106
3000	40.251	338.188	303.934	102.761	229.553	55.557	−0.967
3100	40.456	339.511	305.060	106.797	226.903	49.801	−0.839
3200	40.662	340.798	306.157	110.852	−124.031	51.554	−0.842
3300	40.866	342.053	307.226	114.929	−124.748	57.052	−0.903
3400	41.069	343.276	308.268	119.026	−125.482	62.572	−0.961
3500	41.270	344.469	309.286	123.143	−126.234	68.114	−1.017
3600	41.467	345.634	310.279	127.279	−127.003	73.678	−1.069
3700	41.659	346.773	311.250	131.436	−127.792	79.263	−1.119
3800	41.848	347.887	312.200	135.611	−128.602	84.870	−1.167
3900	42.031	348.976	313.129	139.805	−129.434	90.499	−1.212
4000	42.209	350.043	314.038	144.017	−130.290	96.149	−1.256
4100	42.382	351.087	314.929	148.247	−131.171	101.820	−1.297
4200	42.548	352.110	315.802	152.494	−132.080	107.514	−1.337
4300	42.709	353.113	316.658	156.756	−133.018	113.230	−1.375
4400	42.863	354.097	317.498	161.035	−133.987	118.968	−1.412
4500	43.011	355.062	318.322	165.329	−134.989	124.728	−1.448
4600	43.153	356.009	319.131	169.637	−136.025	130.511	−1.482
4700	43.288	356.938	319.926	173.959	−137.099	136.316	−1.515
4800	43.417	357.851	320.706	178.294	−138.211	142.145	−1.547
4900	43.540	358.748	321.474	182.642	−139.363	147.998	−1.578
5000	43.656	359.628	322.228	187.002	−140.559	153.875	−1.608
5100	43.767	360.494	322.970	191.373	−141.799	159.776	−1.636
5200	43.872	361.345	323.700	195.755	−143.087	165.701	−1.664
5300	43.971	362.182	324.418	200.148	−144.423	171.652	−1.692
5400	44.065	363.004	325.125	204.549	−145.811	177.629	−1.718
5500	44.153	363.814	325.821	208.960	−147.253	183.631	−1.744
5600	44.236	364.610	326.506	213.380	−148.751	189.661	−1.769
5700	44.314	365.394	327.182	217.807	−150.309	195.718	−1.794
5800	44.387	366.165	327.847	222.243	−151.928	201.803	−1.817
5900	44.456	366.924	328.503	226.685	−153.612	207.916	−1.841
6000	44.521	367.672	329.150	231.134	−155.364	214.058	−1.864

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 53.865 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -163.78 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -167.36 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Based on highly accurate adiabatic–shield calorimetry measurements, Gronvold and Westrum[1] reported that the enthalpy of transformation of marcasite to pyrite is -1.05 ± 0.05 kcal·mol^{-1} at 700 K. The adopted value of $\Delta_f H°(298.15\ K)$ is selected to reproduce this enthalpy of reaction within the reported uncertainty. Lipin *et al.*[2] based on combustion calorimetry, reported a value of -5.6 kcal·mol^{-1} for the marcasite pyrite transformation at 298.15 K. Due to the state of the art in combustion calorimetry at the time of this measurement and uncertainty in the products (oxides of sulfur), this value must have a high uncertainty and is given no weight in our selection process.

Heat Capacity and Entropy

The adopted heat capacities of marcasite are based on our analysis of the $C_p°$ measurements (6–700 K) of Gronvold and Westrum.[1] Values above 700 K are extrapolated assuming $C_p°$(marcasite) + 0.075 cal·K^{-1}·mol^{-1}.

The adopted value of $S°(298.15\ K)$ is obtained from the appropriate integration of the adopted $C_p°$ data assuming $S°(6.06\ K) = 0.0008$ cal·K^{-1}·mol^{-1}.

Phase Data

Marcasite has an orthorhombic structure, V_h^{12} = Pnmm, and exists as stoichiometric FeS_2 within the limits of experimental error.[3] Marcasite is known to be metastable with respect to the other known FeS_2 polymorph, cubic pyrite, above 673 K[3] the JANAF Thermochemical Tables[4] indicate it will also be metastable below 673 K. The marcasite to pyrite transformation is kinetically slow at low temperatures and this accounts for the persistence of marcasite in nature. Kjekshus and Rakke[5] found no conversion to pyrite using heat treatments at 573 K for periods up to 14 months. At 673 K the conversion to pyrite is complete in 4 months and is even more rapid (< 1 hour) at 973 K[5]. Indications are that the conversion to pyrite will be complete before the pyrite decomposition temperature of 1016 K is reached.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.753	−163.782	−163.782	INFINITE
100	19.269	7.576	99.375	−9.180	−165.012	−162.658	84.964
200	49.399	31.380	59.227	−5.569	−166.454	−159.685	41.705
298.15	62.390	53.865	53.865	0.	−167.360	−156.159	27.358
300	62.554	54.251	53.866	0.116	−167.375	−156.090	27.178
400	69.169	73.244	56.411	6.733	−172.579	−152.034	19.854
500	72.447	89.075	61.407	13.834	−176.187	−146.504	15.305
600	74.568	102.472	67.163	21.185	−179.092	−140.283	12.213
700	76.959	114.139	73.058	28.757	−181.539	−133.617	9.971
800	78.668	124.569	78.857	36.569	−183.764	−126.619	8.267
900	80.718	133.953	84.466	44.538	−292.337	−117.177	6.801
1000	82.764	142.563	89.851	52.712	−292.623	−97.707	5.104
1100	84.810	150.547	95.010	61.091	−293.630	−78.151	3.711
1200	86.860	158.014	99.952	69.674	−293.910	−58.568	2.549
1300	88.910	165.048	104.692	78.463	−292.370	−39.018	1.568
1400	90.960	171.712	109.243	87.456	−290.740	−19.589	0.731

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 52.916 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -167.86 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -171.54 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K) = -41.0 \pm 0.5\ kcal \cdot mol^{-1}$ is based on our 3rd law analysis of the equilibrium data of Toulmin and Barton.[1] These authors made corrections for the changing stoichiometry of pyrrhotite as a function of temperature in the pyrrhotite–pyrite equilibrium, and also accounted for the changing activity of pyrrhotite as a function of temperature and stoichiometry. These corrections have not been applied to our analysis of the rest of the equilibrium data shown below.

Source	Method	Reaction*	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Toulmin[1]	Electrum–tarnish	A	598– 1016	17**	−71.77 ± 0.12	71.89 ± 0.16	−0.15 ± 0.15	41.0 ± 0.5
DeRudder[2]	Manometric	B	873–962	7	−32.47 ± 1.27	−27.74 ± 0.43	5.17 ± 1.38	43.2 ± 0.6
Ugai[3]	Gravimetric	B	923–1016	equation	−16.70	−26.81 ± 0.93	−10.28	36.0
DeRanter[4]	emf	C	298.15	1		−36.00		42.3 ± 1.0
Schneeberg[5]	emf	B	597–711	4	−28.98 ± 1.10	28.16 ± 0.26	1.26 ± 1.68	43.6 ± 0.5
Rosenqvist[6]	Dew point	B	869–1030	22	−34.03 ± 1.22	−28.04 ± 0.63	6.35 ± 1.29	43.5 ± 0.7

**Point at 1009 K rejected by statistical test.

*Reaction: (A) $Fe(cr) + S_2(g) \rightarrow FeS_2$(cr, pyrite)

(B) $1.14\ Fe_{0.877}S(cr) + 0.43\ S_2(g) \rightarrow FeS_2$(cr, pyrite)

(C) $Fe(cr) + 2\ S(cr) \rightarrow FeS_2$(cr, pyrite).

The value reported by DeRanter[4] is biased since FeS_2 is a semiconductor and DeRanter acknowledged that semiconductors lead to incorrect results in his emf technique. The other values are believed to be biased because the equilibrium is treated as if the composition ($Fe_{0.877}S$) and activity (a=1) of pyrrhotite remain unchanged.

Heat Capacity and Entropy

The adopted values of $C_p°$ are based on our analysis of the calorimetrically measured values of Gronvold and Westrum, 4–346 K[7] and 314–688 K.[8] At higher temperatures the $C_p°$ values are based on our analysis of the enthalpy data of Coughlin,[9] 405–980 K, which merges smoothly with the $C_p°$ data of Gronvold and Westrum. Values above 980 K are extrapolated.

The adopted value of $S°(298.15\ K)$ is obtained from the appropriate integration of the adopted $C_p°$ data assuming $S°(4.6\ K) = 0.0007\ cal \cdot K^{-1} \cdot mol^{-1}$.

Phase Data

Pyrite has a cubic structure, T_h^6 = Pa3, and exits as stoichiometric FeS_2 within the limits of experimental error.[10] The other known FeS_2 polymorph is orthorhombic marcasite which is known to be metastable with respect to pyrite above 673 K[10] the JANAF Thermochemical Tables[11] indicate that pyrite will also be the stable form below 673 K.

Decomposition Data

Pyrite melts incongruently to pyrrhotite, a liquid whose composition is ~FeS_4[3] and vapor at 1016 ± 2 K at the vapor pressure of the system, 10 atm.[3,10] Assuming the vapor to be composed only of $S_2(g)$, we calculate[11] a decomposition temperature of 906 K at 1 atm for the process $2.3263\ FeS_2$(pyrite) $\rightarrow S_2(g) + 2.6525\ Fe_{0.87}S$(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.641	−167.855	−167.855	INFINITE
100	18.712	7.091	98.120	−9.103	−169.119	−166.717	87.084
200	49.056	30.556	58.251	−5.539	−170.607	−163.674	42.747
298.15	62.124	52.916	52.916	0.	−171.544	−160.060	28.042
300	62.289	53.301	52.918	0.115	−171.559	−159.989	27.857
400	68.848	72.213	55.451	6.705	−176.792	−155.835	20.350
500	72.040	87.953	60.425	13.764	−180.441	−150.197	15.691
600	74.307	101.295	66.152	21.086	−183.375	−143.860	12.524
700	76.308	112.899	72.019	28.616	−185.865	−137.074	10.229
800	78.354	123.222	77.786	36.349	−188.169	−129.946	8.485
900	80.404	132.569	83.362	44.287	−296.773	−120.367	6.986
1000	82.450	141.146	88.717	52.429	−297.090	−100.757	5.263
1100	84.496	149.101	93.849	60.777	−298.128	−81.058	3.849
1200	86.546	156.541	98.767	69.329	−298.440	−61.329	2.670
1300	88.592	163.549	103.483	78.086	−296.931	−41.630	1.673
1400	90.642	170.189	108.012	87.047	−295.333	−22.051	0.823

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K)$ = [543.471] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 9.75 ± 20.9 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 8.37 ± 20.9 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[5]
[4200]	[5]
[6800]	[5]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[100](1)	[70](1)	[80](2)
[50](1)	[90](1)	[20](2)
[95](1)	[105](1)	[160](2)

Point Group: $[D_{2h}]$ σ = 4
Bond Distance: Fe–I = [2.43] Å
Bond Angles: $I–Fe–I_{bridge}$ = [135]° $Fe–I_{bridge}–Fe$ = [90]° $I_{bridge}–Fe–I_{bridge}$ = [90]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [8.778988 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

The chemical equilibrium of the interaction of Fe(cr) and I(g) has been studied by a transpiration method by Zaugg and Gregory.[1] Using the reported equilibrium constants in the temperature range from 591 to 751 K, the enthalpy change $\Delta_f H°(298.15\ K)$ of the reaction 2Fe(cr) + 4I(g) = $Fe_2I_4(g)$ was evaluated by both the 2nd and 3rd law method to be −85.3 and −103.75 $kcal·mol^{-1}$, respectively. The corresponding values of the enthalpy of formation, $\Delta_f H°(Fe_2I_4, g, 298.15\ K)$, are calculated as +16.9 and −1.6 $kcal·mol^{-1}$. Mass spectrometric and Knudsen effusion techniques have been used to study the vaporization of $FeI_2(cr)$ by Schoonmaker *et al.*[2] Using the reported vapor pressure, $p = 1.21 \times 10^{-6}$ atm at 714 K for $Fe_2I_4(g)$, the enthalpy change $\Delta_r H°(298.15\ K)$ for the reaction $2FeI_2(cr) = Fe_2I_4(g)$ was evaluated by the 3rd law method as 52.8 $kcal·mol^{-1}$, yielding $\Delta_f H°(298.15\ K)$ = 2.8 $kcal·mol^{-1}$ for $Fe_2I_4(g)$.

The adopted value of $\Delta_f H°(298.15\ K)$ for $Fe_2I_4(g)$ is 2.0 ± 5 $kcal·mol^{-1}$ (8.368 ± 20.9 $kJ·mol^{-1}$).

Heat Capacity and Entropy

The molecular structure was assumed to be the same as that for $Fe_2Br_4(g)$. The Fe–I bond distance was estimated from that in $FeI_2(g)$ molecule. Four vibrational frequencies (ν_i), i.e. i = 2, 4, 5 and 6, were estimated by comparison with those for $K_2I_2(g)$, calculated by Berkowitz.[3] The other frequency values were estimated from those for $FeI_2(g)$. The electronic levels and quantum weights were estimated from those for $FeI_2(g)$. The principal moments of inertia are: $I_A = 124.4358 \times 10^{-39}$, $I_B = 780.0258 \times 10^{-39}$, and $I_C = 904.4616 \times 10^{-39}$ $g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−34.030	9.747	9.747	INFINITE
100	119.470	404.580	658.433	−25.385	11.447	−15.600	8.149
200	129.233	491.411	555.431	−12.804	10.625	−42.494	11.098
250	130.564	520.408	545.629	−6.305	9.593	−55.661	11.630
298.15	131.283	543.471	543.471	0.	8.368	−68.121	11.935
300	131.304	544.284	543.474	0.243	8.316	−68.596	11.944
350	131.756	564.561	545.074	6.820	6.698	−81.293	12.132
400	132.052	582.175	548.635	13.416	−27.043	−92.647	12.098
450	132.258	597.741	553.243	20.024	−31.296	−100.593	11.676
500	132.409	611.684	558.402	26.641	−115.916	−100.461	10.495
600	132.629	635.845	569.357	39.893	−116.344	−97.338	8.474
700	132.820	656.305	580.354	53.166	−117.258	−94.105	7.022
800	133.038	674.054	590.981	66.458	−118.753	−90.704	5.922
900	133.308	689.739	601.100	79.775	−121.074	−87.069	5.053
1000	133.635	703.800	610.679	93.122	−124.826	−83.108	4.341
1100	134.013	716.555	619.733	106.504	−130.359	−78.640	3.734
1200	134.430	728.233	628.295	119.926	−134.783	−73.781	3.212
1300	134.872	739.010	636.402	133.391	−135.917	−68.653	2.759
1400	135.325	749.022	644.093	146.900	−137.235	−63.431	2.367
1500	135.774	758.374	651.404	160.455	−138.756	−58.107	2.023
1600	136.209	767.150	658.366	174.055	−140.500	−52.675	1.720
1700	136.620	775.421	665.011	187.696	−144.386	−47.089	1.447
1800	137.001	783.240	671.364	201.378	−147.300	−41.283	1.198
1900	137.347	790.657	677.449	215.095	−178.679	−33.904	0.932
2000	137.655	797.710	683.287	228.846	−182.614	−26.182	0.684
2100	137.924	804.433	688.897	242.625	−186.656	−18.262	0.454
2200	138.153	810.855	694.296	256.429	−190.797	−10.147	0.241
2300	138.345	817.000	699.498	270.254	−195.027	−1.841	0.042
2400	138.500	822.891	704.518	284.097	−199.330	6.651	−0.145
2500	138.621	828.548	709.367	297.953	−203.686	15.322	−0.320
2600	138.710	833.987	714.056	311.820	−208.077	24.170	−0.486
2700	138.771	839.223	718.595	325.694	−212.481	33.186	−0.642
2800	138.806	844.270	722.994	339.573	−216.879	42.365	−0.790
2900	138.817	849.141	727.260	353.455	−221.251	51.701	−0.931
3000	138.808	853.847	731.402	367.336	−225.581	61.187	−1.065
3100	138.782	858.398	735.426	381.216	−229.853	70.817	−1.193
3200	138.740	862.804	739.338	395.092	−930.654	95.431	−1.558
3300	138.685	867.072	743.144	408.963	−930.973	127.501	−2.018
3400	138.618	871.212	746.850	422.829	−931.267	159.580	−2.452
3500	138.543	875.229	750.461	436.687	−931.529	191.668	−2.860
3600	138.459	879.130	753.981	450.537	−931.758	223.762	−3.247
3700	138.369	882.923	757.415	464.378	−931.950	255.863	−3.612
3800	138.275	886.612	760.767	478.211	−932.106	287.969	−3.958
3900	138.176	890.202	764.040	492.033	−932.225	320.078	−4.287
4000	138.074	893.699	767.238	505.846	−932.311	352.189	−4.599
4100	137.970	897.107	770.364	519.648	−932.365	384.302	−4.896
4200	137.865	900.431	773.421	533.440	−932.392	416.416	−5.179
4300	137.760	903.674	776.413	547.221	−932.396	448.531	−5.449
4400	137.654	906.839	779.341	560.992	−932.380	480.645	−5.706
4500	137.549	909.932	782.209	574.752	−932.351	512.759	−5.952
4600	137.444	912.954	785.019	588.501	−932.312	544.872	−6.187
4700	137.340	915.909	787.772	602.241	−932.270	576.984	−6.412
4800	137.238	918.799	790.472	615.969	−932.230	609.096	−6.628
4900	137.137	921.628	793.120	629.688	−932.197	641.207	−6.835
5000	137.038	924.397	795.718	643.397	−932.178	673.316	−7.034
5100	136.941	927.110	798.268	657.096	−932.178	705.427	−7.225
5200	136.845	929.768	800.771	670.785	−932.204	737.537	−7.409
5300	136.752	932.374	803.230	684.465	−932.260	769.647	−7.585
5400	136.661	934.929	805.645	698.136	−932.354	801.760	−7.755
5500	136.572	937.436	808.018	711.797	−932.492	833.874	−7.919
5600	136.486	939.896	810.351	725.450	−932.681	865.992	−8.078
5700	136.401	942.311	812.645	739.094	−932.927	898.113	−8.230
5800	136.319	944.683	814.902	752.730	−933.238	930.239	−8.378
5900	136.239	947.012	817.121	766.358	−933.621	962.371	−8.520
6000	136.161	949.301	819.305	779.978	−934.083	994.510	−8.658

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

Iron Oxide, Hematite (Fe_2O_3) CRYSTAL M_r = 159.6922

$S°(298.15\ K) = 87.400\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -819.03 \pm 1.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -825.50 \pm 1.3\ kJ·mol^{-1}$

Enthalpy of Formation

The chemical equilibria for the reaction 4 Fe_3O_4(cr) + O_2(g) = 6 Fe_2O_3(cr) have been studied by several investigators. From the reported data the corresponding values of $\Delta_r H°(298.15\ K)$ and $\Delta_f H°(Fe_2O_3, cr, 298.15\ K)$ were evaluated. The results obtained are given as follows:

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Tretyakov and Khomyakov[1]	1373–1728	−106.32 ± 0.19	−111.05	−197.11
Schmahl[2]	1583–1683	−123.95 ± 1.37	−112.94	−197.42
Smiltens[3]	1373–1673	−117.88 ± 0.38	−114.25	−197.64
Darken and Gurry[4]	1723	−110.29		196.98

The value of $\Delta_f H°(298.15\ K)$ adopted for Fe_2O_3(cr) is the weighted average of the $\Delta_f H°(298.15\ K)$ values listed in the above table.

Heat Capacity and Entropy

The low temperature (5.58–345.42 K) heat capacities were determined by Gronvold and Westrum).[5] The high temperature (298–1750 K) $C_p°$ values were obtained from Coughlin *et al.*[6] The two sets of data were plotted and joined smoothly at 298 K. The $C_p°$ values above 1750 K were obtained by graphical extrapolation. The heat capacities of Fe_2O_3(cr) have also been reported by Brown and Furnas (0–650 °C),[7] and Parks and Kelley (88 289 K).[8] $S°(298.15\ K)$ for Fe_2O_3(cr) was derived from the smoothed $C_p°$ data, based on $S°(5\ K) = 0.0003\ calK^{-1}·mol^{-1}$. Coughlin *et al.*[6] measured the enthalpy for hematite and found two anomalies, presumably of megnetic nature, at about 950 and 1050 K, respectively. Both appear to involve maxima in the heat capacity curves rather than isothermal heats of transformation. The complex magnetic properties at low temperatures were discussed by Gronvold and Westrum.[5] No heat capacity anomaly was observed at the magnetic transition about 250 K. The Curie points of the antiferromagnetic α Fe_2O_3 were reported by Aharoni *et al.*[9] and Lielmezs and Chaklader.[10]

Decomposition Data

T_{dcm} = 1735 K is the temperature at which the pressure is 1 atm for the reaction 6 Fe_2O_3(cr) = 4 Fe_3O_4(cr) + O_2(g). In other words, Fe_2O_3(cr) decomposes into Fe_3O_4(cr) and O_2(g) at 1735 K.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}mol^{-1}	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.560	−819.025	−819.025	INFINITE
100	31.497	14.611	159.795	−14.518	−823.186	−797.438	416.539
200	76.567	51.279	96.132	−8.970	−825.542	−770.573	201.253
298.15	103.763	87.400	87.400	0.	−825.503	−743.523	130.262
300	104.182	88.043	87.402	0.192	−825.485	−743.014	129.370
400	120.123	120.299	91.691	11.443	−823.947	−715.727	93.464
500	131.796	148.400	100.284	24.058	−821.626	−688.929	71.972
600	141.168	173.270	110.415	37.713	−818.882	−662.642	57.688
700	149.729	195.675	121.020	52.259	−815.870	−636.837	47.521
800	158.218	216.225	131.653	67.658	−812.705	−611.477	39.925
900	166.490	235.340	142.124	83.894	−809.634	−586.510	34.040
950.000	170.570	244.451	147.271	92.321		I <--> II	
950.000	150.624	245.156	147.271	92.990		TRANSITION	
1000	150.624	252.882	152.360	100.522	−807.695	−561.866	29.349
1050.000	150.624	260.231	157.323	108.053		II <--> III	
1050.000	140.407	260.231	157.323	108.053		TRANSITION	
1100	140.775	266.771	162.150	115.083	−809.682	−537.171	25.508
1200	141.511	279.052	171.388	129.197	−811.071	−512.374	22.303
1300	142.248	290.408	180.112	143.385	−809.145	−487.562	19.590
1400	142.984	300.976	188.372	157.647	−807.358	−462.893	17.271
1500	143.720	310.866	196.212	171.982	−805.706	−438.347	15.265
1600	144.566	320.170	203.671	186.397	−804.180	−413.906	13.513
1700	145.266	328.956	210.785	200.890	−804.681	−389.520	11.968
1800	145.780	337.275	217.583	215.445	−804.094	−365.117	10.595
1900	146.231	345.169	224.092	230.045	−831.859	−339.338	9.329
2000	146.789	352.684	230.335	244.696	−832.056	−313.410	8.185
2100	147.277	359.858	236.334	259.400	−832.235	−287.474	7.151
2200	147.695	366.719	242.105	274.149	−832.403	−261.528	6.209
2300	148.044	373.292	247.667	288.937	−832.566	−235.576	5.350
2400	148.323	379.599	253.034	303.756	−832.731	−209.617	4.562
2500	148.532	385.658	258.219	318.599	−832.905	−183.650	3.837

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = [307.524 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -2582.99 \pm 1.67\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy change, $\Delta_r H°(298.15\ K)$, for the chemical reaction $Fe_2O_3(cr) + 3(H_2SO_4 \cdot 14.855\ H_2O)(sol.) = Fe_2(SO_4)_3(cr) + 47.565\ H_2O(l)$ was measured to be $8.54 + 0.18\ kcal \cdot mol^{-1}$ by solution calorimetry by Barany and Adami.[1] Using $\Delta_f H°(298.15\ K) = -211.178\ kcal \cdot mol^{-1}$ for $H_2SO_4 \cdot 14.855\ H_2O$(sol.) and $-68.315\ kcal \cdot mol^{-1}$ for H_2O(l), obtained from and $-197.3\ kcal \cdot mol^{-1}$ for Fe_2O_3(cr), the enthalpy of formation, $\Delta_f H°(298.15\ K)$, for $Fe_2(SO_4)_3$(cr) was evaluated as $-617.35 \pm 0.40\ kcal \cdot mol^{-1}$ which was adopted here.

The equilibrium pressures for the decomposition of $Fe_2(SO_4)_3$(cr) have been determined by several investigators at different temperatures. The chemical reactions are: (1) $Fe_2(SO_4)_3(cr) = Fe_2O_3(cr) + 3\ SO_3(g)$ and (2) $SO_3(g) = SO_2(g) + 0.5\ O_2(g)$. However, the measured pressure of the chemical equilibrium is the total pressure of three partial pressures, namely, $P(SO_3)$, $P(SO_2)$, and $P(O_2)$. In order to calculate the enthalpy change of Reaction (1), the partial pressures of SO_3(g) were evaluated from the total vapor pressure data at each temperature. Based on the derived values for $P(SO_3)$, the $\Delta_r H°(298.15\ K)$ value for Reaction (1) was calculated by both the 2nd and 3rd law methods. The results obtained are presented in the following table. The $\Delta_f H°(Fe_2(SO_4)_3$, cr, 298.15 K) values were derived, using the 3rd law $\Delta_r H°(298.15\ K)$. These determinations were not given any weight.

Source	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Keppeler and D'Ans[3]	753.15–1013.15	136.8 ± 0.5	139.9 ± 0.5	3.4 ± 0.6	−621.0
Wohler, *et al.*[4]	826.15– 980.15	114.2 ± 6.2	133.1 ± 2.3	19.2 ± 6.9	−614.2
Bodenstein and Suzuki[5]	903.65– 997.15	140.7 ± 6.6	139.1 ± 1.3	−1.2 ± 7.1	−620.2
Wohler and Grunzweig[6]	909.15– 994.15	155.1 ± 1.3	135.5 ± 1.3	−20.4 ± 1.4	−616.6
Neumann and Heintke[7]	793.15– 973.15	136.4 ± 2.3	136.2 ± 1.2	−1.2 ± 2.6	−617.3
Warner and Ingraham[8]	903.15– 997.15	133.9 ± 2.6	135.4 ± 0.5	1.7 ± 2.7	−616.5

The decomposition pressures of $Fe_2(SO_4)_3$(cr) have also been investigated by: Grunzweig (793–994 K),[9] Blanks (845–976 K),[10] and Ingraham (856–995 K).[11] These data together with some of the data mentioned previously were critically reviewed by Kellogg.[12]

Heat Capacity and Entropy

The heat capacities were estimated by comparison with those for $FeSO_4$(cr), assuming their average specific heats, $cal \cdot K^{-1} \cdot g^{-1}$, to be the same. The value of $S°(298.15\ K)$ was estimated so that the 2nd and 3rd law $\Delta_r H°(298.15\ K)$ values, derived from decomposition pressure data, are in reasonable agreement.

Decomposition Data

T_{dcm} is the temperature (1451 K) at which the total pressure of the gaseous products equals one atmosphere, which was obtained by graphical extrapolation of the decomposition pressure data measured by Warner and Ingraham.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	264.722	307.524	307.524	0.	−2582.992	−2262.729	396.421
300	265.851	309.165	307.529	0.491	−2583.047	−2260.742	393.630
400	307.022	391.497	318.475	29.209	−2591.203	−2152.742	281.119
500	339.281	463.626	340.441	61.593	−2594.662	−2042.719	213.401
600	363.297	527.707	366.413	96.776	−2595.362	−1932.225	168.215
700	380.702	585.079	393.626	134.017	−2594.341	−1821.767	135.942
800	393.254	636.776	420.843	172.746	−2592.496	−1711.521	111.751
900	402.041	683.617	447.479	212.524	−2749.978	−1598.273	92.761
1000	409.237	726.359	473.261	253.098	−2745.239	−1470.576	76.815
1100	415.262	765.651	498.080	294.328	−2741.963	−1343.236	63.785
1200	420.659	802.019	521.912	336.128	−2737.297	−1216.322	52.945
1300	425.513	835.884	544.776	378.441	−2729.077	−1089.907	43.793
1400	429.906	867.580	566.714	421.214	−2720.794	−964.127	35.972
1500	434.090	897.385	587.775	464.415	−2712.461	−838.943	29.215
1600	438.065	925.528	608.013	508.025	−2704.089	−714.314	23.320
1700	441.830	952.199	627.482	552.020	−2697.589	−590.172	18.134
1800	445.554	977.560	646.232	596.391	−2689.835	−466.432	13.536
1900	449.069	1001.744	664.311	641.121	−2710.265	−341.717	9.394
2000	452.625	1024.868	681.765	686.206	−2702.965	−217.244	5.674

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 145.266\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1870 \pm 2\ K$

$\Delta_f H°(0\ K) = -1114.58 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1120.89 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = 138.070 \pm 8.4\ kJ·mol^{-1}$

Enthalpy of Formation

The equilibrium constants for the following four reactions, i.e. (A) $3Fe(cr) + 4H_2O(g) = Fe_3O_4(cr) + 4H_2(g)$; (B) $Fe_3O_4(cr) + H_2(g) = 3FeO(cr) + H_2O(g)$; (C) $Fe_3O_4(cr) + CO(g) = 3FeO(cr) + CO_2(g)$; and (D) $2Fe_3O_4(cr) = 6FeO(cr) + O_2(g)$, have been studied by several investigators. Using their reported equilibrium data, the corresponding enthalpy changes, $\Delta_r H°(298.15\ K)$, were evaluated by both 2nd and 3rd law methods. Based on the 3rd law value for $\Delta_r H°(298.15\ K)$, the respective $\Delta_f H°(298.15\ K)$ values for $Fe_3O_4(cr)$ were also derived. The results obtained are presented as follows.

Source	Reactions	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Fricke, *et al.*[1]	A	633.2–823.2	−29.68 ± 1.30	−36.91	−268.10
Eastman[2]	B	873.2–1273.2	22.41 ± 0.09	19.29	−268.01
Eastman and Evans[3]	B	973.2–1273.2	21.56 ± 0.07	18.54	−267.26
Emmett and Shultz[4]	B	973.2–1073.2	—	19.18	−267.90
Eastman[2]	C	873.2–1273.2	11.87 ± 0.03	9.38	−267.93
Eastman and Evans[3]	C	973.2–1273.2	11.63 ± 0.03	9.38	−267.94
Salmon[5]	D	1473.2–1673.2	—	153.73	−267.79

The enthalpy change of the reaction $Fe_{0.947}0(cr) + 0.8215\ Fe(cr) + 0.6787\ O_2(g) = 0.5895\ Fe_3O_4(cr)$ has been determined by Humphrey *et al.*[6] Based on $\Delta_r H°(298.15\ K) = -93.46\ kcal·mol^{-1}$ (average of two separate values derived from two experimental determinations) and $\Delta_f H°(wustite, cr, 298.15\ K) = -63.64\ kcal·mol^{-1}$, the value $\Delta_f H°(Fe_3O_4, cr, 298.15\ K)$ was calculated as $-266.5\ kcal·mol^{-1}$. The enthalpy change, $\Delta_r H°(298.15\ K) = 4.33\ kcal·mol^{-1}$, for the reaction $3Fe(cr) + 4CO_2(g) = Fe_3O_4(cr) + 4CO(g)$ was reported by Darken and Gurry.[7] The corresponding $\Delta_f H°(Fe_3O_4, cr, 298.15\ K)$ was evaluated as $-266.22\ kcal·mol^{-1}$. The adopted value of $\Delta_f H°(298.15\ K)$ for $Fe_3O_4(cr)$ is selected as $-267.9 \pm 0.2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The low temperature heat capacities (60.5–299.7 K) were reported by Millar.[8] The high temperature heat capacities (298–1800 K) were obtained from Coughlin *et al.*[9] These two sets of data were plotted and joined smoothly at 298.15 K. The $C_P°$ values above 1800 K were obtained by graphical extrapolation. Heat capacities (90–295 K) for $Fe_3O_4(cr)$ were also reported by Parks and Kelley.[10] $S°(Fe_3O_4, cr, 298.15\ K)$ was derived from the smoothed $C_p°$ data mentioned previously, using $S°(44.7\ K) = 0.969\ cal·K^{-1}·mol^{-1}$. Coughlin *et al.*[9] measured the heat–content for magnetite and found a magnetic anomaly around 880 K, corresponding to a maximum in heat capacity. A maximum heat capacity of 37.1 $cal·K^{-1}·mol^{-1}$ at 114.15 K was also reported by Millar.[8]

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were obtained from Darken and Gurry.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−24.571	−1114.579	−1114.579	INFINITE
100	56.335	27.611	254.203	−22.659	−1119.743	−1086.024	567.281
114.150	155.535	37.694	226.660	−21.570	____ C_p LAMBDA MAXIMUM ____		
114.150	155.279	37.698	226.660	−21.570	TRANSITION		
200	116.945	92.367	157.872	−13.101	−1121.314	−1051.624	274.656
298.15	147.235	145.266	145.266	0.	−1120.894	−1017.438	178.251
300	147.695	146.179	145.269	0.273	−1120.869	−1016.797	177.040
400	171.126	191.952	151.352	16.240	−1118.728	−982.386	128.286
500	192.380	232.441	163.593	34.424	−1115.219	−948.681	99.108
600	212.547	269.299	178.181	54.671	−1110.550	−915.794	79.727
700	232.714	303.578	193.672	76.934	−1104.774	−883.776	65.948
800	252.881	335.969	209.452	101.214	−1098.011	−852.657	55.673
900	273.050	366.919	225.241	127.510	−1090.611	−822.428	47.732
900.000	273.050	366.919	225.241	127.511	____ C_p LAMBDA MAXIMUM ____		
900.000	200.832	366.919	225.241	127.511	TRANSITION		
1000	200.832	388.079	240.485	147.594	−1091.694	−792.602	41.401
1100	200.832	407.220	254.786	167.677	−1095.556	−762.463	36.206
1200	200.832	424.695	268.228	187.760	−1097.841	−732.139	31.869
1300	200.832	440.770	280.890	207.843	−1095.254	−701.771	28.197
1400	200.832	455.653	292.848	227.927	−1092.980	−671.590	25.057
1500	200.832	469.509	304.169	248.010	−1091.011	−641.562	22.341
1600	200.832	482.471	314.912	268.093	−1089.346	−611.654	19.968
1700	200.832	494.646	325.131	288.176	−1090.831	−581.785	17.876
1800	200.832	506.125	334.870	308.259	−1090.769	−551.846	16.014
1900	200.832	516.984	344.172	328.343	−1133.299	−519.794	14.290
2000	200.832	527.285	353.072	348.426	−1134.548	−487.472	12.731
2100	200.832	537.084	361.603	368.509	−1135.843	−455.087	11.320
2200	200.832	546.426	369.793	388.592	−1137.183	−422.637	10.035
2300	200.832	555.354	377.669	408.675	−1138.568	−390.128	8.860
2400	200.832	563.901	385.252	428.759	−1139.998	−357.557	7.782
2500	200.832	572.099	392.563	448.842	−1141.472	−324.925	6.789
2600	200.832	579.976	399.620	468.925	−1142.988	−292.234	5.871
2700	200.832	587.556	406.441	489.008	−1144.547	−259.482	5.020
2800	200.832	594.859	413.041	509.091	−1146.146	−226.673	4.229
2900	200.832	601.907	419.433	529.175	−1147.786	−193.807	3.491
3000	200.832	608.715	425.629	549.258	−1149.464	−160.882	2.801

PREVIOUS: CURRENT: June 1965

Continued from page 1241

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REFERENCE STATE

0	to	302.920	K	crystal
302.92	to	2476.570	K	liquid
above		2476.570	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.561	0.	0.	0.
100	18.484	16.085	62.261	−4.618	0.	0.	0.
200	23.815	30.912	43.151	−2.448	0.	0.	0.
298.15	26.064	40.838	40.838	0.	0.	0.	0.
300	26.091	41.000	40.839	0.048	0.	0.	0.
302.920	26.133	41.253	40.842	0.124	___ CRYSTAL <--> LIQUID ___		
302.920	28.493	59.706	40.842	5.714	TRANSITION		
400	27.154	67.426	46.408	8.407	0.	0.	0.
500	26.819	73.445	51.237	11.104	0.	0.	0.
600	26.694	78.324	55.358	13.780	0.	0.	0.
700	26.568	82.428	58.939	16.442	0.	0.	0.
800	26.568	85.976	62.102	19.099	0.	0.	0.
900	26.568	89.105	64.932	21.756	0.	0.	0.
1000	26.568	91.904	67.492	24.413	0.	0.	0.
1100	26.568	94.436	69.828	27.069	0.	0.	0.
1200	26.568	96.748	71.976	29.726	0.	0.	0.
1300	26.568	98.875	73.965	32.383	0.	0.	0.
1400	26.568	100.844	75.815	35.040	0.	0.	0.
1500	26.568	102.677	77.546	37.697	0.	0.	0.
1600	26.568	104.391	79.171	40.354	0.	0.	0.
1700	26.568	106.002	80.702	43.010	0.	0.	0.
1800	26.568	107.521	82.150	45.667	0.	0.	0.
1900	26.568	108.957	83.524	48.324	0.	0.	0.
2000	26.568	110.320	84.830	50.981	0.	0.	0.
2100	26.568	111.616	86.075	53.638	0.	0.	0.
2200	26.568	112.852	87.264	56.295	0.	0.	0.
2300	26.568	114.033	88.402	58.951	0.	0.	0.
2400	26.568	115.164	89.494	61.608	0.	0.	0.
2476.570	26.568	115.998	90.301	63.643	___ LIQUID <--> IDEAL GAS ___		
2476.570	21.260	220.462	90.301	322.353	FUGACITY = 1 bar		
2500	21.251	220.662	91.522	322.851	0.	0.	0.
2600	21.215	221.495	96.505	324.974	0.	0.	0.
2700	21.184	222.295	101.149	327.094	0.	0.	0.
2800	21.156	223.065	105.489	329.211	0.	0.	0.
2900	21.131	223.807	109.556	331.325	0.	0.	0.
3000	21.109	224.523	113.377	333.437	0.	0.	0.
3100	21.090	225.214	116.973	335.547	0.	0.	0.
3200	21.073	225.884	120.366	337.655	0.	0.	0.
3300	21.059	226.532	123.574	339.762	0.	0.	0.
3400	21.047	227.160	126.611	341.867	0.	0.	0.
3500	21.036	227.770	129.493	343.971	0.	0.	0.
3600	21.029	228.363	132.231	346.075	0.	0.	0.
3700	21.023	228.939	134.837	348.177	0.	0.	0.
3800	21.020	229.500	137.321	350.279	0.	0.	0.
3900	21.018	230.045	139.691	352.381	0.	0.	0.
4000	21.020	230.578	141.957	354.483	0.	0.	0.
4100	21.024	231.097	144.125	356.585	0.	0.	0.
4200	21.030	231.603	146.202	358.688	0.	0.	0.
4300	21.040	232.098	148.193	360.791	0.	0.	0.
4400	21.052	232.582	150.106	362.896	0.	0.	0.
4500	21.068	233.055	151.944	365.002	0.	0.	0.
4600	21.087	233.519	153.712	367.110	0.	0.	0.
4700	21.109	233.972	155.415	369.219	0.	0.	0.
4800	21.135	234.417	157.056	371.332	0.	0.	0.
4900	21.165	234.853	158.640	373.446	0.	0.	0.
5000	21.198	235.281	160.168	375.565	0.	0.	0.
5100	21.236	235.701	161.645	377.686	0.	0.	0.
5200	21.278	236.114	163.073	379.812	0.	0.	0.
5300	21.324	236.520	164.455	381.942	0.	0.	0.
5400	21.375	236.919	165.793	384.077	0.	0.	0.
5500	21.431	237.312	167.090	386.217	0.	0.	0.
5600	21.491	237.698	168.348	388.363	0.	0.	0.
5700	21.556	238.079	169.568	390.515	0.	0.	0.
5800	21.625	238.455	170.752	392.674	0.	0.	0.
5900	21.700	238.825	171.903	394.841	0.	0.	0.
6000	21.780	239.190	173.021	397.015	0.	0.	0.

PREVIOUS: CURRENT: June 1983 (1 bar)

$S°(298.15\ K) = 40.838 \pm 0.20\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 302.92 \pm 0.02\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 5.59 \pm 0.04\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions are those recommended by Hultgren *et al.*[1] The heat capacity values were based on the studies of Phillips (0.1–4.2 K),[2] Seidel and Kiesom (0.35–4.38 K),[3] Eichenaur and Schulze (5–22 K),[4] Adams *et al.* (15–323 K),[5] and Clusius and Hartick (15–200 K).[6] Refer to Hultgren *et al.*[1] for details.

Enthalpy of Fusion

Refer to the liquid table for details.

Enthalpy of Sublimation

The enthalpy of sublimation is the enthalpy of formation of the gas, $\Delta_{sub} H°(298.15\ K) = \Delta_f H°(g, 298.15\ K)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.561	0.	0.	0.
100	18.484	16.085	62.261	−4.618	0.	0.	0.
200	23.815	30.912	43.151	−2.448	0.	0.	0.
250	24.907	36.338	41.262	−1.231	0.	0.	0.
298.15	26.064	40.838	40.838	0.	0.	0.	0.
300	26.091	41.000	40.839	0.048	0.	0.	0.
302.920	26.133	41.253	40.842	0.124	--- CRYSTAL <--> LIQUID ---		
350	27.004	45.091	41.160	1.376	−5.661	0.875	−0.131
400	27.460	48.726	41.883	2.737	−5.670	1.810	−0.236
450	27.916	51.987	42.827	4.122	−5.638	2.743	−0.318
500	28.372	54.952	43.894	5.529	−5.575	3.672	−0.384

PREVIOUS: CURRENT: June 1983

$S°(298.15\ K) = [59.253]\ J·K^{-1}·mol^{-1}$
$T = 302.92 \pm 0.02\ K$

$\Delta_f H°(298.15\ K) = [5.578]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 5.59 \pm 0.04\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(l, 298.15 K), is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°(302.92\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is based on the recommendations of Hultgren *et al.*[1] These values are based on the enthalpy data of Kochethova and Rezukhina (315–712 K),[2] and the heat capacity data of Chen and Turnbull (245–611 K).[3]

Enthalpy of Fusion

The adopted value for the enthalpy of fusion is derived from the direct calorimetric measurement of Roth *et al.*[4]

The temperature of fusion, $T_{fus} = 302.92 \pm 0.2$ K (corrected to IPTS–68), was derived from the study of Boedtker *et al.*[5]

Enthalpy of Vaporization

The temperature at which $\Delta_f G° = 0$ (1 bar) for the process Ga(l) → Ga(g) is the adopted T_{vap} (1bar). The difference in the enthalpies of formation of the ideal gas and liquid at T_{vap} is $\Delta_{vap} H°$. Refer to the ideal gas table for additional information.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹			kJ·mol⁻¹		
0							
100							
200							
250							
298.15	28.559	59.253	59.253	0.	5.578	0.088	−0.015
300	28.533	59.429	59.253	0.053	5.583	0.054	−0.009
302.920	28.493	59.706	59.256	0.136	--- CRYSTAL <---> LIQUID ---		
350	27.719	63.764	59.598	1.458	0.	0.	0.
400	27.154	67.426	60.353	2.829	0.	0.	0.
450	26.961	70.613	61.320	4.182	0.	0.	0.
500	26.819	73.445	62.393	5.526	0.	0.	0.
600	26.694	78.324	64.655	8.202	0.	0.	0.
700	26.568	82.428	66.908	10.864	0.	0.	0.
800	26.568	85.976	69.075	13.521	0.	0.	0.
900	26.568	89.105	71.130	16.177	0.	0.	0.
1000	26.568	91.904	73.070	18.834	0.	0.	0.
1100	26.568	94.436	74.899	21.491	0.	0.	0.
1200	26.568	96.748	76.625	24.148	0.	0.	0.
1300	26.568	98.875	78.256	26.805	0.	0.	0.
1400	26.568	100.844	79.800	29.462	0.	0.	0.
1500	26.568	102.677	81.264	32.118	0.	0.	0.
1600	26.568	104.391	82.657	34.775	0.	0.	0.
1700	26.568	106.002	83.983	37.432	0.	0.	0.
1800	26.568	107.521	85.249	40.089	0.	0.	0.
1900	26.568	108.957	86.459	42.746	0.	0.	0.
2000	26.568	110.320	87.619	45.403	0.	0.	0.
2100	26.568	111.616	88.731	48.060	0.	0.	0.
2200	26.568	112.852	89.799	50.716	0.	0.	0.
2300	26.568	114.033	90.828	53.373	0.	0.	0.
2400	26.568	115.164	91.818	56.030	0.	0.	0.
2476.570	26.568	115.998	92.553	58.064	----- FUGACITY = 1 bar -----		
2500	26.568	116.249	92.774	58.687	−258.586	2.447	−0.051
2600	26.568	117.291	93.697	61.344	−258.052	12.878	−0.259
2700	26.568	118.293	94.589	64.001	−257.515	23.288	−0.451
2800	26.568	119.260	95.453	66.657	−256.975	33.679	−0.628
2900	26.568	120.192	96.290	69.314	−256.433	44.050	−0.793
3000	26.568	121.093	97.102	71.971	−255.888	54.402	−0.947

PREVIOUS: CURRENT: June 1983

CRYSTAL–LIQUID

0	to	302.92 K	crystal
above		302.92 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−5.561	0.	0.	0.
100	18.484	16.085	62.261	−4.618	0.	0.	0.
200	23.815	30.912	43.151	−2.448	0.	0.	0.
250	24.907	36.338	41.262	−1.231	0.	0.	0.
298.15	26.064	40.838	40.838	0.	0.	0.	0.
300	26.091	41.000	40.839	0.048	0.	0.	0.
302.920	26.133	41.253	40.842	0.124	___ CRYSTAL <--> LIQUID ___		
302.920	28.493	59.706	40.842	5.714	TRANSITION		
350	27.719	63.764	43.660	7.037	0.	0.	0.
400	27.154	67.426	46.408	8.407	0.	0.	0.
450	26.961	70.613	48.924	9.760	0.	0.	0.
500	26.819	73.445	51.237	11.104	0.	0.	0.
600	26.694	78.324	55.358	13.780	0.	0.	0.
700	26.568	82.428	58.939	16.442	0.	0.	0.
800	26.568	85.976	62.102	19.099	0.	0.	0.
900	26.568	89.105	64.932	21.756	0.	0.	0.
1000	26.568	91.904	67.492	24.413	0.	0.	0.
1100	26.568	94.436	69.828	27.069	0.	0.	0.
1200	26.568	96.748	71.976	29.726	0.	0.	0.
1300	26.568	98.875	73.965	32.383	0.	0.	0.
1400	26.568	100.844	75.815	35.040	0.	0.	0.
1500	26.568	102.677	77.546	37.697	0.	0.	0.
1600	26.568	104.391	79.171	40.354	0.	0.	0.
1700	26.568	106.002	80.702	43.010	0.	0.	0.
1800	26.568	107.521	82.150	45.667	0.	0.	0.
1900	26.568	108.957	83.524	48.324	0.	0.	0.
2000	26.568	110.320	84.830	50.981	0.	0.	0.
2100	26.568	111.616	86.075	53.638	0.	0.	0.
2200	26.568	112.852	87.264	56.295	0.	0.	0.
2300	26.568	114.033	88.402	58.951	0.	0.	0.
2400	26.568	115.164	89.494	61.608	0.	0.	0.
2476.570	26.568	115.998	90.301	63.643	----- FUGACITY = 1 bar -----		
2500	26.568	116.249	90.543	64.265	−258.586	2.447	−0.051
2600	26.568	117.291	91.551	66.922	−258.052	12.878	−0.259
2700	26.568	118.293	92.523	69.579	−257.515	23.288	−0.451
2800	26.568	119.260	93.461	72.236	−256.975	33.679	−0.628
2900	26.568	120.192	94.367	74.892	−256.433	44.050	−0.793
3000	26.568	121.093	95.243	77.549	−255.888	54.402	−0.947

PREVIOUS: CURRENT: June 1983

IP(Ga, g) = 48380 ± 5 cm^{-1}
$S°$(298.15 K) = 169.042 ± 0.01 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 270.97 ± 2.1 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 271.96 ± 2.1 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_{1/2}$	0	2
$^3P_{3/2}$	826.24	4
$^2S_{1/2}$	24788.58	2
$^2P_{1/2}$	33044.06	2
$^2P_{3/2}$	33155.03	4

Enthalpy of Formation

The enthalpy of formation of Ga(g), as recommended by Hultgren *et al.*,[1] was derived from the third law analysis of seven vaporization studies and a spectroscopic calculation. The studies are: Matern *et al.* (1081–1213 K),[2] Macur *et al.* (1196–1473 K),[3] Alcock *et al.* (1173–1437 K),[4] Munir and Searcy (1174–1603 K),[5] Cochran and Foster (1179–1383 K),[6] Speiser and Johnston (1230–1518 K),[7] Hartick (1198–1391 K),[8] and the spectroscopic calculaion by Gurvich.[9]

Heat Capacity and Entropy

The thermal functions were calculated using the atomic levels as given by Moore.[10] The resulting thermal functions are those recommended by Hultgren *et al.*[1]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.551	270.970	270.970	INFINITE
100	20.802	144.848	189.570	−4.472	272.105	259.229	−135.407
200	22.311	159.555	171.266	−2.342	272.066	246.337	−64.337
250	23.914	164.703	169.452	−1.187	272.004	239.913	−50.127
298.15	25.346	169.042	169.042	0.	271.960	233.736	−40.950
300	25.394	169.199	169.043	0.047	271.959	233.499	−40.656
350	26.430	173.198	169.356	1.345	266.268	227.966	−34.022
400	26.974	176.768	170.064	2.682	266.234	222.497	−29.055
450	27.120	179.957	170.989	4.035	266.235	217.030	−25.192
500	26.991	182.809	172.031	5.389	266.245	211.563	−22.102
600	26.316	187.676	174.247	8.057	266.237	200.626	−17.466
700	25.489	191.671	176.460	10.648	266.166	189.696	−14.155
800	24.724	195.023	178.576	13.157	266.018	178.781	−11.673
900	24.077	197.896	180.567	15.596	265.801	167.888	−9.744
1000	23.550	200.405	182.428	17.977	265.524	157.023	−8.202
1100	23.125	202.629	184.166	20.310	265.200	146.189	−6.942
1200	22.781	204.626	185.789	22.604	264.838	135.385	−5.893
1300	22.503	206.438	187.309	24.868	264.445	124.613	−5.007
1400	22.275	208.097	188.735	27.107	264.027	113.872	−4.249
1500	22.088	209.627	190.077	29.324	263.588	103.162	−3.592
1600	21.933	211.048	191.344	31.525	263.132	92.482	−3.019
1700	21.802	212.373	192.543	33.712	262.661	81.831	−2.514
1800	21.692	213.616	193.679	35.886	262.179	71.208	−2.066
1900	21.599	214.786	194.760	38.051	261.687	60.611	−1.666
2000	21.519	215.892	195.789	40.207	261.186	50.041	−1.307
2100	21.449	216.940	196.771	42.355	260.677	39.497	−0.982
2200	21.389	217.937	197.711	44.497	260.162	28.976	−0.688
2300	21.337	218.886	198.611	46.633	259.642	18.479	−0.420
2400	21.291	219.794	199.475	48.764	259.116	8.005	−0.174
2476.570	21.260	220.462	200.114	50.394	----- FUGACITY = 1 bar -----		
2500	21.251	220.662	200.305	50.892	0.	0.	0.
2600	21.215	221.495	201.104	53.015	0.	0.	0.
2700	21.184	222.295	201.874	55.135	0.	0.	0.
2800	21.156	223.065	202.618	57.252	0.	0.	0.
2900	21.131	223.807	203.335	59.366	0.	0.	0.
3000	21.109	224.523	204.030	61.478	0.	0.	0.
3100	21.090	225.214	204.702	63.588	0.	0.	0.
3200	21.073	225.884	205.354	65.696	0.	0.	0.
3300	21.059	226.532	205.986	67.803	0.	0.	0.
3400	21.047	227.160	206.599	69.908	0.	0.	0.
3500	21.036	227.770	207.195	72.012	0.	0.	0.
3600	21.029	228.363	207.775	74.115	0.	0.	0.
3700	21.023	228.939	208.339	76.218	0.	0.	0.
3800	21.020	229.500	208.889	78.320	0.	0.	0.
3900	21.018	230.045	209.424	80.422	0.	0.	0.
4000	21.020	230.578	209.947	82.524	0.	0.	0.
4100	21.024	231.097	210.456	84.626	0.	0.	0.
4200	21.030	231.603	210.954	86.729	0.	0.	0.
4300	21.040	232.098	211.440	88.832	0.	0.	0.
4400	21.052	232.582	211.915	90.937	0.	0.	0.
4500	21.068	233.055	212.379	93.043	0.	0.	0.
4600	21.087	233.519	212.834	95.150	0.	0.	0.
4700	21.109	233.972	213.279	97.260	0.	0.	0.
4800	21.135	234.417	213.715	99.372	0.	0.	0.
4900	21.165	234.853	214.142	101.487	0.	0.	0.
5000	21.198	235.281	214.560	103.605	0.	0.	0.
5100	21.236	235.701	214.970	105.727	0.	0.	0.
5200	21.278	236.114	215.373	107.853	0.	0.	0.
5300	21.324	236.520	215.768	109.983	0.	0.	0.
5400	21.375	236.919	216.156	112.118	0.	0.	0.
5500	21.431	237.312	216.537	114.258	0.	0.	0.
5600	21.491	237.698	216.912	116.404	0.	0.	0.
5700	21.556	238.079	217.280	118.556	0.	0.	0.
5800	21.625	238.455	217.642	120.715	0.	0.	0.
5900	21.700	238.825	217.998	122.881	0.	0.	0.
6000	21.780	239.190	218.348	125.055	0.	0.	0.

PREVIOUS: CURRENT: June 1983 (1 bar)

IP(Ga^+, g) = 165458 ± 5 cm^{-1}
$S°$(298.15 K) = 161.790 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 849.8 ± 4.0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [856.648] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1
$^3P_0$	47370	1
$^3P_1$	47816	3
$^3P_2$	48750	5

Enthalpy of Formation

$\Delta_f H°(Ga^+, g, 0 K)$ is calculated from $\Delta_f H°$(Ga, g, 0 K)[1] using the spectroscopic value of IP(Ga) = 48387.63 ± 0.1 cm^{-1}(578.837 ± 0.001 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ga^+, g, 298.15 K)$ is calculated from $\Delta_f H°$(Ga, g, 0 K) by using IP(Ga) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Ga(g), Ga^+(g), and e^-(ref). $\Delta_f H°(Ga \rightarrow Ga^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calcualtions indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first three excited states; the next excited state is 70700 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first three excited states. The position of the $^3P_0$ levels are uncertain by 249 cm^{-1}. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	849.815		
100	20.786	139.083	180.270	−4.119			
200	20.786	153.491	163.691	−2.040			
250	20.786	158.129	162.132	−1.001			
298.15	20.786	161.790	161.790	0.	856.648	814.332	−142.668
300	20.786	161.919	161.790	0.038	856.677	814.069	−141.742
350	20.786	165.123	162.044	1.078	851.767	807.783	−120.555
400	20.786	167.898	162.606	2.117	852.475	801.451	−104.659
450	20.786	170.347	163.333	3.156	853.201	795.030	−92.285
500	20.786	172.537	164.145	4.196	853.935	788.527	−82.377
600	20.786	176.326	165.869	6.274	855.417	775.307	−67.496
700	20.786	179.531	167.598	8.353	856.912	761.837	−56.849
800	20.786	182.306	169.267	10.431	858.413	748.152	−48.849
900	20.786	184.754	170.854	12.510	859.913	734.280	−42.616
1000	20.786	186.944	172.356	14.589	861.413	720.240	−37.621
1100	20.786	188.926	173.774	16.667	862.914	706.050	−33.528
1200	20.786	190.734	175.113	18.746	864.414	691.723	−30.110
1300	20.786	192.398	176.379	20.824	865.914	677.272	−27.213
1400	20.786	193.938	177.579	22.903	867.415	662.705	−24.726
1500	20.786	195.372	178.718	24.982	868.915	648.030	−22.566
1600	20.786	196.714	179.801	27.060	870.415	633.255	−20.674
1700	20.786	197.974	180.834	29.139	871.916	618.387	−19.001
1800	20.786	199.162	181.819	31.217	873.416	603.430	−17.511
1900	20.786	200.286	182.762	33.296	874.917	588.390	−16.176
2000	20.786	201.352	183.665	35.375	876.417	573.271	−14.972
2100	20.786	202.366	184.532	37.453	877.917	558.077	−13.881
2200	20.786	203.333	185.364	39.532	879.418	542.811	−12.888
2300	20.786	204.257	186.166	41.610	880.918	527.477	−11.979
2400	20.786	205.142	186.938	43.689	882.418	512.078	−11.145
2500	20.786	205.991	187.683	45.768	625.333	499.064	−10.427
2600	20.786	206.806	188.403	47.846	627.367	493.973	−9.924
2700	20.786	207.590	189.100	49.925	629.404	488.804	−9.456
2800	20.786	208.346	189.773	52.004	631.444	483.559	−9.021
2900	20.786	209.076	190.427	54.082	633.487	478.241	−8.614
3000	20.786	209.780	191.060	56.161	635.533	472.853	−8.233
3100	20.786	210.462	191.675	58.239	637.580	467.397	−7.876
3200	20.786	211.122	192.272	60.318	639.629	461.874	−7.539
3300	20.786	211.761	192.853	62.397	641.679	456.288	−7.222
3400	20.786	212.382	193.419	64.475	643.731	450.639	−6.923
3500	20.786	212.984	193.969	66.554	645.785	444.930	−6.640
3600	20.786	213.570	194.505	68.632	647.838	439.162	−6.372
3700	20.786	214.140	195.028	70.711	649.893	433.337	−6.118
3800	20.786	214.694	195.539	72.790	651.948	427.457	−5.876
3900	20.786	215.234	196.037	74.868	654.004	421.522	−5.646
4000	20.787	215.760	196.523	76.947	656.059	415.535	−5.426
4100	20.787	216.273	196.999	79.026	658.114	409.497	−5.217
4200	20.787	216.774	197.464	81.104	660.169	403.408	−5.017
4300	20.788	217.263	197.919	83.183	662.223	397.270	−4.826
4400	20.789	217.741	198.364	85.262	664.275	391.085	−4.643
4500	20.790	218.209	198.799	87.341	666.327	384.853	−4.467
4600	20.791	218.665	199.226	89.420	668.377	378.575	−4.299
4700	20.792	219.113	199.645	91.499	670.425	372.253	−4.137
4800	20.794	219.550	200.055	93.578	672.471	365.887	−3.982
4900	20.797	219.979	200.457	95.658	674.514	359.479	−3.832
5000	20.799	220.399	200.852	97.738	676.554	353.029	−3.688
5100	20.803	220.811	201.239	99.818	678.591	346.538	−3.549
5200	20.807	221.215	201.619	101.898	680.625	340.008	−3.415
5300	20.812	221.612	201.993	103.979	682.654	333.438	−3.286
5400	20.818	222.001	202.360	106.061	684.679	326.830	−3.161
5500	20.825	222.383	202.720	108.143	686.700	320.184	−3.041
5600	20.833	222.758	203.075	110.226	688.715	313.502	−2.924
5700	20.843	223.127	203.423	112.310	690.726	306.784	−2.811
5800	20.854	223.489	203.766	114.394	692.730	300.031	−2.702
5900	20.866	223.846	204.104	116.480	694.728	293.243	−2.596
6000	20.880	224.197	204.436	118.568	696.720	286.422	−2.494

PREVIOUS: CURRENT: June 1983 (1 bar)

EA(Ga, g) = 0.30 ± 0.15 eV
$S°(298.15\ K)$ = [175.801 ± 0.1] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 242.025 ± 14.6 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [238.531] $kJ·mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0	1
$^3P_1$	220	3
$^3P_2$	580	5

Enthalpy of Formation

$\Delta_f H°(Ga^-, g, 0\ K)$ is calculated from $\Delta_f H°(Ga, g, 0\ K)$[1] using the adopted electron affinity of EA(Ga) = 0.30 ± 0.15 eV (28.945 ± 14.473 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a photodetachment threshold (using conventional light sources) and semiempirical extrapolation.[3, 4, 5] Additional information on $Ga^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,5] Rosenstock *et al.*[6] and Massey.[7]

$\Delta_f H°(Ga^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ga, g, 0\ K)$ by using EA(Ga) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for $Ga^-(g)$, Ga(g), and e^-(ref). $\Delta_r H°(Ga^- \rightarrow Ga + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[6] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Ga^-(g)$ is given by Hotop and Lineberger,[2, 5] Rosenstocsk *et al.*,[6] and Massey.[7] The fine–structure separation has been calculated via an isoelectronic extrapolation of ratios of fine structure separations and a quadratic isoelectronic extrapolation[4, 5] and is that recommended by Hotop and Lineberger.[2]

A comparison of the isoelectronic sequences – $Ga^-(g)$, Ge(g), $As^+(g)$, $Se^{++}(g)$ – would suggest that a state, $^1D_2$, may exist at low wave numbers. However, this is most likely a metasable state lying at an energy greater than the electron affinity, as in the case of $Al^-(g)$. As discussed by Hotop and Lineberger,[2, 5] Rosenstock *et al.*,[6] and Massey,[7] no stable excited states have been observed. Thus, we assume no stable excited states exist.

References

[1]JANAF Thermochemical Tables: Ga(g); e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.265	242.025		
100	29.645	143.110	201.948	−5.884			
200	30.076	164.238	178.410	−2.834			
250	28.867	170.824	176.263	−1.360			
298.15	27.618	175.801	175.801	0.	238.531	204.547	−35.836
300	27.572	175.972	175.802	0.051	238.496	204.336	−35.578
350	26.407	180.132	176.133	1.400	231.817	199.597	−29.788
400	25.437	183.593	176.855	2.695	230.702	195.070	−25.474
450	24.656	186.542	177.772	3.947	229.562	190.684	−22.134
500	24.034	189.107	178.780	5.163	228.395	186.427	−19.476
600	23.155	193.405	180.872	7.519	225.996	178.257	−15.519
700	22.612	196.930	182.922	9.805	223.542	170.494	−12.722
800	22.287	199.926	184.865	12.049	221.050	163.086	−10.648
900	22.106	202.539	186.687	14.268	218.533	155.991	−9.053
1000	22.021	204.863	188.390	16.473	216.003	149.177	−7.792
1100	21.998	206.961	189.985	18.674	213.469	142.617	−6.772
1200	22.012	208.875	191.480	20.874	210.933	136.288	−5.932
1300	22.049	210.638	192.887	23.077	208.401	130.171	−5.230
1400	22.097	212.274	194.214	25.284	205.873	124.248	−4.636
1500	22.149	213.801	195.469	27.497	203.350	118.505	−4.127
1600	22.199	215.232	196.660	29.714	200.832	112.931	−3.687
1700	22.246	216.579	197.793	31.936	198.318	107.515	−3.304
1800	22.287	217.852	198.872	34.163	195.810	102.246	−2.967
1900	22.323	219.058	199.903	36.394	193.305	97.116	−2.670
2000	22.353	220.203	200.890	38.627	190.803	92.118	−2.406
2100	22.377	221.295	201.836	40.864	188.304	87.245	−2.170
2200	22.395	222.336	202.744	43.103	185.807	82.491	−1.959
2300	22.408	223.332	203.618	45.343	183.312	77.851	−1.768
2400	22.417	224.286	204.459	47.584	180.818	73.319	−1.596
2500	22.422	225.201	205.270	49.826	−80.261	71.339	−1.491
2600	22.423	226.080	206.054	52.068	−82.221	77.442	−1.556
2700	22.422	226.927	206.812	54.311	−84.177	83.620	−1.618
2800	22.417	227.742	207.545	56.553	−86.131	89.870	−1.677
2900	22.410	228.528	208.255	58.794	−88.082	96.190	−1.733
3000	22.402	229.288	208.943	61.035	−90.032	102.578	−1.786
3100	22.391	230.022	209.611	63.274	−91.981	109.030	−1.837
3200	22.379	230.733	210.260	65.513	−93.929	115.545	−1.886
3300	22.366	231.422	210.891	67.750	−95.877	122.122	−1.933
3400	22.351	232.089	211.505	69.986	−97.825	128.757	−1.978
3500	22.336	232.737	212.102	72.220	−99.774	135.449	−2.021
3600	22.320	233.366	212.684	74.453	−101.723	142.198	−2.063
3700	22.303	233.977	213.252	76.684	−103.673	149.000	−2.104
3800	22.286	234.572	213.805	78.914	−105.624	155.855	−2.142
3900	22.268	235.150	214.345	81.141	−107.577	162.762	−2.180
4000	22.250	235.714	214.872	83.367	−109.531	169.718	−2.216
4100	22.232	236.263	215.387	85.591	−111.488	176.724	−2.251
4200	22.214	236.799	215.891	87.814	−113.447	183.777	−2.286
4300	22.195	237.321	216.383	90.034	−115.408	190.877	−2.319
4400	22.176	237.831	216.865	92.253	−117.373	198.022	−2.351
4500	22.158	238.329	217.336	94.469	−119.341	205.213	−2.382
4600	22.139	238.816	217.798	96.684	−121.312	212.447	−2.412
4700	22.120	239.292	218.250	98.897	−123.288	219.724	−2.442
4800	22.102	239.757	218.693	101.108	−125.267	227.043	−2.471
4900	22.083	240.213	219.128	103.318	−127.252	234.403	−2.499
5000	22.065	240.659	219.554	105.525	−129.241	241.804	−2.526
5100	22.047	241.096	219.972	107.731	−131.236	249.245	−2.553
5200	22.029	241.524	220.382	109.934	−133.236	256.724	−2.579
5300	22.011	241.943	220.785	112.136	−135.243	264.243	−2.604
5400	21.993	242.354	221.181	114.336	−137.256	271.799	−2.629
5500	21.976	242.758	221.570	116.535	−139.277	279.393	−2.653
5600	21.958	243.154	221.951	118.732	−141.305	287.023	−2.677
5700	21.941	243.542	222.327	120.927	−143.341	294.690	−2.701
5800	21.924	243.924	222.696	123.120	−145.385	302.393	−2.723
5900	21.908	244.298	223.059	125.311	−147.438	310.131	−2.746
6000	21.891	244.666	223.416	127.501	−149.501	317.903	−2.768

PREVIOUS: CURRENT: June 1983 (1 bar)

$S°(298.15\ K) = 114.716 \pm 0.017\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 216.035 \pm 0.006\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 217.999 \pm 0.006\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2

Enthalpy of Formation

The enthalpy of formation is calculated from the dissociation energy, $D_0°(H_2) = 36118.3 \pm 1\ cm^{-1}$ ($432.071 \pm 0.012\ kJ·mol^{-1}$), from Herzberg[2] and auxiliary data from H_2.[3] The adopted value for the dissociation energy of hydrogen is the value recommended by CODATA.[1]

Earlier experimental values for $D_0°(H_2)$ were obtained by Herzberg and Monfils (36113.0 ± 0.3 cm^{-1}),[4] and Beutler (36116 ± 6 cm^{-1}).[5] Kolos and Wolniewicz[6] calculated the adiabatic dissociation energy of H_2, corrected for relativistic and radiative effects, to be 36117.4 cm^{-1}.

Heat Capacity and Entropy

The electronic levels for H(g) are given in the compilation by Moore.[7] Our calculations indicate that the inclusion of levels through $n = 12$ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the first excited state lies at 82258 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures.[8]

The thermal functions at 298.15 K differ from the CODATA recommendations for two reasons: a difference of 0.001 $J·K^{-1}·mol^{-1}$ in the entropy due to the use of more current fundamental constants and a difference of 0.1094 $J·K^{-1}·mol^{-1}$ in the entropy due to the use of a different standard state pressure.

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[2] G. Herzberg, J. Mol. Spectrosc. **33**, 147 (1970).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	216.035	216.035	INFINITE
100	20.786	92.009	133.197	−4.119	216.614	212.450	−110.972
200	20.786	106.417	116.618	−2.040	217.346	208.004	−54.325
250	20.786	111.055	115.059	−1.001	217.687	205.629	−42.964
298.15	20.786	114.716	114.716	0.	217.999	203.278	−35.613
300	20.786	114.845	114.717	0.038	218.011	203.186	−35.378
350	20.786	118.049	114.970	1.078	218.326	200.690	−29.951
400	20.786	120.825	115.532	2.117	218.637	198.150	−25.876
450	20.786	123.273	116.259	3.156	218.946	195.570	−22.701
500	20.786	125.463	117.072	4.196	219.254	192.957	−20.158
600	20.786	129.253	118.796	6.274	219.868	187.640	−16.335
700	20.786	132.457	120.524	8.353	220.478	182.220	−13.597
800	20.786	135.232	122.193	10.431	221.080	176.713	−11.538
900	20.786	137.681	123.781	12.510	221.671	171.132	−9.932
1000	20.786	139.871	125.282	14.589	222.248	165.485	−8.644
1100	20.786	141.852	126.700	16.667	222.807	159.782	−7.587
1200	20.786	143.660	128.039	18.746	223.346	154.028	−6.705
1300	20.786	145.324	129.305	20.824	223.865	148.230	−5.956
1400	20.786	146.865	130.505	22.903	224.361	142.394	−5.313
1500	20.786	148.299	131.644	24.982	224.836	136.522	−4.754
1600	20.786	149.640	132.728	27.060	225.289	130.620	−4.264
1700	20.786	150.900	133.760	29.139	225.721	124.689	−3.831
1800	20.786	152.088	134.745	31.217	226.132	118.734	−3.446
1900	20.786	153.212	135.688	33.296	226.525	112.757	−3.100
2000	20.786	154.278	136.591	35.375	226.898	106.760	−2.788
2100	20.786	155.293	137.458	37.453	227.254	100.744	−2.506
2200	20.786	156.260	138.291	39.532	227.593	94.712	−2.249
2300	20.786	157.184	139.092	41.610	227.916	88.664	−2.014
2400	20.786	158.068	139.864	43.689	228.224	82.603	−1.798
2500	20.786	158.917	140.610	45.768	228.518	76.530	−1.599
2600	20.786	159.732	141.330	47.846	228.798	70.444	−1.415
2700	20.786	160.516	142.026	49.925	229.064	64.349	−1.245
2800	20.786	161.272	142.700	52.004	229.318	58.243	−1.087
2900	20.786	162.002	143.353	54.082	229.560	52.129	−0.939
3000	20.786	162.706	143.986	56.161	229.790	46.007	−0.801
3100	20.786	163.388	144.601	58.239	230.008	39.877	−0.672
3200	20.786	164.048	145.199	60.318	230.216	33.741	−0.551
3300	20.786	164.688	145.780	62.397	230.413	27.598	−0.437
3400	20.786	165.308	146.345	64.475	230.599	21.449	−0.330
3500	20.786	165.911	146.895	66.554	230.776	15.295	−0.228
3600	20.786	166.496	147.432	68.632	230.942	9.136	−0.133
3700	20.786	167.066	147.955	70.711	231.098	2.973	−0.042
3800	20.786	167.620	148.465	72.790	231.244	−3.195	0.044
3900	20.786	168.160	148.963	74.868	231.381	−9.366	0.125
4000	20.786	168.686	149.450	76.947	231.509	−15.541	0.203
4100	20.786	169.200	149.925	79.025	231.627	−21.718	0.277
4200	20.786	169.700	150.390	81.104	231.736	−27.899	0.347
4300	20.786	170.190	150.845	83.183	231.836	−34.082	0.414
4400	20.786	170.667	151.290	85.261	231.927	−40.267	0.478
4500	20.786	171.135	151.726	87.340	232.009	−46.454	0.539
4600	20.786	171.591	152.153	89.418	232.082	−52.643	0.598
4700	20.786	172.038	152.571	91.497	232.147	−58.834	0.654
4800	20.786	172.476	152.981	93.576	232.204	−65.025	0.708
4900	20.786	172.905	153.383	95.654	232.253	−71.218	0.759
5000	20.786	173.325	153.778	97.733	232.294	−77.412	0.809
5100	20.786	173.736	154.165	99.811	232.327	−83.606	0.856
5200	20.786	174.140	154.546	101.890	232.353	−89.801	0.902
5300	20.786	174.536	154.919	103.969	232.373	−95.997	0.946
5400	20.786	174.924	155.286	106.047	232.386	−102.192	0.989
5500	20.786	175.306	155.646	108.126	232.392	−108.389	1.029
5600	20.786	175.680	156.001	110.204	232.393	−114.584	1.069
5700	20.786	176.048	156.349	112.283	232.389	−120.780	1.107
5800	20.786	176.410	156.692	114.362	232.379	−126.976	1.144
5900	20.786	176.765	157.029	116.440	232.365	−133.172	1.179
6000	20.786	177.114	157.361	118.519	232.348	−139.368	1.213

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

$S°(298.15\ K) = 108.946 \pm 0.02\ J\ K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1528.085 \pm 0.04\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [1536.246]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(H^+, g, 0\ K)$ is calculated from $\Delta_f H°(H, g, 0\ K)$[1] using the spectroscopic value of IP(H) = 109678.764 ± 0.005 cm^{-1} (1312.0498 ± 0.0001 $kJ\cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ\cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ\cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants[3]. Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(H^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(H, g, 0\ K)$ by using IP(H) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for H(g), H^+(g), and e^-(ref). $\Delta_f H°(H \rightarrow H^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ\cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The thermodynamic functions of the proton gas are calculated using the recent CODATA fundamental constants[2] and assuming that the proton is an ideal monatomic gas. Since there is no electron associated with this species, there is only a translational contribution to the thermochemical function.

References

[1]JANAF Thermochemical Tables: H(g), 3-31-82 ; e^-(ref), 3-31-82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1528.085		
100	20.786	86.239	127.427	−4.119			
200	20.786	100.647	110.848	−2.040			
250	20.786	105.285	109.289	−1.001			
298.15	20.786	108.946	108.946	0.	1536.246	1516.990	−265.770
300	20.786	109.075	108.947	0.038	1536.297	1516.871	−264.111
350	20.786	112.279	109.200	1.078	1537.651	1513.526	−225.881
400	20.786	115.055	109.762	2.117	1539.001	1509.987	−197.184
450	20.786	117.503	110.489	3.156	1540.349	1506.280	−174.844
500	20.786	119.693	111.302	4.196	1541.697	1502.422	−156.957
600	20.786	123.483	113.026	6.274	1544.389	1494.314	−130.092
700	20.786	126.687	114.754	8.353	1547.078	1485.755	−110.868
800	20.786	129.463	116.423	10.431	1549.758	1476.812	−96.426
900	20.786	131.911	118.011	12.510	1552.428	1467.533	−85.173
1000	20.786	134.101	119.512	14.589	1555.084	1457.958	−76.156
1100	20.786	136.082	120.930	16.667	1557.721	1448.117	−68.765
1200	20.786	137.891	122.269	18.746	1560.339	1438.038	−62.596
1300	20.786	139.554	123.536	20.824	1562.936	1427.740	−57.367
1400	20.786	141.095	124.735	22.903	1565.511	1417.244	−52.878
1500	20.786	142.529	125.874	24.982	1568.065	1406.564	−48.981
1600	20.786	143.870	126.958	27.060	1570.596	1395.715	−45.565
1700	20.786	145.130	127.990	29.139	1573.107	1384.708	−42.547
1800	20.786	146.319	128.976	31.217	1575.597	1373.554	−39.859
1900	20.786	147.442	129.918	33.296	1578.068	1362.261	−37.451
2000	20.786	148.509	130.821	35.375	1580.520	1350.840	−35.280
2100	20.786	149.523	131.688	37.453	1582.954	1339.296	−33.313
2200	20.786	150.490	132.521	39.532	1585.372	1327.636	−31.522
2300	20.786	151.414	133.322	41.610	1587.774	1315.867	−29.884
2400	20.786	152.298	134.095	43.689	1590.161	1303.994	−28.381
2500	20.786	153.147	134.840	45.768	1592.533	1292.021	−26.995
2600	20.786	153.962	135.560	47.846	1594.891	1279.954	−25.715
2700	20.786	154.747	136.256	49.925	1597.236	1267.797	−24.527
2800	20.786	155.503	136.930	52.004	1599.569	1255.553	−23.423
2900	20.786	156.232	137.583	54.082	1601.889	1243.225	−22.393
3000	20.786	156.937	138.216	56.161	1604.198	1230.818	−21.430
3100	20.786	157.618	138.831	58.239	1606.495	1218.334	−20.529
3200	20.786	158.278	139.429	60.318	1608.781	1205.777	−19.682
3300	20.786	158.918	140.010	62.397	1611.057	1193.148	−18.886
3400	20.786	159.538	140.575	64.475	1613.322	1180.450	−18.135
3500	20.786	160.141	141.125	66.554	1615.576	1167.685	−17.427
3600	20.786	160.726	141.662	68.632	1617.821	1154.857	−16.757
3700	20.786	161.296	142.185	70.711	1620.056	1141.966	−16.122
3800	20.786	161.850	142.695	72.790	1622.281	1129.014	−15.519
3900	20.786	162.390	143.193	74.868	1624.497	1116.005	−14.947
4000	20.786	162.916	143.680	76.947	1626.703	1102.938	−14.403
4100	20.786	163.430	144.155	79.025	1628.899	1089.817	−13.884
4200	20.786	163.931	144.620	81.104	1631.087	1076.642	−13.390
4300	20.786	164.420	145.075	83.183	1633.265	1063.416	−12.918
4400	20.786	164.897	145.520	85.261	1635.435	1050.138	−12.467
4500	20.786	165.365	145.956	87.340	1637.596	1036.812	−12.035
4600	20.786	165.821	146.383	89.418	1639.748	1023.437	−11.621
4700	20.786	166.268	146.801	91.497	1641.891	1010.016	−11.225
4800	20.786	166.706	147.211	93.576	1644.027	996.549	−10.845
4900	20.786	167.135	147.613	95.654	1646.154	983.038	−10.479
5000	20.786	167.555	148.008	97.733	1648.274	969.484	−10.128
5100	20.786	167.966	148.395	99.811	1650.386	955.887	−9.790
5200	20.786	168.370	148.776	101.890	1652.491	942.249	−9.465
5300	20.786	168.766	149.149	103.969	1654.588	928.570	−9.152
5400	20.786	169.154	149.516	106.047	1656.680	914.852	−8.849
5500	20.786	169.536	149.877	108.126	1658.765	901.095	−8.558
5600	20.786	169.910	150.231	110.204	1660.845	887.301	−8.276
5700	20.786	170.278	150.579	112.283	1662.919	873.469	−8.004
5800	20.786	170.640	150.922	114.362	1664.988	859.601	−7.742
5900	20.786	170.995	151.259	116.440	1667.053	845.697	−7.487
6000	20.786	171.344	151.591	118.519	1669.113	831.758	−7.241

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

EA(H, g) = 0.754209 ± 0.000003 eV
$S°$(298.15 K) = 108.960 ± 0.017 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 143.27 ± 0.02 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [139.032] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(H^-, g, 0 K)$ is calculated from $\Delta_f H°(H, g, 0 K)$[1] using the adopted electron affinity of EA(H) = 0.754209 ± 0.000003 eV (72.7695 ± 0.0003 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on extensive Hylleras–type variational calculations on two election systems.[3,4,5] Additional information on H^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 6] Rosenstock *et al.*[7] and Massey.[8] Experimentally, Dehmer and Chupka[9] have reported EA(H) ≥0.7540 ± 0.0003 eV.

$\Delta_f H°(H^-, g, 298.15 K)$ is obtained from $\Delta_f H°(H, g, 0 K)$ by using EA(H) with JANAF[1] enthalpies, $H°(0 K)–H°(298.15 K)$, for H^-(g), H(g), and e^-(ref). $\Delta_r H°(H^- \rightarrow H + e^-, 298.15 K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock et al.[7] $\Delta_f H°$(298.15 K) should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for H^-(g) is given by Hotop and Lineberger[2, 6] and Rosenstock *et al.*[7] A comparison of the isoelectronic sequence – H^-(g), He(g), Li^+(g) – would suggest that stable electronic states may exist at 0.8 EA(H) or roughly 6400 cm^{-1}. This would greatly affect the entropy. However, Pekeris[4] states that he was unable to find any bound states. In addition, Seman and Branscomb[10] state that theoretical and semiempirical evidence suggests that atomic negative ions have very few if any excited states below the continuum. We assume no stable excited states exist.

Reference

[1]JANAF Thermochemical Tables: H(g) and e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
[3]C. L. Pekeris, Phys. Rev. **112**, 1649 (1958).
[4]C. L. Pekeris, Phys. Rev. **126**, 1470 (1962).
[5]K. Aaskamar, Nucl. Instr. Meth. **90**, 263 (1970).
[6]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[7]H. M. Rosenstock, K. Draxel *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
[8]H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
[9]P. M. Dehmer and W. A. Chupka, Bull. Am. Phys. Soc. **20**, 729 (1975).
[10]M. L. Seman and L. M. Branscomb, Phys. Rev. **125**, 1602 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	143.266		
100	20.786	86.253	127.440	−4.119			
200	20.786	100.661	110.861	−2.040			
250	20.786	105.299	109.302	−1.001			
298.15	20.786	108.960	108.960	0.	139.032	132.282	−23.175
300	20.786	109.089	108.960	0.038	139.006	132.240	−23.025
350	20.786	112.293	109.213	1.078	138.281	131.170	−19.576
400	20.786	115.068	109.776	2.117	137.553	130.203	−17.003
450	20.786	117.517	110.502	3.156	136.823	129.328	−15.012
500	20.786	119.707	111.315	4.196	136.091	128.535	−13.428
600	20.786	123.496	113.039	6.274	134.627	127.161	−11.070
700	20.786	126.701	114.768	8.353	133.158	126.033	−9.405
800	20.786	129.476	116.437	10.431	131.682	125.116	−8.169
900	20.786	131.924	118.024	12.510	130.194	124.384	−7.219
1000	20.786	134.114	119.526	14.589	128.692	123.819	−6.468
1100	20.786	136.096	120.943	16.667	127.173	123.405	−5.860
1200	20.786	137.904	122.283	18.746	125.634	123.130	−5.360
1300	20.786	139.568	123.549	20.824	124.073	122.985	−4.942
1400	20.786	141.108	124.749	22.903	122.491	122.960	−4.588
1500	20.786	142.542	125.888	24.982	120.887	123.050	−4.285
1600	20.786	143.884	126.971	27.060	119.262	123.247	−4.024
1700	20.786	145.144	128.004	29.139	117.615	123.546	−3.796
1800	20.786	146.332	128.989	31.217	115.948	123.943	−3.597
1900	20.786	147.456	129.932	33.296	114.262	124.433	−3.421
2000	20.786	148.522	130.835	35.375	112.557	125.012	−3.265
2100	20.786	149.536	131.701	37.453	110.834	125.677	−3.126
2200	20.786	150.503	132.534	39.532	109.094	126.425	−3.002
2300	20.786	151.427	133.336	41.610	107.339	127.252	−2.890
2400	20.786	152.312	134.108	43.689	105.568	128.156	−2.789
2500	20.786	153.160	134.853	45.768	103.783	129.133	−2.698
2600	20.786	153.976	135.573	47.846	101.984	130.183	−2.615
2700	20.786	154.760	136.269	49.925	100.172	131.302	−2.540
2800	20.786	155.516	136.943	52.004	98.348	132.488	−2.472
2900	20.786	156.245	137.596	54.082	96.511	133.740	−2.409
3000	20.786	156.950	138.230	56.161	94.662	135.055	−2.352
3100	20.786	157.632	138.845	58.239	92.802	136.432	−2.299
3200	20.786	158.292	139.442	60.318	90.931	137.869	−2.250
3300	20.786	158.931	140.023	62.397	89.049	139.365	−2.206
3400	20.786	159.552	140.589	64.475	87.157	140.918	−2.165
3500	20.786	160.154	141.139	66.554	85.255	142.527	−2.127
3600	20.786	160.740	141.675	68.632	83.342	144.190	−2.092
3700	20.786	161.309	142.198	70.711	81.420	145.907	−2.060
3800	20.786	161.864	142.709	72.790	79.488	147.676	−2.030
3900	20.786	162.404	143.207	74.868	77.546	149.496	−2.002
4000	20.786	162.930	143.693	76.947	75.595	151.365	−1.977
4100	20.786	163.443	144.169	79.025	73.635	153.284	−1.953
4200	20.786	163.944	144.634	81.104	71.665	155.250	−1.931
4300	20.786	164.433	145.088	83.183	69.686	157.264	−1.910
4400	20.786	164.911	145.534	85.261	67.699	159.323	−1.891
4500	20.786	165.378	145.969	87.340	65.702	161.428	−1.874
4600	20.786	165.835	146.396	89.418	63.697	163.577	−1.857
4700	20.786	166.282	146.815	91.497	61.684	165.770	−1.842
4800	20.786	166.720	147.225	93.576	59.662	168.007	−1.828
4900	20.786	167.148	147.627	95.654	57.632	170.285	−1.815
5000	20.786	167.568	148.022	97.733	55.594	172.604	−1.803
5100	20.786	167.980	148.409	99.811	53.549	174.965	−1.792
5200	20.786	168.383	148.789	101.890	51.497	177.366	−1.782
5300	20.786	168.779	149.163	103.969	49.437	179.806	−1.772
5400	20.786	169.168	149.530	106.047	47.372	182.285	−1.763
5500	20.786	169.549	149.890	108.126	45.300	184.802	−1.755
5600	20.786	169.924	150.245	110.204	43.222	187.358	−1.748
5700	20.786	170.292	150.593	112.283	41.139	189.950	−1.741
5800	20.786	170.653	150.936	114.362	39.051	192.579	−1.734
5900	20.786	171.009	151.273	116.440	36.958	195.244	−1.729
6000	20.786	171.358	151.605	118.519	34.862	197.944	−1.723

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

$S°(298.15\ K) = [219.705]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 243.35 \pm 16.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 238.49 \pm 16.7\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma^+]$	0	[2]

$\omega_e = 1387\ cm^{-1}$ $\omega_e x_e = 83.01\ cm^{-1}$ $\sigma = 1$

$B_e = 5.549\ cm^{-1}$ $\alpha_e = 0.312\ cm^{-1}$ $r_e = 1.74$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from $D_0° = 8.671\ kcal·mol^{-1}$ = taken from Herzberg.[1]

Heat Capacity and Entropy

Molecular constants are taken from Herzberg.[1]

Reference

[1]G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Company, Inc., New York (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.711	243.353	243.353	INFINITE
100	29.132	187.686	245.898	−5.821	243.038	233.028	−121.721
200	29.265	207.901	222.422	−2.904	242.023	223.389	−58.343
250	29.563	214.459	220.197	−1.434	239.098	218.955	−45.748
298.15	30.043	219.705	219.705	0.	238.488	215.132	−37.690
300	30.064	219.891	219.706	0.056	238.465	214.987	−37.433
350	30.708	224.572	220.074	1.574	237.870	211.121	−31.508
400	31.417	228.719	220.900	3.127	237.318	207.338	−27.076
450	32.133	232.461	221.980	4.716	236.810	203.622	−23.636
500	32.822	235.882	223.202	6.340	236.342	199.960	−20.890
600	34.057	241.979	225.835	9.686	235.510	192.763	−16.782
700	35.084	247.308	228.530	13.145	176.026	192.269	−14.347
800	35.931	252.050	231.179	16.697	176.023	194.591	−12.705
900	36.636	256.324	233.739	20.326	176.086	196.908	−11.428
1000	37.233	260.216	236.195	24.020	176.200	199.216	−10.406
1100	37.747	263.789	238.544	27.770	176.352	201.511	−9.569
1200	38.199	267.093	240.787	31.568	176.531	203.790	−8.871
1300	38.603	270.167	242.930	35.408	176.733	206.054	−8.279
1400	38.970	273.042	244.979	39.287	176.951	208.301	−7.772
1500	39.308	275.742	246.941	43.201	177.183	210.533	−7.331
1600	39.623	278.289	248.822	47.148	177.425	212.748	−6.946
1700	39.919	280.700	250.626	51.125	177.677	214.948	−6.605
1800	40.201	282.990	252.361	55.131	177.938	217.133	−6.301
1900	40.471	285.171	254.031	59.165	178.206	219.303	−6.029
2000	40.731	287.253	255.641	63.225	178.483	221.459	−5.784
2100	40.983	289.247	257.194	67.311	178.767	223.601	−5.562
2200	41.227	291.159	258.695	71.422	179.060	225.729	−5.359
2300	41.466	292.997	260.146	75.556	179.361	227.844	−5.174
2400	41.700	294.767	261.552	79.715	179.670	229.945	−5.005
2500	41.930	296.473	262.915	83.896	179.988	232.033	−4.848
2600	42.157	298.122	264.238	88.101	180.315	234.109	−4.703
2700	42.380	299.718	265.522	92.327	180.651	236.171	−4.569
2800	42.601	301.263	266.771	96.576	180.996	238.221	−4.444
2900	42.819	302.762	267.987	100.847	181.352	240.259	−4.328
3000	43.035	304.217	269.170	105.140	181.717	242.284	−4.219
3100	43.249	305.631	270.324	109.454	182.093	244.297	−4.116
3200	43.462	307.008	271.449	113.790	182.479	246.297	−4.020
3300	43.674	308.349	272.547	118.147	182.875	248.285	−3.930
3400	43.884	309.656	273.619	122.525	183.283	250.261	−3.845
3500	44.093	310.931	274.667	126.924	183.700	252.225	−3.764
3600	44.301	312.176	275.691	131.343	184.129	254.177	−3.688
3700	44.508	313.392	276.694	135.784	184.568	256.117	−3.616
3800	44.715	314.582	277.675	140.245	185.018	258.044	−3.547
3900	44.921	315.746	278.637	144.727	185.479	259.960	−3.482
4000	45.126	316.886	279.579	149.229	185.951	261.864	−3.420
4100	45.330	318.003	280.502	153.752	186.434	263.756	−3.360
4200	45.534	319.098	281.408	158.295	186.928	265.636	−3.304
4300	45.738	320.171	282.297	162.859	187.433	267.504	−3.250
4400	45.941	321.225	283.170	167.443	187.949	269.360	−3.198
4500	46.143	322.260	284.027	172.047	188.476	271.204	−3.148
4600	46.346	323.276	284.870	176.671	189.013	273.037	−3.100
4700	46.548	324.275	285.697	181.316	189.562	274.858	−3.055
4800	46.749	325.257	286.511	185.981	190.121	276.667	−3.011
4900	46.950	326.223	287.312	190.666	190.692	278.464	−2.968
5000	47.152	327.174	288.100	195.371	191.274	280.249	−2.928
5100	47.352	328.110	288.875	200.096	191.866	282.022	−2.888
5200	47.553	329.031	289.638	204.841	192.470	283.785	−2.851
5300	47.753	329.939	290.390	209.607	193.085	285.535	−2.814
5400	47.954	330.833	291.131	214.392	193.711	287.273	−2.779
5500	48.154	331.715	291.861	219.197	194.348	289.000	−2.745
5600	48.353	332.584	292.580	224.023	194.996	290.715	−2.712
5700	48.553	333.442	293.290	228.868	195.656	292.419	−2.680
5800	48.753	334.288	293.989	233.733	196.326	294.110	−2.649
5900	48.952	335.123	294.679	238.618	197.008	295.790	−2.619
6000	49.151	335.948	295.360	243.524	197.701	297.459	−2.590

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 206.589\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 28.535 \pm 0.21\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 26.359 \pm 0.21\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 2309.06\ cm^{-1}$ $\omega_e x_e = 39.73\ cm^{-1}$ $\sigma = 2$
$B_e = 6.512\ cm^{-1}$ $\alpha_e = 0.1715\ cm^{-1}$

Enthalpy of Formation

Using the calculated thermal functions and functions for H_2(g) and I_2(g) given in the JANAF tables, equilibrium data from the literature are used to calculate $\Delta_f H°(298.15\ K)$ for the reaction $H_2(g) + I_2(g) \rightarrow 2\ HI(g)$.

Source	$\Delta H°(298.15\ K)$, $kcal·mol^{-1}$
Taylor and Crist[4] (667 to 764 K)	−2.375 ± .005
Bodenstin[5] (556 to 781 K)	−2.053 ± .133
Bright and Hagerty[6] (696 and 779 K)	−2.219 ± .070
Rittenberg and Urey[7] (671 and 741 K)	−2.156 ± .072

The data of Taylor and Crist are the most concordant and are given the most weight. Converting to the solid state of iodine, which has been adopted as a JANAF reference state gives the standard enthalpy of formation of hydrogen iodide.

Heat Capacity and Entropy

Molecular constants are from Cowan and Gordy[1] and Boyd and Thompson.[2] The calculated functions are in reasonable agreement with the compilation of Kelley.[3]

References

[1]M. Cowan and W. Gordy, Phys. Rev. **104**, 551 (1956).
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[3]K. K. Kelley, U. S. Bur. Mines Bull. 584, (1960).
[4]A. H. Taylor and R. H. Crist, J. Amer. Chem. Soc. **65**, 1377 (1941).
[5]M. Bodenstein, Z. physikal. Chem. **29**, 295 (1899).
[6]N. F. H. Bright and R. P. Hagerty, Trans. Faraday Soc. **43**, 697 (1947).
[7]D. Rittenberg and H. C. Urey, J. Amer. Chem. Soc. **56**, 1885 (1934).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.656	28.535	28.535	INFINITE
100	29.114	174.773	232.489	−5.772	28.396	19.004	−9.927
200	29.124	194.956	209.255	−2.860	27.494	9.940	−2.596
250	29.134	201.456	207.069	−1.403	26.939	5.615	−1.173
298.15	29.156	206.589	206.589	0.	26.359	1.560	−0.273
300	29.158	206.770	206.590	0.054	26.336	1.406	−0.245
350	29.216	211.268	206.945	1.513	25.665	−2.698	0.403
400	29.328	215.176	207.735	2.976	16.987	−6.428	0.839
450	29.502	218.640	208.758	4.447	15.710	−9.279	1.077
500	29.736	221.760	209.905	5.928	−5.622	−10.088	1.054
600	30.348	227.233	212.349	8.931	−5.961	−10.948	0.953
700	31.064	231.964	214.820	12.001	−6.243	−11.756	0.877
800	31.798	236.160	217.230	15.144	−6.466	−12.528	0.818
900	32.496	239.946	219.547	18.359	−6.633	−13.275	0.770
1000	33.135	243.404	221.763	21.641	−6.754	−14.006	0.732
1100	33.706	246.589	223.877	24.984	−6.838	−14.727	0.699
1200	34.211	249.544	225.894	28.380	−6.897	−15.441	0.672
1300	34.655	252.300	227.821	31.824	−6.942	−16.151	0.649
1400	35.046	254.883	229.662	35.309	−6.982	−16.858	0.629
1500	35.391	257.313	231.425	38.832	−7.027	−17.562	0.612
1600	35.696	259.607	233.116	42.386	−7.087	−18.263	0.596
1700	35.967	261.780	234.739	45.970	−7.168	−18.959	0.583
1800	36.209	263.842	236.299	49.579	−7.277	−19.649	0.570
1900	36.427	265.806	237.800	53.211	−7.416	−20.333	0.559
2000	36.623	267.680	239.248	56.863	−7.589	−21.009	0.549
2100	36.802	269.471	240.645	60.535	−7.794	−21.675	0.539
2200	36.966	271.187	241.994	64.223	−8.030	−22.330	0.530
2300	37.116	272.833	243.300	67.927	−8.294	−22.975	0.522
2400	37.255	274.416	244.563	71.646	−8.581	−23.607	0.514
2500	37.384	275.939	245.788	75.378	−8.886	−24.227	0.506
2600	37.504	277.408	246.976	79.123	−9.204	−24.834	0.499
2700	37.617	278.825	248.130	82.879	−9.528	−25.429	0.492
2800	37.723	280.195	249.251	86.646	−9.854	−26.012	0.485
2900	37.823	281.521	250.341	90.423	−10.176	−26.583	0.479
3000	37.918	282.805	251.401	94.210	−10.489	−27.144	0.473
3100	38.009	284.050	252.435	98.006	−10.789	−27.694	0.467
3200	38.095	285.258	253.442	101.812	−11.073	−28.235	0.461
3300	38.178	286.431	254.424	105.625	−11.338	−28.767	0.455
3400	38.258	287.572	255.382	109.447	−11.580	−29.291	0.450
3500	38.335	288.682	256.317	113.277	−11.799	−29.809	0.445
3600	38.409	289.763	257.232	117.114	−11.993	−30.321	0.440
3700	38.481	290.817	258.125	120.959	−12.161	−30.828	0.435
3800	38.550	291.844	258.999	124.810	−12.303	−31.330	0.431
3900	38.618	292.846	259.854	128.669	−12.417	−31.829	0.426
4000	38.684	293.825	260.691	132.534	−12.504	−32.326	0.422
4100	38.749	294.781	261.511	136.405	−12.565	−32.821	0.418
4200	38.812	295.715	262.314	140.283	−12.599	−33.314	0.414
4300	38.874	296.629	263.102	144.168	−12.607	−33.807	0.411
4400	38.934	297.523	263.874	148.058	−12.590	−34.300	0.407
4500	38.994	298.399	264.631	151.955	−12.549	−34.794	0.404
4600	39.052	299.257	265.375	155.857	−12.484	−35.289	0.401
4700	39.110	300.097	266.105	159.765	−12.395	−35.786	0.398
4800	39.166	300.921	266.822	163.679	−12.284	−36.284	0.395
4900	39.222	301.729	267.526	167.598	−12.151	−36.786	0.392
5000	39.277	302.522	268.218	171.523	−11.998	−37.290	0.390
5100	39.332	303.301	268.898	175.454	−11.823	−37.798	0.387
5200	39.385	304.065	269.567	179.389	−11.630	−38.309	0.385
5300	39.439	304.816	270.225	183.331	−11.416	−38.824	0.383
5400	39.491	305.553	270.872	187.277	−11.185	−39.343	0.381
5500	39.544	306.278	271.510	191.229	−10.935	−39.867	0.379
5600	39.595	306.991	272.137	195.186	−10.667	−40.395	0.377
5700	39.647	307.693	272.754	199.148	−10.382	−40.929	0.375
5800	39.698	308.383	273.363	203.115	−10.080	−41.467	0.373
5900	39.748	309.062	273.962	207.087	−9.760	−42.011	0.372
6000	39.798	309.730	274.553	211.065	−9.425	−42.561	0.371

PREVIOUS: September 1961 (1 atm) CURRENT: September 1961 (1 bar)

$S°(298.15\ K) = [375.009 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-66.36 \pm 20.9]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-74.48 \pm 20.9]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2190(1)	717(2)
286(1)	399(2)
122(1)	80(2)

Ground State Quantum Weight: [1] $\sigma = 3$

Point Group: C_{3v}

Bond Distances: SiH = [1.50] Å Si–I = [2.435] Å

Bond Angles: H–Si–I = [106.81]° I–Si–I = [112]°

Product of the Moments of Inertia: $I_A I_B I_C = [1.04795 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of $SiI_4(g)$ and $SiH_4(g)$. There are no experimental $\Delta_f H°$ data for SiH_3I, SiH_2I_2, and $SiHI_3$. Data for the iodomethanes[2] have a surprising progression, (SiH_3I, g);[1] they are of doubtful use in predicting $\Delta_f H°$ of the iodosilanes. We conclude, as did Hunt and Sirtl,[3] that the available data justify only linear interpolation.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3I, SiI_4 and the various bormo–, chloro–, and fluorosilanes.[1] The principal moments of inertia are: $I_A = I_B = 174.6 \times 10^{-39}$ and $I_C = 343.48 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are from liquid–phase Raman spectra of Hengge and Hoefler.[4] Infrared data, also presumably for the liquid phase, were reported[4] for ν_1 and ν_4.

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: $H_3ISI(g)$, $HI_3Si(g)$, $BrH_3Si(g)$, $Br_2H_2Si(g)$, $Br_3HSi(g)$, $ClH_3Si(g)$, $Cl_2H_2Si(g)$,$Cl_3HSi(g)$ 12–31–76; $FH_3Si(g)$, $F_2H_2Si(g)$, $F_3HSi(g)$, $I_4Si(g)$, $H_4Si(g)$6–30–76.

[2]S. A. Kudchadker and A. P. Kudchadker, J. Phys. Chem. Ref. Data **4**, 457 (1975).

[3]L. P. Hunt and E. Sirtl, J. Electrochem. Soc. **120**, 806 (1973).

[4]E. Hengge and F. Hoefler, Z. Naturforsch. **A26**, 768 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.135	−66.361	−66.361	INFINITE
100	58.844	297.407	442.714	−14.531	−68.098	−83.270	43.496
200	74.448	343.359	382.414	−7.811	−71.302	−97.213	25.389
250	79.878	360.582	376.369	−3.947	−72.928	−103.503	21.626
298.15	83.884	375.009	375.009	0.	−74.475	−109.250	19.140
300	84.018	375.528	375.011	0.155	−74.535	−109.466	19.060
350	87.179	388.728	376.046	4.439	−76.229	−115.157	17.186
400	89.637	400.536	378.382	8.862	−101.860	−119.782	15.642
450	91.605	411.211	381.446	13.394	−105.232	−121.819	14.140
500	93.228	420.949	384.917	18.016	−168.739	−117.785	12.305
600	95.791	438.185	392.396	27.474	−168.754	−107.590	9.367
700	97.757	453.105	400.026	37.155	−168.641	−97.404	7.268
800	99.322	466.264	407.500	47.012	−168.438	−87.240	5.696
900	100.590	478.039	414.695	57.009	−168.175	−77.105	4.475
1000	101.625	488.692	421.570	67.122	−167.878	−67.002	3.500
1100	102.479	498.419	428.121	77.328	−167.570	−56.930	2.703
1200	103.186	507.367	434.357	87.613	−167.272	−46.885	2.041
1300	103.776	515.651	440.296	97.962	−167.008	−36.863	1.481
1400	104.272	523.360	445.957	108.365	−166.800	−26.860	1.002
1500	104.691	530.569	451.360	118.814	−166.670	−16.870	0.587
1600	105.048	537.337	456.524	129.301	−166.640	−6.885	0.225
1700	105.354	543.715	461.467	139.821	−216.905	3.549	−0.109
1800	105.617	549.744	466.205	150.370	−216.894	16.516	−0.479
1900	105.846	555.461	470.754	160.944	−216.982	29.485	−0.811
2000	106.045	560.896	475.126	171.538	−217.172	42.462	−1.109
2100	106.219	566.074	479.335	182.152	−217.463	55.450	−1.379
2200	106.373	571.019	483.391	192.782	−217.849	68.454	−1.625
2300	106.509	575.750	487.304	203.426	−218.317	81.478	−1.850
2400	106.629	580.286	491.085	214.083	−218.856	94.524	−2.057
2500	106.737	584.641	494.740	224.751	−219.448	107.594	−2.248
2600	106.833	588.829	498.279	235.430	−220.077	120.688	−2.425
2700	106.920	592.863	501.708	246.118	−220.726	133.807	−2.589
2800	106.998	596.752	505.033	256.814	−221.379	146.949	−2.741
2900	107.068	600.508	508.261	267.517	−222.018	160.115	−2.884
3000	107.132	604.139	511.397	278.227	−222.631	173.303	−3.017
3100	107.191	607.653	514.446	288.943	−223.205	186.510	−3.143
3200	107.244	611.057	517.412	299.665	−223.729	199.735	−3.260
3300	107.292	614.358	520.300	310.392	−224.193	212.976	−3.371
3400	107.337	617.562	523.114	321.123	−224.590	226.230	−3.476
3500	107.378	620.674	525.857	331.859	−224.916	239.494	−3.574
3600	107.416	623.699	528.533	342.599	−609.316	263.227	−3.819
3700	107.450	626.643	531.145	353.342	−609.071	287.462	−4.058
3800	107.483	629.509	533.696	364.089	−608.746	311.688	−4.284
3900	107.513	632.301	536.188	374.839	−608.340	335.905	−4.499
4000	107.540	635.023	538.625	385.591	−607.852	360.110	−4.703
4100	107.566	637.679	541.009	396.347	−607.283	384.302	−4.896
4200	107.590	640.271	543.342	407.104	−606.634	408.480	−5.080
4300	107.612	642.803	545.626	417.865	−605.905	432.640	−5.256
4400	107.633	645.278	547.862	428.627	−605.099	456.783	−5.423
4500	107.653	647.697	550.054	439.391	−604.218	480.907	−5.582
4600	107.671	650.063	552.203	450.157	−603.263	505.011	−5.735
4700	107.688	652.379	554.309	460.925	−602.237	529.093	−5.880
4800	107.705	654.646	556.376	471.695	−601.142	553.153	−6.020
4900	107.720	656.867	558.405	482.466	−599.981	577.188	−6.153
5000	107.734	659.043	560.396	493.239	−598.756	601.200	−6.281
5100	107.748	661.177	562.351	504.013	−597.470	625.186	−6.403
5200	107.760	663.269	564.272	514.788	−596.124	649.147	−6.521
5300	107.772	665.322	566.159	525.565	−594.722	673.081	−6.634
5400	107.784	667.337	568.014	536.343	−593.266	696.988	−6.742
5500	107.795	669.315	569.838	547.122	−591.756	720.868	−6.846
5600	107.805	671.257	571.632	557.902	−590.197	744.720	−6.946
5700	107.815	673.165	573.396	568.683	−588.590	768.544	−7.043
5800	107.824	675.040	575.133	579.465	−586.937	792.339	−7.136
5900	107.833	676.884	576.842	590.248	−585.240	816.105	−7.225
6000	107.841	678.696	578.524	601.031	−583.500	839.842	−7.311

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K)$ = [50.208] $J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K)$ = −57.820 ± 0.046 $kJ·mol^{-1}$

Enthalpy of Formation

The value of $\Delta_f H°(298.15\ K)$ is taken from Gunn and Green.[1] The corresponding value reported by Messer *et al.*[2] was −15.16 ± 0.6 $kcal·mol^{-1}$. In this latter paper, the results of the previous investigations were also reviewed.

Heat Capacity and Entropy

$C_p°$ and $S°(298.15\ K)$ are estimated by comparison with those for NaH(cr) and LiH(cr).

Decomposition Data

T_{dcm} = 690 K was assumed to be the temperature at which the value of $\Delta_f G°$ changes from negative to positive.

References

[1]S.R. Gunn and L.G. Green, J. Amer. Chem. Soc. **80**, 4782 (1958).
[2]C.E. Messer, L.G. Fasolino and C.E. Thalmayer, J. Amer. Chem. Soc. 77, 4524 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	37.907	50.208	50.208	0.	−57.820	−53.010	9.287
300	38.074	50.443	50.209	0.070	−57.776	−52.980	9.225
400	44.141	62.267	51.780	4.195	−55.104	−51.768	6.760
500	48.534	72.608	54.933	8.837	−51.924	−51.293	5.359
600	51.923	81.766	58.657	13.865	−48.360	−51.496	4.483
700	54.606	89.977	62.555	19.196	−44.498	−52.320	3.904
800	56.819	97.418	66.455	24.771	−40.400	−53.715	3.507
900	58.440	104.207	70.278	30.536	−36.122	−55.635	3.229
1000	59.831	110.438	73.987	36.451	−31.708	−58.038	3.032
1100	60.966	116.195	77.565	42.493	−27.187	−60.889	2.891
1200	61.923	121.542	81.010	48.639	−22.580	−64.156	2.793
1300	62.701	126.531	84.322	54.871	−17.907	−67.810	2.725
1400	63.301	131.200	87.505	61.173	−13.188	−71.825	2.680
1500	63.722	135.583	90.566	67.526	−8.439	−76.179	2.653

PREVIOUS: CURRENT: March 1963

Potassium Hydride (KH) IDEAL GAS M_r = 40.10624

$S°(298.15\ K) = 198.024\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 125.53 \pm 14.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 123.01 \pm 14.6\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 985.0\ cm^{-1}$ $\omega_e x_e = 14.65\ cm^{-1}$ $\sigma = 1$

$B_e = cm^{-1}$ $\alpha_e = 0.0673\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $D_0° = 1.86 \pm 0.15$ eV as reported by Gaydon.[1]

Heat Capacity and Entropy

All molecular and spectroscopic constants are obtained from Herzberg.[2]

References

[1]A.G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Company, Inc., (1950).

Potassium Hydride (KH) $H_1K_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.795	125.530	125.530	INFINITE
100	29.136	165.689	224.657	−5.897	125.197	117.224	−61.232
200	29.583	185.963	200.811	−2.970	124.183	109.630	−28.632
250	30.243	192.630	198.530	−1.475	123.605	106.058	−22.160
298.15	31.036	198.024	198.024	0.	123.010	102.731	−17.998
300	31.068	198.216	198.025	0.057	122.986	102.606	−17.865
350	31.917	203.069	198.406	1.632	119.945	99.357	−14.828
400	32.711	207.384	199.263	3.248	119.245	96.465	−12.597
450	33.419	211.279	200.386	4.902	118.605	93.656	−10.871
500	34.034	214.832	201.655	6.589	118.017	90.916	−9.498
600	35.019	221.129	204.389	10.044	116.968	85.597	−7.452
700	35.752	226.585	207.179	13.584	116.043	80.443	−6.003
800	36.309	231.397	209.912	17.188	115.194	75.416	−4.924
900	36.746	235.700	212.542	20.842	114.378	70.493	−4.091
1000	37.098	239.590	215.055	24.535	113.556	65.661	−3.430
1100	37.391	243.140	217.450	28.259	33.742	65.523	−3.111
1200	37.640	246.404	219.728	32.011	33.876	68.406	−2.978
1300	37.858	249.426	221.898	35.786	34.012	71.278	−2.864
1400	38.052	252.239	223.966	39.582	34.147	74.140	−2.766
1500	38.228	254.870	225.939	43.396	34.277	76.992	−2.681
1600	38.389	257.342	227.826	47.227	34.402	79.835	−2.606
1700	38.540	259.674	229.631	51.074	34.520	82.671	−2.540
1800	38.681	261.881	231.362	54.935	34.629	85.500	−2.481
1900	38.816	263.976	233.024	58.810	34.728	88.324	−2.428
2000	38.944	265.971	234.622	62.698	34.817	91.142	−2.380
2100	39.068	267.874	236.160	66.598	34.893	93.956	−2.337
2200	39.188	269.694	237.643	70.511	34.956	96.767	−2.298
2300	39.305	271.438	239.075	74.436	35.004	99.576	−2.261
2400	39.419	273.114	240.459	78.372	35.034	102.383	−2.228
2500	39.530	274.725	241.797	82.319	35.045	105.189	−2.198
2600	39.640	276.278	243.094	86.278	35.034	107.994	−2.170
2700	39.747	277.776	244.351	90.247	34.999	110.801	−2.144
2800	39.854	279.223	245.571	94.227	34.937	113.610	−2.119
2900	39.959	280.623	246.755	98.218	34.845	116.421	−2.097
3000	40.062	281.980	247.907	102.219	34.721	119.236	−2.076
3100	40.165	283.295	249.027	106.230	34.561	122.056	−2.057
3200	40.267	284.572	250.118	110.252	34.361	124.881	−2.038
3300	40.369	285.813	251.181	114.284	34.127	127.713	−2.022
3400	40.469	287.019	252.218	118.326	33.841	130.553	−2.006
3500	40.569	288.194	253.229	122.378	33.508	133.402	−1.991
3600	40.669	289.338	254.216	126.440	33.119	136.261	−1.977
3700	40.767	290.454	255.180	130.511	32.672	139.132	−1.964
3800	40.866	291.542	256.123	134.593	32.163	142.016	−1.952
3900	40.964	292.605	257.045	138.685	31.586	144.915	−1.941
4000	41.062	293.643	257.947	142.786	30.944	147.828	−1.930
4100	41.159	294.659	258.830	146.897	30.226	150.759	−1.921
4200	41.256	295.652	259.695	151.018	29.423	153.708	−1.912
4300	41.353	296.623	260.542	155.148	28.535	156.677	−1.903
4400	41.450	297.575	261.373	159.288	27.834	159.641	−1.895
4500	41.546	298.508	262.188	163.438	26.830	162.648	−1.888
4600	41.643	299.422	262.988	167.598	25.740	165.678	−1.881
4700	41.739	300.319	263.772	171.767	24.581	168.731	−1.875
4800	41.835	301.198	264.543	175.945	23.441	171.797	−1.870
4900	41.930	302.062	265.300	180.134	22.107	174.901	−1.864
5000	42.026	302.910	266.044	184.331	20.683	178.034	−1.860
5100	42.121	303.743	266.775	188.539	19.166	181.196	−1.856
5200	42.217	304.562	267.494	192.756	17.557	184.389	−1.852
5300	42.312	305.367	268.201	196.982	15.855	187.613	−1.849
5400	42.407	306.159	268.896	201.218	14.061	190.870	−1.846
5500	42.502	306.938	269.581	205.464	12.177	194.162	−1.844
5600	42.597	307.705	270.255	209.718	10.202	197.488	−1.842
5700	42.692	308.459	270.918	213.983	8.484	200.803	−1.840
5800	42.787	309.203	271.572	218.257	6.379	204.196	−1.839
5900	42.881	309.935	272.216	222.540	4.195	207.625	−1.838
6000	42.976	310.656	272.851	226.833	1.933	211.092	−1.838

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 78.907 \pm 0.84\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 516\ K$
$T_{fus} = 679\ K$

$\Delta_f H°(0\ K) = -421.22 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H(298.15\ K) = -424.72 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 6.443 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 8.619 \pm 0.63\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of KOH(cr) is obtained from its enthalpy of solution in water, the enthalpy of hydrolysis of metallic potassium, and appropriate auxiliary data.

Reshetnikov[1] determined calorimetrically the enthalpy of solution of KOH(cr) in 650 H_2O as -13.665 ± 0.009 kcal·mol^{-1}. Combining this result with enthalpy of dilution data for KOH reported by Parker[2] we derive $\Delta_{sln}H°(KOH, cr) = -13.77 \pm 0.01$ kcal·mol^{-1}.

The enthalpy of hydrolysis of metallic potassium has been determined by various investigators.[3–5] The data are summarized below for the reaction $K(cr) + (n + 1)H_2O(l) \rightarrow KOH \cdot nH_2O + 0.5\ H_2(g)$.

Source	n moles of H_2O	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(KOH, aq, ∞, 298.15 K)* kcal·mol^{-1}	$\Delta_f H°$(KOH, cr, 298.15 K) kcal·mol^{-1}
Gunn and Green[3a,3b]	∞	−46.958 ± 0.22	−115.273 ± 0.22	−101.50 ± 0.02
Messer *et al.*[4]	∞	−47.02 ± 0.15	−115.34 ± 0.15	−101.57 ± 0.16
Ketchen and Wallace[5]	∞	−46.89 ± 0.24	−115.21 ± 0.24	−101.44 ± 0.25

*Based on $\Delta_f H$ (H_2O, l, 298.15 K) = −68.315 kcal·mol^{-1}.[6]

The values of $\Delta_f H°$(KOH, cr, 298.15 K) given in the last column are calculated from $\Delta_f H°$(KOH, aq, ∞, 298.15 K) and the enthalpy of solution of KOH(cr) at infinite dilution given above. The adopted value for $\Delta_f H°$(KOH, cr, 298.15 K) is from the work of Gunn and Green.[3a,3b]

Earlier investigations pertaining to the determination of $\Delta_f H°$(KOH, cr, 298.15 K) have been reviewed by Bichowsky and Rossini[7] and Messer *et al.*[4] and are only of historical interest.

Heat Capacity and Entropy

The low temperature heat capacities for KOH(cr) in the temperature range 20–298 K are from the recent work of Stull *et al.*.[8] These data contain a broad lambda type transition with a heat capacity peak at 227.5 K. Powers and Blalock[9] measured high temperature enthalpy data for KOH(cr) in both the α and β phases in a Bunsen ice calorimeter. Their enthalpy data are scattered and not precise enough to accurately define the heat capacities for the α phase. Therefore, the selected heat capacities between 298 and 516 K are estimated by graphical extrapolation of the low temperature heat capacity data. Heat capacities for the β phase are from Powers and Blalock.[9]

$S°(298.15\ K)$ is calculated from the smoothed C_p^o data and is based on an extrapolation of $S°(20\ K) = 0.199$ cal·K^{-1}·mol^{-1}.

Transition and Fusion Data

Several values for the enthalpy of the α–β transition and the enthalpy of melting of KOH have been reported in the literature.

Source	Method	T_{trs}/K	$\Delta_{trs}H°$ kcal·mol^{-1}	T_{fus}/K	$\Delta_{fus}H°$ kcal·mol^{-1}
Powers and Blalock[9]	Calorimetric	522	1.346	673	2.244
Seward and Martin[10]	Freezing Point			683	1.830
Kelly[11]	Freezing Point			633	1.980
Reshetnikov and Baranskaya[12]	Thermographic	515	1.540 ± 0.5	679	1.980 ± 0.15
Maurice[13]	Freezing Point	517		678	2.13 ± 0.07

The selected values are from the work of Reshetnikov and Baranskaya[12] and Maurice.[13]

Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ for the monomer and dimer are calculated from the selected enthalpies of vaporization and the enthalpy of melting at 298.15 K. See the ideal gas table for details.

References

[1]N. A. Reshetnikov, Zhur. Neorg. Khim. **6**, 682 (1961).
[2]V. B. Parker, NSRDS–NBS 2, 1965.
[3]a) S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. **80**, 4782 (1958). b) S. R. Gunn, J. Phys. Chem. **71**, 1386 (1967).
[4]C. E. Messer, L. C. Fasolino and C. O. Thalmayer, J. Amer. Chem. Soc. **77**, 4524 (1955).

Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.163	−421.223	−421.223	INFINITE
100	34.100	23.857	130.178	−10.632	−424.377	−409.500	213.901
200	53.932	53.620	84.784	−6.233	−425.375	−394.110	102.931
298.15	64.894	78.907	78.907	0.	−424.718	−378.899	66.382
300	65.011	79.309	78.909	0.120	−424.706	−378.615	65.923
400	71.672	98.894	81.534	6.944	−426.299	−362.909	47.391
500	79.580	115.714	86.721	14.496	−424.845	−347.213	36.273
516.000	80.961	118.242	87.660	15.780	ALPHA <–> BETA		
516.000	78.659	130.729	87.660	22.224	TRANSITION		
600	78.659	142.593	94.541	28.831	−416.594	−332.908	28.982
679.000	78.659	152.322	100.709	35.045	BETA <–> LIQUID		
700	78.659	154.718	102.294	36.697	−414.821	−319.100	23.812
800	78.659	165.221	109.518	44.563	−413.076	−305.545	19.950
900	78.659	174.486	116.232	52.429	−411.383	−292.206	16.959
1000	78.659	182.774	122.479	60.295	−409.763	−279.052	14.576
1100	78.659	190.271	128.306	68.161	−487.190	−261.446	12.415
1200	78.659	197.115	133.759	76.027	−484.716	−241.033	10.492
1300	78.659	203.411	138.878	83.893	−482.281	−220.825	8.873
1400	78.659	209.240	143.699	91.758	−479.883	−200.803	7.492
1500	78.659	214.667	148.251	99.624	−477.521	−180.952	6.301

PREVIOUS: March 1966 CURRENT: December 1970

$S°(298.15\ K) = [96.617]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-412.705]\ kJ·mol^{-1}$

$T_{fus} = 679\ K$ $\Delta_{fus}H° = 8.619 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(KOH, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(679\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid phase is obtained from the high temperature enthalpy measurements of Powers and Blalock[1] The constant $C_p°$ is extrapolated below the melting point and up to 2000 K.

$S°$(298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 1596 K for the process KOH(l) = KOH(g) is calculated as the temperature at which the fugacity of KOH(g) is 1 atm. The difference in the enthalpies of formation of KOH(l) and KOH(g) at T_{vap} is the enthalpy of vaporization. If $[KOH]_2$(g) is also considered a minor component in the vapor mixture (approximately 2% of the total vapor pressure at the boiling point) the calculated boiling point is unchanged.

Wartenberg and Albrecht[2] reported a boiling point of 1597 K for KOH from static vapor pressure measurements, while very recently Dubois and Millet[3] determined a boiling point of 1540 K from transpiration vapor pressure measurements.

References

[1]W.D. Powers and G.C. Blalock, Oak Ridge Natl. Lab., ORNL 1653, (January 1954).
[2]H.von Wartenberg and P. Albrecht, Z. Elektrochem. **27**, 162 (1921).
[3]J. Dubois and J. Millet, Compt. Rend. **269**, 1336 (1969).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	83.107	96.617	96.617	0.	−412.705	−372.166	65.202
300	83.107	97.131	96.618	0.154	−412.660	−371.915	64.756
400	83.107	121.039	99.878	8.464	−412.766	−358.234	46.781
500	83.107	139.584	106.034	16.775	−410.553	−344.856	36.027
600	83.107	154.736	112.926	25.086	−408.327	−331.926	28.897
679.000	83.107	165.016	118.401	31.651	---- BETA <--> LIQUID ----		
700	83.107	167.547	119.838	33.396	−406.108	−319.368	23.832
800	83.107	178.644	126.511	41.707	−403.919	−307.127	20.053
900	83.107	188.433	132.858	50.018	−401.781	−295.157	17.130
1000	83.107	197.189	138.861	58.328	−399.716	−283.421	14.804
1100	83.107	205.110	144.529	66.639	−476.698	−267.278	12.692
1200	83.107	212.341	149.883	74.950	−473.780	−248.368	10.811
1300	83.107	218.993	154.947	83.261	−470.900	−229.701	9.230
1400	83.107	225.152	159.744	91.571	−468.057	−211.254	7.882
1500	83.107	230.886	164.298	99.882	−465.250	−193.010	6.721
1600	83.107	236.250	168.629	108.193	−462.480	−174.951	5.712
1700	83.107	241.288	172.757	116.503	−459.744	−157.064	4.826
1800	83.107	246.038	176.697	124.814	−457.043	−139.338	4.043
1900	83.107	250.532	180.466	133.125	−454.378	−121.760	3.347
2000	83.107	254.794	184.077	141.435	−451.748	−104.322	2.725

PREVIOUS: March 1966 CURRENT: December 1970

0	to 516	K	crystal, alpha
516	to 679	K	crystal, beta
above	679	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.163	−421.223	−421.223	INFINITE
100	34.100	23.857	130.178	−10.632	−424.377	−409.500	213.901
200	53.932	53.620	84.784	−6.233	−425.375	−394.110	102.931
298.15	64.894	78.907	78.907	0.	−424.718	−378.899	66.382
300	65.011	79.309	78.909	0.120	−424.706	−378.615	65.923
400	71.672	98.894	81.534	6.944	−426.299	−362.909	47.391
500	79.580	115.714	86.721	14.496	−424.845	−347.213	36.273
516.000	80.961	118.242	87.660	15.780	ALPHA <--> BETA		
516.000	78.659	130.729	87.660	22.224	TRANSITION		
600	78.659	142.593	94.541	28.831	−416.594	−332.908	28.982
679.000	78.659	152.322	100.709	35.045	BETA <--> LIQUID		
679.000	83.107	165.016	100.709	43.664	TRANSITION		
700	83.107	167.547	102.676	45.409	−406.108	−319.368	23.832
800	83.107	178.644	111.494	53.720	−403.919	−307.127	20.053
900	83.107	188.433	119.510	62.031	−401.781	−295.157	17.130
1000	83.107	197.189	126.848	70.342	−399.716	−283.421	14.804
1100	83.107	205.110	133.608	78.652	−476.698	−267.278	12.692
1200	83.107	212.341	139.872	86.963	−473.780	−248.369	10.811
1300	83.107	218.993	145.706	95.274	−470.900	−229.701	9.230
1400	83.107	225.152	151.164	103.584	−468.057	−211.254	7.882
1500	83.107	230.886	156.289	111.895	−465.251	−193.010	6.721
1600	83.107	236.250	161.121	120.206	−462.480	−174.951	5.712
1700	83.107	241.288	165.690	128.516	−459.744	−157.064	4.826
1800	83.107	246.038	170.023	136.827	−457.043	−139.338	4.043
1900	83.107	250.532	174.143	145.138	−454.378	−121.760	3.347
2000	83.107	254.794	178.070	153.448	−451.748	−104.322	2.725

PREVIOUS: CURRENT: December 1970

$S°(298.15\ K) = [236.379 \pm 1.3]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -228.40 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -232.63 \pm 12.6\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
408 (1)
[340] (2)
[3610] (1)

Ground State Quantum Weight: 1 σ = 1
Point Group: $C_{\infty v}$
Bond Distances: K–O = 2.18 ± 0.01 Å O–H = [0.97 ± 0.05] Å
Bond Angle: K–O–H = 180°
Rotational Constant: $B_0 = 0.279902\ cm^{-1}$

Enthalpy of Formation

Mass spectrometric studies[1-5] of the equilibrium gases over pure KOH(cr, l) and mixed KOH–NaOH condensed phases have unequivocally identified the vapor species as monomer and dimer in the temperature range 600–700 K. Absolute partial pressures for KOH(g) and $K_2(OH)_2$ (g) have been determined from peak intensity data by Porter and Schoonmaker[3] and Gusarov and Gorokhov.[5] These data are analyzed by the 3rd law method with JANAF Gibbs energy functions[6] in order to evaluate an enthalpy of dimerization at 298 K. The adopted value is $\Delta_f H°(298.15\ K) = -45.3 \pm 3.0\ kcal·mol^{-1}$ for the reaction 2 KOH(g) = $K_2(OH)_2$ (g).

Vapor pressures for liquid KOH have been determined by static (1443–1600 K)[7] and transpiration (873–1323 K)[8] methods. In order to evaluate $\Delta_{vap}H°$(KOH, l, 298.15 K) we have used a trial and error variation of $\Delta_{vap}H°(298.15\ K)$ for the monomer and dimer, such that these values are in accordance with the adopted enthalpy of dimerization given above, and the sum of the calculated partial pressures for KOH(g) and $[KOH]_2$(g) is in good agreement with the experimental vapor pressure data. Since the dimer to monomer ratio decreases with increasing temperature, more weight is given to the static data of Wartenberg and Albrecht.[7] The selected values are: $\Delta_{vap}H°$(to monomer, 298.15 K) = 43.0 ± 3.0 $kcal·mol^{-1}$ and $\Delta_{vap}H°$(to dimer, 298.15 K) = 40.8 ± 3.0 $kcal·mol^{-1}$. From these results we derive $\Delta_f H°$(KOH, g, 298.15 K) = −55.6 ± 3.0 $kcal·mol^{-1}$ with $\Delta_f H°$(KOH, l, 298.15 K) = −98.64 ± 0.50 $kcal·mol^{-1}$.[6] This value is adopted here and when used in combination with the enthalpy of dimerization results in $\Delta_f H°[KOH]_2$, g, 298.15 K) = −156.5 ± 3.0 $kcal·mol^{-1}$.

The bond dissociation energies of the alkali metal hydroxides have been determined by several workers from flame studies[9-11] and by mass spectrometry.[12] The data for KOH are summarized below.

Source	Method	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 3rd law	$D°_0$(K–OH) $kcal·mol^{-1}$
Smith and Sugden[9]	Flame	86 ± 1	
Jensen and Padley[10]	Flame	36.4	82 ± 2
Cotton and Jenkins[11]	Flame	32.5	86 ± 2
Gorokhov *et al.*[12]	Mass Spec.	80 ± 3	
	Reaction: K(g) + H_2O(g) = KOH(g) + H(g)		

Our adopted enthalpy of formation for KOH(g) leads to $D°_0 = 85.4 \pm 3.0\ kcal·mol^{-1}$, which is in reasonable agreement with the results of the flame studies,[9-11] particularly when one considers the difficulties inherent in this method.

Heat Capacity and Entropy

Kuczkowski *et al.*[13] observed the microwave spectra of gaseous KOH and interpreted the results in terms of a linear geometry. Very recently, microwave studies of gaseous CsOH[14a] and RbOH,[14b] along with infrared spectra of matrix-isolated CsOH,[15a] RbOH[15b] and NaOH[15b] have been reported and interpreted in terms of linear structures for all these molecules. We adopt a linear configuration for KOH(g), along with the bond distances determined by Kuczkowski *et al.*[13] from their microwave studies.

Acquista and Abramowitz[15b] attempted to measure the infrared spectrum of matrix-isolated monomeric KOH but observed bands which could only be ascribable to polymeric species. Spinar and Margrave[16] investigated the infrared spectrum of the equilibrium gases over liquid KOH at temperatures up to 1000 K. An absorption band at 408 ± 10 cm^{-1} was assigned to the K–OH stretching by these workers, and this assignment is adopted here. The doubly degenerate bending and O–H stretching frequencies are estimates taken from the recent work of Jensen.[17]

Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.423	−228.396	−228.396	INFINITE
100	32.946	191.442	275.830	−8.439	−230.096	−231.978	121.173
200	43.677	217.899	240.692	−4.559	−231.613	−233.204	60.907
250	46.658	227.990	237.169	−2.295	−232.150	−233.538	48.795
298.15	48.531	236.379	236.379	0.	−232.630	−233.762	40.954
300	48.589	236.679	236.380	0.090	−232.649	−233.769	40.703
350	49.880	244.273	236.977	2.554	−235.539	−233.819	34.896
400	50.776	250.995	238.317	5.071	−236.084	−233.535	30.497
450	51.424	257.015	240.066	7.627	−236.581	−233.186	27.068
500	51.913	262.460	242.037	10.211	−237.043	−232.784	24.319
600	52.628	271.992	246.258	15.440	−237.898	−231.850	20.184
700	53.187	280.147	250.531	20.732	−238.699	−230.779	17.221
800	53.704	287.283	254.688	26.076	−239.476	−229.594	14.991
900	54.220	293.638	258.669	31.473	−240.252	−228.312	13.251
1000	54.740	299.378	262.457	36.920	−241.050	−226.943	11.854
1100	55.257	304.620	266.056	42.420	−320.843	−220.882	10.489
1200	55.761	309.449	269.473	47.971	−320.684	−211.802	9.220
1300	56.244	313.932	272.723	53.572	−320.514	−202.735	8.146
1400	56.698	318.117	275.817	59.219	−320.335	−193.682	7.226
1500	57.122	322.043	278.769	64.911	−320.147	−184.642	6.430
1600	57.514	325.742	281.591	70.643	−319.955	−175.615	5.733
1700	57.874	329.240	284.292	76.412	−319.761	−166.599	5.119
1800	58.204	332.558	286.882	82.216	−319.567	−157.596	4.573
1900	58.504	335.713	289.369	88.052	−319.376	−148.603	4.085
2000	58.779	338.721	291.762	93.916	−319.192	−139.619	3.646
2100	59.028	341.595	294.067	99.807	−319.018	−130.645	3.250
2200	59.256	344.346	296.291	105.721	−318.858	−121.678	2.889
2300	59.464	346.985	298.438	111.657	−318.714	−112.719	2.560
2400	59.653	349.519	300.514	117.613	−318.591	−103.766	2.258
2500	59.826	351.958	302.523	123.588	−318.491	−94.817	1.981
2600	59.984	354.308	304.470	129.578	−318.418	−85.871	1.725
2700	60.129	356.574	306.358	135.584	−318.375	−76.928	1.488
2800	60.262	358.763	308.191	141.603	−318.366	−67.986	1.268
2900	60.383	360.880	309.971	147.636	−318.395	−59.043	1.063
3000	60.496	362.929	311.703	153.680	−318.465	−50.099	0.872
3100	60.599	364.915	313.387	159.735	−318.579	−41.151	0.693
3200	60.695	366.840	315.028	165.799	−318.743	−32.200	0.526
3300	60.783	368.709	316.626	171.873	−318.950	−23.243	0.368
3400	60.864	370.525	318.185	177.956	−319.220	−14.278	0.219
3500	60.940	372.290	319.706	184.046	−319.546	−5.305	0.079
3600	61.010	374.008	321.190	190.144	−319.939	3.679	−0.053
3700	61.076	375.681	322.641	196.248	−320.401	12.674	−0.179
3800	61.137	377.310	324.058	202.359	−320.935	21.684	−0.298
3900	61.193	378.899	325.444	208.475	−321.548	30.708	−0.411
4000	61.246	380.449	326.800	214.597	−322.237	39.748	−0.519
4100	61.296	381.962	328.127	220.724	−323.014	48.807	−0.622
4200	61.342	383.440	329.426	226.856	−323.886	57.886	−0.720
4300	61.386	384.883	330.699	232.993	−324.855	66.987	−0.814
4400	61.427	386.295	331.947	239.133	−325.648	76.084	−0.903
4500	61.465	387.676	333.170	245.278	−326.756	85.227	−0.989
4600	61.501	389.027	334.369	251.426	−327.963	94.395	−1.072
4700	61.535	390.350	335.547	257.578	−329.250	103.588	−1.151
4800	61.567	391.646	336.702	263.733	−330.531	112.799	−1.227
4900	61.598	392.916	337.836	269.892	−332.019	122.050	−1.301
5000	61.626	394.161	338.950	276.053	−333.611	131.333	−1.372
5100	61.653	395.381	340.045	282.217	−335.308	140.648	−1.441
5200	61.679	396.579	341.121	288.383	−337.111	149.998	−1.507
5300	61.703	397.754	342.178	294.553	−339.022	159.384	−1.571
5400	61.726	398.908	343.218	300.724	−341.039	168.806	−1.633
5500	61.748	400.040	344.241	306.898	−343.163	178.267	−1.693
5600	61.769	401.153	345.247	313.074	−345.392	187.768	−1.751
5700	61.788	402.247	346.238	319.251	−347.381	197.261	−1.808
5800	61.807	403.321	347.213	325.431	−349.774	206.838	−1.863
5900	61.825	404.378	348.173	331.613	−352.264	216.455	−1.916
6000	61.842	405.417	349.118	337.796	−354.849	226.116	−1.969

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [250.331 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 495.60 \pm 41.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 497.896 \pm 41.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[375](1)
[300](2)
[3600](1)

Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distance: K–O = [2.20] Å O–H = [1.03] Å
Bond Angle: K–O–H = [180]°
Rotational Constant: B_0 = [0.27367] cm^{-1}

Heat of Formation

Porter and Schoonmaker[1] obtained an appearance potential curve near threshold for KOH^+ which extrapolates to 7.8 eV at zero ion current. They presented evidence which indicated that a large fraction of KOH^+ was formed by dissociative ionization of the dimer. In a later study, these same workers[2] rejected their earlier results, since it was found that the presence of magnesia in their cell had reduced the activity of the hydroxide. Cusarov and Gorokhov[3] in a similar mass spectrometric study ofthe evaporation products of KOH have shown that KOH^+ is formed primarily from direct ionization of the hydroxide. Very recently, Gorokhov *et al.*[4] reported the appearance potential of KOH^+ from KOH as 7.5 ± 0.2 eV. We adopt this result as $\Delta_r H°$ for the process $e^- + KOH(g) \rightarrow KOH^+(g) + 2e^-$, since it is consistent with the expected mode of ionization. This value leads to $\Delta_f H°(KOH^+, g, 0\ K) = 118 \pm 10\ kcal \cdot mol^{-1}$ when used in conjunction with $\Delta_f H°(KOH, g, 0\ K) = -54.6 \pm 3.0\ kcal \cdot mol^{-1}$.[5]

Heat Capacity and Entropy

The configuration of KOH^+ is predicted to be linear by Walsh,[6] since it has seven valence electrons. The same correlation predicts that the unpaired electron is in a pi orbital, thus, the ground state of KOH^+ is $^2\Pi$. A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecules OH.[5] and SH[5] The vibrational frequencies are estimated from those for KOH with somewhat lower values to account for the effect of weaker bonding predicted for the positive ion. Similarly, the K–O and O–H bond distances are increased slightly over those for KOH.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.760	495.596		
100	34.457	203.689	291.020	−8.733			
200	45.225	231.352	254.747	−4.679			
250	47.868	241.752	251.137	−2.346			
298.15	49.479	250.331	250.331	0.	497.896	486.350	−85.207
300	49.529	250.637	250.332	0.092	497.918	486.278	−84.669
350	50.620	258.359	250.939	2.597	496.108	484.390	−72.291
400	51.369	265.171	252.301	5.148	496.636	482.680	−63.032
450	51.908	271.254	254.075	7.731	497.205	480.902	−55.822
500	52.315	276.745	256.072	10.337	497.804	479.059	−50.047
600	52.917	286.339	260.339	15.600	499.062	475.192	−41.369
700	53.406	294.533	264.653	20.916	500.365	471.111	−35.155
800	53.877	301.696	268.845	26.280	501.686	466.842	−30.482
900	54.362	308.069	272.856	31.692	503.004	462.407	−26.837
1000	54.859	313.822	276.669	37.153	504.298	457.827	−23.914
1100	55.360	319.075	280.289	42.664	426.595	457.729	−21.736
1200	55.851	323.913	283.725	48.225	428.842	460.460	−20.043
1300	56.323	328.402	286.991	53.834	431.099	463.004	−18.604
1400	56.769	332.592	290.101	59.489	433.364	465.373	−17.363
1500	57.186	336.523	293.066	65.187	435.637	467.580	−16.283
1600	57.572	340.227	295.899	70.925	437.914	469.635	−15.332
1700	57.927	343.728	298.610	76.700	440.192	471.548	−14.489
1800	58.252	347.048	301.210	82.509	442.470	473.327	−13.736
1900	58.549	350.206	303.706	88.349	444.744	474.979	−13.058
2000	58.820	353.216	306.107	94.218	447.011	476.512	−12.445
2100	59.067	356.092	308.419	100.113	449.267	477.931	−11.888
2200	59.291	358.845	310.649	106.031	451.510	479.244	−11.379
2300	59.496	361.485	312.802	111.970	453.735	480.454	−10.911
2400	59.684	364.021	314.884	117.929	455.940	481.568	−10.481
2500	59.854	366.461	316.899	123.906	458.122	482.591	−10.083
2600	60.011	368.812	318.850	129.900	460.277	483.528	−9.714
2700	60.154	371.079	320.743	135.908	462.400	484.382	−9.371
2800	60.285	373.269	322.580	141.930	464.490	485.157	−9.051
2900	60.406	375.387	324.365	147.965	466.543	485.859	−8.751
3000	60.517	377.437	326.100	154.011	468.553	486.491	−8.471
3100	60.619	379.423	327.788	160.068	470.519	487.056	−8.207
3200	60.714	381.349	329.432	166.134	472.436	487.559	−7.959
3300	60.801	383.218	331.033	172.210	474.309	488.002	−7.724
3400	60.882	385.035	332.595	178.294	476.121	488.389	−7.503
3500	60.957	386.801	334.119	184.386	477.874	488.724	−7.294
3600	61.027	388.519	335.606	190.486	479.562	489.010	−7.095
3700	61.093	390.192	337.059	196.592	481.181	489.250	−6.907
3800	61.154	391.822	338.479	202.704	482.726	489.448	−6.728
3900	61.211	393.411	339.867	208.822	484.194	489.605	−6.558
4000	61.264	394.962	341.225	214.946	485.585	489.725	−6.395
4100	61.315	396.475	342.554	221.075	486.889	489.812	−6.240
4200	61.362	397.953	343.856	227.209	488.097	489.869	−6.092
4300	61.407	399.397	345.131	233.348	489.209	489.898	−5.951
4400	61.450	400.810	346.380	239.490	490.496	489.874	−5.816
4500	61.491	402.191	347.605	245.638	491.469	489.849	−5.686
4600	61.530	403.543	348.806	251.789	492.344	489.803	−5.562
4700	61.567	404.867	349.985	257.943	493.138	489.737	−5.443
4800	61.602	406.163	351.142	264.102	493.940	489.644	−5.328
4900	61.637	407.434	352.278	270.264	494.534	489.548	−5.219
5000	61.670	408.679	353.394	276.429	495.025	489.441	−5.113
5100	61.702	409.901	354.490	282.598	495.411	489.326	−5.012
5200	61.733	411.099	355.567	288.769	495.691	489.203	−4.914
5300	61.763	412.276	356.626	294.944	495.865	489.077	−4.820
5400	61.793	413.430	357.667	301.122	495.932	488.948	−4.730
5500	61.822	414.564	358.691	307.303	495.895	488.818	−4.642
5600	61.851	415.679	359.699	313.487	495.752	488.691	−4.558
5700	61.879	416.774	360.691	319.673	495.850	488.519	−4.477
5800	61.907	417.850	361.667	325.862	495.545	488.394	−4.398
5900	61.934	418.909	362.628	332.054	495.144	488.273	−4.323
6000	61.961	419.950	363.575	338.249	494.649	488.161	−4.250

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 20.037 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 961.8\ K$

$\Delta_f H°(0\ K) = -85.548 \pm 0.13\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -90.625 \pm 0.13\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 22.594 \pm 0.42\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of Li(cr) and LiH(cr) in water have been measured by Guntz[1] and Moers[2] using an open Dewar flask calorimeter and by Messer[3] and Gunn[4] using closed bomb calorimetry. Based on the reported values of the enthalpy changes ($\Delta_r H°$) for the reaction (A) Li(cr) + H_2O(l) = LiOH(aq) + 1/2 H_2(g), and (B) LiH(cr) + H_2O(l) = LiOH(aq) + H_2(g), the corresponding $\Delta_f H°$(298.15 K) for LiH(cr) are calculated. The results are presented in the table below.

The decomposition pressures of LiH(cr) have been determined by Hurd[5] at temperatures 782–926 K. By use of the 2nd and 3rd law methods, the enthalpy changes for the decomposition reaction (C) LiH(cr) = Li(l) + 1/2 H_2(g) are evaluated as 21.87 ± 0.3 and 22.34 kcal·mol^{-1}, respectively. Based on the 3rd law $\Delta_r H°$(298.15 K) and $\Delta_f H°$(Li, l, 298.15 K) = 0.569 kcal·mol^{-1}, we derive the value $\Delta_f H°$(LiH, cr, 298.15 K) = −21.77 ± 0.2 kcal·mol^{-1}, which is in good agreement with the values obtained by calorimetric method. Gunts[1] measured the decomposition pressure at 953 K for the same reaction. The 3rd law $\Delta_r H°$(298.15 K) and $\Delta_f H°$(LiH, cr, 298.15 K) are evaluated as 21.86 and 21.29 kcal·mol^{-1}, respectively.

Johnson[6] has determined the standard Gibbs energy of formation for LiH(cr) from emf measurements over the temperature range 675–885 K. The cell utilized an Armco iron flag over which H_2 was passed as the cathode and a molten Li anode. LiCl, LiBr and LiI, each saturated with LiH were used as electrolytes. Using the reported emf values at different temperatures (47 data points) for reaction (C) we derive $\Delta_f H°$(298.15 K) = 21.81 kcal·mol^{-1} for LiH(cr).

The $\Delta_f H°$(LiH, cr, 298.15 K) value reported by Gunn[4] is adopted.

Source	$\Delta H°$(298.15 K), kcal·mol^{-1} Reaction A	Reaction B	Reaction C	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Guntz[1]	−53.2	−31.6	–	–	21.6
	–	–	21.86	–	−21.29
Moers[2]	−52.7 ± 0.2	−31.1 ± 0.1	–	–	−21.6 ± 0.25
Messer[3]	−53.10 ± 0.11	−31.76 ± 0.10	–	–	−21.34 ± 0.15
Gunn[4]	−53.14 ± 0.02	−31.48 ± 0.02	–	–	−21.66 ± 0.03
Hurd[5]	–	–	22.34	0.5 ± 0.3	−21.77 ± 0.2
Johnson[6]	–	–	22.38	1.0 ± 0.2	−21.81 ± 0.15

Heat Capacity and Entropy

The low temperature heat capacities are obtained from the data of Kostyukov[7] 3.72–295.5 K. The $C_p°$ data reported by Gunther[8] are consistently lower than the adopted ones in the temperature range 74.0–90.5 K but considerably higher at 292.7 K. The high temperature enthalpies have been determined by Fieldhouse[9] 413.2–914.3 K and Vogt[14] 878.15–953.15 K. The derived high temperature heat capacities are joined smoothly with the low temperature values and extrapolated smoothly above 953.15 K.

$S°$(298.15 K) is calculated based on the adopted low temperature heat capacities, using $S°(7\ K) = 0.0002\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The value of T_{fus} has been reported as 953,[1] 961 ± 1,[10, 12] 959.6[11] and 961.8 ± 0.3.[13] The value reported by Messer[13] is adopted. The heat of melting, $\Delta_{fus} H°$, has been determined as 5.095 ± 0.46[13] and 5.237 ± 0.040 kcal mol.[14] The first $\Delta_{fus} H°$ value was evaluated cryogenically from the lowering of melting point in the systems LiH–LiO_2O and LiH–CaH_2. The second value was derived from enthalpy data measured with copper block calorimeter. The adopted $\Delta_{fus} H°$ value is derived from the enthalpy data of Vogt[14] using the adopted heat capacities for LiH(cr) and LiH(l).

Sublimation Data

The value of $\Delta_{sub} H°$(298.15 K) is calculated as the difference between $\Delta_f H°$(298.15 K) for LiH(g) and LIH(cr).

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Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−3.778	−85.548	−85.548	INFINITE
100	6.381	2.322	38.346	−3.602	−87.367	−81.828	42.743
200	18.778	10.715	22.326	−2.322	−89.275	−75.511	19.722
298.15	27.957	20.037	20.037	0.	−90.625	−68.447	11.992
300	28.083	20.210	20.038	0.052	−90.646	−68.309	11.894
400	34.794	29.236	21.223	3.205	−91.546	−60.718	7.929
500	40.735	37.646	23.676	6.985	−95.160	−52.628	5.498
600	46.380	45.575	26.671	11.342	−95.251	−44.103	3.839
700	51.877	53.138	29.915	16.256	−94.731	−35.611	2.657
800	57.300	60.420	33.276	21.715	−93.644	−27.233	1.778
900	62.676	67.480	36.686	27.715	−92.024	−19.023	1.104
961.800	65.985	71.751	38.802	31.690	--- CRYSTAL <---> LIQUID ---		
1000	68.028	74.361	40.111	34.250	−89.876	−11.022	0.576
1100	73.362	81.095	43.531	41.320	−87.207	−3.261	0.155
1200	78.680	87.706	46.938	48.922	−84.020	4.233	−0.184
1300	83.994	94.214	50.325	57.056	−80.319	11.441	−0.460
1400	89.299	100.633	53.690	65.720	−76.103	18.345	−0.684
1500	94.600	106.974	57.031	74.915	−71.369	24.929	−0.868

PREVIOUS: September 1962 CURRENT: September 1967

$S°(298.15\ K)$ = [22.227] $J·K^{-1}·mol^{-1}$
T_{fus} = 961.8 ± 0.3 K
T_d = 1223 K

$\Delta_f H°(298.15\ K)$ = −[77.714] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 22.594 ± 0.42 $kJ·mol^{-1}$

Heat of Formation

$\Delta_f H°$(l, 298.15 K) is obtained from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference between $H°$(961.8;298.15) for crystal and liquid.

The decomposition pressures of LiH(l) at different temperatures have been investigated by Hill,[1] Perlow,[2] Johnson, and Gibb[4] Based on their reported equilibrium pressures, the enthalpy changes for the reaction LiH(l) = Li(l) + 1/2H_2(g) are evaluated by the second and third law methods. The results are presented in the table below. It should be noted that the measured decomposition pressures are highly sensitive to composition and change extremely rapidly between 99 and 100 percent purity. Therefore we give no weight to the equilibrium data.

Source	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15K)** kcal·mol^{-1}
Hill (1938)	973.2	1	–	16.93	–	−16.36
Perlow (1941)	1043–1098	2	20.10	17.69	−2.2	−17.12
Johnson*	1050–1090	–	24.69	18.36	−5.9	−17.79
Gibb (1951)	1073–1173	2	5.66	15.2	+8.5	−14.63

*The vapor pressure values are calculated from an equation quoted by Gibb[3] but derived from the vapor pressures measured by W.C. Johnson, University of Chicago.

**Based on the third law $\Delta_f H°$(298.15 K).

Heat Capacity and Entropy

The enthalpies of LiH(l) in the temperature range 975.15–1075.15 K have been measured by Vogt.[5] Using the reported enthalpy values, the heat capacity of LiH(l) is derived as 14.9 cal·K^{-1}·mol^{-1}. This $C_p°$ value is adopted and extrapolated above and below the measured range.

$S°$(298.15 K) is obtained in a manner analogous to that of the enthalpy of formation.

Melting Data

Refer to crystal table for details.

Decomposition Data

T_{dcm} = 1223 K is calculated as the temperature at which LiH(l) decomposes into Li(l) and H_2(g) where the fugacity of H_2(g) equals one atmosphere.

References

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[4]T. R. P. Gibb, NEPA 1841, (April 30, 1951).
[5]J. W. Vogt, Thompson Ramo Wooldridge Inc., Cleveland, Ohio, NASA N63 22167, (June 1962).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	62.342	22.227	22.227	0.	−77.714	−56.189	9.844
300	62.342	22.613	22.228	0.115	−77.671	−56.055	9.760
400	62.342	40.547	24.673	6.349	−75.491	−49.187	6.423
500	62.342	54.458	29.291	12.584	−76.651	−42.525	4.443
600	62.342	65.825	34.462	18.818	−74.865	−35.866	3.122
700	62.342	75.435	39.646	25.052	−73.024	−29.511	2.202
800	62.342	83.759	44.651	31.286	−71.163	−23.422	1.529
900	62.342	91.102	49.413	37.520	−69.307	−17.566	1.020
961.800	62.342	95.242	52.226	41.373	--- CRYSTAL <--> LIQUID ---		
1000	62.342	97.670	53.916	43.754	−67.461	−11.916	0.622
1100	62.342	103.612	58.168	49.989	−65.627	−6.451	0.306
1200	62.342	109.036	62.184	56.223	−63.808	−1.151	0.050
1300	62.342	114.026	65.983	62.457	−62.007	3.997	−0.161
1400	62.342	118.646	69.581	68.691	−60.221	9.007	−0.336
1500	62.342	122.948	72.997	74.925	−58.448	13.890	−0.484
1600	62.342	126.971	76.246	81.159	−56.689	18.655	−0.609
1700	62.342	130.750	79.342	87.394	−200.179	30.487	−0.937
1800	62.342	134.314	82.298	93.628	−197.692	43.983	−1.276
1900	62.342	137.684	85.126	99.862	−195.226	57.342	−1.576
2000	62.342	140.882	87.834	106.096	−192.781	70.572	−1.843

PREVIOUS: September 1962 CURRENT: September 1967

0 to 961.8 K crystal
above 961.8 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−3.778	−85.548	−85.548	INFINITE
100	6.381	2.322	38.346	−3.602	−87.367	−81.828	42.743
200	18.778	10.715	22.326	−2.322	−89.275	−75.511	19.722
298.15	27.957	20.037	20.037	0.	−90.625	−68.447	11.992
300	28.083	20.210	20.038	0.052	−90.646	−68.309	11.894
400	34.794	29.236	21.223	3.205	−91.546	−60.718	7.929
500	40.735	37.646	23.676	6.985	−95.160	−52.628	5.498
600	46.380	45.575	26.671	11.342	−95.251	−44.103	3.839
700	51.877	53.138	29.915	16.256	−94.731	−35.611	2.657
800	57.300	60.420	33.276	21.715	−93.644	−27.233	1.778
900	62.676	67.480	36.686	27.715	−92.024	−19.023	1.104
961.800	65.985	71.751	38.802	31.690	___ CRYSTAL <--> LIQUID ___		
961.800	62.342	95.242	38.802	54.284	TRANSITION		
1000	62.342	97.670	41.005	56.665	−67.461	−11.916	0.622
1100	62.342	103.612	46.431	62.900	−65.627	−6.451	0.306
1200	62.342	109.036	51.425	69.134	−63.808	−1.151	0.050
1300	62.342	114.026	56.051	75.368	−62.007	3.997	−0.161
1400	62.342	118.646	60.359	81.602	−60.221	9.007	−0.336
1500	62.342	122.948	64.390	87.836	−58.448	13.890	−0.484
1600	62.342	126.971	68.177	94.070	−56.689	18.655	−0.609
1700	62.342	130.750	71.748	100.305	−200.179	30.487	−0.937
1800	62.342	134.314	75.126	106.539	−197.692	43.983	−1.276
1900	62.342	137.684	78.330	112.773	−195.226	57.342	−1.576
2000	62.342	140.882	81.379	119.007	−192.781	70.572	−1.843

PREVIOUS: CURRENT: September 1967

$S°(298.15\ K) = 170.909\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 140.794 \pm 0.04\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 140.624 \pm 0.04\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
	26513.7	1
	34912.0	2

$\omega_e = 1406.73\ cm^{-1}$ $\omega_e x_e = 23.24\ cm^{-1}$ $\sigma = 1$
$B_e = 7.5247\ cm^{-1}$ $\alpha_e = 0.2137\ cm^{-1}$ $r_e = 1.595$ Å

Enthalpy of Formation

Velasco,[1] observed the absorption spectra of LiH(g) in the near ultraviolet with high dispersion and absorbing path lengths up to 16 meters. He found a new band system involving the ground state and a $^1\Pi$ excited state. Rotational and vibrational analyses of this system were carried out and the observed breaking off of the rotational structure of the bands was interpreted as due to predissociation by rotation. With this assumption very accurate dissociation limits of the $B^1\Pi$ state were obtained. From these dissociation limits the dissociation energy ($D°$) of the ground state of LiH was found to be 2.4288 ± 0.0002 eV. Based on this $D°$ value, we adopt $\Delta_f H°(2981.5\ K) = 33.61\ kcal·mol^{-1}$ for LiH(g)

Kemperer,[2] observed the infrared spectrum of LiH(g) in emission in the frequency region 1500 to 970 cm^{-1}, using a Perkin–Elmer double-pass monochromator with NaCl optics. Estimating the minimum LiH pressure as 10 mm and assuming the maximum possible Li pressure, he reported K = 0.005 (atm) at 1400 K for the reaction $2Li(g) + H_2(g) = 2LiH(g)$. We calculate the corresponding enthalpy change, $\Delta_r H°(1400\ K)$, to be $-9.63\ kcal·mol^{-1}$, employing $\Delta_r S°(1400\ K) = -17.407\ cal·K^{-1}·mol^{-1}$. Incorporating this $\Delta_r H°(1400\ K)$ value with $\Delta_f H°(1400\ K) = 35.601\ kcal·mol^{-1}$ for Li(g), we obtain $\Delta_f H°(298.15\ K) \leq 33.92\ kcal·mol^{-1}$ for LiH(g), which is in good agreement with the adopted value.

Gaydon,[3] derived the value $D°(LiH) = 2.5 \pm 0.2$ eV from earlier spectroscopic data.

Heat Capacity and Entropy

The third electronic level and quantum weight are obtained from Velasco.[1] All the other constants are taken fro Herzberg,[4] and corrected to the average isotopic species.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.686	140.794	140.794	INFINITE
100	29.139	138.955	196.998	−5.804	141.681	133.556	−69.763
200	29.220	159.168	173.607	−2.888	141.409	125.482	−32.773
250	29.401	165.705	171.396	−1.423	141.048	121.540	−25.394
298.15	29.731	170.909	170.909	0.	140.624	117.820	−20.642
300	29.746	171.093	170.910	0.055	140.607	117.679	−20.490
350	30.235	175.714	171.273	1.554	140.119	113.896	−16.998
400	30.811	179.788	172.088	3.080	139.578	110.186	−14.389
450	31.422	183.452	173.150	4.636	138.981	106.547	−12.368
500	32.029	186.794	174.350	6.222	135.326	103.285	−10.790
600	33.144	192.735	176.931	9.482	134.138	96.991	−8.444
700	34.081	197.917	179.567	12.845	133.107	90.883	−6.782
800	34.848	202.519	182.154	16.293	132.182	84.915	−5.544
900	35.472	206.661	184.650	19.810	131.321	79.059	−4.588
1000	35.986	210.426	187.043	23.383	130.507	73.296	−3.829
1100	36.414	213.876	189.327	27.004	129.727	67.613	−3.211
1200	36.776	217.061	191.507	30.664	128.972	62.000	−2.699
1300	37.088	220.017	193.588	34.358	128.233	56.449	−2.268
1400	37.359	222.776	195.576	38.080	127.507	50.954	−1.901
1500	37.600	225.362	197.476	41.828	126.794	45.511	−1.585
1600	37.816	227.795	199.296	45.599	126.090	40.115	−1.310
1700	38.013	230.094	201.040	49.391	−19.843	41.939	−1.289
1800	38.193	232.272	202.715	53.201	−19.780	45.571	−1.322
1900	38.361	234.341	204.326	57.029	−19.720	49.200	−1.353
2000	38.517	236.313	205.876	60.873	−19.665	52.826	−1.380
2100	38.665	238.196	207.371	64.732	−19.615	56.450	−1.404
2200	38.806	239.998	208.813	68.606	−19.571	60.071	−1.426
2300	38.940	241.726	210.207	72.493	−19.534	63.690	−1.446
2400	39.069	243.386	211.555	76.394	−19.506	67.308	−1.465
2500	39.193	244.983	212.860	80.307	−19.486	70.925	−1.482
2600	39.314	246.523	214.126	84.232	−19.478	74.541	−1.498
2700	39.432	248.009	215.353	88.170	−19.481	78.157	−1.512
2800	39.546	249.445	216.545	92.119	−19.498	81.773	−1.526
2900	39.659	250.835	217.704	96.079	−19.530	85.391	−1.538
3000	39.770	252.181	218.831	100.050	−19.578	89.010	−1.550
3100	39.879	253.487	219.928	104.033	−19.644	92.630	−1.561
3200	39.988	254.755	220.996	108.026	−19.729	96.253	−1.571
3300	40.095	255.987	222.038	112.030	−19.835	99.879	−1.581
3400	40.202	257.185	223.054	116.045	−19.963	103.509	−1.590
3500	40.308	258.352	224.046	120.071	−20.114	107.142	−1.599
3600	40.415	259.489	225.015	124.107	−20.290	110.781	−1.607
3700	40.522	260.598	225.962	128.154	−20.492	114.424	−1.615
3800	40.630	261.680	226.888	132.211	−20.722	118.074	−1.623
3900	40.738	262.737	227.793	136.280	−20.980	121.730	−1.630
4000	40.847	263.770	228.680	140.359	−21.268	125.392	−1.637
4100	40.958	264.780	229.548	144.449	−21.587	129.063	−1.644
4200	41.070	265.768	230.399	148.550	−21.939	132.741	−1.651
4300	41.183	266.736	231.233	152.663	−22.324	136.429	−1.657
4400	41.299	267.684	232.050	156.787	−22.723	140.124	−1.663
4500	41.416	268.613	232.852	160.923	−23.169	143.830	−1.670
4600	41.536	269.525	233.640	165.070	−23.653	147.546	−1.675
4700	41.658	270.419	234.413	169.230	−24.173	151.273	−1.681
4800	41.782	271.298	235.172	173.402	−24.732	155.012	−1.687
4900	41.909	272.160	235.918	177.586	−25.329	158.763	−1.692
5000	42.039	273.008	236.652	181.784	−25.965	162.526	−1.698
5100	42.171	273.842	237.373	185.994	−26.637	166.302	−1.703
5200	42.306	274.662	238.082	190.218	−27.354	170.092	−1.709
5300	42.445	275.469	238.780	194.456	−28.114	173.896	−1.714
5400	42.586	276.264	239.467	198.707	−28.918	177.715	−1.719
5500	42.731	277.047	240.143	202.973	−29.766	181.549	−1.724
5600	42.878	277.818	240.809	207.253	−30.659	185.400	−1.729
5700	43.029	278.578	241.465	211.549	−31.598	189.266	−1.734
5800	43.182	279.328	242.111	215.859	−32.584	193.150	−1.740
5900	43.339	280.068	242.748	220.185	−33.618	197.050	−1.745
6000	43.499	280.797	243.376	224.527	−34.700	200.969	−1.750

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 42.821 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -479.14 \pm 0.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -484.93 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of crystalline LiOH is determined from calorimetric studies on the enthalpy of hydrolysis of metallic lithium and the enthalpy of solution of the hydroxide in water.

Reshetnikov[1] determined the enthalpy of solution of LiOH(cr) in (aq, 400 H_2O) as $-5.479 \pm 0.007\ kcal \cdot mol^{-1}$. Combining this result with enthalpy of dilution data for LiOH tabulated by Parker[2] we derive $\Delta_{sol}H°(LiOH, cr) = -5.632 \pm 0.020\ kcal \cdot mol^{-1}$, which is essentially the value recommended by Parker.[2] Lower values by some 600–650 $cal \cdot K^{-1} \cdot mol^{-1}$ for the enthalpy of solution of LiOH(cr) are summarized by Parker.[2] The discrepancy in these values probably arises from carbonate and water impurities in the LiOH samples. Since their presence would tend to reduce the enthalpy of solution, we adopt the higher results of Reshetnikov.[1]

Gunn and Green[3a,3b] and Messer *et al.*[4] measured the enthalpy of hydrolysis of metallic lithium. Their results for the reaction Li(cr) + (n+1) $H_2O \rightarrow LiOHn\ H_2O + 0.5\ H_2(g)$ are summarized below.

Source	Moles of H_2O	$\Delta_{hyd}H°(298.15\ K)$* $kcal \cdot mol^{-1}$	$\Delta_f H°(LiOH, aq, \infty, 298.15\ K)$** $kcal \cdot mol^{-1}$	$\Delta_f H°(298.15K)$ $kcal \cdot mol^{-1}$
Gunn and Green[3a, 3b]	1000	-53.210 ± 0.040	-121.525 ± 0.040	-115.893 ± 0.060
Messer *et al.*[4]	70	-53.05 ± 0.20	-121.37 ± 0.20	-115.74 ± 0.20

*Dilution data from Parker[2]

*Based on $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$ [5]

Combination of the $\Delta_f H°(LiOH, aq, \infty, 298.15\ K)$ values with the enthalpy of solution of LiOH(cr) given above results in the values for $\Delta_f H°(LiOH, cr, 298.15\ K)$ given in the last column. The adopted value is from the work of Gunn and Green[3a,3b] with minor adjustments in the uncertainty interval to include possible errors in some of the auxiliary data used in the calculations.

Heat Capacity and Entropy

Heat capacities for LiOH(cr) in the temperature range 15–300 K are those of Bauer *et al.*[6] Heat capacities above 300 K are calculated from the high temperature (418–879 K) enthalpy data of Shomate and Cohen.[7] Both sets of data were smoothed by computer and joined at 298.15 K. The rapid rise in the enthalpy data of Shomate and Cohen[7] near the melting point is attributed to premelting and data in the temperature range 725–732 K were not used in the fit. Powers and Blalock[8] also measured high temperature (397–1213 K) enthalpy data for LiOH(cr) in a Bunsen ice calorimeter. Although their results are less precise than those of Shomate and Cohen[7] the two sets of measurements are in reasonable agreement.

$S°(298.15\ K)$ is determined from the smoothed $C_p°$ data of Bauer *et al.*[6] and is based on an extrapolation of $S°(16\ K) = 0.027\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition and Fusion Data

The adopted enthalpy of melting and melting point for LiOH are from the enthalpy measurements of Shomate and Cohen.[7] Powers and Blalock[8] reported $\Delta_{fus}H° = 5.029\ kcal \cdot mol^{-1}$ at 746 K from their enthalpy measurements on LiOH. Very recently, Reshetnikov and Baranskaya[9] reported a slightly higher value of 5.29 $kcal \cdot mol^{-1}$ at 747 K which was determined by a thermographic method.

Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ values for the monomer and dimer are calculated from the adopted enthalpies of formation for the gaseous species and the crystal.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.416	−479.144	−479.144	INFINITE
100	14.644	8.561	77.138	−6.858	−482.033	−468.453	244.695
200	35.977	25.632	46.982	−4.270	−484.089	−453.960	118.562
298.15	49.591	42.821	42.821	0.	−484.926	−438.958	76.904
300	49.761	43.128	42.822	0.092	−484.933	−438.672	76.380
400	58.053	58.678	44.886	5.517	−485.047	−423.222	55.267
500	63.647	72.260	49.032	11.614	−487.874	−407.475	42.569
600	68.208	84.277	53.924	18.212	−487.303	−391.441	34.078
700	72.279	95.101	59.045	25.239	−486.298	−375.538	28.023
744.300	73.970	99.588	61.326	28.479	--- CRYSTAL <---> LIQUID ---		
800	76.086	105.002	64.180	32.658	−484.920	−359.805	23.493
900	79.747	114.176	69.231	40.450	−483.208	−344.265	19.981
1000	83.308	122.763	74.159	48.604	−481.174	−328.933	17.182
1100	86.814	130.868	78.950	57.110	−478.823	−313.820	14.902
1200	90.274	138.570	83.600	65.965	−476.158	−298.935	13.012
1300	93.705	145.932	88.113	75.164	−473.183	−284.285	11.423
1400	97.115	153.001	92.497	84.705	−469.897	−269.876	10.069
1500	100.508	159.817	96.759	94.586	−466.298	−255.713	8.905

PREVIOUS: March 1966 CURRENT: June 1971

$S°(298.15\ K) = [47.969]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 744.3\ K$

$\Delta_f H°(298.15\ K) = [-474.422]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 20.878 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiOH, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$and the difference in enthalpy, $H°(744.3\ K)-H°(298.15\ K)$, between the crysal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid phase is obtained from the high temperature enthalpy measurements (750–875 K) of Shomate and Cohen.[1] We derive a constant $C_p°$ of 20.814 $cal·K^{-1}·mol^{-1}$ for LiOH(l) from these enthalpy data. The average percent deviation of the linear fit of the data was 0.2%. Powers and Blalock[2] also determined a constant $C_p° = 22.03\ cal·K^{-1}·mol^{-1}$ for LiOH(l) from enthalpy data (746–1200 K) determined by dromp calorimetry.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Dissociation pressures for LiOH(cr, l) have been measured by static,[4] effusion,[5-6] and transpiration[6] methods. These data are combined with the equilibrium studies of Berkowitz et al.[3] to give either $\Delta_{sub}H°(298.15\ K)$ or $\Delta_{vap}H°(298.15\ K)$. An analysis of the data is summerized below, and further discussion of these results is presented on the ideal gas table under Enthalpy of Formation.

Source	Reaction[a]	Method	T/K	Data Points	$\Delta_f H°(298.15\ K)$,kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_{sub}H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_{vap}H°(298.15\ K)$ kcal·mol^{-1}
Berkowitz *et al.*	A	Mass. Spec.	11201450	18	82.3	82.9 ± 1.0	0.5 ± 2.6		
Johnston[4]	B	Static	793–1176	9[b]	34.7	25.9 ± 2.1	−8.5 ± 0.4		54.4 ± 5.0
Ditmars and	C	Effusion	648–736	11	37.8	39.5 ± 1.0	2.6 ± 5.4	61.2 ± 3.0	
Johnston[5]	B	Effusion	752–795	7	35.5	34.3 ± 0.9	−1.9 ± 12.9		58.6 ± 3.0
Gregory and Mohr[6]	C	Transpiration and Effusion	525–675	Equation	32.1	32.7 ± 0.1	0.9 ± 0.1	57.8 ± 2.0	

[a]A) $Li_2O(cr) + H_2O(g) = 2LiOH(g)$ B) $2LiOH(l) = Li_2O(cr) = H_2O(g)$ C) $2LiOH(cr) = Li_2O(cr) + H_2O(g)$
[b]One point rejected due to failure of a statistical test.

The boiling point, $T_{vap} = 1899$ K, is determined as the temperature at which the fugacity of LiOH(g) becomes 1 atm for the process LiOH(l) = LiOH(g). The difference in their enthalpies of formation at the boiling point is the enthalpy of vaporization, $\Delta_{vap}H° = 44.9$ kcal·mol^{-1}.

References

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[2]W. D. Powers and G. C. Blalock, Oak Ridge Nat. Lab., ORNL 1653, (January 1954).
[3]J. Berkowitz, D. J. Meschi, and W. A. Chupka, J. Chem. Phys. **33**, 533 (1960).
[4]J. Johnston, Z. Phys. Chem. **62**, 339 (1908).
[5]W. E. Ditmars and H. L. Johnston, J. Amer. Chem. Soc. **75**, 1830 (1953).
[6]N. W. Gregory and R. H. Mohr, J. Amer. Chem. Soc. **77**, 2142 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	87.086	47.969	47.969	0.	−474.422	−429.989	75.332
300	87.086	48.508	47.971	0.161	−474.360	−429.713	74.820
400	87.086	73.561	51.386	8.870	−471.191	−415.318	54.235
500	87.086	92.993	57.837	17.578	−471.406	−401.374	41.931
600	87.086	108.871	65.060	26.287	−468.725	−387.619	33.745
700	87.086	122.295	72.302	34.995	−466.038	−374.314	27.932
744.300	87.086	127.639	75.438	38.853	--- CRYSTAL <---> LIQUID ---		
800	87.086	133.924	79.294	43.704	−463.370	−361.393	23.597
900	87.086	144.181	85.945	52.413	−460.743	−348.804	20.244
1000	87.086	153.357	92.235	61.121	−458.153	−336.506	17.577
1100	87.086	161.657	98.175	69.830	−455.600	−324.465	15.408
1200	87.086	169.234	103.786	78.538	−453.081	−312.655	13.610
1300	87.086	176.205	109.092	87.247	−450.596	−301.054	12.096
1400	87.086	182.659	114.119	95.955	−448.142	−289.642	10.807
1500	87.086	188.667	118.891	104.664	−445.716	−278.406	9.695
1600	87.086	194.287	123.429	113.373	−443.316	−267.330	8.727
1700	87.086	199.567	127.754	122.081	−586.177	−249.228	7.658
1800	87.086	204.544	131.883	130.790	−583.074	−229.497	6.660
1900	87.086	209.253	135.833	139.498	−580.004	−209.938	5.772
2000	87.086	213.720	139.616	148.207	−576.965	−190.540	4.976
2100	87.086	217.969	143.247	156.916	−573.958	−171.292	4.261
2200	87.086	222.020	146.736	165.624	−570.983	−152.187	3.613
2300	87.086	225.891	150.094	174.333	−568.041	−133.217	3.025
2400	87.086	229.597	153.330	183.041	−565.130	−114.375	2.489
2500	87.086	233.152	156.453	191.750	−562.253	−95.652	1.999

PREVIOUS: March 1966 CURRENT: June 1971

0 to 744.3 K crystal
above 744.3 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.416	−479.144	−479.144	INFINITE
100	14.644	8.561	77.138	−6.858	−482.033	−468.453	244.695
200	35.977	25.632	46.982	−4.270	−484.089	−453.960	118.562
298.15	49.591	42.821	42.821	0.	−484.926	−438.958	76.904
300	49.761	43.128	42.822	0.092	−484.933	−438.672	76.380
400	58.053	58.678	44.886	5.517	−485.047	−423.222	55.267
500	63.647	72.260	49.032	11.614	−487.874	−407.475	42.569
600	68.208	84.277	53.924	18.212	−487.303	−391.441	34.078
700	72.279	95.101	59.045	25.239	−486.298	−375.538	28.023
744.300	73.970	99.588	61.326	28.479	___ CRYSTAL <--> LIQUID ___		
744.300	87.086	127.639	61.326	49.357	TRANSITION		
800	87.086	133.924	66.164	54.208	−463.370	−361.393	23.597
900	87.086	144.181	74.274	62.916	−460.743	−348.804	20.244
1000	87.086	153.357	81.732	71.625	−458.153	−336.506	17.577
1100	87.086	161.657	88.626	80.333	−455.600	−324.465	15.408
1200	87.086	169.234	95.032	89.042	−453.081	−312.655	13.610
1300	87.086	176.205	101.012	97.751	−450.596	−301.054	12.096
1400	87.086	182.659	106.616	106.459	−448.142	−289.642	10.807
1500	87.086	188.667	111.888	115.168	−445.716	−278.406	9.695
1600	87.086	194.287	116.864	123.876	−443.316	−267.330	8.727
1700	87.086	199.567	121.576	132.585	−586.177	−249.228	7.658
1800	87.086	204.544	126.048	141.294	−583.074	−229.497	6.660
1900	87.086	209.253	130.304	150.002	−580.003	−209.938	5.772
2000	87.086	213.720	134.365	158.711	−576.965	−190.540	4.976
2100	87.086	217.969	138.245	167.419	−573.958	−171.292	4.261
2200	87.086	222.020	141.962	176.128	−570.983	−152.187	3.613
2300	87.086	225.891	145.527	184.836	−568.041	−133.217	3.025
2400	87.086	229.597	148.954	193.545	−565.130	−114.375	2.489
2500	87.086	233.152	152.251	202.254	−562.253	−95.652	1.999

PREVIOUS: CURRENT: June 1971

$S°(298.15\ K) = [210.659 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -231.99 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -234.30 \pm 6.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[630](1)
[362](2)
[3666](1)

Ground State Quantum Weight: 1 σ = 1
Point Group: C
Bond Distances: Li–O = 1.582 Å O–H = [0.97] Å
Bond Angle: Li–O–H = 180°
Rotational Constant: B_0 = [1.192055] cm^{-1}

Enthalpy of Formation

Smith and Sugden[1] provided the first information on the stability of gaseous LiOH by studying its formation in hydrogen–air flames. Very recently, other flame photometric studies[3–5] have been reported on LiOH(g), primarily in connection with establishing its bond dissociation energy. Mass spectrometry[6–7] has also provided additional information on the stability of this species. These investigations have resulted in a wealth of equilibrium data involving this compound. 2nd and 3rd law analyses of these data are presented in tabular form below. Vapor pressure data for LiOH(cr, l) are analyzed under Vaporization Data (see LiOH(l) table); these data lead to $\Delta_f H°$(LiOH, g, 298.15 K) values of −59.0, −54.7, −54.8 and −58.1 kcal·mol^{-1}.

Source	Reaction*	Method	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Smith and Sugden[1]	A	Flame	2200	1		99.6		−51.7
James and Sugden[2]	A	Flame	2200	1		100.0		−53.2
Jensen and Padley[3]	B	Flame	2475	1		15.9		−55.6 ± 2.0
Cotton and Jenkins[4]	B	Flame	2370	1		15.1		−56.4 ± 1.5
McEwan and Phillips[5]	B	Flame	1400–2600	4	15.8	16.7 ± 0.6	0.5 ± 0.2	−54.8 ± 1.6

*Reactions: (A) LiOH(g) = Li(g) + OH(g) (B) Li(g) + H_2O(g) = LiOH(g) + H(g)

The equilibrium data of Sugden and co-workers[1,2] are likely to contain significant errors, since the dissociation constants were calculated with OH concentrations determined from measured flame temperatures and known gas compositions. It is now well established[8,9] that flame radical concentrations vary greatly with the distance from the reaction zone of the flame. The dissociation pressure data of Johnston and Ditmars and Johnston (refer to the LiOH(l) table) show excessive drifts which usually are indications of nonequilibrium measurements. However, even the remaining flame work[3–5] and vapor pressure data still show a scatter of over 3 kcal·mol^{-1} in $\Delta_f H°$(298.15 K) of LiOH(g). Cotton and Jenkins[4] investigated the other alkali metal hydroxides, and their data lead to $\Delta_f H°$(298.15 K) values for these compounds which are quite consistent with JANAF data.[10] On the other hand, the flame studies of McEwan and Phillips[5] as a function of temperature do not show significant drift; yet, the discrepancy between their $\Delta_f H°$(298.15 K) value and that of Cotton and Jenkins[4] is 1.6 kcal·mol^{-1}. We choose to adopt for $\Delta_f H°$(LiOH, g, 298.15 K) a weighted average of the results from the flame work[3–5] and the vapor pressure data. The adopted value $\Delta_f H°$(LiOH, g, 298.15 K) = −56.0 ± 1.5 kcal·mol^{-1} corresponds to a bond dissociation energy of $D_0°$(Li–OH) = 102.8 ± 1.5 kcal·mol^{-}.

Heat Capacity and Entropy

Freund *et al.*[11] measured the molecular beam electric resonance spectra of LiOH and calculated molecular constants on the basis of a linear equilibrium structure. Linear structures for the other alkali metal hydroxides have been proposed from microwave and infrared studies on these molecules. (Refer to the respective tables for details.) We adopt a linear configuration for LiOH and calculate a Li–O bond length from the rotational constant given by Freund *et al.*[11] The O–H bond length is estimated to be the same as for H_2O.

Experimental vibrational frequencies for LiOH have not been reported in the literature at the present time. Acquista and Abramowitz[12] have made matrix-isolation studies of monomeric CsOH, RbOH, and NaOH and provided assignments for the metal–oxygen stretch (ν_1) and the bending modes (ν_2) of these molecules. A Valence Force Treatment of the frequencies by these workers led to metal–oxygen (F_{11}), O–H (F_{33}), and bending (F_{22}) force constants. We extrapolate their data to LiOH with the result; F_{11} = 1.15 mdyn/Å, F_{33} assumed equal to 7.5 mdyn/Å with the interaction constant F_{13} = 0, and F_{22} = 0.060 mdyn Å. These estimated force constants are used to calculate the adopted frequencies by the Valence Force Treatment. Our adopted frequencies when used in an analysis of the equilibrium data from McEwan and Phillips[5] and Berkowitz *et al.*[7] (refer to the LiOH(l) table) lead to reasonable agreement between the 2nd and 3rd law $\Delta_f H°$(298.15 K) values.

Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.879	−231.985	−231.985	INFINITE
100	31.674	168.451	247.699	−7.925	−232.478	−234.887	122.693
200	40.704	193.281	214.729	−4.289	−233.487	−236.888	61.869
250	43.897	202.726	211.407	−2.170	−233.923	−237.687	49.662
298.15	46.129	210.659	210.659	0.	−234.304	−238.377	41.763
300	46.201	210.945	210.660	0.085	−234.318	−238.402	41.510
350	47.864	218.198	211.229	2.439	−234.690	−239.053	35.677
400	49.081	224.673	212.512	4.864	−235.078	−239.651	31.295
450	49.993	230.509	214.193	7.342	−235.512	−240.197	27.881
500	50.696	235.814	216.094	9.860	−239.006	−240.384	25.113
600	51.719	245.154	220.180	14.984	−239.910	−240.573	20.944
700	52.479	253.185	224.335	20.196	−240.720	−240.619	17.955
800	53.130	260.236	228.391	25.477	−241.480	−240.552	15.706
900	53.737	266.529	232.285	30.820	−242.217	−240.392	13.952
1000	54.323	272.222	235.998	36.223	−242.933	−240.151	12.544
1100	54.889	277.426	239.531	41.684	−243.627	−239.838	11.389
1200	55.432	282.225	242.892	47.200	−244.301	−239.464	10.424
1300	55.945	286.683	246.091	52.769	−244.956	−239.034	9.605
1400	56.426	290.846	249.141	58.388	−245.592	−238.555	8.901
1500	56.873	294.755	252.053	64.054	−246.209	−238.031	8.289
1600	57.285	298.439	254.838	69.762	−246.809	−237.466	7.752
1700	57.662	301.923	257.506	75.509	−392.631	−229.688	7.057
1800	58.008	305.229	260.066	81.293	−392.453	−220.108	6.387
1900	58.322	308.374	262.527	87.110	−392.274	−210.538	5.788
2000	58.609	311.373	264.894	92.957	−392.097	−200.978	5.249
2100	58.871	314.239	267.176	98.831	−391.925	−191.426	4.761
2200	59.109	316.983	269.378	104.730	−391.760	−181.882	4.318
2300	59.326	319.615	271.506	110.652	−391.604	−172.346	3.914
2400	59.524	322.145	273.563	116.595	−391.459	−162.816	3.544
2500	59.705	324.578	275.556	122.556	−391.329	−153.292	3.203
2600	59.870	326.923	277.487	128.535	−391.215	−143.773	2.888
2700	60.022	329.186	279.360	134.530	−391.120	−134.258	2.597
2800	60.161	331.371	281.178	140.539	−391.045	−124.746	2.327
2900	60.289	333.484	282.946	146.562	−390.994	−115.236	2.076
3000	60.406	335.530	284.665	152.596	−390.967	−105.728	1.841
3100	60.514	337.513	286.338	158.643	−390.967	−96.220	1.621
3200	60.614	339.436	287.967	164.699	−390.996	−86.712	1.415
3300	60.706	341.302	289.555	170.765	−391.055	−77.202	1.222
3400	60.792	343.116	291.104	176.840	−391.147	−67.690	1.040
3500	60.871	344.879	292.615	182.923	−391.272	−58.175	0.868
3600	60.945	346.595	294.091	189.014	−391.433	−48.656	0.706
3700	61.013	348.266	295.533	195.112	−391.631	−39.132	0.552
3800	61.077	349.894	296.942	201.217	−391.868	−29.601	0.407
3900	61.137	351.481	298.320	207.327	−392.145	−20.064	0.269
4000	61.192	353.030	299.669	213.444	−392.463	−10.520	0.137
4100	61.244	354.541	300.989	219.566	−392.825	−0.967	0.012
4200	61.293	356.018	302.281	225.693	−393.232	8.596	−0.107
4300	61.338	357.460	303.548	231.824	−393.685	18.168	−0.221
4400	61.381	358.871	304.789	237.960	−394.165	27.750	−0.329
4500	61.422	360.251	306.006	244.100	−394.705	37.344	−0.433
4600	61.459	361.601	307.200	250.244	−395.298	46.952	−0.533
4700	61.495	362.923	308.372	256.392	−395.942	56.573	−0.629
4800	61.529	364.218	309.522	262.543	−396.639	66.209	−0.720
4900	61.560	365.487	310.651	268.698	−397.389	75.859	−0.809
5000	61.590	366.731	311.760	274.855	−398.196	85.525	−0.893
5100	61.619	367.951	312.850	281.016	−399.055	95.208	−0.975
5200	61.645	369.148	313.921	287.179	−399.977	104.908	−1.054
5300	61.671	370.323	314.975	293.345	−400.960	114.627	−1.130
5400	61.695	371.476	316.010	299.513	−402.006	124.364	−1.203
5500	61.718	372.608	317.029	305.684	−403.116	134.122	−1.274
5600	61.740	373.720	318.031	311.857	−404.293	143.901	−1.342
5700	61.760	374.813	319.018	318.032	−405.537	153.701	−1.409
5800	61.780	375.887	319.989	324.209	−406.850	163.524	−1.473
5900	61.799	376.944	320.946	330.388	−408.234	173.368	−1.535
6000	61.816	377.982	321.888	336.569	−409.692	183.239	−1.595

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = [221.685 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [774.1 \pm 105]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [778.2 \pm 105]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[600](1)
[325](2)
[3600](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
Bond Distances: Li–O = [1.60] Å O–H = [1.03] Å
Bond Angle: Li–O–H = [180]°
Rotational Constant: B_0 = [1.154155] cm^{-1}

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(LiOH^+, g, 298.15\ K) = 186 \pm 25\ kcal \cdot mol^{-1}$, is calculated from the ionization potential for LiOH and $\Delta_f H°(LiOH, g, 298.15\ K) = -56.0 \pm 1.5\ kcal \cdot mol^{-1}$.[1] The ionization potential is estimated to be 10.5 ± 1.0 eV for LiOH by comparison with similar data[2] for the isoelectronic molecules LiF and LiCl. We note that this estimated value is in accord with the ionization potential of LiO (IP = 9.0 eV),[3] which should be less than LiOH since the electron in the monoxide is unpaired.

Heat Capacity and Entropy

The correlation diagram of Walsh[4] for HAB molecules predicts a linear configuration for $LiOH^+$ (seven valence electrons) with the unpaired electron in a pi orbital. Therefore, the electronic ground state of $LiOH^+$ should be $^2\Pi$. A first excited state ($^2\Sigma$) is estimated at 32000 cm^{-1} by analogy with the isoelectronic molecules OH^1 and SH.[1] The ionization of LiOH is assumed to lead to weaker bonding in $LiOH^+$, since the electron lost is a bonding one. The Li–O and O–H bond distances are increased slightly over those for LiOH to account for this weaker bonding. Similarly, the vibrational frequencies are estimated from those for LiOH with somewhat lower values.

References

[1]JANAF Thermochemical Tables: LiOH(g), 6-30-71; OH(g), 12-31-70; SH(g), 6-30-67.
[2]J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NSRDS-NBS 26, (1969).
[3]C. W. Beckett and E. C. Cassidy, U. S. Nat. Bur. Stand. Report 8628, (1965).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.137	774.087		
90	32.662	178.163	259.751	−8.159			
200	41.973	203.872	225.848	−4.395			
250	44.971	213.579	222.449	−2.217			
298.15	47.019	221.685	221.685	0.	778.224	764.609	−133.956
300	47.085	221.976	221.686	0.087	778.250	764.524	−133.116
350	48.589	229.354	222.265	2.481	778.958	762.181	−113.749
400	49.681	235.917	223.569	4.939	779.642	759.737	−99.211
450	50.495	241.818	225.274	7.444	780.274	757.210	−87.895
500	51.121	247.172	227.201	9.985	777.843	754.923	−78.866
600	52.040	256.578	231.334	15.146	779.055	750.227	−65.313
700	52.739	264.655	235.531	20.386	780.352	745.321	−55.617
800	53.355	271.738	239.623	25.691	781.695	740.225	−48.332
900	53.943	278.056	243.549	31.057	783.057	734.960	−42.656
1000	54.516	283.769	247.290	36.480	784.440	729.542	−38.107
1100	55.074	288.992	250.847	41.959	785.843	723.984	−34.379
1200	55.609	293.807	254.229	47.494	787.267	718.298	−31.267
1300	56.116	298.278	257.447	53.080	788.708	712.492	−28.628
1400	56.590	302.454	260.514	58.716	790.167	706.575	−26.363
1500	57.030	306.374	263.442	64.397	791.645	700.553	−24.395
1600	57.434	310.068	266.242	70.121	793.138	694.431	−22.671
1700	57.805	313.561	268.924	75.883	649.409	695.392	−21.367
1800	58.143	316.875	271.497	81.681	651.680	698.031	−20.256
1900	58.451	320.027	273.968	87.510	653.951	700.544	−19.259
2000	58.731	323.032	276.347	93.370	656.218	702.938	−18.359
2100	58.986	325.904	278.639	99.256	658.481	705.218	−17.541
2200	59.218	328.653	280.850	105.166	660.736	707.391	−16.796
2300	59.429	331.290	282.986	111.099	662.982	709.461	−16.112
2400	59.622	333.824	285.052	117.051	665.215	711.434	−15.484
2500	59.797	336.261	287.052	123.022	667.433	713.314	−14.904
2600	59.958	338.610	288.990	129.010	669.634	715.106	−14.367
2700	60.105	340.875	290.870	135.014	671.817	716.814	−13.868
2800	60.240	343.064	292.695	141.031	673.978	718.441	−13.403
2900	60.363	345.180	294.469	147.061	676.116	719.991	−12.968
3000	60.477	347.228	296.194	153.103	678.228	721.468	−12.562
3100	60.582	349.213	297.872	159.156	680.314	722.875	−12.180
3200	60.679	351.138	299.507	165.219	682.370	724.214	−11.822
3300	60.768	353.006	301.100	171.292	684.396	725.491	−11.484
3400	60.851	354.822	302.653	177.373	686.389	726.706	−11.164
3500	60.928	356.587	304.169	183.462	688.348	727.863	−10.863
3600	61.000	358.304	305.649	189.558	690.271	728.965	−10.577
3700	61.066	359.976	307.095	195.661	692.157	730.013	−10.306
3800	61.129	361.606	308.508	201.771	694.004	731.012	−10.048
3900	61.187	363.194	309.890	207.887	695.811	731.963	−9.804
4000	61.242	364.744	311.242	214.009	697.576	732.867	−9.570
4100	61.294	366.257	312.565	220.135	699.298	733.728	−9.348
4200	61.342	367.735	313.861	226.267	700.975	734.547	−9.135
4300	61.388	369.179	315.131	232.404	702.605	735.327	−8.932
4400	61.432	370.590	316.376	238.545	704.209	736.068	−8.738
4500	61.473	371.971	317.596	244.690	705.752	736.774	−8.552
4600	61.513	373.323	318.793	250.839	707.243	737.447	−8.374
4700	61.550	374.646	319.967	256.992	708.683	738.088	−8.203
4800	61.587	375.942	321.120	263.149	710.071	738.699	−8.039
4900	61.622	377.213	322.252	269.310	711.405	739.281	−7.881
5000	61.655	378.458	323.363	275.474	712.683	739.838	−7.729
5100	61.688	379.679	324.456	281.641	713.909	740.368	−7.583
5200	61.720	380.877	325.529	287.811	715.073	740.875	−7.442
5300	61.751	382.053	326.585	293.985	716.176	741.361	−7.307
5400	61.781	383.208	327.622	300.161	717.217	741.826	−7.176
5500	61.810	384.342	328.643	306.341	718.194	742.272	−7.050
5600	61.839	385.456	329.648	312.523	719.106	742.702	−6.928
5700	61.868	386.551	330.637	318.709	719.951	743.116	−6.810
5800	61.896	387.627	331.610	324.897	720.728	743.516	−6.696
5900	61.924	388.685	332.569	331.088	721.434	743.901	−6.586
6000	61.951	389.726	333.512	337.282	722.068	744.277	−6.480

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 193.200\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 169.58 \pm 48.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 169.03 \pm 48.1\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights					
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	2	35400	2	42070	2
19221.2	2	[38730]	2	48000	4
19224.7	2	41120	4		

$\omega_e = 1495.7\ cm^{-1}$ $\omega_e x_e = 31.5\ cm^{-1}$ $\sigma = 1$
$B_e = 5.8181\ cm^{-1}$ $\alpha_e = 0.1668\ cm^{-1}$ $r_e = 1.73$ Å

Enthalpy of Formation

The enthalpy of formation is calculated using $D_0° = 2.0 \pm 0.5$ eV derived from a graphical extrapolation of the (0–3) energy levels of the $X^2\Sigma^+$ state reported by Gaydon.[1] Herzberg[2] reported $D_0° \leq 2.49$ eV assuming predissociation of the C^2 state of MgH into $Mg(^3P)$ and $H(^2S)$.

Heat Capacity and Entropy

The molecular constants and electronic levels are obtained from Herzberg[2] except for the electronic levels 35400 and 48000 obtained from Khan.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.682	169.583	169.583	INFINITE
100	29.127	161.292	219.230	−5.794	170.330	160.188	−83.673
200	29.181	181.492	195.889	−2.879	169.890	150.162	−39.218
250	29.316	188.016	193.685	−1.417	169.483	145.275	−30.354
298.15	29.583	193.200	193.200	0.	169.034	140.653	−24.642
300	29.596	193.383	193.201	0.055	169.016	140.477	−24.459
350	30.016	197.975	193.562	1.545	168.519	135.759	−20.261
400	30.535	202.016	194.371	3.058	168.011	131.114	−17.122
450	31.103	205.645	195.426	4.599	167.501	126.533	−14.688
500	31.683	208.952	196.615	6.169	166.993	122.008	−12.746
600	32.778	214.828	199.173	9.393	165.986	113.106	−9.847
700	33.724	219.954	201.783	12.719	164.971	104.372	−7.788
800	34.510	224.510	204.345	16.132	163.919	95.786	−6.254
900	35.158	228.613	206.817	19.616	162.798	87.336	−5.069
1000	35.694	232.346	209.186	23.160	152.983	79.728	−4.165
1100	36.141	235.770	211.449	26.752	151.625	72.469	−3.441
1200	36.519	238.931	213.609	30.386	150.289	65.332	−2.844
1300	36.844	241.867	215.671	34.054	148.966	58.306	−2.343
1400	37.127	244.608	217.642	37.753	20.243	54.549	−2.035
1500	37.376	247.178	219.526	41.479	20.286	56.998	−1.985
1600	37.599	249.598	221.330	45.228	20.330	59.443	−1.941
1700	37.800	251.883	223.061	48.998	20.375	61.887	−1.902
1800	37.985	254.049	224.723	52.787	20.419	64.327	−1.867
1900	38.155	256.108	226.321	56.594	20.461	66.765	−1.836
2000	38.314	258.069	227.860	60.418	20.501	69.202	−1.807
2100	38.465	259.942	229.343	64.257	20.538	71.636	−1.782
2200	38.608	261.734	230.775	68.110	20.573	74.068	−1.759
2300	38.746	263.454	232.159	71.978	20.605	76.499	−1.737
2400	38.881	265.106	233.497	75.860	20.636	78.928	−1.718
2500	39.013	266.695	234.794	79.754	20.663	81.357	−1.700
2600	39.144	268.228	236.050	83.662	20.689	83.784	−1.683
2700	39.275	269.708	237.270	87.583	20.712	86.210	−1.668
2800	39.407	271.139	238.454	91.517	20.732	88.636	−1.654
2900	39.541	272.524	239.605	95.464	20.749	91.060	−1.640
3000	39.678	273.867	240.725	99.425	20.763	93.485	−1.628
3100	39.818	275.170	241.815	103.400	20.773	95.909	−1.616
3200	39.962	276.436	242.877	107.389	20.778	98.332	−1.605
3300	40.110	277.668	243.913	111.393	20.778	100.756	−1.595
3400	40.264	278.868	244.923	115.411	20.771	103.179	−1.585
3500	40.423	280.037	245.910	119.445	20.756	105.603	−1.576
3600	40.587	281.178	246.874	123.496	20.733	108.028	−1.567
3700	40.757	282.293	247.816	127.563	20.699	110.453	−1.559
3800	40.933	283.382	248.738	131.648	20.653	112.880	−1.552
3900	41.114	284.448	249.640	135.750	20.595	115.307	−1.544
4000	41.301	285.491	250.523	139.871	20.521	117.737	−1.537
4100	41.494	286.513	251.389	144.010	20.431	120.168	−1.531
4200	41.693	287.515	252.237	148.170	20.323	122.602	−1.525
4300	41.897	288.499	253.069	152.349	20.195	125.039	−1.519
4400	42.106	289.464	253.885	156.549	20.046	127.479	−1.513
4500	42.320	290.413	254.686	160.770	19.874	129.922	−1.508
4600	42.538	291.345	255.473	165.013	19.678	132.370	−1.503
4700	42.761	292.263	256.246	169.278	19.455	134.822	−1.498
4800	42.989	293.165	257.006	173.566	19.205	137.279	−1.494
4900	43.220	294.054	257.753	177.876	18.926	139.742	−1.490
5000	43.455	294.930	258.488	182.210	18.617	142.211	−1.486
5100	43.694	295.792	259.211	186.567	18.277	144.686	−1.482
5200	43.936	296.643	259.922	190.949	17.903	147.168	−1.478
5300	44.181	297.482	260.623	195.355	17.497	149.658	−1.475
5400	44.428	298.311	261.313	199.785	17.056	152.155	−1.472
5500	44.678	299.128	261.994	204.240	16.579	154.661	−1.469
5600	44.931	299.935	262.664	208.721	16.066	157.177	−1.466
5700	45.185	300.733	263.325	213.226	15.516	159.701	−1.463
5800	45.441	301.521	263.977	217.758	14.928	162.236	−1.461
5900	45.699	302.300	264.620	222.315	14.301	164.781	−1.459
6000	45.958	303.070	265.254	226.898	13.636	167.337	−1.457

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = [226.458 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-161.34 \pm 37.7]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-164.75 \pm 37.7]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	2
[27000]	[4]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[718](1)
[492](2)
[3650](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$

Bond Distances: Mg–O = [1.77] Å O–H = [0.96] Å

Bond Angle: Mg–O–H = [180]°

Rotational Constant: B_0 = [0.491925] cm^{-1}

Enthalpy of Formation

From observations made during a flame spectra study of the bond dissociation energy of magnesium oxide, Cotton and Jenkins[1] concluded that $D°_0$(Mg–OH) is less than 90 kcal·mol^{-1}. The analogy between gaseous monohydroxides and monohalides has been recognized.[2-5] Hildenbrand[6] has found that the ratio of $D°_0$(Mg–F)/$D°_0$(F–Mg–F) is 0.45; current JANAF values[7] give 0.448. From the latter ratio and current JANAF data,[7] $D°_0$(Mg–OH) = 84.49 kcal·mol^{-1} is derived. Adding the difference, −16.1 kcal·mol^{-1}, between $D°_0$(Mg–F) and $D°_0$(Ca–F)[7] to $D°_0$(Ca–OH) = 97.5 kcal·mol^{-1}[7] gives $D°_0$(Mg–OH) = 81.4 kcal·mol^{-1}. The average $D°_0$(Mg–OH) = 82.9 ± 5 kcal·mol^{-1} is adopted from which $\Delta_f H°$(MgOH, g, 0 K) = −38.56 ± 9 kcal·mol^{-1} is derived.

The value of $D°_0$(Mg–OH) = 56 ± 5 kcal·mol^{-1} derived by Bulewicz and Sugden[8] from flame spectra studies appears to be too low.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear in accordance with the prediction of Walsh,[9] the evidence that the alkali metal monohydroxides are linear,[10-13] and the ESR spectrum study of MgOH in argon and neon matrices from which Brom and Weltner[13] concluded that MgOH is probably linear with a $^2\Sigma$ ground state. The analogy with MgF and MgCl[7] also indicates a $^2\Sigma^+$ ground state, which is assumed.

Ultraviolet emission spectra near 3800 Å were observed from MgOH and MgOD by Pesic and Gaydon[14] and by Brewer and Trajmar.[15] Brom and Weltner[13] observed absorption spectra of MgOH in an argon matrix in the 3100–3700 Å range. From these observations and from the comparison with MgF and MgCl, the first excited state at 27000 cm^{-1} is estimated.

The Mg–O bond distance is estimated to be slightly larger, 0.02 Å, than the MgF bond distances[7] after noting the close similarity in bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[7]

The Mg–O stretching frequency, 718 cm^{-1}, is estimated to be the same as in MgF.[5,7] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 492 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[5,12]

The entropy in the present table is lower by 0.20 cal·K^{-1}·mol^{-1} at 298 K and 0.25 cal·K^{-1}·mol^{-1} at 1000 K than that proposed by Jackson;[5] the data relevant to the calculation are nearly the same.

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[7] JANAF Thermochemical Tables: $Mg(OH)_2$(g), CaOH(g), 12–31–75; MgF_2(g), 6–30–75; Mg(g), 9–30–62; OH(g), 12–31–70; CaF(g), 12–31–68; H_2O(g), 3–31–61.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.160	−161.341	−161.341	INFINITE
100	29.833	187.913	260.329	−7.242	−162.017	−166.156	86.791
200	36.797	210.512	230.214	−3.940	−163.525	−169.709	44.323
250	40.324	219.114	227.152	−2.010	−164.192	−171.176	35.765
298.15	43.036	226.458	226.458	0.	−164.755	−172.469	30.216
300	43.127	226.725	226.459	0.080	−164.775	−172.517	30.038
350	45.270	233.541	226.992	2.292	−165.287	−173.766	25.933
400	46.900	239.698	228.202	4.598	−165.750	−174.945	22.845
450	48.151	245.297	229.795	6.976	−166.182	−176.068	20.437
500	49.130	250.423	231.605	9.409	−166.597	−177.144	18.506
600	50.561	259.515	235.519	14.398	−167.419	−179.177	15.599
700	51.597	267.390	239.522	19.508	−168.278	−181.069	13.512
800	52.441	274.337	243.448	24.711	−169.208	−182.834	11.938
900	53.189	280.557	247.232	29.993	−170.234	−184.477	10.707
1000	53.879	286.197	250.851	35.347	−179.969	−185.287	9.678
1100	54.524	291.363	254.302	40.767	−181.254	−185.756	8.821
1200	55.128	296.134	257.592	46.250	−182.515	−186.109	8.101
1300	55.690	300.569	260.729	51.792	−183.757	−186.358	7.488
1400	56.209	304.715	263.724	57.387	−312.390	−183.345	6.841
1500	56.686	308.610	266.588	63.032	−312.249	−174.133	6.064
1600	57.123	312.282	269.330	68.723	−312.096	−164.930	5.384
1700	57.521	315.757	271.960	74.455	−311.934	−155.737	4.785
1800	57.883	319.055	274.486	80.226	−311.767	−146.554	4.253
1900	58.212	322.194	276.915	86.031	−311.597	−137.380	3.777
2000	58.511	325.188	279.254	91.867	−311.426	−128.215	3.349
2100	58.783	328.049	281.510	97.732	−311.255	−119.059	2.961
2200	59.030	330.789	283.688	103.623	−311.088	−109.910	2.610
2300	59.254	333.418	285.794	109.537	−310.924	−100.770	2.289
2400	59.459	335.945	287.831	115.473	−310.766	−91.636	1.994
2500	59.646	338.376	289.804	121.428	−310.615	−82.509	1.724
2600	59.817	340.718	291.718	127.401	−310.472	−73.388	1.474
2700	59.973	342.979	293.575	133.391	−310.339	−64.271	1.243
2800	60.117	345.163	295.378	139.396	−310.217	−55.160	1.029
2900	60.250	347.275	297.132	145.414	−310.107	−46.053	0.830
3000	60.373	349.319	298.837	151.445	−310.012	−36.949	0.643
3100	60.486	351.301	300.498	157.488	−309.931	−27.848	0.469
3200	60.592	353.223	302.116	163.542	−309.868	−18.750	0.306
3300	60.692	355.089	303.693	169.607	−309.823	−9.654	0.153
3400	60.785	356.902	305.231	175.681	−309.799	−0.558	0.009
3500	60.874	358.665	306.733	181.764	−309.797	8.537	−0.127
3600	60.958	360.381	308.199	187.855	−309.819	17.633	−0.256
3700	61.038	362.053	309.632	193.955	−309.867	26.729	−0.377
3800	61.116	363.682	311.033	200.063	−309.943	35.828	−0.492
3900	61.192	365.270	312.404	206.178	−310.050	44.929	−0.602
4000	61.266	366.820	313.745	212.301	−310.189	54.032	−0.706
4100	61.338	368.334	315.058	218.431	−310.363	63.140	−0.804
4200	61.410	369.813	316.344	224.569	−310.574	72.252	−0.899
4300	61.482	371.259	317.605	230.713	−310.823	81.370	−0.988
4400	61.553	372.673	318.840	236.865	−311.114	90.494	−1.074
4500	61.625	374.057	320.052	243.024	−311.447	99.624	−1.156
4600	61.698	375.412	321.241	249.190	−311.825	108.763	−1.235
4700	61.772	376.740	322.407	255.364	−312.250	117.911	−1.310
4800	61.846	378.041	323.553	261.544	−312.724	127.069	−1.383
4900	61.923	379.317	324.678	267.733	−313.249	136.236	−1.452
5000	62.000	380.569	325.783	273.929	−313.826	145.416	−1.519
5100	62.079	381.798	326.870	280.133	−314.457	154.607	−1.583
5200	62.160	383.004	327.938	286.345	−315.144	163.810	−1.645
5300	62.243	384.189	328.988	292.565	−315.888	173.028	−1.705
5400	62.328	385.353	330.021	298.794	−316.690	182.260	−1.763
5500	62.415	386.497	331.037	305.031	−317.552	191.507	−1.819
5600	62.503	387.623	332.038	311.277	−318.475	200.772	−1.873
5700	62.593	388.730	333.023	317.531	−319.461	210.053	−1.925
5800	62.686	389.819	333.993	323.795	−320.510	219.352	−1.975
5900	62.780	390.892	334.948	330.069	−321.624	228.668	−2.024
6000	62.876	391.948	335.889	336.351	−322.804	238.006	−2.072

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [220.824 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [581.61 \pm 62.8]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [584.42 \pm 62.8]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[700](1)
[490](2)
[3650](1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: [$C_{\infty v}$]
Bond Distances: Mg–O = [1.77] Å O–H = [0.96] Å
Bond Angle: Mg–O–H = [180]°
Rotational Constant: B_0 = [0.491933] cm^{-1}

Enthalpy of Formation

The enthalpy of formation of $MgOH^+(g)$ is estimated based on trends suggested by the alkaline earth monohydroxide unipositive ions. The estimate is based on the close agreement of the appearance potentials of the alkaline earth monohydroxides and the corresponding monofluoride.[1] In addition, the ionization potentials of the alkaline earth elements are fairly close to the appearance potential of the monohydroxide. We adopt, as the ionization potential for MgOH(g), a value of 7.7 eV (177.57 $kcal \cdot mol^{-1}$). This value is identical to the appearance potential of MgF(g).[1] The ionization potential of Mg(g) is 7.65 eV,[1] which is very close to our adopted value.

The adopted ionization potential of 7.7 eV refers to the process $MgOH(g) + e^- = MgOH^+(g) + 2\ e^-$. Using auxiliary data,[1] we calculate $\Delta_f H°(0\ K) = 139.01 \pm 15\ kcal \cdot mol^{-1}$ for $MgOH^+(g)$. This leads to $\Delta_f H°(298.15\ K) = 139.68 \pm 15.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[1-4] In addition, Walsh[5] had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($MgOH^+$ has 8 valence electrons) will be linear in their ground state. The molecule $MgOH^+$ is isoelectronic with NaOH.

The bond dissociation energy for $MgOH^+$ (81.7 $kcal \cdot mol^{-1}$)[1] for the process $MgOH^+(g) = Mg^+(g) + OH(g)$ is essentially identical to that for MgOH (82.0 $kcal \cdot mol^{-1}$)[1]. This suggests a similar bonding in these two molecules. Thus, the bond distances are assumed to be the same as those adopted for MgOH(g).[1] The vibrational frequencies are assumed to be similar to those adopted for MgOH(g).[1] The ground state quantum weight is assumed to be the same as that of NaOH(g).[1]

References

[1]JANAF Thermochemical Tables: e^-, 3-31-65; NaOH(g) and $Mg^+(g)$, 12-31-70; MgOH(g) and $MgF^+(g)$, 12-31-75.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−9.186	581.611		
100	29.854	182.153	254.830	−7.268			
200	36.949	204.808	224.596	−3.958			
250	40.503	213.448	221.522	−2.018			
298.15	43.216	220.824	220.824	0.	584.421	572.132	−100.235
300	43.306	221.092	220.825	0.080	584.440	572.055	−99.604
350	45.437	227.935	221.361	2.301	584.975	569.950	−85.060
400	47.050	234.113	222.575	4.615	585.560	567.764	−74.142
450	48.284	239.729	224.174	7.000	586.174	565.503	−65.642
500	49.246	244.868	225.990	9.439	586.805	563.172	−58.834
600	50.651	253.979	229.915	14.438	588.071	558.327	−48.607
700	51.668	261.867	233.929	19.557	589.299	553.271	−41.286
800	52.498	268.822	237.864	24.766	590.455	548.044	−35.784
900	53.235	275.048	241.656	30.053	591.512	542.679	−31.496
1000	53.917	280.693	245.282	35.411	583.859	537.914	−28.098
1100	54.556	285.862	248.739	40.835	584.657	533.281	−25.323
1200	55.155	290.635	252.034	46.321	585.477	528.574	−23.008
1300	55.713	295.072	255.176	51.865	586.317	523.798	−21.046
1400	56.229	299.220	258.175	57.462	459.764	522.124	−19.481
1500	56.704	303.116	261.043	63.109	461.986	526.501	−18.334
1600	57.138	306.789	263.788	68.802	464.219	530.729	−17.327
1700	57.535	310.266	266.421	74.536	466.461	534.818	−16.433
1800	57.895	313.564	268.949	80.308	468.708	538.774	−15.635
1900	58.223	316.704	271.381	86.114	470.958	542.605	−14.917
2000	58.521	319.698	273.722	91.951	473.209	546.318	−14.268
2100	58.792	322.560	275.980	97.817	475.459	549.918	−13.678
2200	59.038	325.301	278.160	103.709	477.706	553.411	−13.140
2300	59.262	327.930	280.267	109.624	479.949	556.802	−12.645
2400	59.466	330.456	282.306	115.560	482.187	560.095	−12.190
2500	59.652	332.888	284.281	121.516	484.417	563.295	−11.769
2600	59.822	335.231	286.196	127.490	486.639	566.406	−11.379
2700	59.977	337.491	288.054	133.480	488.851	569.432	−11.016
2800	60.120	339.675	289.859	139.485	491.052	572.377	−10.678
2900	60.250	341.787	291.613	145.504	493.240	575.242	−10.361
3000	60.371	343.832	293.320	151.535	495.414	578.033	−10.064
3100	60.481	345.813	294.982	157.578	497.573	580.752	−9.786
3200	60.583	347.735	296.600	163.631	499.714	583.400	−9.523
3300	60.678	349.601	298.178	169.694	501.837	585.982	−9.275
3400	60.765	351.413	299.717	175.766	503.938	588.501	−9.041
3500	60.846	353.176	301.220	181.847	506.016	590.957	−8.820
3600	60.921	354.891	302.687	187.935	508.070	593.355	−8.609
3700	60.991	356.561	304.121	194.031	510.096	595.696	−8.410
3800	61.056	358.189	305.522	200.133	512.093	597.983	−8.220
3900	61.117	359.775	306.893	206.242	514.058	600.218	−8.039
4000	61.173	361.324	308.234	212.357	515.989	602.402	−7.867
4100	61.226	362.835	309.548	218.477	517.883	604.539	−7.702
4200	61.276	364.311	310.834	224.602	519.739	606.630	−7.545
4300	61.322	365.753	312.095	230.732	521.553	608.678	−7.394
4400	61.366	367.163	313.330	236.866	523.324	610.683	−7.250
4500	61.407	368.543	314.542	243.005	525.050	612.649	−7.111
4600	61.445	369.893	315.731	249.147	526.726	614.577	−6.979
4700	61.482	371.215	316.897	255.294	528.353	616.469	−6.851
4800	61.516	372.510	318.042	261.444	529.926	618.327	−6.729
4900	61.548	373.778	319.167	267.597	531.445	620.153	−6.611
5000	61.579	375.022	320.272	273.753	532.906	621.949	−6.497
5100	61.607	376.242	321.357	279.912	534.309	623.716	−6.388
5200	61.635	377.438	322.424	286.075	535.651	625.455	−6.283
5300	61.660	378.613	323.473	292.239	536.931	627.170	−6.181
5400	61.685	379.765	324.505	298.407	538.146	628.861	−6.083
5500	61.708	380.898	325.520	304.576	539.295	630.530	−5.988
5600	61.730	382.010	326.519	310.748	540.376	632.180	−5.897
5700	61.751	383.102	327.502	316.922	541.389	633.810	−5.808
5800	61.771	384.177	328.470	323.098	542.330	635.423	−5.723
5900	61.790	385.233	329.423	329.276	543.200	637.020	−5.640
6000	61.808	386.271	330.362	335.456	543.996	638.603	−5.560

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = 181.253 \pm 0.04\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 376.51 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 376.56 \pm 16.7\ kJ·mol^{-1}$

Source	State	Electronic States and Molecular Constants (σ = 1) ϵ_i, cm^{-1}	g_i	r_e, A	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}
13,15	$X^3\Sigma^-$	0.0	3	1.038	16.666	0.648	3282.09	78.3
13,14	$a^1\Sigma$	12590	2	1.041	16.439	[0.7]	3303	55
13,16	$b^1\Sigma^+$	21240	1	1.035	16.7326	0.6049	3347	70.7
13,15	$A^3\Pi$	29777	6	1.036	16.6901	0.7440	3231.0	98.5
16,17	$C^1\Pi$	43345	2	1.1005	14.7985	1.267	2503	194
16,17	$d^1\Sigma^+$	82856	1	1.1165	14.3809	0.6119	2665	71.0

Enthalpy of Formation

The electron impact appearance potential of N_2^+ from HN_3 determined by Franklin *et al.*,[1] leads to a value $\Delta_f H°$(NH, g, 298.15 K) = 81.7 ± 0.5 kcal·mol^{-1}. Reed and Snedden[2] determined the electron impact appearance potential of NH^+ from NH_3. This, combined with the directly measured electron impact ionization potential of NH, 13.1 eV, gives $\Delta_f H°$ = 82.9 kcal·mol^{-1}. This value of the ionization potential of NH has also been obtained by Foner and Hudson.[3] However, all of these electron impact experiments are subject to errors of several tenths of an electron volt or more.

More recently, Seal and Gaydon[4] measured the concentration of NH in reflected shock waves in nitrogen–hydrogen–krypton and ammonia–krypton mixtures. These led to $D_0°$(NH) = 3.21 ± 0.16 eV, corresponding to $\Delta_f H°$(NH, g) = 90.13 ± 3 kcal·mol^{-1}. Kaskan and Nadler[5] determined NH, NH_3, and OH concentrations in a flat NH_3–D_2–N_2 flame and concluded $\Delta_f H°$(NH, g) = 90 ± 4 kcal·mol^{-1}. Stedman[6] studied the NH emission spectrum obtained by collision of metastable rare gas atoms with HN_3. Taking the highest level of NH as observed in emission as a limit, he concluded that $\Delta_f H°$(NH, g) > 80 kcal·mol^{-1}. From analogous consideration on N_2 emission observed by collision of metastable argon atoms with HN_3 he concluded that $\Delta_f H°$(NH, g) ≤ 94 kcal·mol^{-1}.

Quantum chemical calculation of the dissociation energy of small molecules is possible with estimated accuracies of 0.1 to 0.2 eV. A theoretical calculation of the dissociation energy of NH($X^3\Sigma^-$), applying the techniques of Wahl and Das[7] has been determined by Stevens[8] to yield D_e = 3.4 eV. This result corroborates the results of Seal and Gaydon and would support $\Delta_f H°$(NH, g) = 90 ± 4 kcal·mol^{-1}. Theoretical calculations of this type can be used to distinquish between disparate experimental results that differ by more than 0.2 eV.

Heat Capacity and Entropy

The vibrational and rotational constants for the ground and excited states are taken from the sources indicated. The splitting between the $X^3\Sigma^-$ and $a^1\Delta$ states is based on the work of Gilles *et al.*[14] who observed the $b^1\Sigma^+$–$X^3\Sigma^-$ band in emission.

The thermodynamic functions are calculated using first-order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_{ti}\Sigma Q_r{}^i Q_v{}^i g_i \exp(-c_2\epsilon_i/T)$. The National Bureau of Standards prepared this table[9] by critical analysis of data existing in 1972 using only the ground electronic state. Using the molecular constants selected here and $\Delta_f H°$ selected by NBS,[9] we recalculate the table in terms of 1973 fundamental constants,[10] 1975 atomic weights[11] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.617	376.511	376.511	INFINITE
100	29.126	149.428	207.157	−5.773	376.405	374.489	−195.613
200	29.133	169.618	183.918	−2.860	376.516	372.532	−97.295
250	29.140	176.119	181.732	−1.403	376.547	371.532	−77.627
298.15	29.147	181.253	181.253	0.	376.560	370.565	−64.921
300	29.147	181.433	181.253	0.054	376.560	370.528	−64.515
350	29.158	185.927	181.608	1.512	376.565	369.522	−55.148
400	29.175	189.821	182.397	2.970	376.565	368.515	−48.123
450	29.208	193.259	183.416	4.429	376.561	367.509	−42.659
500	29.263	196.339	184.557	5.891	376.555	366.504	−38.288
600	29.461	201.690	186.980	8.826	376.534	364.496	−31.732
700	29.787	206.254	189.415	11.787	376.505	362.492	−27.049
800	30.219	210.259	191.775	14.787	376.473	360.492	−23.538
900	30.722	213.847	194.032	17.834	376.444	358.496	−20.807
1000	31.258	217.111	196.179	20.933	376.421	356.503	−18.622
1100	31.798	220.116	198.220	24.085	376.406	354.512	−16.834
1200	32.325	222.906	200.162	27.292	376.399	352.522	−15.345
1300	32.825	225.513	202.013	30.549	376.399	350.532	−14.085
1400	33.294	227.963	203.780	33.856	376.407	348.542	−13.004
1500	33.730	230.275	205.470	37.207	376.420	346.552	−12.068
1600	34.134	232.465	207.089	40.601	376.438	344.560	−11.249
1700	34.507	234.546	208.644	44.033	376.461	342.567	−10.526
1800	34.852	236.528	210.138	47.501	376.488	340.572	−9.883
1900	35.173	238.421	211.577	51.003	376.518	338.576	−9.308
2000	35.473	240.233	212.965	54.535	376.551	336.578	−8.791
2100	35.755	241.970	214.305	58.097	376.587	334.579	−8.322
2200	36.021	243.640	215.601	61.685	376.627	332.578	−7.896
2300	36.274	245.247	216.855	65.300	376.670	330.574	−7.508
2400	36.516	246.796	218.071	68.940	376.716	328.569	−7.151
2500	36.749	248.291	219.250	72.603	376.766	326.562	−6.823
2600	36.975	249.737	220.395	76.290	376.820	324.553	−6.520
2700	37.194	251.136	221.508	79.998	376.879	322.541	−6.240
2800	37.407	252.493	222.590	83.728	376.942	320.528	−5.980
2900	37.616	253.809	223.644	87.479	377.010	318.512	−5.737
3000	37.821	255.088	224.671	91.251	377.084	316.493	−5.511
3100	38.022	256.331	225.672	95.043	377.163	314.472	−5.299
3200	38.220	257.542	226.649	98.855	377.247	312.449	−5.100
3300	38.416	258.721	227.603	102.687	377.338	310.423	−4.914
3400	38.609	259.870	228.536	106.538	377.435	308.393	−4.738
3500	38.799	260.992	229.447	110.409	377.538	306.361	−4.572
3600	38.988	262.088	230.339	114.298	377.648	304.326	−4.416
3700	39.175	263.159	231.211	118.206	377.764	302.288	−4.268
3800	39.360	264.206	232.066	122.133	377.886	300.246	−4.127
3900	39.543	265.231	232.903	126.078	378.015	298.201	−3.994
4000	39.725	266.234	233.724	130.042	378.151	296.153	−3.867
4100	39.905	267.217	234.529	134.023	378.294	294.102	−3.747
4200	40.084	268.181	235.319	138.023	378.443	292.046	−3.632
4300	40.262	269.126	236.094	142.040	378.599	289.987	−3.523
4400	40.439	270.054	236.855	146.075	378.763	287.925	−3.418
4500	40.615	270.965	237.603	150.128	378.933	285.858	−3.318
4600	40.789	271.859	238.338	154.198	379.110	283.788	−3.223
4700	40.963	272.738	239.061	158.286	379.295	281.714	−3.131
4800	41.136	273.603	239.771	162.391	379.486	279.636	−3.043
4900	41.309	274.453	240.470	166.513	379.686	277.553	−2.959
5000	41.480	275.289	241.158	170.652	379.893	275.467	−2.878
5100	41.652	276.112	241.836	174.809	380.108	273.376	−2.800
5200	41.823	276.922	242.503	178.983	380.331	271.281	−2.725
5300	41.993	277.721	243.160	183.173	380.563	269.182	−2.653
5400	42.164	278.507	243.807	187.381	380.803	267.078	−2.583
5500	42.334	279.283	244.445	191.606	381.053	264.970	−2.516
5600	42.504	280.047	245.074	195.848	381.312	262.857	−2.452
5700	42.674	280.801	245.694	200.107	381.581	260.740	−2.389
5800	42.844	281.544	246.306	204.383	381.861	258.617	−2.329
5900	43.015	282.278	246.909	208.676	382.151	256.490	−2.271
6000	43.185	283.003	247.505	212.986	382.451	254.357	−2.214

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 220.722\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 102.501\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 99.579\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2854.17(1)
1570 (1)
1110 (1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: H–N = 1.020 ± 0.02 Å N=O = 1.239 ± 0.005 Å
Bond Angle: H–N=O = 114° 25' ± 2°
Product of the Moments of Inertia: $I_A I_B I_C = 5.939 \times 10^{-118}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°$(HNO, g, 298.15 K) is calculated from $D°_0$(H–NO) = 48.6 kcal·mol^{-1} reported by Clement and Ramsay.[1]

Heat Capacity and Entropy

Vibrational frequencies were assigned by Bancroft *et al.*[2] and Brown and Pimentel[3]. Bond distances and bond angles were taken from Bancroft *et al.*[2] The molecular constants given by Dalby[4] were: r(N=O) = 1.211$_6$ Å; r(N–H) = 1.0628 Å, and a H– N=O bond angle of 108.5$_8$°. The principal moments of inertia are: $I_A = 0.1262 \times 10^{-39}$, $I_B = 2.1070 \times 10^{-39}$, and $I_C = 2.2332 \times 10^{-39}$ g·cm^2.

References

[1]M. J. Y. Clement and D. A. Ramsay, Can. J. Phys. **39**, 205 (1961).
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[3]H. Brown and G. Pimentel, J. Chem. Phys. **29**, 883 (1958).
[4]F. W. Dalby, Can. J. Phys. **36**, 1336 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.988	102.501	102.501	INFINITE
100	33.258	184.104	250.730	−6.663	101.424	104.706	−54.693
200	33.451	207.183	223.843	−3.332	100.497	108.348	−28.298
250	33.911	214.691	221.288	−1.649	100.025	110.366	−23.060
298.15	34.640	220.722	220.722	0.	99.579	112.398	−19.692
300	34.673	220.937	220.723	0.064	99.562	112.478	−19.584
350	35.658	226.353	221.148	1.822	99.129	114.665	−17.113
400	36.768	231.186	222.106	3.632	98.733	116.912	−15.267
450	37.928	235.584	223.363	5.499	98.379	119.206	−13.837
500	39.085	239.640	224.790	7.425	98.065	121.538	−12.697
600	41.289	246.964	227.889	11.445	97.550	126.283	−10.994
700	43.281	253.481	231.087	15.675	97.162	131.104	−9.783
800	45.042	259.378	234.261	20.093	96.881	135.973	−8.878
900	46.583	264.774	237.356	24.676	96.686	140.872	−8.176
1000	47.922	269.753	240.350	29.403	96.560	145.789	−7.615
1100	49.081	274.376	243.235	34.255	96.489	150.716	−7.157
1200	50.083	278.691	246.012	39.214	96.460	155.647	−6.775
1300	50.948	282.734	248.683	44.267	96.464	160.580	−6.452
1400	51.697	286.538	251.252	49.400	96.491	165.511	−6.175
1500	52.346	290.128	253.726	54.603	96.535	170.439	−5.935
1600	52.911	293.524	256.108	59.866	96.590	175.364	−5.725
1700	53.403	296.747	258.404	65.183	96.651	180.286	−5.540
1800	53.834	299.812	260.620	70.545	96.714	185.204	−5.374
1900	54.213	302.733	262.761	75.948	96.776	190.118	−5.227
2000	54.548	305.523	264.829	81.386	96.834	195.029	−5.094
2100	54.843	308.191	266.831	86.856	96.886	199.938	−4.973
2200	55.106	310.749	268.770	92.354	96.930	204.844	−4.864
2300	55.341	313.204	270.649	97.876	96.965	209.748	−4.764
2400	55.550	315.563	272.471	103.421	96.990	214.651	−4.672
2500	55.739	317.835	274.241	108.986	97.004	219.553	−4.587
2600	55.908	320.024	275.960	114.568	97.006	224.455	−4.509
2700	56.061	322.137	277.631	120.167	96.996	229.358	−4.437
2800	56.200	324.179	279.257	125.780	96.974	234.260	−4.370
2900	56.326	326.153	280.840	131.406	96.938	239.164	−4.308
3000	56.440	328.064	282.383	137.045	96.890	244.069	−4.250
3100	56.545	329.917	283.887	142.694	96.828	248.976	−4.195
3200	56.641	331.714	285.353	148.353	96.753	253.885	−4.144
3300	56.729	333.458	286.785	154.022	96.665	258.797	−4.096
3400	56.809	335.153	288.182	159.699	96.564	263.711	−4.051
3500	56.884	336.801	289.548	165.384	96.449	268.629	−4.009
3600	56.953	338.404	290.883	171.075	96.322	273.550	−3.969
3700	57.016	339.965	292.189	176.774	96.181	278.475	−3.931
3800	57.075	341.487	293.466	182.478	96.027	283.404	−3.896
3900	57.130	342.970	294.716	188.189	95.860	288.337	−3.862
4000	57.180	344.417	295.941	193.904	95.681	293.275	−3.830
4100	57.228	345.829	297.140	199.625	95.488	298.217	−3.799
4200	57.272	347.209	298.316	205.350	95.282	303.164	−3.770
4300	57.313	348.557	299.469	211.079	95.063	308.116	−3.743
4400	57.352	349.875	300.600	216.812	94.832	313.073	−3.717
4500	57.388	351.164	301.709	222.549	94.587	318.036	−3.692
4600	57.422	352.426	302.798	228.290	94.330	323.004	−3.668
4700	57.454	353.661	303.867	234.034	94.059	327.978	−3.645
4800	57.484	354.871	304.917	239.780	93.775	332.959	−3.623
4900	57.512	356.057	305.949	245.530	93.478	337.945	−3.603
5000	57.539	357.219	306.963	251.283	93.168	342.937	−3.583
5100	57.564	358.359	307.959	257.038	92.844	347.936	−3.564
5200	57.587	359.477	308.939	262.796	92.507	352.940	−3.545
5300	57.610	360.574	309.903	268.555	92.157	357.953	−3.528
5400	57.631	361.651	310.851	274.317	91.792	362.971	−3.511
5500	57.651	362.709	311.785	280.082	91.414	367.996	−3.495
5600	57.670	363.748	312.703	285.848	91.022	373.028	−3.479
5700	57.688	364.768	313.608	291.616	90.615	378.068	−3.465
5800	57.705	365.772	314.499	297.385	90.195	383.115	−3.450
5900	57.722	366.759	315.376	303.157	89.759	388.168	−3.437
6000	57.737	367.729	316.241	308.930	89.309	393.230	−3.423

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 249.416\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -70.509 \pm 1.34\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -76.735 \pm 1.34\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3462(1)	855(1)
1639(1)	525(1)
1330(1)	638(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.20 Å N–O' = 1.46 Å O–H = 0.98 Å
Bond Angles: O–N–O' = 114° N–O'–H = 103°
Product of the Moments of Inertia: $I_A I_B I_C = 5.51348 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

Ashmore and Tyler[1] reported $\Delta_f H°(298.15\ K) = -9.06 \pm 0.32\ kcal·mol^{-1}$ for the reaction: $NO(g) + NO_2(g) + H_2O(g) = 2\ HNO_2(g)$, yielding $\Delta_f H°(298.15\ K) = -18.57 \pm 0.20\ kcal·mol^{-1}$ for HNO_2(g). Jones *et al.*[2] estimated the difference in energy of cis– and trans– HNO_2(g) to be $506 \pm 250\ cal·K^{-1}·mol^{-1}$. Hence the value of $\Delta_f H°(298.15\ K)$ for cis–HNO_2(g) was calculated.

The heat of reaction and the equilibrium constants for the formation of HNO_2(g) have been calculated by Karavaev and Skvortsov.[3] The value of $\Delta_f H°(298.15\ K)$ reported is $-18.8\ kcal·mol^{-1}$. However, based on the enthalpy of formation of liquid HNO_2, Ashmore and Levitt[4] give $\Delta_f H° = -13.7\ kcal·mol^{-1}$. The corresponding value reported by Rosser and Wise[5] is $-20.0\ kcal·mol^{-1}$, based on the experimental data of Wayne and Yost,[6] and the entropy of the equilibrium mixture of the trans– and cis– HNO_2(g) calculated by Jones, *et al.*[2]

Heat Capacity and Entropy

Vibrational frequencies, bond distances, and bond angles were obtained from Dor and Tarte[7] and Jones *et al.*[2] The principal moments of inertia are: $I_A = 1.0282 \times 10^{-39}$, $I_B = 6.8267 \times 10^{-39}$, and $I_C = 7.8549 \times 10^{-39}\ g·cm^2$.

References

[1]P. G. Ashmore and B. J. Tyler, J. Chem. Soc. 1017 (1961).
[2]L. H. Jones, R. M. Badger and G. E. Moore, J. Chem. Phys. **19**, 1599 (1951).
[3]M. M. Karavaev and G. A. Skvortsov, Russ. J. Phys. Chem. **36**, 566 (1962).
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[5]W. A. Rosser and H. Wise, J. Chem. Phys. **26**, 571 (1957).
[6]L. G. Wayne and D. M. Yost, J. Chem. Phys. **19**, 41 (1951).
[7]L. Dor and P. Tarte, Bull. Soc. Roy. Sci. Lg. 478 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.026	−70.509	−70.509	INFINITE
100	33.585	208.174	285.140	−7.697	−73.034	−63.494	33.166
200	38.653	232.718	253.350	−4.126	−75.178	−53.084	13.864
250	42.127	241.717	250.144	−2.107	−76.042	−47.458	9.916
298.15	45.354	249.416	249.416	0.	−76.735	−41.888	7.339
300	45.473	249.696	249.416	0.084	−76.759	−41.672	7.256
350	48.560	256.942	249.982	2.436	−77.336	−35.776	5.339
400	51.357	263.612	251.274	4.935	−77.790	−29.807	3.892
450	53.870	269.809	252.993	7.567	−78.138	−23.787	2.761
500	56.115	275.603	254.967	10.318	−78.398	−17.733	1.853
600	59.904	286.182	259.305	16.126	−78.705	−5.568	0.485
700	62.943	295.652	263.833	22.273	−78.802	6.632	−0.495
800	65.424	304.225	268.355	28.696	−78.748	18.835	−1.230
900	67.490	312.053	272.782	35.344	−78.580	31.024	−1.801
1000	69.236	319.257	277.074	42.183	−78.326	43.189	−2.256
1100	70.730	325.928	281.215	49.183	−78.003	55.325	−2.627
1200	72.017	332.138	285.203	56.322	−77.626	67.430	−2.935
1300	73.133	337.948	289.039	63.581	−77.208	79.501	−3.194
1400	74.105	343.404	292.730	70.944	−76.757	91.539	−3.415
1500	74.955	348.546	296.281	78.398	−76.283	103.543	−3.606
1600	75.700	353.408	299.701	85.931	−75.791	115.516	−3.771
1700	76.356	358.018	302.997	93.535	−75.289	127.457	−3.916
1800	76.935	362.399	306.176	101.200	−74.781	139.369	−4.044
1900	77.448	366.572	309.246	108.920	−74.272	151.252	−4.158
2000	77.904	370.557	312.213	116.688	−73.766	163.109	−4.260
2100	78.311	374.368	315.083	124.499	−73.266	174.940	−4.351
2200	78.675	378.019	317.861	132.349	−72.774	186.749	−4.434
2300	79.001	381.524	320.553	140.233	−72.292	198.534	−4.509
2400	79.294	384.892	323.164	148.148	−71.823	210.298	−4.577
2500	79.558	388.135	325.699	156.091	−71.369	222.044	−4.639
2600	79.797	391.260	328.160	164.059	−70.929	233.772	−4.697
2700	80.014	394.276	330.554	172.049	−70.506	245.483	−4.749
2800	80.212	397.189	332.882	180.061	−70.099	257.179	−4.798
2900	80.391	400.007	335.148	188.091	−69.709	268.860	−4.843
3000	80.556	402.735	337.356	196.139	−69.337	280.529	−4.884
3100	80.706	405.379	339.508	204.202	−68.983	292.186	−4.923
3200	80.844	407.944	341.606	212.279	−68.646	303.830	−4.960
3300	80.971	410.433	343.655	220.370	−68.327	315.465	−4.993
3400	81.088	412.852	345.654	228.473	−68.026	327.091	−5.025
3500	81.196	415.204	347.608	236.587	−67.743	338.707	−5.055
3600	81.296	417.493	349.518	244.712	−67.478	350.317	−5.083
3700	81.388	419.722	351.385	252.846	−67.230	361.918	−5.109
3800	81.474	421.894	353.212	260.990	−66.999	373.515	−5.134
3900	81.554	424.011	355.000	269.141	−66.786	385.105	−5.158
4000	81.628	426.077	356.752	277.300	−66.590	396.688	−5.180
4100	81.698	428.093	358.467	285.466	−66.411	408.268	−5.201
4200	81.762	430.063	360.149	293.640	−66.249	419.844	−5.222
4300	81.823	431.987	361.797	301.819	−66.105	431.416	−5.241
4400	81.880	433.869	363.414	310.004	−65.977	442.984	−5.259
4500	81.933	435.710	365.000	318.195	−65.867	454.550	−5.276
4600	81.983	437.511	366.557	326.391	−65.775	466.113	−5.293
4700	82.030	439.275	368.085	334.591	−65.700	477.676	−5.309
4800	82.074	441.002	369.586	342.796	−65.643	489.236	−5.324
4900	82.116	442.695	371.061	351.006	−65.604	500.796	−5.339
5000	82.155	444.354	372.510	359.220	−65.583	512.355	−5.353
5100	82.192	445.982	373.935	367.437	−65.582	523.914	−5.366
5200	82.227	447.578	375.336	375.658	−65.600	535.472	−5.379
5300	82.261	449.145	376.714	383.882	−65.637	547.033	−5.391
5400	82.292	450.682	378.069	392.110	−65.696	558.592	−5.403
5500	82.322	452.193	379.403	400.341	−65.774	570.153	−5.415
5600	82.350	453.676	380.717	408.574	−65.874	581.718	−5.426
5700	82.377	455.134	382.009	416.811	−65.997	593.282	−5.437
5800	82.403	456.567	383.283	425.050	−66.142	604.851	−5.447
5900	82.427	457.976	384.537	433.291	−66.311	616.419	−5.457
6000	82.450	459.361	385.772	441.535	−66.504	627.993	−5.467

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 249.261\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -72.674 \pm 1.34\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -78.827 \pm 1.34\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
3590(1)	794(1)
1696(1)	598(1)
1260(1)	543(1)

Ground State Quantum Weight: [1] $\sigma = 1$

Point Group: C_s

Bond Distances: O–N = 1.20 Å N–O' = 1.46 Å O'–H = 0.98 Å

Bond Angles: O–N–O' = 118° N–O'–H = 105°

Product of the Moments of Inertia: $I_A I_B I_C = 4.91660 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

Ashmore and Tyler[1] reported $\Delta_f H°(298.15\ K) = -9.06 \pm 0.32\ kcal·mol^{-1}$ for the reaction: $NO(g) + NO_2(g) + H_2O(g) \rightarrow 2HNO_2$ (g), yielding $\Delta_f H°(298.15\ K) = -18.57 \pm 0.20\ kcal·mol^{-1}$ for HNO_2(g). Jones *et al.*[2] estimated the difference in energy of cis– and trans–HNO_2(g) to be $506 \pm 250\ cal·K^{-1}·mol^{-1}$. Hence the value of $\Delta_f H°(298.15\ K)$ for trans–HNO_2(g) was calculated.

The heat of reaction and the equilibrium constants for the formation of HNO_2(g) have been calculated by Karavaev and Skvortsov.[3] The value of $\Delta_f H°(298.15\ K)$ reported is $-18.8\ kcal·mol^{-1}$. However, based on the enthalpy of formation of liquid HNO_2, Ashmore and Levitt[4] give $\Delta_f H° = -13.7\ kcal·mol^{-1}$. The corresponding value reported by Rosser and Wise[5] is $-20.0\ kcal·mol^{-1}$, based on the experimental data of Wayne and Yost[6] and the entropy of the equilibrium mixture of the trans– and cis– HNO_2(g) calculated by Jones *et al.*[2]

Heat Capacity and Entropy

Vibrational frequencies, bond distances, and bond angles were taken from Jones *et al.*[2] The values of vibrational frequencies were in good agreement to those reported by Dor and Tarte.[7] The principal moments of inertia are: $I_A = 0.7855 \times 10^{-39}$, $I_B = 7.5286 \times 10^{-39}$, and $I_C = 8.3141 \times 10^{-39}\ g·cm^2$.

References

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[7]L. Dor and P. Tarte, Bull. Soc. Roy. Sci. Lg. 478 (1951).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.099	−72.674	−72.674	INFINITE
100	33.588	207.696	285.389	−7.769	−75.199	−65.611	34.272
200	39.045	232.339	253.252	−4.183	−77.326	−55.157	14.405
250	42.718	241.447	250.001	−2.138	−78.165	−49.514	10.345
298.15	46.051	249.261	249.261	0.	−78.827	−43.934	7.697
300	46.173	249.546	249.262	0.085	−78.849	−43.717	7.612
350	49.290	256.902	249.835	2.473	−79.391	−37.817	5.644
400	52.066	263.669	251.147	5.009	−79.809	−31.848	4.159
450	54.528	269.946	252.891	7.675	−80.123	−25.833	2.999
500	56.707	275.807	254.893	10.457	−80.351	−19.788	2.067
600	60.354	286.481	259.286	16.317	−80.606	−7.648	0.666
700	63.260	296.011	263.864	22.503	−80.665	4.519	−0.337
800	65.628	304.618	268.429	28.951	−80.585	16.683	−1.089
900	67.601	312.465	272.892	35.615	−80.402	28.832	−1.673
1000	69.275	319.676	277.215	42.461	−80.139	40.956	−2.139
1100	70.713	326.348	281.382	49.462	−79.816	53.050	−2.519
1200	71.959	332.555	285.391	56.597	−79.443	65.113	−2.834
1300	73.046	338.359	289.245	63.849	−79.032	77.143	−3.100
1400	73.998	343.808	292.949	71.202	−78.591	89.140	−3.326
1500	74.835	348.943	296.513	78.645	−78.128	101.104	−3.521
1600	75.572	353.796	299.943	86.166	−77.649	113.037	−3.690
1700	76.224	358.398	303.247	93.756	−77.160	124.940	−3.839
1800	76.802	362.771	306.433	101.408	−76.665	136.814	−3.970
1900	77.316	366.938	309.509	109.115	−76.170	148.661	−4.087
2000	77.774	370.916	312.481	116.870	−75.676	160.481	−4.191
2100	78.184	374.720	315.355	124.668	−75.189	172.277	−4.285
2200	78.551	378.366	318.136	132.505	−74.709	184.050	−4.370
2300	78.881	381.865	320.832	140.377	−74.240	195.801	−4.447
2400	79.179	385.229	323.445	148.280	−73.783	207.532	−4.517
2500	79.448	388.466	325.982	156.212	−73.340	219.244	−4.581
2600	79.692	391.587	328.445	164.169	−72.911	230.939	−4.640
2700	79.913	394.599	330.840	172.149	−72.498	242.618	−4.694
2800	80.115	397.509	333.169	180.151	−72.101	254.282	−4.744
2900	80.298	400.324	335.437	188.172	−71.720	265.931	−4.790
3000	80.467	403.049	337.645	196.210	−71.358	277.568	−4.833
3100	80.621	405.690	339.798	204.264	−71.012	289.194	−4.873
3200	80.763	408.252	341.897	212.334	−70.684	300.807	−4.910
3300	80.893	410.739	343.946	220.417	−70.373	312.411	−4.945
3400	81.013	413.156	345.946	228.512	−70.080	324.007	−4.978
3500	81.124	415.506	347.900	236.619	−69.804	335.593	−5.008
3600	81.227	417.792	349.810	244.737	−69.545	347.172	−5.037
3700	81.323	420.019	351.678	252.864	−69.304	358.744	−5.065
3800	81.411	422.189	353.505	261.001	−69.080	370.311	−5.090
3900	81.494	424.305	355.293	269.146	−68.873	381.871	−5.115
4000	81.570	426.369	357.044	277.299	−68.683	393.426	−5.138
4100	81.642	428.384	358.760	285.460	−68.509	404.976	−5.159
4200	81.709	430.352	360.441	293.628	−68.353	416.523	−5.180
4300	81.772	432.276	362.089	301.802	−68.214	428.066	−5.200
4400	81.830	434.156	363.706	309.982	−68.092	439.606	−5.219
4500	81.885	435.996	365.292	318.168	−67.986	451.143	−5.237
4600	81.937	437.796	366.849	326.359	−67.898	462.677	−5.254
4700	81.986	439.559	368.377	334.555	−67.828	474.211	−5.270
4800	82.032	441.286	369.878	342.756	−67.775	485.744	−5.286
4900	82.075	442.977	371.353	350.961	−67.740	497.275	−5.301
5000	82.115	444.636	372.802	359.171	−67.724	508.806	−5.315
5100	82.154	446.262	374.226	367.384	−67.727	520.337	−5.329
5200	82.190	447.858	375.627	375.602	−67.748	531.867	−5.343
5300	82.225	449.424	377.005	383.822	−67.789	543.399	−5.356
5400	82.257	450.961	378.360	392.046	−67.851	554.931	−5.368
5500	82.288	452.471	379.694	400.274	−67.933	566.464	−5.380
5600	82.318	453.954	381.007	408.504	−68.037	578.001	−5.391
5700	82.346	455.411	382.299	416.737	−68.162	589.538	−5.403
5800	82.372	456.843	383.572	424.973	−68.311	601.078	−5.413
5900	82.397	458.252	384.826	433.212	−68.482	612.619	−5.424
6000	82.421	459.637	386.061	441.453	−68.679	624.166	−5.434

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 266.400\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -124.492 \pm 0.42\ kJ·mol^{-}$
$\Delta_f H°(298.15\ K) = -134.306 \pm 0.42\ kJ·mol^{-}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
1320(1)	765(1)
886(1)	3560(1)
680(1)	1335(1)
1710(1)	465(1)
583(1)	

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: O–N = 1.206 ± 0.005 N–O' = 1.405 ± 0.005 O–H = [0.96]
Bond Angles: O–N–O = 130° ± 20' N–O' H = 102° ± 30'
Product of the Moments of Inertia: $I_A I_B I_C = 5.988123 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was taken from.[1] Equilibria involving HNO_3 were measured by Jones,[2] Feick,[3] and Abel, *et al.*,[4] yielding $\Delta_f H° = -32.06$, -32.02, and $-32.09\ kcal·mol^{-}$, respectively. Becker and Roth[5] and Thomsen[6] measured the enthalpy of neutralization of HNO_3(aq) with NH_3, combining these values with the data for NH_4NO_3 yields $\Delta_f H° = -32.27$ and $-32.07\ kcal·mol^{-1}$. Berthelot[7] measured the enthalpy of reaction of N_2O_4(g) and Cl_2(g), obtaining $\Delta_f H° = -32.10\ kcal·mol^{-1}$. The value of $\Delta_f H°(298.15\ K)$ reported by Forsythe and Giauque[8] was $-31.994\ kcal·mol^{-1}$. The value adopted is the weighted average of these six values.

Heat Capacity and Entropy

Vibrational frequencies were obtained from Palm and Kilpatrick.[9] Bond distances and bond angles were taken from Millen and Morton.[10] The basic parameters of HNO_3(g) reported by Akishin *et al.*[1] were: r(N=O) = 1.22 ± 0.01 ; r(N–O) = 1.40 ± 0.01 A; and the bond angle (O–N–O) = 135° ± 2.5°. Forsythe and Giauque[8] have calculated the absolute entropy of pure nitric acid (g) from calorimetric data. The value obtained was $S°(298.15\ K) = 63.62\ cal·K^{-1}·mol^{-1}$. The entropy of nitric acid vapor at 298.15 K has also been computed by Cohn *et al.*[9] to be $63.70\ cal·K^{-1}·mol^{-1}$. The prinicpal moments of inertia are: $I_A = 6.3868 \times 10^{-39}$, $I_B = 7.0025 \times 10^{-39}$, and $I_C = 13.3893 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.780	−124.492	−124.492	INFINITE
100	33.920	221.800	306.248	−8.445	−128.465	−111.622	58.305
200	42.298	247.433	270.926	−4.699	−131.888	−93.389	24.391
250	48.008	257.484	267.248	−2.441	−133.243	−83.602	17.468
298.15	53.336	266.400	266.400	0.	−134.306	−73.941	12.954
300	53.534	266.730	266.401	0.099	−134.343	−73.567	12.809
350	58.618	275.371	267.072	2.905	−135.205	−63.366	9.457
400	63.190	283.502	268.622	5.952	−135.858	−53.057	6.928
450	67.252	291.185	270.706	9.215	−136.333	−42.676	4.954
500	70.836	298.460	273.121	12.669	−136.660	−32.251	3.369
600	76.765	311.922	278.485	20.062	−136.963	−11.334	0.987
700	81.382	324.116	284.147	27.979	−136.918	9.605	−0.717
800	85.039	335.231	289.848	36.306	−136.627	30.519	−1.993
900	87.994	345.424	295.465	44.963	−136.154	51.386	−2.982
1000	90.425	354.824	300.937	53.888	−135.544	72.192	−3.771
1100	92.455	363.541	306.237	63.035	−134.829	92.932	−4.413
1200	94.172	371.661	311.354	72.368	−134.032	113.603	−4.945
1300	95.636	379.258	316.289	81.861	−133.172	134.204	−5.392
1400	96.895	386.393	321.044	91.489	−132.263	154.738	−5.773
1500	97.984	393.116	325.627	101.234	−131.318	175.205	−6.101
1600	98.931	399.471	330.045	111.081	−130.347	195.608	−6.386
1700	99.758	405.494	334.308	121.016	−129.358	215.950	−6.635
1800	100.485	411.217	338.423	131.029	−128.361	236.233	−6.855
1900	101.125	416.667	342.399	141.110	−127.360	256.461	−7.051
2000	101.692	421.869	346.243	151.252	−126.362	276.637	−7.225
2100	102.196	426.843	349.964	161.447	−125.370	296.762	−7.382
2200	102.645	431.608	353.567	171.689	−124.389	316.842	−7.523
2300	103.047	436.179	357.060	181.974	−123.423	336.875	−7.651
2400	103.407	440.573	360.449	192.297	−122.472	356.867	−7.767
2500	103.732	444.801	363.739	202.654	−121.541	376.821	−7.873
2600	104.025	448.875	366.936	213.042	−120.629	396.737	−7.971
2700	104.291	452.806	370.044	223.458	−119.739	416.619	−8.060
2800	104.532	456.603	373.068	233.900	−118.871	436.469	−8.142
2900	104.751	460.275	376.012	244.364	−118.026	456.286	−8.219
3000	104.952	463.830	378.880	254.849	−117.205	476.076	−8.289
3100	105.135	467.274	381.676	265.354	−116.407	495.840	−8.355
3200	105.303	470.615	384.404	275.876	−115.633	515.576	−8.416
3300	105.457	473.858	387.066	286.414	−114.882	535.290	−8.473
3400	105.599	477.008	389.665	296.967	−114.155	554.982	−8.526
3500	105.731	480.071	392.204	307.534	−113.452	574.651	−8.576
3600	105.852	483.051	394.687	318.113	−112.771	594.302	−8.623
3700	105.964	485.953	397.114	328.704	−112.114	613.933	−8.667
3800	106.069	488.780	399.489	339.305	−111.479	633.549	−8.709
3900	106.165	491.537	401.814	349.917	−110.866	653.147	−8.748
4000	106.256	494.226	404.091	360.538	−110.276	672.729	−8.785
4100	106.340	496.851	406.322	371.168	−109.708	692.297	−8.820
4200	106.418	499.414	408.508	381.806	−109.162	711.851	−8.853
4300	106.492	501.919	410.651	392.451	−108.638	731.394	−8.885
4400	106.560	504.368	412.753	403.104	−108.136	750.923	−8.915
4500	106.625	506.763	414.816	413.763	−107.657	770.441	−8.943
4600	106.685	509.108	416.840	424.429	−107.199	789.948	−8.970
4700	106.742	511.403	418.828	435.100	−106.765	809.447	−8.996
4800	106.796	513.650	420.780	445.777	−106.354	828.937	−9.021
4900	106.846	515.853	422.698	456.459	−105.966	848.419	−9.044
5000	106.894	518.012	424.583	467.146	−105.603	867.893	−9.067
5100	106.938	520.129	426.436	477.838	−105.264	887.360	−9.088
5200	106.981	522.206	428.257	488.534	−104.951	906.818	−9.109
5300	107.021	524.244	430.049	499.234	−104.665	926.274	−9.129
5400	107.059	526.245	431.812	509.938	−104.406	945.722	−9.148
5500	107.095	528.210	433.547	520.646	−104.174	965.166	−9.166
5600	107.129	530.140	435.255	531.357	−103.973	984.608	−9.184
5700	107.162	532.036	436.936	542.072	−103.801	1004.045	−9.201
5800	107.193	533.900	438.592	552.789	−103.662	1023.481	−9.217
5900	107.222	535.733	440.223	563.510	−103.555	1042.911	−9.233
6000	107.250	537.535	441.830	574.234	−103.482	1062.343	−9.249

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 40.016\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -52.021 \pm 0.08\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -56.442 \pm 0.08\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was obtained from Gunn and Green.[1] The value of $\Delta_f H°(298.15\ K)$ reported by Messer *et al.*[2] was $13.60 \pm 0.27\ kcal·mol^{-1}$ which is in excellent agreement with the value given by Gunn and Green.[1] The results of the previous investigations were also reviewed by Messer, *et al.*[2]

Heat Capacity and Entropy

$C_p°$ below 350 K were measured by Westrum, *et al.*[3] $C_p°$ above 350 K were estimated by comparison with those for LiH(cr). $C_p°$ (59.94–91.84 K) were also measured by Sayre and Beaver.[4] $S°(T)$ at 100, 200, and 298.15 K were taken from Westrum *et al.*[3] using the extrapolated value $S°(10\ K) = 0.008\ cal·K^{-1}·mol^{-1}$.

Decomposition Data

T_{dcm} was estimated from the value of $\Delta_f G°$ in the table. The table of T_{dcm} given by Banus *et al.*[5] was 940 K. It was assumed that NaH would behave similarly to LiH and that decomposition pressures would be purity dependent, and this would produce apparently high decomposition temperatures.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.259	−52.021	−52.021	INFINITE
100	17.497	11.560	66.580	−5.502	−54.103	−47.841	24.990
200	28.234	27.125	43.108	−3.197	−55.600	−40.945	10.694
298.15	36.392	40.016	40.016	0.	−56.442	−33.551	5.878
300	36.535	40.241	40.016	0.067	−56.454	−33.408	5.817
400	42.468	51.636	41.530	4.043	−59.553	−25.444	3.323
500	47.154	61.637	44.571	8.533	−59.625	−16.897	1.765
600	50.710	70.557	48.172	13.431	−59.208	−8.384	0.730
700	53.723	78.609	51.955	18.658	−58.402	0.028	−0.002
800	56.066	85.940	55.751	24.151	−57.294	8.303	−0.542
900	57.948	92.657	59.484	29.855	−55.965	16.425	−0.953
1000	59.413	98.840	63.115	35.725	−54.484	24.390	−1.274
1100	60.668	104.563	66.626	41.731	−52.906	32.201	−1.529
1200	61.641	109.885	70.012	47.848	−148.038	42.307	−1.842
1300	62.425	114.851	73.272	54.053	−145.472	58.065	−2.333
1400	63.021	119.501	76.410	60.327	−142.859	73.624	−2.747
1500	63.429	123.864	79.430	66.651	−140.218	88.995	−3.099

PREVIOUS: CURRENT: March 1963

$S°(298.15\ K) = 188.387\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 126.21 \pm 19.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 124.26 \pm 19.2\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 1172.2\ cm^{-1}$ $\omega_e x_e = 19.72\ cm^{-1}$ $\alpha = 1$
$B_e = 4.9012\ cm^{-1}$ $\alpha_e = 0.1353\ cm^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $D_0^0 = 2.05 \pm 0.2$ eV reported by Gaydon.[1]

Heat Capacity and Entropy

All molecular and spectroscopic constants were obtained from Herzberg.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.731	126.214	126.214	INFINITE
100	29.136	156.294	214.684	−5.839	126.267	118.055	−61.666
200	29.333	176.522	191.121	−2.920	125.384	110.160	−28.771
250	29.724	183.105	188.882	−1.444	124.836	106.416	−22.234
298.15	30.293	188.387	188.387	0.	124.265	102.919	−18.031
300	30.318	188.575	188.388	0.056	124.242	102.787	−17.897
350	31.023	193.300	188.759	1.589	123.598	99.261	−14.814
400	31.753	197.490	189.594	3.159	120.270	96.037	−12.541
450	32.453	201.271	190.684	4.764	119.583	93.050	−10.801
500	33.098	204.725	191.918	6.403	118.952	90.136	−9.416
600	34.191	210.860	194.577	9.770	117.838	84.481	−7.355
700	35.047	216.197	197.292	13.233	116.880	78.999	−5.895
800	35.716	220.923	199.956	16.773	116.035	73.646	−4.809
900	36.249	225.161	202.525	20.372	115.259	68.395	−3.970
1000	36.681	229.003	204.984	24.019	114.517	63.227	−3.303
1100	37.039	232.517	207.330	27.706	113.776	58.134	−2.761
1200	37.344	235.753	209.565	31.425	16.246	55.549	−2.418
1300	37.608	238.753	211.696	35.173	16.355	58.820	−2.363
1400	37.840	241.549	213.730	38.946	16.467	62.083	−2.316
1500	38.049	244.166	215.673	42.741	16.579	65.337	−2.275
1600	38.239	246.628	217.531	46.555	16.689	68.584	−2.239
1700	38.414	248.952	219.312	50.388	16.796	71.824	−2.207
1800	38.577	251.152	221.020	54.237	16.900	75.058	−2.178
1900	38.730	253.242	222.662	58.103	16.999	78.286	−2.152
2000	38.876	255.232	224.241	61.983	17.094	81.510	−2.129
2100	39.015	257.132	225.762	65.878	17.185	84.728	−2.107
2200	39.148	258.950	227.230	69.786	17.272	87.942	−2.088
2300	39.277	260.694	228.647	73.707	17.353	91.153	−2.070
2400	39.402	262.368	230.017	77.641	17.430	94.360	−2.054
2500	39.524	263.979	231.344	81.588	17.500	97.564	−2.038
2600	39.644	265.531	232.629	85.546	17.565	100.765	−2.024
2700	39.760	267.030	233.876	89.516	17.623	103.964	−2.011
2800	39.875	268.478	235.086	93.498	17.674	107.161	−1.999
2900	39.988	269.879	236.261	97.491	17.715	110.356	−1.988
3000	40.099	271.237	237.405	101.496	17.747	113.550	−1.977
3100	40.209	272.553	238.517	105.511	17.768	116.743	−1.967
3200	40.318	273.831	239.601	109.537	17.777	119.935	−1.958
3300	40.426	275.074	240.657	113.575	17.772	123.128	−1.949
3400	40.533	276.282	241.687	117.623	17.752	126.321	−1.941
3500	40.639	277.459	242.693	121.681	17.715	129.514	−1.933
3600	40.744	278.605	243.674	125.750	17.658	132.709	−1.926
3700	40.848	279.723	244.634	129.830	17.581	135.906	−1.919
3800	40.952	280.814	245.571	133.920	17.481	139.106	−1.912
3900	41.056	281.879	246.489	138.020	17.355	142.308	−1.906
4000	41.158	282.919	247.387	142.131	17.202	145.513	−1.900
4100	41.261	283.937	248.266	146.252	17.019	148.724	−1.895
4200	41.363	284.932	249.127	150.383	16.805	151.938	−1.890
4300	41.464	285.907	249.971	154.525	16.555	155.159	−1.885
4400	41.566	286.861	250.799	158.676	16.309	158.382	−1.880
4500	41.667	287.797	251.610	162.838	16.003	161.613	−1.876
4600	41.768	288.713	252.407	167.009	15.649	164.853	−1.872
4700	41.868	289.613	253.189	171.191	15.253	168.101	−1.868
4800	41.968	290.495	253.957	175.383	14.811	171.357	−1.865
4900	42.068	291.362	254.712	179.585	14.322	174.624	−1.862
5000	42.168	292.213	255.453	183.797	13.791	177.900	−1.859
5100	42.268	293.049	256.182	188.018	13.201	181.188	−1.856
5200	42.367	293.870	256.899	192.250	12.556	184.488	−1.853
5300	42.466	294.678	257.604	196.492	11.854	187.801	−1.851
5400	42.566	295.473	258.298	200.743	11.093	191.128	−1.849
5500	42.665	296.255	258.981	205.005	10.271	194.469	−1.847
5600	42.764	297.025	259.654	209.276	9.385	197.826	−1.845
5700	42.862	297.782	260.316	213.558	8.434	201.199	−1.844
5800	42.961	298.529	260.968	217.849	7.416	204.590	−1.843
5900	43.060	299.264	261.611	222.150	6.328	207.999	−1.841
6000	43.158	299.988	262.245	226.461	5.329	211.408	−1.840

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 64.445 \pm 0.84\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 572\ K$
$T_{fus} = 596\ K$

$\Delta_f H°(0\ K) = -421.40 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -425.93 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 7.196 \pm 0.84\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 6.611 \pm 0.84\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of NaOH(cr) is obtained from its enthalpy of solution in water, the enthalpy of hydrolysis of metallic sodium, and appropriate auxiliary data.

Reshetnikov[1] determined calorimetrically the enthalpy of solution of NaOH in aq, 400 H_2O as -10.445 ± 0.015 kcal·mol^{-1}. Combining this result with enthalpy of dilution data for aqueous sodium hydroxide solutions tabulated by Parker[2] we derive $\Delta_{sln}H°$(NaOH, cr) = -10.56 ± 0.02 kcal·mol^{-1}. Murch and Giauque[3] measured the heats of solution in water of a series of solids which contained various amounts of water in the range NaOH·(0.1 to 1) H_2O. Their data indicated a linear relationship between the heat of solution and the ratio of the moles of water to the moles of sodium hydroxide. Upon extrapolation their data gave $\Delta_{sln}H°$(NaOH, cr) = -10.637 ± 0.010 kcal·mol^{-1}.[2] This latter value is adopted here, since the extrapolation to zero moles of water tends to eliminate its effect on the heat of solution.

The enthalpy of hydrolysis of metallic sodium has been determined by various investigators.[4–6] For the reaction Na(cr) + (n+1)H_2O → NaOH·n H_2O + 0.5 H_2(g) data are summarized below.

Source	n moles of H_2O	$\Delta_h H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(NaOH·aq, ∞)* kcal·mol^{-1}	$\Delta_f H°$(NaOH, cr, 298.15 K) kcal·mol^{-1}
Gunn and Green[4a,4b]	∞	−44.124 ± 0.015	−112.439	−101.80
Messer *et al.*[5]	∞	−44.22 ± 0.20	−112.53	−101.88
Ketchen and Wallace[6]	∞	−44.05 ± 0.20	−112.37	−101.72

*Based on $\Delta_f H°(H_2O, l, 298.15\ K) = 68.315$ kcal·mol^{-1}.[7]

Combination of the $\Delta_f H°$(NaOH·aq,∞, 298.15 K) values with the enthalpy of solution of NaOH(cr) at infinite dilution given above, results in the $\Delta_f H°$(NaOH, cr, 298.15 K) values given in the last column. The value determined from the work of Gunn and Green[4] is adopted.

Earlier determinations of $\Delta_f H°$(NaOH, cr, 298.15 K) have been summarized by Bichowsky and Rossini[8] and are not listed here.

Heat Capacity and Entropy

Murch and Giauque[3] determined low temperature heat capacities for NaOH·O.04014 H_2O and NaOH·0.97776 H_2O from 15 to 320 K. From these data heat capacities for anhydrous NaOH(cr) were calculated and joined smoothly at 298.15 K with the high temperature (273–973 K) enthalpy data of Douglas and Dever.[9] These smoothed heat capacities given by Murch and Giauque are adopted. Low temperature heat capacity data for NaOH(cr) in the temperature range 60 to 300 K have also been reported by Kelley and Snyder.[10] The deviations of their data from the adopted values range from a few tenths of a percent (150–300 K) to up to about 30% at the lowest temperatures investigated (60 K). Popov and Ginzburg[11] also determined high temperture enthalpy data (293–1016 K) for NaOH by drop calorimetry. Their reported value $H°(500\ K) - H°(298.15\ K) = 3.112$ kcal·mol^{-1} [11] is in very good agreement with the tabulated value of 3.176 kcal·mol^{-1}.

$S°(298.15\ K)$ is based upon the extrapolated value of 0.020 cal·K^{-1}·mol^{-1} at 15 K.

Transition and Fusion Data

The adopted enthalpies of the polymorphic transformation and fusion of NaOH are mean values from the work of Douglas and Dever[9] Popov and Ginzburg[11] and Reshetnikov and Baranskaya.[12] T_{trs} and T_{fus} are from Reshetnikov and Baranskaya.[12]

Sublimation Data

$\Delta_{sub}H°(298.15\ K)$ for the monomer and dimer are calculated from the adopted enthalpies of formation of the crystal and the respective gaseous species.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.487	−421.396	−421.396	INFINITE
100	27.744	15.513	109.879	−9.437	−424.637	−410.105	214.217
200	49.580	42.588	69.615	−5.406	−425.864	−394.953	103.151
298.15	59.530	64.445	64.445	0.	−425.931	−379.741	66.529
300	59.664	64.814	64.447	0.110	−425.927	−379.454	66.069
400	64.936	82.739	66.856	6.353	−428.244	−363.802	47.508
500	75.157	98.172	71.595	13.288	−427.401	−347.767	36.331
572.000	85.887	108.971	75.620	19.077	I <--> II		
572.000	86.023	121.574	75.620	26.286	TRANSITION		
596.000	86.023	125.110	77.542	28.350	----- II <--> LIQUID -----		
600	86.023	125.685	77.861	28.694	−418.055	−332.373	28.936
700	86.023	138.946	85.665	37.297	−415.502	−318.294	23.751
800	86.023	150.433	93.059	45.899	−412.953	−304.581	19.887
900	86.023	160.565	100.008	54.501	−410.428	−291.187	16.900
1000	86.023	169.628	106.525	63.104	−407.946	−278.071	14.525
1100	86.023	177.827	112.640	71.706	−405.526	−265.202	12.593
1200	86.023	185.312	118.388	80.308	−499.948	−250.109	10.887
1300	86.023	192.198	123.805	88.911	−496.776	−229.418	9.218
1400	86.023	198.573	128.921	97.513	−493.641	−208.970	7.797
1500	86.023	204.508	133.764	106.115	−490.542	−188.745	6.573

PREVIOUS: March 1966 CURRENT: December 1970

$S°(298.15\ K) = [75.891]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-416.878]\ kJ·mol^{-1}$

$T_{fus} = 596\ K$ $\Delta_{fus}H° = 6.611 \pm 0.84\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(NaOH, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(596 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacities for NaOH(l) in the temperature range 596 to 1000 K are from the enthalpy measurements of Douglas and Dever.[1] The heat capacities below the melting point and above 1000 K are extrapolated from the experimental heat capacity curve. Powers and Blalock[2] reported $C_p°$(l) = 19.6 $cal·K^{-1}·mol^{-1}$ from enthalpy measurements, in a short temperature range, by drop calorimetry. The smoothed enthalpy data for NaOH(l) reported by Popov and Ginzburg[3a,3b] are from 0.2 to 0.5 $kcal·mol^{-1}$ less than the adopted values in the temperature range 700 to 1000 K.

$S°$(298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 1830 K (for monomer) is calculated as the temperature at which the fugacity of NaOH(g) is 1 atm for the process NaOH(l) = NaOH(g). The difference in the enthalpies of formation of NaOH(l) and NaOH(g) at the T_{vap} is the enthalpy of vaporization, $\Delta_{vap}H° = 175.310\ kJ·mol^{-1}$.

Wartenberg and Albrecht[4] reported a boiling point of 1661 K from their static vapor pressure data. However, these workers observed the presence of water after each experiment which may indicate some decomposition of the sample. See the ideal gas table for further discussion.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	87.822	75.891	75.891	0.	−416.878	−374.100	65.541
300	87.814	76.434	75.892	0.162	−416.821	−373.835	65.090
400	87.211	101.613	79.329	8.913	−416.631	−359.738	46.977
500	86.651	121.013	85.800	17.606	−414.030	−345.816	36.127
596.000	86.111	136.202	92.791	25.873	----- II <--> LIQUID -----		
600	86.065	136.778	93.024	26.252	−411.445	−332.417	28.939
700	85.479	150.001	100.245	34.829	−408.916	−319.446	23.837
800	84.893	161.377	107.192	43.348	−406.451	−306.834	20.034
900	84.308	171.342	113.777	51.808	−404.068	−294.526	17.094
1000	83.722	180.194	119.985	60.209	−401.787	−282.478	14.755
1100	83.136	188.146	125.826	68.552	−399.626	−270.653	12.852
1200	82.550	195.355	131.324	76.837	−494.366	−256.579	11.169
1300	81.965	201.939	136.507	85.062	−491.571	−236.877	9.518
1400	81.379	207.992	141.400	93.230	−488.871	−217.387	8.111
1500	80.793	213.587	146.028	101.338	−486.266	−198.087	6.898
1600	80.207	218.782	150.415	109.388	−483.754	−178.957	5.842
1700	79.622	223.627	154.580	117.379	−481.334	−159.982	4.916
1800	79.119	228.164	158.544	125.316	−479.001	−141.147	4.096
1900	78.638	232.428	162.321	133.203	−476.749	−122.439	3.366
2000	78.199	236.450	165.928	141.045	−474.574	−103.848	2.712
2100	77.801	240.256	169.378	148.844	−472.471	−85.363	2.123
2200	77.467	243.867	172.682	156.607	−470.434	−66.977	1.590
2300	77.182	247.304	175.853	164.339	−468.457	−48.683	1.106
2400	76.956	250.584	178.899	172.046	−466.535	−30.474	0.663
2500	76.760	253.722	181.829	179.731	−464.662	−12.343	0.258

PREVIOUS: March 1966 CURRENT: December 1970

0	to	572	K crystal, alpha
572	to	596	K crystal, beta
above		596	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.487	−421.396	−421.396	INFINITE
100	27.744	15.513	109.879	−9.437	−424.637	−410.105	214.217
200	49.580	42.588	69.615	−5.406	−425.864	−394.953	103.151
298.15	59.530	64.445	64.445	0.	−425.931	−379.741	66.529
300	59.664	64.814	64.447	0.110	−425.927	−379.454	66.069
400	64.936	82.739	66.856	6.353	−428.244	−363.802	47.508
500	75.157	98.172	71.595	13.288	−427.401	−347.767	36.331
572.000	85.887	108.971	75.620	19.077	I <-> II TRANSITION		
572.000	86.023	121.574	75.620	26.286			
596.000	86.023	125.110	77.542	28.350	II <-> LIQUID TRANSITION		
596.000	86.111	136.202	77.542	34.961			
600	86.065	136.778	77.935	35.305	−411.445	−332.417	28.939
700	85.479	150.001	87.311	43.883	−408.916	−319.446	23.837
800	84.893	161.377	95.875	52.401	−406.451	−306.834	20.034
900	84.308	171.342	103.718	60.861	−404.068	−294.526	17.094
1000	83.722	180.194	110.931	69.263	−401.787	−282.478	14.755
1100	83.136	188.146	117.596	77.606	−399.626	−270.653	12.852
1200	82.550	195.355	123.780	85.890	−494.366	−256.579	11.169
1300	81.965	201.939	129.543	94.116	−491.571	−236.877	9.518
1400	81.379	207.992	134.933	102.283	−488.871	−217.387	8.111
1500	80.793	213.587	139.992	110.392	−486.266	−198.087	6.898
1600	80.207	218.782	144.756	118.442	−483.754	−178.957	5.842
1700	79.622	223.627	149.255	126.432	−481.334	−159.982	4.916
1800	79.119	228.164	153.514	134.369	−479.001	−141.147	4.096
1900	78.638	232.428	157.556	142.257	−476.749	−122.439	3.366
2000	78.199	236.450	161.401	150.098	−474.574	−103.848	2.712
2100	77.801	240.256	165.067	157.898	−472.471	−85.363	2.123
2200	77.467	243.867	168.567	165.661	−470.434	−66.977	1.590
2300	77.182	247.304	171.916	173.393	−468.457	−48.683	1.106
2400	76.956	250.584	175.126	181.099	−466.535	−30.474	0.663
2500	76.760	253.722	178.208	188.785	−464.662	−12.343	0.258

PREVIOUS: CURRENT: December 1970

$S°(298.15\ K) = 228.443 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -194.12 \pm 12.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -197.76 \pm 12.6\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
431 (1)
337 (2)
[3650] (1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distance: Na–O = [1.93] Å; O–H = [0.97] Å
Bond Angle: Na–O–H = 180°
Rotational Constant: $B_0 = 0.426703\ cm^{-1}$

Enthalpy of Formation

The bond dissociation energies of the alkali metal hydroxides have been the subject of a number of investigations[1–4] in recent years. The majority of this work has involved equilibrium studies on the reaction A(g) + H_2O(g) = AOH(g) + H(g), where A is an alkali metal, in hydrogen oxygen nitrogen flames containing water. In the case of NaOH, data are summarized below:

Source	Method	Reaction*	Data Points	T/K	$\Delta_r H°$(298.15 K),kcal·mol^{-1} 3rd law	$D°$(Na–OH, 0 K) kcal·mol^{-1}
Jensen and Padley[2a]	Flames	A	1	2475	40.5	77.9
Cotton and Jenkins[4]	Flames	A	1	2030	36.6	81.8

*(A) Na(g) + H_2O(g) = NaOH(g) + H(g)

We note that Cotton and Jenkins[4] in the same paper reported bond dissociation energies for LiOH(g) and KOH(g) which are in reasonable agreement with JANAF values[5] for the enthalpy of formation of these two compounds. Furthermore, bond dissociation data for the alkali metal halides[6] clearly establish the sodium compound as the least stable within each halide series. The potassium and sodium compounds differ by from 4.3 kcal·mol^{-1} for the fluorides and bromides to 3.6 kcal·mol^{-1} for the chlorides. It seems most likely that this same trend in the bond dissociation energies would apply to the hydroxides as well. Based upon these correlations, we adopt $D_0°$(Na–OH) = 81.5 ± 3.0 kcal·mol^{-1} with $D_0°$(K–OH)–$D_0°$(Na–OH) = 3.9 kcal·mol^{-1}. This value corresponds to $\Delta_f H°$(NaOH, g, 298.15 K) = −47.3 ± 3.0 kcal·mol^{-1}.

Wartenberg and Albrecht[7] determined vapor pressures for NaOH(l) in the temperature range 1283–1681 K by a static method. In order to evaluate $\Delta_{vap}H°$(NaOH, l, 298.15 K), we have used a trial and error variation of $\Delta_{vap}H°$(298.15 K) for the monomer and dimer, such that these values are in accordance with the adopted enthalpy of dimerization (refer to the $Na_2(OH)_2$(g) table), and the sum of the calculated partial pressures for NaOH(g) and $Na_2(OH)_2$(g) in good agreement with the experimental vapor pressure data. The resulting values are: $\Delta_{vap}H°$(to monomer) = 48.25 kcal·mol^{-1} and $\Delta_{vap}H°$(to dimer) = 48.8 kcal·mol^{-1}. From the enthalpy of vaporization of the monomer, we derive $\Delta_f H°$(NaOH, g, 298.15 K) = −51.4 kcal·mol^{-1}. This value corresponds to a bond dissociation energy for NaOH(g) that is slightly greater than the adopted value for KOH(g),[5] and thus not in line with the established trends in $D_0°$ discussed above. Buchler and Berkowitz Mattuck[8] in their review on gaseous ternary compounds of the alkali metals point to the decomposition of NaOH in the condensed phase with a resulting change in composition as the major problem in the interpretation of thermodynamic measurements on this system. Until the nature of the condensed phase and the relationship between the vapor and condensed phase composition for NaOH(l) are established, an accurate enthalpy of vaporization will remain undetermined.

Heat Capacity and Entropy

The infrared spectra of matrix isolated NaOH and NaOD have been recently observed by Acquista and Abramowitz.[9] The alkali–metal–oxygen stretching frequency, ν_1, and the bending mode, ν_2, for NaOH were assigned as 431 and 337 cm^{-1}, respectively, by these workers. The isotope shift of ν_2 was consistent with a linear structure for NaOH having bond lengths of 1.93 and 0.97 Å for the Na–O and O–H bonds. We have adopted a linear configuration for NaOH with the bond lengths and frequencies given above. Spinar and Margrave[10] assigned ν_1 as 437 ± 10 cm^{-1} for NaOH which is in good agreement with the adopted value. The O–H stretching frequency, ν_3, was estimated by Jensen.[2b]

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Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.385	−194.119	−194.119	INFINITE
100	32.864	183.702	267.723	−8.402	−195.428	−197.715	103.276
200	43.462	210.040	232.739	−4.540	−196.824	−199.403	52.079
250	46.468	220.085	229.230	−2.286	−197.322	−199.989	41.785
298.15	48.371	228.443	228.443	0.	−197.757	−200.463	35.120
300	48.431	228.743	228.444	0.090	−197.773	−200.479	34.907
350	49.750	236.314	229.039	2.546	−198.232	−200.895	29.982
400	50.669	243.021	230.376	5.058	−201.365	−201.036	26.253
450	51.334	249.029	232.120	7.609	−201.866	−200.964	23.327
500	51.836	254.465	234.087	10.189	−202.326	−200.839	20.981
600	52.566	263.984	238.299	15.411	−203.165	−200.461	17.452
700	53.130	272.131	242.564	20.696	−203.928	−199.949	14.920
800	53.646	279.259	246.715	26.035	−204.642	−199.332	13.015
900	54.158	285.607	250.690	31.426	−205.329	−198.626	11.528
1000	54.674	291.340	254.473	36.867	−206.008	−197.845	10.334
1100	55.188	296.575	258.066	42.360	−206.697	−196.996	9.355
1200	55.690	301.399	261.478	47.904	−304.177	−193.642	8.429
1300	56.171	305.875	264.723	53.498	−304.014	−184.438	7.411
1400	56.626	310.055	267.814	59.138	−303.842	−175.246	6.539
1500	57.051	313.976	270.762	64.822	−303.661	−166.067	5.783
1600	57.444	317.671	273.579	70.547	−303.474	−156.900	5.122
1700	57.806	321.165	276.277	76.310	−303.282	−147.745	4.540
1800	58.138	324.478	278.863	82.107	−303.089	−138.601	4.022
1900	58.441	327.630	281.348	87.936	−302.895	−129.468	3.559
2000	58.718	330.635	283.738	93.795	−302.703	−120.346	3.143
2100	58.971	333.506	286.040	99.679	−302.515	−111.232	2.767
2200	59.201	336.255	288.260	105.588	−302.332	−102.128	2.425
2300	59.411	338.891	290.405	111.519	−302.157	−93.032	2.113
2400	59.603	341.424	292.478	117.470	−301.990	−83.943	1.827
2500	59.779	343.860	294.485	123.439	−301.834	−74.861	1.564
2600	59.939	346.208	296.429	129.425	−301.689	−65.785	1.322
2700	60.086	348.473	298.315	135.426	−301.559	−56.714	1.097
2800	60.221	350.661	300.146	141.442	−301.444	−47.648	0.889
2900	60.345	352.776	301.924	147.470	−301.346	−38.586	0.695
3000	60.459	354.824	303.654	153.510	−301.266	−29.526	0.514
3100	60.564	356.808	305.336	159.561	−301.207	−20.469	0.345
3200	60.661	358.732	306.975	165.623	−301.171	−11.414	0.186
3300	60.751	360.600	308.572	171.693	−301.157	−2.360	0.037
3400	60.834	362.415	310.129	177.773	−301.170	6.695	−0.103
3500	60.911	364.180	311.648	183.860	−301.211	15.750	−0.235
3600	60.983	365.897	313.131	189.955	−301.281	24.807	−0.360
3700	61.049	367.568	314.580	196.056	−301.383	33.867	−0.478
3800	61.111	369.197	315.996	202.164	−301.520	42.930	−0.590
3900	61.169	370.785	317.381	208.278	−301.693	51.996	−0.696
4000	61.223	372.335	318.735	214.398	−301.905	61.068	−0.797
4100	61.274	373.847	320.061	220.523	−302.159	70.145	−0.894
4200	61.321	375.324	321.359	226.653	−302.454	79.229	−0.985
4300	61.365	376.768	322.631	232.787	−302.798	88.321	−1.073
4400	61.407	378.179	323.878	238.926	−303.150	97.417	−1.156
4500	61.446	379.559	325.100	245.068	−303.574	106.525	−1.237
4600	61.483	380.910	326.298	251.215	−304.058	115.643	−1.313
4700	61.518	382.233	327.475	257.365	−304.597	124.773	−1.387
4800	61.550	383.529	328.629	263.518	−305.195	133.915	−1.457
4900	61.581	384.798	329.762	269.675	−305.853	143.070	−1.525
5000	61.610	386.042	330.875	275.834	−306.567	152.238	−1.590
5100	61.638	387.263	331.969	281.997	−307.354	161.422	−1.653
5200	61.664	388.460	333.044	288.162	−308.209	170.622	−1.714
5300	61.689	389.635	334.101	294.330	−309.137	179.839	−1.772
5400	61.712	390.788	335.140	300.500	−310.138	189.074	−1.829
5500	61.735	391.921	336.162	306.672	−311.217	198.328	−1.884
5600	61.756	393.033	337.168	312.847	−312.375	207.604	−1.936
5700	61.776	394.126	338.157	319.023	−313.616	216.900	−1.988
5800	61.795	395.201	339.132	325.202	−314.940	226.219	−2.037
5900	61.813	396.257	340.091	331.382	−316.352	235.560	−2.085
6000	61.831	397.296	341.036	337.564	−317.694	244.909	−2.132

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [242.626 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [674.9 \pm 105]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [677.8 \pm 105]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	υ_i, cm^{-1}	g_i
$^2\Pi$	0	4
$^2\Sigma^+$	[32000]	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[400](1)
[300](2)
[3600](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
BondDistances: Na–O = [2.00]Å; 0–H = [1.03] Å
Bond Angle: Na–O–H = [180]°
Rotational Constant: B_0 = [0.396362] cm^{-1}

Enthalpy of Formation

Beckett and Cassidy[1] selected the ionization potential of NaOH as 9.0 ± 1.0 eV (207.6 ± 23 kcal·mol^{-1}). A measured value of roughly 9 eV has been reported by Schoonmaker and Porter.[2] Combining this result with JANAF auxiliary data,[3] we derive $\Delta_f H°(NaOH^+, g, 0\ K) = 161 \pm 25$ kcal·mol^{-1}, which is tentatively adopted.

Heat Capacity and Entropy

$NaOH^+$ has seven valence electrons. According to the correlation diagram of Walsh[4] for HAB type molecules, NaOH+ should be linear with the unpaired electron in a pi orbital. Therefore, we assume the ground state to be $^2\Sigma$. A first excited state is estimated at 32000 cm^{-1} to be $^2\Sigma$ by analogy with the isoelectronic molecules OH[3] and SH.[3] The removal of a bonding electron from NaOH to form $NaOH^+$ should lead to weaker bonding in the positive ion. Consequently, the vibrational frequencies are estimated to be somewhat lower than those for NaOH. Similarly, the Na–O and O–H bond distances are increased slightly over those for NaOH.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.693	674.940		
100	34.226	196.325	283.048	−8.672			
200	44.889	223.761	247.019	−4.652			
250	47.591	234.091	243.429	−2.334			
298.15	49.257	242.626	242.626	0.	677.808	664.619	−116.438
300	49.308	242.931	242.627	0.091	677.832	664.537	−115.706
350	50.443	250.623	243.232	2.587	678.451	662.271	−98.839
400	51.226	257.413	244.589	5.130	676.389	660.126	−86.204
450	51.790	263.481	246.357	7.706	676.953	658.060	−76.386
500	52.216	268.960	248.348	10.306	677.552	655.929	−68.524
600	52.846	278.539	252.604	15.561	678.825	651.486	−56.717
700	53.352	286.724	256.908	20.872	680.165	646.825	−48.267
800	53.836	293.880	261.091	26.231	681.550	641.968	−41.916
900	54.328	300.249	265.095	31.639	682.959	636.935	−36.967
1000	54.832	305.999	268.902	37.097	684.375	631.746	−32.999
1100	55.337	311.249	272.517	42.606	685.780	626.415	−29.746
1200	55.832	316.085	275.949	48.164	590.393	623.397	−27.136
1300	56.307	320.573	279.211	53.771	592.648	626.056	−25.155
1400	56.755	324.763	282.316	59.425	594.913	628.541	−23.451
1500	57.174	328.693	285.279	65.121	597.185	630.863	−21.969
1600	57.561	332.395	288.109	70.858	599.463	633.034	−20.666
1700	57.918	335.896	290.818	76.633	601.744	635.062	−19.513
1800	58.244	339.216	293.415	82.441	604.027	636.956	−18.484
1900	58.541	342.373	295.909	88.280	606.310	638.723	−17.560
2000	58.813	345.383	298.308	94.148	608.590	640.371	−16.725
2100	59.060	348.258	300.619	100.042	610.866	641.904	−15.966
2200	59.286	351.011	302.847	105.960	613.136	643.329	−15.275
2300	59.491	353.651	304.999	111.899	615.399	644.650	−14.640
2400	59.679	356.187	307.080	117.857	617.652	645.873	−14.057
2500	59.850	358.627	309.093	123.834	619.894	647.003	−13.518
2600	60.007	360.977	311.044	129.827	622.124	648.043	−13.019
2700	60.150	363.244	312.935	135.835	624.339	648.998	−12.556
2800	60.282	365.434	314.771	141.856	626.539	649.872	−12.124
2900	60.402	367.552	316.555	147.891	628.722	650.666	−11.720
3000	60.514	369.602	318.289	153.937	630.886	651.386	−11.342
3100	60.616	371.587	319.977	159.993	633.029	652.034	−10.987
3200	60.711	373.513	321.620	166.060	635.149	652.613	−10.653
3300	60.798	375.383	323.221	172.135	637.246	653.126	−10.338
3400	60.880	377.199	324.782	178.219	639.316	653.576	−10.041
3500	60.955	378.965	326.305	184.311	641.359	653.966	−9.760
3600	61.025	380.683	327.792	190.410	643.371	654.297	−9.494
3700	61.091	382.356	329.244	196.516	645.352	654.573	−9.241
3800	61.152	383.986	330.663	202.628	647.298	654.797	−9.001
3900	61.209	385.575	332.051	208.746	649.208	654.970	−8.772
4000	61.263	387.126	333.408	214.870	651.078	655.093	−8.555
4100	61.313	388.639	334.737	220.998	652.907	655.171	−8.347
4200	61.361	390.117	336.038	227.132	654.694	655.204	−8.149
4300	61.406	391.562	337.313	233.270	656.432	655.196	−7.959
4400	61.449	392.974	338.562	239.413	658.163	655.144	−7.778
4500	61.489	394.355	339.786	245.560	659.823	655.055	−7.604
4600	61.528	395.707	340.987	251.711	661.421	654.931	−7.437
4700	61.565	397.031	342.166	257.866	662.965	654.774	−7.277
4800	61.601	398.327	343.322	264.024	664.451	654.584	−7.123
4900	61.635	399.598	344.458	270.186	665.877	654.364	−6.976
5000	61.669	400.843	345.573	276.351	667.247	654.114	−6.833
5100	61.701	402.065	346.669	282.520	668.545	653.838	−6.697
5200	61.732	403.263	347.746	288.691	669.775	653.538	−6.565
5300	61.762	404.439	348.804	294.866	670.933	653.215	−6.438
5400	61.792	405.594	349.845	301.044	672.018	652.870	−6.315
5500	61.821	406.728	350.869	307.224	673.026	652.505	−6.197
5600	61.850	407.842	351.877	313.408	673.955	652.124	−6.083
5700	61.878	408.937	352.868	319.594	674.803	651.727	−5.972
5800	61.906	410.014	353.844	325.784	675.568	651.316	−5.866
5900	61.933	411.072	354.805	331.975	676.246	650.890	−5.763
6000	61.961	412.113	355.752	338.170	676.996	650.438	−5.663

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 183.708 \pm 0.04\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 38.390 \pm 1.21\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 38.987 \pm 1.21\ kJ\cdot mol^{-1}$

	Electronic States and Molecular Constants (σ = 1)						
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0	2	3735.21	82.81	18.871	0.714	0.9706
	139.7	2					
$A^2\Sigma^+$	32403	2	3184.28	97.84	17.355	0.807	1.0121
$B^2\Sigma^+$	68372	2	940	105	5.54	0.65	1.80
$C^2\Sigma^+$	89420	2	2339	32	4.20	0.16	2.16

Enthalpy of Formation

$\Delta_f H°$(OH, g, 0 K) is calculated from the relation $\Delta\ H°(OH, g, 0\ K) = 1/2\ D_0°(O_2) + 1/2\ D_0°(H_2) = D_0°(OH)$. are as follows: $D_0°(O_2) = 117.967 \pm 0.042\ kcal\cdot mol^{-1}$ and $D_0°(H_2) = 103.267 \pm 0.003\ kcal\cdot mol^{-1}$ were taken from the CODATA[1] selection. Barrow[2] in a refinement of the work of Barrow and Downie[3] obtains a value of $D_0°$ for $OH(X^2\Pi_{3/2}) \rightarrow O(^3P_2) + H(^2S_{1/2})$ of 35427 cm^{-1} from an extrapolation of $\Delta_{vap}G$ versus v; it was increased to $35450 \pm 100\ cm^{-1}$ to account for the fact that $\Delta_{vap}G$ yields slightly low values at high v. Fehlenbok[4] obtains a value of D_e for $OH(B^2\Sigma^+)$ of 1315 cm^{-1} and G(O) for this state of 441 cm^{-1}. Using $T_e(B^2\Sigma^+)$ given by Rosen[5] and the zero point energy of HO (including the Dunham correction, see Herzberg[6] of 847.0 cm^{-1}, this yields $D_0°(OH) = 35451\ cm^{-1}$ with an estimated uncertainty of 100 cm^{-1}. A value of $D_0°(OH) = 35450 \pm 100\ cm^{-1} = 101.356 \pm 0.29\ kcal\cdot mol^{-1}$ was adopted. Combining the above values, one obtains $\Delta_f H°(OH, g, 0\ K) = 9.261 \pm 0.29\ kcal\cdot mol^{-1}$ which is in good agreement with the last JANAF[7] selection.

A review of earlier work is given in references.[7-9]

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[5] Comparison of the results of these calculations with those of the more exact treatment given by Haar *et al.*[10] suggests that errors in the tables due to approximations in our calculations may be neglected above 400 K. Below this, they may be appreciable. It is recommended that $H°(0\ K)$–$H°(298.15\ K)$, $S°(298.15\ K)$ and $C_p°(298.15\ K)$ be taken as $-2.107\ kcal\cdot mol^{-1}$, $43.890\ kJ\cdot mol^{-1}$, and $7.144\ kJ\cdot mol^{-1}$, respectively. These errors result from dealing with the ground state ($X^2\Pi_i$) as two separate electronic states separated by 139.7 cm^{-1}

The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$. The National Bureau of Standards prepared this table[11] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[11] we recalculate the table in terms of 1973 fundamental constants,[12] 1975 atomic weights[13] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.172	38.390	38.390	INFINITE
100	32.627	149.590	210.980	−6.139	38.471	37.214	−19.438
200	30.777	171.592	186.471	−2.976	38.832	35.803	−9.351
250	30.283	178.402	184.204	−1.450	38.930	35.033	−7.320
298.15	29.986	183.708	183.708	0.	38.987	34.277	−6.005
300	29.977	183.894	183.709	0.055	38.988	34.248	−5.963
350	29.780	188.499	184.073	1.549	39.019	33.455	−4.993
400	29.650	192.466	184.880	3.035	39.029	32.660	−4.265
450	29.567	195.954	185.921	4.515	39.020	31.864	−3.699
500	29.521	199.066	187.082	5.992	38.995	31.070	−3.246
600	29.527	204.447	189.542	8.943	38.902	29.493	−2.568
700	29.663	209.007	192.005	11.902	38.764	27.935	−2.085
800	29.917	212.983	194.384	14.880	38.598	26.399	−1.724
900	30.264	216.526	196.651	17.888	38.416	24.884	−1.444
1000	30.676	219.736	198.801	20.935	38.230	23.391	−1.222
1100	31.124	222.680	200.840	24.024	38.046	21.916	−1.041
1200	31.586	225.408	202.775	27.160	37.867	20.458	−0.891
1300	32.046	227.955	204.615	30.342	37.697	19.014	−0.764
1400	32.492	230.346	206.368	33.569	37.535	17.583	−0.656
1500	32.917	232.602	208.043	36.839	37.381	16.163	−0.563
1600	33.319	234.740	209.645	40.151	37.234	14.753	−0.482
1700	33.694	236.771	211.182	43.502	37.093	13.352	−0.410
1800	34.044	238.707	212.657	46.889	36.955	11.960	−0.347
1900	34.369	240.557	214.078	50.310	36.819	10.575	−0.291
2000	34.670	242.327	215.446	53.762	36.685	9.197	−0.240
2100	34.950	244.026	216.767	57.243	36.551	7.826	−0.195
2200	35.209	245.658	218.043	60.752	36.416	6.462	−0.153
2300	35.449	247.228	219.278	64.285	36.278	5.103	−0.116
2400	35.673	248.741	220.474	67.841	36.137	3.750	−0.082
2500	35.881	250.202	221.635	71.419	35.992	2.404	−0.050
2600	36.075	251.613	222.761	75.017	35.843	1.063	−0.021
2700	36.256	252.978	223.855	78.633	35.689	−0.271	0.005
2800	36.426	254.300	224.918	82.267	35.530	−1.600	0.030
2900	36.586	255.581	225.954	85.918	35.365	−2.924	0.053
3000	36.736	256.824	226.962	89.584	35.194	−4.241	0.074
3100	36.878	258.031	227.945	93.265	35.017	−5.552	0.094
3200	37.013	259.203	228.904	96.960	34.834	−6.858	0.112
3300	37.140	260.344	229.839	100.667	34.644	−8.158	0.129
3400	37.261	261.455	230.753	104.387	34.448	−9.452	0.145
3500	37.376	262.537	231.645	108.119	34.246	−10.741	0.160
3600	37.486	263.591	232.518	111.863	34.037	−12.023	0.174
3700	37.592	264.620	233.372	115.617	33.821	−13.300	0.188
3800	37.693	265.624	234.208	119.381	33.599	−14.570	0.200
3900	37.791	266.604	235.026	123.155	33.371	−15.834	0.212
4000	37.885	267.562	235.827	126.939	33.136	−17.093	0.223
4100	37.976	268.499	236.613	130.732	32.894	−18.346	0.234
4200	38.064	269.415	237.383	134.534	32.646	−19.593	0.244
4300	38.150	270.311	238.138	138.345	32.391	−20.833	0.253
4400	38.233	271.189	238.879	142.164	32.130	−22.068	0.262
4500	38.315	272.050	239.607	145.991	31.862	−23.297	0.270
4600	38.394	272.893	240.322	149.827	31.587	−24.520	0.278
4700	38.472	273.719	241.023	153.670	31.305	−25.737	0.286
4800	38.549	274.530	241.713	157.521	31.017	−26.947	0.293
4900	38.625	275.326	242.391	161.380	30.722	−28.152	0.300
5000	38.699	276.107	243.057	165.246	30.420	−29.350	0.307
5100	38.773	276.874	243.713	169.120	30.111	−30.542	0.313
5200	38.846	277.627	244.358	173.001	29.796	−31.729	0.319
5300	38.919	278.368	244.993	176.889	29.473	−32.909	0.324
5400	38.991	279.096	245.617	180.784	29.144	−34.083	0.330
5500	39.062	279.812	246.233	184.687	28.807	−35.251	0.335
5600	39.134	280.517	246.839	188.597	28.464	−36.412	0.340
5700	39.206	281.210	247.436	192.514	28.113	−37.568	0.344
5800	39.278	281.892	248.024	196.438	27.756	−38.716	0.349
5900	39.350	282.564	248.604	200.369	27.391	−39.860	0.353
6000	39.423	283.226	249.175	204.308	27.019	−40.997	0.357

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 182.776 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1310.88 \pm 0.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 1317.12 \pm 10.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^3\Sigma^-$	0	3
$a^1\Delta$	[17700]	2
$A^3\Pi$	22949	6
$b^1\Sigma^+$	29150	1

$\omega_e = [3135 \pm 100]\ cm^{-1}$ $\omega_e x_e = [89.3 \pm 50]\ cm^{-1}$ $\sigma = 1$

$B_e = 16.776\ cm^{-1}$ $\alpha_e = 0.728\ cm^{-1}$ $r_e = 1.0289$ Å

Enthalpy of Formation

The ionization potential of hydroxyl has been determined by Mann *et al.*[1] as 13.6 eV and by Foner and Hudson[2] as 13.18 ± 0.1 eV, both by electron impact methods. These values correspond to $\Delta_f H°(OH^+, g, 0\ K) = 322.97\ kcal \cdot mol^{-1}$ and 313.28 ± 2.5 $kcal \cdot mol^{-1}$, respectively. Metzger and Cook[3] have reported the photoionization onset of the process $H_2O(g) + h\nu \rightarrow OH^+ + H + e^-$ as 18.3 eV, with JANAF auxiliary data[4] this gives $\Delta_f H°(OH^+, g, 0\ K) = 313.3\ kcal \cdot mol^{-1}$, which is adopted.

Heat Capacity and Entropy

The measured electronic levels are those reported by Merer *et al.*,[5] the rotational constants are derived from this analysis also. The estimated electronic level is from the Hartree–Fock calculations of Cade.[6]

The vibrational constants are estimated so that $\Delta G_{1/2}$ is equal to that reported by Merer *et al.*[5] The anharmonicity, $\omega_e x_e$, is estimated by comparison with OH and NH. Calculations of $\omega_e x_e$ based on the Morse potential curve and the relation $\omega_{e2} = 4B_e^3/D_e$, or $\omega_{o2} = 4\omega_o x_o D_0^{07}$ do not appear to yield values which are preferable to our estimates; this is due to the inexactness of the potential for ionic molecules.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.618	1310.883		
100	29.127	150.948	208.684	−5.774			
200	29.136	171.140	185.442	−2.860			
250	29.144	177.642	183.256	−1.403			
298.15	29.153	182.776	182.776	0.	1317.123	1306.437	−228.882
300	29.153	182.956	182.777	0.054	1317.162	1306.371	−227.459
350	29.167	187.451	183.132	1.512	1318.196	1304.490	−194.685
400	29.192	191.347	183.920	2.971	1319.219	1302.462	−170.084
450	29.237	194.788	184.940	4.431	1320.230	1300.307	−150.936
500	29.311	197.872	186.082	5.895	1321.231	1298.040	−135.605
600	29.566	203.236	188.507	8.838	1323.208	1293.215	−112.584
700	29.959	207.822	190.946	11.813	1325.165	1288.062	−96.116
800	30.456	211.854	193.313	14.833	1327.119	1282.628	−83.747
900	31.013	215.473	195.577	17.906	1329.081	1276.949	−74.112
1000	31.590	218.770	197.734	21.036	1331.057	1271.050	−66.393
1100	32.160	221.808	199.786	24.224	1333.049	1264.954	−60.068
1200	32.706	224.630	201.740	27.467	1335.057	1258.675	−54.789
1300	33.217	227.268	203.604	30.764	1337.081	1252.227	−50.315
1400	33.691	229.747	205.383	34.110	1339.116	1245.624	−46.475
1500	34.127	232.087	207.086	37.501	1341.161	1238.874	−43.141
1600	34.526	234.302	208.719	40.934	1343.214	1231.988	−40.220
1700	34.891	236.407	210.286	44.405	1345.271	1224.974	−37.639
1800	35.226	238.411	211.793	47.911	1347.331	1217.838	−35.341
1900	35.532	240.324	213.245	51.449	1349.391	1210.588	−33.281
2000	35.814	242.153	214.645	55.017	1351.451	1203.229	−31.425
2100	36.074	243.907	215.997	58.611	1353.509	1195.767	−29.743
2200	36.315	245.591	217.304	62.231	1355.563	1188.208	−28.212
2300	36.539	247.210	218.569	65.874	1357.614	1180.555	−26.811
2400	36.749	248.770	219.795	69.538	1359.660	1172.813	−25.526
2500	36.946	250.274	220.985	73.223	1361.701	1164.985	−24.341
2600	37.133	251.727	222.139	76.927	1363.737	1157.076	−23.246
2700	37.311	253.131	223.261	80.649	1365.767	1149.090	−22.230
2800	37.482	254.491	224.352	84.389	1367.792	1141.028	−21.286
2900	37.647	255.810	225.415	88.146	1369.811	1132.893	−20.406
3000	37.806	257.089	226.449	91.918	1371.825	1124.689	−19.583
3100	37.962	258.331	227.458	95.707	1373.834	1116.418	−18.812
3200	38.114	259.538	228.441	99.510	1375.839	1108.082	−18.088
3300	38.265	260.714	229.402	103.329	1377.839	1099.684	−17.407
3400	38.413	261.858	230.340	107.163	1379.836	1091.225	−16.765
3500	38.562	262.974	231.256	111.012	1381.829	1082.707	−16.159
3600	38.709	264.062	232.152	114.876	1383.819	1074.133	−15.585
3700	38.857	265.125	233.029	118.754	1385.806	1065.503	−15.042
3800	39.006	266.163	233.887	122.647	1387.792	1056.820	−14.527
3900	39.156	267.178	234.728	126.555	1389.776	1048.084	−14.038
4000	39.307	268.171	235.552	130.478	1391.759	1039.298	−13.572
4100	39.460	269.144	236.359	134.417	1393.741	1030.462	−13.128
4200	39.615	270.097	237.151	138.371	1395.723	1021.577	−12.705
4300	39.773	271.031	237.928	142.340	1397.706	1012.646	−12.301
4400	39.932	271.947	238.691	146.325	1399.689	1003.668	−11.915
4500	40.094	272.846	239.440	150.326	1401.673	994.644	−11.546
4600	40.258	273.729	240.176	154.344	1403.659	985.577	−11.192
4700	40.425	274.597	240.899	158.378	1405.647	976.467	−10.852
4800	40.595	275.449	241.610	162.429	1407.637	967.315	−10.527
4900	40.767	276.288	242.309	166.497	1409.630	958.121	−10.214
5000	40.942	277.114	242.997	170.583	1411.626	948.887	−9.913
5100	41.120	277.926	243.674	174.686	1413.625	939.612	−9.624
5200	41.299	278.726	244.340	178.807	1415.628	930.298	−9.345
5300	41.482	279.515	244.997	182.946	1417.635	920.946	−9.076
5400	41.666	280.292	245.643	187.103	1419.646	911.555	−8.818
5500	41.853	281.058	246.280	191.279	1421.662	902.127	−8.568
5600	42.042	281.814	246.908	195.474	1423.682	892.663	−8.326
5700	42.233	282.560	247.527	199.688	1425.706	883.163	−8.093
5800	42.425	283.296	248.137	203.920	1427.736	873.627	−7.868
5900	42.619	284.023	248.739	208.173	1429.771	864.055	−7.650
6000	42.815	284.741	249.333	212.444	1431.811	854.450	−7.439

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [172.469 \pm 0.8]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = -137.43 \pm 3.8\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = -143.59 \pm 3.8\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = [3770]\ cm^{-1}$ $\omega_e x_e = [74.7]\ cm^{-1}$ $\sigma = 1$
$B_e = [19.2]\ cm^{-1}$ $\alpha_e = [0.65]\ cm^{-1}$ $r_e = [0.9628]$ Å

Enthalpy of Formation

Branscomb[1] has obtained an electron affinity of OH of 1.83 ± 0.04 eV (42.2 ± 0.9 kcal·mol^{-1}) from the photodetachment spectrum of OH^-. The vibrational state was identified as the ground state since no other absorption sequence could be detected by a thorough search. Kay and Page[2] have also determined the electron affinity by the magnetron method and report 49.1 at 1820 K, which reduces to 40 ± 2.7 kcal·mol^{-1} at 0 K. They also disclaim prior papers, Page[3] and Page and Sugden,[4] which supported higher values. Feugier and Queraud[5] have reported an electron affinity at 2250 K of 2.13 eV (49.1 kcal·mol^{-1}) which reduces to 37.7 kcal·mol^{-1} at 0 K. We adopt the value reported by Branscomb[1] which yields $\Delta_f H°(OH^-, g)$ 0 K = −32.85 kcal·mol^{-1}.

Heat Capacity and Entropy

Branscomb[1] deduced from his photodetachment spectra that ω_e, B_e and r_e are very close to the values for OH(g). Our adopted values are from the calculations of Cade[6] corrected for the mean deviations in OH and HF. The values of $\omega_e x_e$ and α_e were estimated by comparison with OH(g) and other related hydrides. The ground state configuration was assumed to be that of HF(g) with which OH^- is isoelectronic.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.606	−137.429		
100	29.127	140.647	198.369	−5.772			
200	29.130	160.836	175.134	−2.860			
250	29.135	167.336	172.948	−1.403			
298.15	29.141	172.469	172.469	0.	−143.595	−138.698	24.299
300	29.141	172.649	172.469	0.054	−143.633	−138.668	24.144
350	29.148	177.141	172.824	1.511	−144.678	−137.758	20.559
400	29.157	181.034	173.612	2.969	−145.736	−136.697	17.851
450	29.170	184.469	174.631	4.427	−146.806	−135.503	15.729
500	29.194	187.543	175.772	5.886	−147.888	−134.189	14.019
600	29.289	192.873	178.191	8.809	−150.087	−131.244	11.426
700	29.471	197.401	180.620	11.747	−152.325	−127.927	9.546
800	29.749	201.353	182.970	14.707	−154.588	−124.287	8.115
900	30.108	204.877	185.211	17.699	−156.864	−120.363	6.986
1000	30.525	208.070	187.340	20.730	−159.145	−116.185	6.069
1100	30.975	211.001	189.360	23.805	−161.422	−111.779	5.308
1200	31.439	213.716	191.278	26.926	−163.694	−107.165	4.665
1300	31.900	216.250	193.102	30.093	−165.957	−102.363	4.113
1400	32.347	218.631	194.841	33.305	−168.212	−97.386	3.634
1500	32.773	220.877	196.503	36.562	−170.459	−92.249	3.212
1600	33.176	223.005	198.093	39.859	−172.700	−86.962	2.839
1700	33.553	225.028	199.619	43.196	−174.934	−81.535	2.505
1800	33.904	226.956	201.084	46.569	−177.165	−75.976	2.205
1900	34.230	228.798	202.495	49.976	−179.392	−70.294	1.933
2000	34.532	230.561	203.855	53.414	−181.619	−64.494	1.684
2100	34.812	232.253	205.167	56.881	−183.846	−58.583	1.457
2200	35.072	233.879	206.435	60.376	−186.074	−52.566	1.248
2300	35.312	235.443	207.663	63.895	−188.304	−46.448	1.055
2400	35.536	236.951	208.852	67.438	−190.537	−40.232	0.876
2500	35.744	238.406	210.005	71.002	−192.774	−33.924	0.709
2600	35.938	239.811	211.124	74.586	−195.015	−27.525	0.553
2700	36.119	241.171	212.212	78.189	−197.261	−21.041	0.407
2800	36.288	242.488	213.270	81.809	−199.513	−14.473	0.270
2900	36.447	243.764	214.300	85.446	−201.771	−7.825	0.141
3000	36.596	245.002	215.303	89.098	−204.034	−1.098	0.019
3100	36.737	246.204	216.280	92.765	−206.304	5.704	−0.096
3200	36.870	247.373	217.234	96.446	−208.580	12.579	−0.205
3300	36.996	248.509	218.164	100.139	−210.862	19.525	−0.309
3400	37.115	249.616	219.073	103.844	−213.151	26.541	−0.408
3500	37.228	250.693	219.961	107.562	−215.447	33.624	−0.502
3600	37.336	251.743	220.830	111.290	−217.750	40.773	−0.592
3700	37.439	252.768	221.679	115.029	−220.059	47.986	−0.677
3800	37.538	253.768	222.510	118.778	−222.375	55.262	−0.760
3900	37.632	254.744	223.324	122.536	−224.698	62.599	−0.838
4000	37.723	255.698	224.122	126.304	−227.027	69.995	−0.914
4100	37.810	256.630	224.903	130.081	−229.364	77.449	−0.987
4200	37.894	257.542	225.670	133.866	−231.708	84.961	−1.057
4300	37.975	258.435	226.421	137.659	−234.058	92.528	−1.124
4400	38.053	259.309	227.159	141.461	−236.416	100.150	−1.189
4500	38.129	260.165	227.883	145.270	−238.781	107.826	−1.252
4600	38.203	261.004	228.594	149.086	−241.153	115.554	−1.312
4700	38.274	261.826	229.292	152.910	−243.533	123.335	−1.371
4800	38.344	262.633	229.978	156.741	−245.920	131.166	−1.427
4900	38.411	263.424	230.653	160.579	−248.315	139.047	−1.482
5000	38.477	264.201	231.316	164.423	−250.717	146.977	−1.535
5100	38.541	264.963	231.968	168.274	−253.127	154.954	−1.587
5200	38.604	265.712	232.610	172.132	−255.545	162.979	−1.637
5300	38.666	266.448	233.242	175.995	−257.970	171.051	−1.686
5400	38.726	267.172	233.863	179.865	−260.405	179.168	−1.733
5500	38.785	267.883	234.475	183.740	−262.847	187.331	−1.779
5600	38.843	268.582	235.078	187.622	−265.297	195.539	−1.824
5700	38.900	269.270	235.672	191.509	−267.756	203.789	−1.868
5800	38.955	269.947	236.257	195.402	−270.224	212.084	−1.910
5900	39.010	270.613	236.834	199.300	−272.700	220.420	−1.951
6000	39.064	271.270	237.402	203.204	−275.186	228.799	−1.992

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [246.511 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -201.08 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -205.52 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[2]
[14700]	[2]
[15100]	[2]
[16000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[498](1)
[438](2)
[3650](1)

Point Group: $[C_{\infty v}]$ $\sigma = 1$
Bond Distances: Sr–O = [2.10] Å O–H = [0.96] Å
Bond Angle: Sr–O–H = [180]°
Rotational Constant: B_0 = [0.251104] cm^{-1}

Enthalpy of Formation

The adopted enthalpy of formation is based on assessment of $D_0°$ values derived from flame spectra of CaOH, SrOH, and BaOH. Cotton and Jenkins[1] found both the alkaline earth monohydroxides and dihydroxides to be present in significant amounts in fuel– rich hydrogen–oxygen–nitrogen flames. They determined equilibrium constants for the reactions $M(g) + H_2O(g) = MOH(g) + H(g)$ and $M(g) + 2\ H_2O(g) = M(OH)_2(g) + 2\ H(g)$ and derived $D_0°$ values. For $D_0°$(Sr–OH), Cotton and Jenkins[1] gave 103 ± 5 kcal·mol^{-1}. Ryabova and Gurvich[2] considered SrOH to be the dominant compound and reported $D_0° = 95 \pm 8$ kcal·mol^{-1}. Sugden and Schofield[3] interpreted $Sr(OH)_2$ as dominant. Cotton and Jenkins[1] have recalculated the work of Ryabova and Gurvich[2] and of Sugden and Schofield[3] considering both SrOH and $Sr(OH)_2$ to be present and have obtained the recalculated $D_0°$(Sr–OH) values of 96 and 101 kcal·mol^{-1}, respectively. Gurvich *et al.*[4] made further measurements, interpreted SrOH as dominant, and reported $D_0°(Sr–OH) = 93 \pm 3$ kcal·mol^{-1}. Kalff and Alkemade[5] chose flame conditions to minimize the dihydroxide formation and determined a 3rd law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins[1] using current JANAF auxiliary data[7] leads to $D_0°$(Sr–OH) = 103.7 kcal·mol^{-1} which is 0.7 kcal·mol^{-1} higher than the 103 kcal·mol^{-1} given by Cotton and Jenkins.[1] Applying the correction to the value of Ryabova and Gurvich[2] and Sugden and Schofield[3] as recalculated by Cotton and Jenkins[1] gives $D_0°$(Sr–OH) = 96.7 and 101.7 kcal·mol^{-1}, respectively.

Because the corrected dissociation energy of Ryabova and Gurvich was near the adopted value for $Ba(OH)_2(g)$,[7] their corrected value was adopted for $Sr(OH)_2(g)$.[7] While their corrected value for BaOH(g)[7] is not as close to the adopted value as in the dihydroxide case, it is nevertheless the nearest one, and therefore $D_0°$(Sr–OH) = 96.7 kcal·mol^{-1} is adopted.

The ratio of the dissociation energies of the alkaline earth monohalides to those of the corresponding dihalides range from 0.40 to 0.51 with the ratio for the strontium fluorides being 0.49.[7] The similarity between the halides and hydroxides has been established.[8–11] The ratio of the adopted values for the dissociation energies of SrOH(g) and $Sr(OH)_2$ is 0.49 where $D_0°$ of the dihydroxide is defined by the reaction $Sr(OH)_2(g) = Sr(g) + 2\ OH(g)$ and is 198.6 kcal·mol^{-1}.[7]

$\Delta_f H°$(SrOH, g, 0 K) = −48.11 ± 5 kcal·mol^{-1} is calculated from the adopted dissociation energy.

Heat Capacity and Entropy

The analogy between gaseous monohydroxides and monohalides, particularly the monofluorides, has been recognized.[8–11] The molecular configuration is assumed to be linear in accordance with the prediction of Walsh[12] and the evidence that the gaseous alkali metal hydroxide are linear.[13–15] The ground state is assumed to be $^2\Sigma^+$ by analogy with SrF and SrCl.[7] The electronic levels are estimated from the band spectra observed by James and Sugden,[16] Lagerqvist and Huldt,[17] Charton and Gaydon,[18] Zhitkevich *et al.*,[19] and Van der Hurk *et al.*,[20] and the comparison with SrF and SrCl.[7]

The Sr–O bond distance is estimated to be slightly larger, 0.02 Å, than the Sr–F distance[7] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is that in water.[7]

The Sr–O stretching frequency, 498 cm^{-1}, is estimated to be the same as the Sr–F stretching frequency.[7, 11] The O–H stretching frequency, 3650 cm^{-1}, is estimated from the alkali hydroxide series. The bending frequency, 438 cm^{-1}, is estimated by assuming that the ratio of the bending force constant to the stretching force constant is 0.022, which is the average ratio found in the alkali metal monohydroxides by Acquista and Abramowitz.[11, 15]

The entropy in the present table is lower by 0.06 cal·K^{-1}·mol^{-1} at 298.15 K and 0.10 cal·K^{-1}·mol^{-1} at 1000 K than that proposed by Jackson;[11] the data relevant to the calculation are nearly the same.

Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.707	−201.082	−201.082	INFINITE
100	30.646	205.253	282.997	−7.774	−202.600	−206.619	107.927
200	39.954	229.305	250.551	−4.249	−204.366	−209.895	54.819
250	43.517	238.626	247.255	−2.157	−205.004	−211.206	44.129
298.15	45.958	246.511	246.511	0.	−205.518	−212.347	37.202
300	46.036	246.796	246.512	0.085	−205.536	−212.389	36.980
350	47.812	254.034	247.080	2.434	−206.003	−213.494	31.862
400	49.088	260.506	248.361	4.858	−206.431	−214.534	28.015
450	50.028	266.345	250.040	7.337	−206.842	−215.523	25.017
500	50.744	271.654	251.940	9.857	−207.251	−216.465	22.614
600	51.775	281.003	256.026	14.986	−208.096	−218.230	18.999
700	52.534	289.043	260.182	20.203	−209.009	−219.848	16.405
800	53.182	296.101	264.239	25.490	−210.007	−221.329	14.451
900	53.787	302.401	268.136	30.838	−211.722	−222.608	12.920
1000	54.371	308.098	271.852	36.246	−212.581	−223.772	11.689
1100	54.936	313.307	275.387	41.712	−221.325	−224.484	10.660
1200	55.477	318.110	278.750	47.233	−223.064	−224.694	9.781
1300	55.990	322.571	281.951	52.806	−224.789	−224.760	9.031
1400	56.470	326.738	285.003	58.430	−226.501	−224.694	8.383
1500	56.916	330.650	287.917	64.099	−228.202	−224.505	7.818
1600	57.329	334.336	290.704	69.812	−229.895	−224.203	7.319
1700	57.710	337.824	293.374	75.564	−368.496	−222.616	6.840
1800	58.062	341.132	295.936	81.353	−368.318	−214.040	6.211
1900	58.389	344.280	298.398	87.176	−368.143	−205.474	5.649
2000	58.694	347.283	300.768	93.030	−367.974	−196.917	5.143
2100	58.982	350.154	303.052	98.914	−367.817	−188.368	4.685
2200	59.256	352.904	305.256	104.826	−367.677	−179.826	4.270
2300	59.520	355.544	307.385	110.765	−367.560	−171.290	3.890
2400	59.777	358.083	309.445	116.730	−367.471	−162.759	3.542
2500	60.031	360.528	311.440	122.720	−367.418	−154.231	3.222
2600	60.283	362.887	313.374	128.736	−367.409	−145.703	2.927
2700	60.537	365.167	315.250	134.777	−367.452	−137.175	2.654
2800	60.793	367.373	317.072	140.843	−367.556	−128.645	2.400
2900	61.053	369.511	318.844	146.935	−367.728	−120.110	2.163
3000	61.319	371.585	320.567	153.054	−367.979	−111.567	1.943
3100	61.590	373.600	322.246	159.199	−368.317	−103.014	1.736
3200	61.867	375.560	323.881	165.372	−368.750	−94.450	1.542
3300	62.149	377.468	325.477	171.573	−369.288	−85.870	1.359
3400	62.438	379.328	327.033	177.802	−369.938	−77.272	1.187
3500	62.731	381.142	328.553	184.060	−370.707	−68.654	1.025
3600	63.029	382.913	330.039	190.348	−371.602	−60.011	0.871
3700	63.330	384.644	331.491	196.666	−372.629	−51.342	0.725
3800	63.634	386.337	332.912	203.014	−373.792	−42.643	0.586
3900	63.940	387.994	334.304	209.393	−375.094	−33.912	0.454
4000	64.247	389.617	335.666	215.803	−376.539	−25.146	0.328
4100	64.553	391.207	337.002	222.243	−378.127	−16.341	0.208
4200	64.858	392.766	338.311	228.713	−379.856	−7.497	0.093
4300	65.161	394.296	339.595	235.214	−381.729	1.391	−0.017
4400	65.461	395.797	340.855	241.745	−383.744	10.323	−0.123
4500	65.756	397.272	342.093	248.306	−385.896	19.303	−0.224
4600	66.046	398.720	343.308	254.896	−388.117	28.327	−0.322
4700	66.330	400.144	344.502	261.515	−390.513	37.406	−0.416
4800	66.608	401.543	345.676	268.162	−393.029	46.537	−0.506
4900	66.878	402.919	346.830	274.837	−395.659	55.722	−0.594
5000	67.140	404.273	347.966	281.537	−398.390	64.961	−0.679
5100	67.393	405.605	349.083	288.264	−401.201	74.254	−0.761
5200	67.637	406.916	350.182	295.016	−404.123	83.604	−0.840
5300	67.871	408.207	351.265	301.791	−407.129	93.013	−0.917
5400	68.096	409.478	352.331	308.590	−410.210	102.478	−0.991
5500	68.311	410.729	353.382	315.410	−413.360	112.001	−1.064
5600	68.515	411.962	354.417	322.251	−416.571	121.582	−1.134
5700	68.708	413.176	355.437	329.113	−419.835	131.221	−1.203
5800	68.891	414.373	356.443	335.993	−423.145	140.918	−1.269
5900	69.063	415.552	357.435	342.891	−426.285	150.647	−1.334
6000	69.225	416.714	358.413	349.805	−429.638	160.454	−1.397

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [241.049 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 318.99 \pm 62.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 320.80 \pm 62.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[490](1)
[430](2)
[3650](1)

Ground State Quantum Weight: [1] $\sigma = 1$

Point Group: [$C_{\infty v}$]

Bond Distances: Sr–O = [2.1] Å O–H = [0.96] Å

Bond Angle: Sr–O–H = [180]°

Rotational Constant: B_o = [0.251111] cm^{-1}

Enthalpy of Formation

The ionization potential of SrOH(g) was deduced by Kelly an Padley[1] to be 5.55 ± 0.1 eV. Using a rotating single probe, these authors quantitatively examined the total positive ion concentrations produced from Sr aqueous salt solutions in fuel rich, premixed $H_2 + O_2 + N_2$ flames. Using current JANAF auxiliary data,[2] we recalculate the ionization potential to be 5.75 eV.

Jensen[3] determined $\Delta_f H°(0\ K) = 25 \pm 8\ kcal·mol^{-1}$ for $Sr(g) + OH(g) = SrOH^+(g) + e^-$ in atmospheric pressure $H_2 + O_2 + N_2$ flames using the microwave cavity resonance method. This value was calculated assuming a bent molecule for $SrOH^+$; the value is not significantly changed, within the uncertainty, by the change in the configuration. Using auxiliary data[2], we derive an ionization potential of 5.28 eV, which is in fair agreement with the value derived from the data of Kelly and Padly.[1]

We adopt IP = 5.39 eV (124.30 $kcal·mol^{-1}$) which is an average of the above two studies.[1,3] This leads to $\Delta_f H°(0\ K) = 76.19\ kcal·mol^{-1}$ and $\Delta_f H°(298.15\ K) = 76.67\ kcal·mol^{-1}$ for $SrOH^+(g)$. We assign an uncertainty of $\pm 15\ kcal·mol^{-1}$.

In comparison, the ionization potential of SrF(g) is 5.03 eV[2] while that of Sr(g) is 5.692 eV.[4] Note that the average of these two values is very close to our adopted ionization potential.

Heat Capacity and Entropy

The molecular configuration is assumed to be linear, since experimental evidence indicates that the gaseous alkali metal hydroxides are linear.[2,5–7] In addition, Walsh[8] had predicted that BAH molecules (H = hydrogen atom) with ten or less valence electrons ($SrOH+$ has eight valence electrons) will be linear in their ground state. The molecule $SrOH^+$ is isoelectronic with RbOH.

The bond dissociation energy for $SrOH^+$ (103.7 $kcal·mol^{-1}$),[2, 4] for the process $SrOH^+(g) = Sr^+(g) + OH(g)$ is fairly close to that for SrOH (96.7 $kcal·mol^{-1}$).[2] This suggests that the bonding in these two molecules may be quite similar. Thus bond distances are assumed to be the same as those adopted for SrOH(g).[2] The vibrational frequencies are assumed to be similar to those adopted for SrOH(g).[2] The ground state quantum weight is assumed to be the same as that of KOH (g).[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.760	318.986		
100	30.774	199.518	277.769	−7.825			
200	40.248	223.738	245.112	−4.275			
250	43.779	233.120	241.797	−2.169			
298.15	46.180	241.049	241.049	0.	320.800	309.345	−54.196
300	46.256	241.335	241.050	0.085	320.820	309.274	−53.849
350	47.994	248.603	241.620	2.444	321.403	307.304	−45.863
400	49.238	255.098	242.906	4.877	322.023	305.248	−39.861
450	50.154	260.953	244.591	7.363	322.658	303.113	−35.184
500	50.850	266.275	246.498	9.888	323.294	300.907	−31.436
600	51.852	275.640	250.595	15.027	324.537	296.312	−25.796
700	52.592	283.691	254.762	20.250	325.709	291.514	−21.753
800	53.228	290.756	258.828	25.542	326.795	286.553	−18.710
900	53.824	297.060	262.732	30.895	327.162	281.535	−16.340
1000	54.401	302.760	266.454	36.306	328.386	276.399	−14.438
1100	54.961	307.972	269.995	41.774	321.722	271.506	−12.893
1200	55.498	312.777	273.363	47.297	322.064	266.926	−11.619
1300	56.007	317.240	276.568	52.873	322.420	262.317	−10.540
1400	56.484	321.408	279.624	58.498	322.788	257.680	−9.614
1500	56.927	325.320	282.541	64.169	323.167	253.016	−8.811
1600	57.335	329.008	285.331	69.882	323.554	248.327	−8.107
1700	57.710	332.495	288.004	75.635	187.031	244.793	−7.522
1800	58.052	335.803	290.568	81.423	189.288	248.126	−7.200
1900	58.364	338.951	293.033	87.244	191.540	251.333	−6.910
2000	58.648	341.952	295.404	93.095	193.783	254.422	−6.645
2100	58.907	344.819	297.690	98.973	196.013	257.399	−6.402
2200	59.143	347.565	299.895	104.876	198.222	260.271	−6.180
2300	59.358	350.199	302.025	110.801	200.405	263.042	−5.974
2400	59.554	352.730	304.085	116.747	202.553	265.719	−5.783
2500	59.734	355.164	306.080	122.711	204.658	268.307	−5.606
2600	59.897	357.511	308.013	128.693	206.712	270.812	−5.441
2700	60.047	359.774	309.889	134.690	208.704	273.240	−5.286
2800	60.185	361.960	311.710	140.702	210.625	275.595	−5.141
2900	60.311	364.074	313.479	146.727	212.463	277.882	−5.005
3000	60.428	366.121	315.200	152.764	214.210	280.108	−4.877
3100	60.535	368.104	316.875	158.812	215.853	282.278	−4.756
3200	60.634	370.028	318.506	164.870	217.384	284.395	−4.642
3300	60.725	371.895	320.095	170.938	218.792	286.467	−4.534
3400	60.810	373.709	321.646	177.015	220.069	288.499	−4.432
3500	60.888	375.473	323.159	183.100	221.204	290.494	−4.335
3600	60.961	377.189	324.636	189.193	222.192	292.460	−4.243
3700	61.029	378.860	326.079	195.292	223.026	294.399	−4.156
3800	61.092	380.489	327.489	201.398	223.699	296.320	−4.073
3900	61.151	382.076	328.869	207.510	224.209	298.224	−3.994
4000	61.205	383.625	330.218	213.628	224.551	300.116	−3.919
4100	61.257	385.137	331.539	219.751	224.725	302.003	−3.848
4200	61.305	386.614	332.833	225.879	224.732	303.887	−3.779
4300	61.350	388.057	334.101	232.012	224.569	305.774	−3.714
4400	61.392	389.468	335.343	238.149	224.239	307.666	−3.652
4500	61.432	390.848	336.561	244.291	223.746	309.567	−3.593
4600	61.470	392.199	337.756	250.436	223.159	311.475	−3.537
4700	61.505	393.521	338.929	256.584	222.371	313.404	−3.483
4800	61.538	394.816	340.080	262.737	221.439	315.350	−3.432
4900	61.570	396.086	341.210	268.892	220.369	317.318	−3.383
5000	61.599	397.330	342.320	275.050	219.174	319.308	−3.336
5100	61.627	398.550	343.410	281.212	217.876	321.321	−3.291
5200	61.654	399.747	344.482	287.376	216.445	323.363	−3.248
5300	61.679	400.921	345.536	293.542	214.909	325.434	−3.207
5400	61.703	402.074	346.572	299.712	213.277	327.534	−3.168
5500	61.725	403.207	347.592	305.883	211.557	329.666	−3.131
5600	61.747	404.319	348.595	312.057	209.757	331.830	−3.095
5700	61.767	405.412	349.582	318.232	207.886	334.026	−3.061
5800	61.787	406.487	350.554	324.410	205.952	336.256	−3.028
5900	61.805	407.543	351.511	330.590	204.172	338.495	−2.997
6000	61.823	408.582	352.454	336.771	202.164	340.789	−2.967

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 229.106 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 5.01 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 2.09 \pm 8.4\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$\tilde{X}[^2A'']$	0	2
$[^2A']$	7029.764	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
3410(1)
1390(1)
1095(1)

Point Group: C_1 $\sigma = 1$
Bond Distances: H–O = 0.977 Å O–O = 1.335 Å
Bond Angle: H–O–O = 104.1°
Product of the Moments of Inertia: $I_A I_B I_C = 0.9128 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

Wagman[1] and Cohen and Westburg[2] have reviewed the data which leads to the enthalpy of formation for HO_2(g). We adopt the value suggested by Wagman,[1] $\Delta_f H°(HO_2, g, 298.15\ K) = 0.5 \pm 2.0\ kcal \cdot mol^{-1}$. Gurvich *et al.*[3] have also critically reviewed many of the same sources and have adopted the same value for the enthalpy of formation. The analysis by Wagman[1] follows.

Kochubei and Moin[4] made a kinetic determination of the enthalpy of formation of the HO_2 radical by studying the bimolecular radical formation reactions (forward only) $HX(g) + O_2(g) = HO_2(g) + X(g)$, where X = Cl, Br, and I. The basic rate data are not given for this study. However, Wagman corrected their reported results by a small amount due to the improperly used term designated as $\bar{T} d\Delta H/dT$). In the recalculation, the reported E_t–E_r values were used as the $\Delta_r H°$ at the stated mean temperature. Hence the $\Delta_f H°(298.15\ K)$ for HO_2(g) from this study is about 0.7 $kcal \cdot mol^{-1}$.

Calculations for $\Delta_f H°(HO_2, g)$ were also made using the reaction $H_3^+(g) + O_2(g) = HO_2^+(g) + H_2$ (g). For this reaction, Fennelly, *et al.*[5] obtained $\Delta_r H°(0\ K) = -0.05 + 0.07\ kcal \cdot mol^{-1}$. Kim *et al.*,[6] from rate constants for the above, obtain $\Delta_r G°(298.15\ K) = -0.41\ kcal \cdot mol^{-1}$. Estimating $\Delta S°(298.15\ K)$ to be $+0.40\ cal \cdot K^{-1} \cdot mol^{-1}$, and hence $\Delta_r H°(298.15\ K) = -0.3 \pm 0.10\ kcal \cdot mol^{-1}$. The best value is $\Delta_r H°(298.15\ K) = -0.2 \pm 0.2\ kcal \cdot mol^{-1}$. Quantum mechanical calculations of the energy of H_3^+ have been made by a number of people.[7,8] Using the results of Duben and Lowe[8] and ionization potential of HO_2 from Foner and Hudson,[9] Wagman obtained $\Delta_f H°(HO_2, g) = 1.1\ kcal \cdot mol^{-1}$. This yields $\Delta_f H°(HO_2, g, 298.15\ K) = 0.4\ kcal \cdot mol^{-1}$.

An additional calculation can be obtained from the ionization and appearance potentials for HO_2 from H_2O_2. Recent measurements by photoionization at NBS yield $\Delta_r H° = 348.7 \pm 0.2\ kcal \cdot mol^{-1}$ for $H_2O_2(g)$, $H_2O_2 + e^- = HO_2{}_+(g) + H^+ + 2\,e^-$. Combining with the ionization potential of HO_2(g) leads to $\Delta_r H°$ for $H_2O_2(g) = HO_2(g) + H(g)$ and $\Delta_f H°(HO_2, g, 298.15\ K) = 0.6\ kcal \cdot mol^{-1}$.

In these last two calculations, the principal uncertainty lies in the value for the ionization potential of HO_2 reported by Foner and Hudson.[9] However the general consistency of the various paths indicates that a reasonable value for $\Delta_f H°(HO_2, g, 298.15\ K)$ is $0.5 \pm 2.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies adopted are those determined by Paukert and Johnston[11] from infrared absorption measurements on gas phase HO_2. Matrix studies of HO_2 yielded similar results.[12–14] The bond lengths and bond angles are taken from the microwave spectroscopic study of Beers and Howard.[15] Other measurements are in agreement with these values.[11, 14, 16, 17]

The energy separation between the ground and lowest excited electronic state was determined by Freedman and Jones.[18] Their measurements also yield $I_A I_B I_C$ to be $1.090 \times 10^{-117}\ g^3 \cdot cm^6$ and $\nu_3 = 983\ cm^{-1}$ for the $^2A'$ state. This indicates that the structure of this excited state is quite similar to the ground state; thus, for convenience in calculating the entropy and heat capacity, the vibrational frequencies and moments of inertia of the excited state are taken to be the same as the ground state. For the ground electronic state, the principal moments of inertia are: $I_A = 0.1375 \times 10^{-39}$, $I_B = 2.5088 \times 10^{-39}$ and $I_C = 2.6463 \times 10^{-39}\ g \cdot cm^2$.

References

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Continued on page 1358

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.003	5.006	5.006	INFINITE
100	33.258	192.430	259.201	−6.677	3.928	7.052	−3.683
200	33.491	215.515	232.243	−3.346	3.001	10.536	−2.752
250	34.044	223.040	229.676	−1.659	2.532	12.475	−2.606
298.15	34.905	229.106	229.106	0.	2.092	14.430	−2.528
300	34.943	229.322	229.107	0.065	2.076	14.506	−2.526
350	36.072	234.791	229.536	1.839	1.649	16.612	−2.479
400	37.296	239.688	230.504	3.673	1.260	18.777	−2.452
450	38.519	244.151	231.776	5.569	0.908	20.988	−2.436
500	39.687	248.271	233.222	7.524	0.591	23.236	−2.427
600	41.781	255.697	236.363	11.601	0.043	27.819	−2.422
700	43.558	262.275	239.603	15.870	−0.411	32.485	−2.424
800	45.084	268.193	242.813	20.304	−0.790	37.211	−2.430
900	46.418	273.582	245.937	24.880	−1.107	41.981	−2.436
1000	47.604	278.535	248.952	29.583	−1.368	46.783	−2.444
1100	48.672	283.123	251.853	34.397	−1.582	51.609	−2.451
1200	49.643	287.400	254.639	39.314	−1.754	56.452	−2.457
1300	50.535	291.410	257.315	44.323	−1.887	61.308	−2.463
1400	51.360	295.185	259.886	49.419	−1.988	66.173	−2.469
1500	52.128	298.755	262.360	54.593	−2.058	71.045	−2.474
1600	52.845	302.143	264.741	59.842	−2.102	75.920	−2.479
1700	53.518	305.367	267.037	65.161	−2.122	80.797	−2.483
1800	54.149	308.444	269.252	70.545	−2.121	85.674	−2.486
1900	54.742	311.388	271.393	75.989	−2.102	90.551	−2.489
2000	55.299	314.210	273.464	81.492	−2.067	95.427	−2.492
2100	55.820	316.921	275.469	87.048	−2.019	100.301	−2.495
2200	56.308	319.529	277.413	92.655	−1.960	105.172	−2.497
2300	56.763	322.042	279.299	98.309	−1.893	110.040	−2.499
2400	57.186	324.467	281.131	104.006	−1.818	114.905	−2.501
2500	57.578	326.809	282.911	109.745	−1.740	119.767	−2.502
2600	57.940	329.075	284.644	115.521	−1.659	124.625	−2.504
2700	58.274	331.268	286.330	121.332	−1.577	129.481	−2.505
2800	58.580	333.393	287.973	127.175	−1.497	134.334	−2.506
2900	58.860	335.453	289.575	133.047	−1.419	139.183	−2.507
3000	59.115	337.453	291.138	138.946	−1.346	144.030	−2.508
3100	59.347	339.395	292.663	144.869	−1.278	148.876	−2.509
3200	59.557	341.283	294.153	150.814	−1.218	153.718	−2.509
3300	59.745	343.118	295.609	156.780	−1.165	158.558	−2.510
3400	59.915	344.904	297.033	162.763	−1.122	163.398	−2.510
3500	60.066	346.643	298.426	168.762	−1.089	168.236	−2.511
3600	60.200	348.337	299.789	174.775	−1.067	173.074	−2.511
3700	60.318	349.989	301.123	180.801	−1.058	177.910	−2.512
3800	60.423	351.599	302.431	186.839	−1.061	182.748	−2.512
3900	60.513	353.169	303.711	192.886	−1.078	187.586	−2.512
4000	60.592	354.702	304.967	198.941	−1.109	192.423	−2.513
4100	60.659	356.199	306.199	205.004	−1.156	197.262	−2.513
4200	60.716	357.662	307.406	211.072	−1.217	202.102	−2.514
4300	60.764	359.091	308.592	217.146	−1.296	206.945	−2.514
4400	60.803	360.488	309.756	223.225	−1.391	211.788	−2.514
4500	60.834	361.855	310.898	229.307	−1.504	216.634	−2.515
4600	60.858	363.193	312.021	235.391	−1.634	221.482	−2.515
4700	60.876	364.502	313.123	241.478	−1.784	226.335	−2.515
4800	60.888	365.783	314.207	247.566	−1.952	231.190	−2.516
4900	60.895	367.039	315.272	253.656	−2.141	236.050	−2.516
5000	60.897	368.269	316.320	259.745	−2.350	240.913	−2.517
5100	60.894	369.475	317.351	265.835	−2.580	245.780	−2.517
5200	60.888	370.658	318.364	271.924	−2.831	250.652	−2.518
5300	60.879	371.817	319.362	278.012	−3.105	255.530	−2.518
5400	60.866	372.955	320.344	284.100	−3.402	260.412	−2.519
5500	60.851	374.072	321.311	290.185	−3.722	265.300	−2.520
5600	60.834	375.168	322.263	296.270	−4.067	270.195	−2.520
5700	60.814	376.245	323.200	302.352	−4.437	275.096	−2.521
5800	60.792	377.302	324.124	308.432	−4.832	280.004	−2.522
5900	60.769	378.341	325.034	314.511	−5.254	284.917	−2.522
6000	60.745	379.362	325.931	320.586	−5.702	289.839	−2.523

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = 196.344\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 234.6 \pm 33.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 233.6 \pm 33.5\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3\Sigma^-$	0	3
	[7650]	2
	[15150]	1
	29560	6
	[38110]	2
	[57490]	1

$\omega_e = 2380\ cm^{-1}$ $\omega_e x_e = [55]\ cm^{-1}$ $\sigma = 1$
$B_e = 8.412\ cm^{-1}$ $\alpha_e = [0.28]\ cm^{-1}$ $r_e = 1.43$ Å

Enthalpy of Formation

Jordan[1] estimated the dissociation energy of PH(g) as 70.44 kcal·mol^{-1} using a semiempirical theoretical method. The corresponding value for the enthalpy of formation $\Delta_f H°(298.15\ K)$ is 60.6 ± 8 kcal·mol^{-1}.

Heat Capacity and Entropy

Jordan[1] predicted five electronic levels ($X^3\Sigma$, $A^1\Delta$, $B^1\Sigma$, $D^1\Pi$, $E^1\Sigma$) based on the reported value[2] of 29560 cm^{-1} for the $C^3\Pi$ level (this level is designated $A^3\Pi$ by Herzberg.[2] Several qualitative spectroscopic investigations of PH(g) have been reported and are in general accord with the predictions of Jordan.[1] Ishaq and Pearse[3] reported the values of the rotational constant B_e and the fundamental vibrational frequency ω_e. The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The value of the anharmonic vibrational term $\omega_e x_e$ is estimated from the relation $\omega_e x_e = \omega_e^2/(4D° + 2\omega_e)$.

References

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[2]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−8.650	234.555	234.555	INFINITE
100	29.117	164.523	222.248	−5.773	235.045	225.398	−117.736
200	29.130	184.709	199.010	−2.860	234.347	215.772	−56.354
250	29.140	191.210	196.824	−1.404	234.014	211.165	−44.120
298.15	29.162	196.344	196.344	.000	233.611	206.799	−36.230
300	29.163	196.525	196.345	.054	233.594	206.633	−35.978
350	29.217	201.024	196.700	1.513	232.393	202.248	−30.184
400	29.321	204.931	197.490	2.977	231.812	197.981	−25.854
450	29.485	208.394	198.513	4.446	231.235	193.787	−22.494
500	29.709	211.511	199.659	5.926	230.667	189.657	−19.813
600	30.302	216.978	202.102	8.925	229.569	181.559	−15.806
700	31.008	221.701	204.572	11.990	228.533	173.640	−12.957
800	31.742	225.889	206.980	15.128	227.561	165.865	−10.830
900	32.452	229.669	209.294	18.338	226.652	158.208	−9.182
1000	33.111	233.123	211.507	21.616	225.796	150.650	−7.869
1100	33.713	236.308	213.619	24.958	224.985	143.174	−6.799
1200	34.260	239.265	215.634	28.357	160.641	136.850	−5.957
1300	34.759	242.027	217.559	31.808	160.674	134.866	−5.419
1400	35.218	244.620	219.400	35.308	160.728	132.879	−4.958
1500	35.645	247.065	221.164	38.851	160.801	130.887	−4.558
1600	36.046	249.378	222.856	42.436	160.890	128.890	−4.208
1700	36.424	251.575	224.481	46.059	160.993	126.887	−3.899
1800	36.785	253.667	226.045	49.720	161.110	124.878	−3.624
1900	37.131	255.665	227.552	53.416	161.241	122.861	−3.378
2000	37.463	257.578	229.005	57.146	161.385	120.838	−3.156
2100	37.783	259.414	230.410	60.908	161.541	118.807	−2.955
2200	38.090	261.179	231.769	64.702	161.710	116.768	−2.772
2300	38.387	262.878	233.085	68.526	161.891	114.721	−2.605
2400	38.672	264.518	234.360	72.379	162.084	112.666	−2.452
2500	38.947	266.103	235.599	76.260	162.289	110.603	−2.311
2600	39.212	267.635	236.801	80.168	162.506	108.531	−2.180
2700	39.466	269.120	237.971	84.102	162.733	106.451	−2.059
2800	39.709	270.560	239.109	88.061	162.972	104.362	−1.947
2900	39.943	271.957	240.218	92.043	163.220	102.264	−1.842
3000	40.167	273.315	241.299	96.049	163.479	100.158	−1.744
3100	40.382	274.636	242.353	100.077	163.746	98.043	−1.652
3200	40.588	275.921	243.382	104.125	164.022	95.919	−1.566
3300	40.785	277.173	244.387	108.194	164.306	93.786	−1.485
3400	40.973	278.393	245.369	112.282	164.598	91.645	−1.408
3500	41.154	279.584	246.330	116.388	164.896	89.495	−1.336
3600	41.328	280.746	247.270	120.512	165.201	87.336	−1.267
3700	41.494	281.880	248.190	124.654	165.511	85.169	−1.202
3800	41.654	282.989	249.091	128.811	165.827	82.994	−1.141
3900	41.808	284.073	249.974	132.984	166.148	80.810	−1.082
4000	41.956	285.133	250.840	137.172	166.473	78.617	−1.027
4100	42.098	286.171	251.689	141.375	166.802	76.417	−.974
4200	42.237	287.187	252.522	145.592	167.134	74.208	−.923
4300	42.370	288.183	253.340	149.822	167.470	71.992	−.875
4400	42.500	289.158	254.143	154.066	167.809	69.768	−.828
4500	42.627	290.115	254.932	158.322	168.151	67.535	−.784
4600	42.750	291.053	255.707	162.591	168.495	65.296	−.741
4700	42.870	291.974	256.469	166.872	168.842	63.049	−.701
4800	42.988	292.877	257.218	171.165	169.191	60.794	−.662
4900	43.104	293.765	257.955	175.470	169.543	58.532	−.624
5000	43.218	294.637	258.680	179.786	169.897	56.263	−.588
5100	43.331	295.494	259.393	184.113	170.254	53.987	−.553
5200	43.442	296.336	260.096	188.452	170.613	51.704	−.519
5300	43.552	297.165	260.787	192.802	170.976	49.413	−.487
5400	43.661	297.980	261.468	197.162	171.342	47.116	−.456
5500	43.770	298.782	262.140	201.534	171.711	44.812	−.426
5600	43.878	299.572	262.801	205.916	172.085	42.502	−.396
5700	43.985	300.349	263.453	210.309	172.462	40.185	−.368
5800	44.092	301.115	264.096	214.713	172.844	37.861	−.341
5900	44.199	301.870	264.730	219.128	173.232	35.530	−.315
6000	44.307	302.614	265.355	223.553	173.625	33.193	−.289

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = 220.756\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 238.62 \pm 19.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 236.19 \pm 19.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_{1/2}$	0	2
$^2\Pi_{3/2}$	[8000]	2

$\omega_e = 1564.1\ cm^{-1}$ $\omega_e x_e = 29.75\ cm^{-1}$ $\sigma = 1$
$B_e = 4.971\ cm^{-1}$ $\alpha_e = 0.144\ cm^{-1}$ $r_e = 1.8388$ Å

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from the dissociation energy of PbH(g) reported by Gaydon.[1]

Heat Capacity and Entropy

Ground state configuration and spectroscopic data were obtained from Herzberg.[2] Electronic levels and multiplicity were estimated by comparison with those for PbF(g).

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.678	238.620	238.620	INFINITE
100	29.121	188.877	246.747	−5.787	238.246	228.077	−119.135
200	29.160	209.070	223.438	−2.874	237.288	218.270	−57.006
250	29.261	215.585	221.240	−1.414	236.744	213.577	−44.624
298.15	29.476	220.756	220.756	0.	236.187	209.165	−36.645
300	29.487	220.938	220.756	0.055	236.165	208.998	−36.390
350	29.847	225.509	221.116	1.537	235.570	204.517	−30.522
400	30.311	229.524	221.921	3.041	234.970	200.121	−26.133
450	30.836	233.124	222.969	4.569	234.371	195.801	−22.728
500	31.384	236.401	224.151	6.125	233.778	191.548	−20.011
600	32.448	242.218	226.690	9.317	232.617	183.211	−15.950
700	33.390	247.293	229.278	12.610	226.619	175.865	−13.123
800	34.184	251.805	231.817	15.990	225.506	168.692	−11.014
900	34.846	255.871	234.267	19.443	224.486	161.652	−9.382
1000	35.400	259.571	236.616	22.956	223.542	154.722	−8.082
1100	35.872	262.968	238.859	26.520	222.662	147.883	−7.022
1200	36.285	266.107	241.001	30.128	221.837	141.122	−6.143
1300	36.656	269.027	243.045	33.776	221.054	134.427	−5.401
1400	36.999	271.756	245.000	37.459	220.292	127.792	−4.768
1500	37.326	274.320	246.870	41.175	219.540	121.212	−4.221
1600	37.644	276.739	248.662	44.924	218.791	114.681	−3.744
1700	37.957	279.031	250.381	48.704	218.038	108.197	−3.324
1800	38.267	281.209	252.034	52.515	217.281	101.757	−2.953
1900	38.577	283.286	253.625	56.357	216.517	95.360	−2.622
2000	38.886	285.273	255.158	60.230	215.745	89.003	−2.325
2100	39.194	287.178	256.637	64.134	37.745	89.801	−2.234
2200	39.499	289.008	258.067	68.069	37.347	92.288	−2.191
2300	39.800	290.770	259.451	72.034	36.876	94.796	−2.153
2400	40.096	292.471	260.792	76.029	36.328	97.326	−2.118
2500	40.386	294.113	262.092	80.053	35.704	99.880	−2.087
2600	40.667	295.703	263.354	84.106	35.005	102.461	−2.058
2700	40.940	297.243	264.581	88.186	34.232	105.069	−2.033
2800	41.203	298.736	265.774	92.293	33.388	107.708	−2.009
2900	41.456	300.187	266.936	96.426	32.478	110.378	−1.988
3000	41.698	301.596	268.068	100.584	31.507	113.081	−1.969
3100	41.929	302.967	269.172	104.766	30.479	115.817	−1.952
3200	42.149	304.302	270.249	108.970	29.401	118.587	−1.936
3300	42.357	305.602	271.301	113.195	28.279	121.391	−1.921
3400	42.554	306.870	272.328	117.441	27.118	124.230	−1.909
3500	42.739	308.106	273.333	121.705	25.925	127.104	−1.897
3600	42.914	309.312	274.316	125.988	24.705	130.012	−1.886
3700	43.079	310.490	275.277	130.288	23.465	132.954	−1.877
3800	43.233	311.641	276.219	134.604	22.209	135.930	−1.868
3900	43.378	312.766	277.142	138.934	20.942	138.939	−1.861
4000	43.513	313.866	278.046	143.279	19.670	141.981	−1.854
4100	43.640	314.942	278.933	147.637	18.395	145.054	−1.848
4200	43.759	315.995	279.803	152.007	17.121	148.159	−1.843
4300	43.870	317.026	280.657	156.388	15.852	151.294	−1.838
4400	43.973	318.036	281.495	160.780	14.591	154.458	−1.834
4500	44.070	319.025	282.318	165.183	13.340	157.651	−1.830
4600	44.161	319.995	283.127	169.594	12.100	160.872	−1.827
4700	44.246	320.945	283.921	174.014	10.875	164.119	−1.824
4800	44.325	321.878	284.702	178.443	9.664	167.393	−1.822
4900	44.400	322.793	285.470	182.879	8.470	170.691	−1.820
5000	44.470	323.690	286.226	187.323	7.293	174.014	−1.818
5100	44.536	324.572	286.969	191.773	6.133	177.359	−1.817
5200	44.598	325.437	287.700	196.230	4.991	180.728	−1.815
5300	44.657	326.287	288.420	200.693	3.867	184.118	−1.815
5400	44.712	327.122	289.129	205.161	2.762	187.530	−1.814
5500	44.765	327.943	289.828	209.635	1.675	190.961	−1.814
5600	44.815	328.750	290.516	214.114	0.606	194.413	−1.813
5700	44.863	329.544	291.193	218.598	−0.445	197.883	−1.813
5800	44.909	330.325	291.861	223.087	−1.480	201.371	−1.814
5900	44.953	331.093	292.520	227.580	−2.496	204.877	−1.814
6000	44.995	331.849	293.169	232.077	−3.496	208.400	−1.814

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 195.628 \pm 0.04\ J\cdot K^{-1}\cdot mol^{-1}$[(*)]

$\Delta_f H°(0\ K) = 136.49 \pm 5.0\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 139.33 \pm 5.0\ kJ\cdot mol^{-1}$

State	Electronic States and Molecular Constants (σ = 1)						
	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	β_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_i$	0	2	2689.6	45.5	9.601	0.285	1.345
	377.01	2					
$A^2\Sigma^+$	30663	2	1979.8	97.65	8.521	0.464	1.423
$B^2\Sigma$	59622	2	2670.6	56.8	8.785	0.259	1.428
$C^2\Delta$	[63900]	4					
$D^2\Delta$	71195	4					
$E^2\Sigma$	71318	2					
$F^2\Delta$	76708	4	[2689.6]	[45.5]	[9.601]	[0.285]	
$G^2\Delta$	79343	4					
$H^2\Delta$	80848	4					

Enthalpy of Formation

The previous JANAF[1] selection for $\Delta_f H°$(HS, g, 298.15 K) was Mackle's[2] estimate of 34.6 ± 4 kcal·mol^{-1} which he derived from the average of three independent determinations. Of these, the uncertainty can be reduced in the determination involving the calculation of $\Delta H_f°$(HS, g, 298.15 K) from $\Delta_f H°(H_2S, g, 298.15\ K)$, the ionization potential of HS(g), and the appearance potential of HS^+(g) from H_2S(g). A summary of previous work on the ionization potential is given below. From the spectroscopic and photoionization work we arrive at a value of $\Delta_f H°(0\ K)$ for the reaction $H_2S(g) = HS(g) + H(g)$ of 89.02 ± 1.5 kcal·mol^{-1}. Using the appropriate thermal functions for each of the species (see tables for H_2S(g), HS(g), and H(g)[1]) and the selected enthalpies of formation of H_2S(g) of −4.90 ± 2 kcal·mol^{-1} (see H_2S(g) table[1]) and H(g) of 52.103 ± 0.001 kcal·mol^{-1},[8] one obtains 33.3 ± 1.2 kcal·mol^{-1} for $\Delta_f H°$(HS, g, 298.15 K) versus Mackle's[2] values of 33.7 ± 3 kcal·mol^{-1} for this determination. The new value is preferred because it is based on photoionization rather than electron impact studies.

Source	Method	Potential(eV)
$HS(g) \rightarrow HS^+(g) + e^-(g)$:		
Morrow[3]	Rydberg Extrapolation	10.40 ± 0.03
Palmer and Loosing[4]	Electron Impact	10.5 ± 0.1
$H_2S(g) \rightarrow HS^+(g) + H(g) + e^-(g)$		
Dibeler and Liston[5]	Photoionization	14.27 ± 0.04[†]
Dibeler and Rosenstock[6]	Electron Impact	14.43 ± 0.1
Palmer and Lossing[4]	Electron Impact	14.43 ± 0.1
Neuert and Clasen[7]	Electron Impact	15.2 ± 0.5

[†]The uncertainty given by the authors was doubled because the threshold value was not corrected to absolute zero.

Heat Capacity and Entropy*

Calculations were made using the vibrational and rotational constants for the respective electronic levels from Rosen.[12] Comparison of the results of the more exact treatment of Haar *et al.*[13] with those given in the previous JANAF[1] calculations (both used the same molecular constants for the ground state) suggests errors in our calculations are negligible above 400 K. Below this, they can be appreciable. In particular, it is recommended that 0.045 kcal·mol^{-1}, 0.012 cal·K^{-1}·mol^{-1} and −0.028 cal·K^{-1}·mol^{-1} be added to our values of $H°(0\ K) - H°(298.5\ K)$, $S°(298.15\ K)$, and $C_p°(298.15\ K)$. These errors result from dealing with the ground state ($X^2\Pi_i$) as two separate electronic states separated by 377.01 cm^{-1}.

The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$. The National Bureau of Standards prepared this table[9] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[9] we recalculate the table in terms of 1973 fundamental constants,[10] 1975 atomic weights[11] and current JANAF reference states for the elements.

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Continued on page 1359

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.273	136.493	136.493	INFINITE
90	30.185	160.686	224.496	−6.381	137.541	127.135	−66.409
200	32.697	182.575	198.614	−3.208	138.547	116.337	−30.384
250	32.734	189.885	196.164	−1.570	138.977	110.733	−23.136
298.15	32.447	195.628	195.628	0.	139.327	105.260	−18.441
300	32.434	195.829	195.629	0.060	139.340	105.049	−18.291
350	32.052	200.800	196.022	1.672	139.644	99.309	−14.821
400	31.707	205.057	196.892	3.266	138.794	93.573	−12.219
450	31.446	208.775	198.010	4.844	138.679	87.922	−10.206
500	31.283	212.079	199.255	6.412	138.515	82.293	−8.597
600	31.228	217.773	201.881	9.535	138.381	71.064	−6.187
700	31.452	222.601	204.505	12.667	138.370	59.846	−4.466
800	31.844	226.825	207.036	15.831	138.452	48.624	−3.175
900	32.318	230.602	209.448	19.039	112.044	37.927	−2.201
1000	32.814	234.033	211.738	22.295	112.871	29.648	−1.549
1100	33.301	237.184	213.910	25.601	113.722	21.284	−1.011
1200	33.761	240.101	215.972	28.955	114.592	12.843	−0.559
1300	34.185	242.820	217.934	32.352	115.478	4.328	−0.174
1400	34.571	245.368	219.804	35.790	116.376	−4.256	0.159
1500	34.922	247.765	221.589	39.265	117.280	−12.904	0.449
1600	35.239	250.030	223.296	42.774	118.188	−21.613	0.706
1700	35.526	252.175	224.932	46.312	119.099	−30.378	0.933
1800	35.786	254.213	226.503	49.878	120.009	−39.197	1.137
1900	36.021	256.154	228.013	53.468	120.919	−48.067	1.321
2000	36.236	258.007	229.467	57.081	121.826	−56.984	1.488
2100	36.432	259.780	230.868	60.715	122.731	−65.947	1.640
2200	36.611	261.479	232.221	64.367	123.632	−74.953	1.780
2300	36.777	263.110	233.529	68.037	124.530	−83.999	1.908
2400	36.930	264.679	234.794	71.722	125.425	−93.085	2.026
2500	37.072	266.189	236.020	75.422	126.316	−102.208	2.136
2600	37.205	267.646	237.209	79.136	127.203	−111.366	2.237
2700	37.329	269.052	238.362	82.863	128.086	−120.559	2.332
2800	37.445	270.412	239.483	86.602	128.967	−129.784	2.421
2900	37.555	271.728	240.572	90.352	129.843	−139.041	2.504
3000	37.659	273.003	241.632	94.113	130.716	−148.327	2.583
3100	37.758	274.239	242.664	97.883	131.585	−157.643	2.656
3200	37.852	275.439	243.669	101.664	132.451	−166.987	2.726
3300	37.942	276.606	244.650	105.454	133.313	−176.358	2.792
3400	38.028	277.740	245.607	109.252	134.171	−185.755	2.854
3500	38.112	278.843	246.540	113.059	135.025	−195.177	2.913
3600	38.192	279.918	247.453	116.874	135.876	−204.623	2.969
3700	38.270	280.965	248.344	120.698	136.722	−214.093	3.022
3800	38.346	281.987	249.216	124.528	137.565	−223.586	3.073
3900	38.420	282.984	250.069	128.367	138.403	−233.101	3.122
4000	38.492	283.958	250.905	132.212	139.237	−242.637	3.169
4100	38.564	284.909	251.722	136.065	140.066	−252.194	3.213
4200	38.634	285.839	252.524	139.925	140.890	−261.771	3.256
4300	38.703	286.749	253.309	143.792	141.710	−271.368	3.296
4400	38.772	287.640	254.079	147.666	142.526	−280.984	3.336
4500	38.841	288.512	254.835	151.546	143.336	−290.619	3.373
4600	38.909	289.366	255.576	155.434	144.142	−300.271	3.410
4700	38.977	290.204	256.304	159.328	144.943	−309.941	3.445
4800	39.045	291.025	257.019	163.229	145.740	−319.627	3.478
4900	39.114	291.831	257.721	167.137	146.533	−329.331	3.511
5000	39.183	292.622	258.411	171.052	147.321	−339.050	3.542
5100	39.253	293.398	259.090	174.974	148.106	−348.786	3.572
5200	39.323	294.161	259.757	178.902	148.886	−358.536	3.602
5300	39.394	294.911	260.413	182.838	149.664	−368.302	3.630
5400	39.466	295.648	261.059	186.781	150.438	−378.082	3.657
5500	39.539	296.373	261.694	190.732	151.210	−387.877	3.684
5600	39.614	297.086	262.320	194.689	151.980	−397.685	3.709
5700	39.689	297.788	262.936	198.654	152.748	−407.507	3.734
5800	39.766	298.478	263.543	202.627	153.516	−417.343	3.759
5900	39.844	299.159	264.141	206.608	154.283	−427.192	3.782
6000	39.924	299.829	264.730	210.596	155.050	−437.054	3.805

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 198.040 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 374.89 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 376.66 \pm 8.4\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights			
State	ϵ_i, cm^{-1}	g_i	Ref
$A\ ^2\Pi$	0	2	1
	142.83	2	1
$^4\Sigma^-$	[21510]	4	2
$A\ ^2\Delta$	24193.04	4	1
$^2\Sigma^-$	[24730]	2	2
$C\ ^2\Sigma^+$	31899.8	2	3
$B\ ^2\Sigma^+$	31909.7	2	3
$D\ ^2\Delta$	48510.11	4	1
$E\ ^2\Sigma^+$	52399.19	2	1

$\omega_e = 2041.80\ cm^{-1}$ $\omega_e x_e = 35.51\ cm^{-1}$ $\sigma = 1$
$B_e = 7.4996\ cm^{-1}$ $\alpha_e = 0.2190\ cm^{-1}$ $r_e = 1.5201$ Å

Enthalpy of Formation

Verma[4] has derived an upper limit for the dissociation energy of 24680 cm^{-1} (70.6 $kcal·mol^{-1}$) from predissociation in the $B\ ^2\Sigma^+$ state. Hildenbrand[5] has applied an ionic–covalent correction to the linear Birge–Sponer extrapolation and obtained $D_0^\circ = 70\ kcal·mol^{-1}$. Rao and Lakshman[6] have estimated the ground state dissociation energy of 24040 cm^{-1} (68.7 $kcal·mol^{-1}$) from an evaluation of the potential energy curves and Franck–Condon factors. This last number, $D_0^\circ = 68.7\ kcal·mol^{-1}$, is adopted and may be compared with the average per-bond atomization energy of SiH_4(g) of 75.7 $kcal·mol^{-1}$. The $D_0^\circ/\Delta_{at}H°(0\ K)$ ratio is 0.227. For SiF/SiF the ratio is 0.230, for SiCl/$SiCl_4$ it is 0.233 and for SiI/SiI_4 it is 0.245.[7] The adopted D_0° and JANAF auxiliary data[7] lead to $\Delta_f H°(0\ K) = 89.6\ kcal·mol^{-1}$. The allowed error of ±2 $kcal·mol^{-1}$ includes the upper limit value of D_0°.

Heat Capacity and Entropy

The observed and estimated electronic levels are taken from Herzberg *et al.*,[1] Jordan,[2] and Bollmark *et al.*[3] as indicated. Wirsam's[8] ab initio self-consistent-field and configuration-interaction calculations predicted the electronic level for the $^4\Sigma^-$ state at 6430 and 8275 cm^{-1} respectively. Substitution of 6430 cm^{-1} for the adopted Jordan estimate of 21510 cm^{-1} increases the derived entropy starting near 700 K; at 6000 K, the entropy is 0.85 $cal·K^{-1}·mol^{-1}$ higher.

The rotational and vibrational constants are those selected by Rosen.[9] The ground state is treated as two distinct levels because of the splitting of the ground state as expressed by the spin coupling constant ($A = 142.83\ cm^{-1}$). This approximation gives slightly biased results at lower temperatures which are allowed for in the ±0.05 $cal·K^{-1}·mol^{-1}$ error assigned to $S°(298.15\ K)$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.227	374.886	374.886	INFINITE
100	32.654	163.854	225.373	−6.152	376.196	365.230	−190.776
200	30.840	185.896	200.810	−2.983	376.839	353.934	−92.438
250	30.349	192.720	198.537	−1.454	376.819	348.206	−72.754
298.15	30.088	198.040	198.040	0.	376.662	342.708	−60.041
300	30.082	198.226	198.041	0.056	376.654	342.497	−59.634
350	29.989	202.855	198.407	1.557	376.395	336.824	−50.268
400	30.043	206.861	199.219	3.057	376.080	331.192	−43.249
450	30.216	210.409	200.269	4.563	375.732	325.602	−37.795
500	30.480	213.605	201.445	6.080	375.364	320.051	−33.436
600	31.174	219.221	203.952	9.162	374.605	309.060	−26.906
700	31.950	224.085	206.488	12.318	373.844	298.196	−22.252
800	32.707	228.401	208.963	15.551	373.092	287.440	−18.768
900	33.400	232.294	211.342	18.857	372.349	276.778	−16.064
1000	34.013	235.846	213.618	22.228	371.608	266.199	−13.905
1100	34.549	239.113	215.789	25.657	370.861	255.694	−12.142
1200	35.015	242.140	217.860	29.136	370.102	245.258	−10.676
1300	35.420	244.959	219.838	32.658	369.323	234.886	−9.438
1400	35.774	247.597	221.727	36.218	368.519	224.574	−8.379
1500	36.084	250.076	223.535	39.811	367.684	214.321	−7.463
1600	36.359	252.414	225.268	43.434	366.815	204.125	−6.664
1700	36.603	254.626	226.930	47.082	315.731	194.432	−5.974
1800	36.822	256.724	228.528	50.753	315.016	187.317	−5.436
1900	37.020	258.720	230.065	54.446	314.303	180.242	−4.955
2000	37.201	260.624	231.545	58.157	313.589	173.205	−4.524
2100	37.366	262.443	232.974	61.885	312.875	166.203	−4.134
2200	37.519	264.185	234.353	65.630	312.161	159.235	−3.781
2300	37.661	265.856	235.687	69.389	311.445	152.300	−3.459
2400	37.794	267.461	236.977	73.162	310.727	145.396	−3.164
2500	37.920	269.007	238.228	76.947	310.008	138.522	−2.894
2600	38.040	270.496	239.441	80.745	309.288	131.677	−2.645
2700	38.156	271.934	240.618	84.555	308.566	124.860	−2.416
2800	38.268	273.324	241.761	88.376	307.843	118.069	−2.203
2900	38.377	274.669	242.873	92.209	307.119	111.304	−2.005
3000	38.485	275.972	243.954	96.052	306.394	104.564	−1.821
3100	38.592	277.235	245.008	99.906	305.668	97.848	−1.649
3200	38.699	278.462	246.034	103.770	304.942	91.156	−1.488
3300	38.806	279.655	247.035	107.645	304.216	84.487	−1.337
3400	38.916	280.815	248.011	111.531	303.490	77.839	−1.196
3500	39.027	281.944	248.965	115.429	302.765	71.213	−1.063
3600	39.142	283.045	249.896	119.337	−82.110	75.068	−1.089
3700	39.259	284.119	250.807	123.257	−82.418	79.438	−1.121
3800	39.380	285.168	251.697	127.189	−82.726	83.817	−1.152
3900	39.505	286.193	252.569	131.133	−83.032	88.204	−1.181
4000	39.635	287.194	253.422	135.090	−83.336	92.598	−1.209
4100	39.769	288.175	254.258	139.060	−83.637	97.000	−1.236
4200	39.908	289.135	255.077	143.044	−83.934	101.410	−1.261
4300	40.053	290.075	255.880	147.042	−84.226	105.826	−1.286
4400	40.202	290.998	256.667	151.055	−84.512	110.249	−1.309
4500	40.357	291.903	257.440	155.083	−84.792	114.679	−1.331
4600	40.518	292.792	258.199	159.126	−85.064	119.114	−1.353
4700	40.683	293.665	258.944	163.186	−85.328	123.556	−1.373
4800	40.854	294.523	259.677	167.263	−85.583	128.003	−1.393
4900	41.030	295.367	260.397	171.357	−85.829	132.455	−1.412
5000	41.212	296.198	261.104	175.469	−86.064	136.913	−1.430
5100	41.398	297.016	261.800	179.600	−86.288	141.374	−1.448
5200	41.589	297.822	262.485	183.749	−86.499	145.840	−1.465
5300	41.785	298.616	263.160	187.918	−86.699	150.310	−1.481
5400	41.985	299.399	263.824	192.106	−86.885	154.784	−1.497
5500	42.189	300.171	264.477	196.315	−87.056	159.261	−1.513
5600	42.397	300.933	265.122	200.544	−87.213	163.741	−1.527
5700	42.608	301.685	265.757	204.794	−87.355	168.223	−1.542
5800	42.823	302.428	266.382	209.066	−87.482	172.709	−1.555
5900	43.041	303.162	267.000	213.359	−87.592	177.195	−1.569
6000	43.262	303.887	267.608	217.674	−87.686	181.684	−1.582

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 186.789 \pm 0.004\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1140.27 \pm 11.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 1147.67 \pm 11.3\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$A^1\Pi$	25025.2	2

$\omega_e = 2157.1\ cm^{-1}$ $\omega_e x_e = 34.21\ cm^{-1}$ $\sigma = 1$

$B_e = 7.6603\ cm^{-1}$ $\alpha_e = 0.2096\ cm^{-1}$ $r_e = 1.499$ Å

Enthalpy of Formation

According to Douglas and Lutz[1] the A state must have an extremely shallow potential curve since the observed first vibrational quantum is only $\Delta_{1/2}G' = 390.2\ cm^{-1}$. Since no other levels were observed they estimated ω_e' and $\omega_e x_e'$ for the A state from $\Delta_{1/2}G'$, α_e' and B_e'. From the estimated ω_e' and $\omega_e x_e'$ they obtained a dissociation limit of 1180 cm^{-1}. Thus, the dissociation limit of the A state is likely to lie between 390 and 1180 cm^{-1}, on this basis Douglas and Lutz select 780 ± 600 cm^{-1}. Since SiH⁺ can correlate with normal products $Si^+(^2P)$ and $H(^2S)$ in both the X and A states these are assumed to be the products. Thus, the dissociation energy of the ground state to these 294.626 ± 1.0 $kcal \cdot mol^{-1}$[2] we obtain $\Delta_f H°(SiH^+, g) = 272.5 \pm 2.7\ kcal \cdot mol^{-1}$, which is adopted. This gives an ionization potential of 182.9 $kcal \cdot mol^{-1}$ (7.93 eV) with the JANAF value for SiH.[2]

Heat Capacity and Entropy

The electronic levels and vibrational and rotational constants are all from Douglas and Lutz.[1]

References

[1]A. E. Douglas and B. L. Lutz, Can. J. Phys. **48**, 247 (1970).
[2]JANAF Thermochemical Tables; H(g) 9-30-65; Si(g) 3-31-67; SiH(g) 12-31-69; Si^+(g) 12-31-71.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.654	1140.271		
100	29.118	154.962	212.699	−5.774			
200	29.133	175.150	189.456	−2.861			
250	29.148	181.652	187.269	−1.404			
298.15	29.184	186.789	186.789	0.	1147.671	1110.818	−194.611
300	29.186	186.969	186.789	0.054	1147.700	1110.589	−193.371
350	29.273	191.474	187.145	1.515	1148.441	1104.344	−164.814
400	29.427	195.392	187.936	2.982	1149.132	1097.997	−143.384
450	29.652	198.870	188.961	4.459	1149.794	1091.565	−126.706
500	29.941	202.009	190.112	5.949	1150.438	1085.060	−113.355
600	30.651	207.529	192.567	8.977	1151.705	1071.866	−93.314
700	31.436	212.312	195.053	12.081	1152.971	1058.459	−78.983
800	32.208	216.561	197.481	15.264	1154.247	1044.871	−68.223
900	32.922	220.396	199.817	18.521	1155.533	1031.122	−59.845
1000	33.560	223.899	202.053	21.846	1156.823	1017.229	−53.135
1100	34.121	227.124	204.187	25.230	1158.111	1003.207	−47.638
1200	34.611	230.114	206.225	28.668	1159.389	989.068	−43.053
1300	35.039	232.902	208.171	32.151	1160.650	974.824	−39.169
1400	35.413	235.513	210.032	35.674	1161.887	960.483	−35.836
1500	35.741	237.967	211.813	39.232	1163.095	946.054	−32.945
1600	36.031	240.284	213.521	42.820	1164.271	931.546	−30.412
1700	36.288	242.476	215.160	46.437	1115.234	917.413	−28.189
1800	36.518	244.557	216.736	50.077	1116.567	905.738	−26.284
1900	36.725	246.537	218.253	53.739	1117.902	893.989	−24.577
2000	36.912	248.425	219.714	57.421	1119.238	882.169	−23.040
2100	37.083	250.230	221.125	61.121	1120.574	870.283	−21.647
2200	37.240	251.959	222.487	64.838	1121.910	858.333	−20.379
2300	37.385	253.618	223.805	68.569	1123.245	846.322	−19.221
2400	37.520	255.212	225.081	72.314	1124.579	834.254	−18.157
2500	37.646	256.746	226.317	76.073	1125.911	822.130	−17.177
2600	37.764	258.225	227.516	79.843	1127.242	809.952	−16.272
2700	37.876	259.652	228.680	83.625	1128.571	797.723	−15.433
2800	37.983	261.032	229.811	87.418	1129.898	785.445	−14.653
2900	38.085	262.366	230.910	91.222	1131.223	773.120	−13.925
3000	38.184	263.659	231.981	95.035	1132.547	760.749	−13.246
3100	38.280	264.913	233.023	98.859	1133.870	748.334	−12.609
3200	38.374	266.130	234.038	102.691	1135.190	735.876	−12.012
3300	38.467	267.312	235.029	106.533	1136.510	723.377	−11.450
3400	38.558	268.461	235.995	110.385	1137.828	710.838	−10.921
3500	38.649	269.581	236.939	114.245	1139.145	698.261	−10.421
3600	38.740	270.671	237.861	118.114	756.309	696.106	−10.100
3700	38.832	271.733	238.762	121.993	758.038	694.410	−9.803
3800	38.925	272.770	239.644	125.881	759.765	692.667	−9.521
3900	39.019	273.782	240.506	129.778	761.491	690.879	−9.253
4000	39.115	274.771	241.350	133.685	763.215	689.046	−8.998
4100	39.213	275.739	242.177	137.601	764.939	687.171	−8.755
4200	39.314	276.685	242.988	141.528	766.663	685.253	−8.522
4300	39.416	277.611	243.782	145.464	768.389	683.295	−8.300
4400	39.522	278.518	244.561	149.411	770.115	681.296	−8.088
4500	39.630	279.408	245.326	153.369	771.844	679.258	−7.885
4600	39.741	280.280	246.076	157.337	773.575	677.181	−7.690
4700	39.855	281.136	246.813	161.317	775.309	675.067	−7.503
4800	39.973	281.976	247.537	165.308	777.047	672.916	−7.323
4900	40.093	282.802	248.248	169.311	778.789	670.728	−7.150
5000	40.216	283.613	248.947	173.327	780.536	668.505	−6.984
5100	40.343	284.410	249.635	177.355	782.288	666.247	−6.824
5200	40.472	285.195	250.311	181.396	784.047	663.955	−6.670
5300	40.605	285.967	250.977	185.449	785.811	661.629	−6.521
5400	40.740	286.727	251.632	189.517	787.583	659.269	−6.377
5500	40.879	287.476	252.277	193.598	789.362	656.876	−6.238
5600	41.019	288.214	252.912	197.692	791.149	654.451	−6.104
5700	41.163	288.941	253.538	201.802	792.944	651.994	−5.975
5800	41.308	289.659	254.154	205.925	794.748	649.506	−5.849
5900	41.456	290.366	254.762	210.063	796.561	646.986	−5.728
6000	41.606	291.064	255.361	214.216	798.385	644.435	−5.610

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K)$ = [216.158] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [517.346] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [516.306] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
[$^2\Pi$]	0	[4]

ω_e = [1400] cm^{-1} $\omega_e x_e$ = [19] cm^{-1} σ = 1
B_e = [5.1] cm^{-1} α_e = [0.09] cm^{-1} r_e = [1.821] Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as 123.7 $kcal·mol^{-1}$ by Gordon.[1] $\Delta_f H°(298.15\ K)$ is then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] r_e is calculated from the relationship $r_e = (16.858778/\mu B_e)^{1/2}$ Å.

Reference

[1] J. S. Gordon, Astrosystems International, personal communication, (January 10, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.690	517.346	517.346	INFINITE
100	29.126	184.229	242.222	−5.799	517.851	505.870	−264.240
200	29.195	204.430	218.853	−2.885	517.226	494.091	−129.043
250	29.368	210.961	216.645	−1.421	516.775	488.359	−102.037
298.15	29.687	216.158	216.158	0.	516.306	482.928	−84.607
300	29.702	216.342	216.159	0.055	516.287	482.721	−84.049
350	30.178	220.955	216.522	1.551	515.788	477.166	−71.213
400	30.741	225.021	217.335	3.074	515.294	471.682	−61.595
450	31.338	228.676	218.396	4.626	514.811	466.260	−54.122
500	31.930	232.008	219.593	6.208	514.342	460.891	−48.149
600	33.015	237.928	222.168	9.457	513.435	450.286	−39.201
700	33.923	243.088	224.795	12.805	512.548	439.832	−32.821
800	34.661	247.668	227.374	16.236	511.652	429.505	−28.044
900	35.258	251.786	229.861	19.732	510.714	419.292	−24.335
1000	35.743	255.527	232.244	23.283	509.707	409.187	−21.374
1100	36.143	258.953	234.518	26.878	508.611	399.187	−18.956
1200	36.478	262.113	236.688	30.510	503.702	389.513	−16.955
1300	36.762	265.044	238.758	34.172	502.935	380.029	−15.270
1400	37.007	267.778	240.734	37.861	502.131	370.604	−13.827
1500	37.221	270.338	242.623	41.573	501.276	361.239	−12.579
1600	37.411	272.747	244.431	45.304	500.355	351.933	−11.489
1700	37.581	275.020	246.164	49.054	499.357	342.686	−10.529
1800	37.735	277.172	247.828	52.820	498.270	333.501	−9.678
1900	37.876	279.216	249.426	56.601	497.084	324.379	−8.918
2000	38.006	281.162	250.965	60.395	495.786	315.323	−8.235
2100	38.127	283.020	252.448	64.202	494.367	306.334	−7.620
2200	38.242	284.796	253.878	68.020	471.493	298.161	−7.079
2300	38.350	286.498	255.259	71.850	469.383	290.330	−6.594
2400	38.452	288.133	256.595	75.690	467.268	282.590	−6.150
2500	38.551	289.704	257.888	79.540	465.149	274.939	−5.745
2600	38.645	291.218	259.141	83.400	463.026	267.373	−5.372
2700	38.736	292.678	260.357	87.269	460.899	259.888	−5.028
2800	38.824	294.089	261.536	91.147	458.769	252.482	−4.710
2900	38.910	295.453	262.682	95.034	456.634	245.152	−4.416
3000	38.993	296.773	263.797	98.929	454.497	237.896	−4.142
3100	39.075	298.053	264.881	102.832	452.356	230.711	−3.887
3200	39.155	299.295	265.938	106.744	450.213	223.596	−3.650
3300	39.233	300.501	266.967	110.663	448.067	216.547	−3.428
3400	39.310	301.673	267.970	114.590	445.918	209.564	−3.220
3500	39.386	302.814	268.950	118.525	443.766	202.643	−3.024
3600	39.461	303.925	269.906	122.467	441.612	195.785	−2.841
3700	39.535	305.007	270.840	126.417	439.455	188.986	−2.668
3800	39.608	306.062	271.753	130.374	437.296	182.245	−2.505
3900	39.680	307.092	272.646	134.339	435.135	175.561	−2.351
4000	39.752	308.097	273.520	138.310	432.972	168.933	−2.206
4100	39.823	309.080	274.375	142.289	430.806	162.359	−2.068
4200	39.893	310.040	275.213	146.275	428.638	155.838	−1.938
4300	39.963	310.980	276.034	150.268	426.468	149.368	−1.814
4400	40.032	311.899	276.839	154.267	424.296	142.949	−1.697
4500	40.101	312.800	277.628	158.274	422.122	136.579	−1.585
4600	40.170	313.682	278.402	162.288	419.947	130.258	−1.479
4700	40.238	314.546	279.162	166.308	417.770	123.984	−1.378
4800	40.306	315.394	279.908	170.335	−145.346	129.373	−1.408
4900	40.373	316.226	280.641	174.369	−147.177	135.115	−1.440
5000	40.441	317.042	281.360	178.410	−149.027	140.895	−1.472
5100	40.508	317.844	282.068	182.457	−150.893	146.712	−1.503
5200	40.574	318.631	282.764	186.511	−152.774	152.566	−1.533
5300	40.641	319.405	283.448	190.572	−154.668	158.456	−1.562
5400	40.707	320.165	284.121	194.640	−156.574	164.382	−1.590
5500	40.773	320.912	284.783	198.714	−158.489	170.343	−1.618
5600	40.839	321.648	285.434	202.794	−160.413	176.339	−1.645
5700	40.905	322.371	286.076	206.882	−162.343	182.370	−1.671
5800	40.971	323.083	286.708	210.975	−164.278	188.434	−1.697
5900	41.036	323.784	287.331	215.076	−166.216	194.532	−1.722
6000	41.102	324.474	287.944	219.183	−168.156	200.663	−1.747

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

0 to 6000 K Ideal Gas

$D_0^\circ = 432.071 \pm 0.012$ kJ·mol^{-1} $\Delta_f H^\circ(0\text{ K}) = 0$ kJ·mol^{-1}

$S^\circ(298.15\text{ K}) = 130.680 \pm 0.033$ J·K^{-1}·mol^{-1} $\Delta_f H^\circ(298.15\text{ K}) = 0$ kJ·mol^{-1}

Vibrational and Rotational Levels (cm^{-1})
Direct Summation of Electronic Ground State

$E = G - G_0 + F = G - G_0 + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \sim - G - G_0 + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = J(J+1)$, $Y = v + 1/2$, and we omit subscript v on G, F, B, D, H, and L

$G = 4403.566Y - 123.8573Y^2 + 1.87269Y^3 - 0.173514Y^4 + 9.93128 \times 10^{-3}Y^5 - 4.38015 \times 10^{-4}Y^6$

$B = 60.8904 - 3.16997Y + 0.155932Y^2 - 4.60094 \times 10^{-2}Y^3 + 8.72205 \times 10^{-3}Y^4$
$-9.59207 \times 10^{-4}Y^5 + 5.31722 \times 10^{-5}Y^6 - 1.21393 \times 10^{-6}Y^7$

$D = 4.6573 \times 10^{-2} - 1.5085 \times 10^{-3}Y - 2.7385 \times 10^{-4}Y^2 + 1.0242 \times 10^{-4}Y^3 - 1.172 \times 10^{-5}Y^4 + 4.684 \times 10^{-7}Y^5$

$H = 5.224 \times 10^{-5} - 7.240 \times 10^{-6}Y + 9.619 \times 10^{-7}Y^2 - 4.838 \times 10^{-8}Y^3$

$L = 6.70 \times 10^{-8} - 1.426 \times 10^{-8}Y + 1.388 \times 10^{-9}Y^2$

$v_{max} = 14$, $J_{max} = 38 - 32v/v_{max}$

Normalized rotational statistical weights = 1/4 (even J) and 3/4 (odd J)

Ground State Configuration: $^1\Sigma_g^+$ $r_e = 0.7414$ Å

Enthalpy of Formation

Zero by definition. Refer to the monatomic hydrogen gas table for a discussion of the dissociation energy.

Heat Capacity and Entropy

These are calculated by direct summation over vibration–rotation energy levels of the electronic ground state. We performed the direct summation with an extended version of a program written by W. H. Evans and provided through cooperation of D. D. Wagman, both of the U. S. National Bureau of Standards. Contributions of excited states (T_0 >90000 cm^{-1}) are negligible at 6000 K. Polynomials G, B, D, and H are our fits of data from Stoicheff,[1] Herzberg and Howe[2] and Rank *et al.*[3,4] We estimate polynomial L such that our approximation[5,6] for the infinite series F yields high-J rotational levels in reasonable agreement with the theoretical values of Waech and Bernstein.[7] Maximum deviations in our F values are about ±400 cm^{-1}; these occur near $1 \le v \le 4$ and $29 \le J \le 36$ which is far into the extrapolated region of F. Only about one-third of the vibration–rotation levels have been observed spectroscopically and the theoretical calculations[7,6] provide the best available extrapolation to high values of J. Accuracy of the thermodynamic functions near 6000 K depends on this extrapolation and on the rotational cutoff procedure. We assume a linear approximation[5] for the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated from theoretical calculations.[7,6] We omit the nuclear-spin contribution (R ln 4) to entroy and Gibbs energy function.

We adopt ortho–para "equilibrium" H_2 as the reference state at all temperatures. The previous JANAF reference state[8] referred to "normal" H_2 (75% ortho and 25% para). Our new reference state has signficiant changes in C_p°, S° and H°(T)–H°(298.15 K) at 100 K and slight changes at 200 K. Use of "equilibrium" H_2 as a reference state was proposed on the NBS H_2 table[9] which discusses three alternatives. Preferred alternatives are either "equilibrium" H_2 or "normal" H_2. "Normal" H_2 is the form always encountered except in low-temperature generation or catalytic ortho–para equilibrium. Use of "normal" H_2 involves a possible complication, depending on the choice of zero energy for ortho–H_2. If we chose the lowest allowed level (v=0, J=1 instead of v=0, J=0), then H°(298.15 K)–H°(0 K) would be 0.254 kcal·mol^{-1} less for "normal" than for "equilibrium" H_2. This would change the difference between $\Delta_f H^\circ(0\text{ K})$ and $\Delta_f H^\circ(298.15\text{ K})$ for all species involving hydrogen.[8,10] No such change would occur if we chose the lowest level (v=0, J=0) as the energy zero for ortho–H_2. "Equilibrium" H_2 is the form which parallels most substances, i.e., those maintaining equilibrium among all rotational levels.[9]

JANAF values and uncertainties at 298.15 K are the same as those selected by CODATA.[10] Previous thermochemical tables based on direct-summation calculations of Woolley *et al.*[6] include that of Gurvich *et al.*[11] and that of NBS–JANAF.[9,8] Differences of the new JANAF values from the NBS table are greatest near 5300 K, reaching maximum of 0.005 cal·K^{-1}·mol^{-1} in S° and 0.018 kcal·mol^{-1} in H°(T)–H°(298.15 K). Differences from Gurvich *et al.* at 6000 K are 0.006 cal·K^{-1}·mol^{-1} in S° and 0.030 kcal·mol^{-1} in H°(T)–H°(298.15 K). Errors larger than these differences arise from uncertainty in extrapolation of the rotational levels.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.467	0.	0.	0.
100	28.154	100.727	155.408	−5.468	0.	0.	0.
200	27.447	119.412	133.284	−2.774	0.	0.	0.
250	28.344	125.640	131.152	−1.378	0.	0.	0.
298.15	28.836	130.680	130.680	0.	0.	0.	0.
300	28.849	130.858	130.680	0.053	0.	0.	0.
350	29.081	135.325	131.032	1.502	0.	0.	0.
400	29.181	139.216	131.817	2.959	0.	0.	0.
450	29.229	142.656	132.834	4.420	0.	0.	0.
500	29.260	145.737	133.973	5.882	0.	0.	0.
600	29.327	151.077	136.392	8.811	0.	0.	0.
700	29.441	155.606	138.822	11.749	0.	0.	0.
800	29.624	159.548	141.171	14.702	0.	0.	0.
900	29.881	163.051	143.411	17.676	0.	0.	0.
1000	30.205	166.216	145.536	20.680	0.	0.	0.
1100	30.581	169.112	147.549	23.719	0.	0.	0.
1200	30.992	171.790	149.459	26.797	0.	0.	0.
1300	31.423	174.288	151.274	29.918	0.	0.	0.
1400	31.861	176.633	153.003	33.082	0.	0.	0.
1500	32.298	178.846	154.652	36.290	0.	0.	0.
1600	32.725	180.944	156.231	39.541	0.	0.	0.
1700	33.139	182.940	157.743	42.835	0.	0.	0.
1800	33.537	184.846	159.197	46.169	0.	0.	0.
1900	33.917	186.669	160.595	49.541	0.	0.	0.
2000	34.280	188.418	161.943	52.951	0.	0.	0.
2100	34.624	190.099	163.244	56.397	0.	0.	0.
2200	34.952	191.718	164.501	59.876	0.	0.	0.
2300	35.263	193.278	165.719	63.387	0.	0.	0.
2400	35.559	194.785	166.899	66.928	0.	0.	0.
2500	35.842	196.243	168.044	70.498	0.	0.	0.
2600	36.111	197.654	169.155	74.096	0.	0.	0.
2700	36.370	199.021	170.236	77.720	0.	0.	0.
2800	36.618	200.349	171.288	81.369	0.	0.	0.
2900	36.856	201.638	172.313	85.043	0.	0.	0.
3000	37.087	202.891	173.311	88.740	0.	0.	0.
3100	37.311	204.111	174.285	92.460	0.	0.	0.
3200	37.528	205.299	175.236	96.202	0.	0.	0.
3300	37.740	206.457	176.164	99.966	0.	0.	0.
3400	37.946	207.587	177.072	103.750	0.	0.	0.
3500	38.149	208.690	177.960	107.555	0.	0.	0.
3600	38.348	209.767	178.828	111.380	0.	0.	0.
3700	38.544	210.821	179.679	115.224	0.	0.	0.
3800	38.738	211.851	180.512	119.089	0.	0.	0.
3900	38.928	212.860	181.328	122.972	0.	0.	0.
4000	39.116	213.848	182.129	126.874	0.	0.	0.
4100	39.301	214.816	182.915	130.795	0.	0.	0.
4200	39.484	215.765	183.686	134.734	0.	0.	0.
4300	39.665	216.696	184.442	138.692	0.	0.	0.
4400	39.842	217.610	185.186	142.667	0.	0.	0.
4500	40.017	218.508	185.916	146.660	0.	0.	0.
4600	40.188	219.389	186.635	150.670	0.	0.	0.
4700	40.355	220.255	187.341	154.698	0.	0.	0.
4800	40.518	221.106	188.035	158.741	0.	0.	0.
4900	40.676	221.943	188.719	162.801	0.	0.	0.
5000	40.829	222.767	189.392	166.876	0.	0.	0.
5100	40.976	223.577	190.054	170.967	0.	0.	0.
5200	41.117	224.374	190.706	175.071	0.	0.	0.
5300	41.252	225.158	191.349	179.190	0.	0.	0.
5400	41.379	225.931	191.982	183.322	0.	0.	0.
5500	41.498	226.691	192.606	187.465	0.	0.	0.
5600	41.609	227.440	193.222	191.621	0.	0.	0.
5700	41.712	228.177	193.829	195.787	0.	0.	0.
5800	41.806	228.903	194.427	199.963	0.	0.	0.
5900	41.890	229.619	195.017	204.148	0.	0.	0.
6000	41.965	230.323	195.600	208.341	0.	0.	0.

PREVIOUS: March 1961 (1 atm) CURRENT: March 1977 (1 bar)

D_0° = 255.760 ± 0.004 kJ·mol^{-1}
S°(298.15 K) = 142.370 ± 0.04 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 1488.358 ± 0.004 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = [1494.671] kJ·mol^{-1}

Vibrational and Rotational Levels (cm^{-1})
Direct Summation of Electronic Ground State

$E = G - G_0 + F = G - G_0 + BZ - DZ^2 + HZ^3 - LZ^4 + \ldots \approx G - G_0 + BZ - DZ^2 + H^2Z^3/(H+LZ)$,
where $Z = N(N+1)$, $Y = v + 1/2$, and we omit subscript v on G, F, B, D, H, and L
$G = 2323.23\ Y = 67.39\ Y^2 + 0.93\ Y^3 - 0.029\ Y^4$
$B = 29.946 - 1.594\ Y + 0.032\ Y^2 - 0.013\ Y^3$
$D = 0.01991 - 0.00087\ Y + 0.00003\ Y^2$; $H = 1.75 \times 10^{-5} - 6 \times 10^{-7}\ Y$; and $L = 1.6 \times 10^{-8}$
$v_{max} = 18$ and $N_{max} = 41.33v/v_{max}$
Normalized rotational statistical weights = 1/4 (even N) or 3/4 (odd N)

Ground State Configuration: $^2\Sigma_g^+$ $r_e = 1.057$ Å[1,13]

Enthalpy of Formation

The adopted value for the enthalpy of formation of H_2^+(g), $\Delta_f H^\circ$(0 K) = 355.727 ± 0.001 kcal·mol^{-1}, is based on the ionization potential of H_2(g) determined by Herzberg and Jungen.[1] These authors studied in high resolution absorption two Rydberg series of ortho– and para–hydrogen which converge to the $X^2\Sigma_g^+$ ground state of H_2^+(g). This ionization potential, IP = 124417.2 ± 0.4 cm^{-1} is recommended by Rosenstock[2] as the definitive value. The IP or $\Delta_f H^\circ$(0 K) value is converted to a $\Delta_f H^\circ$(298.15 K) value for H_2^+(g) by including JANAF[3] enthalpy differences, H°(0 K)–H°(298.15 K), for H_2^+(g), H_2(ref) and e$^-$(ref). $\Delta_f H^\circ$(298.15 K) should not be interpreted as a room–temperature ionization threshold due to inclusion of these enthalpies and to threshold effects noted by Rosenstock *et al.*[4]

Rosenstock *et al.*[4] had earlier recommened IP = 16.4256 eV (124418.4 cm^{-1}) based on the spectroscopic studies of Takezawa[5] and Herzberg.[6] In both studies the results were derived from extended Rydberg series. The more recent work of Herzberg and Jungen[1] provides a more accurate experimental value for the ionization potential due to the recognition of a pressure shift which was felt to be negligible in the earlier study.[6] The theroetical value, IP = 124417.3 cm^{-1}, is in excellent agreement (0.1 cm^{-1}) with our adopted value. This theoretical value, as discussed by Herzberg and Jungen,[1] is essentially the value of Hunter and Pritchard[7] with the relativistic and Lamb shift corrections of Jeziorski and Kolos[8] and the nonadiabatic correction of Bunker.[9]

Heat Capacity and Entropy

Thermodynamic functions for ortho–para "equilibrim" H_2^+ are calculated, as they were for H_2,[3] by direct summation over energy levels of the electronic ground state. We use 1973 fundamental constants[10] in an extended version of a computer program written by W. H. Evans and provided by D. D. Wagman of the U. S. National Bureau of Standards. Excited electronic states are neglected because they are either repulsive or too high lying[11] to contribute significantly. The electronic statistical weight is taken equal to the multiplicity since we neglect rotational splitting. Assumption of negligible splitting is common practice in theoretical calculation of H_2^+ energy levels[11–13] and it is justified thermodynamically by the small splitting constant.[14]

Coefficients of the energy–level polynomials are those derived from theoretical levels by Beckel *et al.*[13] New calculations[15] yield slightly different levels. The polynomials are confirmed by vibrational (v<3) and rotational (N<4) levels obtained from Rydberg spectra.[1] The value of L was derived[13] from a fit of theoretical levels with v = 0 to 14. Our adopted v_{max}, derived from the G polynomial, is one unit too low.[13,11] Limiting rotaitonal quantum numbers N_{max} are an approximation of values from theoretical calculations.[11,13] The resulting energy–level equations are very approximate near N_{max}, but they do closely reproduce thermodynamic functions[12,11] calculated directly from energy levels. More accurate equations do not signficantly improve the thermodynamic functions up to 6000 K.

We adopt functions closely reproducing those of Iorish and Yungman.[12] The effect of slightly different fundamental constants[12] is barely detectable. Our Gibbs–energy function deviates by less than 0.001 cal·K^{-1}·mol^{-1} at all temperatures. C_p°, S° and H° begin to deviate near 2000 K; differences range from +0.005 to −0.012 cal·K^{-1}·mol^{-1} in C_p°, ±0.001 cal·K^{-1}·mol^{-1} in S° and ±5 cal·K^{-1}·mol^{-1} in H°. C_p° of Patch and McBride[11] is slightly lower at 4000 to 6000 K but well within the probable uncertainty. Due to the high thermal energy (−20% of D_0° at 6000 K), C_p° depends on the number of levels included in the summation. We follow the published references[11,12] which include contributions from quasibound levels lying above D_0°. At 6000 K these levels contribute 0.42 cal·K^{-1}·mol^{-1} to C_p° and 0.05 cal·K^{-1}·mol^{-1} to the Gibbs–energy function.

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Continued on page 1359

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.583	1488.358	1488.358	INFINITE
90	27.510	110.873	168.264	−5.739	1490.282	1489.440	−778.004
200	29.175	130.698	145.046	−2.870	1492.536	1487.743	−388.559
298.15	29.288	142.370	142.370	0.	1494.671	1484.931	−260.154
300	29.292	142.551	142.371	0.054	1494.711	1484.870	−258.539
400	29.525	151.004	143.522	2.993	1496.822	1481.272	−193.434
500	30.016	157.641	145.705	5.968	1498.953	1477.139	−154.316
600	30.719	163.173	148.167	9.003	1501.138	1472.571	−128.199
700	31.529	167.968	150.661	12.115	1503.391	1467.633	−109.516
800	32.357	172.233	153.095	15.310	1505.711	1462.367	−95.483
900	33.152	176.090	155.439	18.586	1508.091	1456.807	−84.551
1000	33.887	179.622	157.684	21.938	1510.518	1450.979	−75.791
1100	34.559	182.884	159.828	25.361	1512.981	1444.906	−68.613
1200	35.168	185.917	161.877	28.848	1515.468	1438.608	−62.621
1300	35.720	188.754	163.837	32.393	1517.971	1432.102	−57.543
1400	36.226	191.420	165.713	35.990	1520.483	1425.402	−53.182
1500	36.691	193.935	167.511	39.636	1522.999	1418.523	−49.397
1600	37.123	196.317	169.238	43.327	1525.518	1411.476	−46.080
1700	37.530	198.580	170.898	47.060	1528.036	1404.271	−43.148
1800	37.918	200.737	172.496	50.833	1530.553	1396.918	−40.538
1900	38.291	202.797	174.037	54.643	1533.069	1389.426	−38.198
2000	38.654	204.770	175.525	58.491	1535.585	1381.800	−36.089
2100	39.011	206.665	176.963	62.374	1538.102	1374.049	−34.178
2200	39.365	208.488	178.355	66.293	1540.620	1366.178	−32.437
2300	39.716	210.245	179.703	70.247	1543.142	1358.193	−30.846
2400	40.065	211.943	181.011	74.236	1545.668	1350.097	−29.384
2500	40.413	213.585	182.282	78.260	1548.201	1341.896	−28.037
2600	40.757	215.177	183.516	82.318	1550.740	1333.594	−26.792
2700	41.096	216.722	184.718	86.411	1553.287	1325.194	−25.637
2800	41.427	218.222	185.888	90.537	1555.843	1316.699	−24.563
2900	41.746	219.682	187.028	94.696	1558.406	1308.113	−23.562
3000	42.050	221.102	188.140	98.886	1560.978	1299.439	−22.625
3100	42.335	222.486	189.226	103.105	1563.556	1290.678	−21.748
3200	42.599	223.834	190.286	107.352	1566.139	1281.834	−20.924
3300	42.836	225.148	191.323	111.624	1568.726	1272.910	−20.148
3400	43.045	226.430	192.337	115.919	1571.315	1263.907	−19.418
3500	43.222	227.681	193.329	120.232	1573.902	1254.828	−18.727
3600	43.366	228.901	194.300	124.562	1576.486	1245.675	−18.074
3700	43.475	230.090	195.251	128.904	1579.062	1236.450	−17.456
3800	43.547	231.251	196.183	133.256	1581.628	1227.156	−16.868
3900	43.583	232.382	197.097	137.612	1584.180	1217.795	−16.311
4000	43.582	233.486	197.993	141.971	1586.715	1208.368	−15.780
4100	43.545	234.562	198.872	146.328	1589.229	1198.878	−15.274
4200	43.473	235.610	199.734	150.679	1591.720	1189.327	−14.791
4300	43.367	236.632	200.581	155.021	1594.183	1179.717	−14.331
4400	43.229	237.627	201.411	159.351	1596.616	1170.050	−13.890
4500	43.060	238.597	202.227	163.666	1599.017	1160.328	−13.469
4600	42.862	239.541	203.028	167.962	1601.381	1150.554	−13.065
4700	42.639	240.461	203.815	172.237	1603.708	1140.728	−12.678
4800	42.391	241.356	204.587	176.489	1605.994	1130.853	−12.306
4900	42.122	242.227	205.347	180.715	1608.239	1120.931	−11.949
5000	41.834	243.075	206.093	184.913	1610.440	1110.964	−11.606
5100	41.528	243.901	206.826	189.081	1612.597	1100.952	−11.276
5200	41.208	244.704	207.547	193.218	1614.708	1090.900	−10.958
5300	40.875	245.486	208.255	197.322	1616.772	1080.807	−10.652
5400	40.532	246.247	208.952	201.393	1618.790	1070.675	−10.357
5500	40.179	246.987	209.637	205.428	1620.760	1060.506	−10.072
5600	39.820	247.708	210.310	209.428	1622.683	1050.303	−9.797
5700	39.456	248.410	210.972	213.392	1624.559	1040.065	−9.531
5800	39.087	249.093	211.624	217.319	1626.389	1029.795	−9.274
5900	38.717	249.758	212.265	221.209	1628.173	1019.493	−9.026
6000	38.346	250.405	212.895	225.063	1629.912	1009.161	−8.786

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

D_0° = 118.0 ± 42 kJ·mol^{-1}
S°(298.15 K) = 143.75 ± 0.4 J K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 241.4 ± 42 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = [235.373] kJ·mol^{-1}

Electonic Levels and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma_u^+$	0	2

ω_e = [1700] cm^{-1} $\omega_e x_e$ = [35] cm^{-1} σ = 2
B_e = [25.3] cm^{-1} α_e = [0.398] cm^{-1} r_e = [1.15] Å

Enthalpy of Formation

The heat of formation at 0 K for H_2^-(g) is based on the electron affinity value derived from a Rydberg–Klein–Rees configuration–interaction calculation.[1] This study by Sharpe[1] led to EA (H_2) = −2.5 eV. Using auxiliary data,[2] we calculate $\Delta_f H^\circ$(0 K) kcal·mol^{-1} and $D_0^\circ(H_2^-)$ = 28.2 ± 10 kcal·mol^{-1}; the latter value assumes dissociation into ground state H(g) and H^-(g). This adopted EA(H_2) value is suggested to be the more reliable value of eight studies considered by Rosenstock *et al.*[3]

In terms of molecular orbitals, the ground state for H_2^-(g) is the $(1s\sigma_g)^2(2p\sigma_u)$ $2\Sigma_u^+$ state involving two bonding electrons and one antibonding electron.[4] We would expect, however, the ground state to be $(1s\sigma_g)^2(2s\sigma_u)$. As stated by Massey,[4] we should expect only a weakly–bound molecule as compared with H_2(g) for which the ground state has no electron in an antibonding orbital. Our calculated EA(H_2) value is consistent with this viewpoint. Further discussion of the H_2^-(g) ion may be found in Massey.[4]

$\Delta_f H^\circ$(0 K) is converted to $\Delta_f H^\circ$(298.15 K) by use of JANAF[2] enthalpies, H°(0 K)–H°(298.15 K), for H_2(g), H_2^-(g), and e^-(ref). $\Delta_f H^\circ$(298.15 K) should not be interpreted as a room temperature electron affinity due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3]

Heat Capacity and Entropy

The vibrational constants for H_2^-(g) are estimated to be the same as in the isoelectronic species He_2^+.[5] The internuclear distance is estimated to be ~8% larger than that for He_2^+(g). The same relationship appeared to exist for the (N_2^-, NO, O_2^+) isoelectronic series. B_e is calculated from r_e whereas α_e is calculated assuming a Morse function for the ground state.

The ground and excited electronic states are discussed in detail by Massey.[4] No excited state contributions are included in this calculation. By assuming the same force constant to exist for H_2^- as in He_2^+, we would calculate ω_e = 3384 cm^{-1}. This leads to an entropy at 298.15 K which is 0.06 cal K^{-1}·mol^{-1} smaller than our adopted value. The vibrational constants derived by Comer and Read[5] for some resonant state of H_2^- suggests ω_e values of 1500, 2300, and 2800 cm^{-1}. Thus, the ω_e value is very uncertain.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.621	241.417		
100	29.209	111.749	169.836	−5.809			
200	29.285	132.014	146.437	−2.885			
250	29.378	138.557	144.231	−1.418			
298.15	29.556	143.746	143.746	0.	235.373	237.732	−41.650
300	29.564	143.928	143.746	0.055	235.335	237.747	−41.395
350	29.866	148.507	144.107	1.540	234.332	238.228	−35.554
400	30.271	152.520	144.913	3.043	233.339	238.852	−31.191
450	30.751	156.113	145.961	4.568	232.365	239.600	−27.812
500	31.272	159.380	147.142	6.119	231.414	240.455	−25.120
600	32.333	165.175	149.677	9.299	229.587	242.437	−21.106
700	33.320	170.235	152.260	12.583	227.854	244.717	−18.261
800	34.187	174.742	154.793	15.959	226.199	247.239	−16.143
900	34.932	178.813	157.240	19.416	224.602	249.966	−14.508
1000	35.568	182.527	159.585	22.942	223.046	252.868	−13.208
1100	36.114	185.944	161.828	26.527	221.513	255.924	−12.153
1200	36.586	189.107	163.971	30.162	219.992	259.119	−11.279
1300	36.999	192.052	166.019	33.842	218.472	262.442	−10.545
1400	37.365	194.807	167.978	37.560	216.948	265.881	−9.920
1500	37.692	197.397	169.854	41.314	215.414	269.430	−9.382
1600	37.988	199.839	171.653	45.098	213.869	273.081	−8.915
1700	38.259	202.150	173.379	48.910	212.309	276.830	−8.506
1800	38.509	204.344	175.039	52.749	210.735	280.670	−8.145
1900	38.742	206.432	176.637	56.612	209.147	284.599	−7.824
2000	38.961	208.425	178.177	60.497	207.543	288.611	−7.538
2100	39.168	210.331	179.663	64.403	205.926	292.705	−7.281
2200	39.365	212.158	181.099	68.330	204.295	296.875	−7.049
2300	39.553	213.912	182.487	72.276	202.652	301.120	−6.839
2400	39.735	215.599	183.832	76.241	200.996	305.437	−6.648
2500	39.910	217.225	185.136	80.223	199.330	309.822	−6.473
2600	40.079	218.793	186.400	84.222	197.653	314.275	−6.314
2700	40.244	220.309	187.628	88.239	195.966	318.793	−6.167
2800	40.406	221.776	188.822	92.271	194.271	323.373	−6.033
2900	40.563	223.196	189.983	96.320	192.567	328.014	−5.908
3000	40.718	224.574	191.113	100.384	190.855	332.713	−5.793
3100	40.869	225.912	192.214	104.463	189.136	337.470	−5.686
3200	41.019	227.212	193.287	108.557	187.410	342.283	−5.587
3300	41.166	228.476	194.335	112.667	185.677	347.149	−5.495
3400	41.311	229.707	195.357	116.791	183.938	352.068	−5.409
3500	41.455	230.907	196.356	120.929	182.193	357.039	−5.329
3600	41.597	232.077	197.332	125.082	180.442	362.059	−5.253
3700	41.738	233.218	198.286	129.248	178.686	367.128	−5.183
3800	41.878	234.333	199.220	133.429	176.924	372.245	−5.117
3900	42.016	235.423	200.135	137.624	175.157	377.408	−5.055
4000	42.154	236.488	201.030	141.832	173.384	382.616	−4.996
4100	42.291	237.531	201.908	146.055	171.607	387.869	−4.942
4200	42.426	238.552	202.768	150.291	169.825	393.166	−4.890
4300	42.562	239.551	203.612	154.540	168.038	398.504	−4.841
4400	42.696	240.531	204.440	158.803	166.247	403.885	−4.795
4500	42.830	241.492	205.253	163.079	164.452	409.306	−4.751
4600	42.963	242.435	206.051	167.369	162.653	414.767	−4.710
4700	43.096	243.361	206.835	171.672	160.850	420.267	−4.671
4800	43.228	244.269	207.605	175.988	159.044	425.806	−4.634
4900	43.360	245.162	208.363	180.317	157.235	431.382	−4.599
5000	43.491	246.039	209.107	184.660	155.423	436.995	−4.565
5100	43.622	246.902	209.840	189.015	153.610	442.644	−4.534
5200	43.753	247.750	210.561	193.384	151.795	448.329	−4.504
5300	43.883	248.585	211.270	197.766	149.980	454.049	−4.475
5400	44.013	249.406	211.969	202.161	148.165	459.804	−4.448
5500	44.143	250.215	212.657	206.569	146.350	465.591	−4.422
5600	44.272	251.012	213.335	210.989	144.537	471.412	−4.397
5700	44.401	251.796	214.003	215.423	142.726	477.265	−4.374
5800	44.530	252.570	214.661	219.870	140.918	483.150	−4.351
5900	44.659	253.332	215.310	224.329	139.114	489.066	−4.330
6000	44.788	254.084	215.950	228.801	137.314	495.013	−4.309

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K)$ = [326.797 ± 3.3] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−28.11 ± 20.9] $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−38.07 ± 20.9] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2205 (1)	[2230](1)
925 (1)	497 (1)
[350](1)	796 (1)
[90](1)	[410](1)
[650](1)	

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Si–H = [1.49] Å Si–I = [2.44] Å
Bond Angles: H–Si–H = [111]° I–Si–I = [110]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.067590 × 10^{-112}] $g^3◀cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated by linear interpolation between the values[1] of SiI_4(g) and SiH_4(g). There are no experimental $\Delta_f H°$ data for SiH_3I, SiH_2I_2 and $SiHI_3$. Data for the iodomethanes[2] have a surprising progression (SiH3I, g);[1] they are of doubtful use in predicting $\Delta_f H°$ of the iodosilanes. We conclude, as did Hunt and Sirtl,[3] that the available data justify only linear interpolation of $\Delta_f H°$.

Heat Capacity and Entropy

The molecular structure is estimated by comparison with SiH_3I, SiI_4 and the various bromo–, chloro– and flurosilanes.[1] The principal moments of inertia are: I_A = 10.2009 × 10^{-39}, I_B = 168.8775 × 10^{-39} and I_C = 178.0688 × 10^{-39} $g·cm^2$.

Five vibrational frequencies are estimated by comparison with the dihalo–, monohalo– and trihalosilanes[1] plus $SiHBrI_2$ and $SiHClI_2$.[4] Frequencies ν_1, ν_2 and ν_8 were observed in gas–phase infrared spectra,[5] while ν_7 was observed in liquid–phase infrared spectra.[6]

We neglect excited states and assume the electronic ground state to be a singlet. We expect that contributions from excited states should be unimportant, as discussed on the tables for SiH_3Br and SiH_2Cl_2.[1]

References

[1]JANAF Thermochemical Tables: H_3ISi(g), HI_3Si(g), BrH_3Si(g), Br_2H_2Si(g), Br_3HSi(g), ClH_3Si(g), Cl2H2Si(g), Cl_3HSi(g) 12–31–76; FH_3Si(g), F_2H_2Si(g), F_3HSi(g), I_4Si(g) 6–30–76
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−14.917	−28.108	−28.108	INFINITE
100	43.099	267.914	379.301	−11.139	−30.645	−40.881	21.354
200	56.780	301.906	332.682	−6.155	−34.466	−49.641	12.965
250	62.986	315.261	327.889	−3.157	−36.342	−53.217	11.119
298.15	67.980	326.797	326.797	0.	−38.074	−56.308	9.865
300	68.153	327.218	326.798	0.126	−38.140	−56.421	9.824
350	72.371	338.051	327.644	3.643	−39.919	−59.328	8.854
400	75.838	347.949	329.572	7.351	−57.581	−61.436	8.023
450	78.748	357.054	332.127	11.217	−60.332	−61.752	7.168
500	81.249	365.483	335.046	15.219	−103.110	−57.968	6.056
600	85.398	380.678	341.413	23.559	−103.829	−48.867	4.254
700	88.749	394.102	348.000	32.272	−104.269	−39.668	2.960
800	91.512	406.139	354.528	41.289	−104.492	−30.422	1.986
900	93.803	417.054	360.878	50.558	−104.550	−21.158	1.228
1000	95.709	427.039	367.002	60.037	−104.488	−11.895	0.621
1100	97.298	436.238	372.884	69.690	−104.345	−2.642	0.125
1200	98.628	444.763	378.523	79.488	−104.157	6.596	−0.287
1300	99.745	452.702	383.927	89.408	−103.954	15.817	−0.636
1400	100.689	460.130	389.108	99.431	−103.764	25.023	−0.934
1500	101.491	467.105	394.077	109.541	−103.614	34.217	−1.192
1600	102.176	473.677	398.849	119.725	−103.524	43.402	−1.417
1700	102.764	479.890	403.435	129.973	−153.690	53.031	−1.629
1800	103.273	485.778	407.847	140.276	−153.542	65.186	−1.892
1900	103.714	491.374	412.097	150.625	−153.455	77.335	−2.126
2000	104.100	496.704	416.196	161.017	−153.434	89.481	−2.337
2100	104.438	501.791	420.151	171.444	−153.480	101.628	−2.528
2200	104.736	506.657	423.974	181.903	−153.590	113.778	−2.701
2300	105.000	511.318	427.671	192.390	−153.758	125.935	−2.860
2400	105.235	515.792	431.250	202.902	−153.977	138.100	−3.006
2500	105.444	520.092	434.718	213.436	−154.237	150.275	−3.140
2600	105.632	524.232	438.082	223.990	−154.527	162.461	−3.264
2700	105.801	528.222	441.347	234.562	−154.835	174.659	−3.379
2800	105.953	532.072	444.519	245.150	−155.153	186.868	−3.486
2900	106.091	535.793	447.602	255.752	−155.468	199.089	−3.586
3000	106.216	539.391	450.602	266.367	−155.773	211.320	−3.679
3100	106.330	542.876	453.523	276.995	−156.059	223.561	−3.767
3200	106.433	546.253	456.368	287.633	−156.318	235.811	−3.849
3300	106.528	549.530	459.142	298.281	−156.546	248.069	−3.927
3400	106.616	552.712	461.847	308.938	−156.738	260.333	−4.000
3500	106.696	555.803	464.488	319.604	−156.889	272.602	−4.068
3600	106.770	558.810	467.066	330.277	−541.150	295.336	−4.285
3700	106.838	561.736	469.586	340.958	−540.800	318.567	−4.497
3800	106.901	564.586	472.048	351.645	−540.406	341.788	−4.698
3900	106.959	567.364	474.457	362.338	−539.967	364.998	−4.889
4000	107.014	570.073	476.814	373.036	−539.483	388.196	−5.069
4100	107.064	572.716	479.121	383.740	−538.954	411.381	−5.241
4200	107.111	575.296	481.380	394.449	−538.381	434.554	−5.404
4300	107.155	577.817	483.593	405.162	−537.764	457.711	−5.560
4400	107.196	580.281	485.763	415.880	−537.105	480.854	−5.708
4500	107.234	582.691	487.890	426.601	−536.404	503.982	−5.850
4600	107.270	585.048	489.977	437.327	−535.664	527.093	−5.985
4700	107.304	587.355	492.024	448.055	−534.885	550.189	−6.115
4800	107.336	589.615	494.034	458.787	−534.068	573.267	−6.238
4900	107.366	591.828	496.007	469.523	−533.216	596.328	−6.357
5000	107.394	593.997	497.945	480.261	−532.330	619.371	−6.471
5100	107.420	596.124	499.850	491.001	−531.411	642.396	−6.579
5200	107.445	598.211	501.721	501.745	−530.461	665.402	−6.684
5300	107.469	600.257	503.561	512.490	−529.480	688.390	−6.784
5400	107.491	602.266	505.370	523.238	−528.470	711.360	−6.881
5500	107.512	604.239	507.150	533.988	−527.431	734.309	−6.974
5600	107.533	606.176	508.901	544.741	−526.366	757.241	−7.063
5700	107.552	608.080	510.625	555.495	−525.275	780.153	−7.149
5800	107.570	609.951	512.321	566.251	−524.159	803.046	−7.232
5900	107.587	611.790	513.991	577.009	−523.019	825.918	−7.312
6000	107.603	613.598	515.636	587.768	−521.854	848.772	−7.389

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [327.996 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -641.95 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -654.80 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[273](1)	[3700](1)
[150](1)	[3700](1)
[235](1)	[1250](1)
[150](1)	[1250](1)
[255](1)	[1250](1)
[258](1)	[1250](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2h}
Bond Distances: K–O = [2.43] Å O–H = [0.96] Å
Bond Angles: K–O–K = [90]° K–O–H = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.758094] \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(K_2(OH)_2, g, 298.15\ K)$ is calculated from the enthalpy of dimerization, $\Delta_{dim} H°(298.15\ K) = -45.3 \pm 3.0\ kcal \cdot mol^{-1}$, and the enthalpy of formation of the monomer, $\Delta_f H°(KOH, g, 298.15\ K) = -55.6 \pm 3.0\ kcal \cdot mol^{-1}$. Refer to the KOH(g) table for details.

Heat Capacity and Entropy

A key to the molecular structure of $K_2(OH)_2$(g) is provided by the work of Buchler *et al.*[1] which involves the electric deflection of molecular beams of $Cs_2(OH)_2$(g) and $Na_2(OH)_2$(g). Their results indicate that these dimers are nonpolar which implies a planar structure for at least the M_2O_2 part of the molecule. The three models proposed thus far for the dimeric alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer *et al.*[2] proposed a model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter[3] adopted the square planar model for the M_2O_2 configuration but did not allow for hydrogen bonding. Berkowitz *et al.*[4] proposed a model for $Li_2(OH)_2$(g) which consisted of a trans configuration with hydrogens above and below the plane of a rhombus formed by the lighium and oxygen atoms, the O–Li–O bond angle being 100°. The adopted molecular structure for $K_2(OH)_2$(g) is similar to the model of Berkowitz *et al.*[4] but with the O–K–O bond angle equal to 90°. The K–O–H bond angle is assumed equal to 110°. The K–O bond distance is estimated as being 10% longer than that in KOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are: $I_A = [17.5192] \times 10^{-39}$, $I_B = [38.5520] \times 10^{-39}$, and $I_C = [55.6426] \times 10^{-39}\ g \cdot cm^2$.

The first six vibrational frequencies are taken equal to those for dimeric K_2F_2(g) (See K_2F_2(g) table), and the remaining O–H stretching and bending modes are estimates taken from the work of Berkowitz *et al.*[4]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.473	−641.954	−641.954	INFINITE
100	56.735	251.157	394.722	−14.357	−647.206	−637.798	333.151
200	73.990	296.990	335.219	−7.646	−651.289	−626.711	163.680
250	78.049	313.955	329.318	−3.841	−653.087	−620.357	129.616
298.15	81.444	327.996	327.996	0.	−654.796	−613.898	107.552
300	81.571	328.500	327.997	0.151	−654.862	−613.644	106.845
350	84.944	341.329	329.003	4.314	−661.407	−606.440	90.506
400	88.173	352.884	331.277	8.643	−663.204	−598.462	78.151
450	91.187	363.446	334.273	13.128	−664.824	−590.271	68.517
500	93.941	373.198	337.684	17.757	−666.286	−581.907	60.791
600	98.651	390.758	345.099	27.395	−668.816	−564.786	49.169
700	102.458	406.261	352.750	37.457	−670.938	−547.275	40.838
800	105.603	420.153	360.322	47.865	−672.774	−529.481	34.572
900	108.278	432.750	367.681	58.562	−674.422	−511.469	29.685
1000	110.604	444.281	374.773	69.509	−675.967	−493.279	25.766
1100	112.656	454.921	381.581	80.674	−835.387	−465.717	22.115
1200	114.482	464.803	388.110	92.033	−834.813	−432.135	18.810
1300	116.113	474.032	394.368	103.564	−834.143	−398.606	16.016
1400	117.572	482.692	400.371	115.249	−833.393	−365.130	13.623
1500	118.878	490.849	406.133	127.073	−832.578	−331.711	11.551
1600	120.048	498.559	411.671	139.020	−831.711	−298.348	9.740
1700	121.097	505.869	416.999	151.079	−830.802	−265.041	8.144
1800	122.039	512.818	422.131	163.236	−829.865	−231.788	6.726
1900	122.885	519.439	427.080	175.483	−828.908	−198.587	5.460
2000	123.647	525.762	431.857	187.810	−827.942	−165.437	4.321
2100	124.333	531.812	436.474	200.210	−826.976	−132.336	3.292
2200	124.953	537.610	440.940	212.675	−826.019	−99.280	2.357
2300	125.513	543.177	445.265	225.199	−825.080	−66.268	1.505
2400	126.021	548.530	449.457	237.776	−824.168	−33.296	0.725
2500	126.483	553.684	453.523	250.401	−823.291	−0.361	0.008
2600	126.903	558.653	457.472	263.071	−822.456	32.540	−0.654
2700	127.286	563.449	461.308	275.781	−821.673	65.409	−1.265
2800	127.635	568.085	465.040	288.527	−820.948	98.251	−1.833
2900	127.956	572.569	468.671	301.307	−820.290	131.067	−2.361
3000	128.250	576.912	472.207	314.117	−819.707	163.863	−2.853
3100	128.520	581.122	475.653	326.956	−819.208	196.640	−3.313
3200	128.768	585.206	479.013	339.820	−818.800	229.402	−3.745
3300	128.998	589.172	482.291	352.709	−818.474	262.152	−4.150
3400	129.210	593.027	485.491	365.619	−818.266	294.895	−4.531
3500	129.406	596.775	488.618	378.550	−818.170	327.633	−4.890
3600	129.588	600.423	491.673	391.500	−818.200	360.370	−5.229
3700	129.757	603.976	494.660	404.467	−818.365	393.110	−5.550
3800	129.914	607.438	497.583	417.451	−818.672	425.857	−5.854
3900	130.060	610.815	500.443	430.450	−819.132	458.614	−6.142
4000	130.197	614.109	503.244	443.463	−819.740	491.382	−6.417
4100	130.325	617.326	505.987	456.489	−820.522	524.169	−6.678
4200	130.444	620.468	508.676	469.527	−821.492	556.978	−6.927
4300	130.556	623.539	511.311	482.577	−822.653	589.812	−7.165
4400	130.660	626.541	513.896	495.638	−823.460	622.621	−7.391
4500	130.759	629.479	516.432	508.709	−824.895	655.501	−7.609
4600	130.851	632.354	518.921	521.790	−826.524	688.416	−7.817
4700	130.939	635.169	521.365	534.879	−828.312	721.365	−8.017
4800	131.021	637.926	523.764	547.977	−830.086	754.331	−8.209
4900	131.098	640.629	526.122	561.083	−832.272	787.362	−8.393
5000	131.171	643.278	528.439	574.197	−834.665	820.440	−8.571
5100	131.240	645.876	530.716	587.317	−837.267	853.568	−8.742
5200	131.305	648.425	532.955	600.445	−840.080	886.748	−8.907
5300	131.367	650.927	535.157	613.578	−843.106	919.985	−9.067
5400	131.426	653.383	537.324	626.718	−846.343	953.281	−9.221
5500	131.482	655.795	539.456	639.864	−849.793	986.638	−9.370
5600	131.535	658.165	541.555	653.014	−853.452	1020.061	−9.515
5700	131.585	660.493	543.621	666.170	−856.629	1053.455	−9.654
5800	131.632	662.782	545.656	679.331	−860.614	1087.001	−9.789
5900	131.678	665.033	547.660	692.497	−864.792	1120.614	−9.921
6000	131.721	667.246	549.635	705.667	−869.158	1154.302	−10.049

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [269.794 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -699.39 \pm 33.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -711.28 \pm 33.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies (ν, cm^{-1}, all singly degenerate)

[400]	[400]	[500]	[500]	[450]	[350]	[3700]	[3700]	[1250]	[1250]	[1250]	[1250]

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: [C_{2h}]

Bond Distances: Li–O = [1.74] Å O–H = [0.97] Å

Bond Angles: Li–O–Li = [90]° Li–O–H = [110]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.293246 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The reaction between water vapor and condensed lithium oxide has been investigated as a function of temperature and water pressure by means of such techniques as mass spectrometry[1,2] and transpiration.[3] At low water pressures (<0.01 Torr) in the temperature range 780–900 K, Schoonmaker and Porter[1] observed only Li^+ and $LiOH^+$ ion species in the mass spectrum of the reaction products. The precursor of these two ions was assumed to be monomeric LiOH. Berkowitz *et al.*[2] in a more extensive mass spectrometric study of the Li_2O(cr)–H_2O(g) equilibrium detected not only monomeric and dimeric LiOH in the vapor phase, but also trace amounts of trimer ($Li_3(OH)_3$). Their work covered the temperature range 1100–1400 K at water pressures of 0.04 and 0.16 Torr. Absolute equilibrium constants were determined for the dimerization reaction, 2 LiOH(g) = $Li_2(OH)_2$(g), by calibrating the mass spectrometer in units of pressure. This was accomplished by measuring the water pressure externally and simultaneously monitoring the intensity of the H_2O^+ peak. In an attempt to investigate the same equilibrium at water pressures inaccessible to mass spectrometry, Berkowitz–Mattuck and Buchler[3] used the transpiration method. Their work covered water pressures of 4.58 and 19.5 Torr at 1095 and 1145 K. An analysis of these equilibrium data are summarized below.

Source	Reaction[a]	Method	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Berkowitz, *et al.*[2]	A	Mass Spec.	1119–1352	9 [b]	−57.2	−63.8 ± 1.4	−5.4 ± 2.8	−175.8 ± 4.0
Berkowitz–Mattock	B	Transp.	1095, 1145	2		12.7		−188.2 ± 4.0

[a]Reactions: A) 2 LiOH(g) = $Li_2(OH)_2$(g) B) H_2O(g) + Li_2O(cr) = $Li_2(OH)_2$(g)

[b]One point rejected due to failure of a statistical test.

It seems most likely that the equilibrium data of Berkowitz–Mattuck and Buchler[3] are in error, since no satisfactory compromise in the flow rates of the inert carrier gas could be found such that saturation was achieved while eliminating thermal diffusion effects. Under these conditions the simple equations relating partial pressures to the masses transported during the transpiration experiment are now longer valid. Furthermore, the authors assumed that under the conditions of their experiment only dimer LiOH would be formed. The work of Berkowitz *et al.*[2] clearly establishes the existence of a trimer at water pressures some 100 times lower than those employed by Berkowitz–Mattuck and Buchler.[3]

Trends in the dimerization energies for the higher alkali metal hydroxides, as well as for the dimeric alkali fluorides and chlorides, suggest that the enthalpy of dimerization for LiOH from the work of Berkowitz *et al.*[2] may be slightly high. Such a comparison results in $\Delta_f H°$(dimerization, 298.15 K) values in the range −(52–61) kcal·mol^{-1}. Further support for a lower value comes from the mass spectral work of Porter and Schoonmaker.[1] They investigated the reaction of H_2O(g) with a mixture of condensed Li_2O–Na_2O. From the reported ion current intensities for the various ions found in the reaction products we calculate, $\Delta_{dim}H°$(NaOH, g, 298.15 K) −$\Delta_{dim}H°$(LiOH, g, 298.15 K) = 5.3 kcal·mol^{-1}. This value yields $\Delta_{dim}H°(298.15\ K) = -56.0 \pm 5$ kcal·mol^{-1}for LiOH(g) when used in combination with the adopted value for NaOH(g).[4] A high enthalpy of dimerization from the mass spectral work of Berkowitz *et al.*[2] is easily reconciled in terms of nonequilibrium measurements. Based upon these findings, we adopt $\Delta_{dim}H°(298.15\ K) = -58.0 \pm 5.0$ kcal mol for LiOH(g). Combining this result with the enthalpy of formation for LiOH(g),[4] that for the dimer is $\Delta_f H°(Li_2(OH)_2, g, 298.15\ K) = -170.0 \pm 8$ kcal·mol^{-1}

Heat Capacity and Entropy

The molecular structure of $Li_2(OH)_2$(g) is assumed identical to that adopted for the higher alkali metal hydroxide dimers. It consists of a planar configuration for the lithium and oxygen atoms with the O–Li–O bond angle equal to 90°. The hydrogen atoms are placed in a trans–configuration above and below the plane of the rhombus formed by the lithium and oxygen atoms. The Li–O–H bond angle is assumed equal to 110°. The Li–O bond distance is estimated as being 10% longer than in LiOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are: $I_A = [3.7044 \times 10^{-39}]$, $I_B = [9.2519 \times 10^{-39}]$, and $I_C = [12.5268 \times 10^{-39}]$ g·cm^2.

The first six vibrational frequencies are estimated by comparison with calculated[5] and experimental[4,6] frequencies for Li_2F_2(g). In the estimation it is assumed that the bulkier OH group would tend to reduce the frequencies of $Li_2(OH)_2$(g) relative to those for Li_2F_2(g). The remaining OH stretching and bending frequencies are estimates from the work of Berkowitz *et al.*[2]

Continued on page 1359

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−14.502	−699.387	−699.387	INFINITE
100	37.588	212.012	323.024	−11.101	−702.880	−695.209	363.140
200	57.261	244.155	275.895	−6.348	−707.415	−685.736	179.096
250	65.023	257.797	270.933	−3.284	−709.461	−680.076	142.094
298.15	71.223	269.794	269.794	0.	−711.280	−674.249	118.126
300	71.443	270.235	269.795	0.132	−711.347	−674.019	117.357
350	76.958	281.672	270.686	3.845	−713.085	−667.659	99.643
400	81.765	292.270	272.730	7.816	−714.741	−661.056	86.325
450	85.956	302.148	275.456	12.011	−716.370	−654.247	75.943
500	89.602	311.397	278.592	16.402	−724.002	−646.643	67.554
600	95.542	328.283	285.495	25.673	−726.787	−630.900	54.925
700	100.130	343.370	292.704	35.466	−729.036	−614.734	45.872
800	103.799	356.988	299.902	45.669	−730.916	−598.274	39.063
900	106.840	369.395	306.945	56.205	−732.542	−581.594	33.755
1000	109.432	380.789	313.767	67.022	−733.963	−564.744	29.499
1100	111.684	391.327	320.345	78.080	−735.215	−547.760	26.011
1200	113.662	401.131	326.674	89.349	−736.324	−530.668	23.099
1300	115.412	410.300	332.758	100.805	−737.317	−513.489	20.632
1400	116.966	418.911	338.607	112.425	−738.207	−496.238	18.515
1500	118.349	427.029	344.234	124.192	−739.004	−478.926	16.678
1600	119.583	434.707	349.650	136.090	−739.723	−461.564	15.069
1700	120.685	441.990	354.870	148.105	−1030.849	−429.806	13.206
1800	121.671	448.917	359.904	160.223	−1029.941	−394.477	11.447
1900	122.554	455.519	364.764	172.435	−1029.005	−359.199	9.875
2000	123.348	461.826	369.460	184.731	−1028.049	−323.971	8.461
2100	124.062	467.862	374.004	197.102	−1027.081	−288.791	7.183
2200	124.705	473.648	378.402	209.541	−1026.110	−253.656	6.023
2300	125.287	479.205	382.665	222.041	−1025.142	−218.567	4.964
2400	125.813	484.548	386.799	234.597	−1024.183	−183.519	3.994
2500	126.291	489.694	390.813	247.202	−1023.240	−148.511	3.103
2600	126.725	494.656	394.712	259.854	−1022.319	−113.540	2.281
2700	127.121	499.446	398.503	272.546	−1021.425	−78.604	1.521
2800	127.482	504.076	402.191	285.277	−1020.564	−43.700	0.815
2900	127.813	508.555	405.782	298.042	−1019.741	−8.827	0.159
3000	128.116	512.893	409.281	310.838	−1018.961	26.019	−0.453
3100	128.395	517.099	412.691	323.664	−1018.227	60.840	−1.025
3200	128.651	521.179	416.018	336.517	−1017.546	95.636	−1.561
3300	128.888	525.142	419.265	349.394	−1016.919	130.413	−2.064
3400	129.106	528.993	422.436	362.293	−1016.352	165.173	−2.538
3500	129.308	532.738	425.534	375.214	−1015.849	199.916	−2.984
3600	129.495	536.384	428.563	388.155	−1015.412	234.646	−3.405
3700	129.669	539.934	431.525	401.113	−1015.046	269.364	−3.803
3800	129.831	543.394	434.424	414.088	−1014.753	304.074	−4.180
3900	129.981	546.769	437.261	427.079	−1014.538	338.778	−4.537
4000	130.122	550.061	440.040	440.084	−1014.403	373.476	−4.877
4100	130.253	553.276	442.763	453.103	−1014.351	408.172	−5.200
4200	130.376	556.416	445.432	466.134	−1014.387	442.868	−5.508
4300	130.491	559.485	448.049	479.178	−1014.513	477.566	−5.801
4400	130.598	562.487	450.616	492.232	−1014.690	512.264	−6.081
4500	130.700	565.423	453.134	505.297	−1014.986	546.970	−6.349
4600	130.795	568.296	455.607	518.372	−1015.385	581.684	−6.605
4700	130.884	571.110	458.034	531.456	−1015.884	616.408	−6.851
4800	130.968	573.867	460.419	544.549	−1016.487	651.144	−7.086
4900	131.048	576.568	462.762	557.649	−1017.197	685.894	−7.312
5000	131.123	579.216	465.065	570.758	−1018.017	720.660	−7.529
5100	131.194	581.813	467.328	583.874	−1018.940	755.441	−7.737
5200	131.261	584.362	469.555	596.997	−1019.988	790.242	−7.938
5300	131.325	586.863	471.744	610.126	−1021.157	825.066	−8.132
5400	131.385	589.318	473.899	623.261	−1022.450	859.912	−8.318
5500	131.442	591.729	476.020	636.403	−1023.870	894.783	−8.498
5600	131.496	594.098	478.107	649.550	−1025.421	929.682	−8.672
5700	131.548	596.426	480.162	662.702	−1027.107	964.609	−8.840
5800	131.597	598.714	482.187	675.859	−1028.930	999.568	−9.002
5900	131.643	600.964	484.181	689.021	−1030.895	1034.557	−9.159
6000	131.688	603.177	486.146	702.188	−1033.005	1069.583	−9.312

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = 31.091 \pm 0.84\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -68.00 \pm 9.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -76.15 \pm 9.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of hydrolysis of MgH_2(cr) was measured by Sinke and Stull.[1] The value of $\Delta_f H°(298.15\ K)$ was calculated to be -19.1 ± 2 kcal·mol^{-1}. From the decomposition pressure measurements for MgH_2(cr) reported by Ellinger[2] and Stampfer *et al.*[3] the values of $\Delta_f H°(298.15\ K)$ for MgH_2(cr) were found to be -17.9 ± 1.0 and -17.7 kcal·mol^{-1}, respectively. The value used was the average of these three.

Heat Capacity and Entropy

The low temperature heat capacities (25–300 K) were measured by Sinke and Hildenbrand.[4] Above 300 K the $C_p°$ values were estimated by comparison with those for MgF_2(cr). $S°(298.15\ K)$ is obtained from Sinke and Hildenbrand[4] using $S°(25\ K) = 0.037$ cal·K^{-1}·mol^{-1} (extrap.).

Decomposition Data

$T_{dcm} = 560$ K is estimated from the value of $\Delta_f G°$ in the table.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−5.314	−67.997	−67.997	INFINITE
100	12.774	6.389	55.049	−4.866	−71.191	−60.806	31.762
200	25.284	19.372	33.974	−2.920	−73.946	−49.309	12.878
298.15	35.334	31.091	31.091	0.	−76.149	−36.716	6.432
300	35.510	31.310	31.092	0.066	−76.183	−36.471	6.350
400	43.304	42.620	32.581	4.015	−77.694	−22.989	3.002
500	49.999	53.029	35.644	8.693	−78.606	−9.195	0.961
600	55.229	62.621	39.352	13.962	−79.033	4.734	−0.412
700	59.538	71.468	43.316	19.706	−79.099	18.705	−1.396
800	63.095	79.659	47.353	25.844	−78.901	32.665	−2.133
900	65.898	87.259	51.370	32.300	−78.539	46.591	−2.704
1000	67.990	94.315	55.316	38.998	−86.701	61.184	−3.196
1100	69.486	100.867	59.163	45.874	−86.295	75.953	−3.607
1200	70.751	106.969	62.896	52.888	−85.790	90.682	−3.947
1300	71.761	112.673	66.508	60.015	−85.214	105.365	−4.234
1400	72.592	118.023	69.998	67.234	−212.000	123.169	−4.595
1500	73.204	123.052	73.369	74.525	−209.996	147.039	−5.120
1600	73.722	127.794	76.624	81.872	−207.978	170.776	−5.575
1700	74.088	132.274	79.767	89.262	−205.960	194.386	−5.973
1800	74.475	136.520	82.803	96.690	−203.945	217.878	−6.323
1900	74.883	140.557	85.737	104.158	−201.929	241.257	−6.633
2000	75.312	144.409	88.575	111.667	−199.908	264.531	−6.909

PREVIOUS: June 1963 CURRENT: September 1963

$S°(298.15\ K) = 63.243\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -915.64 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 924.66 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted value is an average of −221.10 and −220.86 kcal·mol^{-1} obtained from $\Delta_f H°(298.15\ K) = 9.08$ and 8.84 kcal·mol^{-1} for the dehydration reaction $Mg(OH)_2(cr) = MgO(cr) + H_2O(l)$, using auxiliary data.[13, 14] The two values correspond to natually occurring brucite and to synthetic $Mg(OH)_2$ prepared from MgO by hydration at 177 °C under a steam pressure of about 9 atm. The enthalpies of reaction are derived from studies of Taylor and Wells[1] on the enthalpys of solution of various samples of $Mg(OH)_2$and MgO in aqueous HCl. These studies show that the enthalpy of dehydration is quite dependent on the nature of the MgO sample; e.g., values for synthetic $Mg(OH)_2$ vary monotonically from 9.79 to 8.84 kcal·mol^{-1} for MgO ignited at temperatures from 450 to 1425 °C, respectively. The authors ascribe this difference primarily to increase in particle size at the higher ignition temperatures. More recent work[15] suggests that the difference is caused by crystalline disorder rather than particle size alone. We have adopted the results at 1425 °C since they are reasonably consistent with the high temperature samples on which the JANAF enthalpy of formation for MgO is based. The uncertainty is estimated as ±0.5 kcal·mol^{-1}.

Shomate and Huffman[2] have confirmed the enthalpy of solution of MgO (ignited at 1000°C) within about 0.3 kcal·mol^{-1}. Their value may be combined with the enthalpy of solution for synthetic $Mg(OH)_2$, determined under similar conditions by Torgeson and Sahama[3] to obtain $\Delta_r H° = 8.85$ kcal·mol^{-1} for the dehydration reaction. At the other extreme, the enthalpy of solution data of Giauque and Archibald[4] lead to $\Delta_r H° = 9.74$ kcal·mol^{-1}; however, this value corresponds to MgO ignited at 350 °C. The MgO sample was microcrystalline and had significant excess $C_v°$ as suggested by Giauque and Archibald[4] and later confirmed by data of Barron *et al.*[5] Giauque and Archibald[4] intentionally used the microcrystalline form which would be similar to the product in their decomposition pressure measurements (190 and 212 °C). Thus, it is not surprising that 3rd law analysis of their decomposition pressures yields essentially the same enthalpy of formation as their solution data (see summary below). Decomposition data at higher pressures have been reported by Fyfe[6] Roy and Roy[7] Kennedy[8] Zhabrova and Kadenatsi[9] and Berg and Rassonskaya.[10] These data do not significantly affect the enthalpy of formation, however, because of uncertainties in the attainment of equilibrium and in reduction to standard state values.

Source	$Mg(OH)_2$ Sample	Temp. of MgO Formation, °C	Enthalpy of Dehydration $\Delta_r H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$
Taylor & Wells[1])	Brucite	1425	9.08	−221.10
	Synthetic	1425	8.84	−220.86
	Synthetic	1000	9.18	−221.20
	Synthetic	450	9.79	>−221.81
Torgeson[3] Shomate[2]	Synthetic	1000	8.85	−220.87
Giauque & Archibald[4]	Synthetic[a]	350	9.74	>−221.74
K_p data	Synthetic[a]	190, 212	20.10[b]	>−221.59

[a]Prepared by reaction of KOH with $MgCl_2$(aq) at 210 °C, rather than by hydration of MgO.
[b]For $Mg(OH)_2(cr) = MgO(cr) + H_2O(g)$ rather than $Mg(OH)_2(cr) = MgO(cr) + H_2O(l)$.

Heat Capacity and Entropy

The low temperature heat capacities are from the measurements (22–321 K) of Giauque and Archibald[4] who used a synthetic, macrocrystalline sample of magnesium dihydroxide prepared by reacting KOH with aqueous $MgCl_2$ at 210°C. The entropy is derived from the heat capacities starting with $S°(20\ K) = 0.027\ cal·K^{-1}·mol^{-1}$ from a T^3 extrapolation. $S°(298.15\ K) = 15.11\ cal·K^{-1}·mol^{-1}$ compares favorably with 15.09 cal·K^{-1}·mol^{-1} given by Giauque and Archibald.[4] The drop calorimeter enthalpy measurements (350–699 K) of King *et al.*[11] are used to derive heat capacities above 298.15 K. They used a ground sample of natural brucite, which analyzed 98.77% $Mg(OH)_2$. Their published data are corrected for impurities and to one atmosphere total pressure. The low and high temperature heat capacities were joined smoothly by mathematical curve fitting techniques. Heat capacities above 700 K are obtained by extrapolation.

The reference temperature for the enthalpy measurements (393–667 K) of Lashchenko and Kompanskii[12] is uncertain. Their values appear to be near those of King *et al.*[11] up to around 550 K; above 550 K their values average about 5% lower than those of King *et al.*[11]

Decomposition Data

T_{dcm} = 542.2 K is calculated as the temperature at which the fugacity of $H_2O(g)$ is 1 atm for the reaction $Mg(OH)_2(cr) = MgO(cr) + H_2O(g)$.

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Continued on page 1359

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.127	−915.642	−915.642	INFINITE
100	21.618	9.770	116.934	−10.716	−919.778	−892.401	466.142
200	56.868	36.341	69.736	−6.679	−923.352	−863.412	225.500
298.15	77.249	63.242	63.242	0.	−924.664	−833.652	146.052
300	77.555	63.721	63.244	0.143	−924.675	−833.087	145.053
400	91.705	88.120	66.474	8.659	−924.591	−802.538	104.801
500	99.617	109.525	72.994	18.266	−923.632	−772.123	80.663
600	104.441	128.143	80.669	28.484	−922.270	−741.945	64.592
700	107.880	144.513	88.644	39.108	−920.710	−712.012	53.131
800	110.579	159.101	96.556	50.036	−919.060	−682.311	44.550
900	112.847	172.259	104.248	61.210	−917.385	−652.817	37.889
1000	114.851	184.254	111.658	72.597	−924.320	−622.798	32.532

PREVIOUS: March 1967 CURRENT: December 1975

$S°(298.15\ K) = [267.270 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -564.70 \pm 33.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -572.37 \pm 33.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[508](1)
[215](1)
[875](1)
[3650](2)
[492](4)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: $[C_{2v}]$
Bond Distances: Mg–O = [1.79] Å O–H = [0.96] Å
Bond Angles: O–Mg–O = [158]° Mg–O–H = [180]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.092990 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Alexander, *et al.*[1] determined the temperature dependence of the equilibrium constant for the reaction $MgO(cr) + H_2O(g) = Mg(OH)_2(g)$ in the range of 1650 to 2020 K by measuring vapor densities using a transpiration technique. The data are presented graphically and are represented by a linear equation. With auxiliary data,[2] analysis of the equation yields a 2nd law $\Delta_r H°(298.15\ K) = 67.1\ kcal \cdot mol^{-1}$ and a 3rd law $\Delta_f H°(298.15\ K) = 64.70\ kcal \cdot mol^{-1}$ with a drift of $-1.3\ cal \cdot K^{-1} \cdot mol^{-1}$. From the 3rd law heat of reaction, the adopted $\Delta_f H°(298.15\ K) = -136.80\ kcal \cdot mol^{-1}$ is calculated. An uncertainty of $\pm 8.0\ kcal \cdot mol^{-1}$ is assigned to allow for the uncertainty shown in the vapor density measurements and for the uncertainty in the entropy.

The enthalpy of dissociation listed by Jackson[6] leads to $\Delta_f H°(Mg(OH)_2, g, 298.15\ K) = -140.74\ kcal \cdot mol^{-1}$. Another recent compilation[7] lists $\Delta_f H°(298.15\ K) = -134\ kcal \cdot mol^{-1}$.

Based on the adopted $\Delta_f H°(298.15\ K) = -136.80 \pm 8\ kcal \cdot mol^{-1}$, $\Delta_r H°(0\ K) = 188.6\ kcal \cdot mol^{-1}$ is calculated for the reaction $Mg(OH)_2(g) = Mg(g) + 2\ OH(g)$.

Heat Capacity and Entropy

The analogy between gaseous mono– and dihydroxides and gaseous mono– and dihalides, particularly the mono– and difluorides, has been recognized.[3-6] The O–Mg–O bond angle is assumed to be the same as the F–Mg–F bond angle;[2] the Mg–O–H bond is considered to be linear as in MgOH.[2] The Mg–O bond distance is estimated to be slightly larger, 0.02 Å, than the Mg–F distance in MgF_2[2] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is taken to be the same as in water.[2]

The vibrational frequencies are estimated to be the same as in MgF_2[2] (O–Mg–O symmetrical and asymmetrical stretch, and bend) and as in MgOH[2] (O–H stretch and Mg–O–H bend). The principal moments of inertia are: $I_A = 0.3029 \times 10^{-39}$, $I_B = 18.8449 \times 10^{-39}$, and $I_C = 19.1478 \times 10^{-39}\ g \cdot cm^2$.

Jackson[6] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K) = 63.829\ cal \cdot K^{-1} \cdot mol^{-1}$. We assign an uncertainty of $\pm 3.0\ cal \cdot K^{-1} \cdot mol^{-1}$ to the adopted entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−14.472	−564.695	−564.695	INFINITE
100	38.926	209.778	319.782	−11.000	−567.769	−560.393	292.719
200	56.563	242.056	273.257	−6.240	−570.621	−551.824	144.122
250	63.982	255.509	268.385	−3.219	−571.624	−547.003	114.290
298.15	69.476	267.270	267.270	0.	−572.371	−542.190	94.989
300	69.659	267.700	267.271	0.129	−572.396	−542.003	94.371
350	73.933	278.775	268.136	3.724	−572.989	−536.888	80.126
400	77.165	288.868	270.106	7.505	−573.453	−531.698	69.433
450	79.646	298.106	272.711	11.428	−573.828	−526.455	61.109
500	81.588	306.602	275.681	15.460	−574.145	−521.174	54.447
600	84.438	321.746	282.128	23.771	−574.691	−510.528	44.445
700	86.510	334.924	288.749	32.322	−575.204	−499.793	37.295
800	88.203	346.589	295.264	41.060	−575.743	−488.984	31.927
900	89.704	357.066	301.559	49.957	−576.345	−478.104	27.748
1000	91.089	366.590	307.593	58.997	−585.627	−466.440	24.364
1100	92.385	375.333	313.359	68.172	−586.431	−454.482	21.582
1200	93.596	383.424	318.865	77.471	−587.190	−442.452	19.259
1300	94.723	390.961	324.124	86.888	−587.908	−430.362	17.292
1400	95.765	398.020	329.153	96.413	−716.000	−415.050	15.486
1500	96.722	404.660	333.968	106.038	−715.303	−393.578	13.706
1600	97.597	410.930	338.584	115.755	−714.584	−372.153	12.150
1700	98.395	416.871	343.016	125.555	−713.847	−350.773	10.778
1800	99.121	422.516	347.277	135.432	−713.099	−329.438	9.560
1900	99.781	427.894	351.379	145.377	−712.344	−308.144	8.471
2000	100.380	433.027	355.334	155.386	−711.587	−286.889	7.493
2100	100.925	437.938	359.152	165.451	−710.831	−265.673	6.608
2200	101.419	442.645	362.841	175.569	−710.080	−244.492	5.805
2300	101.869	447.163	366.409	185.734	−709.337	−223.346	5.072
2400	102.279	451.507	369.865	195.942	−708.604	−202.232	4.401
2500	102.653	455.690	373.215	206.188	−707.884	−181.148	3.785
2600	102.994	459.723	376.465	216.471	−707.179	−160.093	3.216
2700	103.307	463.616	379.621	226.786	−706.491	−139.064	2.690
2800	103.593	467.379	382.689	237.131	−705.822	−118.060	2.202
2900	103.856	471.018	385.672	247.504	−705.174	−97.081	1.749
3000	104.097	474.543	388.576	257.902	−704.549	−76.122	1.325
3100	104.319	477.960	391.405	268.323	−703.948	−55.184	0.930
3200	104.524	481.276	394.162	278.765	−703.374	−34.266	0.559
3300	104.714	484.495	396.850	289.227	−702.829	−13.365	0.212
3400	104.889	487.624	399.474	299.708	−702.314	7.520	−0.116
3500	105.052	490.667	402.037	310.205	−701.832	28.390	−0.424
3600	105.203	493.628	404.540	320.718	−701.385	49.247	−0.715
3700	105.343	496.512	406.987	331.245	−700.975	70.092	−0.990
3800	105.474	499.324	409.380	341.786	−700.605	90.928	−1.250
3900	105.595	502.065	411.721	352.339	−700.276	111.753	−1.497
4000	105.709	504.740	414.014	362.905	−699.992	132.570	−1.731
4100	105.815	507.351	416.258	373.481	−699.754	153.381	−1.954
4200	105.915	509.902	418.458	384.067	−699.566	174.187	−2.166
4300	106.008	512.396	420.613	394.664	−699.429	194.989	−2.369
4400	106.096	514.834	422.727	405.269	−699.347	215.788	−2.562
4500	106.178	517.219	424.801	415.883	−699.321	236.586	−2.746
4600	106.255	519.554	426.835	426.504	−699.354	257.384	−2.923
4700	106.328	521.839	428.832	437.134	−699.448	278.184	−3.092
4800	106.397	524.079	430.793	447.770	−699.606	298.986	−3.254
4900	106.461	526.273	432.720	458.413	−699.830	319.793	−3.409
5000	106.523	528.425	434.612	469.062	−700.122	340.604	−3.558
5100	106.581	530.535	436.473	479.717	−700.485	361.422	−3.702
5200	106.635	532.605	438.301	490.378	−700.919	382.247	−3.840
5300	106.687	534.637	440.100	501.044	−701.427	403.083	−3.973
5400	106.736	536.631	441.869	511.715	−702.012	423.928	−4.101
5500	106.783	538.590	443.610	522.391	−702.674	444.784	−4.224
5600	106.827	540.515	445.323	533.072	−703.416	465.654	−4.343
5700	106.869	542.406	447.010	543.757	−704.239	486.537	−4.459
5800	106.910	544.265	448.671	554.446	−705.145	507.437	−4.570
5900	106.948	546.093	450.306	565.139	−706.136	528.350	−4.678
6000	106.984	547.890	451.918	575.835	−707.212	549.283	−4.782

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = [355.620 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -842.89 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -851.03 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[2000](1)	[100](1)	[830](1)
[1000](1)	[150](1)	[200](1)
[700](1)	[100](1)	[950](1)
[800](1)	[3600](1)	[200](1)
[250](1)	[600](1)	[250](1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: [C_{2v}]
Bond Distances: Mo–O = [1.83] Å O–H = [0.958] Å
Bond Angles: O–Mo–O = [109.5]° H–O–Mo = [104.5]°
HO–Mo–OH plane perpendicular to O–M–O plane
Product of the Moments of Inertia: $I_A I_B I_C = [1.536748 \times 10^{-113}]\ g^3·cm^6$

Enthalpy of Formation

The enhanced volatility of metallic molybdenum and molybdenum trioxide in the presence of water vapor at high temperatures has been investigated by several workers[1,2,3] using transpiration techniques. Glemser and Haeseler[1] and Bulten[2] have shown that the major volatilization reaction of the oxide is:

A. $MoO_3(cr) + H_2O(g) = MoO_2(OH_2)(g)$.

For the reaction of metallic molybdenum with water vapor, Belton and Jordan[3] reported the existence of $MoO_2(OH)_2(g)$ according to the equilibrium:

B. $Mo(cr) + 4H_2O(g) = MoO_2(OH)_2(g) + 3H_2(g)$.

2nd and 3rd law analyses of these equilibrium data are summarized below.

Source	Reaction	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Glemser and Haeseler[1]	A	873–963	Equation	36.2	31.9 ± 0.3	−4.2	−204.0 ± 0.5
Buiten[2]	A	673–773	Equation	30.0	32.2 ± 0.3	3.6	−203.7 ± 0.5
Belton and Jordan[3]	B	1473–1773	Equation	30.1	28.6 ± 0.1	−0.1	−202.6 ± 0.3

The adopted value, $\Delta_f H°(MoO_2(OH)_2, g) = -203.4 \pm 1.0\ kcal·mol^{-1}$, is an average of these three results.

Heat Capacity and Entropy

The assumed tetrahedral structure for $MoO_2(OH)_2$ is from Jordan.[4] The O–H bond length and H–O–Mo bond angle are assumed to be the same as for $H_2O(g)$. The Mo–O bond length is from the compilation of Sutton[5] and assumed to be the same as for Ag_2MoO_4. Principal moments of inertia are: $I_A = 23.7897 \times 10^{-39}$, $I_B = 25.3843 \times 10^{-39}$, and $I_C = 25.4477 \times 10^{-39}\ g·cm^2$.

The vibrational frequencies are estimated by comparison with those for $H_2SO_4(g)$[6,7] and are adjusted to give $S°(MoO_2(OH)_2, g) = 137.4$ cal·K^{-1}·mol^{-1} at 1600 K. This entropy value is derived from a 2nd law analysis of the equilibrium data for reaction *B* reported by Belton and Jordan.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−22.282	−842.889	−842.889	INFINITE
100	68.112	262.488	437.713	−17.523	−847.429	−828.241	432.629
200	89.457	317.041	364.698	−9.531	−849.796	−808.032	211.036
250	97.403	337.873	357.298	−4.856	−850.551	−797.499	166.628
298.15	104.154	355.620	355.620	0.	−851.026	−787.234	137.920
300	104.395	356.265	355.622	0.193	−851.039	−786.838	137.001
350	110.374	372.819	356.916	5.566	−851.282	−776.115	115.829
400	115.405	387.896	359.860	11.214	−851.321	−765.372	99.947
450	119.623	401.740	363.755	17.093	−851.202	−754.635	87.596
500	123.177	414.532	368.201	23.166	−850.959	−743.917	77.716
600	128.789	437.512	377.882	35.778	−850.212	−722.574	62.906
700	133.009	457.696	387.871	48.877	−849.232	−701.376	52.337
800	136.310	475.681	397.744	62.350	−848.107	−680.329	44.421
900	138.977	491.895	407.319	76.118	−846.891	−659.429	38.272
1000	141.185	506.656	416.526	90.130	−845.620	−638.668	33.361
1100	143.043	520.202	425.344	104.344	−844.325	−618.035	29.348
1200	144.627	532.718	433.777	118.729	−843.034	−597.520	26.009
1300	145.988	544.349	441.840	133.262	−841.770	−577.112	23.189
1400	147.167	555.212	449.554	147.921	−840.552	−556.800	20.774
1500	148.192	565.401	456.941	162.690	−839.398	−536.573	18.685
1600	149.089	574.995	464.023	177.555	−838.326	−516.420	16.859
1700	149.876	584.057	470.820	192.504	−837.349	−496.331	15.250
1800	150.570	592.644	477.351	207.527	−836.483	−476.297	13.822
1900	151.184	600.802	483.636	222.615	−835.741	−456.308	12.545
2000	151.729	608.571	489.690	237.762	−835.136	−436.353	11.396
2100	152.214	615.985	495.529	252.959	−834.682	−416.426	10.358
2200	152.648	623.077	501.166	268.203	−834.389	−396.516	9.414
2300	153.037	629.871	506.615	283.487	−834.271	−376.617	8.553
2400	153.386	636.391	511.888	298.809	−834.340	−356.718	7.764
2500	153.701	642.659	516.994	314.163	−834.609	−336.812	7.037
2600	153.987	648.693	521.944	329.548	−835.100	−316.892	6.366
2700	154.245	654.510	526.747	344.960	−835.854	−296.947	5.745
2800	154.480	660.124	531.411	360.396	−836.934	−276.968	5.167
2900	154.694	665.548	535.943	375.855	−874.304	−256.896	4.627
3000	154.890	670.796	540.351	391.334	−874.242	−235.607	4.102
3100	155.069	675.878	544.642	406.833	−874.221	−214.319	3.611
3200	155.233	680.804	548.820	422.348	−874.241	−193.033	3.151
3300	155.384	685.583	552.892	437.879	−874.301	−171.745	2.718
3400	155.524	690.224	556.864	453.424	−874.401	−150.453	2.311
3500	155.652	694.734	560.739	468.983	−874.540	−129.159	1.928
3600	155.771	699.120	564.522	484.554	−874.718	−107.860	1.565
3700	155.882	703.390	568.218	500.137	−874.933	−86.556	1.222
3800	155.984	707.548	571.830	515.730	−875.187	−65.243	0.897
3900	156.079	711.601	575.362	531.334	−875.477	−43.925	0.588
4000	156.168	715.554	578.818	546.946	−875.803	−22.600	0.295
4100	156.250	719.411	582.200	562.567	−876.166	−1.265	0.016
4200	156.327	723.177	585.512	578.196	−876.564	20.078	−0.250
4300	156.399	726.857	588.756	593.832	−876.998	41.433	−0.503
4400	156.467	730.453	591.936	609.476	−877.468	62.796	−0.745
4500	156.530	733.970	595.053	625.125	−877.972	84.170	−0.977
4600	156.590	737.411	598.111	640.782	−878.513	105.557	−1.199
4700	156.646	740.779	601.111	656.443	−879.089	126.956	−1.411
4800	156.699	744.078	604.055	672.111	−879.701	148.368	−1.615
4900	156.748	747.309	606.945	687.783	−880.350	169.794	−1.810
5000	156.795	750.477	609.785	703.460	−1472.420	196.964	−2.058
5100	156.839	753.582	612.574	719.142	−1474.822	230.376	−2.360
5200	156.881	756.628	615.315	734.828	−1477.409	263.834	−2.650
5300	156.921	759.617	618.009	750.518	−1480.178	297.347	−2.931
5400	156.958	762.550	620.659	766.212	−1483.131	330.912	−3.201
5500	156.994	765.430	623.265	781.910	−1486.263	364.532	−3.462
5600	157.027	768.260	625.829	797.611	−1489.576	398.215	−3.714
5700	157.059	771.039	628.352	813.315	−1493.065	431.955	−3.958
5800	157.090	773.771	630.836	829.023	−1496.731	465.761	−4.195
5900	157.119	776.457	633.281	844.733	−1500.570	499.626	−4.423
6000	157.146	779.098	635.690	860.446	−1504.583	533.563	−4.645

PREVIOUS: June 1970 (1 atm) CURRENT: June 1970 (1 bar)

$S°(298.15\ K) = 194.707\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 193.246 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 190.372 \pm 6.3\ kJ·mol^{-1}$

Electronic Levels (Quantum Weights) and Vibrational Frequencies (Degeneracies)				
State	ϵ, cm^{-1}	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
$\tilde{X}^2B_1$	0(2)	[3173](1)	1497.2(1)	3220 (1)
$\tilde{A}^2A_1(\pi)$	10249(2)	3325 (1)	633 (1)	[3220](1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: N–H = 1.024 Å
Bond Angle: H–N–H = 103°
Product of the Moments of Inertia: $I_A I_B I_C = 0.0085 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

Direct kinetic studies[1-5] onthe decomposition of hydrazine, $N_2H_4(g) = 2\ NH_2(g)$, give activation energies which suggest $\Delta_f H°(NH_2, 298.15\ K) \leq 40\ kcal·mol^{-1}$. [The kinetic rates are discribed by k_d for the the forward reaction and k_r for the reverse reaction]. The pre–exponential factor suggests $k_r \sim 10^7 - 10^8$ l/(mol s). This is exceptionally slow for a radical combination reaction[6] and is at variance with the most recent direct measurements of $k_r = 10^{10.8}$ l/(mol s) (300 K, 1500 mmHg)[7] and $k_r = 10^{9.4}$ l/(mol s) (300 K, 10 mmHg).[8] A possible explanation for this discrepancy is that the hydrazine decomposition studies have been carried out in the energy dependent region.[9,10] This has been confirmed on the basis of RRKM calculations. With $\Delta_f H°(298.15\ K) = 40\ kcal·mol^{-1}$, it is not possible to simultaneously reproduce the measured forward (k_d) and backward (k_r) rates by orders of magnitude. With a value of $\Delta_f H°(298.15\ K) = 45.5\ kcal·mol^{-1}$, all of the rate data can be fitted to a factor of three. For higher values of $\Delta_f H°(298.15\ K)$, the discrepancy increases.

Data on the thermal decomposition of benzylamine from toluene–carrier studies[2,11] yield $\Delta_f H°(298.15\ K) = 36\ kcal·mol^{-1}$. This technique, however, has consistently yielded erroneous rate paramters.[12] Using their very low pressure pyrolysis technique, Golden *et al.*[13] find $\Delta_f H°(NH_2, 298.15\ K) = 47.2\ kcal·mol^{-1}$. This is in reasonable agreement with the recommended value.

Heat Capacity and Entropy

The bond distance and angle are from the electronic absorption spectrum as summarized by Herzberg.[14] The vibrational frequencies are obtained from Herzberg[14] and from matrix–isolation studies of Milligan and Jacox.[15]

The National Bureau of Standards prepared this table[16] by critical analysis of data existing in 1972. Using $S°$, $C_p°$ and $\Delta_f H°$ selected by NBS,[16] we recalculate the table in terms of current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.929	193.246	193.246	INFINITE
100	33.259	158.327	224.351	−6.602	192.122	194.352	−101.519
200	33.280	181.381	197.762	−3.276	191.299	196.904	−51.426
298.15	33.572	194.707	194.707	0.	190.372	199.846	−35.012
300	33.585	194.915	194.708	0.062	190.354	199.905	−34.807
400	34.395	204.680	196.034	3.458	189.386	203.236	−26.540
500	35.533	212.474	198.567	6.953	188.488	206.804	−21.605
600	36.838	219.066	201.448	10.571	187.685	210.545	−18.330
700	38.254	224.851	204.386	14.325	186.980	214.412	−16.000
800	39.715	230.054	207.274	18.224	186.371	218.373	−14.258
900	41.179	234.817	210.074	22.269	185.853	222.405	−12.908
1000	42.597	239.229	212.771	26.458	185.419	226.491	−11.831
1100	43.945	243.353	215.366	30.786	185.059	230.616	−10.951
1200	45.196	247.231	217.861	35.244	184.764	234.771	−10.219
1300	46.355	250.895	220.263	39.822	184.525	238.948	−9.601
1400	47.417	254.370	222.576	44.511	184.333	243.142	−9.072
1500	48.392	257.675	224.807	49.303	184.182	247.348	−8.613
1600	49.292	260.827	226.960	54.187	184.066	251.563	−8.213
1700	50.128	263.841	229.042	59.159	183.982	255.784	−7.859
1800	50.907	266.728	231.056	64.211	183.925	260.010	−7.545
1900	51.647	269.501	233.007	69.339	183.895	264.238	−7.264
2000	52.346	272.168	234.899	74.539	183.891	268.467	−7.012
2100	53.020	274.738	236.735	79.807	183.912	272.695	−6.783
2200	53.664	277.220	238.519	85.142	183.957	276.922	−6.575
2300	54.287	279.619	240.254	90.539	184.027	281.146	−6.385
2400	54.894	281.942	241.943	95.999	184.123	285.366	−6.211
2500	55.484	284.195	243.588	101.518	184.243	289.583	−6.050
2600	56.053	286.383	245.192	107.095	184.389	293.793	−5.902
2700	56.605	288.508	246.757	112.728	184.560	297.998	−5.765
2800	57.145	290.577	248.286	118.415	184.757	302.196	−5.638
2900	57.664	292.591	249.779	124.156	184.977	306.386	−5.519
3000	58.162	294.555	251.239	129.947	185.222	310.569	−5.407
3100	58.643	296.470	252.667	135.788	185.489	314.742	−5.303
3200	59.103	298.339	254.065	141.675	185.778	318.907	−5.206
3300	59.542	300.164	255.435	147.608	186.088	323.063	−5.114
3400	59.961	301.948	256.776	153.583	186.417	327.209	−5.027
3500	60.359	303.692	258.092	159.599	186.763	331.345	−4.945
3600	60.735	305.398	259.383	165.654	187.126	335.471	−4.868
3700	61.087	307.067	260.649	171.746	187.503	339.586	−4.794
3800	61.417	308.700	261.892	177.871	187.892	343.691	−4.724
3900	61.725	310.299	263.113	184.028	188.291	347.786	−4.658
4000	62.011	311.866	264.312	190.215	188.700	351.870	−4.595
4100	62.274	313.400	265.491	196.430	189.115	355.945	−4.535
4200	62.517	314.904	266.649	202.669	189.535	360.009	−4.477
4300	62.740	316.378	267.789	208.932	189.958	364.063	−4.422
4400	62.944	317.822	268.909	215.217	190.383	368.107	−4.370
4500	63.128	319.239	270.012	221.521	190.807	372.141	−4.320
4600	63.291	320.628	271.098	227.842	191.230	376.166	−4.271
4700	63.438	321.991	272.166	234.178	191.650	380.182	−4.225
4800	63.568	323.328	273.218	240.529	192.066	384.189	−4.181
4900	63.684	324.640	274.254	246.891	192.476	388.187	−4.138
5000	63.785	325.928	275.275	253.265	192.879	392.177	−4.097
5100	63.871	327.192	276.280	259.648	193.275	396.159	−4.057
5200	63.944	328.433	277.271	266.039	193.663	400.133	−4.019
5300	64.003	329.651	278.248	272.436	194.042	404.100	−3.983
5400	64.052	330.848	279.211	278.839	194.412	408.060	−3.947
5500	64.091	332.024	280.161	285.246	194.772	412.013	−3.913
5600	64.116	333.179	281.097	291.657	195.122	415.960	−3.880
5700	64.134	334.314	282.021	298.069	195.462	419.901	−3.848
5800	64.143	335.429	282.932	304.483	195.791	423.835	−3.817
5900	64.144	336.526	283.831	310.898	196.110	427.764	−3.787
6000	64.137	337.604	284.718	317.312	196.419	431.688	−3.758

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K)$ = [218.603] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 220.00 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 212.97 \pm 10.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[3095](1)	[3205](1)
[1406](1)	[1495](1)
[1360](1)	[910](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: N–H = [1.014] Å; N–N = [1.23] Å
Bond Angle: H–N–N = [100]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.3981 × 10^{-117}] $g^3·cm^6$

Enthalpy of Formation

The standard enthalpy of formation, $\Delta_f H°(N_2H_2, g, 298.15\ K)$ = 50.9 $kcal·mol^{-1}$, was calculated from the appearance and ionization potentials of di–imide reported by Foner and Hudson[1] using the JANAF $\Delta_f H°(N_2H_4, g, 0\ K)$ = 26.1 $kcal·mol^{-1}$ in calculation. For example:

	$\Delta_r H°(0K)$
$N_2H_4(g) \rightarrow N_2H_2^+ + H_2(g) + e$	11.0 ± 0.2 $cal·K^{-1}·mol^{-1}$
$N_2H_2(g) \rightarrow N_2H_2^+ + e$	9.85 ± 0.1 $cal·K^{-1}·mol^{-1}$
$N_2H_4(g) \rightarrow N_2H_2(g) + H_2$	1.15 ± 0.2 $cal·K^{-1}·mol^{-1}$
	26.5 ± 5 $kcal·mol^{-1}$

From the above enthalpy of formation and that for NH(g) in the JANAF Tables 12–31–65, one can calculate a N–N bond energy of 109.4 ± 5 $kcal·mol^{-1}$ at 0 K. This is in agreement with the N–N bond in molecules such as N_2F_2.

Heat Capacity and Entropy

The bond distances and angle were obtained from a quantum–mechanical calculation by Wheland and Chen.[2] The principal moments of inertia are: I_A = [0.3114] × 10^{-39}, I_B = [1.9689] × 10^{-39} and I_C = [2.2803] × 10^{-39} $g·cm^2$.

Since there are 12 valency electrons in N_2H_2, Walsh[3] has predicted a bent ground state, existing in either a cis or a trans configuration for diimide. Blau and Hochheimer[4] have measured the infrared spectrum of diimide which was frozen in a cold trap as one of the decomposition products of N_2H_4. The spectrum of the solid N_2H_2 at liquid nitrogen temperature agrees with the predicted non–linear planar structure, and the molecule N_2H_2 appears mainly in cis form. They have also assigned six fundamental vibrational frequencies for cis H_2H_4(s) which have been adopted here for gaseous cis N_2H_2. Blau and Hochheimer also observed two gas phase bands (1277–1314 and 3050–3190 cm^{-1}). Rosengren and Pimentel[5] have observed these bands in matrix isolation studies. They assigned ν_1 or ν_4 = 3074 cm^{-1} and ν_3 = 1279 cm^{-1} which are in satisfactory agreement with the selected frequencies.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.107	219.996	219.996	INFINITE
100	33.261	181.498	249.315	−6.782	217.420	225.324	−117.697
200	33.870	204.651	221.843	−3.438	215.159	234.108	−61.143
250	34.966	212.315	219.195	−1.720	214.026	238.977	−49.932
298.15	36.554	218.603	218.603	0.	212.966	243.880	−42.727
300	36.624	218.829	218.604	0.068	212.926	244.071	−42.497
350	38.678	224.625	219.057	1.949	211.901	249.345	−37.213
400	40.937	229.936	220.089	3.939	210.974	254.758	−33.268
450	43.247	234.891	221.461	6.044	210.153	260.282	−30.213
500	45.508	239.565	223.040	8.263	209.436	265.891	−27.777
600	49.713	248.242	226.529	13.028	208.288	277.296	−24.141
700	53.426	256.190	230.206	18.189	207.469	288.866	−21.555
800	56.683	263.541	233.919	23.698	206.916	300.535	−19.623
900	59.540	270.386	237.595	29.512	206.579	312.259	−18.123
1000	62.049	276.792	241.198	35.594	206.417	324.012	−16.925
1100	64.250	282.812	244.710	41.912	206.398	335.773	−15.945
1200	66.179	288.487	248.124	48.435	206.495	347.531	−15.128
1300	67.871	293.852	251.437	55.140	206.685	359.277	−14.436
1400	69.353	298.937	254.650	62.002	206.950	371.005	−13.842
1500	70.655	303.767	257.765	69.004	207.275	382.712	−13.327
1600	71.799	308.365	260.785	76.128	207.649	394.396	−12.876
1700	72.807	312.748	263.713	83.359	208.061	406.055	−12.477
1800	73.697	316.936	266.555	90.686	208.504	417.689	−12.121
1900	74.486	320.942	269.313	98.095	208.972	429.298	−11.802
2000	75.186	324.781	271.991	105.580	209.457	440.882	−11.515
2100	75.809	328.464	274.593	113.130	209.957	452.441	−11.254
2200	76.366	332.004	277.122	120.739	210.468	463.976	−11.016
2300	76.865	335.410	279.583	128.401	210.986	475.487	−10.799
2400	77.313	338.691	281.978	136.111	211.508	486.976	−10.599
2500	77.718	341.855	284.310	143.863	212.034	498.443	−10.414
2600	78.083	344.911	286.583	151.653	212.560	509.889	−10.244
2700	78.413	347.864	288.798	159.478	213.085	521.315	−10.085
2800	78.714	350.721	290.959	167.335	213.608	532.721	−9.938
2900	78.987	353.488	293.067	175.220	214.127	544.109	−9.800
3000	79.237	356.170	295.126	183.131	214.642	555.479	−9.672
3100	79.466	358.772	297.138	191.067	215.151	566.832	−9.551
3200	79.675	361.298	299.103	199.024	215.653	578.168	−9.438
3300	79.868	363.753	301.025	207.001	216.149	589.489	−9.331
3400	80.045	366.140	302.906	214.997	216.636	600.795	−9.230
3500	80.209	368.463	304.746	223.010	217.114	612.087	−9.135
3600	80.360	370.724	306.547	231.038	217.583	623.365	−9.045
3700	80.500	372.928	308.312	239.081	218.041	634.631	−8.959
3800	80.630	375.077	310.040	247.138	218.490	645.884	−8.878
3900	80.751	377.173	311.735	255.207	218.927	657.125	−8.801
4000	80.863	379.219	313.397	263.288	219.352	668.356	−8.728
4100	80.968	381.217	315.026	271.379	219.766	679.576	−8.658
4200	81.066	383.169	316.626	279.481	220.168	690.786	−8.591
4300	81.157	385.077	318.196	287.592	220.557	701.986	−8.527
4400	81.243	386.944	319.737	295.712	220.933	713.178	−8.466
4500	81.323	388.771	321.251	303.841	221.296	724.361	−8.408
4600	81.399	390.559	322.738	311.977	221.646	735.536	−8.352
4700	81.470	392.310	324.200	320.120	221.984	746.704	−8.299
4800	81.536	394.026	325.637	328.271	222.308	757.865	−8.247
4900	81.599	395.708	327.050	336.427	222.619	769.019	−8.198
5000	81.658	397.357	328.439	344.590	222.917	780.168	−8.150
5100	81.714	398.975	329.807	352.759	223.202	791.309	−8.105
5200	81.767	400.562	331.152	360.933	223.475	802.446	−8.061
5300	81.817	402.120	332.476	369.112	223.736	813.578	−8.018
5400	81.865	403.650	333.780	377.296	223.986	824.705	−7.977
5500	81.909	405.153	335.064	385.485	224.224	835.826	−7.938
5600	81.952	406.629	336.329	393.678	224.452	846.945	−7.900
5700	81.992	408.080	337.575	401.875	224.670	858.059	−7.863
5800	82.031	409.506	338.803	410.077	224.878	869.169	−7.828
5900	82.067	410.909	340.013	418.282	225.076	880.275	−7.793
6000	82.102	412.288	341.207	426.490	225.267	891.379	−7.760

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [307.396 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -594.77 \pm 25.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -607.52 \pm 25.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[350](1)	[3700](1)
[209](1)	[3700](1)
[270](1)	[1250](1)
[201](1)	[1250](1)
[294](1)	[1250](1)
[313](1)	[1250](1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2h}
Bond Distances: Na–O = [2.17] Å O–H = [0.96] Å
Bond Angles: Na–O–Na = [90]° Na–O–H = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [8.159128 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

Mass spectrometric studies of the vapors in equilibrium with NaOH(l)[1,2] and mixed NaOH–KOH condensed phases,[3,4] along with a study of the vapor composition by a molecular beam velocity analysis technique,[5] have established the importance of monomeric and dimeric species in the temperature range 573–1050 K. Absolute partial pressures for the monomer and dimer calculated from peak intensity data by Porter and Schoonmaker[3] are analyzed by the 3rd law method with JANAF Gibbs energy functions[6] to give a enthalpy of dimerization of −50.0 $cal·mol^{-1}$ at 298.15 K. Schoonmaker and Porter[4] also calculated differences in the Gibbs energies of dimerization for several alkali metal hydroxide pairs from peak intensity data on mixed systems. A 3rd law analysis of the Gibbs energy data for the NaOH–KOH system leads to a difference in their enthalpies of dimerization of −6.0 $kcal·mol^{-1}$ at 298.15 K. Based upon the adopted value for KOH(g), $\Delta_{dim}H°$(= −45.3 $kcal·mol^{-16}$, we derive $\Delta_{dim}H°$(= −51.3 $kcal·mol^{-1}$ for NaOH(g). For the reaction 2 NaOH(g) = $Na_2(OH)_2$(g), we adopt a mean of these two results, $\Delta_{dim}H°(298.15\ K) = -50.7 \pm 3.0\ kcal·mol^{-1}$. Combining this result with the adopted enthalpy of formation for NaOH(g),[6] that for the dimer is $\Delta_f H°(Na_2(OH)_2, g, 298.15\ K) = -145.2 \pm 6.0\ kcal·mol^{-1}$.

Heat Capacity and Entropy

A key to the molecular structure of $Na_2(OH)_2$(g) is provided by the work of Buchler *et al.*[7] which involves the electric deflection of molecular beams of $Cs_2(OH)_2$(g) and $Na_2(OH)_2$(g). Their results indicate that these dimers are nonpolar which implies a planar structure for at least the M_2O_2 part of the molecule. The three models proposed thus far for the dimeric alkali metal hydroxides each incorporate this planar configuration for the alkali and oxygen atoms. Bauer *et al.*[8] proposed a model consisting of a square planar configuration for the alkali and oxygen atoms with two hydrogen bonded bridges between the oxygens and hydrogens. Schoonmaker and Porter[4] adopted the square planar model for the M_2O_2 configuration but did not allow for hydrogen bonding. Berkowitz *et al.*[9] proposed a model for $Li_2(OH)_2$(g) which consisted of a trans–configuration with hydrogens above and below the plane of a rhombus formed by the lithium and oxygen atoms, the O–Li–O bond angle being 100°. The adopted molecular structure for $Na_2(OH)_2$(g) is similar to the model of Berkowitz *et al.*[9] but with the O–Na–O bond angle equal to 90°. The Na–O–H bond angle is assumed equal to 110°. The Na–O bond distance is estimated as being 12% longer than that in NaOH(g). The O–H bond distance is estimated to be the same as in H_2O(g). The principal moments of inertia are: $I_A = [14.0843] \times 10^{-39}$, $I_B = [18.1898] \times 10^{-39}$, and $I_C = [31.8478] \times 10^{-39}\ g·cm^2$.

The first six vibrational frequencies are estimated by comparison with those for other alkali metal fluorides and hydroxides. The remaining O–H stretching and bending modes are estimates taken from the work of Berkowitz *et al.*[9]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.301	−594.774	−594.774	INFINITE
100	49.910	235.707	370.856	−13.515	−599.571	−590.975	308.694
200	70.007	277.594	314.373	−7.356	−603.928	−580.589	151.634
250	75.172	293.797	308.679	−3.720	−605.796	−574.535	120.043
298.15	79.284	307.396	307.396	0.	−607.517	−568.358	99.574
300	79.433	307.887	307.398	0.147	−607.582	−568.115	98.918
350	83.306	320.426	308.379	4.217	−609.343	−561.398	83.784
400	86.884	331.787	310.606	8.473	−616.377	−554.016	72.347
450	90.149	342.212	313.546	12.900	−618.052	−546.119	63.392
500	93.089	351.866	316.901	17.482	−619.551	−538.044	56.209
600	98.048	369.293	324.213	27.048	−622.106	−521.494	45.400
700	102.010	384.716	331.775	37.058	−624.193	−504.554	37.650
800	105.258	398.556	339.273	47.427	−625.932	−487.341	31.820
900	108.004	411.117	346.568	58.093	−627.420	−469.926	27.274
1000	110.381	422.622	353.606	69.015	−628.738	−452.355	23.629
1100	112.472	433.242	360.369	80.160	−629.958	−434.656	20.640
1200	114.327	443.110	366.858	91.502	−824.665	−411.970	17.933
1300	115.980	452.327	373.082	103.019	−824.009	−377.604	15.172
1400	117.457	460.977	379.055	114.692	−823.270	−343.293	12.808
1500	118.778	469.127	384.790	126.505	−822.464	−309.037	10.762
1600	119.960	476.831	390.304	138.443	−821.602	−274.836	8.972
1700	121.020	484.136	395.611	150.493	−820.694	−240.691	7.396
1800	121.970	491.081	400.723	162.643	−819.752	−206.600	5.995
1900	122.823	497.699	405.655	174.884	−818.783	−172.562	4.744
2000	123.590	504.019	410.416	187.205	−817.794	−138.576	3.619
2100	124.282	510.066	415.018	199.599	−816.793	−104.640	2.603
2200	124.906	515.862	419.471	212.059	−815.785	−70.751	1.680
2300	125.471	521.427	423.784	224.578	−814.776	−36.909	0.838
2400	125.982	526.778	427.965	237.151	−813.771	−3.110	0.068
2500	126.447	531.930	432.021	249.773	−812.775	30.647	−0.640
2600	126.869	536.898	435.960	262.439	−811.792	64.364	−1.293
2700	127.255	541.693	439.787	275.146	−810.828	98.044	−1.897
2800	127.607	546.328	443.510	287.889	−809.885	131.689	−2.457
2900	127.929	550.811	447.133	300.666	−808.968	165.300	−2.977
3000	128.225	555.153	450.662	313.474	−808.082	198.881	−3.463
3100	128.496	559.362	454.101	326.310	−807.230	232.432	−3.916
3200	128.746	563.446	457.454	339.173	−806.417	265.956	−4.341
3300	128.977	567.411	460.727	352.059	−805.646	299.455	−4.740
3400	129.190	571.265	463.921	364.967	−804.921	332.933	−5.115
3500	129.388	575.012	467.042	377.896	−804.248	366.389	−5.468
3600	129.571	578.660	470.092	390.845	−803.630	399.827	−5.801
3700	129.740	582.212	473.075	403.810	−803.073	433.248	−6.116
3800	129.898	585.675	475.992	416.792	−802.580	466.656	−6.415
3900	130.046	589.051	478.848	429.789	−802.156	500.052	−6.697
4000	130.183	592.345	481.645	442.801	−801.808	533.436	−6.966
4100	130.311	595.561	484.384	455.826	−801.540	566.814	−7.221
4200	130.431	598.703	487.069	468.863	−801.354	600.186	−7.464
4300	130.543	601.773	489.701	481.912	−801.262	633.555	−7.696
4400	130.649	604.775	492.282	494.971	−801.184	666.915	−7.917
4500	130.748	607.713	494.815	508.041	−801.246	700.280	−8.129
4600	130.841	610.587	497.300	521.121	−801.428	733.648	−8.331
4700	130.928	613.402	499.741	534.209	−801.719	767.023	−8.525
4800	131.011	616.160	502.137	547.306	−802.123	800.405	−8.710
4900	131.089	618.862	504.492	560.411	−802.648	833.796	−8.888
5000	131.162	621.511	506.806	573.524	−803.283	867.199	−9.060
5100	131.231	624.109	509.081	586.643	−804.061	900.616	−9.224
5200	131.297	626.658	511.317	599.770	−804.976	934.048	−9.383
5300	131.359	629.159	513.517	612.903	−806.033	967.502	−9.535
5400	131.418	631.615	515.682	626.042	−807.238	1000.975	−9.683
5500	131.474	634.027	517.811	639.186	−808.595	1034.472	−9.825
5600	131.527	636.397	519.908	652.336	−810.111	1067.997	−9.962
5700	131.578	638.725	521.972	665.492	−811.790	1101.549	−10.095
5800	131.626	641.014	524.005	678.652	−813.636	1135.133	−10.223
5900	131.671	643.264	526.007	691.817	−815.655	1168.748	−10.347
6000	131.715	645.478	527.980	704.986	−817.534	1202.364	−10.468

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 69.950 \pm 0.079\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -285.830 \pm 0.042\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation and uncertainty are taken from the CODATA recommended values[1] which are, in turn, based on calorimetric measurements by Rossini[2] and King and Armstrong.[3]

Heat Capacity and Entropy

The adopted C_p° data from 273.15 to 373.15 K are taken from the very accurate calorimetric measurements of Osborne *et al.*[4] Heat capacity data taken from the recent equation of state formulation of Haar *et al.*[5] agree with the adopted data to within 0.06% above 320 K with deviations up to 0.12% being noted near 305 K. In the latter region the experimental C_p° data go through a single smooth minimum while data derived from the equation of state exhibit an incipient double minimum behavior. These deviations are very small and would lead to nearly negligible differences in the thermochemical functions.

We have made an approximate extrapolation of C_p° (l, p=1 bar) to temperatures where water is unstable with respect to vaporization by using data derived from Haar's equation of state formulation.[5] From 373.15 to 390 K the adopted C_p°(1 bar) data were taken directly from Haar *et al.*[5] while from 400 to 450 K the adopted C_p° data were derived by taking advantage of the constant difference of 0.0090 $cal \cdot K^{-1} \cdot mol^{-1}$ between C_p(10 bar) and C_p°(1 bar) observed between 320 to 390 K using the data of Haar *et al.*[5] Above 450 K the C_p(100 bar) data[5] were adjusted by a similar procedure although the difference is no longer constant. The C_p° adjustment from 10 bar to 1 bar is less than 0.05% while that from 100 bar to 1 bar ranges from 0.9 to 1.2%.

The adopted value of $S°(298.15\ K) = 16.718 \pm 0.019\ cal \cdot K^{-1} \cdot mol^{-1}$ is taken from the CODATA recommended value.[1] This was calculated by CODATA from the entropy of the ideal gas with appropriate corrections for real gas behavior and vaporization.

Vaporization Data

The boiling point and enthalpy of vaporization to the real gas at p=1 bar are taken from the work of Haar *et al.*[5] see the H_2O (liquid–real gas at p=1 bar) JANAF Table[6] for further details. The enthalpy of vaporization, $\Delta_{vap}H°$, to the ideal gas is calculated as $\Delta_{vap}H° = \Delta_f H°(g) - \Delta_f H°(l, p=1\ bar)$ using JANAF data.[6] The temperature and enthalpy of vaporization at f=1 bar represent the calculated values at the point where $\Delta_r G° = 0$ for the process $H_2O(l) \rightarrow H_2O$(ideal gas). Thus, these values represent boiling to the (hypothetical) ideal vapor at a fugacity of 1 bar.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
280	75.563	65.215	70.102	−1.368	−286.410	−240.123	44.796
298.15	75.351	69.950	69.950	0.	−285.830	−237.141	41.546
300	75.349	70.416	69.952	0.139	−285.771	−236.839	41.237
320	75.344	75.279	70.134	1.646	−285.137	−233.598	38.131
340	75.388	79.847	70.573	3.153	−284.506	−230.396	35.396
360	75.679	84.164	71.209	4.664	−283.874	−227.231	32.970
372.780	75.962	86.808	71.699	5.633	--- LIQUID <--> REAL GAS ---		
380	76.154	88.267	72.000	6.182	−283.237	−224.102	30.805
400	76.770	92.189	72.912	7.711	−282.591	−221.006	28.860
420	77.547	95.952	73.920	9.254	−281.934	−217.943	27.105
440	78.543	99.582	75.004	10.814	−281.262	−214.912	25.513
460	79.793	103.100	76.150	12.397	−280.569	−211.911	24.063
480	81.463	106.530	77.344	14.009	−279.850	−208.941	22.737
500	83.694	109.898	78.579	15.659	−279.095	−206.002	21.521

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$\Delta_{at}H°(0\ K) = 917.769 \pm 0.109\ kJ \cdot mol^{-1}$
$S°(298.15\ K) = 188.834 \pm 0.042\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -238.921 \pm 0.042\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -241.826 \pm 0.042\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies[a] ν, cm^{-1}
3651.1(1)
1594.7(1)
3755.9(1)

Point Group: C_{2v} $\sigma = 2$
Rotational Constants[a]: $A_0 = 27.8847\ cm^{-1}$ $B_0 = 14.5118\ cm^{-1}$ $C_0 = 9.2806\ cm^{-1}$
[a]See Wooley[4] for detailed molecular constants on which this table is based.

Enthalpy of Formaton

The adopted value of $\Delta_f H°(298.15\ K)$ is that recommended by CODATA[1] and was calculated by CODATA from the heat of formation of liquid water at 298.15 K using vaporization data given by Keenan *et al.*[2] The enthalpy of atomization, $\Delta_{at}H°(0\ K) = 219.352 \pm 0.026$ $kcal \cdot mol^{-1}$, is calculated using auxiliary JANAF data.[3]

Heat Capacity and Entropy

The adopted heat capacity and entropy data below 2000 K, which are for water with the natural isotopic abundance, are taken from recent calculations by Woolley.[4] Wooley has done detailed calculations on the thermodynamic functions of light isotopic water ($^1H_2{}^{16}O$) and then corrected those to functions appropriate for water of natural isotopic abundance. Below 240 K, his calculation was a direct summation over rotational levels of the group vibrational state, with small additions above 130 K for the ν_2=1 vibrational level. Above 240 K, individual vibrational partition functions were summed to obtain the total partition function. During this summation the molecule was treated as a rigid rotator with modified corrections of Stripp–Kirkwood and centrifugal effect types, guided by the behavior found for the vibrational ground state. Details are given by Woolley.[4]

Between 2000 and 5000 K we adopt $C_p°$ data calculated by Friedman and Haar[5] for light isotopic water, after a small correction. Our correction consists of adding 0.021 $cal \cdot K^{-1} \cdot mol^{-1}$ to Friedman and Haar's $C_p°$ data. This correction arises from the constant difference of 0.021 ± 0.001 $cal \cdot K^{-1} \cdot mol^{-1}$ between Woolley's $C_p°$ data (natural abundance) and Friedman and Haar's $C_p°$ data (light isotopic water) in the temperature range 1300–2000 K. Above 5000 K, we have linearly extrapolated Friedman and Haar's corrected $C_p°$ data.

Below 2000 K there is good agreement among thermodynamic functions given by Woolley[4], Friedman and Haar[5] and Glushko *et al.*[6] Above 2000 K the $C_p°$ data from references[5] and[6] begin to deviate significantly; at 4000 and 6000 K the differences $[C_p°^{6} - C_p°^{5}]$ are 0.57 and 1.07 $cal \cdot K^{-1} \cdot mol^{-1}$, respectively. Woolley is working on extending his calculations to higher temperature[7] and his initial results[4] yield $C_p°$ values slightly higher than[5] but not nearly so high as.[6]

Values of $S°(298.15\ K)$ and $H°(298.15\ K) - H°(0\ K)$ in the present table are in excellent agreement with CODATA values[1] of 45.106 ± 0.01 $cal \cdot K^{-1} \cdot mol^{-1}$ K) and 2.368 ± 0.002 $kcal \cdot mol^{-1}$, respectively.

References

[1]ICSU–CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972); also refer to, CODATA Bulletin #17,"CODATA Recommended Key Values for Thermodynamics – 1975," (1976).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.904	−238.921	−238.921	INFINITE
100	33.299	152.388	218.534	−6.615	−240.083	−236.584	123.579
200	33.349	175.485	191.896	−3.282	−240.900	−232.766	60.792
298.15	33.590	188.834	188.834	0.	−241.826	−228.582	40.047
300	33.596	189.042	188.835	0.062	−241.844	−228.500	39.785
400	34.262	198.788	190.159	3.452	−242.846	−223.901	29.238
500	35.226	206.534	192.685	6.925	−243.826	−219.051	22.884
600	36.325	213.052	195.550	10.501	−244.758	−214.007	18.631
700	37.495	218.739	198.465	14.192	−245.632	−208.812	15.582
800	38.721	223.825	201.322	18.002	−246.443	−203.496	13.287
900	39.987	228.459	204.084	21.938	−247.185	−198.083	11.496
1000	41.268	232.738	206.738	26.000	−247.857	−192.590	10.060
1100	42.536	236.731	209.285	30.191	−248.460	−187.033	8.881
1200	43.768	240.485	211.730	34.506	−248.997	−181.425	7.897
1300	44.945	244.035	214.080	38.942	−249.473	−175.774	7.063
1400	46.054	247.407	216.341	43.493	−249.894	−170.089	6.346
1500	47.090	250.620	218.520	48.151	−250.265	−164.376	5.724
1600	48.050	253.690	220.623	52.908	−250.592	−158.639	5.179
1700	48.935	256.630	222.655	57.758	−250.881	−152.883	4.698
1800	49.749	259.451	224.621	62.693	−251.138	−147.111	4.269
1900	50.496	262.161	226.526	67.706	−251.368	−141.325	3.885
2000	51.180	264.769	228.374	72.790	−251.575	−135.528	3.540
2100	51.823	267.282	230.167	77.941	−251.762	−129.721	3.227
2200	52.408	269.706	231.909	83.153	−251.934	−123.905	2.942
2300	52.947	272.048	233.604	88.421	−252.092	−118.082	2.682
2400	53.444	274.312	235.253	93.741	−252.239	−112.252	2.443
2500	53.904	276.503	236.860	99.108	−252.379	−106.416	2.223
2600	54.329	278.625	238.425	104.520	−252.513	−100.575	2.021
2700	54.723	280.683	239.952	109.973	−252.643	−94.729	1.833
2800	55.089	282.680	241.443	115.464	−252.771	−88.878	1.658
2900	55.430	284.619	242.899	120.990	−252.897	−83.023	1.495
3000	55.748	286.504	244.321	126.549	−253.024	−77.163	1.344
3100	56.044	288.337	245.711	132.139	−253.152	−71.298	1.201
3200	56.323	290.120	247.071	137.757	−253.282	−65.430	1.068
3300	56.583	291.858	248.402	143.403	−253.416	−59.558	0.943
3400	56.828	293.550	249.705	149.073	−253.553	−53.681	0.825
3500	57.058	295.201	250.982	154.768	−253.696	−47.801	0.713
3600	57.276	296.812	252.233	160.485	−253.844	−41.916	0.608
3700	57.480	298.384	253.459	166.222	−253.997	−36.027	0.509
3800	57.675	299.919	254.661	171.980	−254.158	−30.133	0.414
3900	57.859	301.420	255.841	177.757	−254.326	−24.236	0.325
4000	58.033	302.887	256.999	183.552	−254.501	−18.334	0.239
4100	58.199	304.322	258.136	189.363	−254.684	−12.427	0.158
4200	58.357	305.726	259.252	195.191	−254.876	−6.516	0.081
4300	58.507	307.101	260.349	201.034	−255.078	−0.600	0.007
4400	58.650	308.448	261.427	206.892	−255.288	5.320	−0.063
4500	58.787	309.767	262.486	212.764	−255.508	11.245	−0.131
4600	58.918	311.061	263.528	218.650	−255.738	17.175	−0.195
4700	59.044	312.329	264.553	224.548	−255.978	23.111	−0.257
4800	59.164	313.574	265.562	230.458	−256.229	29.052	−0.316
4900	59.275	314.795	266.554	236.380	−256.491	34.998	−0.373
5000	59.390	315.993	267.531	242.313	−256.763	40.949	−0.428
5100	59.509	317.171	268.493	248.258	−257.046	46.906	−0.480
5200	59.628	318.327	269.440	254.215	−257.338	52.869	−0.531
5300	59.746	319.464	270.373	260.184	−257.639	58.838	−0.580
5400	59.864	320.582	271.293	266.164	−257.950	64.811	−0.627
5500	59.982	321.682	272.199	272.157	−258.268	70.791	−0.672
5600	60.100	322.764	273.092	278.161	−258.595	76.777	−0.716
5700	60.218	323.828	273.973	284.177	−258.930	82.769	−0.758
5800	60.335	324.877	274.841	290.204	−259.272	88.767	−0.799
5900	60.453	325.909	275.698	296.244	−259.621	94.770	−0.839
6000	60.571	326.926	276.544	302.295	−259.977	100.780	−0.877

PREVIOUS: March 1961 (1 atm) CURRENT: March 1979 (1 bar)

$S°(298.15\ K) = 69.950 \pm 0.079\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -285.830 \pm 0.042\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Refer to the H_2O(l, p=1 bar) table for details.[1]

Heat Capacity and Entropy

The adopted heat capacity data in the liquid region are taken from the very accurate calorimetric measurements of Osborne *et al.*[2] The adopted heat capacity data for the real gas at one bar pressure are taken from the recent equation of state formulation of Haar *et al.*[3] Refer to the JANAF Table for H_2O(l, p=1 bar) for details concerning the entropy.

Phase Data

Our table refers to the real fluid existing at the standard–state pressure of 1 bar. Since this pressure is below the critical pressure of water [P_c = 217.6 bar at T_c = 647.14 K][4] there is a first order transition at the normal boiling point. Therefore, this is a two phase (liquid real gas) table for the real fluid at p=1 bar.

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f for the real gas at p=1 bar is given by $f = \exp[\Delta_f G(\text{real gas})\ \Delta_f G°(\text{ideal gas})/(RT)]$ using real gas data from this table and ideal gas data from from JANAF.[1] Since p=1 bar, the fugacity coefficient (f/P) is equal to the fugacity. The fugacity coefficient is 0.986 at 400 K and approaches 1 as temperature increases, indicating nearly ideal behavior at all temperatures.

References

[1]JANAF Thermochemical Tables: H_2O(l, p=1 bar), H_2O(ideal gas), 3–31–79.
[2]N. S. Osborne, H. F. Stimson and D. C. Ginnings, J. Res. Nat. Bur. Stand., 197 (1939).
[3]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).
[4]J. F. Matthews, Chem. Rev. 2, 71 (1972).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
280	75.563	65.215	70.102	−1.368	−286.410	−240.123	44.796
298.15	75.351	69.950	69.950	0.	−285.830	−237.141	41.546
300	75.349	70.416	69.952	0.139	−285.771	−236.839	41.237
320	75.344	75.279	70.134	1.646	−285.137	−233.598	38.131
340	75.388	79.847	70.573	3.153	−284.506	−230.396	35.396
360	75.679	84.164	71.209	4.664	−283.874	−227.231	32.970
372.780	75.962	86.808	71.699	5.633	____ LIQUID <--> REAL GAS ____		
372.780	36.800	195.911	71.699	46.304	PRESSURE = 1 bar		
400	35.982	198.473	80.240	47.293	−243.009	−223.937	29.243
500	35.699	206.428	104.712	50.858	−243.896	−219.069	22.886
600	36.521	213.003	122.227	54.466	−244.797	−214.018	18.632
700	37.596	218.712	135.612	58.170	−245.658	−208.819	15.582
800	38.780	223.809	146.323	61.988	−246.461	−203.501	13.287
900	40.023	228.448	155.194	65.928	−247.198	−198.086	11.497
1000	41.292	232.730	162.736	69.994	−247.868	−192.593	10.060
1100	42.554	236.725	169.283	74.186	−248.468	−187.035	8.882
1200	43.781	240.481	175.061	78.504	−249.004	−181.426	7.897
1300	44.954	244.032	180.231	82.941	−249.479	−175.775	7.063
1400	46.062	247.404	184.910	87.492	−249.899	−170.090	6.346
1500	47.097	250.618	189.184	92.151	−250.269	−164.376	5.724
1600	48.057	253.689	193.120	96.909	−250.595	−158.639	5.179
1700	48.941	256.629	196.770	101.760	−250.884	−152.883	4.698
1800	49.753	259.450	200.175	106.695	−251.141	−147.111	4.269

Since the standard state for a gas is defined as the ideal gas at one bar pressure, the gas phase properties in this table are not standard state properties. The superscript zero, representing standard state, refers only to liquid-phase properties and not to gas-phase properties which are for the real gas at P=1 bar.

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298.15 K, 10 bar) = 69.946 ± 0.084 J·K^{-1}·mol^{-1} $\Delta_f H$(298.15 K, 10 bar) = −285.815 ± 0.042 kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation of H_2O at 298.15 K and p=10 bar [$\Delta_f H$ H(298.15 K, 10 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0.010 kcal·mol^{-1}] by addition of the enthalpy increment [H(298.15 K, 10 bar)–$H°$(298.15 K)]. The enthalpy increment is taken from the recent equation of state formation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H°$, $\Delta_f G°$ and log $K°$ in this table refer to formation of H_2O at p=10 bar from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equiuccirclation of state formulation by less than 0.0001 cal·K^{-1}·mol^{-1} and 0.0001 kcal·mol^{-1}, respectively. The starting point for the entropy integration [S(298.15 K, 10 bar)] is obtained from the CODATA[1] entropy at standard conditions [$S°$(l, 298.15 K) = 16.7184 ± 0.019 cal·K^{-1}·mol^{-1})] by addition of the entropy increment [S(298.15 K, 10 bar) $S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation[2]

Phase Data

Our table refers to the real fluid phase existing at the nonstandard state pressure of 10 bar. Since this pressure is below the critical pressure of water [P_c = 217.6 bar at T_c = 647.14 K[3]] there is a first order transition at the boiling temperature. Therefore this is a two phase (liquid–real gas) table for the real fluid at p=10 bar.

Vaporization Data

The adopted boiling temperature (at 10 bar) and enthalpy of vaporization are taken from the equation of state formulation of Haar *et al.*[2]

Fugacity and Fugacity Coefficients Data

At temperature T the fugacity f of water at p=10 bar is given by f=$K/K°$ or f=exp[($\Delta_f G°$–$\Delta_f G°$)/(RT)], where K and $\Delta_f G°$ are values for H_2O(ideal gas, T).[4] The fugacity coefficient (f/P) at p = 10 bar is given by f/10. At p = 10 bar the fugacity coefficient is 0.99 at 800 K and the gas behaves in a nearly ideal manner above that temperature.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972); see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics 1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. **72**, 71 (1972).

[4]JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H*$	$\Delta_f G*$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
	at P = 10 bar						
0							
100							
200							
298.15	75.313	69.946	69.946	0.	−285.815	−237.125	41.543
300	75.314	70.412	69.948	0.139	−285.756	−236.823	41.235
400	76.732	92.173	72.906	7.707	−282.580	−220.989	28.858
453.070	79.322	101.872	75.740	11.840	___ LIQUID <--> REAL GAS ___		
453.070	46.063	181.988	75.740	48.138	PRESSURE = 10 bar		
500	41.002	186.240	85.919	50.160	−244.579	−209.657	21.903
600	38.430	193.409	103.261	54.089	−245.159	−202.623	17.640
700	38.527	199.326	116.572	57.927	−245.886	−195.477	14.587
800	39.310	204.517	127.247	61.816	−246.618	−188.225	12.290
900	40.357	209.206	136.097	65.798	−247.314	−180.884	10.498
1000	41.517	213.517	143.626	69.891	−247.955	−173.468	9.061
1100	42.714	217.531	150.164	74.103	−248.537	−165.990	7.882
1200	43.900	221.298	155.937	78.434	−249.059	−158.462	6.898
1300	45.045	224.858	161.103	82.881	−249.524	−150.893	6.063
1400	46.134	228.236	165.778	87.441	−249.935	−143.291	5.346
1500	47.155	231.454	170.050	92.106	−250.299	−135.660	4.724
1600	48.104	234.528	173.985	96.869	−250.620	−128.007	4.179
1700	48.981	237.471	177.633	101.724	−250.904	−120.335	3.697
1800	49.786	240.294	181.037	106.663	−251.157	−112.647	3.269

Values of $\Delta_f H*$, $\Delta_f G*$, and Log K_f* in this table refer to formation of H_2O at P = 10 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298.15 K, 100 bar) = 69.903 ± 0.105 J·K^{-1}·mol^{-1} $\Delta_f H$(298.15 K, 100 bar) = −285.666 ± 0.084 kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation of H_2O at 298.15 K and p=100 bar [$\Delta_f H$(298.15 K, 100 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0.10 kcal·mol^{-1}] by addition of the enthalpy increment [H(298.15 K, 100 bar)–$H°$(298.15 K)]The enthalpy increment is taken from the recent equation of state formulation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H*$, $\Delta_f G°$ and log $K°$ in this table refer to formation of H_2O at p=100 bar from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equation of state formulation by less than 0.0012 cal·K^{-1}·mol^{-1} and 0.0008 kcal·mol^{-1}, respectively. The starting point for the entropy integration [S(298.15 K, 100 bar)] is obtained from the CODATA[1] entropy at standard conditions [$S°$(l, 298.15 K) = 16μccircl.7184 ± 0.019 cal·K^{-1}·mol^{-1}] by addition of the entropy increment [S(298.15 K, 100 bar)–$S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation.[2]

Phase Data

Our table refers to the real fluid phase existing at the nonstandard state pressure of 100 bar. Since this pressure is below the critical pressure of water [P_c = 217.6 bar at T_c = 647.14 K][3] there is a first order transition at the boiling temperature. Therefore this is a two phase (liquid real gas) table for the real fluid at p=100 bar.

Vaporization Data

The adopted boiling temperature (at 100 bar) and enthalpy of vaporization are taken from the equation of state formulation of Haar *et al.*[2]

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f of water at p=100 bar is given by f=$K/K°$ or f=exp[$\Delta_f G°$–$\Delta_f G°$)/(RT)], where K and $\Delta_f G°$ are values for H_2O(ideal gas).[4] The fugacity coefficient (f/p) at p=100 bar is given by f/100. At p=100 bar the fugacity coefficient is 0.99 at 1200 K and the gas behaves in a nearly ideal manner above that temperature.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972); see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics 1975," (1976).
[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and personal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).
[3]J. F. Matthews, Chem. Rev. **72**, 71 (1972).
[4] JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H*$	$\Delta_f G*$	log K_f*
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
	at P = 100 bar						
0							
100							
200							
298.15	74.864	69.903	69.903	0.	−285.666	−236.963	41.515
300	74.878	70.366	69.905	0.139	−285.608	−236.661	41.206
400	76.313	92.021	72.848	7.669	−282.468	−220.816	28.836
500	82.696	109.578	78.481	15.548	−279.041	−205.789	21.499
584.180	110.330	123.855	83.972	23.299	LIQUID <--> REAL GAS		
584.180	124.260	164.476	83.972	47.029	PRESSURE = 100 bar		
600	92.684	167.317	86.134	48.710	−250.389	−192.197	16.732
700	51.828	177.340	98.532	55.165	−248.498	−182.699	13.633
800	45.622	183.761	108.802	59.968	−248.317	−173.320	11.317
900	44.071	189.023	117.430	64.434	−248.528	−163.934	9.514
1000	43.949	193.653	124.825	68.828	−248.869	−154.517	8.071
1100	44.414	197.861	131.276	73.244	−249.247	−145.064	6.889
1200	45.145	201.756	136.989	77.721	−249.623	−135.576	5.901
1300	45.991	205.403	142.113	82.277	−249.978	−126.057	5.065
1400	46.872	208.844	146.758	86.920	−250.306	−116.513	4.347
1500	47.745	212.108	151.007	91.651	−250.603	−106.945	3.724
1600	48.586	215.216	154.923	96.468	−250.871	−97.359	3.178
1700	49.380	218.186	158.558	101.367	−251.112	−87.757	2.696
1800	50.123	221.029	161.950	106.343	−251.328	−78.142	2.268

Values of $\Delta_f H*$, $\Delta_f G*$, and Log K_f* in this table refer to formation of H_2O at P = 100 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298.15 K, 500 bar) = 69.696 ± 0.167 J·K^{-1}·mol^{-1} $\Delta_f H$(298.15 K, 500 bar) = −285.014 ± 0.167 kJ·mol^{-1}

Enthalpy of Formation

The enthalpy of formation of H_2O at 298.15 K and p=500 bar [$\Delta_f H°$(298.15 K, 500 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0.010 kcal·mol^{-1}] by addition of the enthalpy increment [H(298.15 K, 500 bar)–$H°$(298.15 K)]. The enthalpy increment is taken from the recent equation of state formulation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H°$, $\Delta_f G°$ and log $K°$ in this table refer to formation of H_2O (real fluid at p = 500 bar) from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equation of state formulation by less than 0.0004 cal·K^{-1}·mol^{-1} and 0.0002 kcal·mol^{-1}, respectively. The starting point for the entropy integration [S(298.15 K, 500 bar)] is obtained from the CODATA[1] entropy at standard condtions [$S°$(l, 298.15 K) = 16.7184 ± 0.019 cal·K^{-1}·mol^{-1}] by addition of the entropy increment [S(298.15 K, 500 bar)–$S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation.[2]

There is a significant maximum in the C_p(500 bar) data which rises to 40.2 cal·K^{-1}·mol^{-1} near 730 K. In this temperature region the density is varying rapidly but continuously with temperature; the maximum in the C_p data is due to a change in sign of the derivative of the density temperature curve. These same density changes are also responsible for large effects on intermolecular interaction as measured by the fugacity coefficient which changes from 0.22 at 600 K to 0.69 at 800 K (refer below).

Phase Data

Our table refers to the fluid phase existing at the nonstandard state pressure of 500 bar. Since 500 bar exceeds the critical pressure of water (P_c = 217.6 bar at T_c = 647.14 K)[3] the properties of the fluid vary continuously with temperature. Thus our table is a single phase table for the compressed fluid. No first order phase transition occurs, even though labels such as compressed liquid and dense gas are sometimes used for the regions below and above T_c.

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f of water at p = 500 bar is given by $f = K/K°$ or f=exp[$(\Delta_f G° - \Delta_f G°)/(RT)$], where K and $\Delta_f G°$ are values for H_2O(ideal gas).[4] The fugacity coefficient (f/p) at p =500 bar is given by f/500.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972); see also, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics–1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and prersonal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. **72**, 71 (1972).

[4]JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H$*	$\Delta_f G$*	log K_f*
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
	at P = 500 bar						
0							
100							
200							
298.15	73.198	69.696	69.696	0.	−285.014	−236.249	41.390
300	73.249	70.149	69.698	0.135	−284.959	−235.947	41.082
400	74.726	91.395	72.585	7.524	−281.962	−220.060	28.737
500	78.518	108.401	78.098	15.152	−278.786	−204.945	21.410
600	90.964	123.595	84.422	23.504	−274.943	−190.519	16.586
700	149.910	140.724	91.172	34.686	−268.326	−176.895	13.200
800	104.930	160.611	98.728	49.507	−258.126	−164.609	10.748
900	67.740	170.291	106.191	57.690	−254.620	−153.167	8.890
1000	57.261	176.794	112.941	63.853	−253.192	−141.981	7.416
1100	53.101	182.029	118.990	69.342	−252.497	−130.897	6.216
1200	51.274	186.560	124.436	74.549	−252.143	−119.860	5.217
1300	50.530	190.631	129.374	79.634	−251.970	−108.845	4.373
1400	50.349	194.367	133.885	84.675	−251.899	−97.838	3.650
1500	50.479	197.844	138.034	89.715	−251.888	−86.835	3.024
1600	50.781	201.111	141.875	94.778	−251.910	−75.831	2.476
1700	51.174	204.201	145.451	99.875	−251.952	−64.824	1.992
1800	51.611	207.138	148.797	105.014	−252.005	−53.816	1.562

Values of $\Delta_f H$*, $\Delta_f G$*, and Log K_f* in this table refer to formation of H_2O at P = 500 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

S(298.15 K, 5000 bar) = 69.627 ± 0.209 $J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H$(298.15 K, 5000 bar) = −278.394 ± 0.418 $kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of H_2O at 298.15 K and p=5000 bar [$\Delta_f H°$(298.15 K, 5000 bar)] is derived from the CODATA[1] enthalpy of formation of the liquid at 298.15 K and 1 bar [$\Delta_f H°$(l, 298.15 K) = −68.315 ± 0.010 $kcal \cdot mol^{-1}$] by addition of the enthalpy increment [H(298.15 K, 5000 bar)–$H°$(298.15 K)]. The enthalpy increment is taken from the recent equation of state formulation of Haar *et al.*[2] which yields enthalpy data at any temperature and pressure referenced to the triple point of water. The values of $\Delta_f H°$, $\Delta_f G°$ and log K in this table refer to formation of H_2O (real fluid at p=5000 bar) from H_2 and O_2 in their standard reference states (ideal gas at a pressure of 1 bar).

Heat Capacity and Entropy

The adopted heat capacity data are taken from the recent equation of state formulation of Haar *et al.*[2] The entropy and enthalpy are obtained by appropriate integration of the C_p data and differ from entropy and enthalpy data calculated directly from the equation of state formulation by less than 0.0002 $cal \cdot K^{-1} \cdot mol^{-1}$ and 0.0001 $kcal \cdot mol^{-1}$, respectively. The starting point for the entropy integration [S(298.15 K, 5000 bar)] is obtained from the CODATA[1] entropy at standard condtions [$S°$(l, 298.15 K) = 16.7184 ± 0.019 $cal \cdot K^{-1} \cdot mol^{-1}$] by addition of the entropy increment [S(298.15 K, 5000 bar)–$S°$(298.15 K)]. The entropy increment is also taken from the equation of state formulation.[2]

There are two rather small maximum in the C_p(5000 bar) data near 420 and 780 K.

Phase Data

Our table refers to the fluid phase existing at the nonstandard–state pressure of 5000 bar. Since 5000 bar exceeds the critical pressure of water (P_c = 217.6 bar at T_c = 647.14 K)[3] the properties of the fluid vary continuously with temperature. Thus our table is a single phase table for the compressed fluid. No first–order phase transition occurs, even though labels such as compressed liquid and dense gas are sometimes used for the regions below and above T_c.

Fugacity and Fugacity Coefficient Data

At temperature T the fugacity f of water at p = 5000 bar is given by $f = K/K°$ or $f = \exp[(\Delta_f G° - \Delta_f G°)/(RT)]$, where K and $\Delta_f G°$ are values for H_2O(ideal gas).[4] The fugacity coefficient (f/p) at p=5000 bar is given by f/5000.

References

[1]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972); also refer to, CODATA Bulletin #17, "CODATA Recommended Key Values for Thermodynamics–1975," (1976).

[2]L. Haar, J. Gallagher and G. S. Kell, Ninth International Conference on Properties of Steam, September 1979, Munich; and prersonal communication from L. Haar and J. Gallagher, U. S. Nat. Bur. Stand., (May 1980).

[3]J. F. Matthews, Chem. Rev. **72**, 71 (1972).

[4]JANAF Thermochemical Tables: H_2O(ideal gas), 3–31–79.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°-[G°-H°(T_r)]/T$ at P = 5000 bar		$H°-H°(T_r)$	$\Delta_f H*$	$\Delta_f G*$	log K_f*
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	62.350	66.927	66.927	0.	−278.394	−228.804	40.086
300	63.153	67.316	66.929	0.116	−278.358	−228.496	39.785
400	67.912	86.697	69.552	6.858	−276.008	−212.226	27.714
500	67.526	101.838	74.553	13.642	−273.676	−196.553	20.534
600	67.186	114.105	80.154	20.370	−271.457	−181.338	15.787
700	67.489	124.482	85.764	27.102	−269.290	−166.490	12.424
800	67.633	133.510	91.180	33.863	−267.150	−151.951	9.921
900	67.178	141.455	96.334	40.609	−265.082	−137.676	7.991
1000	66.153	148.483	101.205	47.278	−263.148	−123.625	6.458
1100	64.807	154.725	105.792	53.826	−261.393	−109.759	5.212
1200	63.396	160.303	110.106	60.236	−259.836	−96.045	4.181
1300	62.089	165.324	114.164	66.508	−258.475	−82.452	3.313
1400	60.968	169.883	117.984	72.659	−257.295	−68.957	2.573
1500	60.056	174.057	121.585	78.709	−256.274	−55.541	1.934
1600	59.344	177.910	124.986	84.678	−255.391	−42.188	1.377
1700	58.804	181.490	128.206	90.584	−254.624	−28.887	0.888
1800	58.408	184.840	131.260	96.443	−253.956	−15.628	0.454

Values of $\Delta_f H*$, $\Delta_f G*$, and Log K_f* in this table refer to formation of H_2O at P = 5000 bar from H_2 and O_2 in their standard reference states (Ideal gas at a pressure of 1 bar).

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

Hydrogen Peroxide (H_2O_2) IDEAL GAS M_r = 34.01468

$\Delta_f H°(0\ K) = -129.808\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 232.991\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -136.106\ kJ \cdot mol^{-1}$

Point Group: C_2

Enthalpy of Formation

The adopted enthalpy of formation is taken from Giguere and Lin[1]. This value was based on the measured enthalpy of decomposition of the liquid,[2] and the enthalpy of vaporization[2].

Heat Capacity and Entropy

$C_p°$ from Giguere and Lin.[1] $C_p°$ below 298.15 K estimated.

Reference

[1]P. A. Giguere and I. D. Lin, J. Amer. Chem. Soc. **77**, 6477 (1955).
[2]P. A. Giguere, B. G. Morissette, A. W. Olmos, and O. Knop, Can. J. Chem. **33**, 804 (1955).

Hydrogen Peroxide (HOOH) $H_2O_2(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.853	−129.808	−129.808	INFINITE
100	33.526	186.540	261.768	−7.523	−132.382	−123.632	64.579
200	36.874	210.632	228.978	−3.669	−134.133	−113.680	29.690
298.15	43.116	232.991	232.991	0.	−136.106	−105.445	18.474
300	43.221	233.258	232.992	0.080	−136.133	−105.255	18.326
400	48.451	246.435	234.753	4.673	−137.417	−94.757	12.374
500	52.551	257.705	238.243	9.731	−138.341	−83.978	8.773
600	55.689	267.576	242.326	15.150	−139.011	−73.039	6.359
700	57.990	276.339	246.571	20.838	−139.515	−62.002	4.627
800	59.831	284.205	250.792	26.731	−139.912	−50.901	3.324
900	61.463	291.349	254.908	32.797	−140.225	−39.755	2.307
1000	62.844	297.897	258.884	39.013	−140.475	−28.578	1.493
1100	64.141	303.949	262.709	45.364	−140.673	−17.378	0.825
1200	65.312	309.580	266.383	51.837	−140.827	−6.162	0.268
1300	66.400	314.852	269.911	58.423	−140.944	5.065	−0.203
1400	67.404	319.810	273.300	65.114	−141.031	16.299	−0.608
1500	68.325	324.492	276.558	71.901	−141.093	27.539	−0.959

PREVIOUS: December 1960 (1 atm) CURRENT: December 1960 (1 bar)

$S°(298.15\ K) = [97.069 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 783.15 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -968.89 \pm 9.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 21.020 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -231.57 \pm 2.2\ kcal \cdot mol^{-1}$ is obtained from the enthalpy of formation adopted for the liquid[1] minus enthalpy of melting and the enthalpy difference of the liquid and the crystal between the melting point and 298.15 K. The dissociation pressure measurements by Johnston[2] and by Tamaru and Shiomi[3] span the melting point, but there is not a definite break in the log P vs 1/T curve at the melting point. The temperatures of the dissociation pressures determined by Sano[4] are all below the melting point. For 2nd and 3rd law analysis, using auxiliary data from the JANAF Thermochemical Tables,[1] the dissociation pressures below the melting point are considered to pertain to the equilibrium $Sr(OH)_2(cr) = SrO(cr) + H_2O(g)$.

Source	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol⁻¹ 2nd law	3rd law	Drift cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15\ K)$ kcal·mol⁻¹
Johnston[2]	4	703–776	18.7	31.65 ± 1.06	17.5 ± 1.4	−230.9 ± 1.9
Tamaru and Shiomi[3]	10	667–782	28.0	31.50 ± 0.42	4.9 ± 0.3	−230.8 ± 1.2
Sano[4]	5	613–743	26.0	31.27 ± 0.75	7.6 ± 0.2	−230.6 ± 1.6

These three 3rd law values for $\Delta_f H°$(cr, 298.15 K) are in excellent agreement, are in reasonable agreement with the adopted value, and are closer to another recent evaluation[5] of −229.2 kcal·mol⁻¹ than is the adopted value. The route taken to derive the adopted value is presently preferred because dissociation pressure measurements of the liquid are judged to be better than those of the solid.

Heat Capacity and Entropy

The heat capacities are derived from a curve fit of the drop calorimeter enthalpy measurements of Powers and Blalock,[6] (545–783 K), extrapolated and forced through zero relative enthalpy at 273.15 K. The change in heat capacity with temperature is larger than it is for the other alkaline earth dihydroxides.[1] There appears to be no definite explanation for this. The purity of the $Sr(OH)_2$ sample, as indicated by total alkalinity, did change more during the enthalpy measurement than other samples in the same report.[6] The total alkalinity of the $Sr(OH)_2$ sample changed from 99.80 to 94.1% while for $Ba(OH)_2$ the change was 100.4 to 99.81%, for NaOH the change was 99.97 to 99.46%, and for KOH the change was 100.00 to 98.68%.[6] The known existence of crystalline allotropy in some of the alkaline earth halides and hydroxides suggests this possibility for $Sr(OH)_2$ crystal also.

The adopted entropy, $S°(298.15\ K) = [23.2 \pm 2]\ cal \cdot K^{-1} \cdot mol^{-1}$, is calculated from Kelley's additive entropy constants for cations and anions.[7]

Fusion Data

From their drop calorimetry, Powers and Blalock[6] selected a melting point of 783.15 K where they derived $\Delta_{fus} H° = 5.23\ kcal \cdot mol^{-1}$. Our smoothing of their data leads to the adopted $\Delta_{fus} H° = 5.024 \pm 0.50\ kcal \cdot mol^{-1}$. Brcic and Jernejcic[8] determined a melting point of 771 K and Berggren and Brown,[9] 723 K. The latter dihydroxide sample contained 5 mole percent $SrCO_3$. $T_{fus} = 783.15 \pm 15$ K is adopted.

References

[1] JANAF Thermochemical Tables: SrO(cr), 12–31–72; H_2O(g), 3–31–61; $Be(OH)_2$ (β–c), $Mg(OH)_2$(cr), $Ca(OH)_2$(cr), $Ba(OH)_2$(cr), $Sr(OH)_2$(l), 12–31–75.
[2] J. Johnston, Z. Physik. Chem. **62**, 330 (1908).
[3] S. Tamaru and K. Shiomi, Z. Physik. Chem. **A171**, 221 (1935).
[4] K. Sano, J. Chem. Soc. Japan **60**, 758 (1939).
[5] U. S. Nat. Bur. Stand. Tech. Note 270–6, (1971).
[6] W. D. Powers an G. C. Blalock, U. S. Atomic Energy Comm., ORNL–1653 (1954).
[7] K. K. Kelley in Chap. 13, D. R. Stull and H. Prophet, "The Characterization of High Temperature Vapors," J. L. Margrave, ed., John Wiley and Sons, New York, (1967).
[8] B. S. Brcic and J. Jernejcic, Vestn. Sloven. Kem. Drustva **9**, 65 (1962).
[9] G. Berggren and A. Brown, Acta Chem. Scand. **25**, 1377 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K⁻¹·mol⁻¹)	$S°$ (J·K⁻¹·mol⁻¹)	$-[G°-H°(T_r)]/T$ (J·K⁻¹·mol⁻¹)	$H°-H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0							
100							
200							
298.15	74.894	97.069	97.069	0.	−968.889	−881.098	154.365
300	75.145	97.533	97.070	0.139	−968.907	−880.553	153.318
400	88.450	120.970	100.176	8.318	−969.335	−851.006	111.130
500	101.755	142.137	106.481	17.828	−968.634	−821.482	85.820
600	115.018	161.859	114.083	28.666	−966.815	−792.204	68.967
700	128.323	180.589	122.256	40.833	−963.874	−763.319	56.960
783.150	139 .370	195.601	129.251	51.963	--- CRYSTAL <--> LIQUID ---		
800	141.628	198.592	130.680	54.330	−959.806	−734.933	47.986
900	154.934	216.041	139.199	69.158	−955.232	−707.052	41.036
1000	168.239	233.054	147.737	85.316	−948.573	−679.822	35.510

PREVIOUS: CURRENT: December 1975

$S°(298.15\ K) = [108.739]\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{fus} = 783.15 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-957.304]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = 21.020 \pm 2.1\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -228.8 \pm 1.7\ kcal\cdot mol^{-1}$ is the average of values derived from the 3rd law analysis of the dissociation pressure measurements of Johnston[1] and of Tamaru and Shiomi.[2] The data from both sources[1,2] span the melting point; only those data above the melting point are used for the 2nd and 3rd law analysis of the reaction $Sr(OH)_2(l) = SrO(cr) + H_2O(g)$.

Source	Data Points	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Johnston[1]	11[a]	806–1038	28.5	30.06 ± 0.28[b]	1.6 ± 0.4	−229.36 ± 1.1
Tamaru and Shioni[2]	6	880–942	30.9	29.93 ± 0.26[b]	−2.3 ± 0.2	−228.23 ± 1.1

[a]One point rejected due to a failure of a statistical test.
[b]Considering all of the data as liquid data (733–1038 K;[1] 667–942 K),[2] yields 3rd law enthalpies of reaction of 29.97 ± 0.48 kcal·mol^{-1} for[1] and 29.08 ± 0.16 kcal·mol^{-1} for[2] leading to standard state enthalpies of formation at 298.15 K of −229.27 ± 1.3 and −228.38 ± 1.0 kcal·mol^{-1}, respectively.

Heat Capacity and Entropy

$C_p°$ is derived from the drop ice calorimeter measurements of Powers and Blalock (789–1187 K)[4] and is assumed constant at 27.7 cal·K^{-1}·mol^{-1} over the range of 520 to 1600 K. A glass transition is assumed at 520 K below which $C_p°$ is that of the crystal. The entropy of 298.15 K is calculated from the value adopted for the crystal.[3]

Decomposition Data

T_{dcm} = 1017 K is calculated as the temperature at which the fugacity of $H_2O(g)$ is 1 atm for the reaction $Sr(OH)_2(l) = SrO(cr) + H_2O(g)$. Auxiliary data used in the calculations are from the JANAF Thermochemical Tables.[3]

References

[1]J. Johnston, Z. physik. Chem. **62**, 330 (1908).
[2]S. Tamaru and K. Shiomi, Z. physik. Chem. **A171**, 221 (1935).
[3]JANAF Thermochemical Tables: SrO(cr), 12–31–72; $H_2O(g)$, 3–31–61; $Sr(OH)_2(cr)$, 12–31–75.
[4]W. D. Powers and G. C. Blalock, U. S. Atomic Energy Comm. ORNL–1653 (1954).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	74.894	108.739	108.739	0.	−957.304	−872.993	152.945
300	75.145	109.203	108.740	0.139	−957.323	−872.470	151.910
400	88.450	132.640	111.846	8.318	−957.750	−844.090	110.227
500	101.755	153.807	118.151	17.828	−957.049	−815.732	85.219
520.000	104.392	157.850	119.600	19.890	GLASS <--> LIQUID TRANSITION		
520.000	157.737	157.850	119.600	19.890			
600	157.737	180.422	126.241	32.509	−951.387	−787.914	68.594
700	157.737	204.737	135.762	48.282	−944.839	−761.189	56.801
783.150	157.737	222.442	144.043	61.398	--- CRYSTAL <--> LIQUID ---		
800	157.737	225.800	145.730	64.056	−938.495	−735.388	48.016
900	157.737	244.379	155.679	79.830	−932.976	−710.299	41.225
1000	157.737	260.998	165.395	95.603	−926.701	−685.895	35.827
1100	157.737	276.032	174.780	111.377	−928.412	−661.749	31.424
1200	157.737	289.757	183.798	127.151	−923.211	−637.737	27.760
1300	157.737	302.382	192.441	142.924	−918.088	−614.156	24.677
1400	157.737	314.072	200.716	158.698	−913.038	−590.966	22.049
1500	157.737	324.955	208.640	174.472	−908.060	−568.135	19.784
1600	157.737	335.135	216.231	190.245	−903.151	−545.634	17.813
1700	157.737	344.697	223.510	206.019	−1035.223	−522.258	16.047
1800	157.737	353.713	230.495	221.793	−1028.585	−492.276	14.285
1900	157.737	362.242	237.207	237.566	−1022.015	−462.660	12.719
2000	157.737	370.333	243.663	253.340	−1015.513	−433.389	11.319

PREVIOUS: CURRENT: December 1975

0 to 783.15 K crystal
above 783.15 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.894	97.069	97.069	0.	−968.889	−881.098	154.365
300	75.145	97.533	97.070	0.139	−968.907	−880.553	153.318
400	88.450	120.970	100.176	8.318	−969.335	−851.006	111.130
500	101.755	142.137	106.481	17.828	−968.634	−821.482	85.820
600	115.018	161.859	114.083	28.666	−966.815	−792.204	68.967
700	128.323	180.589	122.256	40.833	−963.874	−763.319	56.960
783.150	139 .370	195.601	129.251	51.963	____ CRYSTAL <--> LIQUID ____		
783.150	157 .737	222.442	129.251	72.983	TRANSITION		
800	157.737	225.800	131.249	75.641	−938.495	−735.388	48.016
900	157.737	244.379	142.807	91.415	−932.976	−710.299	41.225
1000	157.737	260.998	153.810	107.188	−926.701	−685.895	35.827
1100	157.737	276.032	164.248	122.962	−928.412	−661.749	31.424
1200	157.737	289.757	174.144	138.736	−923.211	−637.737	27.760
1300	157.737	302.382	183.529	154.509	−918.088	−614.156	24.677
1400	157.737	314.072	192.441	170.283	−913.038	−590.966	22.049
1500	157.737	324.955	200.917	186.057	−908.060	−568.135	19.784
1600	157.737	335.135	208.991	201.830	−903.151	−545.634	17.813
1700	157.737	344.697	216.695	217.604	−1035.223	−522.258	16.047
1800	157.737	353.713	224.059	233.378	−1028.585	−492.276	14.285
1900	157.737	362.242	231.110	249.151	−1022.015	−462.660	12.719
2000	157.737	370.333	237.870	264.925	−1015.513	−433.389	11.319

PREVIOUS: CURRENT: December 1975

$S°(298.15\ K)$ = [305.042 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = −588.31 ± 41.8 $kJ·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = −595.80 ± 41.8 $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[442](1)
[82](1)
[443](1)
[3650](2)
[438](4)

Ground State Quantum Weight: [1] σ = [2]
Point Group: [C_{2v}]
Bond Distances: Sr–O = [2.22] Å O–H = [0.96] Å
Bond Angles: O–Sr–O = [108]° Sr–O–H = [180]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [3.824302] × 10^{-114} $g^3·cm^6$

Enthalpy of Formation

Dissociation energies for the reaction $Sr(OH)_2(g) = Sr(g) + 2\ OH(g)$ have been derived from flame spectral measurements.[1-3] Ryabova and Gurvich[1] believed the dominant reaction to be $Sr(g) + H_2O(g) = SrOH(g) + H(g)$ but they also considered the possibility that the reaction $Sr(g) + 2\ H_2O(g) = Sr(OH)_2 + 2\ H(g)$ was dominant and derived $D_0°$ = 180 ± 20 $kcal·mol^{-1}$. Sugden and Schofield[2] considered the dihydroxide to be the dominant product and derived $D_0°$ = 215 ± 12 $kcal·mol^{-1}$. Cotton and Jenkins[3] found both SrOH and $Sr(OH)_2$ to be present in significant amounts in fuel-rich hydrogen–oxygen–nitrogen flames and derived $D_0°$ = 202.2 ± 5 $kcal·mol^{-1}$. Cotton and Jenkins[3] recalculated the work of Ryabova and Gurvich[1] and of Sugden and Schofield[2] considering both SrOH and $Sr(OH)_2$ to be present and obtained the recalculated $D_0°$ values of 196 and 200 $kcal·mol^{-1}$, respectively.

A 3rd law analysis of the experimental equilibrium constants tabulated by Cotton and Jenkins[3] using current JANAF auxiliary data[4] leads to $D_0°$ = 204.8 $kcal·mol^{-1}$ which is 2.6 $kcal·mol^{-1}$ higher than the 202.2 $kcal·mol^{-1}$ derived by Cotton and Jenkins.[3] Applying this difference to the data of Ryabova and Gurvich[1] and of Sugden and Schofield[2] as recalculated by Cottonand Jenkins[3] gives $D_0°$ = 198.6 and 202 $kcal·mol^{-1}$, respectively.

For $Ba(OH)_2(g)$[4] the corrected dissociation energy of Ryabova and Gurvich,[4] $D_0°$ = 208.8 $kcal·mol^{-1}$, is in better agreement with the "adopted" value of 209.6 $kcal·mol^{-1}$, based on good Knudsen cell mass spectrometric measurements, than are the corrected dissociation energies of Sugden and Schofield or Cotton and Jenkins.[4] We adopt $D_0°$ = 198.6 $kcal·mol^{-1}$ for the dissociation of $Sr(OH)_2$ from which $\Delta_f H°(Sr(OH)_2)$ = −140.66 ± 6.0 $kcal·mol^{-1}$ is calculated.

The enthalpy of dissociation listed by Jackson[8] leads to $\Delta_f H°(Sr(OH)_2, g, 298.15\ K)$ = −143.82 $kcal·mol^{-1}$. Another recent compilation[9] lists $\Delta_f H°(298.15\ K)$ = −135 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The analogy between gaseous mono- and dihydroxides and gaseous mono- and dihalides, particularly the mono- and difluorides, has been recognized.[5-8] The O–Sr–O bond angle is assumed to be the same as the F–Sr–F bond angle;[4] the Sr–O–H bond angle is considered to be linear as in SrOH.[4] The Sr–O bond distance is estimated to be slightly larger, 0.02 Å, than the Sr–F distance in SrF_2[4] after noting the close similarity in the bond distance of the alkali metal fluorides and hydroxides. The O–H bond distance is taken to be the same as in water.[4]

The vibrational frequencies are assumed to be the same as in SrF_2 (O–Sr–O symmetrical and asymmetrical stretch, and bend)[4] and as in SrOH (O–H stretch and Sr–O–H bend).[4] The principal moments of inertia are: $I_A = 7.3880 \times 10^{-39}$, $I_B = 19.3556 \times 10^{-39}$, and $I_C = 26.7436 \times 10^{-39}$ $g·cm^2$.

Jackson[8] has used a different molecular configuration and different vibrational frequencies to estimate $S°(298.15\ K)$ = 74.057 $cal·K^{-1}·mol^{-1}$. We assign an uncertainty of ±2.0 $cal·K^{-1}·mol^{-1}$ to the adopted entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−16.235	−588.313	−588.313	INFINITE
100	44.263	239.906	364.080	−12.417	−591.898	−585.681	305.928
200	64.366	276.853	311.694	−6.968	−594.542	−578.292	151.034
250	71.457	292.025	306.273	−3.562	−595.293	−574.142	119.960
298.15	76.209	305.042	305.042	0.	−595.797	−570.013	99.864
300	76.360	305.514	305.044	0.141	−595.813	−569.853	99.220
350	79.769	317.557	305.987	4.049	−596.183	−565.496	84.396
400	82.195	328.375	308.121	8.102	−596.458	−561.092	73.271
450	83.972	338.164	310.924	12.258	−596.681	−556.658	64.615
500	85.321	347.085	314.101	16.492	−596.878	−552.200	57.688
600	87.261	362.823	320.945	25.127	−597.261	−543.229	47.292
700	88.697	376.386	327.918	33.928	−597.687	−534.190	39.862
800	89.938	388.313	334.737	42.860	−598.183	−525.087	34.285
900	91.109	398.974	341.293	51.913	−599.385	−515.844	29.939
1000	92.247	408.632	347.551	61.081	−599.716	−506.544	26.459
1100	93.355	417.477	353.512	70.361	−607.920	−496.846	23.593
1200	94.420	425.645	359.187	79.751	−609.104	−486.696	21.185
1300	95.430	433.243	364.594	89.244	−610.261	−476.448	19.144
1400	96.378	440.351	369.754	98.835	−611.394	−466.112	17.391
1500	97.259	447.030	374.686	108.517	−612.507	−455.696	15.869
1600	98.071	453.334	379.406	118.284	−613.605	−445.206	14.534
1700	98.817	459.302	383.932	128.129	−751.606	−433.468	13.319
1800	99.498	464.970	388.278	138.045	−750.825	−414.777	12.037
1900	100.120	470.366	392.457	148.027	−750.047	−396.129	10.890
2000	100.687	475.516	396.483	158.068	−749.279	−377.521	9.860
2100	101.203	480.442	400.364	168.162	−748.526	−358.952	8.928
2200	101.674	485.161	404.112	178.307	−747.797	−340.418	8.083
2300	102.102	489.690	407.735	188.496	−747.100	−321.917	7.311
2400	102.493	494.044	411.241	198.726	−746.443	−303.445	6.604
2500	102.851	498.235	414.638	208.993	−745.836	−284.999	5.955
2600	103.177	502.275	417.931	219.295	−745.288	−266.577	5.356
2700	103.476	506.175	421.128	229.628	−744.810	−248.174	4.801
2800	103.751	509.943	424.233	239.989	−744.412	−229.787	4.287
2900	104.003	513.588	427.251	250.377	−744.104	−211.414	3.808
3000	104.235	517.118	430.188	260.789	−743.899	−193.049	3.361
3100	104.449	520.540	433.048	271.224	−743.805	−174.689	2.943
3200	104.646	523.859	435.834	281.679	−743.835	−156.331	2.552
3300	104.828	527.082	438.551	292.152	−743.996	−137.969	2.184
3400	104.997	530.214	441.201	302.644	−744.300	−119.600	1.837
3500	105.153	533.260	443.788	313.151	−744.755	−101.221	1.511
3600	105.299	536.224	446.315	323.674	−745.367	−82.826	1.202
3700	105.434	539.111	448.784	334.211	−746.145	−64.412	0.909
3800	105.560	541.924	451.198	344.760	−747.092	−45.974	0.632
3900	105.677	544.668	453.560	355.322	−748.214	−27.509	0.368
4000	105.787	547.345	455.871	365.896	−749.514	−9.014	0.118
4100	105.890	549.958	458.134	376.480	−750.993	9.517	−0.121
4200	105.986	552.511	460.351	387.073	−752.648	28.086	−0.349
4300	106.076	555.006	462.523	397.676	−754.486	46.696	−0.567
4400	106.160	557.446	464.653	408.288	−756.500	65.351	−0.776
4500	106.239	559.832	466.741	418.908	−758.688	84.053	−0.976
4600	106.314	562.168	468.791	429.536	−760.982	102.801	−1.167
4700	106.385	564.455	470.802	440.171	−763.487	121.606	−1.351
4800	106.451	566.696	472.776	450.813	−766.147	140.466	−1.529
4900	106.513	568.891	474.716	461.461	−768.957	159.383	−1.699
5000	106.573	571.044	476.621	472.115	−771.903	178.358	−1.863
5100	106.629	573.155	478.493	482.775	−774.963	197.391	−2.022
5200	106.681	575.226	480.333	493.441	−778.168	216.487	−2.175
5300	106.732	577.258	482.143	504.112	−781.489	235.648	−2.322
5400	106.779	579.254	483.923	514.787	−784.918	254.870	−2.465
5500	106.824	581.214	485.674	525.467	−788.447	274.157	−2.604
5600	106.867	583.139	487.397	536.152	−792.068	293.511	−2.738
5700	106.908	585.031	489.094	546.841	−795.772	312.929	−2.868
5800	106.947	586.890	490.764	557.534	−799.552	332.414	−2.994
5900	106.984	588.719	492.409	568.230	−803.189	351.937	−3.116
6000	107.019	590.517	494.029	578.930	−807.067	371.549	−3.235

PREVIOUS: December 1975 (1 atm) CURRENT: December 1975 (1 bar)

$S°(298.15\ K) = 156.895 \pm 0.08\ J·K^{-1}·mol^{-1}$
$T_{fus} = 283.46 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -811.969 \pm 0.67\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -813.989 \pm 0.67\ kJ·mol^{-1}$
$\Delta_{fus} H° = 10.711 \pm 0.13\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of combustion, $\Delta_c H°(298.15\ K)$, of rhombic sulfur to aqueous sulfuric acid, S(cr, rhombic) + 3/2 O_2(g) + H_2O(l) = H_2SO_4 (n H_2O), has been determined by many investigators. Based on the reported combusion data, values of $\Delta_f H°(298.15\ K)$ for liquid H_2SO_4 are derived using tabulated enthalpy of solution and enthalpy of dilution data.[1,2] The value adopted, $\Delta_f H°(H_2SO_4, l, 298.15\ K) = -194.548 \pm 0.16$ kcal·mol^{-1}, is that recommended by NBS.[2] The uncertainty of ± 0.16 kcal·mol^{-1} not only accounts for the scatter in the combustion data but also the uncertainty arising from conversion of these data to be consistent with the current atomic weights and fundamental constants (~tens of calories/mol). An uncertainty of −0.08 kcal·mol^{-1} may exist due to the difference in the heat of formation of $SO_4^{=}$(aq) as reported by CODATA[11] and NBS.[2]

Source	Product	$\Delta_c H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
McCullough *et al.*[3]	H_2SO_4 (70 H_2O)	−143.58 ± 0.09	−194.400
Scott *et al.*[4]	H_2SO_4 (75 H_2O)	−143.98 ± 0.22	−194.775
Good *et al.*[5]	H_2SO_4 (115 H_2O)	−143.85 ± 0.06	−194.521
Mansson and Sunner[6]	H_2SO_4 (115 H_2O)	−143.93 ± 0.07	−194.601

Heat Capacity and Entropy

The heat capacity has been measured experimentally[7] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[8] based on experimental data (0–300°C). These temperature–dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 290–350 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used for extrapolation of the heat capacity values to 1000 K.

Other heat capacity studies on sulfuric acid and its aqueous solutions are too numerous to mention. However, a recent compilation[9] summarizes much of the work and shows that our adopted heat capacity values for sulfuric acid and its hydrates from room temperature to ~80°C are consistent with the available literature.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, $S°(15\ K) = 0.269$ cal·K^{-1}·mol^{-1} and addition of the entropy of melting.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Rubin and Giauque.[7] The value for T_{fus} used by Giauque *et al.*[1] in their re evaluation and correlation of aqueous sulfuric acid properties was slightly different; the change was 0.07 K. Many other studies have also reported melting data but they are too numerous to mention.

Vaporization Data

$T_{vap} = 610$ K is the temperature at which the fugacity of H_2SO_4(g) is one atm for the reaction H_2SO_4(l) = H_2SO_4(g). $\Delta_{vap} H° = 13.9$ kcal·mol^{-1} is calculated as the difference in the respective $\Delta_f H°$ values at T_{vap}.

According to Luchinskii[10] the total pressure over H_2SO_4(l) reaches one atmosphere at 553 K with a vapor composition of 76.6 mole% SO_3, 22.6 mole% H_2SO_4, and 0.8 mole% H_2O.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−28.226	−811.969	−811.969	INFINITE
100	45.142	42.586	300.474	−25.789	−819.030	−777.302	406.021
200	73.587	82.684	181.887	−19.841	−823.240	−733.773	191.642
283.456	96.902	112.175	157.073	−12.727	____ CRYSTAL <--> LIQUID ____		
283.456	135 .770	149.962	157.073	−2.016	TRANSITION		
298.15	138.584	156.895	156.895	0.	−813.989	−689.918	120.871
300	138.940	157.753	156.897	0.257	−813.936	−689.149	119.991
400	158.205	200.356	162.576	15.112	−812.526	−647.968	84.616
500	177.619	237.744	173.938	31.903	−808.704	−607.248	63.439
600	197.033	271.844	187.451	50.636	−802.804	−567.476	49.403
700	216.447	303.674	201.804	71.310	−794.924	−528.851	39.463
800	235.860	333.844	216.438	93.925	−785.146	−491.486	32.091
900	255.274	362.745	231.099	118.482	−826.632	−454.377	26.371
1000	274.688	390.646	245.666	144.980	−811.918	−413.788	21.614

PREVIOUS: December 1966 CURRENT: September 1977

$S°(298.15\ K) = [298.796 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -721.22 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -735.13 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[3500](1)	[380](1)	883 (1)
1223 (1)	[265](1)	[400](1)
1138 (1)	[390](1)	1450 (1)
834 (1)	3610 (1)	[265](1)
550 (1)	1159 (1)	568 (1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distances: S–O = [1.42] Å S–OH = [1.55] Å O–H = [0.97] Å

Bond Angles: O–S–O = [109.47122]° S–O–H = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [4.510247 \times 10^{-114}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The vapor phase equilibria of the H_2SO_4, H_2O and SO_3 system have been determined by *PVT* studies by Bodenstein and Katayama[5] and Suvorov *et al.*[4] and by vapor pressure measurements by Luchinskii.[3] Using the reported equilibrium values (after correcting a few typographical errors) for the reaction $H_2SO_4(g) = H_2O(g) + SO_3(g)$, we calculate $\Delta_f H°(298.15\ K)$ using a 2nd and 3rd law analysis and auxiliary data.[6] The results are tabulated below. We adopt $\Delta_f H°(H_2SO_4, g, 298.15\ K) = -175.7 \pm 2\ kcal \cdot mol^{-1}$ which is the median of the three values derived from the 3rd law $\Delta_f H°(298.15\ K)$. The analysis of vaporization data of Thomas and Ramsey[1] and Abel[2] leads to $\Delta_f H°(298.15\ K)$ values within 2 $kcal \cdot mol^{-1}$ of our adopted value.

Source	T/K	Data Points	Reaction*	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal^{-1} \cdot mol^{-1}$
[1]	463–493	4	A	18.1 ± 0.1	20.5 ± 0.1	4.9 ± 0.2	−174.0
[2]	523–673	7	A	17.7 ± 0.2	19.7 ± 0.4	3.3 ± 0.3	−174.8
[2]	298–603	9	B	24.2 ± 0.3	23.4 ± 0.5	−1.6 ± 0.1	−175.8
[3]	333–473	8	B	23.7 ± 0.1	23.5 ± 0.1	−0.6 ± 0.3	−175.9
[4]	583–785	40	B	25.1 ± 0.4	23.3 ± 0.3	−2.7 ± 0.7	−175.7
[5]	596–756	53	B	23.3 ± 0.6	23.0 ± 0.5	−0.4 ± 0.9	−175.4

*Reactions: A) $H_2SO_4(l) = H_2SO_4(g)$ B) $H_2SO_4(g) = H_2O(g) + SO_3(g)$

Heat Capacity and Entropy

The molecular structure of $H_2SO_4(g)$ is assumed to be tetrahedral with differing bond lengths for S–O and S–OH. This adopted structure is consistent with the X-ray and electron diffraction studies on $H_2SO_4(cr)$ by Pascard[7] and Pascard–Billy,[8] respectively, and the X-ray scattering study on $H_2SO_4(l)$ by Weidner *et al.*[9] The latter study gave results which could be interpreted by models having point symmetry C_2 and C_{2v}. In both models, the sulfur–oxygen bond distance are equivalent within the experimental uncertainty. For the C_{2v} model, the O–S–O bond angles coincide with the tetrahedral angle. In the C_2 model these angles are split, but not as extremely as in $H_2SO_4(cr)$.[7,8] The OH distance and the S–O–H angle are taken from those for $H_2O(g)$. The principal moments of inertia are: $I_A = 14.9802 \times 10^{-39}$, $I_B = 17.0080 \times 10^{-39}$ and $I_C = 17.7023 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies are from the infrared studies of Chackalackal and Stafford[10] and the comparisons of Giguere and Savoie.[11] The infrared studies led to the assignement of nine vibrational frequencies while the remaining six were estimated[10] by comparison with the infrared frequencies for the crystal and Raman frequencies for the liquid.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−16.340	−721.223	−721.223	INFINITE
100	42.100	232.305	360.452	−12.815	−727.196	−704.440	367.962
200	65.850	269.002	305.914	−7.382	−731.922	−679.718	177.524
250	75.588	284.768	300.131	−3.841	−733.711	−666.453	139.248
298.15	83.761	298.796	298.796	0.	−735.129	−653.366	114.467
300	84.054	299.315	298.798	0.155	−735.178	−652.859	113.673
350	91.435	312.840	299.849	4.547	−736.354	−639.042	95.372
400	97.833	325.477	302.271	9.282	−739.496	−624.986	81.615
450	103.344	337.327	305.515	14.315	−740.883	−610.596	70.876
500	108.076	348.466	309.259	19.604	−742.143	−596.048	62.269
600	115.661	368.875	317.527	30.809	−743.771	−566.661	49.332
700	121.411	387.155	326.191	42.675	−744.699	−537.062	40.076
800	125.932	403.674	334.860	55.051	−745.161	−507.364	33.127
900	129.611	418.725	343.355	67.833	−798.420	−476.548	27.658
1000	132.690	432.545	351.592	80.953	−797.084	−440.854	23.028
1100	135.316	445.318	359.540	94.356	−795.609	−405.301	19.246
1200	137.583	457.192	367.188	108.004	−794.025	−369.888	16.101
1300	139.557	468.284	374.543	121.863	−792.355	−334.610	13.445
1400	141.285	478.691	381.614	135.907	−790.620	−299.464	11.173
1500	142.803	488.492	388.416	150.113	−788.838	−264.444	9.209
1600	144.143	497.751	394.963	164.462	−787.023	−229.543	7.494
1700	145.328	506.526	401.269	178.937	−785.188	−194.756	5.984
1800	146.380	514.863	407.351	193.523	−783.344	−160.079	4.645
1900	147.315	522.803	413.220	208.209	−781.499	−125.503	3.450
2000	148.150	530.381	418.890	222.983	−779.661	−91.024	2.377
2100	148.897	537.628	424.373	237.836	−777.837	−56.638	1.409
2200	149.567	544.570	429.680	252.760	−776.031	−22.336	0.530
2300	150.169	551.232	434.821	267.747	−774.248	11.882	−0.270
2400	150.713	557.635	439.805	282.792	−772.491	46.023	−1.002
2500	151.204	563.798	444.643	297.888	−770.764	80.092	−1.673
2600	151.649	569.737	449.340	313.031	−769.067	114.093	−2.292
2700	152.054	575.468	453.906	328.216	−767.402	148.030	−2.864
2800	152.422	581.005	458.347	343.441	−765.771	181.905	−3.393
2900	152.759	586.359	462.670	358.700	−764.174	215.721	−3.886
3000	153.067	591.543	466.879	373.991	−762.612	249.484	−4.344
3100	153.349	596.567	470.982	389.312	−761.086	283.196	−4.772
3200	153.608	601.440	474.983	404.660	−759.595	316.858	−5.172
3300	153.847	606.170	478.887	420.033	−758.140	350.474	−5.548
3400	154.067	610.766	482.699	435.429	−756.720	384.048	−5.900
3500	154.270	615.235	486.422	450.846	−755.336	417.579	−6.232
3600	154.459	619.584	490.061	466.283	−753.987	451.072	−6.545
3700	154.633	623.818	493.619	481.737	−752.674	484.527	−6.840
3800	154.796	627.944	497.100	497.209	−751.396	517.949	−7.120
3900	154.947	631.967	500.507	512.696	−750.154	551.337	−7.384
4000	155.087	635.892	503.842	528.198	−748.947	584.692	−7.635
4100	155.219	639.723	507.110	543.713	−747.776	618.019	−7.874
4200	155.341	643.465	510.312	559.241	−746.641	651.317	−8.100
4300	155.456	647.121	513.451	574.781	−745.542	684.590	−8.316
4400	155.564	650.697	516.530	590.332	−744.480	717.835	−8.522
4500	155.665	654.194	519.551	605.894	−743.454	751.057	−8.718
4600	155.759	657.616	522.515	621.465	−742.467	784.256	−8.906
4700	155.849	660.967	525.425	637.045	−741.517	817.437	−9.085
4800	155.933	664.249	528.283	652.634	−740.607	850.596	−9.256
4900	156.012	667.465	531.091	668.232	−739.736	883.738	−9.421
5000	156.086	670.618	533.850	683.837	−738.906	916.863	−9.578
5100	156.157	673.709	536.562	699.449	−738.117	949.970	−9.730
5200	156.224	676.742	539.229	715.068	−737.371	983.061	−9.875
5300	156.287	679.718	541.852	730.693	−736.668	1016.141	−10.015
5400	156.347	682.640	544.432	746.325	−736.010	1049.206	−10.149
5500	156.403	685.510	546.971	761.963	−735.398	1082.258	−10.278
5600	156.457	688.328	549.470	777.606	−734.833	1115.303	−10.403
5700	156.508	691.098	551.931	793.254	−734.316	1148.336	−10.523
5800	156.557	693.820	554.354	808.907	−733.848	1181.363	−10.639
5900	156.603	696.497	556.740	824.565	−733.432	1214.376	−10.751
6000	156.647	699.129	559.091	840.228	−733.068	1247.389	−10.859

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = [144.766 \pm 25.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -1131.77 \pm 1.7\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Spitsyn and Patsukova[1] have measured calorimetrically the enthalpy of reaction (1) and (2) at 298.15 K as -13.80 ± 0.01 and -13.05 ± 0.02 kcal·mol^{-1}, respectively. The reactions are given as follows:

(1) $WO_3(cr) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200\ H_2O) + H_2O(l)$
(2) $H_2WO_4(cr) + 2\ NaOH(66H_2O) \rightarrow Na_2WO_4(4200\ H_2O) + 2\ H_2O(l)$

Combination of reactions (1) and (2) gives $\Delta_f H°(298.15\ K) = -0.75 \pm 0.04$ kcal·mol^{-1} for $WO_3(cr) + H_2O(l) \rightarrow H_2WO_4(cr)$, which leads to $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -270.5 \pm 0.4$ kcal·mol^{-1}.

To obtain WO_3(cr) in a form soluble in the calorimetric solution, Spitsyn and Patsukova dehydrated H_2WO_4(cr) at the relatively low temperature of 250°C. The resulting WO_3(cr) was a very fine lemon yellow powder which may have excess surface free energy compared with the JANAF standard state. The latter is WO_3 formed at high temperature in a calorimetric bomb. The actual enthalpy of formation of tungstic acid should be less negative if this effect is significant.

The previously accepted value (2, 3, 4) -280.2 ± 0.4 kcal·mol^{-1}, was based on the pressure temperature composition studies of Huttig and Kurre[5] for the WO_3 H_2O system. We suspect that the data do not correspond to equilibrium (see entropy section) for the reaction $H_2WO_4(cr) = WO_3(cr) + H_2O(g)$.

Heat Capacity and Entropy

$C_p°(300\ K) = 27.0$ cal·K^{-1}·mol^{-1} is estimated using Kopp's rule. Since the decomposition temperature of H_2WO_4(cr) is approximately 400 K, which is relatively low for hydrogen and oxygen to reach their maximum $C_p°$ contribution, we estimate $C_p°(400\ K) = 31.0$ cal·K^{-1}·mol^{-1} for H_2WO_4(cr).

The entropy, $S°(298.15\ K) = 34.6$ cal·K^{-1}·mol^{-1}, is estimated so that the decomposition pressure of water is one atmosphere at 120°C. This value is quite uncertain as suggested by comparison with the following estimates. A lower limit may be obtained from $S°(283.5\ K) = 26.8$ cal·K^{-1}·mol^{-1} for H_2SO_4(cr). Summation of the entropies for WO_3(cr) and H_2O(cr) [10.7 cal·K^{-1}·mol^{-1}] yields 28.8 cal·K^{-1}·mol^{-1}, and estimate which is somewhat larger than the lower limit. An upper limit may be obtained by assuming that the pressure of about 14 mm at 190 °C coresonds to equilibrium for the reaction $H_2WO_4(cr) = WO_3(cr) + H_2O(g)$. This pressure, baseiuccircld on the plateau in the temperature composition data of Huttig and Kurre[5] yields $S°(298.15\ K) = 46.5$ cal·K^{-1}·mol^{-1} when combined with the adopted $\Delta_f H°(298.15\ K)$ and JANAF auxiliary data. Since the estimate appears to be unreasonably large, we suggest that this region of the curve may correspond to the reaction $WO_3 \cdot 0.5\ H_2O(cr) = WO_3(cr) + 0.5\ H_2O(g)$. In contrast, the observed pressures[5] for samples having mole ratios (H_2O/WO_3) of 1.2 1.35 leads to $S°(298.15\ K) = 34$ cal·K^{-1}·mol^{-1}, if the reaction is $WO_3 \cdot H_2O(cr) = WO_3(cr) + H_2O(g)$.

Decomposition Data

$T_{dcm} = 393$ K is calculated as the temperature at which the fugucity of water is 1 atmosphere for the reaction $H_2WO_4(cr) \rightarrow WO_3(cr) + H_2O(g)$ approaches zero.

Spitsyn and Patsukova[1] observed that some dehydration of stoichiometric H_2WO_4(cr) occurs at temperature as low as 90°C. Thermal studies[6,7] on tungstic acid containing some exces water indicated the start of dehydration somewhere in the region of 60–120°C. These temperatures yield a lower limit for T_{dcm} on the presumption that the experiments correspond to a partial pressure of water of less than one atmosphere.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	112.633	144.766	144.766	0.	−1131.772	−1003.905	175.880
300	112.968	145.464	144.769	0.209	−1131.770	−1003.112	174.657
400	129.704	180.255	149.399	12.342	−1130.949	−960.310	125.404
500	146.440	211.003	158.697	26.153	−1128.693	−917.882	95.890
600	159.829	238.972	169.783	41.513	−1125.138	−876.036	76.266
700	170.707	264.509	181.518	58.094	−1120.606	−834.865	62.298
800	176.565	287.724	193.367	75.485	−1115.486	−794.391	51.868
900	182.422	308.889	205.044	93.461	−1109.985	−754.580	43.795
1000	186.606	328.326	216.414	111.912	−1104.195	−715.399	37.369

PREVIOUS: June 1963 CURRENT: March 1967

$S°(298.15\ K)$ = [351.999] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -896.09 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -905.84 \pm 4.2\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
[2200](1)	[100](1)	[570](1)
[1000](1)	[225](1)	[120](1)
[620](1)	[100](1)	[1100](1)
[560](1)	[2500](1)	[300](1)
[500](1)	[630](1)	[540](1)

Ground State Quantum Weight: 1 σ = [2]
Point Group: [C_{2v}]
Bond Distances: W–O = [1.81] Å O–H = [0.97] Å
Bond Angles: O–W–O = [109.47]° W–O–H = [105]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [$1.442326 \times 10^{-113}$] $g^3·cm^6$

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°(298.15\ K) = -216.5 \pm 1.0\ kcal·mol^{-1}$, is derived from equilibrium data[1-5] obtained by the transpiration method. The data are in reasonable agreement and they are summarized below. Belton and McCarron[1] have concluded that $WO_3·H_2O$ is the species responsible for the increased volatilization of W(cr) and WO_3(cr) in the presence of water vapor. Based on their data for W(cr) and the earlier data for WO_3(cr), Belton and McCarron[1] ruled out the possibility of significant amounts of $(WO_3)_2·H_2O$ and $WO_3·2H_2O$.

Source	Reaction*	T/K	Data Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Belton & McCarron[1]	A	1473–1773	Equation	14.70	14.63	−0.1 ± 1.1	−216.56
Glemser & Ackermann[2]	B	673–1173	6	38.56	41.67	3.2 ± 0.9	−217.59
Glemser & Haeseler[3]	B	1173–1373	Equation	38.27	42.27	1.6	−216.99
Glemser & Volz[4]	B	1373	1	–	43.44	–	−215.82
Meyer *et al.*[5]	B	1393–1518	Equation	26.14	43.51	11.9	−215.75

*Reactions: A) $W(cr) + 4H_2O(g) \rightarrow H_2WO_4(g) + 3H_2(g)$ B) $WO_3(cr) + H_2O(g) \rightarrow H_2WO_4(g)$

Heat Capacity and Entropy

The vibrational frequencies are estimated by comparison with those for H_2SO_4(g) reported by Giguere and Savoie,[6] and Chackalackal and Stafford.[7] These frequencies are also adjusted so that $S°(H_2WO_4, g, 1600\ K)$ is 136.7 $cal·K^{-1}·mol^{-1}$ as reported by Belton and McCarron.[1] This entropy was derived a 2nd law analysis of the equilibrium constants for reaction A.

The configuration of WO_4^- group is assumed to be tetrahedral. The bond angle W–O–H is estimated to be the same as the angle of H_2O(g). The bond distances are assumed to be the same as those in WO_3(g) and H_2O(g). The principal moments of inertia are: $I_A = 23.2705 \times 10^{-39}$, $I_B = 24.8660 \times 10^{-39}$, and $I_C = 24.9259 \times 10^{-39}$ $g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J·K^{-1}·mol^{-1}$)	$S°$ ($J·K^{-1}·mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J·K^{-1}·mol^{-1}$)	$H°-H°(T_r)$ ($kJ·mol^{-1}$)	$\Delta_f H°$ ($kJ·mol^{-1}$)	$\Delta_f G°$ ($kJ·mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−21.062	−896.091	−896.091	INFINITE
100	60.677	265.197	430.296	−16.510	−901.000	−881.824	460.618
200	84.476	314.672	360.846	−9.235	−904.248	−861.251	224.936
250	94.555	334.639	353.644	−4.751	−905.233	−850.380	177.677
298.15	102.527	351.999	351.999	0.	−905.836	−839.756	147.122
300	102.802	352.634	352.001	0.190	−905.853	−839.346	146.143
350	109.449	368.999	353.278	5.502	−906.167	−828.233	123.607
400	114.836	383.977	356.193	11.114	−906.241	−817.091	106.701
450	119.269	397.767	360.056	16.970	−906.131	−805.953	93.553
500	122.986	410.531	364.473	23.029	−905.881	−794.834	83.036
600	128.916	433.504	374.107	35.638	−905.077	−772.694	67.269
700	133.483	453.733	384.066	48.767	−903.996	−750.713	56.019
800	137.120	471.804	393.924	62.304	−902.731	−728.900	47.592
900	140.070	488.130	403.499	76.168	−901.341	−707.253	41.048
1000	142.491	503.017	412.717	90.300	−899.871	−685.766	35.821
1100	144.492	516.695	421.557	104.652	−898.355	−664.429	31.551
1200	146.159	529.341	430.018	119.187	−896.820	−643.230	27.999
1300	147.555	541.097	438.116	133.875	−895.289	−622.160	24.999
1400	148.733	552.076	445.868	148.691	−893.780	−601.207	22.431
1500	149.733	562.373	453.296	163.616	−892.309	−580.361	20.210
1600	150.587	572.064	460.419	178.633	−890.887	−559.611	18.269
1700	151.320	581.216	467.258	193.729	−889.525	−538.948	16.560
1800	151.954	589.884	473.832	208.894	−888.231	−518.364	15.043
1900	152.504	598.114	480.158	224.117	−887.011	−497.850	13.687
2000	152.985	605.949	486.253	239.392	−885.872	−477.397	12.468
2100	153.407	613.424	492.132	254.712	−884.818	−457.000	11.367
2200	153.779	620.569	497.809	270.072	−883.853	−436.649	10.367
2300	154.109	627.412	503.297	285.467	−882.979	−416.342	9.455
2400	154.402	633.978	508.606	300.892	−882.199	−396.072	8.620
2500	154.664	640.286	513.748	316.346	−881.513	−375.831	7.853
2600	154.898	646.357	518.732	331.824	−880.921	−355.615	7.144
2700	155.109	652.207	523.568	347.325	−880.448	−335.420	6.489
2800	155.300	657.851	528.263	362.846	−880.131	−315.240	5.881
2900	155.472	663.304	532.826	378.384	−880.008	−295.069	5.315
3000	155.628	668.577	537.264	393.939	−880.106	−274.897	4.786
3100	155.771	673.683	541.583	409.509	−880.467	−254.718	4.292
3200	155.901	678.630	545.789	425.093	−881.123	−234.524	3.828
3300	156.020	683.429	549.887	440.689	−882.098	−214.304	3.392
3400	156.129	688.089	553.884	456.297	−883.426	−194.048	2.981
3500	156.229	692.616	557.783	471.915	−885.171	−173.748	2.593
3600	156.321	697.018	561.590	487.542	−887.428	−153.391	2.226
3700	156.407	701.303	565.308	503.179	−925.062	−132.773	1.874
3800	156.486	705.475	568.942	518.823	−925.055	−111.359	1.531
3900	156.559	709.540	572.495	534.476	−925.087	−89.945	1.205
4000	156.627	713.505	575.971	550.135	−925.157	−68.531	0.895
4100	156.690	717.373	579.373	565.801	−925.266	−47.114	0.600
4200	156.749	721.150	582.704	581.473	−925.412	−25.694	0.320
4300	156.804	724.839	585.967	597.151	−925.595	−4.269	0.052
4400	156.856	728.444	589.164	612.834	−925.816	17.158	−0.204
4500	156.904	731.970	592.299	628.522	−926.073	38.591	−0.448
4600	156.949	735.419	595.372	644.214	−926.368	60.031	−0.682
4700	156.991	738.795	598.388	659.911	−926.699	81.479	−0.906
4800	157.031	742.100	601.348	675.612	−927.068	102.933	−1.120
4900	157.068	745.339	604.254	691.317	−927.475	124.397	−1.326
5000	157.103	748.512	607.107	707.026	−927.920	145.869	−1.524
5100	157.137	751.624	609.910	722.738	−928.403	167.349	−1.714
5200	157.168	754.675	612.665	738.453	−928.926	188.838	−1.897
5300	157.198	757.669	615.373	754.172	−929.488	210.340	−2.073
5400	157.226	760.608	618.035	769.893	−930.092	231.851	−2.243
5500	157.252	763.493	620.654	785.617	−930.737	253.373	−2.406
5600	157.278	766.327	623.230	801.343	−931.425	274.911	−2.564
5700	157.301	769.111	625.765	817.072	−932.156	296.458	−2.717
5800	157.324	771.847	628.260	832.803	−932.933	318.021	−2.864
5900	157.346	774.536	630.716	848.537	−933.755	339.592	−3.007
6000	157.366	777.181	633.136	864.272	−934.625	361.184	−3.144

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K)$ = [212.652] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [112.3 ± 96.2] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [108.5 ± 96.2] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[2327](1)
[1020](1)
[2322](1)

Ground State Quantum Weight: [2] σ = [2]
Point Group = [C_{2v}]
Bond Distance: P–H = [1.419] Å
Bond Angle: H–P–H = [93.7]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [0.0695 × 10^{-117}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°$(298.15 K) was estimated by DiStefano *et al.*[1]. The $\Delta_f H°$(298.15 K) was estimated by taking 63% of the dissociation energy of PH_3 and using it as the dissociation energy of PH_2. Willes and Winkler[2] have estimated $\Delta_f H°(PH_2, g, 298.15\ K)$ to be 30 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The vibratonal spectra of PH_2 from the flash photolysis of PH_3 has been reported by Ramsey[3] and in.[4] Similarities between the spectra of NH_2 and PH_2 were found. For NH_2 and NH_3 bond angles and bond distances were reported to be about the same. Byanalogy then the bond angles and bond distances of PH_2 and PH_3 should be nearly the same. The moments of inertia for PH_2 were therefore calculated from the molecular constants for PH_3. The principal moments of inertia are: $I_A = 0.2960 \times 10^{-39}$, $I_B = 0.3588 \times 10^{-39}$, and $I_C = 0.6548 \times 10^{-39}$ $g·cm^2$.

DiStefano *et al.*[1] have assumed the ground state degeneracy to be 2 because of the unpaired electron. The vibrational frequencies reported by DiStefano *et al.* have been used. They used a simple force field and the force constants of PH_3 to obtain the vibrational frequencies.

References

[1]V. N. DiStefano, R. L. Potter and S. N. Fox, "The Thermodynamic Functions of Some Combustion Products Containing Phosphorus–I.", American Cyanamid Company.
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[3]D. A. Ramsey, Nature **178**, 375 (1956).
[4]N. Y. Acad. Sci. **67**, 485 (1957).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−10.006	112.321	112.321	INFINITE
100	33.258	175.957	242.760	−6.680	111.760	106.006	−55.372
200	33.549	199.055	215.787	−3.347	110.136	100.633	−26.283
250	34.075	206.593	213.221	−1.657	109.338	98.348	−20.549
298.15	34.774	212.652	212.652	.000	108.499	96.306	−16.872
300	34.804	212.868	212.653	.064	108.466	96.231	−16.755
350	35.641	218.295	213.080	1.825	106.842	94.334	−14.079
400	36.535	223.112	214.038	3.629	105.873	92.614	−12.094
450	37.468	227.468	215.292	5.479	104.947	91.012	−10.564
500	38.430	231.466	216.712	7.377	104.065	89.512	−9.351
600	40.400	238.646	219.783	11.318	102.445	86.756	−7.553
700	42.343	245.020	222.941	15.456	101.012	84.257	−6.287
800	44.169	250.796	226.067	19.783	99.754	81.952	−5.351
900	45.820	256.095	229.113	24.284	98.648	79.794	−4.631
1000	47.278	261.000	232.060	28.940	97.668	77.753	−4.061
1100	48.548	265.567	234.901	33.733	96.789	75.805	−3.600
1200	49.645	269.839	237.636	38.644	32.417	75.011	−3.265
1300	50.590	273.851	240.269	43.657	32.452	78.560	−3.157
1400	51.403	277.631	242.804	48.758	32.525	82.104	−3.063
1500	52.104	281.202	245.246	53.934	32.627	85.642	−2.982
1600	52.711	284.584	247.600	59.175	32.747	89.172	−2.911
1700	53.238	287.796	249.871	64.473	32.878	92.695	−2.848
1800	53.696	290.852	252.063	69.821	33.015	96.210	−2.792
1900	54.097	293.767	254.182	75.211	33.153	99.717	−2.741
2000	54.450	296.551	256.231	80.638	33.290	103.217	−2.696
2100	54.760	299.215	258.215	86.099	33.422	106.710	−2.654
2200	55.035	301.769	260.137	91.589	33.548	110.197	−2.616
2300	55.280	304.221	262.001	97.105	33.665	113.678	−2.582
2400	55.498	306.578	263.810	102.644	33.774	117.154	−2.550
2500	55.693	308.848	265.566	108.204	33.873	120.627	−2.520
2600	55.869	311.036	267.273	113.782	33.961	124.095	−2.493
2700	56.027	313.147	268.933	119.377	34.037	127.560	−2.468
2800	56.170	315.187	270.549	124.987	34.102	131.023	−2.444
2900	56.299	317.161	272.122	130.611	34.154	134.483	−2.422
3000	56.417	319.071	273.656	136.247	34.194	137.942	−2.402
3100	56.524	320.923	275.151	141.894	34.221	141.400	−2.383
3200	56.622	322.719	276.609	147.551	34.235	144.857	−2.365
3300	56.712	324.463	278.033	153.218	34.236	148.314	−2.348
3400	56.795	326.157	279.424	158.893	34.222	151.771	−2.332
3500	56.871	327.805	280.783	164.577	34.195	155.229	−2.317
3600	56.941	329.408	282.111	170.267	34.154	158.687	−2.302
3700	57.005	330.969	283.411	175.965	34.098	162.147	−2.289
3800	57.065	332.490	284.682	181.668	34.028	165.609	−2.276
3900	57.121	333.973	285.927	187.377	33.944	169.073	−2.264
4000	57.172	335.419	287.146	193.092	33.844	172.539	−2.253
4100	57.220	336.832	288.341	198.812	33.729	176.008	−2.242
4200	57.265	338.211	289.512	204.536	33.600	179.479	−2.232
4300	57.307	339.559	290.660	210.265	33.455	182.954	−2.222
4400	57.346	340.877	291.787	215.997	33.295	186.433	−2.213
4500	57.383	342.166	292.892	221.734	33.121	189.915	−2.204
4600	57.417	343.428	293.977	227.474	32.931	193.401	−2.196
4700	57.449	344.663	295.042	233.217	32.726	196.892	−2.188
4800	57.480	345.873	296.089	238.964	32.507	200.388	−2.181
4900	57.508	347.058	297.117	244.713	32.274	203.887	−2.173
5000	57.535	348.220	298.127	250.465	32.027	207.392	−2.167
5100	57.560	349.360	299.121	256.220	31.766	210.902	−2.160
5200	57.584	350.478	300.098	261.977	31.491	214.417	−2.154
5300	57.607	351.575	301.059	267.737	31.205	217.938	−2.148
5400	57.628	352.652	302.004	273.499	30.906	221.464	−2.142
5500	57.649	353.710	302.935	279.263	30.596	224.995	−2.137
5600	57.668	354.749	303.851	285.028	30.275	228.533	−2.132
5700	57.686	355.769	304.753	290.796	29.944	232.076	−2.127
5800	57.703	356.773	305.641	296.566	29.604	235.626	−2.122
5900	57.720	357.759	306.516	302.337	29.255	239.180	−2.118
6000	57.736	358.730	307.378	308.110	28.899	242.741	−2.113

PREVIOUS: March 1963 (1 atm) CURRENT: March 1963 (1 bar)

$S°(298.15\ K) = 205.757\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -17.584 \pm 0.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -20.502 \pm 0.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2614.6(1)
1182.7(1)
2626.5(1)

Ground State Quantum Weight: 1 $\sigma = 2$

Point Group: C_{2v}

Bond[uccircl Distance: S–H = 1.328 Å

Bond Angle: H–S–H = 92.2°

Product of the Moments of Inertia: $I_A I_B I_C = 0.0469 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation of $H_2S(g)$ determined by various workers including those reviewed in the previous JANAF analysis[1] were recalculated with the results shown below. No weight was given to the work performed prior to 1934 and less weight was given to the work of Kapustinskii and Kankovskii[7] because of the difficulty of establishing the state of the products.

Source	Reaction*	[from (1)]	$\Delta_f H°$(298.15 K), kcal·mol^{-1} Recalculated
Thomsen[2]	$H_2S(g) + HI_3(aq) = 3\ HI(aq) + S(amorph)$	–	−4.4, −5.1 if S(rhombic)
Thomsen[3]	$*H_2S(g) + O_2(g) = SO_2(g) + H_2SO_4·H_2O$	–	−2.0
Pollitzer[4]	$H_2S(g) + I_2(cr) = 2\ HI(g) + S(rh)$	–	−4.7, − 4.0 if S(amorph)
Lewis and Randall[5]	$3\ S(l) + 2\ H_2O(g) = SO_2(g) + 2\ H_2S(g)$	–	−3.6 ± 0.2
Zeumer and Roth[6]	$*H_2S(g) + O_2(g) = SO_2(g) + H_2SO_4·H_2O$	−4.80 ± 0.15	−4.89 ± 0.24
Kapustinskii and Kankovskii[7]	$*H_2S(g) + 3/2\ O_2(g) = SO_2(g) + H_2O(l) + S(rh)$	−4.9 ± 0.8	−4.92 ± 0.08

*Equations which are not balanced involve two reactions occurring in various proportions.

Heat Capacity and Entropy

The thermodynamic functions were taken from the JANAF table for $H_2S(g)$ dated (December 31, 1965).[1] These in turn were taken from Gordon[8] except below 298 K were they were calculated by the rigid–rotor, harmonic–oscillator approximation. Gordon had calculated $C_p°$ from 298 K to 6000 K by a method which takes into account second–order corrections for vibrational anharmonicity, vibration–rotation interaction, and centrifugal stretching. The spectroscopic constants used were taken from Allen and Plyler.[9]

The National Bureau of Standards prepared this table[10] by critical analysis of data existing in 1972. Using $\Delta_f H°$ selected by NBS,[10] we recalculate the table in terms of current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (1971).
[2]J. Thomsen, "Thermochemical Investigations," Vol. II, p. 60, J. A. Barth, Leipzig, (1882).
[3]J. Thomsen, "Thermochemical Investigations," Vol. IV, p. 188, J. A. Barth, Leipzig, (1882).
[4]F. Pollitzer, Z. Anorg. Chem. **64**, 121 (1909).
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[7]A. F. Kapustinskii and R. T. Kankovskii, Zhur. Fiz. Khim. **32**, 2810 (1958).
[8]J. S. Gordon, Thiokol Chem. Corp., personal communication to D. R. Stull, (February 7, 1961).
[9]H. C. Allen and E. K. Plyler, J. Chem. Phys. **25**, 1132 (1956); **24**, 35 (1956).
[10]S. Abramowitz *et al.*, U. S. Nat. Bur. Stand. Rept. 10904, 239, (July, 1972).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.962	−17.584	−17.584	INFINITE
100	33.259	168.972	235.330	−6.636	−17.947	−23.519	12.285
200	33.380	192.038	208.586	−3.310	−18.957	−28.754	7.510
298.15	34.192	205.757	205.757	0.	−20.502	−33.329	5.839
300	34.208	205.969	205.758	0.063	−20.534	−33.408	5.817
400	35.581	215.992	207.115	3.551	−24.549	−37.343	4.876
500	37.192	224.102	209.726	7.188	−27.762	−40.179	4.197
600	38.936	231.037	212.713	10.994	−30.470	−42.399	3.691
700	40.740	237.174	215.777	14.978	−32.771	−44.201	3.298
800	42.518	242.731	218.804	19.142	−34.771	−45.694	2.984
900	44.212	247.838	221.750	23.479	−89.665	−45.870	2.662
1000	45.786	252.579	224.599	27.980	−90.024	−40.984	2.141
1100	47.200	257.011	227.346	32.631	−90.284	−36.066	1.713
1200	48.467	261.173	229.993	37.415	−90.465	−31.129	1.355
1300	49.593	265.098	232.544	42.320	−90.584	−26.179	1.052
1400	50.593	268.810	235.003	47.330	−90.656	−21.222	0.792
1500	51.476	272.331	237.375	52.434	−90.693	−16.261	0.566
1600	52.262	275.679	239.666	57.622	−90.705	−11.298	0.369
1700	52.961	278.869	241.879	62.883	−90.699	−6.336	0.195
1800	53.589	281.914	244.019	68.212	−90.681	−1.374	0.040
1900	54.145	284.827	246.091	73.599	−90.656	3.587	−0.099
2000	54.656	287.617	248.098	79.039	−90.627	8.547	−0.223
2100	55.107	290.295	250.044	84.528	−90.597	13.505	−0.336
2200	55.522	292.868	251.932	90.059	−90.566	18.461	−0.438
2300	55.898	295.345	253.766	95.631	−90.538	23.416	−0.532
2400	56.250	297.731	255.549	101.238	−90.512	28.370	−0.617
2500	56.568	300.034	257.282	106.879	−90.490	33.323	−0.696
2600	56.861	302.258	258.970	112.551	−90.472	38.275	−0.769
2700	57.133	304.409	260.613	118.251	−90.458	43.227	−0.836
2800	57.384	306.492	262.214	123.977	−90.450	48.178	−0.899
2900	57.618	308.510	263.776	129.727	−90.447	53.129	−0.957
3000	57.840	310.467	265.300	135.500	−90.450	58.080	−1.011
3100	58.049	312.367	266.788	141.294	−90.459	63.031	−1.062
3200	58.245	314.213	268.241	147.109	−90.473	67.982	−1.110
3300	58.430	316.008	269.662	152.943	−90.495	72.935	−1.154
3400	58.605	317.755	271.051	158.795	−90.524	77.887	−1.197
3500	58.773	319.456	272.409	164.664	−90.560	82.841	−1.236
3600	58.932	321.114	273.739	170.549	−90.604	87.796	−1.274
3700	59.086	322.731	275.042	176.450	−90.656	92.752	−1.309
3800	59.229	324.308	276.317	182.366	−90.717	97.710	−1.343
3900	59.371	325.849	277.568	188.296	−90.788	102.670	−1.375
4000	59.509	327.354	278.794	194.240	−90.868	107.631	−1.406
4100	59.639	328.825	279.996	200.197	−90.958	112.595	−1.434
4200	59.768	330.263	281.176	206.168	−91.058	117.561	−1.462
4300	59.890	331.671	282.334	212.151	−91.169	122.529	−1.488
4400	60.011	333.050	283.471	218.146	−91.290	127.500	−1.514
4500	60.128	334.399	284.588	224.153	−91.423	132.474	−1.538
4600	60.237	335.722	285.685	230.171	−91.568	137.451	−1.561
4700	60.346	337.019	286.763	236.200	−91.725	142.431	−1.583
4800	60.459	338.291	287.824	242.240	−91.893	147.416	−1.604
4900	60.563	339.538	288.866	248.292	−92.073	152.403	−1.625
5000	60.668	340.763	289.892	254.353	−92.265	157.394	−1.644
5100	60.764	341.965	290.901	260.425	−92.468	162.389	−1.663
5200	60.869	343.146	291.895	266.506	−92.682	167.388	−1.681
5300	60.965	344.306	292.873	272.598	−92.907	172.392	−1.699
5400	61.061	345.447	293.836	278.699	−93.143	177.400	−1.716
5500	61.153	346.568	294.785	284.810	−93.389	182.412	−1.732
5600	61.250	347.671	295.719	290.930	−93.644	187.429	−1.748
5700	61.342	348.756	296.640	297.060	−93.908	192.451	−1.764
5800	61.429	349.823	297.548	303.198	−94.180	197.477	−1.778
5900	61.526	350.874	298.443	309.346	−94.459	202.507	−1.793
6000	61.609	351.909	299.325	315.503	−94.745	207.543	−1.807

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 29.711\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-136.00 \pm 8.4]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-144.35 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of combustion of $TiH_{1.73}$(cr), the stable species of titanium hydride, was reported to be 247.8 $kcal·mol^{-1}$ by Sieverts and Gotta[1]. From this data the value of $\Delta_f H°(298.15\ K)$ for $TiH_{1.73}$(cr) was calculated to be 29.40 $kcal·mol^{-1}$. The enthalpy of dissociation of titanium hydride having compositions between the rough limits $TiH_{1.75}$ $TiH_{1.93}$ was given as 19.15 $kcal·mol^{-1}$ of H_2 dissociated by Gibb.[2] Assuming this value is applicable to compositions between the limits $TiH_{1.73}$ TiH_2, the difference in the enthalpy of formation of titanium hydride between $TiH_{1.73}$ and TiH_2 was estimated to be 5.17 $kcal·mol^{-1}$. Thus the value of $\Delta_f H°(298.15\ K)$ for TiH_2(cr) was calculated.

Heat Capacity and Entropy

The low temperature $C_p°$ for $TiH_{1.97}$(cr) were measured by Stalinski and Bieganski[3] 24 363 K). This data were adopted for TiH_2(cr) due to lack of the measured $C_p°$ values. A small but well marked type anomaly with a maximal value of $C_p°$ at 288.5 K in the $C_p°$ vs T curve was observed. $S°(298.15\ K)$ was reported by Stalinski and Bieganski[3] based on $S°(\text{extrap } 25\ K) = 0.65\ cal·K^{-1}·mol^{-1}$.

References

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[3]B. Stalinski and Z. Bieganski, Bull. Acad. Polon. Sci., Ser. Sci. Chim. **8**, No. 5, 243 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.945	−135.996	−135.996	INFINITE
100	12.678	6.745	51.513	−4.477	−139.087	−128.863	67.311
200	22.719	19.041	32.284	−2.648	−141.870	−117.550	30.701
298.15	30.087	29.711	29.711	0.	−144.348	−105.073	18.408
300	30.259	29.897	29.711	0.056	−144.392	−104.829	18.252
400	39.330	39.847	31.006	3.536	−146.431	−91.315	11.924
500	47.279	49.504	33.747	7.879	−147.752	−77.368	8.083
600	53.806	58.721	37.148	12.944	−148.441	−63.217	5.504
700	58.994	67.418	40.857	18.593	−148.618	−48.993	3.656
800	63.137	75.577	44.693	24.707	−148.381	−34.773	2.270
900	66.159	83.194	48.553	31.178	−147.877	−20.600	1.196
1000	68.534	90.294	52.376	37.918	−147.261	−6.491	0.339
1100	70.057	96.899	56.127	44.849	−146.684	7.557	−0.359
1200	71.337	103.051	59.784	51.921	−150.185	21.677	−0.944
1300	72.251	108.798	63.336	59.101	−149.106	35.955	−1.445
1400	73.046	114.182	66.777	66.367	−148.063	50.151	−1.871
1500	73.722	119.246	70.108	73.707	−147.082	64.274	−2.238
1600	74.279	124.022	73.330	81.108	−146.187	78.335	−2.557
1700	74.716	128.539	76.446	88.558	−145.402	92.343	−2.837
1800	75.034	132.819	79.460	96.047	−144.751	106.308	−3.085
1900	75.232	136.882	82.376	103.561	−144.257	120.242	−3.306
2000	75.312	140.743	85.199	111.089	−158.631	134.607	−3.516

PREVIOUS: CURRENT: June 1963

$S°(298.15\ K) = 271.022 \pm 0.25\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [8.35 \pm 16.7]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-2.09 \pm 16.7]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2192(1)	2206(2)
903(1)	941(2)
362(1)	592(2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distances: Si–H = 1.486 ± 0.008 Å Si–H = 2.437 Å
Bond Angles: H–Si–H = 110.42° ± 0.5° H–Si–I = 108.5° ± 0.5°
Product of the Moments of Inertia: $I_A I_B I_C = 6.831704 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H$ (298.15 K) is estimated by linear interpolation between the values[1] of SiI_4(g) and SiH_4(g). There are no experimental $\Delta_f H°$ data for SiH_3I, SiH_2I_2 and $SiHI_3$. It is difficult to justify a nonlinear interpolation scheme such as that adopted for the chlorosilanes.[1] A cubic interpolation fits $\Delta_f H°$ data for the chloromethanes and has been proposed for bromomethanes and iodomethanes.[2] Experimental $\Delta_f H°$ values do not seem to eixst for CI_4, CBr_4 and $CHBr_3$, while published values for CBr_4 and $CHBr_3$ are the subject of controversy (SiH_3Br, g).[1] Moreover, the cubic scheme proposed[2] for CH_nI_{4-n} is surprisingly different from those of the other halomethanes;[2] i.e., the first differences in $\Delta_f H°$ exhibit a minimum instead of a maximum. These uncertainties preclude use of the iodomethanes for predicting $\Delta_f H°$ of the iodosilanes. Hunt and Sirtl[3] also concluded that linear interpolation of $\Delta_f H°$ is all that is justified by available data.

Heat Capacity and Entropy

The molecular structure is based on microwave data of Kewley *et al.*[4] for isotopic forms of the four monohalosilanes. The authors concluded that the silyl group is effectively the same in all four halides. We adopt effective (r_o) structural parameters rather than substitutional (r_s) parameters. These are in reasonable agreement with previous structural determinations.[5] The principal moments of inertia are $I_A = 0.9972 \times 10^{-39}$ and $I_B = I_C = 26.1748 \times 10^{-39}\ g \cdot cm^2$.

Vibrational frequencies are from gas-phase infrared spectra.[6,7] Assignments are consistent with liquid-phase Raman spectra[8,9] which yield slightly lower values for most of the frequencies.

We neglect excited states and assume the electronic ground state to be $^1A_1$ by analogy with CH_3I[10]. Comparison of the halosilanes[11] and halomethanes[10, 11] suggests that the lowest excited state of SiH_3I is at ≥30000 cm^{-1}. Contributions from this state should be unimportant.

References

[1]JANAF Thermochemical Tables: ClH_3Si(g), BrH_3Si(g) 12–31–76; H_4Si(g), I_4Si(g) 6–30–76
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.078	8.348	8.348	INFINITE
100	34.754	224.891	312.147	−8.726	5.410	1.463	−0.764
200	43.918	251.491	275.668	−4.835	1.615	−1.031	0.269
250	49.420	261.884	271.890	−2.501	−0.309	−1.469	0.307
298.15	54.401	271.022	271.022	0.	−2.092	−1.529	0.268
300	54.582	271.359	271.023	0.101	−2.159	−1.525	0.266
350	59.178	280.125	271.704	2.947	−3.927	−1.279	0.191
400	63.215	288.296	273.273	6.009	−13.550	−0.514	0.067
450	66.784	295.952	275.372	9.261	−15.629	1.242	−0.144
500	69.979	303.157	277.794	12.681	−37.638	5.122	−0.535
600	75.514	316.420	283.146	19.964	−39.001	13.809	−1.202
700	80.152	328.419	288.770	27.754	−39.950	22.691	−1.693
800	84.055	339.385	294.421	35.970	−40.561	31.685	−2.069
900	87.331	349.480	299.986	44.545	−40.906	40.739	−2.364
1000	90.075	358.827	305.408	53.419	−41.049	49.820	−2.602
1100	92.372	367.523	310.664	62.545	−41.046	58.908	−2.797
1200	94.299	375.646	315.745	71.881	−40.942	67.991	−2.960
1300	95.922	383.260	320.648	81.394	−40.778	77.062	−3.096
1400	97.295	390.420	325.379	91.057	−40.587	86.120	−3.213
1500	98.462	397.173	329.942	100.847	−40.398	95.163	−3.314
1600	99.460	403.561	334.346	110.744	−40.232	104.195	−3.402
1700	100.318	409.617	338.597	120.734	−90.285	113.665	−3.492
1800	101.059	415.372	342.704	130.804	−89.986	125.653	−3.646
1900	101.703	420.854	346.674	140.942	−89.711	137.625	−3.784
2000	102.265	426.085	350.514	151.141	−89.467	149.584	−3.907
2100	102.759	431.087	354.233	161.393	−89.257	161.531	−4.018
2200	103.194	435.877	357.836	171.691	−89.082	173.469	−4.119
2300	103.579	440.473	361.330	182.030	−88.941	185.400	−4.211
2400	103.922	444.889	364.720	192.406	−88.833	197.325	−4.295
2500	104.228	449.138	368.012	202.814	−88.752	209.247	−4.372
2600	104.502	453.231	371.212	213.250	−88.694	221.166	−4.443
2700	104.748	457.179	374.323	223.713	−88.656	233.082	−4.509
2800	104.970	460.993	377.351	234.199	−88.632	244.998	−4.570
2900	105.171	464.680	380.299	244.706	−88.617	256.913	−4.628
3000	105.354	468.249	383.171	255.233	−88.607	268.828	−4.681
3100	105.520	471.706	385.972	265.776	−88.600	280.742	−4.730
3200	105.672	475.059	388.704	276.336	−88.591	292.656	−4.777
3300	105.811	478.312	391.370	286.910	−88.578	304.570	−4.821
3400	105.938	481.473	393.974	297.498	−88.559	316.483	−4.862
3500	106.055	484.546	396.518	308.098	−88.533	328.396	−4.901
3600	106.163	487.535	399.005	318.709	−472.649	350.769	−5.090
3700	106.262	490.445	401.437	329.330	−472.190	373.635	−5.275
3800	106.354	493.280	403.817	339.961	−471.724	396.489	−5.450
3900	106.440	496.044	406.146	350.601	−471.249	419.331	−5.616
4000	106.519	498.740	408.427	361.248	−470.765	442.160	−5.774
4100	106.593	501.371	410.662	371.904	−470.273	464.977	−5.924
4200	106.661	503.940	412.853	382.567	−469.773	487.782	−6.066
4300	106.725	506.451	415.000	393.236	−469.265	510.575	−6.202
4400	106.785	508.905	417.107	403.912	−468.750	533.356	−6.332
4500	106.841	511.305	419.174	414.593	−468.228	556.125	−6.455
4600	106.894	513.654	421.202	425.280	−467.699	578.882	−6.573
4700	106.943	515.954	423.194	435.972	−467.164	601.628	−6.686
4800	106.990	518.206	425.150	446.669	−466.624	624.364	−6.794
4900	107.033	520.412	427.071	457.370	−466.079	647.086	−6.898
5000	107.074	522.575	428.960	468.075	−465.530	669.799	−6.997
5100	107.113	524.696	430.816	478.784	−464.976	692.500	−7.093
5200	107.149	526.776	432.642	489.498	−464.419	715.190	−7.184
5300	107.184	528.817	434.437	500.214	−463.857	737.869	−7.272
5400	107.217	530.821	436.204	510.934	−463.292	760.538	−7.357
5500	107.248	532.789	437.942	521.658	−462.722	783.196	−7.438
5600	107.277	534.721	439.653	532.384	−462.150	805.844	−7.517
5700	107.305	536.620	441.338	543.113	−461.573	828.482	−7.592
5800	107.331	538.487	442.996	553.845	−460.992	851.110	−7.665
5900	107.356	540.322	444.631	564.579	−460.407	873.727	−7.735
6000	107.380	542.126	446.240	575.316	−459.817	896.334	−7.803

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 192.774 \pm 0.025\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -38.907 \pm 0.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -45.898 \pm 0.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3506(1)	1022(1)	3577(2)	1691(2)

Ground State Quantum Weight: 1 σ(internal) = 2
Point Group: C_{3v} σ(external) = 3
Bond Length: N–H = 1.0124 Å
Bond Angle: 106.67°
Product of the Moments of Inertia: $I_A I_B I_C = 0.0348 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

2nd and 3rd law analyses of equilibrium data for the reaction $1/2N_2(g)+3/2H_2(g) = NH_3(g)$ cited in the previous JANAF evaluation[1] plus more recent work of Schulz and Schaefer[6] were made using the revised thermal functions for NH_3(g). All of the previously cited work in reaction calorimetry plus the early work of Berthelot[7,8] and Thomsen[9] were reevaluated. No significant differences in the 3rd law calculations of the equilibrium data or in the corrections to the flow calorimetry data of Haber and Tamaru[12] and Wittig and Schmatz[13] were found. Thus, the 0.1 kcal discrepancy between the results of the equilibrium and reaction calorimetry measurements remains unresolved. The previous JANAF selection[1] for $\Delta_f H°(298.15\ K)$ of NH_3(g) was adopted. A recent evaluation[14] which includes new indirect calorimetry (unpublished) further confirms this selection.

Source	Method	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}*	$\Delta S°$(obs.–calc. 298.15 K)* cal·K^{-1}·mol^{-1}
Larson, Dodge[2]	$K_p^{\circ 4}$ from $K_p°$(10–1,000 atm, 600–800 K)	−10.88	−10.70 ± 0.11	+0.24 ± 0.15[a]
Haber *et al.*[3]	$K_p^{\circ 4}$ from $K_p°$(30 atm, 800–1200 K)	−10.86	−10.88 ± 0.15	−0.02 ± 0.15[b]
Haber, Maschke[5]	$K_p°$(1 atm, 900–1400 K)	−10.85	−10.62 ± 0.22	0.20 ± 0.19[c]
Schulz, Schaefer[6]	$K_p°$(1 atm, 567–673 K)	−10.87	−10.78 ± 0.20	0.14 ± 0.3[d]
Berthelot[7]	Indirect; Reaction of Br_2(aq) and NH_3(aq)	−11.4		
Berthelot[8]	Indirect; Reaction of O_2(g) with NH_3(g)	−12.1		
Thomsen[9]	Indirect; Reaction of O_2(g) with NH_3(g)	−11.9		
Becker, Roth[10]	Indirect; Heat of combustion oxalates	−11.00 ± 0.15		
Haber *et al.*[11]	Flow calorimetry at 298 K	−11.10 ± 0.05		
Haber, Tamaru[12]	Flow calorimetry (739–932 K)	−10.97 ± 0.008		
Wittig, Schmatz[13]	Flow calorimetry at 832 K	−10.99 ± 0.05		

*2nd law analysis assuming $\Delta C_p°$(cal·K^{-1}·mol^{-1}) equals (a)−2.672+0.00591(T−700), (b)−1.236+0.00404(T−1000), (c) − 0.855+0.00305(T−1100), (d) 3.287+0.00651(T−600).

Heat Capacity and Entropy

The thermodynamic functions differ from those of the 1965 JANAF table[1] in being taken directly form the later and more complete work of Haar.[15] Haar treated in detail the contribution of the highly anharmonic out–of–plane vibrational mode, including its large coupling with rotation and its coupling with the other vibrational modes. Haar's values of $C_p°$ pass through a shallow maximum between 4000 and 5000 K; they were extrapolated from 5000 to 6000 K by assuming a constant value (19.300 cal·K^{-1}·mol^{-1}). A summary of Haar's estimated uncertainties and of the differences of the 1965 table from the present table (in cal·K^{-1}·mol^{-1}) is as follows:

	Uncertainities (Haar, 15)		1965 Table minus This Table	
T,K	$C_p°$	$S°$	$C_p°$	$S°$
1000	0.006	0.006	−0.034	−0.033
3000	0.10	0.06	+0.142	−0.122
5000	0.6	0.04	+1.775	+0.265

The National Bureau of Standards prepared this table[16] by critical analysis of data existing in 1972. Using the results of Haar[15] and $\Delta_f H°$ selected by NBS,[16] we recalculate the table in terms of R=1.987192 cal·K^{-1}·mol^{-1} [17] and current JANAF reference states for the elements.

References

[1]JANAF Thermochemical Tables, 2nd ed., NSRDS–NBS 37, (1971).
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Continued on page 1359

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.045	−38.907	−38.907	INFINITE
100	33.284	155.840	223.211	−6.737	−41.550	−34.034	17.777
200	33.757	178.990	195.962	−3.394	−43.703	−25.679	6.707
298.15	35.652	192.774	192.774	0.	−45.898	−16.367	2.867
300	35.701	192.995	192.775	0.066	−45.939	−16.183	2.818
400	38.716	203.663	194.209	3.781	−48.041	−5.941	0.776
500	42.048	212.659	197.021	7.819	−49.857	4.800	−0.501
600	45.293	220.615	200.302	12.188	−51.374	15.879	−1.382
700	48.354	227.829	203.727	16.872	−52.618	27.190	−2.029
800	51.235	234.476	207.160	21.853	−53.621	38.662	−2.524
900	53.948	240.669	210.543	27.113	−54.411	50.247	−2.916
1000	56.491	246.486	213.849	32.637	−55.013	61.910	−3.234
1100	58.859	251.983	217.069	38.406	−55.451	73.625	−3.496
1200	61.048	257.199	220.197	44.402	−55.746	85.373	−3.716
1300	63.057	262.166	223.236	50.609	−55.917	97.141	−3.903
1400	64.893	266.907	226.187	57.008	−55.982	108.918	−4.064
1500	66.564	271.442	229.054	63.582	−55.954	120.696	−4.203
1600	68.079	275.788	231.840	70.315	−55.847	132.469	−4.325
1700	69.452	279.957	234.549	77.193	−55.672	144.234	−4.432
1800	70.695	283.962	237.184	84.201	−55.439	155.986	−4.527
1900	71.818	287.815	239.748	91.328	−55.157	167.725	−4.611
2000	72.833	291.525	242.244	98.561	−54.833	179.447	−4.687
2100	73.751	295.101	244.677	105.891	−54.473	191.152	−4.755
2200	74.581	298.552	247.048	113.309	−54.084	202.840	−4.816
2300	75.330	301.884	249.360	120.805	−53.671	214.509	−4.872
2400	76.009	305.104	251.616	128.372	−53.238	226.160	−4.922
2500	76.626	308.220	253.818	136.005	−52.789	237.792	−4.968
2600	77.174	311.236	255.969	143.695	−52.329	249.406	−5.011
2700	77.672	314.158	258.070	151.438	−51.860	261.003	−5.049
2800	78.132	316.991	260.124	159.228	−51.386	272.581	−5.085
2900	78.529	319.740	262.132	167.062	−50.909	284.143	−5.118
3000	78.902	322.409	264.097	174.933	−50.433	295.689	−5.148
3100	79.228	325.001	266.020	182.840	−49.959	307.218	−5.177
3200	79.521	327.521	267.903	190.778	−49.491	318.733	−5.203
3300	79.785	329.972	269.747	198.744	−49.030	330.233	−5.227
3400	80.011	332.358	271.554	206.734	−48.578	341.719	−5.250
3500	80.216	334.680	273.324	214.745	−48.139	353.191	−5.271
3600	80.400	336.942	275.060	222.776	−47.713	364.652	−5.291
3700	80.550	339.147	276.763	230.824	−47.302	376.101	−5.310
3800	80.684	341.297	278.433	238.886	−46.908	387.539	−5.327
3900	80.793	343.395	280.072	246.960	−46.534	398.967	−5.344
4000	80.881	345.441	281.680	255.043	−46.180	410.385	−5.359
4100	80.956	347.439	283.260	263.136	−45.847	421.795	−5.374
4200	81.006	349.391	284.811	271.234	−45.539	433.198	−5.388
4300	81.048	351.297	286.335	279.337	−45.254	444.593	−5.401
4400	81.065	353.161	287.833	287.442	−44.996	455.981	−5.413
4500	81.073	354.983	289.305	295.550	−44.764	467.364	−5.425
4600	81.057	356.765	290.752	303.656	−44.561	478.743	−5.436
4700	81.032	358.508	292.175	311.761	−44.387	490.117	−5.447
4800	80.990	360.213	293.575	319.862	−44.242	501.488	−5.457
4900	80.931	361.882	294.952	327.958	−44.129	512.856	−5.467
5000	80.856	363.517	296.307	336.048	−44.047	524.223	−5.477
5100	80.751	365.117	297.641	344.127	−43.999	535.587	−5.486
5200	80.751	366.685	298.954	352.202	−43.979	546.951	−5.494
5300	80.751	368.223	300.246	360.277	−43.982	558.315	−5.503
5400	80.751	369.732	301.519	368.352	−44.006	569.680	−5.511
5500	80.751	371.214	302.773	376.428	−44.049	581.044	−5.518
5600	80.751	372.669	304.008	384.503	−44.112	592.410	−5.526
5700	80.751	374.098	305.225	392.578	−44.193	603.778	−5.533
5800	80.751	375.503	306.425	400.653	−44.291	615.147	−5.540
5900	80.751	376.883	307.607	408.728	−44.404	626.516	−5.547
6000	80.751	378.240	308.773	416.803	−44.531	637.889	−5.553

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

Hydronium, Ion (H_3O^+) — IDEAL GAS — M_r = 19.022671

$S°(298.15\ K)$ = [192.257] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 581.99 \pm 12.6\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 581.16 \pm 12.6\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[3760](1)	[3870](2)
[1050](1)	[1550](2)

Ground State Quantum Weight: 1 — σ = [3]
Point Group: [C_{3v}]
Bond Distance: H–O = [0.95] Å
Bond Angle: H–O–H = [109]°
Product of the Moments of Inertia: $I_A I_B I_C = [0.0240 \times 10^{-117}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The proton affinity of water has been measured by the ion impact method as −169 kcal·mol^{-1} by Tal'rose and Frankevitch.[1] The selected enthalpy of formation of hydronium ion, $\Delta_f H°(H_3O^+, g, 0\ K)$ = 139.1 kcal·mol^{-1}, was derived from the $\Delta_r H°(0\ K)$ = −169 kcal·mol^{-1} for $H_2O(g) + H^+(g) \rightarrow H_3O^+(g)$, using the JANAF $\Delta_f H°(H_2O, g, 0\ K)$ = −57.1 and $\Delta_f H°(H^+, g, 0\ K)$ = 365.2 kcal·mol^{-1}.

The values of 195 and 207 kcal·mol^{-1} for the enthalpy of formation of $H_3O^+(g)$ have also been reported by Field and Franklin[2] and Bernecker and Long,[3] respectively. These two values were based on the electron impact studies which may involve unaccounted excitations and excess energy in the fragments. Other literature values have been reviewed by Bishop.[4]

Green and Sugden,[5] based on the studies of the positive ions in flames by mass spectrometry, prefer the value derived from the proton affinity of water obtained by Tal'rose and Frankevitch, rather than the electron impact data. From the approximate equilibrium constant calculations for the reaction $HCO^+(g) + H_2O(g) = H_3O^+(g) + CO(g)$, Clifton[6] has also found that the heat of formation of $H_3O^+(g)$ derived from the proton affinity of water, not from the electron impact data, leads to agreement with the experimental data given by Green and Sugden.

Heat Capacity and Entropy

Since the molecule $H_3O^+(g)$ has the same number of valence electrons as $NH_3(g)$, a pyramidal molecular configuration (C_{3v}) is assumed for $H_3O^+(g)$ in the tabulation. Clifton[7] has obtained a bond distance O–H of 0.95 Å from an application of covalent bond radii and the effect of electric charge, and a bond angle H–O–H of 109° by extrapolating a plot of bond length versus bond angle for $NH_3(g)$ and $PH_3(g)$ to 0.95 Å. Both values are adopted in the tabulation. The principal moments of inertia are: $I_A = I_B 0.2446 \times 10^{-39}$, $I_C = 0.4005 \times 10^{-39}\ g \cdot cm^2$. Bishop[4] has calculated theoretically the bond distance OH of 0.95 Å and the bond angle H–O–H of 114° 26' with a planar D_{3h} molecular configuration. The vibrational frequencies were calculated by the valence force method from the estimated stretching and bending force constants of Clifton.

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Hydronium, Ion ($H_3O_1^+$) — $H_3O_1^+(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.016	581.986		
100	33.258	155.526	222.432	−6.691			
200	33.536	178.619	195.407	−3.358			
250	34.159	186.161	192.829	−1.667			
298.15	35.146	192.257	192.257	0.	581.158	606.607	−106.275
300	35.190	192.474	192.257	0.065	581.154	606.765	−105.647
350	36.540	197.997	192.691	1.857	581.074	611.040	−91.193
400	38.081	202.975	193.670	3.722	581.045	615.324	−80.353
450	39.697	207.554	194.961	5.667	581.080	619.607	−71.922
500	41.309	211.820	196.436	7.692	581.180	623.883	−65.177
600	44.368	219.626	199.663	11.978	581.571	632.391	−55.055
700	47.158	226.678	203.026	16.556	582.194	640.815	−47.818
800	49.727	233.145	206.392	21.402	583.021	649.135	−42.384
900	52.131	239.142	209.702	26.496	584.029	657.341	−38.151
1000	54.401	244.753	212.929	31.824	585.199	665.426	−34.758
1100	56.542	250.040	216.065	37.372	586.513	673.386	−31.976
1200	58.553	255.047	219.107	43.128	587.955	681.221	−29.653
1300	60.428	259.808	222.056	49.078	589.512	688.930	−27.682
1400	62.164	264.351	224.916	55.209	591.168	696.517	−25.987
1500	63.763	268.695	227.691	61.506	592.911	703.981	−24.515
1600	65.229	272.858	230.385	67.957	594.730	711.327	−23.222
1700	66.569	276.853	233.001	74.548	596.614	718.557	−22.079
1800	67.790	280.693	235.545	81.267	598.552	725.674	−21.059
1900	68.903	284.389	238.019	88.102	600.537	732.682	−20.143
2000	69.915	287.949	240.427	95.044	602.561	739.585	−19.316
2100	70.837	291.383	242.772	102.082	604.618	746.386	−18.565
2200	71.676	294.698	245.058	109.209	606.700	753.088	−17.881
2300	72.440	297.901	247.286	116.415	608.803	759.695	−17.253
2400	73.138	300.999	249.460	123.694	610.923	766.210	−16.676
2500	73.775	303.998	251.582	131.041	613.055	772.637	−16.143
2600	74.358	306.903	253.654	138.448	615.196	778.977	−15.650
2700	74.891	309.719	255.678	145.911	617.343	785.236	−15.191
2800	75.381	312.452	257.657	153.424	619.492	791.415	−14.764
2900	75.831	315.105	259.593	160.985	621.642	797.517	−14.365
3000	76.245	317.683	261.486	168.589	623.790	803.545	−13.991
3100	76.626	320.189	263.340	176.233	625.935	809.502	−13.640
3200	76.979	322.628	265.155	183.914	628.074	815.389	−13.310
3300	77.304	325.001	266.932	191.628	630.207	821.210	−12.999
3400	77.606	327.314	268.674	199.374	632.331	826.966	−12.705
3500	77.886	329.567	270.382	207.149	634.445	832.659	−12.427
3600	78.146	331.765	272.057	214.950	636.548	838.293	−12.163
3700	78.387	333.910	273.700	222.777	638.639	843.868	−11.913
3800	78.612	336.003	275.312	230.627	640.718	849.387	−11.676
3900	78.823	338.048	276.894	238.499	642.782	854.852	−11.449
4000	79.019	340.046	278.448	246.391	644.832	860.263	−11.234
4100	79.202	342.000	279.975	254.302	646.866	865.624	−11.028
4200	79.374	343.910	281.474	262.231	648.884	870.935	−10.832
4300	79.535	345.780	282.948	270.177	650.885	876.198	−10.644
4400	79.687	347.610	284.397	278.138	652.869	881.415	−10.464
4500	79.829	349.402	285.822	286.114	654.835	886.586	−10.291
4600	79.962	351.158	287.223	294.103	656.782	891.715	−10.126
4700	80.088	352.880	288.602	302.106	658.712	896.801	−9.967
4800	80.207	354.567	289.958	310.121	660.622	901.847	−9.814
4900	80.319	356.222	291.294	318.147	662.513	906.853	−9.667
5000	80.425	357.846	292.609	326.185	664.386	911.821	−9.526
5100	80.526	359.439	293.904	334.232	666.239	916.751	−9.389
5200	80.621	361.004	295.179	342.290	668.074	921.645	−9.258
5300	80.710	362.540	296.435	350.356	669.890	926.504	−9.131
5400	80.796	364.050	297.674	358.431	671.687	931.329	−9.009
5500	80.877	365.533	298.894	366.515	673.467	936.120	−8.891
5600	80.953	366.991	300.097	374.607	675.228	940.881	−8.776
5700	81.027	368.425	301.283	382.706	676.972	945.609	−8.666
5800	81.096	369.834	302.453	390.812	678.699	950.307	−8.558
5900	81.162	371.221	303.607	398.925	680.410	954.974	−8.455
6000	81.225	372.586	304.745	407.044	682.104	959.614	−8.354

PREVIOUS: June 1966 (1 atm) — CURRENT: June 1966 (1 bar)

Hydronium, Ion ($H_3O_1^+$) — $H_3O_1^+(g)$

$S°(298.15\ K) = 110.544 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 315.5 \pm 5\ K$

$\Delta_f H°(0\ K) = -1265.9 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1284.4 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 13.389 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Recent calorimetric measurements[1,2,3] indicate the National Bureau of Standards' selected values quoted in reference[4] $\Delta_f H°(H_3PO_4, cr, 298.15\ K) = -305.7 \pm 0.3\ kcal \cdot mol^{-1}$, is probably in error. The value was taken from Holmes' work.[5] The data are summarized below, with heat values based on white phosphorus reference state.

Source	Method	n Moles of H_2O	$\Delta_f H°(H_3PO_4, aq, 298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Head[1]	a & b	40	-309.34 ± 0.38	-307.0 ± 0.4
Birley[2]	a	100	-309.8 ± 0.35	-307.18 ± 0.5
Irving[3]	a	0.6416	-305.9 ± 0.5	-307.36 ± 0.5
Holmes[5]	a & b	–	–	-307.4 ± 0.5*

a = solution calorimetry; b = combustion calorimetry
* see text

Head and Lewis[1] determined the enthalpy of combustion of phosphorus and enthalpy of hydrolysis of combustion products which led to $\Delta_f H°(H_3PO_4 \cdot 40\ H_2O, aq, 298.15\ K) = -309.34 \pm 0.38\ kcal \cdot mol^{-1}$. Birley and Skinner[2] measured the enthalpy of hydrolysis of PCl_5 and derived $\Delta_f H°(H_3PO_4 \cdot 100\ H_2O, aq, 298.15\ K) = -309.8 \pm 0.35\ kcal \cdot mol^{-1}$ based on $\Delta_f H°(PCl_5, cr, 298.15\ K) = -106.0\ kcal \cdot mol^{-1}$ obtained by direct chlorination of phosphorus.[4] Irving and McKerrell[3] measured the enthalpy of solution of P_4O_{10} from which they derived $\Delta_f H°(H_3PO_4 \cdot 0.6416\ H_2O, aq, 298.15\ K) = -305.9 \pm 0.5\ kcal \cdot mol^{-1}$. Using enthalpy of solution data for $H_3PO_4(cr) \rightarrow H_3PO_4(363\ H_2O, aq)$,[5] and enthalpy of dilution data for $H_3PO_4(363\ H_2O, aq) \rightarrow H_3PO_4(n\ H_2O, aq)$[6] we obtain enthalpy of formation of H_3PO_4(cr) listed in the last column of the table. (These values are based on white phosphorus as the reference state.) Holmes[5] determined $\Delta_f H°(H_3PO_4, cr, 298.15\ K) = -305.7 \pm 0.3\ kcal \cdot mol^{-1}$ based on his enthalpy of combustion of white phosphorus and related enthalpy of solution data which were combined to form a thermal cycle. Using the white phosphorus based $\Delta_f H°(P_4O_{10}, cr, 298.15\ K) = -719.4\ kcal \cdot mol^{-1}$[7] (instead of his value $-713.2\ kcal \cdot mol^{-1}$, we have recalculated his thermal cycle and find $\Delta_f H°(H_3PO_4, cr, 298.15\ K) = -307.4 \pm 0.5\ kcal \cdot mol^{-1}$ which is in good agreement with the recent calorimetric measurements.[1,2,3]

The value, $307.0 \pm 0.5\ kcal \cdot mol^{-1}$, is tentatively selected for the enthalpy of formation of H_3PO_4(cr), based on white phosphorus as reference state.

Heat Capacity and Entropy

Low temperature heat capacity from 10 to 300 K were measured by Egan and Wakefield.[8] Their smooth $C_p°$ are adopted to the tabulation. Heat capacities above 300 K are estimated graphically based on the measured $C_p°$ curve.

The entropy $S°(298.15\ K)$ is derived from heat capacity data, using $S°(10\ K) = 0.04\ cal\ K^{-1} \cdot mol^{-1}$.

Fusion Data

Egan and Wakefield[8] measured calorimetrically the heat of fusion $\Delta_{fus} H° = 3.1 \pm 0.2\ kcal \cdot mol^{-1}$, but failed to determine the exact melting point due to continuous fusion between 301 to 319 K in their measurements. They suggested the melting point 315.5 K which was found by Ross and Jones.[9]

Holmes[5] derived the enthalpy of fusion $\Delta_{fus} H°(298.15\ K) = 3.2 \pm 0.5\ kcal \cdot mol^{-1}$ from his enthalpy of solution data for crystalline and liquid H_3PO_4 in water and in aq. $HClO_4$ solution, which corresponds to $\Delta_{fus} H° = 3.36\ kcal \cdot mol^{-1}$. We adopt an intermediate value of $\Delta_{fus} H° = 3.2 \pm 0.2\ kcal \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−16.980	−1265.927	−1265.927	INFINITE
100	42.844	34.528	183.578	−14.905	−1275.048	−1226.961	640.899
200	75.856	74.598	119.270	−8.935	−1281.203	−1176.480	307.265
298.15	106.064	110.544	110.544	0.	−1284.375	−1124.314	196.975
300	106.608	111.202	110.546	0.197	−1284.411	−1123.321	195.588
315.500	111.303	116.688	110.713	1.885	--- CRYSTAL <--> LIQUID ---		
400	136.900	146.019	115.089	12.372	−1285.789	−1069.271	139.633
500	167.193	179.822	124.668	27.577	−1283.719	−1015.323	106.070
600	197.485	212.982	136.631	45.811	−1278.830	−962.056	83.754
700	227.777	245.700	149.880	67.074	−1271.116	−909.831	67.892
800	258.069	278.092	163.885	91.366	−1260.559	−858.906	56.081
900	288.361	310.238	178.363	118.688	−1247.143	−809.475	46.981
1000	318.653	342.187	193.149	149.038	−1230.854	−761.692	39.787

PREVIOUS: June 1962 CURRENT: December 1971

$S°(298.15\ K) = [150.775]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 315.5\ K$

$\Delta_f H°(298.15\ K) = [-1271.663]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 13.389 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ (H_3PO_4, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(315.5\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Heat capacities of the liquid are estimated by comparison with those of H_2SO_4(cr, l)[1] and H_3PO_4(cr) $S°(298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.[2]

Decomposition Data

The phosphoric acid tends to be dehydrated to pyro– and meta–phosphoric acids when it is heated.

References

[1]W. F. Giauque, E. W. Hornung, J. E. Kunzler and T. R. Rubin, J. Amer. Chem. Soc. **82**, 62 (1960).
[2]JANAF Thermochemical Tables: H_3PO_4(cr), 12–30–71.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	145.047	150.775	150.775	0.	−1271.663	−1123.597	196.849
300	145.603	151.673	150.777	0.269	−1271.627	−1122.678	195.476
315.500	150.273	159.125	151.005	2.562	--- CRYSTAL <--> LIQUID ---		
400	175.728	197.687	156.848	16.335	−1269.114	−1073.263	140.154
500	205.853	240.135	169.306	35.414	−1263.169	−1024.930	107.074
600	235.978	280.330	184.486	57.506	−1254.423	−978.057	85.147
700	266.102	318.968	200.954	82.610	−1242.867	−932.871	69.612
800	296.227	356.468	218.059	110.726	−1228.486	−889.534	58.081
900	326.352	393.097	235.480	141.855	−1211.263	−848.169	49.226
1000	356.477	429.041	253.044	175.997	−1191.183	−808.875	42.251

PREVIOUS: June 1962 CURRENT: December 1971

0 to 315.5 K crystal
above 315.5 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.980	−1265.927	−1265.927	INFINITE
100	42.844	34.528	183.578	−14.905	−1275.048	−1226.961	640.899
200	75.856	74.598	119.270	−8.935	−1281.203	−1176.480	307.265
298.15	106.064	110.544	110.544	0.	−1284.375	−1124.314	196.975
300	106.608	111.202	110.546	0.197	−1284.411	−1123.321	195.588
315.500	111.303	116.688	110.713	1.885	CRYSTAL <--> LIQUID TRANSITION		
315.500	150.273	159.125	110.713	15.274			
400	175.728	197.687	125.068	29.048	−1269.114	−1073.263	140.154
500	205.853	240.135	143.882	48.127	−1263.169	−1024.930	107.074
600	235.978	280.330	163.299	70.218	−1254.423	−978.057	85.147
700	266.102	318.968	182.794	95.322	−1242.867	−932.871	69.612
800	296.227	356.468	202.169	123.439	−1228.486	−889.534	58.081
900	326.352	393.097	221.356	154.568	−1211.263	−848.169	49.226
1000	356.477	429.041	240.332	188.709	−1191.183	−808.875	42.251

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = 210.243\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 7.2 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 5.4 \pm 1.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
2322.9(1)	2327.7(2)
992 (1)	1122.4(2)

Ground State Quantum Weight: 1 $\sigma = 3$
Point Group: C_{3v}
Bond Distance: P–H = 1.42 Å
Bond Angle: H–P–H = 93° 50'
Product of the Moments of Inertia: $I_A I_B I_C = 0.2826 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation was derived by Gunn and Green.[1] In order to obtain the $\Delta_f H°(298.15\ K)$ they measured the enthalpy of explosive decomposition of phosphine gas. There is a good deal of uncertainty about the enthalpy of formation of PH_3(g), for instance:

$\Delta_f H°(298.15\ K)$	Source
$+3.6\ kcal·mol^{-1}$	The enthalpy of reaction between gaseous PH_3 and saturated bromine water[2]
$+6.3\ kcal·mol^{-1}$	The enthalpy of combustion of PH_3(g) in O_2(g) to form H_3PO_4[3].
$-2.34\ kcal·mol^{-1}$	Equilibrium data of.[4] Their data showed a wide variation in $\Delta_f H°$, as much as 11 $kcal·mol^{-1}$.
$+1.6\ kcal·mol^{-1}$	U.S. Nat. Bur. Stand.[5]

The enthalpy of formation have been reviewed by Cottrell[6] and by Bichowsky and Rossini.[7]

The enthalpy of formation selected was, $+1.3 \pm 0.4\ kcal·mol^{-1}$, as reported by Gunn and Green.[1] The selected enthalpy of formation was based on white (α) phosphorus.

Heat Capacity and Entropy

The fundamental wave number and degeneracy assignments are from the infrared spectral data by McConaghie and Nielsen.[8] The molecular constants are those obtained from infrared data by Nielsen.[9] Nielsen[9] has reported the molecular constants after calculating the Coriolis coupling effect between the wave numbers 2 and 4, or (992 cm^{-1}) and (1122.4 cm^{-1}).

The principal moments of inertia are: $I_A = I_B = 0.6264 \times 10^{-39}\ g·cm^2$ and $I_C = 0.7201 \times 10^{-39}\ g·cm^2$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−10.136	7.166	7.166	INFINITE
100	33.259	173.027	241.134	−6.811	7.185	6.760	−3.531
200	33.933	196.180	213.516	−3.467	6.303	6.780	−1.771
298.15	37.102	210.243	210.243	.000	5.439	7.191	−1.260
300	37.180	210.473	210.244	.069	5.422	7.202	−1.254
350	39.422	216.370	210.704	1.983	4.266	7.605	−1.135
400	41.782	221.787	211.755	4.013	3.834	8.112	−1.059
450	44.151	226.845	213.154	6.161	3.515	8.668	−1.006
500	46.478	231.618	214.764	8.427	3.310	9.252	−.967
600	50.905	240.489	218.323	13.299	3.235	10.455	−.910
700	54.935	248.644	222.080	18.595	3.570	11.637	−.868
800	58.511	256.218	225.879	24.271	4.263	12.746	−.832
900	61.623	263.294	229.648	30.282	5.258	13.750	−.798
1000	64.300	269.929	233.348	36.581	6.498	14.629	−.764
1100	66.585	276.167	236.960	43.128	7.932	15.374	−.730
1200	68.532	282.047	240.474	49.887	−54.053	17.060	−.743
1300	70.191	287.599	243.888	56.825	−51.575	22.886	−.920
1400	71.608	292.854	247.199	63.917	−49.013	28.518	−1.064
1500	72.822	297.837	250.411	71.140	−46.390	33.965	−1.183
1600	73.867	302.571	253.524	78.476	−43.723	39.235	−1.281
1700	74.770	307.077	256.543	85.909	−41.025	44.337	−1.362
1800	75.554	311.374	259.470	93.426	−38.306	49.280	−1.430
1900	76.238	315.477	262.311	101.016	−35.576	54.071	−1.487
2000	76.837	319.404	265.068	108.671	−32.839	58.719	−1.534
2100	77.365	323.165	267.746	116.381	−30.101	63.230	−1.573
2200	77.831	326.775	270.347	124.142	−27.366	67.610	−1.605
2300	78.244	330.244	272.877	131.946	−24.637	71.866	−1.632
2400	78.612	333.582	275.337	139.789	−21.916	76.003	−1.654
2500	78.942	336.798	277.732	147.667	−19.206	80.028	−1.672
2600	79.237	339.900	280.063	155.576	−16.507	83.943	−1.686
2700	79.504	342.896	282.335	163.514	−13.822	87.756	−1.698
2800	79.744	345.792	284.550	171.476	−11.150	91.469	−1.706
2900	79.962	348.594	286.711	179.462	−8.494	95.087	−1.713
3000	80.160	351.308	288.819	187.468	−5.854	98.614	−1.717
3100	80.340	353.939	290.877	195.493	−3.230	102.053	−1.720
3200	80.505	356.493	292.888	203.535	−.624	105.407	−1.721
3300	80.655	358.972	294.853	211.593	1.965	108.681	−1.720
3400	80.794	361.382	296.775	219.666	4.535	111.876	−1.719
3500	80.921	363.726	298.654	227.752	7.087	114.996	−1.716
3600	81.039	366.007	300.494	235.850	9.619	118.043	−1.713
3700	81.147	368.229	302.294	243.959	12.132	121.020	−1.709
3800	81.247	370.395	304.058	252.079	14.624	123.930	−1.704
3900	81.340	372.506	305.786	260.208	17.097	126.774	−1.698
4000	81.427	374.567	307.480	268.347	19.548	129.555	−1.692
4100	81.507	376.578	309.141	276.494	21.979	132.275	−1.685
4200	81.582	378.544	310.770	284.648	24.389	134.936	−1.678
4300	81.652	380.464	312.369	292.810	26.777	137.540	−1.671
4400	81.718	382.342	313.938	300.978	29.144	140.088	−1.663
4500	81.779	384.179	315.478	309.153	31.490	142.583	−1.655
4600	81.836	385.977	316.991	317.334	33.814	145.026	−1.647
4700	81.890	387.738	318.478	325.520	36.118	147.419	−1.638
4800	81.941	389.462	319.939	333.712	38.400	149.763	−1.630
4900	81.988	391.152	321.375	341.908	40.663	152.060	−1.621
5000	82.033	392.809	322.787	350.110	42.905	154.311	−1.612
5100	82.076	394.434	324.176	358.315	45.128	156.516	−1.603
5200	82.116	396.028	325.543	366.525	47.333	158.679	−1.594
5300	82.153	397.593	326.887	374.738	49.519	160.799	−1.585
5400	82.189	399.129	328.211	382.955	51.689	162.879	−1.576
5500	82.223	400.637	329.514	391.176	53.842	164.917	−1.566
5600	82.255	402.119	330.798	399.400	55.980	166.918	−1.557
5700	82.286	403.575	332.062	407.627	58.104	168.880	−1.548
5800	82.315	405.006	333.307	415.857	60.215	170.806	−1.538
5900	82.342	406.414	334.534	424.090	62.314	172.694	−1.529
6000	82.368	407.798	335.744	432.325	64.403	174.547	−1.520

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 112.968 \pm 6.3\ kJ \cdot mol^{-1}$
$T_{trs} = 260\ K$
$T_{fus} = 824\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -202.087\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 2.929\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [20.920]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The $\Delta_f H$, T_{trs} and T_{fus} was taken from U. S. Nat. Bur. Stand.[1] Sublimation data from Luft;[3] $\Delta_{sub} H°(798\ K) = 40.28\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Data extrapolated from Simon *et al.*[4] $S°(298.15\ K)$ was taken from Kelley.[2]

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[1]U. S. Nat. Bur. Stand. Circ. 500, (1952).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	81.755	112.968	112.968	0.	−202.087	−111.966	19.616
300	81.881	113.474	112.970	0.151	−202.120	−111.407	19.398
400	88.998	138.004	116.266	8.695	−211.666	−80.646	10.531
500	96.148	158.632	122.727	17.953	−233.822	−45.736	4.778
600	103.261	176.789	130.252	27.922	−233.079	−8.177	0.712
700	110.458	193.247	138.093	38.608	−231.674	29.204	−2.179
800	117.696	208.468	145.949	50.015	−229.616	66.340	−4.332
900	124.976	222.753	153.697	62.150	−226.914	103.179	−5.988
1000	132.089	236.288	161.285	75.003	−223.590	139.683	−7.296
1100	139.327	249.217	168.695	88.574	−219.652	175.825	−8.349
1200	146.440	261.656	175.927	102.875	−215.099	211.581	−9.210
1300	152.030	273.609	182.984	117.812	−210.029	246.935	−9.922
1400	156.098	285.034	189.869	133.231	−204.598	281.884	−10.517
1500	158.643	295.899	196.579	148.980	−198.962	316.437	−11.019
1600	159.666	306.178	203.110	164.909	−193.275	350.611	−11.446
1700	159.166	315.851	209.461	180.863	−187.688	384.432	−11.812
1800	157.144	324.898	215.626	196.691	−182.352	417.931	−12.128
1900	153.599	333.307	221.601	212.241	−177.418	451.143	−12.403
2000	148.532	341.063	227.383	227.360	−173.034	484.109	−12.644

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = 121.544 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 274.69\ K$

$\Delta_f H°(298.15\ K) = 50.626 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 12.657\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Hughes *et al.*[1] measured the enthalpies of combustion of hydrazine and hydrazine monohydrate. The data, adjusted as suggested by Cole and Gilbert[2] are summarized below. Enthalpies of solution determined by Bushnell *et al.* interrelate N_2H_4(l). An intermediate value was selected from the resulting enthalpies of formation.

Source	Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Hughes[1]	$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$	−148.68 ± 0.06	12.05
Hughes[1]	$N_2H_4 \cdot H_2O(l) + O_2(g) \rightarrow N_2(g) + 3H_2O(l)$	−147.00 ± 0.06	–
Bushnell[3]	$N_2H_4(l) + H_2O(l) \rightarrow N_2H_4 \cdot H_2O(l)$	−1.80	12.17*

*From combination of second and third reactions.

Heat Capacity and Entropy

Heat capacities (12–340 K) of hydrazine crystal and liquid were determined by Scott *et al.*[4] Values beyond the experimental range for the liquid were extrapolated linearly. The entropy was obtained from the enthalpy of melting and the smoothed heat capacities of the crystal using $S°(12) = 0.023\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

Taken from Scott *et al.*[4]

Vaporization Data

The normal boiling point and enthalpy of vaporization are those calculated for the ideal gas from these tables. The boiling point found for the real gas (387.3 K) by Hieber and Woerner is in good agreement. The selected enthalpy of vaporization, $\Delta H°(298.15\ K) = 10.69$ kcal·mol^{-1}, is based on the vapor pressure data of Scott *et al.*,[4] series III. Vapor pressure measurements of Hieber and Woerner[5] are in satisfactory agreement as shown below.

Source	T/K	$\Delta_{vap} H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
Scott, *et al.*[4]	273–343	10.683 ± 0.003	10.696	0.05 ± 0.01
Chang, Gockcen[6]	276–325	10.40 ± 0.03	10.68	0.91 ± 0.09
Hieber, Woerner[5]	293–387	10.82 ± 0.03	10.71	−0.33 ± 0.07

The 2nd law 3rd law consistency of Scott *et al.* reflects the use of these data in selection of the gas phase functions (refer to H_4N_2 gas).

References

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[4] D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Amer. Chem. Soc. **71**, 2293 (1949).
[5] W. Hieber and A. Woerner, Z. Elektrochem. **40**, 252 (1934).
[6] E. T. Chang and N. A. Gokcen, AD 458288, Defense Documentation Center, (January 1964).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100	87.236	21.037	205.395	−18.436	48.895	82.918	−43.312
200	93.094	83.302	130.399	−9.419	49.613	116.715	−30.483
298.15	98.840	121.544	121.544	0.	50.626	149.440	−26.181
300	98.952	122.156	121.546	0.183	50.649	150.054	−26.127
400	107.361	151.693	125.516	10.471	52.208	182.975	−23.894
500	116.566	176.639	133.305	21.667	54.619	215.406	−22.503
600	125.771	198.705	142.398	33.784	57.895	247.270	−21.527
700	134.976	218.784	151.896	46.822	62.013	278.518	−20.783
800	144.181	237.409	161.435	60.779	66.957	309.120	−20.183

PREVIOUS: CURRENT: December 1965

$S°(298.15\ K) = 238.719 \pm 1.7\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 109.43\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 95.35 \pm 0.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
3350(1)	875(1)	3280(1)
3261(1)	780(1)	1275(1)
1312(1)	377(1)	[933](1)
1098(1)	3330(1)	966(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_2
Bond Distances: N–H = 1.022 Å N–N = 1.449 Å
Bond Angles: H–N–H = 109.47° H–N–N = 112.0°
Torsional angle between two NH_2 groups ≥ 90° from eclipsed position.
Product of the Moments of Inertia: $I_A I_B I_C = 7.3095 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

This was obtained from the enthalpy of formation of the liquid and the selected enthalpy of vaporization, $\Delta_f H°(298.15\ K) = 10.69\ kcal·mol^{-1}$, derived from the vapor pressure data (Series III) of Scott *et al.*[1] Other vapor pressure data from Hieber and Woerner[2] and Chang and Gokcen[3] are in satisfactory agreement (refer to the N_2H_4 liquid table).

Heat Capacity and Entropy

Functions were calculated from the constants given above using the rigid rotator harmonic oscillator method. The entropy ws increased by R ln 2 because two rotameric forms are implied by use of the torsional frequency. Small but arbitrary adjustments were made in the assignment of the bending mode frequencies in order to reproduce the vapor pressure data of Scott *et al.*[1] as closely as possible. Calculated values of $S°(298.15\ K) = 57.03$ and $S°(340\ K) = 58.70\ cal·K^{-1}·mol^{-1}$ may be compared with 56.99 and 58.69, respectively, derived from the data of Scott *et al*. Internal rotation calculations would require a complex potential function in order to fit the data. The barrier to inversion ($990\ cm^{-1}$ ~2.8 $kcal·mol^{-1}$) is slightly less than the barrier to internal rotation at the trans position ($1110\ cm^{-1}$ ~3.2 $kcal·mol^{-1}$) according to analyses of the microwave data by Kasuya[4] and Kasuya and Kojima.[5]

From matrix isolation and gas phase infrared studies, Catalano *et al.*[6] have suggested possible uncertainties in the assignment of the bending mode frequencies in the region from 1630 to 740 cm^{-1}. The question hinges on the uncertain existence of a gas phase fundamental at about 1600 cm^{-1} as observed by Giguere and Liu.[7] No corresponding matrix band was found and the gas phase band appeared to be due to absorption on the cell windows. A vapor phase Raman frequency at 1564 cm^{-1} was observed, however, by Kotov and Tatevskii.[8] Catalano *et al.* suggest one assignment based on the uncertain fundamental and a tentative alternative assignment excluding it. The two assignments give entropies that are 0.26 $cal·K^{-1}·mol^{-1}$ lower and 0.12 higher than the 3rd law value. The lower calculated entropy is probably more reasonable, but the higher value could be more easily modified to agree with the 3rd law value. Thus the alternative assignment was adopted with ν_{11} arbitrarily increased from ~810 to 933 cm^{-1}.

The structural constants are based primarily on the electron diffraction study of Morino *et al.*[9] Related analyses of the infrared fine structure of the torsional frequency (377 cm^{-1}), Yamaguchi *et al.*[10] and of the microwave spectra, Kasuya and Kojima[5] are in close agreement. The microwave data give an H–N–H angle of 106° and a torsional angle of 90°2'. Principal moments of inertia of the adopted structure are: $I_A = 0.5741 \times 10^{-39}$, $I_B = 3.5633 \times 10^{-39}$, and $I_C = 3.5734 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.528	109.430	109.430	INFINITE
100	34.368	195.185	277.002	−8.182	103.876	120.484	−62.934
200	40.658	220.673	243.020	−4.469	99.290	138.917	−36.281
250	45.534	230.252	239.526	−2.318	97.193	149.070	−31.146
298.15	50.813	238.719	238.719	0.	95.353	159.232	−27.897
300	51.019	239.034	238.720	0.094	95.287	159.628	−27.794
350	56.531	247.315	239.362	2.784	93.621	170.487	−25.444
400	61.702	255.207	240.853	5.742	92.205	181.567	−23.710
450	66.379	262.749	242.870	8.946	91.023	192.811	−22.381
500	70.544	269.963	245.221	12.371	90.050	204.175	−21.330
600	77.562	283.469	250.487	19.789	88.626	227.144	−19.775
700	83.302	295.869	256.096	27.841	87.760	250.305	−18.678
800	88.202	307.320	261.793	36.422	87.326	273.560	−17.862
900	92.511	317.962	267.449	45.462	87.240	296.848	−17.229
1000	96.356	327.912	273.004	54.908	87.439	320.130	−16.722
1100	99.803	337.260	278.424	64.720	87.875	343.379	−16.306
1200	102.891	346.079	283.698	74.857	88.507	366.581	−15.957
1300	105.653	354.426	288.821	85.287	89.302	389.722	−15.659
1400	108.119	362.348	293.792	95.978	90.231	412.797	−15.402
1500	110.318	369.884	298.616	106.902	91.270	435.802	−15.176
1600	112.279	377.067	303.296	118.034	92.401	458.734	−14.976
1700	114.026	383.928	307.839	129.350	93.606	481.594	−14.798
1800	115.586	390.490	312.250	140.833	94.871	504.380	−14.637
1900	116.980	396.778	316.534	152.462	96.185	527.095	−14.491
2000	118.227	402.810	320.698	164.224	97.538	549.740	−14.358
2100	119.346	408.606	324.747	176.103	98.922	572.316	−14.236
2200	120.352	414.182	328.687	188.089	100.330	594.826	−14.123
2300	121.257	419.552	332.521	200.170	101.756	617.271	−14.019
2400	122.075	424.730	336.256	212.338	103.195	639.654	−13.922
2500	122.815	429.729	339.896	224.583	104.644	661.977	−13.831
2600	123.486	434.559	343.444	236.898	106.097	684.241	−13.747
2700	124.096	439.231	346.906	249.278	107.553	706.450	−13.667
2800	124.652	443.754	350.284	261.716	109.007	728.604	−13.592
2900	125.159	448.137	353.583	274.207	110.459	750.707	−13.522
3000	125.624	452.388	356.806	286.746	111.904	772.760	−13.455
3100	126.050	456.515	359.956	299.330	113.342	794.765	−13.392
3200	126.441	460.523	363.037	311.955	114.770	816.723	−13.332
3300	126.802	464.419	366.050	324.617	116.187	838.638	−13.275
3400	127.134	468.210	368.999	337.314	117.591	860.509	−13.220
3500	127.441	471.899	371.887	350.043	118.980	882.339	−13.168
3600	127.726	475.493	374.715	362.802	120.354	904.130	−13.119
3700	127.989	478.997	377.487	375.588	121.711	925.883	−13.071
3800	128.234	482.413	380.203	388.399	123.050	947.599	−13.026
3900	128.462	485.747	382.867	401.234	124.370	969.281	−12.982
4000	128.675	489.002	385.480	414.091	125.669	990.928	−12.940
4100	128.873	492.182	388.043	426.968	126.948	1012.544	−12.900
4200	129.058	495.290	390.560	439.865	128.205	1034.129	−12.861
4300	129.232	498.329	393.031	452.780	129.440	1055.684	−12.824
4400	129.394	501.302	395.458	465.711	130.652	1077.210	−12.788
4500	129.546	504.211	397.843	478.658	131.841	1098.709	−12.753
4600	129.690	507.060	400.186	491.620	133.007	1120.182	−12.720
4700	129.824	509.851	402.490	504.596	134.149	1141.630	−12.688
4800	129.951	512.585	404.755	517.585	135.268	1163.055	−12.657
4900	130.071	515.266	406.983	530.586	136.364	1184.455	−12.626
5000	130.183	517.895	409.175	543.599	137.436	1205.835	−12.597
5100	130.290	520.474	411.332	556.622	138.487	1227.191	−12.569
5200	130.391	523.005	413.456	569.656	139.515	1248.529	−12.542
5300	130.486	525.489	415.546	582.700	140.522	1269.846	−12.515
5400	130.576	527.929	417.605	595.753	141.509	1291.145	−12.489
5500	130.662	530.326	419.632	608.815	142.477	1312.425	−12.464
5600	130.743	532.681	421.630	621.886	143.426	1333.689	−12.440
5700	130.820	534.996	423.599	634.964	144.359	1354.935	−12.417
5800	130.894	537.272	425.539	648.050	145.275	1376.166	−12.394
5900	130.964	539.510	427.452	661.142	146.177	1397.379	−12.371
6000	131.030	541.712	429.338	674.242	147.065	1418.579	−12.350

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = 211.510 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 281.63 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -1126.433 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1127.621 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.464 \pm 0.042\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the monohydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ using $\Delta_r H°(298.15\ K) = -6.645\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + H_2O(l) = H_2SO_4 \cdot H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been re–analyzed and summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature–dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 290–390 K so as to provide smoothly varying heat capacity values. In the region above 390 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy of 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.190\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Rubin and Giauque.[4] The values used by Giauque *et al.*[1] in their re–evaluation and correlation of aqueous sulfuric acid properties were slightly different from those reported by Rubin and Giauque[4] the changes were 0.01 K in the melting point and 6 cal $K^{-1} \cdot mol^{-1}$ in the enthalpy of melting. In addition, the value for T_{fus} is corrected from IPTS–48 to IPTS–68.

References

[1]W. F. Giauque, E. W. Hornung, J. E. Kinzler, and T. R. Rubin, J. Amer. Chem. Soc. **82**, 62 (1960).
[2]JANAF Thermochemical Tables: H_2SO_4(l), 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972).
[4]T. R. Rubin and W. F. Giauque, J. Amer. Chem. Soc. **74**, 800 (1952).
[5]Om. P. Kharbanda, Ind. Chemist **31**, 538 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−41.866	−1126.433	−1126.433	INFINITE
100	54.220	43.699	436.019	−39.232	−1137.748	−1077.394	562.773
200	92.914	93.433	252.619	−31.837	−1144.661	−1014.113	264.859
281.626	123.973	130.247	211.864	−22.985	CRYSTAL <--> LIQUID		
281.626	211.961	199.360	211.864	−3.521	TRANSITION		
298.15	214.264	211.510	211.510	0.	−1127.621	−950.290	166.487
300	214.523	212.836	211.514	0.397	−1127.510	−949.190	165.269
400	228.538	276.470	220.096	22.550	−1123.193	−890.620	116.303
500	243.601	329.085	236.772	46.157	−1117.007	−833.180	87.042
600	258.663	374.830	256.047	71.270	−1109.236	−777.118	67.654
700	273.726	415.834	275.992	97.889	−1099.975	−722.477	53.912
800	288.788	453.369	295.850	126.015	−1089.308	−669.261	43.698
900	303.850	488.253	315.312	155.647	−1130.396	−616.382	35.774
1000	318.913	521.046	334.261	186.785	−1115.776	−560.042	29.254

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 204.653\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 43.92 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 34.31 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
2185.7 (1)
972.1 (2)
2189.08(3)
913.28 (3)

Ground State Quantum Weight: [1] σ = 12
Point Group: T_d
Bond Distance: Si–H = 1.4806 ± 0.001 Å
Bond Angle: H–Si–H = 109.47122°
Product of the Moments of Inertia: $I_A I_B I_C = 0.9367 \times 10^{-117}\ g^3·cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(SiH_4, g, 298.15\ K) = 8.2 \pm 0.5\ kcal·mol^{-1}$ is derived from the enthalpy of decomposition measurements by Gunn and Green.[1] We have taken the average of the three measurements, $\Delta E = -7.83\ kcal·mol^{-1}$, to obtain $\Delta H = -7.24\ kcal·mol^{-1}$ for the decomposition. Some question exists about the final state of the silicon; we choose to consider it as amorphous and apply a correction of 1 $kcal·mol^{-1}$ to convert to the crystalline state[2] (the authors chose to neglect this correction). The results of Gunn and Green[1] are in good agreement with the value of $\Delta_f H°(SiH_4, g, 298.15\ K) = 7.8 \pm 3.5\ kcal·mol^{-1}$ determined by Brimm and Humphreys[3] from high temperature (680°C) enthalpy of decomposition measurements. We question the earlier negative values for the enthalpy of formation of $SiH_4(g)$[4-6] which range from − 8.7 to $-14.8\ kcal·mol^{-1}$ and the later result of Feher, *et al.*[7], $-11.3\ kcal·mol^{-1}$, because of suspected uncertainty in the final states and/or corrections for the final states.

Heat Capacity and Entropy

The four fundamental vibrational frequencies and the Si–H bond distance are the result of gas–phase infrared and Raman spectral studies by Kattenberg and Oskam.[8] They are in excellent agreement with values selected from earlier work as given in the compilations of Janz and Mikawa[9] and Shimanouchi.[10] The heat capacity and entropy calculations are based on a tetrahedral structure. The $S°(298.15\ K) = 48.89 \pm 0.01\ cal·K^{-1}·mol^{-1}$ is in good agreement with another evaluation.[2]

The principal moments of inertia are $I_A = I_B = I_C = 0.9784 \times 10^{-39}\ g·cm^2$.

References

[1] S. R. Gunn and L. H. Green, J. Phys. Chem. **65**, 779 (1961).
[2] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3] E. O. Brimm and H. M. Humphreys, J. Phys. Chem. **61**, 829 (1957).
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[5] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold, New York, (1936).
[6] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[7] F. Feher, G. Jansen, and H. Rohmer, Z. anorg. allg. Chem. **329**, 31 (1964).
[8] H. W. Kattenberg and A. Oskam, J. Mol. Spectrosc. **49**, 52 (1974).
[9] G. J. Janz and Y. Mikawa, Bull. Chem. Soc. Japan **34**, 1495 (1961).
[10] T. Shimanouchi, NSRDS–NBS 39, (1972).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−10.538	43.923	43.923	INFINITE
100	33.269	165.774	237.899	−7.212	40.984	44.936	−23.472
200	35.520	189.213	208.310	−3.819	37.811	50.067	−13.076
250	38.857	197.475	205.335	−1.965	36.023	53.336	−11.144
298.15	42.827	204.653	204.653	0.	34.309	56.827	−9.956
300	42.985	204.918	204.654	0.079	34.244	56.967	−9.919
350	47.291	211.868	205.193	2.336	32.568	60.888	−9.087
400	51.473	218.458	206.442	4.806	31.038	65.040	−8.493
450	55.431	224.752	208.130	7.480	29.667	69.374	−8.053
500	59.148	230.786	210.096	10.345	28.454	73.853	−7.715
600	65.877	242.179	214.505	16.604	26.478	83.128	−7.237
700	71.715	252.784	219.225	23.491	25.042	92.690	−6.917
800	76.713	262.695	224.046	30.919	24.056	102.426	−6.688
900	80.948	271.982	228.862	38.808	23.433	112.263	−6.516
1000	84.513	280.701	233.614	47.086	23.093	122.153	−6.381
1100	87.507	288.900	238.271	55.692	22.965	132.067	−6.271
1200	90.024	296.625	242.815	64.572	22.989	141.986	−6.180
1300	92.146	303.917	247.238	73.683	23.119	151.897	−6.103
1400	93.942	310.814	251.535	82.990	23.315	161.796	−6.037
1500	95.470	317.348	255.706	92.463	23.548	171.680	−5.978
1600	96.777	323.553	259.755	102.077	23.793	181.547	−5.927
1700	97.901	329.454	263.682	111.812	−26.143	191.846	−5.895
1800	98.872	335.078	267.494	121.652	−25.691	204.656	−5.939
1900	99.716	340.447	271.193	131.582	−25.226	217.440	−5.978
2000	100.454	345.581	274.785	141.592	−24.756	230.200	−6.012
2100	101.101	350.498	278.274	151.670	−24.288	242.937	−6.043
2200	101.671	355.215	281.665	161.809	−23.826	255.651	−6.070
2300	102.176	359.746	284.962	172.002	−23.375	268.344	−6.094
2400	102.625	364.104	288.170	182.243	−22.936	281.018	−6.116
2500	103.026	368.302	291.291	192.526	−22.513	293.674	−6.136
2600	103.385	372.350	294.332	202.847	−22.108	306.313	−6.154
2700	103.708	376.258	297.294	213.202	−21.720	318.937	−6.170
2800	104.000	380.035	300.182	223.587	−21.353	331.548	−6.185
2900	104.264	383.689	302.999	234.001	−21.007	344.145	−6.199
3000	104.503	387.228	305.748	244.439	−20.683	356.731	−6.211
3100	104.721	390.658	308.432	254.900	−20.381	369.306	−6.223
3200	104.920	393.986	311.054	265.383	−20.102	381.872	−6.233
3300	105.102	397.217	313.616	275.884	−19.847	394.430	−6.243
3400	105.269	400.357	316.121	286.402	−19.617	406.980	−6.252
3500	105.422	403.411	318.572	296.937	−19.412	419.524	−6.261
3600	105.564	406.383	320.970	307.486	−403.383	442.523	−6.421
3700	105.694	409.277	323.318	318.049	−402.815	466.013	−6.579
3800	105.815	412.097	325.617	328.625	−402.275	489.488	−6.728
3900	105.927	414.847	327.870	339.212	−401.764	512.949	−6.870
4000	106.031	417.530	330.078	349.810	−401.280	536.396	−7.005
4100	106.127	420.150	332.243	360.418	−400.824	559.833	−7.132
4200	106.217	422.708	334.367	371.035	−400.397	583.258	−7.254
4300	106.302	425.209	336.450	381.661	−399.997	606.674	−7.370
4400	106.380	427.653	338.495	392.295	−399.625	630.080	−7.480
4500	106.454	430.045	340.503	402.937	−399.280	653.478	−7.585
4600	106.522	432.385	342.475	413.586	−398.963	676.869	−7.686
4700	106.587	434.677	344.413	424.242	−398.672	700.254	−7.782
4800	106.648	436.922	346.317	434.903	−398.408	723.633	−7.875
4900	106.705	439.121	348.188	445.571	−398.170	747.006	−7.963
5000	106.759	441.277	350.029	456.244	−397.957	770.375	−8.048
5100	106.810	443.392	351.839	466.923	−397.768	793.739	−8.130
5200	106.858	445.467	353.619	477.606	−397.603	817.101	−8.208
5300	106.903	447.502	355.372	488.294	−397.460	840.459	−8.283
5400	106.946	449.501	357.096	498.986	−397.339	863.815	−8.356
5500	106.986	451.464	358.794	509.683	−397.239	887.168	−8.426
5600	107.025	453.392	360.466	520.384	−397.158	910.521	−8.493
5700	107.061	455.287	362.113	531.088	−397.095	933.872	−8.558
5800	107.096	457.149	363.736	541.796	−397.050	957.222	−8.621
5900	107.129	458.980	365.335	552.507	−397.019	980.570	−8.681
6000	107.160	460.781	366.910	563.222	−397.003	1003.919	−8.740

PREVIOUS: June 1976 (1 atm) CURRENT: June 1976 (1 bar)

$S°(298.15\ K) = 276.363 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 233.70 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -1422.274 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1427.100 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 18.242 \pm 0.17\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the dihydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ for the dihydrate using $\Delta_f H°(298.15\ K) = -9.907\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 2\ H_2O(l) = H_2SO_4 \cdot 2H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature–dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 290–310 K so as to provide smoothly varying heat capacity values. In the region above 310 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.363\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Rubin and Giauque.[4] The melting point adopted in this table differs from that reported by Rubin and Giauque[4] by 0.02 K. This is due to the re analysis of the data by Giauque *et al.*[1] and a conversion of the resulting T_{fus} value from IPTS–48 to IPTS–68.

References

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[2]JANAF Thermochemical Tables: H_2SO_4(l), 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972).
[4]T. R. Rubin and W. F. Giauque, J. Amer. Chem. Soc. **74**, 800 (1952).
[5]Om. P. Kharbanda, Ind. Chemist **31**, 538 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−51.038	−1422.274	−1422.274	INFINITE
100	66.143	56.938	534.191	−47.725	−1437.362	−1359.594	710.179
200	113.413	117.668	311.144	−38.695	−1446.789	−1277.857	333.742
233.700	128 .910	136.505	284.609	−34.612	CRYSTAL <--> LIQUID		
233.700	248 .446	214.564	284.609	−16.370	TRANSITION		
298.15	261.453	276.363	276.363	0.	−1427.100	−1199.560	210.158
300	262.055	277.982	276.368	0.484	−1426.981	−1198.148	208.616
400	294.604	357.829	287.036	28.317	−1421.376	−1122.886	146.634
500	327.155	427.065	308.254	59.405	−1412.161	−1049.281	109.618
600	359.707	489.589	333.342	93.748	−1399.668	−977.824	85.127
700	392.258	547.483	359.845	131.347	−1383.994	−908.713	67.809
800	424.810	601.987	386.737	172.200	−1365.221	−842.061	54.981
900	457.361	653.901	413.559	216.309	−1396.509	−776.864	45.088
1000	489.913	703.774	440.102	263.672	−1370.399	−709.387	37.055

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 345.373 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 236.78 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -1716.249 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1720.402 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 23.999 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the trihydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ for the trihydrate using $\Delta_r H°(298.15\ K) = -11.693\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 3\ H_2O(l) = H_2SO_4 \cdot 3H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4,5] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[6] based on experimental data (273–573 K). These temperature–dependent values are corrected to current atomic weights and converted from IPTS 48 to IPTS 68. Of the five hydrates of sulfuric acid (mono–, di–, tri–, tetra–, and hemihexa–) only in the case of the trihydrate is there a serious discrepancy in the heat capacity values (at ambient temperature) between Giauque *et al.*[6] and Kharbanda.[7] Assuming that the data of Giauque *et al.*[1] are correct and that the linear dependence suggested by the nomograph of Kharbanda[6] is correct, we have shifted the data derived from the nomograph by 0.78 $cal \cdot K^{-1} \cdot mol^{-1}$ to obtain a smooth junction of the low temperature and high temperature heat capacity data. The data are extrapolated linearly to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.398\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Hornung and Giauque.[5] The melting point adopted in this table differs from that reported by Hornung and Giauque[5] by 0.02 K. This is due to the re analysis of the data by Giauque *et al.*[1] and a conversion of the resulting T_{fus} value from IPTS–48 to IPTS–68.

References

[1]W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, J. Amer. Chem. Soc. **82**, 62 (1960).
[2]JANAF Thermochemical Tables: H_2SO_4(l), 9–30–77.
[3]ICSU CODATA Task Group, J. Chem. Thermodyn. **4**, 331 (1972).
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[5]E. W. Hornung and W. F. Giauque, J. Amer. Chem. Soc. **77**, 2983 (1955).
[6]Om. P. Kharbanda, Ind. Chemist **31**, 538 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−64.520	−1716.249	−1716.249	INFINITE
100	82.711	68.614	673.238	−60.462	−1735.045	−1639.705	856.494
200	145.372	145.125	390.475	−49.070	−1746.258	−1539.587	402.099
236.780	169 .746	171.661	354.430	−43.276	___ CRYSTAL <--> LIQUID ___		
236.780	310 .829	273.019	354.430	−19.276	TRANSITION		
298.15	319.090	345.373	345.373	0.	−1720.402	−1443.893	252.964
300	319.320	347.348	345.379	0.591	−1720.258	−1442.178	251.106
400	347.779	442.970	358.216	33.902	−1713.566	−1350.672	176.380
500	376.606	523.671	383.430	70.121	−1703.672	−1261.054	131.741
600	405.434	594.883	412.845	109.223	−1690.930	−1173.680	102.178
700	434.262	659.546	443.535	151.208	−1675.434	−1088.659	81.237
800	463.089	719.415	474.321	196.075	−1657.267	−1006.044	65.688
900	491.917	775.624	504.706	243.825	−1689.591	−924.781	53.673
1000	520.745	828.944	534.486	294.459	−1664.947	−841.100	43.935

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 414.529 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 244.90 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -2007.121 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2011.199 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 30.644 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the tetrahydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ for the tetrahydrate using $\Delta_r H°(298.15\ K) = -12.880\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 4H_2O(l) = H_2SO_4 \cdot 4H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature-dependent values are corrected to current atomic weights, converted from IPTS–48 to IPTS–68, and adjusted graphically in the region 300–330 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.687\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Hornung and Giauque.[4] The values adopted in this table for T_{fus} and $\Delta_{fus}H°$ differ from those reported by Hornung and Giauque[4] by 0.02 K and 2 $cal \cdot mol^{-1}$, respectively. This is due to the re-analysis of this data by Giauque *et al.*[1] and a conversion of the resulting T_{fus} value from IPTS–48 to IPTS–68.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−77.404	−2007.121	−2007.121	INFINITE
100	98.358	88.906	811.941	−72.303	−2029.325	−1917.277	1001.483
200	166.040	177.734	473.245	−59.102	−2042.879	−1799.498	469.981
244.900	197.695	214.443	422.447	−50.940	___ CRYSTAL <--> LIQUID ___		
244.900	376.392	339.570	422.447	−20.297	TRANSITION		
298.15	386.382	414.529	414.529	0.	−2011.199	−1685.764	295.339
300	386.771	416.920	414.536	0.715	−2011.010	−1683.745	293.166
400	410.342	531.343	429.977	40.546	−2002.190	−1576.184	205.829
500	434.525	625.506	459.927	82.789	−1990.724	−1470.981	153.672
600	458.709	706.867	494.448	127.451	−1976.931	−1368.290	119.120
700	482.892	779.393	530.063	174.531	−1960.905	−1268.086	94.626
800	507.076	845.453	565.416	224.030	−1942.729	−1170.328	76.415
900	531.259	906.574	599.967	275.946	−1975.563	−1073.893	62.327
1000	555.443	963.799	633.518	330.281	−1951.951	−974.955	50.926

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 587.819 \pm 0.63\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 220.30 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -2727.58 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2733.26 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 34.116 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the hemihexahydrate of sulfuric acid is derived from the enthalpy of solution data of Giauque *et al.*[1] We calculate $\Delta_f H°(298.15\ K)$ for the hemihexahydrate using $\Delta_r H°(298.15\ K) = -14.669\ kcal \cdot mol^{-1}$ for the solution process $H_2SO_4(l) + 6.5H_2O(l) = H_2SO_4 \cdot 6.5H_2O(l)$ and auxiliary data for H_2SO_4[2] and H_2O.[3]

Heat Capacity and Entropy

The heat capacity has been measured experimentally[4] in the range 15–300 K and has been summarized by Giauque *et al.*[1] Above 300 K, the heat capacity values are derived from a nomograph constructed by Kharbanda[5] based on experimental data (273–573 K). These temperature dependent values are corrected to current atomic weights, converted from IPTS 48 to IPTS 68, and adjusted graphically in the region 300–320 K so as to provide smoothly varying heat capacity values. In the region above 350 K, a linear dependence is assumed (as suggested from a least squares fit of the nomograph data); this linear dependence is used to obtain heat capacity data by extrapolation to 1000 K.

The entropy at 298.15 K is calculated by the appropriate integration of the crystal and liquid heat capacity values, addition of the entropy of melting, and $S°(15\ K) = 0.721\ cal \cdot K^{-1}\ mol^{-1}$.

Fusion Data

The melting point and enthalpy of melting have been measured calorimetrically by Hornung *et al.* These data were reevaluated by Giauque *et al.*[1] We have adopted the revised values and have also corrected T_{fus} to the IPTS–68.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−107.821	−2727.578	−2727.578	INFINITE
100	136.554	115.659	1125.761	−101.010	−2759.200	−2602.982	1359.658
200	239.876	242.053	652.984	−82.186	−2777.504	−2438.910	636.978
220.300	261.042	266.230	616.234	−77.106	___ CRYSTAL <--> LIQUID ___		
220.300	521.282	421.093	616.234	−42.990	TRANSITION		
298.15	570.279	587.819	587.819	0.	−2733.261	−2285.631	400.433
300	570.615	591.348	587.830	1.055	−2732.933	−2282.855	397.480
400	583.250	757.240	610.364	58.750	−2717.228	−2135.430	278.859
500	595.843	888.741	653.331	117.705	−2700.180	−1991.951	208.098
600	608.437	998.489	701.957	177.919	−2682.107	−1851.986	161.230
700	621.031	1093.226	751.237	239.393	−2663.102	−1715.123	127.984
800	633.625	1176.975	799.319	302.125	−2643.243	−1581.044	103.232
900	646.219	1252.333	845.536	366.118	−2675.696	−1448.421	84.064
1000	658.813	1321.071	889.701	431.369	−2653.004	−1313.267	68.598

PREVIOUS: CURRENT: September 1977

Continued from page 1269

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0 to 6000 K Ideal Monatomic Gas

IP(He, g) = 198310.76 ± 0.02 cm^{-1}
$S°(298.15\ K) = 126.152 \pm 0.002\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore[1] and Martin.[9] All predicted levels have been observed through n=4 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[2] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 159000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.[2]

The thermodynamic functions at 298.15 K agree exactly with recent CODATA recommendations[3] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the rare gases arise due to the use of slightly different values for R; this table uses R = 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[4] McBride *et al.*,[5] Gurvich *et al.*,[8] and Wagman *et al.*[12] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants, which are based on the 1981 scale[6] and the 1973 values,[7] respectively.

The thermodynamic functions reported here are calculated assuming that helium gas obeys Boltzmann statistics. In fact helium is a Bose–Einstein gas.[4] However, the differences in thermal properties between the two are very small except at extremely low temperature.[10,11] At 298.15 K the difference in $C_p°$ amounts to only 0.004 $J·K^{-1}·mol^{-1}$ and will be less at higher temperatures. Since $C_p°$ is the most sensitive of the thermodynamic properties, the differences are well within the stated uncertainty. At temperatures below approximately 50 K the differences may become significant and Bose–Einstein statistics should be used.

Phase Data

The boiling point, 4.215 K (1 atm), is taken from Hultgren *et al.* This value should prove reasonably accurate, although it has not been evaluated by the present authors, and is furnished for the convenience of the reader. As a result of this low value, the reference state for helium is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	0.	0.	0.
100	20.786	103.445	144.632	−4.119	0.	0.	0.
200	20.786	117.853	128.053	−2.040	0.	0.	0.
250	20.786	122.491	126.494	−1.001	0.	0.	0.
298.15	20.786	126.152	126.152	0.	0.	0.	0.
300	20.786	126.281	126.152	0.038	0.	0.	0.
350	20.786	129.485	126.405	1.078	0.	0.	0.
400	20.786	132.260	126.968	2.117	0.	0.	0.
450	20.786	134.709	127.694	3.156	0.	0.	0.
500	20.786	136.899	128.507	4.196	0.	0.	0.
600	20.786	140.688	130.231	6.274	0.	0.	0.
700	20.786	143.893	131.960	8.353	0.	0.	0.
800	20.786	146.668	133.629	10.431	0.	0.	0.
900	20.786	149.116	135.216	12.510	0.	0.	0.
1000	20.786	151.306	136.718	14.589	0.	0.	0.
1100	20.786	153.288	138.135	16.667	0.	0.	0.
1200	20.786	155.096	139.475	18.746	0.	0.	0.
1300	20.786	156.760	140.741	20.824	0.	0.	0.
1400	20.786	158.300	141.941	22.903	0.	0.	0.
1500	20.786	159.734	143.080	24.982	0.	0.	0.
1600	20.786	161.076	144.163	27.060	0.	0.	0.
1700	20.786	162.336	145.196	29.139	0.	0.	0.
1800	20.786	163.524	146.181	31.217	0.	0.	0.
1900	20.786	164.648	147.124	33.296	0.	0.	0.
2000	20.786	165.714	148.027	35.375	0.	0.	0.
2100	20.786	166.728	148.893	37.453	0.	0.	0.
2200	20.786	167.695	149.726	39.532	0.	0.	0.
2300	20.786	168.619	150.528	41.610	0.	0.	0.
2400	20.786	169.504	151.300	43.689	0.	0.	0.
2500	20.786	170.352	152.045	45.768	0.	0.	0.
2600	20.786	171.168	152.765	47.846	0.	0.	0.
2700	20.786	171.952	153.461	49.925	0.	0.	0.
2800	20.786	172.708	154.135	52.004	0.	0.	0.
2900	20.786	173.438	154.789	54.082	0.	0.	0.
3000	20.786	174.142	155.422	56.161	0.	0.	0.
3100	20.786	174.824	156.037	58.239	0.	0.	0.
3200	20.786	175.484	156.634	60.318	0.	0.	0.
3300	20.786	176.123	157.215	62.397	0.	0.	0.
3400	20.786	176.744	157.781	64.475	0.	0.	0.
3500	20.786	177.346	158.331	66.554	0.	0.	0.
3600	20.786	177.932	158.867	68.632	0.	0.	0.
3700	20.786	178.501	159.390	70.711	0.	0.	0.
3800	20.786	179.056	159.901	72.790	0.	0.	0.
3900	20.786	179.596	160.399	74.868	0.	0.	0.
4000	20.786	180.122	160.885	76.947	0.	0.	0.
4100	20.786	180.635	161.361	79.025	0.	0.	0.
4200	20.786	181.136	161.826	81.104	0.	0.	0.
4300	20.786	181.625	162.280	83.183	0.	0.	0.
4400	20.786	182.103	162.726	85.261	0.	0.	0.
4500	20.786	182.570	163.161	87.340	0.	0.	0.
4600	20.786	183.027	163.588	89.418	0.	0.	0.
4700	20.786	183.474	164.007	91.497	0.	0.	0.
4800	20.786	183.912	164.417	93.576	0.	0.	0.
4900	20.786	184.340	164.819	95.654	0.	0.	0.
5000	20.786	184.760	165.214	97.733	0.	0.	0.
5100	20.786	185.172	165.601	99.811	0.	0.	0.
5200	20.786	185.575	165.981	101.890	0.	0.	0.
5300	20.786	185.971	166.355	103.969	0.	0.	0.
5400	20.786	186.360	166.722	106.047	0.	0.	0.
5500	20.786	186.741	167.082	108.126	0.	0.	0.
5600	20.786	187.116	167.437	110.204	0.	0.	0.
5700	20.786	187.484	167.785	112.283	0.	0.	0.
5800	20.786	187.845	168.128	114.362	0.	0.	0.
5900	20.786	188.201	168.465	116.440	0.	0.	0.
6000	20.786	188.550	168.797	118.519	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

IP(He^+, g) = 438908.85 ± 0.02 cm^{-1}
$S°$(298.15 K) = 131.913 ± 0.002 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 2372.324 ± 0.001 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [2378.522] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	4

Heat of Formation

The ionization limit of neutral helium (198310.76 ± 0.02 cm^{-1}) reported by Moore[1] and Martin,[10] is adopted as $\Delta_f H°$(0 K) for He^+(g). The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the latest CODATA fundamental constants.[2] The uncertainty in the ionization limit corresponds to an uncertainty of less than 0.001 $kJ·mol^{-1}$ in the heat of formation. Rosenstock *et al.*[9] have summarized additional ionization potential and appearance potential data. Gurvich *et al.*[8] and Wagman *et al.*[11] adopted the same ionization potential, but the use of slightly different fundamental constants by Wagman *et al.*[11] resulted in a heat of formation difference of 0.021 $kJ·mol^{-1}$.

$\Delta_f H°$(He^+, g, 298.15 K) is obtained from $\Delta_f H°$(He, g, 0 K) by using IP(He) with JANAF[3] enthalpies $H°$(0 K)–$H°$(298.15 K) for He^+(g), He(r), and e^-(r). $\Delta_r H°$(He → $He^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights given by Moore[4] is complete to n=14. Our calculations indicate that any reasonable method of including these levels and cutting off the summation in the partition function[5] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the first excited level is over 329000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[5]

The thermodynamic functions reported here agree with those of Green *et al.*,[6] Hilsenrath *et al.*,[7] and Gurvich *et al.*[8] except for one or two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the cited references used a pressure of 1 atm. Second, smaller differences arise from the use of slightly different values for the fundamental constants and the relative ionic mass.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	2372.324		
100	20.786	109.206	150.394	−4.119			
200	20.786	123.614	133.815	−2.040			
250	20.786	128.252	132.256	−1.001			
298.15	20.786	131.913	131.913	0.	2378.522	2370.549	−415.310
300	20.786	132.042	131.914	0.038	2378.560	2370.499	−412.741
350	20.786	135.246	132.167	1.078	2379.599	2369.074	−353.565
400	20.786	138.022	132.729	2.117	2380.639	2367.499	−309.164
450	20.786	140.470	133.456	3.156	2381.678	2365.794	−274.614
500	20.786	142.660	134.269	4.196	2382.717	2363.974	−246.963
600	20.786	146.450	135.993	6.274	2384.796	2360.030	−205.459
700	20.786	149.654	137.721	8.353	2386.874	2355.738	−175.787
800	20.786	152.430	139.390	10.431	2388.953	2351.148	−153.514
900	20.786	154.878	140.978	12.510	2391.032	2346.298	−136.176
1000	20.786	157.068	142.479	14.589	2393.110	2341.216	−122.293
1100	20.786	159.049	143.897	16.667	2395.189	2335.926	−110.924
1200	20.786	160.858	145.236	18.746	2397.267	2330.446	−101.442
1300	20.786	162.521	146.502	20.824	2399.346	2324.794	−93.411
1400	20.786	164.062	147.702	22.903	2401.425	2318.981	−86.522
1500	20.786	165.496	148.841	24.982	2403.503	2313.020	−80.547
1600	20.786	166.837	149.925	27.060	2405.582	2306.920	−75.313
1700	20.786	168.097	150.957	29.139	2407.660	2300.690	−70.692
1800	20.786	169.286	151.943	31.217	2409.739	2294.337	−66.580
1900	20.786	170.409	152.885	33.296	2411.818	2287.869	−62.898
2000	20.786	171.476	153.788	35.375	2413.896	2281.292	−59.581
2100	20.786	172.490	154.655	37.453	2415.975	2274.611	−56.578
2200	20.786	173.457	155.488	39.532	2418.053	2267.830	−53.845
2300	20.786	174.381	156.289	41.610	2420.132	2260.955	−51.348
2400	20.786	175.265	157.062	43.689	2422.211	2253.990	−49.057
2500	20.786	176.114	157.807	45.768	2424.289	2246.938	−46.947
2600	20.786	176.929	158.527	47.846	2426.368	2239.803	−44.998
2700	20.786	177.714	159.223	49.925	2428.446	2232.588	−43.192
2800	20.786	178.469	159.897	52.004	2430.525	2225.296	−41.513
2900	20.786	179.199	160.550	54.082	2432.604	2217.930	−39.949
3000	20.786	179.904	161.183	56.161	2434.682	2210.492	−38.488
3100	20.786	180.585	161.798	58.239	2436.761	2202.985	−37.120
3200	20.786	181.245	162.396	60.318	2438.839	2195.410	−35.836
3300	20.786	181.885	162.977	62.397	2440.918	2187.771	−34.630
3400	20.786	182.505	163.542	64.475	2442.997	2180.069	−33.493
3500	20.786	183.108	164.092	66.554	2445.075	2172.305	−32.420
3600	20.786	183.693	164.629	68.632	2447.154	2164.482	−31.406
3700	20.786	184.263	165.152	70.711	2449.232	2156.602	−30.446
3800	20.786	184.817	165.662	72.790	2451.311	2148.665	−29.535
3900	20.786	185.357	166.160	74.868	2453.390	2140.673	−28.671
4000	20.786	185.883	166.647	76.947	2455.468	2132.629	−27.849
4100	20.786	186.397	167.122	79.025	2457.547	2124.532	−27.067
4200	20.786	186.898	167.587	81.104	2459.625	2116.384	−26.321
4300	20.786	187.387	168.042	83.183	2461.704	2108.187	−25.609
4400	20.786	187.864	168.487	85.261	2463.783	2099.942	−24.929
4500	20.786	188.332	168.923	87.340	2465.861	2091.650	−24.279
4600	20.786	188.788	169.350	89.418	2467.940	2083.311	−23.657
4700	20.786	189.235	169.768	91.497	2470.018	2074.927	−23.060
4800	20.786	189.673	170.178	93.576	2472.097	2066.499	−22.488
4900	20.786	190.102	170.580	95.654	2474.176	2058.027	−21.939
5000	20.786	190.522	170.975	97.733	2476.254	2049.513	−21.411
5100	20.786	190.933	171.362	99.811	2478.333	2040.958	−20.904
5200	20.786	191.337	171.743	101.890	2480.411	2032.362	−20.415
5300	20.786	191.733	172.116	103.969	2482.490	2023.725	−19.945
5400	20.786	192.121	172.483	106.047	2484.569	2015.050	−19.492
5500	20.786	192.503	172.844	108.126	2486.647	2006.336	−19.055
5600	20.786	192.877	173.198	110.204	2488.726	1997.584	−18.633
5700	20.786	193.245	173.546	112.283	2490.804	1988.796	−18.225
5800	20.786	193.607	173.889	114.362	2492.883	1979.970	−17.832
5900	20.786	193.962	174.226	116.440	2494.962	1971.109	−17.451
6000	20.786	194.311	174.558	118.519	2497.040	1962.213	−17.083

PREVIOUS: March 1977 (1 Atm) CURRENT: March 1982 (1 Bar)

REFERENCE STATE

0	to	2054	K	crystal, alpha
2054	to	2500	K	crystal, beta
2500	to	4963.793	K	liquid
4963.793	to	6000	K	Ideal Monatomic Gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹		kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.842	0.	0.	0.
100	20.580	17.753	−65.394	−4.764	0.	0.	0.
200	24.418	33.561	−45.871	−2.462	0.	0.	0.
298.15	25.687	43.560	43.560	0.	0.	0.	0.
300	25.708	43.719	43.560	0.048	0.	0.	0.
400	26.751	51.261	44.581	2.672	0.	0.	0.
500	27.692	57.332	46.543	5.394	0.	0.	0.
600	28.583	62.460	48.780	8.208	0.	0.	0.
700	29.445	66.932	51.060	11.110	0.	0.	0.
800	30.288	70.919	53.298	14.097	0.	0.	0.
900	31.120	74.534	55.459	17.167	0.	0.	0.
1000	31.943	77.856	57.535	20.320	0.	0.	0.
1100	32.759	80.938	59.524	23.556	0.	0.	0.
1200	33.572	83.824	61.430	26.872	0.	0.	0.
1300	34.372	86.543	63.258	30.270	0.	0.	0.
1400	35.064	89.115	65.014	33.741	0.	0.	0.
1500	35.765	91.558	66.703	37.283	0.	0.	0.
1600	36.466	93.889	68.330	40.894	0.	0.	0.
1700	37.167	96.121	69.899	44.576	0.	0.	0.
1800	37.868	98.265	71.416	48.328	0.	0.	0.
1900	38.569	100.331	72.884	52.149	0.	0.	0.
2000	39.269	102.327	74.306	56.041	0.	0.	0.
2054.000	39.648	103.378	75.057	58.172	ALPHA <--> BETA TRANSITION		
2054.000	33.959	106.255	75.057	64.080			
2100	34.384	107.011	75.749	65.652	0.	0.	0.
2200	35.307	108.632	77.207	69.136	0.	0.	0.
2300	36.231	110.222	78.608	72.713	0.	0.	0.
2400	37.154	111.784	79.957	76.383	0.	0.	0.
2500	38.077	113.353	81.262	80.228	0.	0.	0.
2500.000	38.077	113.353	81.262	80.228	BETA <--> LIQUID TRANSITION		
2500.000	37.656	125.068	81.262	109.516			
2600	37.656	126.545	82.976	113.281	0.	0.	0.
2700	37.656	127.966	84.616	117.047	0.	0.	0.
2800	37.656	129.336	86.189	120.813	0.	0.	0.
2900	37.656	130.657	87.699	124.578	0.	0.	0.
3000	37.656	131.934	89.153	128.344	0.	0.	0.
3100	37.656	133.169	90.553	132.109	0.	0.	0.
3200	37.656	134.364	91.903	135.875	0.	0.	0.
3300	37.656	135.523	93.208	139.641	0.	0.	0.
3400	37.656	136.647	94.469	143.406	0.	0.	0.
3500	37.656	137.739	95.690	147.172	0.	0.	0.
3600	37.656	138.799	96.872	150.937	0.	0.	0.
3700	37.656	139.831	98.020	154.703	0.	0.	0.
3800	37.656	140.835	99.133	158.469	0.	0.	0.
3900	37.656	141.814	100.215	162.234	0.	0.	0.
4000	37.656	142.767	101.267	166.000	0.	0.	0.
4100	37.656	143.697	102.291	169.765	0.	0.	0.
4200	37.656	144.604	103.287	173.531	0.	0.	0.
4300	37.656	145.490	104.258	177.297	0.	0.	0.
4400	37.656	146.356	105.205	181.062	0.	0.	0.
4500	37.656	147.202	106.129	184.828	0.	0.	0.
4600	37.656	148.030	107.031	188.593	0.	0.	0.
4700	37.656	148.840	107.912	192.359	0.	0.	0.
4800	37.656	149.632	108.773	196.125	0.	0.	0.
4900	37.656	150.409	109.615	199.890	0.	0.	0.
4963.793	37.656	150.896	110.142	202.292	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
4963.793	37.996	263.754	110.142	762.496			
5000	38.154	264.031	111.256	763.875	0.	0.	0.
5200	39.044	265.544	117.161	771.594	0.	0.	0.
5400	39.964	267.035	122.684	779.494	0.	0.	0.
5600	40.910	268.505	127.866	787.581	0.	0.	0.
5800	41.879	269.958	132.741	795.859	0.	0.	0.
6000	42.870	271.394	137.339	804.334	0.	0.	0.

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$S°(298.15\ K) = 43.560\ J·K^{-1}·mol^{-1}$
$T_{trs} = 2054 \pm 50\ K\ (\alpha–\beta)\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{trs} H° = 5.908 \pm 0.2\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions for α–Hf(cr) are derived from the studies of Collings and Ho,[1] Westrum,[2] Hawkins *et al.*[3] and Cezairliyan and McClure.[4] The mathematical and graphical treatment of these four studies yields a continuous and smooth heat capacity curve.

Roberts[5] surveyed the superconductive properties of the elements and reported a critical temperature of 0.128 K for α–Hf(cr). Since this temperature is so low, the effects of superconductivity on the thermal functions are not considered.

There are four studies[1,6–8] on the heat capaicty of hafnium in the region 1–5 K. Only Wolcott[6] reported the experimental data (56 data points). In the other three states, an equation (with two constants) was given to describe the entire set of experimental data. The second set of constants given by Betterton and Scarbrough[8] are stated to be an average of the two studies of Kneip *et al.*[7] and the more recent study by Betterton and Scarbrough.[8] However, the values appear suspect and may contain a typographical error. Nevertheless the maximum difference in the calculated values for $S°(5\ K)$ is $0.00024\ cal·K^{-1}·mol^{-1}$ with the adopted value being $S°(5\ K) = 0.0038\ cal·K^{-1}·mol^{-1}$. Similarily for $C_p°(5\ K)$ the maximum difference is $0.00024\ cal·K^{-1}·mol^{-1}$, with the adopted value being $C_p°(5\ K) = 0.00638\ cal·K^{-1}·mol^{-1}$

In the region above 5 K, and below 350 K, there are four heat capacity studied.[2,9–11] Cristescu and Simon[9] studies Hf from 13 to 210 K and reported 15 heat capacity values with a peak near 75 K. Burk and Darnell[10] made heat capacity measurements (40–190 K) and reported that the peak is completely absent. The heat capacity measurements of Burk *et al.* (10–200 K),[11] and Westrum (5.82–348.55 K)[1,12] support this latter conclusion, i.e., no peak. The values of Burk *et al.*,[11] after correction for the ~2% Zr in this sample, agree with the data of Westrum[2,12] between 10 and 40 K but deviate above 40 K, becoming ~5% higher at 100 K and decreasing to ~1% higher at 200 K. Above 350 K, there are four heat capacity studies and four enthalpy studies:

	Source (Year)	Data Points	T/K	Wt % Zr in Hf Sample
Enthalpy	Adenstedt (1952)[13]	1	373	0.7
	Fieldhouse and Lang (1961)[14]	14	534–1884	1.0
	Hawkins *et al.* (1963)[3]	50	338–1346	2.8
	Golutvin and Maslennikova (1970)[15]	12	551–1309	0.79
	Golutvin and Maslennikova (1970)[15]	9	695–137	0.79
Heat Capacity	Peletskii *et al.* (1971)[16]	13 (smoothed)	1200–2200	0.66
	Arutyunov *et al.* (1972)[17]	16 (smoothed)	1100–2050	0.65
	Cezairliyand and McClure (1975)[4]	26	1500–2400	3.12
	Rumyantsev *et al.* (1979)[18]	graph	1000–1900	–

The enthalpy studies show an unusually large scatter within each study as well as a lack of agreement between the studies. The heat capacity studies all have a similar temperature dependence in comparison with the adopted values. However, the studies of Arutyunov *et al.*[17,19] and Rumyantsev *et al.*[18] lie roughly 10% higher than the adopted values, whereas the study of Peletskii *et al.*[16] lies 5–24% below. The studies by Arutyunov *et al.*[17,19] and Rumyantsev *et al.*[18] suggest a sharp decrease in the heat capacity values within 50 K of the α–β transition temperature. The experimental results were corrected for this zirconium content.

Transition Data

Refer to the β–crystal table for details.

Sublimation Data

There are no sublimation studies involving α–Hf(cr). The enthalpy of sublimation is calculated as the difference between the enthalpy of formation of the ideal gas and the enthalpy of formation of α–Hf(cr).

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Continued on page 1371

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−5.842	0.	0.	0.
100	20.580	17.753	−65.394	−4.764	0.	0.	0.
200	24.418	33.561	−45.871	−2.462	0.	0.	0.
250	25.110	39.086	−43.979	−1.223	0.	0.	0.
298.15	25.687	43.560	43.560	0.	0.	0.	0.
300	25.708	43.719	43.560	0.048	0.	0.	0.
350	26.247	47.723	43.875	1.347	0.	0.	0.
400	26.751	51.261	44.581	2.672	0.	0.	0.
450	27.230	54.439	45.503	4.021	0.	0.	0.
500	27.692	57.332	46.543	5.394	0.	0.	0.
600	28.583	62.460	48.780	8.208	0.	0.	0.
700	29.445	66.932	51.060	11.110	0.	0.	0.
800	30.288	70.919	53.298	14.097	0.	0.	0.
900	31.120	74.534	55.459	17.167	0.	0.	0.
1000	31.943	77.856	57.535	20.320	0.	0.	0.
1100	32.759	80.938	59.524	23.556	0.	0.	0.
1200	33.572	83.824	61.430	26.872	0.	0.	0.
1300	34.372	86.543	63.258	30.270	0.	0.	0.
1400	35.064	89.115	65.014	33.741	0.	0.	0.
1500	35.765	91.558	66.703	37.283	0.	0.	0.
1600	36.466	93.889	68.330	40.894	0.	0.	0.
1700	37.167	96.121	69.899	44.576	0.	0.	0.
1800	37.868	98.265	71.416	48.328	0.	0.	0.
1900	38.569	100.331	72.884	52.149	0.	0.	0.
2000	39.269	102.327	74.306	56.041	0.	0.	0.
2054.000	39.648	103.378	75.057	58.172	---- ALPHA <--> BETA ----		
2100	39.970	104.260	75.687	60.003	−5.648	0.129	−0.003
2200	40.671	106.136	77.029	64.035	−5.101	0.392	−0.009
2300	41.372	107.959	78.334	68.138	−4.576	0.629	−0.014
2400	42.073	109.734	79.605	72.310	−4.073	0.845	−0.018
2500	42.774	111.466	80.845	76.552	−3.676	1.042	−0.022

PREVIOUS: CURRENT: March 1979

$S°(298.15\ K) = [61.104]\ J·K^{-1}·mol^{-1}$
$T_{trs} = 2054 \pm 50\ K\ (\alpha–\beta)\ J·K^{-1}$
$T_{fus} = 2500 \pm 20\ K\ (\beta–l)\ J·K^{-1}$

$\Delta_f H°(298.15\ K) = [18.686]\ kJ·mol^{-1}$
$\Delta_{trs}H° = 5.908 \pm 0.2\ kJ·mol^{-1}$
$\Delta_{fus}H° = [29.288 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the α–crystal by addition of $\Delta_{trs}H°$ and the difference in enthalpy, $H°(2054\ K)–H°(298.15\ K)$, between the α–crsytal and β–crystal.

Heat Capacity and Entropy

The only heat capacity study for the β–crystal is that of Cezairliyand McClure.[1] Using a pulse heating technique, they studied the heat capacity of a sample containing 3.12% (wt) Zr in the range 2054 to 2400 K. These results were corrected by Cezairliyan and McClure[1] to represent pure β–Hf and are extrapolated linearly to the melting point, 2500 K, and to 298.15 K. The entropy at 298.15 is calculated in a manner similar to that for the enthalpy of formation.

Phase Data

Hafnium, at ambient pressures, exists in two crystal modifications. The low temperature form, α–Hf, is hexagonal close packed, an hcp(A3) structure isotypic with Mg. The high temperature form, β–Hf, is body centered cubic, a bcc(A2) structure isotypic with W. The wide variation in the observed transition temperature is undoubtedly due to the effects of various impurities, in particular, zirconium.

Transition Data

Cezairlivan and McClure[2] have summarized the reported transition temperatures for the α to β transition of hafnium. Their summary is given below. All temperatures were corrected to IPTS–68. The pure hafnium value reported by the cited author was corrected for the zirconium content of the alloy. Hultgren *et al.*,[18] based on data available through 1965, recommended $T_{trs} = 2013 \pm 20$ K. We adopt $T_{trs} = 2054 \pm 50$ K based on the study of Cezairliyan and McClure[2] since we have also adopted their measured heat capacity values. In addition there are many studies of binary phase diagrams which lend support to this adopted value.

Source	Zirconium Content (W/%)	Transformation Temperature (K) Hafnium Alloy	Pure Hafnium
Duwez[3] unknown	1586 ± 10		
Fast (1952)[4]	3	1960–2075	
Gibson *et al.* (1958)[5]	0.01	2011	
Deardorff and Kato (1959)[6]	1.2–8.8		2026 ± 20
Peterson and Beemsten (1960)[7]	0.03	1966–2096	
Giessen *et al.* (1963)[8]	2.3	1991 ± 15	2031 ± 20
Ross and Hume–Rothery (1963)[9]	1.6	2236–2266 50	2271 ± 70
Krikorian and Wallace (1964)[10]	0.02–3.45	2007–2100	2016 ± 14
Taylor and Doyle (1964)[11]	2.3	2226 ± 50	2270 ± 70
Romans *et al.* (1965)[12]	1.5	2028	2053
Bates and Barnes (1967)[13]	3.6	2033	
Peletskii and Druzhinin (1971)[14]	0.66	1970 ± 5	
Carlson *et al.* (1973)[15]	3.3	1990–2003	
Cezairliyan and McClure (1976)[2]	3.12	2012 ± 10	2054

Cezairliyand and McClure,[2] using a millisecond–resolution pulse–heating technique, measured the transformation enthalpy to be 33.1 $J·g^{-1}$ (1.412 ± 0.05 $kcal·mol^{-1}$). Peletskii and Druzhinin[14] measured 29 J g^{-1} (1.237 $kcal·mol^{-1}$), a value which is roughly 12% lower than that of Cezairliyan and McClure.[2] Martynyuk and Tsapkov,[16] using a continuous–pulse heating technique, measured a transformation enthalpy of 1.24 $kcal·mol^{-1}$. The samples used in all three studies contained significant amounts of zirconium wt %,[2] 0.66 wt %,[14] and 0.7 wt %,[16] respectively. Hoerster *et al.*[17] measured an enthalpy of transition of 0.52 $kcal·mol^{-1}$ at 2090 K. We adopted $\Delta_{trs}H° = 1.412 \pm 0.05\ kcal·mol^{-1}$ as derived from the study of Cezairliyan and McClure.[2]

Fusion Data

Refer to the liquid table.

Sublimation Data

The sublimation studies for β–Hf(cr) are summarized on the Hf(g) table. The enthalpy of sublimation for Hf(β,cr) is calculated as the difference in the enthalpies of formation at 298.15 K of Hf(g) and Hf(β,cr).

Continued on page 1371

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	17.747	61.104	61.104	0.	18.686	13.455	−2.357
300	17.764	61.214	61.105	0.033	18.671	13.422	−2.337
350	18.226	63.987	61.323	0.933	18.272	12.579	−1.877
400	18.687	66.451	61.812	1.855	17.869	11.793	−1.540
450	19.149	68.679	62.454	2.801	17.466	11.058	−1.284
500	19.611	70.720	63.180	3.770	17.062	10.368	−1.083
600	20.534	74.377	64.748	5.778	16.255	9.105	−0.793
700	21.457	77.612	66.359	7.877	15.453	7.976	−0.595
800	22.381	80.538	67.951	10.069	14.658	6.963	−0.455
900	23.304	83.227	69.501	12.353	13.872	6.048	−0.351
1000	24.227	85.730	71.000	14.730	13.095	5.221	−0.273
1100	25.151	88.082	72.447	17.199	12.329	4.470	−0.212
1200	26.074	90.310	73.844	19.760	11.573	3.789	−0.165
1300	26.997	92.434	75.193	22.414	10.829	3.171	−0.127
1400	27.921	94.468	76.497	25.160	10.104	2.609	−0.097
1500	28.844	96.426	77.761	27.998	9.401	2.098	−0.073
1600	29.767	98.317	78.987	30.928	8.720	1.634	−0.053
1700	30.691	100.150	80.178	33.951	8.061	1.211	−0.037
1800	31.614	101.930	81.338	37.067	7.424	0.827	−0.024
1900	32.537	103.664	82.467	40.274	6.810	0.477	−0.013
2000	33.461	105.356	83.569	43.574	6.218	0.159	−0.004
2054.000	33.959	106.255	84.154	45.394	---- ALPHA <--> BETA ----		
2100	34.384	107.011	84.646	46.966	0.	0.	0.
2200	35.307	108.632	85.700	50.451	0.	0.	0.
2300	36.231	110.222	86.732	54.028	0.	0.	0.
2400	37.154	111.784	87.743	57.697	0.	0.	0.
2500	38.077	113.353	88.736	61.542	0.	0.	0.
2500.000	38.077	113.353	88.736	61.542	---- BETA <--> LIQUID ----		
2600	39.001	114.865	89.712	65.396	−29.200	1.170	−0.024
2700	39.924	116.354	90.672	69.342	−29.019	2.335	−0.045
2800	40.847	117.822	91.615	73.381	−28.746	3.492	−0.065
2900	41.771	119.272	92.544	77.512	−28.381	4.637	−0.084
3000	42.694	120.704	93.459	81.735	−27.923	5.768	−0.100

PREVIOUS: CURRENT: March 1979

$S°(298.15\ K) = [71.938]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2500 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [46.209]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [29.288 \pm 4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the β–crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2500\ K)–H°(298.15\ K)$, between the β–crystal and liquid.

Heat Capacity and Entropy

There are no heat capacity or enthalpy studies covering the liquid region of hafnium. A constant value of $C_p° = 9.0\ cal·K^{-1}·mol^{-1}$ is assumed for the region 1820–5500 K. A glass transition is assumed at 1820 K below which extrapolated β–Hf heat capacity values are used. The entropy is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Garg and Ackermann,[1] using pyrometric techniques, measured the melting point of hafnium as 2501 ± 3 K. Hultgren *et al.*[2] reviewed nine studies available through 1955 and recommended $T_{fus} = 2500 \pm 20$ K. We adopted $T_{fus} = 2500 \pm 20$ K.

The studies (and the reported melting temperatures in K) examined by Hultgren *et al.*[2] are: DeBoer and Fast,[3] 2503 ± 50; Skinner *et al.*,[4] 2498; Litton,[5] 2403; Adenstedt,[6] 2248; Spedding,[7] 2508 ± 5; Deardoff and Hayes,[8] (2495 ± 20; Gregorovitch,[9] 2116; Taylor *et al.*,[10] 2503 ± 20.

Ackermann and Rauh[11] measured a melting point of 2467 ± 4 K in a HfO_2 container. However, they state that the melting point may be as high as 2495 K since their sample contained 0.7 wt % Zr.

The enthalpy melting for Hf has not been measured. Various estimates and calculations have been made. Martynyuk *et al.*[12] correlated graphically $\Delta_{fus}S°$ versus T_{fus} for many metals and used the resulting linear relationship to estimate $\Delta_{fus}H° = 7.0\ kcal·mol^{-1}$. We adopt this value. Ackermann and Rauh[13] measured vapor pressures over Hf(β,cr) and Hf(l), adjusted the vapor pressures for Hf(β,cr) to match those of Hf(l) at T_{fus}, and derived $\Delta_{fus}H° = 6.2\ kcal·mol^{-1}$.

Vaporization Data

The vaporization studies are summarized on the ideal gas table.

The boiling point is calculated as that temperature for which $\Delta G° = 0$ for Hf(l)=Hf(g). $\Delta_{vap}H°$ is the corresponding enthalpy change. T_{vap} is the temperature at which the fugacity is one bar. The normal boiling point (p=1 bar) would be a slightly lower temperature.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
250							
298.15	17.747	71.938	71.938	0.	46.209	37.748	−6.613
300	17.764	72.048	71.939	0.033	46.194	37.695	−6.563
350	18.226	74.821	72.157	0.933	45.795	36.311	−5.419
400	18.687	77.285	72.646	1.855	45.393	34.983	−4.568
450	19.149	79.513	73.288	2.801	44.989	33.706	−3.912
500	19.611	81.554	74.014	3.770	44.585	32.474	−3.393
600	20.534	85.211	75.582	5.778	43.778	30.128	−2.623
700	21.457	88.446	77.193	7.877	42.976	27.916	−2.083
800	22.381	91.372	78.785	10.069	42.181	25.819	−1.686
900	23.304	94.061	80.335	12.353	41.395	23.821	−1.383
1000	24.227	96.564	81.834	14.730	40.619	21.910	−1.144
1100	25.151	98.916	83.281	17.199	39.852	20.076	−0.953
1200	26.074	101.144	84.678	19.760	39.097	18.312	−0.797
1300	26.997	103.268	86.027	22.414	38.353	16.610	−0.667
1400	27.921	105.302	87.331	25.160	37.627	14.965	−0.558
1500	28.844	107.260	88.595	27.998	36.924	13.371	−0.466
1600	29.767	109.151	89.821	30.928	36.243	11.823	−0.386
1700	30.691	110.984	91.012	33.951	35.584	10.317	−0.317
1800	31.614	112.764	92.172	37.067	34.948	8.849	−0.257
1820.000	31.799	113.114	92.400	37.701	GLASS <--> LIQUID TRANSITION		
1820.000	37.656	113.114	92.400	37.701			
1900	37.656	114.734	93.306	40.713	34.773	7.406	−0.204
2000	37.656	116.666	94.426	44.479	34.646	5.969	−0.156
2100	37.656	118.503	95.529	48.244	28.802	4.669	−0.116
2200	37.656	120.255	96.614	52.010	29.083	3.513	−0.083
2300	37.656	121.929	97.678	55.776	29.271	2.346	−0.053
2400	37.656	123.531	98.722	59.541	29.368	1.173	−0.026
2500	37.656	125.068	99.746	63.307	29.288	0.	0.
2500.000	37.656	125.068	99.746	66.307	BETA <--> LIQUID		
2600	37.656	126.545	100.748	67.072	0.	0.	0.
2700	37.656	127.966	101.730	70.838	0.	0.	0.
2800	37.656	129.336	102.692	74.604	0.	0.	0.
2900	37.656	130.657	103.633	78.369	0.	0.	0.
3000	37.656	131.934	104.556	82.135	0.	0.	0.
3100	37.656	133.169	105.459	85.900	0.	0.	0.
3200	37.656	134.364	106.344	89.666	0.	0.	0.
3300	37.656	135.523	107.210	93.432	0.	0.	0.
3400	37.656	136.647	108.060	97.197	0.	0.	0.
3500	37.656	137.739	108.892	100.963	0.	0.	0.
3600	37.656	138.799	109.708	104.728	0.	0.	0.
3700	37.656	139.831	110.508	108.494	0.	0.	0.
3800	37.656	140.835	111.293	112.260	0.	0.	0.
3900	37.656	141.814	112.063	116.025	0.	0.	0.
4000	37.656	142.767	112.819	119.791	0.	0.	0.
4100	37.656	143.697	113.561	123.556	0.	0.	0.
4200	37.656	144.604	114.289	127.322	0.	0.	0.
4300	37.656	145.490	115.005	131.088	0.	0.	0.
4400	37.656	146.356	115.707	134.853	0.	0.	0.
4500	37.656	147.202	116.398	138.619	0.	0.	0.
4600	37.656	148.030	117.077	142.384	0.	0.	0.
4700	37.656	148.840	117.744	146.150	0.	0.	0.
4800	37.656	149.632	118.400	149.916	0.	0.	0.
4900	37.656	150.409	119.045	153.681	0.	0.	0.
4963.793	37.656	150.896	119.452	156.083	FUGACITY = 1 bar		
5000	37.656	151.170	119.680	157.447	−560.219	4.086	−0.043
5100	37.656	151.915	120.305	161.212	−560.290	15.373	−0.157
5200	37.656	152.646	120.920	164.978	−560.407	26.662	−0.268
5300	37.656	153.364	121.525	168.744	−560.568	37.953	−0.374
5400	37.656	154.068	122.121	172.509	−560.776	49.248	−0.476
5500	37.656	154.759	122.709	176.275	−561.030	60.547	−0.575

PREVIOUS: CURRENT: March 1979

0	to	2054 K	crystal, alpha
2054	to	2500 K	crystal, beta
above		2500 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.842	0.	0.	0.
100	20.580	17.753	−65.394	−4.764	0.	0.	0.
200	24.418	33.561	−45.871	−2.462	0.	0.	0.
250	25.110	39.086	−43.979	−1.223	0.	0.	0.
298.15	25.687	43.560	43.560	0.	0.	0.	0.
300	25.708	43.719	43.560	0.048	0.	0.	0.
350	26.247	47.723	43.875	1.347	0.	0.	0.
400	26.751	51.261	44.581	2.672	0.	0.	0.
450	27.230	54.439	45.503	4.021	0.	0.	0.
500	27.692	57.332	46.543	5.394	0.	0.	0.
600	28.583	62.460	48.780	8.208	0.	0.	0.
700	29.445	66.932	51.060	11.110	0.	0.	0.
800	30.288	70.919	53.298	14.097	0.	0.	0.
900	31.120	74.534	55.459	17.167	0.	0.	0.
1000	31.943	77.856	57.535	20.320	0.	0.	0.
1100	32.759	80.938	59.524	23.556	0.	0.	0.
1200	33.572	83.824	61.430	26.872	0.	0.	0.
1300	34.372	86.543	63.258	30.270	0.	0.	0.
1400	35.064	89.115	65.014	33.741	0.	0.	0.
1500	35.765	91.558	66.703	37.283	0.	0.	0.
1600	36.466	93.889	68.330	40.894	0.	0.	0.
1700	37.167	96.121	69.899	44.576	0.	0.	0.
1800	37.868	98.265	71.416	48.328	0.	0.	0.
1900	38.569	100.331	72.884	52.149	0.	0.	0.
2000	39.269	102.327	74.306	56.041	0.	0.	0.
2054.000	39.648	103.378	75.057	58.172	ALPHA <--> BETA TRANSITION		
2054.000	33.959	106.255	75.057	64.080			
2100	34.384	107.011	75.749	65.652	0.	0.	0.
2200	35.307	108.632	77.207	69.136	0.	0.	0.
2300	36.231	110.222	78.608	72.713	0.	0.	0.
2400	37.154	111.784	79.957	76.383	0.	0.	0.
2500	38.077	113.353	81.262	80.228	0.	0.	0.
2500.000	38.077	113.353	81.262	80.228	BETA <--> LIQUID TRANSITION		
2500.000	37.656	125.068	81.262	109.516			
2600	37.656	126.545	82.976	113.281	0.	0.	0.
2700	37.656	127.966	84.616	117.047	0.	0.	0.
2800	37.656	129.336	86.189	120.813	0.	0.	0.
2900	37.656	130.657	87.699	124.578	0.	0.	0.
3000	37.656	131.934	89.153	128.344	0.	0.	0.
3100	37.656	133.169	90.553	132.109	0.	0.	0.
3200	37.656	134.364	91.903	135.875	0.	0.	0.
3300	37.656	135.523	93.208	139.641	0.	0.	0.
3400	37.656	136.647	94.469	143.406	0.	0.	0.
3500	37.656	137.739	95.690	147.172	0.	0.	0.
3600	37.656	138.799	96.872	150.937	0.	0.	0.
3700	37.656	139.831	98.020	154.703	0.	0.	0.
3800	37.656	140.835	99.133	158.469	0.	0.	0.
3900	37.656	141.814	100.215	162.234	0.	0.	0.
4000	37.656	142.767	101.267	166.000	0.	0.	0.
4100	37.656	143.697	102.291	169.765	0.	0.	0.
4200	37.656	144.604	103.287	173.531	0.	0.	0.
4300	37.656	145.490	104.258	177.297	0.	0.	0.
4400	37.656	146.356	105.205	181.062	0.	0.	0.
4500	37.656	147.202	106.129	184.828	0.	0.	0.
4600	37.656	148.030	107.031	188.593	0.	0.	0.
4700	37.656	148.840	107.912	192.359	0.	0.	0.
4800	37.656	149.632	108.773	196.125	0.	0.	0.
4900	37.656	150.409	109.615	199.890	0.	0.	0.
4963.793	37.656	150.896	110.142	202.292	----- FUGACITY = 1 bar -----		
5000	37.656	151.170	110.438	203.656	−560.219	4.086	−0.043
5100	37.656	151.915	111.244	207.421	−560.290	15.373	−0.157
5200	37.656	152.646	112.034	211.187	−560.407	26.662	−0.268
5300	37.656	153.364	112.807	214.953	−560.568	37.953	−0.374
5400	37.656	154.068	113.564	218.718	−560.776	49.248	−0.476
5500	37.656	154.759	114.307	222.484	−561.030	60.547	−0.575

PREVIOUS: CURRENT: March 1979

IP(Hf, g) = 54700 ± 600 cm^{-1}
$S°(298.15\ K)$ = 186.897 ± 0.2 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 618.0 ± 6.3 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 618.4 ± 6.3 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_2$	0.00	5
$^3F_3$	2356.68	7
$^3F_4$	4567.64	9
.	.	.
	53853.61	
IP	54700	

Enthalpy of Formation

There are six sublimation studies and two vaporization studies from which an enthalpy of formation for Hf(g) could be derived. A plot of these vapor pressure data, log p vs $1/T$, reveals considerable discrepancy between the various studies. In the liquid region, the vapor pressure values of Koch *et al.*[1] and Ackermann and Rauh[2] are in close agreement. The pressures of the former study are 5% higher at 2500 K but become 10% lower at 2800 K. The measured temperatures in the former study[1] were adjusted (i.e., the pyrometer reading) by Koch *et al.*[1] so that at the observed melting point the temperature would be 2500 K. The sample purity was not stated. In the latter study[2] the reported vapor pressures were corrected pressures (assuming ideal solution) from a eutectic of Hf and W. The Hf sample had a measured melting point of 2464 K; the purity was not reported.

The sublimation studies of Golubtsov and Mikul'skaya[3] and Ackermann and Rauh[2] spanned a temperature range which involved the α- and β-phases of hafnium, yet neither study mentioned the characterization of the condensed phase. The study of Golubtsov and Mikul'skaya[3] is not considered further since their reported vapor pressure equation is ambiguous and cannot be easily modified to yield reasonable vapor pressures. In general terms, the sublimation pressures of Ackermann and Rauh,[2] Kibler *et al.*[4] and McClaine and Blackburn[5] are in reasonable agreement. The pressures of Panish and Reif[6] are 60% above these three studies;[2,4,5] there is considerable scatter with one distinctly low pressure point at 2113 K. On the other hand, the results of Trulson *et al.*[7] are substantially lower by 50% than the three studies[2,4,5] with two distinctly lower points.

A 2nd and 3rd law analysis is given in the following table. We adopt $\Delta_f H°$ (Hf, g, 298.15 K) = 147.8 ± 1.5 $kcal·mol^{-1}$. This result is based on the reasonable consistency of the two vapor pressure studies[2,4] with each other and with our adopted thermodynamic functions as evidenced by the small values of the drift. Hultgren *et al.*,[8] using different thermodynamic functions and data available through 1966, recommended an enthalpy of formation of 148.0 ± 1.0 $kcal·mol^{-1}$ based heavily on the study by Kibler *et al.*[4] Other values for $\Delta_f H°(298.15\ K)$, also derived from vapor pressure studies, have been reported by Krupka,[9] Krikorian[10] and Kibler *et al.*[11]

Source (Year)	Reaction*	Pts	T/K	Method	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Kibler *et al.* (1963)[11]	A	8	2035–2325	Langmuir	141.5 ± 2.4	143.4 ± 0.5	0.9 ± 1.1	147.8
Panish and Reif (1963)[6]	A	6	2066–2274	Langmuir	160.3 ± 15.5	140.9 ± 2.7	−9.0 ± 7.2	145.4
McClaine (1964)[6]	A	5	2200–2363	Langmuir	124.3 ± 5.7	144.5 ± 1.3	8.8 ± 2.5	149.0
Trulson *et al.* (1965)[7]	A	15[b]	2075–2273	Knudsen	145.1 ± 4.2	145.9 ± 0.7	0.4 ± 1.9	150.4
Ackermann and Rauh (1972)[2]	A	eqn	1950–2464	mass eff.	145.4	143.6	−0.8	148.0
Koch *et al.* (1968)[1]	B	17	2500–2810	Langmuir	131.6 ± 3.4	136.9 ± 1.2	2.0 ± 1.3	147.9
Ackermann and Rauh (1972)[2]	B	eqn	1464–2800	mass eff.	140.1	136.7	−1.3	147.8

*Reaction: A) Hf(β,cr) = Hf(g) B) Hf(l) = Hf(g)
[b]Two points discarded due to a statistical test.

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Meggers and Moore.[12] Although we have listed only the ground state, the lowest two excited states, the highest observed excited state (below the ionization potential), and the ionization potential for Hf(g), all levels listed by Meggers and Moore,[12] as well as estimated levels (for n = 5,6,7), are used in the calculation. The 233 observed levels, two of which lie above the ionization potential, are too numerous to list completely. In our calculations, the missing levels for n = 6 and 7 have been arbitrarily added near the ionization limit. The calculations indicate that for Hf(g) the thermodynamic functions up to at least 3000 K are independent of the estimated missing levels (for n = 6 and 7), the cut–off procedure, and the inclusion of n = 7 levels. At this temperature there are no experimental heat capacity enthalpy, or vapor pressure data. The Gibbs energy function is essentially unaffected up to 5500 K.

References

[1]R. K. Koch, W. E. Anable and R. A. Beall, U. S. Bur. Mines RI–7125, 24 pp. (1968).
[2]R. J. Ackerman and E. G. Rauh, J., Chem. Thermodyn. **4**, 521 (1972).
[3]I. V. Golubtsov and G. Yu. Mikul'skaya, Svoistva Metal Splavov **75**, 62 (1975).

Continued on page 1371

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.198	618.040	618.040	INFINITE
100	20.786	164.188	205.380	−4.119	619.040	604.397	−315.704
200	20.786	178.596	188.799	−2.041	618.816	589.809	−154.042
250	20.789	183.235	187.240	−1.001	618.617	582.580	−121.723
298.15	20.803	186.897	186.897	0.	618.395	575.659	−100.853
300	20.804	187.026	186.898	0.038	618.386	575.394	−100.185
350	20.854	190.236	187.151	1.080	618.128	568.249	−84.806
400	20.960	193.027	187.715	2.125	617.848	561.142	−73.278
450	21.140	195.505	188.445	3.177	617.551	554.071	−64.315
500	21.397	197.745	189.265	4.240	617.241	547.034	−57.148
600	22.113	201.706	191.017	6.414	616.600	533.053	−46.406
700	23.012	205.181	192.797	8.669	615.954	519.180	−38.742
800	23.991	208.317	194.544	11.019	615.317	505.398	−32.999
900	24.978	211.200	196.236	13.467	614.695	491.696	−28.537
1000	25.925	213.881	197.868	16.013	614.088	478.062	−24.971
1100	26.806	216.394	199.439	18.650	613.490	464.489	−22.057
1200	27.603	218.761	200.952	21.371	612.894	450.969	−19.630
1300	28.305	220.999	202.409	24.167	612.293	437.500	−17.579
1400	28.912	223.119	203.813	27.029	611.683	424.077	−15.823
1500	29.424	225.132	205.168	29.947	611.059	410.698	−14.302
1600	29.847	227.045	206.476	32.911	610.412	397.362	−12.973
1700	30.190	228.865	207.740	35.913	609.733	384.067	−11.801
1800	30.465	230.599	208.962	38.947	609.014	370.813	−10.761
1900	30.681	232.252	210.144	42.004	608.250	357.600	−9.831
2000	30.852	233.830	211.290	45.081	607.435	344.429	−8.996
2100	30.986	235.339	212.399	48.174	600.917	331.429	−8.244
2200	31.095	236.783	213.475	51.278	600.537	318.605	−7.565
2300	31.187	238.167	214.519	54.392	600.074	305.800	−6.945
2400	31.270	239.496	215.532	57.515	599.528	293.017	−6.377
2500	31.351	240.775	216.516	60.646	598.813	280.260	−5.856
2600	31.436	242.006	217.473	63.785	568.899	268.702	−5.398
2700	31.528	243.194	218.404	66.933	568.282	257.168	−4.975
2800	31.632	244.342	219.310	70.091	567.674	245.656	−4.583
2900	31.750	245.454	220.192	73.260	567.077	234.166	−4.218
3000	31.884	246.533	221.052	76.442	566.493	222.696	−3.877
3100	32.037	247.581	221.891	79.638	565.924	211.246	−3.559
3200	32.208	248.601	222.710	82.850	565.370	199.814	−3.262
3300	32.399	249.595	223.510	86.080	564.835	188.398	−2.982
3400	32.610	250.565	224.291	89.330	564.319	176.999	−2.719
3500	32.841	251.513	225.056	92.603	563.826	165.614	−2.472
3600	33.090	252.442	225.803	95.899	563.357	154.243	−2.238
3700	33.359	253.352	226.536	99.221	562.914	142.885	−2.017
3800	33.645	254.246	227.253	102.571	562.498	131.539	−1.808
3900	33.948	255.124	227.957	105.951	562.112	120.203	−1.610
4000	34.267	255.987	228.647	109.362	561.757	108.877	−1.422
4100	34.602	256.837	229.324	112.805	561.435	97.559	−1.243
4200	34.951	257.675	229.989	116.282	561.147	86.248	−1.073
4300	35.313	258.502	230.642	119.796	560.894	74.944	−0.910
4400	35.688	259.318	231.285	123.345	560.678	63.645	−0.756
4500	36.074	260.124	231.917	126.933	560.501	52.351	−0.608
4600	36.471	260.921	232.539	130.561	560.362	41.061	−0.466
4700	36.878	261.710	233.151	134.228	560.264	29.773	−0.331
4800	37.294	262.491	233.754	137.936	560.207	18.486	−0.201
4900	37.720	263.264	234.348	141.687	560.192	7.201	−0.077
4963.793	37.996	263.754	234.723	144.102	----- FUGACITY = 1 bar -----		
5000	38.154	264.031	234.934	145.481	0.	0.	0.
5100	38.595	264.790	235.512	149.318	0.	0.	0.
5200	39.044	265.544	236.083	153.200	0.	0.	0.
5300	39.501	266.292	236.646	157.127	0.	0.	0.
5400	39.964	267.035	237.202	161.100	0.	0.	0.
5500	40.434	267.773	237.751	165.120	0.	0.	0.
5600	40.910	268.505	238.293	169.187	0.	0.	0.
5700	41.392	269.234	238.830	173.302	0.	0.	0.
5800	41.879	269.958	239.360	177.465	0.	0.	0.
5900	42.372	270.678	239.885	181.678	0.	0.	0.
6000	42.870	271.394	240.404	185.940	0.	0.	0.

PREVIOUS: March 1979 (1 atm) CURRENT: March 1979 (1 bar)

$IP(Hf^+, g) = 120000 \pm 1000\ cm^{-1}$
$S°(298.15\ K) = 185.040 \pm 0.01\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1272.4 \pm 4.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [1278.950]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2D_{3/2}$	0.00	4
$^2D_{5/2}$	3050.88	6
.	.	.
.	.	.
.	.	.
	83129.8	10
IP	120000	

Enthalpy of Formation

$\Delta_f H°(Hf^+, g\ 0\ K)$ is calculated from $\Delta_f H°(Hf, g, 0\ K)$[1] using the spectroscopic value of $IP(Hf) = 54700 \pm 600\ cm^{-1}$ ($654.358 \pm 1.18\ kJ·mol^{-1}$) from Meggers and Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, $1\ cm^{-1} = 0.01196266\ kJ·cm^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Hf^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Hf, g, 0\ K)$ by using IP (Hf) with JANAF[1] enthalpies, $H°(0\ K)–H°(298.15\ K)$, for Hf(g), $Hf^+(g)$, and $e^-(g)$. $\Delta_f H°(Hf \rightarrow Hf^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by $-6.197\ kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Moore.[6] Although we have listed only the ground state, the first excited state, the highest observed excited state, and the ionization potential for $Hf^+(g)$, all levels listed by Moore,[6] as well as estimated levels (for $n = 6$ and 7), are used in the calculation. The 121 observed levels are too numerous to list completely. In our calculations the missing levels for $n = 6$ and 7 have been arbitrarily added near the ionization limit. The calculations indicate that for $Hf^+(g)$ the thermodyanmic functions up to 5000 K are independent of the estimated missing levels (for $n = 6$ and 7), the cut–off procedure, and the inclusion of n=7 levels. The free energy function is unaffected up to 10000 K. The reported uncertainty in $S°_{298}$ is due to uncertainties in the gram formula weight and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>7), more precise estimation of the missing levels (for all n), and utilization of proper fill and cut–off procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
T/K	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.		INFINITE	−6.197	1272.397		
100	20.786	162.333	203.521	−4.119			
200	20.786	176.741	186.942	−2.040			
250	20.786	181.379	185.382	−1.001			
298.15	20.786	185.040	185.040	0.	1278.950	1230.512	−215.581
300	20.786	185.169	185.041	0.038	1278.979	1230.212	−214.199
350	20.786	188.373	185.294	1.078	1279.758	1222.022	−182.377
400	20.786	191.149	185.856	2.117	1280.512	1213.722	−158.496
450	20.786	193.597	186.583	3.156	1281.241	1205.329	−139.911
500	20.786	195.787	187.396	4.196	1281.946	1196.857	−125.035
600	20.786	199.577	189.120	6.274	1283.290	1179.711	−102.703
700	20.786	202.781	190.848	8.353	1284.545	1162.347	−86.735
800	20.786	205.556	192.517	10.431	1285.716	1144.810	−74.748
900	20.786	208.005	194.105	12.510	1286.802	1127.130	−65.417
1000	20.786	210.195	195.606	14.589	1287.806	1109.334	−57.946
1100	20.787	212.176	197.024	16.667	1288.729	1091.442	−51.828
1200	20.789	213.985	198.363	18.746	1289.569	1073.469	−46.727
1300	20.794	215.649	199.629	20.825	1290.329	1055.429	−42.408
1400	20.804	217.190	200.829	22.905	1291.016	1037.334	−38.703
1500	20.823	218.626	201.968	24.986	1291.635	1019.192	−35.491
1600	20.857	219.971	203.052	27.070	1292.186	1001.010	−32.680
1700	20.910	221.237	204.085	29.158	1292.671	982.797	−30.198
1800	20.991	222.434	205.071	31.253	1293.092	964.556	−27.991
1900	21.107	223.572	206.015	33.358	1293.454	946.294	−26.015
2000	21.264	224.658	206.920	35.476	1293.759	928.015	−24.237
2100	21.472	225.701	207.790	37.612	1288.363	909.850	−22.631
2200	21.737	226.705	208.627	39.772	1289.117	891.808	−21.174
2300	22.065	227.679	209.434	41.962	1289.808	873.733	−19.843
2400	22.462	228.626	210.214	44.187	1290.444	855.629	−18.622
2500	22.931	229.552	210.970	46.456	1290.946	837.501	−17.499
2600	23.477	230.462	211.702	48.776	1262.291	820.523	−16.485
2700	24.100	231.359	212.413	51.154	1262.982	803.519	−15.545
2800	24.800	232.248	213.106	53.599	1263.739	786.488	−14.672
2900	25.576	233.132	213.781	56.117	1264.571	769.429	−13.859
3000	26.424	234.013	214.441	58.716	1265.483	752.340	−13.099
3100	27.341	234.894	215.086	61.404	1266.484	735.219	−12.388
3200	28.320	235.778	215.719	64.187	1267.579	718.064	−11.721
3300	29.355	236.665	216.340	67.070	1268.776	700.873	−11.094
3400	30.437	237.557	216.951	70.059	1270.078	683.645	−10.503
3500	31.559	238.455	217.553	73.159	1271.490	666.376	−9.945
3600	32.711	239.360	218.146	76.372	1273.017	649.066	−9.418
3700	33.883	240.273	218.732	79.702	1274.659	631.712	−8.918
3800	35.066	241.192	219.311	83.149	1276.420	614.312	−8.444
3900	36.249	242.118	219.884	86.715	1278.298	596.863	−7.994
4000	37.424	243.051	220.451	90.399	1280.295	579.366	−7.566
4100	38.580	243.989	221.014	94.199	1282.409	561.816	−7.158
4200	39.710	244.932	221.572	98.114	1284.636	544.214	−6.768
4300	40.805	245.880	222.126	102.140	1286.975	526.558	−6.396
4400	41.857	246.830	222.677	106.273	1289.422	508.846	−6.041
4500	42.862	247.782	223.224	110.510	1291.971	491.077	−5.700
4600	43.812	248.734	223.768	114.844	1294.618	473.250	−5.374
4700	44.704	249.686	224.310	119.270	1297.358	455.365	−5.061
4800	45.534	250.636	224.848	123.783	1300.183	437.420	−4.760
4900	46.299	251.583	225.384	128.375	1303.088	419.416	−4.471
5000	46.999	252.526	225.918	133.040	745.848	405.438	−4.236
5100	47.631	253.463	226.449	137.772	748.821	398.601	−4.083
5200	48.197	254.393	226.977	142.564	751.810	391.704	−3.935
5300	48.696	255.316	227.503	147.409	754.807	384.751	−3.792
5400	49.130	256.231	228.027	152.301	757.804	377.740	−3.654
5500	49.501	257.136	228.548	157.233	760.795	370.675	−3.520
5600	49.811	258.030	229.066	162.199	763.772	363.555	−3.391
5700	50.063	258.914	229.582	167.194	766.730	356.382	−3.266
5800	50.260	259.787	230.095	172.210	769.662	349.157	−3.144
5900	50.405	260.647	230.606	177.244	772.562	341.882	−3.027
6000	50.502	261.495	231.114	182.290	775.424	334.558	−2.913

PREVIOUS: March 1979 (1 atm) CURRENT: March 1984 (1 bar)

EA(Hf, g) = 0.0 eV
$S°(298.15\ K) = 185.040 \pm 0.002\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 618.040 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [612.197]\ kJ \cdot mol^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^4F_{3/2}$	0.0	4

Enthalpy of Formation

$\Delta_f H°(Hf^-, g, 0\ K)$ is calculated from $\Delta_f H°(Hf, g, 0\ K)$[1] using the adopted electron affinity of EA(Hf) = ~0.0 eV. This value, recommended by Hotop and Lineberger,[2] is based on a semiempirical extrapolation.[3,4] Additional information on Hf^-(g) and may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Hf^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Hf, g, 0\ K)$ by using EA(Hf) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for Hf^-(g), Hf(g), and e^-(ref). $\Delta_f H°(Hf^- \rightarrow Hf + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Hf^-(g) is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	618.040		
100	20.786	162.333	203.521	−4.119			
200	20.786	176.741	186.942	−2.040			
250	20.786	181.379	185.383	−1.001			
298.15	20.786	185.040	185.040	0.	612.197	576.270	−100.960
300	20.786	185.169	185.041	0.038	612.150	576.047	−100.299
350	20.786	188.373	185.294	1.078	610.851	570.132	−85.088
400	20.786	191.149	185.856	2.117	609.526	564.405	−73.704
450	20.786	193.597	186.583	3.156	608.176	558.846	−64.869
500	20.786	195.787	187.396	4.196	606.803	553.438	−57.817
600	20.786	199.577	189.120	6.274	603.989	543.028	−47.275
700	20.786	202.781	190.848	8.353	601.087	533.096	−39.780
800	20.786	205.556	192.517	10.431	598.101	523.586	−34.187
900	20.786	208.005	194.105	12.510	595.030	514.455	−29.858
1000	20.786	210.195	195.606	14.589	591.877	505.671	−26.414
1100	20.786	212.176	197.024	16.667	588.642	497.206	−23.610
1200	20.786	213.984	198.363	18.746	585.325	489.040	−21.287
1300	20.786	215.648	199.629	20.824	581.928	481.153	−19.333
1400	20.786	217.189	200.829	22.903	578.456	473.531	−17.668
1500	20.786	218.623	201.968	24.982	574.915	466.159	−16.233
1600	20.786	219.964	203.052	27.060	571.303	459.026	−14.986
1700	20.786	221.224	204.084	29.139	567.621	452.121	−13.892
1800	20.786	222.412	205.069	31.217	563.870	445.435	−12.926
1900	20.786	223.536	206.012	33.296	560.048	438.959	−12.068
2000	20.786	224.602	206.915	35.375	556.156	432.687	−11.301
2100	20.786	225.617	207.782	37.453	546.546	426.740	−10.615
2200	20.786	226.584	208.615	39.532	543.061	421.116	−9.999
2300	20.786	227.508	209.416	41.610	539.484	415.653	−9.440
2400	20.786	228.392	210.188	43.689	535.815	410.347	−8.931
2500	20.786	229.241	210.934	45.768	531.970	405.198	−8.466
2600	20.786	230.056	211.654	47.846	498.916	401.373	−8.064
2700	20.786	230.840	212.350	49.925	495.150	397.693	−7.694
2800	20.786	231.596	213.024	52.004	491.385	394.153	−7.353
2900	20.786	232.326	213.677	54.082	487.619	390.747	−7.038
3000	20.786	233.030	214.310	56.161	483.854	387.470	−6.746
3100	20.786	233.712	214.925	58.239	480.088	384.320	−6.476
3200	20.786	234.372	215.523	60.318	476.322	381.290	−6.224
3300	20.786	235.012	216.104	62.397	472.557	378.379	−5.989
3400	20.786	235.632	216.669	64.475	468.791	375.581	−5.770
3500	20.786	236.235	217.219	66.554	465.026	372.895	−5.565
3600	20.786	236.820	217.756	68.632	461.260	370.316	−5.373
3700	20.786	237.390	218.279	70.711	457.494	367.841	−5.193
3800	20.786	237.944	218.789	72.790	453.729	365.469	−5.024
3900	20.786	238.484	219.287	74.868	449.963	363.195	−4.864
4000	20.786	239.010	219.774	76.947	446.198	361.018	−4.714
4100	20.786	239.524	220.249	79.025	442.432	358.936	−4.573
4200	20.786	240.024	220.714	81.104	438.666	356.945	−4.439
4300	20.786	240.514	221.169	83.183	434.901	355.043	−4.313
4400	20.786	240.991	221.614	85.261	431.135	353.230	−4.193
4500	20.786	241.459	222.050	87.340	427.370	351.501	−4.080
4600	20.786	241.915	222.477	89.418	423.604	349.857	−3.973
4700	20.786	242.362	222.895	91.497	419.838	348.294	−3.871
4800	20.786	242.800	223.305	93.576	416.073	346.812	−3.774
4900	20.786	243.229	223.707	95.654	412.307	345.408	−3.682
5000	20.786	243.649	224.102	97.733	−151.677	348.167	−3.637
5100	20.786	244.060	224.489	99.811	−155.514	358.202	−3.669
5200	20.786	244.464	224.870	101.890	−159.396	368.313	−3.700
5300	20.786	244.860	225.243	103.969	−163.324	378.499	−3.730
5400	20.786	245.248	225.610	106.047	−167.297	388.759	−3.760
5500	20.786	245.630	225.970	108.126	−171.317	399.093	−3.790
5600	20.786	246.004	226.325	110.204	−175.384	409.501	−3.820
5700	20.786	246.372	226.673	112.283	−179.499	419.982	−3.849
5800	20.786	246.734	227.016	114.362	−183.662	430.535	−3.877
5900	20.786	247.089	227.353	116.440	−187.874	441.161	−3.906
6000	20.786	247.438	227.685	118.519	−192.136	451.858	−3.934

PREVIOUS: March 1979 (1 atm) CURRENT: March 1984 (1 bar)

Continued from page 1364

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REFERENCE STATE

0	to	234.29	K crystal
234.29	to	629.839	K liquid
above		629.839	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.343	0.	0.	0.
100	24.255	37.219	113.592	−7.637	0.	0.	0.
200	27.275	55.022	80.284	−5.052	0.	0.	0.
234.290	28.485	59.428	76.915	−4.097	CRYSTAL <--> LIQUID		
234.290	28.476	69.225	76.915	−1.802	TRANSITION		
298.15	27.978	76.028	76.028	0.	0.	0.	0.
300	27.963	76.201	76.028	0.052	0.	0.	0.
400	27.414	84.161	77.118	2.817	0.	0.	0.
500	27.175	90.248	79.158	5.545	0.	0.	0.
600	27.139	95.197	81.432	8.259	0.	0.	0.
629.839	27.164	96.514	82.115	9.069	LIQUID <--> IDEAL GAS		
629.839	20.786	190.515	82.115	68.274	FUGACITY = 1 bar		
700	20.786	192.710	93.092	69.733	0.	0.	0.
800	20.786	195.486	105.722	71.811	0.	0.	0.
900	20.786	197.934	115.834	73.890	0.	0.	0.
1000	20.786	200.124	124.156	75.969	0.	0.	0.
1100	20.786	202.105	131.153	78.047	0.	0.	0.
1200	20.786	203.914	137.143	80.126	0.	0.	0.
1300	20.786	205.578	142.344	82.204	0.	0.	0.
1400	20.786	207.118	146.916	84.283	0.	0.	0.
1500	20.786	208.552	150.978	86.362	0.	0.	0.
1600	20.786	209.894	154.619	88.440	0.	0.	0.
1700	20.786	211.154	157.908	90.519	0.	0.	0.
1800	20.786	212.342	160.899	92.597	0.	0.	0.
1900	20.786	213.466	163.636	94.676	0.	0.	0.
2000	20.786	214.532	166.155	96.755	0.	0.	0.
2100	20.786	215.546	168.483	98.833	0.	0.	0.
2200	20.786	216.513	170.644	100.912	0.	0.	0.
2300	20.786	217.437	172.659	102.990	0.	0.	0.
2400	20.786	218.322	174.543	105.069	0.	0.	0.
2500	20.786	219.170	176.311	107.148	0.	0.	0.
2600	20.786	219.986	177.975	109.226	0.	0.	0.
2700	20.786	220.770	179.546	111.305	0.	0.	0.
2800	20.786	221.526	181.032	113.383	0.	0.	0.
2900	20.786	222.255	182.441	115.462	0.	0.	0.
3000	20.786	222.960	183.780	117.541	0.	0.	0.
3100	20.786	223.642	185.055	119.619	0.	0.	0.
3200	20.786	224.302	186.271	121.698	0.	0.	0.
3300	20.787	224.941	187.433	123.776	0.	0.	0.
3400	20.787	225.562	188.546	125.855	0.	0.	0.
3500	20.787	226.164	189.612	127.934	0.	0.	0.
3600	20.788	226.750	190.635	130.013	0.	0.	0.
3700	20.789	227.319	191.619	132.091	0.	0.	0.
3800	20.790	227.874	192.566	134.170	0.	0.	0.
3900	20.791	228.414	193.478	136.249	0.	0.	0.
4000	20.793	228.940	194.358	138.329	0.	0.	0.
4100	20.795	229.454	195.208	140.408	0.	0.	0.
4200	20.798	229.955	196.029	142.488	0.	0.	0.
4300	20.802	230.444	196.824	144.568	0.	0.	0.
4400	20.807	230.923	197.594	146.648	0.	0.	0.
4500	20.813	231.390	198.339	148.729	0.	0.	0.
4600	20.820	231.848	199.063	150.811	0.	0.	0.
4700	20.829	232.296	199.765	152.893	0.	0.	0.
4800	20.839	232.734	200.448	154.977	0.	0.	0.
4900	20.851	233.164	201.111	157.061	0.	0.	0.
5000	20.866	233.586	201.756	159.147	0.	0.	0.
5100	20.882	233.999	202.384	161.234	0.	0.	0.
5200	20.902	234.405	202.996	163.324	0.	0.	0.
5300	20.924	234.803	203.593	165.415	0.	0.	0.
5400	20.949	235.194	204.174	167.508	0.	0.	0.
5500	20.978	235.579	204.742	169.605	0.	0.	0.
5600	21.010	235.957	205.296	171.704	0.	0.	0.
5700	21.046	236.329	205.837	173.807	0.	0.	0.
5800	21.087	236.696	206.366	175.913	0.	0.	0.
5900	21.132	237.057	206.883	178.024	0.	0.	0.
6000	21.182	237.412	207.389	180.140	0.	0.	0.

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

$S°(298.15\ K) = 76.03 \pm 0.2\ J·K^{-1}·mol^{-1}$
$T_{fus} = 234.29\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 2.2953 \pm 0.0004\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacities of Smith and Wolcott, (1.2-20.2 K),[1] Busey and Giaugue (15-330 K),[2] and Douglas *et al.* (300-770 K),[3] have been smoothly joined. There is fair agreement between the selected values and those of Pickard and Simon,[4] Carpenter and Oakley,[5] Carpenter and Stoodley,[6] Cohen *et al.*,[7] Dixon and Rodebush,[8] Simon,[9] Bronsted,[10] and Pollitzer.[11]

Fusion Data

The results of Busey and Giauque[2] are adopted.

Vaporization Data

Refer to the gas phase tables for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−9.343	0.	0.	0.
100	24.255	37.219	113.592	−7.637	0.	0.	0.
200	27.275	55.022	80.284	−5.052	0.	0.	0.
234.290	28.485	59.428	76.915	−4.097	CRYSTAL <--> LIQUID		
234.290	28.476	69.225	76.915	−1.802	TRANSITION		
250	28.351	71.069	76.490	−1.355	0.	0.	0.
298.15	27.978	76.028	76.028	0.	0.	0.	0.
300	27.963	76.201	76.028	0.052	0.	0.	0.
350	27.639	80.486	76.368	1.441	0.	0.	0.
400	27.414	84.161	77.118	2.817	0.	0.	0.
450	27.267	87.381	78.083	4.184	0.	0.	0.
500	27.175	90.248	79.158	5.545	0.	0.	0.
600	27.139	95.197	81.432	8.259	0.	0.	0.
629.839	27.164	96.514	82.115	9.069	----- FUGACITY = 1 bar -----		
700	27.291	99.389	83.705	10.979	−58.754	6.571	−0.490
800	27.582	103.052	85.899	13.722	−58.089	15.858	−1.035
900	27.896	106.318	87.990	16.496	−57.394	25.060	−1.454
1000	28.210	109.274	89.973	19.301	−56.667	34.183	−1.786
1100	28.523	111.977	91.852	22.138	−55.909	43.232	−2.053
1200	28.837	114.472	93.634	25.006	−55.120	52.210	−2.273
1300	29.151	116.793	95.328	27.905	−54.299	61.121	−2.456
1400	29.465	118.965	96.939	30.836	−53.447	69.968	−2.611
1500	29.778	121.008	98.476	33.798	−52.563	78.752	−2.742
1600	30.092	122.940	99.945	36.792	−51.649	87.477	−2.856
1700	30.406	124.774	101.352	39.816	−50.702	96.144	−2.954
1800	30.719	126.521	102.703	42.873	−49.725	104.754	−3.040
1900	31.033	128.190	104.000	45.960	−48.716	113.308	−3.115
2000	31.347	129.790	105.250	49.079	−47.675	121.809	−3.181

PREVIOUS: CURRENT: December 1961

IP(Hg, g) = 84184.1 ± 0.5 cm^{-1}
$S°$(298.15 K) = 174.970 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 64.53 ± 0.04 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 61.38 ± 0.04 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.000	1
$^3P_0$	37645.080	1
$^3P_1$	39412.300	3
$^3P_2$	44042.977	5

Enthalpy of Formation

The value adopted for the enthalpy of formation of Hg(g) is that recommended by CODATA.[1] This value was derived from the vapor pressure studies summarized by Hultgren *et al.*[2] Of the 24 studies examined, most weight was given to the following studies: Spedding and Dye (533–630 K),[3] Menzies (395 625 K),[4] Beattie *et al.* (623–635 K),[5] Burlingame (343–474 K),[6] Rodebush and Dixon (444–476 K),[7] and Mayer (262–298 K).[8]

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[9,10] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[11] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the three levels below 45000 cm^{-1}; the next excited state is approximately 54000 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the three P levels. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[11]

The thermal functions at 298.15 K agree with the CODATA recommendations[1] except that the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$, since this table uses a standard state pressure of 1 bar (CODATA recommendations are based on 1 atm).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	64.526	64.526	INFINITE
100	20.786	152.263	193.450	−4.119	64.899	53.394	−27.890
200	20.786	166.670	176.871	−2.040	64.392	42.062	−10.986
250	20.786	171.309	175.312	−1.001	61.735	36.675	−7.663
298.15	20.786	174.970	174.970	0.	61.380	31.880	−5.585
300	20.786	175.098	174.970	0.038	61.367	31.697	−5.519
350	20.786	178.303	175.223	1.078	61.016	26.781	−3.997
400	20.786	181.078	175.786	2.117	60.680	21.913	−2.862
450	20.786	183.526	176.512	3.156	60.352	17.087	−1.983
500	20.786	185.717	177.325	4.196	60.031	12.297	−1.285
600	20.786	189.506	179.049	6.274	59.395	2.810	−0.245
629.839	20.786	190.515	179.569	6.894	----- FUGACITY = 1 bar -----		
700	20.786	192.710	180.778	8.353	0.	0.	0.
800	20.786	195.486	182.447	10.431	0.	0.	0.
900	20.786	197.934	184.034	12.510	0.	0.	0.
1000	20.786	200.124	185.536	14.589	0.	0.	0.
1100	20.786	202.105	186.953	16.667	0.	0.	0.
1200	20.786	203.914	188.292	18.746	0.	0.	0.
1300	20.786	205.578	189.559	20.824	0.	0.	0.
1400	20.786	207.118	190.759	22.903	0.	0.	0.
1500	20.786	208.552	191.898	24.982	0.	0.	0.
1600	20.786	209.894	192.981	27.060	0.	0.	0.
1700	20.786	211.154	194.013	29.139	0.	0.	0.
1800	20.786	212.342	194.999	31.217	0.	0.	0.
1900	20.786	213.466	195.942	33.296	0.	0.	0.
2000	20.786	214.532	196.845	35.375	0.	0.	0.
2100	20.786	215.546	197.711	37.453	0.	0.	0.
2200	20.786	216.513	198.544	39.532	0.	0.	0.
2300	20.786	217.437	199.346	41.610	0.	0.	0.
2400	20.786	218.322	200.118	43.689	0.	0.	0.
2500	20.786	219.170	200.863	45.768	0.	0.	0.
2600	20.786	219.986	201.583	47.846	0.	0.	0.
2700	20.786	220.770	202.279	49.925	0.	0.	0.
2800	20.786	221.526	202.953	52.004	0.	0.	0.
2900	20.786	222.255	203.606	54.082	0.	0.	0.
3000	20.786	222.960	204.240	56.161	0.	0.	0.
3100	20.786	223.642	204.855	58.239	0.	0.	0.
3200	20.786	224.302	205.452	60.318	0.	0.	0.
3300	20.787	224.941	206.033	62.397	0.	0.	0.
3400	20.787	225.562	206.598	64.475	0.	0.	0.
3500	20.787	226.164	207.149	66.554	0.	0.	0.
3600	20.788	226.750	207.685	68.633	0.	0.	0.
3700	20.789	227.319	208.208	70.712	0.	0.	0.
3800	20.790	227.874	208.719	72.790	0.	0.	0.
3900	20.791	228.414	209.217	74.869	0.	0.	0.
4000	20.793	228.940	209.703	76.949	0.	0.	0.
4100	20.795	229.454	210.179	79.028	0.	0.	0.
4200	20.798	229.955	210.644	81.108	0.	0.	0.
4300	20.802	230.444	211.098	83.188	0.	0.	0.
4400	20.807	230.923	211.544	85.268	0.	0.	0.
4500	20.813	231.390	211.979	87.349	0.	0.	0.
4600	20.820	231.848	212.406	89.431	0.	0.	0.
4700	20.829	232.296	212.825	91.513	0.	0.	0.
4800	20.839	232.734	213.235	93.597	0.	0.	0.
4900	20.851	233.164	213.637	95.681	0.	0.	0.
5000	20.866	233.586	214.032	97.767	0.	0.	0.
5100	20.882	233.999	214.420	99.855	0.	0.	0.
5200	20.902	234.405	214.800	101.944	0.	0.	0.
5300	20.924	234.803	215.174	104.035	0.	0.	0.
5400	20.949	235.194	215.541	106.129	0.	0.	0.
5500	20.978	235.579	215.902	108.225	0.	0.	0.
5600	21.010	235.957	216.256	110.324	0.	0.	0.
5700	21.046	236.329	216.605	112.427	0.	0.	0.
5800	21.087	236.696	216.949	114.534	0.	0.	0.
5900	21.132	237.057	217.286	116.644	0.	0.	0.
6000	21.182	237.412	217.619	118.760	0.	0.	0.

PREVIOUS: December 1961 (1 atm) CURRENT: September 1984 (1 bar)

$IP(Hg^+, g) = 151280 \pm 10\ cm^{-1}$
$S°(298.15\ K) = 224.617 \pm 0.025\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1071.57 \pm 4.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [1074.623]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2
$^2D_{5/2}$	35514	6
$^2D_{3/2}$	50552	4
$^2P_{1/2}$	51485	2
$^2P_{3/2}$	60608	4

Enthalpy of Formation

$\Delta_f H°(Hg^+, g, 0\ K)$ is calculated from $\Delta_f H°(Hg, g, 0\ K)$[1] using the spectroscopic value of IP(Hg) = 84184.1 ± 0.5 cm^{-1}(1007.066 ± 0.006 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Hg^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Hg, g, 0\ K)$ by using IP(Hg) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for Hg(g), $Hg^+(g)$, and e^-(ref). $\Delta_f H°(Hg \rightarrow Hg^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting of the summation in the partition functions[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is approximately 79704 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−6.197	1071.571		
100	20.786	158.026	199.213	−4.119			
150	20.786	166.454	186.983	−3.079			
200	20.786	172.434	182.634	−2.040			
250	20.786	177.072	181.075	−1.001			
298.15	20.786	180.733	180.733	.000	1074.623	1037.151	−181.704
300	20.786	180.862	180.733	.038	1074.648	1036.918	−180.543
350	20.786	184.066	180.986	1.078	1075.337	1030.575	−153.805
400	20.786	186.841	181.549	2.117	1076.040	1024.133	−133.738
450	20.786	189.290	182.275	3.156	1076.752	1017.602	−118.120
500	20.786	191.480	183.088	4.196	1077.470	1010.991	−105.618
600	20.786	195.269	184.812	6.274	1078.913	997.560	−86.845
700	20.786	198.474	186.541	8.353	1021.596	990.459	−73.909
800	20.786	201.249	188.210	10.431	1023.675	985.868	−64.371
900	20.786	203.697	189.797	12.510	1025.753	981.018	−56.937
1000	20.786	205.887	191.299	14.589	1027.832	975.936	−50.978
1100	20.786	207.869	192.716	16.667	1029.911	970.646	−46.092
1200	20.786	209.677	194.056	18.746	1031.989	965.166	−42.013
1300	20.786	211.341	195.322	20.824	1034.068	959.513	−38.554
1400	20.786	212.881	196.522	22.903	1036.146	953.700	−35.583
1500	20.786	214.315	197.661	24.982	1038.225	947.739	−33.003
1600	20.786	215.657	198.744	27.060	1040.304	941.639	−30.741
1700	20.786	216.917	199.777	29.139	1042.382	935.408	−28.742
1800	20.786	218.105	200.762	31.217	1044.461	929.056	−26.960
1900	20.786	219.229	201.705	33.296	1046.539	922.588	−25.364
2000	20.786	220.295	202.608	35.375	1048.618	916.010	−23.924
2100	20.786	221.309	203.474	37.453	1050.697	909.329	−22.618
2200	20.786	222.276	204.307	39.532	1052.775	902.548	−21.429
2300	20.786	223.200	205.109	41.611	1054.854	895.673	−20.341
2400	20.786	224.085	205.881	43.689	1056.932	888.708	−19.342
2500	20.786	224.933	206.626	45.768	1059.011	881.656	−18.421
2600	20.786	225.749	207.346	47.846	1061.090	874.520	−17.569
2700	20.786	226.533	208.042	49.925	1063.168	867.305	−16.779
2800	20.786	227.289	208.716	52.004	1065.247	860.013	−16.044
2900	20.786	228.019	209.369	54.082	1067.325	852.646	−15.358
3000	20.786	228.723	210.003	56.161	1069.404	845.208	−14.716
3100	20.787	229.405	210.618	58.239	1071.483	837.701	−14.115
3200	20.787	230.065	211.215	60.318	1073.561	830.126	−13.550
3300	20.787	230.704	211.796	62.397	1075.640	822.487	−13.019
3400	20.788	231.325	212.362	64.476	1077.719	814.784	−12.518
3500	20.788	231.928	212.912	66.554	1079.797	807.021	−12.044
3600	20.789	232.513	213.448	68.633	1081.876	799.198	−11.596
3700	20.791	233.083	213.971	70.712	1083.955	791.317	−11.171
3800	20.793	233.637	214.482	72.791	1086.034	783.380	−10.768
3900	20.795	234.177	214.980	74.871	1088.113	775.388	−10.385
4000	20.798	234.704	215.466	76.950	1090.192	767.343	−10.020
4100	20.801	235.218	215.942	79.030	1092.271	759.246	−9.673
4200	20.805	235.719	216.407	81.111	1094.350	751.099	−9.341
4300	20.811	236.208	216.862	83.191	1096.429	742.901	−9.024
4400	20.817	236.687	217.307	85.273	1098.509	734.656	−8.721
4500	20.824	237.155	217.743	87.355	1100.589	726.363	−8.431
4600	20.833	237.613	218.170	89.438	1102.668	718.024	−8.153
4700	20.843	238.061	218.588	91.521	1104.748	709.640	−7.887
4800	20.855	238.500	218.998	93.606	1106.828	701.211	−7.631
4900	20.868	238.930	219.401	95.693	1108.909	692.739	−7.385
5000	20.883	239.352	219.796	97.780	1110.989	684.225	−7.148
5100	20.901	239.765	220.183	99.869	1113.069	675.669	−6.920
5200	20.920	240.171	220.564	101.960	1115.150	667.072	−6.701
5300	20.942	240.570	220.937	104.053	1117.230	658.435	−6.489
5400	20.966	240.962	221.305	106.149	1119.311	649.759	−6.285
5500	20.993	241.347	221.665	108.247	1121.391	641.045	−6.088
5600	21.022	241.725	222.020	110.347	1123.471	632.292	−5.898
5700	21.054	242.098	222.369	112.451	1125.550	623.503	−5.714
5800	21.089	242.464	222.713	114.558	1127.630	614.677	−5.536
5900	21.127	242.825	223.050	116.669	1129.708	605.815	−5.363
6000	21.168	243.180	223.383	118.784	1131.786	596.918	−5.197

PREVIOUS: CURRENT: September 1984 (1 bar)

$S°(298.15\ K) = 280.752\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 138.82\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 133.47 \pm 4.6\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma$	0	2

$\omega_e = 125.0\ cm^{-1}$ $\omega_e x_e = 1.00\ cm^{-1}$ $\sigma = 1$

$B_e = [0.0351]\ cm^{-1}$ $\alpha_e = [0.0003]\ cm^{-1}$ $r_e = [2.49]$ Å

Enthalpy of Formation

Wieland and Herczog[1] gave 8.3 ± 1.1 kcal·mol^{-1} for the enthalpy of dissociation into gaseous atoms.

Heat Capacity and Entropy

Vibrational constants were taken from Wieland.[2] Rotational constants are estimated using equation III–123 in Herzberg.[3] The bond length was estimated to be 0.965 of the mercuric bond length by analogy with the mercury chlorides.

References

[1]K. Wieland and A Herczog, Helv. Chim. Acta, **32**, 889, (1949).
[2]K. Wieland, Zeits, F. Electrochemie **64**, 761 (1960).
[3]G. Herzberg, "Spectra of Diatomic Molecules," D. van Nostrand, New York, (1950); refer to p 108.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.595	138.817	138.817	INFINITE
100	35.757	240.288	314.043	−7.375	138.805	121.548	−63.490
200	37.382	265.715	284.205	−3.698	137.432	104.789	−27.368
250	37.696	274.092	281.375	−1.821	134.298	96.877	−20.241
298.15	37.919	280.752	280.752	0.	133.470	89.745	−15.723
300	37.926	280.986	280.752	0.070	133.438	89.474	−15.579
350	38.116	286.847	281.215	1.971	132.543	82.216	−12.270
400	38.284	291.948	282.245	3.881	123.664	75.362	−9.841
450	38.438	296.466	283.578	5.799	122.199	69.412	−8.057
500	38.585	300.524	285.074	7.725	100.682	65.524	−6.845
600	38.864	307.583	288.254	11.598	99.964	58.561	−5.098
700	39.132	313.594	291.455	15.497	40.506	58.287	−4.349
800	39.394	318.837	294.557	19.424	40.464	60.830	−3.972
900	39.653	323.492	297.518	23.376	40.443	63.377	−3.678
1000	39.910	327.683	300.329	27.354	40.441	65.926	−3.444
1100	40.166	331.499	302.992	31.358	40.459	68.474	−3.252
1200	40.420	335.005	305.515	35.387	40.493	71.019	−3.091
1300	40.674	338.250	307.910	39.442	40.541	73.561	−2.956
1400	40.928	341.274	310.186	43.522	40.599	76.099	−2.839
1500	41.181	344.106	312.354	47.628	40.663	78.633	−2.738
1600	41.434	346.772	314.423	51.759	40.726	81.162	−2.650
1700	41.687	349.291	316.400	55.915	40.786	83.687	−2.571
1800	41.940	351.681	318.295	60.096	40.838	86.209	−2.502
1900	42.192	353.956	320.112	64.303	40.881	88.729	−2.439
2000	42.444	356.126	321.859	68.534	40.914	91.246	−2.383
2100	42.697	358.203	323.541	72.791	40.938	93.762	−2.332
2200	42.949	360.195	325.162	77.074	40.957	96.277	−2.286
2300	43.201	362.110	326.727	81.381	40.973	98.791	−2.244
2400	43.453	363.954	328.240	85.714	40.992	101.305	−2.205
2500	43.705	365.733	329.704	90.072	41.020	103.817	−2.169
2600	43.957	367.452	331.123	94.455	41.061	106.328	−2.136
2700	44.209	369.116	332.500	98.863	41.122	108.838	−2.106
2800	44.461	370.728	333.836	103.297	41.209	111.344	−2.077
2900	44.713	372.293	335.136	107.756	41.327	113.847	−2.051
3000	44.965	373.813	336.400	112.239	41.481	116.345	−2.026
3100	45.217	375.291	337.630	116.749	41.674	118.837	−2.002
3200	45.469	376.731	338.830	121.283	41.912	121.323	−1.980
3300	45.721	378.134	340.000	125.842	42.196	123.800	−1.960
3400	45.973	379.502	341.142	130.427	42.530	126.268	−1.940
3500	46.225	380.839	342.257	135.037	42.915	128.726	−1.921
3600	46.476	382.144	343.347	139.672	43.352	131.171	−1.903
3700	46.728	383.421	344.413	144.332	43.844	133.604	−1.886
3800	46.980	384.671	345.456	149.018	44.389	136.023	−1.870
3900	47.232	385.894	346.477	153.728	44.990	138.427	−1.854
4000	47.484	387.093	347.477	158.464	45.645	140.814	−1.839
4100	47.736	388.269	348.458	163.225	46.355	143.185	−1.824
4200	47.988	389.422	349.420	168.011	47.119	145.537	−1.810
4300	48.239	390.554	350.363	172.823	47.936	147.871	−1.796
4400	48.491	391.666	351.289	177.659	48.806	150.185	−1.783
4500	48.743	392.759	352.199	182.521	49.729	152.479	−1.770
4600	48.995	393.833	353.092	187.408	50.702	154.751	−1.757
4700	49.247	394.889	353.970	192.320	51.726	157.003	−1.745
4800	49.498	395.929	354.834	197.257	52.799	159.231	−1.733
4900	49.750	396.952	355.683	202.219	53.920	161.437	−1.721
5000	50.002	397.960	356.518	207.207	55.088	163.619	−1.709
5100	50.254	398.952	357.341	212.220	56.302	165.778	−1.698
5200	50.506	399.931	358.150	217.258	57.561	167.913	−1.687
5300	50.757	400.895	358.948	222.321	58.864	170.022	−1.676
5400	51.009	401.846	359.733	227.409	60.210	172.107	−1.665
5500	51.261	402.784	360.507	232.523	61.598	174.166	−1.654
5600	51.513	403.710	361.271	237.661	63.025	176.201	−1.644
5700	51.765	404.624	362.023	242.825	64.493	178.208	−1.633
5800	52.016	405.527	362.766	248.014	65.998	180.190	−1.623
5900	52.268	406.418	363.498	253.229	67.541	182.146	−1.613
6000	52.520	407.299	364.221	258.468	69.120	184.075	−1.603

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

Mercury Iodide (HgI_2) CRYSTAL $M_r = 454.3990$

$S°(298.15\ K) = [181.326 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 402\ K$
$T_{fus} = 530\ K$

$\Delta_f H°(298.15\ K) = -105.437 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 2.515 \pm 0.17\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 18.966 \pm 0.21\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The value recommended by NBS[1] is adopted.

Heat Capacity and Entropy

The heat capacity is calculated from the enthalpy data of Guinchant[2] and Ewald.[3] The entropy is estimated by adjusting its value to provide the best fit of the melting, sublimation and vaporization phenomena.

Transition and Fusion Data

The enthalpy of transition, $\Delta_{trs} H° = 0.601 \pm 0.04\ kcal \cdot mol^{-1}$, and the temperature of transition are taken from NBS.[1] The enthalpy of melting, $\Delta_{fus} H° = 4.533 \pm 0.05\ kcal \cdot mol^{-1}$ was taken from Guinchant,[2] the temperature of melting from NBS.[1]

References

[1]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[2]M. Guinchant, Comp. Rend. **68**, 145 (1907).
[3]R. Ewald, Ann. d. Physik (4) **44**, 1213 (1914).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	77.747	181.326	181.326	0.	−105.437	−102.204	17.906
300	77.822	181.807	181.328	0.144	−105.445	−102.184	17.792
400	82.006	204.768	184.430	8.135	−121.858	−100.476	13.121
402.000	82.090	205.178	184.532	8.299	I <--> II		
402.000	84.119	211.433	184.532	10.814	TRANSITION		
500	84.119	229.784	191.669	19.058	−161.859	−91.667	9.576
530.000	84.119	234.686	193.966	21.581	----- II <--> LIQUID -----		
600	84.119	245.121	199.338	27.470	−159.916	−77.812	6.774
700	84.119	258.088	206.828	35.882	−216.745	−57.709	4.306
800	84.119	269.320	213.954	44.294	−214.191	−35.164	2.296
900	84.119	279.228	220.667	52.705	−211.648	−12.939	0.751
1000	84.119	288.091	226.974	61.117	−209.116	9.004	−0.470
1100	84.119	296.109	232.900	69.529	−206.598	30.694	−1.458
1200	84.119	303.428	238.477	77.941	−204.098	52.156	−2.270
1300	84.119	310.161	243.735	86.353	−201.620	73.410	−2.950
1400	84.119	316.395	248.706	94.765	−199.174	94.474	−3.525
1500	84.119	322.199	253.414	103.177	−196.768	115.364	−4.017

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = [215.663]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 530\ K$

$\Delta_f H°(298.15\ K) = [-87.287]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 18.966 \pm 0.21\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(HgI_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(HgI_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(530\ K) H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Heat capacity measurements were obtained from the data of Guinchant[1] in the range 540–600 K and were assumed constant above and below this range. A glass type transition is assumed at 353 K below which the heat capacity is assumed to be that of HgI_2(cr). $S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion and Vaporization Data

$T_{vap} = 627$ K (1 atm) is taken from NBS,[2] $\Delta_{vap} H° = 14.141 \pm 0.25\ kcal·mol^{-1}$ (for $T_{vap} = 627$ K) was obtained from the data of Prideaux[3] and Johnson.[4]

References

[1]M. Guinchant, Compt. Rend. **68**, 145 (1907).
[2]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).
[3]E. B. R. Prideaux, J. Chem. Soc. (London) **97**, 2032 (1910).
[4]F. M. G. Johnson, J. Amer. Chem. Soc. **33**, 777 (1911).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹			kJ·mol⁻¹		
0							
100							
200							
250							
298.15	77.747	215.663	215.663	0.	−87.287	−94.291	16.519
300	77.822	216.144	215.665	0.144	−87.295	−94.335	16.425
353.000	80.040	228.980	216.722	4.327	GLASS <--> LIQUID		
353.000	102 .090	228.980	216.722	4.327	TRANSITION		
400	102.090	241.741	218.928	9.125	−102.717	−96.125	12.553
500	102.090	264.522	225.853	19.334	−143.432	−90.609	9.466
530.000	102 .090	270.471	228.212	22.397	----- II <--> LIQUID -----		
600	102.090	283.135	233.896	29.543	−139.692	−80.396	6.999
700	102.090	298.872	242.083	39.752	−194.724	−64.237	4.793
800	102.090	312.504	250.053	49.961	−190.373	−45.893	2.997
900	102.090	324.529	257.673	60.170	−186.033	−28.094	1.631
1000	102.090	335.285	264.906	70.379	−181.704	−10.778	0.563
1100	102.090	345.015	271.753	80.588	−177.389	6.106	−0.290
1200	102.090	353.898	278.234	90.797	−173.091	22.597	−0.984
1300	102.090	362.070	284.373	101.006	−168.817	38.731	−1.556
1400	102.090	369.635	290.196	111.215	−164.574	54.537	−2.035
1500	102.090	376.679	295.729	121.424	−160.371	70.041	−2.439

PREVIOUS: CURRENT: March 1962

0	to	402 K	crystal, I
402	to	530 K	crystal, II
above		530 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	77.747	181.326	181.326	0.	−105.437	−102.204	17.906
300	77.822	181.807	181.328	0.144	−105.445	−102.184	17.792
400	82.006	204.768	184.430	8.135	−121.858	−100.476	13.121
402.000	82.090	205.178	184.532	8.299	I <--> II TRANSITION		
402.000	84.119	211.433	184.532	10.814			
500	84.119	229.784	191.669	19.058	−161.859	−91.667	9.576
530.000	84.119	234.686	193.966	21.581	II <--> LIQUID TRANSITION		
530.000	102 .090	270.471	193.966	40.547			
600	102.090	283.135	203.646	47.694	−139.692	−80.396	6.999
700	102.090	298.872	216.154	57.903	−194.724	−64.237	4.793
800	102.090	312.504	227.365	68.112	−190.373	−45.893	2.997
900	102.090	324.529	237.506	78.321	−186.033	−28.094	1.631
1000	102.090	335.285	246.756	88.529	−181.704	−10.778	0.563
1100	102.090	345.015	255.253	98.738	−177.389	6.106	−0.290
1200	102.090	353.898	263.109	108.947	−173.091	22.597	−0.984
1300	102.090	362.070	270.411	119.156	−168.817	38.731	−1.556
1400	102.090	369.635	277.232	129.365	−164.574	54.537	−2.035
1500	102.090	376.679	283.629	139.574	−160.371	70.041	−2.439

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = 336.206\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -9.84\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -16.13 \pm 2.1\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
156 (1)
33 (2)
[233](1)

Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distance: Hg–I = 2.58 Å
Bond Angle: I–Hg–I = 180°
Rotational Constant: $B_o = 0.009978\ cm^{-1}$

Enthalpy of Formation

The enthalpy of formation of the crystal as given in National Bureau of Standards[1] was combined with the 3rd law heat of sublimation at 298.15 K derived from the data of Niwa and Shibata,[2] Magee[3] and Johnson.[4]

Heat Capacity and Entropy

The vibrational constants were given by Klemperer and Lindeman.[5] The anti-symmetric stretching frequency is estimated by analogy with the bromide and chloride. The bond length is an average of the values given by Braune and Knoke,[6] Gregg *et al.*[7] and Akishin *et al.*[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.253	−9.841	−9.841	INFINITE
100	54.486	272.205	389.418	−11.721	−10.065	−27.465	14.346
200	59.759	312.043	341.763	−5.944	−11.805	−44.218	11.549
250	60.630	325.481	337.210	−2.932	−15.118	−52.052	10.876
298.15	61.118	336.206	336.206	0.	−16.129	−59.074	10.349
300	61.132	336.584	336.207	0.113	−16.169	−59.340	10.332
350	61.446	346.033	336.952	3.178	−17.305	−66.448	9.917
400	61.654	354.252	338.612	6.256	−34.430	−72.842	9.512
450	61.798	361.523	340.762	9.342	−36.743	−77.504	8.996
500	61.903	368.040	343.169	12.435	−79.175	−78.110	8.160
600	62.040	379.339	348.284	18.633	−79.445	−77.872	6.779
700	62.124	388.909	353.422	24.841	−138.478	−71.017	5.299
800	62.178	397.209	358.388	31.057	−138.120	−61.404	4.009
900	62.216	404.534	363.116	37.276	−137.769	−51.836	3.008
1000	62.243	411.091	367.592	43.499	−137.427	−42.306	2.210
1100	62.263	417.024	371.820	49.725	−137.095	−32.810	1.558
1200	62.278	422.443	375.816	55.952	−136.780	−23.344	1.016
1300	62.290	427.428	379.597	62.180	−136.486	−13.903	0.559
1400	62.299	432.044	383.180	68.410	−136.222	−4.484	0.167
1500	62.307	436.343	386.583	74.640	−135.997	4.918	−0.171
1600	62.313	440.364	389.820	80.871	−135.822	14.307	−0.467
1700	62.318	444.142	392.905	87.103	−135.705	23.686	−0.728
1800	62.322	447.704	395.852	93.335	−135.652	33.060	−0.959
1900	62.326	451.074	398.670	99.567	−135.669	42.433	−1.167
2000	62.329	454.271	401.371	105.800	−135.755	51.808	−1.353
2100	62.332	457.312	403.963	112.033	−135.909	61.190	−1.522
2200	62.334	460.212	406.454	118.266	−136.124	70.580	−1.676
2300	62.336	462.983	408.852	124.500	−136.395	79.982	−1.816
2400	62.338	465.636	411.164	130.733	−136.710	89.396	−1.946
2500	62.340	468.181	413.394	136.967	−137.058	98.824	−2.065
2600	62.341	470.626	415.548	143.201	−137.429	108.267	−2.175
2700	62.342	472.978	417.632	149.435	−137.811	117.724	−2.278
2800	62.343	475.246	419.649	155.670	−138.191	127.195	−2.373
2900	62.344	477.433	421.604	161.904	−138.560	136.680	−2.462
3000	62.345	479.547	423.501	168.139	−138.907	146.177	−2.545
3100	62.346	481.591	425.342	174.373	−139.225	155.685	−2.623
3200	62.347	483.571	427.131	180.608	−139.505	165.203	−2.697
3300	62.347	485.489	428.870	186.842	−139.742	174.729	−2.766
3400	62.348	487.350	430.563	193.077	−139.931	184.261	−2.831
3500	62.349	489.158	432.211	199.312	−140.067	193.799	−2.892
3600	62.349	490.914	433.818	205.547	−140.149	203.339	−2.950
3700	62.350	492.622	435.384	211.782	−140.173	212.881	−3.005
3800	62.350	494.285	436.912	218.017	−140.138	222.422	−3.057
3900	62.350	495.905	438.404	224.252	−140.044	231.962	−3.107
4000	62.351	497.483	439.862	230.487	−139.891	241.499	−3.154
4100	62.351	499.023	441.286	236.722	−139.679	251.031	−3.198
4200	62.352	500.526	442.679	242.957	−139.409	260.558	−3.241
4300	62.352	501.993	444.041	249.192	−139.082	270.077	−3.281
4400	62.352	503.426	445.374	255.428	−138.698	279.588	−3.319
4500	62.352	504.827	446.680	261.663	−138.261	289.090	−3.356
4600	62.353	506.198	447.959	267.898	−137.771	298.581	−3.390
4700	62.353	507.539	449.213	274.133	−137.230	308.061	−3.424
4800	62.353	508.852	450.441	280.369	−136.640	317.529	−3.455
4900	62.353	510.137	451.647	286.604	−136.003	326.985	−3.486
5000	62.353	511.397	452.829	292.839	−135.320	336.426	−3.515
5100	62.354	512.632	453.990	299.075	−134.595	345.854	−3.542
5200	62.354	513.842	455.129	305.310	−133.828	355.268	−3.569
5300	62.354	515.030	456.248	311.545	−133.021	364.665	−3.594
5400	62.354	516.196	457.347	317.781	−132.178	374.048	−3.618
5500	62.354	517.340	458.428	324.016	−131.298	383.414	−3.641
5600	62.354	518.463	459.490	330.252	−130.385	392.765	−3.664
5700	62.355	519.567	460.534	336.487	−129.440	402.098	−3.685
5800	62.355	520.651	461.561	342.722	−128.465	411.415	−3.705
5900	62.355	521.717	462.572	348.958	−127.462	420.715	−3.725
6000	62.355	522.765	463.567	355.193	−126.432	429.997	−3.743

PREVIOUS: March 1962 (1 atm) CURRENT: March 1962 (1 bar)

$S°(298.15\ K) = 70.270 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -86.208 \pm 0.100\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -90.789 \pm 0.100\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Calculated from the entropy obtained by Bauer and Johnston[1] and the Gibbs energy of formation as determined from the numerous cell measurements described by Bauer and Johnston. The value adopted for $\Delta_f H°(298.15\ K)$ is $-42707 \pm 14\ cal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacity has been measured from 15 to 298.15 K by Bauer and Johnston.[1] The extrapolation below 15 K was done assuming a T^3 law and gave $S°(15\ K) = 0.264\ cal \cdot K^{-1} \cdot mol^{-1}$. Above 298.15 the data was extrapolated smoothly and adjusted to give the observed decomposition vapor pressures of Taylor and Hulett.[2]

Decomposition Data

According to Taylor and Hulett,[2] the vapor pressure reaches 1.89 atmospheres at 749 K. This corresponds to the decomposition to 2 Hg(g) + O_2(g), the equilibrium constant being unity at 1.89 atm.

References

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[2]G. B. Taylor and G. A. Hulett, J. Phys. Chem. **17**, 565 (1913).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.104	−86.208	−86.208	INFINITE
100	28.434	30.840	105.148	−7.431	−87.693	−78.390	40.947
200	38.171	53.856	74.128	−4.054	−88.357	−68.775	17.962
298.15	44.062	70.270	70.270	0.	−90.789	−58.490	10.247
300	44.145	70.543	70.271	0.082	−90.786	−58.289	10.149
400	48.325	83.836	72.055	4.712	−90.406	−47.502	6.203
500	51.631	94.990	75.556	9.717	−89.659	−36.856	3.850
600	54.120	104.632	79.617	15.009	−88.660	−26.386	2.297
700	56.066	113.127	83.809	20.523	−146.248	−9.526	0.711
800	57.509	120.711	87.956	26.204	−144.314	9.874	−0.645
900	58.626	127.553	91.982	32.013	−142.285	29.027	−1.685
1000	59.413	133.773	95.855	37.918	−140.190	47.950	−2.505

PREVIOUS: CURRENT: June 1962

$S°(298.15\ K) = [239.161]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [46.514]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [41.840]\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = [680]\ cm^{-1}$ $\omega_e x_e = [4.7]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.336]\ cm^{-1}$ $\alpha_e = [0.0027]\ cm^{-1}$ $r_e = [1.84]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(HgO, g, 298.15 K), is estimated to be 10 ± 15 kcal·mol^{-1}. This value is obtained from the enthalpy of formation of PbO(g) and comparison of the enthalpy of formation of analogous lead and mercury compounds using the method of Karapet'yants.[1] The corresponding dissociation energy, $D_0°$(HgO,g) is 64 ± 15 kcal·mol^{-1}.

Heat Capacity and Entropy

The equilibrium internuclear separation (r_e) of HgO(g) is estimated from the corresponding quantity for PbO(g) and comparison of Hg–X and Pb–X bond distances for cases in which values of both distances are known. The rotational constant B_e is calculated from r_e. The fundamental vibrational frequency ω_e is estimated from Guggenheimer's relation for multiple bonded molecules.[2] The anharmonic vibrational term $\omega_e x_e$ is calculated from $\omega_e x_e = \omega_e^2/(4D_0 + 2\ \omega_e)$. The value of α_e is calculated from the Morse potential function. The ground state configuration is estimated from the building–up principle,[3] the united atom theory,[3] and from analogy with BeO.

References

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[2]K. M. Guggenheimer, Proc. Phys. Soc. (London) **58**, 456 (1946).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.010	46.514	46.514	INFINITE
100	29.158	205.913	266.918	−6.101	46.266	38.062	−19.882
200	30.709	226.480	242.102	−3.124	45.202	30.259	−7.903
250	31.874	233.459	239.697	−1.560	42.341	26.742	−5.587
298.15	32.883	239.161	239.161	0.	41.840	23.784	−4.167
300	32.918	239.365	239.162	0.061	41.822	23.672	−4.122
350	33.776	244.506	239.566	1.729	41.362	20.684	−3.087
400	34.460	249.063	240.474	3.436	40.945	17.759	−2.319
450	35.002	253.154	241.659	5.173	40.557	14.884	−1.728
500	35.435	256.865	242.997	6.934	40.187	12.052	−1.259
600	36.068	263.385	245.867	10.511	39.470	6.492	−0.565
700	36.501	268.980	248.778	14.141	−20.001	7.624	−0.569
800	36.811	273.875	251.616	17.807	−20.082	11.575	−0.756
900	37.045	278.225	254.335	21.501	−20.170	15.538	−0.902
1000	37.229	282.138	256.923	25.215	−20.265	19.510	−1.019
1100	37.379	285.693	259.380	28.945	−20.368	23.493	−1.116
1200	37.504	288.951	261.710	32.690	−20.476	27.485	−1.196
1300	37.613	291.958	263.923	36.446	−20.591	31.486	−1.265
1400	37.708	294.749	266.026	40.212	−20.710	35.496	−1.324
1500	37.794	297.353	268.029	43.987	−20.834	39.515	−1.376
1600	37.873	299.795	269.938	47.770	−20.963	43.543	−1.422
1700	37.946	302.093	271.763	51.561	−21.096	47.579	−1.462
1800	38.014	304.264	273.509	55.359	−21.235	51.622	−1.498
1900	38.079	306.321	275.182	59.164	−21.378	55.674	−1.531
2000	38.141	308.276	276.788	62.975	−21.527	59.733	−1.560
2100	38.201	310.138	278.333	66.792	−21.681	63.800	−1.587
2200	38.258	311.917	279.819	70.615	−21.841	67.874	−1.612
2300	38.314	313.619	281.252	74.444	−22.006	71.956	−1.634
2400	38.369	315.250	282.635	78.278	−22.177	76.044	−1.655
2500	38.422	316.818	283.971	82.117	−22.354	80.141	−1.674
2600	38.474	318.326	285.263	85.962	−22.536	84.244	−1.692
2700	38.526	319.779	286.515	89.812	−22.723	88.355	−1.709
2800	38.577	321.181	287.728	93.667	−22.915	92.472	−1.725
2900	38.627	322.535	288.905	97.528	−23.113	96.596	−1.740
3000	38.676	323.846	290.048	101.393	−23.315	100.728	−1.754
3100	38.725	325.115	291.159	105.263	−23.521	104.866	−1.767
3200	38.774	326.345	292.239	109.138	−23.731	109.011	−1.779
3300	38.822	327.539	293.291	113.018	−23.946	113.162	−1.791
3400	38.870	328.698	294.315	116.902	−24.164	117.320	−1.802
3500	38.918	329.826	295.314	120.792	−24.385	121.485	−1.813
3600	38.965	330.923	296.288	124.686	−24.609	125.656	−1.823
3700	39.013	331.991	297.239	128.585	−24.836	129.832	−1.833
3800	39.060	333.032	298.167	132.488	−25.066	134.016	−1.842
3900	39.106	334.047	299.074	136.397	−25.297	138.206	−1.851
4000	39.153	335.038	299.961	140.310	−25.531	142.401	−1.860
4100	39.199	336.005	300.828	144.227	−25.767	146.602	−1.868
4200	39.246	336.951	301.677	148.150	−26.005	150.809	−1.876
4300	39.292	337.875	302.508	152.076	−26.245	155.022	−1.883
4400	39.338	338.778	303.322	156.008	−26.487	159.240	−1.890
4500	39.384	339.663	304.120	159.944	−26.731	163.464	−1.897
4600	39.430	340.529	304.902	163.885	−26.977	167.693	−1.904
4700	39.476	341.378	305.669	167.830	−27.226	171.927	−1.911
4800	39.521	342.209	306.422	171.780	−27.477	176.167	−1.917
4900	39.567	343.025	307.160	175.734	−27.731	180.413	−1.923
5000	39.613	343.824	307.886	179.693	−27.988	184.663	−1.929
5100	39.658	344.609	308.598	183.657	−28.249	188.919	−1.935
5200	39.704	345.380	309.298	187.625	−28.514	193.179	−1.941
5300	39.749	346.137	309.986	191.598	−28.784	197.446	−1.946
5400	39.794	346.880	310.662	195.575	−29.060	201.717	−1.951
5500	39.840	347.611	311.328	199.556	−29.342	205.993	−1.956
5600	39.885	348.329	311.982	203.543	−29.631	210.275	−1.961
5700	39.930	349.035	312.626	207.533	−29.927	214.561	−1.966
5800	39.975	349.730	313.260	211.529	−30.232	218.853	−1.971
5900	40.021	350.414	313.883	215.529	−30.547	223.150	−1.976
6000	40.066	351.087	314.498	219.533	−30.872	227.453	−1.980

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = 241.29 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 563\ K$

$\Delta_f H°(298.15\ K) = -119.085 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [27.196 \pm 8.4]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The average value of the cell measurements of Vosburgh,[1] Cohen,[2] Yoshida,[3] Oholm[4] and the calorimetric values of Varet[5] and Nernst[6] is adopted.

Heat Capacity and Entropy

The heat capacity at 298.15 K is taken from NBS[7] and is estimated above this by analogy with mercurous chloride. The entropy is obtained from the enthalpy and Gibbs energy of formation obtained from the cell measurements listed under enthalpy of formation.

Fusion Data

Yvon[8] gives 563 K for the melting point. The enthalpy of melting is estimated by assuming the entropy of melting per atom to be the same as that for mercuric iodide.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	105.855	241.291	241.291	0.	−119.085	−111.063	19.458
300	105.868	241.946	241.293	0.196	−119.093	−111.013	19.329
400	110.416	273.066	245.506	11.024	−135.435	−107.707	14.065
500	113.679	298.073	253.599	22.237	−177.873	−96.702	10.102
563.000	115 .244	311.658	259.349	29.450	--- CRYSTAL <---> LIQUID ---		
600	116.064	319.018	262.804	33.729	−175.564	−80.680	7.024
700	117.905	337.052	272.152	45.430	−290.578	−51.920	3.874
800	119.411	352.898	281.275	57.298	−286.646	−18.092	1.181
900	120.625	367.034	290.033	69.301	−282.590	15.235	−0.884
1000	121.713	379.800	298.381	81.419	−278.432	48.104	−2.513
1100	122.687	391.447	306.320	93.640	−274.183	80.553	−3.825
1200	123.554	402.161	313.866	105.953	−269.860	112.611	−4.902
1300	124.236	412.076	321.044	118.341	−265.485	144.307	−5.798
1400	125.143	421.314	327.880	130.808	−261.062	175.664	−6.554
1500	126.273	429.986	334.401	143.377	−256.578	206.702	−7.198

PREVIOUS: CURRENT: March 1962

$S°$(298.15 K) = [273.258] J·K^{-1}·mol^{-1}
T_{fus} = 563 K

$\Delta_f H°$(298.15 K) = [−98.564] kJ·mol^{-1}
$\Delta_{fus} H°$ = [27.196 ± 8.4] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(Hg_2I_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(Hg_2I_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(563\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 1.33 times the heat capacity of mercuric iodide. $S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point was given by Yvon.[1] The enthalpy of melting was estimated from that of mercuric iodide, by assuming the entropies of melting per atom to be equal.

Vaporization Data

Mercurous iodide decomposes to Hg(g) and HgI_2(g) at the boiling point which was estimated from the Gibbs energy change of the reaction. For 1 atm, T_{vap} = [630] K (decomposition).

Reference

[1] P. Yvon, Comp. Rend. **76**, 1607 (1873).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	136.398	273.258	273.258	0.	−98.564	−100.073	17.532
300	136.398	274.101	273.260	0.252	−98.516	−100.082	17.426
400	136.398	313.341	278.610	13.892	−112.046	−100.428	13.115
500	136.398	343.777	288.713	27.532	−152.057	−93.738	9.793
563.000	136.398	359.964	295.798	36.125	--- CRYSTAL <--> LIQUID ---		
600	136.398	368.646	300.026	41.172	−147.600	−82.493	7.182
700	136.398	389.672	311.369	54.812	−260.675	−58.850	4.391
800	136.398	407.885	322.321	68.452	−254.971	−30.408	1.985
900	136.398	423.950	332.738	82.091	−249.279	−2.679	0.155
1000	136.398	438.321	342.590	95.731	−243.598	24.416	−1.275
1100	136.398	451.322	351.893	109.371	−237.931	50.943	−2.419
1200	136.398	463.190	360.681	123.011	−232.281	76.955	−3.350
1300	136.398	474.107	368.992	136.651	−226.654	102.496	−4.118
1400	136.398	484.216	376.865	150.291	−221.059	127.605	−4.761
1500	136.398	493.626	384.339	163.930	−215.503	152.316	−5.304

PREVIOUS: CURRENT: March 1962

0	to	563 K	crystal
above		563 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0							
100							
200							
250							
298.15	105.855	241.291	241.291	0.	−119.085	−111.063	19.458
300	105.868	241.946	241.293	0.196	−119.093	−111.013	19.329
400	110.416	273.066	245.506	11.024	−135.435	−107.707	14.065
500	113.679	298.073	253.599	22.237	−177.873	−96.702	10.102
563.000	115.244	311.658	259.349	29.450	CRYSTAL <--> LIQUID		
563.000	136.398	359.964	259.349	56.646	TRANSITION		
600	136.398	368.646	265.824	61.693	−147.600	−82.493	7.182
700	136.398	389.672	282.053	75.333	−260.675	−58.850	4.391
800	136.398	407.885	296.669	88.972	−254.971	−30.408	1.985
900	136.398	423.950	309.937	102.612	−249.279	−2.679	0.155
1000	136.398	438.321	322.069	116.252	−243.598	24.416	−1.275
1100	136.398	451.322	333.238	129.892	−237.931	50.943	−2.419
1200	136.398	463.190	343.580	143.532	−232.281	76.955	−3.350
1300	136.398	474.107	353.206	157.172	−226.654	102.496	−4.118
1400	136.398	484.216	362.207	170.811	−221.059	127.605	−4.761
1500	136.398	493.626	370.659	184.451	−215.503	152.316	−5.304

PREVIOUS: CURRENT: March 1962

IP(I, g) = 84295.1 ± 0.2 cm^{-1}
$S°(298.15\ K)$ = 180.786 ± 0.002 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 107.16 ± 0.04 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 106.76 ± 0.04 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^2P°_{1/2}$	0.0	4
$^2P°_{1/2}$	7603.15	2

Enthalpy of Formation

The adopted value for the enthalpy of formation of I(g) is derived from the spectroscopically determined dissociation energy of I_2(g) as reported by Barrow *et al.*[1,2] This value is also recommended by Brewer and Winn[3] and Huber and Herzberg.[4] The adopted value is $D°_0(I_2, g)$ = 12440.06 ± 0.03 cm^{-1} (148.816 ± 0.001 $kJ·mol^{-1}$). The convergence limit in the absorption spectrum of the $^3\Pi_{0^+_u} - {}^1\Sigma_{+g}$ system corresponds to dissociation to a ground state iodine atom ($^3P_{3/2}$) and an excited state iodine atom ($^3P_{1/2}$).

Using earlier data, the CODATA recommended value[5] was calculated using $D°_0(I_2, g)$ = 12440.9 ± 1.1 cm^{-1} from LeRoy,[6] Brown,[7] LeRoy and Bernstein,[8] and Sitterley.[9] LeRoy,[6] LeRoy and Bernstein,[8] and a recent study by LeRoy and Bernstein[10] obtained the dissociation energy from the analysis of the distribution of the uppermost vibrational levels. Their calculations were based on the data of Brown,[7] with reference to the study by Verma.[11]

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[12,13] Only two levels are included in the calculation. All other levels (observed and predicted) lie above 54633 cm^{-1}. Our calculations indicate that any reasonable method of filling in the missing levels and cutting off the summation in the partition function[14] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels. Therefore, we list only the ground state and the first excited state. Extension to higher temperatures may require consideration of the higher excited states and utilization of different fill and cutoff procedures.

The thermodynamic functions at 298.15 K are in agreement with recent CODATA recommendations[15] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the monatomic halogens arise due to the use of slightly different values for the relative atomic mass and for R; this table uses R 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[16] Gurvich *et al.*[17] and Wagman *et al.*[20] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[18] and the 1973 values,[19] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	107.164	107.164	INFINITE
100	20.786	158.079	199.267	−4.119	107.717	94.959	−49.601
200	20.786	172.487	182.688	−2.040	107.330	82.328	−21.502
250	20.786	177.125	181.128	−1.001	107.055	76.109	−15.902
298.15	20.786	180.786	180.786	0.	106.762	70.174	−12.294
300	20.786	180.915	180.787	0.038	106.750	69.947	−12.179
350	20.786	184.119	181.040	1.078	106.383	63.841	−9.528
400	20.786	186.895	181.602	2.117	98.010	58.064	−7.582
450	20.786	189.343	182.329	3.156	97.032	53.130	−6.167
500	20.786	191.533	183.142	4.196	75.990	50.203	−5.245
600	20.786	195.323	184.866	6.274	76.191	45.027	−3.920
700	20.786	198.527	186.594	8.353	76.386	39.818	−2.971
800	20.787	201.302	188.263	10.432	76.575	34.580	−2.258
900	20.789	203.751	189.851	12.510	76.759	29.320	−1.702
1000	20.795	205.942	191.352	14.589	76.937	24.039	−1.256
1100	20.806	207.924	192.770	16.669	77.110	18.741	−0.890
1200	20.824	209.735	194.109	18.751	77.275	13.428	−0.584
1300	20.851	211.403	195.376	20.835	77.430	8.101	−0.325
1400	20.889	212.949	196.577	22.921	77.574	2.762	−0.103
1500	20.936	214.392	197.717	25.013	77.701	−2.586	0.090
1600	20.994	215.745	198.802	27.109	77.809	−7.942	0.259
1700	21.062	217.020	199.836	29.212	77.894	−13.304	0.409
1800	21.137	218.226	200.825	31.322	77.954	−18.671	0.542
1900	21.220	219.371	201.771	33.440	77.986	−24.040	0.661
2000	21.308	220.461	202.679	35.566	77.992	−29.410	0.768
2100	21.399	221.503	203.550	37.701	77.974	−34.780	0.865
2200	21.493	222.501	204.389	39.846	77.933	−40.148	0.953
2300	21.588	223.458	205.198	42.000	77.875	−45.514	1.034
2400	21.682	224.379	205.978	44.163	77.803	−50.877	1.107
2500	21.775	225.266	206.732	46.336	77.724	−56.237	1.175
2600	21.865	226.122	207.461	48.518	77.643	−61.594	1.237
2700	21.953	226.949	208.168	50.709	77.565	−66.948	1.295
2800	22.036	227.749	208.853	52.909	77.497	−72.299	1.349
2900	22.116	228.523	209.518	55.116	77.442	−77.648	1.399
3000	22.191	229.274	210.164	57.332	77.406	−82.995	1.445
3100	22.261	230.003	210.792	59.554	77.392	−88.342	1.489
3200	22.327	230.711	211.404	61.784	77.403	−93.688	1.529
3300	22.387	231.399	211.999	64.019	77.442	−99.035	1.568
3400	22.443	232.068	212.580	66.261	77.511	−104.384	1.604
3500	22.494	232.720	213.146	68.508	77.612	−109.735	1.638
3600	22.540	233.354	213.698	70.760	77.745	−115.090	1.670
3700	22.581	233.972	214.238	73.016	77.911	−120.448	1.700
3800	22.618	234.575	214.765	75.276	78.110	−125.812	1.729
3900	22.651	235.163	215.281	77.539	78.342	−131.181	1.757
4000	22.679	235.736	215.785	79.806	78.608	−136.557	1.783
4100	22.704	236.297	216.279	82.075	78.905	−141.940	1.808
4200	22.725	236.844	216.762	84.346	79.234	−147.330	1.832
4300	22.743	237.379	217.235	86.620	79.593	−152.729	1.855
4400	22.757	237.902	217.699	88.895	79.983	−158.136	1.877
4500	22.769	238.414	218.153	91.171	80.400	−163.552	1.898
4600	22.777	238.914	218.599	93.448	80.846	−168.979	1.919
4700	22.783	239.404	219.037	95.726	81.318	−174.415	1.938
4800	22.787	239.884	219.466	98.005	81.816	−179.861	1.957
4900	22.788	240.354	219.888	100.284	82.338	−185.318	1.976
5000	22.787	240.814	220.302	102.562	82.883	−190.786	1.993
5100	22.784	241.265	220.708	104.841	83.450	−196.265	2.010
5200	22.780	241.708	221.108	107.119	84.039	−201.755	2.027
5300	22.774	242.142	221.501	109.397	84.648	−207.257	2.043
5400	22.766	242.567	221.887	111.674	85.276	−212.770	2.058
5500	22.757	242.985	222.267	113.950	85.922	−218.296	2.073
5600	22.747	243.395	222.640	116.225	86.586	−223.833	2.088
5700	22.736	243.797	223.008	118.500	87.266	−229.382	2.102
5800	22.724	244.193	223.370	120.773	87.962	−234.943	2.116
5900	22.711	244.581	223.726	123.044	88.673	−240.517	2.129
6000	22.697	244.963	224.077	125.315	89.399	−246.102	2.143

PREVIOUS: June 1974 (1 atm) CURRENT: June 1982 (1 bar)

IP(I^+, g) = 154304 ± 1 cm^{-1}
$S°$(298.15 K) = 182.642 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1115.557 ± 0.05 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1121.353] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
^3P_P	0.0	5
$^3P_1$	7087.0	3
$^3P_0$	6447.9	1
$^1D_2$	13731	5
$^1S_0$	32629	1

Enthalpy of Formation

$\Delta_f H°(I^+, g, 0 K)$ is calculated from $\Delta_f H°(I, g, 0 K)$[1] using the spectroscopic value of IP(I) = 84295.1 ± 0.2 cm^{-1}(1008.39 ± 0.01 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization potential and appearance potential data.

$\Delta_f H°(I^+, g, 298.15 K)$ is calculated from $\Delta_f H°(I, g, 0 K)$ by using IP(I) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for I(g), $I^+(g)$, and e^-(ref). $\Delta_f H°(I \rightarrow I^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the lowest four excited states; the next lowest level is approximately 81040 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and four excited states, with the energy of these states taken from recent study by Moore.[2,6] The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, fundamental constants, and the position of the four lowest excited states. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1115.557		
100	20.786	159.934	201.122	−4.119			
200	20.786	174.342	184.543	−2.040			
250	20.786	178.980	182.984	−1.001			
298.15	20.786	182.642	182.642	0.	1121.353	1077.957	−188.854
300	20.786	182.770	182.642	0.038	1121.379	1077.688	−187.642
350	20.786	185.974	182.895	1.078	1122.052	1070.352	−159.741
400	20.786	188.750	183.457	2.117	1114.718	1063.195	−138.839
450	20.786	191.198	184.184	3.156	1114.780	1056.751	−122.664
500	20.786	193.388	184.997	4.196	1094.777	1052.200	−109.923
600	20.786	197.178	186.721	6.274	1097.057	1043.470	−90.842
700	20.787	200.382	188.449	8.353	1099.330	1034.359	−77.185
800	20.790	203.158	190.118	10.432	1101.598	1024.923	−66.921
900	20.800	205.607	191.706	12.511	1103.861	1015.203	−58.921
1000	20.819	207.800	193.208	14.592	1106.119	1005.231	−52.508
1100	20.852	209.785	194.626	16.675	1108.374	995.032	−47.250
1200	20.903	211.602	195.966	18.763	1110.624	984.629	−42.860
1300	20.974	213.277	197.234	20.857	1112.868	974.039	−39.137
1400	21.065	214.835	198.436	22.959	1115.105	963.276	−35.940
1500	21.176	216.292	199.578	25.070	1117.332	952.353	−33.164
1600	21.305	217.663	200.666	27.194	1119.546	941.282	−30.730
1700	21.450	218.959	201.705	29.332	1121.744	930.073	−28.578
1800	21.608	220.189	202.698	31.485	1123.925	918.735	−26.661
1900	21.776	221.362	203.649	33.654	1126.088	907.277	−24.943
2000	21.952	222.483	204.563	35.840	1128.233	895.705	−23.393
2100	22.134	223.559	205.442	38.045	1130.361	884.026	−21.989
2200	22.320	224.593	206.289	40.267	1132.477	872.246	−20.710
2300	22.506	225.589	207.107	42.509	1134.585	860.370	−19.540
2400	22.693	226.551	207.897	44.769	1136.688	848.403	−18.465
2500	22.879	227.481	208.662	47.047	1138.793	836.348	−17.475
2600	23.062	228.382	209.403	49.344	1140.906	824.208	−16.559
2700	23.241	229.256	210.122	51.659	1143.031	811.987	−15.709
2800	23.416	230.104	210.821	53.992	1145.175	799.687	−14.918
2900	23.587	230.929	211.500	56.343	1147.341	787.310	−14.181
3000	23.751	231.731	212.161	58.710	1149.535	774.858	−13.491
3100	23.910	232.513	212.805	61.093	1151.760	762.332	−12.845
3200	24.062	233.274	213.433	63.491	1154.019	749.734	−12.238
3300	24.208	234.017	214.046	65.905	1156.315	737.065	−11.667
3400	24.346	234.741	214.644	68.333	1158.649	724.325	−11.128
3500	24.478	235.449	215.228	70.774	1161.022	711.517	−10.619
3600	24.603	236.140	215.799	73.228	1163.436	698.639	−10.137
3700	24.720	236.816	216.358	75.694	1165.891	685.695	−9.680
3800	24.830	237.477	216.905	78.172	1168.387	672.683	−9.247
3900	24.933	238.123	217.441	80.660	1170.922	659.605	−8.834
4000	25.029	238.756	217.966	83.158	1173.498	646.462	−8.442
4100	25.118	239.375	218.481	85.666	1176.112	633.254	−8.068
4200	25.200	239.981	218.986	88.182	1178.764	619.981	−7.711
4300	25.276	240.575	219.481	90.705	1181.452	606.645	−7.369
4400	25.345	241.157	219.967	93.236	1184.176	593.246	−7.043
4500	25.407	241.727	220.444	95.774	1186.934	579.785	−6.730
4600	25.464	242.286	220.913	98.318	1189.725	566.262	−6.430
4700	25.514	242.834	221.373	100.867	1192.546	552.678	−6.142
4800	25.559	243.372	221.826	103.420	1195.398	539.034	−5.866
4900	25.598	243.899	222.271	105.978	1198.277	525.330	−5.600
5000	25.632	244.417	222.709	108.540	1201.184	511.567	−5.344
5100	25.661	244.925	223.140	111.104	1204.116	497.746	−5.098
5200	25.685	245.423	223.563	113.672	1207.072	483.866	−4.860
5300	25.705	245.913	223.980	116.241	1210.052	469.930	−4.631
5400	25.720	246.393	224.391	118.813	1213.052	455.937	−4.410
5500	25.732	246.865	224.795	121.385	1216.074	441.889	−4.197
5600	25.739	247.329	225.194	123.959	1219.115	427.786	−3.990
5700	25.743	247.785	225.586	126.533	1222.174	413.628	−3.790
5800	25.743	248.233	225.973	129.107	1225.249	399.416	−3.597
5900	25.740	248.673	226.354	131.682	1228.342	385.151	−3.410
6000	25.734	249.105	226.729	134.255	1231.449	370.833	−3.228

PREVIOUS: CURRENT: June 1982 (1 bar)

EA(I, g) = 3.0591 ± 0.0004 eV
$S°$(298.15 K) = 169.260 ± 0.005 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −187.992 ± 0.4 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [−194.591] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

$\Delta_f H°(I^-, g, 0\ K)$ is calculated from $\Delta_f H°$ (I, g, 0 K)[1] using the adopted electron affinity of EA (I) = 3.0591 ± 0.0004 eV (295.156 ± 0.039 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[6] is based on laser optogalvanic spectroscopy.[5] Additional information on I^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,6] Rosenstock *et al.*[3] and Massey.[4]

$\Delta_f H°(I^-, g, 298.15\ K)$ is obtained from $\Delta_f H°$(I, g, 0 K) by using EA(I) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for I^-(g), I(g), and e^-(ref). $\Delta_r H°(I^- \rightarrow I + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for I^-(g) is given by Hotop and Lineberger,[2,6] Rosenstock *et al.*[3] and Massey.[4] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

The entropy at all temperatures (0–6000 K) agrees within 0.001 J·K^{-1}·mol^{-1} with the values of Gurvich *et al.*[8] except for one minor difference. The entropy differs by 0.1094 J·K^{-1}·mol^{-1} because this table uses a standard-state pressure of 1 bar, whereas the tabulation of Gurvich, *et al.*[8] is based on 1 atm. The estimated uncertainty is due to uncertainties in the relative ionic mass and the fundamental constants which are based on the 1981 scale[9] and the 1973 values,[7] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	−187.992		
100	20.786	146.553	187.740	−4.119			
200	20.786	160.961	171.161	−2.040			
250	20.786	165.599	169.602	−1.001			
298.15	20.786	169.260	169.260	0.	−194.591	−221.488	38.804
300	20.786	169.389	169.260	0.038	−194.642	−221.654	38.593
350	20.786	172.593	169.514	1.078	−196.048	−226.047	33.736
400	20.786	175.368	170.076	2.117	−205.461	−229.961	30.030
450	20.786	177.817	170.803	3.156	−207.477	−232.902	27.035
500	20.786	180.007	171.615	4.196	−229.559	−233.720	24.417
600	20.786	183.796	173.339	6.274	−231.436	−234.376	20.404
700	20.786	187.001	175.068	8.353	−233.320	−234.717	17.515
800	20.786	189.776	176.737	10.431	−235.209	−234.788	15.330
900	20.786	192.224	178.324	12.510	−237.104	−234.621	13.617
1000	20.786	194.414	179.826	14.589	−239.005	−234.243	12.236
1100	20.786	196.396	181.244	16.667	−240.913	−233.675	11.096
1200	20.786	198.204	182.583	18.746	−242.829	−232.932	10.139
1300	20.786	199.868	183.849	20.824	−244.757	−232.029	9.323
1400	20.786	201.408	185.049	22.903	−246.701	−230.977	8.618
1500	20.786	202.842	186.188	24.982	−248.664	−229.786	8.002
1600	20.786	204.184	187.271	27.060	−250.653	−228.463	7.459
1700	20.786	205.444	188.304	29.139	−252.671	−227.014	6.975
1800	20.786	206.632	189.289	31.217	−254.721	−225.446	6.542
1900	20.786	207.756	190.232	33.296	−256.807	−223.763	6.152
2000	20.786	208.822	191.135	35.375	−258.927	−221.969	5.797
2100	20.786	209.836	192.001	37.453	−261.081	−220.068	5.474
2200	20.786	210.803	192.834	39.532	−263.266	−218.064	5.178
2300	20.786	211.727	193.636	41.610	−265.479	−215.960	4.905
2400	20.786	212.612	194.408	43.689	−267.714	−213.759	4.652
2500	20.786	213.461	195.153	45.768	−269.966	−211.465	4.418
2600	20.786	214.276	195.873	47.846	−272.229	−209.080	4.200
2700	20.786	215.060	196.570	49.925	−274.497	−206.608	3.997
2800	20.786	215.816	197.243	52.004	−276.765	−204.053	3.807
2900	20.786	216.546	197.897	54.082	−279.027	−201.416	3.628
3000	20.786	217.250	198.530	56.161	−281.279	−198.701	3.460
3100	20.786	217.932	199.145	58.239	−283.516	−195.912	3.301
3200	20.786	218.592	199.742	60.318	−285.734	−193.050	3.151
3300	20.786	219.231	200.323	62.397	−287.931	−190.120	3.009
3400	20.786	219.852	200.889	64.475	−290.103	−187.123	2.875
3500	20.786	220.454	201.439	66.554	−292.249	−184.063	2.747
3600	20.786	221.040	201.975	68.632	−294.368	−180.942	2.625
3700	20.786	221.610	202.498	70.711	−296.458	−177.762	2.510
3800	20.786	222.164	203.009	72.790	−298.519	−174.527	2.399
3900	20.786	222.704	203.507	74.868	−300.550	−171.237	2.293
4000	20.786	223.230	203.993	76.947	−302.551	−167.896	2.192
4100	20.786	223.743	204.469	79.025	−304.523	−164.505	2.096
4200	20.786	224.244	204.934	81.104	−306.466	−161.067	2.003
4300	20.786	224.733	205.389	83.183	−308.380	−157.582	1.914
4400	20.786	225.211	205.834	85.261	−310.265	−154.053	1.829
4500	20.786	225.678	206.269	87.340	−312.124	−150.482	1.747
4600	20.786	226.135	206.696	89.418	−313.956	−146.870	1.668
4700	20.786	226.582	207.115	91.497	−315.762	−143.218	1.592
4800	20.786	227.020	207.525	93.576	−317.543	−139.528	1.518
4900	20.786	227.448	207.927	95.654	−319.299	−135.801	1.448
5000	20.786	227.868	208.322	97.733	−321.033	−132.039	1.379
5100	20.786	228.280	208.709	99.811	−322.744	−128.241	1.313
5200	20.786	228.684	209.089	101.890	−324.434	−124.411	1.250
5300	20.786	229.079	209.463	103.969	−326.103	−120.549	1.188
5400	20.786	229.468	209.830	106.047	−327.752	−116.655	1.128
5500	20.786	229.849	210.190	108.126	−329.381	−112.731	1.071
5600	20.786	230.224	210.545	110.204	−330.993	−108.777	1.015
5700	20.786	230.592	210.893	112.283	−332.587	−104.795	0.960
5800	20.786	230.953	211.236	114.362	−334.164	−100.784	0.908
5900	20.786	231.309	211.573	116.440	−335.724	−96.747	0.857
6000	20.786	231.658	211.905	118.519	−337.269	−92.684	0.807

PREVIOUS: CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 106.387\ J·K^{-1}·mol^{-1}$
$T_{fus} = 954\ K$

$\Delta_f H°(0\ K) = -326.93 \pm 0.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -327.90 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 24.016\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of KI(cr) have been critically reviewed by Parker.[1] Six pertinent results are quoted in the table below. Adopting the best value, $\Delta_\infty H°(298.15\ K) = 4.86 \pm 0.03\ kcal·mol^{-1}$, reported by Parker, and $\Delta_f H°(298.15\ K) = -60.32$ and $-13.19\ kcal·mol^{-1}$ for K^+(aq, ∞) and I (aq, ∞), respectively, obtained from,[2] we obtain $\Delta_f H°$(KI, cr, 298.15 K) = $-78.37 \pm 0.1\ kcal·mol^{-1}$, which is adopted.

$\Delta_f H°$, kcal·mol^{-1}(a)	T/°C	n(b)	Source
4.830 ± 0.05	19	200	Thomsen[3]
4.897 ± 0.04	25	18	Wust and Lange[4]
4.873	25	500	Lange and Martin[5]
4.790 ± 0.10	20.5	600	Popov *et al.*[6]
5.020	24.5	18.5	Bobtelsky and Lairsch[7]
4.830 ± 0.07	25	75000	Kapustinskii and Drakin[8]

a Values are adjusted to 298.15 K and to infinite dilution.
b n is the number of moles of H_2O per mole of KI(cr) in solution.

Heat Capacity and Entropy

The low temperature heat capacities are based on those measured by Berg and Morrison,[9] 2.86–268.0 K. The adopted values are in good agreement with the $C_p°$ values reported by Scales,[10] 2–7 K. The data of Clusius *et al.*,[11] 10.27–269.9 K, appear to be too low in the temperature range 70–270 K and are not used. Low temperature enthalpies, 83–273 K, have been measured by Koref.[12] The value of $S°(298.15\ K)$ is derived based on the adopted low temperature heat capacities, using $S°(2.86\ K) = 0.0033\ cal·K^{-1}·mol^{-1}$.

The high temperature enthalpies were determined by Skuratov and Lapushkin,[13] 623–923 K; Dworkin,[14] 854–954 K; and Cooper,[15] 297–973 K. Heat capacities are derived from the enthalpies by a curve fitting method which requires a smooth joint with the low temperature $C_p°$. Enthalpy values used in the curve fit include smooth values calculated from the equation of Skuratov and the value $H°(954)-H°(298.15) = 9.2\ kcal·mol^{-1}$ from Dworkin. Deviation of the input values from the selected enthalpies are all less than 0.3 percent, while the deviations of the data of Cooper range from +1.0 at 570 K to −1.6 percent at 974 K. Since the latter point is 20 above the melting point, there appears to be an error in Cooper's measurement of temperature. $C_p°$ above the melting point is obtained by graphical extrapolation.

Fusion Data

T_{fus} has been reported to be 953, 952, and 954 K by Ray and Dayal,[16] Phipps and Partridge,[17] and Johnson and Bredig,[18] respectively. The latter value is adopted. The enthalpy of fusion was determined by Dworkin and Bredig,[19] using drop calorimetry

Sublimation Data

The difference between $\Delta_f H°(298.15\ K)$ for KI(g) and KI(cr) is $\Delta_{sub} H°$(to monomer, 298.15 K). The $\Delta_{sub} H°$(to dimer, 298.15 K K) is calculated as the enthalpy change for the following reaction: $2KI(cr) = K_2I_2(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.711	−326.930	−326.930	INFINITE
100	45.003	52.413	151.616	−9.920	−327.397	−326.028	170.300
200	50.518	85.772	111.148	−5.075	−327.612	−324.572	84.770
298.15	52.777	106.387	106.387	0.	−327.900	−323.024	56.592
300	52.806	106.713	106.388	0.098	−327.907	−322.994	56.238
400	53.932	122.054	108.472	5.433	−338.870	−320.549	41.859
500	55.363	134.235	112.446	10.894	−360.614	−313.870	32.790
600	57.300	144.490	116.953	16.522	−359.903	−304.584	26.516
700	59.777	153.503	121.543	22.372	−358.933	−295.437	22.046
800	62.639	161.668	126.055	28.490	−357.681	−286.448	18.703
900	65.793	169.225	130.437	34.909	−356.140	−277.633	16.113
954.000	67.594	173.111	132.743	38.510	--- CRYSTAL <--> LIQUID ---		
1000	69.036	176.329	134.674	41.654	−354.308	−269.006	14.051
1100	71.546	183.033	138.769	48.691	−431.198	−255.964	12.155
1200	73.136	189.332	142.723	55.930	−427.954	−240.176	10.455
1300	74.090	195.226	146.537	63.295	−424.595	−224.663	9.027
1400	74.601	200.737	150.214	70.732	−421.182	−209.412	7.813
1500	74.927	205.895	153.756	78.209	−417.748	−194.405	6.770
1600	75.145	210.739	157.168	85.713	−414.313	−179.628	5.864
1700	75.234	215.297	160.454	93.232	−410.894	−165.065	5.072
1800	75.291	219.599	163.622	100.759	−407.503	−150.702	4.373
1900	75.317	223.671	166.676	108.290	−404.146	−136.527	3.753
2000	75.312	227.534	169.623	115.821	−400.829	−122.528	3.200

PREVIOUS: December 1961 CURRENT: June 1967

$S°(298.15\ K) = [114.098]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 954\ K$

$\Delta_f H°(298.15\ K) = [-312.846]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 24.016\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(KI, l, 298.15 K), is calculated from $\Delta_f H°$(KI, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(954\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived as 17.3 cal $K^{-1}·mol^{-1}$ from the enthalpy measurements, 954–1014K, by Dworkin.[1] This $C_p°$ value is adopted in the temperature range 298.15 K. $S°$(298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point, T_{vap} = 1618 K (1 atm), is calculated as the temperature at which the sum of the partial pressure of KI(g) and K_2I_2(g) over KI(l) equals one atmosphere. The value of $\Delta_{vap}H°$ is calculated as the heat required to produce one mole of vapor mixture, which contains 78 percent monomer (KI) and 22 percent dimer (K_2I_2) at T_{vap}.

T_{vap} was reported as 1603 and 1590 K by Wartenberg and Albrecht,[2] and Ruff and Mugdan,[3] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	72.383	114.098	114.098	0.	−312.846	−310.269	54.358
300	72.383	114.546	114.100	0.134	−312.817	−310.253	54.020
400	72.383	135.369	116.939	7.372	−321.876	−308.881	40.336
500	72.383	151.521	122.300	14.611	−341.844	−303.743	31.732
600	72.383	164.718	128.303	21.849	−339.522	−296.340	25.799
700	72.383	175.876	134.323	29.087	−337.163	−289.329	21.590
800	72.383	185.541	140.135	36.326	−334.792	−282.657	18.456
900	72.383	194.067	145.663	43.564	−332.431	−276.282	16.035
954.000	72.383	198.285	148.523	47.473	--- CRYSTAL <--> LIQUID ---		
1000	72.383	201.693	150.891	50.802	−330.106	−270.169	14.112
1100	72.383	208.592	155.828	58.040	−406.794	−259.675	12.331
1200	72.383	214.890	160.491	65.279	−403.551	−246.444	10.727
1300	72.383	220.684	164.902	72.517	−400.320	−233.483	9.381
1400	72.383	226.048	169.080	79.755	−397.104	−220.770	8.237
1500	72.383	231.042	173.046	86.994	−393.909	−208.286	7.253
1600	72.383	235.714	176.819	94.232	−390.740	−196.015	6.399
1700	72.383	240.102	180.413	101.470	−387.602	−183.941	5.652
1800	72.383	244.239	183.845	108.709	−384.499	−172.051	4.993
1900	72.383	248.153	187.128	115.947	−381.435	−160.332	4.408
2000	72.383	251.866	190.273	123.185	−378.411	−148.773	3.886
2100	72.383	255.397	193.291	130.424	−375.428	−137.365	3.417
2200	72.383	258.764	196.191	137.662	−372.485	−126.098	2.994
2300	72.383	261.982	198.982	144.900	−369.581	−114.963	2.611
2400	72.383	265.063	201.671	152.139	−366.713	−103.955	2.263
2500	72.383	268.017	204.267	159.377	−363.879	−93.065	1.944

PREVIOUS: December 1961 CURRENT: June 1967

0 to 954 K crystal
above 954 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.711	−326.930	−326.930	INFINITE
100	45.003	52.413	151.616	−9.920	−327.397	−326.028	170.300
200	50.518	85.772	111.148	−5.075	−327.612	−324.572	84.770
298.15	52.777	106.387	106.387	0.	−327.900	−323.024	56.592
300	52.806	106.713	106.388	0.098	−327.907	−322.994	56.238
400	53.932	122.054	108.472	5.433	−338.870	−320.549	41.859
500	55.363	134.235	112.446	10.894	−360.614	−313.870	32.790
600	57.300	144.490	116.953	16.522	−359.903	−304.584	26.516
700	59.777	153.503	121.543	22.372	−358.933	−295.437	22.046
800	62.639	161.668	126.055	28.490	−357.681	−286.448	18.703
900	65.793	169.225	130.437	34.909	−356.140	−277.633	16.113
954.000	67.594	173.111	132.743	38.510	CRYSTAL <--> LIQUID		
954.000	72.383	198.285	132.743	62.527	TRANSITION		
1000	72.383	201.693	135.837	65.856	−330.106	−270.169	14.112
1100	72.383	208.592	142.143	73.095	−406.794	−259.675	12.331
1200	72.383	214.890	147.946	80.333	−403.551	−246.444	10.727
1300	72.383	220.684	153.322	87.571	−400.320	−233.483	9.381
1400	72.383	226.048	158.327	94.810	−397.104	−220.770	8.237
1500	72.383	231.042	163.010	102.048	−393.909	−208.286	7.253
1600	72.383	235.714	167.410	109.286	−390.740	−196.015	6.399
1700	72.383	240.102	171.558	116.524	−387.602	−183.941	5.652
1800	72.383	244.239	175.482	123.763	−384.499	−172.051	4.993
1900	72.383	248.153	179.205	131.001	−381.435	−160.332	4.408
2000	72.383	251.866	182.746	138.239	−378.411	−148.773	3.886
2100	72.383	255.397	186.122	145.478	−375.428	−137.365	3.417
2200	72.383	258.764	189.348	152.716	−372.485	−126.098	2.994
2300	72.383	261.982	192.437	159.954	−369.581	−114.963	2.611
2400	72.383	265.063	195.399	167.193	−366.713	−103.955	2.263
2500	72.383	268.017	198.245	174.431	−363.879	−93.065	1.944

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 258.283\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -122.08 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -125.52 \pm 2.1\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 186.287 \pm 0.04\ cm^{-1}$ $\omega_e x_e = 0.5725 \pm 0.006\ cm^{-1}$ $\sigma = 1$
$B_e = 0.06072\ cm^{-1}$ $\alpha_e = 0.000267\ cm^{-1}$ $r_e = 3.0478$ Å

Enthalpy of Formation

The enthalpy of formation is derived from the sublimation and vaporization data analyzed below. Many investigators have determined the total pressures of KI(g) and K_2I_2(g) over KI(cr) or KI(l) by static methods or "apparent" pressures by Knudsen effusion or transpiration. These pressures are converted to monomer pressures by use of functions [refer to K_2I_2(g) table] which are consistent with the dimer monomer equilibrium data of Datz.[9] 2nd and 3rd law analyses of the monomer pressures show reasonable agreement. The selected value of $\Delta_f H°(298.15\ K) = -30.0 \pm 0.5\ kcal·mol^{-1}$ is also in good agreement with -30.23 ± 1.15 and $-30.46\ kcal·mol^{-1}$ derived from $D_0° = 3.32 \pm 0.05$ and 3.33 eV reported by Gaydon[10] and Herzberg[11] respectively.

Source	Reactions*	T/K	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
Wartenberg–Albrecht[1]	(B)	1336.2–1606.2	9	47.79 ± 0.38	44.76	−2.1 ± 0.2	−30.01
Ruff–Mugdan[2]	(B)	1319.2–1590.2	12	49.38 ± 1.03	44.59	−3.3 ± 0.7	−30.18
Flock–Rodebush[3]	(B)	1116.1–1275.7	8	45.43 ± 0.03	44.75	−0.6 ± 0.1	−30.02
Greiner–Jellinek[4]	(B)	1453.2	1	–	45.24	–	−29.53
Niwa[5]	(A)	803.2–873.2	8	46.11 ± 0.35	48.30	2.6 ± 0.4	−30.07
Zimm–Mayer[6]	(A)	618.4–892.9	10	48.66 ± 0.25	48.47	−0.4 ± 0.3	−29.90
Cogin–Kimball[7]	(A)	721.5–897.7	29	48.52 ± 0.40	47.73	1.1 ± 0.5	−30.64
Bridgers[8]	(A)	697.5–891.7	25	48.48 ± 0.22	47.72	−1.1 ± 0.3	−30.65

*Reactions: (A) KI(cr) = KI(g); (B) KI(l) = KI(g).

Heat Capacity and Entropy

The ground state configuration is obtained from Herzberg.[11] The adopted values of ω_e, $\omega_e x_e$, B_e, α_e, and r_e were determined using millimeter wave molecular beam spectroscopy by Rusk and Gordy[12] and corrected to the average isotopic species. Similar values were reported by Honig *et al.*[13] from microwave spectra, except ω_e which was given as 199.74 cm^{-1}. The value of ω_e was derived to be 200 and 173 cm^{-1} by Barrow and Caunt[14] and Rice and Klemperer.[15] The moment of inertia is 4.5979×10^{-38} g cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.242	−122.081	−122.081	INFINITE
100	33.908	219.083	290.729	−7.165	−122.261	−137.559	71.854
200	36.441	243.584	261.662	−3.615	−123.772	−152.295	39.775
250	36.869	251.766	258.893	−1.782	−124.627	−159.328	33.290
298.15	37.122	258.283	258.283	0.	−125.520	−165.932	29.071
300	37.130	258.513	258.284	0.069	−125.556	−166.182	28.935
350	37.308	264.251	258.737	1.930	−128.992	−172.775	25.785
400	37.439	269.241	259.745	3.799	−138.124	−178.678	23.333
450	37.543	273.657	261.050	5.673	−139.830	−183.644	21.317
500	37.629	277.617	262.512	7.553	−161.576	−186.523	19.486
600	37.771	284.491	265.619	11.323	−162.722	−191.403	16.663
700	37.889	290.322	268.742	15.106	−163.818	−196.097	14.633
800	37.994	295.389	271.763	18.900	−164.891	−200.634	13.100
900	38.093	299.870	274.642	22.705	−165.964	−205.038	11.900
1000	38.186	303.888	277.369	26.519	−167.064	−209.321	10.934
1100	38.277	307.532	279.948	30.342	−247.167	−208.881	9.919
1200	38.366	310.866	282.388	34.174	−247.330	−205.394	8.941
1300	38.453	313.940	284.698	38.015	−247.496	−201.892	8.112
1400	38.539	316.793	286.890	41.864	−247.669	−198.378	7.402
1500	38.624	319.455	288.973	45.723	−247.854	−194.851	6.785
1600	38.709	321.951	290.957	49.589	−248.056	−191.311	6.246
1700	38.793	324.300	292.850	53.464	−248.282	−187.757	5.769
1800	38.877	326.520	294.660	57.348	−248.534	−184.190	5.345
1900	38.961	328.624	296.392	61.240	−248.816	−180.608	4.965
2000	39.044	330.624	298.054	65.140	−249.130	−177.010	4.623
2100	39.128	332.531	299.651	69.049	−249.477	−173.396	4.313
2200	39.211	334.353	301.187	72.966	−249.856	−169.764	4.031
2300	39.294	336.098	302.667	76.891	−250.265	−166.114	3.773
2400	39.377	337.772	304.095	80.824	−250.702	−162.446	3.536
2500	39.459	339.381	305.475	84.766	−251.163	−158.760	3.317
2600	39.542	340.931	306.809	88.716	−251.647	−155.054	3.115
2700	39.625	342.425	308.101	92.675	−252.149	−151.329	2.928
2800	39.707	343.867	309.352	96.641	−252.668	−147.586	2.753
2900	39.790	345.262	310.567	100.616	−253.201	−143.824	2.591
3000	39.872	346.612	311.746	104.599	−253.746	−140.043	2.438
3100	39.955	347.921	312.892	108.590	−254.303	−136.243	2.296
3200	40.037	349.191	314.006	112.590	−254.872	−132.426	2.162
3300	40.119	350.424	315.091	116.598	−255.445	−128.591	2.035
3400	40.202	351.623	316.148	120.614	−256.037	−124.738	1.916
3500	40.284	352.790	317.179	124.638	−256.642	−120.868	1.804
3600	40.366	353.925	318.184	128.671	−257.266	−116.980	1.697
3700	40.449	355.033	319.165	132.712	−257.912	−113.074	1.596
3800	40.531	356.112	320.123	136.761	−258.583	−109.151	1.500
3900	40.613	357.166	321.059	140.818	−259.283	−105.209	1.409
4000	40.696	358.196	321.975	144.883	−260.011	−101.250	1.322
4100	40.778	359.201	322.871	148.957	−260.778	−97.272	1.239
4200	40.860	360.185	323.747	153.039	−261.593	−93.274	1.160
4300	40.942	361.148	324.606	157.129	−262.457	−89.257	1.084
4400	41.025	362.090	325.447	161.227	−263.098	−85.246	1.012
4500	41.107	363.013	326.272	165.334	−264.006	−81.193	0.942
4600	41.189	363.917	327.080	169.449	−264.968	−77.120	0.876
4700	41.271	364.804	327.874	173.572	−265.965	−73.028	0.812
4800	41.353	365.673	328.652	177.703	−266.911	−68.925	0.750
4900	41.436	366.527	329.416	181.842	−268.021	−64.789	0.691
5000	41.518	367.365	330.167	185.990	−269.192	−60.630	0.633
5100	41.600	368.188	330.904	190.146	−270.426	−56.447	0.578
5200	41.682	368.996	331.629	194.310	−271.726	−52.238	0.525
5300	41.764	369.791	332.342	198.482	−273.091	−48.005	0.473
5400	41.846	370.573	333.042	202.663	−274.523	−43.744	0.423
5500	41.929	371.341	333.732	206.852	−276.022	−39.457	0.375
5600	42.011	372.097	334.410	211.048	−277.589	−35.142	0.328
5700	42.093	372.842	335.078	215.254	−278.876	−30.846	0.283
5800	42.175	373.574	335.735	219.467	−280.531	−26.480	0.238
5900	42.257	374.296	336.383	223.689	−282.246	−22.085	0.196
6000	42.339	375.007	337.021	227.918	−284.019	−17.661	0.154

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = [85.772]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 742\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -270.08 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 14.644\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation. $\Delta_f H°$(LiI, cr, 298.15 K) = −64.55 kcal·mol^{-1}, was calculated from the heat of solution of lithium iodide (cr) at infinite dilution and the ionic heats of formation of Li^+(aq,∞) and I^-(aq,∞).

Parker[1] reviewed the literature heat of solution data and gave the "best" value, $\Delta_{sol} H°$(aq,linfl) = −15.130 ± 75 cal·K^{-1}·mol^{-1} for LiI(cr) → LiI(aq,linfl) at 298.15 K. The ionic heat of formation, $\Delta_f H°(Li^+, aq, ∞, 298.15\ K)$ = −66.49 kcal·mol^{-1} was calculated from $\Delta H°$(LiOH·aq, ∞, 298.15 K) = −121.46 kcal·mol^{-1} (see JANAF LiOH(cr) table, Mar. 31, 1966) with $\Delta_f H°(OH^-\cdot aq, ∞, 298.15\ K)$ = −54.97 kcal·mol^{-1} from.[2] The value $\Delta_f H°(I^-\cdot aq, ∞, 298.15\ K)$ = 13.19 kcal·mol^{-1} was also obtained from[2] Combination of the ionic heats of formation of Li^+(aq, ∞) and I^- (aq, ∞) gives the heat of formation of LiI(aq, ∞), $\Delta_f H°$(298.15 K) = −79.68 kcal·mol^{-1}.

Heat Capacity and Entropy

Dworkin[3] has measured the enthalpy changes by the drop method (642–802 K), yielding $H°(742\ K) - H°(298.15\ K)$ = 6.0 kcal·mol^{-1} for the crystal at the melting point. Heat capacities derived from his data were $C_p°(692\ K)$ = 14.8 and $C_p°(772\ K)$ = 15.1 cal·K^{-1}mol^{-1} for the crystal and liquid, respectively. The tabulated heat capacities were estimated based on these values and on the heat capacities of LiCl(cr), NaCl(cr) and NaI(cr).

The entropy, $S°(298.15\ K)$ = 20.5 cal·K^{-1}·mol^{-1}, was estimated by adding the entropy difference at 298.15 K between NaI(cr) and NaCl(cr) to the entropy of LiCl(cr). Comparisons with other alkali halides give results within ±0.5 cal·K^{-1}·mol^{-1} of this value.

Kelley[4] has estimated the heat capacities ($C_p° = 12.30 + 2.44 \times 10^{-3} T$ cal·K^{-1}·mol^{-1}) and the entropy, $S°(298.15\ K)$ = 17.50 cal·K^{-1}·mol^{-1}.

Fusion Data

The selected enthalpy of fusion, $\Delta H°(823\ K)$ = 350 kcal·mol^{-1}) was obtained from enthalpy measurements in a drop calorimeter by Dworkin and Bredig.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	50.082	85.772	85.772	0.	−270.077	−269.665	47.244
300	50.187	86.082	85.773	0.093	−270.080	−269.662	46.952
400	53.430	100.875	87.767	5.243	−278.350	−269.208	35.155
500	55.948	113.073	91.645	10.714	−302.910	−264.545	27.637
600	58.660	123.499	96.104	16.437	−302.047	−256.948	22.369
700	62.258	132.807	100.693	22.480	−300.814	−249.523	18.620
800	66.107	141.363	105.248	28.891	−299.188	−242.302	15.821
900	69.517	149.355	109.710	35.680	−297.185	−235.308	13.657
1000	71.965	156.815	114.052	42.763	−294.889	−228.553	11.938
1100	73.534	163.751	118.259	50.042	−292.399	−222.039	10.544
1200	74.559	170.195	122.321	57.448	−289.785	−215.757	9.392
1300	75.375	176.196	126.237	64.946	−287.087	−209.697	8.426
1400	75.877	181.801	130.008	72.510	−284.333	−203.847	7.606
1500	76.191	187.049	133.638	80.116	−281.548	−198.195	6.902
1600	76.191	191.966	137.132	87.735	−278.767	−192.729	6.292
1700	76.191	196.585	140.494	95.354	−421.243	−180.261	5.539
1800	76.191	200.940	143.733	102.974	−417.755	−166.186	4.823
1900	76.191	205.060	146.853	110.593	−414.303	−152.304	4.187
2000	76.191	208.968	149.862	118.212	−410.888	−138.603	3.620
2100	76.191	212.685	152.766	125.831	−407.509	−125.072	3.111
2200	76.191	216.229	155.570	133.450	−404.165	−111.702	2.652
2300	76.191	219.616	158.282	141.069	−400.854	−98.482	2.237
2400	76.191	222.859	160.906	148.688	−397.571	−85.406	1.859
2500	76.191	225.969	163.446	156.307	−394.313	−72.466	1.514

PREVIOUS: September 1961 CURRENT: June 1966

$S°(298.15\ K) = [98.611]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 742\ K$

$\Delta_f H°(298.15\ K) = [-258.349]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 14.644\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(LiI, l, 298.15 K) is calculated from $\Delta_f H°$(LiI, cr, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(742\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Dworkin[1] has derived the heat capacity ($C_p°$ = 15.1 $cal·K^{-1}·mol^{-1}$) from enthalpy measurements (742–802 K) by the drop method. The liquid heat capacity was assumed to be constant as 15.1 $cal·K^{-1}·mol^{-1}$. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap}(to monomer only) = 1497 K is determined as the temperature at which the fugacity is 1 atm for the reaction LiI(l) = LiI(g). The corresponding enthalpy change ($\Delta_r H°$) at boiling point is the enthalpy of vaporization $\Delta_{vap}H°$(to monomer only).

T_{vap}(to equilibrium mixture) = 1447 K is the temperature at which the sum of the calculated partial vapor pressures of LiI(g) and Li_2I_2(g) reaches one atmosphere (trimer and higher polymer have been neglected in calculation). This value is in good agreement with the boiling point of 1444 K from the least squares fit of the total vapor pressure data measured by Ruff and Mugdan.[2] $\Delta_{vap}H°$(to equilibrium mixture) at the boiling point is calculated as the heat of vaporization of one mole of liquid to vapor containing 30.44 mole percent of dimer. For detailed information see LiI(g) and Li_2I_2(g) tables.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	63.178	98.611	98.611	0.	−258.349	−261.764	45.860
300	63.178	99.002	98.612	0.117	−258.328	−261.785	45.581
400	63.178	117.177	101.090	6.435	−265.430	−262.809	34.319
500	63.178	131.275	105.770	12.753	−289.143	−259.879	27.149
600	63.178	142.794	111.010	19.070	−287.685	−254.163	22.127
700	63.178	152.533	116.264	25.388	−286.177	−248.694	18.558
742.000	63.178	156.214	118.422	28.042	--- CRYSTAL <--> LIQUID ---		
800	63.178	160.969	121.336	31.706	−284.644	−243.444	15.895
900	63.178	168.410	126.162	38.024	−283.113	−238.386	13.836
1000	63.178	175.067	130.725	44.342	−281.582	−233.498	12.197
1100	63.178	181.088	135.034	50.660	−280.053	−228.764	10.863
1200	63.178	186.586	139.104	56.977	−278.527	−224.169	9.758
1300	63.178	191.643	142.954	63.295	−277.010	−219.700	8.828
1400	63.178	196.325	146.601	69.613	−275.502	−215.348	8.035
1500	63.178	200.683	150.063	75.931	−274.005	−211.104	7.351
1600	63.178	204.761	153.355	82.249	−272.525	−206.959	6.757
1700	63.178	208.591	156.493	88.567	−416.302	−195.730	6.014
1800	63.178	212.202	159.489	94.884	−414.116	−182.818	5.305
1900	63.178	215.618	162.354	101.202	−411.965	−170.027	4.674
2000	63.178	218.859	165.099	107.520	−409.851	−157.349	4.110
2100	63.178	221.941	167.733	113.838	−407.773	−144.775	3.601
2200	63.178	224.880	170.264	120.156	−405.731	−132.299	3.141
2300	63.178	227.689	172.700	126.474	−403.721	−119.916	2.723
2400	63.178	230.378	175.048	132.792	−401.739	−107.619	2.342
2500	63.178	232.957	177.313	139.109	−399.782	−95.404	1.993

PREVIOUS: September 1961 CURRENT: June 1966

0 to 742 K crystal
above 742 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	50.082	85.772	85.772	0.	−270.077	−269.665	47.244
300	50.187	86.082	85.773	0.093	−270.080	−269.662	46.952
400	53.430	100.875	87.767	5.243	−278.350	−269.208	35.155
500	55.948	113.073	91.645	10.714	−302.910	−264.545	27.637
600	58.660	123.499	96.104	16.437	−302.047	−256.948	22.369
700	62.258	132.807	100.693	22.480	−300.814	−249.523	18.620
742.000	63.764	136.478	102.615	25.126	____ CRYSTAL <−−> LIQUID ____		
742.000	63.178	156.214	102.615	39.770	TRANSITION		
800	63.178	160.969	106.676	43.435	−284.644	−243.444	15.895
900	63.178	168.410	113.130	49.752	−283.113	−238.386	13.836
1000	63.178	175.067	118.997	56.070	−281.582	−233.498	12.197
1100	63.178	181.088	124.372	62.388	−280.053	−228.764	10.863
1200	63.178	186.586	129.331	68.706	−278.527	−224.169	9.758
1300	63.178	191.643	133.932	75.024	−277.010	−219.700	8.828
1400	63.178	196.325	138.224	81.342	−275.502	−215.348	8.035
1500	63.178	200.684	142.244	87.659	−274.005	−211.104	7.351
1600	63.178	204.761	146.025	93.977	−272.525	−206.959	6.757
1700	63.178	208.591	149.594	100.295	−416.302	−195.730	6.014
1800	63.178	212.202	152.973	106.613	−414.116	−182.818	5.305
1900	63.178	215.618	156.181	112.931	−411.965	−170.027	4.674
2000	63.178	218.859	159.234	119.249	−409.851	−157.349	4.110
2100	63.178	221.941	162.148	125.566	−407.773	−144.775	3.601
2200	63.178	224.880	164.933	131.884	−405.731	−132.299	3.141
2300	63.178	227.689	167.601	138.202	−403.721	−119.916	2.723
2400	63.178	230.378	170.161	144.520	−401.739	−107.619	2.342
2500	63.178	232.957	172.622	150.838	−399.782	−95.404	1.993

PREVIOUS: CURRENT: June 1966

$S°(298.15\ K) = 232.262\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -89.08 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -91.00 \pm 8.4\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 498.16\ cm^{-1}$ $\omega_e x_e = 3.39\ cm^{-1}$ $\sigma = 1$
$B_e = 0.44837\ cm^{-1}$ $\alpha_e = 0.00416\ cm^{-1}$ $r_e = 2.3919$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(LiI, g, 298.15 K) = −21.75 ± 2 kcal·mol^{-1}, was calculated from the selected heat of sublimation and the enthalpy of formation for lithium iodide (cr). The heat of sublimation has been determined mass spectrometrically from the ion intensity measurement (2nd law method) by Gorokhov as $\Delta_{sub}H°$(cr → monomer, 298.15 K) = 42.9 ± 0.6 and $\Delta_{sub}H°$(cr → dimer, 298.15 K) = 43.2 ± 0.4 kcal·mol^{-1} in the temperature range from 626–722 K. Gorokhov also reported the partial vapor pressure of monomeric lithium iodide ($P_{monomer} = 3 \times 10^{3}$ mm Hg) and the ratio of dimer to monomer ($P_{dimer}/P_{monomer} = 6$) which have been used for 3rd law calculation. Using the same technique, Friedman reported the heats of sublimation as $\Delta_{sub}H°$(cr → monomer, 727 K) = 41.9 ± 0.5 and $\Delta_{sub}H°$(cr → dimer, 727 K) = 40.8 ± 0.5 kcal·mol^{-1} in the temperature range from 630 to 730 K. Berkowitz *et al.* have also studied the lithium iodide vapor in the mass spectrometer and reported the 2nd law and 3rd law values of the heat of dimerization at 800 K as 37.9 and 40.4 kcal·mol^{-1}, respectively. Using the JANAF thermodynamic functions, all the heats of sublimation and dimerization at different temperatures have been reduced to 298.15 K and summarized in the following table. The total vapor pressure over the liquid has been measured by a boiling point method in the temperature range 1223 to 1413 K by Ruff and Mugdan[4] (Their data have been quoted by Wartenberg and Schulz.)[5] In order to have good agreement between the calculated vapor pressure and the observed total vapor pressure, the heats of sublimation have been so chosen as $\Delta_{sub}H°(298.15\ K) = 42.8$ kcal·mol^{-1} and $\Delta_{sub}H°$(cr → dimer, 298.15 K) = 42.6 kcal·mol^{-1} and the heat of dissociation of dimer, $\Delta_d H°$(cr → monomer, 298.15 K) = 43.0 kcal·mol^{-1}. The calculated boiling point (to equilibrium mixture) is 1449 K which agrees with 1443 K reported by Wartenberg and Schulz, and also 1462 K by Ruff and Mugdan.

Reaction	Source	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law
LiI(cr) → LiI(g)	Gorokhov	44.7	42.2
	Friedman	43.9	–
2 LiI(cr) → Li_2I_2(g)	Gorokhov	46.0	41.3
	Friedman	44.1	–
Li_2I_2(g) → 2 LiI(g)	Berkowitz *et al.*	38.8	41.3
	Friedman	43.7	–
	Gorokov	43.2	43.1

Heat Capacity and Entropy

The bond distance and the rotational constants (B_e and ν_e), corrected to the isotopic abundance of 7.4% Li^6 and 92.6% Li^7 were obtained from the microwave studies by Honig *et al.*[6] The vibrational constants (ω_e and $\omega_e x_e$) were determined from the infrared spectrum by Klemperer *et al.*[7]

The tabulated thermodynamic functions are in reasonable agreement with those calculated by Wilkins who used slightly different molecular constants.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.297	−89.078	−89.078	INFINITE
100	29.475	197.607	261.437	−6.383	−88.184	−104.161	54.408
200	32.394	218.879	235.363	−3.297	−89.405	−119.720	31.268
250	33.663	226.251	232.826	−1.644	−90.194	−127.209	26.579
298.15	34.572	232.262	232.262	0.	−91.002	−134.265	23.523
300	34.602	232.476	232.262	0.064	−91.034	−134.534	23.424
350	35.289	237.864	232.686	1.812	−91.955	−141.713	21.149
400	35.798	242.611	233.636	3.590	−100.928	−148.480	19.390
450	36.185	246.851	234.873	5.390	−102.568	−154.327	17.914
500	36.485	250.679	236.265	7.207	−127.342	−157.780	16.483
600	36.921	257.372	239.241	10.879	−128.530	−163.755	14.256
700	37.223	263.088	242.250	14.587	−129.631	−169.537	12.651
800	37.448	268.074	245.173	18.321	−130.683	−175.166	11.437
900	37.627	272.495	247.967	22.075	−131.715	−180.664	10.485
1000	37.777	276.467	250.622	25.845	−132.732	−186.048	9.718
1100	37.906	280.074	253.138	29.629	−133.736	−191.331	9.086
1200	38.022	283.377	255.522	33.426	−134.732	−196.523	8.554
1300	38.128	286.425	257.784	37.234	−135.725	−201.632	8.102
1400	38.227	289.254	259.932	41.051	−136.717	−206.665	7.711
1500	38.321	291.895	261.976	44.879	−137.710	−211.627	7.369
1600	38.410	294.371	263.924	48.715	−138.712	−216.522	7.069
1700	38.496	296.702	265.784	52.561	−284.962	−214.178	6.581
1800	38.580	298.905	267.563	56.415	−285.239	−210.006	6.094
1900	38.662	300.993	269.268	60.277	−285.543	−205.819	5.658
2000	38.742	302.978	270.905	64.147	−285.877	−201.614	5.266
2100	38.821	304.870	272.477	68.025	−286.239	−197.392	4.910
2200	38.899	306.678	273.991	71.911	−286.629	−193.152	4.586
2300	38.976	308.409	275.450	75.805	−287.043	−188.894	4.290
2400	39.052	310.069	276.858	79.706	−287.478	−184.617	4.018
2500	39.128	311.665	278.219	83.615	−287.930	−180.322	3.768
2600	39.203	313.201	279.535	87.532	−288.394	−176.009	3.536
2700	39.277	314.682	280.810	91.456	−288.867	−171.677	3.321
2800	39.352	316.112	282.045	95.387	−289.345	−167.328	3.122
2900	39.426	317.494	283.244	99.326	−289.824	−162.962	2.935
3000	39.499	318.832	284.408	103.272	−290.300	−158.580	2.761
3100	39.572	320.128	285.539	107.226	−290.771	−154.181	2.598
3200	39.645	321.386	286.640	111.187	−291.236	−149.768	2.445
3300	39.718	322.607	287.711	115.155	−291.693	−145.340	2.301
3400	39.791	323.794	288.755	119.131	−292.140	−140.898	2.165
3500	39.863	324.948	289.773	123.113	−292.578	−136.443	2.036
3600	39.936	326.072	290.766	127.103	−293.007	−131.976	1.915
3700	40.008	327.167	291.735	131.100	−293.426	−127.497	1.800
3800	40.080	328.235	292.681	135.105	−293.838	−123.007	1.691
3900	40.152	329.277	293.606	139.116	−294.242	−118.506	1.587
4000	40.224	330.295	294.511	143.135	−294.641	−113.995	1.489
4100	40.296	331.289	295.396	147.161	−295.035	−109.474	1.395
4200	40.368	332.261	296.262	151.194	−295.428	−104.943	1.305
4300	40.439	333.211	297.110	155.235	−295.821	−100.404	1.220
4400	40.511	334.142	297.941	159.282	−296.194	−95.856	1.138
4500	40.583	335.053	298.756	163.337	−296.583	−91.299	1.060
4600	40.654	335.946	299.555	167.399	−296.980	−86.732	0.985
4700	40.726	336.821	300.338	171.468	−297.383	−82.158	0.913
4800	40.797	337.679	301.107	175.544	−297.796	−77.574	0.844
4900	40.869	338.521	301.862	179.627	−298.222	−72.981	0.778
5000	40.940	339.347	302.604	183.718	−298.661	−68.380	0.714
5100	41.011	340.159	303.332	187.815	−299.111	−63.771	0.653
5200	41.083	340.956	304.048	191.920	−299.585	−59.152	0.594
5300	41.154	341.739	304.752	196.032	−300.081	−54.523	0.537
5400	41.225	342.509	305.444	200.151	−300.600	−49.885	0.483
5500	41.296	343.266	306.125	204.277	−301.145	−45.238	0.430
5600	41.368	344.011	306.795	208.410	−301.719	−40.579	0.379
5700	41.439	344.744	307.454	212.550	−302.324	−35.911	0.329
5800	41.510	345.465	308.103	216.698	−302.962	−31.231	0.281
5900	41.581	346.175	308.743	220.852	−303.636	−26.541	0.235
6000	41.652	346.875	309.372	225.014	−304.347	−21.838	0.190

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 252.647 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [26.45 \pm 41.8]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [24.61 \pm 41.8]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Sigma^+$	0	2
$A[^2\Pi]$	24319	2
	25294	2

$\omega_e = 312\ cm^{-1}$ $\omega_e x_e = [1.09]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.13014]\ cm^{-1}$ $\alpha_e = [0.00062]\ cm^{-1}$ $r_e = [2.52]$ Å

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = 6.309 \pm 10\ kcal·mol^{-1}$ is calculated from a $D_0°$ value of 54.3 $kcal·mol^{-1}$ (2.35 $cal·K^{-1}·mol^{-1}$). An approximate value of 312 cm^{-1} has been given for ω_e.[1] A value of $\omega_e x_e$, 1.09 cm^{-1}, is calculated from an average value of $x_e\mu^{1/2}$ calculated from data for CaI, SrI, BaI, MgBr, and MgCl.[1,2] A linear Birge–Sponer extrapolation of these ω_e and $\omega_e x_e$data is corrected for the ionic character of the molecule as described by Hildenbrand to give the adopted value of $D_0° = 54.3\ kcal·mol^{-1}$.

From a consideration of ionic bonding forces, Krasnov and Karaseva[4] calculated $D_0° \geq 55 \pm 10\ kcal·mol^{-1}$.

Using JANAF data, $D_0°(MgI)$ $D_0°(MgI_2) = 0.44$, in reasonable agreement with the ratios found by Blue *et. al.*[5] for the alkali earth fluorides and by Hildenbrand for the alkaline with fluorides and chlorides.

$\Delta_f H°(298.15\ K) = 5.883 \pm 10\ kcal·mol^{-1}$ is calculated from the adopted $\Delta_f H°(0\ K) = 6.309\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The ground state vibrational constants are as given in the Enthalpy of Formation section above. The adopted value of $r_e = 2.52$ Å is the bond distance in MgI_2.[7] Margrave[8] has estimated 2.72 Å from additive ionic radii. B_e is calculated from the adopted r_e, and α_e is calculated assuming a Morse potential function.

The electronic levels and their designation are those given by Rosen.[1] The possibility of additional electronic levels near 15000 cm^{-1} is suggested by a comparison with CaI, SrI, and BaI.[2] Including these levels does not change the entropy at 298.15 K and increases the entropy at 6000 K by only 0.69 $cal·K^{-1}·mol^{-1}$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.765	26.446	26.446	INFINITE
100	31.085	215.601	283.716	−6.811	27.233	9.673	−5.053
200	34.773	238.459	255.920	−3.492	26.079	−7.488	1.956
250	35.645	246.320	253.240	−1.730	25.356	−15.798	3.301
298.15	36.178	252.647	252.647	0.	24.614	−23.658	4.145
300	36.195	252.871	252.648	0.067	24.585	−23.957	4.171
350	36.562	258.480	253.090	1.886	23.736	−31.982	4.773
400	36.821	263.380	254.076	3.721	14.865	−39.608	5.172
450	37.013	267.728	255.356	5.567	13.374	−46.327	5.378
500	37.160	271.636	256.792	7.422	−8.199	−50.980	5.326
600	37.376	278.431	259.849	11.149	−9.116	−59.452	5.176
700	37.530	284.205	262.926	14.895	−10.126	−67.763	5.057
800	37.651	289.224	265.907	18.654	−11.245	−75.922	4.957
900	37.751	293.665	268.749	22.425	−12.488	−83.933	4.871
1000	37.840	297.647	271.443	26.204	−22.466	−91.086	4.758
1100	37.920	301.257	273.992	29.992	−24.016	−97.873	4.648
1200	37.994	304.560	276.404	33.788	−25.568	−104.519	4.550
1300	38.064	307.604	278.688	37.591	−27.123	−111.035	4.461
1400	38.132	310.427	280.855	41.401	−156.097	−114.264	4.263
1500	38.197	313.060	282.916	45.217	−156.323	−111.268	3.875
1600	38.261	315.528	284.878	49.040	−156.567	−108.257	3.534
1700	38.324	317.849	286.750	52.869	−156.835	−105.229	3.233
1800	38.385	320.041	288.539	56.705	−157.128	−102.185	2.965
1900	38.446	322.118	290.252	60.546	−157.451	−99.124	2.725
2000	38.506	324.092	291.895	64.394	−157.802	−96.045	2.508
2100	38.565	325.972	293.473	68.247	−158.181	−92.948	2.312
2200	38.625	327.768	294.992	72.107	−158.586	−89.833	2.133
2300	38.684	329.486	296.454	75.972	−159.013	−86.698	1.969
2400	38.743	331.133	297.865	79.844	−159.458	−83.544	1.818
2500	38.802	332.716	299.228	83.721	−159.914	−80.372	1.679
2600	38.861	334.239	300.545	87.604	−160.378	−77.181	1.551
2700	38.921	335.707	301.821	91.493	−160.843	−73.972	1.431
2800	38.981	337.123	303.056	95.388	−161.305	−70.747	1.320
2900	39.042	338.492	304.255	99.289	−161.759	−67.504	1.216
3000	39.104	339.817	305.418	103.197	−162.202	−64.247	1.119
3100	39.168	341.100	306.549	107.110	−162.630	−60.974	1.027
3200	39.232	342.345	307.648	111.030	−163.041	−57.688	0.942
3300	39.299	343.553	308.718	114.957	−163.433	−54.390	0.861
3400	39.368	344.727	309.760	118.890	−163.806	−51.080	0.785
3500	39.439	345.869	310.775	122.831	−164.158	−47.759	0.713
3600	39.512	346.982	311.765	126.778	−164.491	−44.429	0.645
3700	39.588	348.065	312.732	130.733	−164.805	−41.090	0.580
3800	39.667	349.122	313.676	134.696	−165.101	−37.742	0.519
3900	39.750	350.153	314.598	138.667	−165.380	−34.387	0.461
4000	39.835	351.161	315.499	142.646	−165.646	−31.024	0.405
4100	39.925	352.146	316.381	146.634	−165.899	−27.656	0.352
4200	40.017	353.109	317.244	150.631	−166.142	−24.281	0.302
4300	40.114	354.052	318.089	154.637	−166.378	−20.901	0.254
4400	40.214	354.975	318.917	158.654	−166.609	−17.515	0.208
4500	40.318	355.880	319.729	162.680	−166.837	−14.124	0.164
4600	40.427	356.767	320.524	166.718	−167.066	−10.728	0.122
4700	40.539	357.638	321.305	170.766	−167.298	−7.326	0.081
4800	40.654	358.492	322.070	174.826	−167.535	−3.920	0.043
4900	40.774	359.332	322.822	178.897	−167.780	−0.509	0.005
5000	40.897	360.157	323.561	182.980	−168.035	2.907	−0.030
5100	41.024	360.968	324.286	187.076	−168.303	6.329	−0.065
5200	41.155	361.766	324.999	191.185	−168.586	9.756	−0.098
5300	41.289	362.551	325.701	195.308	−168.885	13.188	−0.130
5400	41.427	363.324	326.390	199.443	−169.204	16.626	−0.161
5500	41.567	364.086	327.069	203.593	−169.544	20.071	−0.191
5600	41.711	364.836	327.736	207.757	−169.908	23.521	−0.219
5700	41.857	365.575	328.394	211.935	−170.296	26.979	−0.247
5800	42.006	366.305	329.041	216.128	−170.711	30.443	−0.274
5900	42.158	367.024	329.679	220.337	−171.155	33.915	−0.300
6000	42.312	367.734	330.307	224.560	−171.628	37.395	−0.326

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [278.974 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [499.74 \pm 41.8]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [498.73 \pm 41.8]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights					
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[15199]	[6]	[15890]	[2]
[11783]	[2]	[15331]	[8]	[16796]	[2]
[12034]	[4]	[15428]	[10]	[16947]	[8]
[12417]	[6]	[15447]	[12]	[17174]	[4]
[12900]	[8]	[15691]	[6]	[17344]	[6]
[13461]	[10]	[15699]	[4]		

$\omega_e = [200]\ cm^{-1}$ $\omega_e x_e = [0.41]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.04361]\ cm^{-1}$ $\alpha_e = [0.00013]\ cm^{-1}$ $r_e = [2.66]$ Å

Enthalpy of Formation

The adopted value of $\Delta_f H°$ at 298.15 K is that estimated by Brewer.[1] The estimated value is consistent with the low volatility of solid molybdenum in iodine vapor reported by Schafer *et al.*[2] Brewer's estimated value is given as $\Delta_f H°(298.15\ K)/R = 60000 \pm 5000$. The assigned uncertainty ($\pm 10\ kcal·mol^{-1}$) is determined from the product $500 \times R$ which has been rounded to the nearest $kcal·mol^{-1}$. The value of $\Delta_f H°(0\ K)$ combined with JANAF data[3] for Mo(g) and I(g) gives $D_0°(Mo–I) = 63 \pm 11\ kcal·mol^{-1}$.

Heat Capacity and Entropy

We use values of r_e and ω_e estimated by Brewer.[1] The electronic contribution is taken to be the same as that for the free gaseous Mo^+ ion, as suggested by Brewer.[1] The levels listed by Moore[4] below 17334 cm^{-1} are used in the calculations. Our thermodynamic functions differ slightly from those reported by Brewer[1] due to the use of non–zero values for $\omega_e x_e$ and α_e. Estimates for α_e and ω_e are based on the empirical correlations of Calder and Ruedenberg.[5]

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication; September 28, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]H. Schafer, T. Grofe, and M. Trenkel, J. Solid State Chem. **8**, 14 (1973).
[3]JANAF Thermochemical Tables: Mo(g), 3–31–78; I(g) and SrI(g), 6–30–74.
[4]C. E. Moore, NSRDS NBS 34, 1970; NSRDS NBS 35, Vol. III, Reissued (1971).
[5]G. V. Calder and K. Ruedenberg, J. Chem. Phys. **49**, 5399 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.173	499.744	499.744	INFINITE
100	33.511	240.056	311.234	−7.118	500.783	480.529	−251.003
200	36.229	264.348	282.337	−3.598	499.994	460.516	−120.274
250	36.692	272.487	279.581	−1.774	499.386	450.715	−94.172
298.15	36.962	278.974	278.974	0.	498.733	441.399	−77.331
300	36.970	279.203	278.975	0.068	498.707	441.043	−76.792
350	37.154	284.917	279.426	1.922	497.940	431.492	−64.397
400	37.285	289.887	280.429	3.783	489.146	422.328	−55.150
450	37.384	294.284	281.729	5.650	487.732	414.060	−48.063
500	37.463	298.227	283.185	7.521	466.237	407.851	−42.608
600	37.586	305.069	286.279	11.274	465.497	396.242	−34.496
700	37.682	310.870	289.389	15.037	464.704	384.762	−28.711
800	37.764	315.907	292.395	18.810	463.865	373.398	−24.380
900	37.837	320.360	295.260	22.590	462.984	362.142	−21.018
1000	37.905	324.350	297.973	26.377	462.057	350.987	−18.334
1100	37.970	327.966	300.538	30.171	461.081	339.926	−16.142
1200	38.035	331.272	302.963	33.971	460.046	328.958	−14.319
1300	38.100	334.319	305.259	37.778	458.944	318.078	−12.781
1400	38.170	337.145	307.437	41.591	457.764	307.286	−11.465
1500	38.249	339.781	309.507	45.412	456.496	296.581	−10.328
1600	38.342	342.253	311.477	49.241	455.130	285.964	−9.336
1700	38.456	344.580	313.356	53.081	453.656	275.436	−8.463
1800	38.599	346.782	315.153	56.933	452.067	264.997	−7.690
1900	38.780	348.874	316.873	60.802	450.356	254.651	−7.001
2000	39.007	350.869	318.523	64.691	448.518	244.397	−6.383
2100	39.288	352.778	320.109	68.605	446.552	234.239	−5.826
2200	39.630	354.614	321.636	72.550	444.456	224.177	−5.323
2300	40.040	356.384	323.109	76.533	442.232	214.214	−4.865
2400	40.523	358.098	324.531	80.561	439.881	204.350	−4.448
2500	41.082	359.763	325.907	84.640	437.405	194.587	−4.066
2600	41.718	361.387	327.241	88.780	434.796	184.925	−3.715
2700	42.430	362.974	328.535	92.987	432.027	175.367	−3.393
2800	43.218	364.531	329.793	97.268	429.050	165.915	−3.095
2900	44.075	366.063	331.017	101.632	389.911	156.623	−2.821
3000	44.997	367.572	332.210	106.086	388.347	148.605	−2.587
3100	45.975	369.064	333.375	110.634	386.893	140.638	−2.370
3200	47.001	370.539	334.514	115.282	385.557	132.716	−2.166
3300	48.065	372.002	335.628	120.035	384.348	124.834	−1.976
3400	49.156	373.453	336.719	124.896	383.271	116.986	−1.797
3500	50.263	374.894	337.789	129.867	382.330	109.168	−1.629
3600	51.375	376.325	338.839	134.949	381.528	101.375	−1.471
3700	52.481	377.748	339.872	140.142	380.865	93.603	−1.321
3800	53.568	379.162	340.887	145.444	380.341	85.846	−1.180
3900	54.628	380.567	341.887	150.854	379.955	78.102	−1.046
4000	55.649	381.963	342.871	156.369	379.702	70.366	−0.919
4100	56.625	383.350	343.842	161.983	379.579	62.634	−0.798
4200	57.546	384.725	344.799	167.692	379.579	54.904	−0.683
4300	58.407	386.090	345.743	173.490	379.698	47.172	−0.573
4400	59.202	387.441	346.675	179.371	379.928	39.437	−0.468
4500	59.928	388.780	347.596	185.328	380.261	31.695	−0.368
4600	60.581	390.105	348.506	191.354	380.689	23.944	−0.272
4700	61.161	391.414	349.405	197.442	381.206	16.183	−0.180
4800	61.665	392.707	350.294	203.584	381.801	8.411	−0.092
4900	62.096	393.983	351.172	209.772	382.467	0.625	−0.007
5000	62.454	395.241	352.041	216.001	−208.189	−1.444	0.015
5100	62.742	396.481	352.900	222.261	−209.085	2.700	−0.028
5200	62.961	397.701	353.750	228.547	−210.080	6.862	−0.069
5300	63.116	398.902	354.591	234.851	−211.179	11.044	−0.109
5400	63.210	400.083	355.422	241.168	−212.390	15.249	−0.148
5500	63.247	401.243	356.245	247.491	−213.714	19.476	−0.185
5600	63.231	402.383	357.059	253.815	−215.157	23.729	−0.221
5700	63.166	403.502	357.864	260.136	−216.720	28.008	−0.257
5800	63.057	404.599	358.660	266.447	−218.408	32.316	−0.291
5900	62.908	405.676	359.448	272.746	−220.219	36.654	−0.325
6000	62.723	406.732	360.227	279.028	−222.160	41.024	−0.357

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

Nitrosyl Iodide (NOI) **IDEAL GAS** $M_r = 156.9106$ **Nitrosyl Iodide (ONI)** $I_1N_1O_1(g)$

$S°(298.15\ K) = [282.960]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [115.30 \pm 20.9]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [112.13 \pm 20.9]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1780](1)
[440](1)
[200](1)

Ground State Quantum Weight: 1 $\alpha = 1$

Point Group: C_s

Bond Distances: O–N = [1.15] Å N–I = [2.3] Å

Bond Angle: O–N–I = [120]°

Product of the Moments of Inertia: $I_A I_B I_C = [7.908120 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation $\Delta_f H°(298.15\ K)$ for INO(g) is estimated by comparison with those for FNO(g), ClNO(g), BrNO(g), and the related cyanogen halides.

Heat Capacity and Entropy

The molecular structure and bond angle are estimated by comparison with those for ClNO(g) and BrNO(g). The N–O bond distance is assumed to be the same as that in NO(g). The N–I bond distance, r(N–I) is calculated based on an assumption that r(ON–Cl) r(ON–I) = r(I–Cl r(I–I). The vibrational frequencies are estimated by comparison with those for FNO(g), ClNO(g) and BrNO(g). The three principal moments of inertia are: $I_A = 0.8962 \times 10^{-39}$, $I_B = 29.2605 \times 10^{-39}$, and $I = 30.1568 \times 10^{-39}$ g·cm^2.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.107	115.300	115.300	INFINITE
100	38.203	236.247	322.541	−8.629	114.349	110.430	−57.683
200	44.111	264.773	287.171	−4.480	113.122	107.010	−27.948
250	45.744	274.803	283.726	−2.231	112.600	105.543	−22.052
298.15	46.856	282.960	282.960	0.	112.131	104.227	−18.260
300	46.893	283.250	282.961	0.087	112.113	104.178	−18.139
350	47.790	290.548	283.535	2.455	111.608	102.894	−15.356
400	48.566	296.981	284.822	4.864	103.127	101.957	−13.314
450	49.279	302.743	286.498	7.310	102.065	101.875	−11.825
500	49.950	307.970	288.388	9.791	80.957	103.810	−10.845
600	51.181	317.188	292.440	14.849	81.066	108.371	−9.435
700	52.248	325.160	296.558	20.022	81.207	112.911	−8.425
800	53.146	332.197	300.581	25.293	81.365	117.429	−7.667
900	53.890	338.501	304.451	30.646	81.532	121.927	−7.076
1000	54.503	344.212	308.146	36.066	81.701	126.407	−6.603
1100	55.006	349.431	311.665	41.543	81.866	130.869	−6.214
1200	55.422	354.236	315.015	47.065	82.023	135.317	−5.890
1300	55.767	358.686	318.205	52.625	82.166	139.752	−5.615
1400	56.055	362.829	321.246	58.216	82.291	144.177	−5.379
1500	56.297	366.705	324.149	63.834	82.390	148.594	−5.174
1600	56.502	370.345	326.924	69.474	82.459	153.005	−4.995
1700	56.677	373.776	329.580	75.133	82.492	157.413	−4.837
1800	56.827	377.020	332.126	80.809	82.484	161.820	−4.696
1900	56.956	380.096	334.571	86.498	82.434	166.229	−4.570
2000	57.069	383.020	336.921	92.199	82.339	170.641	−4.457
2100	57.167	385.807	339.183	97.911	82.202	175.059	−4.354
2200	57.253	388.469	341.363	103.632	82.024	179.486	−4.262
2300	57.329	391.015	343.467	109.362	81.808	183.920	−4.177
2400	57.397	393.457	345.499	115.098	81.561	188.365	−4.100
2500	57.457	395.801	347.465	120.841	81.286	192.820	−4.029
2600	57.511	398.056	349.367	126.589	80.990	197.288	−3.964
2700	57.559	400.227	351.211	132.343	80.678	201.767	−3.903
2800	57.602	402.321	352.999	138.101	80.357	206.258	−3.848
2900	57.641	404.343	354.735	143.863	80.032	210.759	−3.796
3000	57.677	406.298	356.422	149.629	79.708	215.273	−3.748
3100	57.709	408.190	358.061	155.398	79.390	219.797	−3.704
3200	57.738	410.022	359.656	161.171	79.081	224.331	−3.662
3300	57.765	411.799	361.210	166.946	78.785	228.875	−3.623
3400	57.790	413.524	362.723	172.724	78.504	233.427	−3.586
3500	57.812	415.200	364.199	178.504	78.241	237.988	−3.552
3600	57.833	416.829	365.638	184.286	77.997	242.555	−3.519
3700	57.852	418.414	367.043	190.070	77.775	247.129	−3.489
3800	57.870	419.957	368.415	195.856	77.574	251.710	−3.460
3900	57.886	421.460	369.756	201.644	77.395	256.295	−3.433
4000	57.902	422.926	371.067	207.434	77.239	260.884	−3.407
4100	57.916	424.356	372.350	213.225	77.105	265.476	−3.382
4200	57.929	425.751	373.605	219.017	76.994	270.072	−3.359
4300	57.941	427.115	374.833	224.810	76.904	274.671	−3.337
4400	57.953	428.447	376.037	230.605	76.836	279.270	−3.315
4500	57.964	429.749	377.216	236.401	76.788	283.872	−3.295
4600	57.974	431.023	378.372	242.198	76.760	288.474	−3.276
4700	57.983	432.270	379.505	247.996	76.752	293.076	−3.257
4800	57.992	433.491	380.617	253.794	76.761	297.679	−3.239
4900	58.000	434.687	381.709	259.594	76.786	302.282	−3.222
5000	58.008	435.859	382.780	265.394	76.828	306.883	−3.206
5100	58.015	437.008	383.832	271.195	76.884	311.484	−3.190
5200	58.022	438.134	384.866	276.997	76.954	316.083	−3.175
5300	58.029	439.240	385.881	282.800	77.037	320.681	−3.160
5400	58.035	440.324	386.879	288.603	77.130	325.277	−3.146
5500	58.041	441.389	387.861	294.407	77.234	329.871	−3.133
5600	58.047	442.435	388.826	300.211	77.346	334.464	−3.120
5700	58.052	443.463	389.775	306.016	77.466	339.054	−3.107
5800	58.057	444.472	390.710	311.822	77.592	343.642	−3.095
5900	58.062	445.465	391.629	317.628	77.723	348.228	−3.083
6000	58.066	446.441	392.535	323.434	77.858	352.812	−3.072

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 98.500\ J·K^{-1}·mol^{-1}$
$T_{fus} = 933\ K$

$\Delta_f H°(0\ K) = -287.34 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -287.86 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = 23.598\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was obtained as follows:

	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
(1) $HI·100H_2O + NaOH·100H_2O \rightarrow NaI·201H_2O$	-13.51 ± 0.02[1]
(2) $Na(cr) + 1001H_2O(l) \rightarrow NaOH·1000H_2O + 1/2H_2(g)$	-44.069 ± 0.006[2]
(3) $NaOH·1000H_2O \rightarrow NaOH·100H_2O + 900H_2O(l)$	$+0.031 \pm 0.004$[3]
(4) $1/2H_2(g) + 1/2I_2(s) \rightarrow HI(g)$	$+6.30 \pm 0.05$[4]
(5) $HI(g) + 100H_2O(l) \rightarrow HI·100H_2O$	19.30 ± 0.05[5]
(6) $NaI·201H_2O(l) \rightarrow NaI(cr) + 201\ H_2O(\ell)$	$+1.75 \pm 0.06$[6,7,8]
(1) + (2) + (3) + (4) + (5) + (6) gives $Na(cr) + 1/2I_2(s) \rightarrow NaI(cr)$	-68.80 ± 0.2

Heat Capacity and Entropy

Smoothed heat capacities between 3 and 270 K have been presented by Berg and Morrison.[9] Above 270 K the heat capacity was obtained by comparing with KI(cr) on a reduced temperature plot of C_p/T versus T. The values so obtained were increased by 1.4% to bring them into line with the low temperature data.

Fusion Data

Dworkin and Bredig[10] have measured both T_{fus} and $\Delta_{fus}H$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.523	−287.336	−287.336	INFINITE
100	43.032	45.601	143.089	−9.749	−287.427	−286.556	149.681
200	49.852	78.103	103.207	−5.021	−287.621	−285.606	74.593
298.15	52.225	98.500	98.500	0.	−287.859	−284.572	49.856
300	52.258	98.823	98.501	0.097	−287.865	−284.551	49.545
400	53.806	114.077	100.570	5.403	−299.000	−282.898	36.943
500	55.020	126.213	104.526	10.844	−320.758	−276.772	28.914
600	56.233	136.353	109.008	16.407	−320.088	−268.035	23.335
700	57.363	145.106	113.554	22.087	−319.244	−259.424	19.358
800	58.492	152.840	117.990	27.880	−318.250	−250.945	16.385
900	59.580	159.793	122.255	33.784	−317.128	−242.598	14.080
933.000	59.939	161.945	123.621	35.756	− − − CRYSTAL <− −> LIQUID − − −		
1000	60.675	166.127	126.330	39.796	−315.904	−234.381	12.243
1100	61.764	171.961	130.217	45.918	−314.598	−226.292	10.746
1200	62.844	177.381	133.924	52.149	−409.994	−215.884	9.397
1300	63.914	182.454	137.464	58.487	−407.663	−199.802	8.028
1400	64.974	187.229	140.850	64.931	−405.241	−183.903	6.861
1500	66.024	191.748	144.093	71.481	−402.733	−168.180	5.857
1600	67.064	196.042	147.207	78.136	−400.146	−152.627	4.983
1700	68.095	200.139	150.201	84.894	−397.484	−137.238	4.217
1800	69.116	204.060	153.085	91.754	−394.753	−122.008	3.541
1900	70.127	207.824	155.868	98.717	−391.956	−106.931	2.940
2000	71.128	211.446	158.557	105.779	−389.093	−92.004	2.403

PREVIOUS: CURRENT: September 1963

$S°(298.15\ K) = [120.754]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 933\ K$

$\Delta_f H°(298.15\ K) = [-266.508]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 23.598\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta H°$(NaI, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(933\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated assuming each atom contributed 7.75 $cal·K^{-1}·mol^{-1}$. $S°$(NaI, l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point, T_{vap} = 1577 K (l → equilibrium mixture, 1 atm), is that given by Kelley[1] from examination of the high temperature vapor pressure.

Reference

[1]K. K. Kelley, U. S. Bur. of Mines Bull. 383, (1935).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	52.225	120.754	120.754	0.	−266.508	−269.856	47.278
300	52.258	121.077	120.755	0.097	−266.514	−269.876	46.990
400	53.806	136.331	122.824	5.403	−277.649	−270.448	35.317
500	55.020	148.468	126.780	10.844	−299.407	−266.548	27.846
600	56.233	158.606	131.262	16.407	−298.737	−260.036	22.638
600.000	56.233	158.606	131.262	16.407	GLASS <---> LIQUID		
600.000	64.852	158.606	131.262	16.407	TRANSITION		
700	64.852	168.603	135.901	22.892	−297.088	−253.716	18.933
800	64.852	177.263	140.542	29.377	−295.401	−247.635	16.169
900	64.852	184.902	145.055	35.862	−293.699	−241.766	14.032
933.000	64.852	187.237	146.506	38.002	--- CRYSTAL <---> LIQUID ---		
1000	64.852	191.734	149.387	42.347	−292.002	−236.087	12.332
1100	64.852	197.915	153.522	48.833	−290.333	−230.576	10.949
1200	64.852	203.558	157.460	55.318	−385.474	−222.776	9.697
1300	64.852	208.749	161.208	61.803	−382.995	−209.318	8.411
1400	64.852	213.555	164.778	68.288	−380.532	−196.051	7.315
1500	64.852	218.030	168.181	74.773	−378.089	−182.959	6.371
1600	64.852	222.215	171.428	81.259	−375.672	−170.030	5.551
1700	64.852	226.147	174.533	87.744	−373.283	−157.250	4.832
1800	64.852	229.854	177.504	94.229	−370.927	−144.611	4.196
1900	64.852	233.360	180.352	100.714	−368.607	−132.101	3.632
2000	64.852	236.686	183.087	107.199	−366.322	−119.713	3.127
2100	64.852	239.851	185.715	113.685	−364.071	−107.438	2.672
2200	64.852	242.867	188.245	120.170	−361.854	−95.269	2.262
2300	64.852	245.750	190.683	126.655	−359.666	−83.201	1.890
2400	64.852	248.510	193.035	133.140	−357.503	−71.227	1.550
2500	64.852	251.158	195.308	139.625	−355.360	−59.343	1.240
2600	64.852	253.701	197.505	146.111	−353.233	−47.544	0.955
2700	64.852	256.149	199.632	152.596	−351.116	−35.827	0.693
2800	64.852	258.507	201.693	159.081	−349.005	−24.188	0.451
2900	64.852	260.783	203.691	165.566	−346.897	−12.625	0.227
3000	64.852	262.982	205.631	172.051	−344.787	−1.134	0.020

PREVIOUS: CURRENT: September 1963

0 to 933 K crystal
above 933 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.523	−287.336	−287.336	INFINITE
100	43.032	45.601	143.089	−9.749	−287.427	−286.556	149.681
200	49.852	78.103	103.207	−5.021	−287.621	−285.606	74.593
298.15	52.225	98.500	98.500	0.	−287.859	−284.572	49.856
300	52.258	98.823	98.501	0.097	−287.865	−284.551	49.545
400	53.806	114.077	100.570	5.403	−299.000	−282.898	36.943
500	55.020	126.213	104.526	10.844	−320.758	−276.772	28.914
600	56.233	136.353	109.008	16.407	−320.088	−268.035	23.335
700	57.363	145.106	113.554	22.087	−319.244	−259.424	19.358
800	58.492	152.840	117.990	27.880	−318.250	−250.945	16.385
900	59.580	159.793	122.255	33.784	−317.128	−242.598	14.080
933.000	59.939	161.945	123.621	35.756	CRYSTAL <--> LIQUID TRANSITION		
933.000	64.852	187.237	123.621	59.354			
1000	64.852	191.734	128.036	63.699	−292.002	−236.087	12.332
1100	64.852	197.915	134.112	70.184	−290.333	−230.576	10.949
1200	64.852	203.558	139.667	76.669	−385.474	−222.776	9.697
1300	64.852	208.749	144.784	83.154	−382.995	−209.318	8.411
1400	64.852	213.555	149.527	89.639	−380.532	−196.051	7.315
1500	64.852	218.030	153.946	96.125	−378.089	−182.959	6.371
1600	64.852	222.215	158.084	102.610	−375.672	−170.030	5.551
1700	64.852	226.147	161.973	109.095	−373.283	−157.250	4.832
1800	64.852	229.854	165.642	115.580	−370.927	−144.611	4.196
1900	64.852	233.360	169.115	122.065	−368.607	−132.101	3.632
2000	64.852	236.686	172.411	128.551	−366.322	−119.713	3.127
2100	64.852	239.850	175.548	135.036	−364.071	−107.438	2.672
2200	64.852	242.867	178.540	141.521	−361.854	−95.269	2.262
2300	64.852	245.750	181.400	148.006	−359.666	−83.201	1.890
2400	64.852	248.510	184.139	154.491	−357.503	−71.227	1.550
2500	64.852	251.158	186.767	160.977	−355.360	−59.343	1.240
2600	64.852	253.701	189.293	167.462	−353.233	−47.544	0.955
2700	64.852	256.149	191.724	173.947	−351.116	−35.827	0.693
2800	64.852	258.507	194.067	180.432	−349.005	−24.188	0.451
2900	64.852	260.783	196.329	186.917	−346.897	−12.625	0.227
3000	64.852	262.982	198.514	193.403	−344.787	−1.134	0.020

PREVIOUS: CURRENT: September 1963

D_0° = 18892 ± 1500 cm^{-1}
S°(298.15 K) = 239.6 ± 1 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 128 ± 18 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 126 ± 18 kJ·mol^{-1}

		Electronic Levels and Molecular Constants ($^{127}I^{16}O$), cm^{-1}					
State	T_e	g_i	ω_e	$\omega_e x_e$	B_e	α_e	$D_e \cdot 10^6$	r_e/Å
$X^2\Pi_{3/2}$	0	2	681.6004	4.3699	0.340206	0.0026296	3.6	1.8676
$X^2\Pi_{1/2}$	2091	2	681.6004	4.3699	0.340206	0.0026296	3.6	1.8676
$A^2\Pi_{3/2}$	21557.81	2	514.57	5.52	0.27635	0.00273	[3.2]	2.0723
$A^2\Pi_{1/2}$	[24698]	2	514.57	5.52	0.27635	0.00273	[3.2]	2.0723

Point Group: $C_{\infty v}$ σ=1

Enthalpy of Formation

The dissociation energy has been calculated by many different techniques. The derived values range from 176 to 250 kJ·mol^{-1}. The values may be grouped into two types: (1) derived from a treatment of the observed vibrational energy levels and (2) extracted from kinetic studies.

The two existing spectroscopic studies by Coleman *et al.*[1] and Durie and Ramsay[2] yield dissociation energy values for IO(g). One should note that the first bound excited state $A^2\Pi$ of IO(g) dissociates into $I(^2P_{3/2}) + O(^1D_2)$. Coleman *et al.*,[1] from their study of the IO spectrum in flames, used a graphical Birge–Sponer technique to give 1.92 ± 0.2 eV (185 ± 19 kJ·mol^{-1}). Durie and Ramsay[2] stated that since only six bands were observed in their study of the absorption spectrum of IO, it was not possible to obtain an accurate value for the dissociation of the ground state. They derived an upper limit of <21976 cm^{-1} (2.72 eV or 262.9 kJ·mol^{-1}) from the observed predissociation. Durie and Ramsay felt that a better estimate could be obtained from a Birge–Sponer extrapolation of the first four vibrational levels in the upper state leading to D_0° = 10200 cm^{-1} for the excited state. However, since the accepted values (at that time, 1958) for ClO and BrO were approximately 10% less than the values calculated by the same procedure, they applied the same correction to IO and calculated 14800 ± 1800 cm^{-1} (1.8 ± 0.2 eV or 175.7 ± 21 kJ·mol^{-1}).

Using flame photometry, Phillips and Sugden[3] measured the intensity of the (0,4) band of IO at 5307 to determine the temperature dependent (1900–2700 K) equilibrium constant for the dissociation energy of IO and obtained D_0° = 238.5 ± 25 kJ·mol^{-1}. This value was calculated from the assumed enthalpy of formation value (relative to the monoatomic gases) of 263.6 kJ·mol^{-1} at 2000 K and is considerably higher than the earlier determined spectroscopic values. Using current thermal functions and auxiliary data we calculate D_0° = 256 kJ·mol^{-1} or 21400 cm^{-1}.

Herron and Huie[4] and Huie and Laszlo,[5] in their kinetic studies, questioned the validity of these spectroscopically derived dissociation energy values. The value from the Durie and Ramsay study is too small to be consistent with the kinetic studies. Herron and Huie preferred the results of Phillips and Sugden. Huie and Laszlo adopted an enthalpy of formation based on the molecular beam studies of Radlein *et al.*,[6] D_0° = 222 ± 13 kJ·mol^{-1}, and Buss *et al.*,[7] D_0° = 230 ± 8 kJ·mol^{-1}. Ruscic and Berkowitz,[8] in determining experimentally the ethalpy of formation and ionization potential of HOBr, inferred a new value for the enthalpy of formation of IO; $\Delta_f H^\circ$(IO, 0 K) = 145 kJ·mol^{-1}. This value was a mean of the Radlein *et al.*[6] and the spectroscopic results.[1,2] In concurrence with the arguments of Huie, Herron and Laszlo we adopt D_0° = 226 kJ·mol^{-1} which leads to $\Delta_f H^\circ$(0 K) = 128 ± 18 kJ·mol^{-1}. Additional data needed for the calculations presented here, e.g. thermal functions for I(g), and I_2(ref), O(g), and O_2(ref), are taken from JANAF Thermochemical Tables.[9] A recent photoionization study[10] confirms our adopted value.

Heat Capacity and Entropy

The spectroscopic results tabulated above are for the $^{127}I^{16}O$ isotopomer. Isotopic relationships[11] are used to convert the above constants to those natural abundance species. The latter values are then used in the calculation of the thermal functions. Only the X and A states are included in the calculation; a sum–over–states technique is used. Values of ω_e and $\omega_e x_e$ are from Bekooy *et al.*[12] and Gilles *et al.*,[13] but the value of D_e for the excited state is estimated.[11] The dissociation energy of the A state is estimated to be 12900 cm^{-1}.

The electronic ground state configuration, $X^2\Pi_{3/2}$ (inverted doublet) was confirmed by the EPR measurements of Carrington *et al.*[14] An earlier EPR spectra result, 2330 cm^{-1}, was reported by Brown *et al.*[16] The recent measured value of Gilles *et al.*,[13] 2091 cm^{-1}, for the spin–orbit splitting of the ground state is adopted here. For ClO the spin–orbit splitting of the A state was estimated to be 1.5 times the value found for the ground state.[17] Using the same factor of 1.5 the spin–orbit splitting for the A state in IO is estimated to be 3140 cm^{-1}. The position of the first excited state, $A^2\Pi_{3/2}$, was provided by Bekooy *et al.*,[12] Loewenschuss *et al.*,[18] Vaidya[19] and Durie *et al.*[20] We adopt the 21557.81 cm^{-1} value of Durie *et al.* Additional excited states have been mentioned by Callear and Metcalf[21] and Saito.[15] The higher states were not included in the thermal function calculations.

References

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Continued on page 1463

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	.000	.000	INFINITE	−9.003	127.954	127.954	INFINITE
50	29.104	186.214	337.315	−7.555	128.200	123.526	−129.047
100	29.157	206.394	267.387	−6.099	127.880	118.956	−62.136
150	29.663	218.290	249.166	−4.631	127.421	114.590	−39.904
200	30.696	226.957	242.576	−3.124	126.934	110.387	−28.830
250	31.865	233.933	240.172	−1.560	126.455	106.305	−22.211
298.15	32.900	239.636	239.636	.000	126.016	102.465	−17.951
300	32.938	239.839	239.636	.061	125.999	102.319	−17.815
400	34.700	249.567	240.951	3.446	117.080	94.840	−12.385
500	36.155	257.470	243.488	6.991	94.997	91.415	−9.550
600	37.433	264.177	246.391	10.672	95.221	90.680	−7.894
700	38.533	270.032	249.359	14.472	95.510	89.901	−6.708
800	39.430	275.239	252.274	18.371	95.851	89.075	−5.816
900	40.121	279.925	255.091	22.351	96.233	88.207	−5.119
1000	40.624	284.180	257.790	26.389	96.639	87.292	−4.560
1100	40.968	288.069	260.369	30.470	97.058	86.338	−4.100
1200	41.187	291.644	262.828	34.579	97.476	85.345	−3.715
1300	41.311	294.946	265.173	38.704	97.882	84.317	−3.388
1400	41.366	298.010	267.410	42.839	98.267	83.259	−3.106
1500	41.371	300.864	269.547	46.976	98.619	82.175	−2.862
1600	41.344	303.533	271.588	51.112	98.933	81.069	−2.647
1700	41.294	306.038	273.542	55.244	99.202	79.944	−2.456
1800	41.229	308.397	275.413	59.370	99.419	78.803	−2.287
1900	41.154	310.624	277.208	63.490	99.584	77.654	−2.135
2000	41.071	312.733	278.932	67.601	99.694	76.496	−1.998
2100	40.980	314.735	280.590	71.703	99.749	75.334	−1.874
2200	40.882	316.639	282.186	75.797	99.754	74.172	−1.761
2300	40.774	318.454	283.723	79.879	99.708	73.009	−1.658
2400	40.655	320.186	285.207	83.951	99.618	71.852	−1.564
2500	40.524	321.844	286.639	88.010	99.488	70.695	−1.477
2600	40.380	323.430	288.024	92.055	99.322	69.548	−1.397
2700	40.221	324.951	289.364	96.086	99.125	68.408	−1.323
2800	40.048	326.411	290.661	100.099	98.902	67.272	−1.255
2900	39.859	327.813	291.918	104.095	98.657	66.147	−1.191
3000	39.656	329.161	293.137	108.071	98.392	65.031	−1.132
3100	39.438	330.458	294.320	112.025	98.112	63.922	−1.077
3200	39.208	331.706	295.469	115.958	97.820	62.826	−1.026
3300	38.966	332.909	296.586	119.867	97.517	61.736	−0.977
3400	38.713	334.068	297.671	123.751	97.204	60.659	−0.932
3500	38.452	335.187	298.727	127.609	96.884	59.586	−0.889
3600	38.184	336.266	299.755	131.441	96.558	58.527	−0.849
3700	37.912	337.309	300.756	135.246	96.226	57.473	−0.811
3800	37.635	338.316	301.731	139.023	95.888	56.432	−0.776
3900	37.358	339.290	302.682	142.773	95.546	55.399	−0.742
4000	37.080	340.233	303.609	146.495	95.198	54.371	−0.710
4100	36.803	341.145	304.513	150.189	94.846	53.355	−0.680
4200	36.529	342.028	305.396	153.855	94.489	52.349	−0.651
4300	36.259	342.885	306.258	157.495	94.128	51.348	−0.624
4400	35.993	343.715	307.100	161.107	93.762	50.359	−0.598
4500	35.734	344.521	307.923	164.693	93.390	49.376	−0.573
4600	35.480	345.304	308.727	168.254	93.014	48.401	−0.550
4700	35.234	346.064	309.513	171.790	92.633	47.437	−0.527
4800	34.996	346.803	310.282	175.301	92.246	46.481	−0.506
4900	34.765	347.523	311.035	178.789	91.853	45.528	−0.485
5000	34.543	348.223	311.772	182.254	91.454	44.586	−0.466
5100	34.328	348.905	312.493	185.698	91.050	43.653	−0.447
5200	34.123	349.569	313.200	189.120	90.638	42.730	−0.429
5300	33.925	350.217	313.892	192.523	90.220	41.814	−0.412
5400	33.736	350.850	314.571	195.906	89.795	40.901	−0.396
5500	33.556	351.467	315.236	199.270	89.362	40.001	−0.380
5600	33.383	352.070	315.889	202.617	88.922	39.109	−0.365
5700	33.218	352.660	316.528	205.947	88.474	38.219	−0.350
5800	33.061	353.236	317.156	209.261	88.017	37.344	−0.336
5900	32.911	353.800	317.773	212.559	87.551	36.472	−0.323
6000	32.768	354.352	318.378	215.843	87.076	35.611	−0.310

PREVIOUS: CURRENT: March 1996 (1 bar)

$\Delta_{at}H°(0\ K)$ = [438 ± 25] kJ·mol^{-1}
$S°(298.15\ K)$ = [281.5 ± 4] J·K^{-1}·mol^{-1}

$\Delta_fH°(0\ K)$ = [162.7 ± 25] kJ·mol^{-1}
$\Delta_fH°(298.15\ K)$ = [159.3 ± 25] kJ·mol^{-1}

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
X^2B_1	0.0	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
765(1)
192(1)
[800](1)

Point Group: C_{2v} σ = 2
Bond Distance: I–O = [1.8]Å
Bond Angle: O–I–O = [120]°
Product of the Moments of Inertia: $I_AI_BI_C$ = 725.5989 × 10^{-117} g^3·cm^6

Enthalpy of Formation

For the series OXO(g) [where X = F, Cl, Br, I], there are only reliable experimental data for OClO(g). Assuming that the values $D_0°$(ClO) and $\Delta_{at}H°$(OClO,g) are reasonable, we adopt the ratio of the numbers (~1.94) to apply for a similar relationship between IO(g) and OIO(g). Thus, $\Delta_{at}H°$(OIO,g, 0 K) = 1.94 $D_0°$(IO) = 438 kJ·mol^{-1}.

Heat Capacity and Entropy

Based on the ESR study by Byberg,[1] the ground state of the free IO_2 molecule belongs to the representation B_1 of the point group C_{2v}. This symmetric, bent molecule is estimated to have an O–I–O angle of [120]° and a bond length of [1.8] Å in analogy with the corresponding fluorine, chlorine, and bromine oxide molecules.[2] The principal moments of inertia in g·cm^2 are: I_A = 3.4373 × 10^{-39}, I_B = 12.1991 × 10^{-39}, and I_C = 16.3491 × 10^{-39}.

Two of the three vibrational frequencies have been derived by Gilles *et al.*[3] who used photoelectron spectroscopic techniques. ν_3 is estimated based on anticipated trends with the OXO(g) family[2] and assuming $\nu_3 > \nu_1$.

References

[1]J. R. Byberg, J. Chem. Phys. **88**(4), 2129–34 (1988).
[2]NIST–JANAF Thermochemical Tables: OFO(g): (September 1995); OClO(g): (March 1996); OBrO(g): (March 1996).
[3]M. K. Gilles, M. L. Polak, and W. C. Lineberger, J. Chem. Phys. **96**(11), 8012–20 (1992)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−11.861	162.744	162.744	INFINITE
50	34.278	211.198	414.979	−10.189	162.490	160.395	−167.564
100	37.850	236.126	319.929	−8.380	161.795	158.563	−82.825
150	40.093	251.918	294.779	−6.429	161.091	157.100	−54.707
200	42.280	263.746	285.600	−4.371	160.427	155.871	−40.709
250	44.599	273.429	282.225	−2.199	159.828	154.803	−32.344
298.15	46.697	281.468	281.468	.000	159.323	153.882	−26.959
300	46.772	281.757	281.468	.086	159.304	153.848	−26.787
400	50.184	295.711	283.348	4.945	150.373	152.450	−19.908
500	52.445	307.170	287.000	10.085	128.355	155.097	−16.203
600	53.929	316.872	291.191	15.408	128.642	160.419	−13.966
700	54.929	325.265	295.473	20.854	128.950	165.691	−12.364
800	55.626	332.648	299.668	26.384	129.253	170.919	−11.160
900	56.127	339.230	303.705	31.973	129.542	176.109	−10.221
1000	56.498	345.164	307.559	37.605	129.811	181.269	−9.469
1100	56.779	350.562	311.226	43.270	130.059	186.403	−8.852
1200	56.997	355.513	314.714	48.959	130.283	191.515	−8.336
1300	57.168	360.082	318.030	54.668	130.480	196.609	−7.900
1400	57.306	364.324	321.187	60.391	130.647	201.690	−7.525
1500	57.419	368.281	324.196	66.128	130.779	206.759	−7.200
1600	57.511	371.990	327.069	71.875	130.870	211.821	−6.915
1700	57.588	375.479	329.815	77.630	130.915	216.879	−6.664
1800	57.653	378.773	332.444	83.392	130.911	221.935	−6.440
1900	57.709	381.891	334.965	89.160	130.855	226.993	−6.240
2000	57.756	384.853	337.386	94.933	130.745	232.056	−6.061
2100	57.797	387.672	339.714	100.711	130.583	237.125	−5.898
2200	57.832	390.361	341.955	106.492	130.371	242.204	−5.751
2300	57.863	392.933	344.116	112.277	130.113	247.293	−5.616
2400	57.891	395.396	346.202	118.065	129.813	252.393	−5.493
2500	57.915	397.760	348.217	123.855	129.476	257.508	−5.380
2600	57.936	400.031	350.167	129.648	129.109	262.636	−5.276
2700	57.955	402.218	352.054	135.442	128.718	267.780	−5.181
2800	57.972	404.326	353.884	141.239	128.309	272.938	−5.092
2900	57.988	406.361	355.659	147.037	127.887	278.110	−5.009
3000	58.002	408.327	357.382	152.836	127.458	283.297	−4.933
3100	58.014	410.229	359.056	158.637	127.026	288.500	−4.861
3200	58.026	412.071	360.684	164.439	126.596	293.715	−4.794
3300	58.036	413.857	362.268	170.242	126.172	298.943	−4.732
3400	58.046	415.590	363.811	176.046	125.756	304.186	−4.673
3500	58.055	417.272	365.315	181.851	125.351	309.439	−4.618
3600	58.063	418.908	366.781	187.657	124.959	314.705	−4.566
3700	58.070	420.499	368.211	193.464	124.581	319.980	−4.517
3800	58.077	422.048	369.608	199.271	124.219	325.267	−4.471
3900	58.083	423.556	370.972	205.079	123.874	330.563	−4.427
4000	58.089	425.027	372.305	210.888	123.546	335.866	−4.386
4100	58.094	426.461	373.608	216.697	123.234	341.178	−4.347
4200	58.099	427.861	374.883	222.507	122.940	346.497	−4.309
4300	58.104	429.228	376.131	228.317	122.663	351.824	−4.274
4400	58.108	430.564	377.353	234.128	122.402	357.155	−4.240
4500	58.112	431.870	378.550	239.939	122.156	362.493	−4.208
4600	58.116	433.147	379.724	245.750	121.926	367.836	−4.177
4700	58.120	434.397	380.874	251.562	121.709	373.185	−4.147
4800	58.123	435.621	382.001	257.374	121.505	378.538	−4.119
4900	58.126	436.819	383.108	263.186	121.313	383.895	−4.092
5000	58.129	437.994	384.194	268.999	121.132	389.256	−4.067
5100	58.132	439.145	385.260	274.812	120.959	394.620	−4.042
5200	58.135	440.274	386.307	280.626	120.795	399.987	−4.018
5300	58.137	441.381	387.336	286.439	120.636	405.358	−3.995
5400	58.140	442.468	388.347	292.253	120.483	410.731	−3.973
5500	58.142	443.535	389.341	298.067	120.333	416.107	−3.952
5600	58.144	444.582	390.318	303.882	120.184	421.487	−3.931
5700	58.146	445.612	391.279	309.696	120.036	426.868	−3.912
5800	58.148	446.623	392.224	315.511	119.886	432.253	−3.893
5900	58.150	447.617	393.155	321.326	119.733	437.639	−3.875
6000	58.151	448.594	394.071	327.141	119.575	443.029	−3.857

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [296.4 \pm 4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [119 \pm 40]\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [116.5 \pm 40]\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
X[^{2}A"]	0.0	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1500](1)
[150](1)
[275](1)

Point Group: C_s $\sigma = 1$
Bond Distances: I–O = [2.4]Å; O–O = [1.25]Å
Bond Angle: I–O–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [1314.2931 \times 10^{-117}]\ g^3{\cdot}cm^6$

Enthalpy of Formation

Following trends[1] in the reaction XOO(g) → X(g) + 2O(g), a reasonable estimate for the iodine reaction would be 470 kJ·mol which yields $\Delta_f H°(0\ K) = -91.25\ kJ{\cdot}mol^{-1}$. However, looking at the trends in the reaction XOO(g) → XO(g) + O(g), a reasonable estimate for the iodine reaction would be 260 $kJ{\cdot}mol^{-1}$ which leads to a $\Delta_f H°(0\ K) = 119\ kJ{\cdot}mol^{-1}$. This large discrepancy in estimates is a result of the estimates and uncertainties in all XOO enthalpies of formation. We adopt the value based on the reaction involving an X–O bond breakage.

Heat Capacity and Entropy

The vibrational frequencies and structure are estimated based on the existing data for FOO(g), ClOO(g), and BrOO(g).[1] The principal moments of inertia in $g{\cdot}cm^2$ are: $I_A = 1.1391 \times 10^{-39}$, $I_B = 33.4021 \times 10^{-39}$, and $I_C = 34.5412 \times 10^{-39}$.

References

[1]NIST–JANAF Thermochemical Tables: FOO(g): Sept. 1995; ClOO(g): March 1996; BrOO(g): (March 1996).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J{\cdot}K^{-1}{\cdot}mol^{-1}$			$kJ{\cdot}mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−12.806	119.000	119.000	INFINITE
50	35.573	219.838	442.181	−11.117	118.762	116.235	−121.430
100	41.565	246.433	338.245	−9.181	118.195	113.932	−59.512
150	45.076	264.029	310.732	−7.005	117.715	111.907	−38.970
200	46.892	277.272	300.780	−4.702	117.297	110.035	−28.738
250	47.962	287.859	297.172	−2.328	116.899	108.266	−22.621
298.15	48.727	296.374	296.374	.000	116.523	106.638	−18.682
300	48.754	296.676	296.375	.090	116.509	106.576	−18.557
400	50.151	310.895	298.305	5.036	107.664	103.667	−13.538
500	51.463	322.229	301.993	10.118	85.589	104.801	−10.948
600	52.620	331.717	306.178	15.323	85.758	108.628	−9.457
700	53.581	339.903	310.424	20.635	85.931	112.426	−8.389
800	54.355	347.110	314.568	26.033	86.103	116.199	−7.587
900	54.973	353.549	318.548	31.501	86.270	119.950	−6.962
1000	55.467	359.368	322.344	37.024	86.430	123.684	−6.461
1100	55.863	364.674	325.954	42.591	86.580	127.402	−6.050
1200	56.184	369.548	329.387	48.194	86.718	131.107	−5.707
1300	56.446	374.056	332.652	53.826	86.839	134.801	−5.416
1400	56.662	378.248	335.761	59.482	86.938	138.487	−5.167
1500	56.842	382.163	338.725	65.157	87.009	142.166	−4.951
1600	56.993	385.837	341.556	70.849	87.045	145.842	−4.761
1700	57.121	389.296	344.263	76.555	87.041	149.517	−4.594
1800	57.230	392.564	346.857	82.273	86.992	153.192	−4.446
1900	57.324	395.661	349.345	88.001	86.895	156.873	−4.313
2000	57.405	398.603	351.735	93.737	86.749	160.559	−4.193
2100	57.475	401.406	354.034	99.481	86.554	164.254	−4.086
2200	57.537	404.081	356.248	105.232	86.311	167.961	−3.988
2300	57.591	406.640	358.384	110.988	86.024	171.678	−3.899
2400	57.639	409.092	360.446	116.750	85.698	175.408	−3.818
2500	57.681	411.446	362.439	122.516	85.337	179.154	−3.743
2600	57.719	413.709	364.368	128.286	84.948	182.914	−3.675
2700	57.753	415.888	366.236	134.059	84.536	186.690	−3.612
2800	57.784	417.988	368.047	139.836	84.107	190.481	−3.553
2900	57.812	420.017	369.804	145.616	83.667	194.288	−3.499
3000	57.836	421.977	371.511	151.399	83.220	198.110	−3.449
3100	57.859	423.874	373.170	157.183	82.773	201.948	−3.403
3200	57.880	425.711	374.783	162.970	82.328	205.798	−3.359
3300	57.899	427.492	376.353	168.759	81.889	209.663	−3.319
3400	57.916	429.221	377.883	174.550	81.460	213.542	−3.281
3500	57.932	430.900	379.374	180.342	81.042	217.433	−3.245
3600	57.946	432.532	380.828	186.136	80.638	221.336	−3.211
3700	57.960	434.120	382.247	191.932	80.249	225.249	−3.180
3800	57.972	435.666	383.632	197.728	79.876	229.174	−3.150
3900	57.983	437.172	384.986	203.526	79.521	233.108	−3.122
4000	57.994	438.640	386.309	209.325	79.183	237.049	−3.096
4100	58.004	440.072	387.603	215.125	78.862	241.000	−3.070
4200	58.013	441.470	388.869	220.926	78.559	244.958	−3.047
4300	58.022	442.835	390.108	226.727	78.274	248.924	−3.024
4400	58.030	444.169	391.322	232.530	78.004	252.895	−3.002
4500	58.037	445.474	392.511	238.333	77.751	256.873	−2.982
4600	58.044	446.749	393.676	244.137	77.513	260.855	−2.962
4700	58.051	447.998	394.819	249.942	77.290	264.844	−2.943
4800	58.057	449.220	395.939	255.747	77.079	268.837	−2.926
4900	58.063	450.417	397.039	261.553	76.880	272.834	−2.908
5000	58.068	451.590	398.118	267.360	76.693	276.835	−2.892
5100	58.073	452.740	399.178	273.167	76.514	280.840	−2.876
5200	58.078	453.868	400.219	278.974	76.344	284.847	−2.861
5300	58.083	454.974	401.242	284.783	76.180	288.859	−2.847
5400	58.087	456.060	402.247	290.591	76.021	292.873	−2.833
5500	58.091	457.126	403.235	296.400	75.866	296.890	−2.820
5600	58.095	458.172	404.207	302.209	75.712	300.911	−2.807
5700	58.099	459.201	405.162	308.019	75.559	304.933	−2.794
5800	58.102	460.211	406.103	313.829	75.405	308.959	−2.782
5900	58.105	461.204	407.028	319.639	75.247	312.986	−2.771
6000	58.109	462.181	407.939	325.450	75.085	317.018	−2.760

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [293.0 \pm 4]\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [248 \pm 50]\ kJ{\cdot}mol^{-1}$
$\Delta_f H°(298.15\ K) = [241.9 \pm 50]\ kJ{\cdot}mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
$[^2A_1]$	0	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[780](1)
[357](1)
[809](2)
[326](2)

Point Group: C_{3v} σ=3
Bond Distance: I–O = [1.79]Å
Bond Angle: O–I–O = [89]°
Product of the Moments of Inertia: $I_A I_B I_C = 3642.3539 \times 10^{-117}\ g^3{\cdot}cm^6$

Enthalpy of Formation

We adopt an enthalpy of formation value which is based on an assumed relationship of $\Delta_{at}H°(IO_3,g)/3 = 0.9D°_0(IO)$.

An enthalpy of formation value has been reported by Farkas and Klein.[1] This value, − 28 kcal·mol^{-1} (−117 kJ·mol^{-1}), is derived from absorption spectra measurements of iodate ions in solutions. There is considerable uncertainty in this value, both in terms of the experimental measurements and the fact that the authors have interchanged IO_3 and IO_3^-. This corresponds to an average bond energy of 241.9 kJ·mol^{-1}. Since this value is greater than $D°_0(IO)$, it is suspect.

Heat Capacity and Entropy

The structure of this molecule is estimated to be pyramidal with a O–I–O angle of [89]° and a bond length of 1.79Å in analogy with the corresponding chlorine and bromine oxide molecules. Venkateswarlu and Sundaram,[2] Venkateswarlu and Rajalakshmi,[3] Rao and Santhamma,[4] Rao,[5] and Thirugnanasambandam and Mohan[6] assumed the same structure and bond angle for ClO_3, BrO_3 and IO_3. Using Badger's rule, the authors examined the relationship between the vibrational frequencies and force constants for the three pyramidal molecules $-ClO_3$, BrO_3, and IO_3. Although these authors refer to early measurements of the vibrational frequencies, the values appear to be in part those of the ion IO_3^-. Their reported values are adopted here although we treat them as estimated values. The vibrational frequencies are derived from the force constants which describe the other halogen oxide molecules. The principal moments of inertia in g·cm^2 are: $I_A = 14.7650 \times 10^{-39}$, $I_B = 14.7650 \times 10^{-39}$, and $I_C = 16.7280 \times 10^{-39}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C°_p$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.505	248.000	248.000	INFINITE
50	33.412	215.531	452.355	−11.841	247.013	248.530	−259.637
100	38.019	239.747	340.560	−10.081	245.542	250.613	−130.907
150	45.140	256.517	309.858	−8.001	244.239	253.441	−88.256
200	51.557	270.403	298.303	−5.580	243.210	256.671	−67.036
250	57.096	282.519	293.959	−2.860	242.430	260.131	−54.351
298.15	61.560	292.970	292.970	.000	241.881	263.593	−46.180
300	61.714	293.351	292.971	.114	241.863	263.727	−45.919
400	68.430	312.098	295.481	6.647	233.120	271.416	−35.443
500	72.681	327.860	300.424	13.718	211.505	283.075	−29.573
600	75.418	341.371	306.149	21.133	212.303	297.316	−25.884
700	77.245	353.143	312.040	28.772	213.176	311.416	−23.238
800	78.511	363.545	317.841	36.563	214.073	325.389	−21.246
900	79.417	372.847	323.445	44.462	214.968	339.249	−19.690
1000	80.086	381.251	328.812	52.439	215.851	353.011	−18.439
1100	80.592	388.909	333.933	60.474	216.715	366.685	−17.412
1200	80.984	395.939	338.811	68.553	217.555	380.282	−16.553
1300	81.293	402.434	343.458	76.668	218.367	393.809	−15.823
1400	81.541	408.467	347.889	84.810	219.145	407.275	−15.196
1500	81.742	414.100	352.117	92.975	219.884	420.687	−14.650
1600	81.908	419.381	356.158	101.157	220.578	434.051	−14.170
1700	82.047	424.351	360.025	109.355	221.220	447.373	−13.746
1800	82.163	429.044	363.730	117.566	221.806	460.658	−13.368
1900	82.262	433.489	367.286	125.787	222.334	473.913	−13.029
2000	82.347	437.711	370.702	134.018	222.800	487.142	−12.723
2100	82.420	441.731	373.989	142.256	223.207	500.349	−12.446
2200	82.484	445.566	377.156	150.502	223.554	513.539	−12.193
2300	82.540	449.234	380.211	158.753	223.847	526.712	−11.962
2400	82.589	452.748	383.161	167.010	224.089	539.875	−11.750
2500	82.632	456.120	386.012	175.271	224.286	553.028	−11.555
2600	82.670	459.362	388.771	183.536	224.443	566.175	−11.375
2700	82.704	462.483	391.444	191.804	224.568	579.316	−11.208
2800	82.735	465.491	394.035	200.076	224.665	592.454	−11.052
2900	82.763	468.395	396.550	208.351	224.742	605.586	−10.908
3000	82.788	471.201	398.991	216.629	224.802	618.718	−10.773
3100	82.810	473.916	401.365	224.909	224.852	631.849	−10.647
3200	82.831	476.545	403.673	233.191	224.895	644.976	−10.528
3300	82.849	479.095	405.920	241.475	224.936	658.103	−10.417
3400	82.866	481.568	408.109	249.761	224.977	671.229	−10.312
3500	82.882	483.970	410.242	258.048	225.023	684.353	−10.213
3600	82.896	486.306	412.323	266.337	225.074	697.476	−10.120
3700	82.910	488.577	414.353	274.627	225.133	710.597	−10.032
3800	82.922	490.788	416.336	282.919	225.201	723.718	−9.948
3900	82.933	492.942	418.273	291.212	225.280	736.836	−9.869
4000	82.943	495.042	420.166	299.506	225.369	749.951	−9.793
4100	82.953	497.090	422.017	307.800	225.469	763.065	−9.722
4200	82.962	499.089	423.828	316.096	225.580	776.175	−9.653
4300	82.971	501.042	425.601	324.393	225.703	789.284	−9.588
4400	82.978	502.949	427.338	332.690	225.835	802.388	−9.526
4500	82.986	504.814	429.039	340.988	225.978	815.489	−9.466
4600	82.993	506.638	430.706	349.287	226.130	828.587	−9.409
4700	82.999	508.423	432.341	357.587	226.290	841.683	−9.354
4800	83.005	510.170	433.944	365.887	226.456	854.775	−9.302
4900	83.011	511.882	435.517	374.188	226.629	867.864	−9.252
5000	83.016	513.559	437.061	382.489	226.805	880.949	−9.203
5100	83.021	515.203	438.577	390.791	226.984	894.031	−9.157
5200	83.026	516.815	440.066	399.093	227.165	907.107	−9.112
5300	83.030	518.397	441.530	407.396	227.344	920.182	−9.069
5400	83.034	519.949	442.967	415.699	227.521	933.252	−9.027
5500	83.038	521.472	444.381	424.003	227.693	946.319	−8.987
5600	83.042	522.969	445.771	432.307	227.859	959.385	−8.949
5700	83.046	524.439	447.138	440.611	228.016	972.445	−8.911
5800	83.049	525.883	448.484	448.916	228.162	985.505	−8.875
5900	83.052	527.303	449.807	457.221	228.296	998.559	−8.841
6000	83.055	528.698	451.111	465.527	228.414	1011.615	−8.807

PREIVOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = 280.094 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 110.88 \pm 37.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 107.74 \pm 37.7\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$2\Pi_{3/2}$	[8300]	2
$A[^2\Delta]$	20528.5	[4]
$B[^2\Sigma]$	33488	[2]

$\omega_e = 160.5\ cm^{-1}$ $\omega_e x_e = 0.25\ cm^{-1}$ $\sigma = 1$

$B_e = [0.02861]\ cm^{-1}$ $\alpha_e = [0.00006]\ cm^{-1}$ $r_e = [2.736]$ Å

Enthalpy of Formation

$\Delta_f H°$(PbI, g, 0 K) = 26.50 ± 9 kcal·mol^{-1} is calculated from $D_0° = 46 \pm 9$ kcal·mol^{-1} with $\Delta_f H°$(Pb, g) = 46.91 ± 0.13 kcal·mol^{-1} [1] and $\Delta_f H°$(I, g, 0 K) = 25.633 kcal·mol^{-1}).[1] The dissociation energy is uncertain. Both Rosen[2] and Gaydon[3] referred to the most probable value of $D_0° = 1.98$ eV determined by Wieland and Newburgh[4] from emission and absorption spectra. Interpretation is difficult and Wieland and Newburgh[4,5] have given possible values of 2.84, 1.98, and 1.36 eV with 1.98 eV given as the most probable value. The linear Birge–Sponer extrapolation of the adopted ground state vibrational constants, derived from emission and absorption spectra (ν, 0 36)[5] gives a dissociation energy of 3.18 eV. Correction for the ionic character of PbI as suggested by Hildenbrand[6] gives $D_0° = 2.7$ eV (62.3 kcal·mol^{-1}). This is in better agreement with the original $D_0° = 2.84$ eV given by Wieland and Newburgh[5] than it is with $D_0° = 1.98$ eV recommended later.[4] An intercomparison of the dissociaiton energies of lead[1] mercury[2] and potassium[1] halides suggests a $D_0°$ value near 45 kcal·mol^{-1}. The rounded value $D_0° = 2.0 \pm 0.4$ eV (46 ± 9 kcal·mol^{-1}) listed by Gaydon[3] is adopted. $\Delta_f H°$(PbI, g, 298.15 K) = 25.75 ± 9 kcal·mol^{-1} is calculated from the selected $\Delta_f H°$(PbI, g, 0 K) = 26.5 ± 9 kcal·mol^{-1}.

Heat Capacity and Entropy

The vibrational constants are taken from the compilation of Rosen.[2] The electronic states and levels are from Rosen[2] except that the $^2\Pi_{3/2}$ state at 8300 cm^{-1} is added in analogy to Pb[1] and PbCl.[1] The value of $r_e = 2.736$ Å is estimated from a comparison of the sums of the ionic radii of the lead halides with the adopted r_e values for PbF, PbCl, and PbBr.[1] B_e is calculated from the adopted r_e. The value for α_e is estimated assuming a Morse potential function.

References

[1]JANAF Thermochemical Tables: Pb(g), 3–31–62; I(g), 12–31–61; PbF(g), 12–31–73; PbCl(g), 6–30–73; PbBr(g), 12–31–73; KF(g), 6–30–69; KCl(g), 3–31–66; KBr(g), 3–31–67; KI(g), 6–30–67.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.339	110.877	110.877	INFINITE
100	34.581	240.551	312.703	−7.215	110.709	93.387	−48.780
200	36.646	265.350	283.479	−3.626	109.308	76.588	−20.003
250	36.968	273.565	280.704	−1.785	108.530	68.497	−14.312
298.15	37.155	280.094	280.094	0.	107.738	60.858	−10.662
300	37.160	280.323	280.094	0.069	107.707	60.567	−10.546
350	37.288	286.062	280.547	1.930	106.809	52.780	−7.877
400	37.380	291.047	281.555	3.797	97.887	45.399	−5.929
450	37.451	295.454	282.859	5.668	96.345	38.930	−4.519
500	37.508	299.403	284.320	7.542	74.720	34.534	−3.608
600	37.601	306.250	287.421	11.297	73.710	26.591	−2.315
700	37.676	312.052	290.536	15.061	67.768	19.620	−1.464
800	37.742	317.087	293.547	18.832	66.632	12.820	−0.837
900	37.803	321.536	296.415	22.610	65.529	6.160	−0.358
1000	37.865	325.522	299.130	26.393	64.457	−0.379	0.020
1100	37.931	329.134	301.696	30.183	63.414	−6.812	0.323
1200	38.004	332.438	304.122	33.979	62.401	−13.151	0.572
1300	38.088	335.483	306.419	37.784	61.407	−19.407	0.780
1400	38.187	338.309	308.597	41.597	60.414	−25.586	0.955
1500	38.301	340.948	310.666	45.422	59.410	−31.694	1.104
1600	38.433	343.424	312.637	49.258	58.386	−37.734	1.232
1700	38.582	345.758	314.518	53.109	57.333	−43.709	1.343
1800	38.747	347.968	316.315	56.975	56.247	−49.622	1.440
1900	38.926	350.068	318.037	60.859	55.126	−55.473	1.525
2000	39.119	352.069	319.689	64.761	53.968	−61.264	1.600
2100	39.322	353.983	321.276	68.683	−124.446	−59.882	1.489
2200	39.533	355.817	322.805	72.625	−125.282	−56.788	1.348
2300	39.750	357.579	324.279	76.590	−126.211	−53.654	1.219
2400	39.972	359.275	325.702	80.576	−127.232	−50.478	1.099
2500	40.196	360.911	327.078	84.584	−128.338	−47.258	0.987
2600	40.421	362.492	328.410	88.615	−129.524	−43.991	0.884
2700	40.645	364.022	329.700	92.668	−130.780	−40.678	0.787
2800	40.867	365.504	330.953	96.744	−132.099	−37.317	0.696
2900	41.086	366.942	332.169	100.842	−133.470	−33.908	0.611
3000	41.303	368.339	333.352	104.961	−134.882	−30.450	0.530
3100	41.515	369.696	334.502	109.102	−136.327	−26.946	0.454
3200	41.724	371.018	335.623	113.264	−137.795	−23.394	0.382
3300	41.928	372.305	336.715	117.447	−139.275	−19.796	0.313
3400	42.128	373.560	337.780	121.649	−140.759	−16.153	0.248
3500	42.323	374.784	338.820	125.872	−142.238	−12.467	0.186
3600	42.514	375.978	339.836	130.114	−143.704	−8.738	0.127
3700	42.702	377.146	340.828	134.375	−145.151	−4.969	0.070
3800	42.885	378.287	341.799	138.654	−146.572	−1.161	0.016
3900	43.064	379.403	342.749	142.951	−147.962	2.684	−0.036
4000	43.240	380.496	343.679	147.267	−149.314	6.564	−0.086
4100	43.412	381.566	344.590	151.599	−150.626	10.477	−0.133
4200	43.580	382.614	345.483	155.949	−151.892	14.422	−0.179
4300	43.746	383.641	346.359	160.315	−153.111	18.396	−0.223
4400	43.908	384.649	347.217	164.698	−154.280	22.398	−0.266
4500	44.068	385.637	348.060	169.097	−155.397	26.426	−0.307
4600	44.224	386.608	348.888	173.511	−156.460	30.478	−0.346
4700	44.378	387.560	349.701	177.942	−157.468	34.553	−0.384
4800	44.529	388.496	350.499	182.387	−158.421	38.649	−0.421
4900	44.678	389.416	351.284	186.847	−159.318	42.764	−0.456
5000	44.824	390.320	352.056	191.322	−160.160	46.897	−0.490
5100	44.967	391.209	352.815	195.812	−160.947	51.046	−0.523
5200	45.108	392.084	353.561	200.316	−161.679	55.210	−0.555
5300	45.247	392.944	354.296	204.834	−162.357	59.387	−0.585
5400	45.383	393.791	355.020	209.365	−162.982	63.577	−0.615
5500	45.516	394.625	355.732	213.910	−163.556	67.778	−0.644
5600	45.647	395.447	356.434	218.468	−164.080	71.989	−0.671
5700	45.776	396.256	357.126	223.039	−164.555	76.209	−0.698
5800	45.902	397.053	357.807	227.623	−164.983	80.436	−0.724
5900	46.025	397.839	358.479	232.220	−165.364	84.671	−0.750
6000	46.147	398.613	359.142	236.828	−165.702	88.912	−0.774

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 253.854\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 313.51 \pm 41.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 313.63 \pm 41.8\ kJ·mol^{-1}$

Electronic Levels and Molecular Constants (σ = 1)								
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X^2\Pi_{1/2}$	0	2	363.2	1.25	0.123	[0.001]	2.45	1
$^2\Pi_{3/2}$	650	2	358.5	1.1	0.123	[0.001]	2.45	1,6
$A'^4\Sigma_{1/2}$	20939.1	4	275.3	5.6	0.118	[0.001]	2.50	1
$A^2\Sigma^+$	21204.9	2	208.3	1.66	0.085	[0.001]	2.95	1
$B^2\Sigma^+$	32380.3	2	471.0	0.9	[0.123]	[0.001]	[2.45]	1
$C^2\Pi$	42710	4	485	3.5	[0.123]	[0.001]	[2.45]	6

Enthalpy of Formation

The adopted value is $\Delta_f H°(298.15\ K) = 75.0 \pm 10\ kcal·mol^{-1}$. The value is based on a Birge–Sponer extrapolation of the $A^2\Sigma$ state by Billingsley[1] who obtains a dissociation limit of 69.76 $kcal·mol^{-1}$. Correction for the ionic character of the bond according to Hildenbrand[2] yields $D_0° = 57.3\ kcal·mol^{-1}$ which, with auxiliary JANAF data,[3] gives the adopted value. An uncertainty of $\pm 10\ kcal·mol^{-1}$ is assigned to $\Delta_f H°(298.15\ K)$ due to the approximate nature of Birge–Sponer extrapolation based on data from the first few vibrational levels only. The adopted value of $D_0° = 57.3 \pm 8\ kcal·mol^{-1}$ is in good agreement with $D_0° = 56.9$ and 61.8 $kcal·mol^{-1}$ obtained in a similar manner from the $A'\ ^4\Sigma$ state and ground state data, respectively. The value is also in reasonable agreement with $D_0° = 72.4$ and $65 \pm 10\ kcal·mol^{-1}$ obtained by theoretical and empirical procedures, respectively.[4,5] The upper limit for $D_0° = 4.02$ ev (92.7 $kcal·mol^{-1}$) is based on the observed predissociation of the $B^2\Sigma$ state.[1] The adopted value of $D_0°$ is also in good agreement with the average (per bond) heat of atomization of SiI_4(g) of 58.6 $kcal·mol^{-1}$.[3]

Heat Capacity and Entropy

Electronic levels and molecular constants are taken from the studies by Oldershaw and Robinson[6] and Billingsley.[1] Several systems above 40,000 cm^{-1} have been observed by Oldershaw and Robinson[7] but are not included since their states and degeneracies are not known. They would make only a minor contribution to the thermodynamic properties at 6000 K and a negligible contribution at lower temperatures. Of more importance is the uncertainty in the value of the ground state spin splitting constant and the energy of the $A'^4\Sigma^-$ state. Billingsley[1] interprets the observed A'–X emission spectrum as terminating at the upper level of the split ground state and calculates the ground state splitting of 646.4 cm^{-1} from the observation of one absorption line. Lakshminarayana and Haranath[8] observe a second emission series 650.3 cm^{-1} to the red of that observed by Billingsley, and although the ground state splittings are in agreement, this would place the A' state approximately 650 cm^{-1} lower than reported. We favor Billingsley's interpretation while recognizing the need for additional work to resolve this paradox. In addition the $B'\ ^2\Delta$ state observed for the other silicon monohalides[3] is not observed for SiI. Its energy is difficult to predict due to the rapidly dropping energy of this state across the series and the possible misidentification of this state for SiBr. Accordingly, we have assigned an uncertainty of $\pm 0.1\ cal·K^{-1}·mol^{-1}$ to $S°(298.15\ K)$ to account for this uncertainty. Since no information is available on the rotational constants for the B and C states, the ground state $B_e = .123\ cm^{-1}$ was used in our calculations. Likewise, values of $\alpha_e = .001\ cm^{-1}$ are estimated for all states. The ground state is treated as two distinct levels due to the splitting of this state as expressed by the spin coupling constant ($A = 650\ cm^{-1}$). This leads to slightly biased results at low temperature; the stated uncertainty in $S°(298.15\ K)$ should account for this also. All molecular constants have been corrected to reflect the natural abundance of Si.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.936	313.510	313.510	INFINITE
100	30.446	216.152	286.167	−7.001	314.654	296.471	−154.861
200	35.736	238.883	257.338	−3.691	314.319	278.371	−72.703
250	37.748	247.087	254.491	−1.851	313.995	269.420	−56.292
298.15	39.038	253.854	253.854	0.	313.629	260.868	−45.703
300	39.076	254.096	253.855	0.072	313.614	260.540	−45.364
350	39.850	260.184	254.334	2.047	313.148	251.730	−37.569
400	40.238	265.534	255.407	4.051	304.652	243.264	−31.767
450	40.381	270.283	256.801	6.067	303.527	235.658	−27.354
500	40.380	274.539	258.366	8.087	282.312	230.077	−24.036
600	40.179	281.886	261.692	12.116	282.088	219.650	−19.122
700	39.905	288.059	265.030	16.120	281.761	209.268	−15.616
800	39.652	293.370	268.248	20.098	281.339	198.940	−12.989
900	39.442	298.028	271.304	24.052	280.837	188.669	−10.950
1000	39.276	302.175	274.187	27.987	280.260	178.458	−9.322
1100	39.151	305.912	276.904	31.909	279.618	168.309	−7.992
1200	39.057	309.314	279.465	35.819	278.913	158.220	−6.887
1300	38.989	312.438	281.883	39.721	278.147	148.193	−5.954
1400	38.943	315.325	284.170	43.617	277.317	138.228	−5.157
1500	38.913	318.011	286.338	47.510	276.422	128.324	−4.469
1600	38.897	320.522	288.397	51.400	275.458	118.481	−3.868
1700	38.891	322.880	290.356	55.290	224.244	109.149	−3.354
1800	38.895	325.103	292.226	59.179	223.363	102.403	−2.972
1900	38.906	327.206	294.012	63.069	222.449	95.708	−2.631
2000	38.924	329.202	295.722	66.960	221.500	89.062	−2.326
2100	38.948	331.102	297.362	70.854	220.520	82.464	−2.051
2200	38.976	332.914	298.937	74.750	219.512	75.914	−1.802
2300	39.010	334.647	300.452	78.649	218.479	69.409	−1.576
2400	39.049	336.308	301.912	82.552	217.427	62.951	−1.370
2500	39.093	337.903	303.320	86.459	216.362	56.536	−1.181
2600	39.143	339.438	304.679	90.371	215.292	50.164	−1.008
2700	39.199	340.916	305.994	94.288	214.221	43.833	−0.848
2800	39.262	342.343	307.267	98.211	213.156	37.542	−0.700
2900	39.333	343.722	308.501	102.141	212.104	31.289	−0.564
3000	39.412	345.056	309.697	106.078	211.070	25.072	−0.437
3100	39.500	346.350	310.859	110.024	210.059	18.888	−0.318
3200	39.598	347.606	311.987	113.978	209.076	12.737	−0.208
3300	39.708	348.826	313.085	117.944	208.125	6.617	−0.105
3400	39.829	350.013	314.154	121.920	207.210	0.524	−0.008
3500	39.963	351.169	315.195	125.910	206.333	−5.542	0.083
3600	40.110	352.297	316.210	129.913	−178.653	−1.123	0.016
3700	40.271	353.398	317.200	133.932	−179.030	3.814	−0.054
3800	40.448	354.475	318.167	137.968	−179.362	8.760	−0.120
3900	40.640	355.528	319.112	142.022	−179.648	13.714	−0.184
4000	40.848	356.559	320.035	146.097	−179.885	18.675	−0.244
4100	41.072	357.571	320.938	150.193	−180.071	23.642	−0.301
4200	41.314	358.563	321.822	154.312	−180.206	28.612	−0.356
4300	41.572	359.538	322.688	158.456	−180.287	33.585	−0.408
4400	41.848	360.497	323.537	162.627	−180.313	38.559	−0.458
4500	42.141	361.441	324.368	166.826	−180.283	43.533	−0.505
4600	42.452	362.370	325.185	171.056	−180.196	48.506	−0.551
4700	42.781	363.287	325.985	175.317	−180.051	53.477	−0.594
4800	43.127	364.191	326.772	179.612	−179.847	58.443	−0.636
4900	43.491	365.084	327.545	183.943	−179.583	63.405	−0.676
5000	43.872	365.967	328.304	188.311	−179.258	68.361	−0.714
5100	44.269	366.839	329.051	192.718	−178.871	73.310	−0.751
5200	44.683	367.703	329.786	197.166	−178.422	78.250	−0.786
5300	45.113	368.558	330.510	201.655	−177.910	83.181	−0.820
5400	45.559	369.406	331.222	206.189	−177.334	88.102	−0.852
5500	46.020	370.246	331.924	210.768	−176.693	93.012	−0.883
5600	46.496	371.079	332.616	215.393	−175.988	97.909	−0.913
5700	46.985	371.906	333.298	220.067	−175.217	102.793	−0.942
5800	47.488	372.728	333.971	224.791	−174.380	107.664	−0.970
5900	48.003	373.544	334.635	229.565	−173.478	112.519	−0.996
6000	48.531	374.355	335.290	234.392	−172.508	117.358	−1.022

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 272.213 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -27.61 \pm 83.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -30.49 \pm 83.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X\ ^2\Sigma^+$	0	2
$A\ ^2\Pi$	14422.7	2
	14815.9	
$B\ ^2\Sigma$	14748.8	2
$C\ ^2\Pi$	22666.1	2
	23223.4	2
$D\ ^2\Sigma$	28928.3	2

$\omega_e = 173.9\ cm^{-1}$ $\omega_e x_e = 0.42\ cm^{-1}$ $\sigma = 1$

$B_e = [0.0354]\ cm^{-1}$ $\alpha_e = [0.00011]\ cm^{-1}$ $r_e = [3.03]$ Å

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -6.65 \pm 20$ kcal·mol^{-1} is obtained from $D_0° = 71.5$ kcal·mol^{-1} calculated from the ratio $D_0°(SrI)/D_0°(SrI_2) = 0.46$. This value for the ratio was found for a series of mono and difluorides[1] and for other alkaline earth halide systems.[2] Other values for $D_0°$ i kcal·mol^{-1} are 54.6 obtained from a linear Birge–Sponer extrapolation of ω_e and $\omega_e x_e$ data[3] with a correction for the ionic character of the molecule as described by Hildenbrand,[4] 67.3 obtained by Krasnov and Karaseva[5] as a lower bound from a consideration of ionic bonding forces, and 65 obtained by Mims *et al.*[6] as a lower bound from a consideration of energy conservation and measured reaction threshold relative kinetic energy from crossed molecular beam experiments. $\Delta_f H°(298.15\ K) = -7.29 \pm 20$ kcal·mol^{-1} from the adopted $\Delta_f H°(0\ K) = -6.65$ kcal·mol^{-1}.

Heat Capacity and Entropy

The ground state vibrational constants are from the compilation of Rosen.[3] The value of $r_e = 3.03$ Å is assumed the same as the bond distance in SrI_2.[7] B_e is calculated from the adopted r_e. α_e is calculated assuming a Morse potential function.

The electronic levels and their designations are from Ashrafunnisa *et al.*[8,9] and Reddy *et al.*[10] The data are similar to the values in Rosen[2] but are more complete. The $D^2\Sigma$ level is confirmed by Shah *et al.*[11]

References

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[9]Ashrafunnisa, D. V. K. Rao and P. T. Rao, J. Phys. B **6**, 2653 (1973).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.287	−27.614	−27.614	INFINITE
100	34.228	232.849	304.737	−7.189	−27.540	−44.971	23.490
200	36.539	257.493	275.595	−3.620	−28.926	−61.887	16.163
250	36.915	265.691	272.824	−1.783	−29.705	−70.044	14.635
298.15	37.135	272.213	272.213	0.	−30.494	−77.736	13.619
300	37.141	272.443	272.214	0.069	−30.526	−78.029	13.586
350	37.294	278.181	272.667	1.930	−31.423	−85.877	12.816
400	37.405	283.168	273.675	3.797	−40.345	−93.318	12.186
450	37.492	287.579	274.979	5.670	−41.891	−99.847	11.590
500	37.563	291.533	276.440	7.546	−63.522	−104.304	10.897
600	37.679	298.392	279.544	11.309	−64.567	−112.364	9.782
700	37.774	304.208	282.663	15.081	−65.712	−120.241	8.972
800	37.859	309.257	285.678	18.863	−66.959	−127.946	8.354
900	37.936	313.721	288.551	22.653	−68.939	−135.418	7.859
1000	38.010	317.722	291.272	26.450	−70.076	−142.744	7.456
1100	38.082	321.348	293.843	30.255	−79.115	−149.590	7.103
1200	38.152	324.664	296.276	34.067	−81.166	−155.906	6.786
1300	38.220	327.721	298.579	37.885	−83.221	−162.051	6.511
1400	38.289	330.556	300.763	41.711	−85.286	−168.038	6.270
1500	38.358	333.200	302.838	45.543	−87.363	−173.876	6.055
1600	38.428	335.678	304.814	49.382	−89.459	−179.575	5.863
1700	38.502	338.010	306.699	53.229	−228.491	−183.963	5.653
1800	38.580	340.212	308.500	57.083	−228.773	−181.336	5.262
1900	38.663	342.301	310.224	60.945	−229.088	−178.692	4.913
2000	38.755	344.286	311.878	64.816	−229.437	−176.031	4.597
2100	38.857	346.179	313.467	68.696	−229.822	−173.351	4.312
2200	38.970	347.989	314.995	72.587	−230.244	−170.652	4.052
2300	39.097	349.725	316.468	76.491	−230.704	−167.934	3.814
2400	39.238	351.391	317.888	80.407	−231.201	−165.194	3.595
2500	39.395	352.996	319.261	84.339	−231.737	−162.433	3.394
2600	39.570	354.545	320.588	88.287	−232.312	−159.649	3.207
2700	39.762	356.042	321.874	92.253	−232.927	−156.843	3.034
2800	39.972	357.491	323.120	96.240	−233.585	−154.013	2.873
2900	40.200	358.898	324.330	100.248	−234.288	−151.159	2.723
3000	40.447	360.265	325.505	104.281	−235.039	−148.280	2.582
3100	40.711	361.596	326.648	108.338	−235.843	−145.375	2.450
3200	40.992	362.892	327.760	112.423	−236.705	−142.443	2.325
3300	41.289	364.158	328.844	116.537	−237.629	−139.483	2.208
3400	41.601	365.396	329.901	120.682	−238.620	−136.494	2.097
3500	41.928	366.606	330.932	124.858	−239.683	−133.475	1.992
3600	42.267	367.792	331.940	129.068	−240.824	−130.425	1.892
3700	42.618	368.955	332.925	133.312	−242.045	−127.342	1.798
3800	42.980	370.096	333.888	137.592	−243.350	−124.224	1.708
3900	43.350	371.217	334.831	141.908	−244.744	−121.071	1.622
4000	43.727	372.320	335.754	146.262	−246.226	−117.882	1.539
4100	44.110	373.404	336.659	150.654	−247.800	−114.654	1.461
4200	44.498	374.472	337.547	155.084	−249.461	−111.386	1.385
4300	44.888	375.523	338.418	159.553	−251.215	−108.079	1.313
4400	45.280	376.560	339.273	164.062	−253.057	−104.729	1.243
4500	45.673	377.582	340.113	168.609	−254.985	−101.336	1.176
4600	46.064	378.590	340.938	173.196	−256.931	−97.905	1.112
4700	46.454	379.585	341.750	177.822	−259.001	−94.425	1.049
4800	46.840	380.567	342.549	182.487	−261.141	−90.901	0.989
4900	47.221	381.536	343.334	187.190	−263.345	−87.332	0.931
5000	47.598	382.494	344.108	191.931	−265.601	−83.718	0.875
5100	47.967	383.440	344.870	196.709	−267.890	−80.059	0.820
5200	48.330	384.375	345.621	201.524	−270.242	−76.353	0.767
5300	48.684	385.299	346.361	206.375	−272.630	−72.602	0.716
5400	49.030	386.213	347.090	211.261	−275.048	−68.805	0.666
5500	49.367	387.115	347.810	216.181	−277.489	−64.964	0.617
5600	49.693	388.008	348.520	221.134	−279.946	−61.077	0.570
5700	50.010	388.890	349.220	226.119	−282.413	−57.147	0.524
5800	50.316	389.763	349.912	231.135	−284.882	−53.173	0.479
5900	50.611	390.625	350.595	236.182	−287.138	−49.181	0.435
6000	50.894	391.478	351.269	241.257	−289.565	−45.128	0.393

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 268.827 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [275.34 \pm 41.8]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [274.05 \pm 41.8]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^4\Sigma]$	0	[4]
	[1000]	[4]
	[2000]	[4]
	[4000]	[4]
	[6000]	[4]
	[8000]	[4]
	[10000]	[4]

$\omega_e = [240]\ cm^{-1}$ $\omega_e x_e = [1.67]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.062]\ cm^{-1}$ $\alpha_e = [0.00043]\ cm^{-1}$ $r_e = [2.8]$ Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$, of TiI(g) is calculated from the dissocation energy, $D_0°$, which is estimated as 73 $kcal \cdot mol^{-1}$. This estimate is obtained from the relation $\Delta_{at}H°(TiI_4, 0\ K)/4 < D_0°(TiI) < \Delta_{at}H°(TiI_3, 0\ K)/3)$, which is valid for the titanium flourides. The dissociation energy of TiF(g) from which the relation is derived was estimated relative to that of TiF_2(g) by Zmbov and Margrave.[1]

Heat Capacity and Entropy

The vibrational frequency, ω_e, and the anharmonic vibrational term, $\omega_e x_e$, are estimated from those of TiCl(g) and comparisons of the mercury and alkali monohalides. The interatomic distance is estimated from Guggenheimer's relation.[2] B_e is calculated from r_e. The ground state term and electronic levels are estimated from the ground state multiplet of Ti^{+}.[3] α_e is estimated from the Morse potential function.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.138	275.343	275.343	INFINITE
100	32.578	230.074	301.372	−7.130	276.266	257.134	−134.313
200	36.180	253.948	272.273	−3.665	275.347	238.299	−62.237
250	37.373	262.151	269.455	−1.826	274.709	229.109	−47.870
298.15	38.459	268.827	268.827	0.	274.052	220.386	−38.611
300	38.500	269.065	268.828	0.071	274.026	220.053	−38.315
350	39.542	275.080	269.301	2.023	273.284	211.115	−31.507
400	40.464	280.421	270.363	4.023	264.546	202.559	−26.451
450	41.251	285.234	271.752	6.067	263.215	194.890	−22.622
500	41.902	289.615	273.323	8.146	241.830	189.269	−19.773
600	42.842	297.345	276.700	12.387	241.368	178.800	−15.566
700	43.407	303.995	280.135	16.702	240.911	168.409	−12.567
800	43.728	309.815	283.489	21.060	240.455	158.082	−10.322
900	43.903	314.976	286.706	25.443	239.952	147.815	−8.579
1000	44.002	319.607	289.769	29.838	239.325	137.609	−7.188
1100	44.066	323.804	292.675	34.242	238.506	127.476	−6.053
1200	44.119	327.641	295.431	38.651	233.504	117.545	−5.117
1300	44.175	331.174	298.047	43.066	233.011	107.902	−4.336
1400	44.238	334.450	300.531	47.487	232.429	98.299	−3.668
1500	44.312	337.505	302.896	51.914	231.743	88.742	−3.090
1600	44.395	340.367	305.149	56.349	230.934	79.234	−2.587
1700	44.487	343.062	307.301	60.793	229.988	69.781	−2.144
1800	44.585	345.607	309.359	65.247	228.887	60.388	−1.752
1900	44.687	348.020	311.331	69.710	227.618	51.061	−1.404
2000	44.791	350.315	313.223	74.184	211.480	42.258	−1.104
2100	44.896	352.503	315.042	78.669	209.086	33.856	−0.842
2200	45.001	354.594	316.792	83.163	206.672	25.568	−0.607
2300	45.103	356.597	318.480	87.669	204.241	17.391	−0.395
2400	45.203	358.518	320.108	92.184	201.797	9.319	−0.203
2500	45.299	360.366	321.682	96.709	199.347	1.349	−0.028
2600	45.391	362.144	323.204	101.244	196.895	−6.522	0.131
2700	45.479	363.859	324.678	105.787	194.446	−14.299	0.277
2800	45.562	365.514	326.107	110.339	192.006	−21.986	0.410
2900	45.641	367.115	327.494	114.900	189.581	−29.585	0.533
3000	45.716	368.663	328.841	119.468	187.173	−37.102	0.646
3100	45.787	370.163	330.150	124.043	184.788	−44.538	0.750
3200	45.854	371.618	331.423	128.625	182.428	−51.898	0.847
3300	45.917	373.030	332.662	133.213	180.096	−59.185	0.937
3400	45.977	374.402	333.870	137.808	177.795	−66.401	1.020
3500	46.034	375.735	335.047	142.409	175.525	−73.550	1.098
3600	46.089	377.033	336.195	147.015	173.289	−80.635	1.170
3700	46.141	378.296	337.316	151.626	−238.012	−79.870	1.128
3800	46.191	379.528	338.411	156.243	−238.945	−75.583	1.039
3900	46.240	380.728	339.481	160.864	−239.900	−71.271	0.955
4000	46.287	381.899	340.527	165.491	−240.874	−66.935	0.874
4100	46.333	383.043	341.550	170.122	−241.866	−62.575	0.797
4200	46.378	384.160	342.551	174.757	−242.875	−58.190	0.724
4300	46.422	385.252	343.531	179.397	−243.901	−53.780	0.653
4400	46.466	386.319	344.492	184.042	−244.941	−49.347	0.586
4500	46.510	387.364	345.433	188.691	−245.996	−44.890	0.521
4600	46.554	388.387	346.356	193.344	−247.063	−40.409	0.459
4700	46.597	389.388	347.261	198.001	−248.142	−35.905	0.399
4800	46.641	390.370	348.148	202.663	−249.231	−31.378	0.341
4900	46.686	391.332	349.020	207.330	−250.329	−26.828	0.286
5000	46.731	392.276	349.876	212.000	−251.435	−22.255	0.232
5100	46.776	393.202	350.716	216.676	−252.548	−17.660	0.181
5200	46.823	394.110	351.542	221.356	−253.667	−13.044	0.131
5300	46.869	395.003	352.354	226.040	−254.789	−8.406	0.083
5400	46.917	395.879	353.152	230.730	−255.915	−3.747	0.036
5500	46.966	396.741	353.936	235.424	−257.043	0.933	−0.009
5600	47.015	397.587	354.708	240.123	−258.172	5.634	−0.053
5700	47.066	398.420	355.468	244.827	−259.300	10.355	−0.095
5800	47.117	399.239	356.215	249.536	−260.427	15.096	−0.136
5900	47.170	400.045	356.951	254.250	−261.551	19.856	−0.176
6000	47.223	400.838	357.676	258.970	−262.672	24.635	−0.214

PREVIOUS: December 1968 (a atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [275.805]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [593.20 \pm 41.8]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [591.20 \pm 41.8]\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^4\Sigma$	0	4

$\omega_e = [223]\ cm^{-1}$ $\omega_e x_e = [1.2]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.03789]\ cm^{-1}$ $\alpha_e = [0.00020]\ cm^{-1}$ $r_e = [2.9]$ Å

Enthalpy of Formation

The dissociation energy was estimated from a correlation of the JANAF values for TiCl(g), TiI(g), and ZrCl(g). The resulting value, 29.7 $kcal·mol^{-1}$, was employed with auxiliary JANAF enthalpies of formation for Zr(g) and I(g) in calculating $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

The vibrational frequency was estimated from those of TiI(g), TiCl(g), ZrCl(g), and the alkali halides. The ground state configuration was assumed to be analogous to the ground term of TiCl(g) as given by Shenyavskaya *et al.*[1] The interatomic distance was estiamted from those of TiBr(g), TiI_4(g) and ZrI_4(g).

Reference

[1]E. A. Shenyavskaya *et al.*, Optics and Spectroscopy **12**, 359 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.097	593.198	593.198	INFINITE
100	32.964	237.198	307.908	−7.071	593.813	574.549	−300.113
200	36.028	261.223	279.160	−3.587	592.637	555.699	−145.134
250	36.593	269.329	276.411	−1.771	591.925	546.545	−114.194
298.15	36.931	275.805	275.805	0.	591.199	537.871	−94.233
300	36.941	276.033	275.806	0.068	591.171	537.540	−93.594
350	37.177	281.747	276.256	1.922	590.347	528.665	−78.899
400	37.349	286.723	277.260	3.785	581.508	520.185	−67.929
450	37.483	291.130	278.561	5.656	580.058	512.607	−59.502
500	37.592	295.085	280.019	7.533	558.533	507.090	−52.975
600	37.767	301.955	283.120	11.301	557.733	496.875	−43.257
700	37.910	307.788	286.237	15.085	556.867	486.800	−36.325
800	38.034	312.858	289.255	18.882	555.925	476.853	−31.135
900	38.148	317.345	292.132	22.692	554.892	467.031	−27.106
1000	38.256	321.370	294.858	26.512	553.755	457.328	−23.888
1100	38.360	325.021	297.436	30.343	552.507	447.745	−21.262
1200	38.460	328.363	299.876	34.184	547.430	438.502	−19.088
1300	38.559	331.445	302.188	38.035	546.484	429.463	−17.256
1400	38.656	334.306	304.381	41.895	545.491	420.498	−15.689
1500	38.751	336.976	306.466	45.766	544.434	411.607	−14.333
1600	38.847	339.480	308.452	49.646	543.298	402.788	−13.150
1700	38.941	341.838	310.347	53.535	542.069	394.043	−12.107
1800	39.035	344.067	312.159	57.434	540.732	385.374	−11.183
1900	39.128	346.180	313.894	61.342	539.274	376.782	−10.358
2000	39.221	348.189	315.559	65.260	537.685	368.270	−9.618
2100	39.314	350.105	317.159	69.186	535.954	359.842	−8.951
2200	39.407	351.936	318.699	73.122	512.752	352.244	−8.363
2300	39.499	353.690	320.182	77.068	510.300	345.003	−7.835
2400	39.592	355.373	321.613	81.022	507.836	337.869	−7.354
2500	39.684	356.991	322.996	84.986	505.364	330.838	−6.912
2600	39.776	358.549	324.334	88.959	502.889	323.906	−6.507
2700	39.868	360.052	325.629	92.941	500.419	317.069	−6.134
2800	39.960	361.503	326.885	96.933	497.959	310.323	−5.789
2900	40.052	362.907	328.103	100.933	495.513	303.665	−5.470
3000	40.143	364.267	329.286	104.943	493.087	297.091	−5.173
3100	40.235	365.584	330.435	108.962	490.685	290.598	−4.897
3200	40.327	366.863	331.554	112.990	488.311	284.181	−4.639
3300	40.418	368.106	332.643	117.027	485.968	277.838	−4.398
3400	40.510	369.314	333.704	121.074	483.658	271.566	−4.172
3500	40.602	370.489	334.738	125.129	481.383	265.361	−3.960
3600	40.693	371.634	335.747	129.194	479.145	259.221	−3.761
3700	40.785	372.751	336.732	133.268	476.945	253.142	−3.574
3800	40.876	373.839	337.694	137.351	474.783	247.123	−3.397
3900	40.968	374.902	338.635	141.443	472.660	241.159	−3.230
4000	41.059	375.941	339.555	145.544	470.576	235.250	−3.072
4100	41.150	376.956	340.454	149.655	468.531	229.392	−2.922
4200	41.242	377.948	341.335	153.774	466.524	223.584	−2.781
4300	41.333	378.920	342.198	157.903	464.555	217.823	−2.646
4400	41.425	379.871	343.044	162.041	462.623	212.107	−2.518
4500	41.516	380.803	343.872	166.188	460.728	206.435	−2.396
4600	41.607	381.717	344.685	170.344	458.868	200.805	−2.280
4700	41.699	382.612	345.483	174.510	457.043	195.215	−2.170
4800	41.790	383.491	346.265	178.684	−105.684	201.280	−2.190
4900	41.881	384.354	347.034	182.868	−107.093	207.690	−2.214
5000	41.973	385.201	347.789	187.060	−108.486	214.128	−2.237
5100	42.064	386.033	348.531	191.262	−109.864	220.594	−2.259
5200	42.155	386.851	349.260	195.473	−111.225	227.087	−2.281
5300	42.247	387.655	349.977	199.693	−112.570	233.606	−2.302
5400	42.338	388.445	350.682	203.923	−113.897	240.150	−2.323
5500	42.429	389.223	351.375	208.161	−115.206	246.718	−2.343
5600	42.521	389.988	352.058	212.408	−116.496	253.311	−2.363
5700	42.612	390.742	352.730	216.665	−117.768	259.926	−2.382
5800	42.703	391.483	353.392	220.931	−119.020	266.563	−2.401
5900	42.795	392.214	354.044	225.206	−120.252	273.221	−2.419
6000	42.886	392.934	354.686	229.490	−121.463	279.901	−2.437

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

REFERENCE STATE

0	to	386.75	K crystal
386.75	to	457.666	K liquid
above		457.666	K diatomic ideal gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.198	0.	0.	0.
100	45.650	60.992	162.472	−10.148	0.	0.	0.
200	51.566	94.958	121.036	−5.216	0.	0.	0.
298.15	54.436	116.142	116.142	0.	0.	0.	0.
300	54.506	116.479	116.143	0.101	0.	0.	0.
386.750	63.545	131.224	117.899	5.153	___ CRYSTAL <--> LIQUID ___		
386.750	80.669	171.344	117.899	20.670	TRANSITION		
400	80.669	174.062	119.714	21.739	0.	0.	0.
457.666	80.669	184.926	127.262	26.391	___ LIQUID <--> IDEAL GAS ___		
457.666	37.386	276.609	127.262	68.351	FUGACITY = 1 bar		
500	37.464	279.920	140.049	69.935	0.	0.	0.
600	37.612	286.764	163.948	73.690	0.	0.	0.
700	37.735	292.571	181.918	77.457	0.	0.	0.
800	37.847	297.618	196.072	81.236	0.	0.	0.
900	37.959	302.082	207.608	85.027	0.	0.	0.
1000	38.081	306.087	217.259	88.828	0.	0.	0.
1100	38.232	309.724	225.502	92.644	0.	0.	0.
1200	38.431	313.058	232.661	96.476	0.	0.	0.
1300	38.699	316.144	238.966	100.332	0.	0.	0.
1400	39.055	319.025	244.583	104.219	0.	0.	0.
1500	39.507	321.734	249.637	108.146	0.	0.	0.
1600	40.051	324.301	254.224	112.124	0.	0.	0.
1700	40.674	326.747	258.418	116.159	0.	0.	0.
1800	41.352	329.091	262.280	120.260	0.	0.	0.
1900	42.054	331.346	265.856	124.431	0.	0.	0.
2000	42.748	333.521	269.185	128.671	0.	0.	0.
2100	43.404	335.622	272.299	132.979	0.	0.	0.
2200	43.994	337.655	275.224	137.349	0.	0.	0.
2300	44.494	339.622	277.981	141.775	0.	0.	0.
2400	44.890	341.525	280.589	146.245	0.	0.	0.
2500	45.171	343.363	283.064	150.749	0.	0.	0.
2600	45.335	345.139	285.417	155.275	0.	0.	0.
2700	45.382	346.851	287.661	159.812	0.	0.	0.
2800	45.319	348.500	289.805	164.348	0.	0.	0.
2900	45.154	350.088	291.856	168.872	0.	0.	0.
3000	44.897	351.615	293.823	173.376	0.	0.	0.
3100	44.561	353.082	295.711	177.849	0.	0.	0.
3200	44.157	354.490	297.526	182.286	0.	0.	0.
3300	43.697	355.842	299.273	186.679	0.	0.	0.
3400	43.193	357.139	300.956	191.024	0.	0.	0.
3500	42.654	358.384	302.579	195.316	0.	0.	0.
3600	42.091	359.577	304.146	199.554	0.	0.	0.
3700	41.510	360.723	305.660	203.734	0.	0.	0.
3800	40.919	361.822	307.123	207.855	0.	0.	0.
3900	40.325	362.877	308.539	211.917	0.	0.	0.
4000	39.731	363.891	309.911	215.920	0.	0.	0.
4100	39.143	364.864	311.239	219.864	0.	0.	0.
4200	38.563	365.801	312.527	223.749	0.	0.	0.
4300	37.995	366.701	313.777	227.577	0.	0.	0.
4400	37.439	367.568	314.989	231.348	0.	0.	0.
4500	36.899	368.404	316.167	235.065	0.	0.	0.
4600	36.374	369.209	317.311	238.729	0.	0.	0.
4700	35.866	369.986	318.424	242.341	0.	0.	0.
4800	35.375	370.736	319.506	245.903	0.	0.	0.
4900	34.901	371.460	320.559	249.416	0.	0.	0.
5000	34.444	372.161	321.584	252.883	0.	0.	0.
5100	34.005	372.838	322.582	256.306	0.	0.	0.
5200	33.582	373.495	323.555	259.685	0.	0.	0.
5300	33.176	374.130	324.503	263.023	0.	0.	0.
5400	32.785	374.747	325.428	266.321	0.	0.	0.
5500	32.410	375.345	326.330	269.580	0.	0.	0.
5600	32.051	375.926	327.211	272.803	0.	0.	0.
5700	31.705	376.490	328.071	275.991	0.	0.	0.
5800	31.374	377.038	328.910	279.145	0.	0.	0.
5900	31.056	377.572	329.730	282.266	0.	0.	0.
6000	30.751	378.091	330.532	285.356	0.	0.	0.

PREVIOUS: September 1961 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = 116.142 \pm 0.080\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 386.75 \pm 0.3\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 15.517 \pm 0.16\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity measurements of Shirley and Giauque[1] over the temperature range 13 to 327 K are adopted. No weight is given to the earlier work of Lange[2] which deviate by 1% or more. Carpenter and Harle[3] measured the heat capacity of crystalline and liquid iodine by an adiabatic method. Their data are in poor agreement with Shirley and Giauque[1] in the range 275–330 K and are given no weight. Frederick and Hildebrand[4] measured the enthalpy of crystalline and liquid iodine relative to 298.15 K by the method of mixtures. For calibration they used a slug of copper. The enthalpy of copper which they used appears to be too high.[5] The results are corrected by a factor which varies from 0 at 300 K to 0.995 at 400 K, and 0.990 at 500 K. Using these corrected enthalpies and the heat capacities of Shirley and Giaugue[1] avove 298.15 K, the following equation is derived for I_2(cr). $H°(T)–H°(298.15\ K) = -50.646T + 0.12345T^2 - 27.97 \times 10^5\ T^{-1} + 13508.7$.

The CODATA recommendation[6] for $S°(298.15\ K)$ is within 0.003 $J \cdot K^{-1} \cdot mol^{-1}$ of our calculated value and is based on the same heat capacity study.[1]

Fusion Data

T_{fus} = 113.6 °C is given by Frederick and Hildebrand.[4] The difference in the enthalpy equations at T_{fus} is the enthalpy of fusion.

Sublimation Data

Refer to the I_2(g) table for details.

References

[1]D. A. Shirley and W. F. Giauque, J. Am. Chem. Soc. **81**, 4778 (1959).
[2]E. Lange, Z. physik. Chem. **110**, 343 (1924).
[3]L. G. Carpenter and T. F. Harle, Phil. Mag. **23**, 193 (1937).
[4]K. J. Frederick and J. H. Hildebrand, J. Am. Chem. Soc. **60**, 1436 (1939).
[5]JANAF Thermochemical Tables: Cu(cr), 6–30–77.
[6]J. D. Cox, Chairman, CODATA Task Group on Key Values for Chemical Thermodynamics, J. Chem. Thermodyn. **10**, 903 (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.198	0.	0.	0.
100	45.650	60.992	162.472	−10.148	0.	0.	0.
200	51.566	94.958	121.036	−5.216	0.	0.	0.
250	53.244	106.678	117.030	−2.588	0.	0.	0.
298.15	54.436	116.142	116.142	0.	0.	0.	0.
300	54.506	116.479	116.143	0.101	0.	0.	0.
350	58.605	125.140	116.818	2.913	0.	0.	0.
386.750	63.545	131.224	117.899	5.153	--- CRYSTAL <--> LIQUID ---		
400	65.598	133.398	118.376	6.009	−15.730	0.535	−0.070
450	73.402	141.575	120.500	9.484	−16.288	2.606	−0.303
500	81.207	149.713	123.015	13.349	−56.586	8.517	−0.890
600	96.816	165.898	128.815	22.250	−51.439	21.080	−1.835
700	112.425	181.995	135.263	32.712	−44.745	32.659	−2.437

PREVIOUS: CURRENT: June 1982

$S°(298.15\ K) = [150.356]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 386.75 \pm 0.03\ K$

$\Delta_f H°(298.15\ K) = [13.523]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 15.517 \pm 0.16\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(I_2, l, 298.15\ K)$, is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(386.75\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of the liquid is adopted to be a constant value, 80.672 $J·K^{-1}·mol^{-1}$, based on the data of Frederick and Hildebrand.[1] Their enthalpy data was corrected as discussed in the I_2(cr) table. The enthalpy equation is $H°(T)–H°(298.15\ K) = 80.672\ T–10529$.

The entropy is calcualted in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

Refer to the I_2(g) table for details.

References

[1]K. J. Frederick and J. H. Hidebrand, J. Am., Chem. Soc. **60**, 1436 (1938).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	80.669	150.356	150.356	0.	13.523	3.322	−0.582
300	80.669	150.855	150.357	0.149	13.571	3.259	−0.567
350	80.669	163.290	151.339	4.183	14.793	1.440	−0.215
386.750	80.669	171.344	152.864	7.147	--- CRYSTAL <--> LIQUID ---		
400	80.669	174.062	153.521	8.216	0.	0.	0.
450	80.669	183.563	156.342	12.250	0.	0.	0.
457.666	80.669	184.926	156.809	12.868	----- FUGACITY = 1 bar -----		
500	80.669	192.062	159.496	16.283	−40.130	3.799	−0.397
600	80.669	206.770	166.187	24.350	−35.817	12.179	−1.060
700	80.669	219.205	172.895	32.417	−31.518	19.839	−1.480
800	80.669	229.977	179.372	40.484	−27.230	26.883	−1.755
900	80.669	239.478	185.533	48.550	−22.953	33.390	−1.938
1000	80.669	247.978	191.360	56.617	−18.688	39.421	−2.059

PREVIOUS: September 1961 CURRENT: June 1982

CRYSTAL-LIQUID

0 to 386.75 K crystal
above 386.75 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.198	0.	0.	0.
100	45.650	60.992	162.472	−10.148	0.	0.	0.
200	51.566	94.958	121.036	−5.216	0.	0.	0.
250	53.244	106.678	117.030	−2.588	0.	0.	0.
298.15	54.436	116.142	116.142	0.	0.	0.	0.
300	54.506	116.479	116.143	0.101	0.	0.	0.
350	58.605	125.140	116.818	2.913	0.	0.	0.
386.750	63.545	131.224	117.899	5.153	___ CRYSTAL <--> LIQUID ___		
386.750	80.669	171.344	117.899	20.670	TRANSITION		
400	80.669	174.062	119.714	21.739	0.	0.	0.
450	80.669	183.563	126.291	25.772	0.	0.	0.
457.666	80.669	184.926	127.262	26.391	----- FUGACITY = 1 bar -----		
500	80.669	192.062	132.451	29.806	−40.130	3.799	−0.397
600	80.669	206.770	143.649	37.873	−35.817	12.179	−1.060
700	80.669	219.205	153.577	45.940	−31.518	19.839	−1.480
800	80.669	229.977	162.469	54.006	−27.230	26.883	−1.755
900	80.669	239.478	170.508	62.073	−22.953	33.390	−1.938
1000	80.669	247.978	177.837	70.140	−18.688	39.421	−2.059

PREVIOUS: CURRENT: June 1982

$D_0°$ = 148.816 ± 0.001 kJ·mol^{-1}
$S°$(298.15 K) = 260.685 ± 0.062 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 65.504 ± 0.092 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 62.421 ± 0.079 kJ·mol^{-1}

State	T_e	$D°$	ω_e	Spectroscopic Data for I_2 in cm^{-1} $\omega_e x_e$	B_e	$10^3\,\alpha_e$	$10^6\,D_e$	r_e, Å	References
$^1\Sigma_g^+$	0	12440	214.5481	0.616259(a)	0.037395	0.12435(b)	0.00454(c)	2.6657	[1] $^4D_0°$
$^3\Pi_{2u}$	10200	12440	110.366	1.3927[d]	0.028	0.1	0.04	3.104	[2]
$^3\Pi_{1u}$	11059	12440	90.6	2.57[e]	0.02763	0.542[f]	0.03	3.101	[3]
$^3\Pi_{0^+u}$	15769.01	20043.15	125.697	0.7642[g]	0.029039	0.1582[h]	0.00543[i]	3.0247	[4]

(a) $+7.507 \times 10^{-5}(v+1/2)^3 - 1.263643 \times 10^{-4}(v+1/2)^4 + 6.198129 \times 10^{-6}(v+1/2)^5 - 2.0255975 \times 10^{-7}(v+1/2)^6 + 3.9662824 \times 10^{-9}(v+1/2)^7$
(b) $+4.a498 \times 10^{-7}(v+1/2)^2 - 1.482 \times 10^{-8}(v+1/2)^3$
(c) $+1.7 \times 10^{-11}(v+1/2) + 7 \times 10^{-12}(v+1/2)^2$
(d) $-3.45 \times 10^{-3}(v+1/2)^3$
(e) $+3.36 \times 10^{-2}(v+1/2)^3$
(f) $+2.46 \times 10^{-6}(v+1/2)^2$
(g) $-1.78 \times 10^{-3}(v+1/2)^3 + 1.03 \times 10^{-6}(v+1/2)^4$
(h) $-3.36 \times 10^{-7}(v+1/2)^2 - 4.78 \times 10^{-8}(v+1/2)^3$
(i) $+3.0 \times 10^{-10}(v+1/2)$

The dissociation energy of each state is relative to the lowest level of the ground state; the $3\Pi_{0^+u}$ state dissociates to $I(^2P_{3/2}) + I(^2P_{1/2})$.

Enthalpy of Formation

We adopt the enthalpy of formation values of CODATA[5] as follows: $\Delta_f H°$(298.15 K) = 62.421 ± 0.079 kJ·mol^{-1} and $\Delta_f H°$(0 K) = 65.500 ± 0.092 kJ·mol^{-1}. These values are based on the heat capacity study of Shirley and Giauque[8] and the vapor pressure data of Baxter *et al.*,[9] Baxter and Grose,[10] Gillespie and Fraser,[11] and Stern.[12] Note that the latter value of $\Delta_f H°$ is deduced from the former using the CODATA values of $H°$(298.15 K)–$H°$(0 K) for I_2(g) and I_2(cr). Our calculated value of $H°$(298.15 K)–$H°$(0 K) for I_2(g) is only 1.5 J·mol^{-1} smaller than that recommended by CODATA. We adopted the dissociation energy for the $^1\Sigma_g^+$, $^3\Pi_{2u}$, and $^3\Pi_{1u}$ states as given by Huber *et al.*[4] The $D_0°$ value for the $^3\Pi_0^+$ state was deduced fro mthe dissociative state energies given by Gurvich *et al.*[2] (table 10.1). Refer to the monatomic iodine gas table for additional disscussion of the dissociation energy.

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique. Included in the calculation are the ground state and the three lowest lying excited electronic states. Spectroscopic constants for the ground state are from Leroy;[1] however, we truncate the B_v expression at the $(v+1/2)^3$ term. The $^3\Pi_{2u}$ constants were taken from Gurvich *et. al.*[2] We adopt the spectroscopic constants of Ashby[3] for the $^3\Pi_{1u}$ state and of Huber and Herzberg[1] for the $^3\Pi_{0^+u}$ state. For the ground state and the $^3\Pi_{0^+u}$ state, the calculation is performed including the quasi–bound rotational levels above the dissociation limit (see Cl_2(g) table). The values of J_{lim} and v_{max} for the ground state are those given by Gurvich *et al.*[2] The corresponding values for the $^3\Pi_{0^+u}$ state were estimated as J_{lim} = 500 and v_{max} = 69 based on the spectroscopic constants given by Gurvich *et al.*[2] and Ashby.[3]

Splitting of the rotational levels due to the rotational–electronic interaction is taken into account only insofar as the statistical weight of the rotational levels is increased appropriately. The rotational levels are extrapolated to high J values according to the method of Khachkurozov[6] who proposed a simpler form of Wooley's method.[7] Our calculated value of $S°$(298.15 K) is only 0.112 J·K^{-1}·mol^{-1} larger than that given by Gurvich[2] and CODATA.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.116	65.504	65.504	INFINITE
100	33.135	222.004	292.808	−7.080	65.489	49.387	−25.797
200	36.062	246.105	264.038	−3.587	64.050	33.821	−8.833
250	36.582	254.213	261.291	−1.769	63.240	26.356	−5.507
298.15	36.887	260.685	260.685	0.	62.421	19.325	−3.386
300	36.897	260.913	260.686	0.068	62.388	19.058	−3.318
350	37.105	266.617	261.136	1.919	61.427	11.910	−1.777
400	37.256	271.582	262.138	3.778	44.460	5.452	−0.712
450	37.371	275.977	263.436	5.644	42.292	0.706	−0.082
457.666	37.386	276.609	263.651	5.930	----- FUGACITY = 1 bar -----		
500	37.464	279.920	264.891	7.515	0.	0.	0.
600	37.612	286.764	267.983	11.269	0.	0.	0.
700	37.735	292.571	271.091	15.036	0.	0.	0.
800	37.847	297.618	274.098	18.815	0.	0.	0.
900	37.959	302.082	276.964	22.606	0.	0.	0.
1000	38.081	306.087	279.680	26.407	0.	0.	0.
1100	38.232	309.724	282.248	30.223	0.	0.	0.
1200	38.431	313.058	284.679	34.055	0.	0.	0.
1300	38.699	316.144	286.982	37.911	0.	0.	0.
1400	39.055	319.025	289.169	41.798	0.	0.	0.
1500	39.507	321.734	291.251	45.726	0.	0.	0.
1600	40.051	324.301	293.237	49.703	0.	0.	0.
1700	40.674	326.747	295.136	53.738	0.	0.	0.
1800	41.352	329.091	296.958	57.839	0.	0.	0.
1900	42.054	331.346	298.709	62.010	0.	0.	0.
2000	42.748	333.521	300.396	66.250	0.	0.	0.
2100	43.404	335.622	302.023	70.558	0.	0.	0.
2200	43.994	337.655	303.597	74.929	0.	0.	0.
2300	44.494	339.622	305.121	79.354	0.	0.	0.
2400	44.890	341.525	306.598	83.824	0.	0.	0.
2500	45.171	343.363	308.032	88.328	0.	0.	0.
2600	45.335	345.139	309.425	92.854	0.	0.	0.
2700	45.382	346.851	310.780	97.391	0.	0.	0.
2800	45.319	348.500	312.098	101.927	0.	0.	0.
2900	45.154	350.088	313.381	106.451	0.	0.	0.
3000	44.897	351.615	314.630	110.955	0.	0.	0.
3100	44.561	353.082	315.847	115.428	0.	0.	0.
3200	44.157	354.490	317.033	119.865	0.	0.	0.
3300	43.697	355.842	318.188	124.258	0.	0.	0.
3400	43.193	357.139	319.315	128.603	0.	0.	0.
3500	42.654	358.384	320.414	132.895	0.	0.	0.
3600	42.091	359.577	321.485	137.133	0.	0.	0.
3700	41.510	360.723	322.530	141.313	0.	0.	0.
3800	40.919	361.822	323.550	145.434	0.	0.	0.
3900	40.325	362.877	324.545	149.496	0.	0.	0.
4000	39.731	363.891	325.516	153.499	0.	0.	0.
4100	39.143	364.864	326.464	157.443	0.	0.	0.
4200	38.563	365.801	327.389	161.328	0.	0.	0.
4300	37.995	366.701	328.293	165.156	0.	0.	0.
4400	37.439	367.568	329.176	168.928	0.	0.	0.
4500	36.899	368.404	330.038	172.644	0.	0.	0.
4600	36.374	369.209	330.881	176.308	0.	0.	0.
4700	35.866	369.986	331.705	179.920	0.	0.	0.
4800	35.375	370.736	332.510	183.482	0.	0.	0.
4900	34.901	371.460	333.298	186.995	0.	0.	0.
5000	34.444	372.161	334.068	190.462	0.	0.	0.
5100	34.005	372.838	334.822	193.885	0.	0.	0.
5200	33.582	373.495	335.559	197.264	0.	0.	0.
5300	33.176	374.130	336.281	200.602	0.	0.	0.
5400	32.785	374.747	336.988	203.900	0.	0.	0.
5500	32.410	375.345	337.680	207.159	0.	0.	0.
5600	32.051	375.926	338.357	210.382	0.	0.	0.
5700	31.705	376.490	339.022	213.570	0.	0.	0.
5800	31.374	377.038	339.672	216.724	0.	0.	0.
5900	31.056	377.572	340.310	219.845	0.	0.	0.
6000	30.751	378.091	340.936	222.935	0.	0.	0.

PREVIOUS: September 1961 (1 atm) CURRENT: June 1982 (1 bar)

$S°(298.15\ K) = [395.773]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -416.48 \pm 4.2\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -422.17 \pm 4.2\ kJ\cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[90](1)	[80](1)
[60](1)	[105](1)
[110](1)	[120](1)

Ground State Quantum Weight: [1] σ = [4]
Point Group: [D_{2h}]
Bond Distances: K–I = [3.29]Å K–K = [4.00]Å
Bond Angles: K–I–K = [75°] I–K–I = [105°]
Product of the Moments of Inertia: $I_A I_B I_C = [5.073451 \times 10^{111}]\ g^3\cdot cm^6$

Enthalpy of Formation

The chemical equilibrium for the reaction $K_2I_2(g) = 2\ KI(g)$ has been studied by Datz and Datz *et al.*[2] They measured the temperature dependence of the molecular weight of KI(g) which was determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. Based on the reported P–V–T measurements, the enthalpy change of the reaction at 298.15 K is evaluated by the 2nd and 3rd law methods. The results are given in the table below.

Miller and Kusch determined the molecular composition of KI vapor by measurement of the velocity distribution of the molecules in the beam produced as the vapor effused through a small slit in a source. The analysis was based on an assumption that the velocity distribution within the oven is Maxwellian and that the vapor effuses through the ideal slit of kinetic theory. The velocity distributions of potassium and thallium atomic beams were found to be in excellent agreement with the theoretical distributions so the determination of the molecular composition of KI beams was tried. Using the derived equilibrium constants, we calculate the enthalpy change of the dissociation reaction by the 2nd and 3rd law methods. The results are presented in the following table.

The value of $\Delta_f H°(K_2I_2, g, 298.15\ K)$ is adopted as $-100.9 \pm 1\ kcal\cdot mol^{-1}$.

Source	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
Datz[1]	1226–1385	10	40.09 ± 0.82	40.66	0.4 ± 0.6	−100.66
	1292–1408	6	41.37 ± 1.91	41.01	−0.2 ± 1.4	−101.01
Miller Kusch[2]	816–921	10	54.62 ± 2.46	36.28	−21.4 ± 2.8	−96.28

Heat Capacity

The molecular structure and bond distance and angles were estimated by Berkowitz.[4] The vibrational frequences are estimated by comparison with those calculated by Berkowitz and adjusted to give good agreement between 2nd and 3rd law evaluations of the equilibrium data. The three principal moments of inertia are: $I_A = 52.0871 \times 10^{-39}$, $I_B = 287.1362 \times 10^{-39}$, and $I_C = 339.2233 \times 10^{-39}\ g\cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−21.676	−416.480	−416.480	INFINITE
100	75.971	308.279	467.994	−15.972	−417.290	−434.898	227.167
200	81.203	363.113	403.271	−8.032	−419.471	−451.705	117.973
250	81.890	381.315	397.125	−3.953	−420.768	−459.616	96.032
298.15	82.258	395.772	395.772	0.	−422.166	−466.974	81.812
300	82.268	396.281	395.774	0.152	−422.223	−467.252	81.356
350	82.499	408.982	396.777	4.272	−428.698	−474.433	70.805
400	82.649	420.008	399.007	8.401	−446.570	−480.288	62.719
450	82.752	429.749	401.892	12.536	−449.596	−484.321	56.218
500	82.826	438.472	405.121	16.675	−492.707	−484.220	50.586
600	82.923	453.583	411.977	24.963	−494.252	−482.375	41.995
700	82.982	466.370	418.857	33.259	−495.716	−480.279	35.839
800	83.020	477.453	425.504	41.559	−497.149	−477.976	31.209
900	83.046	487.233	431.831	49.862	−498.601	−475.493	27.597
1000	83.064	495.984	437.816	58.168	−500.123	−472.845	24.699
1100	83.078	503.901	443.470	66.475	−659.668	−460.819	21.882
1200	83.089	511.131	448.811	74.783	−659.350	−442.756	19.273
1300	83.097	517.782	453.864	83.093	−659.054	−424.718	17.065
1400	83.103	523.940	458.652	91.403	−658.789	−406.703	15.174
1500	83.109	529.674	463.198	99.713	−658.565	−388.705	13.536
1600	83.113	535.038	467.522	108.025	−658.393	−370.720	12.103
1700	83.116	540.076	471.644	116.336	−658.282	−352.744	10.839
1800	83.119	544.827	475.579	124.648	−658.241	−334.773	9.715
1900	83.122	549.321	479.343	132.960	−658.277	−316.802	8.709
2000	83.124	553.585	482.949	141.272	−658.394	−298.827	7.805
2100	83.126	557.641	486.410	149.585	−658.592	−280.844	6.986
2200	83.128	561.508	489.736	157.897	−658.871	−262.850	6.241
2300	83.129	565.203	492.938	166.210	−659.227	−244.841	5.561
2400	83.130	568.741	496.023	174.523	−659.655	−226.815	4.937
2500	83.131	572.135	499.000	182.836	−660.149	−208.771	4.362
2600	83.132	575.395	501.876	191.149	−660.703	−190.704	3.831
2700	83.133	578.533	504.657	199.463	−661.311	−172.616	3.339
2800	83.134	581.556	507.350	207.776	−661.968	−154.505	2.882
2900	83.135	584.473	509.960	216.089	−662.670	−136.369	2.456
3000	83.135	587.292	512.491	224.403	−663.413	−118.208	2.058
3100	83.136	590.018	514.948	232.717	−664.196	−100.022	1.685
3200	83.136	592.657	517.335	241.030	−665.020	−81.809	1.335
3300	83.137	595.215	519.657	249.344	−665.868	−63.572	1.006
3400	83.137	597.697	521.916	257.657	−666.770	−45.307	0.696
3500	83.138	600.107	524.115	265.971	−667.714	−27.016	0.403
3600	83.138	602.449	526.259	274.285	−668.714	−8.696	0.126
3700	83.138	604.727	528.349	282.599	−669.773	9.652	−0.136
3800	83.139	606.944	530.388	290.913	−670.899	28.030	−0.385
3900	83.139	609.104	532.379	299.227	−672.101	46.438	−0.622
4000	83.139	611.209	534.324	307.540	−673.373	64.877	−0.847
4100	83.139	613.262	536.224	315.854	−674.741	83.350	−1.062
4200	83.140	615.265	538.082	324.168	−676.221	101.857	−1.267
4300	83.140	617.221	539.900	332.482	−677.815	120.402	−1.463
4400	83.140	619.133	541.679	340.796	−678.979	138.930	−1.649
4500	83.140	621.001	543.421	349.110	−680.696	157.538	−1.829
4600	83.140	622.829	545.128	357.424	−682.534	176.185	−2.001
4700	83.140	624.617	546.800	365.738	−684.461	194.870	−2.166
4800	83.141	626.367	548.439	374.052	−686.302	213.574	−2.324
4900	83.141	628.081	550.047	382.366	−688.486	232.343	−2.477
5000	83.141	629.761	551.625	390.681	−690.809	251.159	−2.624
5100	83.141	631.407	553.173	398.995	−693.275	270.023	−2.766
5200	83.141	633.022	554.693	407.309	−695.888	288.936	−2.902
5300	83.141	634.605	556.186	415.623	−698.649	307.901	−3.035
5400	83.141	636.160	557.653	423.937	−701.560	326.919	−3.162
5500	83.141	637.685	559.094	432.251	−704.622	345.993	−3.286
5600	83.142	639.183	560.511	440.565	−707.835	365.124	−3.406
5700	83.142	640.655	561.904	448.879	−710.506	384.218	−3.521
5800	83.142	642.101	563.274	457.194	−713.928	403.454	−3.633
5900	83.142	643.522	564.622	465.508	−717.486	422.749	−3.743
6000	83.142	644.919	565.949	473.822	−721.178	442.106	−3.849

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = [330.628]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -356.74 \pm 16.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -361.92 \pm 16.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[166](1)	[310](1)
[160](1)	248 (1)
[383](1)	375 (1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distances: Li–I = 2.54 Å; Li–Li = 2.71 Å
Bond Angles: I–Li–I = 116° ± 4° Li–I–Li = 64°
Product of the Moments of Inertia: $I_A I_B I_C = 1.631229 \times 10^{-112}\ g^3·cm^6$

Enthalpy of Formation

This was obtained from the enthalpy of formation of the crystal and the enthalpy of sublimation to the dimer, which derivation has been given in the LiI(g) table.

Heat Capacity and Entropy

Berkowitz has calculated the molecular structure and vibrational frequencies based on the ionic model. The planar rhombic structure proposed by Berkowitz has been confirmed by the lack of polarity in electric deflection by Buchler *et al.*[2] The selected bond distances and angle were obtained from the electron diffraction studies of monomer dimer vapor by Akischin and Rambidi.[3] The bond distances, r(Li–Li) = 2.712 Å and r(I–I) = 4.520 Å, calculated by Berkowitz are in good agreement with those from Akischin and Rambidi.[3] The principal moments of inertia are: $I_A = 4.1763 \times 10^{-39}$, $I_B = 195.5561 \times 10^{-39}$ and $I_C = 199.7324 \times 10^{-39}\ g·cm^2$.

Bauer *et al.* have estimated six vibrational frequencies (501, 501, 148, 200, 294, 360 cm^{-1}) for Li_2I_2(g) in the electron diffraction studies of the Li_2Cl_2(g). Klemperer and Norris have observed two fundamental vibrational frequencies (248 and 375 cm^{-1}) in the infrared spectrum and tentatively assigned them as B_{2u} and B_{3u} modes; these have been adopted in the tabulation. The remaining four vibrational frequencies were obtained from Berkowitz because his model and derivation are self consistent.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.267	−356.740	−356.740	INFINITE
100	51.234	259.423	393.015	−13.359	−356.873	−375.247	196.009
200	69.370	301.482	337.413	−7.186	−359.315	−392.689	102.560
250	73.525	317.446	331.867	−3.605	−360.618	−400.883	83.760
298.15	76.044	330.628	330.628	0.	−361.916	−408.522	71.571
300	76.121	331.098	330.629	0.141	−361.967	−408.811	71.180
350	77.820	342.969	331.563	3.992	−363.454	−416.504	62.160
400	78.982	353.441	333.656	7.914	−381.033	−423.426	55.294
450	79.808	362.794	336.383	11.885	−383.942	−428.552	49.745
500	80.414	371.235	339.453	15.891	−433.119	−428.934	44.810
600	81.222	385.974	346.014	23.976	−434.754	−427.940	37.256
700	81.720	398.535	352.642	32.125	−436.223	−426.686	31.840
800	82.048	409.470	359.076	40.315	−437.605	−425.229	27.765
900	82.275	419.147	365.224	48.531	−438.961	−423.601	24.585
1000	82.438	427.825	371.057	56.767	−440.299	−421.822	22.034
1100	82.559	435.688	376.581	65.018	−441.626	−419.910	19.940
1200	82.652	442.876	381.810	73.278	−442.950	−417.877	18.190
1300	82.724	449.494	386.766	81.547	−444.281	−415.734	16.704
1400	82.782	455.627	391.468	89.823	−445.625	−413.488	15.427
1500	82.828	461.340	395.938	98.103	−446.987	−411.145	14.317
1600	82.866	466.687	400.194	106.388	−448.378	−408.710	13.343
1700	82.898	471.712	404.255	114.676	−740.280	−391.835	12.040
1800	82.924	476.451	408.135	122.968	−740.251	−371.340	10.776
1900	82.947	480.935	411.850	131.261	−740.291	−350.844	9.645
2000	82.966	485.190	415.412	139.557	−740.403	−330.344	8.628
2100	82.983	489.238	418.832	147.854	−740.587	−309.837	7.707
2200	82.997	493.099	422.120	156.153	−740.839	−289.320	6.869
2300	83.009	496.789	425.287	164.454	−741.154	−268.789	6.104
2400	83.020	500.322	428.340	172.755	−741.525	−248.244	5.403
2500	83.030	503.711	431.288	181.058	−741.944	−227.682	4.757
2600	83.039	506.968	434.136	189.361	−742.403	−207.103	4.161
2700	83.046	510.102	436.892	197.665	−742.893	−186.505	3.608
2800	83.053	513.122	439.561	205.970	−743.406	−165.889	3.095
2900	83.059	516.037	442.148	214.276	−743.936	−145.254	2.616
3000	83.065	518.852	444.658	222.582	−744.475	−124.600	2.169
3100	83.070	521.576	447.096	230.889	−745.018	−103.929	1.751
3200	83.074	524.214	449.465	239.196	−745.562	−83.240	1.359
3300	83.079	526.770	451.769	247.504	−746.104	−62.534	0.990
3400	83.082	529.250	454.012	255.812	−746.642	−41.812	0.642
3500	83.086	531.659	456.196	264.120	−747.175	−21.074	0.315
3600	83.089	533.999	458.325	272.429	−747.703	−0.320	0.005
3700	83.092	536.276	460.401	280.738	−748.227	20.448	−0.289
3800	83.095	538.492	462.427	289.047	−748.750	41.230	−0.567
3900	83.097	540.650	464.405	297.357	−749.272	62.025	−0.831
4000	83.099	542.754	466.338	305.667	−749.797	82.834	−1.082
4100	83.102	544.806	468.226	313.977	−750.329	103.657	−1.321
4200	83.104	546.809	470.074	322.287	−750.870	124.492	−1.548
4300	83.105	548.764	471.881	330.597	−751.425	145.341	−1.766
4400	83.107	550.675	473.650	338.908	−751.957	166.199	−1.973
4500	83.109	552.542	475.383	347.219	−752.533	187.072	−2.171
4600	83.110	554.369	477.080	355.530	−753.139	207.959	−2.361
4700	83.112	556.157	478.744	363.841	−753.773	228.859	−2.543
4800	83.113	557.906	480.375	372.152	−754.441	249.773	−2.718
4900	83.114	559.620	481.974	380.464	−755.146	270.702	−2.886
5000	83.116	561.299	483.544	388.775	−755.894	291.645	−3.047
5100	83.117	562.945	485.085	397.087	−756.679	312.603	−3.202
5200	83.118	564.559	486.598	405.398	−757.524	333.577	−3.351
5300	83.119	566.142	488.084	413.710	−758.427	354.568	−3.494
5400	83.120	567.696	489.544	422.022	−759.391	375.577	−3.633
5500	83.120	569.221	490.979	430.334	−760.422	396.604	−3.767
5600	83.121	570.719	492.389	438.646	−761.525	417.651	−3.896
5700	83.122	572.190	493.776	446.958	−762.703	438.718	−4.020
5800	83.123	573.636	495.141	455.271	−763.962	459.806	−4.141
5900	83.124	575.057	496.483	463.583	−765.306	480.917	−4.258
6000	83.124	576.454	497.805	471.895	−766.738	502.052	−4.371

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = [129.704 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 907 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -366.94 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 29.288 \pm 8.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Finch *et al.*[1] measured the enthalpy of solution of MgO(cr) in aqueous HI and of MgI_2(cr) in the same solvent. Combining and correcting for a concentration change gives $\Delta_r H°(298.15\ K) = 14.53\ kcal \cdot mol^{-1}$ for the process MgO(cr) + 2 HI (0.5m) = MgI_2(cr) + H_2O(l) from which $\Delta_f H°(MgI_2, cr, 298.15\ K) = -87.70 \pm 1.5\ kcal \cdot mol^{-1}$ is calculated. The auxiliary data used are $\Delta_f H°(MgO, cr, 298.15\ K) = -143.7\ kcal \cdot mol^{-1}$,[1,2] $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$,[3] and $\Delta_f H°(HI, 0.5m, 298.15\ K) = -13.42\ kcal \cdot mol^{-1}$. This last value was calculated from the CODATA value of −13.60 for $\Delta_f H°(I^-, aq, std.\ state, 298.15\ K)$[3] = $\Delta_f H°(HI, aq, std.\ state, 298.15\ K)$ and the enthalpy of dilution of HI.[4]

Combination of $\Delta_f H°(Mg^{+2}, aq, std.\ state, 298.15\ K) = -111.58\ kcal \cdot mol^{-1}$ selected by Parker[4,5] with the CODATA value of $\Delta_f H°(I^-, aq, std.\ state, 298.15\ K) = -13.60\ kcal \cdot mol^{-1}$ gives $\Delta_f H°(MgI_2, aq, std.\ state, 298.15\ K) = -138.78\ kcal \cdot mol^{-1}$. Further combination with the enthalpy of solution, $-50.96\ kcal \cdot mol^{-1}$,[4] gives $\Delta_f H°(MgI_2, cr, 298.15\ K) = -87.82\ kcal \cdot mol^{-1}$. We adopt $\Delta_f H°(MgI_2, cr, 298.15\ K) = -87.7 \pm 1.5\ kcal \cdot mol^{-1}$ to retain internal consistency.

Heat Capacity and Entropy

$C_p°(298.15\ K) = 17.88\ cal \cdot K^{-1} \cdot mol^{-1}$ is calculated from the reaction $MgCl_2$(cr) + 2 NaI(cr) = MgI_2(cr) + 2 NaCl(cr) assuming no net change in heat capacity. $C_p° = 21.0\ cal\ K^{-1} \cdot mol^{-1}$ at $T_{fus} = 907$ K estimated from a Kopp's rule value of 7.0 cal K^{-1} g atom appears reasonable in comparison with a $C_p°$ vs. T plot for $MgBr_2$(cr), $MgCl_2$(cr) and CaI_2(cr).[2] Values of $C_p°$ between 298.15 and 907 K are read from the graphical comparison curve. The adopted values lead to $H°(500\ K) - H°(298.15\ K) = 3.77\ kcal \cdot mol^{-1}$, in reasonable agreement with the estimate of 4.0 by Brewer *et al.*[6]

$S°(298.15\ K) = 31.0 \pm 1.0\ cal \cdot K^{-1} \cdot mol^{-1}$ is adopted from Kelley and King.[7]

Fusion Data

The melting point of 650 °C (923 K) quoted in the literature appears to be based on the assumed value of Devoto and Jeny[8] In a study of molten electrolytes, Bockris *et al.*[9] found MgI_2 to be molten at 910 K; a graph in the same paper infers that a $T_{fus} = 907$ K was chosen. We adopt $T_{fus} = 907 \pm 15$ K.

From the KI/MgI_2 phase diagram by Klemm *et al.*[10] values of $\Delta_{fus} H°(MgI_2)$ ranging from 7 to 9 $kcal \cdot mol^{-1}$ are calculated. Brewer[11] earlier estimated 5.3 $kcal \cdot mol^{-1}$. We adopt $7.0 \pm 2.0\ kcal \cdot mol^{-1}$.

Sublimation Data

By a mass spectrometric–Knudsen cell technique, Berkowitz and Marguart[12] found the sublimation pressure of MgI_2(cr) to be 5.18×10^{-6} atm at 734 K and 2.02×10^{-5} atm at 757 K. A 3rd law analysis of these two points gives $\Delta_{sub} H°(298.15\ K) = 49.4 \pm 0.8\ kcal \cdot mol^{-1}$. The 2nd law analysis of these two points gives 67.5 $kcal \cdot mol^{-1}$ but other data covering an approximate range of 550 to 750 K are shown graphically by Berkowitz and Marguardt[12] from which they calculate $\Delta_{sub} H°(550–750\ K) = 45\ kcal \cdot mol^{-1}$. We adopt $\Delta_{sub} H°(298.15\ K) = 49.4 \pm 0.8$ $kcal \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	74.810	129.704	129.704	0.	−366.937	−361.240	63.288
300	74.977	130.167	129.705	0.139	−366.945	−361.204	62.891
400	78.408	152.229	132.690	7.815	−383.462	−358.661	46.836
500	80.919	170.002	138.432	15.785	−426.355	−348.339	36.391
600	83.011	184.946	144.971	23.985	−424.677	−332.893	28.981
700	84.726	197.873	151.626	32.373	−422.928	−317.733	23.710
800	86.274	209.290	158.134	40.925	−421.144	−302.826	19.773
900	87.655	219.502	164.395	49.596	−419.381	−288.143	16.723
907.000	87.864	220.182	164.823	50.210	− − − CRYSTAL <− − > LIQUID − − −		
1000	88.994	228.812	170.378	58.434	−426.201	−272.943	14.257
1100	90.249	237.354	176.084	67.396	−424.485	−257.700	12.237
1200	91.462	245.259	181.523	76.482	−422.663	−242.617	10.561
1300	92.634	252.626	186.713	85.687	−420.744	−227.690	9.149
1400	93.763	259.532	191.670	95.008	−546.151	−209.748	7.826
1500	94.851	266.039	196.413	104.439	−542.726	−185.838	6.471

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = [155.737]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 907 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-342.252]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 29.288 \pm 8.4\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgI_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgI_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(907\ K)\ H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

The liquid heat capacity of 24.0 $cal·K^{-1}·mol^{-1}$ (8 $cal·K^{-1}$ g·atom) follows the trend of the liquid heat capacities of the alkaline earth chlorides and bromides and the other alkaline earth iodides. This value is adopted and assumed constant over a 600–2000 K range. A glass transition is assumed at 600 K below which the heat capacity is that of the crystal.

$S°(MgI_2, l, 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} = 1255 K is calculated as the temperature at which the fugacity is 1 atm for the reaction $MgI_2(l) = MgI_2(g)$. $\Delta_{vap}H° = 36.126\ kcal·mol^{-1}$ is the calculated difference between the enthalpies of formation of the ideal gas and the liquid at T_{vap}.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.810	155.737	155.737	0.	−342.252	−344.316	60.323
300	74.977	156.200	155.738	0.139	−342.260	−344.329	59.953
400	78.408	178.261	158.723	7.815	−358.776	−344.389	44.973
500	80.919	196.035	164.464	15.785	−401.669	−336.671	35.172
600	83.011	210.980	171.004	23.985	−399.991	−323.827	28.192
600.000	83.011	210.980	171.004	23.985	GLASS <- -> LIQUID		
600.000	100.416	210.980	171.004	23.985	TRANSITION		
700	100.416	226.459	177.849	34.027	−396.589	−311.403	23.237
800	100.416	239.867	184.782	44.068	−393.315	−299.459	19.553
900	100.416	251.695	191.572	54.110	−390.182	−287.917	16.710
907.000	100.416	252.473	192.040	54.813	--- CRYSTAL <- -> LIQUID ---		
1000	100.416	262.275	198.123	64.152	−395.798	−276.003	14.417
1100	100.416	271.845	204.397	74.193	−393.003	−264.159	12.544
1200	100.416	280.583	210.387	84.235	−390.225	−252.568	10.994
1300	100.416	288.620	216.100	94.276	−387.470	−241.209	9.692
1400	100.416	296.062	221.549	104.318	−512.156	−226.893	8.465
1500	100.416	302.990	226.750	114.360	−508.120	−206.658	7.196
1600	100.416	309.471	231.720	124.401	−504.134	−186.691	6.095
1700	100.416	315.558	236.474	134.443	−500.207	−166.972	5.130
1800	100.416	321.298	241.029	144.484	−496.345	−147.481	4.280
1900	100.416	326.727	245.398	154.526	−492.552	−128.204	3.525
2000	100.416	331.878	249.594	164.568	−488.830	−109.124	2.850

PREVIOUS: CURRENT: December 1974

0 to 907 K crystal
above 907 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.810	129.704	129.704	0.	−366.937	−361.240	63.288
300	74.977	130.167	129.705	0.139	−366.945	−361.204	62.891
400	78.408	152.229	132.690	7.815	−383.462	−358.661	46.836
500	80.919	170.002	138.432	15.785	−426.355	−348.339	36.391
600	83.011	184.946	144.971	23.985	−424.677	−332.893	28.981
700	84.726	197.873	151.626	32.373	−422.928	−317.733	23.710
800	86.274	209.290	158.134	40.925	−421.144	−302.826	19.773
900	87.655	219.502	164.395	49.596	−419.381	−288.143	16.723
907.000	87.864	220.182	164.823	50.210	CRYSTAL <--> LIQUID TRANSITION		
907.000	100.416	252.473	164.823	79.498			
1000	100.416	262.275	173.438	88.837	−395.798	−276.003	14.417
1100	100.416	271.845	181.956	98.879	−393.003	−264.159	12.544
1200	100.416	280.583	189.816	108.920	−390.225	−252.568	10.994
1300	100.416	288.620	197.111	118.962	−387.470	−241.209	9.692
1400	100.416	296.062	203.917	129.003	−512.156	−226.893	8.465
1500	100.416	302.990	210.293	139.045	−508.120	−206.658	7.196
1600	100.416	309.471	216.291	149.087	−504.134	−186.691	6.095
1700	100.416	315.558	221.953	159.128	−500.207	−166.972	5.130
1800	100.416	321.298	227.315	169.170	−496.345	−147.481	4.280
1900	100.416	326.727	232.405	179.211	−492.552	−128.204	3.525
2000	100.416	331.878	237.251	189.253	−488.830	−109.124	2.850

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 317.5 \pm 2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -157.56 \pm 10.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -160.25 \pm 10.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[125](1)
[60](2)
[423](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: $D_{\infty h}$

Bond Distance: Mg–I = 2.52 ± 0.03 Å

Bond Angle: I–Mg–I = 180°

Rotational Constant: B_o = [0.010459] cm^{-1}

Enthalpy of Formation

$\Delta_f H°(MgI_2, g, 298.15\ K)$ is obtained from that of the crystal by addition of $\Delta_{sub} H°(298.15\ K) = 49.4 \pm 0.8$ kcal·mol^{-1}. The enthalpy of sublimation is derived from the sublimation pressure measurements of Berkowitz and Marquart.[1] Refer to the MgI_2(cr) table.

Heat Capacity and Entropy

The bond distance is taken from the electron diffraction study of Akishin and Spiridonov.[2] From an electric deflection study of mass spectrometrically detected molecular beams, Buechler *et al.*[3] concluded that MgI_2 is linear.

The equality of the stretching force constant of the alkaline earth monohalide and the stretching force constant of the alkaline earth dihalide has been indicated as a reasonable assumption.[4,5] The stretching force constant for MgI(g) is calculated, using the valence force model, from the ground state vibrational frequency given by Rosen.[6] The bending force constant for MgI_2(g) is taken as 0.01 of the stretching force constant. Brewer *et al.*[4] used a factor of 0.1 for MgI_2; however, a factor of 0.01 appears more reasonable.[7] The adopted vibrational frequencies are calculated from the estimated force constants. Other estimates for ν_1, ν_2, and ν_3 are 132, 199, 446[4] and 137, 140, 464.[8]

We assign an uncertainty of ±2 cal·K^{-1}·mol^{-1} to the entropy to allow for error in estimating the vibrational frequencies.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−15.512	−157.563	−157.563	INFINITE
100	51.832	256.256	368.725	−11.247	−156.990	−175.566	91.706
200	57.298	294.115	322.882	−5.753	−158.436	−193.639	50.573
250	58.718	307.064	318.466	−2.850	−159.332	−202.337	42.276
298.15	59.623	317.489	317.489	0.	−160.247	−210.538	36.885
300	59.651	317.858	317.490	0.110	−160.284	−210.850	36.712
350	60.281	327.104	318.219	3.110	−161.359	−219.196	32.713
400	60.721	335.183	319.845	6.135	−178.452	−226.834	29.621
450	61.038	342.355	321.955	9.180	−180.762	−232.743	27.016
500	61.273	348.798	324.323	12.238	−223.213	−234.595	24.508
600	61.590	360.000	329.363	18.382	−223.590	−236.838	20.619
700	61.787	369.510	334.436	24.552	−224.060	−239.010	17.835
800	61.917	377.770	339.348	30.737	−224.641	−241.108	15.743
900	62.008	385.068	344.030	36.934	−225.354	−243.125	14.111
1000	62.073	391.605	348.467	43.138	−234.808	−244.342	12.763
1100	62.122	397.523	352.662	49.348	−235.844	−245.245	11.646
1200	62.159	402.930	356.629	55.562	−236.893	−246.054	10.710
1300	62.189	407.907	360.384	61.780	−237.962	−246.774	9.916
1400	62.212	412.517	363.945	68.000	−366.470	−244.244	9.113
1500	62.230	416.809	367.328	74.222	−366.253	−235.521	8.202
1600	62.246	420.826	370.548	80.446	−366.085	−226.812	7.405
1700	62.259	424.600	373.617	86.671	−365.974	−218.111	6.702
1800	62.269	428.159	376.550	92.897	−365.928	−209.414	6.077
1900	62.278	431.526	379.355	99.125	−365.949	−200.719	5.518
2000	62.286	434.721	382.044	105.353	−366.040	−192.021	5.015
2100	62.293	437.760	384.626	111.582	−366.198	−183.316	4.560
2200	62.298	440.658	387.107	117.811	−366.418	−174.602	4.146
2300	62.304	443.427	389.496	124.042	−366.693	−165.878	3.767
2400	62.308	446.079	391.799	130.272	−367.014	−157.140	3.420
2500	62.312	448.623	394.021	136.503	−367.368	−148.388	3.100
2600	62.315	451.067	396.169	142.734	−367.747	−139.621	2.805
2700	62.318	453.418	398.246	148.966	−368.138	−130.840	2.531
2800	62.321	455.685	400.257	155.198	−368.531	−122.044	2.277
2900	62.324	457.872	402.206	161.430	−368.916	−113.234	2.040
3000	62.326	459.985	404.097	167.663	−369.285	−104.411	1.818
3100	62.328	462.028	405.933	173.896	−369.631	−95.576	1.610
3200	62.330	464.007	407.717	180.128	−369.947	−86.730	1.416
3300	62.332	465.925	409.452	186.362	−370.230	−77.875	1.233
3400	62.333	467.786	411.141	192.595	−370.475	−69.012	1.060
3500	62.334	469.593	412.785	198.828	−370.680	−60.142	0.898
3600	62.336	471.349	414.387	205.062	−370.846	−51.268	0.744
3700	62.337	473.057	415.950	211.295	−370.971	−42.388	0.598
3800	62.338	474.719	417.475	217.529	−371.057	−33.507	0.461
3900	62.339	476.339	418.964	223.763	−371.104	−24.623	0.330
4000	62.340	477.917	420.418	229.997	−371.117	−15.739	0.206
4100	62.341	479.456	421.839	236.231	−371.095	−6.855	0.087
4200	62.342	480.959	423.229	242.465	−371.044	2.029	−0.025
4300	62.342	482.426	424.589	248.699	−370.966	10.911	−0.133
4400	62.343	483.859	425.919	254.934	−370.865	19.790	−0.235
4500	62.344	485.260	427.223	261.168	−370.744	28.668	−0.333
4600	62.344	486.630	428.499	267.402	−370.608	37.542	−0.426
4700	62.345	487.971	429.750	273.637	−370.459	46.413	−0.516
4800	62.346	489.283	430.977	279.871	−370.302	55.281	−0.602
4900	62.346	490.569	432.180	286.106	−370.140	64.146	−0.684
5000	62.347	491.829	433.360	292.341	−369.978	73.007	−0.763
5100	62.347	493.063	434.519	298.575	−369.819	81.865	−0.838
5200	62.347	494.274	435.657	304.810	−369.665	90.721	−0.911
5300	62.348	495.461	436.774	311.045	−369.521	99.572	−0.981
5400	62.348	496.627	437.871	317.279	−369.390	108.422	−1.049
5500	62.349	497.771	438.950	323.514	−369.275	117.269	−1.114
5600	62.349	498.894	440.011	329.749	−369.179	126.115	−1.176
5700	62.349	499.998	441.053	335.984	−369.105	134.959	−1.237
5800	62.349	501.082	442.079	342.219	−369.055	143.801	−1.295
5900	62.350	502.148	443.088	348.454	−369.032	152.643	−1.351
6000	62.350	503.196	444.081	354.689	−369.039	161.485	−1.406

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = [149.662 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{dcm} = 1305$ K (total $p = 1$ atm)

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -103.93 \pm 12.6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Barnes *et al.*[1] have measured calorimetrically the enthalpy of formation of $MoI_{2.76}$ by reacting iodine vapor with $Mo(CO)_6$ at 539 K. The products were shown to consist of MoI_3, MoI_2, and Mo by chemical analysis. Assuming a difference in the enthalpies of formation of MoI_3 and MoI_2 of $-1.5\ kcal \cdot mol^{-1}$, Barnes *et al.*[1] determined $\Delta_f H°(MoI_2, cr, 298.15\ K) = -24.7 \pm 2\ kcal \cdot mol^{-1}$. Brewer[2] has estimated that the difference $\Delta_f H°(MoI_3)-\Delta_f H°(MoI_2)$ may be as large as $-5\ kcal \cdot mol^{-1}$, and he reanalyzed the enthalpy of iodination data with the result $\Delta_f H°(MoI_2, cr, 298.15\ K)/R = -12500 \pm 1500$ K which is adoptedThe assigned uncertainty ($\pm 3\ kcal \cdot mol^{-1}$) is determined from the product 1500xR which has been rounded to the nearest $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Values of $S°(298.15\ K)$ and $C_p°$ over the temperature range 298–1500 K are estimates reported by Brewer.[2] We treat his reported value of $S°(298.15\ K)/R$ in a manner similar to that for the heat of formation.

Phase Data

The crystal structure[2] of α–MoI_2 in the Pearson classification system of oC72. Glicksman and Walton[3] have reported preparing a new molybdenum diiodide phase (β–MoI_2) by reacting $Mo_2(O_2CCH_3)_4$ with HI gas at 573 K. We assume that this new phase is unstable with respect to α–MoI_2 at all temperatures.

Decomposition Data

T_{dcm} is calculated as the temperature at which the partial pressures of I_2(g) and I(g) reach one atmosphere over crystalline MoI_2 and Mo. At $T_{dcm} = 1305$ K, we calculate the vapor composition to consist of 0.63 atm of I_2 and 0.37 atm of I. Saturated vapor pressure measurements by Drobot *et al.*[4] on MoI_2(cr) prepared by thermal decomposition of MoI_3(cr) show that initial decomposition to the metal and iodine occurs at 1063 K and 0.33 atm.

References

[1] D. S. Barnes, G. Pilcher, D. A. Pittam, H. A. Skinner, D. Todd, and Y. Virmani, J. Less Common Met. **6**, 177 (1974).
[2] L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 28, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[3] H. D. Glicksman and R. A. Walton, Inorg. Chem. **7**, 200 (1978).
[4] D. V. Drobot, L. G. Mikhailova, K. A. Bol'shakov, and V. L. Sbitnev, Russ. J. Inorg. Chem. **3**, 643 (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	82.705	149.662	149.662	0.	−103.931	−105.396	18.465
300	82.730	150.173	149.663	0.153	−103.923	−105.405	18.353
400	83.977	174.144	152.923	8.488	−119.681	−105.390	13.763
500	85.224	193.017	159.120	16.948	−161.966	−97.768	10.214
600	86.471	208.665	166.110	25.533	−159.752	−85.135	7.412
700	87.718	222.089	173.171	34.243	−157.483	−72.878	5.438
800	88.964	233.883	180.037	43.077	−155.149	−60.950	3.980
900	90.211	244.433	186.616	52.035	−152.747	−49.318	2.862
1000	91.458	254.003	192.884	61.119	−150.278	−37.958	1.983
1100	92.705	262.778	198.844	70.327	−147.748	−26.848	1.275
1200	93.952	270.898	204.515	79.660	−145.166	−15.971	0.695
1300	95.199	278.467	209.915	89.117	−142.546	−5.310	0.213
1400	96.445	285.568	215.068	98.700	−139.900	5.147	−0.192
1500	97.696	292.264	219.993	108.407	−137.246	15.415	−0.537

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K) = [339.290 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [257.38 \pm 41.8]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [257.73 \pm 41.8]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[1]
[243.1]	[3]
[669.6]	[5]
[1225.2]	[7]
[1873.0]	[9]
[11471.3]	[1]
[12590.8]	[3]
[12630.3]	[9]
[13201.3]	[11]
[13741.5]	[13]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[200](1)
[50](2)
[200](1)

Point Group: $[D_{\infty h}]$ σ = [2]
Bond Distance: Mo–I = [2.66] Å
Bond Angle: I–Mo–I = [180]°
Rotational Constant: B_0 = [0.009387] cm^{-1}

Enthalpy of Formation

The adopted value of $\Delta_f H°$ at 298.15 K is that estimated by Brewer.[1] The estimated value is consistent with the low volatility of solid molybdenum in iodine vapor reported by Schafer *et al.*[2] Brewer has given no weight to the equilibrium data reported by Allen and Yost[3] for the formation of MoI_2(g) from Mo(cr) and I(g) since the product formed may have been MoO_2I_2 rather than the diiodide.[2] Brewer's estimated value is given as $\Delta_f H°(298.15\ K/F) = 31000 \pm 5000$ K. The assigned uncertainty ($\pm 10\ kcal·mol^{-1}$) is determined from the product 5000 × R which has been rounded to the nearest $kcal·mol^{-1}$. The value of $\Delta_f H°(0\ K)$ combined with JANAF data for Mo(g) and I(g) gives $\Delta_{at} H°(0\ K) = 147 \pm 11\ kcal·mol^{-1}$ and an average Mo–I bond energy of $\Delta_{at} H°(0\ K/2) = 73.4 \pm 5.5\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The bond length and vibrational frequencies are values estimated by Brewer.[1] A linear structure has been predicted for MoI_2 by Drake and Rosenblatt.[5] The electronic contribution is taken to be the same as that for the free gaseous Mo^{+2} ion, as estimated by Brewer.[1] The levels listed by Rico[6] below 1374 cm^{-1} are used in the calculations.

Our heat capacity and enthalpy values up to 3000 K are in agreement with those determined by Brewer.[1] However, his entropies and free energy functions differ from our values by about 1 $cal·K^{-1}·mol^{-1}$ at all temperatures over the range 298 3000 K. We believe that his results are erroneous due to the use of an incorrect value for the molecular weight of MoI_2. We reproduce his entropies and free energy functions if we use a molecular weight of 476.65 which corresponds to MoI_3.

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley: personal communication, September 20, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]H. Schafer, T. Grofe, and M. Trenkel, J. Solid State Chem. **8**, 14 (1973).
[3]T. L. Allen and D. M. Yost, J. Chem. Phys. **22**, 855 (1954).
[4]JANAF Thermochemical Tables: Mo(g), 3–31–78; I(g), 6–30–74.
[5]M. C. Drake and G. M. Rosenblatt, Paper 388, The Electrochemical Society, Atlanta, Georgia, (October 1977).
[6]F. R. Rico, An. Real Soc. Espan. Fis. Quim., Ser. A **61**, 103 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.140	257.377	257.377	INFINITE
100	61.708	265.272	400.919	−13.565	258.411	238.686	−124.677
200	69.265	311.318	345.722	−6.881	258.321	218.944	−57.182
250	70.171	326.880	340.452	−3.393	258.063	209.128	−43.695
298.15	70.717	339.290	339.290	0.	257.734	199.731	−34.992
300	70.733	339.728	339.291	0.131	257.720	199.372	−34.714
350	71.082	350.660	340.154	3.677	257.241	189.682	−28.308
400	71.254	360.164	342.074	7.236	240.732	180.614	−23.586
450	71.268	368.559	344.560	10.800	238.997	173.204	−20.105
500	71.146	376.063	347.342	14.361	197.111	169.786	−17.737
600	70.599	388.991	353.240	21.451	197.830	164.252	−14.299
700	69.827	399.818	359.142	28.473	198.412	158.607	−11.835
800	68.995	409.087	364.820	35.414	198.853	152.889	−9.983
900	68.198	417.167	370.197	42.273	199.156	147.124	−8.539
1000	67.478	424.314	375.258	49.056	199.324	141.332	−7.382
1100	66.847	430.715	380.014	55.772	199.362	135.530	−6.436
1200	66.305	436.508	384.484	62.429	199.267	129.731	−5.647
1300	65.842	441.796	388.692	69.035	199.037	123.944	−4.980
1400	65.449	446.661	392.662	75.599	198.664	118.181	−4.409
1500	65.118	451.165	396.414	82.127	198.140	112.450	−3.916
1600	64.840	455.358	399.968	88.625	197.453	106.758	−3.485
1700	64.609	459.282	403.343	95.097	196.594	101.115	−3.107
1800	64.422	462.970	406.554	101.548	195.553	95.528	−2.772
1900	64.272	466.449	409.616	107.982	194.322	90.004	−2.474
2000	64.157	469.742	412.540	114.403	192.897	84.549	−2.208
2100	64.075	472.870	415.339	120.815	191.274	79.171	−1.969
2200	64.022	475.850	418.023	127.219	189.452	73.875	−1.754
2300	63.996	478.695	420.599	133.620	187.433	68.666	−1.559
2400	63.995	481.419	423.077	140.019	185.219	63.549	−1.383
2500	64.017	484.031	425.463	146.420	182.812	58.528	−1.223
2600	64.059	486.543	427.765	152.823	180.204	53.607	−1.077
2700	64.120	488.962	429.987	159.232	177.369	48.791	−0.944
2800	64.198	491.295	432.135	165.648	174.257	44.085	−0.822
2900	64.289	493.549	434.214	172.072	134.916	39.545	−0.712
3000	64.393	495.730	436.228	178.506	133.082	36.288	−0.632
3100	64.507	497.844	438.182	184.951	131.287	33.091	−0.558
3200	64.630	499.894	440.079	191.408	129.542	29.952	−0.489
3300	64.760	501.884	441.921	197.878	127.853	26.866	−0.425
3400	64.895	503.820	443.714	204.360	126.225	23.830	−0.366
3500	65.034	505.703	445.458	210.857	124.663	20.841	−0.311
3600	65.175	507.537	447.157	217.367	123.171	17.896	−0.260
3700	65.317	509.324	448.813	223.892	121.750	14.992	−0.212
3800	65.458	511.068	450.429	230.430	120.401	12.125	−0.167
3900	65.599	512.770	452.005	236.983	119.126	9.292	−0.124
4000	65.738	514.433	453.545	243.550	117.925	6.491	−0.085
4100	65.873	516.058	455.050	250.131	116.796	3.719	−0.047
4200	66.005	517.647	456.522	256.725	115.739	0.974	−0.012
4300	66.133	519.201	457.962	263.332	114.753	−1.746	0.021
4400	66.257	520.723	459.371	269.951	113.835	−4.445	0.053
4500	66.375	522.214	460.751	276.583	112.984	−7.123	0.083
4600	66.487	523.674	462.103	283.226	112.198	−9.784	0.111
4700	66.594	525.105	463.428	289.880	111.475	−12.428	0.138
4800	66.695	526.508	464.728	296.545	110.812	−15.056	0.164
4900	66.790	527.884	466.003	303.219	110.207	−17.672	0.188
5000	66.879	529.234	467.254	309.902	−481.727	−14.545	0.152
5100	66.962	530.559	468.482	316.595	−483.902	−5.180	0.053
5200	67.038	531.860	469.688	323.295	−486.173	4.229	−0.042
5300	67.109	533.138	470.874	330.002	−488.538	13.681	−0.135
5400	67.173	534.393	472.038	336.716	−491.000	23.180	−0.224
5500	67.232	535.626	473.183	343.436	−493.557	32.725	−0.311
5600	67.284	536.838	474.309	350.162	−496.210	42.318	−0.395
5700	67.331	538.029	475.417	356.893	−498.956	51.959	−0.476
5800	67.373	539.201	476.506	363.628	−501.797	61.649	−0.555
5900	67.409	540.353	477.579	370.368	−504.729	71.388	−0.632
6000	67.440	541.486	478.634	377.110	−507.755	81.178	−0.707

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$\Delta_{at}H°(0\ K) = 348 \pm 25$ kJ·mol^{-1}
$S°(298.15\ K) = [308.1 \pm 4]$ J·K^{-1}·mol^{-1}

$\Delta_fH°(0\ K) = [124 \pm 25]$ kJ·mol^{-1}
$\Delta_fH°(298.15\ K) = [119.5 \pm 25]$ kJ·mol^{-1}

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
X^1A	0.0	1

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[475](1)
[100](1)
[525](1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: I–O = [2.0]Å
Bond Angle: I–O–I = [115]°
Product of the Moments of Inertia: $I_AI_BI_C = 42498.6720 \times 10^{-117}$ g^3·cm^6

Enthalpy of Formation

For the series XOX(g) [where X = F, Cl, Br, I], there are only reliable experimental data for ClOCl(g). Assuming that the values $D_0°$(ClO) and $\Delta_{at}H°$(ClOCl,g) are reasonable, we adopt the ratio of the numbers (1.52) to apply for a similar relationship between IO(g) and IOI(g). The ratio for the corresponding bromine oxides is approximately 1.6.

Heat Capacity and Entropy

The structure of this molecule is estimated to be bent with a I–O–I angle of [115]° and a bond length of [2.0]Å in analogy with the corresponding fluorine, chlorine, and bromine oxide molecules.[1] The principal moments of inertia in g·cm^2 are: $I_A = 2.8860 \times 10^{-39}$, $I_B = 119.9153 \times 10^{-39}$, and $I_C = 122.8013 \times 10^{-39}$.

The vibrational frequencies are estimated from known frequencies of FOF(g), ClOCl(g), and BrOBr(g)[1] and expected trends in this halogen oxide family.

References

[1]NIST–JANAF Thermochemical Tables: FOF(g): September 1995; ClOCl(g): March 1996; BrOBr(g): (March 1996).

Enthalpy Reference Temperature = T_r = 298.15 K					Standard State Pressure = $p°$ = 0.1 MPa		
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
0	.000	.000	INFINITE	−13.025	124.000	124.000	INFINITE
50	37.610	230.650	456.463	−11.291	124.056	117.968	−123.241
100	40.943	257.873	351.050	−9.318	123.205	112.182	−58.598
150	44.204	275.070	323.013	−7.192	122.204	106.886	−37.221
200	47.472	288.246	312.734	−4.898	121.237	101.928	−26.621
250	50.053	299.131	308.955	−2.456	120.322	97.207	−20.310
298.15	51.874	308.111	308.111	.000	119.485	92.832	−16.264
300	51.933	308.432	308.112	.096	119.453	92.667	−16.135
400	54.269	323.727	310.181	5.418	101.652	84.560	−11.042
500	55.547	335.988	314.157	10.915	57.423	84.562	−8.834
600	56.302	346.187	318.670	16.511	57.684	89.965	−7.832
700	56.780	354.905	323.239	22.166	57.945	95.325	−7.113
800	57.100	362.509	327.682	27.861	58.193	100.648	−6.572
900	57.324	369.248	331.933	33.583	58.422	105.941	−6.149
1000	57.487	375.297	335.972	39.324	58.630	111.209	−5.809
1100	57.608	380.782	339.801	45.079	58.815	116.458	−5.530
1200	57.701	385.799	343.428	50.845	58.973	121.691	−5.297
1300	57.774	390.420	346.867	56.619	59.100	126.912	−5.099
1400	57.832	394.704	350.133	62.399	59.187	132.125	−4.930
1500	57.879	398.695	353.239	68.185	59.224	137.333	−4.782
1600	57.918	402.432	356.198	73.975	59.204	142.541	−4.653
1700	57.950	405.944	359.022	79.768	59.115	147.752	−4.540
1800	57.977	409.258	361.722	85.565	58.953	152.970	−4.439
1900	58.000	412.393	364.307	91.364	58.712	158.199	−4.349
2000	58.019	415.368	366.786	97.165	58.391	163.444	−4.269
2100	58.036	418.200	369.167	102.967	57.993	168.706	−4.196
2200	58.051	420.900	371.458	108.772	57.523	173.989	−4.131
2300	58.064	423.481	373.664	114.578	56.988	179.294	−4.072
2400	58.075	425.952	375.792	120.384	56.399	184.624	−4.018
2500	58.085	428.323	377.846	126.192	55.765	189.980	−3.969
2600	58.094	430.601	379.831	132.001	55.100	195.361	−3.925
2700	58.101	432.794	381.753	137.811	54.414	200.769	−3.884
2800	58.108	434.907	383.613	143.622	53.720	206.203	−3.847
2900	58.115	436.946	385.418	149.433	53.027	211.660	−3.812
3000	58.120	438.916	387.168	155.245	52.347	217.142	−3.781
3100	58.125	440.822	388.868	161.057	51.688	222.646	−3.752
3200	58.130	442.668	390.521	166.870	51.058	228.171	−3.725
3300	58.134	444.457	392.128	172.683	50.462	233.715	−3.699
3400	58.138	446.192	393.693	178.496	49.907	239.277	−3.676
3500	58.142	447.877	395.217	184.311	49.397	244.854	−3.654
3600	58.145	449.515	396.703	190.125	48.934	250.445	−3.634
3700	58.148	451.109	398.152	195.940	48.522	256.048	−3.615
3800	58.151	452.659	399.566	201.754	48.161	261.663	−3.597
3900	58.153	454.170	400.947	207.570	47.853	267.285	−3.580
4000	58.156	455.642	402.296	213.385	47.598	272.915	−3.564
4100	58.158	457.078	403.615	219.201	47.395	278.550	−3.549
4200	58.160	458.480	404.904	225.017	47.245	284.190	−3.534
4300	58.162	459.848	406.166	230.833	47.147	289.833	−3.521
4400	58.164	461.185	407.401	236.649	47.099	295.477	−3.508
4500	58.165	462.493	408.611	242.466	47.099	301.122	−3.495
4600	58.167	463.771	409.797	248.282	47.147	306.766	−3.483
4700	58.168	465.022	410.958	254.099	47.241	312.410	−3.472
4800	58.170	466.247	412.097	259.916	47.378	318.050	−3.461
4900	58.171	467.446	413.215	265.733	47.558	323.688	−3.451
5000	58.172	468.621	414.311	271.550	47.777	329.321	−3.440
5100	58.173	469.773	415.387	277.367	48.035	334.950	−3.431
5200	58.174	470.903	416.444	283.185	48.329	340.572	−3.421
5300	58.175	472.011	417.482	289.002	48.658	346.189	−3.412
5400	58.176	473.098	418.502	294.820	49.018	351.799	−3.403
5500	58.177	474.166	419.504	300.638	49.409	357.403	−3.394
5600	58.178	475.214	420.490	306.455	49.828	363.000	−3.386
5700	58.179	476.244	421.459	312.273	50.274	368.588	−3.378
5800	58.180	477.256	422.412	318.091	50.744	374.168	−3.370
5900	58.181	478.250	423.350	323.909	51.237	379.740	−3.362
6000	58.181	479.228	424.274	329.727	51.751	385.304	−3.354

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = [330.6 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [110.5 \pm 40]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [106.7 \pm 40]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
state	ϵ_i, cm^{-1}	g_i
[^{3}A'']	0.0	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[750](1)
[100](1)
[170](1)

Point Group: C_s $\sigma = 1$
Bond Distances: I–O = [1.9]Å ; I–I = [3.0]Å
Bond Angle: I–O–I = [125]°
Product of the Moments of Inertia: $I_A I_B I_C = 67538.6868 \times 10^{-117}\ g^3 \cdot cm^6$

Enthalpy of Formation

For the four halogen oxide species, XXO(g) where X = F, Cl, Br, I, there are no experimental data related to the enthalpy of formation. Thus the enthalpy of formation is estimated based on assumption that the X–X bond in XXO(g) is 0.6 $D_0°(X_2)$. This leads to a $\Delta_f H°$(IIO,g,0 K) = 110.5 kJ·mol^{-1}.

Heat Capacity and Entropy

The structure of this molecule is estimated to be bent with a I–I–O angle of [125]° and bond distances r(I–I) = [3.0]Å and r(I–O) = [1.9]Å. This structure is estimated in anlogy with the corresponding chlorine and bromine molecules.[1] The vibrational frequencies are estimated from the known frequencies of ClClO and BrBrO. The principal moments of inertia in g·cm^2 are: $I_A = 5.1010 \times 10^{-39}$, $I_B = 112.5438 \times 10^{-39}$, and $I_C = 117.6448 \times 10^{-39}$.

References

[1]NIST–JANAF Thermochemical Tables: ClClO(g): March 1996; BrBrO(g): (March 1996).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−13.691	110.500	110.500	INFINITE
50	39.124	247.843	486.678	−11.942	110.572	103.624	−108.255
100	45.462	277.274	375.278	−9.800	109.889	96.926	−50.629
150	47.981	296.239	345.956	−7.458	109.104	90.611	−31.554
200	49.683	310.283	335.356	−5.015	108.286	84.570	−22.087
250	51.153	321.531	331.503	−2.493	107.452	78.737	−16.451
298.15	52.359	330.647	330.647	.000	106.652	73.279	−12.838
300	52.401	330.971	330.648	.097	106.621	73.072	−12.723
400	54.230	346.316	332.728	5.435	88.835	62.708	−8.189
500	55.386	358.551	336.710	10.920	44.594	60.452	−6.315
600	56.127	368.719	341.221	16.499	44.839	63.601	−5.537
700	56.620	377.411	345.786	22.138	45.083	66.708	−4.978
800	56.961	384.995	350.223	27.818	45.315	69.782	−4.556
900	57.205	391.719	354.467	33.527	45.531	72.827	−4.227
1000	57.384	397.756	358.499	39.257	45.728	75.849	−3.962
1100	57.520	403.232	362.321	45.002	45.904	78.852	−3.744
1200	57.625	408.241	365.942	50.759	46.054	81.841	−3.562
1300	57.707	412.857	369.375	56.526	46.174	84.818	−3.408
1400	57.773	417.136	372.636	62.300	46.254	87.787	−3.275
1500	57.827	421.124	375.737	68.080	46.286	90.753	−3.160
1600	57.872	424.857	378.692	73.866	46.261	93.718	−3.060
1700	57.909	428.367	381.511	79.655	46.168	96.686	−2.971
1800	57.940	431.678	384.207	85.447	46.002	99.662	−2.892
1900	57.966	434.811	386.789	91.242	45.757	102.649	−2.822
2000	57.989	437.785	389.265	97.040	45.433	105.652	−2.759
2100	58.008	440.615	391.643	102.840	45.032	108.672	−2.703
2200	58.025	443.314	393.931	108.642	44.559	111.714	−2.652
2300	58.040	445.894	396.135	114.445	44.022	114.778	−2.607
2400	58.053	448.364	398.260	120.250	43.430	117.867	−2.565
2500	58.065	450.734	400.312	126.056	42.795	120.981	−2.528
2600	58.075	453.012	402.295	131.863	42.127	124.122	−2.494
2700	58.084	455.204	404.214	137.671	41.440	127.289	−2.463
2800	58.092	457.316	406.073	143.479	40.744	130.481	−2.434
2900	58.100	459.355	407.876	149.289	40.050	133.698	−2.408
3000	58.106	461.325	409.625	155.099	39.369	136.939	−2.384
3100	58.112	463.230	411.323	160.910	38.708	140.202	−2.362
3200	58.118	465.075	412.974	166.722	38.076	143.486	−2.342
3300	58.123	466.863	414.581	172.534	37.480	146.789	−2.323
3400	58.127	468.599	416.144	178.346	36.924	150.110	−2.306
3500	58.131	470.284	417.667	184.159	36.412	153.447	−2.290
3600	58.135	471.921	419.151	189.973	35.948	156.797	−2.275
3700	58.139	473.514	420.599	195.786	35.535	160.160	−2.261
3800	58.142	475.065	422.012	201.600	35.173	163.534	−2.248
3900	58.145	476.575	423.392	207.415	34.864	166.916	−2.236
4000	58.148	478.047	424.740	213.229	34.608	170.305	−2.224
4100	58.150	479.483	426.058	219.044	34.405	173.700	−2.213
4200	58.153	480.884	427.346	224.859	34.255	177.099	−2.203
4300	58.155	482.253	428.607	230.675	34.155	180.502	−2.193
4400	58.157	483.590	429.842	236.490	34.106	183.906	−2.183
4500	58.159	484.897	431.051	242.306	34.106	187.310	−2.174
4600	58.161	486.175	432.235	248.122	34.154	190.714	−2.166
4700	58.163	487.426	433.396	253.938	34.247	194.117	−2.157
4800	58.164	488.650	434.535	259.755	34.384	197.517	−2.149
4900	58.166	489.850	435.652	265.571	34.563	200.914	−2.142
5000	58.167	491.025	436.747	271.388	34.782	204.307	−2.134
5100	58.168	492.177	437.823	277.205	35.039	207.695	−2.127
5200	58.170	493.306	438.879	283.022	35.333	211.077	−2.120
5300	58.171	494.414	439.916	288.839	35.660	214.454	−2.114
5400	58.172	495.502	440.936	294.656	36.020	217.824	−2.107
5500	58.173	496.569	441.938	300.473	36.411	221.187	−2.101
5600	58.174	497.617	442.923	306.290	36.830	224.544	−2.094
5700	58.175	498.647	443.891	312.108	37.275	227.891	−2.088
5800	58.176	499.659	444.844	317.925	37.745	231.232	−2.082
5900	58.177	500.653	445.782	323.743	38.238	234.563	−2.077
6000	58.178	501.631	446.704	329.561	38.751	237.886	−2.071

PREVIOUS: CURRENT: March 1996 (1 bar)

$S°(298.15\ K) = 174.836 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 683 \pm 2\ K$

$\Delta_f H°(0\ K) = -174.817 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -175.393 \pm 0.42\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 23.430 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Koref and Braune[1] determined $\Delta_f H°(PbI_2, cr, 298.15\ K) = -41.850\ kcal \cdot mol^{-1}$ by enthalpy of solution calorimetry. 3rd law analyses of emf data at 298.15 K reported by Gerke[2] and Cann and Taylor[3] for the reaction $Pb(cr) + I_2(cr) = PbI_2(cr)$ lead to $\Delta_f H°(PbI_2, cr, 298.15\ K) = -41.923$ and $-41.925\ kcal \cdot mol^{-1}$, respectively. $\Delta_f H°(PbI_2, cr, 298.15\ K) = -41.92 \pm 0.10\ kcal \cdot mol^{-1}$ is adopted.

Heat Capacity and Entropy

McBride[4] measured the low temperature heat capacity (4.52–291.00 K) of PbI_2. Enthalpies have been measured by Ehrhardt[5] (448–776 K), Magnus[6] (373–523 K), and Linsey[7] (323–877 K). The enthalpy data of Linsey[7] is subjected to a curve fitting procedure subject to the constraint that it join smoothly in the region of 298.15 K with the enthalpy derived from the heat capacity data of McBride.[4] $S°(10\ K) = 0.662\ cal \cdot K^{-1} \cdot mol^{-1}$ is adopted from McBride.[4] The data of Linsey[7] did not indicate any transitions other than the solid liquid transition at 683 K.

Fusion Data

Germann and Metz[8] van Klooster and Stearns[9] and Popovkin, Odin, and Novoselova[10] determined $T_{fus} = 685 \pm 1$ K. Blanc and Petit[11] found $T_{fus} = 680$ K. Sumarokova and Modestova[12] found PbI_2 to exist in two crystalline forms with the α–B transition at 645 K. On a DTA cooling curve, Popovkin *et al.*[10] observed a peak at 656 K which they attribute to the B–α transition. Modestova and Sumarokova[13] observed the B form to melt at 669 K. Ehrhardt's[5] drop calorimetry data and his interpretation of the enthalpy increase at 648 K as indicating the melting points are consistent with the existence of a B–phase. The observation by Novoselova *et al.*[14] that only the α form crystallizes on cooling melts of the PbI_2 rich region of the PbI_2–PbSe system is consistent with the interpretation that the reference state for Ehrhardt's work is α–PbI_2. The enthalpy measurements by Linsey[7] led to a reported value of $T_{fus} = 683$ K. This value is adopted.

From a plot of Ehrhardt's enthalpy data, $\Delta_{fus} H° = 5.43\ kcal \cdot mol^{-1}$ at 685 K is obtained. Kelley[15] derived 5.57, 5.67, and 5.80 $kcal \cdot mol^{-1}$ from phase diagram information and also gives 6.01 $kcal \cdot mol^{-1}$.[16] Another analysis[17] has resulted in $\Delta_{fus} H° = 5.20\ kcal \cdot mol^{-1}$. Blanc and Petit's[11] value of 3.87 $kcal \cdot mol^{-1}$ is too low. The enthalpy data of Linsey[7] was analyzed to yield $\Delta_{fus} H° = 5.6\ kcal \cdot mol^{-1}$. $\Delta_{fus} H° = 5.6 \pm 0.2\ kcal \cdot mol^{-1}$ is adopted.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is calculated from the difference between the adopted values for $\Delta_f H°(298.15\ K)$ of the gas and crystal. Refer to $PbI_2(g)$ table.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.501	−174.817	−174.817	INFINITE
100	69.789	93.717	242.109	−14.839	−174.972	−174.562	91.182
200	75.396	144.332	181.860	−7.506	−175.096	−174.116	45.474
298.15	77.573	174.836	174.836	0.	−175.393	−173.577	30.410
300	77.613	175.316	174.838	0.144	−175.400	−173.566	30.221
400	78.856	197.846	177.901	7.978	−191.933	−172.328	22.504
500	80.391	215.574	183.723	15.925	−234.996	−163.287	17.059
600	83.713	230.498	190.305	24.116	−233.448	−149.087	12.979
683.000	87.780	241.591	195.872	31.226	--- CRYSTAL <--> LIQUID ---		
700	88.743	243.761	197.009	32.726	−236.428	−134.371	10.027
800	95.102	256.015	203.627	41.910	−234.040	−119.947	7.832
900	102.428	267.637	210.098	51.784	−230.941	−105.864	6.144
1000	110.064	278.821	216.415	62.406	−227.076	−92.166	4.814

PREVIOUS: March 1962 CURRENT: December 1973

$S°$(298.15 K) = [198.902] J·K^{-1}·mol^{-1}
T_{fus} = 683 ± 2 K

$\Delta_f H°$(298.15 K) = [−157.679] kJ·mol^{-1}
$\Delta_{fus}H°$ = 23.430 ± 0.8 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(PbI_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(PbI_2, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in the enthalpy, $H°(683\ K) - H°(298.15\ K)$, between the crystal and the liquid.

$\Delta_f H°$(l) can also be obtained from a 2nd and 3rd law analysis of emf data for the cell reaction Pb(l) + I_2(g) = PbI_2(l) as reported by Murgulescu *et al.*[1] in the form of an equation covering a range of 723 to 923 K. The enthalpy changes for the reaction are $\Delta_r H°$(298.15 K) = 57.65 ± 0.18 kcal·mol^{-1} (2nd law) and −52.74 ± 1.08 kcal·mol^{-1} (3rd law) with a drift of 5.8 ± 0.2 cal·K^{-1}·mol^{-1}. With auxiliary data $\Delta_f H°$(Pb, l, 298.15 K) = 1.025 kcal·mol^{-1}[2] and $\Delta_f H°(I_2, g, 298.15\ K)$ = 14.924 kcal mol^{-1},[2] $\Delta_f H°(PbI_2, l, 298.15\ K)$ = 41.70 kcal·mol^{-1} and −36.79 kcal·mol^{-1} from the 2nd and 3rd law calculations, respectively.

Heat Capacity and Entropy

The heat capacity is assumed to be constant at 25.95 cal·K^{-1}·mol^{-1} from 460 to 2000 K and is based on a linear least squares fit of the liquid range enthalpy measurements (683–877 K) of Linsey.[4] The enthalpy measurements of Ehrhardt[3] for the liquid range covered a smaller temperature region (687–776 K) and are considered less reliable. A least squares fit of the Ehrhardt data[3] leads to a heat capacity value of 32.5 cal·K^{-1}·mol^{-1}. A glass transition is assumed at 460 K below which the heat capacity is that of the crystal.

$S°(PbI_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

T_{vap} = 1105 K is calculated as the temperature at which the fugacity is 1 atm for the reaction PbI_2(cr) = PbI_2(g). $\Delta_{vap}H°$ = 28.34 kcal·mol^{-1} is calculated as the difference between $\Delta_f H°$ at T_{vap} for the gas and the liquid.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.571	198.902	198.902	0.	−157.679	−163.038	28.564
300	77.613	199.382	198.904	0.144	−157.686	−163.072	28.393
400	78.856	221.912	201.967	7.978	−174.219	−164.241	21.448
460.000	79.592	232.980	205.306	12.730	GLASS <--> LIQUID TRANSITION		
460.000	108.575	232.980	205.306	12.730			
500	108.575	242.033	207.887	17.073	−216.134	−157.655	16.470
600	108.575	261.829	215.278	27.930	−211.920	−146.357	12.741
683.000	108.575	275.896	221.808	36.942	--- CRYSTAL <--> LIQUID ---		
700	108.575	278.565	223.154	38.788	−212.652	−134.959	10.071
800	108.575	293.064	231.007	49.645	−208.591	−124.137	8.105
900	108.575	305.852	238.627	60.503	−204.509	−113.825	6.606
1000	108.575	317.291	245.931	71.360	−200.408	−103.969	5.431
1100	108.575	327.640	252.896	82.218	−196.290	−94.524	4.489
1200	108.575	337.087	259.524	93.075	−192.159	−85.455	3.720
1300	108.575	345.778	265.829	103.933	−188.028	−76.730	3.083
1400	108.575	353.824	271.831	114.790	−183.920	−68.323	2.549
1500	108.575	361.315	277.550	125.648	−179.855	−60.208	2.097

PREVIOUS: March 1962 CURRENT: December 1973

CRYSTAL-LIQUID

0 to 683 K crystal
above 683 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.501	−174.817	−174.817	INFINITE
100	69.789	93.717	242.109	−14.839	−174.972	−174.562	91.182
200	75.396	144.332	181.860	−7.506	−175.096	−174.116	45.474
298.15	77.573	174.836	174.836	0.	−175.393	−173.577	30.410
300	77.613	175.316	174.838	0.144	−175.400	−173.566	30.221
400	78.856	197.846	177.901	7.978	−191.933	−172.328	22.504
500	80.391	215.574	183.723	15.925	−234.996	−163.287	17.059
600	83.713	230.498	190.305	24.116	−233.448	−149.087	12.979
683.000	87.780	241.591	195.872	31.226	CRYSTAL <-> LIQUID TRANSITION		
683.000	108.575	275.896	195.872	54.656			
700	108.575	278.565	197.848	56.502	−212.652	−134.959	10.071
800	108.575	293.064	208.864	67.359	−208.591	−124.137	8.105
900	108.575	305.852	218.944	78.217	−204.509	−113.825	6.606
1000	108.575	317.291	228.217	89.074	−200.408	−103.969	5.431
1100	108.575	327.640	236.792	99.932	−196.290	−94.524	4.489
1200	108.575	337.087	244.762	110.789	−192.159	−85.455	3.720
1300	108.575	345.778	252.203	121.647	−188.028	−76.730	3.083
1400	108.575	353.824	259.178	132.504	−183.920	−68.323	2.549
1500	108.575	361.315	265.740	143.362	−179.855	−60.208	2.097

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [359.552 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1.16 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -3.18 \pm 4.2\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[100](1)
[40](1)
[160](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Pb–I = 2.79 ± 0.02 Å

Bond Angle: Br–Pb–Br = [95]°

Product of the Moments of Inertia: $I_A I_B I_C = [2.948087 \times 10^{-111}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value of $\Delta_f H°(298.15\ K) = 0.76 \pm 1.0\ kcal \cdot mol^{-1}$ is the average of results from 3rd law analyses of two sets[1,2] of sublimation data and one set[3] of vaporization data. Auxiliary data $\Delta H°(PbI_2, cr, 298.15\ K) = -41.92\ kcal \cdot mol^{-1}$ [4] and $\Delta_f H°(PbI_2, l, 298.15\ K) = -37.686\ kcal \cdot mol^{-1}$ [4] are used in the calculations. The adopted enthalpy of formation for PbI_2(g) yields an atomization energy of $\Delta_{at} H°(0\ K) = 4.29$ eV for the process $PbI_2(g) = Pb(g) + 2\ I(g)$.

Source	Reaction	Data Points	T/K	$\Delta_r H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(PbI_2, g, 298.15\ K)$ kcal·mol^{-1}
Niwa *et al.*[1]	A	7	579–650	39.77 ± 0.37	41.54 ± 0.16	2.9 ± 0.60	0.38
Duncan and Thomas[2]	A	13	563–613	39.44 ± 0.40	40.24 ± 0.09	1.4 ± 0.7	1.69
Jellinek and Rudat[3]	B	4	923–1073	35.19 ± 0.52	37.49 ± 0.32	2.3 ± 0.6	0.20

*Reactions: (A) $PbI_2(cr) = PbI_2(g)$ (B) $PbI_2(l) = PbI_2(g)$

Heat Capacity and Entropy

Molecular dimensions are those given by Sutton.[5] Vibrational frequencies are estimated by comparison with the corresponding values for HgI_2(g) and with the lead dihalide series.[4] The electronic ground state is assumed to be A_1 based on analogy with $PbCl_2$(g).[4] The principal moments of inertia are: $I_A = 67.3005 \times 10^{-39}$, $I_B = 178.3336 \times 10^{-39}$ and $I_C = 245.6341 \times 10^{-39}\ g \cdot cm^2$.

References

[1]K. Niva, M. Sato, and M. Yosiyama, J. Chem. Soc. Japan **60**, 918 (1939).

[2]J. F. Duncan and F. G. Thomas, J. Chem. Soc. **1964**, 360 (1964).

[3]K. Jellinek and A. Rudat, Z. physik. Chem. **143**, 55 (1929).

[4]JANAF Thermochemical Tables: PbI_2(cr), 12–31–73; PbI_2(l), 12–31–73; HgI_2(g), 3–31–62; PbF_2(g), 12–31–73; $PbCl_2$(g), 6–30–73; $PbBr_2$(g), 12–31–73.

[5]L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−15.736	1.161	1.161	INFINITE
100	53.807	298.094	410.195	−11.210	0.870	−19.157	10.007
200	56.934	336.667	364.806	−5.628	−1.005	−38.492	10.053
250	57.375	349.424	360.499	−2.769	−2.078	−47.741	9.975
298.15	57.615	359.552	359.552	0.	−3.180	−56.437	9.888
300	57.622	359.908	359.553	0.107	−3.224	−56.767	9.884
350	57.773	368.803	360.255	2.992	−4.504	−65.593	9.789
400	57.872	376.524	361.817	5.883	−21.814	−73.681	9.622
450	57.940	383.345	363.837	8.778	−24.349	−80.012	9.288
500	57.989	389.452	366.099	11.677	−67.031	−82.262	8.594
600	58.054	400.031	370.899	17.479	−67.872	−85.230	7.420
700	58.092	408.983	375.717	23.287	−73.654	−87.253	6.511
800	58.118	416.742	380.371	29.097	−74.639	−89.128	5.819
900	58.135	423.588	384.800	34.910	−75.602	−90.882	5.275
1000	58.148	429.714	388.990	40.724	−76.545	−92.529	4.833
1100	58.157	435.257	392.948	46.539	−77.469	−94.082	4.468
1200	58.164	440.317	396.688	52.355	−78.380	−95.552	4.159
1300	58.169	444.973	400.226	58.172	−79.290	−96.946	3.895
1400	58.174	449.284	403.578	63.989	−80.222	−98.270	3.666
1500	58.177	453.298	406.760	69.807	−81.196	−99.525	3.466
1600	58.180	457.053	409.787	75.625	−82.228	−100.714	3.288
1700	58.182	460.580	412.672	81.443	−83.331	−101.836	3.129
1800	58.184	463.906	415.427	87.261	−84.515	−102.890	2.986
1900	58.186	467.052	418.062	93.080	−85.787	−103.877	2.856
2000	58.188	470.036	420.587	98.898	−87.149	−104.794	2.737
2100	58.189	472.875	423.010	104.717	−265.820	−98.526	2.451
2200	58.190	475.582	425.338	110.536	−266.964	−90.534	2.150
2300	58.191	478.169	427.580	116.355	−268.251	−82.486	1.873
2400	58.192	480.645	429.739	122.174	−269.674	−74.379	1.619
2500	58.192	483.021	431.823	127.993	−271.222	−66.210	1.383
2600	58.193	485.303	433.837	133.813	−272.882	−57.977	1.165
2700	58.194	487.499	435.784	139.632	−274.641	−49.678	0.961
2800	58.194	489.616	437.669	145.451	−276.484	−41.313	0.771
2900	58.195	491.658	439.496	151.271	−278.395	−32.881	0.592
3000	58.195	493.631	441.267	157.090	−280.359	−24.381	0.425
3100	58.195	495.539	442.987	162.910	−282.362	−15.816	0.266
3200	58.196	497.387	444.659	168.729	−284.390	−7.185	0.117
3300	58.196	499.177	446.284	174.549	−286.430	1.509	−0.024
3400	58.196	500.915	447.865	180.368	−288.470	10.265	−0.158
3500	58.197	502.602	449.405	186.188	−290.498	19.081	−0.285
3600	58.197	504.241	450.906	192.008	−292.506	27.954	−0.406
3700	58.197	505.836	452.369	197.827	−294.484	36.884	−0.521
3800	58.197	507.388	453.796	203.647	−296.425	45.866	−0.630
3900	58.197	508.899	455.190	209.467	−298.323	54.898	−0.735
4000	58.198	510.373	456.551	215.287	−300.172	63.979	−0.835
4100	58.198	511.810	457.882	221.106	−301.969	73.105	−0.931
4200	58.198	513.212	459.182	226.926	−303.708	82.274	−1.023
4300	58.198	514.582	460.455	232.746	−305.387	91.484	−1.111
4400	58.198	515.920	461.700	238.566	−307.005	100.732	−1.196
4500	58.198	517.228	462.920	244.386	−308.559	110.017	−1.277
4600	58.198	518.507	464.114	250.205	−310.048	119.335	−1.355
4700	58.198	519.758	465.285	256.025	−311.473	128.685	−1.430
4800	58.199	520.984	466.433	261.845	−312.832	138.065	−1.502
4900	58.199	522.184	467.558	267.665	−314.127	147.472	−1.572
5000	58.199	523.359	468.662	273.485	−315.357	156.904	−1.639
5100	58.199	524.512	469.746	279.305	−316.525	166.362	−1.704
5200	58.199	525.642	470.810	285.125	−317.630	175.841	−1.766
5300	58.199	526.751	471.855	290.945	−318.675	185.340	−1.827
5400	58.199	527.838	472.882	296.764	−319.661	194.860	−1.885
5500	58.199	528.906	473.891	302.584	−320.590	204.396	−1.941
5600	58.199	529.955	474.883	308.404	−321.463	213.950	−1.996
5700	58.199	530.985	475.858	314.224	−322.284	223.518	−2.048
5800	58.199	531.997	476.817	320.044	−323.052	233.100	−2.099
5900	58.199	532.992	477.761	325.864	−323.771	242.695	−2.149
6000	58.199	533.970	478.690	331.684	−324.442	252.302	−2.196

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [320.972 \pm 4.2]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 95.09 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H(298.15\ K) = 92.47 \pm 8.4\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1A_1]$	0	[1]
$[^3B_1]$	[20000]	[3]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[350](1)
[90](1)
[350](1)

Point Group: $[C_{2v}]$ σ = [2]
Bond Distance: Si–I = [2.44] Å
Bond Angle: I–Si–I = [113]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.419819 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

An equilibrium system involving SiI_2(g) has been studied by Schafer *et al.*[1] and Wolf and Herbst.[2] They both used a flow technique in an argon atmosphere. A 2nd and 3rd law analysis of their results (reported only in equation form) is summarized below. As in the case of $SiCl_2$(g) and $SiBr_2$(g),[3] there is acceptable agreement between the 3rd law results of these two studies. Using the mean $\Delta_f H°$(298.15 K), we calculate and adopt $\Delta_f H°(SiI_2, g, 298.15\ K) = 22.1\ kcal·mol^{-1}$. This corresponds to $\Delta_{at} H° = 135.2\ kcal·mol^{-1}$ and an average bond energy of 67.6 $kcal·mol^{-1}$. In comparison, the average bond energy of SiI_4(g) is 58.6 $kcal·mol^{-1}$. This implies that the average bond energy is 15% stronger in SiI_2 than in SiI_4.

Source	Reaction	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(g, 298.15 K)* kcal·mol^{-1}
1	$SiI_4(g) = SiI_2(g) + 2I(g)$	1361–1526	98.92	101.04	1.46	23.60
2	$Si(cr) + I_2(g) = SiI_2(g)$	1300–1470	3.21	5.14	1.38	20.60
4	$SiI_4(g) + Si(cr) = 2SiI_2(g)$	1173–1373	83.90	68.09	−12.42	20.84

*Based on 3rd law $\Delta_f H°$(298.15 K) value and auxiliary data[3].

Uchimura *et al.*[4] also studied SiI_2(g). An analysis of their equilibrium data yields $\Delta_f H°(SiI_2, g, 298.15\ K) = 20.84\ kcal·mol^{-1}$ which is in good agreement with our adopted value. However, because of the large drift ($-12.42\ cal·K^{-1}·mol^{-1}$), no weight was given to this study.

Heat Capacity and Entropy

The Si–I bond distance is assumed to be the same as in SiH_2I_2.[3] The bond angle is estimated to be 113° based on the trend observed in SiF_2, $SiCl_2$, and $SiBr_2$.[3] C_{2v} symmetry is also assumed to be consistent with the other three silicon dihalides. The principal moments of inertia are: $I_A = 7.6158 \times 10^{-39}$, $I_B = 174.4841 \times 10^{-39}$, and $I_C = 182.0999 \times 10^{-39}\ g·cm^2$.

The vibrational frequencies are estimated based on trends observed in the SiX_2 and SiH_2X_2 species, where X = F, Cl, Br, and *I*.[3] As suggested by SiF_2 and $SiCl_2$, an electronic excited state is included at 20000 cm^{-1}.

References

[1]H. Schafer, H. Bruderrick, and B. Morcher, Z. anorg. allg. Chem. **352**, 122 (1967).
[2]E. Wolf and C. Herbst, Z. Chem. **7**, 34 (1967).
[3]JANAF Thermochemical Tables: Si(g), 3–31–67; I(g), 6–30–74; SiH_2F_2(g) and SiI_4(g), 6–30–76, $SiBr_4$(g), SiH_2X_2(g), X = Cl, Br, I, 12–31–76; SiF_2(g), $SiCl_2$(g), and $SiBr_2$(g), 12–31–77.
[4]K. Uchimura, T. Takuma, M. Yuizumi, and T. Kunugi, Denki Kagaku **35**, 876 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.792	95.090	95.090	INFINITE
100	43.279	266.948	367.003	−10.006	95.561	75.348	−39.358
200	51.344	299.763	325.883	−5.224	94.231	55.603	−14.522
250	53.375	311.456	321.865	−2.602	93.375	46.042	−9.620
298.15	54.624	320.972	320.972	0.	92.466	37.008	−6.484
300	54.663	321.310	320.973	0.101	92.430	36.664	−6.384
350	55.512	329.804	321.641	2.857	91.339	27.452	−4.097
400	56.096	337.257	323.137	5.648	74.217	18.952	−2.475
450	56.512	343.889	325.081	8.464	71.875	12.184	−1.414
500	56.817	349.860	327.266	11.297	29.392	9.477	−0.990
600	57.226	360.259	331.923	17.001	28.966	5.533	−0.482
700	57.478	369.100	336.618	22.737	28.486	1.665	−0.124
800	57.644	376.787	341.170	28.494	27.955	−2.131	0.139
900	57.759	383.584	345.512	34.265	27.373	−5.858	0.340
1000	57.842	389.674	349.629	40.045	26.741	−9.517	0.497
1100	57.904	395.190	353.524	45.832	26.057	−13.110	0.623
1200	57.951	400.230	357.209	51.625	25.318	−16.638	0.724
1300	57.988	404.870	360.699	57.422	24.519	−20.103	0.808
1400	58.017	409.169	364.010	63.222	23.650	−23.503	0.877
1500	58.040	413.172	367.155	69.025	22.701	−26.838	0.935
1600	58.060	416.919	370.150	74.830	21.663	−30.108	0.983
1700	58.076	420.439	373.005	80.637	−29.651	−32.862	1.010
1800	58.090	423.759	375.734	86.445	−30.663	−33.022	0.958
1900	58.102	426.900	378.345	92.255	−31.743	−33.124	0.911
2000	58.113	429.881	380.848	98.066	−32.892	−33.167	0.866
2100	58.124	432.716	383.251	103.878	−34.108	−33.151	0.825
2200	58.135	435.420	385.561	109.691	−35.385	−33.076	0.785
2300	58.147	438.005	387.785	115.505	−36.716	−32.942	0.748
2400	58.160	440.480	389.930	121.320	−38.090	−32.748	0.713
2500	58.176	442.854	392.000	127.137	−39.497	−32.497	0.679
2600	58.195	445.136	394.000	132.955	−40.925	−32.189	0.647
2700	58.218	447.333	395.935	138.776	−42.360	−31.825	0.616
2800	58.245	449.451	397.808	144.599	−43.793	−31.409	0.586
2900	58.278	451.495	399.625	150.425	−45.211	−30.942	0.557
3000	58.317	453.472	401.387	156.255	−46.604	−30.426	0.530
3100	58.363	455.385	403.098	162.089	−47.963	−29.864	0.503
3200	58.416	457.238	404.761	167.928	−49.280	−29.259	0.478
3300	58.477	459.037	406.379	173.772	−50.548	−28.614	0.453
3400	58.546	460.784	407.953	179.623	−51.762	−27.931	0.429
3500	58.624	462.482	409.487	185.482	−52.916	−27.213	0.406
3600	58.710	464.134	410.982	191.349	−438.158	−16.002	0.232
3700	58.805	465.744	412.440	197.224	−438.768	−4.267	0.060
3800	58.909	467.314	413.864	203.110	−439.311	7.484	−0.103
3900	59.022	468.846	415.254	209.006	−439.786	19.248	−0.258
4000	59.143	470.341	416.613	214.915	−440.190	31.023	−0.405
4100	59.273	471.803	417.941	220.835	−440.523	42.808	−0.545
4200	59.411	473.233	419.241	226.769	−440.785	54.600	−0.679
4300	59.557	474.633	420.513	232.718	−440.976	66.397	−0.807
4400	59.710	476.004	421.758	238.681	−441.096	78.198	−0.928
4500	59.870	477.348	422.979	244.660	−441.145	90.001	−1.045
4600	60.036	478.665	424.175	250.655	−441.124	101.804	−1.156
4700	60.208	479.958	425.348	256.667	−441.034	113.606	−1.263
4800	60.385	481.228	426.499	262.697	−440.877	125.405	−1.365
4900	60.567	482.475	427.629	268.745	−440.652	137.201	−1.463
5000	60.753	483.700	428.738	274.811	−440.363	148.990	−1.556
5100	60.943	484.905	429.827	280.896	−440.010	160.774	−1.647
5200	61.135	486.090	430.898	286.999	−439.594	172.551	−1.733
5300	61.330	487.257	431.950	293.123	−439.117	184.318	−1.817
5400	61.526	488.405	432.985	299.265	−438.581	196.076	−1.897
5500	61.723	489.536	434.003	305.428	−437.986	207.823	−1.974
5600	61.920	490.650	435.005	311.610	−437.335	219.560	−2.048
5700	62.118	491.747	435.991	317.812	−436.630	231.284	−2.119
5800	62.315	492.829	436.961	324.034	−435.873	242.995	−2.188
5900	62.511	493.896	437.917	330.275	−435.064	254.693	−2.255
6000	62.705	494.948	438.859	336.536	−434.206	266.376	−2.319

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 159.120 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 811 \pm 10\ K$

$\Delta_f H°(0\ K) = -560.65 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -561.49 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.665 \pm 0.38\ kJ \cdot mol^{-1}$
$\Delta_{sub} H°(298.15\ K) = 286.604\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Ehrlich *et al.*[1] derived $\Delta_f H°(SrI_2, cr, 298.15\ K) = -133.8 \pm 0.4\ kcal \cdot mol^{-1}$ from enthalpy of solution measurements of Sr(cr) and SrI_2(cr) in 0.1 N HI. An auxiliary HI enthalpy of solution value, $-13.22\ kcal \cdot mol^{-1}$, calculated from data in reference[2] was used in the derivation. This auxiliary value will be changed by incorporation of the accepted CODATA key value of $\Delta_f H°(I^-, aq.\ std.\ state) = -13.60\ kcal \cdot mol^{-1}$[13] in the $\Delta_f H°$(HI, aq, 298.15 K) table so that the above derived enthalpy of formation of SrI_2 (cr) will be approximately $-134.3\ kcal \cdot mol^{-1}$.

Combining $\Delta_f H°(Sr^{+2}, aq, std.\ state, 298.15\ K) = -130.45\ kcal \cdot mol^{-1}$ selected by Parker[4,5] with the CODATA value for I (aq, std. state)[3] gives $\Delta_f H°(SrI_2, aq, std.\ state, 298.15\ K) = 157.65\ kcal \cdot mol^{-1}$. Further combination with the enthalpy of solution, $23.43\ kcal \cdot mol^{-1}$ [5] gives $\Delta_f H°(SrI_2, cr, 298.15\ K) = -134.22\ kcal \cdot mol^{-1}$. This enthalpy of solution value is based solely on the work of Ehrlich *et al.*[6]

To be consistent with the selection of the enthalpies of formation of BaI_2(cr) and CaI_2(cr), we adopt $\Delta_f H°(SrI_2, cr, 298.15\ K) = -134.2 \pm 0.5\ kcal \cdot mol^{-1}$ calculated via the combination of aqueous ions.

Heat Capacity and Entropy

$C_p°$(13.9–300.9 K) has been measured by Paukov *et al.*[7] and smoothed values have been published. Starting values of entropy and enthalpy, $S°$(14 K) and $H°$(14 K) $H°$(0 K), were not given. Our T^3 extrapolation leads to $S°(8\ K) = 0.148\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(8\ K)\ H(0\ K) = 0.891\ cal \cdot K^{-1} \cdot mol^{-1}$, which, when combined with our $C_p°$ extrapolation from 14 K to 8 K and with the Paukov *et al.*[7] data, gives $S°(298.15\ K) = 38.03\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(298.15\ K) - H°(0\ K) = 4522\ cal \cdot K^{-1} \cdot mol^{-1}$. Paukov *et al.*[7] gave $37.42 \pm 0.06\ cal \cdot K^{-1} \cdot mol^{-1}$ and $4156 \pm 7\ kcal \cdot mol^{-1}$ for the entropy and enthalpy at 298.15 K. In as much as our integration of their data gives $S°(298.15\ K) - S°(14\ K) = 37.26\ cal \cdot K^{-1} \cdot mol^{-1}$ it appears unlikely that their published value for $S°(298.15\ K)$ is correct.

The low temperature heat capacity joins smoothly with a linear extrapolation from $C_p° = 18.45$ at 270 K to $C_p° = 22.0$ at the adopted T_{fus} of 811 K. The linearly extrapolated heat capacity at 298 K is 0.6% higher than the published smoothed value[7] Dworkin and Bredig[8] determined the heat capacity of the crystal near the melting point to be $22.9 \pm 5\%$. The graphically selected $C_p°(811\ K) = 22.0$ is within the experimental error and gives $H°(811\ K) - H°(298.15\ K) = 10.42\ kcal \cdot mol^{-1}$ in agreement with Dworkin and Bredig's measured value of $10.4\ kcal \cdot mol^{-1}$.[8]

Fusion Data

Emons and Loeffelholz[9] determined $\Delta_{fus} H° = 4.580\ kcal \cdot mol^{-1}$ ($\pm 5\%$) and $T_{fus} = 802$ K by high temperature cryoscopy, in good agreement with the drop calorimetry $\Delta_{fus} H° = 4.70\ kcal \cdot mol^{-1}$ ($\pm 2\%$) and $T_{fus} = 811$ K by Dworkin and Bredig.[8] Hutchison[10] found $T_{fus} = 793$ K, noting that his melting point data were only approximate.

Because drop calorimetry is a more direct measure of the enthalpy of melting, we adopt $\Delta_{fus} H° = 4.70 \pm 0.09\ kcal \cdot mol^{-1}$ at $T_{fus} = 811 \pm 10$ K.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ is derived as the difference between the enthalpies of formation of the ideal gas and the crystal state at 298.15 K.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−18.919	−560.645	−560.645	INFINITE
100	67.404	78.914	226.165	−14.725	−561.001	−559.988	292.508
200	75.019	128.568	166.164	−7.519	−561.216	−558.896	145.969
298.15	77.948	159.120	159.120	0.	−561.493	−557.702	97.707
300	78.032	159.603	159.122	0.144	−561.499	−557.678	97.100
400	80.751	182.421	162.214	8.083	−577.928	−555.790	72.579
500	83.513	200.737	168.145	16.296	−620.739	−546.142	57.055
600	86.274	216.207	174.898	24.785	−618.933	−531.390	46.262
700	88.994	229.710	181.784	33.548	−616.972	−516.953	38.575
800	91.755	241.776	188.542	42.587	−614.852	−502.807	32.830
811.000	92.048	243.031	189.272	43.598	--- CRYSTAL <--> LIQUID ---		
900	94.492	252.741	195.075	51.899	−613.204	−488.864	28.373
1000	97.236	262.839	201.353	61.486	−610.453	−475.194	24.822
1100	99.971	272.234	207.374	71.346	−615.344	−461.446	21.912
1200	102.717	281.051	213.150	81.480	−612.989	−447.557	19.482
1300	105.493	289.382	218.697	91.891	−610.380	−433.876	17.433
1400	108.240	297.301	224.031	102.578	−607.527	−420.404	15.685
1500	110.960	304.861	229.169	113.538	−604.440	−407.144	14.178

PREVIOUS: CURRENT: June 1974

$S°(298.15\ K) = [172.440]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 811 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-548.748]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 19.665 \pm 0.38\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(SrI_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(SrI_2, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(811\ K) - H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

The liquid heat capacity near the melting point, 26.3 $cal·K^{-1}·mol^{-1}$, was determined by Dworkin and Bredig[1] from drop calorimeter measurements. This value is adopted and assumed constant over a 500–2600 K range. A glass transition is assumed at 500 K below which the heat capacity is that of the crystal.

$S°(SrI_2, l, 298.15\ K)$ is calculated in a manner similar to that used for the enthalpy of formation.

Vaporization Data

The temperature at which the fugacity is 1 atm for the reaction $SrI_2(l) = SrI_2(g)$ is 2181 K, the adopted T_{vap}. Peterson and Hutchison have extrapolated Knudsen effusion cell measurements in the 1061–1308 K range to obtain a normal boiling point of 2046 K.

$\Delta_{vap} H° = 45.35\ kcal·mol^{-1}$ is the calculated difference between the enthalpies of formation of the ideal gas and the liquid at T_{vap}. Refer to the ideal gas table for details.

References

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[2] D. T. Peterson and J. F. Hutchison, J. Chem. Eng. Data **15**, 320 (1970).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	77.948	172.440	172.440	0.	−548.748	−548.928	96.170
300	78.032	172.923	172.442	0.144	−548.754	−548.929	95.577
400	80.751	195.741	175.534	8.083	−565.183	−548.373	71.610
499.990	83.513	214.055	181.464	16.295	GLASS <--> LIQUID		
499.990	110.039	214.055	181.464	16.295	TRANSITION		
500	110.039	214.057	181.465	16.296	−607.994	−540.057	56.419
600	110.039	234.120	188.620	27.300	−603.674	−526.878	45.869
700	110.039	251.082	196.362	38.304	−599.471	−514.413	38.386
800	110.039	265.776	204.141	49.308	−595.386	−502.542	32.813
811.000	110.039	267.279	204.987	50.518	--- CRYSTAL <--> LIQUID ---		
900	110.039	278.737	211.724	60.312	−592.047	−491.103	28.503
1000	110.039	290.330	219.015	71.316	−587.878	−480.111	25.078
1100	110.039	300.818	225.982	82.320	−591.626	−469.170	22.279
1200	110.039	310.393	232.623	93.323	−588.401	−458.180	19.944
1300	110.039	319.201	238.949	104.327	−585.199	−447.459	17.979
1400	110.039	327.356	244.976	115.331	−582.028	−436.982	16.304
1500	110.039	334.948	250.724	126.335	−578.898	−426.731	14.860
1600	110.039	342.049	256.212	137.339	−575.818	−416.688	13.603
1700	110.039	348.720	261.460	148.343	−709.710	−405.655	12.464
1800	110.039	355.010	266.484	159.347	−704.893	−387.909	11.257
1900	110.039	360.960	271.301	170.351	−700.151	−370.429	10.184
2000	110.039	366.604	275.926	181.355	−695.487	−353.196	9.225
2100	110.039	371.973	280.373	192.359	−690.902	−336.194	8.362
2200	110.039	377.092	284.654	203.363	−686.397	−319.410	7.584
2300	110.039	381.983	288.780	214.367	−681.969	−302.828	6.877
2400	110.039	386.666	292.762	225.370	−677.614	−286.437	6.234
2500	110.039	391.158	296.609	236.374	−673.330	−270.226	5.646
2600	110.039	395.474	300.329	247.378	−669.112	−254.185	5.107

PREVIOUS: CURRENT: June 1974

0 to 811 K crystal
above 811 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.919	−560.645	−560.645	INFINITE
100	67.404	78.914	226.165	−14.725	−561.001	−559.988	292.508
200	75.019	128.568	166.164	−7.519	−561.216	−558.896	145.969
298.15	77.948	159.120	159.120	0.	−561.493	−557.702	97.707
300	78.032	159.603	159.122	0.144	−561.499	−557.678	97.100
400	80.751	182.421	162.214	8.083	−577.928	−555.790	72.579
500	83.513	200.737	168.145	16.296	−620.739	−546.142	57.055
600	86.274	216.207	174.898	24.785	−618.933	−531.390	46.262
700	88.994	229.710	181.784	33.548	−616.972	−516.953	38.575
800	91.755	241.776	188.542	42.587	−614.852	−502.807	32.830
811.000	92.048	243.031	189.272	43.598	___ CRYSTAL <--> LIQUID ___		
811.000	110.039	267.279	189.272	63.263	TRANSITION		
900	110.039	278.737	197.563	73.057	−592.047	−491.103	28.503
1000	110.039	290.330	206.270	84.061	−587.878	−480.111	25.078
1100	110.039	300.818	214.396	95.064	−591.626	−469.170	22.279
1200	110.039	310.393	222.003	106.068	−588.401	−458.180	19.944
1300	110.039	319.201	229.145	117.072	−585.199	−447.459	17.979
1400	110.039	327.356	235.873	128.076	−582.028	−436.982	16.304
1500	110.039	334.948	242.227	139.080	−578.898	−426.731	14.860
1600	110.039	342.049	248.247	150.084	−575.818	−416.688	13.603
1700	110.039	348.720	253.963	161.088	−709.710	−405.655	12.464
1800	110.039	355.010	259.403	172.092	−704.893	−387.909	11.257
1900	110.039	360.960	264.593	183.096	−700.151	−370.429	10.184
2000	110.039	366.604	269.554	194.100	−695.487	−353.196	9.225
2100	110.039	371.973	274.304	205.104	−690.902	−336.194	8.362
2200	110.039	377.092	278.861	216.108	−686.397	−319.410	7.584
2300	110.039	381.983	283.239	227.111	−681.969	−302.828	6.877
2400	110.039	386.666	287.452	238.115	−677.614	−286.437	6.234
2500	110.039	391.158	291.511	249.119	−673.330	−270.226	5.646
2600	110.039	395.474	295.427	260.123	−669.112	−254.185	5.107

PREVIOUS: CURRENT: June 1974

298.15 K) = [339.554 ± 8.4] J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = −271.66 ± 6.3 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = −274.89 ± 6.3 kJ·mol^{-1}

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[111](1)
[31](2)
[219](1)

Ground State Quantum Weight: [1] σ = 2
Point Group: $D_{\infty h}$
Bond Distance: Sr–I = 3.03 ± 0.03 Å
Bond Angle: I–Sr–I = [180]°
Rotational Constant: B_0 = 0.007234 cm^{-1}

Enthalpy of Formation

Peterson and Hutchison[1,2] used a weight loss Knudsen effusion technique to observe vapor pressures of the liquid at 20 temperatures ranging from 1061 to 1308 K. Our 2nd and 3rd law analyses of these data give $\Delta_{vap}H°$(298.15 K) (2nd law) = 65.72 ± 1.48 kcal·mol^{-1} and $\Delta_{vap}H°$(298.15 K) (3rd law) = 65.48 ± 0.68 kcal·mol^{-1} with a drift of −0.2 ± 1.2 cal·K^{-1}·mol^{-1}. We adopt $\Delta_{vap}H°$(298.15 K) = 65.5 ± 0.7 kcal·mol^{-1} and combine this with the adopted enthalpy of formation of the liquid to obtain $\Delta_f H°$(SrI_2, g, 298.15 K) = −65.7 ± 1.5 kcal·mol^{-1}.

Heat Capacity and Entropy

The bond distance, as determined from an electron diffraction study, is taken from Akishin *et al.*[3] who also judged that the bond angle was 180° ± 10°. We have assumed a linear structure.

An analysis of the trend of the ratio of the stretching force constants, k(monohalide)/k_1(dihalide), has indicated that k(SrI)/k_1(SrI_2) = 1 is a reasonable approximation.[4] The bending force constant is taken as 0.01 times the stretching force constant. These approximations have been used by Brewer *et al.*[5] Our vibrational frequencies calculated from the force constants, using k for SrI calculated from the ground state vibrational frequency given by Rosen,[6] are in exact agreement with those calculated by Brewer *et al.*,[5] which are adopted. Other estimates of ν_1, ν_2, and ν_3 are 111, 49, and 220.[7]

We assign an uncertainty of ±2 cal·K^{-1}·mol^{-1} to the entropy to allow for error in bond angle and vibrational frequency estimates.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−16.542	−271.664	−271.664	INFINITE
100	56.065	274.673	393.256	−11.858	−271.530	−290.093	151.529
200	60.336	315.227	345.144	−5.983	−273.076	−308.088	80.464
250	61.019	328.771	340.563	−2.948	−273.971	−316.744	66.180
298.15	61.399	339.554	339.554	0.	−274.889	−324.894	56.920
300	61.410	339.934	339.555	0.114	−274.926	−325.204	56.623
350	61.653	349.420	340.304	3.191	−276.013	−333.501	49.772
400	61.814	357.664	341.970	6.278	−293.129	−341.088	44.542
450	61.926	364.951	344.126	9.371	−295.470	−346.943	40.272
500	62.007	371.480	346.541	12.470	−337.961	−348.736	36.432
600	62.113	382.796	351.669	18.676	−338.439	−350.848	30.544
700	62.177	392.376	356.817	24.891	−339.025	−352.872	26.332
800	62.220	400.681	361.793	31.111	−339.724	−354.804	23.166
900	62.248	408.011	366.529	37.334	−341.165	−356.569	20.695
1000	62.269	414.571	371.011	43.560	−341.774	−358.248	18.713
1100	62.285	420.507	375.245	49.788	−350.298	−359.500	17.071
1200	62.296	425.927	379.246	56.017	−351.848	−360.268	15.682
1300	62.305	430.914	383.031	62.247	−353.420	−360.906	14.501
1400	62.313	435.531	386.618	68.478	−355.022	−361.422	13.485
1500	62.318	439.830	390.024	74.710	−356.664	−361.822	12.600
1600	62.323	443.853	393.264	80.942	−358.356	−362.111	11.822
1700	62.327	447.631	396.352	87.174	−497.020	−361.113	11.096
1800	62.331	451.194	399.301	93.407	−496.974	−353.120	10.247
1900	62.333	454.564	402.121	99.640	−497.002	−345.128	9.488
2000	62.336	457.761	404.824	105.874	−497.108	−337.132	8.805
2100	62.338	460.803	407.418	112.108	−497.294	−329.129	8.187
2200	62.340	463.703	409.911	118.341	−497.559	−321.115	7.624
2300	62.341	466.474	412.310	124.576	−497.901	−313.088	7.110
2400	62.343	469.127	414.623	130.810	−498.316	−305.044	6.639
2500	62.344	471.672	416.854	137.044	−498.801	−296.981	6.205
2600	62.345	474.117	419.010	143.278	−499.353	−288.897	5.804
2700	62.346	476.470	421.095	149.513	−499.968	−280.792	5.432
2800	62.347	478.737	423.113	155.748	−500.646	−272.662	5.087
2900	62.347	480.925	425.069	161.982	−501.384	−264.507	4.764
3000	62.348	483.039	426.967	168.217	−502.185	−256.325	4.463
3100	62.349	485.083	428.808	174.452	−503.049	−248.116	4.181
3200	62.349	487.063	430.598	180.687	−503.979	−239.877	3.916
3300	62.350	488.981	432.338	186.922	−504.978	−231.609	3.666
3400	62.350	490.843	434.032	193.157	−506.051	−223.309	3.431
3500	62.351	492.650	435.681	199.392	−507.202	−214.976	3.208
3600	62.351	494.407	437.288	205.627	−508.436	−206.610	2.998
3700	62.352	496.115	438.855	211.862	−509.756	−198.208	2.798
3800	62.352	497.778	440.384	218.097	−511.167	−189.769	2.609
3900	62.352	499.397	441.876	224.333	−512.672	−181.292	2.428
4000	62.352	500.976	443.334	230.568	−514.275	−172.775	2.256
4100	62.353	502.516	444.759	236.803	−515.977	−164.216	2.092
4200	62.353	504.018	446.152	243.038	−517.776	−155.615	1.935
4300	62.353	505.485	447.515	249.274	−519.677	−146.970	1.785
4400	62.353	506.919	448.849	255.509	−521.678	−138.280	1.642
4500	62.354	508.320	450.155	261.744	−523.777	−129.543	1.504
4600	62.354	509.691	451.434	267.980	−525.906	−120.763	1.371
4700	62.354	511.032	452.688	274.215	−528.173	−111.931	1.244
4800	62.354	512.344	453.917	280.451	−530.523	−103.050	1.121
4900	62.354	513.630	455.123	286.686	−532.952	−94.120	1.003
5000	62.355	514.890	456.306	292.921	−535.447	−85.140	0.889
5100	62.355	516.125	457.466	299.157	−537.990	−76.110	0.780
5200	62.355	517.335	458.606	305.392	−540.611	−67.028	0.673
5300	62.355	518.523	459.725	311.628	−543.283	−57.896	0.571
5400	62.355	519.689	460.825	317.863	−546.001	−48.712	0.471
5500	62.355	520.833	461.906	324.099	−548.756	−39.477	0.375
5600	62.355	521.956	462.968	330.334	−551.542	−30.192	0.282
5700	62.355	523.060	464.013	336.570	−554.352	−20.858	0.191
5800	62.355	524.145	465.040	342.805	−557.179	−11.474	0.103
5900	62.356	525.210	466.051	349.041	−559.807	−2.064	0.018
6000	62.356	526.259	467.046	355.276	−562.618	7.413	−0.065

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = [122.591 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -266.10 \pm 12.6\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of TiI_2(cr) is calculated from the enthalpy of reaction for the process $2TiI_2(cr) = Ti(cr) + TiI_4(g)$, and the enthalpy of formation of TiI_4(cr). Vapor pressure data for this reaction were reported by Herczog and Pidgeon[1] over the temperature range 750 to 902 K. 2nd and 3rd law analyses of these data give values for $\Delta_r H°(298.15\ K)$ of 60.5 ± 0.8 and 60.85 kcal·mol^{-1}, respectively, the 3rd law drift being 0.4 ± 1.0 cal·K^{-1}·mol^{-1}. The 3rd law $\Delta_f H°(298.15\ K)$ is used to obtain the adopted value of $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

The estimated heat capacity is that reported by Kelley.[2] The value of $S°(298.15\ K)$ is estimated from that of $TiCl_2$(cr) and the difference between ionic entropy contributions of Cl^- and I^-.

Sublimation Data

The enthalpy of sublimation of TiI_2(cr) is taken as the difference in the enthalpies of formation of TiI_2(cr) and TiI_2(g) at the sublimation temperature. The sublimation temperature is taken as the point at which $\Delta_r G° = 0$ for the reaction $TiI_2(cr) = TiI_2(g)$.

References

[1] A. Herczog and L. M. Pidgeon, Can. J. Chem. **34**, 1687 (1956).
[2] K. K. Kelley, U. S. Bur. Mines Bull. 584, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	86.228	122.591	122.591	0.	−266.102	−258.854	45.350
300	86.241	123.125	122.593	0.160	−266.090	−258.810	45.063
400	86.969	148.034	125.984	8.820	−281.682	−255.901	33.417
500	87.697	167.519	132.412	17.553	−323.885	−245.418	25.639
600	88.425	183.572	139.640	26.359	−321.659	−229.934	20.018
700	89.153	197.258	146.917	35.238	−319.435	−214.822	16.030
800	89.881	209.210	153.973	44.190	−317.188	−200.030	13.061
900	90.609	219.838	160.711	53.214	−314.944	−185.521	10.767
1000	91.337	229.423	167.111	62.312	−312.770	−171.258	8.946
1100	92.065	238.162	173.179	71.482	−310.730	−157.207	7.465
1200	92.793	246.204	178.933	80.725	−312.815	−143.215	6.234
1300	93.521	253.660	184.398	90.040	−310.336	−129.182	5.191
1400	94.249	260.617	189.597	99.429	−307.893	−115.339	4.303
1500	94.977	267.145	194.551	108.890	−305.509	−101.669	3.540
1600	95.705	273.298	199.282	118.424	−303.207	−88.155	2.878
1700	96.433	279.121	203.809	128.031	−301.008	−74.782	2.298
1800	97.161	284.654	208.148	137.711	−298.933	−61.535	1.786
1900	97.889	289.927	212.315	147.463	−296.999	−48.400	1.331
2000	98.617	294.966	216.322	157.288	−309.906	−34.909	0.912

PREVIOUS: June 1964 CURRENT: December 1968

$S°(298.15\ K) = [323.673 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-17.15 \pm 33.5]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-19.66 \pm 33.5]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[7000]	[6]
[17000]	[6]
[22000]	[15]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[134](1)
[92](2)
[290](1)

Ground State Quantum Weight: [3] $\sigma = 2$
Point Group: [$D_{\infty h}$]
Bond Distance: Ti–I = [2.7] Å
Bond Angle: I–Ti–I = [180]°
Rotational Constant: B_0 = [0.009111] cm^{-1}

Enthalpy of Formation

The enthalpy of formation of TiI_2(g) is calculated from that of TiI_2(cr) and the enthalpy of vaporization. Vapor pressure data over the temperature range 750 K to 902 K have been reported by Herczog and Pidgeon.[1] 2nd and 3rd law analyses of these data give values for $\Delta_{vap}H°(298.15\ K)$ of 51.9 and 58.9 kcal·mol^{-1}, respectively. The 3rd law drift for these data is 8.3 ± 1.1 cal·K^{-1}·mol^{-1}, with one point rejected due to failure of a statistical test. The adopted value of $\Delta_f H°(298.15\ K)$ is calculated from the 3rd law enthalpy of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiCl_2$(g), $TiCl_4$(g), $TiBr_2$(g), $TiBr_4$(g) and TiI_4(g). The vibrational frequencies are estimated from a valence force field model. The force constant K is estimated as 1.0 millidynes/Å and the constant K_s/I^2 is assumed to be 0.05 millidynes/Å.

The electronic levels are assumed to be the same as $TiCl_2$(g). The levels of $TiCl_2$ are estimated by assuming they correspond to the inverted states of $NiCl_2$(g).[2] The linear configuration is adopted, since experimental evidence indicates that other transition metal dihalides are linear,[3-6].

References

[1] A. Herczog and L. M. Pidgeon, Can. J. Chem. **34**, 1687 (1956).
[2] C. W. DeKock and D. M. Gruen, J. Chem. Phys. **44**, 4387 (1966).
[3] R. A. Berg and O. Sinanoghi, J. Chem. Phys. **32**, 1082 (1960).
[4] J. T. Houghen, G. E. Leroi and T. C. James, J. Chem. Phys. **34**, 1670 (1961).
[5] G. E. Leroi, T. C. James, J. T. Hougen and W. Klemperer, J. Chem. Phys. **36**, 2879 (1962).
[6] A. Buchler, J. L. Stauffer, and W. Klemperer, J. Chem. Phys. **40**, 3471 (1964).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.514	−17.151	−17.151	INFINITE
100	51.957	261.203	375.991	−11.479	−16.726	−35.921	18.763
200	58.692	299.824	329.167	−5.869	−17.965	−54.693	14.284
250	59.887	313.062	324.667	−2.901	−18.789	−63.782	13.327
298.15	60.570	323.673	323.673	0.	−19.665	−72.369	12.679
300	60.591	324.048	323.674	0.112	−19.700	−72.696	12.658
350	61.036	333.424	324.414	3.154	−20.758	−81.449	12.156
400	61.333	341.595	326.062	6.213	−37.851	−89.495	11.687
450	61.542	348.832	328.197	9.285	−40.170	−95.811	11.121
500	61.693	355.324	330.591	12.366	−82.634	−98.070	10.245
600	61.893	366.591	335.680	18.547	−83.034	−101.120	8.803
700	62.016	376.142	340.795	24.742	−83.493	−104.099	7.768
800	62.103	384.429	345.743	30.949	−83.991	−107.009	6.987
900	62.178	391.748	350.456	37.163	−84.558	−109.853	6.376
1000	62.260	398.303	354.919	43.384	−85.260	−112.628	5.883
1100	62.365	404.242	359.137	49.615	−86.159	−115.323	5.476
1200	62.505	409.674	363.125	55.859	−91.243	−117.807	5.128
1300	62.688	414.684	366.901	62.118	−91.820	−119.998	4.822
1400	62.916	419.338	370.482	68.398	−92.486	−122.141	4.557
1500	63.188	423.688	373.886	74.703	−93.259	−124.233	4.326
1600	63.500	427.775	377.127	81.037	−94.157	−126.269	4.122
1700	63.845	431.635	380.221	87.404	−95.198	−128.245	3.940
1800	64.215	435.295	383.180	93.806	−96.400	−130.155	3.777
1900	64.603	438.777	386.015	100.247	−97.777	−131.994	3.629
2000	65.000	442.101	388.737	106.727	−114.029	−133.302	3.481
2100	65.400	445.282	391.355	113.247	−116.541	−134.204	3.338
2200	65.795	448.334	393.876	119.807	−119.076	−134.985	3.205
2300	66.182	451.267	396.308	126.406	−121.626	−135.652	3.081
2400	66.555	454.091	398.657	133.043	−124.183	−136.207	2.964
2500	66.913	456.816	400.929	139.717	−126.737	−136.655	2.855
2600	67.254	459.447	403.129	146.425	−129.278	−137.001	2.752
2700	67.576	461.991	405.263	153.167	−131.797	−137.251	2.655
2800	67.879	464.454	407.333	159.940	−134.284	−137.407	2.563
2900	68.164	466.841	409.344	166.742	−136.730	−137.475	2.476
3000	68.431	469.157	411.299	173.572	−139.127	−137.460	2.393
3100	68.681	471.405	413.202	180.428	−141.469	−137.366	2.315
3200	68.916	473.589	415.055	187.308	−143.749	−137.197	2.240
3300	69.137	475.713	416.861	194.211	−145.963	−136.958	2.168
3400	69.346	477.780	418.623	201.135	−148.107	−136.652	2.099
3500	69.543	479.793	420.342	208.079	−150.179	−136.285	2.034
3600	69.730	481.755	422.021	215.043	−152.176	−135.860	1.971
3700	69.908	483.668	423.661	222.025	−563.197	−127.591	1.801
3800	70.078	485.534	425.265	229.024	−563.808	−115.810	1.592
3900	70.242	487.357	426.834	236.040	−564.399	−104.013	1.393
4000	70.399	489.137	428.369	243.072	−564.969	−92.201	1.204
4100	70.551	490.877	429.872	250.120	−565.516	−80.375	1.024
4200	70.697	492.579	431.345	257.182	−566.042	−68.536	0.852
4300	70.839	494.244	432.789	264.259	−566.544	−56.684	0.689
4400	70.977	495.875	434.204	271.350	−567.024	−44.822	0.532
4500	71.110	497.471	435.592	278.455	−567.481	−32.948	0.382
4600	71.240	499.035	436.955	285.572	−567.916	−21.065	0.239
4700	71.365	500.569	438.292	292.702	−568.328	−9.172	0.102
4800	71.486	502.073	439.605	299.845	−568.717	2.729	−0.030
4900	71.603	503.548	440.895	306.999	−569.084	14.638	−0.156
5000	71.716	504.996	442.162	314.165	−569.428	26.554	−0.277
5100	71.825	506.417	443.408	321.343	−569.751	38.477	−0.394
5200	71.928	507.813	444.634	328.530	−570.051	50.406	−0.506
5300	72.028	509.184	445.839	335.728	−570.330	62.340	−0.614
5400	72.122	510.531	447.024	342.936	−570.586	74.280	−0.719
5500	72.212	511.855	448.191	350.152	−570.822	86.224	−0.819
5600	72.296	513.157	449.339	357.378	−571.035	98.173	−0.916
5700	72.375	514.437	450.470	364.611	−571.228	110.125	−1.009
5800	72.449	515.697	451.584	371.853	−571.400	122.080	−1.099
5900	72.517	516.936	452.681	379.101	−571.550	134.037	−1.187
6000	72.580	518.155	453.762	386.356	−571.681	145.998	−1.271

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [150.206]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-259.408]\ kJ·mol^{-1}$
$T_{fus} = [700]\ K$ $\Delta_{fus}H° = [25.104]\ kJ·mol^{-1}$

Enthalpy of Formation

Estimated from a consideration of $\Delta_f H°(ZrI_4, cr)$ and of the disproportionation data given by Rolsten.[1]

Heat Capacity and Entropy

Heat capacity estimated by comparison to the other zirconium halides and titanium halides. Entropy estimated from additive constants.

Fusion and Vaporization Data

$\Delta_{fus}H°$ was estimated. T_{fus}, T_{vap} and $\Delta_{vap}H°$ from Brewer.[2]

Reference

[1]R. F. Rolsten, "Iodide Metals and Metal Iodides," John Wiley and Sons, Inc., New York, (1961).
[2]L. Brewer, National Nuclear Energy Series, Div. IV, **19B**, paper 7, McGraw-Hill Book Co., Inc., (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	94.140	150.206	150.206	0.	−259.408	−257.975	45.196
300	94.349	150.789	150.207	0.174	−259.381	−257.966	44.916
400	95.019	178.019	153.915	9.641	−274.112	−257.141	33.579
500	95.855	199.313	160.942	19.186	−315.389	−248.966	26.009
600	96.609	216.855	168.841	28.808	−312.211	−235.980	20.544
700	97.445	231.809	176.794	38.510	−309.043	−223.526	16.680
700.000	97.445	231.809	176.794	38.510	--- CRYSTAL <--> LIQUID ---		
800	98.157	244.862	184.504	48.286	−305.897	−211.524	13.811
900	99.621	256.520	191.870	58.185	−302.735	−199.917	11.603
1000	99.830	267.022	198.869	68.153	−299.625	−188.661	9.855
1100	100.583	276.571	205.505	78.173	−296.592	−177.712	8.439
1200	101.420	285.359	211.798	88.274	−297.326	−166.815	7.261
1300	102.215	293.509	217.774	98.455	−293.868	−156.079	6.271
1400	103.010	301.113	223.458	108.717	−290.405	−145.609	5.433
1500	103.805	308.247	228.875	119.057	−286.955	−135.387	4.715

PREVIOUS: CURRENT: June 1962

S K) = [186.168] J·K^{-1}·mol^{-1}
T_{fus} = [700] K

$\Delta_f H°$(298.15 K) = [−234.239] kJ·mol^{-1}
$\Delta_{fus} H°$ = [25.104] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(ZrI_2, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(700\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid phase heat capacity is estimated. $S°(ZrI_2, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion and Vaporization Data

$\Delta_{fus}H°$ was estimated. T_{fus}, T_{vap} and $\Delta_{vap}H°$ from Brewer.[1]

Reference

[1]L. Brewer, National Nuclear Energy Series, Div. IV, **19B**, paper 7, McGraw Hill Book Co., Inc., (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	94.140	186.168	186.168	0.	−234.239	−243.529	42.665
300	94.349	186.751	186.170	0.174	−234.212	−243.586	42.412
400	95.019	213.982	189.878	9.641	−248.943	−246.357	32.171
500	95.855	235.276	196.904	19.186	−290.220	−241.779	25.258
600	96.609	252.818	204.804	28.808	−287.043	−232.389	20.231
700	97.445	267.672	212.750	38.445	−283.939	−223.526	16.680
700.000	97.445	267.672	212.750	38.445	--- CRYSTAL <--> LIQUID ---		
800	106.148	281.251	220.471	48.625	−280.389	−215.128	14.046
900	114.893	294.259	227.951	59.677	−276.075	−207.222	12.027
1000	123.595	306.815	235.213	71.602	−271.008	−199.836	10.438
1100	132.298	319.003	242.279	84.396	−265.200	−192.994	9.165
1200	141.001	330.887	249.170	98.061	−262.369	−186.492	8.118
1300	149.704	342.517	255.905	112.596	−254.559	−180.480	7.252
1400	158.448	353.931	262.500	128.004	−245.949	−175.099	6.533
1500	167.151	365.160	268.971	144.284	−236.560	−170.362	5.933
1600	175.854	376.225	275.329	161.434	−226.413	−166.275	5.428
1700	184.556	387.148	281.586	179.455	−215.529	−162.846	5.004
1800	193.259	397.943	287.751	198.345	−203.925	−160.078	4.645
1900	202.004	408.626	293.832	218.108	−191.613	−157.975	4.343
2000	210.706	419.209	299.837	238.744	−178.604	−156.538	4.088

PREVIOUS: CURRENT: June 1962

0 to 700 K crystal
above 700 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K^{-1}mol^{-1}		kJ·mol^{-1}			
0							
100							
200							
298.15	94.140	150.206	150.206	0.	−259.408	−257.975	45.196
300	94.349	150.789	150.207	0.174	−259.381	−257.966	44.916
400	95.019	178.019	153.915	9.641	−274.112	−257.141	33.579
500	95.855	199.313	160.942	19.186	−315.389	−248.966	26.009
600	96.609	216.855	168.841	28.808	−312.211	−235.980	20.544
700	97.445	231.809	176.794	38.510	−309.043	−223.526	16.680
700.000	97.445	231.809	176.794	38.510	___ CRYSTAL <--> LIQUID ___		
700.000	97.445	267.672	176.794	63.614	TRANSITION		
800	106.148	281.251	189.009	73.794	−280.389	−215.128	14.046
900	114.893	294.259	199.986	84.846	−276.075	−207.222	12.027
1000	123.595	306.815	210.044	96.770	−271.008	−199.836	10.438
1100	132.298	319.003	219.398	109.565	−265.200	−192.994	9.165
1200	141.001	330.887	228.196	123.230	−262.369	−186.492	8.118
1300	149.704	342.517	236.544	137.765	−254.559	−180.480	7.252
1400	158.448	353.931	244.522	153.173	−245.949	−175.099	6.533
1500	167.151	365.160	252.191	169.453	−236.560	−170.362	5.933
1600	175.854	376.225	259.598	186.603	−226.413	−166.275	5.428
1700	184.556	387.148	266.781	204.623	−215.529	−162.846	5.004
1800	193.259	397.943	273.768	223.514	−203.925	−160.078	4.645
1900	202.004	408.626	280.585	243.277	−191.613	−157.975	4.343
2000	210.706	419.209	287.252	263.913	−178.604	−156.538	4.088

PREVIOUS: CURRENT: June 1962

$S°(298.15\ K)$ = [344.782] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = [−63.262] $kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−66.643] $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[60](1)
[120](1)
[210](1)

Ground State Quantum Weight: [1] $\sigma = 2$

Point Group: C_{2v}

Bond Distance: Zr–I = [2.66] Å

Bond Angle: I–Zr–I = 120°

Product of the Moments of Inertia: $I_A I_B I_C = 1.072892 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

Based upon the estimated value of the $\Delta_f H°$ for the crystal and the appropriate crystal and gas functions.

Heat Capacity and Entropy

Molecular constants were all estimated by comparison to similar molecules of zirconium and titanium. The principal moments of inertia are: $I_A = 19.7106 \times 10^{-39}$, $I_B = 223.6596 \times 10^{-39}$ and $I_C = 243.3703 \times 10^{-39}\ g \cdot cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.315	−63.262	−63.262	INFINITE
100	51.686	284.507	394.767	−11.026	−62.910	−83.856	43.802
200	56.159	322.118	349.992	−5.575	−64.584	−104.206	27.216
250	56.854	334.733	345.723	−2.748	−65.600	−113.996	23.818
298.15	57.238	344.782	344.782	0.	−66.643	−123.223	21.588
300	57.249	345.136	344.783	0.106	−66.684	−123.574	21.516
350	57.495	353.981	345.481	2.975	−67.898	−132.963	19.844
400	57.656	361.670	347.035	5.854	−85.134	−141.624	18.494
450	57.769	368.468	349.046	8.740	−87.586	−148.538	17.242
500	57.850	374.558	351.298	11.630	−130.179	−151.379	15.814
600	57.956	385.116	356.081	17.421	−130.833	−155.559	13.543
700	58.020	394.055	360.883	23.220	−131.568	−159.623	11.911
800	58.062	401.806	365.525	29.024	−132.393	−163.576	10.680
900	58.091	408.646	369.944	34.832	−133.323	−167.419	9.717
1000	58.112	414.768	374.125	40.642	−134.371	−171.152	8.940
1100	58.127	420.307	378.076	46.454	−135.545	−174.774	8.299
1200	58.139	425.366	381.809	52.268	−140.566	−178.062	7.751
1300	58.148	430.020	385.341	58.082	−141.476	−181.151	7.279
1400	58.156	434.329	388.688	63.897	−142.459	−184.166	6.871
1500	58.161	438.342	391.866	69.713	−143.534	−187.108	6.516
1600	58.166	442.095	394.889	75.530	−144.721	−189.975	6.202
1700	58.170	445.622	397.771	81.346	−146.041	−192.764	5.923
1800	58.173	448.947	400.523	87.164	−147.510	−195.471	5.672
1900	58.176	452.092	403.155	92.981	−149.144	−198.092	5.446
2000	58.179	455.076	405.677	98.799	−150.953	−200.622	5.240
2100	58.181	457.915	408.097	104.617	−152.947	−203.057	5.051
2200	58.182	460.621	410.424	110.435	−176.452	−204.647	4.859
2300	58.184	463.208	412.663	116.253	−179.243	−205.866	4.675
2400	58.185	465.684	414.821	122.072	−182.079	−206.963	4.504
2500	58.187	468.059	416.903	127.890	−184.948	−207.941	4.345
2600	58.188	470.342	418.915	133.709	−187.840	−208.804	4.195
2700	58.189	472.538	420.861	139.528	−190.742	−209.555	4.054
2800	58.190	474.654	422.744	145.347	−193.643	−210.199	3.921
2900	58.190	476.696	424.570	151.166	−196.532	−210.739	3.796
3000	58.191	478.668	426.340	156.985	−199.401	−211.180	3.677
3100	58.192	480.577	428.059	162.804	−202.239	−211.526	3.564
3200	58.192	482.424	429.729	168.623	−205.040	−211.780	3.457
3300	58.193	484.215	431.353	174.442	−207.798	−211.948	3.355
3400	58.193	485.952	432.934	180.262	−210.508	−212.033	3.257
3500	58.194	487.639	434.473	186.081	−213.165	−212.039	3.165
3600	58.194	489.278	435.973	191.900	−215.767	−211.970	3.076
3700	58.194	490.873	437.435	197.720	−218.312	−211.829	2.990
3800	58.195	492.425	438.862	203.539	−220.798	−211.621	2.909
3900	58.195	493.936	440.255	209.359	−223.225	−211.347	2.831
4000	58.195	495.410	441.615	215.178	−225.592	−211.013	2.756
4100	58.196	496.847	442.945	220.998	−227.900	−210.620	2.683
4200	58.196	498.249	444.245	226.817	−230.150	−210.171	2.614
4300	58.196	499.618	445.517	232.637	−232.342	−209.669	2.547
4400	58.196	500.956	446.762	238.457	−234.478	−209.117	2.483
4500	58.196	502.264	447.981	244.276	−236.559	−208.517	2.420
4600	58.197	503.543	449.175	250.096	−238.587	−207.872	2.360
4700	58.197	504.795	450.345	255.916	−240.563	−207.182	2.303
4800	58.197	506.020	451.492	261.735	−803.426	−194.834	2.120
4900	58.197	507.220	452.617	267.555	−804.955	−182.139	1.942
5000	58.197	508.396	453.721	273.375	−806.456	−169.414	1.770
5100	58.197	509.548	454.804	279.195	−807.927	−156.658	1.605
5200	58.198	510.678	455.868	285.014	−809.369	−143.874	1.445
5300	58.198	511.787	456.913	290.834	−810.782	−131.063	1.292
5400	58.198	512.875	457.939	296.654	−812.168	−118.225	1.144
5500	58.198	513.943	458.947	302.474	−813.525	−105.362	1.001
5600	58.198	514.991	459.939	308.293	−814.855	−92.474	0.863
5700	58.198	516.021	460.914	314.113	−816.157	−79.562	0.729
5800	58.198	517.034	461.873	319.933	−817.432	−66.629	0.600
5900	58.198	518.028	462.816	325.753	−818.680	−53.673	0.475
6000	58.198	519.007	463.744	331.573	−819.901	−40.696	0.354

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = [195.393 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -124.68 \pm 8.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Barnes *et al.*[1] have measured calorimetrically the enthalpy of formation of $MoI_{2.76}$ by reacting iodine vapor with $Mo(CO)_6$ at 539 K. The products were found to consist of MoI_3, MoI_2, and Mo by chemical analysis. Assuming a difference in the enthalpies of formation of MoI_3 and MoI_2 of 1.5 $kcal \cdot mol^{-1}$, Barnes *et al.*[1] determined that the $\Delta_f H°(MoI_3, cr, 298.15\ K) = 26.2 \pm 2.0\ kcal \cdot mol^{-1}$. Brewer[2] has estimated that the difference $\Delta_f H°(MoI_3)\ \Delta_f H°(MoI_2)$ may be as large as $-5\ kcal \cdot mol^{-1}$ and reanalyzed the heat of iodination data with the result $\Delta_f H°(MoI_3, cr, 298.15\ K)/R = -15000 \pm 1000$ K which is adopted. We adopt the estimate of Brewer.[2] The assigned uncertainty ($\pm 2.0\ kcal \cdot mol^{-1}$) is determined from the product $1000 \times R$ which has been rounded to the nearest $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The values of $S°(298.15\ K)$ and $C_p°$ over the temperature range 298–1000 K are estimates reported by Brewer.[2] We treat the estimated entropy value given as $S°(298.15\ K)/R$ in a manner similar to that for the enthalpy of formation.

Phase Data

Drobot *et al.*[3] have studied the thermal decomposition of MoI_3 in evacuated sealed ampoules at various temperatures. X–ray diffraction and chemical analyses of the condensed decomposition products showed the existence of a homogeneity range in which the atomic ratio of I/Mo varied from 3.00 to 2.5. The crystal structure of MoI_3 is oP16[2] in the Pearson classification system.

Decomposition Data

T_{dcm} of 629.5 K is calculated as the decomposition temperature at which the fugacity of iodine is 1 atm for the dissociation reaction $MoI_3(cr) = MoI_2(cr) + 0.5\ I_2(g)$. Saturated vapor pressure measurements by Drobot *et al.*[3] indicate that MoI_3(cr) decomposes to a non stoichiometric triiodide phase beginning at a temperature near 363.2 K.

References

[1]D. S. Barnes, G. Pilcher, D. A. Pittam, H. A. Skinner, D. Todd, and Y. Virmani, J. Less Common Met. **36**, 177 (1974).
[2]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[3]D. V. Drobot, L. G. Mikhailova, K. A. Bol'shakov, and V. L. Sbitnev, Russ. J. Inorg. Chem. **23**, (5), 643 (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	108.889	195.393	195.393	0.	−124.683	−122.469	21.456
300	108.918	196.066	195.395	0.201	−124.677	−122.456	21.321
400	110.583	227.628	199.687	11.177	−148.615	−120.905	15.789
500	112.244	252.483	207.847	22.318	−212.317	−107.872	11.269
600	113.909	273.094	217.052	33.626	−209.257	−87.269	7.597
700	115.570	290.778	226.350	45.100	−206.107	−67.185	5.013
800	117.231	306.319	235.394	56.740	−202.857	−47.559	3.105
900	118.897	320.223	244.061	68.546	−199.502	−28.347	1.645
1000	120.558	332.836	252.317	80.519	−196.045	−9.515	0.497

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K) = [403.532 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [186.15 \pm 41.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [182.84 \pm 41.8]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
[0]	2
[3505.4]	2
[10861.0]	4
[11062.0]	4

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[110](1)
[75](1)
[200](2)
[60](2)

Point Group: $[D_{3h}]$ $\sigma = [6]$
Bond Distance: Mo–I = [2.66] Å
Bond Angle: I–Mo–I = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.237654 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value of $\Delta_f H°$ at 298.15 K is that estimated by Brewer.[1] The estimated value is consistent with the low volatility of solid molybdenum in iodine vapor reported by Schafer *et al.*[2] The estimated value given by Brewer is $\Delta_f H°(298.15\ K)/R = 22000 \pm 5000$ K. The assigned uncertainty ($\pm 10\ kcal \cdot mol^{-1}$) is determined from the product $5000 \times R$ which has been rounded to the nearest $kcal \cdot mol^{-1}$. The value of $\Delta_f H°(0\ K)$ combined with JANAF data for Mo(g) and I(g) gives $\Delta_{at} H°(0\ K) = 189 \pm 11\ kcal \cdot mol^{-1}$ and an average Mo–I bond energy of $\Delta_{at} H°(0\ K)/3 = 63 \pm 4\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The bond length and vibrational frequencies are values estimated by Brewer.[1] A planar structure has been predicted for MoI_3 by Drak and Rosenblatt.[4] The electronic contribution is taken to be the same as that for TaO, as estimated by Brewer[1] The levels are taken from the latest JANAF table[3] however, we only include four levels. The principal moments of inertia are: $I_A = I_B = 223.6596 \times 10^{-39}$, and $I_C = 447.3193 \times 10^{-39}\ g \cdot cm^2$.

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]H. Schafer, T. Grofe, and M. Trenkel, J. Solid State Chem. **8**, 14 (1973).
[3]JANAF Thermochemical Tables: Mo(g), 3–31–78; I(g), 3–30–74; TaO(g), 12–31–73.
[4]M. C. Drake and G. M. Rosenblatt, Paper 388, The Electrochemical Society, Atlanta, Georgia, (October 1977).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.071	186.152	186.152	INFINITE
100	71.920	318.351	474.458	−15.611	186.546	164.562	−85.958
200	79.674	371.309	410.943	−7.927	184.989	143.110	−37.377
250	80.859	389.229	404.871	−3.910	183.946	132.758	−27.738
298.15	81.513	403.532	403.532	0.	182.841	122.998	−21.549
300	81.532	404.036	403.533	0.151	182.796	122.627	−21.351
350	81.949	416.638	404.528	4.239	181.452	112.700	−16.820
400	82.227	427.600	406.742	8.343	156.076	103.797	−13.554
450	82.427	437.297	409.608	12.460	152.878	97.454	−11.312
500	82.585	445.990	412.819	16.585	89.474	97.166	−10.151
600	82.861	461.072	419.642	24.858	89.499	98.701	−8.593
700	83.159	473.867	426.497	33.159	89.476	100.236	−7.480
800	83.512	484.994	433.129	41.492	89.419	101.777	−6.645
900	83.914	494.853	439.450	49.863	89.338	103.326	−5.997
1000	84.342	503.716	445.441	58.275	89.236	104.886	−5.479
1100	84.772	511.775	451.110	66.731	89.106	106.457	−5.055
1200	85.183	519.169	456.478	75.229	88.936	108.041	−4.703
1300	85.562	526.002	461.566	83.767	88.709	109.642	−4.405
1400	85.906	532.356	466.399	92.340	88.402	111.264	−4.151
1500	86.214	538.294	470.996	100.947	87.992	112.910	−3.932
1600	86.492	543.867	475.378	109.582	87.455	114.588	−3.741
1700	86.745	549.118	479.563	118.244	86.768	116.304	−3.574
1800	86.980	554.083	483.566	126.931	85.912	118.065	−3.426
1900	87.205	558.792	487.402	135.640	84.871	119.879	−3.296
2000	87.425	563.270	491.085	144.371	83.636	121.753	−3.180
2100	87.644	567.541	494.625	153.125	82.201	123.693	−3.077
2200	87.865	571.624	498.032	161.900	80.565	125.706	−2.985
2300	88.090	575.534	501.318	170.698	78.730	127.798	−2.902
2400	88.318	579.288	504.489	179.519	76.702	129.974	−2.829
2500	88.550	582.898	507.553	188.362	74.486	132.239	−2.763
2600	88.784	586.376	510.519	197.229	72.078	134.596	−2.704
2700	89.018	589.731	513.391	206.119	69.455	137.050	−2.651
2800	89.250	592.972	516.175	215.032	66.574	139.605	−2.604
2900	89.479	596.108	518.878	223.969	27.483	142.318	−2.563
3000	89.702	599.146	521.503	232.928	25.922	146.305	−2.547
3100	89.917	602.090	524.055	241.909	24.427	150.343	−2.533
3200	90.122	604.948	526.539	250.911	23.008	154.427	−2.521
3300	90.316	607.725	528.957	259.933	21.675	158.555	−2.510
3400	90.498	610.424	531.314	268.973	20.433	162.721	−2.500
3500	90.666	613.049	533.612	278.032	19.287	166.924	−2.491
3600	90.819	615.606	535.854	287.106	18.239	171.157	−2.483
3700	90.957	618.096	538.043	296.195	17.293	175.418	−2.476
3800	91.081	620.523	540.182	305.297	16.447	179.703	−2.470
3900	91.188	622.890	542.272	314.411	15.701	184.009	−2.465
4000	91.280	625.200	544.317	323.534	15.055	188.333	−2.459
4100	91.357	627.455	546.317	332.666	14.506	192.672	−2.455
4200	91.418	629.658	548.275	341.805	14.052	197.023	−2.450
4300	91.466	631.809	550.193	350.949	13.689	201.384	−2.446
4400	91.499	633.912	552.072	360.098	13.414	205.752	−2.443
4500	91.519	635.969	553.914	369.249	13.224	210.126	−2.439
4600	91.527	637.980	555.719	378.401	13.116	214.503	−2.436
4700	91.522	639.949	557.491	387.554	13.085	218.881	−2.433
4800	91.507	641.876	559.229	396.705	13.128	223.260	−2.430
4900	91.481	643.762	560.935	405.855	13.241	227.637	−2.427
5000	91.446	645.610	562.610	415.001	−577.964	237.741	−2.484
5100	91.402	647.420	564.255	424.144	−579.400	254.070	−2.602
5200	91.349	649.195	565.871	433.281	−580.922	270.427	−2.716
5300	91.290	650.934	567.460	442.413	−582.532	286.814	−2.827
5400	91.223	652.640	569.022	451.539	−584.231	303.233	−2.933
5500	91.151	654.313	570.557	460.658	−586.019	319.683	−3.036
5600	91.073	655.955	572.068	469.769	−587.898	336.168	−3.136
5700	90.991	657.566	573.554	478.872	−589.866	352.686	−3.232
5800	90.904	659.148	575.016	487.967	−591.925	369.240	−3.325
5900	90.813	660.701	576.455	497.053	−594.070	385.830	−3.416
6000	90.720	662.227	577.872	506.129	−596.307	402.457	−3.504

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = [378.305 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [39.75 \pm 62.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [35.31 \pm 62.8]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[286](1)
[122](1)
[399](2)
[80](2)

Ground State Quantum Weight: [2] σ = [3]
Point Group: [C_{3v}]
Bond Distance: Si–I = [2.435] Å
Bond Angle: I–Si–I = [112]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.038908 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of $SiI_3(g)$ is based on an assumed average bond energy of 58 ± 5 $kcal \cdot mol^{-1}$.[1] This average bond energy is that of SiI (g), i.e. $\Delta_{at}H°(SiI_4, g, 0\ K)/4$. The rationale for this assumption is based on the same relationship existing for the silicon chloride and fluoride species.[1]

Heat Capacity and Entropy

The molecular structure is assumed to be identical to the SiI_3 group in $SiHI_3$.[1] From this structure we estimate the following principal moments of inertia: $I_A = I_B = 173.9077 \times 10^{-39}$, and $I_C = 343.5099 \times 10^{-39}\ g \cdot cm^2$. The vibrational frequencies are assumed to be those of the SiI_3 group in $SiHI_3(g)$.

Reference

[1]JANAF Thermochemical Tables: $SiI_4(g)$, $SiCl_3(g)$ and $SiF_3(g)$, 12–31–77; $SiHI_3(g)$, 12–31–76.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.578	39.751	39.751	INFINITE
100	58.786	303.097	442.837	−13.974	39.514	18.736	−9.787
200	71.873	348.463	385.228	−7.353	37.557	−1.315	0.343
250	75.152	364.881	379.565	−3.671	36.448	−10.907	2.279
298.15	77.191	378.305	378.305	0.	35.314	−19.925	3.491
300	77.254	378.783	378.306	0.143	35.268	−20.268	3.529
350	78.652	390.803	379.253	4.043	33.916	−29.421	4.391
400	79.619	401.373	381.370	8.001	8.548	−37.551	4.904
450	80.310	410.793	384.126	12.000	5.373	−43.123	5.006
500	80.820	419.282	387.224	16.029	−57.997	−42.643	4.455
600	81.503	434.083	393.836	24.148	−57.885	−39.583	3.446
700	81.926	446.681	400.508	32.321	−57.811	−36.539	2.727
800	82.206	457.640	406.979	40.529	−57.781	−33.503	2.188
900	82.399	467.334	413.157	48.759	−57.798	−30.467	1.768
1000	82.539	476.023	419.017	57.007	−57.864	−27.428	1.433
1100	82.643	483.895	424.563	65.266	−57.984	−24.379	1.158
1200	82.722	491.090	429.811	73.534	−58.163	−21.316	0.928
1300	82.784	497.714	434.783	81.810	−58.412	−18.236	0.733
1400	82.833	503.850	439.500	90.091	−58.744	−15.134	0.565
1500	82.873	509.567	443.983	98.376	−59.174	−12.004	0.418
1600	82.906	514.916	448.251	106.665	−59.717	−8.843	0.289
1700	82.933	519.943	452.321	114.957	−110.563	−5.196	0.160
1800	82.955	524.684	456.211	123.252	−111.140	1.018	−0.030
1900	82.975	529.170	459.934	131.548	−111.818	7.267	−0.200
2000	82.991	533.426	463.503	139.846	−112.600	13.554	−0.354
2100	83.005	537.476	466.930	148.146	−113.482	19.883	−0.495
2200	83.018	541.338	470.225	156.447	−114.456	26.256	−0.623
2300	83.028	545.028	473.398	164.750	−115.511	32.676	−0.742
2400	83.038	548.562	476.456	173.053	−116.632	39.142	−0.852
2500	83.046	551.952	479.409	181.357	−117.804	45.657	−0.954
2600	83.053	555.209	482.262	189.662	−119.008	52.219	−1.049
2700	83.060	558.344	485.022	197.968	−120.227	58.828	−1.138
2800	83.066	561.365	487.695	206.274	−121.444	65.482	−1.222
2900	83.071	564.280	490.286	214.581	−122.644	72.179	−1.300
3000	83.076	567.096	492.800	222.888	−123.811	78.917	−1.374
3100	83.080	569.820	495.241	231.196	−124.933	85.693	−1.444
3200	83.084	572.458	497.613	239.505	−125.999	92.505	−1.510
3300	83.088	575.014	499.920	247.813	−127.000	99.349	−1.573
3400	83.091	577.495	502.165	256.122	−127.928	106.222	−1.632
3500	83.094	579.904	504.352	264.431	−128.777	113.121	−1.688
3600	83.097	582.244	506.483	272.741	−513.695	130.504	−1.894
3700	83.099	584.521	508.562	281.051	−513.961	148.403	−2.095
3800	83.102	586.737	510.590	289.361	−514.140	166.307	−2.286
3900	83.104	588.896	512.570	297.671	−514.232	184.215	−2.467
4000	83.106	591.000	514.505	305.981	−514.236	202.124	−2.639
4100	83.108	593.052	516.396	314.292	−514.151	220.032	−2.803
4200	83.109	595.055	518.245	322.603	−513.979	237.937	−2.959
4300	83.111	597.010	520.054	330.914	−513.721	255.837	−3.108
4400	83.112	598.921	521.825	339.225	−513.378	273.730	−3.250
4500	83.114	600.789	523.559	347.536	−512.953	291.614	−3.385
4600	83.115	602.616	525.257	355.848	−512.448	309.488	−3.514
4700	83.116	604.403	526.922	364.160	−511.865	327.350	−3.638
4800	83.117	606.153	528.555	372.471	−511.206	345.199	−3.757
4900	83.119	607.867	530.156	380.783	−510.475	363.033	−3.870
5000	83.120	609.546	531.727	389.095	−509.673	380.851	−3.979
5100	83.121	611.192	533.269	397.407	−508.804	398.654	−4.083
5200	83.121	612.806	534.783	405.719	−507.869	416.438	−4.183
5300	83.122	614.390	536.270	414.031	−506.872	434.203	−4.279
5400	83.123	615.943	537.732	422.343	−505.815	451.950	−4.372
5500	83.124	617.469	539.167	430.656	−504.700	469.676	−4.461
5600	83.125	618.966	540.579	438.968	−503.531	487.382	−4.546
5700	83.125	620.438	541.967	447.281	−502.310	505.066	−4.628
5800	83.126	621.883	543.333	455.593	−501.038	522.728	−4.708
5900	83.126	623.304	544.676	463.906	−499.719	540.368	−4.784
6000	83.127	624.701	545.998	472.219	−498.353	557.985	−4.858

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

Titanium Iodide (TiI_3) **CRYSTAL** **M_r = 428.5935** **Titanium Iodide (TiI_3)** **I_3Ti_1(cr)**

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K)$ [192.464 ± 8.4] $J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K)$ = [−322.17 ± 20.9] $kJ \cdot mol^{-1}$

T_{sub} = [1000] K

Enthalpy of Formation

The enthalpy of formation of TiI_3(cr) is calculated from the free energy of formation at 623 K combined with the increment $\Delta_f G°(623\ K)$ $\Delta_f G°(298.15\ K)$ and the entropies, $S°(298.15\ K)$, of TiI_2(cr), TiI_3(cr) and TiI_4(g). The free energy of formation, $\Delta_f G°(623\ K)$, is estimated such that $\Delta_r G°(623\ K) = 0$ for the process $2TiI_3(cr) = TiI_2(cr) + TiI_4(g)$. This assumption is based on the observations of Hercog and Pidgeon[1] and Fast[2].

Heat Capacity and Entropy

The heat capacities of TiI_3(cr) and the value of $S°(298.15\ K)$ estimated by Kelley[3] have been adopted.

Sublimation Data

The enthalpy of sublimation of TiI_3(cr) is taken as the difference in the enthalpies of formation of TiI_3(cr) and TiI_3(g) at the sublimation temperature. The sublimation temperature is estimated as the point at which $\Delta_r G° = 0$ for the process $TiI_3(cr) = TiI_3(g)$.

References

[1]A. Herczog and L. M. Pidgeon, Can. J. Chem. **34**, 1687 (1956).

[2]J. P. Fast, Rec. Trav. Chim. **58**, 174 (1939).

[3]K. K. Kelley, U. S. Bur. Mines Bull. 584, 232 pp. 1960; U. S. Bur. Mines Bull. 592, 149 pp. (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	116.771	192.464	192.464	0.	−322.168	−318.439	55.789
300	116.784	193.186	192.466	0.216	−322.150	−318.416	55.441
400	117.512	226.883	197.056	11.931	−345.506	−316.453	41.324
500	118.240	253.183	205.746	23.718	−408.753	−303.138	31.669
600	118.968	274.805	215.507	35.579	−405.350	−282.335	24.579
700	119.696	293.199	225.324	47.512	−401.956	−262.101	19.558
800	120.424	309.229	234.832	59.518	−398.543	−242.354	15.824
900	121.152	323.455	243.903	71.597	−395.141	−223.035	12.945
1000	121.880	336.257	252.509	83.748	−391.813	−204.092	10.661
1100	122.608	347.908	260.660	95.973	−388.627	−185.476	8.808
1200	123.336	358.607	268.383	108.270	−389.573	−167.022	7.270
1300	124.064	368.508	275.708	120.640	−385.968	−148.623	5.972
1400	124.792	377.729	282.670	133.083	−382.414	−130.499	4.869
1500	125.520	386.364	289.298	145.598	−378.940	−112.627	3.922

PREVIOUS: June 1964 CURRENT: December 1968

$S°(298.15\ K) = [382.164 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-144.51 \pm 33.5]\ kJ \cdot mol^{-1}$

$\Delta\ H°(298.15\ K) = [-150.21 \pm 33.5]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[2]	4000	[2]
600	[2]	10000	[2]
1500	[2]		

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[341](1)	[383](2)
[123](1)	[74](2)

Ground State Quantum Weight: [2] $\sigma = 3$
Point Group: [C_{3v}]
Bond Distance: Ti–I = [2.7] Å
Bond Angle: I–Ti–I = [100]°
Product of the Moments of Inertia: $I_A I_B I_C = 1.322449 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(TiI_3, g, 298.15\ K)$, is estimated from the average Ti–I bond energy. The bond energy is estimated from the corresponding quantities for $TiBr_4$(g), $TiBr_3$(g) and TiI_4(g).

Heat Capacity and Entropy

The interatomic distance is estimated from those of TiI_4, $TiCl_4$ and $TiCl_3$. The pyramidal bond angle is estimated by assuming that TiI_3(g) is similar to the group V trihalides. The principal moments of inertia are: $I_A = I_B = 191.5028 \times 10^{-39}$ and $I_C = 360.6023 \times 10^{-39}\ g \cdot cm^2$. The vibrational frequencies are estimated from valence force field predictions and comparisons with group V trihalides. The electronic levels are estimated from the levels of Ti^{+3} reported by Moore.[1]

Reference

[1]C. E. Moore, U. S. Nat. Bur. Stand. Circ. 467, (1949).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.933	−144.511	−144.511	INFINITE
100	58.519	305.563	448.602	−14.304	−145.018	−165.600	86.500
200	73.632	351.232	389.367	−7.627	−147.657	−185.170	48.362
250	78.018	368.168	383.480	−3.828	−148.963	−194.397	40.617
298.15	80.800	382.164	382.164	0.	−150.206	−203.035	35.571
300	80.886	382.664	382.166	0.150	−150.254	−203.363	35.409
350	82.769	395.284	383.158	4.244	−151.664	−212.107	31.655
400	84.024	406.424	385.384	8.416	−177.058	−219.822	28.706
450	84.870	416.373	388.284	12.640	−180.242	−224.976	26.114
500	85.440	425.346	391.549	16.899	−243.611	−224.077	23.409
600	86.063	440.987	398.523	25.478	−243.488	−220.183	19.169
700	86.303	454.275	405.563	34.099	−243.407	−216.305	16.141
800	86.363	465.804	412.388	42.733	−243.366	−212.437	13.871
900	86.344	475.976	418.900	51.369	−243.407	−208.570	12.105
1000	86.297	485.071	425.070	60.001	−243.598	−204.690	10.692
1100	86.242	493.293	430.904	68.628	−244.010	−200.782	9.534
1200	86.187	500.795	436.420	77.249	−248.632	−196.705	8.562
1300	86.133	507.691	441.641	85.865	−248.780	−192.373	7.730
1400	86.083	514.073	446.590	94.476	−249.058	−188.024	7.015
1500	86.034	520.010	451.289	103.082	−249.494	−183.651	6.395
1600	85.988	525.561	455.759	111.683	−250.113	−179.242	5.852
1700	85.943	530.773	460.020	120.279	−250.943	−174.788	5.371
1800	85.900	535.684	464.088	128.871	−252.006	−170.279	4.941
1900	85.860	540.327	467.980	137.459	−253.321	−165.704	4.556
2000	85.822	544.730	471.708	146.044	−269.590	−160.599	4.194
2100	85.787	548.917	475.286	154.624	−272.195	−155.086	3.858
2200	85.754	552.907	478.724	163.201	−274.898	−149.447	3.548
2300	85.723	556.718	482.033	171.775	−277.685	−143.683	3.263
2400	85.695	560.366	485.221	180.346	−280.543	−137.795	2.999
2500	85.669	563.863	488.298	188.914	−283.455	−131.788	2.754
2600	85.644	567.223	491.269	197.479	−286.402	−125.663	2.525
2700	85.622	570.455	494.142	206.043	−289.368	−119.424	2.310
2800	85.600	573.568	496.924	214.604	−292.335	−113.076	2.109
2900	85.580	576.571	499.619	223.163	−295.286	−106.621	1.920
3000	85.561	579.472	502.232	231.720	−298.208	−100.066	1.742
3100	85.543	582.278	504.770	240.275	−301.086	−93.414	1.574
3200	85.525	584.993	507.234	248.829	−303.911	−86.669	1.415
3300	85.507	587.625	509.631	257.380	−306.673	−79.838	1.264
3400	85.490	590.177	511.962	265.930	−309.364	−72.923	1.120
3500	85.473	592.655	514.233	274.478	−311.979	−65.931	0.984
3600	85.456	595.063	516.445	283.025	−314.512	−58.865	0.854
3700	85.439	597.404	518.601	291.569	−726.060	−43.941	0.620
3800	85.422	599.682	520.705	300.112	−727.189	−25.490	0.350
3900	85.404	601.901	522.759	308.654	−728.285	−7.010	0.094
4000	85.386	604.063	524.764	317.193	−729.349	11.498	−0.150
4100	85.369	606.171	526.724	325.731	−730.378	30.032	−0.383
4200	85.350	608.228	528.641	334.267	−731.372	48.590	−0.604
4300	85.332	610.236	530.515	342.801	−732.332	67.172	−0.816
4400	85.313	612.198	532.349	351.333	−733.256	85.776	−1.018
4500	85.294	614.115	534.145	359.864	−734.146	104.400	−1.212
4600	85.275	615.989	535.904	368.392	−735.001	123.044	−1.397
4700	85.255	617.823	537.627	376.919	−735.823	141.706	−1.575
4800	85.235	619.617	539.317	385.443	−736.611	160.386	−1.745
4900	85.215	621.375	540.974	393.966	−737.367	179.081	−1.909
5000	85.195	623.096	542.599	402.486	−738.090	197.791	−2.066
5100	85.174	624.783	544.194	411.005	−738.783	216.516	−2.218
5200	85.154	626.437	545.760	419.521	−739.444	235.254	−2.363
5300	85.133	628.059	547.297	428.035	−740.075	254.004	−2.503
5400	85.112	629.650	548.808	436.548	−740.676	272.766	−2.638
5500	85.091	631.211	550.292	445.058	−741.247	291.538	−2.769
5600	85.070	632.744	551.750	453.566	−741.790	310.322	−2.895
5700	85.049	634.250	553.185	462.072	−742.304	329.114	−3.016
5800	85.028	635.729	554.595	470.576	−742.790	347.915	−3.133
5900	85.007	637.182	555.983	479.077	−743.248	366.724	−3.247
6000	84.986	638.611	557.348	487.577	−743.678	385.541	−3.356

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [204.585]\ J·K^{-1}·mol^{-1}$
$T_{sub} = [970]\ K$

$\Delta_f H°(0\ K) = [-396.545]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-397.480]\ kJ·mol^{-1}$

Enthalpy of Formation

Larsen and Leddy[1] studied the reaction Zr(cr) + 3 ZeI_4(g) = 4 ZrI_3(cr) in the temperature range 473 to 973 K and pressure range 5 to 15 atm. They present a plot of the fractional reaction, at a number of temperatures, as a function of reaction time; however, they express doubt concerning the attainment of thermodynamic equilibrium.

The Gibbs energy function change for this reaction was calculated at 100 K from 500 to 1100 K. At each temperature the equilibrium constant was assumed to be 1, and $\Delta_f H°(298.15\ K)$ accordingly calculated. These values and the enthalpy of formation of ZrI_4(g) [see ZrI_4 table] were used to compute a series of values for the enthalpy of formation of ZrI_3(cr) at 298.15 K. The following table gives representative values at four temperatures.

T/K	K_p	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
500	1	−66.0	−80.2
700	1	−90.3	−86.2
900	1	−113.5	−92.1
1100	1	−135.9	−97.7

If one assumes an initial pressure of from 5 to 10 atm. for ZrI_4 and stoichiometric amounts of reactants, then, on the basis of zirconium, the reaction must proceed to the extent of 80 to 90% for the pressure of ZrI_4 to attain a value of 1 atm. and hence an equilibrium constant of 1. The data of Larsen and Leddy indicate that the reaction proceeds to the extent of 88% at 973 K. From this it was assumed that at around 1000 K the equilibrium constant attains a value of 1 giving −95 kcal·mol^{-1} for the enthalpy of formation of ZrI_3 at 298.15 K.

Their data were subjected to a 2nd law calculation but the results are of doubtful value in view of the uncertainty in the attainment of thermodynamic equilibrium at the lower temperature. The limits of error assigned to the enthalpy of formation are ±15 kcal·mol^{-1} corresponding to a temperature spread of ±500 in the above table.

Heat Capacity and Entropy

The heat capacity was estimated in the same manner as for $ZrBr_4$(cr) [refer to the $ZrBr_4$(cr) table]. The value θ_D = 60 K and θ_E = 115 K were taken to be the same as those estimated for ZrI_4(cr). The internal contribution was obtained from the estimated ZrI_3 vibrational frequencies and the anharmonicity factor "a" was taken to be 2.5×10^{-3}. The specific heat above 300 K was obtained by graphical extrapolation.

For the above estimation, it was assumed that the crystalline lattice is made up of ZrI_3 molecules. However, Holze[2] came to the conclusion that crystalline ZrI_3 is composed of a chain lattice of $(Zr_2I_6)_n$ units. The results of an analysis for a crystalline lattice composed of Zr_2I_6 units would probably not differ significantly from that for a crystalline lattice composed of ZrI_3 units since both are approaching the classical harmonic heat capacity of 12R calories per formula weight of ZrI_3 at relatively low temperatures.

Until more quantitative information becomes available, it is felt that the above analysis gives a fair approximation to the heat capacity of ZrI_3.

Decomposition Data

As described in the "Enthalpy of Formation" section, the temperature of decomposition was assumed to be 1000 ± 500 K.

Liquid Data

It is assumed that the liquid phase is thermodynamically unstable under ordinary conditions.

Sublimation Data

The enthalpy of sublimation at 298.15 K was obtained from the difference in the enthalpies of formation of the gas and solid at 298.15 K. The sublimation point was obtained from the free energy crossover between gas and solid.

References

[1]E. M. Larsen and J. J. Leddy, J. Amer. Chem. Soc. **78**, 5983 (1956).
[2]E. Holze: see R. F. Rolsten, "Iodide Metals and Metal Iodides," John Wiley & Sons, Inc., New York, **46**, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−24.359	−396.545	−396.545	INFINITE
100	83.366	100.663	292.625	−19.196	−396.843	−396.355	207.035
200	98.328	164.189	213.936	−9.950	−397.188	−395.728	103.354
298.15	103.818	204.585	204.585	0.	−397.480	−394.947	69.193
300	103.897	205.227	204.587	0.192	−397.486	−394.931	68.764
400	105.855	235.422	208.690	10.693	−422.002	−393.180	51.344
500	106.274	259.088	216.490	21.299	−486.315	−379.800	39.677
600	106.692	278.504	225.255	31.949	−483.987	−358.717	31.229
700	106.901	294.966	234.068	42.629	−481.726	−338.018	25.223
800	107.110	309.254	242.593	53.329	−479.544	−317.638	20.740
900	107.320	321.883	250.715	64.051	−477.454	−297.526	17.268
1000	107.445	333.197	258.407	74.790	−475.474	−277.642	14.503
1100	107.529	343.442	265.679	85.539	−473.620	−257.949	12.249
1200	107.612	352.802	272.555	96.296	−475.614	−238.198	10.368
1300	107.696	361.419	279.064	107.062	−473.500	−218.500	8.779
1400	107.738	369.401	285.235	117.833	−471.470	−198.961	7.423
1500	107.780	376.836	291.097	128.609	−469.548	−179.564	6.253
1600	107.822	383.793	296.675	139.389	−467.761	−160.291	5.233
1700	107.864	390.331	301.994	150.174	−466.131	−141.124	4.336
1800	107.905	396.498	307.074	160.962	−464.679	−122.049	3.542
1900	107.947	402.333	311.936	171.755	−463.423	−103.050	2.833
2000	107.989	407.871	316.595	182.551	−462.373	−84.111	2.197

PREVIOUS: June 1962 CURRENT: June 1964

$S°(298.15\ K)$ = [397.776] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−216.860] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−221.752] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[195](1)
[88](1)
[220](2)
[65](2)

Ground State Quantum Weight: [2] σ = [3]
Point Group: [C_{3v}]
Bond Distance: Zr–I = [2.59] Å
Bond Angle: I–Zr–I = [101]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [1.155142 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

The enthalpies of formation, from the gaseous atoms, of the gaseous zirconium tetrahalides were computed from data issued in these tables. The zirconium–halide bond energy, taken as 1/4 of this enthalpy of formation, was found to be linear with internuclear separation. From gaseous titanium tri– and tetrachloride, it was found that the bond energy of the trichloride was around 7 $kcal·mol^{-1}$ greater than that for titanium tetrachloride. This amount was added to the bond energy of zirconium tetrachloride to get that of zirconium trichloride which, when used with its estimated internuclear distance, was found to lie almost exactly on the bond energy versus internuclear distance curve for the tetrahalides. The bond energy for each of the gaseous trihalides of zirconium was determined from this curve and their estimated bond distances.

For zirconium triiodide, the enthalpy of formation from the gaseous atoms was −275 $kcal·mol^{-1}$ and from the elements in their standard state, −53 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The measured internuclear distances for the triiodides of phosphorus, arsenic, and antimony were plotted as a function of the atomic weight of these elements and a smooth curve was drawn through the points. The bond distance in ZrI_3 was taken from this plot. The bond angle was assumed to be 101°. The principal moments of inertia are: $I_A = I_B$ = 185.2317 × 10^{-39} and I_C = 336.6703 × 10^{-39} $g·cm^2$.

Force constants for ZrI_3 were estimated from those of the triiodides of phosphorus and arsenic. These were used in a valence force field calculation giving ν_1 = 195, ν_2 = 88, ν_3 = 181, and ν_4 = 65 cm^{-1} for the fluorides and chlorides of P, As, and Sb, ν_1 is greater than ν_3 but there appears to be a reversal as one goes to the bromides and iodides with ν_3 becoming greater than ν_1. An empirical correlation procedure for ZrI_3 gave ν_1 = 195, ν_2 = 90, ν_3 = 220, and ν_4 = 65 cm^{-1} in which $\nu_3 > \nu_1$. Since $\nu_3 > \nu_1$ for PI_3 and AsI_3, the correlation value for ν_3 was used to represent this frequency in ZrI_3.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−20.403	−216.860	−216.860	INFINITE
100	68.161	314.735	467.501	−15.277	−217.195	−238.115	124.378
200	78.257	365.960	405.106	−7.829	−219.340	−258.234	67.444
250	79.902	383.617	399.102	−3.871	−220.539	−267.821	55.958
298.15	80.820	397.776	397.776	0.	−221.752	−276.819	48.497
300	80.847	398.276	397.778	0.150	−221.800	−277.160	48.258
350	81.436	410.786	398.764	4.208	−223.231	−286.278	42.725
400	81.826	421.688	400.963	8.290	−248.677	−294.361	38.440
450	82.097	431.342	403.812	12.388	−251.933	−299.876	34.809
500	82.292	440.002	407.006	16.498	−315.388	−299.330	31.271
600	82.549	455.031	413.795	24.741	−315.467	−296.112	25.779
700	82.706	467.768	420.619	33.005	−315.621	−292.875	21.855
800	82.808	478.819	427.218	41.281	−315.864	−289.610	18.910
900	82.878	488.577	433.504	49.565	−316.212	−286.309	16.617
1000	82.928	497.312	439.456	57.856	−316.681	−282.962	14.780
1100	82.966	505.218	445.081	66.151	−317.280	−279.563	13.275
1200	82.994	512.438	450.397	74.449	−321.733	−275.881	12.009
1300	83.016	519.082	455.428	82.749	−322.085	−272.046	10.931
1400	83.034	525.235	460.198	91.052	−322.523	−268.181	10.006
1500	83.048	530.964	464.727	99.356	−323.074	−264.281	9.203
1600	83.060	536.324	469.036	107.661	−323.761	−260.340	8.499
1700	83.069	541.360	473.143	115.968	−324.609	−256.351	7.877
1800	83.077	546.108	477.066	124.275	−325.638	−252.307	7.322
1900	83.084	550.600	480.819	132.583	−326.866	−248.201	6.824
2000	83.090	554.862	484.416	140.892	−328.305	−244.024	6.373
2100	83.095	558.916	487.868	149.201	−329.961	−239.770	5.964
2200	83.099	562.782	491.186	157.511	−353.161	−234.687	5.572
2300	83.103	566.476	494.380	165.821	−355.672	−229.245	5.206
2400	83.107	570.013	497.458	174.131	−358.251	−223.694	4.869
2500	83.109	573.405	500.428	182.442	−360.880	−218.033	4.556
2600	83.112	576.665	503.298	190.753	−363.542	−212.267	4.264
2700	83.114	579.802	506.074	199.065	−366.220	−206.397	3.993
2800	83.116	582.824	508.761	207.376	−368.897	−200.429	3.739
2900	83.118	585.741	511.366	215.688	−371.556	−194.365	3.501
3000	83.120	588.559	513.892	224.000	−374.183	−188.211	3.277
3100	83.122	591.284	516.345	232.312	−376.765	−181.969	3.066
3200	83.123	593.923	518.728	240.624	−379.291	−175.645	2.867
3300	83.124	596.481	521.046	248.937	−381.753	−169.242	2.679
3400	83.125	598.963	523.301	257.249	−384.141	−162.767	2.501
3500	83.126	601.372	525.498	265.562	−386.452	−156.222	2.331
3600	83.127	603.714	527.638	273.874	−388.679	−149.612	2.171
3700	83.128	605.992	529.725	282.187	−390.821	−142.942	2.018
3800	83.129	608.209	531.761	290.500	−392.874	−136.214	1.872
3900	83.130	610.368	533.749	298.813	−394.838	−129.434	1.734
4000	83.131	612.473	535.691	307.126	−396.714	−122.605	1.601
4100	83.131	614.525	537.589	315.439	−398.500	−115.730	1.474
4200	83.132	616.529	539.445	323.752	−400.199	−108.813	1.353
4300	83.132	618.485	541.260	332.065	−401.811	−101.856	1.237
4400	83.133	620.396	543.037	340.379	−403.339	−94.862	1.126
4500	83.133	622.264	544.777	348.692	−404.785	−87.835	1.020
4600	83.134	624.091	546.482	357.005	−406.151	−80.777	0.917
4700	83.134	625.879	548.152	365.319	−407.439	−73.689	0.819
4800	83.135	627.630	549.789	373.632	−969.589	−54.957	0.598
4900	83.135	629.344	551.396	381.946	−970.382	−35.894	0.383
5000	83.135	631.023	552.971	390.259	−971.122	−16.816	0.176
5100	83.136	632.670	554.518	398.573	−971.810	2.278	−0.023
5200	83.136	634.284	556.037	406.886	−972.448	21.384	−0.215
5300	83.136	635.868	557.528	415.200	−973.037	40.501	−0.399
5400	83.137	637.422	558.993	423.514	−973.577	59.630	−0.577
5500	83.137	638.947	560.433	431.827	−974.071	78.767	−0.748
5600	83.137	640.445	561.848	440.141	−974.518	97.915	−0.913
5700	83.137	641.917	563.240	448.455	−974.920	117.069	−1.073
5800	83.138	643.362	564.609	456.769	−975.278	136.229	−1.227
5900	83.138	644.784	565.956	465.082	−975.593	155.396	−1.376
6000	83.138	646.181	567.282	473.396	−975.865	174.568	−1.520

PREVIOUS: June 1964 (1 atm) CURRENT: June 1964 (1 bar)

$S°(298.15\ K) = [266.061 \pm 16.7]\ J·K^{-1}·mol^{-1}$
$T_{dcm} = [293]\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [-123.010 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

We adopt the $\Delta_f H°(298.15\ K)$ value estimated by Brewer.[1] This value predicts that MoI_4(cr) is unstable with respect to MoI_3(cr) at temperatures above 293 K.[1] This is consistent with the observations of Lewis *et al.*[2] who found that only the crystalline triiodide is formed by heating pure Mo metal in excess iodine in a sealed tube to 573 K. Brewer's estimated value is given as $\Delta_f H°(298.15\ K)/R = -14800 \pm 1000$ K. The assigned uncertainty ($\pm 2\ kcal·mol^{-1}$) is determined from the product $1000 \times R$ which has been rounded to the nearest $kcal·mol^{-1}$.

Heat Capacity and Entropy

The values of $C_p°$ and $S°$ at 298.15 K are estimates reported by Brewer.[1] We assume a constant $C_p°$ of 32.79 $cal·K^{-1}·mol^{-1}$ over the temperature range 298–600 K. The value of $S°(298.15\ K)/R$ reported by Brewer[1] is treated in a manner similar to that for the enthalpy of formation.

Phase Data

The preparation of MoI_4(cr) has been reported by Guichard[3] but the sample was impure. The stability range of the tetraiodide appears to be small based on the observations of Lewis *et al.*[2] who found that MoI_4 could not be formed by heating Mo in excess iodine in a sealed tube to 573 K.

Decomposition Data

Brewer[1] estimated a T_{dcm} of 293 K from free energy data for the dissociation reaction MoI_4(cr) = MoI_3(cr) + 0.5 I_2(cr). We adopt this value since T_{dcm} appears to lie outside the temperature range selected for our MoI_4(cr) phase table.

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]J. Lewis, D. J. Machin, R. S. Nyholm, P. Pauling, and P. W. Smith, Chemistry and Industry, **1960**, 259 (1960).
[3]M. Guichard, Annales de Chimie et de Physique, **23**, 498 (1901).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	137.193	266.061	266.061	0.	−123.010	−124.552	21.821
300	137.193	266.909	266.063	0.254	−123.002	−124.561	21.688
400	137.193	306.377	271.444	13.973	−155.014	−123.992	16.192
500	137.193	336.991	281.606	27.692	−240.237	−108.065	11.290
600	137.193	362.004	292.985	41.412	−236.642	−81.970	7.136

PREVIOUS: CURRENT: September 1978

$S°(298.15\ K)$ = [452.812 ± 12.6] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [129.32 ± 41.8] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [124.68 ± 41.8] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[15000]	[11]
[20000]	[9]

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[150](1)	[240](3)
[50](2)	[60](3)

Point Group: [T_d] σ = [12]
Bond Distance: Mo–I = [2.66] Å
Bond Angle: I–Mo–I = [109°28']
Product of the Moments of Inertia: $I_A I_B I_C$ = [6.286307 × 10^{-110}] $g^3·cm^6$

Enthalpy of Formation

We adopt the $\Delta_f H°(298.15\ K)$ value estimated by Brewer.[1] This estimated value is consistent with the low volatility of metallic molybdenum in iodine vapor reported by Schafer *et al.*[2] Brewer's estimated value is given as $\Delta_f H°(298.15\ K)/R$ = 15000 ± 5000 K. The assigned uncertainty (10 $kcal·mol^{-1}$) is determined from the product 5000xR which has been rounded to the nearest $kcal·mol^{-1}$. Combining the $\Delta_f H°(0\ K)$ value with JANAF data on Mo(g) and I(g), we calculate a heat of atomization $\Delta_{at} H°(0\ K)$ of 228.7 ± 11 $kcal·mol^{-1}$ and a mean bond dissociation energy $\Delta_{at} H°(0\ K)/4$=57.2 ± 2.5 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies and molecular structural data are estimates taken from Brewer.[1] The principal moments of inertia are: $I_A = I_B = I_C$ = 397.6172 × 10^{-39} $g·cm^2$. The electronic levels and degeneracies are those predicted by Brewer for MoF_4(g) from crystal field theory. The upper levels contribute 0.23 $cal·K^{-1}·mol^{-1}$ to the Gibbs energy function at 6000 K.

References

[1]L. Brewer, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication, September 29, 1978, preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria.
[2]H. Schafer, T. Grofe, and M. Trenkel, J. Solid State Chem. **8**, 14 (1973).
[3]JANAF Thermochemical Tables: Mo(g), 3–31–78, I(g), 6–30–74.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−26.344	129.320	129.320	INFINITE
100	88.395	345.225	543.185	−19.796	129.277	107.655	−56.233
200	101.392	411.558	462.319	−10.152	127.214	86.781	−22.665
250	103.615	434.446	454.532	−5.022	125.971	76.814	−16.049
298.15	104.869	452.812	452.812	0.	124.683	67.461	−11.819
300	104.906	453.461	452.814	0.194	124.631	67.106	−11.684
350	105.716	469.698	454.095	5.461	123.061	57.638	−8.602
400	106.254	483.851	456.948	10.761	89.467	49.499	−6.464
450	106.629	496.389	460.647	16.084	85.458	44.744	−5.194
500	106.901	507.639	464.794	21.422	1.186	48.034	−5.018
600	107.258	527.163	473.610	32.132	1.771	57.347	−4.993
700	107.476	543.715	482.473	42.869	2.301	66.567	−4.967
800	107.618	558.076	491.045	53.625	2.776	75.715	−4.944
900	107.716	570.758	499.212	64.392	3.196	84.807	−4.922
1000	107.786	582.111	506.944	75.167	3.555	93.855	−4.902
1100	107.838	592.386	514.252	85.948	3.843	102.870	−4.885
1200	107.878	601.771	521.159	96.734	4.045	111.863	−4.869
1300	107.909	610.407	527.697	107.524	4.142	120.843	−4.856
1400	107.935	618.405	533.894	118.316	4.110	129.820	−4.844
1500	107.957	625.853	539.779	129.110	3.925	138.805	−4.834
1600	107.977	632.821	545.379	139.907	3.560	147.808	−4.825
1700	107.998	639.367	550.717	150.706	2.992	156.840	−4.819
1800	108.022	645.541	555.815	161.507	2.200	165.911	−4.815
1900	108.051	651.382	560.693	172.310	1.169	175.033	−4.812
2000	108.088	656.925	565.367	183.117	−0.111	184.216	−4.811
2100	108.135	662.200	569.853	193.928	−1.643	193.469	−4.812
2200	108.195	667.232	574.166	204.745	−3.424	202.800	−4.815
2300	108.270	672.043	578.318	215.568	−5.445	212.219	−4.820
2400	108.363	676.653	582.320	226.399	−7.697	221.730	−4.826
2500	108.476	681.079	586.182	237.241	−10.167	231.339	−4.834
2600	108.611	685.336	589.914	248.095	−12.851	241.052	−4.843
2700	108.768	689.438	593.525	258.964	−15.763	250.872	−4.853
2800	108.950	693.396	597.022	269.850	−18.940	260.805	−4.865
2900	109.156	697.223	600.411	280.755	−58.325	270.905	−4.880
3000	109.388	700.928	603.700	291.682	−60.170	282.290	−4.915
3100	109.644	704.518	606.895	302.633	−61.931	293.735	−4.949
3200	109.924	708.004	610.000	313.611	−63.591	305.234	−4.982
3300	110.228	711.391	613.022	324.619	−65.136	316.784	−5.014
3400	110.554	714.686	615.964	335.658	−66.552	328.379	−5.045
3500	110.901	717.896	618.830	346.730	−67.830	340.014	−5.074
3600	111.267	721.025	621.626	357.838	−68.963	351.683	−5.103
3700	111.650	724.079	624.354	368.984	−69.943	363.382	−5.130
3800	112.049	727.062	627.017	380.169	−70.767	375.105	−5.156
3900	112.460	729.978	629.620	391.394	−71.431	386.847	−5.181
4000	112.882	732.830	632.165	402.661	−71.935	398.604	−5.205
4100	113.313	735.623	634.654	413.971	−72.279	410.372	−5.228
4200	113.749	738.359	637.091	425.324	−72.462	422.147	−5.250
4300	114.189	741.040	639.477	436.721	−72.486	433.924	−5.271
4400	114.630	743.671	641.816	448.162	−72.354	445.699	−5.291
4500	115.071	746.252	644.108	459.647	−72.068	457.470	−5.310
4600	115.508	748.786	646.356	471.176	−71.632	469.233	−5.328
4700	115.940	751.274	648.562	482.748	−71.048	480.985	−5.346
4800	116.365	753.720	650.727	494.364	−70.323	492.724	−5.362
4900	116.780	756.123	652.854	506.021	−69.458	504.445	−5.377
5000	117.185	758.487	654.943	517.719	−659.845	521.878	−5.452
5100	117.578	760.811	656.996	529.458	−660.396	545.519	−5.587
5200	117.957	763.098	659.014	541.234	−660.969	569.170	−5.717
5300	118.321	765.348	661.000	553.048	−661.566	592.831	−5.843
5400	118.669	767.563	662.953	564.898	−662.190	616.505	−5.964
5500	119.000	769.744	664.874	576.782	−662.843	640.190	−6.080
5600	119.314	771.891	666.766	588.697	−663.529	663.889	−6.192
5700	119.609	774.005	668.629	600.644	−664.248	687.599	−6.301
5800	119.886	776.088	670.464	612.619	−665.003	711.321	−6.406
5900	120.144	778.140	672.272	624.620	−665.794	735.058	−6.508
6000	120.383	780.161	674.053	636.647	−666.625	758.808	−6.606

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

$S°(298.15\ K) = [466.266 \pm 12.6]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-218.82 \pm 83.7]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-224.47 \pm 83.7]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν_i, cm^{-1}
[137](1)
[37](2)
[168](3)
[48](3)

Ground State Quantum Weight: [1] σ = [12]
Point Group: [T_d]
Bond Distance: Pb–I = [2.77] Å
Bond Angle: I–Pb–I = [109°28']
Product of the Moments of Inertia: $I_A I_B I_C = [8.016506 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted $\Delta_f H°(0\ K) = -52.3 \pm 20$ kcal·mol^{-1} is derived from the atomization energy for the process $PbI_4(g) = Pb(g) + 4\ I(g)$. $\Delta_{at}H°(0\ K) = 8.75$ eV is estimated from an intercomparison of the lead mono–, di–, and tetra– halides.[1] This adopted value for $PbI_4(g)$ is greater than the $\Delta_{at}H°(0\ K)$ value for PbI (g) by a factor of 2.04. The auxiliary values $\Delta f H°(Pb,g,0K) = 46.91$kcal·mol^{-1} and $\Delta_f H°(I, g, 0\ K) = 25.633$ kcal·mol^{-1} are used. $\Delta_f H°(PbI_4, g, 298.15\ K) = -53.6 \pm 20$ kcal·mol^{-1} is calculated from $\Delta_f H°(0\ K)$.

Heat Capacity and Entropy

The molecular constants and vibrational frequencies are those calculated by Aleksandrovskaya *et al.*[2] Later works[4, 5] mistakenly cite this work as observed data.

The principal moments of inertia are: $I_A = I_B = I_C = 431.1831 \times 10^{-39}$ g·cm^2.

References

[1]JANAF Thermochemical Tables: PbF(g), PbF_2(g), PbF_4(g), PbBr(g), $PbBr_2$(g), PbI(g) and PbI_2(g), 12–31l73; PbCl(g) and $PbCl_2$(g), 6–30–73; Pb(g), 3–31–62; I(g), 12–31–61.
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[4]M. Radhakrishnan, Indian J. Pure Appl. Phys. **1**, 402 (1963).
[5]S. P. Singh, Labdev, Part A **7**, 185 (1969).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−27.627	−218.820	−218.820	INFINITE
100	95.214	354.506	559.058	−20.455	−219.515	−239.084	124.885
200	104.275	424.175	475.941	−10.353	−221.802	−257.799	67.330
250	105.593	447.600	468.013	−5.103	−223.112	−266.650	55.713
298.15	106.313	466.266	466.266	0.	−224.467	−274.914	48.164
300	106.334	466.924	466.268	0.197	−224.522	−275.226	47.921
350	106.790	483.352	467.565	5.526	−226.170	−283.553	42.318
400	107.089	497.633	470.450	10.873	−259.851	−290.536	37.940
450	107.296	510.259	474.185	16.233	−263.954	−294.126	34.141
500	107.445	521.572	478.368	21.602	−348.329	−289.659	30.261
600	107.640	541.180	487.252	32.357	−347.971	−277.961	24.199
700	107.758	557.782	496.172	43.127	−352.558	−265.517	19.813
800	107.835	572.177	504.793	53.907	−352.353	−253.096	16.525
900	107.888	584.881	513.000	64.693	−352.133	−240.702	13.970
1000	107.926	596.250	520.766	75.484	−351.901	−228.333	11.927
1100	107.954	606.538	528.103	86.278	−351.662	−215.988	10.256
1200	107.975	615.932	535.037	97.075	−351.424	−203.664	8.865
1300	107.991	624.576	541.596	107.873	−351.208	−191.360	7.689
1400	108.005	632.579	547.813	118.673	−351.045	−179.070	6.681
1500	108.015	640.031	553.715	129.474	−350.963	−166.790	5.808
1600	108.024	647.002	559.330	140.276	−350.988	−154.512	5.044
1700	108.031	653.552	564.682	151.079	−351.142	−142.228	4.370
1800	108.037	659.727	569.792	161.882	−351.442	−129.931	3.770
1900	108.042	665.568	574.681	172.686	−351.899	−117.613	3.233
2000	108.047	671.110	579.365	183.491	−352.515	−105.267	2.749
2100	108.051	676.382	583.860	194.295	−530.508	−85.771	2.133
2200	108.054	681.408	588.181	205.101	−531.036	−64.582	1.533
2300	108.057	686.212	592.339	215.906	−531.762	−43.364	0.985
2400	108.059	690.810	596.347	226.712	−532.669	−22.110	0.481
2500	108.061	695.222	600.215	237.518	−533.733	−0.816	0.017
2600	108.063	699.460	603.951	248.324	−534.933	20.525	−0.412
2700	108.065	703.538	607.564	259.131	−536.242	41.913	−0.811
2800	108.067	707.468	611.062	269.937	−537.633	63.351	−1.182
2900	108.068	711.261	614.452	280.744	−539.081	84.840	−1.528
3000	108.069	714.924	617.741	291.551	−540.562	106.380	−1.852
3100	108.070	718.468	620.933	302.358	−542.051	127.969	−2.156
3200	108.071	721.899	624.035	313.165	−543.528	149.606	−2.442
3300	108.072	725.225	627.051	323.972	−544.973	171.289	−2.711
3400	108.073	728.451	629.986	334.779	−546.370	193.015	−2.965
3500	108.074	731.584	632.845	345.587	−547.703	214.782	−3.205
3600	108.075	734.628	635.630	356.394	−548.960	236.585	−3.433
3700	108.075	737.589	638.346	367.202	−550.131	258.422	−3.648
3800	108.076	740.472	640.995	378.009	−551.206	280.290	−3.853
3900	108.077	743.279	643.582	388.817	−552.178	302.184	−4.047
4000	108.077	746.015	646.109	399.625	−553.042	324.102	−4.232
4100	108.078	748.684	648.578	410.432	−553.794	346.040	−4.409
4200	108.078	751.288	650.993	421.240	−554.430	367.995	−4.577
4300	108.079	753.831	653.355	432.048	−554.950	389.964	−4.737
4400	108.079	756.316	655.667	442.856	−555.351	411.943	−4.890
4500	108.079	758.745	657.931	453.664	−555.633	433.931	−5.037
4600	108.080	761.120	660.148	464.472	−555.798	455.923	−5.177
4700	108.080	763.445	662.322	475.280	−555.847	477.917	−5.311
4800	108.080	765.720	664.452	486.088	−555.780	499.913	−5.440
4900	108.081	767.949	666.542	496.896	−555.600	521.905	−5.564
5000	108.081	770.132	668.592	507.704	−555.309	543.891	−5.682
5100	108.081	772.273	670.604	518.512	−554.911	565.872	−5.796
5200	108.081	774.371	672.579	529.320	−554.407	587.843	−5.905
5300	108.082	776.430	674.519	540.128	−553.802	609.803	−6.010
5400	108.082	778.450	676.425	550.936	−553.097	631.752	−6.111
5500	108.082	780.434	678.298	561.745	−552.298	653.686	−6.208
5600	108.082	782.381	680.140	572.553	−551.406	675.606	−6.302
5700	108.082	784.294	681.950	583.361	−550.425	697.508	−6.392
5800	108.083	786.174	683.731	594.169	−549.359	719.392	−6.479
5900	108.083	788.022	685.483	604.978	−548.211	741.257	−6.563
6000	108.083	789.838	687.207	615.786	−546.984	763.103	−6.643

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [258.153 \pm 3.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 393.65 \pm 3.0\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -189.54 \pm 16.7\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.665 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	108.035	258.153	258.153	0.	−189.535	−191.637	33.574
300	108.198	258.822	258.155	0.200	−189.574	−191.650	33.369
393.650	116.388	289.279	262.056	10.716	--- CRYSTAL <--> LIQUID ---		
400	116.943	291.146	262.503	11.457	−223.715	−190.911	24.930
500	125.687	318.180	271.003	23.589	−310.254	−174.369	18.216

PREVIOUS: CURRENT: June 1976

Enthalpy of Formation

Schafer and Heine[1] measured the enthalpies of solution of Si(cr) and SiI_4(cr) in an HF solution containing AgF. For the overall reaction $SiI_4(cr) + 4Ag(cr) = Si(cr) + 4AgI(cr)$, they reported $\Delta_r H°(298.15\ K) = -13.80 \pm 0.44\ kcal \cdot mol^{-1}$. Using auxiliary data for AgI[2] we calculate $\Delta_f H°(298.15\ K) = 45.3\ kcal \cdot mol^{-1}$ for SiI_4(cr). We adopt this value and assign an uncertainty of $\pm 4.0\ kcal \cdot mol^{-1}$ due to the overall inconsistency in the SiI_4 thermochemical data. Refer to the SiI_4(g) table for more details.

Wolf[3] studied the enthalpies of solution of SiI_4(cr) and Na_2SiO_3(cr) in caustic solution. The net reaction of interest $SiI_4(cr) + 6NaOH(cr) = Na_2SiO_3(cr) + 4NaI(cr) + 3H_2O(l)$ yielded a enthalpy of reaction of $\Delta_r H°(298.15\ K) = -191.5 \pm 1.5\ kcal \cdot mol^{-1}$ based on the appropriate combination of results from five solution studies. Using current auxiliary data,[4,5] we calculate $\Delta_f H°(298.15\ K) = -51.0\ kcal \cdot mol^{-1}$ for SiI_4(cr). This data is suspect due to uncertainties in how Wolf converted his data from Na_2SiO_3(calorimetric solution) to Na_2SiO_3(cr).

Heat Capacity and Entropy

The adopted heat capacity values are from the study of Kurosawa, *et al.*[6] The data was obtained from an adiabatic calorimeter of a type used for specific heat measurements and differential thermal analysis. Similar studies on Cr(cr) and Si(cr) would suggest uncertainties of the order of 3% near room temperature and 0 10% at 600 70 K.

There is no low temperature heat capacity data for T<298.15 K. The entropy at 298.15 K is chosen from a consideration of the sublimation and vaporization data. Refer to the SiI_4(g) table for additional information. However, the discrepancies in the various vapor pressure studies are such that a precise estimate of the entropy is not possible.

Fusion Data

Kurosawa *et al.*[6] using differential thermal analysis (DTA) techniques, determined $\Delta_{fus}H° = 4.7\ kcal \cdot mol^{-1}$, an average of eight measurements with a standard deviation of $0.08\ kcal \cdot mol^{-1}$. The same study reported T_{fus} = 120.5°C as determined from the cooling curve. McCarty *et al.*[7] reported $T_{fus} = 123.68 \pm 0.06$°C for 99.998% (mole) pure SiI_4. Other studies have listed melting points in the range 120–127°C as reported by Kurosawa *et al.*[6] The sublimation and vaporization studies of Bartsch and Wolf[8] suggest a melting point of 123.5°C and a heat of melting of $4.1 \pm 0.6\ kcal \cdot mol^{-1}$. Due to the short temperature range of measurement in each condensed phase, precise melting data is not expected. In general, the vapor pressure studies, as discussed in the SiI_4(g) table[5] show poor agreement in the vicinity of T_{fus}.

We adopt T_{fus} = 120.5°C and $\Delta_{fus}H° = 4.7\ kcal \cdot mol^{-1}$ as derived from Kurosawa *et al.*[6] We assign respective uncertainties of ±3.0 K and $0.5\ kcal \cdot mol^{-1}$ due to the variances among the various studies.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, is the difference between the $\Delta_f H°(298.15\ K)$ values for SiI_4(g) and SiI_4(cr). Three sublimation studies are summarized in the SiI_4(g) table.

References

[1]H. Schafer and H. Heine, Z. anorg. allg. Chem. **332**, 25 (1964).
[2]U. S. Nat. Bur. Stand. Tech. Note 270–4, 141 pp. (1969).
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[4]J. D. Cox, ICSU CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. **4**, 331 (1972).
[5]JANAF Thermochemical Tables: NaI(cr), 9–30–63; NaOH(cr), 12–31–70; Na_2SiO_3(cr), 9–30–67; $SiCl_4$(g), 12–31–70; SiI_4(cr), 6–30–76.
[6]T. Kurosawa, R. Hasegawa, and T. Yagihashi, Trans. Japan Inst. Metals. **6**, 229 (1965); Trans. Natl. Res. Inst. Metals. (Tokyo) **7**, 222 (1965).
[7]L. V. McCarty, L. C. Landauer, and J. M. Binkowski, J. Chem. Eng. Data **5**, 365–6 (1960).
[8]K. Bartsch and E. Wolf, Z. anorg. allg. Chem. **383**, 66 (1971).

$S°(298.15\ K) = [294.309]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 393.65 \pm 3.0\ K$

$\Delta_f H°(298.15\ K) = [-174.603]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 19.665 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(SiI_4, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of melting, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(393.65\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Kurosawa *et al.*[1] measured the heat capacity of SiI_4 from the melting point (unspecified). No data was presented but rather smoothed results were represented by an equation, linear in T. This equation is extrapolated to 700 K and to 298.15 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°(298.15\ K)$.

Vaporization Data

$T_{vap} = -576$ K is calculated as that temperature at which the fugacity is one atmosphere for the process $SiI_4(l) = SiI_4(g)$. $\Delta_{vap}H°$ is calculated as the difference between the $\Delta_f H°$ values for the ideal gas and the liquid at T_{vap}. The vaporization studies near T_{vap} are discussed in the $SiI_4(g)$ table; they yielded normal boiling points (p = 760 mm Hg) of 574.7 K and 573.7 K[3] The normal boiling point should be slightly lower than our calculated T_{vap} which corresponds to f = 760 mm Hg.

References

[1]T. Kurosawa, R. Hasegawa, and T. Yagihanshi, Trans. Japan Inst. Metals. **6**, 229 (1965); Trans. Natl. Res. Metals (Toyko) **7**, 222 (1965).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	159.800	294.309	294.309	0.	−174.603	−187.485	32.847
300	159.875	295.298	294.312	0.296	−174.546	−187.565	32.658
393.650	163.744	339.234	299.988	15.449	--- CRYSTAL <--> LIQUID ---		
400	164.004	341.856	300.632	16.490	−203.750	−191.230	24.972
500	168.134	378.897	312.703	33.097	−285.814	−180.287	18.834
600	172.264	409.916	326.389	50.117	−278.678	−159.847	13.916
700	176.393	436.781	340.282	67.549	−271.228	−140.627	10.494

PREVIOUS: June 1976 CURRENT: December 1977

0 to 393.65 K crystal
above 393.65 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	108.035	258.153	258.153	0.	−189.535	−191.637	33.574
300	108.198	258.822	258.155	0.200	−189.574	−191.650	33.369
393.650	116.388	289.279	262.056	10.716	CRYSTAL <--> LIQUID		
393.650	163.744	339.234	262.056	30.381	TRANSITION		
400	164.004	341.856	263.302	31.422	−203.750	−191.230	24.972
500	168.134	378.897	282.839	48.029	−285.814	−180.287	18.834
600	172.264	409.916	301.502	65.049	−278.678	−159.847	13.916
700	176.393	436.781	318.950	82.481	−271.228	−140.627	10.494

PREVIOUS: CURRENT: December 1977

$S°(298.15\ K) = [416.449 \pm 0.21]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -105.04 \pm 16.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -110.46 \pm 16.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
165.9(1)	404 (3)
57.4(2)	88.8(3)

Ground State Quantum Weight: [1] $\sigma = 12$

Point Group: T_d

Bond Distance: Si–I = 2.43 ± 0.02 Å

Bond Angle: I–Si–I = 109° 28'

Product of the Moments of Inertia: $I_A I_B I_C = [3.653782 \times 10^{-110}]\ g^3·cm^6$

Enthalpy of Formation

The sublimation, vaporization, and decomposition studies on SiI_4 are summarized in the following table. The vapor pressure data from the sublimation and vaporization studies are corrected for vapor non-ideality by means of the equation $\Delta G°/T = -R \ln p - Bp/T$. The Berthelot equation of state and critical constants Tc = 850 K and Pc = 42.1 atm as suggested by Lapidus *et al.*[1] are used to calculate B.

Source	Reaction	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} T/K	2nd law	Drift 3rd law	$\Delta_f H°$(g, 298.15 K) cal·K^{-1}·mol^{-1}	kcal·mol^{-1}
[2]	A	13	343–396	16.23 ± 0.32	18.82 ± 0.28	6.9 ± 0.9	−26.48
[3]	A	eqn (flow)	373–392	18.75	19.08	0.9	−26.22
[3]	A	eqn (static)	370–395	18.33	19.08	2.0	−26.22
[3]	B	eqn (static)	398–425	15.68	15.49	−0.5	−26.24
[4]	B	10	399–572	15.50 ± 0.06	15.38 ± 0.05	−0.2 ± 0.1	−26.35
[5]	B	eqn	393–573	14.82	15.27	0.9	−26.46
[6]	C	6	1313–1513	59.09 ± 1.14	59.91 ± 0.26	0.6 ± 0.8	−30.06
[7]	C	eqn	1300–1470	59.44	59.84	0.3	−29.99

Reactions: A) $SiI_4(cr) = SiI_4(g)$ B) $SiI_4(l) = SiI_4(g)$ C) $SiI_4(g) = Si(cr) + 2I_2(g)$

The 3rd law results of the sublimation and vaporization studies (reactions A and B) perhaps imply a better agreement among the studies than actually exists. For example, the vaporization studies of Andersen and Belz[4] and Uchimura *et al.*[5] agree very well near T_{vap} but diverge by up to 33% as T decreases to T_{fus}. The vapor pressure results of Bartsch and Wolf[3] cover a very small temperature range and lie 10–15% lower than those of Andersen and Belz[4] and Krichevskii *et al.*[2] In addition, the decomposition studies (reaction C) suggest a $\Delta_f H°$(g, 298.15 K) value 3.6 kcal·mol^{-1} more negative than the vapor pressure studies.

We adopt $\Delta_f H°$(g, 298.15 K) = −26.4 kcal·mol^{-1} based primarily on Andersen and Belz[4] and Krichevskii *et al.*[2] Anderson and Belz[4] are also given primary weight in our selection of $S°$(cr, 298.15 K). We assign an uncertainty of ±4 kcal·mol^{-1} to include the possibility that the decomposition studies[6,7] may be correct.

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark and Rippon,[8] who recorded the Raman spectra in the vapor phase (210°C). The spectral data were interpreted in terms of a tetrahedral structure. This structure is consistent with the electron diffraction data of Liston and Sutton[9] which suggested a tetrahedral structure with a Si–I bond distance of 2.43 ± 0.02 Å. We adopt this bond distance. The principal moments of inertia are: $I_A = I_B = I_C = 331.8289 \times 10^{-39}$ g·cm^2.

Shimanouchi, in a recent compilation of molecular vibrational frequencies,[10] suggested somewhat different values (168, 63, 405, 94 cm^{-1}), based on earlier infrared and Raman studies by Delwaulle[11] and Delwaulle and Francois.[12] Much literature has been published on the inter-relationships between force constants and vibrational frequencies. Since the majority of this work was published prior to the Clark and Rippon study,[8] it will not be further discussed or referenced. The same situation exists for temperature dependent thermochemical tabulations for SiI_4(g).

References

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[2] I. R. Krichevskii, G. F. Ivanovskii, and E. K. Safronov, Zh. Fiz. Khim **39**, 2594 (1965).

Continued on page 1463

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−24.199	−105.043	−105.043	INFINITE
100	78.597	317.592	500.874	−18.328	−105.538	−124.716	65.145
200	94.049	377.499	425.478	−9.596	−107.849	−143.032	37.356
250	98.051	398.948	418.092	−4.786	−109.144	−151.681	31.692
298.15	100.574	416.449	416.449	0.	−110.458	−159.755	27.988
300	100.653	417.071	416.451	0.186	−110.510	−160.061	27.869
350	102.399	432.726	417.683	5.265	−112.090	−168.200	25.102
400	103.613	446.484	420.441	10.417	−145.677	−175.008	22.854
450	104.485	458.741	424.028	15.621	−149.664	−178.435	20.712
500	105.129	469.784	428.060	20.862	−233.903	−173.820	18.159
600	105.996	489.035	436.665	31.422	−233.227	−161.867	14.092
700	106.534	505.418	445.346	42.050	−232.582	−150.026	11.195
800	106.889	519.668	453.765	52.723	−231.977	−138.274	9.028
900	107.136	532.273	461.801	63.425	−231.417	−126.595	7.347
1000	107.314	543.570	469.423	74.147	−230.909	−114.976	6.006
1100	107.447	553.805	476.636	84.886	−230.457	−103.405	4.910
1200	107.548	563.159	483.462	95.636	−230.071	−91.872	3.999
1300	107.627	571.770	489.928	106.395	−229.765	−80.368	3.229
1400	107.690	579.749	496.062	117.161	−229.555	−68.885	2.570
1500	107.741	587.180	501.892	127.932	−229.462	−57.412	1.999
1600	107.782	594.135	507.442	138.708	−229.506	−45.942	1.500
1700	107.817	600.670	512.736	149.488	−279.883	−34.017	1.045
1800	107.846	606.834	517.794	160.272	−280.021	−19.551	0.567
1900	107.871	612.665	522.635	171.058	−280.295	−5.074	0.139
2000	107.892	618.199	527.276	181.846	−280.707	9.422	−0.246
2100	107.910	623.464	531.732	192.636	−281.253	23.941	−0.596
2200	107.926	628.484	536.017	203.428	−281.922	38.489	−0.914
2300	107.939	633.282	540.142	214.221	−282.699	53.070	−1.205
2400	107.951	637.876	544.119	225.015	−283.564	67.687	−1.473
2500	107.962	642.283	547.958	235.811	−284.496	82.342	−1.720
2600	107.971	646.517	551.668	246.608	−285.471	97.035	−1.949
2700	107.980	650.592	555.257	257.405	−286.467	111.765	−2.162
2800	107.987	654.520	558.732	268.204	−287.460	126.533	−2.360
2900	107.994	658.309	562.101	279.003	−288.430	141.335	−2.546
3000	108.000	661.970	565.369	289.803	−289.356	156.171	−2.719
3100	108.006	665.512	568.543	300.603	−290.222	171.036	−2.882
3200	108.011	668.941	571.627	311.404	−291.014	185.928	−3.035
3300	108.015	672.265	574.627	322.205	−291.719	200.844	−3.179
3400	108.019	675.489	577.546	333.007	−292.326	215.779	−3.315
3500	108.023	678.621	580.389	343.809	−292.829	230.731	−3.443
3600	108.027	681.664	583.161	354.611	−677.373	256.156	−3.717
3700	108.030	684.624	585.863	365.414	−677.236	282.087	−3.982
3800	108.033	687.505	588.500	376.217	−676.983	308.011	−4.234
3900	108.036	690.311	591.075	387.021	−676.612	333.928	−4.472
4000	108.038	693.046	593.590	397.825	−676.124	359.833	−4.699
4100	108.041	695.714	596.048	408.628	−675.518	385.724	−4.914
4200	108.043	698.317	598.452	419.433	−674.795	411.600	−5.119
4300	108.045	700.860	600.805	430.237	−673.958	437.456	−5.314
4400	108.047	703.344	603.107	441.042	−673.008	463.292	−5.500
4500	108.049	705.772	605.361	451.846	−671.948	489.106	−5.677
4600	108.050	708.147	607.570	462.651	−670.781	514.894	−5.847
4700	108.052	710.470	609.735	473.456	−669.510	540.656	−6.009
4800	108.053	712.745	611.857	484.262	−668.139	566.391	−6.164
4900	108.055	714.973	613.939	495.067	−666.670	592.095	−6.312
5000	108.056	717.156	615.982	505.873	−665.108	617.768	−6.454
5100	108.057	719.296	617.987	516.678	−663.456	643.410	−6.590
5200	108.058	721.394	619.955	527.484	−661.718	669.018	−6.720
5300	108.059	723.453	621.888	538.290	−659.896	694.591	−6.846
5400	108.060	725.473	623.788	549.096	−657.994	720.130	−6.966
5500	108.061	727.455	625.655	559.902	−656.016	745.632	−7.081
5600	108.062	729.402	627.490	570.708	−653.964	771.099	−7.193
5700	108.063	731.315	629.295	581.514	−651.843	796.528	−7.299
5800	108.064	733.195	631.070	592.321	−649.654	821.918	−7.402
5900	108.065	735.042	632.817	603.127	−647.402	847.271	−7.501
6000	108.066	736.858	634.536	613.934	−645.088	872.585	−7.597

PREVIOUS: December 1977 (1 atm) CURRENT: December 1977 (1 bar)

$S°(298.15\ K) = 246.150 \pm 6.7\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 379\ K$
$T_{fus} = 428\ K$

$\Delta_f H°(0\ K) = -373.64 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -375.72 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 9.916 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.832 \pm 0.63\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of TiI_4(cr) was measured by Johnson *et al.*[1] based on the enthalpies of hydrolysis of $TiBr_4$(cr) and TiI_4(cr) in sulfuric acid. These data result in a enthalpy of reaction of $-57.88\ kcal \cdot mol^{-1}$ for the process $TiI_4(cr) + 2Br_2(l) = TiBr_4(cr) + 2I_2(cr)$, when recalculated with revised values of $\Delta_f H°(298.15\ K)$ for HBr(aq) and HI(aq)[2]. Combination of $\Delta_r H°(298.15\ K)$ with auxiliary JANAF data gives the adopted value of $\Delta_f H°(298.15\ K)$.

Heat Capacity and Entropy

King *et al.*[3] reported the heat capacity and enthalpy of TiI_4(cr) over the temperature range 51 to 428 K. The value of $S°(298.15\ K)$ is calculated from these data based on $S°(51\ K) = 14.62\ cal \cdot K^{-1} \cdot mol^{-1}$. The value of $H°(51\ K) - H°(0\ K)$ is calculated to be $0.356\ kcal \cdot mol^{-1}$ from a Debye Einstein extrapolation of the measured heat capacities.

Transition Data

A first order transition was observed by King *et al.*[2] at 379 K. They reported the measured value of $2.37\ kcal \cdot mol^{-1}$, noting that this uncircl value had an uncertainty of $0.15\ kcal \cdot mol^{-1}$ due to hysteresis in the transition.

Fusion Data

The melting temperature and enthalpy of fusion were reported by King *et al.*[2] The large uncertainty of $\Delta_{fus} H°$ is due to the uncertainty and close proximity of the transition at 379 K.

References

[1]W. H. Johsnon, A. A. Gilliland, and E. J. Prosen, J. Res. Nat. Bur. Stand. **63A**, 161 (1959).
[2]U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3]E. G. King, W. W. Weller, A. U. Christensen and K. K. Kelley, U. S. Bur. Mines RI 5799, (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−29.141	−373.638	−373.638	INFINITE
100	100.671	120.059	352.958	−23.290	−374.448	−373.429	195.059
200	119.349	197.192	257.466	−12.055	−374.995	−372.204	97.210
298.15	125.629	246.150	246.150	0.	−375.723	−370.687	64.943
300	125.947	246.928	246.153	0.233	−375.739	−370.655	64.537
379.000	139.608	277.904	249.613	10.722		I <- -> II	
379.000	148.114	304.068	249.613	20.639		TRANSITION	
400	148.114	312.056	252.683	23.749	−398.112	−368.316	48.097
428.000	148.114	322.077	256.899	27.896	- - - - - II <- -> LIQUID - - - - -		
500	148.114	345.106	267.986	38.560	−482.434	−352.801	36.857
600	148.114	372.111	283.158	53.372	−477.957	−327.296	28.494
700	148.114	394.942	297.538	68.183	−473.568	−302.534	22.575
800	148.114	414.720	310.977	82.994	−469.240	−278.397	18.177
900	148.114	432.166	323.492	97.806	−465.000	−254.797	14.788
1000	148.114	447.771	335.154	112.617	−460.914	−231.662	12.101
1100	148.114	461.888	346.044	127.428	−457.048	−208.926	9.921
1200	148.114	474.775	356.242	142.240	−457.397	−186.412	8.114
1300	148.114	486.631	365.822	157.051	−453.278	−163.998	6.590
1400	148.114	497.607	374.848	171.863	−449.299	−141.896	5.294
1500	148.114	507.826	383.376	186.674	−445.492	−120.072	4.181

PREVIOUS: June 1964 CURRENT: December 1968

Titanium Iodide (TiI_4) LIQUID $M_r = 555.4980$ Titanium Iodide (TiI_4) $I_4Ti_1(l)$

$S°(298.15\ K) = [311.841]\ J·K^{-1}·mol^{-1}$ $\Delta_fH°(298.15\ K) = [-348.314]\ kJ·mol^{-1}$

$T_{fus} = 428\ K$ $\Delta_{fus}H° = 19.832 \pm 0.63\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_fH°(TiI_4, l, 298.15\ K)$ is calculated from $\Delta_fH°(TiI_4, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(428\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

King *et al.* reported the enthalpy of $TiI_4(l)$ above the melting temperature. The heat capacity derived from these data is constant. $S°(TiI_4, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting temperature and enthalpy of fusion were reported by King *et al.*[1]

Vaporization Data

The boiling temperature, T_{vap}, is taken as the temperature at which the fugacity is 1 bar for the reaction $TiI_4(l) = TiI_4(g)$. The enthalpy of vaporization is calculated as the difference between $\Delta_fH°$ of the liquid and gas at the boiling temperature. The vapor pressure data are discussed in the table for $TiI_4(g)$.

Reference

[1]E. G. King, W. W. Weller, A. U. Christensen, and K. K. Kelley, U. S. Bur. Mines RI 5799, 20 pp. (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
298.15	156.482	311.841	311.841	0.	−348.314	−362.863	63.572
300	156.482	312.809	311.844	0.289	−348.273	−362.954	63.196
400	156.482	357.826	317.982	15.938	−378.515	−367.027	47.929
428.000	156.482	368.414	320.939	20.319	----- II <--> LIQUID -----		
500	156.482	392.744	329.573	31.586	−462.000	−356.185	37.210
600	156.482	421.274	342.551	47.234	−456.685	−335.523	29.210
700	156.482	445.396	355.564	62.882	−451.460	−315.744	23.561
800	156.482	466.291	368.128	78.530	−446.295	−296.709	19.373
900	156.482	484.722	380.079	94.178	−441.219	−278.316	16.153
1000	156.482	501.209	391.382	109.827	−436.295	−260.482	13.606
1100	156.482	516.123	402.055	125.475	−431.593	−243.130	11.545
1200	156.482	529.739	412.137	141.123	−431.105	−226.076	9.841
1300	156.482	542.264	421.671	156.771	−426.149	−209.193	8.405
1400	156.482	553.861	430.704	172.419	−421.333	−192.685	7.189
1500	156.482	564.657	439.279	188.067	−416.690	−176.516	6.147

PREVIOUS: June 1964 CURRENT: December 1968

0 to 379 K crystal, I
379 to 428 K crystal, II
above 428 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−29.141	−373.638	−373.638	INFINITE
100	100.671	120.059	352.958	−23.290	−374.448	−373.429	195.059
200	119.349	197.192	257.466	−12.055	−374.995	−372.204	97.210
298.15	125.629	246.150	246.150	0.	−375.723	−370.687	64.943
300	125.947	246.928	246.153	0.233	−375.739	−370.655	64.537
379.000	139.608	277.904	249.613	10.722		I <--> II	
379.000	148.114	304.068	249.613	20.639		TRANSITION	
400	148.114	312.056	252.683	23.749	−398.112	−368.316	48.097
428.000	148.114	322.077	256.899	27.896		II <--> LIQUID	
428.000	156.482	368.414	256.899	47.728		TRANSITION	
500	156.482	392.744	274.754	58.995	−462.000	−356.185	37.210
600	156.482	421.274	296.869	74.643	−456.685	−335.523	29.210
700	156.482	445.396	316.408	90.291	−451.460	−315.744	23.561
800	156.482	466.291	333.867	105.939	−446.295	−296.709	19.373
900	156.482	484.722	349.625	121.588	−441.219	−278.316	16.153
1000	156.482	501.209	363.973	137.236	−436.295	−260.482	13.606
1100	156.482	516.123	377.138	152.884	−431.593	−243.130	11.545
1200	156.482	529.739	389.296	168.532	−431.105	−226.076	9.841
1300	156.482	542.264	400.587	184.180	−426.149	−209.193	8.405
1400	156.482	553.861	411.126	199.828	−421.333	−192.685	7.189
1500	156.482	564.657	421.006	215.477	−416.690	−176.516	6.147

PREVIOUS: CURRENT: December 1968

$S°(298.15\ K) = 433.072 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -271.86 \pm 8.4\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -277.27 \pm 8.4\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[175](1)	[260](3)
[55](2)	[69](3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distance: Ti–I = [2.5] Å
Bond Angle: I–Ti–I = [109°28']
Product of the Moments of Inertia: $I_A I_B I_C = [4.332573 \times 10^{-110}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation of $TiI_4(g)$ is calculated from that of $TiI_4(l)$ and the enthalpy of vaporization of the liquid. Blocher and Campbell[1] reported vapor pressure data for $TiI_4(l)$ over the temperature range 473 to 655 K. 2nd and 3rd law analyses of these data give values for $\Delta_{vap}H°(298.15\ K)$ of 17.2 ± 0.1 and 16.98 $kcal \cdot mol^{-1}$, respectively, the 3rd law drift being $-0.4 \pm 0.2\ cal \cdot K^{-1} \cdot mol^{-1}$. The adopted value of $\Delta_f H°(298.15\ K)$ is based on the 3rd law enthalpy of vaporization.

Heat Capacity and Entropy

The interatomic distances are estimated from those of $TiBr_4(cr)$, $TiBr_4(g)$ and $TiI_4(cr)$.[2] The tetrahedral model is assumed by analogy with $TiCl_4(g)$ and $TiBr_4(g)$. The principal moments of inertia are: $I_A = I_B = I_C = 351.2222 \times 10^{-39}\ g \cdot cm^2$.

The vibrational frequencies of $TiI_4(g)$ have been estimated by Ushanova *et al.*[3] The given estimates are based on their predictions and valence force field calculations.

References

[1] J. M. Blocher, Jr. and I. E. Campbell, J. Amer. Chem. Soc. **69**, 2100 (1947).
[2] O. Hasoel and H. Kringstand, Z. Phys. Chem. **1315**, 274 (1932).
[3] N. I. Ushanova, I. N. Godnev and I. V. Orlova, Opt. Spektrosk. **5**, 567 (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−25.812	−271.860	−271.860	INFINITE
100	85.757	327.171	522.445	−19.527	−272.236	−291.928	152.488
200	100.193	392.170	442.507	−10.068	−274.558	−310.763	81.163
250	102.779	414.832	434.781	−4.987	−275.896	−319.662	66.790
298.15	104.254	433.072	433.072	0.	−277.274	−327.968	57.459
300	104.298	433.717	433.074	0.193	−277.329	−328.282	57.159
350	105.256	449.872	434.347	5.433	−278.999	−336.648	50.242
400	105.895	463.971	437.188	10.713	−312.699	−343.668	44.878
450	106.342	476.471	440.871	16.020	−316.816	−347.292	40.313
500	106.666	487.693	445.002	21.345	−401.200	−342.859	35.818
600	107.093	507.181	453.789	32.035	−400.844	−331.226	28.836
700	107.354	523.711	462.627	42.759	−400.543	−319.647	23.852
800	107.524	538.058	471.179	53.503	−400.282	−308.109	20.117
900	107.641	550.730	479.328	64.262	−400.095	−296.600	17.214
1000	107.726	562.075	487.045	75.030	−400.051	−285.104	14.892
1100	107.788	572.346	494.340	85.806	−400.221	−273.603	12.992
1200	107.836	581.727	501.237	96.587	−404.600	−261.957	11.403
1300	107.873	590.360	507.765	107.373	−404.507	−250.074	10.048
1400	107.902	598.355	513.954	118.162	−404.550	−238.194	8.887
1500	107.926	605.800	519.832	128.953	−404.764	−226.305	7.881
1600	107.945	612.766	525.425	139.747	−405.179	−214.396	6.999
1700	107.962	619.311	530.757	150.542	−405.828	−202.453	6.221
1800	107.975	625.482	535.850	161.339	−406.737	−190.465	5.527
1900	107.987	631.320	540.722	172.137	−407.927	−178.419	4.905
2000	107.996	636.860	545.392	182.936	−424.101	−165.849	4.332
2100	108.005	642.129	549.874	193.736	−426.640	−152.874	3.803
2200	108.012	647.154	554.182	204.537	−429.304	−139.776	3.319
2300	108.019	651.955	558.330	215.339	−432.077	−126.554	2.874
2400	108.024	656.552	562.327	226.141	−434.939	−113.210	2.464
2500	108.029	660.962	566.185	236.943	−437.868	−99.744	2.084
2600	108.034	665.199	569.912	247.747	−440.841	−86.160	1.731
2700	108.037	669.277	573.517	258.550	−443.835	−72.462	1.402
2800	108.041	673.206	577.008	269.354	−446.827	−58.653	1.094
2900	108.044	676.997	580.391	280.158	−449.795	−44.737	0.806
3000	108.047	680.660	583.672	290.963	−452.721	−30.719	0.535
3100	108.049	684.203	586.859	301.768	−455.587	−16.605	0.280
3200	108.052	687.633	589.954	312.573	−458.378	−2.400	0.039
3300	108.054	690.958	592.965	323.378	−461.083	11.891	−0.188
3400	108.056	694.184	595.895	334.184	−463.691	26.263	−0.403
3500	108.058	697.316	598.748	344.989	−466.194	40.711	−0.608
3600	108.059	700.361	601.529	355.795	−468.587	55.227	−0.801
3700	108.061	703.321	604.240	366.601	−879.963	77.598	−1.095
3800	108.062	706.203	606.885	377.407	−880.890	103.491	−1.423
3900	108.063	709.010	609.468	388.213	−881.752	129.407	−1.733
4000	108.065	711.746	611.991	399.020	−882.550	155.344	−2.029
4100	108.066	714.414	614.457	409.826	−883.283	181.301	−2.310
4200	108.067	717.019	616.868	420.633	−883.949	207.274	−2.578
4300	108.068	719.561	619.227	431.440	−884.549	233.263	−2.834
4400	108.069	722.046	621.535	442.247	−885.085	259.265	−3.078
4500	108.069	724.475	623.796	453.053	−885.557	285.278	−3.311
4600	108.070	726.850	626.011	463.860	−885.965	311.301	−3.535
4700	108.071	729.174	628.181	474.667	−886.312	337.333	−3.749
4800	108.072	731.449	630.309	485.475	−886.599	363.372	−3.954
4900	108.072	733.678	632.396	496.282	−886.827	389.415	−4.151
5000	108.073	735.861	634.443	507.089	−886.997	415.462	−4.340
5100	108.073	738.001	636.453	517.896	−887.112	441.513	−4.522
5200	108.074	740.100	638.426	528.704	−887.172	467.565	−4.697
5300	108.074	742.158	640.364	539.511	−887.178	493.617	−4.865
5400	108.075	744.178	642.268	550.319	−887.133	519.670	−5.027
5500	108.075	746.162	644.139	561.126	−887.037	545.721	−5.183
5600	108.076	748.109	645.978	571.934	−886.892	571.770	−5.333
5700	108.076	750.022	647.786	582.741	−886.698	597.816	−5.478
5800	108.077	751.901	649.565	593.549	−886.457	623.858	−5.618
5900	108.077	753.749	651.316	604.356	−886.170	649.896	−5.754
6000	108.077	755.565	653.038	615.164	−885.838	675.928	−5.884

PREVIOUS: December 1968 (1 atm) CURRENT: December 1968 (1 bar)

$S°(298.15\ K) = [260.270 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 772 \pm 2\ K$
$T_{sub} = 705.6\ K$

$\Delta_f H°(0\ K) = [-487.24 \pm 8.4]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -488.69 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = Unknown$
$\Delta_{sub} H°(298.15\ K) = 126.357 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Turnbull[1] measured the enthalpies of reaction for the dissolution of the zirconium tetrahalides in caustic and in water. The reported enthalpies of reaction and the corresponding reactions may be combined to yield the following:

$$ZrI_4(cr) + 4\ NaCl(aq) = ZrCl_4(cr) + 4\ NaI(aq),\ \Delta_r H°(298.15\ K) = -12.50\ kcal \cdot mol^{-1}$$
$$ZrI_4(cr) + 4\ Cl\ (aq) = ZrCl_4(cr) + 4\ I\ (aq),\ \Delta_r H°(298.15\ K) = -11.97\ kcal \cdot mol^{-1}$$

Using auxiliary data,[2,4] we calculate $\Delta_f H°(298.15\ K) = -116.52$ and $-117.05\ kcal \cdot mol^{-1}$ for ZrI_4(cr) from these two reactions. We adopt a mean of these two values, $\Delta_f H°(298.15\ K) = -116.8\ kcal \cdot mol^{-1}$, and assign an uncertainty of $\pm 1.5\ kcal \cdot mol^{-1}$. The value suggested by NBS[3] is $1.7\ kcal \cdot mol^{-1}$ more positive.

Baev and Shelton[5] reference an enthalpy of formation value for ZrI_4(cr). The reported $\Delta_f H°(298.15\ K) = 105.9\ kcal \cdot mol^{-1}$ as supposedly extracted from Karapet'yants and Karapet'yants.[6] We tentatively discard this value due to the large number of inconsistencies in the reported tabular results of Baev and Shelton.[5]

Heat Capacity and Entropy

There is no heat capacity and enthalpy data reported in the literature for ZrI_4(cr). The adopted heat capacity values are estimated such they they parallel those adopted for $ZrCl_4$(cr) and $ZrBr_4$(cr)[2] and are consistent with the sublimation data.

The crystal data compilation of Donnay and Ondik[8] does not list the crystal structure of ZrI_4(cr) but does tabulate both $ZrCl_4$ and $ZrBr_4$ as cubic structures. The literature data related to the crystal structure of ZrI_4 is not definitive. Assuming ZrI_4(cr) also has a cubic structure, the adopted heat capacity values are estimated so as to parallel those for $ZrCl_4$ and $ZrBr_4$. The values below 300 K are calculated in the same manner as for $ZrBr_4$(cr).[2] The high temperature heat capacities are obtained graphically.

Fusion Data

The melting point was observed by Rahlfs and Fischer[9] to be 772 ± 2 K and by Nisel'son[10] to be 773 K.

Sublimation Data

The sublimation data are treated in the ZrI_4(g) table.[2] The sublimation temperature, T_{sub}, is calculated from the Gibbs energy crossover between the crystal and gas. Since T_{sub} is less than T_{fus}, the liquid phase is thermodynamically unstable at one atmosphere pressure.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−30.439	−487.236	−487.236	INFINITE
100	104.207	131.545	369.071	−23.753	−487.537	−487.087	254.428
200	121.579	210.426	271.784	−12.272	−488.114	−486.406	127.036
298.15	127.800	260.270	260.270	0.	−488.691	−485.446	85.048
300	127.880	261.061	260.272	0.236	−488.703	−485.426	84.520
400	131.001	298.303	265.329	13.190	−521.586	−483.104	63.087
500	133.009	327.759	274.971	26.394	−607.399	−465.240	48.603
600	134.599	352.154	285.860	39.776	−604.216	−437.106	38.053
700	135.938	373.005	296.856	53.304	−600.990	−409.509	30.558
800	137.152	391.236	307.537	66.959	−597.743	−382.376	24.967
900	138.365	407.460	317.755	80.735	−594.496	−355.650	20.641
1000	139.578	422.101	327.469	94.632	−591.258	−329.285	17.200

PREVIOUS: June 1964 CURRENT: June 1975

$S°(298.15\ K) = 446.563 \pm 0.13\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -356.75 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -362.33 \pm 8.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
158 (1)
43 (2)
254 (3)
55 (3)

Ground State Quantum Weight: [1] $\sigma = 12$

Point Group: T_d

Bond Distance: Zr–I = 2.660 ± 0.005 Å

Bond Angle: I–Zr–I = 109° 28'

Product of the Moments of Inertia: $I_A I_B I_C = 6.286307 \times 10^{-110}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation for ZrI_4(g) is calculated from the enthalpies of formation and sublimation at 298.15 K. The adopted value for the heat of sublimation, $\Delta_{sub}H°(298.15\ K) = 30.2 \pm 0.5\ kcal·mol^{-1}$, is based on the 2nd and 3rd law analyses of the sublimation data of Sale and Shelton[1] and Rahlfs and Fischer[2]. Using Knudsen effusion techniques, Sale and Shelton[1] studied effusion in a nickel effusion cell for three different orifice areas. The results were then extrapolated to zero orifice area (refer to last line in the following table). Other sublimation studies have been conducted by Rahlfs and Fischer,[2] using a liquid tin tensimeter, and by Gerlach *et al.*,[3] using the oscillating quartz fiber method. It should be noted that the work of Rahlfs and Fischer[2] covered an observed pressure range of 4.0–272 mm Hg, which is much wider than range covered by Sale and Shelton.[1] The adopted $\Delta_{sub}H°(298.15\ K)$ is based on the mean of the 3rd law results of Sale and Shelton (30.01 $kcal·mol^{-1}$),[1] and Rahlfs and Fischer (30.32 $kcal·mol^{-1}$).[2]

The effusion studies (membrane method) by Baev and Shelton[4] are discarded due to the large number of discrepancies in their tabulated results.

In analyzing the vapor pressures for the three sublimation studies,[1,2,3] corrections were made for non–ideality by means of the equation $\Delta G°/T = -R\ln p - Bp/T$. The Bertholet equation of state and the critical constants T_c = 959 K and p_c = 40.7 atm as determined by Nisel'son and Sokolova[5] are used to calculate B.

Source	T/K	Data Points	$\Delta_{sub}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
2	558–671	15*	31.33 ± 0.24	30.32 ± 0.12	−1.62 ± 0.38
3	393–453	eqn	26.91	29.98	7.25
1	426–474A**	12*	29.84 ± 1.28	31.22 ± 0.30	3.09 ± 2.84
	432–500B**	14*	30.81 ± 0.57	30.86 ± 0.15	0.10 ± 1.24
	436–480C**	12	30.24 ± 0.76	30.51 ± 0.17	0.61 ± 1.66
	423–503	eqn	29.97	30.01	0.08

*One point rejected due to a statistical test

**Orifice area (cm^2 10^2) A = 0.5364 B = 0.0935

Heat Capacity and Entropy

The adopted vibrational frequencies are from the work of Clark *et al.*[6,7] who recorded the Raman spectra of ZrI_4 in the vapor phase (380–420°C). These studies indicated that ZrI_4 is a tetrahedral monomer in the vapor phase. Shimanouchi, in his compilation of molecular vibrational frequencies,[8] also adopted the values of Clark *et al.*[6,7] for ZrI_4(g). Rahlfs and Fischer,[2] though vapor density measurements had earlier concluded that ZrI_4 was monomeric in the vapor phase.

An electron diffraction study of ZrI_4(g) at 250–270°C was conducted by Zasorin *et al.*[9] This study confirmed the tetrahedral structure and determined the Zr–I bond length to be 2.660 ± 0.005 Å. We adopt this value. Other interatomic distances reported in the literature are estimates. The principal moments of inertia are: $I_A = I_B = I_C = 397.6172 \times 10^{-39}\ g·cm^2$.

Much literature has been published on the inter–relationships between force constants and vibrational frequencies. Since the majority of these are based on estimated frequencies, they will not be further discussed or referenced. The same situation is true for thermodynamic tabulations of ZrI_4(g). One exception is that Clark *et al.*[6] calculated thermodynamic properties based on their experimental vibrational frequencies. Their tabulation is very similar to ours: the differences in the entropy being 0.04 $cal·K^{-1}·mol^{-1}$ in the range 100–1000 K.

Continued on page 1463

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−26.311	−356.752	−356.752	INFINITE
100	87.629	339.627	536.514	−19.689	−357.116	−377.475	197.173
200	100.873	405.465	456.038	−10.115	−359.600	−396.900	103.660
250	103.241	428.254	448.278	−5.006	−360.962	−406.069	84.843
298.15	104.589	446.563	446.563	0.	−362.334	−414.633	72.642
300	104.629	447.210	446.565	0.194	−362.389	−414.957	72.250
350	105.504	463.409	447.843	5.448	−364.029	−423.594	63.218
400	106.088	477.538	450.690	10.739	−397.679	−430.892	56.269
450	106.496	490.058	454.382	16.054	−401.736	−434.800	50.470
500	106.791	501.295	458.521	21.387	−486.049	−430.658	44.991
600	107.181	520.803	467.324	32.087	−485.549	−419.628	36.532
700	107.418	537.344	476.175	42.818	−485.119	−408.676	30.496
800	107.574	551.698	484.738	53.568	−484.777	−397.780	25.972
900	107.681	564.375	492.896	64.331	−484.542	−386.921	22.456
1000	107.758	575.725	500.622	75.103	−484.430	−376.081	19.644
1100	107.814	585.998	507.924	85.882	−484.453	−365.246	17.344
1200	107.858	595.381	514.826	96.666	−488.336	−354.181	15.417
1300	107.892	604.016	521.359	107.453	−488.129	−343.011	13.782
1400	107.919	612.012	527.553	118.244	−488.023	−331.852	12.382
1500	107.940	619.459	533.434	129.037	−488.048	−320.697	11.168
1600	107.958	626.426	539.031	139.832	−488.235	−309.536	10.105
1700	107.973	632.971	544.366	150.628	−488.610	−298.356	9.167
1800	107.985	639.143	549.462	161.426	−489.200	−287.149	8.333
1900	107.996	644.982	554.337	172.225	−490.022	−275.903	7.585
2000	108.005	650.521	559.009	183.025	−491.089	−264.607	6.911
2100	108.012	655.791	563.493	193.826	−492.408	−253.251	6.299
2200	108.019	660.816	567.803	204.628	−515.301	−241.082	5.724
2300	108.025	665.618	571.953	215.430	−517.533	−228.567	5.191
2400	108.030	670.215	575.952	226.233	−519.855	−215.954	4.700
2500	108.034	674.625	579.811	237.036	−522.243	−203.243	4.247
2600	108.038	678.863	583.540	247.839	−524.676	−190.435	3.826
2700	108.042	682.940	587.146	258.643	−527.130	−177.532	3.435
2800	108.045	686.869	590.638	269.448	−529.582	−164.540	3.070
2900	108.048	690.661	594.022	280.252	−532.010	−151.460	2.728
3000	108.050	694.324	597.305	291.057	−534.395	−138.296	2.408
3100	108.053	697.867	600.492	301.863	−536.721	−125.054	2.107
3200	108.055	701.298	603.589	312.668	−538.973	−111.739	1.824
3300	108.057	704.623	606.600	323.474	−541.137	−98.354	1.557
3400	108.059	707.848	609.531	334.279	−543.205	−84.905	1.304
3500	108.060	710.981	612.385	345.085	−545.169	−71.397	1.066
3600	108.062	714.025	615.166	355.891	−547.021	−57.834	0.839
3700	108.063	716.986	617.878	366.698	−548.759	−44.221	0.624
3800	108.064	719.868	620.525	377.504	−550.380	−30.563	0.420
3900	108.066	722.675	623.108	388.310	−551.882	−16.864	0.226
4000	108.067	725.411	625.631	399.117	−553.265	−3.128	0.041
4100	108.068	728.079	628.098	409.924	−554.529	10.641	−0.136
4200	108.069	730.683	630.509	420.731	−555.677	24.441	−0.304
4300	108.069	733.226	632.869	431.537	−556.710	38.265	−0.465
4400	108.070	735.711	635.178	442.344	−557.630	52.113	−0.619
4500	108.071	738.139	637.439	453.152	−558.441	65.980	−0.766
4600	108.072	740.515	639.654	463.959	−559.144	79.863	−0.907
4700	108.072	742.839	641.825	474.766	−559.745	93.762	−1.042
4800	108.073	745.114	643.953	485.573	−1121.182	119.289	−1.298
4900	108.074	747.343	646.040	496.380	−1121.238	145.133	−1.547
5000	108.074	749.526	648.088	507.188	−1121.218	170.977	−1.786
5100	108.075	751.666	650.098	517.995	−1121.123	196.821	−2.016
5200	108.075	753.765	652.072	528.803	−1120.957	222.661	−2.237
5300	108.076	755.823	654.010	539.610	−1120.720	248.497	−2.449
5400	108.076	757.844	655.914	550.418	−1120.416	274.329	−2.654
5500	108.076	759.827	657.786	561.225	−1120.045	300.154	−2.851
5600	108.077	761.774	659.625	572.033	−1119.610	325.973	−3.041
5700	108.077	763.687	661.434	582.841	−1119.112	351.782	−3.224
5800	108.077	765.567	663.213	593.649	−1118.553	377.582	−3.400
5900	108.078	767.414	664.964	604.456	−1117.934	403.372	−3.571
6000	108.078	769.231	666.687	615.264	−1117.257	429.152	−3.736

PREVIOUS: June 1975 (1 atm) CURRENT: June 1975 (1 bar)

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REFERENCE STATE

0	to	336.35 K	crystal
336.35	to	1039.540 K	liquid
above		1039.540 K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−7.082	0.	0.	0.
100	24.631	35.603	89.101	−5.350	0.	0.	0.
200	27.004	53.493	67.270	−2.755	0.	0.	0.
298.15	29.497	64.670	64.670	0.	0.	0.	0.
300	29.573	64.853	64.671	0.055	0.	0.	0.
336.350	34.567	68.370	64.880	1.174	___ CRYSTAL <--> LIQUID ___		
336.350	32.139	75.310	64.880	3.508	TRANSITION		
400	31.499	80.825	66.993	5.533	0.	0.	0.
500	30.695	87.763	70.482	8.641	0.	0.	0.
600	30.136	93.306	73.840	11.680	0.	0.	0.
700	29.824	97.925	76.960	14.676	0.	0.	0.
800	29.757	101.901	79.834	17.653	0.	0.	0.
900	29.936	105.413	82.485	20.636	0.	0.	0.
1000	30.361	108.587	84.939	23.648	0.	0.	0.
1039.540	30.604	109.769	85.861	24.854	___ LIQUID <--> IDEAL GAS ___		
1039.540	20.786	186.300	85.861	104.410	FUGACITY = 1 bar		
1100	20.786	187.475	91.414	105.667	0.	0.	0.
1200	20.787	189.284	99.496	107.746	0.	0.	0.
1300	20.789	190.948	106.467	109.825	0.	0.	0.
1400	20.793	192.488	112.557	111.904	0.	0.	0.
1500	20.801	193.923	117.934	113.983	0.	0.	0.
1600	20.814	195.266	122.726	116.064	0.	0.	0.
1700	20.836	196.529	127.031	118.146	0.	0.	0.
1800	20.868	197.720	130.925	120.231	0.	0.	0.
1900	20.914	198.850	134.471	122.320	0.	0.	0.
2000	20.975	199.924	137.717	124.415	0.	0.	0.
2100	21.056	200.949	140.703	126.516	0.	0.	0.
2200	21.157	201.931	143.464	128.627	0.	0.	0.
2300	21.281	202.874	146.027	130.748	0.	0.	0.
2400	21.431	203.783	148.415	132.884	0.	0.	0.
2500	21.606	204.661	150.647	135.035	0.	0.	0.
2600	21.809	205.512	152.741	137.206	0.	0.	0.
2700	22.043	206.340	154.711	139.398	0.	0.	0.
2800	22.307	207.146	156.569	141.615	0.	0.	0.
2900	22.605	207.934	158.327	143.861	0.	0.	0.
3000	22.936	208.706	159.993	146.137	0.	0.	0.
3100	23.306	209.464	161.577	148.449	0.	0.	0.
3200	23.714	210.210	163.085	150.800	0.	0.	0.
3300	24.123	210.943	164.524	153.184	0.	0.	0.
3400	24.599	211.670	165.900	155.619	0.	0.	0.
3500	25.107	212.390	167.218	158.102	0.	0.	0.
3600	25.666	213.105	168.483	160.640	0.	0.	0.
3700	26.270	213.816	169.698	163.236	0.	0.	0.
3800	26.920	214.526	170.869	165.896	0.	0.	0.
3900	27.618	215.234	171.997	168.622	0.	0.	0.
4000	28.345	215.940	173.087	171.414	0.	0.	0.
4100	29.124	216.649	174.141	174.283	0.	0.	0.
4200	29.962	217.361	175.161	177.237	0.	0.	0.
4300	30.848	218.076	176.151	180.277	0.	0.	0.
4400	31.145	218.726	177.106	183.131	0.	0.	0.
4500	32.003	219.436	178.039	186.288	0.	0.	0.
4600	32.892	220.149	178.946	189.532	0.	0.	0.
4700	33.767	220.861	179.830	192.846	0.	0.	0.
4800	34.464	221.553	180.689	196.143	0.	0.	0.
4900	35.385	222.273	181.531	199.635	0.	0.	0.
5000	36.319	222.997	182.353	203.220	0.	0.	0.
5100	37.263	223.725	183.157	206.899	0.	0.	0.
5200	38.212	224.458	183.944	210.673	0.	0.	0.
5300	39.163	225.195	184.715	214.542	0.	0.	0.
5400	40.111	225.936	185.472	218.506	0.	0.	0.
5500	41.052	226.681	186.214	222.564	0.	0.	0.
5600	41.980	227.429	186.944	226.716	0.	0.	0.
5700	42.477	228.111	187.652	230.615	0.	0.	0.
5800	43.337	228.857	188.356	234.906	0.	0.	0.
5900	44.172	229.605	189.049	239.281	0.	0.	0.
6000	44.978	230.354	189.731	243.739	0.	0.	0.

PREVIOUS: December 1961 (1 atm) CURRENT: December 1961 (1 bar)

$S°(298.15\ K) = 64.67\ J·K^{-1}·mol^{-1}$
$T_{fus} = 336.35\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 2.334\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Low temperature heat capacity measurements have been reported by Roberts (1.5 20 K),[1] Krier, Craig, and Wallace (12–320 K),[2] Dauphinee, Martin, and Preston Thomas (20–330 K),[3] Simon and Zeidler (15–300 K),[4] and Eastman and Rodebush, (70–290 K)[5] A smooth curve was drawn through a large scale plot of the data, giving the most weight to the first three references. Above 300 K, the heat capacity data were adjusted to join smoothly with the enthalpy measurements of Douglas *et al.*[6]

Fusion Data

The enthalpy of fusion is from the enthalpy measurements of Douglas *et al.*[6]

Sublimation Data

Refer to the K(g) and K_2(g) tables for details.

References

[1]L. M. Roberts, Proc. Phys. Soc. (London) **70B**, 744 (1957).
[2]C. A. Krier, R. S. Craig, and W. E. Wallace, J. Phys. Chem. **61**, 522 (1957).
[3]T. M. Dauphinee, D. L. Martin, and H. Preston Thomas, Proc. Roy. Soc. (London) **A233**, 214 (1955).
[4]F. Simon and W. Zeidler, Z. Physik. Chem. **123**, 383 (1926).
[5]E. D. Eastman and W. H. Rodebush, J. Am. Chem. Soc. **40**, 489 (1918).
[6]T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis, J. Am. Chem. Soc. **74**, 2472 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−7.082	0.	0.	0.
100	24.631	35.603	89.101	−5.350	0.	0.	0.
200	27.004	53.493	67.270	−2.755	0.	0.	0.
250	28.008	59.623	65.146	−1.381	0.	0.	0.
298.15	29.497	64.670	64.670	0.	0.	0.	0.
300	29.573	64.853	64.671	0.055	0.	0.	0.
336.350	34.567	68.370	64.880	1.174	--- CRYSTAL <--> LIQUID ---		
350	38.484	69.819	65.044	1.671	−2.275	0.094	−0.014
400	52.287	75.858	66.008	3.940	−1.593	0.394	−0.051

PREVIOUS: CURRENT: December 1961

$S°(298.15\ K)$ = [71.403] $J·K^{-1}·mol^{-1}$
T_{fus} = 336.35 K

$\Delta_f H°(298.15\ K)$ = [2.270] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 2.334 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(K, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°(336.35\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The liquid heat capacity values are derived from the enthalpy measurements of Douglas *et al.*[1] The heat capactiy curve was extropolated to 298.15 K and 200 K in a reasonable manner.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

Potassium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm. at 1037 K. The vapor composition at this temperature is 94.5 mole % monatomic and 5.5 mole % diatomic gas. The enthalpy of vaporization of 39.1 grams of liquid potassium to this equilibrium mixture is 18.38 kcal.

Reference

[1]T. B. Douglas, A. F. Ball, D. C. Ginnings, and W. D. Davis, J. Am. Chem. Soc. **74**, 2472 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	32.702	71.403	71.403	0.	2.270	0.263	−0.046
300	32.677	71.605	71.404	0.060	2.276	0.250	−0.044
336.350	32.139	75.310	71.630	1.238	--- CRYSTAL <--> LIQUID ---		
350	31.993	76.586	71.799	1.676	0.	0.	0.
400	31.499	80.825	72.669	3.263	0.	0.	0.
450	31.067	84.510	73.784	4.827	0.	0.	0.
500	30.695	87.763	75.023	6.370	0.	0.	0.
600	30.136	93.306	77.623	9.410	0.	0.	0.
700	29.824	97.925	80.203	12.406	0.	0.	0.
800	29.757	101.901	82.672	15.383	0.	0.	0.
900	29.936	105.413	85.007	18.365	0.	0.	0.
1000	30.361	108.587	87.209	21.378	0.	0.	0.
1039.540	30.604	109.769	88.045	22.583	---- FUGACITY = 1 bar ------		
1100	31.031	111.511	89.287	24.446	−78.951	4.610	−0.219
1200	31.882	114.247	91.254	27.591	−77.884	12.160	−0.529
1300	32.803	116.835	93.123	30.825	−76.729	19.617	−0.788
1400	33.723	119.300	94.906	34.152	−75.482	26.982	−1.007
1500	34.644	121.658	96.611	37.570	−74.143	34.255	−1.193

PREVIOUS: CURRENT: December 1961

0 to 336.35 K crystal
above 336.35 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.082	0.	0.	0.
100	24.631	35.603	89.101	−5.350	0.	0.	0.
200	27.004	53.493	67.270	−2.755	0.	0.	0.
250	28.008	59.623	65.146	−1.381	0.	0.	0.
298.15	29.497	64.670	64.670	0.	0.	0.	0.
300	29.573	64.853	64.671	0.055	0.	0.	0.
336.3150	34.567	68.370	64.880	1.174	___ CRYSTAL <--> LIQUID ___		
336.3150	32.139	75.310	64.880	3.508	TRANSITION		
350	31.993	76.586	65.312	3.946	0.	0.	0.
400	31.499	80.825	66.993	5.533	0.	0.	0.
450	31.067	84.510	68.739	7.097	0.	0.	0.
500	30.695	87.763	70.482	8.641	0.	0.	0.
600	30.136	93.306	73.840	11.680	0.	0.	0.
700	29.824	97.925	76.960	14.676	0.	0.	0.
800	29.757	101.901	79.834	17.653	0.	0.	0.
900	29.936	105.413	82.485	20.636	0.	0.	0.
1000	30.361	108.587	84.939	23.648	0.	0.	0.
1039.540	30.604	109.769	85.861	24.854	----- FUGACITY = 1 bar -----		
1100	31.031	111.511	87.223	26.716	−78.951	4.610	−0.219
1200	31.882	114.247	89.362	29.862	−77.884	12.160	−0.529
1300	32.803	116.835	91.377	33.096	−76.729	19.617	−0.788
1400	33.723	119.300	93.284	36.422	−75.482	26.982	−1.007
1500	34.644	121.658	95.098	39.840	−74.143	34.255	−1.193

PREVIOUS: CURRENT: December 1961

IP(K, g) = 35009.78 ± 0.02 cm^{-1}
$S°$(298.15 K) = 160.340 ± 0.025 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 89.9 ± 0.4 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 89.0 ± 0.4 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2
$^2P_{1/2}$	12985.170	2
$^2P_{3/2}$	13042.876	4
$^2S_{1/2}$	21026.551	2
.	.	.
$^2P_{3/2}$	34991.2	4
IP	35009.78	

Enthalpy of Formation

The enthalpy of formation of potassium gas, $\Delta_f H°$(298.15 K) = 89.0 ± 0.4 $kJ·mol^{-1}$, is chosen to be the value recommended by CODATA.[1] This value was obtained from 2nd and 3rd law treatments of vapor pressure data. The reported vapor pressures were corrected for the effects of K_2(g), using $D_0°$ = 49.01 $kJ·mol^{-1}$. At higher pressures an alternate virial treatment was employed.

As stated by CODATA,[1] the selected value is the weighted average of the 3rd law values of $\Delta_{sub}H°$(298.15 K) calculated from the following studies:

Source	$\Delta_{sub}H°$(298.15 K), $kJ·mol^{-1}$	Source	$\Delta_{sub}H°$(298.15 K), $kJ·mol^{-1}$
Haycock and Lamplough[2]	89.31 ± 0.65	Venogradov and Volyak[13]	89.27 ± 0.65
Fiock and Rodenbush[3]	89.41 ± 0.65	Achener[14]	88.97 ± 0.69
Edmondson and Egerton[4]	89.71 ± 0.25	Ahpil'rain *et al.*[15]	88.94 ± 0.47
Weiler[5]	89.71 ± 0.65	Bowles[16]	88.50 ± 1.35
Mayer[6]	88.58 ± 1.00	Gerasimov *et al.*[17]	89.43 ± 0.50
Neumann and volker[7]	89.56 ± 0.25	Sphil'rain and Nikanorov[18]	88.70 ± 0.85
Walling[8]	88.59 ± 0.75	Schins *et al.*[19]	88.94 ± 0.50
Makansi *et al.*[9]	88.73 ± 0.72	Bonilla[20]	88.75 ± 0.65
Buck and Pauly[10]	89.72 ± 0.35	Roeder and Morawitz[21]	89.59 ± 0.38
Stone *et al.*[11]	88.81 ± 0.90	Kondrat'ev[22]	88.27 ± 0.55
Rigney *et al.*[12]	88.90 ± 0.93		

The 2nd law calculations from the above sources led to somewhat more positive values.

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP–kT) technique as the cutoff procedure in the energy level summation.[24]

The lowest lying levels for these metals [14904 cm^{-1} (Li), 16956 cm^{-1} (Na), 12985 cm^{-1} (K), 12578 cm^{-1} (Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm^{-1} cm for Li to 31406.1 cm^{-1} for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.[24]

The atomic energy levels have been taken from the compilation of Corliss and Sugar.[14] Our calculated values for the thermal functions are similar to those recommended by CODATA.[1] They do differ for two reasons, however. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 $J·K^{-1}·mol^{-1}$, presumably due to the use of slightly different values for auxiliary data.

References

1J. D. Cox, chairman, CODATA Task Group on Key Values for Thermodynamics, J. Chem. Thermodyn. **10**, 903 (1978).
[2]C. T. Heycock and F. E. E. Lamplough, Proc. Chem. Soc. **28**, 3 (1912).
[3]E. F. Fiock and W. H. Rodebush, J. Am. Chem. Soc. **48**, 2522 (1926).

Continued on page 1489

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	89.885	89.885	INFINITE
100	20.786	137.632	178.820	−4.119	90.231	80.028	−41.802
200	20.786	152.040	162.241	−2.040	89.715	70.006	−18.284
250	20.786	156.678	160.682	−1.001	89.380	65.116	−13.605
298.15	20.786	160.340	160.340	0.	89.000	60.476	−10.595
300	20.786	160.468	160.340	0.038	88.984	60.299	−10.499
350	20.786	163.672	160.593	1.078	86.132	55.652	−8.306
400	20.786	166.448	161.155	2.117	85.584	51.335	−6.704
450	20.786	168.896	161.882	3.156	85.060	47.086	−5.466
500	20.786	171.086	162.695	4.196	84.555	42.894	−4.481
600	20.786	174.876	164.419	6.274	83.594	34.652	−3.017
700	20.786	178.080	166.147	8.353	82.677	26.568	−1.983
800	20.786	180.856	167.816	10.431	81.778	18.614	−1.215
900	20.786	183.304	169.404	12.510	80.875	10.773	−0.625
1000	20.786	185.494	170.905	14.589	79.940	3.034	−0.158
1039.540	20.786	186.300	171.476	15.411	----- FUGACITY = 1 bar -----		
1100	20.786	187.475	172.323	16.667	0.	0.	0.
1200	20.787	189.284	173.662	18.746	0.	0.	0.
1300	20.789	190.948	174.929	20.825	0.	0.	0.
1400	20.793	192.488	176.129	22.904	0.	0.	0.
1500	20.801	193.923	177.268	24.983	0.	0.	0.
1600	20.814	195.266	178.351	27.064	0.	0.	0.
1700	20.836	196.529	179.384	29.147	0.	0.	0.
1800	20.868	197.720	180.369	31.232	0.	0.	0.
1900	20.914	198.850	181.313	33.321	0.	0.	0.
2000	20.975	199.924	182.217	35.415	0.	0.	0.
2100	21.056	200.949	183.084	37.516	0.	0.	0.
2200	21.157	201.931	183.919	39.627	0.	0.	0.
2300	21.281	202.874	184.723	41.748	0.	0.	0.
2400	21.431	203.783	185.498	43.884	0.	0.	0.
2500	21.606	204.661	186.247	46.035	0.	0.	0.
2600	21.809	205.512	186.972	48.206	0.	0.	0.
2700	22.043	206.340	187.674	50.398	0.	0.	0.
2800	22.307	207.146	188.355	52.615	0.	0.	0.
2900	22.605	207.934	189.017	54.861	0.	0.	0.
3000	22.936	208.706	189.660	57.137	0.	0.	0.
3100	23.306	209.464	190.287	59.449	0.	0.	0.
3200	23.714	210.210	190.898	61.800	0.	0.	0.
3300	24.123	210.943	191.494	64.184	0.	0.	0.
3400	24.599	211.670	192.077	66.619	0.	0.	0.
3500	25.107	212.390	192.647	69.102	0.	0.	0.
3600	25.666	213.105	193.205	71.640	0.	0.	0.
3700	26.270	213.816	193.752	74.237	0.	0.	0.
3800	26.920	214.526	194.290	76.896	0.	0.	0.
3900	27.618	215.234	194.818	79.622	0.	0.	0.
4000	28.345	215.940	195.337	82.414	0.	0.	0.
4100	29.124	216.649	195.848	85.283	0.	0.	0.
4200	29.962	217.361	196.352	88.237	0.	0.	0.
4300	30.848	218.076	196.849	91.277	0.	0.	0.
4400	31.145	218.726	197.333	94.131	0.	0.	0.
4500	32.003	219.436	197.816	97.288	0.	0.	0.
4600	32.892	220.149	198.294	100.532	0.	0.	0.
4700	33.767	220.861	198.766	103.847	0.	0.	0.
4800	34.464	221.553	199.231	107.143	0.	0.	0.
4900	35.385	222.273	199.694	110.635	0.	0.	0.
5000	36.319	222.997	200.153	114.220	0.	0.	0.
5100	37.263	223.725	200.608	117.899	0.	0.	0.
5200	38.212	224.458	201.059	121.673	0.	0.	0.
5300	39.163	225.195	201.508	125.542	0.	0.	0.
5400	40.111	225.936	201.953	129.506	0.	0.	0.
5500	41.052	226.681	202.396	133.564	0.	0.	0.
5600	41.980	227.429	202.837	137.716	0.	0.	0.
5700	42.477	228.111	203.266	141.615	0.	0.	0.
5800	43.337	228.857	203.701	145.906	0.	0.	0.
5900	44.172	229.605	204.134	150.281	0.	0.	0.
6000	44.978	230.354	204.564	154.739	0.	0.	0.

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

$IP(K^+, g) = 255100 \pm 100\ cm^{-1}$
$S°(298.15\ K) = 154.576 \pm 0.025\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 508.7 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [514.007]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

$\Delta_f H°(K^+, g, 0\ K)$ is calculated from $\Delta_f H°(K, g, 0\ K)$[1] using the spectroscopic value of IP(K) = 35009.78 ± 0.02 cm^{-1} (418.810 ± 0.000 $kJ \cdot mol^{-1}$) from Corliss and Sugar[2]. The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(K^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(K, g, 0\ K)$ by using IP(K) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for K(g), $K^+(g)$, and e^-(ref). $\Delta_f H°(K \rightarrow K^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state; the first excited state is approximately 162507 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: K(g), 12–31–83; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	508.695		
100	20.786	131.869	173.057	−4.119			
200	20.786	146.277	156.478	−2.040			
250	20.786	150.915	154.919	−1.001			
298.15	20.786	154.576	154.576	0.	514.007	480.947	−84.260
300	20.786	154.705	154.577	0.038	514.030	480.742	−83.705
350	20.786	157.909	154.830	1.078	512.217	475.245	−70.926
400	20.786	160.685	155.392	2.117	512.709	469.930	−61.367
450	20.786	163.133	156.119	3.156	513.223	464.552	−53.924
500	20.786	165.323	156.932	4.196	513.758	459.116	−47.963
600	20.786	169.113	158.656	6.274	514.876	448.083	−39.009
700	20.786	172.317	160.384	8.353	516.037	436.860	−32.599
800	20.786	175.092	162.053	10.431	517.217	425.468	−27.780
900	20.786	177.541	163.641	12.510	518.392	413.929	−24.024
1000	20.786	179.731	165.142	14.589	519.536	402.260	−21.012
1100	20.786	181.712	166.560	16.667	441.675	395.089	−18.761
1200	20.786	183.520	167.899	18.746	443.753	390.762	−17.009
1300	20.786	185.184	169.165	20.824	445.832	386.262	−15.520
1400	20.786	186.725	170.365	22.903	447.910	381.602	−14.238
1500	20.786	188.159	171.504	24.982	449.988	376.793	−13.121
1600	20.786	189.500	172.588	27.060	452.064	371.845	−12.140
1700	20.786	190.760	173.620	29.139	454.139	366.768	−11.269
1800	20.786	191.948	174.605	31.217	456.211	361.569	−10.492
1900	20.786	193.072	175.548	33.296	458.279	356.255	−9.794
2000	20.786	194.138	176.451	35.375	460.342	350.832	−9.163
2100	20.786	195.153	177.318	37.453	462.398	345.305	−8.589
2200	20.786	196.120	178.151	39.532	464.445	339.682	−8.065
2300	20.786	197.044	178.952	41.610	466.480	333.965	−7.585
2400	20.786	197.928	179.724	43.689	468.502	328.160	−7.142
2500	20.786	198.777	180.470	45.768	470.508	322.271	−6.733
2600	20.786	199.592	181.190	47.846	472.494	316.302	−6.355
2700	20.786	200.376	181.886	49.925	474.459	310.258	−6.002
2800	20.786	201.132	182.560	52.004	476.399	304.141	−5.674
2900	20.786	201.862	183.213	54.082	478.311	297.955	−5.367
3000	20.786	202.566	183.846	56.161	480.192	291.703	−5.079
3100	20.786	203.248	184.461	58.239	482.037	285.390	−4.809
3200	20.786	203.908	185.059	60.318	483.844	279.017	−4.554
3300	20.786	204.548	185.640	62.397	485.617	272.589	−4.315
3400	20.786	205.168	186.205	64.475	487.339	266.107	−4.088
3500	20.786	205.771	186.755	66.554	489.013	259.576	−3.874
3600	20.786	206.356	187.292	68.632	490.632	252.997	−3.671
3700	20.786	206.926	187.815	70.711	492.193	246.375	−3.478
3800	20.786	207.480	188.325	72.790	493.691	239.711	−3.295
3900	20.786	208.020	188.823	74.868	495.122	233.008	−3.121
4000	20.786	208.546	189.310	76.947	496.487	226.269	−2.955
4100	20.786	209.060	189.785	79.025	497.775	219.497	−2.796
4200	20.786	209.560	190.250	81.104	498.978	212.695	−2.645
4300	20.786	210.050	190.705	83.183	500.095	205.866	−2.501
4400	20.786	210.527	191.150	85.261	501.399	198.984	−2.362
4500	20.786	210.995	191.586	87.340	502.399	192.099	−2.230
4600	20.786	211.451	192.013	89.418	503.312	185.194	−2.103
4700	20.786	211.898	192.431	91.497	504.155	178.267	−1.981
4800	20.786	212.336	192.841	93.576	505.016	171.311	−1.864
4900	20.786	212.765	193.243	95.654	505.680	164.352	−1.752
5000	20.786	213.185	193.638	97.733	506.253	157.380	−1.644
5100	20.786	213.596	194.025	99.811	506.731	150.398	−1.540
5200	20.786	214.000	194.406	101.890	507.114	143.407	−1.441
5300	20.786	214.396	194.779	103.969	507.403	136.410	−1.344
5400	20.786	214.784	195.146	106.047	507.596	129.408	−1.252
5500	20.786	215.166	195.506	108.126	507.695	122.403	−1.162
5600	20.786	215.540	195.861	110.204	507.701	115.398	−1.076
5700	20.786	215.908	196.209	112.283	507.959	108.345	−0.993
5800	20.786	216.270	196.552	114.362	507.825	101.336	−0.913
5900	20.786	216.625	196.889	116.440	507.607	94.329	−0.835
6000	20.786	216.974	197.221	118.519	507.306	87.327	−0.760

PREVIOUS: March 1965 (1 atm) CURRENT: December 1983 (1 bar)

EA(K, g) = 0.50147 ± 0.00010 eV
$S°$(298.15 K) = 154.577 ± 0.005 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 41.5 ± 1 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [34.419] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for K^-(g) is calculated from the adopted electron affinity, EA(K, g) = 0.50147 ± 0.00010 eV (48.384 ± 0.010 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[6] was measured by a tunable laser photodetachment threshold technique.[2] Additional discussion on K^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[1,6] Rosenstock *et al.*,[3] and Massey.[4]

$\Delta_f H°(K^-, g, 298.15\ K)$ is obtained from $\Delta_f H°$(K, g, 0 K) by using EA(K, g) with JANAF[5] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for K^-(g), K(g), and e^-(ref). $\Delta_r H°(K^- \rightarrow K + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°$(298.15 K) should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for K^-(g) is given by Hotop and Lineberger[1,6] and Rosenstock *et al.*[3] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

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[6]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	41.501		
100	20.786	131.869	173.057	−4.119			
200	20.786	146.277	156.478	−2.040			
250	20.786	150.916	154.919	−1.001			
298.15	20.786	154.577	154.577	0.	34.419	13.868	−2.430
300	20.786	154.705	154.577	0.038	34.364	13.740	−2.392
350	20.786	157.909	154.830	1.078	30.473	10.519	−1.570
400	20.786	160.685	155.392	2.117	28.886	7.777	−1.016
450	20.786	163.133	156.119	3.156	27.322	5.232	−0.607
500	20.786	165.323	156.932	4.196	25.778	2.861	−0.299
600	20.786	169.113	158.656	6.274	22.738	−1.437	0.125
700	20.786	172.317	160.385	8.353	19.743	−5.228	0.390
800	20.786	175.093	162.053	10.431	16.766	−8.592	0.561
900	20.786	177.541	163.641	12.510	13.783	−11.583	0.672
1000	20.786	179.731	165.142	14.589	10.770	−14.241	0.744
1100	20.786	181.712	166.560	16.667	−71.249	−11.984	0.569
1200	20.786	183.521	167.899	18.746	−73.327	−6.504	0.283
1300	20.786	185.185	169.166	20.824	−75.406	−0.851	0.034
1400	20.786	186.725	170.366	22.903	−77.485	4.961	−0.185
1500	20.786	188.159	171.505	24.982	−79.565	10.923	−0.380
1600	20.786	189.501	172.588	27.060	−81.645	17.023	−0.556
1700	20.786	190.761	173.620	29.139	−83.728	23.254	−0.715
1800	20.786	191.949	174.606	31.217	−85.813	29.607	−0.859
1900	20.786	193.073	175.548	33.296	−87.902	36.076	−0.992
2000	20.786	194.139	176.451	35.375	−89.996	42.656	−1.114
2100	20.786	195.153	177.318	37.453	−92.098	49.340	−1.227
2200	20.786	196.120	178.151	39.532	−94.208	56.125	−1.333
2300	20.786	197.044	178.952	41.610	−96.330	63.005	−1.431
2400	20.786	197.929	179.725	43.689	−98.465	69.979	−1.523
2500	20.786	198.777	180.470	45.768	−100.617	77.041	−1.610
2600	20.786	199.592	181.190	47.846	−102.787	84.190	−1.691
2700	20.786	200.377	181.886	49.925	−104.980	91.423	−1.769
2800	20.786	201.133	182.560	52.004	−107.197	98.738	−1.842
2900	20.786	201.862	183.213	54.082	−109.442	106.132	−1.912
3000	20.786	202.567	183.847	56.161	−111.719	113.605	−1.978
3100	20.786	203.248	184.462	58.239	−114.030	121.153	−2.041
3200	20.786	203.908	185.059	60.318	−116.381	128.777	−2.102
3300	20.786	204.548	185.640	62.397	−118.765	136.475	−2.160
3400	20.786	205.168	186.205	64.475	−121.201	144.246	−2.216
3500	20.786	205.771	186.756	66.554	−123.683	152.089	−2.270
3600	20.786	206.357	187.292	68.632	−126.221	160.004	−2.322
3700	20.786	206.926	187.815	70.711	−128.818	167.990	−2.372
3800	20.786	207.480	188.325	72.790	−131.477	176.047	−2.420
3900	20.786	208.020	188.823	74.868	−134.204	184.176	−2.467
4000	20.786	208.547	189.310	76.947	−136.995	192.374	−2.512
4100	20.786	209.060	189.785	79.025	−139.865	200.643	−2.556
4200	20.786	209.561	190.250	81.104	−142.819	208.984	−2.599
4300	20.786	210.050	190.705	83.183	−145.859	217.396	−2.641
4400	20.786	210.528	191.150	85.261	−148.712	225.852	−2.681
4500	20.786	210.995	191.586	87.340	−151.869	234.401	−2.721
4600	20.786	211.452	192.013	89.418	−155.114	243.020	−2.760
4700	20.786	211.899	192.431	91.497	−158.428	251.709	−2.797
4800	20.786	212.336	192.841	93.576	−161.724	260.457	−2.834
4900	20.786	212.765	193.244	95.654	−165.217	269.289	−2.871
5000	20.786	213.185	193.638	97.733	−168.802	278.192	−2.906
5100	20.786	213.596	194.026	99.811	−172.481	287.169	−2.941
5200	20.786	214.000	194.406	101.890	−176.254	296.218	−2.976
5300	20.786	214.396	194.779	103.969	−180.123	305.341	−3.009
5400	20.786	214.785	195.146	106.047	−184.087	314.537	−3.043
5500	20.786	215.166	195.507	108.126	−188.145	323.808	−3.075
5600	20.786	215.541	195.861	110.204	−192.297	333.154	−3.108
5700	20.786	215.908	196.210	112.283	−196.196	342.527	−3.139
5800	20.786	216.270	196.552	114.362	−200.487	352.015	−3.170
5900	20.786	216.625	196.890	116.440	−204.863	361.579	−3.201
6000	20.786	216.975	197.221	118.519	−209.320	371.217	−3.232

PREVIOUS: CURRENT: December 1983 (1 bar)

Potassium Oxide (KO) — IDEAL GAS — $M_r = 55.0977$

$S°(298.15\ K) = [238.027 \pm 2.1]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [72.89 \pm 41.8]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [71.13 \pm 41.8]\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^2\Pi]$	0	[4]

$\omega_e = [350]\ cm^{-1}$ $\quad \omega_e x_e = [2.2]\ cm^{-1}$ $\quad \sigma = 1$

$B_e = [0.3068]\ cm^{-1}$ $\quad \alpha_e = [0.0027]\ cm^{-1}$ $\quad r_e = [2.2]$ Å

Enthalpy of Formation

Brewer and Margrave[1] suggested that the $\Delta_f H°$ value for MO(g) from the gaseous ions can be taken as the mean of the corresponding $\Delta_f H°$ values for the alkali fluoride and chloride with a maximum uncertainty of 10 $kcal\cdot mol^{-1}$. We obtain the values $\Delta_f H°(0\ K) = -137.94$ and $-117.7\ kcal\cdot mol^{-1}$ for the reactions $K^+(g) + F^-(g) = KF(g)$ and $K^+(g) + Cl^-(g) = KCl(g)$, respectively. Assuming $\Delta_f H°(0\ K) = -127.83\ kcal\cdot mol^{-1}$ for the reaction $K^+(g) + O^-(g) = KO(g)$, we calculate $\Delta_f H°(KO, g, 298.15\ K) = 19.0\ kcal\cdot mol^{-1}$ with the JANAF auxiliary values for the gaseous ions.

Based on the assumption that $D°_0(KO) = 1/2[D°_0(K_2) + D°_0(O_2)]$, or $\Delta_r H°(0\ K) = 64.9\ kcal\cdot mol^{-1}$ for the reaciton $KO(g) = K(g) + O(g)$, we evaluate $\Delta_f H°(KO, g, 0\ K) = 15.6\ kcal\cdot mol^{-1}$ or $\Delta_f H°(KO, g, 298.15\ K) = 15.2\ kcal\cdot mol^{-1}$.

According to Somayajulu,[2] in a sequence of similar diatomic molecules, $k_e r_e / D°_0 =$ constant, where k_e = force constant and r_e = equilibrium bond distance. Using $r_e = 1.62$ Å, $D°_0 = 77.9\ kcal\cdot mol^{-1}$ for LiO(g), $r_e = 2.2$ Å and $k_e(KO)/k_e(LiO) = 0.3015$, we calculate $D°_0 = 55\ kcal\cdot mol^{-1}$ for KO(g), yielding $\Delta_f H°(KO, g, 298.15\ K) = 26.1\ kcal\cdot mol^{-1}$. The value k_e is derived from the relation $k_e = 4\ ^2\mu^2$ where is the vibrational frequency for the diatomic molecule and μ is the reduced mass.

The value of $\Delta_f H°(KO, g, 298.15\ K)$ is tentatively adopted as $17 \pm 10\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for the OH(g) molecule, which has the same number of valence electrons. The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for LiF(g) and KF(g). The bond distance is estimated from those for HO(g), HF(g) and KF(g). B_e and α_e are derived from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg.[3]

References

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Potassium Oxide (KO) — $K_1O_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.666	72.886	72.886	INFINITE
100	30.583	201.486	268.756	−6.727	72.640	64.717	−33.805
200	34.332	223.966	241.275	−3.462	71.855	57.109	−14.915
250	35.340	231.744	238.616	−1.718	71.496	53.464	−11.171
298.15	35.981	238.027	238.027	0.	71.128	50.024	−8.764
300	36.001	238.249	238.028	0.067	71.113	49.893	−8.687
350	36.455	243.835	238.468	1.879	68.295	46.487	−6.938
400	36.782	248.725	239.451	3.710	67.792	43.407	−5.668
450	37.029	253.073	240.727	5.555	67.315	40.387	−4.688
500	37.223	256.984	242.160	7.412	66.857	37.420	−3.909
600	37.514	263.798	245.215	11.150	65.976	31.616	−2.752
700	37.731	269.598	248.295	14.912	65.115	25.957	−1.937
800	37.906	274.648	251.280	18.694	64.252	20.422	−1.333
900	38.056	279.121	254.130	22.493	63.365	14.996	−0.870
1000	38.191	283.138	256.833	26.305	62.433	9.671	−0.505
1100	38.316	286.784	259.393	30.130	−17.515	9.053	−0.430
1200	38.433	290.123	261.816	33.968	−17.530	11.469	−0.499
1300	38.546	293.204	264.114	37.817	−17.552	13.886	−0.558
1400	38.655	296.064	266.295	41.677	−17.577	16.305	−0.608
1500	38.761	298.735	268.370	45.548	−17.607	18.727	−0.652
1600	38.865	301.240	270.347	49.429	−17.640	21.150	−0.690
1700	38.968	303.599	272.234	53.321	−17.676	23.575	−0.724
1800	39.070	305.829	274.039	57.223	−17.717	26.003	−0.755
1900	39.170	307.944	275.768	61.135	−17.764	28.433	−0.782
2000	39.270	309.956	277.428	65.057	−17.818	30.866	−0.806
2100	39.369	311.874	279.023	68.989	−17.880	33.302	−0.828
2200	39.467	313.708	280.558	72.930	−17.953	35.741	−0.849
2300	39.565	315.465	282.038	76.882	−18.038	38.183	−0.867
2400	39.663	317.151	283.466	80.843	−18.139	40.629	−0.884
2500	39.760	318.772	284.846	84.815	−18.256	43.080	−0.900
2600	39.857	320.333	286.181	88.795	−18.394	45.536	−0.915
2700	39.954	321.839	287.474	92.786	−18.555	47.998	−0.929
2800	40.050	323.294	288.727	96.786	−18.741	50.467	−0.941
2900	40.147	324.701	289.944	100.796	−18.955	52.942	−0.954
3000	40.243	326.064	291.125	104.815	−19.201	55.425	−0.965
3100	40.339	327.385	292.274	108.845	−19.481	57.918	−0.976
3200	40.435	328.667	293.391	112.883	−19.800	60.419	−0.986
3300	40.531	329.913	294.479	116.932	−20.151	62.930	−0.996
3400	40.627	331.124	295.539	120.990	−20.552	65.454	−1.006
3500	40.723	332.303	296.573	125.057	−20.999	67.990	−1.015
3600	40.819	333.452	297.581	129.134	−21.500	70.539	−1.024
3700	40.914	334.571	298.566	133.221	−22.057	73.103	−1.032
3800	41.010	335.664	299.528	137.317	−22.674	75.684	−1.040
3900	41.105	336.730	300.468	141.423	−23.356	78.281	−1.048
4000	41.201	337.772	301.388	145.538	−24.101	80.896	−1.056
4100	41.296	338.791	302.288	149.663	−24.919	83.530	−1.064
4200	41.392	339.787	303.169	153.797	−25.819	86.186	−1.072
4300	41.487	340.762	304.032	157.941	−26.802	88.865	−1.079
4400	41.582	341.717	304.877	162.095	−27.595	91.539	−1.087
4500	41.678	342.652	305.706	166.258	−28.688	94.259	−1.094
4600	41.773	343.570	306.519	170.430	−29.865	97.004	−1.102
4700	41.868	344.469	307.317	174.612	−31.109	99.773	−1.109
4800	41.964	345.351	308.101	178.804	−32.331	102.558	−1.116
4900	42.059	346.218	308.870	183.005	−33.746	105.383	−1.123
5000	42.154	347.068	309.625	187.216	−35.251	108.238	−1.131
5100	42.249	347.904	310.368	191.436	−36.847	111.123	−1.138
5200	42.344	348.725	311.097	195.665	−38.535	114.040	−1.146
5300	42.440	349.533	311.815	199.905	−40.316	116.992	−1.153
5400	42.535	350.327	312.521	204.153	−42.191	119.977	−1.161
5500	42.630	351.108	313.215	208.412	−44.158	122.998	−1.168
5600	42.725	351.877	313.899	212.679	−46.217	126.056	−1.176
5700	42.820	352.634	314.572	216.957	−48.024	129.103	−1.183
5800	42.915	353.380	315.234	221.243	−50.222	132.230	−1.191
5900	43.010	354.114	315.887	225.540	−52.505	135.395	−1.199
6000	43.105	354.838	316.530	229.845	−54.871	138.600	−1.207

PREVIOUS: December 1967 (1 atm) — CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = [226.308 \pm 1.3]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-130.09 \pm 83.7]\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [-138.07 \pm 83.7]\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma]$	0	[1]

$\omega_e = [360]\ cm^{-1}$ $\omega_e x_e = [2.3]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.3068]\ cm^{-1}$ $\alpha_e = [0.0027]\ cm^{-1}$ $r_e = [2.2]$ Å

Enthalpy of Formation

Since the electron affinity of KO(g) is unavailable, the value of $\Delta_f H°(KO^-, g, 298.15\ K)$ is estimated. Assuming that the enthalpy change $\Delta_r H°(0\ K)$ of the reaction (1) $KO^-(g) = K(g) + O^-(g)$ is approximately the average of the $\Delta_r H°(0\ K)$ value for the reaction (2) KO(g) = K(g) + O(g) and (3) KF(g) = K(g) + F(g), we obtain $\Delta_r H°(0\ K) = 1/2(63.5 + 117.3) = 90.4\ kcal·mol^{-1}$ for reaction (1). However, we compare the $\Delta_r H°(0\ K)$ values for the reactions (4) HO(g) = H(g) + O(g), (5) $HO^-(g) = H(g) + O^-(g)$, and (6) HF(g) = H(g) + F(g), and find that $\Delta_r H°(0\ K)$ for reaction (5) is experimentally determined as 109.7 $kcal·mol^{-1}$ which is about 8 $kcal·mol^{-1}$ more negative than the average of $\Delta_r H°(0\ K)$ values for reactions (4) and (6). Based on this fact we estimated $\Delta_r H°(0\ K) = 80\ kcal·mol^{-1}$ for reaction (1), yielding $\Delta_f H°(KO^-, g, 298.15\ K) = -33\ kcal·mol^{-1}$. The value of $\Delta_f H°(KO^-, g, 298.15\ K)$ is tentatively adopted as $-33 \pm 20\ kcal·mol^{-1}$. The electronic affinity of KO(g) is derived to be 2.2 ± 0.9 eV. The value of EA for HO(g) is determined as 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of KF(g) which is isoelectronic with $KO^-(g)$. The values of ω_e, $\omega_e x_e$ and r_e are estimated by comparison with those for KF(g). The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ using the method recommended by Herzberg.[1]

Reference

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.636	−130.087		
100	30.460	189.920	256.923	−6.700			
200	34.190	212.295	229.546	−3.450			
250	35.226	220.044	226.896	−1.713			
298.15	35.888	226.308	226.308	0.	−138.072	−149.427	26.179
300	35.909	226.530	226.309	0.066	−138.126	−149.498	26.030
350	36.379	232.103	226.748	1.874	−141.987	−151.180	22.562
400	36.717	236.984	227.729	3.702	−143.533	−152.387	19.900
450	36.973	241.324	229.003	5.545	−145.052	−153.402	17.806
500	37.173	245.230	230.433	7.398	−146.552	−154.250	16.114
600	37.473	252.036	233.483	11.132	−149.517	−155.510	13.538
700	37.693	257.830	236.558	14.890	−152.460	−156.276	11.661
800	37.870	262.875	239.539	18.669	−155.405	−156.621	10.226
900	38.021	267.344	242.385	22.464	−158.375	−156.595	9.089
1000	38.155	271.357	245.085	26.272	−161.388	−156.236	8.161
1100	38.279	275.000	247.641	30.094	−243.418	−150.962	7.169
1200	38.395	278.335	250.062	33.928	−245.516	−142.465	6.201
1300	38.506	281.413	252.357	37.773	−247.620	−133.792	5.376
1400	38.614	284.271	254.535	41.629	−249.728	−124.957	4.662
1500	38.718	286.938	256.608	45.496	−251.841	−115.971	4.038
1600	38.820	289.440	258.582	49.373	−253.957	−106.844	3.488
1700	38.921	291.797	260.467	53.260	−256.076	−97.584	2.998
1800	39.020	294.024	262.270	57.157	−258.201	−88.200	2.559
1900	39.118	296.137	263.998	61.064	−260.331	−78.697	2.164
2000	39.215	298.145	265.655	64.980	−262.469	−69.082	1.804
2100	39.312	300.061	267.248	68.907	−264.615	−59.360	1.477
2200	39.408	301.892	268.782	72.843	−266.772	−49.535	1.176
2300	39.504	303.646	270.260	76.788	−268.942	−39.613	0.900
2400	39.599	305.329	271.686	80.743	−271.128	−29.595	0.644
2500	39.694	306.948	273.065	84.708	−273.331	−19.486	0.407
2600	39.788	308.506	274.398	88.682	−275.554	−9.289	0.187
2700	39.883	310.010	275.689	92.666	−277.800	0.995	−0.019
2800	39.977	311.462	276.941	96.659	−280.071	11.362	−0.212
2900	40.071	312.866	278.156	100.661	−282.372	21.811	−0.393
3000	40.165	314.226	279.336	104.673	−284.704	32.340	−0.563
3100	40.258	315.545	280.482	108.694	−287.071	42.947	−0.724
3200	40.352	316.825	281.598	112.725	−289.477	53.631	−0.875
3300	40.445	318.068	282.685	116.764	−291.915	64.390	−1.019
3400	40.538	319.277	283.743	120.814	−294.403	75.224	−1.156
3500	40.632	320.453	284.775	124.872	−296.938	86.132	−1.285
3600	40.725	321.599	285.782	128.940	−299.527	97.114	−1.409
3700	40.818	322.716	286.765	133.017	−302.172	108.167	−1.527
3800	40.911	323.806	287.726	137.103	−304.877	119.294	−1.640
3900	41.004	324.870	288.665	141.199	−307.648	130.493	−1.748
4000	41.097	325.909	289.583	145.304	−310.481	141.762	−1.851
4100	41.190	326.925	290.481	149.419	−313.389	153.104	−1.951
4200	41.283	327.919	291.361	153.542	−316.378	164.518	−2.046
4300	41.376	328.891	292.222	157.675	−319.451	176.004	−2.138
4400	41.468	329.843	293.067	161.817	−322.334	187.535	−2.226
4500	41.561	330.776	293.894	165.969	−325.517	199.158	−2.312
4600	41.654	331.691	294.706	170.130	−328.784	210.854	−2.394
4700	41.747	332.588	295.503	174.300	−332.118	222.619	−2.474
4800	41.839	333.467	296.284	178.479	−335.432	234.444	−2.551
4900	41.932	334.331	297.052	182.667	−338.938	246.353	−2.626
5000	42.025	335.179	297.806	186.865	−342.534	258.334	−2.699
5100	42.117	336.012	298.547	191.072	−346.222	270.388	−2.769
5200	42.210	336.831	299.276	195.289	−350.002	282.515	−2.838
5300	42.302	337.636	299.992	199.514	−353.875	294.716	−2.905
5400	42.395	338.428	300.696	203.749	−357.842	306.990	−2.970
5500	42.488	339.206	301.389	207.993	−361.902	319.339	−3.033
5600	42.580	339.973	302.071	212.247	−366.054	331.763	−3.095
5700	42.673	340.727	302.743	216.509	−369.954	344.213	−3.154
5800	42.765	341.470	303.404	220.781	−374.245	356.780	−3.213
5900	42.858	342.202	304.056	225.062	−378.622	369.421	−3.271
6000	42.950	342.923	304.698	229.353	−383.082	382.137	−3.327

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = 122.499 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1} = 193.5\ K$
$T_{trs2} = 230.9\ K$
$T_{fus} = 782 \pm 20\ K$

$\Delta_f H°(0\ K) = -285.48 \pm 21\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -284.51 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = 0.302\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 0.157\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

D'Orazio and Wood[1] measured the enthalpy of solution, $\Delta_{sln} H°(25°C) = -13.0 \pm 0.4\ kcal \cdot mol^{-1}$ for KO_2(cr) + 1/2 H_2O(l). KOH(aq, 12,000 H_2O) + 3/4 O_2(g) which leads to $\Delta_f H°(KO_2, cr, 298.15\ K) = -68.09 \pm 0.4\ kcal \cdot mol^{-1}$, using the following auxiliary data. $\Delta_f H°$(KOHaq, 12,000 H_2O, 298.15 K) = −115.243 kcal·mol^{-1} [2] and $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal \cdot mol^{-1}$.[3] Giles and Margrave[4] also measured the enthalpy of solution as $-13.2 \pm 0.8\ kcal \cdot mol^{-1}$ from which we obtain $\Delta_f H°(KO_2, cr, 298.15\ K) = -67.88 \pm 0.8\ kcal \cdot mol^{-1}$. Both $\Delta_{sol} H°$ values have been corrected for impurites present in their samples. The value $\Delta_f H°(KO_2, cr, 298.15\ K) = -68.0 \pm 0.5\ kcal \cdot mol^{-1}$ is adopted in the tabulation.

Kazarnovskaya and Kazarnovskii[5] and deForcrand[6] determined the enthalpy of solution in H_2SO_4(aq) and derived the heat of formation of KO_2(cr) as $-67.9\ kcal \cdot mol^{-1}$ and $-66.8\ kcal \cdot mol^{-1}$, respectively. The former is reliable since their sample was well characterized and corrections for the impurities were included in the $\Delta_{sln} H°$ data.[5] The latter did not give enough experimental details to check their derivation.

Heat Capacity and Entropy

The low temperature heat capacities in the temperature range from 52 298 K are obtained from Todd's measurements.[7] Two peaks at 193.5 K and 230.9 K were found in his heat capacity data. Below 50 K, the heat capacities were extrapolated using a combination of 1 Debye (θ = 139) and 2 Einstein (θ = 260) functions as suggested by Todd. This extrapolation yields the entropy from lattice contribution as 3.278 $cal \cdot K^{-1} \cdot mol^{-1}$ at 50 K. By neutron diffraction, Smith *et al.*[8] found an antiferromagnetic transition at 7 K which indicates the existence of an unpaired electron in KO_2(cr). We tentatively adopt $S°(50\ K) = 4.656 \pm 1\ cal \cdot K^{-1} \cdot mol^{-1}$ which includes both lattice (3.278 $cal \cdot K^{-1} \cdot mol^{-1}$) and unpaired electron (Rln2) contributions. Heat capacities above 298 K are estimated graphically.

The entropy at 298 K is calculated from the $C_p°$ data and is based on an extrapolation of $S°(50\ K) = 4.656\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

Todd[7] observed two anomalies in the heat capacity at 193.5 and 230.9 K which are adopted as two phase transitions in the tabulation. The heats of transition are calculated from the total heats of absorption given by Todd between 180 and 208 K for transition 1 and 217–240 K for transition 2 with extrapolated $C_p°$ below 176 K and above 250 K.

Smith *et al.*[8] confirmed these two transitions in the neutron diffraction measurements. In addition, they found an antiferromagnetic transition at 7.1 ± 0.5 K and an unusually low temperature phase transition at 12 K. Neuman[9] observed a color change at 75.7 ± 15°C in the warming and cooling curves for KO_2(cr). This color change represents a phase transition which is in good agreement with Todd's observation.

Fusion Data

Firsova *et al.*[10] studied the thermograms of KO_2(cr) and found the melting point 509 ± 20°C under atmospheric pressure which is adopted in the tabulation. Earlier melting point data were reported as 380°C by Bluemental[11] and 440°C by deForcrand.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.734	−285.480	−285.480	INFINITE
100	52.400	46.225	188.849	−14.262	−287.646	−271.377	141.753
200	69.454	92.567	129.436	−7.374	−286.263	−255.381	66.699
298.15	77.530	122.499	122.499	0.	−284.512	−240.589	42.150
300	77.613	122.979	122.500	0.144	−284.478	−240.316	41.843
400	83.889	146.226	125.627	8.240	−284.831	−225.443	29.440
500	87.655	165.373	131.719	16.827	−282.410	−210.868	22.029
600	90.165	181.588	138.714	25.724	−279.712	−196.810	17.134
700	91.922	195.625	145.864	34.833	−276.854	−183.217	13.672
800	93.220	207.987	152.872	44.092	−273.908	−170.041	11.103
900	94.224	219.028	159.620	53.467	−270.921	−157.237	9.126
1000	94.893	228.992	166.067	62.924	−267.939	−144.765	7.562
1100	95.395	238.061	172.206	72.440	−343.951	−127.980	6.077
1200	95.730	246.376	178.045	81.997	−340.021	−108.520	4.724
1300	95.981	254.049	183.600	91.583	−336.097	−89.388	3.592
1400	96.148	261.169	188.890	101.191	−332.182	−70.557	2.633
1500	96.232	267.806	193.932	110.810	−328.284	−52.006	1.811

PREVIOUS: June 1962 CURRENT: June 1971

D_0° = 53.48 ± 1.20 kJ·mol^{-1} (natural abundance)
$S°$(298.15 K) = 249.690 ± 0.042 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 127.11 ± 2.0 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = 123.68 ± 2.0 kJ·mol^{-1}

Spectroscopic Data for $^{39}K_2$ (Ground State: $^1\Sigma_g^+$) in cm^{-1}

ω_e = 92.021	$\omega_e x_e$ = 0.2829	$\omega_e y_e$ = −2.055 × 10
B_e = 0.056743	α_e = 1.65 × 10^{-4} (a)	
D_e = 8.63 × 10^{-8}	r_e = 3.9051 Å	

(a) − 7.2 × 10^{-6} (v + 1/2)^2 + 1.5 × 10^{-7} (v + 1/2).[3]

Enthalpy of Formation

Using the adopted value of the dissociation energy for natural abundance K_2(g), D_0° = 53.477 kJ·mol^{-1} [D_0° for $^{39}K_2$ = 53.474 kJ·mol^{-1} as determined by Tango *et al.*[2]], and the recommended $\Delta_f H°$(K, g, 0 K) = 90.14 kJ·mol^{-1} from NBS,[4] we calculate $\Delta_f H°$(K_2, g, 0 K) = 126.80 kJ·mol^{-1}. Since this value is only 0.31 kJ·mol^{-1} smaller than the NBS recommended value of 127.1 kJ·mol^{-1}, we adopt the NBS result. Correcting this value to 298.15 K using the current $H°$(298.15 K)−$H°$(0 K) = 1.0738 kJ·mol^{-1} for K_2(g) and the NBS value of $H°$(298.15 K)−$H°$(0 K) = 7.092 kJ·mol^{-1} for K(cr),[4] we obtain $\Delta_f H°$(K_2, g, 298.15 K) = 123.68 kJ·mol^{-1}.

Heat Capacity and Entropy

The heat capacity and entropy were calculated using a direct summation technique similar to the Li_2(g) species (see Li_2(g) table) using data given above.[1,2] Since insufficient spectroscopic data exist for the lower lying excited electronic states, weperformed the calculation in the ground state only. Based on the results of Li_2 and Na_2, we expect that the neglect of these excited states results in only ca. 1–2% lower free energy functions near 6000 K. The heat capacity, however, above 2000 K will be seriously deficient. The actual C_p will probably exhibit temperature dependence similar to that calculated for Li_2 and Na_2. Likewise, the actual entropy will be somewhat larger than given here but these effects will not manifest themselves at temperatures less than ca. 3000 K (for Na_2(g) the entropy of the ground state only at 3000 K is only 1.3 J·K^{-1} less than that calculated including the excited states). Separate calculations were performed on the isotopic species $^{39}K_2$, $^{41}K_2$, and $^{39}K^{41}K$ and the results combined according to the natural atomic isotopic abundances[3]: ^{39}K, 93.258%; ^{41}K, 6.730% (the diatomic species $^{40}K_2$ was neglected due to the small isotopic abundance of .011%). The spectroscopic input data for the calculation of the isotopic species were calculated from the $^{39}K_2$(g) data using mass reduced scaling. The rotational levels were weighted according to the nuclear spins of the individual atoms (^{39}K, I=3/2; ^{41}K, I=4) as follows: $^{39}K_2$, even J weight = 0.625, odd J weight = 0.375; $^{41}K_2$, even J weight = 0.556, odd J weight = 0.444. The adopted value of $S°$(298.15 K) is only 0.15 J·K^{-1}·mol^{-1} lower than that adopted by NBS.[4]

References

[1]W. C. Stwalley, Director: Iowa Laser Facility and Professor of Chemistry and Physics, University of Iowa, personal communication, (1982).
[2]W. J. Tango, J. K. Link and R. N. Zare, J. Chem. Phys. **49**, 4264 (1968).
[3]Pure Appl. Chem. **47**, 75 (1976).
[4]D. D. Wagman, *et al.*, J. Phys. Chem. Ref. Data **11**, Supp. 2 (1982).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.738	127.110	127.110	INFINITE
100	36.488	208.920	283.115	−7.420	126.963	113.192	−59.125
200	37.533	234.619	253.150	−3.706	125.488	99.961	−26.107
298.15	37.962	249.690	249.690	0.	123.683	87.801	−15.382
300	37.969	249.925	249.691	0.070	123.644	87.579	−15.249
400	38.347	260.900	251.185	3.886	116.504	76.804	−10.030
500	38.698	269.496	254.018	7.739	114.141	67.157	−7.016
600	38.895	276.572	257.204	11.621	111.944	57.968	−5.047
700	38.769	282.563	260.411	15.507	109.838	49.139	−3.667
800	38.242	287.710	263.509	19.361	107.738	40.611	−2.652
900	37.358	292.167	266.452	23.143	105.556	32.350	−1.878
1000	36.231	296.046	269.222	26.824	103.211	24.340	−1.271
1100	34.982	299.441	271.817	30.386	−57.265	25.795	−1.225
1200	33.710	302.430	274.247	33.820	−57.988	33.377	−1.453
1300	32.482	305.079	276.519	37.129	−58.837	41.024	−1.648
1400	31.337	307.444	278.644	40.319	−59.805	48.742	−1.819
1500	30.292	309.570	280.637	43.400	−60.884	56.532	−1.969
1600	29.352	311.494	282.506	46.381	−62.064	64.397	−2.102
1700	28.514	313.248	284.264	49.274	−63.336	72.339	−2.223
1800	27.771	314.856	285.919	52.087	−64.693	80.359	−2.332
1900	27.114	316.340	287.482	54.831	−66.127	88.456	−2.432
2000	26.533	317.716	288.960	57.512	−67.634	96.631	−2.524
2100	26.020	318.998	290.360	60.140	−69.209	104.883	−2.609
2200	25.566	320.197	291.689	62.718	−70.851	113.211	−2.688
2300	25.162	321.325	292.953	65.254	−72.559	121.616	−2.762
2400	24.804	322.388	294.158	67.752	−74.332	130.096	−2.831
2500	24.485	323.394	295.307	70.217	−76.171	138.651	−2.897
2600	24.199	324.348	296.406	72.651	−78.078	147.282	−2.959
2700	23.944	325.257	297.458	75.057	−80.055	155.986	−3.018
2800	23.715	326.124	298.466	77.440	−82.107	164.766	−3.074
2900	23.508	326.952	299.434	79.801	−84.237	173.621	−3.127
3000	23.321	327.746	300.365	82.143	−86.449	182.549	−3.178
3100	23.153	328.508	301.261	84.466	−88.749	191.553	−3.228
3200	22.999	329.240	302.124	86.774	−91.142	200.633	−3.275
3300	22.860	329.946	302.956	89.066	−93.617	209.788	−3.321
3400	22.733	330.626	303.760	91.346	−96.209	219.021	−3.365
3500	22.617	331.284	304.537	93.613	−98.907	228.331	−3.408
3600	22.510	331.919	305.289	95.870	−101.727	237.720	−3.449
3700	22.412	332.535	306.017	98.116	−104.674	247.189	−3.490
3800	22.322	333.131	306.723	100.352	−107.755	256.740	−3.529
3900	22.240	333.710	307.407	102.580	−110.980	266.375	−3.568
4000	22.163	334.272	308.072	104.801	−114.344	276.091	−3.605
4100	22.092	334.818	308.718	107.013	−117.870	285.896	−3.642
4200	22.026	335.350	309.345	109.219	−121.572	295.788	−3.679
4300	21.966	335.868	309.956	111.419	−125.452	305.769	−3.714
4400	21.909	336.372	310.551	113.612	−128.965	315.791	−3.749
4500	21.856	336.864	311.130	115.801	−133.091	325.944	−3.783
4600	21.807	337.343	311.695	117.984	−137.397	336.192	−3.818
4700	21.761	337.812	312.245	120.162	−141.847	346.532	−3.851
4800	21.718	338.270	312.783	122.336	−146.267	356.944	−3.884
4900	21.677	338.717	313.308	124.506	−151.081	367.477	−3.917
5000	21.640	339.155	313.820	126.672	−156.086	378.110	−3.950
5100	21.604	339.583	314.321	128.834	−161.281	388.847	−3.983
5200	21.571	340.002	314.811	130.993	−166.670	399.684	−4.015
5300	21.539	340.412	315.290	133.148	−172.252	410.629	−4.047
5400	21.510	340.815	315.759	135.301	−178.027	421.681	−4.079
5500	21.482	341.209	316.218	137.450	−183.994	432.841	−4.111
5600	21.456	341.596	316.668	139.597	−190.151	444.111	−4.142
5700	21.431	341.976	317.109	141.741	−195.805	455.399	−4.173
5800	21.407	342.348	317.541	143.883	−202.245	466.878	−4.205
5900	21.385	342.714	317.964	146.023	−208.856	478.472	−4.236
6000	21.364	343.073	318.380	148.160	−215.634	490.178	−4.267

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

Potassium Oxide (K_2O) CRYSTAL M_r = 94.1960

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [94.14 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -363.17 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was reported by Rengade[1] based on the measurements of the enthalpy of solution of K(cr) and K_2O(cr) in H_2O. The same value of $\Delta_f H°(298.15\ K)$ was also given by de Forcrand.[2]

Heat Capacity and Entropy

Both $C_p°$ and $S°(298.15\ K)$ were estimated by comparison with those of the Na_2O(cr).

Decomposition Data

T_{dcm} = 1154 K(600mmHg) was taken from NRC Bulletin.[3]

References

[1]M. Rengade, Ann. Chim. et phys. [8] **14**, 540 (1908).
[2]R. de Forcrand, Compt. rend. **158**, 991 (1914).
[3]"Data on Chemicals for Ceramic Use," National Research Council Bulletin 118 (1949).

Potassium Oxide (K_2O) K_2O_1(cr)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	83.680	94.140	94.140	0.	−363.171	−322.094	56.429
300	83.889	94.658	94.142	0.155	−363.153	−321.839	56.037
400	91.546	119.958	97.539	8.968	−366.782	−307.331	40.133
500	94.266	140.671	104.161	18.255	−365.240	−292.638	30.572
600	97.404	158.126	111.736	27.834	−363.320	−278.292	24.227
700	101.384	173.439	119.478	37.773	−361.000	−264.299	19.722
800	105.395	187.239	127.099	48.111	−358.283	−250.665	16.367
900	109.455	199.887	134.494	58.854	−355.209	−237.394	13.778
1000	113.512	211.629	141.627	70.002	−351.817	−224.482	11.726
1100	117.549	222.637	148.496	81.555	−506.056	−202.704	9.626
1200	121.592	233.038	155.112	93.512	−500.031	−175.390	7.635
1300	125.642	242.931	161.489	105.874	−493.618	−148.594	5.971
1400	129.699	252.390	167.647	118.641	−486.816	−122.306	4.563
1500	133.762	261.477	173.601	131.814	−479.623	−96.519	3.361
1600	137.833	270.240	179.369	145.394	−472.038	−71.223	2.325
1700	141.910	278.718	184.965	159.381	−464.062	−46.415	1.426
1800	145.993	286.945	190.403	173.776	−455.695	−22.087	0.641
1900	150.083	294.948	195.696	188.580	−446.939	1.766	−0.049
2000	154.180	302.751	200.854	203.793	−437.796	25.147	−0.657

PREVIOUS: CURRENT: June 1963

Potassium Oxide (K_2O) K_2O_1(cr)

$S°(298.15\ K) = [112.968 \pm 6.3]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 763$ K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = [495.80 \pm 4.2]$ kJ·mol^{-1}
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was reported by NBS.[1] The value was based on the measured decomposition pressure of K_2O_2(cr) by Centnerzwer and Blumenthal.[2]

Heat Capacity and Entropy

The heat capacities and $S°(298.15\ K)$ were estimated by comparison with those for Na_2O_2(cr), Na_2O(cr), and K_2O(cr).

Fusion Data

T_{fus} was reported by Centnerzwer and Blumenthal.[2]

References

[1]D. D. Wagman, U. S. Nat. Bur. Stand., Report 7437, Table 4, Chap. B4, p 95, (January 1, 1962).
[2]M. Centnerzwer and M. Blumenthal, IX Congr. IUPAC, **3A**, 201 (1935).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	100.165	112.968	112.968	0.	−495.804	−429.758	75.292
300	100.374	113.588	112.970	0.185	−495.782	−429.348	74.756
400	107.110	143.348	116.982	10.546	−499.349	−406.479	53.081
500	115.478	168.206	124.802	21.702	−497.468	−383.461	40.060
600	120.708	189.704	133.869	33.501	−494.907	−360.891	31.418
700	127.952	208.862	143.236	45.938	−491.716	−338.798	25.281
800	134.725	226.395	152.550	59.076	−487.870	−317.208	20.712
900	140.798	242.614	161.667	72.852	−483.464	−296.134	17.187
1000	146.858	257.762	170.527	87.235	−478.569	−275.578	14.395
1100	152.917	272.043	179.112	102.224	−631.126	−246.314	11.696
1200	158.959	285.608	187.426	117.818	−623.239	−211.675	9.214
1300	164.983	298.569	195.481	134.015	−614.782	−177.717	7.141
1400	170.992	311.016	203.292	150.814	−605.755	−144.431	5.389
1500	176.983	323.018	210.876	168.213	−596.156	−111.812	3.894
1600	182.958	334.631	218.249	186.210	−585.988	−79.850	2.607
1700	188.916	345.901	225.428	204.804	−575.251	−48.542	1.492
1800	194.857	356.868	232.427	223.993	−563.948	−17.883	0.519
1900	200.782	367.562	239.259	243.775	−552.083	12.133	−0.334
2000	206.690	378.011	245.937	264.148	−539.660	41.509	−1.084

PREVIOUS: June 1963 CURRENT: September 1963

$S°(298.15\ K) = 146.147 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1249\ K$

$\Delta_f H°(0\ K) = -1539.54 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1548.08 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [50.208 \pm 12.6]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Hatton *et al.*[1] conducted enthalpy of solution measurements on K_2SiO_3(cr) and KOH(cr) in HF(aq) at 50°C to determine the enthalpy of formation of the silicate. The results of this work gave a $\Delta_r H°(298.15\ K) = -17.5 \pm 0.5\ kcal \cdot mol^{-1}$ for the process 2 KOH(cr) + SiO_2(cr, quartz) → K_2SiO_3(cr) + H_2O(l). When combined with the auxiliary data for H_2O(l) KOH(cr) and SiO_2(cr),[2,3] we calculate $\Delta_f H°(K_2SiO_3, cr, 298.15\ K) = -369.9 \pm 1\ kcal \cdot mol^{-1}$.

Urusov[4] summarized the various methods of estimating the enthalpies of formation of silicates using the Born Haber cycle and energies of atomization. His estimate for $\Delta_f H°(K_2SiO_3, cr, 298.15\ K)$ is $-369\ kcal \cdot mol^{-1}$.

An earlier estimate by Wilcox and Bromley[5] based upon ionic contributions to crystal lattice energies gave $\Delta_f H°(K_2SiO_3, cr, 298.15\ K) = -367 \pm 15\ kcal \cdot mol^{-1}$.

An attempt to calculate the $\Delta_f H°(K_2SiO_3, cr, 298.15\ K)$ from HF solution experiments on higher potassium silicates ($K_2Si_2O_5$, $K_2Si_3O_7$) and sodium silicates[6] yielded a value of $-383.8\ kcal \cdot mol^{-1}$ which is discrepant with the former values.

A value for $\Delta_f H°(K_2SiO_3, cr, 298.15\ K) = -370 \pm 2\ kcal \cdot mol^{-1}$ has been selected.

Heat Capacity and Entropy

The low temperature heat capacity of K_2SiO_3(cr) has been measured and reported by Stull *et al.*[7] in the range 15 298 K. They report $S°(298.15\ K) = 34.93\ cal \cdot K^{-1} \cdot mol^{-1}$ which is derived from $C_p°$ and an extrapolation of $S°(15\ K) = 0.18\ cal\ k^{-1} \cdot mol^{-1}$.

Heat capacities above 298.15 K have been estimated by analogy with other alkali metal silicates and borates.

Fusion Data

A melting temperature of 1249 K for K_2SiO_3 was measured by Morey and Bowen.[8] The enthalpy of fusion, $\Delta_{fus} H° = 12 \pm 3\ kcal \cdot mol^{-1}$, was estimated by comparison with other silicates.

References

[1]W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, unpublished data, The Dow Chemical Company, Midland, MI (1959).
[2]U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[3]JANAF Thermochemical Tables: KOH(cr), 12–31–70; SiO_2(cr), 6–30–67.
[4]V. S. Urusov, Geokhimiya, No. 5, 551 (1965).
[5]D. E. Wilcox and L. A. Bromley, Ind. Eng. Chem. **55**, No. 7, 32 (1963).
[6]G. W. Morey, Geophysical Laboratory, Carnegie Institute of Washington, Paper No. 1215 (1952–1953).
[7]D. R. Stull, D. L. Hildenbrand, F. L. Oetting and G. C. Sinke, J. Chem. Eng. Data **15**, 15 (1970).
[8]G. W. Morey and H. L. Bowen, J. Phys. Chem. **28**, 1167 (1924).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.870	−1539.542	−1539.542	INFINITE
100	63.262	46.944	236.438	−18.949	−1544.710	−1515.904	791.827
200	98.198	103.052	156.335	−10.657	−1547.151	−1485.986	388.100
298.15	118.407	146.147	146.147	0.	−1548.080	−1455.733	255.038
300	118.758	146.881	146.149	0.219	−1548.089	−1455.160	253.366
400	135.562	183.448	151.021	12.971	−1552.872	−1423.255	185.858
500	148.114	215.101	160.743	27.179	−1551.745	−1390.957	145.312
600	157.737	242.994	172.173	42.492	−1549.626	−1358.985	118.310
700	164.850	267.859	184.099	58.632	−1546.808	−1327.426	99.054
800	170.707	290.268	195.992	75.420	−1543.488	−1296.307	84.640
900	175.310	310.648	207.617	92.728	−1539.816	−1265.627	73.455
1000	179.075	329.321	218.867	110.455	−1535.919	−1235.369	64.529
1100	182.004	346.523	229.700	128.505	−1689.825	−1196.287	56.807
1200	185.351	362.515	240.110	146.887	−1683.623	−1151.692	50.132
1249.000	186 .376	369.955	245.059	155.996	--- CRYSTAL <--> LIQUID ---		
1300	187.443	377.434	250.106	165.526	−1677.256	−1107.622	44.505
1400	189.535	391.401	259.705	184.375	−1670.768	−1064.047	39.700
1500	191.627	404.549	268.927	203.434	−1664.155	−1020.940	35.552
1600	193.719	416.983	277.795	222.701	−1657.416	−978.278	31.937
1700	195.811	428.790	286.333	242.177	−1700.727	−935.594	28.747
1800	197.903	440.042	294.562	261.863	−1693.505	−890.795	25.850
1900	199.995	450.798	302.504	281.758	−1686.116	−846.400	23.269
2000	202.087	461.110	310.179	301.862	−1678.564	−802.399	20.957
2100	204.179	471.020	317.603	322.175	−1670.852	−758.780	18.874
2200	206.271	480.567	324.795	342.698	−1662.982	−715.531	16.989

PREVIOUS: CURRENT: June 1972

$S°(298.15\ K)$ = [184.256] $J·K^{-1}·mol^{-1}$
T_{fus} = 1249 K

$\Delta_f H°(298.15\ K)$ = [−1499.290] $kJ·mol^{-1}$
$\Delta_{fus}H°$[50.208 ± 12.6] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(K_2SiO_3, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1249\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of K_2SiO_3(l) has been estimated. A constant $C_p°$ of 43 $cal·K^{-1}·mol^{-1}$ for K_2SiO_3(l) was selected above a hypothetical glass transition temperature of 700 K. Below this temperature the heat capacity was taken as that of the crystal. $S°(K_2SiO_3, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	118.407	184.256	184.256	0.	−1499.291	−1418.306	248.481
300	118.758	184.990	184.259	0.219	−1499.299	−1417.803	246.861
400	135.562	221.557	189.130	12.971	−1504.082	−1389.709	181.477
500	148.114	253.210	198.852	27.179	−1502.956	−1361.222	142.206
600	157.737	281.103	210.282	42.492	−1500.837	−1333.061	116.053
700	164.850	305.985	222.209	58.643	−1498.008	−1305.314	97.404
700.000	164.850	305.985	222.209	58.643	GLASS <- -> LIQUID		
700.000	179.912	305.985	222.209	58.643	TRANSITION		
800	179.912	330.008	234.216	76.634	−1493.485	−1278.097	83.451
900	179.912	351.199	246.060	94.625	−1489.129	−1251.437	72.632
1000	179.912	370.155	257.538	112.616	−1484.968	−1225.251	64.001
1100	179.912	387.302	268.568	130.607	−1638.934	−1190.252	56.520
1200	179.912	402.956	279.124	148.599	−1633.122	−1149.720	50.046
1249.000	179.912	410.154	284.121	157.414	--- CRYSTAL <- -> LIQUID ---		
1300	179.912	417.357	289.211	166.590	−1627.403	−1109.670	44.587
1400	179.912	430.690	298.846	184.581	−1621.773	−1070.056	39.924
1500	179.912	443.103	308.055	202.572	−1616.227	−1030.842	35.897
1600	179.912	454.714	316.862	220.563	−1610.764	−991.994	32.385
1700	179.912	465.621	325.295	238.555	−1655.560	−953.040	29.283
1800	179.912	475.905	333.379	256.546	−1650.032	−911.875	26.462
1900	179.912	485.632	341.139	274.537	−1644.548	−871.016	23.946
2000	179.912	494.860	348.596	292.528	−1639.109	−830.445	21.689
2100	179.912	503.638	355.772	310.519	−1633.718	−790.144	19.654
2200	179.912	512.008	362.685	328.511	−1628.380	−750.098	17.810
2300	179.912	520.005	369.352	346.502	−1623.098	−710.296	16.131
2400	179.912	527.662	375.790	364.493	−1617.876	−670.721	14.598
2500	179.912	535.006	382.013	382.484	−1612.720	−631.363	13.192
2600	179.912	542.063	388.034	400.475	−1607.634	−592.209	11.898
2700	179.912	548.853	393.865	418.467	−1602.623	−553.249	10.703
2800	179.912	555.396	399.518	436.458	−1597.692	−514.474	9.598
2900	179.912	561.709	405.002	454.449	−1592.847	−475.874	8.571
3000	179.912	567.808	410.328	472.440	−1588.095	−437.438	7.616

PREVIOUS: CURRENT: June 1972

0 to 1249 K crystal
above 1249 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.870	−1539.542	−1539.542	INFINITE
100	63.262	46.944	236.438	−18.949	−1544.710	−1515.904	791.827
200	98.198	103.052	156.335	−10.657	−1547.151	−1485.986	388.100
298.15	118.407	146.147	146.147	0.	−1548.080	−1455.733	255.038
300	118.758	146.881	146.149	0.219	−1548.089	−1455.160	253.366
400	135.562	183.448	151.021	12.971	−1552.872	−1423.255	185.858
500	148.114	215.101	160.743	27.179	−1551.745	−1390.957	145.312
600	157.737	242.994	172.173	42.492	−1549.626	−1358.985	118.310
700	164.850	267.859	184.099	58.632	−1546.808	−1327.426	99.054
800	170.707	290.268	195.992	75.420	−1543.488	−1296.307	84.640
900	175.310	310.648	207.617	92.728	−1539.816	−1265.627	73.455
1000	179.075	329.321	218.867	110.455	−1535.919	−1235.369	64.529
1100	182.004	346.523	229.700	128.505	−1689.825	−1196.287	56.807
1200	185.351	362.515	240.110	146.887	−1683.623	−1151.692	50.132
1249.000	186.376	369.955	245.059	155.996	CRYSTAL <--> LIQUID TRANSITION		
1249.000	179.912	410.154	245.059	206.204			
1300	179.912	417.354	251.677	215.379	−1627.403	−1109.665	44.587
1400	179.912	430.687	263.994	233.370	−1621.773	−1070.051	39.924
1500	179.912	443.099	275.525	251.362	−1616.227	−1030.837	35.897
1600	179.912	454.711	286.365	269.353	−1610.764	−991.989	32.385
1700	179.912	465.618	296.592	287.344	−1655.560	−953.034	29.283
1800	179.912	475.901	306.271	305.335	−1650.032	−911.869	26.462
1900	179.912	485.629	315.457	323.326	−1644.548	−871.010	23.946
2000	179.912	494.857	324.198	341.318	−1639.109	−830.438	21.689
2100	179.912	503.635	332.535	359.309	−1633.718	−790.137	19.654
2200	179.912	512.004	340.504	377.300	−1628.380	−750.091	17.809
2300	179.912	520.002	348.136	395.291	−1623.098	−710.288	16.131
2400	179.912	527.659	355.458	413.282	−1617.876	−670.713	14.598
2500	179.912	535.003	362.494	431.274	−1612.720	−631.354	13.191
2600	179.912	542.059	369.265	449.265	−1607.634	−592.200	11.897
2700	179.912	548.849	375.791	467.256	−1602.623	−553.240	10.703
2800	179.912	555.392	382.090	485.247	−1597.692	−514.464	9.597
2900	179.912	561.706	388.175	503.238	−1592.847	−475.865	8.571
3000	179.912	567.805	394.062	521.230	−1588.095	−437.429	7.616

PREVIOUS: CURRENT: June 1972

$S°(298.15\ K) = 175.544 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 857 \pm 1\ K$

$\Delta_f H°(0\ K) = -1427.20 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1437.71 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(\alpha \rightarrow \beta) = 8.452 \pm 0.418\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Shibata *et al.*[1] measured the emf of the cell: K (amalgam, 0.2201%)|K_2SO_4(sat. soln.), Hg_2SO_4|Hg at 298 303 K. From their results at 298 K, correcting the observed voltage for the formation of the K–amalgam, and converting to absolute volts, we have $E_{cell} = 3.59172$ volts for the reaction at 298 K, 2 K(cr) + Hg_2SO_4(cr) = 2 Hg(l) + K_2SO_4(cr). From this voltage, we calculate $\Delta_r G°(298.15\ K) = -165.656\ kcal \cdot mol^{-1}$. Taking $\Delta_f G°(Hg_2SO_4,\ cr,\ 298.15\ K) = -149.658\ kcal \cdot mol^{-1}$ [2] and reference entropies from,[3] we calculate $\Delta_f G°(K_2SO_4,\ cr,\ 298.15\ K) = -315.314\ kcal \cdot mol^{-1}$ and $\Delta_f H°(K_2SO_4,\ cr,\ 298.15\ K) = -343.525 \pm 0.2\ kcal \cdot mol^{-1}$.

The enthalpy of solution at infinite dilution, $\Delta_{sol} H°(K_2SO_4,\ cr,\ 298.15\ K) = 5.677 \pm 0.020\ kcal \cdot mol^{-1}$, adopted in this tabulation is based on our reanalysis of the enthalpy of solution measurements of Mishchenko and Pronina,[4] Tsvetkov and Rabinovich,[5] Romanova and Samoilov,[6] Cohen and Kooy,[7] Bronsted,[8] Samilov *et al.*,[9] and Gritsus *et al.*[10] Enthalpies of dilution are taken from Lange and Streeck.[11] When this result is combined with enthalpy of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(K_2SO_4,\ aq,\ \infty,\ 298.15\ K) = -337.940 \pm 0.10\ kcal \cdot mol^{-1}$ and $\Delta_f H°(K_2SO_4,\ cr,\ 298.15\ K) = -343.617 \pm 0.10\ kcal \cdot mol^{-1}$.

The solubility of K_2SO_4(cr) in water at 298 K has been measured by many workers.[4,12,14–16] When the solubility of 0.6919 molal is combined with the activity coefficient data of Stokes,[13] we obtain $\Delta_r G°(298.15\ K) = 2423 \pm 20\ cal \cdot mol^{-1}$ for the reaction K_2SO_4(cr) = 2 K^+(aq, ∞) + $SO_4^{\ 2}$(aq, ∞). When this result is combined with enthalpies of formation and entropies from,[3] we obtain $\Delta_f H°(K_2SO_4,\ cr,\ 298.15\ K) = 343.595 \pm 0.2\ kcal \cdot mol^{-1}$.

We adopt the value of $\Delta_f H°(298.15\ K)$ obtained from the enthalpy of solution measurements.

Heat Capacity and Entropy

Low temperature heat capacities of K_2SO_4(cr, α) have been measured by Moore and Kelley[17] from 52.7–295.4 K and by Paukov[18] from 12.5–299.5 K. The heat capacities reported by Moore and Kelley are systematically lower by about 0.5% than those of Paukov. Our adopted value of $S°(298.15\ K) = 41.956 \pm 0.2\ cal \cdot K^{-1} \cdot mol^{-1}$ is based on $S°(12.5\ K) = 0.068\ cal \cdot K^{-1} \cdot mol^{-1}$ [18] and $H°(12.5\ K) - H°(0\ K) = 0.640\ cal \cdot K^{-1} \cdot mol^{-1}$ derived from a Debye T^3 law extrapolation.

Heat capacity data measured by adiabatic calorimetry in the range 298.5–773.7 K have been reportd by Shmidt.[19] In addition, drop calorimetric measurements have been reported by the following workers; Shomate and Naylor,[20] Dworkin and Bredig,[21] Denielou *et al.*,[22] and Rubinchik *et al.*[23] The heat capacity and enthalpy curves between 298 K and 857 K are obtained by orthogonal polynomial curve fitting of all the data listed above. These data are in good agreement.

Transition Data

K_2SO_4(cr, α) is the low temperature form (sometimes denoted as K_2SO_4, II). The mineral is known as arcanite and exists in the form of orthorhombic crystals (space group D^{16h} –Pnma).[24] The orthorhombic–to–hexagonal transition temperature for K_2SO_4 is selected as 857 ± 1 K from the calorimetric work of Dworkin and Bredig[21] and Rubinchik *et al.*[23] and the polymorphism study of Pistorius and Rapoport.[25] The enthalpy of transition is determined by taking the difference between the adopted enthalpy curves of α and β–K_2SO_4 extrapolated to 857 K.

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Continued on page 1489

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−25.436	−1427.199	−1427.199	INFINITE
100	79.195	61.609	277.387	−21.578	−1433.305	−1396.431	729.421
200	110.667	127.344	186.920	−11.915	−1436.295	−1358.245	354.737
298.15	131.319	175.544	175.544	0.	−1437.706	−1319.595	231.188
300	131.666	176.357	175.546	0.243	−1437.723	−1318.862	229.634
400	147.649	216.494	180.911	14.233	−1445.229	−1278.152	166.909
500	160.733	250.870	191.544	29.663	−1446.060	−1236.272	129.153
600	172.527	281.186	204.005	46.309	−1445.397	−1194.353	103.978
700	186.368	308.829	217.031	64.259	−1443.295	−1152.659	86.012
800	199.619	334.580	230.132	83.558	−1439.835	−1111.361	72.564
857.000	207.169	348.575	237.547	95.151	--- ALPHA <--> BETA -----		
900	212.865	358.856	243.098	104.182	−1488.244	−1069.491	62.072
1000	226.116	381.969	255.838	126.131	−1481.100	−1023.335	53.454
1100	239.365	404.142	268.319	149.405	−1630.753	−968.729	46.001
1200	252.613	425.538	280.534	174.004	−1619.296	−909.041	39.570

PREVIOUS: December 1971 CURRENT: June 1978

$S°(298.15\ K) = [192.279]\ J\ K^{-1}\cdot mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 857 \pm 1\ K$
$T_{fus}H°(\beta \rightarrow l) = 1342 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1424.243]\ kJ\cdot mol^{-1}$
$\Delta_{trs}H°(\alpha \rightarrow \beta) = 8.452 \pm 0.418\ kJ\cdot mol^{-1}$
$\Delta_{fus}H°(\beta \rightarrow l) = 34.392\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(K_2SO_4, cr, \beta, 298.15\ K)$ is calculated from $\Delta_f H°(K_2SO_4, cr, \alpha, 298.15\ K)$ by adding the enthalpy of transition ($\alpha \rightarrow \beta$), $\Delta_{trs}H°$, and the difference in enthalpy, $H°(857\ K)–H°(298.15\ K)$, between the alpha and beta crystalline forms.[1]

Heat Capacity and Entropy

High temperature enthalpy measurements by drop calorimetry were carried out by Shomate and Naylor,[2] 872.4–1258.8 K), Rubinchik *et al.*,[3] 859.0–1340.7 K) Dworkin and Bredig,[4] 868.5–979.9 K), and Denielou *et al.*,[5] 864–1300 K). The data of[2] are systematically higher by about 0.5% than the data from.[3–5] $C_p°$ values are derived from the smoothed curves and extrapolated to 298.15 K and 1500 K. $S°(K_2SO_4, \beta, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

The high temperature β–modification of K_2SO_4 is of hexagonal structure, space group D^3_{3d}–P3ml.[6] The transition from the low temperature orthorhombic pseudohexagonal modification occurs at 857 ± 1 K.[1]

Fusion Data

The adopted melting point of 1342 K was determined by Shomate and Naylor[2] and Rubinchik *et al.*[3] The heat of fusion, $\Delta_{fus}H° = 8.220 \pm 0.400\ kcal\cdot mol^{-1}$, is calculated from the difference between the smoothed relative enthalpy of the liquid (refer to the K_2SO_4(l) table) and the adopted enthalpy value for the β–crystalline form at T_{fus}.

References

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[2]C. H. Shomate and B. F. Naylor, J. Amer. Chem. Soc. **67**, 72 (1945).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	138.574	192.279	192.279	0.	−1424.243	−1311.121	229.703
300	138.741	193.137	192.282	0.257	−1424.246	−1310.419	228.164
400	146.858	234.162	197.820	14.537	−1431.462	−1271.452	166.035
500	154.975	267.803	208.548	29.628	−1432.632	−1231.311	128.634
600	163.134	296.781	220.891	45.534	−1432.709	−1191.022	103.688
700	171.251	322.537	233.605	62.253	−1431.838	−1150.797	85.874
800	179.368	345.935	246.205	79.784	−1430.146	−1110.755	72.525
857.000	184.000	358.437	253.257	90.140	--- ALPHA <--> BETA -----		
900	187.485	367.530	258.500	98.127	−1480.836	−1069.890	62.095
1000	195.602	387.703	270.423	117.281	−1476.487	−1024.456	53.512
1100	203.761	406.729	281.957	137.249	−1629.446	−970.268	46.074
1200	211.878	424.807	293.114	158.031	−1621.806	−910.674	39.641
1300	219.995	442.087	303.914	179.625	−1613.438	−851.747	34.224
1342.000	223.384	449.136	308.349	188.936	---- BETA <--> LIQUID -----		
1400	228.112	458.687	314.380	202.030	−1604.337	−793.492	29.606
1500	236.229	474.702	324.537	225.247	−1594.495	−735.914	25.627

PREVIOUS: CURRENT: June 1978

$S°(298.15\ K) = [211.505]\ J·K^{-1}·mol^{-1}$
$T_{fus}(\beta \rightarrow l) = 1342 \pm 1\ K$
$T_{dcm} = 2567\ K$

$\Delta_f H°(298.15\ K) = [-1393.668]\ kJ·mol^{-1}$
$\Delta_{fus}H°(\beta \rightarrow l) = 34.392\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(K_2SO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(K_2SO_4, \beta, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1342\ K)–H°(298.15\ K)$, between the β–crystal and liquid.[1]

Heat Capacity and Entropy

Enthalpies for K_2SO_4(l) have been measured by drop calorimetry by Shomate and Naylor (1358–1698 K),[2] Denielou *et al.* (1350–1550 K),[3] and Rubinchik *et al.* (single point at 1344.84 K).[4] A constant heat capacity of 46.15 $cal·K^{-1}·mol^{-1}$ is selected above a hypothetical glass transition at 800 K. Below the glass transition, the heat capacity is taken as that of the orthorhombic crystal.

$S°(K_2SO_4, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the K_2SO_4(cr, β) table for details.

Vaporization and Decomposition Data

K_2SO_4(l) can vaporize to the gaseous monomer K_2SO_4(g) or decompose according to $K_2SO_4(l) = 2\ K(g) + SO_2(g) + O_2(g)$. Vaporization pressures from the two processes are of comparable magnitude in the vicinity of the melting point.[6] Recent experimental data for vaporization of K_2SO_4(cr)[5,6] are in good agreement with dissociation pressures and the heat of reaction calculated from the JANAF Thermochemical Tables.[1] Molecular vaporization data are discussed on the K_2SO_4(g) table.[1] $T_{vap} = 2975$ K is the calculated temperature at which the Gibbs energy difference is zero for the reaction $K_2SO_4(l) = 2\ K(g) + SO_2(g) + O_2(g)$. Decomposition to the oxides of potassium produces significantly lower decomposition pressures than decomposition to the metal. Significant decomposition can occur in the presence of water vapor according to $K_2SO_4(l) + H_2O(g) = 2\ KOH(g) + SO_2(g) + 1/2\ O_2(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	131.319	211.505	211.505	0.	−1393.668	−1286.278	225.351
300	131.666	212.319	211.508	0.243	−1393.685	−1285.612	223.845
400	147.649	252.455	216.872	14.233	−1401.191	−1248.498	163.037
500	160.733	286.831	227.505	29.663	−1402.022	−1210.215	126.430
600	172.527	317.148	239.966	46.309	−1401.359	−1171.892	102.022
700	186.368	344.790	252.992	64.259	−1399.257	−1133.794	84.605
800	199.619	370.547	266.094	83.563	−1395.792	−1096.092	71.567
800.000	199.619	370.547	266.094	83.563	GLASS <--> LIQUID TRANSITION		
800.000	201.460	370.547	266.094	83.563			
900	201.460	394.276	279.044	103.709	−1444.679	−1057.804	61.393
1000	201.460	415.502	291.647	123.855	−1439.338	−1015.106	53.024
1100	201.460	434.703	303.793	144.001	−1592.120	−963.712	45.763
1200	201.460	452.232	315.443	164.147	−1585.116	−906.894	39.476
1300	201.460	468.358	326.594	184.293	−1578.196	−850.657	34.180
1342.000	201.460	474.763	331.132	192.754	---- BETA <--> LIQUID -----		
1400	201.460	483.287	337.260	204.439	−1571.353	−794.950	29.660
1500	201.460	497.187	347.464	224.585	−1564.582	−739.730	25.760
1600	201.460	510.189	357.232	244.731	−1557.880	−684.958	22.362
1700	201.460	522.402	366.592	264.877	−1551.245	−630.604	19.376
1800	201.460	533.917	375.571	285.022	−1544.678	−576.639	16.734
1900	201.460	544.809	384.195	305.168	−1538.178	−523.036	14.379
2000	201.460	555.143	392.486	325.314	−1531.747	−469.774	12.269
2100	201.460	564.972	400.467	345.460	−1525.387	−416.833	10.368
2200	201.460	574.344	408.159	365.606	−1519.101	−364.191	8.647
2300	201.460	583.299	415.581	385.752	−1512.892	−311.835	7.082
2400	201.460	591.873	422.749	405.898	−1506.763	−259.747	5.653
2500	201.460	600.097	429.680	426.044	−1500.719	−207.913	4.344
2600	201.460	607.999	436.387	446.190	−1494.762	−156.318	3.140
2700	201.460	615.602	442.885	466.336	−1488.898	−104.951	2.030
2800	201.460	622.929	449.185	486.482	−1483.129	−53.799	1.004
2900	201.460	629.998	455.299	506.628	−1477.463	−2.853	0.051
3000	201.460	636.828	461.237	526.774	−1471.903	47.901	−0.834

PREVIOUS: December 1971 CURRENT: June 1978

0	to	857	K	crystal, alpha
857	to	1342	K	crystal, beta
above 1342	to	T_{dem}	K	liquid

Refer to the single phase tables for the alpha, beta, liquid phases for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−25.436	−1427.199	−1427.199	INFINITE
100	79.195	61.609	277.387	−21.578	−1433.305	−1396.431	729.421
200	110.667	127.344	186.920	−11.915	−1436.295	−1358.245	354.737
298.15	131.319	175.544	175.544	0.	−1437.706	−1319.595	231.188
300	131.666	176.357	175.546	0.243	−1437.723	−1318.862	229.634
400	147.649	216.494	180.911	14.233	−1445.229	−1278.152	166.909
500	160.733	250.870	191.544	29.663	−1446.060	−1236.272	129.153
600	172.527	281.186	204.005	46.309	−1445.397	−1194.353	103.978
700	186.368	308.829	217.031	64.259	−1443.295	−1152.659	86.012
800	199.619	334.580	230.132	83.558	−1439.835	−1111.361	72.564
857.000	207.169	348.575	237.547	95.151	ALPHA <--> BETA		
857.000	184.000	358.437	237.547	103.603	TRANSITION		
900	187.485	367.530	243.541	111.590	−1480.836	−1069.890	62.095
1000	195.602	387.703	256.959	130.744	−1476.487	−1024.456	53.512
1100	203.761	406.729	269.718	150.713	−1629.446	−970.268	46.074
1200	211.878	424.807	281.895	171.494	−1621.806	−910.674	39.641
1300	219.995	442.087	293.557	193.089	−1613.438	−851.747	34.224
1342.000	223.384	449.136	298.316	202.400	BETA <--> LIQUID		
1342.000	201.460	474.763	298.316	236.792	TRANSITION		
1400	201.460	483.287	305.804	248.477	−1571.353	−794.950	29.660
1500	201.460	497.187	318.105	268.623	−1564.582	−739.730	25.760
1600	201.460	510.189	329.708	288.769	−1557.880	−684.958	22.362
1700	201.460	522.402	340.688	308.915	−1551.245	−630.604	19.376
1800	201.460	533.917	351.106	329.061	−1544.678	−576.639	16.734
1900	201.460	544.809	361.017	349.207	−1538.178	−523.037	14.379
2000	201.460	555.143	370.467	369.353	−1531.747	−469.774	12.269
2100	201.460	564.972	379.497	389.499	−1525.387	−416.833	10.368
2200	201.460	574.344	388.142	409.644	−1519.101	−364.191	8.647
2300	201.460	583.299	396.434	429.790	−1512.892	−311.835	7.082
2400	201.460	591.873	404.400	449.936	−1506.763	−259.747	5.653
2500	201.460	600.097	412.064	470.082	−1500.719	−207.913	4.344
2600	201.460	607.999	419.449	490.228	−1494.762	−156.318	3.140
2700	201.460	615.602	426.574	510.374	−1488.898	−104.951	2.030
2800	201.460	622.929	433.457	530.520	−1483.129	−53.799	1.004
2900	201.460	629.998	440.113	550.666	−1477.463	−2.853	0.051
3000	201.460	636.828	446.557	570.812	−1471.903	47.901	−0.834

PREVIOUS: CURRENT: June 1978

$S°(298.15\ K) = 366.152 \pm 16.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1080.64 \pm 16.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1094.12 \pm 16.7\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Symmetries, and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
A_1 962 (1)	B_1 [450] (1)	E 1098 (2)
[458](1)	B_2 1124 (1)	613 (2)
[190](1)	639 (1)	[230](2)
	[262](1)	[62](2)

Ground State Quantum Weight: [1] $\sigma = 4$

Point Group: D_{2h}

Bond Distances: S–O = 1.47 Å K–O = 1.45 Å

Bond Angles: O–S–O = 109.47° O–K–O = 58.67°

Product of the Moments of Inertia: $I_A I_B I_C = 2.626307 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value of the enthalpy of formation is based on JANAF analyses of the vaporization data given below. Earlier data on the vaporizaiton of K_2SO_4 is extremely discordant (for a review, refer to reference [10]). Dissociation and other reactions play an important role in K_2SO_4 vaporization (refer to the K_2SO_4(l) table).

Torsion–effusion studies on the vaporization of K_2SO_4(g) by Lau *et al.*[3] showed an orifice dependence which was reproduced in four separate runs. Plante *et al.*[2] did not observe this orifice size dependence in their effusion study, obtaning similar total pressures in two separate experiments. Calculated dissociation pressures were subtracted in both studies to obtain K_2SO_4(g) pressures. Similar results were obtained by Efimova and Gorokhov.[1] We have corrected the effusion data of Kosugi[11] for dissociation. The 3rd law enthalpy of sublimation from the three studies[1–3] are in very good agreement indicating similar $K_2S_2O_4$(g) pressures. The studies of Lau *et al.*[3] and Efimova and Gorokhov[1] yield 2nd law enthalpy of sublimation (from K_2SO_4(cr, β)) some 6 $kcal \cdot mol^{-1}$ greater than our calculated 3rd law enthalpy.

Lau *et al.*[3] and Efimova and Gorokhov[1] also carried out mass spectrometric measurements of the $K_2SO_4^+$ ion intensity as a function of temperature. The 2nd law enthalpy of sublimation of Lau *et al.*[3] obtained in two separate mass spectrometric experiments tend to corroborate their 2nd law enthalpy from the torsion–effusion measurements. The 2nd law enthalpy of Efimova and Gorokhov[1] as well as that of Ficalora *et al.*[12] are more in line with our 3rd law effusion values. Kosugi[11] did not observe the $K_2SO_4^+$ ion in his mass spectrometric experiments. The appearance potential of $K_2SO_4^+$ has been measured as 7.40 ± 0.5 eV,[12] 8.40 ± 0.3 eV[3] and 8.0 eV.[1]

We have discounted the transpiration experiments of Halstead[13] and Dubois and Millet.[14] The calculated 3rd law $\Delta_f H°(298.15\ K)$ may have an uncertainty of 3 $kcal \cdot mol^{-1}$ since the JANAF Gibbs energy functions are partially based on the estimated molecular constants of K_2SO_4(g). Our adopted $\Delta_f H°$ is based on a weighted average of the 3rd law results from.[1–3]

Source	Method	Reaction*	T/K	Data Points	δS $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(K_2SO_4, g, 298.15\ K)$ $kcal \cdot mol^{-1}$
Efimova[1]	effusion	A	1171–1331	equation	4.38	84.77	79.02 ± 0.11	−261.38 ± 1.5
Lau *et al.*[3]	torsion–effusion	A	1180–1274	37	5.18	85.36	78.93 ± 0.45	−261.47 ± 1.5
Plante[2]	effusion	A	1166–1322	26	−1.42 ± 0.8	77.03 ± 0.9	78.78 ± 0.42	−261.62 ± 1.5
Plante[2]	effusion	A	1196–1321	15	−0.76 ± 2.0	77.87 ± 2.0	78.83 ± 0.51	−261.57 ± 1.0
Halstead	effusion	A	1180–1340	equation	1.07	75.75	74.39 ± 0.15	−266.02 ± 1.0
Kosugi[11]	effusion	B	1409–1530	12	2.70 ± 2.8	73.67 ± 4.2	69.66 ± 0.76	−263.43 ± 2.0
Efimova[1]	mass spec	A	1171–1331	?	—	78.0 ± 1.0	—	−262.4 ± 2
Lau *et al.*[3]	mass spec	A	1183–1248	9	—	84.12 ± 2.02	—	−256.28 ± 2.0
Lau *et al.*[3]	mass spec	A	1180–1314	10	—	81.96 ± 0.40	—	−258.44 ± 1.5
Ficalora[12]	mass spec	A	1080–1230	?	—	79.8 ± 2.0	—	−260.6 ± 4

*Reactions: A) K_2SO_4(cr, β) = K_2SO_4(g) B) K_2SO_4(l) = K_2SO_4(g)

Heat Capacity and Entropy

The adopted structure (D_{2h} symmetry) is based on the high temperature electron diffraction study of Spiridonov and Lutoshkin.[5] This symmetry is supported by the similar work of Ugarov *et al.*[4] on Cs_2SO_4 and the IR and Raman study of Atkins and Gingerich[7] on K_2SO_4 and Na_2SO_4. The molecule can be pictured as having a central sulfur atom surrounded at the corners of a tetrahedron by four oxygen atoms with bridging potassium atoms between two pairs of oxygens forming two planar mutually perpendicular KO_2S rings. The sulfate core is fairly

Continued on page 1489

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−22.463	−1080.636	−1080.636	INFINITE
100	64.770	273.209	449.682	−17.647	−1085.784	−1070.071	558.948
200	90.384	326.456	375.546	−9.818	−1090.608	−1052.380	274.854
250	100.439	347.734	367.897	−5.041	−1092.515	−1042.597	217.839
298.15	108.730	366.152	366.152	0.	−1094.116	−1032.835	180.948
300	109.023	366.826	366.154	0.201	−1094.175	−1032.454	179.766
350	116.277	384.193	367.509	5.839	−1100.439	−1021.853	152.503
400	122.342	400.128	370.604	11.809	−1104.063	−1010.439	131.950
450	127.380	414.838	374.713	18.056	−1105.903	−998.632	115.918
500	131.555	428.481	379.416	24.533	−1107.600	−986.618	103.071
600	137.903	453.063	389.688	38.025	−1110.091	−962.173	83.765
700	142.345	474.674	400.317	52.050	−1111.914	−937.369	69.947
800	145.525	493.901	410.835	66.452	−1113.351	−912.333	59.569
900	147.859	511.183	421.041	81.127	−1167.708	−886.050	51.425
1000	149.612	526.856	430.851	96.005	−1167.636	−854.758	44.648
1100	150.956	541.181	440.239	111.036	−1325.533	−814.251	38.666
1200	152.006	554.363	449.208	126.186	−1323.524	−767.860	33.424
1300	152.842	566.564	457.772	141.430	−1321.507	−721.636	28.996
1400	153.515	577.917	465.953	156.749	−1319.491	−675.568	25.206
1500	154.067	588.527	473.775	172.129	−1317.486	−629.644	21.926
1600	154.523	598.486	481.261	187.559	−1315.500	−583.853	19.061
1700	154.904	607.865	488.435	203.031	−1313.539	−538.185	16.536
1800	155.226	616.729	495.319	218.538	−1311.610	−492.632	14.296
1900	155.500	625.129	501.932	234.075	−1309.720	−447.185	12.294
2000	155.736	633.111	508.293	249.637	−1307.873	−401.836	10.495
2100	155.940	640.715	514.419	265.221	−1306.075	−356.579	8.869
2200	156.117	647.973	520.326	280.824	−1304.332	−311.405	7.394
2300	156.272	654.916	526.028	296.444	−1302.649	−266.310	6.048
2400	156.409	661.570	531.538	312.078	−1301.032	−221.288	4.816
2500	156.529	667.957	536.868	327.725	−1299.487	−176.330	3.684
2600	156.637	674.099	542.028	343.383	−1298.017	−131.433	2.641
2700	156.733	680.012	547.030	359.052	−1296.630	−86.591	1.675
2800	156.819	685.714	551.882	374.729	−1295.330	−41.798	0.780
2900	156.896	691.218	556.592	390.415	−1294.124	2.948	−0.053
3000	156.966	696.538	561.169	406.108	−1293.017	47.656	−0.830
3100	157.029	701.686	565.619	421.808	−1292.015	92.329	−1.556
3200	157.087	706.673	569.950	437.514	−1291.126	136.970	−2.236
3300	157.139	711.507	574.166	453.225	−1290.336	181.583	−2.874
3400	157.187	716.199	578.275	468.942	−1289.682	226.178	−3.475
3500	157.231	720.756	582.281	484.663	−1289.155	270.753	−4.041
3600	157.272	725.186	586.189	500.388	−1288.769	315.316	−4.575
3700	157.309	729.496	590.005	516.117	−1288.530	359.870	−5.080
3800	157.343	733.691	593.731	531.850	−1288.445	404.421	−5.559
3900	157.375	737.779	597.372	547.586	−1288.523	448.972	−6.013
4000	157.404	741.764	600.932	563.325	−1288.761	493.523	−6.445
4100	157.432	745.651	604.415	579.066	−1289.181	538.085	−6.855
4200	157.457	749.445	607.823	594.811	−1289.798	582.659	−7.246
4300	157.481	753.150	611.160	610.558	−1290.615	627.252	−7.620
4400	157.503	756.771	614.428	626.307	−1291.086	671.809	−7.975
4500	157.523	760.310	617.631	642.058	−1292.192	716.432	−8.316
4600	157.543	763.773	620.770	657.812	−1293.501	761.081	−8.642
4700	157.561	767.161	623.849	673.567	−1294.978	805.758	−8.955
4800	157.578	770.479	626.869	689.324	−1296.449	850.445	−9.255
4900	157.594	773.728	629.834	705.082	−1298.342	895.192	−9.543
5000	157.609	776.912	632.743	720.842	−1300.452	939.979	−9.820
5100	157.623	780.033	635.601	736.604	−1302.781	984.812	−10.087
5200	157.636	783.094	638.408	752.367	−1305.334	1029.689	−10.343
5300	157.649	786.097	641.166	768.131	−1308.111	1074.621	−10.591
5400	157.660	789.044	643.878	783.897	−1311.116	1119.605	−10.830
5500	157.672	791.937	646.543	799.663	−1314.347	1164.647	−11.061
5600	157.682	794.778	649.165	815.431	−1317.805	1209.752	−11.284
5700	157.693	797.569	651.744	831.200	−1320.800	1254.823	−11.499
5800	157.702	800.311	654.282	846.969	−1324.621	1300.044	−11.708
5900	157.711	803.007	656.780	862.740	−1328.659	1345.328	−11.911
6000	157.720	805.658	659.239	878.512	−1332.909	1390.687	−12.107

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

$S°(298.15\ K) = 115.06 \pm 16.7\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1050 \pm 10\ K$ (diffuse lambda transition)
$T_{fus} = 1221 \pm 10\ K$

$\Delta_f H°(298.15\ K) = -376.56 \pm 12.6\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 16.150 \pm 0.17\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Experimental measurements leading to the enthalpy of formation of K_2S(cr) are summarized below.

Source	Reaction	$\Delta_f H°$(298.15 K), kcal·mol^{-1}
Sabatier[1]	$\Delta_{sln} H°$ K_2S(cr) and K(cr); $\Delta_n H°$ KOH(aq) + H_2S(aq)	−103.4
Rengade and Costeanu[2]		−87.3
Letoffe *et al.*[3]	H_2SO_4(aq, 1100 H_2O) + K_2S(cr) = K SO (soln.) + H S(g)	−92.1[a]

a. The authors' value of −91.1 ± 0.9 kcal·mol^{-1} is changed by new $\Delta_f H°$(298.15 K) values for H_2SO_4(aq, 1100 H_2O), K_2SO_4(cr) and H_2S(g).[4,5]

Since Sabatier himself has expressed reservations because of impure material, we eliminate his value and adopt the average of the other two values, $\Delta_f H°(K_2S, cr, 298.15\ K) = -90 \pm 3$ kcal·mol^{-1}.

Heat Capacity and Entropy

The heat capacity is taken from the drop calorimetry of Dworkin and Bredig (384 to 1260 K).[6] Between 298 and 820 K, the observed enthalpy differences and the constraint of passing through zero at 298.15 K are fit by a linear least squares technique; $C_p° = 15.99 + 6.22 \times 10^{-3}\ T$ cal·K^{-1}·mol^{-1} (298 820 K). The heat capacity in the observed diffuse lambda transition region, 820–1100 K, was adjusted to properly reproduce the observed enthalpies. The sharp heat capacity maximum occurs at 1050 K[6] and 46.60 cal·K^{-1}·mol^{-1}. From 1100 K to the melting point, 1221 K,[7] the heat capacity was found to be constant at uccircl34.02 cal·K^{-1}mol^{-1}.

Freeman[8] has estimated $S°(K_2S, cr, 298.15\ K) = 27$ cal·K^{-1}·mol^{-1}; Voronin[9] also has estimated 27 cal·K^{-1}·mol^{-1}. Kelley's additive entropy constants give 28.0 We adopt $S°(K_2S, cr, 298.15\ K) = 27.5 \pm 4$ cal·K^{-1}·mol^{-1}.

Transition and Fusion Data

A crystal II to crystal I transition at 419.6 K with a enthalpy change of 0.085 kcal·mol^{-1} has been listed[10] from Bridgman.[11] However, West[12] found no change in the x-ray powder diffraction pattern over the 298–473 K range. Although not definitive because of the small heat change listed, the drop calorimetric enthalpy measurements of Dworkin and Bredig[6] do not show this transition. Therefore, we do not indicate any solid state transition at 419.6 K.

The diffuse lambda transition has been discussed above.

A melting point of 1221 K was determined by thermal analysis (cooling curves) of the K–K_2S system by Dworkin and Bredig.[7] This is considerably higher than earlier values of 1108 K[13] and 1185 K,[14] but it is confirmed by their drop calometric measurements.[6] A melting point of 1221 ± 10 K is adopted with $\Delta_{fus} H° = 3.86 \pm 0.04$ kcal·mol^{-1}.[6]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
250							
298.15	74.684	115.060	115.060	0.	−376.560	−362.745	63.551
300	74.726	115.522	115.061	0.138	−376.573	−362.659	63.145
400	77.320	137.375	118.023	7.741	−384.524	−356.897	46.606
500	79.914	154.907	123.702	15.602	−386.806	−349.730	36.536
600	82.508	169.706	130.167	23.723	−388.349	−342.158	29.787
700	85.144	182.621	136.757	32.105	−389.306	−334.377	24.952
800	87.738	194.161	143.224	40.749	−389.826	−326.490	21.318
900	103.554	205.100	149.486	50.053	−442.745	−317.488	18.427
1000	156.063	218.274	155.672	62.602	−438.078	−303.773	15.867
1050.000	194.982	226.816	158.850	71.364	___ C_p HUMP MAXIMUM ___		
1050.000	194.985	226.816	158.850	71.364	TRANSITION		
1100	142.340	234.558	162.127	79.675	−586.914	−281.577	13.371
1200	142.340	246.943	168.686	93.908	−578.724	−254.180	11.064
1221.000	142.340	249.413	170.053	96.898	--- CRYSTAL <--> LIQUID ---		
1300	142.340	258.336	175.150	108.142	−570.550	−227.467	9.140
1400	142.340	268.885	181.473	122.376	−562.393	−201.382	7.514
1500	142.340	278.705	187.632	136.610	−554.251	−175.879	6.125
1600	142.340	287.892	193.614	150.844	−546.127	−150.920	4.927
1700	142.340	296.521	199.416	165.078	−538.021	−126.467	3.886
1800	142.340	304.657	205.039	179.312	−529.933	−102.492	2.974
1900	142.340	312.353	210.486	193.546	−521.866	−78.965	2.171
2000	142.340	319.654	215.764	207.780	−513.823	−55.863	1.459

PREVIOUS: CURRENT: March 1978

$S°(298.15\ K) = [141.172]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1221 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-346.506]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 16.150 \pm 0.17\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(K_2S, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1221\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was derived from drop calorimetric enthalpy measurements by Dworkin and Bredig,[2] (1221–1260 K) and is constant at 24.13 $cal·K^{-1}·mol^{-1}$ over the range measured. A glass transition temperature is assumed at 820 K with $C_p° = 24.13$ above this temperature and $C_p°$ equal to that of the crystal below this temperature.

$S°(K_2S, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	74.684	141.172	141.172	0.	−346.506	−340.476	59.650
300	74.726	141.634	141.174	0.138	−346.519	−340.439	59.276
400	77.320	163.487	144.136	7.741	−354.470	−337.288	44.045
500	79.914	181.019	149.815	15.602	−356.752	−332.732	34.760
600	82.508	195.819	156.280	23.723	−358.295	−327.771	28.535
700	85.144	208.734	162.869	32.105	−359.252	−322.602	24.073
800	87.738	220.273	169.336	40.749	−359.773	−317.326	20.719
820.010	88.241	222.447	170.606	42.510	GLASS <--> LIQUID		
820.010	100.960	222.447	170.606	42.510	TRANSITION		
900	100.960	231.844	175.637	50.586	−412.158	−310.970	18.048
1000	100.960	242.481	181.799	60.682	−409.944	−299.847	15.662
1100	100.960	252.103	187.760	70.778	−565.757	−279.720	13.283
1200	100.960	260.888	193.493	80.874	−561.705	−253.895	11.052
1221.000	100.960	262.640	194.667	82.994	--- CRYSTAL <--> LIQUID ---		
1300	100.960	268.969	198.992	90.970	−557.669	−228.408	9.178
1400	100.960	276.451	204.261	101.066	−553.649	−203.231	7.583
1500	100.960	283.417	209.309	111.162	−549.646	−178.341	6.210
1600	100.960	289.932	214.146	121.258	−545.660	−153.717	5.018
1700	100.960	296.053	218.786	131.354	−541.691	−129.343	3.974
1800	100.960	301.824	223.241	141.450	−537.742	−105.201	3.053
1900	100.960	307.282	227.521	151.546	−533.813	−81.278	2.234
2000	100.960	312.461	231.640	161.642	−529.907	−57.562	1.503
2100	100.960	317.387	235.607	171.738	−526.026	−34.040	0.847
2200	100.960	322.083	239.432	181.834	−522.174	−10.702	0.254
2300	100.960	326.571	243.124	191.930	−518.353	12.461	−0.283
2400	100.960	330.868	246.691	202.026	−514.569	35.458	−0.772
2500	100.960	334.990	250.141	212.122	−510.825	58.299	−1.218
2600	100.960	338.949	253.481	222.218	−507.125	80.991	−1.627
2700	100.960	342.760	256.717	232.314	−503.476	103.541	−2.003
2800	100.960	346.431	259.856	242.410	−499.882	125.957	−2.350
2900	100.960	349.974	262.903	252.506	−496.350	148.246	−2.670
3000	100.960	353.397	265.863	262.602	−492.887	170.414	−2.967

PREVIOUS: CURRENT: March 1978

0	to 1050	K*crystal
1050	to 1221	K crystal
above	1221	K liquid

Refer to the individual tables for details.

*There is a diffuse transition at 1030 K.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	74.684	115.060	115.060	0.	−376.560	−362.745	63.551
300	74.726	115.522	115.061	0.138	−376.573	−362.659	63.145
400	77.320	137.375	118.023	7.741	−384.524	−356.897	46.606
500	79.914	154.907	123.702	15.602	−386.806	−349.730	36.536
600	82.508	169.706	130.167	23.723	−388.349	−342.158	29.787
700	85.144	182.621	136.757	32.105	−389.306	−334.377	24.952
800	87.738	194.161	143.224	40.749	−389.826	−326.490	21.318
900	103.554	205.100	149.486	50.053	−442.745	−317.488	18.427
1000	156.063	218.274	155.672	62.602	−438.078	−303.773	15.867
1050.000	194.982	226.816	158.850	71.364	____ C_p HUMP MAXIMUM ____		
1050.000	194.985	226.816	158.850	71.364	TRANSITION		
1100	142.340	234.558	162.127	79.675	−586.914	−281.577	13.371
1200	142.340	246.943	168.686	93.908	−578.724	−254.180	11.064
1221.000	142.340	249.413	170.053	96.898	____ CRYSTAL <--> LIQUID ____		
1221.000	100.960	262.640	170.053	113.048	TRANSITION		
1300	100.960	268.969	175.874	121.024	−557.669	−228.408	9.178
1400	100.960	276.451	182.794	131.120	−553.649	−203.231	7.583
1500	100.960	283.417	189.273	141.216	−549.646	−178.341	6.210
1600	100.960	289.932	195.363	151.312	−545.660	−153.717	5.018
1700	100.960	296.053	201.107	161.408	−541.691	−129.343	3.974
1800	100.960	301.824	206.544	171.504	−537.742	−105.201	3.053
1900	100.960	307.282	211.704	181.600	−533.813	−81.278	2.234
2000	100.960	312.461	216.613	191.696	−529.907	−57.562	1.503
2100	100.960	317.387	221.296	201.792	−526.026	−34.040	0.847
2200	100.960	322.084	225.771	211.888	−522.174	−10.702	0.254
2300	100.960	326.571	230.057	221.984	−518.353	12.461	−0.283
2400	100.960	330.868	234.168	232.080	−514.569	35.458	−0.772
2500	100.960	334.990	238.119	242.176	−510.825	58.299	−1.218
2600	100.960	338.949	241.922	252.272	−507.125	80.991	−1.627
2700	100.960	342.760	245.586	262.368	−503.476	103.541	−2.003
2800	100.960	346.431	249.123	272.464	−499.882	125.957	−2.350
2900	100.960	349.974	252.540	282.560	−496.350	148.246	−2.670
3000	100.960	353.397	255.845	292.656	−492.887	170.414	−2.967

PREVIOUS: CURRENT: March 1978

Continued from page 1469

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Continued from page 1485

rigid while the metal atoms undergo large amplitude motions. The internuclear distances of 1.47 Å for S–O and 2.45 Å for K–O are from[5] as are the O–S–O and O–K–O angles. The principal moments of inertia are $I_A = 15.3096 \times 10^{-39}$ and $I_B = I_C = 130.9758 \times 10^{-39}$ g·cm^2.

Atkins and Gingerich[7] have observed the infrared and Raman spectra of K_2SO_4 and Na_2SO_4 isolated in oxygen and nitrogen matrices at 12 K. Five of the eleven fundamental frequencies were observed in this work. Good agreement exists between these observations and the frequencies adopted by Gurvich *et al.*[6] The two other sulfate–ion group fundamentals are taken from the Raman study of Davies and Sandford.[9] The low–frequency fundamentals involving the metal atoms are taken from the infrared study of Belyaeva *et al.*[8] These authors observed the spectra of K_2SO_4, Rb_2SO_4 and Cs_2SO_4 isolated in Ar, Kr, and Xe matrices at 4.2 K. Uncertainties in the location of the gas phase frequencies may contribute 4 cal·K^{-1}·mol^{-1} to $S°$(298.15 K).

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0 to 6000 K Ideal Monatomic Gas

IP(Kr, g) = 112914.5 ± 0.1 cm^{-1}
$S°$(298.15 K) = 164.084 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[1,9] All predicted levels have been observed for n=4 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[2] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is nearly 80000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.[2]

The thermodynamic functions at 298.15 K agree exactly with recent CODATA recommendations[3] except for two minor differences First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the rare gases arise due to the use of slightly different values for R; this table uses R = 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[4] Hilsenrath *et al.*,[5] Gurvich *et al.*,[8] and Wagman *et al.*[12] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[6] and the 1973 values,[7] respectively.

Phase Data

The triple point, 115.770 K, and boiling point, 119.800 K, are secondary fixed points of IPTS–68.[10,11] Hultgren *et al.*[4] had recommended a triple point of 115.78 K (0.7220 atm) and a boiling point of 119.86 K (1 atm). These values are provided for the convenience of the reader and have not been evaluated by the present authors. As a result of these low values, the reference state for krypton is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ ($J·K^{-1}·mol^{-1}$)	$S°$ ($J·K^{-1}·mol^{-1}$)	$-[G°-H°(T_r)]/T$ ($J·K^{-1}·mol^{-1}$)	$H°-H°(T_r)$ ($kJ·mol^{-1}$)	$\Delta_f H°$ ($kJ·mol^{-1}$)	$\Delta_f G°$ ($kJ·mol^{-1}$)	log K_f
0	0.	0.	INFINITE	−6.197	0.	0.	0.
100	20.786	141.377	182.565	−4.119	0.	0.	0.
200	20.786	155.785	165.986	−2.040	0.	0.	0.
250	20.786	160.423	164.427	−1.001	0.	0.	0.
298.15	20.786	164.084	164.084	0.	0.	0.	0.
300	20.786	164.213	164.085	0.038	0.	0.	0.
350	20.786	167.417	164.338	1.078	0.	0.	0.
400	20.786	170.193	164.900	2.117	0.	0.	0.
450	20.786	172.641	165.627	3.156	0.	0.	0.
500	20.786	174.831	166.440	4.196	0.	0.	0.
600	20.786	178.621	168.164	6.274	0.	0.	0.
700	20.786	181.825	169.892	8.353	0.	0.	0.
800	20.786	184.600	171.561	10.431	0.	0.	0.
900	20.786	187.049	173.149	12.510	0.	0.	0.
1000	20.786	189.239	174.650	14.589	0.	0.	0.
1100	20.786	191.220	176.068	16.667	0.	0.	0.
1200	20.786	193.028	177.407	18.746	0.	0.	0.
1300	20.786	194.692	178.673	20.824	0.	0.	0.
1400	20.786	196.233	179.873	22.903	0.	0.	0.
1500	20.786	197.667	181.012	24.982	0.	0.	0.
1600	20.786	199.008	182.096	27.060	0.	0.	0.
1700	20.786	200.268	183.128	29.139	0.	0.	0.
1800	20.786	201.456	184.113	31.217	0.	0.	0.
1900	20.786	202.580	185.056	33.296	0.	0.	0.
2000	20.786	203.646	185.959	35.375	0.	0.	0.
2100	20.786	204.661	186.826	37.453	0.	0.	0.
2200	20.786	205.628	187.659	39.532	0.	0.	0.
2300	20.786	206.552	188.460	41.610	0.	0.	0.
2400	20.786	207.436	189.232	43.689	0.	0.	0.
2500	20.786	208.285	189.978	45.768	0.	0.	0.
2600	20.786	209.100	190.698	47.846	0.	0.	0.
2700	20.786	209.884	191.394	49.925	0.	0.	0.
2800	20.786	210.640	192.068	52.004	0.	0.	0.
2900	20.786	211.370	192.721	54.082	0.	0.	0.
3000	20.786	212.074	193.354	56.161	0.	0.	0.
3100	20.786	212.756	193.969	58.239	0.	0.	0.
3200	20.786	213.416	194.567	60.318	0.	0.	0.
3300	20.786	214.056	195.148	62.397	0.	0.	0.
3400	20.786	214.676	195.713	64.475	0.	0.	0.
3500	20.786	215.279	196.263	66.554	0.	0.	0.
3600	20.786	215.864	196.800	68.632	0.	0.	0.
3700	20.786	216.434	197.323	70.711	0.	0.	0.
3800	20.786	216.988	197.833	72.790	0.	0.	0.
3900	20.786	217.528	198.331	74.868	0.	0.	0.
4000	20.786	218.054	198.818	76.947	0.	0.	0.
4100	20.786	218.567	199.293	79.025	0.	0.	0.
4200	20.786	219.068	199.758	81.104	0.	0.	0.
4300	20.786	219.557	200.213	83.183	0.	0.	0.
4400	20.786	220.035	200.658	85.261	0.	0.	0.
4500	20.786	220.502	201.094	87.340	0.	0.	0.
4600	20.786	220.959	201.521	89.418	0.	0.	0.
4700	20.786	221.406	201.939	91.497	0.	0.	0.
4800	20.786	221.844	202.349	93.576	0.	0.	0.
4900	20.786	222.273	202.751	95.654	0.	0.	0.
5000	20.786	222.692	203.146	97.733	0.	0.	0.
5100	20.786	223.104	203.533	99.811	0.	0.	0.
5200	20.786	223.508	203.914	101.890	0.	0.	0.
5300	20.786	223.904	204.287	103.969	0.	0.	0.
5400	20.786	224.292	204.654	106.047	0.	0.	0.
5500	20.786	224.674	205.014	108.126	0.	0.	0.
5600	20.786	225.048	205.369	110.204	0.	0.	0.
5700	20.786	225.416	205.717	112.283	0.	0.	0.
5800	20.786	225.778	206.060	114.362	0.	0.	0.
5900	20.786	226.133	206.397	116.440	0.	0.	0.
6000	20.786	226.482	206.729	118.519	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

IP(Kr^+, g) = 196474.8 ± 0.1 cm^{-1}
$S°$(298.15 K) = 175.610 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1350.758 ± 0.012 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1356.955] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	5371.00	2

Heat of Formation

The ionization limit of neutral krypton (112914.5 ± 0.1 cm^{-1}) reported by Moore[1] is adopted as $\Delta_f H°$(0 K) for Kr^+(g). The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the latest CODATA fundamental constants.[2] The uncertainty in the ionization limit is estimated to be ±0.1 cm^{-1} which corresponds to an uncertainty of ±0.012 $kJ·mol^{-1}$ in the heat of formation. Rosenstock *et al.*[9] and Levin and Lias[11] have summarized additional ionization potential and appearance potential data. The recent spectroscopic study by Yoshino *et al.*[12] is in agreement with our adopted value. Gurvich *et al.*[8] and Wagman *et al.*[10] adopted the same ionization potential, but the use of slightly different fundamental constants by Wagman *et al.*[10] resulted in a heat of formation difference of 0.012 $kJ·mol^{-1}$. However, the study by Chaghtai *et al.*[13] suggests an ionization potential which is larger by 10 cm^{-1}.

$\Delta_f H°$(Kr^+, g, 298.15 K) is obtained from $\Delta_f H°$(Kr, g, 0 K) by using IP(Kr) with JANAF[3] enthalpies $H°$(0 K)–$H°$(298.15 K) for Kr^+(g), Kr(r), and e^-(r). $\Delta_r H°$($Kr \rightarrow Kr^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights given by Moore[4] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[5] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 109000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore.[1] The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[5]

The thermodynamic functions reported here agree with those of Green *et al.*,[6] Hilsenrath *et al.*,[7] and Gurvich *et al.*[8] except for one or two minor changes. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the cited references used a pressure of 1 atm. Second, smaller differences arise from the use of slightly different values for the fundamental constants, the relative ionic mass, and the position of the $^2P_{1/2}$ electronic level.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1350.758		
100	20.786	152.903	194.091	−4.119			
200	20.786	167.311	177.512	−2.040			
250	20.786	171.949	175.953	−1.001			
298.15	20.786	175.610	175.610	0.	1356.955	1347.264	−236.035
300	20.786	175.739	175.611	0.038	1356.994	1347.204	−234.569
350	20.786	178.943	175.864	1.078	1358.033	1345.490	−200.803
400	20.786	181.719	176.426	2.117	1359.072	1343.627	−175.460
450	20.786	184.167	177.153	3.156	1360.111	1341.634	−155.733
500	20.786	186.357	177.966	4.196	1361.151	1339.525	−139.939
600	20.788	190.147	179.690	6.274	1363.229	1335.005	−116.222
700	20.794	193.352	181.418	8.353	1365.308	1330.136	−99.256
800	20.811	196.129	183.087	10.434	1367.389	1324.970	−86.512
900	20.843	198.582	184.675	12.516	1369.471	1319.542	−76.584
1000	20.895	200.781	186.178	14.603	1371.558	1313.883	−68.630
1100	20.968	202.776	187.598	16.696	1373.651	1308.014	−62.112
1200	21.061	204.604	188.940	18.797	1375.752	1301.954	−56.673
1300	21.170	206.294	190.210	20.909	1377.864	1295.719	−52.063
1400	21.291	207.867	191.416	23.032	1379.987	1289.321	−48.105
1500	21.421	209.340	192.562	25.167	1382.122	1282.770	−44.670
1600	21.555	210.727	193.655	27.316	1384.271	1276.077	−41.660
1700	21.688	212.038	194.698	29.478	1386.433	1269.248	−38.999
1800	21.819	213.281	195.696	31.653	1388.609	1262.292	−36.631
1900	21.944	214.464	196.653	33.842	1390.797	1255.215	−34.508
2000	22.062	215.593	197.572	36.042	1392.997	1248.022	−32.595
2100	22.171	216.672	198.456	38.254	1395.209	1240.719	−30.861
2200	22.271	217.706	199.308	40.476	1397.431	1233.311	−29.283
2300	22.361	218.698	200.129	42.707	1399.663	1225.801	−27.839
2400	22.441	219.651	200.923	44.948	1401.903	1218.194	−26.513
2500	22.512	220.569	201.691	47.195	1404.151	1210.493	−25.292
2600	22.573	221.453	202.434	49.450	1406.405	1202.702	−24.163
2700	22.626	222.306	203.154	51.710	1408.665	1194.824	−23.115
2800	22.669	223.130	203.853	53.975	1410.930	1186.863	−22.141
2900	22.705	223.926	204.531	56.243	1413.199	1178.821	−21.233
3000	22.734	224.696	205.191	58.515	1415.471	1170.700	−20.384
3100	22.756	225.442	205.832	60.790	1417.745	1162.503	−19.588
3200	22.771	226.164	206.456	63.066	1420.021	1154.233	−18.841
3300	22.782	226.865	207.064	65.344	1422.299	1145.892	−18.138
3400	22.787	227.546	207.657	67.623	1424.578	1137.482	−17.475
3500	22.788	228.206	208.234	69.901	1426.856	1129.005	−16.849
3600	22.785	228.848	208.798	72.180	1429.135	1120.463	−16.257
3700	22.778	229.472	209.348	74.458	1431.413	1111.857	−15.697
3800	22.768	230.080	209.886	76.735	1433.690	1103.190	−15.164
3900	22.755	230.671	210.411	79.012	1435.967	1094.463	−14.659
4000	22.740	231.247	210.925	81.286	1438.241	1085.677	−14.177
4100	22.723	231.808	211.428	83.560	1440.515	1076.835	−13.719
4200	22.704	232.355	211.919	85.831	1442.786	1067.938	−13.282
4300	22.684	232.889	212.401	88.100	1445.056	1058.986	−12.864
4400	22.662	233.411	212.873	90.368	1447.323	1049.981	−12.465
4500	22.640	233.920	213.335	92.633	1449.588	1040.925	−12.083
4600	22.616	234.417	213.788	94.896	1451.851	1031.819	−11.717
4700	22.591	234.903	214.232	97.156	1454.111	1022.663	−11.366
4800	22.566	235.378	214.667	99.414	1456.369	1013.460	−11.029
4900	22.541	235.844	215.095	101.669	1458.624	1004.209	−10.705
5000	22.515	236.299	215.514	103.922	1460.877	994.912	−10.394
5100	22.489	236.744	215.926	106.172	1463.127	985.571	−10.094
5200	22.463	237.181	216.331	108.420	1465.375	976.185	−9.806
5300	22.436	237.608	216.728	110.665	1467.620	966.756	−9.528
5400	22.410	238.027	217.119	112.907	1469.862	957.285	−9.260
5500	22.384	238.438	217.503	115.147	1472.102	947.772	−9.001
5600	22.357	238.841	217.880	117.384	1474.339	938.219	−8.751
5700	22.332	239.237	218.251	119.618	1476.573	928.625	−8.510
5800	22.306	239.625	218.617	121.850	1478.805	918.992	−8.276
5900	22.280	240.006	218.976	124.079	1481.034	909.321	−8.051
6000	22.255	240.380	219.329	126.306	1483.261	899.613	−7.832

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

REFERENCE STATE

0	to	453.69	K crystal
453.69	to	1620.120	K liquid
above		1620.120	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.622	0.	0.	0.
100	13.360	7.342	48.615	−4.127	0.	0.	0.
107.250	16.491	8.370	45.859	−4.021	C_p HUMP MAXIMUM TRANSITION		
107.250	16.494	8.370	45.859	−4.021			
200	21.573	19.826	31.255	−2.286	0.	0.	0.
298.15	24.623	29.085	29.085	0.	0.	0.	0.
300	24.669	29.237	29.085	0.046	0.	0.	0.
400	27.610	36.698	30.083	2.646	0.	0.	0.
453.690	29.387	40.288	31.080	4.178	CRYSTAL <--> LIQUID TRANSITION		
453.690	30.392	46.902	31.080	7.178			
500	30.125	49.843	32.684	8.579	0.	0.	0.
600	29.539	55.283	36.013	11.562	0.	0.	0.
700	28.987	59.794	39.097	14.487	0.	0.	0.
800	28.937	63.661	41.931	17.384	0.	0.	0.
900	28.886	67.066	44.539	20.275	0.	0.	0.
1000	28.836	70.107	46.946	23.161	0.	0.	0.
1100	28.786	72.853	49.179	26.042	0.	0.	0.
1200	28.736	75.356	51.257	28.918	0.	0.	0.
1300	28.702	77.655	53.201	31.790	0.	0.	0.
1400	28.619	79.779	55.024	34.656	0.	0.	0.
1500	28.535	81.750	56.741	37.514	0.	0.	0.
1600	28.451	83.589	58.362	40.363	0.	0.	0.
1620.120	28.431	83.945	58.678	40.936	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1620.120	20.794	173.965	58.678	186.779			
1700	20.799	174.966	64.118	188.441	0.	0.	0.
1800	20.810	176.155	70.310	190.521	0.	0.	0.
1900	20.826	177.281	75.911	192.603	0.	0.	0.
2000	20.849	178.349	81.006	194.687	0.	0.	0.
2100	20.882	179.367	85.666	196.773	0.	0.	0.
2200	20.925	180.340	89.947	198.863	0.	0.	0.
2300	20.980	181.271	93.898	200.958	0.	0.	0.
2400	21.049	182.165	97.557	203.060	0.	0.	0.
2500	21.132	183.026	100.959	205.169	0.	0.	0.
2600	21.231	183.857	104.131	207.287	0.	0.	0.
2700	21.347	184.660	107.099	209.415	0.	0.	0.
2800	21.479	185.439	109.883	211.556	0.	0.	0.
2900	21.628	186.195	112.502	213.712	0.	0.	0.
3000	21.794	186.931	114.970	215.883	0.	0.	0.
3100	21.977	187.649	117.303	218.071	0.	0.	0.
3200	22.177	188.350	119.513	220.278	0.	0.	0.
3300	22.391	189.035	121.609	222.506	0.	0.	0.
3400	22.622	189.707	123.602	224.757	0.	0.	0.
3500	22.868	190.366	125.500	227.031	0.	0.	0.
3600	23.130	191.014	127.311	229.331	0.	0.	0.
3700	23.406	191.652	129.041	231.658	0.	0.	0.
3800	23.697	192.280	130.697	234.013	0.	0.	0.
3900	24.003	192.899	132.284	236.398	0.	0.	0.
4000	24.323	193.511	133.807	238.814	0.	0.	0.
4100	24.658	194.115	135.271	241.263	0.	0.	0.
4200	25.009	194.714	136.679	243.746	0.	0.	0.
4300	25.375	195.307	138.036	246.265	0.	0.	0.
4400	25.696	195.889	139.344	248.800	0.	0.	0.
4500	26.069	196.470	140.607	251.386	0.	0.	0.
4600	26.464	197.047	141.827	254.012	0.	0.	0.
4700	26.873	197.621	143.008	256.679	0.	0.	0.
4800	27.297	198.191	144.152	259.387	0.	0.	0.
4900	27.736	198.758	145.261	262.139	0.	0.	0.
5000	28.191	199.323	146.336	264.935	0.	0.	0.
5200	29.134	200.446	148.396	270.661	0.	0.	0.
5400	30.152	201.564	150.344	276.588	0.	0.	0.
5600	31.233	202.680	152.193	282.726	0.	0.	0.
5800	32.377	203.796	153.954	289.086	0.	0.	0.
6000	33.581	204.914	155.634	295.681	0.	0.	0.

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 29.085\ J·K^{-1}·mol^{-1}$
$T_{fus} = 453.69\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 3.000 \pm 0.015\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Heat capacities have been reported by the following authors for the temperature ranges indicated: Roberts,[1] 1.5 to 20 K (Li 99.5% pure); Simon and Swain[2] 15 to 300 K; Martin[3] 22 to 300 K(Li 99.95% pure); Douglas *et al.*[4] 289.15 K to 1200 K (Li 99.98% pure). Martin[3] in a series of determinations, found that C_p depended on the thermal history of the sample; a peak at roughly 107 K was ascribed to a martensitic transformation. There is excellent continuty between the results of Roberts[1] and of Martin,[3] while those of Martin[3] and Douglas *et al.*[4] differ by 1% at 300 K and have been smoothly joined. The values of Simon and Swain[2] were not used as they were 5% lower than Martin's[3] and did not show the peak at 107 K; also their values for Al_2O_3, reported at the same time, are lower than recent measurements. Heat capacities between 1200 K and the normal boiling point were obtained from the enthalpy equation given by Douglas *et al.*[4] between 420–900°C.

Fusion Data

Douglas *et al.*[4] report the triple point to be 180.54°C, which is here adopted as the melting point since the densities of solid and liquid lithium at 180°C are not available for calculating dT_{fus}/dP. The same authors[4] give the enthalpy of melting as $432.3 \pm 2.2\ J·g^{-1}$.

Sublimation Data

Lithium vapor contains an appreciable amount of dimer, whose enthalpy of dissociation has been selected by Evans,[5] from spectroscopic and molecular beam measuresments to be $25.76 \pm 0.10\ kcal·mol^{-1}$ at 0 K. This enthalpy of dissociation, together with the thermodynamic functions calculated in this work, has been used to find the partial pressures of Li(g) and Li_2(g) from the measured total vapor pressures. Hartmann and Schneider,[6] report values from 1204 to 1353 K; while Mancherat[7] reports effusion measurements from 735 to 915 K. Mancherat's[7] pressures are calculated on the assumption of monatomic vapor and have been recalculated to fine the true total pressure. Effusion measurements by Lewis[8] and Bogros[9] have been disregarded. Mancherat[7] considers them to be inaccurate because of impurities in the lithium used, and Lewis[8] used a doubtful calibration method. Enthalpy of sublimation to monatomic vapor calculated from the vapor pressures of Hartmann and Schneider[6] and of Mancherat[7] agree to within 2% and the average value has been adopted. The enthalpy of sublimation of the dimer was then calculated using this value.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.622	0.	0.	0.
100	13.360	7.342	48.615	−4.127	0.	0.	0.
107.250	16.491	8.370	45.859	−4.021	___ C_p HUMP MAXIMUM ___		
107.250	16.494	8.370	45.859	−4.021	TRANSITION		
200	21.573	19.826	31.255	−2.286	0.	0.	0.
250	23.406	24.854	29.484	−1.157	0.	0.	0.
298.15	24.623	29.085	29.085	0.	0.	0.	0.
300	24.669	29.237	29.085	0.046	0.	0.	0.
350	25.930	33.128	29.390	1.308	0.	0.	0.
400	27.610	36.698	30.083	2.646	0.	0.	0.
450	29.280	40.049	31.006	4.069	0.	0.	0.
453.690	29.387	40.288	31.080	4.178	--- CRYSTAL <--> LIQUID ---		
500	30.217	43.188	32.069	5.559	−3.020	0.308	−0.032
600	30.380	48.714	34.396	8.591	−2.972	0.970	−0.084
700	30.384	53.397	36.785	11.629	−2.859	1.619	−0.121
800	30.384	57.455	39.121	14.667	−2.716	2.249	−0.147
900	30.384	61.033	41.360	17.706	−2.569	2.860	−0.166
1000	30.384	64.235	43.491	20.744	−2.417	3.456	−0.180

PREVIOUS: CURRENT: June 1962

$S°(298.15\ K)$ = [33.938] $J·K^{-1}·mol^{-1}$
T_{fus} = 1843 K

$\Delta_f H°(298.15\ K)$ = [2.380] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 3.000 ± 0.015 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(Li, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°$(453.69 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The liquid heat capacity values are derived from the enthalpy measurements of Douglas *et al.*[1] The heat capacity curve was extrapolated to 298.15 K and 2000 K in a reasonable manner.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The enthalpy of fusion and the melting point were measured by Douglas *et al.*[1]

Vaporization Data

Lithium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm at 1620 K; the vapor pressure of the monatomic gas reaches 1 atm at 1638 K and the enthalpy of vaporization to monatomic gas is 35.16 $kcal·mol^{-1}$.

Reference

[1]T. B. Douglas, L. F. Epstein, J. L. Dever, and W. H. Howland, J. Am. Chem. Soc. **77**, 2144 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	31.300	33.938	33.938	0.	2.380	0.933	−0.163
300	31.284	34.131	33.938	0.058	2.392	0.924	−0.161
350	31.000	38.933	34.318	1.615	2.686	0.655	−0.098
400	30.711	43.053	35.159	3.158	2.891	0.349	−0.046
450	30.414	46.653	36.240	4.686	2.996	0.024	−0.003
453.690	30.392	46.902	36.335	4.794	--- CRYSTAL <--> LIQUID ---		
500	30.125	49.843	37.444	6.199	0.	0.	0.
600	29.539	55.283	39.979	9.182	0.	0.	0.
700	28.987	59.793	42.497	12.108	0.	0.	0.
800	28.937	63.661	44.906	15.004	0.	0.	0.
900	28.886	67.066	47.183	17.895	0.	0.	0.
1000	28.836	70.107	49.326	20.781	0.	0.	0.
1100	28.786	72.853	51.342	23.662	0.	0.	0.
1200	28.736	75.356	53.240	26.538	0.	0.	0.
1300	28.702	77.655	55.031	29.410	0.	0.	0.
1400	28.619	79.779	56.724	32.276	0.	0.	0.
1500	28.535	81.750	58.327	35.134	0.	0.	0.
1600	28.451	83.589	59.850	37.983	0.	0.	0.
1620.120	28.431	83.945	60.147	38.556	----- FUGACITY = 1 bar -----		
1700	28.368	85.311	61.297	40.824	−145.237	7.176	−0.220
1800	28.326	86.931	62.677	43.658	−144.483	16.120	−0.468
1900	28.326	88.463	63.994	46.491	−143.732	25.022	−0.688
2000	28.326	89.916	65.254	49.323	−142.983	33.884	−0.885
2100	28.326	91.298	66.462	52.156	−142.237	42.709	−1.062
2200	28.326	92.615	67.621	54.989	−141.495	51.499	−1.223

PREVIOUS: CURRENT: June 1962

0	to	453.69	K	crystal
above		453.69	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.622	0.	0.	0.
100	13.360	7.342	48.615	−4.127	0.	0.	0.
107.250	16.491	8.370	45.859	−4.021	____ C_p HUMP MAXIMUM ____		
107.250	16.494	8.370	45.859	−4.021	TRANSITION		
200	21.573	19.826	31.255	−2.286	0.	0.	0.
250	23.406	24.854	29.484	−1.157	0.	0.	0.
298.15	24.623	29.085	29.085	0.	0.	0.	0.
300	24.669	29.237	29.085	0.046	0.	0.	0.
350	25.930	33.128	29.390	1.308	0.	0.	0.
400	27.610	36.698	30.083	2.646	0.	0.	0.
450	29.280	40.049	31.006	4.069	0.	0.	0.
453.690	29.387	40.288	31.080	4.178	____ CRYSTAL <--> LIQUID ____		
453.690	30.392	46.902	31.080	7.178	TRANSITION		
500	30.125	49.843	32.684	8.579	0.	0.	0.
600	29.539	55.283	36.013	11.562	0.	0.	0.
700	28.987	59.794	39.097	14.487	0.	0.	0.
800	28.937	63.661	41.931	17.384	0.	0.	0.
900	28.886	67.066	44.539	20.275	0.	0.	0.
1000	28.836	70.107	46.946	23.161	0.	0.	0.
1100	28.786	72.853	49.179	26.042	0.	0.	0.
1200	28.736	75.356	51.257	28.918	0.	0.	0.
1300	28.702	77.655	53.201	31.790	0.	0.	0.
1400	28.619	79.779	55.024	34.656	0.	0.	0.
1500	28.535	81.750	56.741	37.514	0.	0.	0.
1600	28.451	83.589	58.362	40.363	0.	0.	0.
1620.120	28.431	83.945	58.678	40.936	- - - - - FUGACITY = 1 bar - - - - -		
1700	28.368	85.311	59.897	43.204	−145.237	7.176	−0.220
1800	28.326	86.931	61.355	46.038	−144.483	16.120	−0.468
1900	28.326	88.463	62.741	48.871	−143.732	25.022	−0.688
2000	28.326	89.916	64.064	51.703	−142.983	33.884	−0.885
2100	28.326	91.298	65.328	54.536	−142.237	42.709	−1.062
2200	28.326	92.615	66.539	57.368	−141.495	51.499	−1.223

PREVIOUS: CURRENT: June 1962

IP(Li, g) = 43487.150 ± 0.005 cm^{-1}
$S°(298.15\ K)$ = 138.781 ± 0.025 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = 157.7 ± 1.0 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 159.3 ± 1.0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2
$^2P_{1/2}$	14903.66	2
$^2P_{3/2}$	14904.00	4
$^2S_{1/2}$	27206.12	2
.	.	.
.	.	.
.	.	.
$^2P_{3/2}$	43424.3	4
IP	43487.150	

Enthalpy of Formation

The enthalpy of formation of lithium gas is chosen to be the value recommended by CODATA.[1] This value was obtained from 2nd and 3rd law treatments of vapor pressure data. The reported vapor pressures were corrected for the effects of $Li_2(g)$, using D_0^0 = 101.02 $kJ·mol^{-1}$.

As stated by CODATA,[2] the selected value is the weighted average of the 3rd law values of $\Delta_{sub}H°(298.15\ K)$ calculated from the following data:

Source	$\Delta_{sub}H°(298.15\ K)$, $kJ·mol^{-1}$
Hartmann and Sckneider[3]	159.04 ± 1.56
Bohdansky and Schins[4]	159.54 ± 1.85
Schins *et al.*[5]	159.22 ± 1.81
Rigney *et al.*[6]	159.34 ± 1.85
Anisimov and Volyak[7]	159.60 ± 1.58
Shpilrain and Belova[8]	159.06 ± 1.99

The weighted average is $\Delta_{sub}H°(298.15\ K)$ = 159.3 ± 1.0 $kJ·mol^{-1}$.

The 2nd law values calculated from the above sources lead to more positive values. 3rd law values in reasonable agreement with the selected value were calculated from the data of Bogros,[9] Maucherat,[10] Achener,[11] Wu,[12] and Bonilla.[13]

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP–kT) technique as the cutoff procedure in the energy level summation.[16]

The lowest lying levels for these metals [14904 cm^{-1} (Li), 16956 cm^{-1} (Na), 12985 cm^{-1} (K), 12578 cm^{-1} (Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm^{-1} for Li to 31406.1 cm^{-1} for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.[16]

The atomic energy levels have been taken from the compilation of Moore.[14,15] Our calculated values for the thermal functions are similar to those recommended by CODATA.[1] They do differ for two reasons, however. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 $J·K^{-1}·mol^{-1}$, presumably due to the use of slightly different values for auxiliary data.

References

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Continued on page 1527

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	157.725	157.725	INFINITE
100	20.786	116.074	157.261	−4.119	159.308	148.435	−77.535
200	20.786	130.481	140.682	−2.040	159.545	137.415	−35.889
250	20.786	135.120	139.123	−1.001	159.457	131.890	−27.557
298.15	20.786	138.781	138.781	0.	159.300	126.594	−22.179
300	20.786	138.909	138.781	0.038	159.293	126.391	−22.007
350	20.786	142.114	139.034	1.078	159.069	120.924	−18.047
400	20.786	144.889	139.596	2.117	158.771	115.495	−15.082
450	20.786	147.337	140.323	3.156	158.387	110.107	−12.781
500	20.786	149.527	141.136	4.196	154.917	105.074	−10.977
600	20.786	153.317	142.860	6.274	154.012	95.192	−8.287
700	20.786	156.521	144.589	8.353	153.165	85.456	−6.377
800	20.786	159.297	146.258	10.431	152.348	75.839	−4.952
900	20.786	161.745	147.845	12.510	151.535	66.324	−3.849
1000	20.786	163.935	149.346	14.589	150.728	56.900	−2.972
1100	20.786	165.916	150.764	16.667	149.925	47.556	−2.258
1200	20.786	167.725	152.103	18.746	149.128	38.285	−1.666
1300	20.786	169.389	153.370	20.825	148.334	29.080	−1.168
1400	20.787	170.929	154.570	22.903	147.547	19.936	−0.744
1500	20.789	172.363	155.709	24.982	146.768	10.848	−0.378
1600	20.793	173.705	156.792	27.061	145.998	1.812	−0.059
1620.120	20.794	173.965	157.004	27.479	----- FUGACITY = 1 bar -----		
1700	20.799	174.966	157.824	29.141	0.	0.	0.
1800	20.810	176.155	158.810	31.221	0.	0.	0.
1900	20.826	177.281	159.753	33.303	0.	0.	0.
2000	20.849	178.349	160.656	35.386	0.	0.	0.
2100	20.882	179.367	161.523	37.473	0.	0.	0.
2200	20.925	180.340	162.356	39.563	0.	0.	0.
2300	20.980	181.271	163.159	41.658	0.	0.	0.
2400	21.049	182.165	163.932	43.760	0.	0.	0.
2500	21.132	183.026	164.679	45.868	0.	0.	0.
2600	21.231	183.857	165.401	47.986	0.	0.	0.
2700	21.347	184.660	166.099	50.115	0.	0.	0.
2800	21.479	185.439	166.776	52.256	0.	0.	0.
2900	21.628	186.195	167.433	54.412	0.	0.	0.
3000	21.794	186.931	168.070	56.582	0.	0.	0.
3100	21.977	187.649	168.690	58.771	0.	0.	0.
3200	22.177	188.350	169.294	60.978	0.	0.	0.
3300	22.391	189.035	169.882	63.206	0.	0.	0.
3400	22.622	189.707	170.455	65.457	0.	0.	0.
3500	22.868	190.366	171.014	67.731	0.	0.	0.
3600	23.130	191.014	171.561	70.031	0.	0.	0.
3700	23.406	191.652	172.095	72.358	0.	0.	0.
3800	23.697	192.280	172.618	74.713	0.	0.	0.
3900	24.003	192.899	173.130	77.098	0.	0.	0.
4000	24.323	193.511	173.632	79.514	0.	0.	0.
4100	24.658	194.115	174.125	81.963	0.	0.	0.
4200	25.009	194.714	174.608	84.446	0.	0.	0.
4300	25.375	195.307	175.082	86.965	0.	0.	0.
4400	25.696	195.889	175.548	89.500	0.	0.	0.
4500	26.069	196.470	176.007	92.086	0.	0.	0.
4600	26.464	197.047	176.458	94.712	0.	0.	0.
4700	26.873	197.621	176.902	97.379	0.	0.	0.
4800	27.297	198.191	177.339	100.087	0.	0.	0.
4900	27.736	198.758	177.771	102.839	0.	0.	0.
5000	28.191	199.323	178.196	105.635	0.	0.	0.
5100	28.650	199.885	178.616	108.472	0.	0.	0.
5200	29.134	200.446	179.030	111.361	0.	0.	0.
5300	29.635	201.006	179.440	114.299	0.	0.	0.
5400	30.152	201.564	179.844	117.288	0.	0.	0.
5500	30.684	202.122	180.244	120.330	0.	0.	0.
5600	31.233	202.680	180.640	123.426	0.	0.	0.
5700	31.798	203.238	181.031	126.577	0.	0.	0.
5800	32.377	203.796	181.419	129.786	0.	0.	0.
5900	32.972	204.354	181.803	133.053	0.	0.	0.
6000	33.581	204.914	182.184	136.381	0.	0.	0.

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

IP(Li^+, g) = 610079.0 ± 0.1 cm^{-1}
$S°$(298.15 K) = 133.017 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 677.947 ± 0.002 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [685.719] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

$\Delta_f H°(Li^+, g, 0 K)$ is calculated from $\Delta_f H°$(Li, g, 0 K)[1] using the spectroscopic value of IP(Li) = 43487.150 ± 0.005 cm^{-1} (520.222 ± .000 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Li^+, g, 298.15 K)$ is calculated from $\Delta_f H°$(Li, g, 0 K) by using IP(Li) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for Li(g), $Li^+(g)$, and e^-(ref). $\Delta_f H°(Li \rightarrow Li^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state; the first excited state is approximately 476046 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	677.947		
100	20.786	110.309	151.497	−4.119			
200	20.786	124.717	134.918	−2.040			
250	20.786	129.356	133.359	−1.001			
298.15	20.786	133.017	133.017	0.	685.719	648.477	−113.611
300	20.786	133.145	133.017	0.038	685.751	648.246	−112.870
350	20.786	136.349	133.270	1.078	686.566	641.930	−95.803
400	20.786	139.125	133.832	2.117	687.307	635.502	−82.988
450	20.786	141.573	134.559	3.156	687.963	628.986	−73.011
500	20.786	143.763	135.372	4.196	685.532	622.709	−65.054
600	20.786	147.553	137.096	6.274	686.706	610.035	−53.108
700	20.786	150.757	138.825	8.353	687.938	597.160	−44.561
800	20.786	153.533	140.493	10.431	689.199	584.105	−38.138
900	20.786	155.981	142.081	12.510	690.465	570.893	−33.134
1000	20.786	158.171	143.582	14.589	691.736	557.539	−29.123
1100	20.786	160.152	145.000	16.667	693.012	544.057	−25.835
1200	20.786	161.961	146.339	18.746	694.293	530.460	−23.090
1300	20.786	163.625	147.606	20.824	695.578	516.755	−20.763
1400	20.786	165.165	148.806	22.903	696.869	502.951	−18.765
1500	20.786	166.599	149.945	24.982	698.169	489.054	−17.030
1600	20.786	167.941	151.028	27.060	699.477	475.070	−15.509
1700	20.786	169.201	152.060	29.139	555.556	468.181	−14.385
1800	20.786	170.389	153.046	31.217	557.633	462.981	−13.435
1900	20.786	171.513	153.988	33.296	559.709	457.666	−12.582
2000	20.786	172.579	154.891	35.375	561.782	452.242	−11.811
2100	20.786	173.593	155.758	37.453	563.853	446.714	−11.111
2200	20.786	174.560	156.591	39.532	565.920	441.087	−10.473
2300	20.786	175.484	157.392	41.610	567.982	435.367	−9.887
2400	20.786	176.369	158.165	43.689	570.038	429.557	−9.349
2500	20.786	177.217	158.910	45.768	572.086	423.661	−8.852
2600	20.786	178.032	159.630	47.846	574.125	417.684	−8.391
2700	20.786	178.817	160.326	49.925	576.154	411.629	−7.963
2800	20.786	179.573	161.000	52.004	578.170	405.498	−7.565
2900	20.786	180.302	161.653	54.082	580.172	399.296	−7.192
3000	20.786	181.007	162.287	56.161	582.158	393.025	−6.843
3100	20.786	181.688	162.902	58.239	584.127	386.688	−6.516
3200	20.786	182.348	163.499	60.318	586.077	380.288	−6.208
3300	20.786	182.988	164.080	62.397	588.006	373.827	−5.917
3400	20.786	183.608	164.645	64.475	589.913	367.308	−5.643
3500	20.786	184.211	165.196	66.554	591.795	360.733	−5.384
3600	20.786	184.797	165.732	68.632	593.653	354.105	−5.138
3700	20.786	185.366	166.255	70.711	595.483	347.426	−4.905
3800	20.786	185.920	166.765	72.790	597.286	340.697	−4.683
3900	20.786	186.460	167.263	74.868	599.058	333.922	−4.472
4000	20.786	186.987	167.750	76.947	600.799	327.101	−4.272
4100	20.786	187.500	168.225	79.025	602.507	320.238	−4.080
4200	20.786	188.001	168.690	81.104	604.181	313.333	−3.897
4300	20.786	188.490	169.145	83.183	605.819	306.388	−3.722
4400	20.786	188.968	169.590	85.261	607.441	299.405	−3.554
4500	20.786	189.435	170.026	87.340	609.013	292.386	−3.394
4600	20.786	189.892	170.453	89.418	610.544	285.333	−3.240
4700	20.786	190.339	170.871	91.497	612.034	278.247	−3.092
4800	20.786	190.776	171.281	93.576	613.483	271.129	−2.950
4900	20.786	191.205	171.684	95.654	614.889	263.982	−2.814
5000	20.786	191.625	172.078	97.733	616.250	256.807	−2.683
5100	20.786	192.036	172.466	99.811	617.570	249.605	−2.556
5200	20.786	192.440	172.846	101.890	618.838	242.377	−2.435
5300	20.786	192.836	173.219	103.969	620.057	235.126	−2.317
5400	20.786	193.225	173.586	106.047	621.225	227.852	−2.204
5500	20.786	193.606	173.947	108.126	622.341	220.557	−2.095
5600	20.786	193.981	174.301	110.204	623.402	213.242	−1.989
5700	20.786	194.348	174.650	112.283	624.408	205.909	−1.887
5800	20.786	194.710	174.992	114.362	625.357	198.558	−1.788
5900	20.786	195.065	175.330	116.440	626.246	191.192	−1.693
6000	20.786	195.415	175.661	118.519	627.076	183.811	−1.600

PREVIOUS: March 1965 (1 atm) CURRENT: December 1983 (1 bar)

EA(Li, g) = 0.6180 ± 0.0005 eV
$S°$(298.15 K) = 133.019 ± 0.005 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 98.10 ± 0.1 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [93.475] kJ·mol^{-1}

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for Li^-(g) is calculated from the adopted electron affinity, EA(Li, g) = 0.6180 ± 0.0005 eV (59.627 ± 0.048 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[1] was measured by a tunable laser photodetachment threshold technique.[2,3] Additional discussion on Li^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[1,4] Rosenstock *et al.*,[5] and Massey.[6]

$\Delta_f H°$(Li^-, g, 298.15 K) is obtained from $\Delta_f H°$(Li, g, 0 K) by using EA(Li, g) with JANAF[7] enthalpies, $H°$(0 K)–$H°$(298.15 K), for Li^-(g), Li(g), and e^-(ref). $\Delta_r H°$($Li^- \rightarrow Li + e^-$, 298.15 K) differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°$(298.15 K) should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Li^-(g) is given by Hotop and Lineberger[1,4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

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[6] H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, (1976).
[7] JANAF Thermochemical Tables: Li(g), 3-31-82; e^-(ref), 3-31-82.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	98.097		
100	20.786	110.311	151.499	−4.119			
200	20.786	124.719	134.920	−2.040			
250	20.786	129.357	133.361	−1.001			
298.15	20.786	133.019	133.019	0.	93.475	68.742	−12.043
300	20.786	133.147	133.019	0.038	93.430	68.589	−11.942
350	20.786	136.351	133.272	1.078	92.167	64.548	−9.633
400	20.786	139.127	133.834	2.117	90.829	60.692	−7.926
450	20.786	141.575	134.561	3.156	89.406	57.010	−6.618
500	20.786	143.765	135.374	4.196	84.896	53.797	−5.620
600	20.786	147.555	137.098	6.274	81.913	47.859	−4.166
700	20.786	150.759	138.827	8.353	78.988	42.415	−3.165
800	20.786	153.535	140.495	10.431	76.092	37.388	−2.441
900	20.786	155.983	142.083	12.510	73.200	32.724	−1.899
1000	20.786	158.173	143.584	14.589	70.314	28.381	−1.482
1100	20.786	160.154	145.002	16.667	67.433	24.328	−1.155
1200	20.786	161.963	146.341	18.746	64.557	20.536	−0.894
1300	20.786	163.627	147.608	20.824	61.685	16.984	−0.682
1400	20.786	165.167	148.808	22.903	58.819	13.653	−0.509
1500	20.786	166.601	149.947	24.982	55.961	10.527	−0.367
1600	20.786	167.943	151.030	27.060	53.112	7.591	−0.248
1700	20.786	169.203	152.062	29.139	−94.965	12.009	−0.369
1800	20.786	170.391	153.048	31.217	−97.046	18.361	−0.533
1900	20.786	171.515	153.990	33.296	−99.128	24.829	−0.683
2000	20.786	172.581	154.893	35.375	−101.211	31.407	−0.820
2100	20.786	173.595	155.760	37.453	−103.298	38.090	−0.947
2200	20.786	174.562	156.593	39.532	−105.388	44.871	−1.065
2300	20.786	175.486	157.394	41.610	−107.483	51.748	−1.175
2400	20.786	176.371	158.167	43.689	−109.584	58.716	−1.278
2500	20.786	177.219	158.912	45.768	−111.693	65.772	−1.374
2600	20.786	178.034	159.632	47.846	−113.811	72.913	−1.465
2700	20.786	178.819	160.328	49.925	−115.940	80.135	−1.550
2800	20.786	179.575	161.002	52.004	−118.081	87.436	−1.631
2900	20.786	180.304	161.655	54.082	−120.236	94.814	−1.708
3000	20.786	181.009	162.289	56.161	−122.407	102.266	−1.781
3100	20.786	181.690	162.904	58.239	−124.596	109.791	−1.850
3200	20.786	182.350	163.501	60.318	−126.803	117.387	−1.916
3300	20.786	182.990	164.082	62.397	−129.031	125.053	−1.979
3400	20.786	183.610	164.647	64.475	−131.282	132.786	−2.040
3500	20.786	184.213	165.198	66.554	−133.556	140.586	−2.098
3600	20.786	184.799	165.734	68.632	−135.856	148.451	−2.154
3700	20.786	185.368	166.257	70.711	−138.183	156.380	−2.208
3800	20.786	185.922	166.767	72.790	−140.538	164.373	−2.259
3900	20.786	186.462	167.265	74.868	−142.922	172.428	−2.309
4000	20.786	186.989	167.752	76.947	−145.339	180.544	−2.358
4100	20.786	187.502	168.227	79.025	−147.788	188.722	−2.404
4200	20.786	188.003	168.692	81.104	−150.271	196.959	−2.450
4300	20.786	188.492	169.147	83.183	−152.790	205.256	−2.493
4400	20.786	188.970	169.592	85.261	−155.325	213.611	−2.536
4500	20.786	189.437	170.028	87.340	−157.910	222.024	−2.577
4600	20.786	189.894	170.455	89.418	−160.537	230.496	−2.617
4700	20.786	190.341	170.873	91.497	−163.204	239.026	−2.656
4800	20.786	190.778	171.283	93.576	−165.912	247.612	−2.695
4900	20.786	191.207	171.686	95.654	−168.664	256.256	−2.732
5000	20.786	191.627	172.080	97.733	−171.460	264.956	−2.768
5100	20.786	192.038	172.468	99.811	−174.297	273.712	−2.803
5200	20.786	192.442	172.848	101.890	−177.186	282.524	−2.838
5300	20.786	192.838	173.221	103.969	−180.124	291.393	−2.872
5400	20.786	193.227	173.588	106.047	−183.113	300.317	−2.905
5500	20.786	193.608	173.949	108.126	−186.155	309.298	−2.937
5600	20.786	193.982	174.303	110.204	−189.251	318.334	−2.969
5700	20.786	194.350	174.652	112.283	−192.402	327.426	−3.001
5800	20.786	194.712	174.994	114.362	−195.611	336.573	−3.031
5900	20.786	195.067	175.332	116.440	−198.878	345.777	−3.061
6000	20.786	195.417	175.663	118.519	−202.206	355.036	−3.091

PREVIOUS: CURRENT: December 1983 (1 bar)

$\Delta_f H°(0\ K) = 334.7 \pm 167\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [208.245]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = 334.7 \pm 167\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^3\Sigma]$	0	[3]

$\omega_e = [700]\ cm^{-1}$ $\omega_e x_e = [7]\ cm^{-1}$ $\sigma = 1$

$B_e = [1.25]\ cm^{-1}$ $\alpha_e = [0.0183]\ cm^{-1}$ $r_e = [1.71]$ Å

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = 80 \pm 40\ kcal \cdot mol^{-1}$ is calculated from the following estimates:

Method	$D_0°$, kcal·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
Estimate $D_0°$ from geometric means for Li_2 and N_2	76	75
Estimate from $D_0°$ for series N_2(g), CN(g), BN(g), and BeN(g)	40 – 100	110 – 50
Estimate from $D_0°$ for series HN(g), HO(g), HF(g), LiF(g) and LiO(g)	20 – 60	130 – 90

Margrave and Sthapitanonda[1] report estimated dissociation energies in the range 111–178 kcal·mol^{-1} based on approximate ionic binding energies calculated from ionic radii for N^- in the range 0.70 to 1.08 Å.

Heat Capacity and Entropy

The molecular constants, ω_e, r_e and $\omega_e x_e$ are estimated by comparison with those of CN, BN, CO, BO and LiO. The values of α_e and B_e are calculated from the above constants. The ground state configuration is assumed to be $^3\Sigma$ by analogy with NH and OH^+.

Reference

[1] J. L. Margrave and P. Sthapitanonda, J. Phys. Chem. 59, 1231 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.999	334.678	334.678	INFINITE
100	29.167	175.034	235.957	−6.092	335.639	326.860	−170.734
200	30.651	195.587	211.181	−3.119	335.316	318.162	−83.095
250	31.812	202.552	208.780	−1.557	335.021	313.907	−65.587
298.15	32.838	208.245	208.245	0.	334.720	309.868	−54.288
300	32.875	208.448	208.246	0.061	334.708	309.713	−53.926
350	33.762	213.585	208.649	1.727	334.383	305.573	−45.604
400	34.479	218.142	209.556	3.434	334.022	301.481	−39.369
450	35.056	222.237	210.742	5.173	333.605	297.438	−34.526
500	35.521	225.956	212.080	6.938	330.123	293.752	−30.688
600	36.215	232.497	214.952	10.527	329.238	286.562	−24.947
700	36.702	238.118	217.870	14.174	328.438	279.514	−20.858
800	37.064	243.044	220.715	17.863	327.676	272.577	−17.797
900	37.345	247.426	223.444	21.584	326.918	265.735	−15.423
1000	37.574	251.373	226.043	25.330	326.158	258.977	−13.528
1100	37.767	254.964	228.511	29.098	325.396	252.296	−11.981
1200	37.935	258.257	230.855	32.883	324.631	245.684	−10.694
1300	38.084	261.300	233.081	36.684	323.862	239.137	−9.609
1400	38.221	264.127	235.199	40.499	323.095	232.648	−8.680
1500	38.347	266.768	237.216	44.328	322.332	226.214	−7.877
1600	38.466	269.247	239.142	48.169	321.573	219.831	−7.177
1700	38.578	271.582	240.982	52.021	175.586	220.671	−6.780
1800	38.686	273.791	242.744	55.884	175.594	223.323	−6.481
1900	38.790	275.885	244.434	59.758	175.601	225.975	−6.212
2000	38.890	277.877	246.056	63.642	175.607	228.626	−5.971
2100	38.989	279.777	247.617	67.536	175.612	231.277	−5.753
2200	39.085	281.593	249.121	71.440	175.616	233.927	−5.554
2300	39.179	283.333	250.570	75.353	175.617	236.578	−5.373
2400	39.273	285.002	251.971	79.275	175.616	239.228	−5.207
2500	39.364	286.607	253.324	83.207	175.611	241.879	−5.054
2600	39.455	288.153	254.634	87.148	175.600	244.530	−4.913
2700	39.545	289.643	255.903	91.098	175.584	247.181	−4.782
2800	39.634	291.083	257.134	95.057	175.559	249.833	−4.661
2900	39.722	292.476	258.329	99.025	175.526	252.486	−4.548
3000	39.810	293.824	259.490	103.002	175.482	255.141	−4.442
3100	39.898	295.131	260.619	106.987	175.426	257.797	−4.344
3200	39.984	296.399	261.717	110.981	175.356	260.455	−4.251
3300	40.071	297.630	262.787	114.984	175.271	263.116	−4.165
3400	40.157	298.828	263.829	118.995	175.170	265.779	−4.083
3500	40.243	299.993	264.846	123.015	175.051	268.446	−4.006
3600	40.328	301.128	265.838	127.044	174.912	271.116	−3.934
3700	40.414	302.234	266.807	131.081	174.753	273.791	−3.865
3800	40.499	303.313	267.753	135.127	174.571	276.470	−3.800
3900	40.584	304.366	268.679	139.181	174.366	279.154	−3.739
4000	40.668	305.395	269.584	143.243	174.136	281.844	−3.681
4100	40.753	306.400	270.470	147.314	173.880	284.540	−3.625
4200	40.837	307.383	271.337	151.394	173.596	287.242	−3.572
4300	40.921	308.345	272.186	155.482	173.282	289.952	−3.522
4400	41.006	309.287	273.019	159.578	172.959	292.667	−3.474
4500	41.090	310.209	273.835	163.683	172.592	295.392	−3.429
4600	41.173	311.113	274.636	167.796	172.191	298.125	−3.385
4700	41.257	311.999	275.421	171.918	171.757	300.867	−3.344
4800	41.341	312.869	276.192	176.048	171.287	303.619	−3.304
4900	41.425	313.722	276.950	180.186	170.781	306.381	−3.266
5000	41.508	314.560	277.693	184.332	170.236	309.154	−3.230
5100	41.592	315.383	278.424	188.487	169.658	311.938	−3.195
5200	41.675	316.191	279.143	192.651	169.034	314.733	−3.162
5300	41.759	316.986	279.849	196.822	168.367	317.542	−3.130
5400	41.842	317.767	280.544	201.003	167.657	320.363	−3.099
5500	41.925	318.536	281.228	205.191	166.900	323.198	−3.069
5600	42.009	319.292	281.901	209.388	166.096	326.047	−3.041
5700	42.092	320.036	282.564	213.593	165.243	328.910	−3.014
5800	42.175	320.769	283.216	217.806	164.339	331.789	−2.988
5900	42.258	321.491	283.859	222.028	163.383	334.685	−2.963
6000	42.341	322.201	284.492	226.258	162.373	337.597	−2.939

PREVIOUS: December 1966 (1 atm) CURRENT: December 1966 (1 bar)

$S°(298.15\ K) = 245.332\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [181.91 \pm 41.8]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [179.91 \pm 41.8]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1350(1)
330(1)
650(1)

Ground State Quantum Weight: [1] $\sigma = 1$
Point Group: C_s
Bond Distances: O–Li = 1.63 ± 0.07 Å O–N = 1.30 ± 0.05 Å
Bond Angle: Li–O–N = 100 ± 10°
Product of the Moments of Inertia: $I_A I_B I_C = 2.65370 \times 10^{-116}\ g^3·cm^6$

Enthalpy of Formation

In order to estimate the $\Delta_f H°$(298.15 K) of LiON(g) a comparison with the known $\Delta_f H°$(LiOH, g, 298.15 K) = −59 kcal·mol^{-1} was made. This was estimated from bond energies using D(Li–O) = 88 kcal·mol^{-1}, the average value in Li_2O(g), and D(O–H) = 111 kcal·mol^{-1}, the average value in H_2O(g), which yields an estimated $\Delta_f H°$(LiOH, g, 298.15 K) = −49 kcal·mol^{-1} or a difference of −10 kcal·mol^{-1}. Using D(N=O) = 69 kcal·mol^{-1} from NO_2Cl(g)(equation 1) and D(Li–O) = 88 kcal·mol^{-1} from Li_2O(g), the estimated $\Delta_f H°$(298.15 K) = 53 kcal·mol^{-1} of LiON(g) was obtained (equation 2). Thus adding the −10 kcal·mol^{-1} correction from the above comparison a $\Delta_f H°$(298.15 K) = 43 kcal·mol^{-1} for LiON(g) was obtained.

The justification for using a N=O bond energy is from the 1.7 bond order reported by Andrews and Pimentel[1] and a comparison of bond lengths.

Equations:	1. $NO_2Cl(g) \rightarrow NOCl(g) + O(g)$
	2. $LiON(g) \rightarrow Li(g) + O(g) + N(g)$

Heat Capacity and Entropy

The vibration frequencies, bond distances and bond angle were obtained from Andrews and Pimentel.[1] The principal moments of inertia are: $I_A = 1.2707 \times 10^{-39}$, $I_B = 3.9785 \times 10^{-39}$ and $I_C = 5.2492 \times 10^{-39}$ g·cm.^{2}

Reference

[1]W. L. S. Andrews and G. C. Pimentel, J. Chem. Phys. **44**, 2361 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.301	181.910	181.910	INFINITE
100	34.974	202.507	281.906	−7.940	181.873	179.012	−93.506
200	40.335	228.423	249.272	−4.170	180.890	176.518	−46.102
250	42.576	237.671	246.053	−2.096	180.380	175.484	−36.665
298.15	44.424	245.332	245.332	0.	179.912	174.584	−30.586
300	44.490	245.607	245.333	0.082	179.895	174.551	−30.392
350	46.144	252.592	245.881	2.349	179.432	173.698	−25.923
400	47.585	258.850	247.117	4.693	178.961	172.910	−22.580
450	48.838	264.529	248.741	7.104	178.457	172.184	−19.987
500	49.925	269.732	250.584	9.574	174.909	171.823	−17.950
600	51.676	278.997	254.566	14.658	173.939	171.299	−14.913
700	52.982	287.066	258.645	19.895	173.101	170.927	−12.755
800	53.962	294.208	262.653	25.244	172.332	170.669	−11.144
900	54.706	300.608	266.521	30.679	171.585	170.506	−9.896
1000	55.280	306.403	270.224	36.180	170.848	170.426	−8.902
1100	55.729	311.694	273.757	41.731	170.115	170.419	−8.093
1200	56.085	316.559	277.124	47.322	169.382	170.479	−7.421
1300	56.371	321.060	280.332	52.946	168.644	170.601	−6.855
1400	56.605	325.246	283.393	58.595	167.904	170.779	−6.372
1500	56.797	329.158	286.315	64.265	167.162	171.010	−5.955
1600	56.957	332.829	289.108	69.953	166.417	171.291	−5.592
1700	57.092	336.286	291.783	75.656	20.434	178.795	−5.494
1800	57.206	339.553	294.347	81.371	20.436	188.110	−5.459
1900	57.304	342.649	296.808	87.097	20.425	197.425	−5.428
2000	57.388	345.590	299.174	92.831	20.401	206.742	−5.400
2100	57.461	348.392	301.452	98.574	20.362	216.060	−5.374
2200	57.525	351.066	303.647	104.323	20.307	225.380	−5.351
2300	57.581	353.625	305.765	110.079	20.235	234.703	−5.330
2400	57.630	356.076	307.810	115.839	20.145	244.029	−5.311
2500	57.674	358.430	309.788	121.604	20.036	253.360	−5.294
2600	57.713	360.693	311.703	127.374	19.906	262.695	−5.278
2700	57.747	362.871	313.558	133.147	19.754	272.036	−5.263
2800	57.779	364.972	315.357	138.923	19.578	281.383	−5.249
2900	57.807	367.000	317.103	144.702	19.377	290.737	−5.237
3000	57.832	368.960	318.799	150.484	19.150	300.098	−5.225
3100	57.855	370.857	320.448	156.269	18.895	309.467	−5.214
3200	57.876	372.694	322.052	162.055	18.611	318.845	−5.205
3300	57.895	374.475	323.614	167.844	18.296	328.232	−5.195
3400	57.913	376.204	325.135	173.634	17.950	337.629	−5.187
3500	57.929	377.883	326.618	179.426	17.571	347.037	−5.179
3600	57.943	379.515	328.065	185.220	17.158	356.456	−5.172
3700	57.957	381.103	329.477	191.015	16.709	365.887	−5.165
3800	57.970	382.649	330.856	196.811	16.224	375.331	−5.159
3900	57.981	384.155	332.204	202.609	15.702	384.788	−5.154
4000	57.992	385.623	333.521	208.408	15.140	394.258	−5.148
4100	58.002	387.055	334.809	214.207	14.538	403.744	−5.144
4200	58.011	388.453	336.070	220.008	13.894	413.244	−5.139
4300	58.020	389.818	337.304	225.809	13.207	422.761	−5.136
4400	58.028	391.152	338.513	231.612	12.497	432.292	−5.132
4500	58.035	392.456	339.697	237.415	11.730	441.841	−5.129
4600	58.042	393.732	340.858	243.219	10.915	451.407	−5.126
4700	58.049	394.980	341.996	249.023	10.052	460.993	−5.123
4800	58.055	396.202	343.113	254.829	9.140	470.597	−5.121
4900	58.061	397.399	344.208	260.634	8.177	480.220	−5.119
5000	58.067	398.572	345.284	266.441	7.162	489.864	−5.118
5100	58.072	399.722	346.340	272.248	6.099	499.529	−5.116
5200	58.077	400.850	347.378	278.055	4.975	509.214	−5.115
5300	58.081	401.956	348.397	283.863	3.793	518.923	−5.114
5400	58.086	403.042	349.399	289.672	2.551	528.653	−5.114
5500	58.090	404.108	350.384	295.480	1.248	538.407	−5.113
5600	58.094	405.154	351.353	301.289	−0.119	548.187	−5.113
5700	58.097	406.183	352.306	307.099	−1.552	557.990	−5.113
5800	58.101	407.193	353.243	312.909	−3.053	567.820	−5.114
5900	58.104	408.186	354.166	318.719	−4.624	577.675	−5.114
6000	58.107	409.163	355.075	324.530	−6.268	587.559	−5.115

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

Lithium Sodium Oxide (LiONa) **IDEAL GAS** $M_r = 45.93017$

$\Delta_f H°(0\ K) = [-100.16 \pm 125.5]\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = [256.459]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [-104.60 \pm 125.5]\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[400](1)
[1000](1)
[900](1)

Ground State Quantum Weight: [1] $\sigma = 1$

Point Group: C_s

Bond Distances: O–Li = [1.82] Å O–Na = [2.21] Å

Bond Angle: Li–O–Na = [105]°

Product of the Moments of Inertia: $I_A I_B I_C = [3.182324 \times 10^{-115}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Estimated from bond energies derived from enthalpies of formation used in the JANAF Thermochemical Tables.

Heat Capacity and Entropy

The molecular constants have been estimated by comparison of similar molecules. The principal moments of inertia are: $I_A = 1.9618 \times 10^{-39}$, $I_B = 11.7930 \times 10^{-39}$, and $I_C = 13.7548 \times 10^{-39}\ g \cdot cm^2$.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.966	−100.156	−100.156	INFINITE
100	34.139	215.303	291.557	−7.625	−100.102	−109.851	57.380
200	38.470	240.232	260.252	−4.004	−102.233	−118.826	31.034
250	40.849	249.071	257.156	−2.021	−103.432	−122.836	25.665
298.15	43.079	256.459	256.459	0.	−104.600	−126.468	22.157
300	43.161	256.726	256.460	0.080	−104.645	−126.604	22.044
350	45.267	263.540	256.993	2.292	−105.887	−130.166	19.426
400	47.099	269.708	258.203	4.602	−109.831	−133.340	17.412
450	48.652	275.348	259.799	6.997	−111.180	−136.198	15.809
500	49.952	280.543	261.617	9.463	−115.534	−138.598	14.479
600	51.941	289.837	265.564	14.564	−118.012	−142.973	12.447
700	53.334	297.955	269.624	19.831	−120.249	−146.954	10.966
800	54.331	305.145	273.623	25.217	−122.337	−150.625	9.835
900	55.060	311.589	277.490	30.689	−124.346	−154.040	8.940
1000	55.607	317.419	281.196	36.223	−126.316	−157.234	8.213
1100	56.026	322.740	284.734	41.806	−128.278	−160.230	7.609
1200	56.353	327.629	288.108	47.425	−227.019	−160.608	6.991
1300	56.613	332.151	291.324	53.074	−228.112	−155.029	6.229
1400	56.822	336.354	294.392	58.746	−229.192	−149.367	5.573
1500	56.993	340.280	297.322	64.437	−230.258	−143.628	5.002
1600	57.134	343.963	300.123	70.144	−231.313	−137.818	4.499
1700	57.252	347.431	302.805	75.863	−377.595	−124.767	3.834
1800	57.352	350.706	305.376	81.594	−377.882	−109.886	3.189
1900	57.437	353.809	307.844	87.333	−378.174	−94.990	2.611
2000	57.510	356.757	310.217	93.081	−378.471	−80.078	2.091
2100	57.573	359.565	312.500	98.835	−378.777	−65.151	1.621
2200	57.628	362.244	314.701	104.595	−379.094	−50.208	1.192
2300	57.676	364.807	316.824	110.360	−379.423	−35.252	0.801
2400	57.718	367.262	318.875	116.130	−379.768	−20.281	0.441
2500	57.755	369.619	320.858	121.904	−380.132	−5.295	0.111
2600	57.788	371.885	322.777	127.681	−380.515	9.706	−0.195
2700	57.818	374.067	324.637	133.461	−380.922	24.723	−0.478
2800	57.844	376.170	326.440	139.244	−381.356	39.755	−0.742
2900	57.868	378.200	328.190	145.030	−381.819	54.802	−0.987
3000	57.890	380.162	329.890	150.818	−382.314	69.866	−1.216
3100	57.910	382.061	331.542	156.608	−382.845	84.948	−1.431
3200	57.927	383.900	333.150	162.400	−383.414	100.047	−1.633
3300	57.943	385.683	334.715	168.193	−384.024	115.164	−1.823
3400	57.958	387.413	336.240	173.988	−384.680	130.301	−2.002
3500	57.972	389.093	337.726	179.785	−385.383	145.457	−2.171
3600	57.984	390.726	339.175	185.583	−386.138	160.635	−2.331
3700	57.996	392.315	340.590	191.382	−386.947	175.834	−2.482
3800	58.006	393.862	341.972	197.182	−387.814	191.056	−2.626
3900	58.016	395.369	343.322	202.983	−388.743	206.301	−2.763
4000	58.025	396.838	344.641	208.785	−389.738	221.571	−2.893
4100	58.034	398.271	345.932	214.588	−390.802	236.867	−3.018
4200	58.041	399.669	347.195	220.392	−391.937	252.189	−3.136
4300	58.049	401.035	348.431	226.196	−393.151	267.540	−3.250
4400	58.056	402.369	349.642	232.002	−394.384	282.914	−3.359
4500	58.062	403.674	350.828	237.807	−395.733	298.322	−3.463
4600	58.068	404.950	351.991	243.614	−397.179	313.761	−3.563
4700	58.073	406.199	353.131	249.421	−398.715	329.232	−3.659
4800	58.079	407.422	354.249	255.229	−400.344	344.738	−3.752
4900	58.084	408.620	355.347	261.037	−402.073	360.278	−3.841
5000	58.088	409.793	356.424	266.845	−403.897	375.854	−3.927
5100	58.093	410.943	357.482	272.654	−405.828	391.468	−4.009
5200	58.097	412.072	358.521	278.464	−407.876	407.120	−4.090
5300	58.101	413.178	359.542	284.274	−410.040	422.814	−4.167
5400	58.104	414.264	360.545	290.084	−412.325	438.549	−4.242
5500	58.108	415.330	361.531	295.895	−414.735	454.328	−4.315
5600	58.111	416.378	362.502	301.705	−417.275	470.153	−4.385
5700	58.114	417.406	363.456	307.517	−419.949	486.023	−4.454
5800	58.117	418.417	364.395	313.328	−422.762	501.942	−4.520
5900	58.120	419.410	365.319	319.140	−425.716	517.909	−4.585
6000	58.123	420.387	366.228	324.952	−428.659	533.911	−4.648

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = [210.963]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 84.12 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 84.10 \pm 20.9\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^2\Pi]$	0	4

$\omega_e = 745\ cm^{-1}$ $\omega_e x_e = [4.835]\ cm^{-1}$ $\sigma = 1$
$B_e = [1.333]\ cm^{-1}$ $\alpha_e = [0.01288]\ cm^{-1}$ $r_e = [1.62]$ Å

Enthalpy of Formation

White *et al.*[1] calculated the enthalpy of formation from their mass spectral data by two different methods.

For the first calculation (a) they combined the slope of the log IT vs $1/T$ curve for LiO^+ with the slopes for Li^+ and Li_2O^+ for the reaction $Li_2O(g) \rightarrow Li(g) + LiO(g)$. For the second calculation (b) they assumed a cross section σ LiO/σ Li_2O = 1 and from this they calculated a partial pressure for LiO(g) at 1500 K and an equilibrium constant for the reaction $Li_2O(g) \rightarrow Li(g) + LiO(g)$. They obtained (a) $\Delta_f H°(298.15\ k) = 18.3$ $kcal·mol^{-1}$ and (b) $\Delta_f H°(298.15\ K) = 16.3\ kcal·mol^{-1}$, and used the average value from the two methods for the enthalpy of formation of LiO(g). The JANAF enthalpy of formation, $20.1 \pm 5\ kcal·mol^{-1}$, was obtained in the same way using their data and the present tables i.e. (a) $\Delta_f H°(298.15\ K) = 22.0\ kcal·mol^{-1}$ and (b) $\Delta_f H°(298.15\ K) = 18.3\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The molecular constants, $\omega_e x_e$, B_e and α_e, were calculated from ω_e and r_e, reported by White *et al.*[1] The ground state configuration, $^2\Pi$, was estimated by Gordon,[2] Buchler and Stauffer[3] and White *et al.*[1]

References

[1]D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963).
[2]J. S. Gordon, Thiokol Chemical Corp., Reaction Motor Division, Denville, N.J., "Thermodynamic Data for Combustion Products," (Janaury 1960).
[3]A. Buchler and J. L. Stauffer, J. Chem. Phys. **39**, 2299 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.945	84.118	84.118	INFINITE
100	29.147	178.000	238.387	−6.039	85.076	76.676	−40.051
200	30.343	198.459	213.861	−3.080	84.737	68.359	−17.854
250	31.411	205.343	211.491	−1.537	84.424	64.300	−13.435
298.15	32.406	210.963	210.963	0.	84.098	60.454	−10.591
300	32.442	211.163	210.963	0.060	84.086	60.307	−10.500
350	33.332	216.233	211.362	1.705	83.729	56.372	−8.413
400	34.067	220.733	212.257	3.391	83.330	52.490	−6.855
450	34.664	224.782	213.427	5.109	82.867	48.662	−5.649
500	35.148	228.460	214.750	6.855	79.332	45.197	−4.722
600	35.872	234.936	217.589	10.408	78.323	38.466	−3.349
700	36.376	240.506	220.474	14.022	77.384	31.898	−2.380
800	36.744	245.389	223.290	17.679	76.476	25.462	−1.663
900	37.024	249.733	225.991	21.368	75.571	19.140	−1.111
1000	37.246	253.646	228.564	25.082	74.668	12.918	−0.675
1100	37.428	257.205	231.008	28.816	73.766	6.787	−0.322
1200	37.582	260.468	233.329	32.567	72.867	0.738	−0.032
1300	37.716	263.482	235.534	36.332	71.968	−5.237	0.210
1400	37.834	266.281	237.632	40.109	71.073	−11.142	0.416
1500	37.942	268.895	239.630	43.898	70.183	−16.983	0.591
1600	38.041	271.347	241.536	47.697	69.300	−22.766	0.743
1700	38.133	273.656	243.358	51.506	−76.815	−21.317	0.655
1800	38.219	275.838	245.103	55.324	−76.936	−18.049	0.524
1900	38.302	277.907	246.775	59.150	−77.061	−14.774	0.406
2000	38.381	279.874	248.381	62.984	−77.192	−11.492	0.300
2100	38.457	281.748	249.926	66.826	−77.329	−8.204	0.204
2200	38.530	283.539	251.414	70.675	−77.474	−4.909	0.117
2300	38.602	285.253	252.848	74.532	−77.628	−1.607	0.036
2400	38.672	286.897	254.233	78.396	−77.792	1.702	−0.037
2500	38.741	288.477	255.571	82.266	−77.967	5.017	−0.105
2600	38.808	289.998	256.866	86.144	−78.156	8.340	−0.168
2700	38.875	291.464	258.120	90.028	−78.359	11.671	−0.226
2800	38.941	292.879	259.337	93.919	−78.579	15.010	−0.280
2900	39.005	294.247	260.517	97.816	−78.815	18.356	−0.331
3000	39.070	295.570	261.664	101.720	−79.071	21.711	−0.378
3100	39.133	296.852	262.778	105.630	−79.347	25.075	−0.423
3200	39.196	298.096	263.862	109.547	−79.645	28.448	−0.464
3300	39.259	299.303	264.918	113.469	−79.966	31.831	−0.504
3400	39.321	300.476	265.947	117.398	−80.311	35.224	−0.541
3500	39.383	301.616	266.950	121.334	−80.682	38.627	−0.576
3600	39.445	302.727	267.928	125.275	−81.080	42.042	−0.610
3700	39.506	303.808	268.883	129.223	−81.506	45.467	−0.642
3800	39.567	304.863	269.816	133.176	−81.962	48.906	−0.672
3900	39.628	305.891	270.728	137.136	−82.448	52.356	−0.701
4000	39.689	306.895	271.620	141.102	−82.966	55.819	−0.729
4100	39.749	307.876	272.492	145.074	−83.517	59.295	−0.755
4200	39.810	308.835	273.346	149.052	−84.103	62.785	−0.781
4300	39.870	309.772	274.182	153.036	−84.725	66.290	−0.805
4400	39.930	310.689	275.002	157.026	−85.364	69.808	−0.829
4500	39.990	311.587	275.805	161.022	−86.052	73.342	−0.851
4600	40.049	312.467	276.592	165.024	−86.781	76.891	−0.873
4700	40.109	313.329	277.365	169.031	−87.551	80.458	−0.894
4800	40.169	314.174	278.123	173.045	−88.364	84.041	−0.915
4900	40.228	315.003	278.867	177.065	−89.219	87.642	−0.934
5000	40.287	315.816	279.598	181.091	−90.120	91.260	−0.953
5100	40.347	316.615	280.316	185.123	−91.062	94.897	−0.972
5200	40.406	317.399	281.022	189.160	−92.058	98.552	−0.990
5300	40.465	318.169	281.715	193.204	−93.104	102.228	−1.008
5400	40.524	318.926	282.397	197.253	−94.203	105.924	−1.025
5500	40.583	319.670	283.068	201.309	−95.357	109.640	−1.041
5600	40.642	320.402	283.728	205.370	−96.567	113.379	−1.058
5700	40.701	321.122	284.378	209.437	−97.835	117.139	−1.073
5800	40.760	321.830	285.018	213.510	−99.165	120.922	−1.089
5900	40.819	322.527	285.648	217.589	−100.557	124.728	−1.104
6000	40.878	323.214	286.268	221.674	−102.013	128.559	−1.119

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

Lithium Oxide, Ion (LiO^-) — IDEAL GAS — $M_r = 22.94095$

$S°(298.15\ K) = [199.241 \pm 1.3]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-60.7 \pm 62.8]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-66.944]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma]$	0	[1]

$\omega_e = [750]\ cm^{-1}$ $\quad \omega_e x_e = [4.5]\ cm^{-1}$ $\quad \sigma = 1$

$B_e = [1.360]\ cm^{-1}$ $\quad \alpha_e = [0.0121]\ cm^{-1}$ $\quad r_e = [1.6]$ Å

Enthalpy of Formation

Data on the electron affinity of LiO(g) are unavailable, therefore the value of $\Delta_f H°(LiO^-, g, 298.15\ K)$ is estimated. We first assume that the enthalpy change $\Delta_r H°(0\ K)$ of the reaction (1) $LiO^-(g) = Li(g) + O^-(g)$ is close to the average of the $\Delta_r H°(0\ K)$ values for the reactions (2) $LiO(g) = Li(g) + O(g)$ and (3) $LiF(g) = Li(g) + F(g)$. The atom F(g) is isoelectronic with $O^-(g)$. In other words, the $\Delta_r H°(0\ K)$ for reaction (1) is approximately $1/2(776.91 + 135.84) = 106.4\ kcal \cdot mol^{-1}$. Then we compare the $\Delta_r H°(0\ K)$ values for the reactions (4) $HO(g) = H(g) + O(g)$, (5) $HO^-(g) = H(g) + O^-(g)$, and (6) $HF(g) + H(g) + F(g)$, and find that $\Delta_r H°(0\ K)$ for reaction (5) is experimentally determined as $109.7\ kcal \cdot mol^{-1}$ which is about $8\ kcal \cdot mol^{-1}$ more negative than the average of $\Delta_r H°(0\ K)$ values for reactions (4) and (6). Based on this fact we estimate $\Delta_r H°(0\ K) = 96.4\ kcal \cdot mol^{-1}$ for reaction (1), yielding $\Delta_f H°(LiO^-, g, 298.15\ K) = -15.5\ kcal \cdot mol^{-1}$.

Applying the difference in electron affinity between H(g) and Li(g) to OH(g) gives an approximate value, EA = 1.7 eV ($39.2\ kcal \cdot mol^{-1}$) for LiO(g). The values of EA for H(g), Li(g) and OH(g) are taken from.[1] Based on $\Delta_r H°(0\ K) = 39.2\ kcal \cdot mol^{-1}$ for the reaction $LiO^-(g) = LiO(g) + e^-(g)$, we derive $\Delta_f H°(298.15\ K) = -19.1\ kcal \cdot mol^{-1}$ for $LiO^-(g)$, which is in reasonable agreement with the above estimated value.

The value of $\Delta_f H°(298.15\ K)$ for $LiO^-(g)$ is tentatively adopted as $-16 \pm 15\ kcal \cdot mol^{-1}$. Using this $\Delta_f H°(298.15\ K)$ value, we derive EA = 1.6 ± 0.7 eV for LiO(g). The electron affinity of OH(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of LiF(g) which is isoelectronic with $LiO^-(g)$. The values of ω_e, $\omega_e x_e$ and r_e are estimated by comparison with the observed data for LiF(g). The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ by use of the method suggested by Herzberg.[2]

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Lithium Oxide, Ion (LiO^-) — $Li_1O_1^-(g)$

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−8.939	−60.722		
100	29.145	166.304	226.636	−6.033			
200	30.312	186.754	202.136	−3.076			
250	31.369	193.630	199.769	−1.535			
298.15	32.359	199.241	199.241	.000	−66.944	−80.839	14.163
300	32.395	199.442	199.242	.060	−66.995	−80.925	14.090
350	33.284	204.504	199.640	1.703	−68.393	−83.137	12.407
400	34.020	208.998	200.534	3.386	−69.834	−85.145	11.119
450	34.619	213.041	201.703	5.102	−71.339	−86.969	10.095
500	35.106	216.715	203.023	6.846	−75.915	−88.315	9.226
600	35.833	223.184	205.859	10.395	−79.008	−90.504	7.879
700	36.339	228.748	208.740	14.005	−82.029	−92.180	6.879
800	36.707	233.625	211.552	17.658	−85.019	−93.426	6.100
900	36.986	237.965	214.250	21.343	−88.006	−94.297	5.473
1000	37.207	241.874	216.821	25.054	−90.991	−94.836	4.954
1100	37.388	245.429	219.262	28.784	−93.976	−95.076	4.515
1200	37.541	248.689	221.581	32.530	−96.958	−95.045	4.137
1300	37.672	251.699	223.783	36.291	−99.940	−94.765	3.808
1400	37.789	254.495	225.878	40.064	−102.918	−94.255	3.517
1500	37.894	257.106	227.874	43.848	−105.890	−93.532	3.257
1600	37.991	259.555	229.778	47.643	−108.858	−92.611	3.023
1700	38.080	261.861	231.598	51.446	−257.056	−84.329	2.591
1800	38.165	264.040	233.341	55.259	−259.261	−74.105	2.150
1900	38.244	266.106	235.011	59.079	−261.470	−63.759	1.753
2000	38.321	268.069	236.615	62.908	−263.685	−53.296	1.392
2100	38.394	269.941	238.158	66.743	−265.907	−42.721	1.063
2200	38.465	271.728	239.644	70.586	−268.137	−32.041	.761
2300	38.534	273.440	241.076	74.436	−270.376	−21.260	.483
2400	38.602	275.081	242.459	78.293	−272.626	−10.380	.226
2500	38.668	276.658	243.796	82.157	−274.887	.593	−.012
2600	38.732	278.176	245.089	86.027	−277.162	11.657	−.234
2700	38.796	279.639	246.342	89.903	−279.452	22.809	−.441
2800	38.859	281.051	247.556	93.786	−281.758	34.046	−.635
2900	38.921	282.416	248.735	97.675	−284.081	45.365	−.817
3000	38.982	283.736	249.880	101.570	−286.424	56.766	−.988
3100	39.043	285.016	250.993	105.471	−288.788	68.245	−1.150
3200	39.104	286.256	252.075	109.379	−291.173	79.799	−1.303
3300	39.164	287.460	253.129	113.292	−293.582	91.429	−1.447
3400	39.223	288.630	254.156	117.211	−296.016	103.133	−1.584
3500	39.282	289.768	255.158	121.137	−298.475	114.908	−1.715
3600	39.341	290.876	256.135	125.068	−300.962	126.754	−1.839
3700	39.399	291.954	257.088	129.005	−303.477	138.670	−1.958
3800	39.458	293.006	258.020	132.948	−306.022	150.654	−2.071
3900	39.516	294.032	258.930	136.896	−308.598	162.706	−2.179
4000	39.573	295.033	259.820	140.851	−311.206	174.823	−2.283
4100	39.631	296.011	260.691	144.811	−313.848	187.007	−2.382
4200	39.689	296.966	261.543	148.777	−316.524	199.255	−2.478
4300	39.746	297.901	262.378	152.749	−319.237	211.568	−2.570
4400	39.803	298.815	263.196	156.726	−321.967	223.942	−2.659
4500	39.860	299.710	263.997	160.709	−324.746	236.379	−2.744
4600	39.917	300.587	264.783	164.698	−327.568	248.880	−2.826
4700	39.974	301.446	265.554	168.693	−330.430	261.442	−2.906
4800	40.031	302.288	266.311	172.693	−333.334	274.066	−2.982
4900	40.087	303.114	267.053	176.699	−336.282	286.751	−3.057
5000	40.144	303.925	267.783	180.710	−339.276	299.496	−3.129
5100	40.200	304.720	268.499	184.727	−342.311	312.301	−3.199
5200	40.257	305.501	269.203	188.750	−345.400	325.166	−3.266
5300	40.313	306.269	269.895	192.779	−348.540	338.092	−3.332
5400	40.369	307.023	270.576	196.813	−351.733	351.077	−3.396
5500	40.425	307.764	271.245	200.853	−354.981	364.122	−3.458
5600	40.482	308.493	271.904	204.898	−358.286	377.226	−3.519
5700	40.538	309.210	272.552	208.949	−361.649	390.390	−3.578
5800	40.594	309.915	273.190	213.005	−365.073	403.614	−3.635
5900	40.650	310.610	273.819	217.068	−368.561	416.896	−3.691
6000	40.706	311.294	274.438	221.135	−372.113	430.239	−3.746

PREVIOUS: December 1967 (1 atm) — CURRENT: December 1967 (1 bar)

Lithium Oxide, Ion (LiO^-) — $Li_1O_1^-(g)$

D_0° = 99.833 ± 0.096 kJ·mol^{-1} (natural abundance)
S°(298.15 K) = 196.998 ± 0.030 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 215.5 ± 3.0 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 215.9 ± 3.0 kJ·mol^{-1}

Spectroscopic Data for $^7Li_2$ in cm^{-1}

State	T_e	D_0°	ω_e	$\omega_e x_e$	B_e	$10^3\alpha_e$	$10^6 D_e$	r_e, Å	References
$^1\Sigma^+_g$	0	8346.45	351.39	2.5779[a]	0.67257	7.0173[b]	9.8478[c]	2.6730	5(D°)9
$^3\Sigma^+_u$	8229.5	8346.45	61.0	3.2	0.26806	[17.35][d]	[20.706][d]	4.234	10
$^3\Pi^+_u$	11942.5	23250.4	339.0	2.5	0.69368	[7.65][d]	[11.618][d]	2.632	10
$^1\Sigma^+_u$	14068.3	23250.4	255.47	1.58	0.4975	5.4	7.54	3.107	9
$^3\Sigma^+_g$	16614.5	23250.4	245.0	2.2	0.50134	[6.74][d]	[8.385][d]	3.096	10

(a) -6.4724×10^{-3} (v + 1/2)^3 − 9.712×10^{-5} (v + 1/2).[4]
(b) -3.6071×10^{-5} (v + 1/2)^2 − 4.2570×10^{-7}(v + 1/2).[3]
(c) $+5.672 \times 10^{-8}$ (v + 1/2) − 1.9002×10^{-9}(v + 1/2).[2]
(d) These values of α_e and D_e were approximated: equations III,118 and III,123.[4]

Enthalpy of Formation

We adopt the $\Delta_f H^\circ$(Li_2, g, 298.15 K) of 215.9 kJ·mol^{-1} as recommended by NBS.[12] The value adopted for $\Delta_f H^\circ$(Li_2, g, 0 K) was obtained using the values of H°(298.15 K)–H°(0 K) for Li_2(g) and Li(cr), from JANAF and NBS,[12] respectively. This results in $\Delta_f H^\circ$(Li_2, g, 0 K) = 215.474 kJ·mol^{-1}. Note that this adoption of the NBS value results in a minor inconsistency in the value of D_0° for the ground state. In the calculation of C_p° and S° described below, we used D_0° = 99.846 kJ·mol^{-1} (for $^7Li_2$) whereas the above procedure results in D_0° = 100.125 kJ·mol^{-1} based on $\Delta_f H^\circ$(Li, g, 0 K) from NBS.[12] This results in uncertainties in the calculated C_p° and S° of less than 0.002 J·K^{-1}·mol^{-1} at 6000 K.

Heat Capacity and Entropy

The thermal functions were calculated using a direct summation technique. Included in the calculation were the ground state plus the four lowest lying excited electronic states. Of these excited states, only the $^1\Sigma^+_u$ has been observed spectroscopically. All spectroscopic data for $^7Li_2$ used in this calculation are those recommended by Stwalley.[1, 2] Separate calculations were performed for each of the three isotopic species $^6Li_2$, $^7Li_2$, and $^6Li^7Li$ and the results were combined according to the natural abundances of the atoms, ^{7}Li: 92.3191%, ^{6}Li: 7.6809%.[3] Calculation of the $^6Li_2$ and $^6Li^7Li$ species were carried out by adjusting the spectroscopic constants for $^7Li_2$ using a standard reduced mass scaling routine. The summation was extended to the dissociation limit of each state, and thus did not include any of the so–called quasi–bound levels above D° that owe their existence to rotational barriers. A detailed study of the effects of the quasi–bound levels on the thermodynamic properties of diatomic molecules has been recently performed by Mies and Julienne.[11] According to their approach, the metastable and "free" contribution to the Gibbs energy function for Li_2(g) at 6000 K is only ca. 4 J·K^{-1}·mol^{-1}.[13]

The excited states contribute significantly to the heat capacity above 2000 K but the affect on the Gibbs energy function is considerably less, only 0.5 J·K^{-1}·mol^{-1} larger than the ground state contribution at 6000 K. The ground state and $^1\Sigma^+_u$ excited state rotational levels were weighted in accordance with the nuclear spin–rotation interaction[4] as follows: even J weight = 0.625, odd J weight = 0.375 for the $^7Li_2$ species; even J weight = 0.667, odd J weight = 0.333 for the $^6Li_2$ species. Note also that although the Dunham coefficients for the ground state are known to higher order than used here,[5] the neglect of these data leads to small errors in the computed functions as follows: S°(6000 K) is 0.4 J·K^{-1}·mol^{-1} larger than the nontruncated ro– vibrational constant calculation (based on a ground state calculation). The rotational levels were extrapolated to high J values according to the method of Khachkuruzov[6] who proposed a simpler form of Wooley's method.[7] Splitting of the rotational levels in the $^3\Sigma$ and $^3\Pi$ states due to rotational–electronic coupling was taken into account only insofar as the electronic degeneracy of these states was increased accordingly. The errors invoked by this approximation are much less than the other uncertainties. The adopted value of S°(298.15 K) is only 0.013 J·K^{-1}·mol^{-1} lower than that adopted by NBS.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p° (J·K^{-1}·mol^{-1})	S° (J·K^{-1}·mol^{-1})	$-[G^\circ-H^\circ(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H^\circ-H^\circ(T_r)$ (kJ·mol^{-1})	$\Delta_f H^\circ$ (kJ·mol^{-1})	$\Delta_f G^\circ$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.675	215.469	215.469	INFINITE
100	30.583	160.414	227.785	−6.737	217.417	202.844	−105.955
200	34.380	182.905	200.255	−3.470	217.001	188.351	−49.192
250	35.426	190.697	197.589	−1.723	216.492	181.244	−37.869
298.15	36.103	196.998	196.998	0.	215.900	174.508	−30.573
300	36.125	197.222	196.999	0.067	215.876	174.251	−30.340
350	36.617	202.830	197.441	1.886	215.169	167.368	−24.978
400	36.985	207.744	198.428	3.726	214.334	160.595	−20.972
450	37.274	212.118	199.711	5.583	213.344	153.935	−17.868
500	37.513	216.058	201.151	7.453	206.195	148.009	−15.462
600	37.902	222.933	204.225	11.225	204.000	136.580	−11.890
700	38.225	228.800	207.327	15.031	201.956	125.507	−9.365
800	38.499	233.923	210.338	18.868	200.001	114.720	−7.490
900	38.714	238.471	213.216	22.729	198.080	104.175	−6.046
1000	38.843	242.557	215.949	26.608	196.186	93.843	−4.902
1100	38.859	246.261	218.539	30.494	194.310	83.700	−3.975
1200	38.744	249.638	220.992	34.375	192.439	73.727	−3.209
1300	38.498	252.731	223.316	38.238	190.558	63.910	−2.568
1400	38.133	255.571	225.520	42.071	188.658	54.239	−2.024
1500	37.675	258.187	227.612	45.862	186.734	44.705	−1.557
1600	37.155	260.602	229.599	49.604	184.777	35.300	−1.152
1700	36.607	262.838	231.490	53.292	−107.689	40.370	−1.240
1800	36.067	264.915	233.290	56.926	−108.217	49.095	−1.425
1900	35.569	266.851	235.006	60.507	−108.799	57.850	−1.590
2000	35.142	268.665	236.644	64.042	−109.431	66.637	−1.740
2100	34.814	270.371	238.209	67.539	−110.107	75.457	−1.877
2200	34.610	271.985	239.708	71.009	−110.818	84.310	−2.002
2300	34.547	273.522	241.145	74.465	−111.551	93.196	−2.117
2400	34.643	274.993	242.525	77.924	−112.296	102.114	−2.222
2500	34.909	276.412	243.853	81.400	−113.037	111.063	−2.321
2600	35.350	277.790	245.131	84.911	−113.762	120.041	−2.412
2700	35.970	279.135	246.366	88.476	−114.455	129.047	−2.497
2800	36.765	280.457	247.560	92.111	−115.102	138.077	−2.576
2900	37.728	281.763	248.717	95.834	−115.689	147.130	−2.650
3000	38.846	283.061	249.840	99.662	−116.203	156.202	−2.720
3100	40.103	284.355	250.933	103.608	−116.634	165.289	−2.785
3200	41.479	285.649	251.997	107.686	−116.971	174.389	−2.847
3300	42.948	286.948	253.037	111.907	−117.206	183.498	−2.905
3400	44.483	288.253	254.053	116.278	−117.336	192.612	−2.959
3500	46.057	289.565	255.049	120.805	−117.358	201.729	−3.011
3600	47.640	290.884	256.026	125.490	−117.272	210.845	−3.059
3700	49.201	292.211	256.986	130.332	−117.083	219.957	−3.105
3800	50.713	293.543	257.931	135.328	−116.797	229.062	−3.149
3900	52.149	294.879	258.861	140.472	−116.423	238.159	−3.190
4000	53.485	296.217	259.778	145.755	−115.973	247.246	−3.229
4100	54.702	297.553	260.683	151.165	−115.460	256.320	−3.266
4200	55.781	298.884	261.577	156.691	−114.901	265.381	−3.300
4300	56.711	300.208	262.460	162.317	−114.314	274.428	−3.334
4400	57.483	301.521	263.333	168.028	−113.673	283.459	−3.365
4500	58.092	302.820	264.196	173.808	−113.063	292.477	−3.395
4600	58.537	304.102	265.049	179.640	−112.484	301.483	−3.423
4700	58.822	305.364	265.894	185.510	−111.948	310.476	−3.451
4800	58.950	306.604	266.729	191.400	−111.475	319.459	−3.476
4900	58.930	307.820	267.555	197.295	−111.083	328.432	−3.501
5000	58.772	309.009	268.373	203.181	−110.789	337.399	−3.525
5100	58.487	310.170	269.181	209.045	−110.599	346.360	−3.547
5200	58.086	311.302	269.980	214.875	−110.547	355.319	−3.569
5300	57.582	312.404	270.770	220.659	−110.640	364.279	−3.590
5400	56.988	313.475	271.551	226.388	−110.889	373.242	−3.610
5500	56.317	314.514	272.323	232.054	−111.306	382.210	−3.630
5600	55.580	315.523	273.085	237.649	−111.903	391.188	−3.649
5700	54.789	316.499	273.838	243.168	−112.686	400.179	−3.667
5800	53.955	317.445	274.582	248.606	−113.666	409.185	−3.685
5900	53.087	318.360	275.316	253.958	−114.849	418.209	−3.703
6000	52.196	319.245	276.041	259.222	−116.239	427.256	−3.720

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

$S°(298.15\ K) = 37.890\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1843\ K$

$\Delta_f H°(0\ K) = -592.39 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -598.73 \pm 2.1\ kJ·mol^{-1}$
$\Delta_{fus} H° = [58.576]\ kJ·mol^{-1}$

Enthalpy of Formation

The selected enthalpy of formation was calculated as follows:

Reaction	$\Delta_r H°(298.15K)$ kcal·mol^{-1}	Source
(A) Li O(c_2r) + H O($_2$) = 2 LiOH(aq, ∞)	−31.74 ± 0.08	1
(B) Li(cr) + 1/2 O_2(g) = LiOH(aq, ∞)	−121.572 ± 0.019	2
(C) H_2(g) + 1/2 O_2(g) = H_2O(l)	−68.3174	3
(D) 2 Li(cr) + 1/2 O_2(g) = Li_2O(cr)*	−143.1 ± 0.5	

* Reaction (D) is the sum of −(A) + 2(B) − (C).

Kolesov *et al.*[1] measured the enthalpy of the reaction of Li_2O with water at 20° in 5 experiments. The mean $\Delta_r H°$ was −31.41 ± 0.08 kcal·mol^{-1}. This was brought to 298.15 K by Kolesov using enthalpy data of Johnston and Bauer[4] for Li_2O, Osborne *et al.*[5] for H_2O, Gucker and Schminke[6] for $C_p°$ of LiOH(aq) and Rossini *et al.*[3] for aqueous LiOH. In addition to the above, Beketov[7] and Forcrand[8] have reported experimental enthalpies for Li_2O. Rossini *et al.* and Johnston and Bauer[4] have reported enthalpies of formation for Li_2O recalculated from older data. Fasolino[9] reported a $\Delta_f H°(298.15\ K)$ of −141.1 ± 4.2 kcal·mol^{-1}. He measured the enthalpy of combustion of Li(cr) in O (g) in a Parr bomb.

Heat Capacity and Entropy

The low temperature $C_p°$ data of Johnston and Bauer[4] from [179–298 K] was joined graphically to the high temperature $C_p°$ data of Shomate and Cohen,[10] (425–1045 K) and Rodigina and Gomelskii,[11] (370–1125 K). $S°(298.15\ K)$ was reported by Johnston and Bauer using $S°(16\ K) = 0.003\ cal·K^{-1}·mol^{-1}$ (extrap.).

Fusion Data

The melting point of Li_2O is uncertain. The selected melting point, 1843 K, was measured by van Arkel *et al.*[12] Brewer and Margrave[13] reported the melting point 1700 K. They also stated that van Kooster and Jaeger[14] had reported 1700 (1973 K) as the melting point. The heat of melting, [14] kcal·mol^{-1}, was estimated by Glassner.[15]

Sublimation Data

Li_2O(cr) vaporizes to Li_2O(g), LiO(g), Li_2O_2(g) and O_2(g).[16–20] The major species (0–1700 K) are reported to be Li_2O(g), Li(g), and O_2(g) with lesser amounts of LiO(g) and Li_2O_2(g). Hildenbrand *et al.*,[18] U–2298, have reported about equal amounts of Li_2O^+ and Li^+ (1300 to 1550 K) and about 1/30th of this amount of LiO^+. White *et al.*[17] calculated $\Delta_{sub} H°$ from their mass spectra data. They made two different calculations: (I) for Li_2O(cr) → Li_2O(g), and (II) for Li_2O(g) → 2 LI(g) + 1/2 O_2(g), and found: (a) 102.5 kcal·mol^{-1} and (b) 99.0 kcal·mol^{-1}. They used a weighted average of (a) and (b) and obtained 101.6 kcal·mol^{-1} at 0 K. The selected $\Delta_{sub} H°(298.15\ K)$ of 102.3 ± 3 kcal·mol^{-1} was obtained in the same manner using their data and the present JANAF functions, i.e., (a) 104.2 kcal·mol^{-1} and (b) 100.3 kcal·mol^{-1}. Knudson–effusion data of White *et al.*, corrected for dissociation gave 3rd law heats at 298 K of 101.9 kcal·mol^{-1} and a 2nd law heat of 94 kcal·mol^{-1}. Recalculation of Hildenbrand's dissociation pressure with JANAF values give Li_2O pressures slightly different than those reported. The recalculated pressures give a 3rd law $\Delta_{sub} H°(298.15\ K)$ of 101.7 kcal·mol^{-1} for both cells. The corresponding 2nd law values are 85 and 95.5 kcal·mol^{-1} for cell 7 and 8. The 3rd law treatment of both sets of data show relatively large trends of $\Delta_{sub} H°$ with T which are probably too large to be only due to errors in the function.

A sample of $LiAlO_2$ was melted 7 times in argon in an arc–image furnace, Prophet.[21] The sample decomposed on fusion and successive melting points approached that of Al_2O_3. The residue was found to be 95% Al_2O_3 and 5% $LiAl_5O_8$. The sample and residue were characterized by X–ray diffraction. A reasonable assumption from this is that $\Delta_r F°(2000\ K) = 0$ for $2LiAlO_2(cr) = Al_2O_3(cr) + Li_2O(g)$. From this ΔF, a $\Delta_{sub} H°(298.15\ K)$ for Li_2O of 50 kcal·mol^{-1} was calculated. A vapor pressure study of the molecular species over the decomposing $LiAlO_2$ might help resolve the discrepancies in lithium oxide $\Delta_{sub} H°$ values.

References

[1] V. P. Kolesov, S. M. Skuratov, and I. D. Zaikin, Russian J. Inorganic Chemistry **4**, 558 (1959).
[2] S. R. Gunn and L. G. Green, J. Amer. Chem. Soc. **80**, 4782 (1958).
[3] U. S. Nat. Bur. Stand. Circ. 500, (1952).
[4] H. L. Johnston and T. W. Bauer, J. Amer. Chem. Soc. **73**, 1119 (1951).
[5] N. S. Osborne, J. F. Stimson, and D. C. Ginnings, J. Res. Nat. Bur. Stand. A **23**, 197 (1939).

Continued on page 1527

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−7.248	−592.392	−592.392	INFINITE
100	10.447	3.632	73.417	−6.979	−594.565	−584.794	305.465
200	37.204	19.581	42.362	−4.556	−597.282	−573.919	149.892
298.15	54.087	37.890	37.890	0.	−598.730	−562.102	98.478
300	54.379	38.226	37.891	0.100	−598.748	−561.875	97.831
400	64.003	55.315	40.156	6.064	−599.472	−549.465	71.753
500	69.580	70.232	44.714	12.759	−606.172	−536.272	56.024
600	73.822	83.284	50.077	19.924	−606.553	−522.248	45.466
700	77.404	94.940	55.668	27.490	−606.464	−508.198	37.922
800	80.563	105.484	61.246	35.390	−606.026	−494.187	32.267
900	83.429	115.137	66.705	43.589	−605.311	−480.247	27.873
1000	86.211	124.073	72.001	52.073	−604.331	−466.401	24.362
1100	88.805	132.415	77.118	60.827	−603.094	−452.666	21.495
1200	91.211	140.244	82.055	69.826	−601.621	−439.054	19.112
1300	93.199	147.625	86.818	79.049	−599.934	−425.574	17.100
1400	94.872	154.595	91.413	88.455	−598.066	−412.230	15.381
1500	96.232	161.189	95.847	98.013	−596.045	−399.026	13.895
1600	97.320	167.434	100.127	107.691	−593.899	−385.961	12.600
1700	98.332	173.364	104.262	117.473	−882.118	−358.681	11.021
1800	99.454	179.017	108.260	127.363	−878.247	−328.002	9.518
1843.000	99.914	181.370	109.938	131.649	--- CRYSTAL <--> LIQUID ---		
1900	100.542	184.423	112.127	137.363	−874.280	−297.541	8.180
2000	101.420	189.603	115.872	147.461	−870.230	−267.290	6.981
2100	102.287	194.572	119.502	157.646	−866.111	−237.244	5.901
2200	103.143	199.350	123.024	167.918	−861.924	−207.396	4.924
2300	103.988	203.954	126.443	178.274	−857.673	−177.740	4.037
2400	104.821	208.397	129.766	188.715	−853.361	−148.270	3.227
2500	105.642	212.693	132.997	199.238	−848.993	−118.981	2.486
2600	106.452	216.852	136.143	209.843	−844.572	−89.867	1.805
2700	107.251	220.884	139.207	220.528	−840.103	−60.925	1.179
2800	108.038	224.799	142.195	231.293	−835.590	−32.149	0.600
2900	108.814	228.604	145.109	242.136	−831.036	−3.535	0.064
3000	109.579	232.306	147.954	253.055	−826.447	24.922	−0.434

PREVIOUS: December 1960 CURRENT: March 1964

$S°(298.15\ K) = [55.083]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1843\ K$

$\Delta_f H°(298.15\ K) = [-553.247]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [58.576]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_2O, l, 298.15\ K)$ is calculated from $\Delta_f H°(Li_2O, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°(1843\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated at 8 $cal·K^{-1}·mol^{-1}$ from comparisons with similar compounds and from Kopp's rule. $S°(Li_2O, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The vapor over $Li_2O(cr)$ at 1700 K is composed of $Li_2O(g)$, Li(g), $O_2(g)$, LiO(g), and $Li_2O_2(g)$. Thus a boiling point becomes almost meaningless. The value, T_{vap} = 2836 K, listed above is the temperature at which the fugacity of $Li_2O(g)$ reaches one atm. Brewer[1] estimated a boiling point of 2600 K.

Reference

[1] L. Brewer, Chem. Rev. **52**, (1953).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	54.087	55.083	55.083	0.	−553.247	−521.744	91.407
300	54.379	55.419	55.084	0.100	−553.265	−521.549	90.810
400	64.003	72.477	57.344	6.053	−553.999	−510.857	66.711
500	69.580	87.383	61.896	12.743	−560.704	−499.380	52.170
600	73.822	100.464	67.256	19.925	−561.069	−487.072	42.403
600.000	73.822	100.464	67.256	19.925	GLASS <--> LIQUID TRANSITION		
600.000	100.416	100.464	67.256	19.925			
700	100.416	115.943	73.134	29.966	−558.505	−474.941	35.441
800	100.416	129.352	79.342	40.008	−555.924	−463.180	30.243
900	100.416	141.179	85.569	50.049	−553.368	−451.741	26.218
1000	100.416	151.759	91.668	60.091	−550.829	−440.585	23.014
1100	100.416	161.330	97.573	70.133	−548.304	−429.683	20.404
1200	100.416	170.067	103.255	80.174	−545.789	−419.010	18.239
1300	100.416	178.105	108.708	90.216	−543.284	−408.547	16.416
1400	100.416	185.546	113.934	100.257	−540.781	−398.277	14.860
1500	100.416	192.474	118.942	110.299	−538.275	−388.185	13.518
1600	100.416	198.955	123.742	120.341	−535.766	−378.261	12.349
1700	100.416	205.043	128.347	130.382	−823.725	−354.142	10.881
1800	100.416	210.782	132.769	140.424	−819.702	−326.636	9.479
1843.000	100.416	213.153	134.617	144.742	CRYSTAL <--> LIQUID		
1900	100.416	216.212	137.019	150.465	−815.694	−299.352	8.230
2000	100.416	221.362	141.109	160.507	−811.701	−272.280	7.111
2100	100.416	226.262	145.048	170.549	−807.725	−245.407	6.104
2200	100.416	230.933	148.847	180.590	−803.768	−218.722	5.193
2300	100.416	235.397	152.513	190.632	−799.832	−192.218	4.365
2400	100.416	239.670	156.056	200.673	−795.919	−165.884	3.610
2500	100.416	243.770	159.483	210.715	−792.033	−139.712	2.919
2600	100.416	247.708	162.801	220.757	−788.175	−113.696	2.284
2700	100.416	251.498	166.017	230.798	−784.350	−87.827	1.699
2800	100.416	255.150	169.135	240.840	−780.559	−62.099	1.158
2900	100.416	258.673	172.162	250.881	−776.807	−36.506	0.658
3000	100.416	262.078	175.103	260.923	−773.096	−11.042	0.192
3100	100.416	265.370	177.962	270.965	−769.429	14.299	−0.241
3200	100.416	268.558	180.744	281.006	−765.809	39.523	−0.645
3300	100.416	271.648	183.452	291.048	−762.239	64.634	−1.023
3400	100.416	274.646	186.090	301.089	−758.722	89.638	−1.377
3500	100.416	277.557	188.662	311.131	−755.261	114.539	−1.709
3600	100.416	280.386	191.171	321.173	−751.859	139.342	−2.022
3700	100.416	283.137	193.619	331.214	−748.518	164.051	−2.316
3800	100.416	285.815	196.011	341.256	−745.240	188.672	−2.593
3900	100.416	288.423	198.347	351.297	−742.029	213.207	−2.856
4000	100.416	290.965	200.631	361.339	−738.888	237.660	−3.104

PREVIOUS: December 1960 CURRENT: March 1964

0 to 1843 K crystal
above 1843 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.248	−592.392	−592.392	INFINITE
100	10.447	3.632	73.417	−6.979	−594.565	−584.794	305.465
200	37.204	19.581	42.362	−4.556	−597.282	−573.919	149.892
298.15	54.087	37.890	37.890	0.	−598.730	−562.102	98.478
300	54.379	38.226	37.891	0.100	−598.748	−561.875	97.831
400	64.003	55.315	40.156	6.064	−599.472	−549.465	71.753
500	69.580	70.232	44.714	12.759	−606.172	−536.272	56.024
600	73.822	83.284	50.077	19.924	−606.553	−522.248	45.466
700	77.404	94.940	55.668	27.490	−606.464	−508.198	37.922
800	80.563	105.484	61.246	35.390	−606.026	−494.187	32.267
900	83.429	115.137	66.705	43.589	−605.311	−480.247	27.873
1000	86.211	124.073	72.001	52.073	−604.331	−466.401	24.362
1100	88.805	132.415	77.118	60.827	−603.094	−452.666	21.495
1200	91.211	140.244	82.055	69.826	−601.621	−439.054	19.112
1300	93.199	147.625	86.818	79.049	−599.934	−425.574	17.100
1400	94.872	154.595	91.413	88.455	−598.066	−412.230	15.381
1500	96.232	161.189	95.847	98.013	−596.045	−399.026	13.895
1600	97.320	167.434	100.127	107.691	−593.899	−385.961	12.600
1700	98.332	173.364	104.262	117.473	−882.118	−358.681	11.021
1800	99.454	179.017	108.260	127.363	−878.247	−328.002	9.518
1843.000	99.914	181.370	109.938	131.649	CRYSTAL <−−> LIQUID TRANSITION		
1843.000	100.416	213.153	109.938	190.225			
1900	100.416	216.212	113.081	195.949	−815.694	−299.352	8.230
2000	100.416	221.362	118.367	205.990	−811.701	−272.280	7.111
2100	100.416	226.262	123.389	216.032	−807.725	−245.407	6.104
2200	100.416	230.933	128.172	226.074	−803.768	−218.722	5.193
2300	100.416	235.397	132.738	236.115	−799.832	−192.218	4.365
2400	100.416	239.670	137.105	246.157	−795.919	−165.884	3.610
2500	100.416	243.769	141.290	256.198	−792.033	−139.712	2.919
2600	100.416	247.708	145.308	266.240	−788.175	−113.696	2.284
2700	100.416	251.498	149.171	276.282	−784.350	−87.827	1.699
2800	100.416	255.150	152.891	286.323	−780.559	−62.099	1.158
2900	100.416	258.673	156.478	296.365	−776.807	−36.506	0.658
3000	100.416	262.077	159.942	306.406	−773.096	−11.042	0.192
3100	100.416	265.370	163.290	316.448	−769.429	14.299	−0.241
3200	100.416	268.558	166.530	326.490	−765.809	39.523	−0.645
3300	100.416	271.648	169.669	336.531	−762.239	64.634	−1.023
3400	100.416	274.646	172.713	346.573	−758.722	89.638	−1.377
3500	100.416	277.557	175.667	356.614	−755.261	114.539	−1.709
3600	100.416	280.386	178.537	366.656	−751.859	139.342	−2.022
3700	100.416	283.137	181.327	376.698	−748.518	164.052	−2.316
3800	100.416	285.815	184.041	386.739	−745.240	188.672	−2.593
3900	100.416	288.423	186.684	396.781	−742.029	213.207	−2.856
4000	100.416	290.965	189.260	406.822	−738.888	237.660	−3.104

PREVIOUS: CURRENT: March 1964

$S°$ (298.15 K) = 229.108 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = −165.84 ± 10.5 $kJ·mol^{-1}$
$\Delta_f H$ (298.15 K) = −166.94 ± 1.5 $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[760](1)
[140](2)
987 (1)

Ground State Quantum Weight: [1] $\sigma = 2$
Point Group: D_{2h}
Bond Distance: Li–O = [1.59] Å
Bond Angle: Li–O–Li = 180°
Rotational Constant: B_0 = 0.480342 cm^{-1}

Enthalpy of Formation

The enthalpy of formation was calculated from the enthalpy of formation of the crystal and the enthalpy of sublimation.

Heat Capacity and Entropy

White *et al.*[1] made an estimate of the bond distance Li–O = 1.59 Å based on an analysis of their vibrational spectra. They found that Li_2O was a linear molecule. Buchler and Stauffer[2] have shown from electric deflection experiments that Li_2O is very probably linear. They also report from the results of an effusion experiment evidence that the electron diffraction data and Li–O bond distance, 1.82 Å reported by Akishin and Rambidi[3] are for Mo–O in Li_2MoO_4 rather than for Li–O in Li_2O. Buchler and Stauffer[2] estimate an Li–O distance of 1.55 Å. White, *et al.*,[1] have estimated the vibrational frequencies ν_1 = [760] cm^{-1} and ν_2 = [140] cm^{-1} and assigned ν_3 = 987 cm^{-1} from their infrared matrix spectra.

References

[1]D. White, K. S. Seshadri, D. F. Dever, D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963).
[2]A. Buchler and J. L. Stauffer, J. Chem. Phys. **39**, 2299 (1963).
[3]P. A. Akishin and N. G. Rambidi, Dokl. Akad. Nauk. SSSR **118**, 973 (1958) [English Translation, Proc. Acad. Sci. USSR, Phys. Chem. Sect. **118**, 83 (1958)].

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.485	−165.840	−165.840	INFINITE
100	41.106	179.969	270.575	−9.061	−164.858	−172.721	90.220
200	45.797	210.079	233.532	−4.691	−165.627	−180.364	47.106
250	47.836	220.517	229.917	−2.350	−166.272	−183.975	38.440
298.15	49.758	229.108	229.108	0.	−166.942	−187.325	32.818
300	49.829	229.416	229.109	0.092	−166.968	−187.451	32.638
350	51.633	237.236	229.723	2.630	−167.694	−190.808	28.477
400	53.190	244.235	231.107	5.251	−168.495	−194.056	25.341
450	54.500	250.578	232.923	7.945	−169.407	−197.198	22.890
500	55.590	256.378	234.983	10.698	−176.444	−199.618	20.854
600	57.243	266.669	239.428	16.344	−178.344	−204.070	17.766
700	58.393	275.584	243.971	22.130	−180.036	−208.221	15.538
800	59.211	283.438	248.423	28.012	−181.615	−212.139	13.851
900	59.808	290.448	252.710	33.964	−183.147	−215.863	12.528
1000	60.254	296.774	256.805	39.968	−184.646	−219.417	11.461
1100	60.595	302.533	260.705	46.012	−186.120	−222.822	10.581
1200	60.861	307.818	264.414	52.085	−187.573	−226.095	9.842
1300	61.072	312.698	267.942	58.182	−189.012	−229.247	9.211
1400	61.242	317.230	271.303	64.298	−190.435	−232.288	8.667
1500	61.380	321.460	274.507	70.429	−191.840	−235.228	8.191
1600	61.495	325.425	277.567	76.573	−193.228	−238.076	7.772
1700	61.591	329.156	280.493	82.728	−485.074	−226.484	6.959
1800	61.672	332.679	283.295	88.891	−484.930	−211.278	6.131
1900	61.740	336.016	285.983	95.062	−484.792	−196.078	5.391
2000	61.799	339.184	288.565	101.239	−484.664	−180.886	4.724
2100	61.850	342.200	291.047	107.421	−484.547	−165.700	4.122
2200	61.895	345.079	293.439	113.608	−484.444	−150.519	3.574
2300	61.933	347.831	295.744	119.800	−484.358	−135.343	3.074
2400	61.968	350.467	297.970	125.995	−484.292	−120.170	2.615
2500	61.998	352.998	300.120	132.193	−484.249	−104.999	2.194
2600	62.025	355.430	302.201	138.394	−484.232	−89.830	1.805
2700	62.049	357.771	304.216	144.598	−484.245	−74.660	1.444
2800	62.070	360.028	306.170	150.804	−484.290	−59.490	1.110
2900	62.089	362.207	308.065	157.012	−484.371	−44.317	0.798
3000	62.107	364.312	309.905	163.222	−484.492	−29.141	0.507
3100	62.123	366.349	311.693	169.433	−484.655	−13.960	0.235
3200	62.137	368.321	313.432	175.646	−484.864	1.227	−0.020
3300	62.150	370.233	315.124	181.861	−485.121	16.421	−0.260
3400	62.162	372.089	316.772	188.076	−485.430	31.624	−0.486
3500	62.173	373.891	318.379	194.293	−485.794	46.836	−0.699
3600	62.183	375.643	319.945	200.511	−486.215	62.060	−0.900
3700	62.192	377.346	321.474	206.730	−486.697	77.296	−1.091
3800	62.201	379.005	322.966	212.949	−487.241	92.547	−1.272
3900	62.209	380.621	324.424	219.170	−487.852	107.813	−1.444
4000	62.216	382.196	325.848	225.391	−488.531	123.094	−1.607
4100	62.223	383.732	327.241	231.613	−489.281	138.394	−1.763
4200	62.229	385.232	328.604	237.836	−490.105	153.713	−1.912
4300	62.235	386.696	329.938	244.059	−491.007	169.053	−2.054
4400	62.241	388.127	331.245	250.283	−491.947	184.411	−2.189
4500	62.246	389.526	332.524	256.507	−492.992	199.793	−2.319
4600	62.251	390.894	333.778	262.732	−494.125	215.201	−2.444
4700	62.255	392.233	335.008	268.957	−495.345	230.634	−2.563
4800	62.259	393.544	336.214	275.183	−496.653	246.094	−2.678
4900	62.263	394.827	337.397	281.409	−498.054	261.583	−2.789
5000	62.267	396.085	338.558	287.636	−499.550	277.100	−2.895
5100	62.271	397.318	339.698	293.862	−501.134	292.648	−2.997
5200	62.274	398.528	340.818	300.090	−502.830	308.228	−3.096
5300	62.277	399.714	341.918	306.317	−504.630	323.843	−3.192
5400	62.280	400.878	342.999	312.545	−506.540	339.492	−3.284
5500	62.283	402.021	344.062	318.773	−508.562	355.178	−3.373
5600	62.285	403.143	345.107	325.002	−510.701	370.902	−3.460
5700	62.288	404.245	346.135	331.230	−512.959	386.664	−3.543
5800	62.290	405.329	347.146	337.459	−515.342	402.468	−3.625
5900	62.293	406.394	348.141	343.688	−517.851	418.313	−3.703
6000	62.295	407.441	349.121	349.918	−520.490	434.203	−3.780

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

$\Delta_f H°(0\ K)$ = Unknown

$S°(298.15\ K) = [56.484 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [632.62 \pm 8.4]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was reported by Forcrand,[1] based on the measured enthalpies of the reactions of Li_2O_2(cr) with HCl(aq) and LiOH(aq) with H_2O_2(aq).

Heat Capacity and Entropy

Both $C_p°$ and $S°(298.15\ K)$ were estimated by comparison with those of the Na_2O_2(cr), respectively.

Decomposition Data

T_{dcm} was reported to be about 300°C by Wiederhorn *et. al.*[2] The value adopted, T_{dcm} = 468 K, was reported by[3] obtained from Centnerzwer and Blumenthal.[4]

References

[1]R. de Forcrand, Compt. Rend. **130**, 1465 (1900).
[2]N. M. Wiederhorn, N. F. Surprenant, and A. J. Leffler, "Research on New Methods of Separation of Air into O_2 and N_2 Components," C 63825, First Quarterly Progress Report, September 1961, Arthur D. Little, Inc.
[3]Bulletin of the National Research Council, No. 118, "Data on Chemicals for Ceramic Use", (June 1949).
[4]M. Centnerzwer and M. Blementhal, Bull. Intern. Acad. Polonaise, Classe. Sci. Math. Nat., A 499 (1933).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	70.626	56.484	56.484	0.	−632.621	−570.954	100.029
300	70.919	56.922	56.485	0.131	−632.635	−570.571	99.345
400	82.676	79.021	59.419	7.841	−633.098	−549.799	71.796
500	90.793	98.369	65.316	16.527	−639.337	−528.332	55.194
600	97.445	115.520	72.280	25.944	−639.045	−506.147	44.064
700	103.428	130.995	79.580	35.991	−638.104	−484.063	36.121
800	109.077	145.178	86.905	46.618	−636.605	−462.154	30.176
900	114.432	158.336	94.120	57.794	−634.617	−440.462	25.564
1000	119.704	170.666	101.164	69.502	−632.144	−419.017	21.887
1100	124.892	182.319	108.017	81.733	−629.184	−397.844	18.892
1200	129.997	193.406	114.674	94.478	−625.740	−376.961	16.409
1300	134.980	204.008	121.141	107.727	−621.818	−356.385	14.320
1400	139.905	214.192	127.426	121.472	−617.419	−336.129	12.541
1500	144.766	224.010	133.540	135.706	−612.541	−316.205	11.011
1600	149.570	233.507	139.492	150.423	−607.190	−296.621	9.684
1700	154.318	242.717	145.295	165.618	−891.841	−263.034	8.082
1800	159.005	251.671	150.957	181.285	−884.052	−226.268	6.566
1900	163.628	260.392	156.488	197.417	−875.822	−189.947	5.222
2000	168.197	268.902	161.897	214.009	−867.160	−154.070	4.024

PREVIOUS: June 1963 CURRENT: September 1963

$S°(298.15\ K)$ = [273.562] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = [−240.60 ± 25.1] $kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−242.67 ± 25.1] $kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[400](1)	[270](1)
[250](1)	330 (1)
[300](1)	530 (1)

Ground State Quantum Weight: [1] $\sigma = 4$
Point Group: [D_{2h}]
Bond Distance: Li–O = [1.90] Å
Bond Angle: O–Li–O = [116]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [5.200811 × 10^{-115}] $g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation, −58 $kcal \cdot mol^{-1}$, was calculated from an equilibrium constant for the reaction 1/2 $O_2(g)$ + $Li_2O(g) \rightarrow Li_2O_2(g)$ and the current JANAF functions. The equilibrium constant, 0.39, was estimated by White *et al.*,[1] from their mass spectrometric data.

Heat Capacity and Entropy

White, *et al.*,[1] from their spectral data have assigned two observed frequencies and estimated the remaining frequencies using the ionic model calculations of Berkowitz[2] as a guide. They proposed a planar rhombic structure of D_{2h} symmetry, similar to the alkali halide dimers, for the previously undetected Li_2O_2 molecule, and estimated the angle, 116°, and bond distance, 1.90 Å, from their matrix spectra. The principal moments calculated from these molecular constants are: $I_A = 2.3369 \times 10^{-39}$, $I_B = 13.7955 \times 10^{-39}$, and $I_C = 16.1324 \times 10^{-39}$ $g \cdot cm^2$.

References

[1]D. White, K. S. Seshadri, D. F. Dever, and D. E. Mann, and M. J. Linevsky, J. Chem. Phys. **39**, 2463 (1963).
[2]J. Berkowitz, J. Chem. Phys. **29**, 1386 (1958); **32**, 1519 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−15.854	−240.598	−240.598	INFINITE
100	43.954	208.779	331.528	−12.275	−240.914	−242.992	126.926
200	63.946	246.153	279.984	−6.766	−241.999	−244.602	63.884
250	69.312	261.042	274.742	−3.425	−242.372	−245.208	51.233
298.15	72.730	273.562	273.562	0.	−242.672	−245.727	43.050
300	72.837	274.012	273.563	0.135	−242.683	−245.746	42.788
350	75.223	285.431	274.460	3.840	−242.980	−246.233	36.748
400	76.893	295.591	276.478	7.645	−243.345	−246.674	32.212
450	78.098	304.720	279.117	11.521	−243.832	−247.062	28.678
500	78.993	312.998	282.098	15.450	−250.465	−246.774	25.780
600	80.201	327.516	288.491	23.415	−251.626	−245.925	21.410
700	80.955	339.940	294.975	31.475	−252.670	−244.891	18.274
800	81.454	350.784	301.288	39.597	−253.678	−243.711	15.913
900	81.801	360.399	307.332	47.761	−254.702	−242.404	14.069
1000	82.052	369.032	313.078	55.954	−255.743	−240.982	12.588
1100	82.239	376.861	318.526	64.169	−256.799	−239.455	11.371
1200	82.381	384.023	323.690	72.400	−257.868	−237.831	10.353
1300	82.493	390.622	328.588	80.644	−258.952	−236.117	9.487
1400	82.582	396.739	333.240	88.898	−260.044	−234.320	8.743
1500	82.654	402.439	337.665	97.160	−261.138	−232.444	8.094
1600	82.713	407.775	341.882	105.429	−262.236	−230.496	7.525
1700	82.762	412.791	345.907	113.702	−553.809	−214.126	6.579
1800	82.803	417.523	349.756	121.981	−553.407	−194.157	5.634
1900	82.838	422.001	353.441	130.263	−553.028	−174.209	4.789
2000	82.867	426.250	356.976	138.548	−552.672	−154.280	4.029
2100	82.893	430.294	360.372	146.836	−552.343	−134.369	3.342
2200	82.915	434.151	363.639	155.127	−552.041	−114.472	2.718
2300	82.935	437.837	366.785	163.419	−551.769	−94.589	2.148
2400	82.952	441.367	369.820	171.713	−551.531	−74.717	1.626
2500	82.967	444.754	372.750	180.009	−551.327	−54.854	1.146
2600	82.980	448.008	375.582	188.307	−551.162	−34.999	0.703
2700	82.992	451.140	378.323	196.605	−551.038	−15.148	0.293
2800	83.003	454.158	380.978	204.905	−550.959	4.698	−0.088
2900	83.012	457.071	383.552	213.206	−550.926	24.541	−0.442
3000	83.021	459.886	386.050	221.507	−550.943	44.386	−0.773
3100	83.029	462.608	388.476	229.810	−551.013	64.231	−1.082
3200	83.036	465.244	390.834	238.113	−551.139	84.079	−1.372
3300	83.042	467.799	393.127	246.417	−551.322	103.932	−1.645
3400	83.048	470.278	395.360	254.722	−551.566	123.792	−1.902
3500	83.053	472.686	397.535	263.027	−551.874	143.660	−2.144
3600	83.058	475.026	399.656	271.332	−552.247	163.538	−2.373
3700	83.063	477.301	401.724	279.638	−552.688	183.426	−2.590
3800	83.067	479.517	403.742	287.945	−553.200	203.328	−2.795
3900	83.071	481.674	405.712	296.252	−553.785	223.245	−2.990
4000	83.075	483.778	407.638	304.559	−554.446	243.176	−3.176
4100	83.078	485.829	409.520	312.867	−555.184	263.126	−3.352
4200	83.081	487.831	411.361	321.175	−556.004	283.094	−3.521
4300	83.084	489.786	413.162	329.483	−556.908	303.084	−3.682
4400	83.087	491.696	414.925	337.791	−557.856	323.091	−3.836
4500	83.089	493.563	416.652	346.100	−558.915	343.124	−3.983
4600	83.092	495.390	418.344	354.409	−560.069	363.181	−4.124
4700	83.094	497.177	420.002	362.719	−561.316	383.265	−4.260
4800	83.096	498.926	421.628	371.028	−562.659	403.377	−4.390
4900	83.098	500.639	423.224	379.338	−564.100	423.518	−4.515
5000	83.100	502.318	424.789	387.648	−565.643	443.689	−4.635
5100	83.101	503.964	426.325	395.958	−567.281	463.891	−4.751
5200	83.103	505.577	427.834	404.268	−569.038	484.126	−4.863
5300	83.105	507.160	429.316	412.578	−570.907	504.398	−4.971
5400	83.106	508.714	430.772	420.889	−572.893	524.705	−5.076
5500	83.107	510.239	432.203	429.199	−575.000	545.049	−5.176
5600	83.109	511.736	433.609	437.510	−577.232	565.435	−5.274
5700	83.110	513.207	434.993	445.821	−579.593	585.859	−5.369
5800	83.111	514.653	436.354	454.132	−582.086	606.328	−5.461
5900	83.112	516.073	437.693	462.443	−584.717	626.839	−5.550
6000	83.113	517.470	439.011	470.755	−587.489	647.398	−5.636

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

$S°(298.15\ K) = 80.295 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1474 \pm 1\ K$

$\Delta_f H°(0\ K) = -1638.57 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1649.50 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = 28.033 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of LiCl(cr), Li_2SO_4(cr), SiO_2(quartz) and Li_2SO_3(cr) in 20 percent hydrofluoric acid at 74.7°C were measured by Kracek.[1] The authors derived two values of $\Delta_{sln}H°$ of Li_2O(cr) from those of LiCl(cr) and Li_2SO_4(cr), presumably employing auxiliary data from.[2] We recalculate $\Delta_{sln}H°$ of Li_2O(cr) as −58.74 (chloride scheme, originally −59.36) and −59.83 kcal·mol^{-1} (sulfate scheme, originally −60.86), using recent $\Delta_f H°(298.15\ K)$ values for LiCl(cr), Li_2SO_4(cr), HCl(aq), H_2SO_4(aq) and Li_2O(cr). The corresponding enthalpy changes, $\Delta_r H°(298.15\ K)$, for the reaction $Li_2O(cr) + SiO_2(quartz) = Li_2SiO_3(cr)$ are derived as −33.08 and −34.17 kcal·mol^{-1}. Adopting the weighted average $\Delta_r H°(298.15\ K) = -33.44$ kcal·mol^{-1} with $\Delta_f H°(Li_2O, cr, 298.15\ K) = -143.1$ kcal·mol^{-1} and $\Delta_f H°(SiO_2, quartz, 298.15\ K) = -217.7$ kcal·mol^{-1}, we obtain $\Delta_f H°(298.15\ K) = -394.24$ kcal·mol^{-1} for Li_2SiO_3(cr). This $\Delta_f H°(Li_2SiO_3, cr, 298.15\ K)$ value is independent of future changes in $\Delta_f H°(298.15\ K)$ of Li_2O(cr) but the values of $\Delta_{sln}H°$ and $\Delta_f H°$ are not independent.

The enthalpies of solution of LiOH(cr) and Li_2SiO_3(cr) in 20 percent HF(aq) at 50°C were measured by Hatton*et al.*[2] The Li_2SiO_3 sample was prepared from lithium carbonate and silica by fusion under vacuum at 1500 K. Analysis gave 66.74 percent $SiO_2$and 15.12 percent Li. The corresponding calculated values are 66.79 and 15.43. Also present were 0.5 percent K and 0.06 percent Na. Corrections were made for impurities in the enthalpy of formation measurements. The results are given as follows:

	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}
2 LiOH(cr, 25°C) + 2HF(sol, 50°C) + 2 LiF(sol, 50°C) + 2 H_2O(sol, 50°C)	−38.728
SiO_2(cr, 25°C) + 6 HF(sol, 50°C) → H_2SiF_6(sol, 50°C) + 2 H_2O(sol, 50°C)	−32.810
3 H_2O(sol, 50°C) + 2 LiF(sol, 50°C) + H_2SiF_6(sol, 50°C) → Li_2SiO_3(cr, 25°C) + 8 HF(sol, 50°C)	+58.850
H_2O(sol, 50°C) → H_2O(l, 25°C)	−0.450
2 LiOH(cr, 25 °C) + SiO_2(cr, 25 °C) → Li_2SO_3(cr, 25 °C) + H_2O(l, 25 °C)	−13.14 ± 0.70

The $\Delta_r H°(298.15\ K)$ for the second reaction was determined by Torgeon and Sahama.[4] Based on the calculated enthalpy change for the overall reaction, $\Delta_r H°(298.15\ K) = -13.14$ kcal·mol^{-1} and $\Delta_f H°(298.15\ K) = -115.84$, −217.7 and −68.33 kcal·mol^{-1} for LiOH(cr), SiO_2(low quartz), and H_2O(l), respectively, we derived $\Delta_f H°(Li_2SO_3, cr, 298.15\ K) = -394.21 \pm 1.0$ kcal·mol^{-1}, which is in agreement with the adopted value.

Kroger and Fingas[5] measured the equilibrium pressure of CO_2 over a mixture of Li_2CO_3(cr), SiO_2(quartz) and Li_2SiO_3(cr) from 585 to 781 K. The enthalpy change $\Delta_r H°(298.15\ K)$ of the reaction $Li_2CO_3(cr) + SiO_2(cr) \rightarrow Li_2SiO_3(cr) + CO_2(g)$ is evaluated by the second and third law methods to be 30.94 and 29.47 kcal·mol^{-1}, respectively. Using $\Delta_f H°(298.15\ K) = -290.64$, −217.7 and −94.05 kcal·mol^{-1} for Li_2CO_3(cr), SiO_2(cr), and CO_2(g), respectively, and 3rd law $\Delta_r H°(298.15\ K)$, we obtain $\Delta_f H°(Li_2SiO_3, cr, 298.15\ K) = -384.82 \pm 5$ kcal·mol^{-1}, which is not used.

Heat Capacity and Entropy

The low temperature heat capacities, 25–340 K, were measured by Hatton*et al.*[3] with an adiabatic vacuum calorimeter, using a nickel plated copper sample container. During the filling and sealing of the calorimeter, the compound was handled in an anhydrous, CO_2 free atmosphere so as to avoid contamination. The purity of the sample is not well established. The high temperature heat capacities are estimated by summation of the $C_p°$'s of the constituent oxides, Li_2O and SiO_2, and a subsequent correction based upon a comparison of the heat capacities of Na_2SiO_3(cr) and its constituent oxides. These estimated $C_p°$ values are plotted and the resulting curve is joined smoothly with the low temperature $C_p°$ curve at 298 K. The entropy, $S°(298.15\ K)$, is derived using the measured low temperature heat capacities, based on $S°(25\ K) = 0.023\ cal·K^{-1}·mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

References

[1]F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69 (1953).
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[3]W. E. Hatton, D. L. Hildenbrand, G. C. Sinke and D. R. Stull, unpublished work, The Dow Chemical Co., Midland, Michigan, (1959).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−14.554	−1638.567	−1638.567	INFINITE
100	27.669	12.276	148.950	−13.667	−1643.293	−1616.673	844.463
200	72.036	45.798	88.665	−8.573	−1647.428	−1588.278	414.816
298.15	100.567	80.295	80.295	0.	−1649.500	−1558.739	273.085
300	101.010	80.919	80.297	0.186	−1649.524	−1558.176	271.303
400	118.826	112.628	84.499	11.252	−1650.237	−1527.594	199.483
500	127.809	140.155	92.946	23.604	−1656.617	−1496.277	156.315
600	134.306	164.049	102.850	36.720	−1656.584	−1464.203	127.470
700	139.649	185.161	113.129	50.422	−1656.061	−1432.175	106.870
800	144.432	204.128	123.338	64.632	−1655.158	−1400.249	91.427
900	148.565	221.382	133.288	79.285	−1653.958	−1368.455	79.423
1000	152.302	237.232	142.900	94.331	−1652.487	−1336.808	69.828
1100	155.576	251.903	152.151	109.728	−1650.773	−1305.321	61.985
1200	158.574	265.571	161.040	125.437	−1648.837	−1274.001	55.456
1300	161.293	278.371	169.578	141.431	−1646.703	−1242.850	49.938
1400	163.942	290.422	177.783	157.694	−1644.375	−1211.870	45.215
1474.000	165.856	298.915	183.653	169.896	--- CRYSTAL <---> LIQUID ---		
1500	166.523	301.821	185.676	174.217	−1641.853	−1181.064	41.128
1600	169.034	312.649	193.276	190.996	−1639.140	−1150.432	37.558
1700	171.502	322.971	200.604	208.023	−1976.890	−1105.177	33.958
1800	173.887	332.841	207.678	225.293	−1972.074	−1054.038	30.587
1900	176.188	342.305	214.517	242.798	−1967.061	−1003.172	27.579
2000	178.406	351.399	221.135	260.528	−1961.862	−952.574	24.879
2100	180.537	360.155	227.548	278.476	−1956.485	−902.241	22.442
2200	182.590	368.602	233.768	296.633	−1950.940	−852.168	20.233
2300	184.565	376.762	239.809	314.991	−1945.238	−802.351	18.222
2400	186.461	384.657	245.681	333.543	−1939.387	−752.786	16.384
2500	188.280	392.306	251.394	352.281	−1933.399	−703.467	14.698

PREVIOUS: March 1964 CURRENT: June 1967

$S°(298.15\ K) = [96.064]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1474 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1625.231]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 28.033 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_2SiO_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(Li_2SiO_3, cr, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1474\ K)–H°(298.15\ K)$, between the crystal and liquid.

Tschernobaeff[1] measured the enthalpy of reaction between SiO_2 and Li_2CO_3 in a bomb calorimeter, using carbon as the auxiliary combustible material. Based on the derived $\Delta_r H°(298.15\ K) = 24.99\ kcal·mol^{-1}$ for the reaction $Li_2CO_3(cr) + SiO_2(cr) \rightarrow Li_2SiO_3(g) + CO_2(g)$, the enthalpy of formation for $Li_2SiO_3(g)$ is evaluated as $-389.30\ kcal·mol^{-1}$, which is in fair agreement with the adopted value.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for Na_2SiO_3(l), Na_2O(l) and Li_2O(l). A glass transition is assumed at 1000 K; i.e., the heat capacities below 1000 K are taken to be the same as those for Li_2SiO_3(cr).

$S°(Li_2SiO_3, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point has been reported as 1474 ± 1 and 1461 K by Fracek[2] and Van Klooster,[3] respectively. The value reported by Kracek is adopted.

Schwartz and Sturm[4] used a cooling–curve method to compare the heats of fusion of Li_2SiO_3(cr) and NaCl(cr). From the reported ratio, $\epsilon(Li_2SiO_3)/\epsilon(NaCl) = 0.261/0.402$, where ϵ = heat of fusion in $kcal·g^{-1}$ and heat of fusion of NaCl(cr), the value $\Delta_{fus}H° = 6.7\ kcal·mol^{-1}$ is derived.

References

[1]Tschernobaeff, Rev. Met. **21**, 729 (1905).
[2]F. C. Kracek, J. Phys. Chem. **34**, 2641 (1930).
[3]H. S. Van Klooster, Z. Anorg. Chem. **69**, 135 (1911).
[4]R. Schwarz and H. Sturm, Ber. **47**, 1730 (1914).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	100.567	96.064	96.064	0.	−1625.231	−1539.171	269.656
300	101.010	96.688	96.066	0.186	−1625.254	−1538.637	267.901
400	118.826	128.398	100.268	11.252	−1625.968	−1509.633	197.138
500	127.809	155.924	108.716	23.604	−1632.348	−1479.892	154.603
600	134.306	179.818	118.619	36.720	−1632.314	−1449.396	126.181
700	139.649	200.930	128.898	50.422	−1631.792	−1418.944	105.883
800	144.432	219.897	139.108	64.632	−1630.889	−1388.595	90.666
900	148.565	237.151	149.057	79.285	−1629.689	−1358.378	78.838
1000	152.302	253.001	158.670	94.331	−1628.218	−1328.309	69.384
1000.000	152.302	253.001	158.670	94.331	GLASS <--> LIQUID		
1000.000	167.360	253.001	158.670	94.331	TRANSITION		
1100	167.360	268.952	167.982	111.067	−1625.164	−1298.466	61.659
1200	167.360	283.514	177.012	127.803	−1622.201	−1268.898	55.234
1300	167.360	296.910	185.726	144.539	−1619.325	−1239.573	49.807
1400	167.360	309.313	194.116	161.275	−1616.524	−1210.467	45.163
1474.000	167.360	317.933	200.118	173.660	--- CRYSTAL <--> LIQUID ---		
1500	167.360	320.860	202.185	178.011	−1613.789	−1181.559	41.146
1600	167.360	331.661	209.944	194.747	−1611.119	−1152.831	37.636
1700	167.360	341.807	217.405	211.483	−1949.160	−1109.469	34.090
1800	167.360	351.373	224.584	228.219	−1944.879	−1060.199	30.766
1900	167.360	360.422	231.498	244.955	−1940.635	−1011.166	27.799
2000	167.360	369.006	238.160	261.691	−1936.429	−962.356	25.134
2100	167.360	377.172	244.587	278.427	−1932.264	−913.755	22.728
2200	167.360	384.957	250.792	295.163	−1928.141	−865.350	20.546
2300	167.360	392.397	256.788	311.899	−1924.060	−817.134	18.558
2400	167.360	399.519	262.588	328.635	−1920.026	−769.094	16.739
2500	167.360	406.351	268.203	345.371	−1916.040	−721.220	15.069
2600	167.360	412.915	273.643	362.107	−1912.104	−673.505	13.531
2700	167.360	419.232	278.919	378.843	−1908.221	−625.940	12.110
2800	167.360	425.318	284.040	395.579	−1904.393	−578.518	10.792
2900	167.360	431.191	289.013	412.315	−1900.623	−531.233	9.569
3000	167.360	436.865	293.848	429.051	−1896.915	−484.076	8.429
3100	167.360	442.352	298.550	445.787	−1893.268	−437.041	7.364
3200	167.360	447.666	303.127	462.523	−1889.688	−390.124	6.368
3300	167.360	452.816	307.586	479.259	−1886.174	−343.318	5.434
3400	167.360	457.812	311.931	495.995	−1882.730	−296.616	4.557
3500	167.360	462.663	316.169	512.731	−1879.358	−250.015	3.731
3600	167.360	467.378	320.304	529.467	−2260.212	−193.048	2.801
3700	167.360	471.964	324.341	546.203	−2256.576	−135.678	1.915
3800	167.360	476.427	328.285	562.939	−2253.020	−78.403	1.078
3900	167.360	480.774	332.139	579.675	−2249.546	−21.221	0.284
4000	167.360	485.011	335.908	596.411	−2246.155	35.871	−0.468

PREVIOUS: March 1964 CURRENT: June 1967

0 to 1474 K crystal
above 1474 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−14.554	−1638.567	−1638.567	INFINITE
100	27.669	12.276	148.950	−13.667	−1643.293	−1616.673	844.463
200	72.036	45.798	88.665	−8.573	−1647.428	−1588.278	414.816
298.15	100.567	80.295	80.295	0.	−1649.500	−1558.739	273.085
300	101.010	80.919	80.297	0.186	−1649.524	−1558.176	271.303
400	118.826	112.628	84.499	11.252	−1650.237	−1527.594	199.483
500	127.809	140.155	92.946	23.604	−1656.617	−1496.277	156.315
600	134.306	164.049	102.850	36.720	−1656.584	−1464.203	127.470
700	139.649	185.161	113.129	50.422	−1656.061	−1432.175	106.870
800	144.432	204.128	123.338	64.632	−1655.158	−1400.249	91.427
900	148.565	221.382	133.288	79.285	−1653.958	−1368.455	79.423
1000	152.302	237.232	142.900	94.331	−1652.487	−1336.808	69.828
1100	155.576	251.903	152.151	109.728	−1650.773	−1305.321	61.985
1200	158.574	265.571	161.040	125.437	−1648.837	−1274.001	55.456
1300	161.293	278.371	169.578	141.431	−1646.703	−1242.850	49.938
1400	163.942	290.422	177.783	157.694	−1644.375	−1211.870	45.215
1474.000	165.856	298.915	183.653	169.896	CRYSTAL <--> LIQUID TRANSITION		
1474.000	167.360	317.933	183.653	197.929			
1500	167.360	320.860	186.006	202.281	−1613.789	−1181.559	41.146
1600	167.360	331.661	194.775	219.017	−1611.119	−1152.831	37.636
1700	167.360	341.807	203.129	235.753	−1949.160	−1109.469	34.090
1800	167.360	351.373	211.102	252.489	−1944.879	−1060.199	30.766
1900	167.360	360.422	218.725	269.225	−1940.635	−1011.166	27.799
2000	167.360	369.006	226.026	285.961	−1936.429	−962.356	25.134
2100	167.360	377.172	233.030	302.697	−1932.264	−913.755	22.728
2200	167.360	384.957	239.761	319.433	−1928.141	−865.350	20.546
2300	167.360	392.397	246.236	336.169	−1924.060	−817.134	18.558
2400	167.360	399.519	252.476	352.905	−1920.026	−769.094	16.739
2500	167.360	406.351	258.495	369.641	−1916.040	−721.220	15.069
2600	167.360	412.915	264.309	386.377	−1912.104	−673.505	13.531
2700	167.360	419.232	269.931	403.113	−1908.221	−625.940	12.110
2800	167.360	425.318	275.372	419.849	−1904.393	−578.518	10.792
2900	167.360	431.191	280.645	436.585	−1900.623	−531.233	9.569
3000	167.360	436.865	285.758	453.321	−1896.915	−484.076	8.429
3100	167.360	442.352	290.721	470.057	−1893.268	−437.041	7.364
3200	167.360	447.666	295.543	486.793	−1889.688	−390.124	6.368
3300	167.360	452.816	300.231	503.529	−1886.174	−343.318	5.434
3400	167.360	457.812	304.793	520.265	−1882.730	−296.616	4.557
3500	167.360	462.663	309.235	537.001	−1879.358	−250.015	3.731
3600	167.360	467.378	313.562	553.737	−2260.212	−193.048	2.801
3700	167.360	471.964	317.782	570.473	−2256.576	−135.678	1.915
3800	167.360	476.427	321.898	587.209	−2253.020	−78.403	1.078
3900	167.360	480.774	325.916	603.945	−2249.546	−21.221	0.284
4000	167.360	485.011	329.841	620.681	−2246.155	35.871	−0.468

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 91.755 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1485\ K$
$T_{fus} = 1820\ K$

$\Delta_f H°(0\ K) = -1660.065\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1670.671\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 11.506\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 110.165\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was calculated from measurements of solution calorimetry by Todd and Kelley[1] according to the following equation: $TiO_2(cr) + Li_2SO_4(cr) + 13.312\ H_2O(l) = Li_2TiO_3(cr) + H_2SO_4(aq,\ 12.312\ H_2O)$ $\Delta_r H°(298.15\ K) = 27.04\ kcal \cdot mol^{-1}$ $\Delta_f H°(TiO_2,\ cr,\ 298.15\ K)$ value for rutile was obtained from the JANAF tables and the other $\Delta_f H(298.15\ K)$ values were obtained from.[2]

Heat Capacity and Entropy

The low temperature heat capacities were taken from King.[3] These low temperature heat capacities were fit to the high temperature enthalpies from Christensen *et al.*[4]

$S°(298.15\ K) = 21.9\ cal \cdot K^{-1} \cdot mol^{-1}$ was obtained from King[3] based on the measured heat capacities and the extrapolated $S°(51\ K)$ value.

Transition Data

Christensen *et al.*[4] reported that lithium metatitanate undergoes a transition from the α to the β form at 1,485 K with an absorption of 2.750 $kcal \cdot mol^{-1}$.

Fusion Data

The T_{fus} and $\Delta_{fus} H°$ were obtained from Christensen *et al.*[4]

References

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[2]U. S. Nat. Bur. Stand. Circ. 500, (1952).
[3]E. G. King, J. Amer. Chem. Soc. 77, 2150 (1955).
[4]A. U. Christensen, K. C. Conway and K. K. Kelley, U. S. Bur. Mines RI 5565, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.493	−1660.065	−1660.065	INFINITE
100	31.142	14.129	169.105	−15.498	−1664.977	−1638.099	855.655
200	82.663	52.886	101.316	−9.686	−1669.132	−1609.488	420.355
298.15	109.855	91.755	91.755	0.	−1670.671	−1579.767	276.769
300	110.750	92.437	91.757	0.204	−1670.687	−1579.203	274.964
400	127.361	126.619	96.309	12.124	−1671.038	−1548.635	202.231
500	135.645	156.002	105.388	25.307	−1677.049	−1517.421	158.524
600	141.503	181.283	115.979	39.182	−1676.706	−1485.520	129.326
700	145.854	203.436	126.924	53.559	−1675.949	−1453.710	108.477
800	149.034	223.130	137.741	68.311	−1674.920	−1422.030	92.849
900	151.670	240.839	148.229	83.349	−1673.763	−1390.488	80.702
1000	153.888	256.936	158.307	98.628	−1672.570	−1359.077	70.991
1100	155.812	271.696	167.954	114.117	−1671.422	−1327.783	63.051
1200	157.318	285.322	177.174	129.778	−1674.331	−1296.471	56.434
1300	158.490	297.965	185.985	145.574	−1672.635	−1265.052	50.830
1400	159.494	309.751	194.410	161.478	−1670.942	−1233.763	46.032
1485.000	160.344	319.174	201.284	175.067	ALPHA <--> BETA		
1485.000	176.063	326.922	201.284	186.573	TRANSITION		
1500	176.565	328.694	202.549	189.218	−1657.529	−1202.712	41.882
1600	179.912	340.196	210.795	207.042	−1654.160	−1172.500	38.278
1700	183.259	351.204	218.733	225.200	−1941.066	−1128.152	34.664
1800	186.606	361.773	226.388	243.693	−1935.811	−1080.485	31.355
1820.000	187.276	363.839	227.887	247.432	---- BETA <--> LIQUID -----		
1900	189.954	371.952	233.783	262.521	−1930.404	−1033.113	28.402
2000	193.301	381.781	240.939	281.684	−1939.544	−985.576	25.741
2100	196.648	391.293	247.873	301.182	−1934.622	−937.998	23.331
2200	199.995	400.518	254.603	321.014	−1929.406	−890.660	21.147
2300	203.342	409.482	261.143	341.181	−1923.899	−843.567	19.158
2400	206.690	418.207	267.506	361.682	−1918.103	−796.720	17.340
2500	210.037	426.712	273.705	382.519	−1912.021	−750.119	15.673
2600	213.384	435.015	279.750	403.690	−1905.654	−703.768	14.139
2700	216.731	443.131	285.652	425.195	−1899.005	−657.666	12.723
2800	220.078	451.074	291.418	447.036	−1892.077	−611.816	11.414
2900	223.426	458.855	297.058	469.211	−1884.873	−566.220	10.199
3000	226.773	466.486	302.579	491.721	−1877.394	−520.876	9.069

PREVIOUS: June 1961 CURRENT: March 1964

$S°(298.15\ K)$ = [147.656] $J·K^{-1}·mol^{-1}$
T_{fus} = 1820 K

$\Delta_f H°(298.15\ K)$ = [−1566.760] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 110.165 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_2TiO_3, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1820\ K)$–$H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacities were reported by Christensen *et al.*[1] The measured heat capacity is extrapolated to an assumed glass transition temperature of 1214 K, below which the heat capacity is taken to be equal to that of the crystal.

$S°(Li_2TiO_3, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The T_{fus} and $\Delta_{fus}H°$ were obtained from Christensen *et al.*[1]

Reference

[1]A. U. Christensen, K. C. Conway and K. K. Kelley, U. S. Bur. Mines RI 5565, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	109.855	147.656	147.656	0.	−1566.760	−1492.523	261.484
300	110.750	148.338	147.658	0.204	−1566.775	−1492.062	259.791
400	127.361	182.520	152.209	12.124	−1567.127	−1467.084	191.582
500	135.645	211.903	161.289	25.307	−1573.138	−1441.460	150.588
600	141.503	237.183	171.880	39.182	−1572.795	−1415.149	123.200
700	145.854	259.337	182.824	53.559	−1572.038	−1388.930	103.643
800	149.034	279.031	193.642	68.311	−1571.009	−1362.840	88.984
900	151.670	296.740	204.130	83.349	−1569.852	−1336.887	77.591
1000	153.888	312.837	214.208	98.628	−1568.659	−1311.066	68.483
1100	155.812	327.597	223.855	114.117	−1567.511	−1285.363	61.037
1200	157.318	341.223	233.075	129.778	−1570.420	−1259.641	54.831
1214.000	157.569	343.049	234.333	131.982	GLASS <--> LIQUID		
1214.000	200.832	343.049	234.333	131.982	TRANSITION		
1300	200.832	356.795	241.984	149.253	−1565.044	−1233.940	49.580
1400	200.832	371.678	250.723	169.336	−1559.172	−1208.691	45.097
1500	200.832	385.534	259.254	189.420	−1553.416	−1183.859	41.226
1600	200.832	398.495	267.556	209.503	−1547.787	−1159.406	37.851
1700	200.832	410.671	275.620	229.586	−1832.769	−1120.948	34.443
1800	200.832	422.150	283.445	249.669	−1825.924	−1079.275	31.320
1820.000	200.832	424.369	284.965	253.716	BETA <--> LIQUID		
1900	200.832	433.008	291.033	269.752	−1819.262	−1037.977	28.536
2000	200.832	443.310	298.392	289.836	−1827.482	−996.572	26.028
2100	200.832	453.108	305.528	309.919	−1821.974	−955.162	23.758
2200	200.832	462.451	312.450	330.002	−1816.507	−914.012	21.701
2300	200.832	471.378	319.167	350.085	−1811.084	−873.112	19.829
2400	200.832	479.926	325.689	370.168	−1805.706	−832.447	18.118
2500	200.832	488.124	332.023	390.252	−1800.377	−792.004	16.548
2600	200.832	496.001	338.180	410.335	−1795.098	−751.773	15.103
2700	200.832	503.580	344.166	430.418	−1789.872	−711.744	13.770
2800	200.832	510.884	349.991	450.501	−1784.701	−671.908	12.535
2900	200.832	517.931	355.661	470.584	−1779.588	−632.257	11.388
3000	200.832	524.740	361.184	490.668	−1774.536	−592.780	10.321
3100	200.832	531.325	366.567	510.751	−1769.547	−553.470	9.326
3200	200.832	537.701	371.816	530.834	−1764.623	−514.321	8.395
3300	200.832	543.881	376.937	550.917	−1759.766	−475.325	7.524
3400	200.832	549.877	381.935	571.000	−1754.979	−436.474	6.706
3500	200.832	555.698	386.817	591.084	−1750.265	−397.763	5.936
3600	200.832	561.356	391.587	611.167	−1745.624	−359.186	5.212
3700	200.832	566.859	396.250	631.250	−2150.157	−312.949	4.418
3800	200.832	572.214	400.811	651.333	−2144.436	−263.371	3.620
3900	200.832	577.431	405.273	671.416	−2138.850	−213.942	2.865
4000	200.832	582.516	409.641	691.500	−2133.402	−164.655	2.150

PREVIOUS: June 1961 CURRENT: March 1964

0	to 1485	K	crystal, alpha
1485	to 1820	K	crystal, beta
above	1820	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−16.493	−1660.065	−1660.065	INFINITE
100	31.142	14.129	169.105	−15.498	−1664.977	−1638.099	855.655
200	82.663	52.886	101.316	−9.686	−1669.132	−1609.488	420.355
298.15	109.855	91.755	91.755	0.	−1670.671	−1579.767	276.769
300	110.750	92.437	91.757	0.204	−1670.687	−1579.203	274.964
400	127.361	126.619	96.309	12.124	−1671.038	−1548.635	202.231
500	135.645	156.002	105.388	25.307	−1677.049	−1517.421	158.524
600	141.503	181.283	115.979	39.182	−1676.706	−1485.520	129.326
700	145.854	203.436	126.924	53.559	−1675.949	−1453.710	108.477
800	149.034	223.130	137.741	68.311	−1674.920	−1422.030	92.849
900	151.670	240.839	148.229	83.349	−1673.763	−1390.488	80.702
1000	153.888	256.936	158.307	98.628	−1672.570	−1359.077	70.991
1100	155.812	271.696	167.954	114.117	−1671.422	−1327.783	63.051
1200	157.318	285.322	177.174	129.778	−1674.331	−1296.471	56.434
1300	158.490	297.965	185.985	145.574	−1672.635	−1265.052	50.830
1400	159.494	309.751	194.410	161.478	−1670.942	−1233.763	46.032
1485.000	160.344	319.174	201.284	175.067	ALPHA <--> BETA TRANSITION		
1485.000	176.063	326.922	201.284	186.573			
1500	176.565	328.694	202.549	189.218	−1657.529	−1202.712	41.882
1600	179.912	340.196	210.795	207.042	−1654.160	−1172.500	38.278
1700	183.259	351.204	218.733	225.200	−1941.066	−1128.152	34.664
1800	186.606	361.773	226.388	243.693	−1935.811	−1080.485	31.355
1820.000	187.276	363.839	227.887	247.432	BETA <--> LIQUID TRANSITION		
1820.000	200.832	424.369	227.887	357.597			
1900	200.832	433.008	236.343	373.664	−1819.262	−1037.977	28.536
2000	200.832	443.310	246.436	393.747	−1827.482	−996.572	26.028
2100	200.832	453.108	256.046	413.830	−1821.974	−955.162	23.758
2200	200.832	462.451	265.218	433.913	−1816.507	−914.012	21.701
2300	200.832	471.378	273.989	453.996	−1811.084	−873.112	19.829
2400	200.832	479.926	282.392	474.080	−1805.706	−832.447	18.118
2500	200.832	488.124	290.459	494.163	−1800.377	−792.004	16.548
2600	200.832	496.001	298.214	514.246	−1795.098	−751.773	15.103
2700	200.832	503.580	305.681	534.329	−1789.872	−711.744	13.770
2800	200.832	510.884	312.880	554.412	−1784.701	−671.908	12.535
2900	200.832	517.931	319.830	574.496	−1779.588	−632.257	11.388
3000	200.832	524.740	326.547	594.579	−1774.536	−592.780	10.321
3100	200.832	531.325	333.047	614.662	−1769.547	−553.470	9.326
3200	200.832	537.701	339.344	634.745	−1764.623	−514.321	8.395
3300	200.832	543.881	345.449	654.828	−1759.766	−475.325	7.524
3400	200.832	549.877	351.373	674.912	−1754.979	−436.474	6.706
3500	200.832	555.698	357.128	694.995	−1750.265	−397.763	5.936
3600	200.832	561.356	362.723	715.078	−1745.624	−359.186	5.212
3700	200.832	566.859	368.166	735.161	−2150.157	−312.949	4.418
3800	200.832	572.214	373.466	755.244	−2144.436	−263.371	3.620
3900	200.832	577.431	378.629	775.328	−2138.850	−213.942	2.865
4000	200.832	582.516	383.663	795.411	−2133.402	−164.655	2.150

PREVIOUS: CURRENT: March 1964

$S°(298.15\ K) = 113.947 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 848 \pm 1\ K$

$\Delta_f H°(0\ K) = -1423.980 \pm 1.7\ kJ\ mol^{-1}$
$\Delta_f H°(298.15\ K) = -1436.367 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(\alpha \rightarrow \beta) = 28.451 \pm 1.7\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of solution of Li_2SO_4(cr, α) has been measured by Ueda,[1] Thomsen,[2] Pickering,[3] Romanova and Samoilov[4] and Tsvetkov and Rabinovich.[5] Adopting the results from[1,4,5] we have $\Delta_{sln}H°(298.15\ K) = -7.300 \pm 0.1$ kcal·mol^{-1} for the enthalpy of solution at infinite dilution. We have used data from Thompson *et. al.*[6] to correct the enthalpy of solution data to infinite dilution. When this result is combined with enthalpies of formation of the infinitely dilute ions from CODATA[7] we obtain $\Delta_f H°(Li_2SO_4, aq, \infty, 298.15\ K) = 350.504 \pm 0.2$ kcal·mol^{-1} and $\Delta_f H°(Li_2SO_4, cr, 298.15\ K) = -343.20 \pm 0.3$ kcal·mol^{-1}.

Lithium sulfate was studied by hydrochloric acid solution calorimetry by Barany and Adami[8] who obtained $\Delta_r H°(298.15\ K) = -16.020 \pm 0.120$ kcal·mol^{-1} for the reaction 2 LiCl(cr) + H_2SO_4·7.068 H_2O(l) + 18.394 H_2O(l) = Li_2SO_4(cr) + 2 HCL·12.731 H_2O(l). When this result is combined with auxiliary data from,[9,10] we obtain $\Delta_f H°(Li_2SO_4, cr, 298.15\ K) = -343.30 \pm 0$ kcal·mol^{-1}. Auxiliary data used in the analysis are (in kcal·mol^{-1}): $\Delta_f H°(H_2SO_4 \cdot 7.068\ H_2O, 298.15\ K) = -209.566 \pm 0.10$ and $\Delta_f H°(HCl \cdot 12.731\ H_2O, 298.15\ K) = 38.792 \pm 0.010$.

Ueda[1] measured the emf of the cell: Li (amalgam, 0.035%)|$Li_2SO_4 \cdot H_2O$ (sat. soln.), Hg_2SO_4|Hg at 298 K as $E_{cell} = 2.67489$ volts. Kelley[17] used this value along with other data to determine $\Delta_f H°(298.15\ K)$ for Li_2SO_4(cr). Adopting results given in Kelley,[17] we calculate $\Delta_r G°(298.15\ K) = -165.780$ kcal·mol^{-1} for the reaction 2 Li(cr) + Hg_2SO_4(cr) = 2 Hg(l) + Li_2SO_4(cr). Taking $\Delta_f G°(Hg_2SO_4, cr, 298.15\ K) = 149.658$ kcal·mol^{-1} [7] and reference entropies from,[7] we calculate $\Delta_f G°(Li_2SO_4, cr, 298.15\ K) = -315.438$ and $\Delta_f H°(Li_2SO_4, cr, 298.15\ K) = -343.0 \pm 0.5$ kcal·mol^{-1}.

We adopt a value for the enthalpy of reaction based on the solution work of Barany and Adami.[8]

Heat Capacity and Entropy

Low temperature heat capacities of Li_2SO_4(cr, α) have been measured by Paukov[11] in an adiabatic calorimeter from 12.00–311.11 K. We have smoothed the experimental $C_p°$ data by fitting to orthogonal polynomials over selected temperature intervals. Our adopted value of $S°(298.15\ K) = 27.234 \pm 0.10$ kcal·mol^{-1} is based on $S°(14\ K) = 0.051$ kcal·mol^{-1} and $H°(14;0) = 0.540$ cal·K^{-1}·mol^{-1} derived from a Debye T^3 law extrapolation.

Heat capacity data measured by adiabatic calorimetry have been reported by Shmidt,[12] (298.5–774.3) and by Sjoblom,[13] (430–845 K). In addition, drop calorimetric enthalpy measurements have been performed by Denielou *et al.*,[14] (400–848 K), by Clark,[15] (488.0–848.7 K) and by Voskresenskaya and Banashek,[16] (360–859 K). The data of Clark is systematically low by 15% while the data from Sjoblom is too high by 10%. There is good agreement among the other three studies.[12,14,16] We adopt heat capacities above 300 K based on a smooth fit to the combined data from.[11,12,14,and16]

Transition Data

Li_2SO_4(cr, α) is the low–temperature form of lithium sulfate (sometimes denoted Li_2SO_4 II). The crystals are monoclinic (space group C_{2h}, $P2_1/c$). The transformation to the high–temperature β phase (cubic form) occurs at 848 ± 1 K.[14,15] The enthalpy of transition is determined by taking the difference between the adopted enthalpy curves of α and β Li_2SO_4 extrapolated to 848 K (see the discussion on the Li_2SO_4(cr, β) table.[18]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.636	−1423.980	−1423.980	INFINITE
100	43.869	28.932	196.627	−16.769	−1429.603	−1395.114	728.733
200	86.872	73.028	123.821	−10.159	−1434.139	−1358.693	354.854
298.15	117.608	113.947	113.947	0.	−1436.367	−1321.111	231.453
300	118.026	114.676	113.949	0.218	−1436.391	−1320.395	229.901
400	139.244	151.679	118.850	13.131	−1439.218	−1281.517	167.349
500	154.473	184.409	128.754	27.827	−1446.434	−1241.336	129.682
600	168.469	213.812	140.519	43.975	−1446.156	−1200.315	104.497
700	182.360	240.827	152.943	61.518	−1444.320	−1159.466	86.520
800	196.062	266.069	165.522	80.437	−1441.078	−1118.979	73.062
848.000	202.732	277.686	171.544	90.008	---- ALPHA <--> BETA ----		
900	209.702	289.957	178.033	100.732	−1489.633	−1077.896	62.559
1000	223.384	312.760	190.373	122.387	−1482.531	−1032.517	53.933
1100	237.051	334.692	202.502	145.408	−1474.161	−987.910	46.912
1200	250.705	355.903	214.406	169.796	−1464.510	−944.121	41.097

PREVIOUS: CURRENT: December 1978

$S°(298.15\ K) = [113.802]\ J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 848 \pm 1\ K$
$T_{fus}(\beta \rightarrow l) = 1132 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1425.373]\ kJ·mol^{-1}$
$\Delta_{trs}H°(\alpha \rightarrow \beta) = 28.451 \pm kJ·mol^{-1}$
$\Delta_{fus}H°(\beta \rightarrow l) = 8.577 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_2SO_4, cr, \beta, 298.15\ K)$ is calculated from $\Delta_f H°(Li_2SO_4, cr, \alpha, 298.15\ K)$ by adding the enthalpy of transition ($\alpha \rightarrow \beta$), $\Delta_{trs}H°$, and the difference in enthalpy, $H°(848\ K)–H°(298.15\ K)$, between the alpha and beta crystalline forms.[1]

Heat Capacity and Entropy

High temperature enthalpy measurements by drop calorimetry were carried out by Denielou *et al.*,[2] (860–1110 K), by Clark,[3] (874–1103 K), and by Voskresenskaya and Banashek,[4] (859–1133 K). In addition, heat capacities have been measured in an adiabatic calorimeter by Sjoblom,[5] (873–1073 K). All of the data indicate that C_p° is nearly constant over the temperature interval 848– 1132 K. The data of Clark[3] is systematically low by 15% while the other studies[2,4,5] are in substantial agreement. We have adopted enthalpies from Denielou *et al.*[2] for our curve fits, but have neglected points near T_{trs} and T_{fus} where the data shows pronounced curvature. This leads to a constant heat capacity of 51.0 $cal·K^{-1}·mol^{-1}$ over the range 909–1119 K. Our adopted enthalpies are 1.5% higher than those from Denielou *et al.*[2] at 848 K and 0.5% higher at 1132 K. We have extrapolated a constant heat capacity below T_{trs} to 700 K at which point we slowly bend C_p° until it is only 5% higher than C_p° for the α–form at 298.15 K. We also extrapolate a constant heat capacity above T_{fus}.

Transition Data

The high temperature β–modification of lithium sulfate (sometimes denoted Li_2SO_4 I) is of cubic structure, space group T_{d2}.[6] The α–β transition at 848 K is somewhat gradual and shows a second order rather than first order behavior. We have treated the transition as a first order transition, taking some of the curvature in the enthalpy data (see above) and lumping it into the heat of transition. Reasonable C_p° curves are obtained by omitting from the curve fits those enthalpy data in the vicinity of T_{trs}. T_{trs} = 848 K is selected as the peak of the transition. $\Delta_{trs}H°$ is calculated as the difference in the enthalpy curve fits at T_{trs}.

Fusion Data

The adopted melting point, T_{fus} = 1132 ± 1 K, was determined from the work of Denielou *et al.*,[2] (1130 ± 3 K), Voskresenskaya and Banashek,[4] (1133 ± 1 K), and Rea,[7] (1132 K). The heat of fusion, $\Delta_{fus}H° = 2.050 \pm 0.2\ kcal·mol^{-1}$, is calculated from the difference between the smoothed relative enthalpy of the liquid and the adopted enthalpy value for the β–crystalline form at T_{fus}.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	129.704	113.802	113.802	0.	−1425.373	−1310.073	229.519
300	132.214	114.612	113.804	0.242	−1425.373	−1309.358	227.979
400	176.565	159.302	119.593	15.883	−1425.472	−1270.820	165.952
500	196.648	201.029	131.788	34.621	−1428.646	−1231.859	128.691
600	207.526	237.933	146.469	54.878	−1424.259	−1192.891	103.850
700	212.547	270.354	161.901	75.917	−1418.927	−1154.743	86.168
800	213.384	298.803	177.274	97.223	−1413.298	−1117.386	72.958
848.000	213.384	311.237	184.509	107.465	---- ALPHA <--> BETA ----		
900	213.384	323.936	192.201	118.561	−1460.810	−1079.654	62.661
1000	213.384	346.418	206.518	139.900	−1454.024	−1037.668	54.202
1100	213.384	366.756	220.176	161.238	−1447.337	−996.357	47.313
1132.000	213 .384	372.875	224.406	168.066	---- BETA <--> LIQUID ----		
1200	213.384	385.323	233.176	182.576	−1440.735	−955.650	41.598
1300	213.384	402.402	245.545	203.915	−1434.210	−915.492	36.785
1400	213.384	418.216	257.321	225.253	−1427.749	−875.833	32.678
1500	213.384	432.938	268.543	246.592	−1421.342	−836.635	29.134
1600	213.384	446.709	279.253	267.930	−1414.985	−797.862	26.048
1700	213.384	459.646	289.488	289.268	−1699.147	−745.133	22.895
1800	213.384	471.842	299.283	310.607	−1691.378	−689.240	20.001
1900	213.384	483.379	308.671	331.945	−1683.671	−633.776	17.424
2000	213.384	494.325	317.683	353.284	−1676.027	−578.716	15.115

PREVIOUS: CURRENT: December 1978

$S°(298.15\ K) = [154.332]\ J·K^{-1}·mol^{-1}$
$T_{fus}(\beta \rightarrow l) = 1132 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1399.296]\ kJ·mol^{-1}$
$\Delta_f H°(\beta \rightarrow l) = \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Li_2SO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(Li_2SO_4, \beta, 298.15\ K)$ by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1132\ K)-H°(298.15\ K)$, between the β crystal and liquid.

Heat Capacity and Entropy

Enthalpies for $Li_2SO_4(l)$ have been measured by Clark,[2] (1145–1179 K), by Voskresenskaya and Banashek,[3] (1133–1270 K), and by Denielou *et al.*,[4] (1138–1530 K). The data of Clark is systematically low by 15% while the other two studies[3,4] are in substantial agreement. We adopt enthalpies based on the work of Denielou *et al.*[4] We adopt a constant heat capacity of 49.00 $cal·K^{-1}·mol^{-1}$ at temperatures above a hypothetical glass transition at 680 K. Below the glass transition, the heat capacity is taken as that of the alpha phase. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the β–crystal table for details.

Vaporization and Decomposition Data

$Li_2SO_4(l)$ can vaporize to the gaseous monomer, $Li_2SO_4(g)$, or decompose according to $Li_2SO_4(l) = Li_2O(cr) + SO_2(g) + 1/2\ O_2(g)$ or according to $Li_2SO_4(l) = 2\ Li(g) + SO_2(g) + O_2(g)$. Ficalora *et al.*[5] did not observe ions from Li_2O or Li_2SO_4 in their effusion mass–spectrometric experiments, indicating decomposition occurs to the metal. They determined $\Delta_{dcm}H°(1080\ K) = 324 \pm 12\ kcal·mol^{-1}$. This is in substantial agreement with JANAF thermodynamic data[1] which indicates $\Delta_{dcm}H°(1080\ K) = 332.3\ kcal·mol^{-1}$. Effusion and transpiration results of Jagannathan and Wyatt[6] also indicate that decomposition to the oxide is less important then decomposition to the metal. $T_{dcm} = \sim 2466\ K$ is the temperature at which the Gibbs energy change is zero for the reaction $Li_2SO_4(l) = Li_2O(l) + SO_2(g) + 1/2\ O_2(g)$ and $T_{dcm} = 2800\ K$ for the reaction $Li_2SO_4(l) = 2\ Li(g) + SO_2(g) + O_2(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	117.608	154.332	154.332	0.	−1399.296	−1296.080	227.068
300	118.026	155.061	154.334	0.218	−1399.320	−1295.439	225.556
400	139.244	192.064	159.235	13.131	−1402.147	−1260.599	164.617
500	154.473	224.794	169.139	27.827	−1409.362	−1224.457	127.918
600	168.469	254.196	180.904	43.975	−1409.085	−1187.475	103.379
680.000	179.619	275.966	190.820	57.899	_____ GLASS <−−> LIQUID _____		
680.000	205.016	275.966	190.820	57.899	TRANSITION		
700	205.016	281.909	193.338	61.999	−1406.767	−1150.671	85.864
800	205.016	309.285	206.159	82.501	−1401.943	−1114.416	72.764
900	205.016	333.432	218.985	103.002	−1450.291	−1077.682	62.547
1000	205.016	355.033	231.529	123.504	−1444.342	−1036.601	54.146
1100	205.016	374.573	243.659	144.006	−1438.492	−996.110	47.301
1132.000	205.016	380.452	247.443	150.566	−−−− BETA <−−> LIQUID −−−−		
1200	205.016	392.412	255.322	164.507	−1432.727	−956.149	41.620
1300	205.016	408.822	266.507	185.009	−1427.039	−916.665	36.832
1400	205.016	424.015	277.222	205.510	−1421.414	−877.617	32.744
1500	205.016	438.160	287.485	226.012	−1415.844	−838.970	29.216
1600	205.016	451.391	297.320	246.514	−1410.324	−800.692	26.140
1700	205.016	463.820	306.752	267.015	−1695.323	−748.405	22.996
1800	205.016	475.538	315.807	287.517	−1688.391	−692.905	20.108
1900	205.016	486.623	324.508	308.018	−1681.521	−637.788	17.534
2000	205.016	497.139	332.879	328.520	−1674.713	−583.031	15.227
2100	205.016	507.142	340.941	349.022	−1667.968	−528.613	13.149
2200	205.016	516.679	348.714	369.523	−1661.285	−474.513	11.266
2300	205.016	525.792	356.216	390.025	−1654.667	−420.718	9.555
2400	205.016	534.518	363.465	410.526	−1648.115	−367.210	7.992
2500	205.016	542.887	370.476	431.028	−1641.630	−313.972	6.560
2600	205.016	550.928	377.263	451.530	−1635.212	−260.993	5.243
2700	205.016	558.665	383.839	472.031	−1628.865	−208.258	4.029
2800	205.016	566.121	390.217	492.533	−1622.589	−155.758	2.906
2900	205.016	573.315	396.407	513.034	−1616.386	−103.482	1.864
3000	205.016	580.266	402.420	533.536	−1610.259	−51.417	0.895

PREVIOUS: CURRENT: December 1978

0	to	848	K crystal, alpha
848	to	1132	K crystal, beta
above		1132	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.636	−1423.980	−1423.980	INFINITE
100	43.869	28.932	196.627	−16.769	−1429.603	−1395.114	728.733
200	86.872	73.028	123.821	−10.159	−1434.139	−1358.693	354.854
298.15	117.608	113.947	113.947	0.	−1436.367	−1321.111	231.453
300	118.026	114.676	113.949	0.218	−1436.391	−1320.395	229.901
400	139.244	151.679	118.850	13.131	−1439.218	−1281.517	167.349
500	154.473	184.409	128.754	27.827	−1446.434	−1241.336	129.682
600	168.469	213.812	140.519	43.975	−1446.156	−1200.315	104.497
700	182.360	240.827	152.943	61.518	−1444.320	−1159.466	86.520
800	196.062	266.069	165.522	80.437	−1441.078	−1118.979	73.062
848.000	202.732	277.686	171.544	90.008	ALPHA <--> BETA		
848.000	213.384	311.237	171.544	118.459	TRANSITION		
900	213.384	323.936	179.985	129.555	−1460.810	−1079.654	62.661
1000	213.384	346.418	195.524	150.894	−1454.024	−1037.668	54.202
1100	213.384	366.756	210.181	172.232	−1447.337	−996.357	47.313
1132.000	213.384	372.875	214.694	179.060	BETA <--> LIQUID		
1132.000	205.016	380.452	214.694	187.638	TRANSITION		
1200	205.016	392.412	224.429	201.579	−1432.727	−956.149	41.620
1300	205.016	408.822	237.991	222.080	−1427.039	−916.665	36.832
1400	205.016	424.015	250.742	242.582	−1421.414	−877.617	32.744
1500	205.016	438.159	262.770	263.084	−1415.844	−838.970	29.216
1600	205.016	451.391	274.150	283.585	−1410.324	−800.691	26.140
1700	205.016	463.820	284.945	304.087	−1695.323	−748.405	22.996
1800	205.016	475.538	295.211	324.588	−1688.391	−692.905	20.108
1900	205.016	486.623	304.997	345.090	−1681.521	−637.788	17.534
2000	205.016	497.139	314.343	365.592	−1674.713	−583.031	15.227
2100	205.016	507.142	323.288	386.093	−1667.968	−528.613	13.149
2200	205.016	516.679	331.863	406.595	−1661.285	−474.513	11.266
2300	205.016	525.792	340.098	427.096	−1654.667	−420.718	9.555
2400	205.016	534.518	348.019	447.598	−1648.115	−367.210	7.992
2500	205.016	542.887	355.647	468.100	−1641.630	−313.972	6.560
2600	205.016	550.928	363.004	488.601	−1635.212	−260.993	5.243
2700	205.016	558.665	370.109	509.103	−1628.865	−208.258	4.029
2800	205.016	566.121	376.977	529.604	−1622.589	−155.758	2.906
2900	205.016	573.315	383.624	550.106	−1616.386	−103.482	1.864
3000	205.016	580.266	390.063	570.608	−1610.259	−51.417	0.895

PREVIOUS: CURRENT: December 1978

$S°(298.15\ K) = [322.820 \pm 41.8]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-1030.445 \pm 83.7]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-1041.816 \pm 83.7]\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Symmetries, and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
A_1 [1020](1)	B_1 [460](1)	E [1115](2)
[500](1)	B_2 [1150](1)	[61](2)
[380](1)	[660](1)	[410](2)
	[420](1)	[100](2)

Ground State Quantum Weight: [1] σ = [4]
Point Group: [D_{2d}]
Bond Distances: S–O = [1.48] Å Li–O = [1.90] Å
Bond Angles: O–S–O = [109.47]° O–Li–O = [79.0]°
Product of the Moments of Inertia: $I_A I_B I_C = [1.210866 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

Vaporization experiments on Li_2SO_4 have been carried out by Ficalora *et al.*,[1] by Vasilev and Dmitrievskaya,[2] (73–1223 K), and by Jagannathan and Wyatt,[3] (1227–1371 K). Ficalora *et al.*[1] did not observe the $Li_2SO_4^+$ ion nor ions from Li_2O in their Knudsen effusion mass–spectrometric experiments. Decomposition to Li(g) was the dominant process observed. Vasilev and Dmitrievskaya[2] carried out Langmuir method experiments on solid and liquid lithium sulfate. Their experimental pressures are less than JANAF calculated dissociation pressures from the two reactions $Li_2SO_4(l) = Li_2O(cr) + SO_2(g) + 1/2\ O_2(g)$ and $Li_2SO_4(l) = 2\ Li(g) + SO_2(g) + O_2(g)$. We have discounted their results.

Jagannathan and Wyatt[3] carried out Knudsen effusion weight–loss experiments and transpiration experiments (in N_2) on molten lithium sulfate. Their transpiration experiments identified high lithium concentrations in the vapor, so that $Li_2O(cr)$ formation cannot be the major reaction. The effusion experiments yield apparent $Li_2SO_4(g)$ pressures of the same order of magnitude as our calculated decomposition pressures (to $Li_2O(cr)$. The data from[3] leads to $\Delta_r H°(1300\ K) = 58 \pm 20\ kcal \cdot mol^{-1}$ for molecular vaporization. When this result is combined with auxiliary JANAF data,[7] we obtain $\Delta_f H°(Li_2SO_4, g, 298.15\ K) = -266 \pm 20\ kcal \cdot mol^{-1}$.

From trends in the enthalpies and entropies of sublimation for the other alkali sulfates[4] we would estimate $\Delta_r H°(1200\ K) = 75 \pm 15\ kcal \cdot mol^{-1}$ and $\Delta_r S°(1200\ K) = 35 \pm 5\ cal \cdot K^{-1} \cdot mol^{-1}$ for $Li_2SO_4(l) = Li_2SO_4(g)$. This estimate leads to $\Delta_f H°(Li_2SO_4, g, 298.15\ K) = -249 \pm 28\ kcal \cdot mol^{-1}$. We adopt this estimate for this tabulation.

Heat Capacity and Entropy

The adopted structure (D_{2d} symmetry) is based on the similar symmetry assigned to $Cs_2SO_4(g)$ and $K_2SO_4(g)$ in the high–temperature electron diffraction studies of Ugarov *et al.*[5] and Spiridonov and Lutoshkin.[6] The internuclear distance of 1.48 Å for S–O is taken from data on other sulfates[7] while Li–O = 1.90 Å is an estimate based on trends among lithium and sodium compounds. The Li–O distance of 1.96 Å found by Alcock *et al.*[8] seems a bit long. The principal moments of inertia are: $I_A = 15.5185 \times 10^{-39}\ g\ cm^2$ and $I_B = I_C = 27.9333 \times 10^{-39}\ g \cdot cm^2$.

Estimates of the eleven fundamental frequencies of Li_2SO_4 are based on comparisons with $Na_2SO_4(g)$ and $K_2SO_4(g)$,[7] data on crystalline Li_2SO_4,[9] and on a normal coordinate analysis of Devlin.[10] Uncertainties in the estimates of the molecular constants and gas–phase frequencies may contribute 10 $cal \cdot K^{-1} \cdot mol^{-1}$ to $S°(298.15\ K)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−19.652	−1030.445	−1030.445	INFINITE
100	51.737	242.404	397.499	−15.509	−1033.791	−1020.650	533.133
200	79.551	286.652	331.470	−8.963	−1038.393	−1005.671	262.654
250	91.859	305.764	324.443	−4.670	−1040.290	−997.264	208.367
298.15	101.804	322.820	322.820	0.	−1041.816	−988.835	173.240
300	102.151	323.451	322.822	0.189	−1041.869	−988.506	172.114
350	110.669	339.858	324.098	5.516	−1043.187	−979.505	146.183
400	117.688	355.110	327.033	11.231	−1046.568	−970.239	126.700
450	123.463	369.316	330.951	17.264	−1048.340	−960.600	111.504
500	128.218	382.578	335.458	23.560	−1056.150	−950.137	99.260
600	135.407	406.631	345.359	36.763	−1058.817	−928.668	80.848
700	140.417	427.903	355.661	50.569	−1060.718	−906.818	67.668
800	143.997	446.899	365.900	64.799	−1062.165	−884.730	57.767
900	146.621	464.019	375.867	79.337	−1116.477	−861.396	49.994
1000	148.589	479.574	385.472	94.102	−1116.264	−833.064	43.515
1100	150.099	493.810	394.683	109.040	−1115.979	−804.757	38.215
1200	151.278	506.922	403.497	124.111	−1115.644	−776.479	33.799
1300	152.216	519.070	411.926	139.287	−1115.281	−748.230	30.064
1400	152.972	530.379	419.987	154.548	−1114.897	−720.009	26.864
1500	153.591	540.954	427.703	169.877	−1114.499	−691.817	24.091
1600	154.102	550.884	435.095	185.262	−1114.095	−663.651	21.666
1700	154.530	560.239	442.184	200.695	−1404.164	−621.159	19.086
1800	154.891	569.083	448.990	216.166	−1402.261	−575.156	16.691
1900	155.199	577.466	455.533	231.671	−1400.388	−529.256	14.550
2000	155.463	585.433	461.831	247.205	−1398.549	−483.455	12.627
2100	155.692	593.024	467.899	262.763	−1396.747	−437.744	10.888
2200	155.891	600.271	473.752	278.342	−1394.987	−392.118	9.310
2300	156.065	607.205	479.405	293.940	−1393.273	−346.572	7.871
2400	156.218	613.850	484.869	309.554	−1391.607	−301.100	6.553
2500	156.354	620.230	490.157	325.183	−1389.995	−255.696	5.342
2600	156.474	626.365	495.279	340.825	−1388.438	−210.355	4.226
2700	156.582	632.272	500.244	356.477	−1386.939	−165.072	3.194
2800	156.678	637.969	505.061	372.141	−1385.501	−119.843	2.236
2900	156.765	643.468	509.740	387.813	−1384.128	−74.667	1.345
3000	156.843	648.784	514.286	403.493	−1382.822	−29.535	0.514
3100	156.915	653.928	518.708	419.181	−1381.586	15.555	−0.262
3200	156.979	658.911	523.012	434.876	−1380.422	60.604	−0.989
3300	157.038	663.742	527.204	450.577	−1379.331	105.618	−1.672
3400	157.092	668.431	531.289	466.283	−1378.317	150.602	−2.314
3500	157.141	672.986	535.273	481.995	−1377.382	195.556	−2.919
3600	157.186	677.413	539.160	497.711	−1376.528	240.485	−3.489
3700	157.228	681.721	542.955	513.432	−1375.757	285.390	−4.029
3800	157.266	685.914	546.662	529.157	−1375.072	330.279	−4.540
3900	157.302	690.000	550.285	544.885	−1374.475	375.149	−5.025
4000	157.335	693.983	553.828	560.617	−1373.968	420.003	−5.485
4100	157.366	697.868	557.294	576.352	−1373.554	464.847	−5.922
4200	157.394	701.660	560.687	592.090	−1373.236	509.682	−6.339
4300	157.421	705.364	564.008	607.831	−1373.017	554.512	−6.736
4400	157.445	708.984	567.262	623.574	−1372.858	599.332	−7.115
4500	157.468	712.522	570.451	639.320	−1372.826	644.153	−7.477
4600	157.490	715.983	573.577	655.068	−1372.904	688.974	−7.824
4700	157.510	719.371	576.643	670.818	−1373.092	733.801	−8.155
4800	157.529	722.687	579.651	686.570	−1373.391	778.631	−8.473
4900	157.547	725.935	582.604	702.324	−1373.808	823.470	−8.778
5000	157.564	729.118	585.502	718.079	−1374.344	868.318	−9.071
5100	157.580	732.239	588.349	733.837	−1374.993	913.177	−9.353
5200	157.595	735.299	591.146	749.595	−1375.781	958.048	−9.624
5300	157.609	738.301	593.894	765.356	−1376.701	1002.940	−9.885
5400	157.622	741.247	596.596	781.117	−1377.761	1047.848	−10.136
5500	157.635	744.139	599.252	796.880	−1378.962	1092.776	−10.378
5600	157.647	746.980	601.865	812.644	−1380.312	1137.731	−10.612
5700	157.658	749.770	604.435	828.409	−1381.815	1182.708	−10.838
5800	157.669	752.512	606.965	844.176	−1383.476	1227.715	−11.057
5900	157.679	755.207	609.454	859.943	−1385.299	1272.748	−11.268
6000	157.689	757.858	611.906	875.712	−1387.292	1317.818	−11.473

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

$S°(298.15\ K)$ = [125.520] $J·K^{-1}·mol^{-1}$
T_{trs} = 1209 K
T_{fus} = 1307 ± 1 K

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −2560.90 ± 4.2 $kJ·mol^{-1}$
$\Delta_{trs} H°$ = 0.941 $kJ·mol^{-1}$
$\Delta_{fus} H°$ = [53.806] $kJ·mol^{-1}$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	138.072	125.520	125.520	0.	−2560.901	−2416.848	423.422
300	138.909	126.377	125.523	0.256	−2560.946	−2415.954	420.655
400	174.891	171.701	131.457	16.098	−2561.976	−2367.401	309.151
500	192.673	212.726	143.694	34.516	−2567.627	−2318.171	242.178
600	205.685	249.062	158.287	54.466	−2566.295	−2268.388	197.481
700	214.890	281.479	173.613	75.507	−2564.136	−2218.898	165.576
800	222.589	310.685	188.951	97.387	−2561.408	−2169.759	141.671
900	229.492	337.312	203.978	120.000	−2558.215	−2120.990	123.099
1000	235.350	361.800	218.552	143.248	−2554.617	−2072.599	108.261
1100	240.617	384.483	232.618	167.052	−2550.660	−2024.585	96.140
1200	245.182	405.621	246.164	191.347	−2546.385	−1976.947	86.054
1209.000	245.559	407.454	247.358	193.556	I <--> II		
1209.000	245.559	408.233	247.358	194.497	TRANSITION		
1300	248.195	426.145	259.253	216.960	−2540.956	−1929.746	77.538
1307.000	248.417	427.478	260.150	218.698	------ II <--> LIQUID -----		
1400	251.207	444.648	271.841	241.929	−2536.318	−1882.902	70.252
1500	254.868	462.109	283.949	267.239	−2531.474	−1836.398	63.949
1600	257.734	478.653	295.606	292.876	−2526.436	−1790.223	58.445
1700	259.617	494.337	306.839	318.747	−2912.119	−1729.121	53.129
1800	261.082	509.220	317.672	344.786	−2904.970	−1659.740	48.164
1900	262.075	523.364	328.129	370.946	−2897.761	−1590.756	43.733
2000	262.755	536.825	338.230	397.190	−2890.530	−1522.153	39.755
2100	262.978	549.650	347.995	423.477	−2883.319	−1453.912	36.164
2200	263.174	561.889	357.441	449.785	−2876.151	−1386.012	32.908
2300	263.341	573.591	366.586	476.111	−2869.031	−1318.439	29.943
2400	263.480	584.802	375.447	502.452	−2861.964	−1251.174	27.231
2500	263.592	595.560	384.038	528.806	−2854.954	−1184.202	24.743

PREVIOUS: CURRENT: June 1967

Enthalpy of Formation

The enthalpies of solution of LiCl(cr), Li_2SO_4(cr), SiO_2(quartz) and $Li_2Si_2O_5$(cr) in 20 per cent hydrofluoric acid at 74.7°C were measured by Kracek.[1] The authors derived two values of $\Delta_{soln}H$ of Li_2O(cr) from those of LiCl(cr) and Li_2SO_4(cr), presumably employing auxiliary data from.[2] We recalculate $\Delta_{soln}H$ of Li_2O(cr) as −58.74 (chloride scheme, originally −59.36) and −59.83 $kcal·mol^{-1}$ (sulfate scheme, originally −60.86), using recent $\Delta_f H°(298.15\ K)$ values for LiCl(cr), Li_2SO_4(cr), HCl(aq), H_2SO_4(aq), and Li_2O(cr). The corresponding enthalpy changes, $\Delta_r H°(298.15\ K)$, for the reaction $Li_2O(cr) + 2SiO_2(quartz) = Li_2Si_2O_5(cr)$ are derived as −33.21 and −34.30 $kcal·mol^{-1}$. Adopting the weighted average $\Delta_r H°(298.15\ K)$ = −33.57 $kcal·mol^{-1}$ with $\Delta_f H°(Li_2O, cr, 298.15\ K)$ = −143.1 $kcal·mol^{-1}$ and $\Delta_f H°(SiO_2, quartz, 298.15\ K)$ = −217.7 $kcal·mol^{-1}$, we obtain $\Delta_f H°(298.15\ K)$ = −612.07 $kcal·mol^{-1}$ for $Li_2Si_2O_5$(cr). This value is independent of future changes in $\Delta_f H°(298.15\ K)$ of Li_2O(cr) but the values of $\Delta_{soln}H$ and $\Delta_r H°$ are not independent.

The enthalpies of solution of LiOH(cr) and $Li_2Si_2O_6$(cr) in 20 per cent HF(aq) at 50°C were measured by Hatton *et al.*[3] By use of a reaction scheme similar to that described on the Li_2SiO_3(cr) table, the enthalpy change at 298.15 K for the reaction $2LiOH(cr) + 2SiO_2(cr) \rightarrow Li_2Si_2O_5(cr) + H_2O(l)$ was calculated to be −13.44 $kcal·mol^{-1}$. Incorporating this value with $\Delta_f H°(298.15\ K)$ = −115.84, − 217.7 and −68.315 $kcal·mol^{-1}$ for LiOH(cr), SiO_2(cr), and H_2O(l), respectively, we obtain $\Delta_f H°(Li_2Si_2O_5, cr, 298.15\ K)$ = −612.20 ± 2.0 $kcal·mol^{-1}$, which is in excellent agreement with the adopted value.

Heat Capacity and Entropy

Both heat capacities and $S°(298.15\ K)$ are estimated by comparison with those for $Na_2Si_2O_5$(cr), Na_2O(cr) and Li_2O(cr).

Transition Data

The transition temperature, T_{trs} = 1209 K, is taken from Kracek.[4] The author estimated a enthalpy of transition of 1 to 2 $cal·K^{-1}·mol^{-1}$ based on the arrest in the cooling and heating curves. The value of $\Delta_{trs}H°$ is calculated assuming the enthalpy of transition at 1209 K is 1.5 $cal·K^{-1}·mol^{-1}$.

Fusion Data

Incongruent melting of $Li_2Si_2O_5$(cr) at 1033°C has been reported by Kracek[5] and Kracek.[4] The liquidus temperature of 1034°C at the composition 19.92 per cent Li_2O and 80.08 per cent SiO_2, reported by Kracek,[4] is adopted as T_{fus}. The enthalpy of melting is evaluated such that $\Delta_{fus}H°(298.15\ K) + \Delta_{trs}H°(298.15\ K)$ = 11.43 $kcal·mol^{-1}$, where the value 11.43 $kcal·mol^{-1}$ is the difference between $\Delta_f H°(298.15\ K)$ for $Li_2Si_2O_5$(cr) and $Li_2Si_2O_5$(l). The latter were determined by solution calorimetry by Kracek (refer to the Enthalpy of Formation sections in crystal and liquid tables).

References

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[2]U. S. Nat. Bur. Stand. Circ. 500, (1952).
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[5]F. C. Kracek, J. Phys. Chem. **34**, 2641 (1930).

$S°(298.15\ K)$ = [160.243] $J·K^{-1}·mol^{-1}$
T_{fus} = 1307 ± 1 K

$\Delta_f H°(298.15\ K)$ = [−2513.068] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [53.806] $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of LiCl(cr), Li_2SO_4(cr), SiO_2(quartz) and $Li_2Si_2O_5$(gl) in 20 per cent hydrofluoric acid at 74.7°C were measured by Kracek.[1] Following the same procedure as described in Li2Si2O5(cr) table, we derived the enthalpy changes, $\Delta_r H°(298.15\ K)$, for the reaction $Li_2O(cr) + 2SiO_2(quartz) = Li2Si2O5(gl)$ as −21.78 and −22.87 kcal mol^{-1}. Adopting the weighted average $\Delta_r H°(298.15\ K)$ = −22.14 $kcal·mol^{-1}$ with $\Delta_f H°(Li_2O, cr, 298.15\ K)$ = −143.1 $kcal·mol^{-1}$ and $\Delta_f H°(SiO_2, quartz, 298.15\ K)$ = −217.7 $kcal·mol^{-1}$, we obtain $\Delta_f H°(298.15\ K)$ = −600.640 $kcal·mol^{-1}$ for $Li_2Si_2O_5$(gl). This $\Delta H°(Li_2Si_2O_5, gl, 298.15\ K)$ value is independent of future changes in $\Delta_f H°(298.15\ K)$ of Li_2O(cr) but the values of $\Delta_{sol}H°$ and $\Delta_r H°$ are not independent.

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for $Na_2Si_2O_5$(l), Na_2SiO_3(l) and Li_2SiO_3(l). A glass transition temperature at 800 K is assumed, i.e. the heat capacities below 800 K are taken from those for $Li_2Si_2O_5$(cr) and above 800 K are assumed to be constant.

$S°(Li_2Si_2O_5, l, 298.15\ K)$ is calculated from $S°(Li_2Si_2O_5, cr, 298.15\ K)$ by adding the entropy of fusion, $\Delta_{fus}S°(1307\ K)$, and the fidderence in entropy, $S°(1307\ K)–S°298.15\ K)$, between the crystal and liquid.

Fusion Data

Refer to the crystal table for details.

References

[1]F. C. Kracek, Ann. Rept. Director of the Geophysical Laboratory, No. 1215, 69, (1953).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	138.072	160.243	160.243	0.	−2513.068	−2379.367	416.855
300	138.909	161.099	160.245	0.256	−2513.113	−2378.537	414.140
400	174.891	206.424	166.179	16.098	−2514.143	−2333.457	304.718
500	192.673	247.448	178.417	34.516	−2519.794	−2287.699	238.994
600	205.685	283.785	193.009	54.466	−2518.462	−2241.388	195.130
700	214.890	316.202	208.335	75.507	−2516.303	−2195.371	163.821
800	222.589	345.416	223.674	97.393	−2513.569	−2149.704	140.361
800.000	222.589	345.416	223.674	97.393	_____ GLASS <--> LIQUID _____		
800.000	251.040	345.416	223.674	97.393	TRANSITION		
900	251.040	374.984	238.876	122.497	−2507.885	−2104.565	122.146
1000	251.040	401.434	253.833	147.601	−2502.430	−2060.046	107.606
1100	251.040	425.361	268.356	172.705	−2497.173	−2016.063	95.735
1200	251.040	447.204	282.363	197.809	−2492.090	−1972.552	85.863
1300	251.040	467.298	295.826	222.913	−2487.169	−1929.458	77.527
1307.000	251.040	468.646	296.748	224.671	----- II <--> LIQUID -----		
1400	251.040	485.902	308.747	248.017	−2482.396	−1886.737	70.395
1500	251.040	503.222	321.141	273.121	−2477.759	−1844.353	64.226
1600	251.040	519.424	333.033	298.225	−2473.253	−1802.273	58.838
1700	251.040	534.643	344.449	323.329	−2859.704	−1745.226	53.624
1800	251.040	548.992	355.418	348.433	−2853.489	−1679.849	48.748
1900	251.040	562.565	365.966	373.537	−2847.336	−1614.814	44.394
2000	251.040	575.442	376.121	398.641	−2841.245	−1550.102	40.485
2100	251.040	587.690	385.906	423.745	−2835.217	−1485.694	36.955
2200	251.040	599.368	395.346	448.849	−2829.253	−1421.569	33.752
2300	251.040	610.527	404.461	473.953	−2823.356	−1357.717	30.835
2400	251.040	621.212	413.271	499.057	−2817.526	−1294.119	28.166
2500	251.040	631.460	421.795	524.161	−2811.766	−1230.763	25.715
2600	251.040	641.306	430.050	549.265	−2806.078	−1167.635	23.458
2700	251.040	650.780	438.050	574.369	−2800.463	−1104.724	21.372
2800	251.040	659.910	445.812	599.473	−2794.925	−1042.020	19.439
2900	251.040	668.719	453.347	624.577	−2789.465	−979.515	17.643
3000	251.040	677.230	460.669	649.681	−2784.085	−917.194	15.970

PREVIOUS: CURRENT: June 1967

0	to 1209	K	crystal, I
1209	to 1307	K	crystal, II
above	1307	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	138.072	125.520	125.520	0.	−2560.901	−2416.848	423.422
300	138.909	126.377	125.523	0.256	−2560.946	−2415.954	420.655
400	174.891	171.701	131.457	16.098	−2561.976	−2367.401	309.151
500	192.673	212.726	143.694	34.516	−2567.627	−2318.171	242.178
600	205.685	249.062	158.287	54.466	−2566.295	−2268.388	197.481
700	214.890	281.479	173.613	75.507	−2564.136	−2218.898	165.576
800	222.589	310.685	188.951	97.387	−2561.408	−2169.759	141.671
900	229.492	337.312	203.978	120.000	−2558.215	−2120.990	123.099
1000	235.350	361.800	218.552	143.248	−2554.617	−2072.599	108.261
1100	240.617	384.483	232.618	167.052	−2550.660	−2024.585	96.140
1200	245.182	405.621	246.164	191.347	−2546.385	−1976.947	86.054
1209.000	245.559	407.454	247.358	193.556	I <--> II		
1209.000	245.559	408.233	247.358	194.497	TRANSITION		
1300	248.195	426.145	259.253	216.960	−2540.956	−1929.746	77.538
1307.000	248.417	427.478	260.150	218.698	II <--> LIQUID		
1307.000	251.040	468.646	260.150	272.504	TRANSITION		
1400	251.040	485.902	274.580	295.851	−2482.396	−1886.737	70.395
1500	251.040	503.222	289.252	320.955	−2477.759	−1844.353	64.226
1600	251.040	519.424	303.137	346.059	−2473.253	−1802.273	58.838
1700	251.040	534.643	316.312	371.163	−2859.704	−1745.226	53.624
1800	251.040	548.992	328.844	396.267	−2853.489	−1679.849	48.748
1900	251.040	562.565	340.791	421.371	−2847.336	−1614.814	44.394
2000	251.040	575.442	352.204	446.475	−2841.245	−1550.102	40.485
2100	251.040	587.690	363.129	471.579	−2835.217	−1485.694	36.955
2200	251.040	599.368	373.603	496.683	−2829.253	−1421.569	33.752
2300	251.040	610.527	383.664	521.787	−2823.356	−1357.717	30.835
2400	251.040	621.212	393.341	546.891	−2817.526	−1294.119	28.166
2500	251.040	631.460	402.662	571.995	−2811.766	−1230.763	25.715
2600	251.040	641.306	411.652	597.099	−2806.078	−1167.635	23.458
2700	251.040	650.780	420.334	622.203	−2800.463	−1104.724	21.372
2800	251.040	659.910	428.729	647.307	−2794.925	−1042.020	19.439
2900	251.040	668.719	436.853	672.411	−2789.465	−979.515	17.643
3000	251.040	677.230	444.725	697.515	−2784.085	−917.194	15.970

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 62.593 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1086\ K$

$\Delta_f H°(0\ K) = -157.57 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -164.56 \pm 1.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation for Li_3N(cr) is derived from the solution calorimetric study of O'Hare and Johnson.[1] The reported values have been revised by Osborne and Flotow[2] to correct for the current atomic weight of lithium to give $\Delta_f H°(298.15\ K) = -39.33 \pm 0.26$ kcal·mol^{-1}. This uncertainty is derived from the experimental studies.

Previous studies on the measurement of the enthalpy of reaction of lithium with nitrogen[4] and the enthalpy of solution of Li_3N in water[3] are currently thought to be less reliable.[1] Both these studies[3,4] yielded $\Delta_f H°(298.15\ K)$ values of approximately 47 kjuccirclcal·mol^{-1}. Yonco *et al.*[5] studied the solubility of nitrogen in liquid lithium (468–714 K) and the equilibrium pressure of nitrogen over solid Li_3N (933–1051 K). A 2nd and 3rd law analysis of their reported $\Delta_f G°(T)$ values supports our adopted $S°(298.15\ K)$ value, to within 0.1 cal·K^{-1}·mol^{-1}, but suggests a 3rd law $\Delta_f H°(298.15$ k) value which is more positive by roughly 1.5 kcal·mol^{-1} than our adopted value. Emf measurements (823–973 K) of Bonomi *et al.*[6] gave $\Delta_f G°(T)$ values which are also more positive than our adopted values by roughly 2 kcal·mol^{-1} at 900 K. These are suspect since $Li_9N_2Cl_3$ may be involved in the reaction.[6] A 2nd and 3rd law analysis of this latter data suggests a $S°(298.15\ K)$ value which is 1.8 cal·K^{-1}·mol^{-1} smaller than our adopted value and a 3rd law $\Delta_f H°(298.15\ K)$ value which is more positive by 2 kcal·mol^{-1} than our adopted value. The $S°(298.15\ K)$ discrepancy is very difficult to reconcile without a unreasonable change in the heat capacity values.

Heat Capacity and Entropy

The thermal functions adopted are those tabulated by Osborne and Flotow.[2] These authors determined the heat capacity of a well characterized sample of Li_3N between 5 and 350 K. They used the results of Satoh,[7] ice calorimetric data from 273 to 773 K, to extend the heat capacity results to 773 K and then extrapolate to 1086 K, the melting point of Li_3N.[1,5]

As a check, the low temperature experimental heat capacity values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure gave an $S°(298.15\ K)$ identical to that reported by Osborne and Flotow.[2] The ice calorimetric data of Satoh[7] are not extensive enough to reliably define the entire heat capacity dependence from 350 to 1086 K, however the three data prints at 373 K, 578 K, and 773 K are sufficient to define a reasonable temperature dependence.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.212	−157.567	−157.567	INFINITE
100	22.204	10.114	114.995	−10.488	−159.779	−150.597	78.664
200	55.417	36.403	68.917	−6.503	−162.774	−140.160	36.606
298.15	75.266	62.593	62.593	0.	−164.557	−128.640	22.537
300	75.544	63.059	62.594	0.139	−164.581	−128.417	22.359
400	87.100	86.504	65.713	8.316	−165.664	−116.192	15.173
500	96.940	107.004	71.961	17.521	−175.728	−102.781	10.737
600	106.430	125.522	79.367	27.693	−175.998	−88.148	7.674
700	115.580	142.620	87.197	38.796	−175.191	−73.556	5.489
800	124.380	158.632	95.135	50.797	−173.434	−59.146	3.862
900	132.840	173.773	103.039	63.661	−170.832	−45.008	2.612
1000	140.950	188.192	110.839	77.353	−167.418	−31.203	1.630
1100	148.693	201.995	118.503	91.841	−163.222	−17.779	0.844
1200	156.108	215.253	126.016	107.084	−158.281	−4.769	0.208
1300	163.177	228.030	133.375	123.051	−152.628	7.799	−0.313

PREVIOUS: September 1966 CURRENT: March 1978

Continued from page 1497

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REFERENCE STATE

0	to	923 K	crystal
923	to	1366.104 K	liquid
above		1366.104 K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.998	0.	0.	0.
100	15.762	9.505	53.066	−4.356	0.	0.	0.
200	22.724	23.143	34.888	−2.349	0.	0.	0.
298.15	24.869	32.671	32.671	0.	0.	0.	0.
300	24.897	32.825	32.671	0.046	0.	0.	0.
400	26.144	40.167	33.664	2.601	0.	0.	0.
500	27.171	46.113	35.578	5.268	0.	0.	0.
600	28.184	51.156	37.764	8.035	0.	0.	0.
700	29.279	55.581	39.999	10.907	0.	0.	0.
800	30.507	59.569	42.200	13.895	0.	0.	0.
900	31.895	63.241	44.336	17.014	0.	0.	0.
923.000	32.238	64.050	44.818	17.751	CRYSTAL <--> LIQUID TRANSITION		
923.000	34.309	73.234	44.818	26.228			
1000	34.309	75.983	47.113	28.870	0.	0.	0.
1100	34.309	79.253	49.888	32.301	0.	0.	0.
1200	34.309	82.238	52.462	35.732	0.	0.	0.
1300	34.309	84.984	54.859	39.163	0.	0.	0.
1366.104	34.309	86.686	56.358	41.431	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1366.104	20.786	180.286	56.359	169.298			
1400	20.786	180.796	59.365	170.003	0.	0.	0.
1500	20.786	182.230	67.509	172.082	0.	0.	0.
1600	20.786	183.571	74.721	174.160	0.	0.	0.
1700	20.786	184.832	81.162	176.239	0.	0.	0.
1800	20.787	186.020	86.954	178.317	0.	0.	0.
1900	20.787	187.144	92.198	180.396	0.	0.	0.
2000	20.789	188.210	96.972	182.475	0.	0.	0.
2100	20.791	189.224	101.341	184.554	0.	0.	0.
2200	20.795	190.192	105.358	186.633	0.	0.	0.
2300	20.802	191.116	109.067	188.713	0.	0.	0.
2400	20.812	192.002	112.504	190.794	0.	0.	0.
2500	20.826	192.851	115.701	192.875	0.	0.	0.
2600	20.846	193.669	118.684	194.959	0.	0.	0.
2700	20.874	194.456	121.476	197.045	0.	0.	0.
2800	20.909	195.216	124.096	199.134	0.	0.	0.
2900	20.956	195.950	126.561	201.227	0.	0.	0.
3000	21.014	196.661	128.886	203.326	0.	0.	0.
3100	21.085	197.352	131.084	205.430	0.	0.	0.
3200	21.172	198.022	133.165	207.543	0.	0.	0.
3300	21.275	198.675	135.140	209.665	0.	0.	0.
3400	21.396	199.312	137.019	211.799	0.	0.	0.
3500	21.537	199.934	138.807	213.945	0.	0.	0.
3600	21.697	200.543	140.514	216.107	0.	0.	0.
3700	21.879	201.140	142.144	218.285	0.	0.	0.
3800	22.083	201.726	143.705	220.483	0.	0.	0.
3900	22.310	202.303	145.200	222.703	0.	0.	0.
4000	22.559	202.871	146.634	224.946	0.	0.	0.
4100	22.832	203.431	148.013	227.215	0.	0.	0.
4200	23.128	203.985	149.339	229.513	0.	0.	0.
4300	23.447	204.533	150.616	231.842	0.	0.	0.
4400	23.789	205.076	151.848	234.203	0.	0.	0.
4500	24.152	205.614	153.037	236.600	0.	0.	0.
4600	24.537	206.149	154.185	239.034	0.	0.	0.
4700	24.944	206.681	155.297	241.508	0.	0.	0.
4800	25.372	207.211	156.373	244.023	0.	0.	0.
4900	25.820	207.739	157.416	246.583	0.	0.	0.
5000	26.287	208.265	158.427	249.188	0.	0.	0.
5100	26.773	208.790	159.410	251.841	0.	0.	0.
5200	27.276	209.315	160.364	254.543	0.	0.	0.
5300	27.794	209.839	161.293	257.296	0.	0.	0.
5400	28.329	210.364	162.197	260.102	0.	0.	0.
5500	28.878	210.888	163.077	262.962	0.	0.	0.
5600	29.442	211.414	163.936	265.878	0.	0.	0.
5700	30.020	211.940	164.773	268.851	0.	0.	0.
5800	30.610	212.467	165.591	271.882	0.	0.	0.
5900	31.213	212.996	166.390	274.973	0.	0.	0.
6000	31.827	213.525	167.171	278.125	0.	0.	0.

PREVIOUS: September 1962 (1 atm) CURRENT: September 1983 (1 bar)

Magnesium (Mg) CRYSTAL A_r = 24.3057

Pearson Notation: hP2
$S°(298.15\ K) = 32.671 \pm 0.10\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 923 \pm 1\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(923\ K) = 8.477 \pm 0.418\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted heat capacities are derived from heat capacity[1,2] and enthalpy data[3] by fitting the experimental data with orthogonal polynomials over selected overlapping temperature intervals. The temperature region of 1 14 K is described by the equation: $C_p° = 0.3 \times 10^{-4} T + 0.8 \times 10^{-6} T^3$ cal·K^{-1}·mol^{-1}. The $S°(298.15\ K)$ value calculated from the polynomials agrees with those of Hultgren *et al.*,[4] Gurvich *et al.*,[5] and CODATA[6] to within 0.01 J·K^{-1}·mol^{-1}.

Craig *et al.*[1] measured the heat capacity in the region 12–320 K. Only smoothed values at 10 K intervals were reported and these were based on an incorrect relative atomic mass. Furukawa *et al.*[4] stated that the heat capacity values should be multiplied by 24.32/24.22 = 1.0041 to be consistent with the atomic mass of 1954. The current value for the relative atomic mass of magnesium requires a multiplier of 24.305/24.22 = 1.0035. Our analysis of this smoothed data (with orthogonal polynomials) suggests that the reported values at 18 K and 200 K may be in error.

The heat capacity study of Saba *et al.*[2] consisted of 37 determinations covering the range 293–548 K. Again only smoothed values at 10 K intervals were given. Using the current relative atomic mass for magnesium, this data should be multiplied by 24.305/24.32 = 0.99938. The enthalpy data of McDonald,[3] 6 values in the range 404 914 K, also need to be corrected by a factor of 24.305/24.312 = 0.99971. In the region 300–320 K, the corrected results of Craig *et al.*[1] lie 0.1% higher and Saba *et. al.*[2] 0.2% lower than the adopted values. The maximum deviation in the enthalpy data of McDonald[3] in comparison with our derived enthalpy values is 0.1%, except for the point at 403 K which is 0.7%. At the melting point, the entropies of JANAF, Hultgren *et. al.*,[4] and Gurvich *et al.*[5] are 15.308, 15.34, and 15.313 cal·K^{-1}·mol^{-1}, respectively.

Other studies[8–13] are considered for comparison with and confirmation of the adopted values, but they are not included in the polynomial fitting procedure. The heat capacity results of Mannchen and Bornkessel,[8] 12–300 K, were presented only graphically and support the results of Craig *et. al.*[1] The quantitative agreement is uncertain since it is not clear if the authors[8] were aware of the correction required for the data of Craig *et. al.*[1] Clusius and Vaughn[9] made experimental heat capacity determinations in the range 11–228 K. These data scatter about the selected values within ±2–4%.

Phase Data

According to Pearson,[15] magnesium has the hcp(A3) prototype structure. In the alkaline earth metal series, only α–Be has a similar structure.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation of magnesium is the enthalpy of formation of the gas. It is chosen to be that adopted by CODATA[6] based on numerous experimental studies which are discussed in the ideal gas table.[14]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−4.998	0.	0.	0.
100	15.762	9.505	53.066	−4.356	0.	0.	0.
200	22.724	23.143	34.888	−2.349	0.	0.	0.
250	24.018	28.364	33.076	−1.178	0.	0.	0.
298.15	24.869	32.671	32.671	0.	0.	0.	0.
300	24.897	32.825	32.671	0.046	0.	0.	0.
350	25.568	36.715	32.977	1.308	0.	0.	0.
400	26.144	40.167	33.664	2.601	0.	0.	0.
450	26.668	43.277	34.562	3.922	0.	0.	0.
500	27.171	46.113	35.578	5.268	0.	0.	0.
600	28.184	51.156	37.764	8.035	0.	0.	0.
700	29.279	55.581	39.999	10.907	0.	0.	0.
800	30.507	59.569	42.200	13.895	0.	0.	0.
900	31.895	63.241	44.336	17.014	0.	0.	0.
923.000	32.238	64.050	44.818	17.751	--- CRYSTAL <--> LIQUID ---		
1000	33.460	66.681	46.401	20.280	−8.590	0.712	−0.037
1100	35.214	69.951	48.394	23.712	−8.589	1.644	−0.078
1200	37.164	73.097	50.322	27.330	−8.402	2.567	−0.112
1300	39.316	76.155	52.192	31.152	−8.011	3.467	−0.139
1400	41.673	79.154	54.011	35.200	−134.803	7.496	−0.280
1500	44.238	82.115	55.786	39.493	−132.588	17.584	−0.612
1600	47.013	85.058	57.524	44.054	−130.106	27.516	−0.898
1700	50.000	87.996	59.230	48.903	−127.336	37.284	−1.146
1800	53.199	90.944	60.910	54.061	−124.256	46.881	−1.360
1900	56.613	93.911	62.568	59.550	−120.846	56.297	−1.548
2000	60.241	96.906	64.210	65.391	−117.084	65.524	−1.711

PREVIOUS: September 1962 CURRENT: September 1983

$S°(298.15\ K) = [34.464]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [4.790]\ kJ·mol^{-1}$
$T_{fus} = 923 \pm 1\ K$ $\Delta_{fus}H°(923\ K) = 8.477 \pm 0.418\ kJ·mol^{-1}$

Enthalpy of Formation

The heat of formation is calculated from that of the crystal by addition of the heat of fusion, $\Delta_{fus}H°(923\ K)$, and the enthalpy differences, $H°(923;298.15)$, for the crystal and the liquid. This value is dependent on the arbitrary choice of the liquid phase heat capacity values for temperatures less than 923 K.

Heat Capacity and Entropy

The enthalpy measurements of McDonald,[1] five observations in the temperature range 954–1263 K, are used to derive a constant liquid phase heat capacity of 8.2 $cal·K^{-1}·mol^{-1}$. This constant value is adopted for the entire liquid region and the region between 298.15 and 923 K. Gurvich *et al.*[13] have adopted the same value. Kubaschewski[2] quoted an unpublished study by Reinartz which gave $C_p°(l) = 8.1 \pm 0.3$ $cal·K^{-1}·mol^{-1}$. The enthalpies measured by McDonald deviate by −0.2 to +0.3% from the adopted values. The enthalpy study of Awbery and Griffiths[3] extended only 100 K into the liquid region (3 data points) and cannot be used to reliably predict the heat capacity; in addition, their reported enthalpies are 15% lower than the adopted values.

Fusion Data

The melting point is adopted as 923 ± 1 K. Charlesworth[4] and Geschneider[5] both adopted this value after critically reviewing the available data in 1964 and 1970, respectively. The primary studies are by Chadwick[6] (923 K), Jones[7] (920.5 K), and Haughton and Payne[8] (922 ± 0.5 K)].

The adopted heat of melting, $\Delta_{fus}H° = 2.026\ kcal·mol^{-1}$, is derived from the enthalpy study of McDonald.[1] Although McDonald[1] reports an uncertainty of ±50 $cal·mol^{-1}$, we feel a value of ±100 $cal·mol^{-1}$ reflects better the scatter of the various studies. Kubaschewski[2] quoted values for $\Delta_{fus}H°$ of 2.030 ± 0.080 and 1.830 ± 0.090 $kcal·mol^{-1}$ from the unpublished work of Reinartz and a thesis of Wittig, respectively. The calorimetric studies of Ginsberg and Wrigge[9] and the DTA study of Chiotte *et al.*[10] led to values of 90.6 ± 2 cal/g (2.202 ± 0.049 $kcal·mol^{-1}$) and 1.970 ± 0.016 $kcal·mol^{-1}$, respectively. An enthalpy study of Siuccirctull and McDonald[11] led to a heat of melting of 2.14 $kcal·mol^{-1}$; however, this value was thought to be in error due to a container reaction. These reported values all support the adopted value. The enthalpy study of Awbery and Griffiths[3] led to a miuccircluch lower value of 1.130 $kcal·mol^{-1}$.

Vaporization Data

T_b is calculated as the temperature for which $\Delta_{vap}G° = 0$ for the liquid vaporizing to the ideal monatomic gas. $T_b$corresponds to a fugacity of one bar. The heat of vaporization is calculated from the heat of formation of the liquid and the gas at T_b. Vaporization studies are discussed in the Mg(g) single phase table.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	34.309	34.464	34.464	0.	4.790	4.256	−0.746
300	34.309	34.676	34.465	0.063	4.808	4.252	−0.740
350	34.309	39.965	34.882	1.779	5.261	4.124	−0.615
400	34.309	44.546	35.810	3.494	5.684	3.932	−0.513
450	34.309	48.587	37.010	5.210	6.078	3.689	−0.428
500	34.309	52.202	38.352	6.925	6.448	3.403	−0.356
600	34.309	58.457	41.197	10.356	7.111	2.731	−0.238
700	34.309	63.746	44.050	13.787	7.670	1.955	−0.146
800	34.309	68.327	46.805	17.218	8.113	1.107	−0.072
900	34.309	72.368	49.425	20.649	8.425	0.211	−0.012
923.000	34.309	73.234	50.008	21.438	--- CRYSTAL <--> LIQUID ---		
1000	34.309	75.983	51.903	24.080	0.	0.	0.
1100	34.309	79.253	54.243	27.511	0.	0.	0.
1200	34.309	82.238	56.454	30.941	0.	0.	0.
1300	34.309	84.984	58.544	34.372	0.	0.	0.
1366.104	34.309	86.686	59.865	36.640	----- FUGACITY = 1 bar -----		
1400	34.309	87.527	60.525	37.803	−127.409	3.167	−0.118
1500	34.309	89.894	62.405	41.234	−126.057	12.447	−0.433
1600	34.309	92.108	64.193	44.665	−124.705	21.636	−0.706
1700	34.309	94.188	65.897	48.096	−123.352	30.741	−0.945
1800	34.309	96.149	67.523	51.527	−122.000	39.766	−1.154
1900	34.309	98.004	69.079	54.958	−120.648	48.717	−1.339
2000	34.309	99.764	70.570	58.388	−119.296	57.596	−1.504

PREVIOUS: September 1962 CURRENT: September 1983

0 to 923 K crystal
above 923 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.998	0.	0.	0.
100	15.762	9.505	53.066	−4.356	0.	0.	0.
200	22.724	23.143	34.888	−2.349	0.	0.	0.
250	24.018	28.364	33.076	−1.178	0.	0.	0.
298.15	24.869	32.671	32.671	0.	0.	0.	0.
300	24.897	32.825	32.671	0.046	0.	0.	0.
350	25.568	36.715	32.977	1.308	0.	0.	0.
400	26.144	40.167	33.664	2.601	0.	0.	0.
450	26.668	43.277	34.562	3.922	0.	0.	0.
500	27.171	46.113	35.578	5.268	0.	0.	0.
600	28.184	51.156	37.764	8.035	0.	0.	0.
700	29.279	55.581	39.999	10.907	0.	0.	0.
800	30.507	59.569	42.200	13.895	0.	0.	0.
900	31.895	63.241	44.336	17.014	0.	0.	0.
923.000	32.238	64.050	44.818	17.751	____ CRYSTAL <--> LIQUID ____		
923.000	34.309	73.234	44.818	26.228	TRANSITION		
1000	34.309	75.983	47.113	28.870	0.	0.	0.
1100	34.309	79.253	49.888	32.301	0.	0.	0.
1200	34.309	82.238	52.462	35.732	0.	0.	0.
1300	34.309	84.984	54.859	39.163	0.	0.	0.
1366.104	34.309	86.686	56.358	41.431	----- FUGACITY = 1 bar -----		
1400	34.309	87.527	57.103	42.594	−127.409	3.167	−0.118
1500	34.309	89.894	59.211	46.024	−126.057	12.447	−0.433
1600	34.309	92.108	61.199	49.455	−124.705	21.636	−0.706
1700	34.309	94.188	63.079	52.886	−123.352	30.741	−0.945
1800	34.309	96.149	64.862	56.317	−122.000	39.766	−1.154
1900	34.309	98.004	66.558	59.748	−120.648	48.717	−1.339
2000	34.309	99.764	68.175	63.179	−119.296	57.596	−1.504

PREVIOUS: CURRENT: September 1983

IP(Mg, g) = 61671.02 ± 0.10 cm^{-1}
$S°$(298.15 K) = 148.648 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 145.90 ± 0.80 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 147.10 ± 0.80 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.00	1
$^3P_0$	21850.405	1
$^3P_1$	21870.464	3
$^3P_2$	21911.178	5
$^1P_1$	35051.264	3

Enthalpy of Formation

The adopted enthalpy of formation values for Mg(g), $\Delta_f H°$(298.15 K) = 147.10 ± 0.80 $kJ·mol^{-1}$, is that recommended by CODATA.[1] This value was calculated, according to CODATA, from the vapor pressure measurements by Priselkov (673–773 K),[2] Gilbreath (495–658 K),[3] McCreary and Thorn (716–800 K),[4] Pahlman and Smith (650–930 K),[5] and others cited in Hultgren *et al.*[6]

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Martin and Zulubas,[7] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of fitting in these missing levels (for $n < 60$) and cutting off the summation in the partition function[8] has no effect on the thermodynamic functions to 4000 K. This is a result of the high energy of all levels other than the ground state and the levels listed above; the next excited state is approximately 41197 cm^{-1} above the ground state. Although we list only a few levels, all levels listed by Martin and Zulubas[7] and estimated levels (for $n < 60$) are considered in the calculation. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the additional states and use of different fill and cutoff procedures.[8]

The thermal functions at 298.15 K differ from the CODATA recommendations[1] for two reasons. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas CODATA recommendations are based on 1 atm. Second, small changes, ~0.002 $J·K^{-1}·mol^{-1}$, arise due to the use of slightly different values for the fundamental constants.

References

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[2] Yu. A. Priselkov, Moscow State University, Dissertation, 1954; cited by A. N. Nesmeyanov, "Vapor Pressures of the Chemical Elements," Moscow, (1961).
[3] W. P. Gilbreath, NASA TN-D-2723, (1965).
[4] J. R. McCreary and R. J. Thorn, High Temp. Sci. **3**, 300 (1971).
[5] J. E. Pahlman and J. F. Smith, Met. Trans. **3**, 2423 (1972).
[6] R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," American Society of Metals, Metals Park, Ohio, (1973).
[7] W. C. Martin and R. Zalubas, J. Phys. Chem. Ref. Data **9**, 1 (1980).
[8] J. R. Downey, Jr., The Dow Chemical Company, Report AFOSR-TR-78-0960, Contract No. F44670-75-1-0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	145.901	145.901	INFINITE
100	20.786	125.940	167.128	−4.119	147.337	135.694	−70.879
200	20.786	140.348	150.549	−2.040	147.409	123.968	−32.377
250	20.786	144.986	148.990	−1.001	147.277	118.122	−24.680
298.15	20.786	148.648	148.648	0.	147.100	112.522	−19.713
300	20.786	148.776	148.648	0.038	147.092	112.307	−19.554
350	20.786	151.980	148.901	1.078	146.870	106.527	−15.898
400	20.786	154.756	149.463	2.117	146.616	100.780	−13.161
450	20.786	157.204	150.190	3.156	146.335	95.067	−11.035
500	20.786	159.394	151.003	4.196	146.028	89.387	−9.338
600	20.786	163.184	152.727	6.274	145.339	78.122	−6.801
700	20.786	166.388	154.455	8.353	144.546	66.981	−4.998
800	20.786	169.164	156.124	10.431	143.636	55.961	−3.654
900	20.786	171.612	157.712	12.510	142.596	45.062	−2.615
1000	20.786	173.802	159.213	14.589	132.819	35.000	−1.828
1100	20.786	175.783	160.631	16.667	131.466	25.283	−1.201
1200	20.786	177.592	161.970	18.746	130.114	15.690	−0.683
1300	20.786	179.255	163.237	20.824	128.762	6.209	−0.249
1366.104	20.786	180.286	164.037	22.199	----- FUGACITY = 1 bar -----		
1400	20.786	180.796	164.437	22.903	0.	0.	0.
1500	20.786	182.230	165.575	24.982	0.	0.	0.
1600	20.786	183.571	166.659	27.060	0.	0.	0.
1700	20.786	184.832	167.691	29.139	0.	0.	0.
1800	20.787	186.020	168.677	31.218	0.	0.	0.
1900	20.787	187.144	169.619	33.296	0.	0.	0.
2000	20.789	188.210	170.522	35.375	0.	0.	0.
2100	20.791	189.224	171.389	37.454	0.	0.	0.
2200	20.795	190.192	172.222	39.533	0.	0.	0.
2300	20.802	191.116	173.023	41.613	0.	0.	0.
2400	20.812	192.002	173.796	43.694	0.	0.	0.
2500	20.826	192.851	174.541	45.776	0.	0.	0.
2600	20.846	193.669	175.261	47.859	0.	0.	0.
2700	20.874	194.456	175.958	49.945	0.	0.	0.
2800	20.909	195.216	176.632	52.034	0.	0.	0.
2900	20.956	195.950	177.285	54.127	0.	0.	0.
3000	21.014	196.661	177.920	56.226	0.	0.	0.
3100	21.085	197.352	178.535	58.331	0.	0.	0.
3200	21.172	198.022	179.134	60.443	0.	0.	0.
3300	21.275	198.675	179.716	62.566	0.	0.	0.
3400	21.396	199.312	180.283	64.699	0.	0.	0.
3500	21.537	199.934	180.836	66.845	0.	0.	0.
3600	21.697	200.543	181.375	69.007	0.	0.	0.
3700	21.879	201.140	181.901	71.186	0.	0.	0.
3800	22.083	201.726	182.415	73.384	0.	0.	0.
3900	22.310	202.303	182.918	75.603	0.	0.	0.
4000	22.559	202.871	183.409	77.846	0.	0.	0.
4100	22.832	203.431	183.891	80.116	0.	0.	0.
4200	23.128	203.985	184.363	82.413	0.	0.	0.
4300	23.447	204.533	184.825	84.742	0.	0.	0.
4400	23.789	205.076	185.279	87.103	0.	0.	0.
4500	24.152	205.614	185.725	89.500	0.	0.	0.
4600	24.537	206.149	186.164	91.934	0.	0.	0.
4700	24.944	206.681	186.594	94.408	0.	0.	0.
4800	25.372	207.211	187.018	96.923	0.	0.	0.
4900	25.820	207.739	187.436	99.483	0.	0.	0.
5000	26.287	208.265	187.847	102.088	0.	0.	0.
5100	26.773	208.790	188.253	104.741	0.	0.	0.
5200	27.276	209.315	188.653	107.443	0.	0.	0.
5300	27.794	209.839	189.048	110.196	0.	0.	0.
5400	28.329	210.364	189.437	113.002	0.	0.	0.
5500	28.878	210.888	189.823	115.862	0.	0.	0.
5600	29.442	211.414	190.204	118.778	0.	0.	0.
5700	30.020	211.940	190.580	121.751	0.	0.	0.
5800	30.610	212.467	190.953	124.782	0.	0.	0.
5900	31.213	212.996	191.322	127.873	0.	0.	0.
6000	31.827	213.525	191.688	131.025	0.	0.	0.

PREVIOUS: September 1962 (1 atm) CURRENT: September 1983 (1 bar)

$IP(Mg^+, g) = 121267.61 \pm 0.05\ cm^{-1}$
$S°(298.15\ K) = 154.410 \pm 0.02\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 883.65 \pm 1.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [891.047]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2
$^2P_{1/2}$	35669.31	2
$^2P_{3/2}$	35760.88	4

Enthalpy of Formation

$\Delta_f H°(Mg^+, g, 0\ K)$ is calculated from $\Delta_f H°(Mg, g, 0\ K)$[1] using the spectroscopic value of IP(Mg) = 61671.02 ± 0.10 cm^{-1}(737.749 ± 0.001 $kJ·mol^{-1}$) from Martin and Zolubas.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Mg^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Mg, g, 0\ K)$ by using IP(Mg) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, for Mg(g), $Mg^+(g)$, and e^-(ref). $\Delta_r H°(Mg \rightarrow Mg^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Martin and Zolubas,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first two excited states; the next excited state is 69804.95 cm^{-1} above the ground state. Since inclusion of these higher excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first two excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: Mg(g), 9–30–83; e^-(ref), 3–31–82.
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[6]J. R. Downey, Jr., The Dow Chemical Company, AFOSRS–TR–78–0960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	883.650		
100	20.786	131.703	172.891	−4.119			
200	20.786	146.111	156.312	−2.040			
250	20.786	150.749	154.753	−1.001			
298.15	20.786	154.410	154.410	0.	891.047	848.495	−148.653
300	20.786	154.539	154.411	0.038	891.078	848.231	−147.690
350	20.786	157.743	154.664	1.078	891.894	841.025	−125.516
400	20.786	160.519	155.226	2.117	892.680	833.704	−108.871
450	20.786	162.967	155.953	3.156	893.438	826.287	−95.913
500	20.786	165.157	156.766	4.196	894.170	818.786	−85.538
600	20.786	168.947	158.490	6.274	895.560	803.577	−69.958
700	20.786	172.151	160.218	8.353	896.845	788.143	−58.812
800	20.786	174.926	161.887	10.431	898.014	772.533	−50.441
900	20.786	177.375	163.475	12.510	899.053	756.784	−43.923
1000	20.786	179.565	164.976	14.589	891.354	741.639	−38.739
1100	20.786	181.546	166.394	16.667	892.080	726.633	−34.505
1200	20.786	183.354	167.733	18.746	892.807	711.560	−30.973
1300	20.786	185.018	168.999	20.824	893.533	696.427	−27.983
1400	20.786	186.559	170.199	22.903	766.850	684.404	−25.535
1500	20.786	187.993	171.338	24.982	768.929	678.443	−23.625
1600	20.786	189.334	172.422	27.060	771.007	672.343	−21.950
1700	20.786	190.594	173.454	29.139	773.086	666.113	−20.467
1800	20.786	191.783	174.439	31.217	775.164	659.760	−19.146
1900	20.786	192.906	175.382	33.296	777.243	653.292	−17.960
2000	20.786	193.973	176.285	35.375	779.321	646.714	−16.890
2100	20.786	194.987	177.152	37.453	781.400	640.033	−15.920
2200	20.786	195.954	177.985	39.532	783.477	633.253	−15.035
2300	20.786	196.878	178.786	41.610	785.555	626.378	−14.225
2400	20.786	197.762	179.558	43.689	787.631	619.412	−13.481
2500	20.786	198.611	180.304	45.768	789.707	612.361	−12.795
2600	20.786	199.426	181.024	47.846	791.780	605.226	−12.159
2700	20.786	200.211	181.720	49.925	793.852	598.011	−11.569
2800	20.786	200.966	182.394	52.004	795.920	590.720	−11.020
2900	20.786	201.696	183.047	54.082	797.984	583.355	−10.507
3000	20.786	202.401	183.680	56.161	800.043	575.919	−10.028
3100	20.786	203.082	184.295	58.239	802.095	568.414	−9.578
3200	20.787	203.742	184.893	60.318	804.140	560.844	−9.155
3300	20.787	204.382	185.474	62.397	806.175	553.209	−8.757
3400	20.788	205.002	186.039	64.475	808.199	545.513	−8.381
3500	20.788	205.605	186.589	66.554	810.210	537.758	−8.026
3600	20.789	206.191	187.126	68.633	812.205	529.945	−7.689
3700	20.790	206.760	187.649	70.712	814.184	522.077	−7.370
3800	20.792	207.315	188.159	72.791	816.144	514.156	−7.068
3900	20.794	207.855	188.657	74.871	818.083	506.184	−6.780
4000	20.797	208.381	189.144	76.950	819.998	498.162	−6.505
4100	20.800	208.895	189.619	79.030	821.887	490.093	−6.244
4200	20.804	209.396	190.084	81.110	823.748	481.978	−5.994
4300	20.809	209.886	190.539	83.191	825.578	473.818	−5.756
4400	20.815	210.364	190.984	85.272	827.377	465.617	−5.528
4500	20.822	210.832	191.420	87.354	829.141	457.375	−5.309
4600	20.830	211.290	191.847	89.436	830.868	449.095	−5.100
4700	20.839	211.738	192.265	91.520	832.556	440.777	−4.899
4800	20.850	212.177	192.676	93.604	834.203	432.424	−4.706
4900	20.862	212.607	193.078	95.690	835.808	424.037	−4.520
5000	20.876	213.028	193.473	97.777	837.368	415.617	−4.342
5100	20.892	213.442	193.860	99.865	838.882	407.167	−4.170
5200	20.910	213.848	194.241	101.955	840.349	398.688	−4.005
5300	20.930	214.246	194.615	104.047	841.767	390.181	−3.845
5400	20.952	214.638	194.982	106.141	843.133	381.647	−3.692
5500	20.976	215.022	195.343	108.238	844.448	373.089	−3.543
5600	21.003	215.400	195.697	110.337	845.710	364.508	−3.400
5700	21.032	215.772	196.046	112.438	846.918	355.904	−3.261
5800	21.063	216.138	196.390	114.543	848.069	347.279	−3.128
5900	21.098	216.499	196.727	116.651	849.165	338.636	−2.998
6000	21.134	216.854	197.060	118.763	850.203	329.974	−2.873

PREVIOUS: December 1970 (1 atm) CURRENT: September 1983 (1 bar)

$S°(298.15\ K)$ = [224.835] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = [289.04 ± 25.1] $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [288.70 ± 25.1] $kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
[$^2\Pi$]	0	[4]

ω_e = [700] cm^{-1} $\omega_e x_e$ = [4.8] cm^{-1} σ = 1
B_e = [0.5542] cm^{-1} α_e = [0.0052] cm^{-1} r_e = [1.85] Å

Enthalpy of Formation

$\Delta_f H°$(MgN, g, 298.15 K) was estimated from bond strengths using MgO and comparison with analogous pairs of compounds such as, PN and PO, and also the bond strengths of C–N and C–O in organic compounds.

Heat Capacity and Entropy

The r_e value for MgN was estimated from MgO by comparison with similar pairs PO and PN, SiO and SiN, and AlO and AlN. Using Guggenheimer.[1] ω for MgO was found to lie between the single and multiple bonding cases. Magnesium nitride was assumed to be similar to MgO and ω_e 700 cm^{-1} was obtained. It was assumed that the $x_e\mu^{1/2}$ value for MgN was equal to that for MgO thus giving $\omega_e x_e$ = 4.8 cm^{-1}. B_e was calculated from r_e. The α_e value was calculated from B_e, ω_e and $\omega_e x_e$.

Reference

[1]Guggenheimer's Relation, Proc. Phys. Soc. (London) **58**, 456 (1946).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.989	289.040	289.040	INFINITE
100	29.151	191.683	252.482	−6.080	289.856	279.629	−146.063
200	30.587	212.211	227.762	−3.110	289.363	269.548	−70.399
250	31.725	219.159	225.368	−1.552	289.023	264.634	−55.292
298.15	32.733	224.835	224.835	0.	288.696	259.966	−45.545
300	32.768	225.037	224.835	0.061	288.684	259.788	−45.233
350	33.639	230.156	225.238	1.722	288.354	254.999	−38.056
400	34.340	234.696	226.141	3.422	288.031	250.256	−32.680
450	34.901	238.774	227.322	5.153	287.709	245.553	−28.503
500	35.350	242.475	228.655	6.910	287.383	240.886	−25.165
600	36.013	248.983	231.516	10.480	286.694	231.651	−20.167
700	36.468	254.570	234.420	14.106	285.926	222.536	−16.606
800	36.797	259.463	237.251	17.770	285.047	213.539	−13.943
900	37.045	263.812	239.965	21.462	284.033	204.660	−11.878
1000	37.241	267.725	242.548	25.177	274.271	196.614	−10.270
1100	37.401	271.282	245.001	28.909	272.924	188.914	−8.971
1200	37.536	274.543	247.329	32.656	271.566	181.337	−7.893
1300	37.653	277.552	249.540	36.416	270.198	173.873	−6.986
1400	37.756	280.346	251.642	40.186	141.411	169.682	−6.331
1500	37.849	282.954	253.643	43.967	141.379	171.702	−5.979
1600	37.935	285.400	255.552	47.756	141.340	173.725	−5.672
1700	38.014	287.702	257.376	51.553	141.296	175.751	−5.400
1800	38.089	289.877	259.122	55.359	141.248	177.779	−5.159
1900	38.159	291.938	260.795	59.171	141.197	179.809	−4.943
2000	38.227	293.897	262.402	62.990	141.143	181.843	−4.749
2100	38.292	295.764	263.947	66.816	141.088	183.879	−4.574
2200	38.355	297.547	265.434	70.649	141.031	185.918	−4.414
2300	38.417	299.253	266.867	74.487	140.973	187.960	−4.269
2400	38.477	300.889	268.251	78.332	140.914	190.004	−4.135
2500	38.535	302.461	269.588	82.183	140.855	192.051	−4.013
2600	38.593	303.974	270.882	86.039	140.795	194.100	−3.900
2700	38.649	305.431	272.134	89.901	140.733	196.151	−3.795
2800	38.705	306.838	273.349	93.769	140.669	198.205	−3.698
2900	38.761	308.197	274.527	97.642	140.603	200.261	−3.607
3000	38.815	309.512	275.672	101.521	140.534	202.319	−3.523
3100	38.870	310.786	276.784	105.405	140.460	204.380	−3.444
3200	38.923	312.021	277.866	109.295	140.381	206.443	−3.370
3300	38.977	313.219	278.919	113.190	140.294	208.509	−3.300
3400	39.030	314.383	279.945	117.090	140.199	210.577	−3.235
3500	39.082	315.516	280.945	120.996	140.093	212.649	−3.174
3600	39.135	316.617	281.921	124.907	139.975	214.724	−3.116
3700	39.187	317.690	282.873	128.823	139.843	216.802	−3.061
3800	39.239	318.736	283.803	132.744	139.694	218.884	−3.009
3900	39.290	319.756	284.712	136.670	139.527	220.970	−2.960
4000	39.342	320.751	285.601	140.602	139.339	223.060	−2.913
4100	39.393	321.723	286.470	144.539	139.128	225.156	−2.869
4200	39.444	322.673	287.321	148.481	138.891	227.257	−2.826
4300	39.496	323.602	288.154	152.428	138.627	229.364	−2.786
4400	39.546	324.511	288.970	156.380	138.334	231.477	−2.748
4500	39.597	325.400	289.769	160.337	138.008	233.598	−2.712
4600	39.648	326.271	290.553	164.299	137.649	235.726	−2.677
4700	39.699	327.124	291.323	168.267	137.253	237.862	−2.644
4800	39.749	327.960	292.077	172.239	136.818	240.008	−2.612
4900	39.800	328.780	292.818	176.216	136.343	242.162	−2.581
5000	39.850	329.585	293.545	180.199	135.826	244.327	−2.552
5100	39.901	330.375	294.260	184.186	135.264	246.502	−2.525
5200	39.951	331.150	294.962	188.179	134.656	248.689	−2.498
5300	40.001	331.911	295.652	192.177	134.001	250.889	−2.473
5400	40.051	332.659	296.330	196.179	133.296	253.101	−2.448
5500	40.101	333.395	296.997	200.187	132.541	255.326	−2.425
5600	40.152	334.118	297.654	204.200	131.733	257.566	−2.402
5700	40.202	334.829	298.300	208.217	130.871	259.820	−2.381
5800	40.252	335.529	298.936	212.240	129.953	262.090	−2.360
5900	40.302	336.217	299.562	216.268	128.979	264.377	−2.341
6000	40.351	336.895	300.178	220.300	127.947	266.680	−2.322

PREVIOUS: March 1964 (1 atm) CURRENT: March 1964 (1 bar)

$S°(298.15\ K) = 26.924 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 3105 \pm 30\ K$

$\Delta_f H°(0\ K) = -597.060 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -601.241 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [77.822 \pm 16.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is based on oxygen bomb calorimetry of Holley and Huber[1] and HCl–solution calorimetry of Shomate and Huffman.[2] The reported values of -143.70 ± 0.12[1] and -143.84 ± 0.05[2] kcal·mol^{-1} become $\Delta_f H°(298.15\ K) = -143.61 \pm 0.12$ and -143.78 ± 0.08 kcal·mol^{-1} when adjusted to 1969 atomic weights. We adopt the median value of -143.70 ± 0.15 kcal·mol^{-1}.

NBS[3] adopted -143.81 kcal·mol^{-1} for macrocrystalline periclase, based on the data of Shomate and Huffman[2] converted to 1961 atomic weights. Parker[3] preferred the data of Shomate and Huffman because of the inference that their sample corresponded more closely to the macrocrystalline standard state. New $\Delta_{sln} H°$ data[4] suggest that excess energy of up to ~1.1 kcal·mol^{-1} arises mainly from disorder (defects) in MgO rather than from high surface area and small particle size. Since the excess energy is eliminated at T>~1000°C,[4] it is unlikely that this effect would bias the combustion data of Holley and Huber.[1]

Other data for $\Delta_f H°$ were reviewed by Parker.[3] New measurements exist for $\Delta_{sln} H°$ of MgO[4] and Mg,[5] but we have not attempted to derive $\Delta_f H°$ because of difference in the final states of the solutions.

Heat Capacity and Entropy

$C_p°$ below 270 K is based on data (3–270 K) for single crystals measured by Barron *et al.*[6] Values above 270 K are from a constrained fit of $C_p°$[6] and enthalpies (373–1173 K) of fused MgO measured in a Bunsen ice calorimeter by Victor & Douglas.[7] $S°$(298.15 K) is obtained from $C_p°$ based on a negligible extrapolation to absolute zero.

Maximum deviatons of the $C_p°$ data[6] from the adopted curve are ±1.7% near 15 K, ±1.0% near 20 K, ±0.4% near 40 K, and ~0.2% at higher temperatures. Gmelin[8] later reported smoothed $C_p°$ values (2–320 K) derived from data for MgO sintered at high temperature. These values are in good agreement with the adopted curve except from 70 to 140 K, where deviations are all positive and reach a maximum of almost 7% at 90 K. Gmelin's values gave $S°(298.15\ K) = 6.50$, i.e., higher by ~0.06 cal·K^{-1}·mol^{-1}. Larger positive deviations in $C_p°$ exist at all temperatures (20–301 K) for the non standard state MgO used by Giauque and Archibald.[9] Their sample was prepared from hydroxide in vacuo at ~350 °C and was not annealed at high temperature. The microcrystalline product presumably was disordered, leading to excess $C_p°$ and $S°(298.15\ K) = 6.66$ cal·K^{-1}·mol^{-1}. Limited data of Parks and Kelley[10] for fused MgO tend to confirm the adopted curve.

Deviations of the enthalpy data from the adopted curve are ±0.15% (373–1173 K),[7] $-0.3 \pm 0.3\%$ (402–1799 K),[11] $+0.8 \pm 0.9\%$ (370–1591 K)[12] and -2.8 to +1.0% (equation for 1200–2500 K).[13] Microcalorimetric $C_p°$ data (305–455 K)[14] agree with the adopted curve at the mid temperature but have a temperature derivative which is too small.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−5.159	−597.060	−597.060	INFINITE
100	7.802	2.548	52.212	−4.966	−598.962	−589.601	307.976
200	26.681	14.096	30.037	−3.188	−600.646	−579.488	151.347
298.15	37.106	26.924	26.924	0.	−601.241	−568.945	99.677
300	37.244	27.154	26.925	0.069	−601.245	−568.745	99.027
400	42.561	38.678	28.460	4.087	−601.268	−557.898	72.854
500	45.544	48.523	31.513	8.505	−601.046	−547.078	57.153
600	47.430	57.006	35.072	13.160	−600.738	−536.312	46.690
700	48.748	64.420	38.746	17.972	−600.426	−525.600	39.221
800	49.740	70.996	42.374	22.898	−600.156	−514.930	33.621
900	50.539	76.902	45.888	27.913	−599.962	−504.289	29.268
1000	51.208	82.262	49.262	33.001	−608.462	−492.952	25.749
1100	51.794	87.171	52.488	38.151	−608.496	−481.399	22.860
1200	52.325	91.701	55.569	43.358	−608.495	−469.844	20.452
1300	52.810	95.908	58.512	48.615	−608.461	−458.291	18.414
1400	53.262	99.839	61.325	53.918	−735.804	−443.575	16.550
1500	53.693	103.528	64.017	59.266	−734.355	−422.752	14.722
1600	54.107	107.007	66.596	64.656	−732.877	−402.026	13.125
1700	54.509	110.299	69.071	70.087	−731.371	−381.394	11.719
1800	54.898	113.426	71.449	75.558	−729.837	−360.851	10.472
1900	55.278	116.404	73.737	81.067	−728.277	−340.395	9.358
2000	55.651	119.249	75.942	86.613	−726.690	−320.021	8.358
2100	56.019	121.973	78.070	92.197	−725.079	−299.727	7.455
2200	56.379	124.587	80.125	97.816	−723.442	−279.510	6.636
2300	56.738	127.101	82.114	103.472	−721.781	−259.368	5.890
2400	57.094	129.524	84.039	109.164	−720.097	−239.300	5.208
2500	57.445	131.862	85.905	114.891	−718.389	−219.301	4.582
2600	57.797	134.121	87.716	120.653	−716.659	−199.372	4.005
2700	58.145	136.309	89.476	126.450	−714.906	−179.509	3.473
2800	58.491	138.430	91.187	132.282	−713.132	−159.712	2.979
2900	58.836	140.489	92.851	138.148	−711.338	−139.979	2.521
3000	59.177	142.489	94.473	144.049	−709.524	−120.308	2.095
3100	59.516	144.436	96.053	149.987	−707.689	−100.697	1.697
3105.000	59.523	144.532	96.131	150.284	--- CRYSTAL <--> LIQUID ---		
3200	59.859	146.331	97.595	155.955	−705.840	−81.147	1.325
3300	60.201	148.178	99.100	161.958	−703.975	−61.654	0.976
3400	60.541	149.980	100.570	167.995	−702.095	−42.218	0.649
3500	60.878	151.740	102.007	174.066	−700.203	−22.837	0.341
3600	61.214	153.460	103.412	180.171	−698.299	−3.511	0.051
3700	61.551	155.142	104.788	186.309	−696.387	15.763	−0.223
3800	61.888	156.787	106.135	192.481	−694.467	34.985	−0.481
3900	62.225	158.399	107.454	198.687	−692.542	54.156	−0.725
4000	62.561	159.979	108.748	204.926	−690.613	73.277	−0.957

PREVIOUS: December 1965 CURRENT: December 1974

$S°(298.15\ K) = [48.366]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3105 \pm 30\ K$

$\Delta_f H°(298.15\ K) = [-532.609]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [77.822 \pm 16.7]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(MgO, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(3105\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is assumed to be 16 $cal·K^{-1}·mol^{-1}$ except below the glass transition (2100 K) where $C_p°$(l) is taken equal to $C_p°$(cr). Enthalpy data yield $C_p° \geq 19\ cal·K^{-1}·mol^{-1}$ for liquid BeO[1] but there may be a positive bias due to volatilization. $S°(298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Documented values for T_{fus} (in °C, IPTS–48) include 2800 ± 20,[2] 2827 ± 20[3] and 2852.[4,5] We adopt the median value[3] which becomes 2832°C = 3105 K on IPTS–68.

Calorimetric data for $\Delta_{fus} H°$ are not available. Kelley[6] derived an apparent $\Delta_{fus} H° = 18.5\ kcal·mol^{-1}$ at $T_{fus} = 2915$ K from liquidus data for the MgO–ZrO_2 binary.[7] The old[7] and new[8,9] data for MgO–ZrO_2 imply gross non–ideality which makes the system unsuitable for obtaining the enthalpy of fusion. Apparent $\Delta_{fus} H°$ values ranging from 8 to 30 $kcal·mol^{-1}$ are obtained from more suitable binary systems[9,10] involving CaO, Al_2O_3, Cr_2O_3, PuO_2 and UO_2. These values are so uncertain that we assume $\Delta_{fus} H° = 18.6\ kcal·mol^{-1}$ based on $\Delta_{fus} = 6$ cal $k^{-1}·mol^{-1}$. $\Delta_{fus} H° = 20\ kcal·mol^{-1}$ was measured calorimetrically for BeO,[1] but the crystal is hexagonal or tetragonal rather than cubic as in the case of MgO.

Vaporization Data

Vaporization rates based on weight loss at T_{fus} were repoted by Noguchi[8] for MgO and six other refractory oxides. Vaporization of MgO near 2000 K has been studied by Langmuir–torsion,[11] Langmuir–weight–loss,[12,13] Knudsen–mass– spectrometric,[14] Knudsen–effusion[15] and transpiration[15,16] methods. Vaporization near 2000 K is primarily to the elements,[14] Mg(g) and presumably O(g) and O_2(g), rather than to MgO(g). Quantitative interpretation of the vaporization species is uncertain. The adopted tables[1] predict that MgO(g) is insignificant near 2000 K but should become one of the significant components of the vapor near T_{fus}.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	37.106	48.366	48.366	0.	−532.609	−506.707	88.773
300	37.244	48.596	48.367	0.069	−532.614	−506.546	88.197
400	42.561	60.120	49.902	4.087	−532.636	−497.843	65.012
500	45.544	69.966	52.956	8.505	−532.414	−489.167	51.103
600	47.430	78.448	56.514	13.160	−532.106	−480.546	41.835
700	48.748	85.862	60.188	17.972	−531.794	−471.978	35.219
800	49.740	92.439	63.816	22.898	−531.525	−463.452	30.260
900	50.539	98.344	67.330	27.913	−531.331	−454.955	26.405
1000	51.208	103.705	70.704	33.001	−539.830	−445.763	23.284
1100	51.794	108.613	73.930	38.151	−539.865	−436.354	20.721
1200	52.325	113.143	77.012	43.358	−539.864	−426.943	18.584
1300	52.810	117.351	79.955	48.615	−539.829	−417.535	16.777
1400	53.262	121.281	82.768	53.918	−667.172	−404.962	15.109
1500	53.693	124.970	85.459	59.266	−665.724	−386.284	13.452
1600	54.107	128.449	88.039	64.656	−664.246	−367.702	12.004
1700	54.509	131.741	90.513	70.087	−662.740	−349.214	10.730
1800	54.898	134.868	92.891	75.558	−661.206	−330.816	9.600
1900	55.278	137.846	95.180	81.067	−659.645	−312.503	8.591
2000	55.651	140.691	97.385	86.613	−658.059	−294.274	7.686
2100	56.019	143.415	99.512	92.197	−656.447	−276.124	6.868
2100.001	56.019	143.415	99.512	92.197	GLASS <--> LIQUID		
2100.001	66.944	143.415	99.512	92.197	TRANSITION		
2200	66.944	146.530	101.579	98.891	−653.736	−258.077	6.128
2300	66.944	149.505	103.599	105.585	−651.037	−240.153	5.454
2400	66.944	152.354	105.571	112.280	−648.350	−222.346	4.839
2500	66.944	155.087	107.498	118.974	−645.674	−204.651	4.276
2600	66.944	157.713	109.379	125.669	−643.012	−187.062	3.758
2700	66.944	160.239	111.216	132.363	−640.362	−169.576	3.281
2800	66.944	162.674	113.011	139.057	−637.725	−152.188	2.839
2900	66.944	165.023	114.764	145.752	−635.103	−134.894	2.430
3000	66.944	167.293	116.477	152.446	−632.496	−117.690	2.049
3100	66.944	169.488	118.152	159.140	−629.904	−100.572	1.695
3105.000	66.944	169.595	118.235	159.475	--- CRYSTAL <--> LIQUID ---		
3200	66.944	171.613	119.790	165.835	−627.329	−83.538	1.364
3300	66.944	173.673	121.391	172.529	−624.772	−66.584	1.054
3400	66.944	175.671	122.959	179.224	−622.235	−49.708	0.764
3500	66.944	177.612	124.493	185.918	−619.719	−32.905	0.491
3600	66.944	179.498	125.994	192.612	−617.226	−16.174	0.235
3700	66.944	181.332	127.465	199.307	−614.757	0.487	−0.007
3800	66.944	183.117	128.906	206.001	−612.315	17.083	−0.235
3900	66.944	184.856	130.319	212.696	−609.901	33.615	−0.450
4000	66.944	186.551	131.704	219.390	−607.518	50.084	−0.654
4100	66.944	188.204	133.062	226.084	−605.167	66.495	−0.847
4200	66.944	189.817	134.394	232.779	−602.851	82.849	−1.030
4300	66.944	191.393	135.701	239.473	−600.572	99.149	−1.204
4400	66.944	192.932	136.984	246.168	−598.332	115.395	−1.370
4500	66.944	194.436	138.244	252.862	−596.133	131.591	−1.527
4600	66.944	195.907	139.482	259.556	−593.978	147.739	−1.678
4700	66.944	197.347	140.698	266.251	−591.869	163.840	−1.821
4800	66.944	198.756	141.893	272.945	−589.807	179.897	−1.958
4900	66.944	200.137	143.067	279.640	−587.796	195.912	−2.088
5000	66.944	201.489	144.222	286.334	−585.838	211.886	−2.214

PREVIOUS: December 1965 CURRENT: December 1974

0 to 3105 K crystal
above 3105 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.159	−597.060	−597.060	INFINITE
100	7.802	2.548	52.212	−4.966	−598.962	−589.601	307.976
200	26.681	14.096	30.037	−3.188	−600.646	−579.488	151.347
298.15	37.106	26.924	26.924	0.	−601.241	−568.945	99.677
300	37.244	27.154	26.925	0.069	−601.245	−568.745	99.027
400	42.561	38.678	28.460	4.087	−601.268	−557.898	72.854
500	45.544	48.523	31.513	8.505	−601.046	−547.078	57.153
600	47.430	57.006	35.072	13.160	−600.738	−536.312	46.690
700	48.748	64.420	38.746	17.972	−600.426	−525.600	39.221
800	49.740	70.996	42.374	22.898	−600.156	−514.930	33.621
900	50.539	76.902	45.888	27.913	−599.962	−504.289	29.268
1000	51.208	82.262	49.262	33.001	−608.462	−492.952	25.749
1100	51.794	87.171	52.488	38.151	−608.496	−481.399	22.860
1200	52.325	91.701	55.569	43.358	−608.495	−469.844	20.452
1300	52.810	95.908	58.512	48.615	−608.461	−458.291	18.414
1400	53.262	99.839	61.325	53.918	−735.804	−443.575	16.550
1500	53.693	103.528	64.017	59.266	−734.355	−422.752	14.722
1600	54.107	107.007	66.596	64.656	−732.877	−402.026	13.125
1700	54.509	110.299	69.071	70.087	−731.371	−381.394	11.719
1800	54.898	113.426	71.449	75.558	−729.837	−360.851	10.472
1900	55.278	116.404	73.737	81.067	−728.277	−340.395	9.358
2000	55.651	119.249	75.942	86.613	−726.690	−320.021	8.358
2100	56.019	121.973	78.070	92.197	−725.079	−299.727	7.455
2200	56.379	124.587	80.125	97.816	−723.442	−279.510	6.636
2300	56.738	127.101	82.114	103.472	−721.781	−259.368	5.890
2400	57.094	129.524	84.039	109.164	−720.097	−239.300	5.208
2500	57.445	131.862	85.905	114.891	−718.389	−219.301	4.582
2600	57.797	134.121	87.716	120.653	−716.659	−199.372	4.005
2700	58.145	136.309	89.476	126.450	−714.906	−179.509	3.473
2800	58.491	138.430	91.187	132.282	−713.132	−159.712	2.979
2900	58.836	140.489	92.851	138.148	−711.338	−139.979	2.521
3000	59.177	142.489	94.473	144.049	−709.524	−120.308	2.095
3100	59.516	144.436	96.053	149.987	−707.689	−100.697	1.697
3105.000	59.523	144.532	96.131	150.284	CRYSTAL <--> LIQUID TRANSITION		
3105.000	66.944	169.595	96.131	228.107			
3200	66.944	171.613	98.342	234.466	−627.329	−83.538	1.364
3300	66.944	173.673	100.594	241.161	−624.772	−66.584	1.054
3400	66.944	175.671	102.773	247.855	−622.235	−49.708	0.764
3500	66.944	177.612	104.884	254.550	−619.719	−32.905	0.491
3600	66.944	179.498	106.930	261.244	−617.226	−16.174	0.235
3700	66.944	181.332	108.916	267.938	−614.757	0.487	−0.007
3800	66.944	183.117	110.846	274.633	−612.315	17.083	−0.235
3900	66.944	184.856	112.721	281.327	−609.901	33.615	−0.450
4000	66.944	186.551	114.546	288.022	−607.518	50.084	−0.654
4100	66.944	188.204	116.322	294.716	−605.167	66.495	−0.847
4200	66.944	189.817	118.053	301.410	−602.851	82.849	−1.030
4300	66.944	191.393	119.740	308.105	−600.572	99.149	−1.204
4400	66.944	192.932	121.386	314.799	−598.332	115.395	−1.370
4500	66.944	194.436	122.993	321.494	−596.133	131.591	−1.527
4600	66.944	195.907	124.562	328.188	−593.978	147.739	−1.678
4700	66.944	197.347	126.095	334.882	−591.869	163.840	−1.821
4800	66.944	198.756	127.595	341.577	−589.807	179.897	−1.958
4900	66.944	200.137	129.061	348.271	−587.796	195.912	−2.088
5000	66.944	201.489	130.496	354.966	−585.838	211.886	−2.214

PREVIOUS: CURRENT: December 1974

$S°(298.15\ K) = 213.269 \pm 3.3\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 58.59 \pm 25.1\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 58.16 \pm 25.1\ kJ\cdot mol^{-1}$

	Electronic States and Molecular Constants (σ=1)							
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X^1\Sigma^+$	0.0	1	785.1	5.18	0.5743	0.0050	1.749	1
$^3\Pi$	[2300]	6	[664.4]	[3.9]	[0.5050]	[0.0040]	[1.864]	2–7
$A^1\Pi$	3503.3	2	664.4	3.9	0.5050	0.0040	1.864	1
$^3\Sigma^+$	[14000]	3	[824.1]	[4.8]	[0.5822]	[0.0045]	[1.737]	2–5
$B^1\Sigma^+$	20004.	1	824.1	4.76	0.5822	0.0045	1.737	1
$^3\Sigma^+$	[28000]	3	[632.5]	[5.3]	[0.501]	[0.0048]	[1.872	4,3
$^3\Sigma$	[29000]	6	[632.5]	[5.3]	[0.501]	[0.0048]	[1.872]	4,3
$D^1\Delta$	29775.	2	632.5	5.3	0.5014	0.0048	1.872	1,8,9
$^3\Sigma^-$	[30000]	3	[632.5]	[5.3]	[0.501]	[0.0048]	[1.872]	4,3
$C^1\Sigma^{-*}$	30004.	1	632.4	5.2	0.5008	0.0048	1.873	1
$E^1\Sigma^+$	37684.	1	[632.4]	[5.2]	0.5273	[0.0048]	1.825	10,3,4
$^3\Pi$	[37000]	6	[710]	[5.]	[0.5615]	[0.005]	[1.768]	4,3
$F^1\Pi$	37879.	2	710	[5.]	0.5615	[0.005]	1.768	10,3,4
$^3\Pi$	[39000]	6	[790]	[5.]	[0.5249]	[0.005]	[1.83]	4,3
$G^1\Pi$	39868.	2	790	[5.]	0.5249	[0.005]	1.83	10,3,4

Enthalpy of Formation

We adopt $D_0° = 80 \pm 6\ kcal\cdot mol^{-1}$ and $\Delta_f H°(298.15\ K) = 13.9 \pm 6\ kcal\cdot mol^{-1}$ based on equilibria analyzed below. Greatest weight is given to mass–spectrometric data[11] for reactions A and B. We give "<" or ">" for $\Delta_f H°$ and $D_0°$ values which may have a systematic bias. The JANAF differences in $\Delta_f H°(298.15\ K)$ for WO_3–WO_2[3] may be biased by as much as $-3.5\ kcal\cdot mol^{-1}$, leading to a positive bias in $D_0°$ from reaction B. Mass spectra[12] and transpiration data[13] yield an upper limit to $D_0°$; we neglect $Mg(OH)_2$ and MgOH which probably are important in.[13] Cotton and Jenkins[15] concluded that hydroxides were negligible in their H_2–O_2–N_2 flames; we doubt this conclusion and presume that reaction D yields an upper limit to $D_0°$. Our adopted value is comparable with those of Richards *et al.*[7,1] and Brewer & Rosenblatt,[16] considering the difference in functions for MgO.

Other published values of $D_0°$ are dismissed for reasons cited in critical reviews.[17,18,11] Schofield's criticism[17] of flame studies is supported by new evidence for importance of hydroxides (CaO, g).[3] Inadequate allowance for hydroxides may bias a recent flame result of $D_0° = 88 \pm 2.3\ kcal\cdot mol^{-1}$,[19] furthermore, we cannot firm this $D_0°$ from the published information. $D_0° = 83\ kcal\cdot mol^{-1}$ was derived[20] by fitting an electronegativity potential function to X'Σ. This state is predicted[18,4,11] to dissociate to excited state $0(^1D)$ at $45.4\ kcal\cdot mol^{-1}$. Theoretical calculations[21] support this prediction. Linear Birge–Sponer extrapolation yields a very low estimate for $D_0°$, just as it does for the alkali halides,[18] unless $X^1\Sigma$ fails to dissociate to $0^1(D)$ as predicted.

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K⁻¹·mol⁻¹	$\Delta_f H°(298.15\ K)$ kcal·mol⁻¹ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol⁻¹	$D_0°$
11	Knudsen mass spec.	A	2026–2274	8	−13 ± 5	12 ± 11	39.5 ± 3	15.3	78.6 ± 3
	Knudsen mass spec.	B	2106–2225	6	−18 ± 8	23 ± 16	63.1 ± 3	>10.1	<83.8 ± 5
12	Knudsen mass spec.	C	1950	1	—	—	>148.7	>5.0	<86.9 ± 5
13	Transpiration	C	1780–2010	7	−8 ± 3	132 ± 5	>148.3 ± 2	>4.7	<89.2 ± 2
14	Transpiration	C	2033–2175	8	−52 ± 32	53 ± 68	162.8 ± 8	19.1	74.7 ± 8
15	Flame spec.	D	1570–2370	4	−9 ± 1	−11 ± 2	>5.7 ± 6	>−1.6	<95.4 ± 6

[a]Reactions: A) $Mg(g) + O_2(g) = MgO(g) + O(g)$; B) $Mg(g) + WO_3(g) = MgO(g) + WO_2(g)$; C) $MgO(cr) = MgO(g)$; D) $Mg(g) + OH(g) = MgO(g) + H(g)$

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational–rotational constants of observed states are from Rosen[1] and other recent sources.[3–10] States are listed in the isoconfigurational order given by Schamps and Lefebvre–Brion.[4] Designations[3] of the new E, F and G states are based on theoretical calculations.[4] Field[2] concluded that calculations[4–6] of the isoconfigurational $A^1\Pi$–$^3\Pi$ separation should be adequate for estimating the low–lying $^3\Pi$ state. The other potentially low–lying state ($^3\Sigma^+$) is estimated[4] similarly from isoconfigurational $B^1\Sigma^+$. Higher estimated levels are also based on calculations.[4] Vibrational–rotational constants are estimated in isoconfigurational groups by comparison with BeO, CaO, SrO and BaO.[3] Low–lying levels and their vibrational–rotational constants cause marked changes in the thermodynamic functions, which are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_{ii}\Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

Continued on page 1569

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.909	58.588	58.588	INFINITE
100	29.124	180.485	240.493	−6.001	59.402	50.970	−26.624
200	30.117	200.873	216.143	−3.054	58.886	42.689	−11.149
250	31.121	207.699	213.793	−1.524	58.517	38.682	−8.082
298.15	32.173	213.269	213.269	0.	58.158	34.895	−6.113
300	32.215	213.468	213.270	0.060	58.144	34.750	−6.051
350	33.401	218.522	213.666	1.699	57.783	30.880	−4.609
400	34.783	223.069	214.562	3.403	57.446	27.060	−3.534
450	36.452	227.259	215.743	5.182	57.147	23.280	−2.702
500	38.434	231.200	217.093	7.053	56.901	19.531	−2.040
600	43.078	238.608	220.068	11.124	56.624	12.088	−1.052
700	47.785	245.608	223.221	15.671	56.672	4.666	−0.348
800	51.560	252.250	226.439	20.649	56.994	−2.783	0.182
900	53.890	258.472	229.657	25.934	57.457	−10.282	0.597
1000	54.795	264.208	232.829	31.379	49.315	−17.121	0.894
1100	54.608	269.429	235.923	36.857	49.607	−23.779	1.129
1200	53.729	274.147	238.915	42.278	49.823	−30.461	1.326
1300	52.496	278.400	241.792	47.591	49.914	−37.156	1.493
1400	51.139	282.241	244.546	52.773	−77.551	−40.685	1.518
1500	49.802	285.723	247.177	57.820	−76.404	−38.093	1.327
1600	48.558	288.897	249.687	62.737	−75.399	−35.573	1.161
1700	47.439	291.807	252.080	67.535	−74.525	−33.111	1.017
1800	46.454	294.490	254.363	72.229	−73.768	−30.697	0.891
1900	45.599	296.978	256.541	76.831	−73.114	−28.323	0.779
2000	44.862	299.298	258.621	81.353	−72.552	−25.980	0.679
2100	44.230	301.471	260.611	85.806	−72.070	−23.664	0.589
2200	43.691	303.516	262.515	90.202	−71.658	−21.368	0.507
2300	43.231	305.447	264.340	94.547	−71.308	−19.091	0.434
2400	42.841	307.279	266.091	98.850	−71.012	−16.827	0.366
2500	42.509	309.021	267.774	103.117	−70.764	−14.574	0.305
2600	42.229	310.682	269.392	107.354	−70.559	−12.331	0.248
2700	41.993	312.272	270.951	111.565	−70.393	−10.095	0.195
2800	41.795	313.795	272.454	115.754	−70.262	−7.864	0.147
2900	41.629	315.259	273.905	119.925	−70.163	−5.637	0.102
3000	41.493	316.668	275.307	124.081	−70.094	−3.414	0.059
3100	41.381	318.026	276.664	128.224	−70.053	−1.191	0.020
3200	41.291	319.339	277.977	132.357	−70.040	1.029	−0.017
3300	41.220	320.608	279.250	136.483	−70.052	3.250	−0.051
3400	41.167	321.838	280.484	140.602	−70.090	5.472	−0.084
3500	41.128	323.030	281.683	144.717	−70.154	7.695	−0.115
3600	41.103	324.189	282.848	148.828	−70.243	9.921	−0.144
3700	41.091	325.315	283.980	152.938	−70.359	12.149	−0.172
3800	41.090	326.411	285.082	157.047	−70.503	14.381	−0.198
3900	41.099	327.478	286.156	161.156	−70.674	16.617	−0.223
4000	41.117	328.519	287.202	165.267	−70.874	18.858	−0.246
4100	41.144	329.534	288.222	169.380	−71.105	21.104	−0.269
4200	41.179	330.526	289.218	173.496	−71.367	23.356	−0.290
4300	41.222	331.496	290.190	177.616	−71.662	25.615	−0.311
4400	41.272	332.444	291.139	181.741	−71.992	27.881	−0.331
4500	41.329	333.372	292.067	185.871	−72.358	30.154	−0.350
4600	41.393	334.281	292.975	190.007	−72.761	32.437	−0.368
4700	41.463	335.172	293.864	194.149	−73.203	34.729	−0.386
4800	41.539	336.046	294.733	198.300	−73.686	37.030	−0.403
4900	41.621	336.903	295.585	202.458	−74.212	39.342	−0.419
5000	41.709	337.745	296.420	206.624	−74.781	41.665	−0.435
5100	41.802	338.572	297.238	210.800	−75.395	44.000	−0.451
5200	41.901	339.384	298.041	214.985	−76.057	46.347	−0.466
5300	42.004	340.183	298.829	219.180	−76.766	48.709	−0.480
5400	42.113	340.970	299.602	223.386	−77.525	51.083	−0.494
5500	42.227	341.743	300.361	227.603	−78.335	53.471	−0.508
5600	42.345	342.505	301.107	231.831	−79.198	55.876	−0.521
5700	42.467	343.256	301.840	236.072	−80.115	58.296	−0.534
5800	42.594	343.995	302.560	240.325	−81.087	60.733	−0.547
5900	42.725	344.725	303.269	244.591	−82.116	63.186	−0.559
6000	42.860	345.444	303.966	248.870	−83.202	65.658	−0.572

PREVIOUS: December 1974 (1 atm) CURRENT: December 1974 (1 bar)

$S°(298.15\ K) = 67.77 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1} = 903\ K = 0.67\ kJ \cdot mol^{-1}$
$T_{trs2} = 1258\ K$
$T_{fus} = 1850 \pm 2\ K$

$\Delta_f H°(0\ K) = -1539.79 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1548.92 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = 0.67\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 1.632\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [75.312 \pm 20.9]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Torgeson *et al.*[1] report a $\Delta_f H°(298.15\ K) = -8.69 \pm 0.15\ kcal \cdot mol^{-1}$ for reaction (a). They used a hydrofluoric acid solution calorimeter and measured the enthalpies of solution of each component. They appear to have made the water–absorption correction to the enthalpy of solution of SiO_2(cr) in the wrong direction. We reverse the correction so that the new $\Delta_{sol} H$ almost overlaps the range observed by King.[11] We derive $\Delta_f H°(MgSiO_3, cr, 298.15\ K) = -370.20 \pm 1.0\ kcal \cdot mol^{-1}$ using the $\Delta_f H°(298.15\ K)$ of MgO(cr) and SiO_2(cr, low quartz) from the JANAF tables.

Reesman *et al.*[2] calculated a $\Delta_f G°(298.15\ K) = 23.72\ kcal \cdot mol^{-1}$ for reaction (b) using aqueous solubility data. We use the $\Delta_f G°(298.15\ K)$ of H_2O(l) and OH^- (aq) from source 3, $\Delta_f G°(298.15\ K)$ of H_4SIO_4(aq) from source 4 and $\Delta_f G°(298.15\ K)$ of Mg^{++}(aq) from source 5 and we obtain a $\Delta_f G°(MgSiO_3, cr, 298.15\ K) = -352.534\ kcal \cdot mol^{-1}$. We derive $\Delta_f H°(MgSiO_3, cr, 298.15\ K) = -373.293\ kcal \cdot mol^{-1}$ using the above $\Delta_f G°(298.15\ K)$ of $MgSiO_3$(cr) and the entropies of Mg(cr), Si(cr) and O_2(g) from the JANAF tables.

We choose the enthalpy of formation derived from the result of Torgeson *et al.*[1] which is considered to be better since it relates directly to the oxides. Also the $\Delta_f G°(MgSiO_3, l, 1873\ K)$ thus calculated is in very good agreement with that derived from the activities of SiO_2 and MgO (in the SiO_2–MgO system) measured by Rein *et al.*[6] The $\Delta_f H°(MgSiO_3, cr, 298.15\ K)$ derived from the work of Reesman *et al.* is less accurate and involves uncertainties in the auxiliary data used to calculate the value.

Source	Method	Reaction	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f G°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15)$ kcal·mol^{-1}
1	HF solution calorimeter	(a) $MgO(cr) + SiO_2(cr) = MgSiO_3(cr)$	-8.7 ± 0.15		-370.20
2	Aqueous solubility	(b) $MgSiO_3(cr) + 3H_2O(l) = Mg^{++}(aq) + H_4SiO_4(aq) + 2OH^-(aq)$		23.72	-373.3

Heat Capacity and Entropy

Low temperature heat capacities are from the data (53–295 K) of Kelley.[7] Wagner[8] measured the average heat capacities in the temperature range 580–1570 K. Using his data we derive the high temperature heat capacities which are joined smoothly with the low temperature values by a constrained fitting technique. The $C_p°$ values at 903 = 1258 K and above 1258 K are derived as 28.762 and 29.262 $cal \cdot K^{-1} \cdot mol^{-1}$, respectively, by assuming that the data of Wagner[8] pertain to the stable phase in these regions. The entropy is based on $S°(50\ K) = 0.49\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

$T_{trs1} = 903$ K is obtained from Boyd *et al.*[9] The authors determined the phase diagram boundary at high pressures and extrapolated to one atmosphere. $T_{trs2} = 1258$ K is taken from Atlas.[10] Below 903 K the phase is known as clinoenstatite. Between 903 and 1258 K it is rhombic enstatite and above 1258 K it is protoenstatite. We calculate $\Delta_{trs1} H°$ and $\Delta_{trs2} H°$ (from dT/dP (slopes of the inversion) = 2.6/kbar and 84/kbar reported by Boyd *et al.*[9,13] and from the densities of clinoenstatite (3.210 gm/cc) and rhombic enstatite (3.208 gm/cc) reported by Stephenson *et al.*[11] and the density of protoenstatite (3.10 gm/cc) reported by Smith.[12]

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−12.113	−1539.788	−1539.788	INFINITE
100	23.912	11.117	124.420	−11.330	−1544.271	−1518.053	792.950
200	59.643	39.430	74.617	−7.037	−1547.531	−1490.410	389.255
298.15	81.927	67.768	67.768	0.	−1548.917	−1462.023	256.140
300	82.228	68.276	67.770	0.152	−1548.930	−1461.484	254.467
400	94.194	93.738	71.160	9.031	−1549.184	−1432.276	187.036
500	101.512	115.590	77.915	18.838	−1548.910	−1403.073	146.578
600	106.997	134.600	85.812	29.273	−1548.358	−1373.955	119.613
700	111.621	151.449	94.008	40.208	−1547.624	−1344.943	100.361
800	115.780	166.629	102.152	51.581	−1546.754	−1316.047	85.929
900	119.675	180.492	110.097	63.356	−1545.768	−1287.267	74.711
903.000	119.788	180.891	110.332	63.715	I <--> II		
903.000	120.340	181.632	110.332	64.384	TRANSITION		
1000	120.340	193.911	117.854	76.057	−1552.726	−1257.958	65.709
1100	120.340	205.381	125.298	88.091	−1552.043	−1228.515	58.337
1200	120.340	215.852	132.414	100.125	−1551.461	−1199.129	52.197
1258.000	120.340	221.532	136.393	107.105	II <--> III		
1258.000	122.432	222.829	136.393	108.737	TRANSITION		
1300	122.432	226.850	139.250	113.879	−1549.254	−1169.845	47.005
1400	122.432	235.923	145.836	126.122	−1676.053	−1137.516	42.441
1500	122.432	244.370	152.126	138.365	−1674.175	−1099.115	38.275
1600	122.432	252.271	158.141	150.609	−1672.377	−1060.837	34.633
1700	122.432	259.694	163.899	162.852	−1720.835	−1022.222	31.409
1800	122.432	266.692	169.417	175.095	−1718.964	−981.182	28.473
1850.000	122.432	270.046	172.091	181.217	----- III <--> LIQUID -----		
1900	122.432	273.311	174.712	187.338	−1717.128	−940.244	25.849
2000	122.432	279.591	179.801	199.581	−1715.327	−899.402	23.490
2100	122.432	285.565	184.696	211.825	−1713.561	−858.649	21.358
2200	122.432	291.260	189.411	224.068	−1711.829	−817.979	19.421
2300	122.432	296.703	193.959	236.311	−1710.131	−777.388	17.655
2400	122.432	301.913	198.349	248.554	−1708.467	−736.870	16.038
2500	122.432	306.911	202.592	260.798	−1706.838	−696.421	14.551

PREVIOUS: September 1964 CURRENT: December 1967

$S°(298.15\ K) = [92.515]\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 903$ K
$T_{trs2} = 1258$ K
$T_{fus} = 1850 \pm 2$ K

$\Delta_f H°(298.15\ K) = [-1494.862 \pm 20.9]\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 0.67\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 1.632\ kJ·mol^{-1}$
$\Delta_{fus} H° = [75.312 \pm 20.9]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgSiO_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgSiO_3, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1850\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 900 K. Below 900 K the heat capacity is obtained from the heat capacity of the crystal. Above 900 K the heat capacity is assumed constant and estimated as 35 $cal·K^{-1}·mol^{-1}$ or 7 $cal·K^{-1}$ g–atom^{-1}. $S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Transition Data

Refer to the crystal table for details.

Fusion Data

T_{fus} is taken from Bowen and Andersen.[1] $MgSiO_3$(cr) melts incongruently in the temperature range 1830–1850 K at atmospheric pressure. $\Delta_{fus} H°$ is estimated from the phase diagrams of the $MgSiO_3$–TiO_2 system reported by MacGregor.[2] The phase diagrams were determined at 10 and 20 kbars pressure where $MgSiO_3$(cr) melts congruently.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	81.927	92.515	92.515	0.	−1494.862	−1415.346	247.963
300	82.228	93.022	92.516	0.152	−1494.875	−1414.853	246.348
400	94.194	118.484	95.906	9.031	−1495.129	−1388.120	181.270
500	101.512	140.337	102.661	18.838	−1494.855	−1361.392	142.224
600	106.997	159.347	110.559	29.273	−1494.303	−1334.747	116.200
700	111.621	176.195	118.754	40.208	−1493.569	−1308.211	97.620
800	115.780	191.375	126.899	51.581	−1492.699	−1281.789	83.692
900	119.675	205.239	134.844	63.356	−1491.713	−1255.483	72.866
900.000	119.675	205.239	134.844	63.356	GLASS <--> LIQUID		
900.000	146.440	205.239	134.844	63.356	TRANSITION		
1000	146.440	220.668	142.668	78.000	−1496.729	−1228.717	64.182
1100	146.440	234.625	150.404	92.644	−1493.435	−1202.076	57.082
1200	146.440	247.367	157.961	107.288	−1490.244	−1175.731	51.178
1300	146.440	259.088	165.295	121.932	−1487.146	−1149.648	46.193
1400	146.440	269.941	172.387	136.576	−1611.545	−1120.632	41.811
1500	146.440	280.044	179.231	151.220	−1607.265	−1085.717	37.808
1600	146.440	289.495	185.830	165.864	−1603.067	−1051.085	34.314
1700	146.440	298.373	192.192	180.508	−1649.124	−1016.266	31.226
1800	146.440	306.743	198.326	195.152	−1644.852	−979.163	28.415
1850.000	146.440	310.756	201.310	202.474	----- III <--> LIQUID		-----
1900	146.440	314.661	204.242	209.796	−1640.616	−942.295	25.906
2000	146.440	322.172	209.952	224.440	−1636.414	−905.650	23.653
2100	146.440	329.317	215.468	239.084	−1632.247	−869.215	21.621
2200	146.440	336.129	220.799	253.728	−1628.114	−832.976	19.777
2300	146.440	342.639	225.956	268.372	−1624.015	−796.926	18.099
2400	146.440	348.871	230.948	283.016	−1619.951	−761.053	16.564
2500	146.440	354.849	235.786	297.660	−1615.921	−725.349	15.155
2600	146.440	360.593	240.476	312.304	−1611.924	−689.805	13.858
2700	146.440	366.120	245.028	326.948	−1607.962	−654.414	12.660
2800	146.440	371.445	249.448	341.592	−1604.033	−619.169	11.551
2900	146.440	376.584	253.744	356.236	−1600.138	−584.065	10.520
3000	146.440	381.549	257.922	370.880	−1596.278	−549.093	9.561

PREVIOUS: September 1964 CURRENT: December 1967

0	to 903	K	crystal, I
903	to 1258	K	crystal, II
1258	to 1850	K	crystal, III
above	1850	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.113	−1539.788	−1539.788	INFINITE
100	23.912	11.117	124.420	−11.330	−1544.271	−1518.053	792.950
200	59.643	39.430	74.617	−7.037	−1547.531	−1490.410	389.255
298.15	81.927	67.768	67.768	0.	−1548.917	−1462.023	256.140
300	82.228	68.276	67.770	0.152	−1548.930	−1461.484	254.467
400	94.194	93.738	71.160	9.031	−1549.184	−1432.276	187.036
500	101.512	115.590	77.915	18.838	−1548.910	−1403.073	146.578
600	106.997	134.600	85.812	29.273	−1548.358	−1373.955	119.613
700	111.621	151.449	94.008	40.208	−1547.624	−1344.943	100.361
800	115.780	166.629	102.152	51.581	−1546.754	−1316.047	85.929
900	119.675	180.492	110.097	63.356	−1545.768	−1287.267	74.711
903.000	119.788	180.891	110.332	63.715	I <--> II		
903.000	120 .340	181.632	110.332	64.384	TRANSITION		
1000	120.340	193.911	117.854	76.057	−1552.726	−1257.958	65.709
1100	120.340	205.381	125.298	88.091	−1552.043	−1228.515	58.337
1200	120.340	215.852	132.414	100.125	−1551.461	−1199.129	52.197
1258.000	120.340	221.532	136.393	107.105	II <--> III		
1258.000	122.432	222.829	136.393	108.737	TRANSITION		
1300	122.432	226.850	139.250	113.879	−1549.254	−1169.845	47.005
1400	122.432	235.923	145.836	126.122	−1676.053	−1137.516	42.441
1500	122.432	244.370	152.126	138.365	−1674.175	−1099.115	38.275
1600	122.432	252.271	158.141	150.609	−1672.377	−1060.837	34.633
1700	122.432	259.694	163.899	162.852	−1720.835	−1022.222	31.409
1800	122.432	266.692	169.417	175.095	−1718.964	−981.182	28.473
1850.000	122.432	270.046	172.091	181.217	III <--> LIQUID		
1850.000	146.440	310.756	172.091	256.529	TRANSITION		
1900	146.440	314.661	175.792	263.851	−1640.616	−942.295	25.906
2000	146.440	322.172	182.925	278.495	−1636.414	−905.650	23.653
2100	146.440	329.317	189.727	293.139	−1632.247	−869.215	21.621
2200	146.440	336.129	196.228	307.783	−1628.114	−832.976	19.777
2300	146.440	342.639	202.453	322.427	−1624.015	−796.926	18.099
2400	146.440	348.871	208.425	337.071	−1619.951	−761.053	16.564
2500	146.440	354.849	214.164	351.715	−1615.921	−725.349	15.155
2600	146.440	360.593	219.686	366.359	−1611.924	−689.805	13.858
2700	146.440	366.120	225.007	381.003	−1607.962	−654.414	12.660
2800	146.440	371.445	230.143	395.647	−1604.033	−619.169	11.551
2900	146.440	376.584	235.104	410.291	−1600.138	−584.065	10.520
3000	146.440	381.549	239.904	424.935	−1596.278	−549.093	9.561

PREVIOUS: CURRENT: December 1967

$S°(298.15\ K) = 74.56 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1953 \pm 20$

$\Delta_f H°(0\ K) = -1563.26 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1572.56 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [90.374]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is calculated from $\Delta_f H°(298.15\ K) = -6.35 \pm 0.25\ kcal \cdot mol^{-1}$ for the reaction MgO(cr) + TiO_2(rutile → $MgTiO_3$(cr) measured by Kelley *et al.*,[1] using a solution calorimetric method. For the same reaction a value of $\Delta_f H°(298.15\ K) = -5.5 \pm 0.1\ kcal \cdot mol^{-1}$ was obtained with a calorimetric bomb method by Ronfilov and Feodos'ev.[2] These authors used the oxidation of lampblack in order to initiate the formation of the titanate from the oxides. Unfortunately the desired enthalpy of reaction was only 1.2 to 1.5 percent of the total measured heat, and consequently this result appears to be more uncertain than that measured by the solution calorimetric method.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52–296 K) of Shomate.[3] High temperature enthalpies have been measured (402–1720 K) by Naylor and Cook.[4] High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S°(52\ K) = 0.45\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.556	−1563.260	−1563.260	INFINITE
100	25.510	10.857	138.595	−12.774	−1568.037	−1541.350	805.119
200	67.873	42.539	82.308	−7.954	−1571.507	−1513.096	395.180
298.15	91.881	74.559	74.559	0.	−1572.556	−1484.128	260.013
300	92.203	75.128	74.561	0.170	−1572.560	−1483.579	258.314
400	105.244	103.609	78.355	10.102	−1572.255	−1453.939	189.865
500	113.123	128.001	85.906	21.047	−1571.304	−1424.461	148.812
600	118.453	149.124	94.722	32.641	−1570.043	−1395.208	121.464
700	122.353	167.690	103.847	44.690	−1568.636	−1366.179	101.946
800	125.382	184.233	112.880	57.082	−1567.162	−1337.357	87.320
900	127.846	199.147	121.650	69.747	−1565.714	−1308.719	75.956
1000	129.938	212.728	130.089	82.639	−1572.993	−1279.523	66.835
1100	131.775	225.200	138.177	95.726	−1571.915	−1250.229	59.368
1200	133.432	236.738	145.915	108.987	−1574.903	−1220.909	53.145
1300	134.972	247.480	153.319	122.408	−1573.268	−1191.476	47.874
1400	136.423	257.536	160.408	135.979	−1699.017	−1159.002	43.243
1500	137.821	266.996	167.202	149.691	−1695.995	−1120.536	39.021
1600	139.185	275.934	173.721	163.542	−1692.979	−1082.270	35.333
1700	140.532	284.413	179.985	177.527	−1689.982	−1044.193	32.084
1800	141.879	292.483	186.012	191.648	−1687.017	−1006.291	29.202
1900	143.231	300.191	191.820	205.903	−1684.097	−968.553	26.627
1953.000	143.949	304.141	194.815	213.514	--- CRYSTAL <---> LIQUID ---		
2000	144.595	307.572	197.425	220.294	−1695.921	−930.513	24.303
2100	145.980	314.660	202.840	234.823	−1693.874	−892.293	22.195
2200	147.394	321.484	208.078	249.491	−1691.721	−854.172	20.281
2300	148.833	328.067	213.153	264.302	−1689.459	−816.152	18.535
2400	150.310	334.433	218.074	279.259	−1687.086	−778.233	16.938
2500	151.825	340.599	222.853	294.366	−1684.598	−740.415	15.470
2600	153.381	346.584	227.497	309.626	−1681.989	−702.699	14.117
2700	154.975	352.402	232.016	325.043	−1679.257	−665.085	12.867
2800	156.615	358.068	236.417	340.622	−1676.398	−627.574	11.708
2900	158.302	363.593	240.708	356.368	−1673.405	−590.170	10.630
3000	160.038	368.989	244.894	372.284	−1670.277	−552.869	9.626

PREVIOUS: June 1961 CURRENT: June 1967

$S°(298.15\ K) = [111.082]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1953 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-1497.631 \pm 6.3]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [90.374]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgTiO_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgTiO_3, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1953\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300 K. The heat capacity below 1300 K is obtained from the heat capacity of the crystal. Above 1300 K the heat capacity is assumed constant and estimated as 39 $cal·K^{-1}·mol^{-1}$ or 7.8 $cal·K^{-1}$ g–atom^{-1}. $S°(l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The incongruent melting point is obtained from Massazza.[1] Previous work by Coughanour[2] indicates congruent melting point at 1903 K. The $\Delta_{fus} H°$ is estimated from those of $Na_2O·2TiO_2$ and $Na_2O·TiO_2$ observed by Naylor[3] and $CaO·TiO_2·SiO_2$ observed by King.[4]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	91.881	111.082	111.082	0.	−1497.631	−1420.091	248.794
300	92.203	111.651	111.083	0.170	−1497.635	−1419.610	247.176
400	105.244	140.132	114.878	10.102	−1497.329	−1393.623	181.988
500	113.123	164.524	122.429	21.047	−1496.378	−1367.797	142.893
600	118.453	185.647	131.245	32.641	−1495.117	−1342.196	116.849
700	122.353	204.213	140.370	44.690	−1493.710	−1316.819	98.262
800	125.382	220.756	149.403	57.082	−1492.236	−1291.649	84.336
900	127.846	235.670	158.173	69.747	−1490.789	−1266.664	73.515
1000	129.938	249.251	166.612	82.639	−1498.067	−1241.121	64.829
1100	131.775	261.723	174.699	95.726	−1496.990	−1215.479	57.718
1200	133.432	273.261	182.438	108.987	−1499.977	−1189.811	51.791
1300	134.972	284.003	189.842	122.409	−1498.342	−1164.030	46.771
1300.000	134.972	284.003	189.842	122.409	GLASS <--> LIQUID		
1300.000	163.176	284.003	189.842	122.409	TRANSITION		
1400	163.176	296.095	197.005	138.726	−1621.344	−1135.313	42.359
1500	163.176	307.353	203.991	155.044	−1615.717	−1100.794	38.333
1600	163.176	317.884	210.784	171.361	−1610.233	−1066.645	34.822
1700	163.176	327.777	217.378	187.679	−1604.905	−1032.835	31.735
1800	163.176	337.104	223.772	203.997	−1599.743	−999.334	29.000
1900	163.176	345.926	229.971	220.314	−1594.761	−966.115	26.560
1953.000	163.176	350.416	233.179	228.963	--- CRYSTAL <--> LIQUID ---		
2000	163.176	354.296	235.980	236.632	−1604.658	−932.699	24.360
2100	163.176	362.258	241.805	252.949	−1600.822	−899.195	22.366
2200	163.176	369.848	247.454	269.267	−1597.019	−865.873	20.558
2300	163.176	377.102	252.935	285.585	−1593.251	−832.724	18.912
2400	163.176	384.047	258.254	301.902	−1589.518	−799.738	17.406
2500	163.176	390.708	263.420	318.220	−1585.818	−766.907	16.024
2600	163.176	397.108	268.439	334.537	−1582.152	−734.223	14.751
2700	163.176	403.266	273.320	350.855	−1578.520	−701.679	13.575
2800	163.176	409.200	278.067	367.173	−1574.922	−669.269	12.485
2900	163.176	414.926	282.688	383.490	−1571.357	−636.988	11.473
3000	163.176	420.458	287.189	399.808	−1567.828	−604.829	10.531
3100	163.176	425.809	291.575	416.125	−1564.332	−572.786	9.651
3200	163.176	430.989	295.851	432.443	−1560.871	−540.857	8.829
3300	163.176	436.011	300.023	448.761	−1557.446	−509.035	8.057
3400	163.176	440.882	304.094	465.078	−1554.057	−477.315	7.333
3500	163.176	445.612	308.070	481.396	−1550.706	−445.695	6.652
3600	163.176	450.209	311.955	497.713	−1547.392	−414.170	6.009
3700	163.176	454.680	315.752	514.031	−1953.217	−374.949	5.293
3800	163.176	459.031	319.466	530.349	−1948.749	−332.352	4.568
3900	163.176	463.270	323.099	546.666	−1944.379	−289.872	3.882
4000	163.176	467.401	326.655	562.984	−1940.107	−247.504	3.232

PREVIOUS: CURRENT: June 1967

0 to 1953 K crystal
above 1953 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.556	−1563.260	−1563.260	INFINITE
100	25.510	10.857	138.595	−12.774	−1568.037	−1541.350	805.119
200	67.873	42.539	82.308	−7.954	−1571.507	−1513.096	395.180
298.15	91.881	74.559	74.559	0.	−1572.556	−1484.128	260.013
300	92.203	75.128	74.561	0.170	−1572.560	−1483.579	258.314
400	105.244	103.609	78.355	10.102	−1572.255	−1453.939	189.865
500	113.123	128.001	85.906	21.047	−1571.304	−1424.461	148.812
600	118.453	149.124	94.722	32.641	−1570.043	−1395.208	121.464
700	122.353	167.690	103.847	44.690	−1568.636	−1366.179	101.946
800	125.382	184.233	112.880	57.082	−1567.162	−1337.357	87.320
900	127.846	199.147	121.650	69.747	−1565.714	−1308.719	75.956
1000	129.938	212.728	130.089	82.639	−1572.993	−1279.523	66.835
1100	131.775	225.200	138.177	95.726	−1571.915	−1250.229	59.368
1200	133.432	236.738	145.915	108.987	−1574.903	−1220.909	53.145
1300	134.972	247.480	153.319	122.408	−1573.268	−1191.476	47.874
1400	136.423	257.536	160.408	135.979	−1699.017	−1159.002	43.243
1500	137.821	266.996	167.202	149.691	−1695.995	−1120.536	39.021
1600	139.185	275.934	173.721	163.542	−1692.979	−1082.270	35.333
1700	140.532	284.413	179.985	177.527	−1689.982	−1044.193	32.084
1800	141.879	292.483	186.012	191.648	−1687.017	−1006.291	29.202
1900	143.231	300.191	191.820	205.903	−1684.097	−968.553	26.627
1953.000	143.949	304.141	194.815	213.514	CRYSTAL <--> LIQUID TRANSITION		
1953.000	163.176	350.416	194.815	303.888			
2000	163.176	354.296	198.517	311.557	−1604.658	−932.699	24.360
2100	163.176	362.258	206.127	327.875	−1600.822	−899.195	22.366
2200	163.176	369.848	213.397	344.193	−1597.019	−865.873	20.558
2300	163.176	377.102	220.358	360.510	−1593.251	−832.724	18.912
2400	163.176	384.047	227.035	376.828	−1589.518	−799.739	17.406
2500	163.176	390.708	233.450	393.145	−1585.818	−766.907	16.024
2600	163.176	397.108	239.622	409.463	−1582.152	−734.223	14.751
2700	163.176	403.266	245.570	425.781	−1578.520	−701.679	13.575
2800	163.176	409.200	251.308	442.098	−1574.922	−669.269	12.485
2900	163.176	414.926	256.852	458.416	−1571.357	−636.988	11.473
3000	163.176	420.458	262.214	474.733	−1567.828	−604.829	10.531
3100	163.176	425.809	267.405	491.051	−1564.332	−572.786	9.651
3200	163.176	430.989	272.437	507.369	−1560.871	−540.857	8.829
3300	163.176	436.011	277.318	523.686	−1557.446	−509.035	8.057
3400	163.176	440.882	282.057	540.004	−1554.057	−477.315	7.333
3500	163.176	445.612	286.663	556.321	−1550.706	−445.695	6.652
3600	163.176	450.209	291.142	572.639	−1547.392	−414.170	6.009
3700	163.176	454.680	295.502	588.957	−1953.217	−374.949	5.293
3800	163.176	459.031	299.749	605.274	−1948.749	−332.352	4.568
3900	163.176	463.270	303.887	621.592	−1944.379	−289.872	3.882
4000	163.176	467.401	307.924	637.909	−1940.107	−247.504	3.232

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 91.40 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1400\ K$

$\Delta_f H°(0\ K) = -1250.40 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1261.79 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 14.644\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°(298.15\ K) = -301.6 \pm 5\ kcal \cdot mol^{-1}$ was calculated from the $\Delta_r H°(298.15\ K) = 63.3 \pm 5\ kcal \cdot mol^{-1}$ for the reaction $MgO(cr) + SO_3(g) = MgSO_4(cr)$. The value of $\Delta_r H°(298.15\ K)$ was calculated by the 3rd law method using the equilibrium data obtained from a transpiration study by Knopf and Staude.[1] In addition Marchal[2] measured the total pressure of $SO_3(g)$, $SO_2(g)$ and $O_2(g)$ above $MgSO_4(cr)$ and partial pressures were obtained by application of the SO_3–SO_2 equilibrium data. Another value of $\Delta_f H°(MgSO_4, cr, 298.15\ K)$ may be derived from the measured enthalpy of solution of $MgSO_4(cr)$ by Thomsen[3] and the measured enthalpies of mixing of $MgCl_2(aq, 200\ H_2O)$ with $H_2SO_4(aq, 200\ H_2O)$ and $MgSO_4(aq, 200\ H_2O)$ with $2HCl(100\ H_2O)$ by Thomsen.[4]

Source	Reaction	T/K	Drift $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_r H°(298.15\ K)$ $kcal \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
1	$MgO(cr) + SO_3(g) = MgSO_4(cr)$	1144–1313	0.514	63.284	−301.574
2	$MgO(cr) + SO_3(g) = MgSO_4(cr)$	1223–1428	0.525	72.394	−310.867
3	$MgSO_4(cr) = MgSO_4(aq, 200\ H_2O)$	298.15	−20.84		
4	$MgCl_2(aq, 200\ H_2O) + H_2SO_4(aq, 200\ H_2O)$ $= MgSO_4(aq, 200\ H_2O) + 2HCl(aq, 100 H_2O)$	298.15		−3.52	−305.1*

*Combination of the reactions 3 and 4 with the following $\Delta_f H°(298.15\ K)$:
$H_2SO_4(aq, 200\ H_2O) = -212.387$, $HCl(aq, 100\ H_2O) = -39.74$ and $MgCl_2(aq, 200\ H_2O) = -189.5\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The low temperature heat capacities 53.3–295.4 K were measured by Moore and Kelley.[4] The heat capacities in the temperature range 298–1400 K were estimated from the equation $MgSO_4(cr) = CaSO_4(cr) + MgO(cr) - CaO(cr)$. $CaSO_4(cr)$ and $CaO(cr)$ $C_p°$ were calculated using the equation $C_p° = 16.78 + 23.60 \times 10^{-3} T$ and $C_p° = 11.67 + 1.08 \times 10^{-3} T - 1.56 \times 10^5 T^{-2}$ respectively, Kelley.[5] The heat capacity of MgO(cr) was calculated from the correlation of the low temperature heat capacities. The values from the two sources join smoothly at 298.15 K. Above the melting point (1400 K) the heat capacity was graphically extrapolated. The entropy was calculated at 50.12 K using the Debye and Einstein function $D(242/T) + 2E(378/T) + 2E(866/T) + E(1683/T)$ given by Moore and Kelley.[4] The value of $S°(50.12\ K) = 1.08\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} and $\Delta_{fus} H°$ from Kelley.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−15.390	−1250.399	−1250.399	INFINITE
100	36.313	19.979	160.297	−14.032	−1256.182	−1221.316	637.950
200	73.309	57.532	99.534	−8.400	−1260.022	−1184.778	309.432
298.15	96.232	91.396	91.396	0.	−1261.786	−1147.408	201.021
300	96.441	91.992	91.398	0.178	−1261.804	−1146.698	199.658
400	109.997	121.692	95.355	10.535	−1264.542	−1108.138	144.708
500	119.411	147.271	103.240	22.015	−1265.774	−1068.894	111.667
600	127.612	169.790	112.492	34.379	−1266.082	−1029.474	89.624
700	134.306	189.970	122.143	47.479	−1265.710	−990.061	73.879
800	140.499	208.314	131.785	61.223	−1264.839	−950.737	62.077
900	146.231	225.196	141.238	75.562	−1316.686	−910.467	52.842
1000	151.670	240.888	150.428	90.461	−1322.424	−864.769	45.171
1100	156.691	255.582	159.326	105.881	−1319.324	−819.150	38.898
1200	161.419	269.424	167.930	121.793	−1315.827	−773.831	33.684
1300	165.352	282.504	176.245	138.137	−1311.983	−728.819	29.284
1400	168.619	294.881	184.281	154.840	−1435.265	−680.946	25.406
1400.000	168.619	294.882	184.281	154.841	--- CRYSTAL <--> LIQUID ---		
1500	171.389	306.611	192.049	171.843	−1429.556	−627.265	21.843
1600	173.787	317.750	199.560	189.105	−1423.656	−573.970	18.738
1700	175.895	328.350	206.826	206.591	−1417.595	−521.049	16.010
1800	177.778	338.458	213.861	224.276	−1411.397	−468.490	13.595
1900	179.477	348.117	220.675	242.140	−1405.080	−416.278	11.444
2000	181.033	357.363	227.279	260.166	−1398.658	−364.401	9.517
2100	182.468	366.230	233.686	278.342	−1392.145	−312.848	7.782
2200	183.807	374.750	239.906	296.657	−1385.549	−261.606	6.211
2300	185.067	382.949	245.948	315.101	−1378.878	−210.668	4.784
2400	186.259	390.850	251.822	333.668	−1372.138	−160.021	3.483
2500	187.393	398.477	257.537	352.351	−1365.335	−109.656	2.291

PREVIOUS: December 1960 CURRENT: March 1966

$S°(298.15\ K)$ = [102.125] $J·K^{-1}·mol^{-1}$
T_{fus} = 1400 K

$\Delta_f H°(298.15\ K)$ = [−1246.587] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 14.644 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgSO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgSO_4, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1400\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition was assumed at 1000 K. The heat capacity below 1000 K was obtained from the heat capacity of the crystal. Above 100 K the heat capacity was assumed constant and estimated as 38.0 $cal·K^{-1}·mol^{-1}$ by comparison with those for $MgCl_2$(l), KCl(l) and K_2SO_4(l). $S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	96.232	102.125	102.125	0.	−1246.587	−1135.408	198.919
300	96.441	102.721	102.127	0.178	−1246.605	−1134.718	197.572
400	109.997	132.421	106.084	10.535	−1249.343	−1097.231	143.284
500	119.411	158.000	113.970	22.015	−1250.575	−1059.059	110.639
600	127.612	180.519	123.221	34.379	−1250.883	−1020.713	88.861
700	134.306	200.700	132.873	47.479	−1250.511	−982.373	73.306
800	140.499	219.043	142.514	61.223	−1249.640	−944.122	61.645
900	146.231	235.858	151.964	75.505	−1301.545	−904.921	52.520
1000	158.574	251.845	161.156	90.690	−1306.996	−860.299	44.937
1000.000	158.574	251.845	161.156	90.690	GLASS <--> LIQUID TRANSITION		
1000.000	158.992	251.845	161.156	90.690			
1100	158.992	266.999	170.100	106.589	−1303.417	−815.802	38.739
1200	158.992	280.833	178.760	122.488	−1299.933	−771.628	33.588
1300	158.992	293.559	187.108	138.387	−1296.534	−727.741	29.241
1400	158.992	305.342	195.137	154.286	−1420.620	−680.946	25.406
1400.000	158.992	305.342	195.137	154.286	--- CRYSTAL <--> LIQUID ---		
1500	158.992	316.311	202.854	170.186	−1416.015	−628.274	21.878
1600	158.992	326.572	210.269	186.085	−1411.477	−575.906	18.801
1700	158.992	336.211	217.397	201.984	−1407.003	−523.820	16.095
1800	158.992	345.299	224.253	217.883	−1402.590	−471.996	13.697
1900	158.992	353.895	230.852	233.782	−1398.238	−420.415	11.558
2000	158.992	362.050	237.209	249.682	−1393.944	−369.062	9.639
2100	158.992	369.808	243.340	265.581	−1389.707	−317.923	7.908
2200	158.992	377.204	249.258	281.480	−1385.526	−266.982	6.339
2300	158.992	384.271	254.976	297.379	−1381.400	−216.233	4.911
2400	158.992	391.038	260.505	313.278	−1377.328	−165.662	3.606
2500	158.992	397.528	265.857	329.178	−1373.310	−115.258	2.408

PREVIOUS: December 1960 CURRENT: March 1966

0 to 1400 K crystal
above 1400 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−15.390	−1250.399	−1250.399	INFINITE
100	36.313	19.979	160.297	−14.032	−1256.182	−1221.316	637.950
200	73.309	57.532	99.534	−8.400	−1260.022	−1184.778	309.432
298.15	96.232	91.396	91.396	0.	−1261.786	−1147.408	201.021
300	96.441	91.992	91.398	0.178	−1261.804	−1146.698	199.658
400	109.997	121.692	95.355	10.535	−1264.542	−1108.138	144.708
500	119.411	147.271	103.240	22.015	−1265.774	−1068.894	111.667
600	127.612	169.790	112.492	34.379	−1266.082	−1029.474	89.624
700	134.306	189.970	122.143	47.479	−1265.710	−990.061	73.879
800	140.499	208.314	131.785	61.223	−1264.839	−950.737	62.077
900	146.231	225.196	141.238	75.562	−1316.686	−910.467	52.842
1000	151.670	240.888	150.428	90.461	−1322.424	−864.769	45.171
1100	156.691	255.582	159.326	105.881	−1319.324	−819.150	38.898
1200	161.419	269.424	167.930	121.793	−1315.827	−773.831	33.684
1300	165.352	282.504	176.245	138.137	−1311.983	−728.819	29.284
1400	168.619	294.882	184.281	154.841	−1435.264	−680.946	25.406
1400.000	168.619	294.882	184.281	154.841	CRYSTAL <--> LIQUID		
1400.000	158.992	305.342	184.281	169.485	TRANSITION		
1500	158.992	316.311	192.721	185.385	−1416.015	−628.274	21.878
1600	158.992	326.572	200.770	201.284	−1411.477	−575.906	18.801
1700	158.992	336.211	208.456	217.183	−1407.003	−523.820	16.095
1800	158.992	345.299	215.809	233.082	−1402.590	−471.996	13.697
1900	158.992	353.895	222.852	248.981	−1398.238	−420.415	11.558
2000	158.992	362.050	229.610	264.881	−1393.944	−369.062	9.639
2100	158.992	369.808	236.103	280.780	−1389.707	−317.923	7.908
2200	158.992	377.204	242.350	296.679	−1385.526	−266.982	6.339
2300	158.992	384.271	248.368	312.578	−1381.400	−216.233	4.911
2400	158.992	391.038	254.172	328.477	−1377.328	−165.662	3.606
2500	158.992	397.528	259.778	344.377	−1373.310	−115.258	2.408

PREVIOUS: CURRENT: March 1966

$S°(298.15\ K) = 101.19 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = Unknown

$\Delta_f H°(0\ K) = -1505.74 \pm 33.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ k) = -1515.86 \pm 33.5\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

Rezukhina and Levitskii[1] measured the emf, E = 0.2433–0.0001264T, for the cell reaction $MgO(cr) + W(cr) + 3Fe_{0.95}O(cr) = MgWO_4(cr) + 2.85\ Fe(cr)$, in the temperature range 1220–1370 K. Incorporating the results with auxiliary thermal data, the authors obtained $\Delta_r G° = -224{,}370 + 65.67T\ (cal \cdot K^{-1} \cdot mol^{-1})$ for $MgO(cr) + W(cr) + 3/2O_2(g) \rightarrow MgWO_4(cr)$. 3rd law analysis of the $\Delta_r G°$ equation gives $\Delta_r H°(298.15\ K) = -218.6\ kcal \cdot mol^{-1}$, from which the adopted $\Delta_f H°(MgWO_4, cr, 298.15\ K)$, $-362.3\ kcal \cdot mol^{-1}$, is calculated. The 2nd law analysis gives $\Delta_f H°(MgWO_4, cr, 298.15\ K) = -372.7\ kcal \cdot mol^{-1}$. The drift is $8.0\ cal \cdot K^{-1} \cdot mol^{-1}$.

Rezukhina, *et. al.*[2] determined the Gibbs energy changes $\Delta_r G° = 51{,}300 - 27.67T\ (cal \cdot K^{-1} \cdot mol^{-1})$ for the reaction $MgWO_4(cr) + 3H_2(g) \rightarrow MgO(cr) + W(cr) + 3H_2O(g)$ in the temperature range 1073 K–1273 K by a circulation method. This leads to heats of formation of 366.1 $kcal \cdot mol^{-1}$ by the 3rd law method and 377.2 $kcal \cdot mol^{-1}$ by the 2nd law method. Both determinations were performed by Rezukhina and his co workers, but they considered the data obtained by the emf method to be more reliable than that derived from heterogeneous equilibria.

Heat Capacity and Entropy

Low temperature heat capacities, 52.92–296.09 K, were measured calorimetrically by King and Weller.[3] The heat capacities above 300 K are estimated by comparison with those of $CaWO_4$(cr),[4] CaO(cr)[5] and MgO(cr).[6] These two sets of data are joined smoothly at 298.15 K by a graphical method.

The entropy, $S°(298.15\ K) = 21.184\ cal \cdot K^{-1} \cdot mol^{-1}$, is taken from King and Weller,[3] based on an extrapolation of $S°(51\ K) = 1.27\ cal \cdot K^{-1} \cdot mol^{-1}$. No spin magnetic entropy is predicted below 51 K based on the diamagnetism observed by Gerasimov.[7]

References

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[4]R. A. Yakovleva and T. N. Rezukhina, Russ. J. Phys. Chem. **34**, 390 (1960).
[5]K. K. Kelley, U.S. Bur. Mines Bull. 584, (1960).
[6]JANAF Thermochemical Tables: MgO, 12–31–65.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.218	−1505.744	−1505.744	INFINITE
100	38.221	21.150	179.146	−15.800	−1511.429	−1476.970	771.490
200	83.220	62.706	110.418	−9.542	−1515.008	−1440.872	376.317
298.15	109.077	101.186	101.186	0.	−1515.863	−1404.224	246.014
300	109.621	101.862	101.188	0.202	−1515.861	−1403.532	244.377
400	123.428	135.424	105.670	11.902	−1515.122	−1366.171	178.404
500	131.587	163.893	114.543	24.675	−1513.648	−1329.093	138.849
600	137.026	188.377	124.856	38.112	−1511.854	−1292.348	112.509
700	141.670	209.851	135.496	52.049	−1509.900	−1255.916	93.718
800	146.147	229.063	146.011	66.441	−1507.815	−1219.774	79.643
900	150.415	246.522	156.223	81.268	−1505.606	−1183.900	68.712
1000	154.808	262.595	166.067	96.528	−1511.860	−1147.567	59.943
1100	159.410	277.566	175.530	112.239	−1509.378	−1111.254	52.769
1200	164.013	291.633	184.625	128.410	−1506.559	−1075.183	46.801
1300	168.615	304.945	193.373	145.043	−1503.393	−1039.361	41.762
1400	173.008	317.600	201.798	162.122	−1627.297	−1000.628	37.334
1500	177.611	329.694	209.924	179.655	−1622.088	−956.046	33.292
1600	182.004	341.296	217.775	197.634	−1616.532	−911.823	29.768
1700	186.606	352.469	225.371	216.066	−1610.619	−867.958	26.669
1800	191.000	363.259	232.734	234.945	−1604.355	−824.451	23.925
1900	195.602	373.710	239.880	254.277	−1597.733	−781.302	21.479
2000	199.995	383.855	246.826	274.058	−1590.756	−738.511	19.288

PREVIOUS: June 1963 CURRENT: March 1967

$S°(298.15\ K) = 135.60 \pm 6.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1963 \pm 20$

$\Delta_f H°(0\ K) = -2495.43 \pm 10.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2509.35 \pm 10.5\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [146.440]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from $\Delta_r H°(298.15\ K) = -4.45 \pm 0.45\ kcal \cdot mol^{-1}$ for the reaction $MgO(cr) + 2TiO_2(rutile) = MgTi_2O_5(cr)$ measured by Kelley *et al.*,[1] using a solution calorimetric method. The uncertainty of $\pm 2.5\ kcal \cdot mol^{-1}$ assigned to the enthalpy of formation is due primarily to TiO_2(rutile).

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52–296 K) of Todd.[2] High temperature enthalpies have been measured (397–1812 K) by Orr and Coughlin.[3] High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S°(51\ K) = 1.11\ cal \cdot K^{-1} \cdot mol^{-1}$.

Kelley *et al.*,[1] suggested that there may be a zero-point entropy due to randomness of the cations. The authors estimated $S°(0\ K)$ from the following alternative assumptions: (a) all the Mg and Ti ions are randomly distributed among the latice sites giving $3.79\ cal \cdot K^{-1} \cdot mol^{-1}$ and (b) all the Mg and one-half of the Ti ions are randomly distributed giving $2.75\ cal \cdot K^{-1} \cdot mol^{-1}$. These assumptions were proposed in order to make $MgTi_2O_5$ stable relative to $MgTiO_3$ at high temperatures. Phase data of Massazza and Sirchia,[4] indicate that $MgTi_2O_5$ melts congruently at 1963 ± 20 K and that there is a temperature range. To make $\Delta_r G°(1800\ K) < 0$ would require that $S°(0\ K) \geq 0.35\ cal \cdot K^{-1} \cdot mol^{-1}$. We adopt a compromise zero-point entropy of $2\ cal \cdot K^{-1} \cdot mol^{-1}$ between the upper ($3.79\ cal \cdot K^{-1} \cdot mol^{-1}$) and the lower ($0.35\ cal \cdot K^{-1} \cdot mol^{-1}$) limits.

Fusion Data

Refer to the liquid table for details.

References

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[2] S. S. Todd, J. Amer. Chem. Soc. **74**, 4669 (1952).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.439	−2495.427	−2495.427	INFINITE
100	46.129	22.217	231.124	−20.891	−2502.903	−2459.195	1284.552
200	110.533	75.638	139.695	−12.811	−2507.943	−2413.208	630.265
298.15	146.858	135.603	135.603	0.	−2509.354	−2368.790	415.002
300	147.335	136.513	135.606	0.272	−2509.357	−2367.918	412.291
400	165.753	181.688	141.640	16.019	−2508.821	−2320.819	303.068
500	176.665	219.925	153.575	33.175	−2507.459	−2273.965	237.559
600	184.498	252.858	167.441	51.250	−2505.701	−2227.426	193.915
700	190.807	281.785	181.751	70.024	−2503.712	−2181.202	162.763
800	196.276	307.628	195.899	89.383	−2501.533	−2135.276	139.419
900	201.238	331.036	209.634	109.262	−2499.268	−2089.630	121.279
1000	205.870	352.481	222.861	129.620	−2505.664	−2043.521	106.743
1100	210.284	372.311	235.557	150.429	−2503.688	−1997.403	94.849
1200	214.539	390.791	247.732	171.671	−2509.739	−1951.222	84.934
1300	218.681	408.127	259.410	193.332	−2506.427	−1904.812	76.536
1400	222.739	424.482	270.622	215.404	−2630.346	−1855.496	69.229
1500	226.731	439.986	281.401	237.878	−2625.354	−1800.324	62.693
1600	230.672	454.745	291.777	260.748	−2620.240	−1745.488	56.984
1700	234.572	468.847	301.781	284.011	−2615.031	−1690.975	51.957
1800	238.438	482.364	311.441	307.662	−2609.756	−1636.771	47.498
1900	242.279	495.359	320.781	331.698	−2604.443	−1582.861	43.516
1963.000	244.685	503.301	326.512	347.037	--- CRYSTAL <-- -> LIQUID ---		
2000	246.099	507.883	329.825	356.116	−2628.493	−1528.324	39.916
2100	249.902	519.982	338.593	380.917	−2624.683	−1473.408	36.649
2200	253.688	531.695	347.106	406.096	−2620.551	−1418.679	33.684
2300	257.458	543.055	355.380	431.654	−2616.098	−1364.148	30.981
2400	261.220	554.092	363.431	457.588	−2611.324	−1309.817	28.507
2500	264.973	564.832	371.273	483.897	−2606.231	−1255.691	26.236
2600	268.713	575.297	378.919	510.582	−2600.818	−1201.776	24.144
2700	272.450	585.508	386.383	537.640	−2595.087	−1148.073	22.211
2800	276.177	595.484	393.673	565.071	−2589.036	−1094.589	20.420
2900	279.901	605.241	400.801	592.875	−2582.667	−1041.330	18.756
3000	283.621	614.792	407.775	621.051	−2575.979	−988.292	17.208

PREVIOUS: June 1961 CURRENT: June 1967

$S°(298.15\ K) = [197.783]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1963 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-2382.31 \pm 8.4]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [146.440]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(MgTi_2O_5, l, 298.15\ K)$ is calculated from $\Delta_f H°(MgTi_2O_5, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1963\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1300 K. Below 1300 K the heat capacity is obtained from the heat capacity of the crystal. Above 1300 K the heat capacity is assumed constant and estimated as 62.4 $cal·K^{-1}·mol^{-1}$ or 7.8 $cal·K^{-1}$ g–atom^{-1}. $S°(l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The congruent melting point is obtained from Massazza.[1] Previous work by Coughanour[2] indicates congruent melting at 1925 K. The $\Delta_{fus} H°$ is estimated from those of $Na_2O·2TiO_2$ and $Na_2O·TiO_2$ observed by Naylor[3] and $CaO·TiO_2·SiO_2$ observed by King.[4]

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Magnesium Titanium Oxide ($MgTi_2O_5$) $Mg_1O_5Ti_2(l)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	146.858	197.783	197.783	0.	−2382.307	−2260.282	395.992
300	147.335	198.692	197.785	0.272	−2382.310	−2259.525	393.418
400	165.753	243.867	203.819	16.019	−2381.773	−2218.643	289.725
500	176.665	282.105	215.754	33.175	−2380.411	−2178.007	227.535
600	184.498	315.037	229.620	51.250	−2378.654	−2137.686	186.102
700	190.807	343.964	243.931	70.024	−2376.665	−2097.680	156.531
800	196.276	369.807	258.078	89.383	−2374.486	−2057.972	134.372
900	201.238	393.215	271.813	109.262	−2372.221	−2018.544	117.153
1000	205.870	414.660	285.040	129.620	−2378.616	−1978.653	103.354
1100	210.284	434.490	297.736	150.429	−2376.641	−1938.752	92.064
1200	214.539	452.970	309.911	171.671	−2382.691	−1898.789	82.652
1300	218.681	470.307	321.589	193.333	−2379.379	−1858.597	74.679
1300.000	218.681	470.307	321.589	193.333	GLASS <--> LIQUID		
1300.000	261.082	470.307	321.589	193.333	TRANSITION		
1400	261.082	489.655	332.911	219.441	−2499.262	−1815.654	67.743
1500	261.082	507.668	343.968	245.549	−2490.636	−1767.128	61.537
1600	261.082	524.518	354.732	271.657	−2482.284	−1719.168	56.125
1700	261.082	540.345	365.189	297.765	−2474.229	−1671.721	51.366
1800	261.082	555.268	375.339	323.873	−2466.497	−1624.740	47.149
1900	261.082	569.384	385.184	349.982	−2459.112	−1578.179	43.387
1963.000	261.082	577.901	391.233	366.430	--- CRYSTAL <--> LIQUID ---		
2000	261.082	582.776	394.731	376.090	−2481.473	−1531.089	39.988
2100	261.082	595.514	403.992	402.198	−2476.355	−1483.696	36.905
2200	261.082	607.660	412.975	428.306	−2471.294	−1436.544	34.108
2300	261.082	619.265	421.694	454.414	−2466.290	−1389.624	31.559
2400	261.082	630.377	430.159	480.522	−2461.342	−1342.919	29.228
2500	261.082	641.035	438.383	506.631	−2456.451	−1296.419	27.087
2600	261.082	651.275	446.375	532.739	−2451.614	−1250.113	25.115
2700	261.082	661.128	454.148	558.847	−2446.832	−1203.992	23.293
2800	261.082	670.623	461.710	584.955	−2442.105	−1158.047	21.604
2900	261.082	679.785	469.073	611.063	−2437.431	−1112.272	20.034
3000	261.082	688.636	476.245	637.171	−2432.812	−1066.655	18.572
3100	261.082	697.196	483.235	663.280	−2428.245	−1021.190	17.207
3200	261.082	705.485	490.052	689.388	−2423.732	−975.875	15.930
3300	261.082	713.519	496.702	715.496	−2419.271	−930.700	14.732
3400	261.082	721.313	503.195	741.604	−2414.863	−885.656	13.606
3500	261.082	728.882	509.535	767.712	−2410.508	−840.744	12.547
3600	261.082	736.236	515.731	793.820	−2406.207	−795.954	11.549
3700	261.082	743.390	521.788	819.928	−3220.157	−735.708	10.386
3800	261.082	750.352	527.711	846.037	−3213.497	−668.648	9.191
3900	261.082	757.134	533.507	872.145	−3207.003	−601.763	8.060
4000	261.082	763.744	539.181	898.253	−3200.675	−535.044	6.987

PREVIOUS: June 1961 CURRENT: June 1967

Magnesium Titanium Oxide ($MgTi_2O_5$) $Mg_1O_5Ti_2(l)$

0 to 1963 K crystal
above 1963 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−22.439	−2495.427	−2495.427	INFINITE
100	46.129	22.217	231.124	−20.891	−2502.903	−2459.195	1284.552
200	110.533	75.638	139.695	−12.811	−2507.943	−2413.208	630.265
298.15	146.858	135.603	135.603	0.	−2509.354	−2368.790	415.002
300	147.335	136.513	135.606	0.272	−2509.357	−2367.918	412.291
400	165.753	181.688	141.640	16.019	−2508.821	−2320.819	303.068
500	176.665	219.925	153.575	33.175	−2507.459	−2273.965	237.559
600	184.498	252.858	167.441	51.250	−2505.701	−2227.426	193.915
700	190.807	281.785	181.751	70.024	−2503.712	−2181.202	162.763
800	196.276	307.628	195.899	89.383	−2501.533	−2135.276	139.419
900	201.238	331.036	209.634	109.262	−2499.268	−2089.630	121.279
1000	205.870	352.481	222.861	129.620	−2505.664	−2043.521	106.743
1100	210.284	372.311	235.557	150.429	−2503.688	−1997.403	94.849
1200	214.539	390.791	247.732	171.671	−2509.739	−1951.222	84.934
1300	218.681	408.127	259.410	193.332	−2506.427	−1904.812	76.536
1400	222.739	424.482	270.622	215.404	−2630.346	−1855.496	69.229
1500	226.731	439.986	281.401	237.878	−2625.354	−1800.324	62.693
1600	230.672	454.745	291.777	260.748	−2620.240	−1745.488	56.984
1700	234.572	468.847	301.781	284.011	−2615.031	−1690.975	51.957
1800	238.438	482.364	311.441	307.662	−2609.756	−1636.771	47.498
1900	242.279	495.359	320.781	331.698	−2604.443	−1582.861	43.516
1963.000	244.685	503.301	326.512	347.037	CRYSTAL <--> LIQUID TRANSITION		
1963.000	261.082	577.901	326.512	493.477			
2000	261.082	582.776	331.208	503.137	−2481.473	−1531.089	39.988
2100	261.082	595.514	343.493	529.245	−2476.355	−1483.696	36.905
2200	261.082	607.660	355.227	555.353	−2471.294	−1436.544	34.108
2300	261.082	619.265	366.456	581.462	−2466.290	−1389.624	31.559
2400	261.082	630.377	377.223	607.570	−2461.342	−1342.919	29.228
2500	261.082	641.035	387.564	633.678	−2456.451	−1296.419	27.087
2600	261.082	651.275	397.511	659.786	−2451.614	−1250.113	25.115
2700	261.082	661.128	407.093	685.894	−2446.832	−1203.992	23.293
2800	261.082	670.623	416.336	712.002	−2442.105	−1158.047	21.604
2900	261.082	679.785	425.264	738.110	−2437.431	−1112.272	20.034
3000	261.082	688.636	433.896	764.219	−2432.812	−1066.655	18.572
3100	261.082	697.196	442.252	790.327	−2428.245	−1021.190	17.207
3200	261.082	705.485	450.350	816.435	−2423.732	−975.875	15.930
3300	261.082	713.519	458.203	842.543	−2419.271	−930.700	14.732
3400	261.082	721.313	465.828	868.651	−2414.863	−885.656	13.606
3500	261.082	728.882	473.236	894.759	−2410.508	−840.744	12.547
3600	261.082	736.236	480.440	920.868	−2406.207	−795.954	11.549
3700	261.082	743.390	487.450	946.976	−3220.157	−735.708	10.386
3800	261.082	750.352	494.278	973.084	−3213.497	−668.648	9.191
3900	261.082	757.134	500.931	999.192	−3207.003	−601.763	8.060
4000	261.082	763.744	507.419	1025.300	−3200.675	−535.044	6.987

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 50.33 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -344.65 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -345.72 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Sabatier[1] determined $\Delta_r H°(286\ K) = -37.8 \pm 1.0$ kcal·mol^{-1} while Mourlot[2] determined $\Delta_r H°(291\ K) = -38.0 \pm 1.0$ kcal·mol^{-1} for MgS(cr) + 2 HCl(aq, 100 H_2O) → $MgCl_2$(aq, 100 H_2O) + H_2S(aq). We derive $\Delta_f H°$(MgS, cr, 298.15 K) = -83.0 ± 2.0 kcal·mol^{-1} and $\Delta_f H°$(MgS, cr, 298.15 K) = 82.8 ± 2.0 kcal·mol^{-1} respectively based on the following auxiliary data: $\Delta_f H°$(HCl·100 H_2O, aq, 298.15 K) = −39.657 kcal·mol^{-1},[3] $\Delta_f H°$(H_2S, aq, 298.15 K) = −9.5 kcal·mol^{-1},[3] and $\Delta_f H°$($MgCl_2$·100 H_2O, aq, 298.15 K) = −190.59 kcal·mol^{-1}.[4] The uncertainty reflects the correction to 298.15 K and the ambiguity of the exact solution composition. Von Wartenberg[5] measured $\Delta_r H°(293\ K) = -33.95 \pm 0.79$ kcal·mol^{-1} for MgS(cr) + 2 HCl(30 H_2O, aq) → $MgCl_2$(30 H_2O, aq) + H_2S(g). We derive $\Delta_f H°$(MgS, cr, 298.15 K) = -82.0 ± 1.0 kcal·mol^{-1} based on the following auxiliary data: $\Delta_f H°$(HCl·30 H_2O, aq, 298.15 K) = 39.357 kcal·mol^{-1},[3] $\Delta_f H°$(H_2S, g, 298.15 K) = −4.90 kcal·mol^{-1},[3] and $\Delta_f H°$($MgCl_2$·30 H_2O, aq, 298.15 K) = 189.78 kcal·mol^{-1}.[4]

Kapustinskii and Korshunov[6] performed calorimetric measurements of the enthalpy of formation of MgS(cr) from the pure elements. They determined $\Delta_f H°(298.15\ K) = -84.33 \pm 0.27$ kcal·mol^{-1} for Mg(cr) + S(cr, rhombic) = MgS(cr).

Our analyses of equilibrium studies of Curlock and Pidgeon[7] and of Dewing and Richardson[8] are given below. The two studies are in reasonable agreement. The 3rd law $\Delta_r H°(298.15\ K)$ may be in error by as much as 0.5 kcal·mol^{-1} since the Gibbs energy functions employed in the calculations are partially based on estimated high temperature $C_p°$ values.

Source	Method	Data Points	Reaction[a]	T/K	δS cal·K^{-1}·mol^{-1}	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Curlock[7]	Equilibrium	6	A	1180–1483	−0.60 ± 0.45	−8.49 ± 0.59	−9.19 ± 0.24	−81.59 ± 0.4
Dewing[8]	Equilibrium	6	A	1267–1768	−2.23 ± 0.22	−5.53 ± 0.38	−8.73 ± 1.01	−82.05 ± 1.2

[a]Reaction: A) MgS(cr) + H_2O(g) = MgO(cr) + H_2S(g)

Our adopted value is based on a weighted average of all the data.

Heat Capacity and Entropy

Stull *et al.*[9] measured the low temperature heat capacities in an adiabatic calorimeter from 15–320 K. Their smooth values are adopted in the tabulation. The entropy $S°(298.15\ K) = 12.03 \pm 0.1$ cal·K^{-1}·mol^{-1} is based on $S° = 0.010$ cal·K^{-1}·mol^{-1} at 15 K.[9] The $C_p°$ values above 320 K are estimated by graphical extrapolation combined with method B of Kubaschewski *et. al.*[10]

Fusion Data

MgS melts above 2300 K [11]and no other literature melting data are available.

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[12]JANAF Thermochemical Tables: MgO(cr) 12-13-74; H_2O(g) 3-31-61; H_2S(g) 6-30-77.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−8.333	−344.647	−344.647	INFINITE
100	22.677	10.920	86.467	−7.555	−345.200	−344.090	179.734
200	40.125	33.095	54.342	−4.249	−345.544	−342.807	89.532
298.15	45.564	50.334	50.334	0.	−345.724	−341.433	59.818
300	45.647	50.616	50.334	0.084	−345.728	−341.406	59.444
400	47.614	64.032	52.150	4.753	−348.212	−339.840	44.379
500	48.953	74.807	55.639	9.584	−349.975	−337.556	35.264
600	49.915	83.823	59.606	14.530	−351.381	−334.934	29.159
700	50.543	91.566	63.631	19.555	−352.575	−332.097	24.781
800	51.003	98.346	67.556	24.632	−353.697	−329.094	21.488
900	51.463	104.380	71.318	29.756	−407.949	−324.871	18.855
1000	51.882	109.823	74.901	34.923	−416.494	−314.931	16.450
1100	52.347	114.790	78.305	40.134	−416.585	−304.770	14.472
1200	52.802	119.365	81.538	45.392	−416.645	−294.602	12.824
1300	53.252	123.609	84.613	50.694	−416.676	−284.431	11.429
1400	53.681	127.571	87.542	56.041	−544.087	−271.091	10.115
1500	54.073	131.288	90.335	61.429	−542.712	−251.639	8.763
1600	54.476	134.791	93.005	66.856	−541.311	−232.279	7.583
1700	54.910	138.106	95.562	72.326	−539.883	−213.008	6.545
1800	55.312	141.256	98.014	77.837	−538.427	−193.822	5.625
1900	55.647	144.256	100.369	83.385	−536.947	−174.718	4.803
2000	56.024	147.120	102.636	88.968	−535.444	−155.692	4.066
2100	56.468	149.864	104.820	94.593	−533.911	−136.742	3.401
2200	56.902	152.501	106.927	100.261	−532.344	−117.866	2.798
2300	57.326	155.039	108.964	105.973	−530.744	−99.062	2.250
2400	57.739	157.488	110.935	111.726	−529.112	−80.328	1.748
2500	58.131	159.853	112.845	117.520	−527.450	−61.662	1.288
2600	58.534	162.141	114.697	123.353	−525.756	−43.064	0.865
2700	58.953	164.358	116.496	129.227	−524.029	−24.532	0.475
2800	59.371	166.509	118.244	135.143	−522.270	−6.064	0.113
2900	59.789	168.600	119.944	141.101	−520.479	12.341	−0.222
3000	60.208	170.634	121.600	147.101	−518.656	30.683	−0.534

PREVIOUS: December 1971 CURRENT: September 1977

$S°(298.15\ K) = 225.483 \pm 4.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$

$\Delta_f H°(0\ K) = [145.39 \pm 66.9]\ kJ{\cdot}mol^{-1}$

$\Delta_f H°(298.15\ K) = [145.23 \pm 66.9]\ kJ{\cdot}mol^{-1}$

Electronic States and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X^1\Sigma^+$	0.0	1	526.47	2.681	0.26570	0.00174	2.1425	1
$^3\Pi$	[2000]	6	[430]	[2.2]	[0.237]	[0.0015]	[2.27]	2
$^1\Pi$	[3000]	2	[430]	[2.2]	[0.237]	[0.0015]	[2.27]	3
$^3\Sigma^+$	[17000]	3	[493.20]	[2.313]	[0.2530]	[0.00153]	[2.1956]	1,2
$A^1\Sigma^+$	23036.98	1	495.20	2.313	0.2530	0.00153	2.1956	1

Enthalpy of Formation

Colin *et al.*[1] searched unsuccessfully for gaseous MgS in a Knudsen effusion mass–spectrometric experiment. They set the upper limit $D_0°(MgS, g) = 55$ kcal·mol^{-1}. There are no other equilibrium or positive mass spectrometric data involving MgS(g); consequently $D_0°(MgS, g)$ must be estimated. The Birge–Sponer extrapolation is of little utility in this case. Gaydon[2] has gone into great detail concerning the problems inherent in linear–Birge–Sponer extrapolations (LBX) on the oxides and sulfides of the alkaline earths. The normal LBX yields $D_0°(MgS, g) = 73$ kcal·mol^{-1}. When adjusted for ionic character with the Hildenbrand correction,[3] $D_0°(MgS, g) = 65$ kcal·mol^{-1}. The ground state of MgS cannot dissociate into ground state atoms. After correcting for the excited atomic products, $D_0°(MgS, g) = 42$ kcal·mol^{-1}. A more reliable method of estimation is that of Hauge and Margrave[4] based on the observation that the ratio $D_{MS}K_{MO}/D_{MO}K_{MS}$ is very similar for elements within a given group. Based on data involving known bond energies and force constants of the gaseous diatomic oxides and sulfides, we calculate $D_0°(MgS, g) = 78 \pm 10$ kcal·mol^{-1}. Dissociation energies of the alkaline earth monoxides were taken from Srivastava,[5] dissociation energies for the alkaline earth sulfides were taken the JANAF Thermochemical Tables[6] and force constants were calculated from spectroscopic data of Barrow and Cousins.[7] Further comparisons of vapor pressures and enthalpies of sublimation for the other alkaline earth oxides and sulfides[6] suggest lower values of $D_0°(MgS, g)$ than the Hauge and Margrave method leads to. We adopt $D_0°(MgS, g) \leq 66 \pm 16$ kcal·mol^{-1}. Using auxiliary JANAF data,[6] we calculate $\Delta_f H°(MgS, g, 298.15\ K) = 34.71 \pm 16$ kcal·mol^{-1}.

Heat Capacity and Entropy

The spectroscopic constants of the observed states, taken from Marcano and Barrow[8] for the isotopic species $Mg^{24}S^{32}$, are corrected to account for the natural abundances of the elements. Other low–lying electronic states and their vibrational–rotational constants are estimated in isoconfigurational groups by analogy with MgO[6] and from trends observed in the known states of the other alkaline–earth oxides and sulfides.[6] Uncertainty in the energy and molecular constants for the estimated states may contribute significantly, perhaps as much as 1.0 cal·K^{-1}·mol^{-1} to the entropy at 298.15 K.

The ground state of gaseous MgS is taken as $^1\Sigma^+$. There should be low–lying triplet states. A $^1\Pi$ state is predicted for MgS at 3000 cm^{-1} based on experimentally observed $^1\Pi$ states for MgO,[9] BeO,[6] and BeS.[10] The corresponding triplet, $^3\Pi$, is assumed to lie 1000 cm^{-1} lower in energy based on trends in the triplet–singlet splitting observed by Field[11] for the alkaline– earth oxides. Similar trends in the triplet–singlet splitting of the isoconfigurational Σ states are used to place the $^3\Sigma^+$ state 6000 cm^{-1} below the experimentally observed[8] $A^1\Sigma^+$ state. By analogy with MgO[6] we do not feel that a $^1\Delta$ state exists below 25000 cm^{-1}. The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_t \sum_i Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.245	145.392	145.392	INFINITE
100	29.371	191.105	254.427	−6.332	146.973	130.065	−67.939
200	32.039	212.204	228.567	−3.273	146.383	113.299	−29.591
250	33.380	219.500	226.046	−1.636	145.829	105.090	−21.957
298.15	34.599	225.483	225.483	0.	145.227	97.297	−17.046
300	34.648	225.697	225.484	0.064	145.203	97.000	−16.889
350	36.111	231.144	225.911	1.832	144.542	89.018	−13.285
400	37.972	236.082	226.878	3.682	141.668	81.219	−10.606
450	40.277	240.684	228.159	5.636	140.377	73.732	−8.559
500	42.922	245.062	229.632	7.715	139.107	66.399	−6.937
600	48.397	253.377	232.903	12.284	137.324	52.038	−4.530
700	52.741	261.186	236.392	17.356	136.177	37.921	−2.830
800	55.100	268.406	239.950	22.765	135.386	23.941	−1.563
900	55.594	274.940	243.481	28.313	81.559	11.133	−0.646
1000	54.817	280.766	246.924	33.842	73.375	3.996	−0.209
1100	53.380	285.926	250.240	39.255	73.486	−2.948	0.140
1200	51.717	290.500	253.408	44.510	73.424	−9.896	0.431
1300	50.079	294.574	256.421	49.599	73.179	−16.830	0.676
1400	48.585	298.230	259.279	54.531	−54.647	−20.572	0.768
1500	47.278	301.536	261.988	59.323	−53.867	−18.166	0.633
1600	46.161	304.551	264.555	63.993	−53.224	−15.808	0.516
1700	45.217	307.320	266.990	68.560	−52.698	−13.486	0.414
1800	44.426	309.881	269.303	73.042	−52.272	−11.192	0.325
1900	43.765	312.265	271.502	77.450	−51.931	−8.920	0.245
2000	43.213	314.496	273.596	81.798	−51.663	−6.663	0.174
2100	42.752	316.592	275.594	86.096	−51.457	−4.419	0.110
2200	42.368	318.572	277.503	90.351	−51.304	−2.183	0.052
2300	42.048	320.448	279.330	94.572	−51.195	0.048	−0.001
2400	41.781	322.232	281.081	98.763	−51.126	2.274	−0.049
2500	41.559	323.933	282.761	102.929	−51.090	4.498	−0.094
2600	41.375	325.559	284.376	107.076	−51.082	6.721	−0.135
2700	41.225	327.118	285.931	111.205	−51.101	8.945	−0.173
2800	41.102	328.615	287.428	115.321	−51.141	11.169	−0.208
2900	41.003	330.055	288.874	119.426	−51.203	13.396	−0.241
3000	40.925	331.444	290.270	123.523	−51.284	15.625	−0.272
3100	40.865	332.785	291.620	127.612	−51.383	17.857	−0.301
3200	40.820	334.081	292.926	131.696	−51.499	20.092	−0.328
3300	40.790	335.337	294.193	135.776	−51.633	22.331	−0.353
3400	40.772	336.554	295.421	139.854	−51.784	24.575	−0.378
3500	40.764	337.736	296.613	143.931	−51.955	26.823	−0.400
3600	40.766	338.885	297.771	148.008	−52.144	29.077	−0.422
3700	40.776	340.002	298.898	152.085	−52.354	31.335	−0.442
3800	40.793	341.089	299.994	156.163	−52.587	33.600	−0.462
3900	40.817	342.149	301.061	160.243	−52.843	35.872	−0.480
4000	40.847	343.183	302.101	164.327	−53.125	38.150	−0.498
4100	40.882	344.192	303.116	168.413	−53.434	40.436	−0.515
4200	40.921	345.178	304.105	172.503	−53.773	42.729	−0.531
4300	40.965	346.141	305.072	176.597	−54.143	45.031	−0.547
4400	41.012	347.083	306.016	180.696	−54.548	47.342	−0.562
4500	41.062	348.005	306.939	184.800	−54.987	49.663	−0.576
4600	41.115	348.909	307.841	188.909	−55.466	51.993	−0.590
4700	41.170	349.793	308.725	193.023	−55.984	54.335	−0.604
4800	41.228	350.661	309.589	197.143	−56.545	56.688	−0.617
4900	41.287	351.511	310.436	201.269	−57.150	59.053	−0.630
5000	41.348	352.346	311.266	205.400	−57.801	61.431	−0.642
5100	41.410	353.166	312.080	209.538	−58.500	63.823	−0.654
5200	41.473	353.970	312.878	213.682	−59.250	66.229	−0.665
5300	41.537	354.761	313.660	217.833	−60.050	68.649	−0.677
5400	41.602	355.538	314.429	221.990	−60.905	71.085	−0.688
5500	41.668	356.302	315.183	226.153	−61.814	73.538	−0.698
5600	41.734	357.053	315.924	230.323	−62.779	76.007	−0.709
5700	41.801	357.792	316.652	234.500	−63.803	78.495	−0.719
5800	41.868	358.520	317.368	238.683	−64.886	81.001	−0.729
5900	41.935	359.236	318.071	242.874	−66.029	83.526	−0.739
6000	42.002	359.942	318.763	247.070	−67.234	86.070	−0.749

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$D_0^\circ = 4.84 \pm 0.01$ kJ·mol^{-1} (natural abundance)
$S^\circ(298.15\ K) = 240.19 \pm 0.50$ J·K^{-1}·mol^{-1}

(0 K) = 288.16 ± 0.80 kJ·mol^{-1}
$\Delta_f H^\circ(298.15\ K) = 287.63 \pm 0.80$ kJ·mol^{-1}

State	T_e	D°	Spectroscopic Constants for $^{24}Mg_2$ in cm^{-1} ω_e	$\omega_e x_e$	B_e	$10^3\alpha_e$	$10^6 D_e$	r_e, Å	References
$^1\Sigma_g^{++}$	0	404	51.121	1.6448[a]	0.092866	3.7758[b]	1.2166[c]	3.8905	1
$^3\Pi_g$	[15645]	[21740]	[220.1]	[1.95]	[0.171]	[1.89]	[0.413]	[2.91]	4[d]
$^3\Sigma_u^+$	[16773]	[21740]	[184.2]	[1.67]	[0.145]	[1.64]	[0.359]	[3.18]	4[d]
$^1\Pi_g$	[20267]	[34941]	[263.1]	[1.17]	[0.181]	[1.15]	[0.343]	[2.91]	4[d]

(a) $+1.6244 \times 10^{-2}\ (v + 1/2)^3 - 6.106 \times 10^{-4}\ (v + 1/2)^4$.
(b) $+1.0679 \times 10^{-4}\ (v + 1/2)^2 - 9.6831 \times 10^{-6}\ (v + 1/2)^3$.
(c) $-3.0768 \times 10^{-8}\ (v + 1/2) + 2.1344 \times 10^{-8}\ (v + 1/2)^2$.
(d) These values are estimated based on the theoretical potential curves of Stevens and Krauss.[4]

Enthalpy of Formation

The ground state dissociation energy for $^{24}Mg_2$ was determined by Li and Stwalley[2] to be 404.1 ± 0.5 cm^{-1}. This value was corrected to natural abundance Mg_2 with the result $D_0^\circ = 404.3$ cm^{-1}. Using this value and the recommended value for $\Delta_f H^\circ(Mg, g, 0) = 146.499$ kJ·mol^{-1} from CODATA,[13] we calculate the adopted value of $\Delta_f H^\circ(Mg_2, g, 0) = 288.16$ kJ·mol^{-1}. Our adopted D° is in essential agreement with the value adopted by Brewer[12] and by Wagman *et al.*[3] It should be noted that a value of $D_0^\circ = 11.3 \pm 4.1$ kJ·mol^{-1} was determined by a mass spectrometric study of Wu, Ihle and Gingerich.[7] In light of the spectroscopic evidence, this value appears to be too large.

Heat Capacity and Entropy

The thermal functions are calculated using a direct summation technique analogous to the alkali dimers and diatomic halogens. Included in the calculation are the ground state and the three lowest excited states. Spectrocopic constants for the $^1\Sigma_g^+$ ground state are taken from an experimental study from Balfour and Douglas.[1] No known spectroscopic data exists for the three lowest excited electronic states of $Mg_2(g)$. In order to generate the spectroscopic constants of these states, a Morse potential was least squares fit to the calculated potential curves of Stevens and Krause,[4] an **ab initio** investigation which included configuration interaction. Although this procedure for estimating the spectroscopic data results in substantial uncertainty in the generated constants, the inclusion of the excited states results in thermal functions which are more realistic at temperatures greater than 1000 K. The large maximum in the heat capacity at 5000 K, for example, would not be present if the excited states were not included. Also, it should be noted that $Mg_2(g)$ is an example of a molecule where the traditional integration methods of calculating the thermal functions fail due to the shallow ground state.

The rotational levels are extrapolated to high J values according to the method of Khachkuruzov[5] who proposed a simpler form of Wooley's method.[6] For the ground state only, we included the so-called quasi-bound rotational levels above the dissociation limit.[9] The values used for J_{lim} and v_{max} are 93 and 17, respectively, as determined by.[8] Separate calculations were performed for each of the six isotopic dimeric species (made up from the three atomic isotopes ^{24}Mg, ^{25}Mg, ^{26}Mg) by adjusting the spectroscopic constants of ^{24}Mg using a standard reduced mass scaling routine.[10] The results were combined according to the natural abundance of the atoms, ^{24}Mg: 78.99%, ^{25}Mg: 10.00%, ^{26}Mg: 11.01%.[11] Splitting of the rotational levels in the $^3\Pi_g$ and $^3\Sigma_u^+$ states was taken into account only insofar as the degeneracy of these states were increased accordingly. The adopted value of $S^\circ(298.15\ K)$ is 0.64 J·K^{-1}·mol^{-1} smaller than that adopted by.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−9.463	288.158	288.158	INFINITE
100	38.343	206.636	264.861	−5.822	290.515	271.752	−141.949
200	28.193	229.790	242.505	−2.543	289.780	253.079	−66.098
250	25.711	235.789	240.594	−1.201	288.780	244.015	−50.984
298.15	24.293	240.186	240.186	0.000	287.625	235.495	−41.258
300	24.250	240.337	240.187	0.045	287.578	235.172	−40.947
350	23.340	244.001	240.478	1.233	286.242	226.541	−33.809
400	22.742	247.076	241.116	2.384	284.806	218.110	−28.482
450	22.329	249.730	241.929	3.510	283.292	209.863	−24.360
500	22.034	252.066	242.828	4.619	281.708	201.788	−21.081
600	21.649	256.046	244.711	6.801	278.356	186.115	−16.203
700	21.418	259.365	246.574	8.954	274.764	171.022	−12.762
800	21.268	262.214	248.355	11.088	270.922	156.461	−10.216
900	21.166	264.713	250.036	13.209	266.806	142.398	−8.265
1000	21.093	266.939	251.617	15.322	245.207	130.233	−6.803
1100	21.039	268.947	253.103	17.428	240.451	118.966	−5.649
1200	20.999	270.776	254.501	19.530	235.691	108.132	−4.707
1300	20.967	272.455	255.818	21.628	230.928	97.696	−3.925
1400	20.944	274.008	257.063	23.724	−28.657	93.960	−3.506
1500	20.927	275.452	258.241	25.817	−30.721	102.790	−3.579
1600	20.919	276.803	259.359	27.909	−32.786	111.758	−3.649
1700	20.923	278.071	260.423	30.001	−34.851	120.856	−3.713
1800	20.946	279.267	261.437	32.095	−36.915	130.074	−3.775
1900	20.998	280.401	262.406	34.192	−38.976	139.408	−3.833
2000	21.094	281.480	263.333	36.296	−41.029	148.850	−3.888
2100	21.253	282.513	264.221	38.413	−43.070	158.394	−3.940
2200	21.497	283.507	265.076	40.549	−45.092	168.035	−3.990
2300	21.853	284.470	265.898	42.716	−47.085	177.767	−4.037
2400	22.351	285.410	266.692	44.925	−49.038	187.585	−4.083
2500	23.024	286.336	267.459	47.192	−50.934	197.484	−4.126
2600	23.904	287.255	268.203	49.536	−52.757	207.457	−4.168
2700	25.023	288.177	268.925	51.980	−54.485	217.498	−4.208
2800	26.412	289.112	269.629	54.550	−56.093	227.601	−4.246
2900	28.096	290.067	270.318	57.273	−57.557	237.760	−4.283
3000	30.094	291.052	270.992	60.179	−58.847	247.966	−4.317
3100	32.417	292.076	271.656	63.302	−59.934	258.211	−4.351
3200	35.067	293.146	272.310	66.674	−60.788	268.488	−4.383
3300	38.032	294.270	272.959	70.326	−61.380	278.788	−4.413
3400	41.290	295.453	273.603	74.290	−61.683	289.101	−4.442
3500	44.805	296.700	274.245	78.593	−61.673	299.419	−4.469
3600	48.526	298.014	274.887	83.258	−61.331	309.732	−4.494
3700	52.393	299.396	275.530	88.303	−60.643	320.031	−4.518
3800	56.336	300.845	276.177	93.739	−59.603	330.306	−4.540
3900	60.277	302.360	276.829	99.570	−58.211	340.549	−4.561
4000	64.134	303.935	277.487	105.792	−56.475	350.753	−4.580
4100	67.825	305.564	278.152	112.391	−54.414	360.908	−4.598
4200	71.274	307.240	278.824	119.349	−52.053	371.010	−4.614
4300	74.410	308.955	279.505	126.636	−49.423	381.053	−4.629
4400	77.176	310.698	280.194	134.218	−46.563	391.031	−4.642
4500	79.525	312.460	280.891	142.057	−43.517	400.942	−4.654
4600	81.426	314.229	281.597	150.108	−40.335	410.785	−4.665
4700	82.864	315.996	282.310	158.327	−37.064	420.556	−4.674
4800	83.838	317.752	283.030	166.666	−33.756	430.258	−4.682
4900	84.358	319.487	283.756	175.079	−30.462	439.891	−4.689
5000	84.450	321.193	284.488	183.523	−27.228	449.457	−4.695
5100	84.145	322.863	285.224	191.956	−24.101	458.959	−4.701
5200	83.481	324.491	285.964	200.340	−21.121	468.402	−4.705
5300	82.502	326.072	286.706	208.641	−18.326	477.789	−4.709
5400	81.254	327.603	287.449	216.831	−15.748	487.125	−4.712
5500	79.780	329.081	288.193	224.885	−13.414	496.415	−4.715
5600	78.126	330.504	288.936	232.781	−11.349	505.665	−4.717
5700	76.331	331.871	289.677	240.505	−9.571	514.882	−4.718
5800	74.435	333.182	290.416	248.044	−8.095	524.070	−4.720
5900	72.470	334.438	291.151	255.390	−6.931	533.234	−4.721
6000	70.466	335.639	291.883	262.537	−6.088	542.382	−4.722

PREVIOUS: December 1974 (1 atm) CURRENT: September 1983 (1 bar)

Magnesium Silicate (Mg_2SiO_4) $Mg_2O_4Si_1$(cr)

$S°(298.15\ K) = 95.14 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2171 \pm 11\ K$

$\Delta_f H°(0\ K) = -2163.63 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2176.94 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [71.128 \pm 20.9]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Torgeson *et al.*[1] have reported a $\Delta_f H°(298.15\ K) = -15.1 \pm 0.2$ kcal·mol^{-1} for reaction (a). They used an HF solution calorimeter and measured the enthalpies of solution of each component. We derive $\Delta_f H°(Mg_2SiO_4, cr, 298.15\ K) = -520.30 \pm 1.0$ kcal·mol^{-1} using the $\Delta_f H°(298.15\ K)$ of MgO(cr) and SiO_2(cr, low quartz) from JANAF tables.

Kapustinskii *et al.*[2] used the same method but measured only $\Delta_f H°(298.15\ K) = 95.00 \pm 0.47$ kcal·mol^{-1} for reaction (b). We calculate $\Delta_f H°(Mg_2SiO_4, cr, 298.15\ K) = -522.27$ kcal·mol^{-1} using the $\Delta_f H°(298.15\ K)$ of H_2SiF_6(aq) from source 3 and the $\Delta_f H°(298.15\ K)$ of H_2O(l) and HF(aq) from source 4.

Reesman *et al.*[5] calculated a $\Delta_f G°(298.15\ K) = 42.46$ kcal·mol^{-1} for reaction (c) using aqueous solubility data. We use the $\Delta_f G°(298.15\ K)$ of H_2O(l) and OH (aq) from source 4, $\Delta_f G°(298.15\ K)$ of H_4SiO_4(aq) from source 3 and $\Delta_f G°(298.15\ K)$ of Mg^{++}(aq) from source 6 and we obtain a $\Delta_f G°(Mg_2SiO_4, cr, 298.15\ K) = -498.764$ kcal·mol^{-1}. We derive a $\Delta_f H°(Mg_2SiO_4, cr, 298.15\ K) = -524.848$ kcal·mol^{-1} using the above $\Delta_f G°(298.15\ K)$ of Mg_2SiO_4(cr) and the entropies of Mg(cr), Si(cr) and O_2(g) from the JANAF tables.

The adopted value is from the work of Torgeson *et al.*[1] which is considered to be the most reliable since it relates directly to the oxides. The other reported values are less accurate and involve uncertainties in the auxiliary data used to derive the heat of formation.

Source	Method	Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f G°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	hydrofluoric acid solution calorimeter	(a) 2 MgO(cr) + SiO_2(cr) = Mg_2SiO_4(cr)	−15.10 ± 0.2		−520.3
2	hydrofluoric acid solution calorimeter	(b) Mg_2SiO_4(cr) + 10 HF(aq, 4.44 H_2O) = 2 MgF_2(cr) + H_2SiF_6(714 HF(aq) + 322 OH_2O) + 4 H_2O(l)	95.0 ± 0.47	−522.27	
5	aqueous solubility	(c) Mg_2SiO_4(cr) + 4 H_2O( ) = 2 Mg^{++}(aq) + H_4SiO_4(aq) + 4 OH (aq)	42.46	−524.848	

Heat Capacity and Entropy

Low temperature heat capacities are from the data (53–295 K) of Kelley.[7] High temperature enthalpies have been measured (398–1808 K) by Orr.[8] High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. The entropy is based on $S°(50\ K) = 0.60$ cal·K^{-1}·mol^{-1}.

Fusion Data

T_{fus} is obtained from Davis *et al.*[9] $\Delta_{fus} H°$ is estimated from MacGregor's[10] phase diagrams of the Mg_2SiO_4–TiO_2system. The phase diagrams were determined at 10 and 20 kbars pressure.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−17.280	−2163.634	−2163.634	INFINITE
100	32.317	14.050	176.849	−16.280	−2169.994	−2134.453	1114.924
200	86.144	54.162	105.060	−10.180	−2174.908	−2096.757	547.617
298.15	118.688	95.140	95.140	0.	−2176.935	−2057.879	360.532
300	119.148	95.876	95.142	0.220	−2176.953	−2057.141	358.180
400	137.557	132.920	100.068	13.141	−2177.207	−2017.131	263.410
500	148.695	164.894	109.913	27.491	−2176.585	−1977.171	206.554
600	156.431	192.724	121.447	42.767	−2175.539	−1937.382	168.664
700	162.310	217.297	133.419	58.715	−2174.292	−1897.786	141.615
800	167.063	239.291	145.302	75.191	−2172.975	−1858.375	121.339
900	171.088	259.206	156.869	92.104	−2171.673	−1819.128	105.579
1000	174.607	277.418	168.026	109.392	−2187.632	−1778.598	92.904
1100	177.770	294.210	178.744	127.013	−2186.547	−1737.746	82.519
1200	180.665	309.804	189.024	144.936	−2185.281	−1697.000	73.868
1300	183.360	324.372	198.881	163.139	−2183.847	−1656.367	66.554
1400	185.895	338.054	208.338	181.602	−2437.073	−1609.516	60.052
1500	188.309	350.962	217.420	200.314	−2432.626	−1550.560	53.995
1600	190.619	363.190	226.152	219.261	−2428.036	−1491.904	48.706
1700	192.845	374.813	234.558	238.434	−2473.488	−1433.093	44.034
1800	195.008	385.897	242.660	257.828	−2468.404	−1372.040	39.816
1900	197.108	396.497	250.480	277.434	−2463.154	−1311.273	36.049
2000	199.163	406.660	258.036	297.248	−2457.742	−1250.787	32.667
2100	201.175	416.426	265.348	317.264	−2452.175	−1190.575	29.614
2171.000	202.673	423.139	270.399	331.600	--- CRYSTAL <--> LIQUID ---		
2200	203.154	425.833	272.430	337.487	−2446.445	−1130.631	26.845
2300	205.100	434.907	279.298	357.900	−2440.573	−1070.953	24.322
2400	207.020	443.676	285.965	378.506	−2434.554	−1011.534	22.015
2500	208.915	452.166	292.445	399.303	−2428.390	−952.367	19.899
2600	210.790	460.396	298.747	420.289	−2422.084	−893.451	17.950
2700	212.648	468.386	304.883	441.461	−2415.638	−834.778	16.150
2800	214.490	476.153	310.861	462.818	−2409.054	−776.348	14.483
2900	216.315	483.712	316.692	484.358	−2402.334	−718.156	12.935
3000	218.124	491.076	322.382	506.080	−2395.483	−660.197	11.495

PREVIOUS: September 1964 CURRENT: December 1967

Magnesium Silicate (Mg_2SiO_4) $Mg_2O_4Si_1$(cr)

$S°(298.15\ K) = [123.044]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2171 \pm 11\ K$

$\Delta_f H°(298.15\ K) = [-2113.88 \pm 20.9]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [71.128 \pm 20.9]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Mg_2SiO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(Mg_2SiO_4, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(2171\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1400 K. Below 1400 K the heat capacity is obtained from the heat capacity of the crystal. Above 1400 K the heat capacity is assumed constant and estimated as 49 $cal·K^{-1}·mol^{-1}$ or 7 $cal·K^{-1}$ g–atom^{-1}. $S°(l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	118.688	123.044	123.044	0.	−2113.878	−2003.141	350.942
300	119.148	123.780	123.046	0.220	−2113.895	−2002.454	348.658
400	137.557	160.824	127.972	13.141	−2114.149	−1965.234	256.633
500	148.695	192.798	137.817	27.491	−2113.528	−1928.065	201.424
600	156.431	220.628	149.351	42.767	−2112.482	−1891.067	164.632
700	162.310	245.201	161.323	58.715	−2111.235	−1854.261	138.367
800	167.063	267.195	173.206	75.191	−2109.918	−1817.640	118.680
900	171.088	287.110	184.773	92.104	−2108.615	−1781.184	103.377
1000	174.607	305.322	195.930	109.392	−2124.574	−1743.445	91.068
1100	177.770	322.114	206.648	127.013	−2123.489	−1705.382	80.982
1200	180.665	337.708	216.928	144.936	−2122.224	−1667.427	72.581
1300	183.360	352.276	226.785	163.139	−2120.789	−1629.585	65.478
1400	185.895	365.958	236.242	181.603	−2374.015	−1585.524	59.157
1400.000	185.895	365.958	236.242	181.603	GLASS <--> LIQUID		
1400.000	205.016	365.958	236.242	181.603	TRANSITION		
1500	205.016	380.103	245.367	202.104	−2367.777	−1529.422	53.259
1600	205.016	393.334	254.206	222.606	−2361.633	−1473.732	48.112
1700	205.016	405.763	262.759	243.108	−2405.758	−1417.978	43.569
1800	205.016	417.482	271.032	263.609	−2399.565	−1360.052	39.468
1900	205.016	428.567	279.035	284.111	−2393.419	−1302.469	35.807
2000	205.016	439.082	286.776	304.612	−2387.319	−1245.209	32.522
2100	205.016	449.085	294.269	325.114	−2381.266	−1188.252	29.556
2171.000	205.016	455.902	299.444	339.670	--- CRYSTAL <--> LIQUID ---		
2200	205.016	458.623	301.525	345.616	−2375.259	−1131.582	26.867
2300	205.016	467.736	308.555	366.117	−2369.298	−1075.186	24.418
2400	205.016	476.461	315.370	386.619	−2363.384	−1019.047	22.179
2500	205.016	484.830	321.982	407.120	−2357.515	−963.154	20.124
2600	205.016	492.871	328.401	427.622	−2351.693	−907.495	18.232
2700	205.016	500.609	334.637	448.124	−2345.917	−852.058	16.484
2800	205.016	508.065	340.699	468.625	−2340.189	−796.834	14.865
2900	205.016	515.259	346.595	489.127	−2334.508	−741.816	13.362
3000	205.016	522.209	352.333	509.628	−2328.877	−686.991	11.962
3100	205.016	528.932	357.922	530.130	−2323.296	−632.353	10.655
3200	205.016	535.441	363.368	550.632	−2317.767	−577.896	9.433
3300	205.016	541.749	368.679	571.133	−2312.291	−523.610	8.288
3400	205.016	547.870	373.860	591.635	−2306.872	−469.488	7.213
3500	205.016	553.813	378.917	612.136	−2301.510	−415.527	6.201
3600	205.016	559.588	383.855	632.638	−2680.362	−351.255	5.097
3700	205.016	565.205	388.681	653.140	−2674.711	−286.637	4.047
3800	205.016	570.673	393.399	673.641	−2669.130	−222.167	3.054
3900	205.016	575.998	398.013	694.143	−2663.620	−157.845	2.114
4000	205.016	581.189	402.528	714.644	−2658.186	−93.665	1.223

PREVIOUS: September 1964 CURRENT: December 1967

0 to 2171 K crystal
above 2171 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−17.280	−2163.634	−2163.634	INFINITE
100	32.317	14.050	176.849	−16.280	−2169.994	−2134.453	1114.924
200	86.144	54.162	105.060	−10.180	−2174.908	−2096.757	547.617
298.15	118.688	95.140	95.140	0.	−2176.935	−2057.879	360.532
300	119.148	95.876	95.142	0.220	−2176.953	−2057.141	358.180
400	137.557	132.920	100.068	13.141	−2177.207	−2017.131	263.410
500	148.695	164.894	109.913	27.491	−2176.585	−1977.171	206.554
600	156.431	192.724	121.447	42.767	−2175.539	−1937.382	168.664
700	162.310	217.297	133.419	58.715	−2174.292	−1897.786	141.615
800	167.063	239.291	145.302	75.191	−2172.975	−1858.375	121.339
900	171.088	259.206	156.869	92.104	−2171.673	−1819.128	105.579
1000	174.607	277.418	168.026	109.392	−2187.632	−1778.598	92.904
1100	177.770	294.210	178.744	127.013	−2186.547	−1737.746	82.519
1200	180.665	309.804	189.024	144.936	−2185.281	−1697.000	73.868
1300	183.360	324.372	198.881	163.139	−2183.847	−1656.367	66.554
1400	185.895	338.054	208.338	181.602	−2437.073	−1609.516	60.052
1500	188.309	350.962	217.420	200.314	−2432.626	−1550.560	53.995
1600	190.619	363.190	226.152	219.261	−2428.036	−1491.904	48.706
1700	192.845	374.813	234.558	238.434	−2473.488	−1433.093	44.034
1800	195.008	385.897	242.660	257.828	−2468.404	−1372.040	39.816
1900	197.108	396.497	250.480	277.434	−2463.154	−1311.273	36.049
2000	199.163	406.660	258.036	297.248	−2457.742	−1250.787	32.667
2100	201.175	416.426	265.348	317.264	−2452.175	−1190.575	29.614
2171.000	202.673	423.139	270.399	331.600	CRYSTAL <--> LIQUID TRANSITION		
2171.000	205.016	455.902	270.399	402.728			
2200	205.016	458.623	272.862	408.673	−2375.259	−1131.582	26.867
2300	205.016	467.736	281.138	429.175	−2369.298	−1075.186	24.418
2400	205.016	476.461	289.096	449.676	−2363.384	−1019.047	22.179
2500	205.016	484.830	296.759	470.178	−2357.515	−963.154	20.124
2600	205.016	492.871	304.148	490.680	−2351.693	−907.495	18.232
2700	205.016	500.609	311.282	511.181	−2345.917	−852.058	16.484
2800	205.016	508.065	318.178	531.683	−2340.189	−796.834	14.865
2900	205.016	515.259	324.850	552.184	−2334.508	−741.816	13.362
3000	205.016	522.209	331.314	572.686	−2328.877	−686.991	11.962
3100	205.016	528.932	337.581	593.188	−2323.296	−632.353	10.655
3200	205.016	535.441	343.663	613.689	−2317.767	−577.896	9.433
3300	205.016	541.749	349.570	634.191	−2312.291	−523.610	8.288
3400	205.016	547.870	355.313	654.692	−2306.872	−469.488	7.213
3500	205.016	553.813	360.900	675.194	−2301.510	−415.527	6.201
3600	205.016	559.588	366.339	695.696	−2680.362	−351.255	5.097
3700	205.016	565.205	371.639	716.197	−2674.711	−286.637	4.047
3800	205.016	570.673	376.805	736.699	−2669.130	−222.167	3.054
3900	205.016	575.998	381.844	757.200	−2663.620	−157.845	2.114
4000	205.016	581.189	386.763	777.702	−2658.186	−93.665	1.223

PREVIOUS: CURRENT: December 1967

$S°(298.15\ K) = 115.10 \pm 6.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2013 \pm 20\ K$

$\Delta_f H°(0\ K) = -2151.03 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2164.38 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [129.704]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from $\Delta_f H°(298.15\ K) = -4.1 \pm 0.25\ kcal \cdot mol^{-1}$ for the reaction $2\ MgO(cr) + TiO_2(rutile) \rightarrow Mg_2TiO_4(cr)$ measured by Kelley,[1] using a solution calorimetric method. The uncertainty of $\pm 1.5\ kcal \cdot mol^{-1}$ assigned to the enthalpy of formation is due primarily to TiO_2(rutile)

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52–296 K) of Todd.[2]

High temperature enthalpies have been measured (392–1817 K) by Orr.[3] High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values.

The entropy is based on $S°(51\ K) = 0.66 + 2.75 = 3.41\ cal \cdot K^{-1} \cdot mol^{-1}$, where the first term is a lattice contribution and the second term is a zero–point entropy of $2R\ln 2$ corresponding to random distribution of Ti and Mg on the octahedral sites of the spinel lattice. The adopted value is $S°(298.15\ K) = 27.51 \pm 1.5\ cal \cdot K^{-1} \cdot mol^{-1}$ instead of $24.76 \pm 0.15\ cal \cdot K^{-1} \cdot mol^{-1}$ as given by Todd.

Barth[4] showed from intensities of the x–ray diffraction lines that Mg_2TiO_4 is a spinel of the inverse (or variate) class. Thus, half of the Mg ions occupy the tetrahedral interstices in the oxygen lattice, while the remaining Mg ions and the Ti ions are (presumably) randomly located in the octahedral interstices. This conclusion was confirmed by Romeijn.[5]

King and Kelley[6] suggested that the degree of structural randomness is not established and that it may vary with the sample of Mg_2TiO_4; thus, they recommended an intermediate value of $R\ln 2$ for the zero–point entropy. In a previous review, however, Kelley[1] used the theoretical value of $2R\ln 2$ in order to make Mg_2TiO_4 stable relative to $MgTiO_3$ at high temperatures. We choose to adopt $2R\ln 2$, although the evidence is not conclusive. Recent studies of solid state reactions by Bautsch and Werner[7] indicate that $\Delta_r G°$ is negative for $MgTiO_3(cr) + MgO(cr) \rightarrow Mg_2TiO_4(cr)$ at 1673 K and above. Both $R\ln 2$ and $2R\ln 2$ are consistent with this evidence.

Fusion Data

Refer to the liquid table for details.

References

[1] K. K. Kelley, S. S. Todd and E. G. King, U. S. Bur. Mines RI 5059, (1954).
[2] S. S. Todd, J. Amer. Chem. Soc. **74**, 4669 (1952).
[3] R. L. Orr and J. P. Coughlin, J. Amer. Chem. Soc. **74**, 3186 (1952).
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[5] F. C. Romeijn, Philips Res. Rep. **8**, 304 (1953).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−18.836	−2151.027	−2151.027	INFINITE
100	34.639	26.740	204.267	−17.753	−2157.597	−2122.882	1108.880
200	94.320	70.337	125.901	−11.113	−2162.710	−2085.881	544.776
298.15	128.574	115.102	115.102	0.	−2164.383	−2047.719	358.752
300	129.026	115.899	115.104	0.238	−2164.393	−2046.995	356.414
400	146.285	155.637	120.405	14.093	−2164.204	−2007.859	262.199
500	156.410	189.441	130.920	29.260	−2163.228	−1968.875	205.687
600	163.686	218.628	143.161	45.280	−2161.887	−1930.126	168.032
700	169.582	244.316	155.813	61.952	−2160.357	−1891.618	141.154
800	174.707	267.301	168.337	79.171	−2158.713	−1853.339	121.011
900	179.360	288.151	180.509	96.877	−2157.045	−1815.267	105.355
1000	183.686	307.275	192.243	115.032	−2172.648	−1775.953	92.766
1100	187.778	324.975	203.515	133.607	−2171.269	−1736.349	82.452
1200	191.690	341.483	214.332	152.581	−2173.748	−1696.756	73.858
1300	195.456	356.976	224.714	171.940	−2171.398	−1657.101	66.583
1400	199.091	371.594	234.689	191.668	−2423.636	−1611.300	60.118
1500	202.614	385.451	244.282	211.754	−2418.140	−1553.467	54.097
1600	206.041	398.637	253.520	232.188	−2412.452	−1496.007	48.840
1700	209.367	411.229	262.429	252.959	−2406.595	−1438.908	44.212
1800	212.610	423.288	271.033	274.058	−2400.588	−1382.158	40.109
1900	215.765	434.868	279.353	295.478	−2394.453	−1325.745	36.447
2000	218.840	446.014	287.410	317.209	−2402.896	−1269.205	33.148
2013.000	219.233	447.433	288.438	320.056	− − − CRYSTAL <− −> LIQUID − − −		
2100	221.831	456.764	295.220	339.243	−2397.315	−1212.657	30.163
2200	224.752	467.151	302.800	361.573	−2391.484	−1156.379	27.456
2300	227.593	477.205	310.165	384.191	−2385.411	−1100.373	24.990
2400	230.358	486.950	317.329	407.089	−2379.103	−1044.637	22.736
2500	233.049	496.408	324.304	430.260	−2372.570	−989.168	20.668
2600	235.668	505.600	331.101	453.696	−2365.816	−933.964	18.764
2700	238.212	514.542	337.730	477.391	−2358.852	−879.024	17.006
2800	240.685	523.250	344.201	501.336	−2351.684	−824.346	15.378
2900	243.086	531.738	350.522	525.525	−2344.320	−769.929	13.868
3000	245.417	540.018	356.701	549.951	−2336.769	−715.767	12.463

PREVIOUS: June 1961 CURRENT: June 1967

$S°(298.15\ K) = [172.412]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2013 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-2046.33 \pm 6.3]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [129.704]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Mg_2TiO_4, l, 298.15\ K)$ is calculated from $\Delta_f H°(Mg_2TiO_4, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(2013\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 1400 K. Below 1400 K the heat capacity is obtained from the heat capacity of the crystal. Above 1400 K the heat capacity is assumed constant and estimated as 54.6 $cal·K^{-1}·mol^{-1}$ or 7.8 $cal·K^{-1}$ g–atom^{-1}. $S°(l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The incongruent melting point is obtained from Massazza[1]. Previous work by Coughanour[2] suggested congruent melting at 2005 K. $\Delta_{fus} H°$ is estimated from those of $Na_2O·2TiO_2$ and $Na_2O·TiO_2$ observed by Naylor[3] and $CaO·TiO_2·SiO_2$ observed by King.[4]

References

[1]F. Massazza and E. Sirchia, 16th Int. Congress of Pure and Appl. Chem., Inorg. Sect., Paris (1957), pp 161–8, Butterworths Scientific Publications, London, (1958).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	128.574	172.412	172.412	0.	−2046.329	−1946.752	341.063
300	129.026	173.209	172.415	0.238	−2046.338	−1946.134	338.852
400	146.285	212.948	177.716	14.093	−2046.150	−1912.729	249.777
500	156.410	246.751	188.230	29.260	−2045.173	−1879.476	196.347
600	163.686	275.939	200.472	45.280	−2043.833	−1846.458	160.748
700	169.582	301.626	213.124	61.952	−2042.303	−1813.681	135.339
800	174.707	324.612	225.648	79.171	−2040.658	−1781.133	116.296
900	179.360	345.462	237.820	96.877	−2038.991	−1748.792	101.497
1000	183.686	364.585	249.553	115.032	−2054.594	−1715.209	89.593
1100	187.778	382.286	260.825	133.607	−2053.214	−1681.336	79.840
1200	191.690	398.793	271.642	152.581	−2055.694	−1647.475	71.713
1300	195.456	414.286	282.025	171.940	−2053.344	−1613.550	64.833
1400	199.091	428.905	291.999	191.668	−2305.581	−1573.481	58.707
1400.000	199.091	428.905	291.999	191.668	GLASS <--> LIQUID TRANSITION		
1400.000	228.446	428.905	291.999	191.668			
1500	228.446	444.666	301.658	214.513	−2297.326	−1521.477	52.983
1600	228.446	459.410	311.061	237.357	−2289.228	−1470.019	47.991
1700	228.446	473.259	320.199	260.202	−2281.297	−1419.062	43.602
1800	228.446	486.317	329.069	283.047	−2273.545	−1368.568	39.715
1900	228.446	498.668	337.673	305.891	−2265.985	−1318.498	36.248
2000	228.446	510.386	346.018	328.736	−2273.315	−1268.368	33.126
2013.000	228.446	511.866	347.084	331.706	--- CRYSTAL <--> LIQUID ---		
2100	228.446	521.532	354.113	351.580	−2266.923	−1218.278	30.303
2200	228.446	532.159	361.966	374.425	−2260.577	−1168.490	27.743
2300	228.446	542.314	369.588	397.270	−2254.277	−1118.992	25.413
2400	228.446	552.037	376.989	420.114	−2248.023	−1069.766	23.283
2500	228.446	561.362	384.179	442.959	−2241.816	−1020.800	21.328
2600	228.446	570.322	391.167	465.804	−2235.654	−972.081	19.529
2700	228.446	578.944	397.963	488.648	−2229.540	−923.598	17.868
2800	228.446	587.252	404.576	511.493	−2223.473	−875.340	16.330
2900	228.446	595.268	411.014	534.338	−2217.453	−827.300	14.901
3000	228.446	603.013	417.286	557.182	−2211.483	−779.465	13.572
3100	228.446	610.504	423.398	580.027	−2205.563	−731.828	12.331
3200	228.446	617.757	429.359	602.872	−2199.695	−684.383	11.171
3300	228.446	624.786	435.175	625.716	−2193.881	−637.120	10.085
3400	228.446	631.606	440.853	648.561	−2188.122	−590.031	9.065
3500	228.446	638.228	446.398	671.405	−2182.422	−543.113	8.106
3600	228.446	644.664	451.817	694.250	−2176.783	−496.355	7.202
3700	228.446	650.923	457.114	717.095	−2580.306	−441.966	6.239
3800	228.446	657.015	462.294	739.939	−2573.563	−384.261	5.282
3900	228.446	662.949	467.364	762.784	−2566.947	−326.734	4.376
4000	228.446	668.733	472.326	785.629	−2560.458	−269.377	3.518

PREVIOUS: June 1961 CURRENT: June 1967

0 to 2013 K crystal
above 2013 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.836	−2151.027	−2151.027	INFINITE
100	34.639	26.740	204.267	−17.753	−2157.597	−2122.882	1108.880
200	94.320	70.337	125.901	−11.113	−2162.710	−2085.881	544.776
298.15	128.574	115.102	115.102	0.	−2164.383	−2047.719	358.752
300	129.026	115.899	115.104	0.238	−2164.393	−2046.995	356.414
400	146.285	155.637	120.405	14.093	−2164.204	−2007.859	262.199
500	156.410	189.441	130.920	29.260	−2163.228	−1968.875	205.687
600	163.686	218.628	143.161	45.280	−2161.887	−1930.126	168.032
700	169.582	244.316	155.813	61.952	−2160.357	−1891.618	141.154
800	174.707	267.301	168.337	79.171	−2158.713	−1853.339	121.011
900	179.360	288.151	180.509	96.877	−2157.045	−1815.267	105.355
1000	183.686	307.275	192.243	115.032	−2172.648	−1775.953	92.766
1100	187.778	324.975	203.515	133.607	−2171.269	−1736.349	82.452
1200	191.690	341.483	214.332	152.581	−2173.748	−1696.756	73.858
1300	195.456	356.976	224.714	171.940	−2171.398	−1657.101	66.583
1400	199.091	371.594	234.689	191.668	−2423.636	−1611.300	60.118
1500	202.614	385.451	244.282	211.754	−2418.140	−1553.467	54.097
1600	206.041	398.637	253.520	232.188	−2412.452	−1496.007	48.840
1700	209.367	411.229	262.429	252.959	−2406.595	−1438.908	44.212
1800	212.610	423.288	271.033	274.058	−2400.588	−1382.158	40.109
1900	215.765	434.868	279.353	295.478	−2394.453	−1325.745	36.447
2000	218.840	446.014	287.410	317.209	−2402.896	−1269.205	33.148
2013.000	219.233	447.433	288.438	320.056	CRYSTAL <--> LIQUID TRANSITION		
2013.000	228.446	511.866	288.438	449.760			
2100	228.446	521.532	297.896	469.635	−2266.923	−1218.278	30.303
2200	228.446	532.159	308.305	492.480	−2260.577	−1168.490	27.743
2300	228.446	542.314	318.260	515.324	−2254.277	−1118.992	25.413
2400	228.446	552.037	327.800	538.169	−2248.023	−1069.766	23.283
2500	228.446	561.362	336.957	561.013	−2241.816	−1020.800	21.328
2600	228.446	570.322	345.761	583.858	−2235.654	−972.081	19.529
2700	228.446	578.944	354.239	606.703	−2229.540	−923.598	17.868
2800	228.446	587.252	362.414	629.547	−2223.473	−875.340	16.330
2900	228.446	595.268	370.306	652.392	−2217.453	−827.300	14.901
3000	228.446	603.013	377.934	675.237	−2211.483	−779.465	13.572
3100	228.446	610.504	385.316	698.081	−2205.563	−731.828	12.331
3200	228.446	617.757	392.467	720.926	−2199.695	−684.383	11.171
3300	228.446	624.786	399.401	743.771	−2193.881	−637.120	10.085
3400	228.446	631.606	406.131	766.615	−2188.122	−590.031	9.065
3500	228.446	638.228	412.668	789.460	−2182.422	−543.113	8.106
3600	228.446	644.664	419.024	812.305	−2176.783	−496.355	7.202
3700	228.446	650.923	425.207	835.149	−2580.306	−441.966	6.239
3800	228.446	657.015	431.227	857.994	−2573.563	−384.261	5.282
3900	228.446	662.949	437.093	880.838	−2566.947	−326.734	4.376
4000	228.446	668.733	442.812	903.683	−2560.458	−269.377	3.518

PREVIOUS: CURRENT: June 1967

Magnesium Silicide (Mg_2Si) CRYSTAL $M_r = 76.6955$

$S°(298.15\ K) = [81.588]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1375\ K$

$\Delta_f H°(298.15\ K) = [-77.822]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [85.772]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ and T_{fus} from NBS.[1]

Heat Capacity and Entropy

$C_p°$ and $\Delta_{fus} H°$ from Kubaschewski and Evans.[2] $S°(298.15\ K)$ estimated.

References

[1]U. S. Nat. Bur. Stand., Circ. 500, (1952).
[2]O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," 3rd ed., Pergamon Press Ltd., New York, (1958).

Magnesium Silicide (Mg_2Si) $Mg_2Si_1(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	67.864	81.588	81.588	0.	−77.822	−77.055	13.500
300	67.994	82.008	81.589	0.126	−77.826	−77.050	13.416
400	73.764	102.413	84.332	7.232	−77.951	−76.770	10.025
500	77.278	119.268	89.683	14.793	−78.002	−76.468	7.989
600	79.831	133.589	95.837	22.651	−78.054	−76.157	6.630
700	82.006	146.062	102.140	30.745	−78.152	−75.833	5.659
800	83.889	157.137	108.335	39.041	−78.342	−75.491	4.929
900	85.688	167.122	114.321	47.520	−78.661	−75.117	4.360
1000	87.404	176.239	120.064	56.175	−96.329	−73.274	3.827
1100	89.077	184.649	125.558	65.000	−97.022	−70.933	3.368
1200	90.667	192.468	130.812	73.987	−97.596	−68.536	2.983
1300	92.257	199.788	135.839	83.134	−98.052	−66.095	2.656
1375.000	93.450	204.996	139.470	90.098	--- CRYSTAL <--> LIQUID ---		
1400	93.805	206.684	140.655	92.439	−353.209	−57.289	2.137
1500	95.312	213.207	145.277	101.896	−350.734	−36.237	1.262
1600	96.776	219.405	149.718	111.500	−348.152	−15.354	0.501
1700	98.198	225.315	153.992	121.249	−395.645	5.811	−0.179
1800	99.579	230.967	158.113	131.139	−392.633	29.339	−0.851
1900	100.918	236.387	162.091	141.164	−389.485	52.697	−1.449
2000	102.215	241.597	165.937	151.321	−386.205	75.886	−1.982
2100	103.470	246.615	169.660	161.606	−382.798	98.907	−2.460
2200	104.684	251.456	173.268	172.014	−379.268	121.763	−2.891
2300	105.855	256.136	176.770	182.541	−375.620	144.456	−3.281
2400	106.985	260.665	180.172	193.183	−371.859	166.988	−3.634
2500	108.073	265.054	183.480	203.936	−367.989	189.360	−3.956

PREVIOUS: CURRENT: December 1960

$S°(298.15\ K)$ = [123.472] $J \cdot K^{-1} \cdot mol^{-1}$
T_{fus} = 1375 K

$\Delta_f H°(298.15\ k)$ = [−3.327] $kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = [85.772] $kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Mg_2Si, l, 298.15\ K)$ is calculated from $\Delta_f H°(Mg_2Si, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1375\ K) - H°(298.15\ K)$, between the crystal and liquid.

Fusion Data

T_{fus} from.[1] $\Delta_{fus} H°$ from Kubaschewski and Evans.[2] Other data estimated.

References

[1]U. S. Nat. Bur. Stand., Circ. 500, (1952).
[2]O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry", 3rd ed., Pergamon Press. Ltd., New York, (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	94.140	123.472	123.472	0.	−3.327	−15.048	2.636
300	94.140	124.054	123.474	0.174	−3.282	−15.121	2.633
400	94.140	151.136	127.166	9.588	−1.100	−19.408	2.534
500	94.140	172.143	134.139	19.002	0.703	−24.201	2.528
600	94.140	189.307	141.947	28.416	2.206	−29.327	2.553
700	94.140	203.819	149.776	37.830	3.428	−34.683	2.588
800	94.140	216.389	157.334	47.244	4.357	−40.195	2.624
900	94.140	227.477	164.524	56.658	4.971	−45.804	2.658
1000	94.140	237.396	171.324	66.072	−11.938	−50.039	2.614
1100	94.140	246.369	177.745	75.486	−12.041	−53.844	2.557
1200	94.140	254.560	183.810	84.900	−12.188	−57.638	2.509
1300	94.140	262.095	189.546	94.314	−12.376	−61.418	2.468
1375.000	94.140	267.375	193.648	101.375	--- CRYSTAL <--> LIQUID ---		
1400	94.140	269.072	194.980	103.728	−267.425	−58.848	2.196
1500	94.140	275.567	200.138	113.142	−264.992	−44.035	1.533
1600	94.140	281.642	205.045	122.556	−262.602	−29.383	0.959
1700	94.140	287.349	209.720	131.970	−310.430	−14.432	0.443
1800	94.140	292.730	214.184	141.384	−307.893	2.906	−0.084
1900	94.140	297.820	218.453	150.798	−305.356	20.104	−0.553
2000	94.140	302.649	222.543	160.212	−302.819	37.168	−0.971
2100	94.140	307.242	226.468	169.626	−300.282	54.105	−1.346
2200	94.140	311.621	230.240	179.040	−297.747	70.921	−1.684
2300	94.140	315.806	233.870	188.454	−295.212	87.622	−1.990
2400	94.140	319.813	237.368	197.868	−292.679	104.212	−2.268
2500	94.140	323.656	240.743	207.282	−290.148	120.697	−2.522
2600	94.140	327.348	244.003	216.696	−287.621	137.081	−2.754
2700	94.140	330.901	247.156	226.110	−285.098	153.368	−2.967
2800	94.140	334.324	250.209	235.524	−282.582	169.562	−3.163
2900	94.140	337.628	253.167	244.938	−280.074	185.665	−3.344
3000	94.140	340.819	256.035	254.352	−277.576	201.683	−3.512
3100	94.140	343.906	258.820	263.766	−275.091	217.617	−3.667
3200	94.140	346.895	261.526	273.180	−272.623	233.471	−3.811
3300	94.140	349.792	264.157	282.594	−270.173	249.249	−3.945
3400	94.140	352.602	266.718	292.008	−267.745	264.952	−4.070
3500	94.140	355.331	269.211	301.422	−265.344	280.585	−4.188
3600	94.140	357.983	271.640	310.836	−647.124	306.610	−4.449
3700	94.140	360.563	274.008	320.250	−644.373	333.065	−4.702
3800	94.140	363.073	276.319	329.664	−641.662	359.445	−4.941
3900	94.140	365.518	278.575	339.078	−638.996	385.756	−5.167
4000	94.140	367.902	280.779	348.492	−636.378	411.998	−5.380

PREVIOUS: CURRENT: December 1960

0 to 1375 K crystal
above 1375 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	67.864	81.588	81.588	0.	−77.822	−77.055	13.500
300	67.994	82.008	81.589	0.126	−77.826	−77.050	13.416
400	73.764	102.413	84.332	7.232	−77.951	−76.770	10.025
500	77.278	119.268	89.683	14.793	−78.002	−76.468	7.989
600	79.831	133.589	95.837	22.651	−78.054	−76.157	6.630
700	82.006	146.062	102.140	30.745	−78.152	−75.833	5.659
800	83.889	157.137	108.335	39.041	−78.342	−75.491	4.929
900	85.688	167.122	114.321	47.520	−78.661	−75.117	4.360
1000	87.404	176.239	120.064	56.175	−96.329	−73.274	3.827
1100	89.077	184.649	125.558	65.000	−97.022	−70.933	3.368
1200	90.667	192.468	130.812	73.987	−97.596	−68.536	2.983
1300	92.257	199.788	135.839	83.134	−98.052	−66.095	2.656
1375.000	93.450	204.996	139.470	90.098	CRYSTAL <--> LIQUID		
1375.000	94.140	267.375	139.470	175.870	TRANSITION		
1400	94.140	269.072	141.769	178.223	−267.425	−58.848	2.196
1500	94.140	275.567	150.475	187.637	−264.992	−44.035	1.533
1600	94.140	281.642	158.485	197.051	−262.602	−29.383	0.959
1700	94.140	287.349	165.899	206.465	−310.430	−14.432	0.443
1800	94.140	292.730	172.797	215.879	−307.893	2.906	−0.084
1900	94.140	297.820	179.245	225.293	−305.356	20.104	−0.553
2000	94.140	302.649	185.295	234.707	−302.819	37.168	−0.971
2100	94.140	307.242	190.994	244.121	−300.282	54.105	−1.346
2200	94.140	311.621	196.378	253.535	−297.747	70.921	−1.684
2300	94.140	315.806	201.480	262.949	−295.212	87.622	−1.990
2400	94.140	319.813	206.328	272.363	−292.679	104.212	−2.268
2500	94.140	323.656	210.945	281.777	−290.148	120.697	−2.522
2600	94.140	327.348	215.351	291.191	−287.621	137.081	−2.754
2700	94.140	330.901	219.566	300.605	−285.098	153.368	−2.967
2800	94.140	334.324	223.603	310.019	−282.582	169.562	−3.163
2900	94.140	337.628	227.479	319.433	−280.074	185.665	−3.344
3000	94.140	340.819	231.204	328.847	−277.576	201.683	−3.512
3100	94.140	343.906	234.790	338.261	−275.091	217.617	−3.667
3200	94.140	346.895	238.247	347.675	−272.623	233.471	−3.811
3300	94.140	349.792	241.583	357.089	−270.173	249.249	−3.945
3400	94.140	352.602	244.807	366.503	−267.745	264.952	−4.070
3500	94.140	355.331	247.926	375.917	−265.344	280.585	−4.188
3600	94.140	357.983	250.947	385.331	−647.124	306.610	−4.449
3700	94.140	360.563	253.875	394.745	−644.373	333.065	−4.702
3800	94.140	363.073	256.715	404.159	−641.662	359.445	−4.941
3900	94.140	365.518	259.474	413.573	−638.996	385.756	−5.167
4000	94.140	367.902	262.155	422.987	−636.378	411.998	−5.380

PREVIOUS: CURRENT: December 1960

$S°(298.15\ K) = [87.864 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -461.08 \pm 4.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation
Data from Douglas *et al.*[1]

Heat Capacity and Entropy
Data from Douglas *et al.*[1]

Reference
[1]F. B. Douglas, A. C. Victor, and A. R. Beaudoin, U. S. Nat. Bur. Stand., Report 6928, Appendix B, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.516	87.864	87.864	0.	−461.077	−400.923	70.240
300	104.600	88.511	87.866	0.193	−461.075	−400.549	69.742
400	107.654	119.021	92.005	10.806	−461.046	−380.381	49.673
500	110.709	143.371	99.922	21.724	−461.067	−360.213	37.631
600	113.763	163.826	108.913	32.948	−461.128	−340.037	29.603
700	116.817	181.592	118.053	44.477	−461.258	−319.846	23.867
800	119.872	197.390	127.001	56.311	−461.498	−299.630	19.564
823.000	120.574	200.797	129.016	59.076		I <-> II	
823.000	123.846	201.916	129.016	59.997		TRANSITION	
900	123.846	212.993	135.733	69.533	−460.808	−279.470	16.220
1000	123.846	226.041	144.123	81.918	−487.232	−257.154	13.432
1061.000	123.846	233.374	149.046	89.472		II <-> III	
1061.000	123.595	234.399	149.046	90.560		TRANSITION	
1100	123.595	238.861	152.152	95.380	−487.359	−234.128	11.118
1200	123.595	249.615	159.832	107.740	−488.641	−211.050	9.187
1300	123.595	259.508	167.124	120.100	−489.968	−187.864	7.548
1400	123.595	268.668	174.054	132.459	−873.563	−155.073	5.786
1500	123.595	277.195	180.649	144.819	−870.908	−103.845	3.616
1600	123.595	285.171	186.935	157.178	−868.283	−52.793	1.724
1700	123.595	292.664	192.936	169.538	−865.684	−1.905	0.059
1800	123.595	299.729	198.675	181.897	−863.110	48.831	−1.417
1900	123.595	306.411	204.171	194.257	−860.556	99.425	−2.733
2000	123.595	312.751	209.443	206.616	−858.022	149.885	−3.915
2100	123.595	318.781	214.507	218.976	−855.504	200.218	−4.980
2200	123.595	324.531	219.378	231.335	−853.002	250.432	−5.946
2300	123.595	330.025	224.071	243.695	−850.516	300.532	−6.825
2400	123.595	335.285	228.596	256.054	−848.043	350.524	−7.629
2500	123.595	340.330	232.965	268.414	−845.586	400.414	−8.366

PREVIOUS: CURRENT: December 1960

$S°(298.15\ K) = [188.280]\ J·K^{-1}·mol^{-1}$
$T_{fus} \approx 1621\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -3745.10 \pm 10.5\ kJ·mol^{-1}$
$\Delta_{fus} H° = [121.336 \pm 41.8]\ kJ·mol^{-1}$

Enthalpy of Formation

The selected $\Delta_f H°(298.15\ K)$ is a weighted average of a revised calorimetric determination and a 3rd law calculation using equilibrium data.

A calorimetric determination of the enthalpy of formation reported by Stevens and Turkdogan[1] was revised three ways:

1. The enthalpy of reaction for the reaction $3MgO(cr) + P_2O_5(orthorohombic) \rightarrow Mg_3P_2O_8(cr)$ had been evaluated at 348 K. A small temperature correction to 298.15 K was made with thermal data not available to Stevens and Turkdogan[1] on MgO (Giauque (2)), P_2O_5 JANAF Table, December 31, 1962) and $Mg_3P_2O_8$ (this table).

2. A new $\Delta_f H°(298.15\ K)$ for P_2O_5(hexagonal) as reported by Holmes[3] was combined with the enthalpy of reaction, -6.85 ± 1.0 $kcal·mol^{-1}$, for the reaction: P_2O_5(hexagonal) $\rightarrow$ P_2O_5(orthorhombic) as reported by Hill *et. al.*[4].

3. A correction of $+8.35\ kcal·mol^{-1}$ was made for the change in phosphorus reference state from white (α) $\rightarrow$ red (V). (The correction is $+8.35\ kcal·mol^{-1}$ of $Mg_3P_2O_8$ or $+4.173\ kcal·mol^{-1}$ of P.)

This revised $\Delta_f H°(298.15\ K)$, $897.60 \pm 2.0\ kcal·mol^{-1}$, would appear to be more reliable than the original value reported by Stevens and Turkdogan[1].

For the reaction $Mg_3P_2O_8(cr) + 5\ H_2(g) \rightarrow 3\ MgO(cr) + P_2(g) + 5\ H_2O(g)$, the 3rd law treatment of the equilibrium data of Bookey[5] and the JANAF table free energy functions gave a $\Delta_f H°(298.15\ K) = -893.11\ kcal·mol^{-1}$.

The quantity, $-895.10 \pm 2.50\ kcal·mol^{-1}$, is taken as the most probable value for the enthalpy of formation of magnesium orthophosphate.

Heat Capacity and Entropy

The entropy at 298.15 was estimated by considering the additive entropy constants of Kelley[6] and Evans and Kubaschewski.[7] The heat capacity was estimated in a similar manner by considering the heat capacities of the constituent elements and related compounds such as Mg, O_2, MgO, P, P_2O_5, $Ca_2P_2O_7$, and $Ca_3P_2O_8$.

Fusion Data

The melting point, 1621 K, as reported by Stevens and Turkdogan[1] was selected. There is disagreement on the melting point in the literature. From the work of Winter,[8] Kelley[9] has quoted a melting point of 1457 K and has calculated a "rather uncertain value" of $11.300\ kcal·mol^{-1}$ for the heat of fusion. Bookey[5] has found a melting point of 1703 K. Berak[10] gives 1630 K as the melting point.

References

[1]C. G. Stevens and E. T. Turkdogan, Trans. Faraday Soc. **50**, 370 (1954).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	212.756	188.280	188.280	0.	−3745.098	−3502.859	613.686
300	213.384	189.598	188.284	0.394	−3745.148	−3501.356	609.640
400	240.162	254.762	196.988	23.110	−3748.487	−3419.399	446.528
500	262.337	310.777	214.270	48.254	−3748.843	−3337.054	348.620
600	282.211	360.377	234.563	75.488	−3747.814	−3254.772	283.353
700	301.248	405.305	255.793	104.658	−3745.544	−3172.761	236.754
800	320.620	446.840	277.109	135.785	−3741.994	−3091.163	201.832
900	335.975	485.488	298.140	168.613	−3737.409	−3010.075	174.700
1000	351.540	521.754	318.706	203.048	−3757.656	−2927.411	152.912
1100	360.075	555.683	338.726	238.653	−3751.645	−2844.671	135.082
1200	365.682	587.236	358.136	274.920	−3872.275	−2760.346	120.155
1300	373.757	616.851	376.909	311.925	−3863.611	−2668.032	107.203
1400	377.899	644.714	395.053	349.525	−4236.710	−2566.904	95.772
1500	379.907	670.862	412.578	387.425	−4223.344	−2448.098	85.250
1600	380.744	695.407	429.496	425.458	−4209.957	−2330.185	76.073
1621.000	380.920	700.373	432.973	433.455	--- CRYSTAL <---> LIQUID ---		
1700	381.581	718.517	445.824	463.578	−4196.587	−2213.109	68.001
1800	381.581	740.328	461.585	501.736	−4183.281	−2096.819	60.848
1900	381.581	760.959	476.804	539.894	−4170.074	−1981.265	54.469
2000	381.581	780.531	491.505	578.052	−4156.965	−1866.404	48.745
2100	381.581	799.149	505.715	616.210	−4143.953	−1752.196	43.583
2200	381.581	816.900	519.460	654.368	−4131.036	−1638.604	38.905
2300	381.581	833.862	532.763	692.526	−4118.215	−1525.600	34.647
2400	381.581	850.102	545.650	730.685	−4105.489	−1413.152	30.756
2500	381.581	865.679	558.142	768.843	−4092.858	−1301.231	27.188
2600	381.581	880.644	570.260	807.001	−4080.321	−1189.814	23.904
2700	381.581	895.045	582.024	845.159	−4067.878	−1078.876	20.872
2800	381.581	908.923	593.452	883.317	−4055.529	−968.398	18.066
2900	381.581	922.313	604.563	921.475	−4043.276	−858.362	15.461
3000	381.581	935.249	615.371	959.633	−4031.118	−748.744	13.037

PREVIOUS: December 1960 CURRENT: March 1963

$S°(298.15\ K) = [235.102]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1621\ K$

$\Delta_f H°(298.15\ K) = [-3663.190]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [121.336 \pm 41.8]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Mg_3P_2O_8, l, 298.15\ K)$ is calculated from $\Delta_f H°(Mg_3P_2O_8, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1621\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated as 13/11 of the corresponding heat capacity of $Ca_2P_2O_7$ as given in Kelley,[1] $S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The enthalpy of fusion was estimated by taking 13/11 of the $\Delta_{fus} H°$ of $Ca_2P_2O_7$ as given in Kelley.[1]

Reference

[1]K. K. Kelley, U. S. Bur. Mines Bull. 5841, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	212.756	235.102	235.102	0.	−3663.190	−3434.910	601.782
300	213.384	236.420	235.106	0.394	−3663.240	−3433.494	597.824
400	240.162	301.584	243.810	23.110	−3666.578	−3356.219	438.277
500	262.337	357.600	261.092	48.254	−3666.934	−3278.557	342.508
600	282.211	407.199	281.385	75.488	−3665.905	−3200.957	278.668
700	301.248	452.127	302.615	104.658	−3663.635	−3123.628	233.088
800	320.620	493.663	323.931	135.785	−3660.086	−3046.712	198.930
900	335.975	532.311	344.962	168.613	−3655.500	−2970.306	172.392
1000	351.540	568.576	365.529	203.048	−3675.747	−2892.324	151.080
1100	360.075	602.505	385.548	238.653	−3669.736	−2814.266	133.638
1200	365.682	634.097	404.960	274.965	−3790.321	−2734.626	119.035
1220.000	366.451	640.148	408.766	282.287	GLASS <--> LIQUID		
1220.000	475.302	640.148	408.766	282.287	TRANSITION		
1300	475.302	670.336	423.944	320.311	−3773.316	−2647.268	106.369
1400	475.302	705.560	442.817	367.841	−4136.486	−2551.863	95.211
1500	475.302	738.353	461.439	415.371	−4113.490	−2439.480	84.950
1600	475.302	769.028	479.715	462.901	−4090.605	−2328.626	76.022
1621.000	475.302	775.226	483.503	472.883	--- CRYSTAL <--> LIQUID ---		
1700	475.302	797.843	497.589	510.432	−4067.825	−2219.200	68.188
1800	475.302	825.011	515.032	557.962	−4045.147	−2111.114	61.263
1900	475.302	850.709	532.029	605.492	−4022.568	−2004.284	55.102
2000	475.302	875.089	548.577	653.022	−4000.086	−1898.640	49.587
2100	475.302	898.279	564.682	700.553	−3977.702	−1794.118	44.626
2200	475.302	920.390	580.352	748.083	−3955.413	−1690.659	40.141
2300	475.302	941.518	595.599	795.613	−3933.220	−1588.214	36.069
2400	475.302	961.747	610.437	843.143	−3911.122	−1486.733	32.358
2500	475.302	981.149	624.880	890.674	−3889.119	−1386.169	28.962
2600	475.302	999.791	638.943	938.204	−3867.209	−1286.483	25.846
2700	475.302	1017.729	652.642	985.734	−3845.394	−1187.638	22.976
2800	475.302	1035.015	665.992	1033.264	−3823.673	−1089.599	20.327
2900	475.302	1051.694	679.006	1080.795	−3802.047	−992.339	17.874
3000	475.302	1067.807	691.699	1128.325	−3780.518	−895.818	15.598
3100	475.302	1083.392	704.084	1175.855	−3759.085	−800.013	13.480
3200	475.302	1098.482	716.175	1223.385	−3737.751	−704.902	11.506
3300	475.302	1113.108	727.982	1270.916	−3716.518	−610.456	9.663
3400	475.302	1127.298	739.519	1318.446	−3695.387	−516.648	7.937
3500	475.302	1141.075	750.797	1365.976	−3674.363	−423.464	6.320
3600	475.302	1154.465	761.824	1413.506	−3653.448	−330.876	4.801
3700	475.302	1167.488	772.613	1461.036	−3632.647	−238.871	3.372
3800	475.302	1180.163	783.172	1508.567	−3611.963	−147.421	2.026
3900	475.302	1192.510	793.510	1556.097	−3591.401	−56.516	0.757
4000	475.302	1204.543	803.636	1603.627	−3570.967	33.860	−0.442
4100	475.302	1216.280	813.558	1651.157	−3550.666	123.729	−1.576
4200	475.302	1227.733	823.284	1698.688	−3530.503	213.104	−2.650
4300	475.302	1238.917	832.820	1746.218	−3510.485	302.002	−3.669
4400	475.302	1249.844	842.174	1793.748	−3490.617	390.433	−4.635
4500	475.302	1260.526	851.353	1841.278	−3470.904	478.414	−5.553

PREVIOUS: December 1960 CURRENT: March 1963

0 to 1621 K crystal
above 1621 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	212.756	188.280	188.280	0.	−3745.098	−3502.859	613.686
300	213.384	189.598	188.284	0.394	−3745.148	−3501.356	609.640
400	240.162	254.762	196.988	23.110	−3748.487	−3419.399	446.528
500	262.337	310.777	214.270	48.254	−3748.843	−3337.054	348.620
600	282.211	360.377	234.563	75.488	−3747.814	−3254.772	283.353
700	301.248	405.305	255.793	104.658	−3745.544	−3172.761	236.754
800	320.620	446.840	277.109	135.785	−3741.994	−3091.163	201.832
900	335.975	485.488	298.140	168.613	−3737.409	−3010.075	174.700
1000	351.540	521.754	318.706	203.048	−3757.656	−2927.411	152.912
1100	360.075	555.683	338.726	238.653	−3751.645	−2844.671	135.082
1200	365.682	587.236	358.136	274.920	−3872.275	−2760.346	120.155
1300	373.757	616.851	376.909	311.925	−3863.611	−2668.032	107.203
1400	377.899	644.714	395.053	349.525	−4236.710	−2566.904	95.772
1500	379.907	670.862	412.578	387.425	−4223.344	−2448.098	85.250
1600	380.744	695.407	429.496	425.458	−4209.957	−2330.185	76.073
1621.000	380.920	700.373	432.973	433.455	CRYSTAL <--> LIQUID		
1621.000	475.302	775.226	432.973	554.791	TRANSITION		
1700	475.302	797.843	449.408	592.340	−4067.825	−2219.200	68.188
1800	475.302	825.011	469.527	639.870	−4045.147	−2111.114	61.263
1900	475.302	850.709	488.919	687.401	−4022.568	−2004.284	55.102
2000	475.302	875.089	507.623	734.931	−4000.086	−1898.640	49.587
2100	475.302	898.279	525.678	782.461	−3977.702	−1794.118	44.626
2200	475.302	920.390	543.121	829.991	−3955.413	−1690.659	40.141
2300	475.302	941.518	559.987	877.522	−3933.220	−1588.214	36.069
2400	475.302	961.747	576.308	925.052	−3911.122	−1486.733	32.358
2500	475.302	981.149	592.116	972.582	−3889.119	−1386.169	28.962
2600	475.302	999.791	607.440	1020.112	−3867.209	−1286.483	25.846
2700	475.302	1017.729	622.306	1067.643	−3845.394	−1187.638	22.976
2800	475.302	1035.015	636.739	1115.173	−3823.673	−1089.599	20.327
2900	475.302	1051.694	650.762	1162.703	−3802.047	−992.339	17.874
3000	475.302	1067.807	664.396	1210.233	−3780.518	−895.818	15.598
3100	475.302	1083.392	677.662	1257.764	−3759.085	−800.013	13.480
3200	475.302	1098.482	690.578	1305.294	−3737.751	−704.902	11.506
3300	475.302	1113.108	703.162	1352.824	−3716.518	−610.456	9.663
3400	475.302	1127.298	715.429	1400.354	−3695.387	−516.648	7.937
3500	475.302	1141.075	727.394	1447.885	−3674.363	−423.464	6.320
3600	475.302	1154.465	739.072	1495.415	−3653.448	−330.876	4.801
3700	475.302	1167.488	750.476	1542.945	−3632.647	−238.871	3.372
3800	475.302	1180.163	761.617	1590.475	−3611.963	−147.421	2.026
3900	475.302	1192.510	772.508	1638.006	−3591.401	−56.516	0.757
4000	475.302	1204.543	783.159	1685.536	−3570.967	33.860	−0.442
4100	475.302	1216.280	793.581	1733.066	−3550.666	123.729	−1.576
4200	475.302	1227.733	803.782	1780.596	−3530.503	213.104	−2.650
4300	475.302	1238.917	813.772	1828.126	−3510.485	302.002	−3.669
4400	475.302	1249.844	823.559	1875.657	−3490.617	390.433	−4.635
4500	475.302	1260.526	833.151	1923.187	−3470.904	478.414	−5.553

PREVIOUS: CURRENT: March 1963

Continued from page 1539

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REFERENCE STATE

0	to	980 K	crystal, alpha
980	to	1360 K	crystal, beta
1360	to	1410 K	crystal, gamma
1410	to	1517 K	crystal, delta
1517	to	2335 K	liquid
2335	to	6000 K	ideal gas, monatomic

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.994	0.	0.	0.
100	14.723	8.875	52.876	−4.400	0.	0.	0.
200	23.054	22.133	34.325	−2.438	0.	0.	0.
298.15	26.299	32.010	32.010	0.	0.	0.	0.
300	26.347	32.173	32.010	0.049	0.	0.	0.
400	28.527	40.066	33.072	2.798	0.	0.	0.
500	30.292	46.696	35.152	5.772	0.	0.	0.
600	31.899	52.362	37.559	8.882	0.	0.	0.
700	33.426	57.395	40.039	12.149	0.	0.	0.
800	34.915	61.956	42.498	15.566	0.	0.	0.
900	36.384	66.153	44.896	19.131	0.	0.	0.
980.000	37.545	69.300	46.761	22.088	ALPHA <--> BETA TRANSITION		
980.000	37.572	71.572	46.761	24.314			
1000	37.698	72.332	47.265	25.067	0.	0.	0.
1100	38.116	75.945	49.710	28.858	0.	0.	0.
1200	38.535	79.279	52.037	32.690	0.	0.	0.
1300	38.953	82.380	54.253	36.565	0.	0.	0.
1361.000	39.204	84.172	55.554	38.948	BETA <--> GAMMA TRANSITION		
1361.000	43.095	85.731	55.554	41.070			
1400	43.430	86.953	56.412	42.757	0.	0.	0.
1412.000	43.514	87.324	56.673	43.279	GAMMA <--> DELTA TRANSITION		
1412.000	45.229	88.655	56.673	45.158			
1500	45.982	91.413	58.631	49.173	0.	0.	0.
1519.000	46.108	91.993	59.045	50.048	DELTA <--> LIQUID TRANSITION		
1519.000	46.024	99.931	59.045	62.106			
1600	46.024	102.322	61.176	65.834	0.	0.	0.
1700	46.024	105.112	63.679	70.436	0.	0.	0.
1800	46.024	107.743	66.055	75.039	0.	0.	0.
1900	46.024	110.231	68.315	79.641	0.	0.	0.
2000	46.024	112.592	70.470	84.244	0.	0.	0.
2100	46.024	114.837	72.530	88.846	0.	0.	0.
2200	46.024	116.978	74.502	93.448	0.	0.	0.
2300	46.024	119.024	76.393	98.051	0.	0.	0.
2334.526	46.024	119.710	77.029	99.640	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
2334.526	20.951	216.509	77.029	325.620			
2400	20.997	217.089	80.842	326.993	0.	0.	0.
2500	21.085	217.948	86.309	329.097	0.	0.	0.
2600	21.198	218.777	91.388	331.211	0.	0.	0.
2700	21.341	219.580	96.121	333.338	0.	0.	0.
2800	21.515	220.359	100.545	335.480	0.	0.	0.
2900	21.726	221.118	104.689	337.642	0.	0.	0.
3000	21.976	221.858	108.583	339.827	0.	0.	0.
3100	22.269	222.583	112.248	342.039	0.	0.	0.
3200	22.606	223.296	115.708	344.282	0.	0.	0.
3300	22.990	223.997	118.978	346.561	0.	0.	0.
3400	23.424	224.690	122.077	348.882	0.	0.	0.
3500	23.909	225.376	125.019	351.248	0.	0.	0.
3600	24.445	226.056	127.816	353.665	0.	0.	0.
3700	25.034	226.734	130.480	356.139	0.	0.	0.
3800	25.675	227.410	133.022	358.674	0.	0.	0.
3900	26.370	228.086	135.451	361.275	0.	0.	0.
4000	27.118	228.763	137.776	363.949	0.	0.	0.
4200	28.772	230.125	142.141	369.535	0.	0.	0.
4400	30.635	231.506	146.171	375.472	0.	0.	0.
4600	32.606	232.907	149.912	381.777	0.	0.	0.
4800	34.798	234.340	153.399	388.514	0.	0.	0.
5000	37.153	235.808	156.666	395.707	0.	0.	0.
5200	39.664	237.313	159.739	403.386	0.	0.	0.
5400	42.327	238.860	162.641	411.582	0.	0.	0.
5600	43.514	240.321	165.382	419.658	0.	0.	0.
5800	45.714	241.887	167.993	428.580	0.	0.	0.
6000	47.832	243.472	170.483	437.936	0.	0.	0.

PREVIOUS: CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 32.01 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}\ (\alpha \rightarrow \beta) = 980 \pm 20\ K$
$T_{trs}(\beta \rightarrow \gamma) = 1361 \pm 10\ K$
$T_{trs}(\gamma\text{–}\delta) = 1412 \pm 5\ K$
$T_{fus}(\delta\text{–}l) = 1519 \pm 5\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs}H°(\alpha \rightarrow \beta) = 2.226 \pm 0.21\ kJ \cdot mol^{-1}$
$\Delta_{trs}H°(\beta \rightarrow \gamma) = 2.122 \pm 0.33\ kJ \cdot mol^{-1}$
$\Delta_{trs}H°(\gamma \rightarrow \delta) = 1.879 \pm 0.33\ kJ \cdot mol^{-1}$
$\Delta_{fus}H°(\delta \rightarrow l) = 12.058 \pm 1.0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

A thorough re examination of the manganese thermal functions is in process. Temporarily, the recommendations of Hultgren *et al.*[1] are adotped. These results are based on the heat capacity studies of Scurlock and Stevens (0.3–1.0 K),[2] Gaumer (0.64–3 K),[3] Guthrie *et al.* (1.7–4.2 K),[4] Booth *et al.* (12–20 K),[5] Kelley (52–298 K),[6] and Shomate (52–298 K),[7] and the enthalpy study of Naylor (373–1436 K).[8] As Hultgren *et al.*[1] states, the study of Naylor was chosen because it covers all forms of Mn in a self consistant manner. It is not stated why Hultgren, *et al.*[1] altered Naylor's equations,[8] which appear more appropriate than the current values.

Phase and Fusion Data

As we are temporarily adopting the analysis of Hultgren, *et al.*,[1] we rely on his analysis of the transition and fusion temperatures. Ten studies are analyzed by Hultgren *et al.*[1] The temperatures were adjusted to IPTS–68.

Sublimation Data

Refer to the ideal gas table for details.

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals," Metals Park, Ohio, (1973).
[2]R. G. Scurlock and W. N. R. Stevens, Proc. Phys. Soc. **86**, 331 (1965).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−4.994	0.	0.	0.
100	14.723	8.875	52.876	−4.400	0.	0.	0.
200	23.054	22.133	34.325	−2.438	0.	0.	0.
250	24.948	27.493	32.436	−1.236	0.	0.	0.
298.15	26.299	32.010	32.010	0.	0.	0.	0.
300	26.347	32.173	32.010	0.049	0.	0.	0.
350	27.516	36.325	32.336	1.396	0.	0.	0.
400	28.527	40.066	33.072	2.798	0.	0.	0.
450	30.020	43.524	34.043	4.266	0.	0.	0.
500	30.292	46.696	35.152	5.772	0.	0.	0.
600	31.899	52.362	37.559	8.882	0.	0.	0.
700	33.426	57.395	40.039	12.149	0.	0.	0.
800	34.915	61.956	42.498	15.566	0.	0.	0.
900	36.384	66.153	44.896	19.131	0.	0.	0.
980.000	37.545	69.300	46.761	22.088	ALPHA <--> BETA TRANSITION		
980.000	37.572	71.572	46.761	24.314			
1000	37.698	72.332	47.265	25.067	0.	0.	0.
1100	38.116	75.945	49.710	28.858	0.	0.	0.
1200	38.535	79.279	52.037	32.690	0.	0.	0.
1300	38.953	82.380	54.253	36.565	0.	0.	0.
1361.000	39.204	84.172	55.554	38.948	BETA <--> GAMMA TRANSITION		
1361.000	43.095	85.731	55.554	41.070			
1400	43.430	86.953	56.412	42.757	0.	0.	0.
1412.000	43.514	87.324	56.673	43.279	GAMMA <--> DELTA TRANSITION		
1412.000	45.229	88.655	56.673	45.158			
1500	45.982	91.413	58.631	49.173	0.	0.	0.
1519.000	46.108	91.993	59.045	50.048	--- DELTA <--> LIQUID ---		
1600	46.803	94.406	60.774	53.811	−12.023	0.642	−0.021
1700	47.624	97.268	62.837	58.532	−11.904	1.431	−0.044
1800	48.446	100.013	64.827	63.336	−11.703	2.210	−0.064
1900	49.267	102.655	66.749	68.221	−11.420	2.975	−0.082

PREVIOUS: CURRENT: September 1967

$S°(298.15\ K) = [43.499]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1519 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [16.289]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 12.058 \pm 1.0\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Mn(l), $\Delta_f H°(298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1519\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Hultgren[1] adopted $C_p°(l) = 11.0\ cal·K^{-1}·mol^{-1}$ based on the recommendation of Kelly.[2] A glass transition temperature is assumed at 1125 K, below which the heat capacity values of α–Mn(cr) are adopted. a re–examination of Mn(l) is in progress. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

T_{vap}(1 bar) is calculated as the temperature at which $\Delta_r G° = 0$ for the process Mn(l) = Mn(g). $\Delta_{vap} H°$ is calculated as the difference in the enthalpies of formation of Mn(l) and Mn(g) at T_{vap}.

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio, (1973).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	26.299	43.499	43.499	0.	16.289	12.863	−2.254
300	26.347	43.662	43.500	0.049	16.289	12.842	−2.236
350	27.516	47.814	43.825	1.396	16.289	12.267	−1.831
400	28.527	51.555	44.561	2.798	16.289	11.693	−1.527
450	30.020	55.013	45.533	4.266	16.289	11.118	−1.291
500	30.292	58.185	46.642	5.772	16.289	10.544	−1.102
600	31.899	63.852	49.048	8.882	16.289	9.395	−0.818
700	33.426	68.884	51.529	12.149	16.289	8.246	−0.615
800	34.915	73.445	53.988	15.566	16.289	7.097	−0.463
900	36.384	77.643	56.386	19.131	16.289	5.948	−0.345
1000	37.834	81.551	58.709	22.842	14.064	4.845	−0.253
1100	39.275	85.225	60.954	26.698	14.129	3.921	−0.186
1125.000	39.634	86.111	61.503	27.684	GLASS <--> LIQUID TRANSITION		
1125.000	46.024	86.111	61.503	27.684			
1200	46.024	89.082	63.135	31.136	14.734	2.971	−0.129
1300	46.024	92.766	65.275	35.738	15.462	1.961	−0.079
1400	46.024	96.176	67.362	40.341	13.872	0.960	−0.036
1500	46.024	99.352	69.390	44.943	12.059	0.151	−0.005
1519.000	46.024	99.931	69.768	45.817	DELTA <--> LIQUID		
1600	46.024	102.322	71.356	49.545	0.	0.	0.
1700	46.024	105.112	73.260	54.148	0.	0.	0.
1800	46.024	107.743	75.104	58.750	0.	0.	0.
1900	46.024	110.231	76.888	63.353	0.	0.	0.
2000	46.024	112.592	78.614	67.955	0.	0.	0.
2100	46.024	114.837	80.286	72.557	0.	0.	0.
2200	46.024	116.978	81.906	77.160	0.	0.	0.
2300	46.024	119.024	83.476	81.762	0.	0.	0.
2334.526	46.024	119.710	84.006	83.351	FUGACITY = 1 bar		
2400	46.024	120.983	84.998	86.365	−224.340	6.315	−0.137
2500	46.024	122.862	86.475	90.967	−221.841	15.874	−0.332
2600	46.024	124.667	87.909	95.569	−219.353	25.334	−0.509
2700	46.024	126.404	89.303	100.172	−216.877	34.698	−0.671
2800	46.024	128.078	90.658	104.774	−214.417	43.970	−0.820
2900	46.024	129.693	91.977	109.377	−211.977	53.155	−0.957
3000	46.024	131.253	93.260	113.979	−209.559	62.256	−1.084

PREVIOUS: CURRENT: September 1967

CRYSTAL(α, β, γ, δ)–LIQUID

0	to	980 K	crystal, alpha
980	to	1361 K	crystal, beta
1361	to	1412 K	crystal, gamma
1412	to	1519 K	crystal, delta
above		1519 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0	0.	0. INFINITE	−4.994	0.	0.	0.
100	14.723	8.875 52.876	−4.400	0.	0.	0.
200	23.054	22.133 34.325	−2.438	0.	0.	0.
250	24.948	27.493 32.436	−1.236	0.	0.	0.
298.15	26.299	32.010 32.010	0.	0.	0.	0.
300	26.347	32.173 32.010	0.049	0.	0.	0.
350	27.516	36.325 32.336	1.396	0.	0.	0.
400	28.527	40.066 33.072	2.798	0.	0.	0.
450	30.020	43.524 34.043	4.266	0.	0.	0.
500	30.292	46.696 35.152	5.772	0.	0.	0.
600	31.899	52.362 37.559	8.882	0.	0.	0.
700	33.426	57.395 40.039	12.149	0.	0.	0.
800	34.915	61.956 42.498	15.566	0.	0.	0.
900	36.384	66.153 44.896	19.131	0.	0.	0.
980.000	37.545	69.300 46.761	22.088	ALPHA <--> BETA TRANSITION		
980.000	37.572	71.572 46.761	24.314			
1000	37.698	72.332 47.265	25.067	0.	0.	0.
1100	38.116	75.945 49.710	28.858	0.	0.	0.
1200	38.535	79.279 52.037	32.690	0.	0.	0.
1300	38.953	82.380 54.253	36.565	0.	0.	0.
1361.000	39.204	84.172 55.554	38.948	BETA <--> GAMMA TRANSITION		
1361.000	43.095	85.731 55.554	41.070			
1400	43.430	86.953 56.412	42.757	0.	0.	0.
1412.000	43.514	87.324 56.673	43.279	GAMMA <--> DELTA TRANSITION		
1412.000	45.229	88.655 56.673	45.158			
1500	45.982	91.413 58.631	49.173	0.	0.	0.
1519.000	46.108	91.993 59.045	50.048	DELTA <--> LIQUID TRANSITION		
1519.000	46.024	99.931 59.045	62.106			
1600	46.024	102.322 61.176	65.834	0.	0.	0.
1700	46.024	105.112 63.679	70.436	0.	0.	0.
1800	46.024	107.743 66.055	75.039	0.	0.	0.
1900	46.024	110.231 68.315	79.641	0.	0.	0.
2000	46.024	112.592 70.470	84.244	0.	0.	0.
2100	46.024	114.837 72.530	88.846	0.	0.	0.
2200	46.024	116.978 74.502	93.448	0.	0.	0.
2300	46.024	119.024 76.393	98.051	0.	0.	0.
2334.526	46.024	119.710 77.029	99.640	FUGACITY = 1 bar		
2400	46.024	120.983 78.211	102.653	−224.340	6.315	−0.137
2500	46.024	122.862 79.960	107.256	−221.841	15.874	−0.332
2600	46.024	124.667 81.645	111.858	−219.353	25.334	−0.509
2700	46.024	126.404 83.270	116.460	−216.877	34.698	−0.671
2800	46.024	128.078 84.841	121.063	−214.417	43.970	−0.820
2900	46.024	129.693 86.360	125.665	−211.977	53.155	−0.957
3000	46.024	131.253 87.830	130.268	−209.559	62.256	−1.084

PREVIOUS: CURRENT: September 1967

IP (Mn, g) = 59981 ± 1 cm^{-1}
$S°(298.15\ K)$ = 173.716 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 282.1 ± 4.2 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 283.3 ± 4.2 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0.00	6
$^6D_{9/2}$	17052.29	10
$^6D_{7/2}$	17282.00	8
$^6D_{5/2}$	17451.52	6
$^6D_{3/2}$	17568.48	4
$^6D_{1/2}$	17637.15	2

Enthalpy of Formation

The value adopted for the enthalpy of formation of Mn(g), $\Delta_f H°(298.15\ K)$ = 283.3 ± 4.2 $kJ·mol^{-1}$, is that recommended by Hultgren *et al.*[1] This value is a weighted mean of sublimation and vaporization studies. The studies are: Bogatyrev and Golubtsov (1043–1168 K),[2] Pratt and Spencer (1248–1620 K),[3] Wiedemeier (1269–1448 K),[4] Butler *et al.* (1075–1335 K),[5] Woolf, *et al.* (1523–1823 K),[6] McCabe and Hudson (1075–1235 K),[7] and Baur and Brunner (1587–1987 K).[8]

A reanalysis of the vapor pressure data is in progress.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[9] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only a few of the lowest lying levels for Mn(g), all levels listed by Corliss and Sugar,[9] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Mn(g), the thermodynamic functions are independent of the estimated missing levels (for n = 4–8), the cut–off procedure, and the inclusion of n<9 levels up to 4000 K; the Gibbs energy function showing no significant variations at this temperature. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>8), and use of different fill and cut–off procedures.[10]

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values for Thermodynamic Properties of Metals," American Society of Metals, Metals Park, Ohio, (1973).
[2]V. L. Bogatyrev and I. V. Golubtsev, Zh. Fiz. Khim. **40**, 938 (1966).
[3]J. N. Pratt and P. J. Spencer, Q.T.S.R. No. 1, U.S. Dept. of the Army, Contract No. DA–91–591–EVC–3762, (1966).
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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	282.053	282.053	INFINITE
100	20.786	151.009	192.196	−4.119	283.538	269.325	−140.681
200	20.786	165.416	175.617	−2.040	283.655	254.998	−66.599
250	20.786	170.055	174.058	−1.001	283.492	247.851	−51.786
298.15	20.786	173.716	173.716	0.	283.257	241.007	−42.223
300	20.786	173.844	173.716	0.038	283.247	240.745	−41.917
350	20.786	177.049	173.969	1.078	282.938	233.685	−34.876
400	20.786	179.824	174.532	2.117	282.576	226.673	−29.600
450	20.786	182.272	175.258	3.156	282.147	219.710	−25.503
500	20.786	184.462	176.071	4.196	281.681	212.797	−22.231
600	20.786	188.252	177.795	6.274	280.649	199.115	−17.335
700	20.786	191.456	179.524	8.353	279.461	185.618	−13.851
800	20.786	194.232	181.193	10.431	278.122	172.301	−11.250
900	20.786	196.680	182.780	12.510	276.636	159.161	−9.237
1000	20.786	198.870	184.282	14.589	272.778	146.240	−7.639
1100	20.786	200.851	185.699	16.667	271.066	133.669	−6.347
1200	20.786	202.660	187.038	18.746	269.312	121.255	−5.278
1300	20.786	204.324	188.305	20.824	267.517	108.990	−4.379
1400	20.786	205.864	189.505	22.903	263.403	96.927	−3.616
1500	20.787	207.298	190.644	24.982	259.066	85.238	−2.968
1600	20.788	208.640	191.727	27.061	244.483	74.375	−2.428
1700	20.791	209.900	192.759	29.139	241.960	63.820	−1.961
1800	20.797	211.089	193.745	31.219	239.437	53.414	−1.550
1900	20.806	212.213	194.688	33.299	236.914	43.148	−1.186
2000	20.822	213.281	195.591	35.380	234.393	33.015	−0.862
2100	20.845	214.297	196.458	37.464	231.874	23.008	−0.572
2200	20.880	215.268	197.291	39.550	229.358	13.121	−0.312
2300	20.930	216.197	198.093	41.640	226.846	3.348	−0.076
2334.526	20.951	216.509	198.363	42.363	----- FUGACITY = 1 bar -----		
2400	20.997	217.089	198.866	43.736	0.	0.	0.
2500	21.085	217.948	199.612	45.840	0.	0.	0.
2600	21.198	218.777	200.333	47.954	0.	0.	0.
2700	21.341	219.580	201.031	50.081	0.	0.	0.
2800	21.515	220.359	201.708	52.223	0.	0.	0.
2900	21.726	221.118	202.364	54.385	0.	0.	0.
3000	21.976	221.858	203.002	56.570	0.	0.	0.
3100	22.269	222.583	203.622	58.782	0.	0.	0.
3200	22.606	223.296	204.225	61.025	0.	0.	0.
3300	22.990	223.997	204.814	63.305	0.	0.	0.
3400	23.424	224.690	205.388	65.625	0.	0.	0.
3500	23.909	225.376	205.950	67.991	0.	0.	0.
3600	24.445	226.056	206.499	70.408	0.	0.	0.
3700	25.034	226.734	207.036	72.882	0.	0.	0.
3800	25.675	227.410	207.564	75.417	0.	0.	0.
3900	26.370	228.086	208.081	78.019	0.	0.	0.
4000	27.118	228.763	208.590	80.693	0.	0.	0.
4100	27.919	229.442	209.090	83.444	0.	0.	0.
4200	28.772	230.125	209.583	86.278	0.	0.	0.
4300	29.678	230.813	210.068	89.200	0.	0.	0.
4400	30.635	231.506	210.548	92.216	0.	0.	0.
4500	31.574	232.201	211.021	95.311	0.	0.	0.
4600	32.606	232.907	211.489	98.520	0.	0.	0.
4700	33.681	233.619	211.952	101.834	0.	0.	0.
4800	34.798	234.340	212.411	105.258	0.	0.	0.
4900	35.956	235.069	212.866	108.795	0.	0.	0.
5000	37.153	235.808	213.318	112.450	0.	0.	0.
5100	38.389	236.556	213.766	116.227	0.	0.	0.
5200	39.664	237.313	214.211	120.129	0.	0.	0.
5300	40.976	238.081	214.655	124.161	0.	0.	0.
5400	42.327	238.860	215.096	128.325	0.	0.	0.
5500	43.716	239.649	215.535	132.627	0.	0.	0.
5600	43.514	240.321	215.964	136.401	0.	0.	0.
5700	44.624	241.101	216.398	140.808	0.	0.	0.
5800	45.714	241.887	216.831	145.324	0.	0.	0.
5900	46.784	242.677	217.262	149.948	0.	0.	0.
6000	47.832	243.472	217.692	154.679	0.	0.	0.

PREVIOUS: CURRENT: June 1984 (1 bar)

IP(Mn^+, g) = 126145.0 ± 0.6 cm^{-1}
$S°$(298.15 K) = 174.997 ± 0.05 J K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 999.6 ± 0.5 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [10006.986] kJ·mol^{-1}

Electronic Level and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^7S_3$	0.00	7
$^5S_2$	9472.97	5
$^5D_4$	14325.86	9
.	.	.
.	.	.
.	.	.
$^7H_8$	120721.9	17
IP	126145.0	

Enthalpy of Formation

$\Delta_f H°$(Mn^+, g, 0 K) is calculated from $\Delta_f H°$(Mn, g, 0 K)[1] using the spectroscopic value of IP(Mn) = 59981 ± 1 cm^{-1} (717.532 ± 0.012 mol^{-1}) from Corliss and Sugar.[2] The ionization limit is converted from cm^{-1} to kJ·mol^{-1} using the factor, 1 cm^{-1} = 0.01196266 kJ·mol^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°$(Mn^+, g, 298.15 K) is calculated from $\Delta_f H°$(Mn, g, 0 K) by using IP(Mn) with JANAF[1] enthalpies, $H°$(0 K)–$H°$(298.15 K), for Mn(g), Mn^+(g), and e^-(ref). $\Delta_f H°$(Mn → $Mn^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for Mn^+(g), all levels listed by Corliss and Sugar,[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Mn^+(g), the thermodynamic functions are independent of the estimated missing levels (for n = 4–7), the cut–off procedure, and the inclusion of n<8 levels up to 6000 K; the Gibbs energy function showing no significant variations at this temperature. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>7), and use of different fill and cut–off procedures.[6]

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[1]JANAF Thermochemical Tables: Mn(g), 6–30–84; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	999.586		
100	20.786	152.290	193.478	−4.119			
200	20.786	166.698	176.899	−2.040			
250	20.786	171.336	175.340	−1.001			
298.15	20.786	174.997	174.997	0.	1006.986	958.100	−167.855
300	20.786	175.126	174.998	0.038	1007.015	957.797	−166.767
350	20.786	178.330	175.251	1.078	1007.746	949.535	−141.710
400	20.786	181.106	175.813	2.117	1008.423	941.172	−122.904
450	20.786	183.554	176.540	3.156	1009.033	932.728	−108.268
500	20.786	185.744	177.353	4.196	1009.606	924.219	−96.553
600	20.786	189.534	179.077	6.274	1010.653	907.041	−78.965
700	20.786	192.738	180.805	8.353	1011.543	889.700	−66.390
800	20.786	195.514	182.474	10.431	1012.283	872.241	−56.952
900	20.786	197.962	184.062	12.510	1012.875	854.699	−49.605
1000	20.787	200.152	185.563	14.589	1011.097	837.144	−43.728
1100	20.790	202.133	186.981	16.668	1011.464	819.731	−38.926
1200	20.795	203.942	188.320	18.747	1011.789	802.286	−34.923
1300	20.805	205.607	189.587	20.827	1012.073	784.815	−31.534
1400	20.821	207.150	190.787	22.908	1010.040	767.387	−28.632
1500	20.846	208.587	191.926	24.991	1007.787	750.184	−26.124
1600	20.882	209.933	193.010	27.078	995.290	733.668	−23.952
1700	20.932	211.201	194.043	29.168	994.857	717.330	−22.041
1800	20.996	212.399	195.030	31.265	994.430	701.017	−20.343
1900	21.078	213.536	195.974	33.368	994.009	684.728	−18.824
2000	21.179	214.620	196.880	35.481	993.598	668.461	−17.458
2100	21.301	215.656	197.749	37.605	993.198	652.214	−16.223
2200	21.445	216.650	198.586	39.742	992.812	635.985	−15.100
2300	21.611	217.607	199.392	41.894	992.440	619.774	−14.076
2400	21.800	218.531	200.171	44.065	767.747	609.894	−13.274
2500	22.011	219.425	200.923	46.255	769.912	603.272	−12.605
2600	22.246	220.293	201.651	48.468	772.090	596.564	−11.985
2700	22.503	221.137	202.357	50.705	774.279	589.771	−11.410
2800	22.782	221.960	203.043	52.969	776.479	582.898	−10.874
2900	23.080	222.765	203.709	55.262	778.689	575.945	−10.374
3000	23.398	223.553	204.358	57.586	780.906	568.916	−9.906
3100	23.735	224.325	204.989	59.942	783.130	561.813	−9.466
3200	24.088	225.085	205.605	62.333	785.356	554.638	−9.054
3300	24.457	225.831	206.207	64.761	787.582	547.394	−8.665
3400	24.841	226.567	206.795	67.225	789.805	540.082	−8.297
3500	25.238	227.293	207.370	69.729	792.021	532.705	−7.950
3600	25.648	228.010	207.934	72.273	794.227	525.265	−7.621
3700	26.070	228.718	208.486	74.859	796.418	517.763	−7.310
3800	26.504	229.419	209.028	77.488	798.590	510.203	−7.013
3900	26.948	230.113	209.559	80.160	800.739	502.586	−6.731
4000	27.402	230.801	210.082	82.878	802.861	494.914	−6.463
4100	27.866	231.484	210.595	85.641	804.952	487.189	−6.207
4200	28.341	232.161	211.101	88.451	807.007	479.414	−5.962
4300	28.825	232.833	211.598	91.310	809.021	471.590	−5.729
4400	29.319	233.502	212.089	94.217	810.992	463.720	−5.505
4500	29.822	234.166	212.572	97.174	812.932	455.805	−5.291
4600	30.336	234.827	213.049	100.181	814.809	447.848	−5.085
4700	30.859	235.485	213.519	103.241	816.634	439.851	−4.888
4800	31.391	236.140	213.983	106.354	818.401	431.815	−4.699
4900	31.934	236.793	214.442	109.520	820.108	423.744	−4.517
5000	32.485	237.444	214.896	112.741	821.753	415.638	−4.342
5100	33.046	238.093	215.344	116.017	823.331	407.500	−4.174
5200	33.616	238.740	215.788	119.350	824.841	399.331	−4.011
5300	34.195	239.386	216.227	122.741	826.278	391.135	−3.855
5400	34.781	240.030	216.662	126.189	827.641	382.911	−3.704
5500	35.375	240.674	217.093	129.697	828.926	374.664	−3.558
5600	35.976	241.317	217.520	133.265	830.798	366.345	−3.417
5700	36.583	241.959	217.943	136.893	832.097	358.040	−3.281
5800	37.195	242.600	218.362	140.581	833.349	349.712	−3.149
5900	37.810	243.241	218.778	144.332	834.553	341.363	−3.022
6000	38.429	243.882	219.192	148.144	835.713	332.994	−2.899

PREVIOUS: CURRENT: June 1984 (1 bar)

REFERENCE STATE

0	to 2896	K	crystal
2896	to 4951.969	K	liquid
above	4951.969	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−4.585	0.	0.	0.
100	13.495	7.026	47.961	−4.094	0.	0.	0.
200	21.507	19.478	30.735	−2.251	0.	0.	0.
298.15	23.933	28.605	28.605	0.	0.	0.	0.
300	23.958	28.753	28.606	0.044	0.	0.	0.
400	25.080	35.810	29.560	2.500	0.	0.	0.
500	25.850	41.494	31.397	5.049	0.	0.	0.
600	26.460	46.263	33.487	7.665	0.	0.	0.
700	26.980	50.382	35.613	10.338	0.	0.	0.
800	27.440	54.015	37.691	13.059	0.	0.	0.
900	27.890	57.272	39.689	15.825	0.	0.	0.
1000	28.370	60.235	41.597	18.638	0.	0.	0.
1100	28.900	62.963	43.417	21.501	0.	0.	0.
1200	29.490	65.502	45.153	24.419	0.	0.	0.
1300	30.140	67.888	46.811	27.400	0.	0.	0.
1400	30.860	70.148	48.398	30.450	0.	0.	0.
1500	31.650	72.304	49.920	33.575	0.	0.	0.
1600	32.500	74.373	51.384	36.782	0.	0.	0.
1700	33.420	76.371	52.796	40.078	0.	0.	0.
1800	34.420	78.309	54.160	43.469	0.	0.	0.
1900	35.490	80.198	55.481	46.964	0.	0.	0.
2000	36.650	82.048	56.763	50.570	0.	0.	0.
2100	37.900	83.866	58.010	54.297	0.	0.	0.
2200	39.240	85.659	59.226	58.152	0.	0.	0.
2300	40.670	87.435	60.414	62.147	0.	0.	0.
2400	42.210	89.198	61.577	66.290	0.	0.	0.
2500	43.890	90.954	62.717	70.594	0.	0.	0.
2600	45.880	92.713	63.837	75.079	0.	0.	0.
2700	48.370	94.490	64.939	79.786	0.	0.	0.
2800	51.570	96.304	66.027	84.777	0.	0.	0.
2896.000	54.835	98.098	67.060	89.885	CRYSTAL <--> LIQUID TRANSITION		
2896.000	37.656	110.522	67.060	125.867			
2900	37.656	110.574	67.120	126.018	0.	0.	0.
3000	37.656	111.851	68.590	129.784	0.	0.	0.
3100	37.656	113.086	70.005	133.549	0.	0.	0.
3200	37.656	114.281	71.370	137.315	0.	0.	0.
3300	37.656	115.440	72.688	141.080	0.	0.	0.
3400	37.656	116.564	73.962	144.846	0.	0.	0.
3500	37.656	117.656	75.195	148.612	0.	0.	0.
3600	37.656	118.716	76.389	152.377	0.	0.	0.
3700	37.656	119.748	77.547	156.143	0.	0.	0.
3800	37.656	120.752	78.671	159.908	0.	0.	0.
3900	37.656	121.731	79.763	163.674	0.	0.	0.
4000	37.656	122.684	80.824	167.440	0.	0.	0.
4100	37.656	123.614	81.856	171.205	0.	0.	0.
4200	37.656	124.521	82.861	174.971	0.	0.	0.
4300	37.656	125.407	83.841	178.736	0.	0.	0.
4400	37.656	126.273	84.795	182.502	0.	0.	0.
4500	37.656	127.119	85.726	186.268	0.	0.	0.
4600	37.656	127.947	86.635	190.033	0.	0.	0.
4700	37.656	128.757	87.523	193.799	0.	0.	0.
4800	37.656	129.549	88.390	197.564	0.	0.	0.
4900	37.656	130.326	89.238	201.330	0.	0.	0.
4951.969	37.656	130.723	89.671	203.287	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
4951.969	53.001	249.995	89.671	793.918			
5000	53.713	250.510	91.214	796.481	0.	0.	0.
5100	55.185	251.588	94.348	801.926	0.	0.	0.
5200	56.640	252.674	97.382	807.517	0.	0.	0.
5300	58.072	253.766	100.322	813.252	0.	0.	0.
5400	59.485	254.865	103.174	819.130	0.	0.	0.
5500	60.874	255.969	105.942	825.148	0.	0.	0.
5600	62.239	257.078	108.631	831.303	0.	0.	0.
5700	63.577	258.191	111.245	837.593	0.	0.	0.
5800	64.887	259.308	113.788	844.015	0.	0.	0.
5900	66.164	260.428	116.264	850.565	0.	0.	0.
6000	67.413	261.550	118.676	857.243	0.	0.	0.

PREVIOUS: March 1978 (1 atm) CURRENT: March 1978 (1 bar)

$S°(298.15\ K) = 28.605 \pm 0.050\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2896 \pm 8\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 36.0 \pm 5.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacities of Mo(cr) have been measured by Clusius and Franzosini[1] between 16 and 256 K (63 measured C_p points). The reported C_p values are smoothed by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. This fitting procedure also includes the smoothed $C_p°$ values (275–335 K) reported in the critical evaluation by Ditmars *et al.*[2] so as to provide smoothly varying heat capacity values in the range 256–275 K. The data of Simon and Zeidler,[3] 15–238 K, are as much as 2.5% high below 78 K and as much as 1% low above 78 K.

Below 20 K several investigators[4-7] have determined the heat capacity. Heiniger *et al.*[8] have summarized and critically reviewed this work as well as other studies. These sources give $S°(20\ K)$ values in the range 0.021–0.025 $cal \cdot K^{-1} \cdot mol^{-1}$. Adopting $S°(20\ K) = 0.024$ $cal \cdot K^{-1} \cdot mol^{-1}$ and combining this with our analysis of the Clusius and Franzosoni work,[1] we calculate $S°(298.15\ K) = 6.836 \pm 0.012$ $cal \cdot K^{-1} \cdot mol^{-1}$. This result agrees with the review of the heat capacity data ($T < 298.15$ K) by Reilly and Furukawa[9] for Brewer.[10]

The high temperature heat capacity values, 273–2800 K, are those selected by Ditmars *et al.*[2] This study reports three recent NBS heat capacity/enthalpy studies covering the 270–2800 K on NBS Standard Reference Material No. 781. In addition, the report contains a bibliography of publications on the high temperature enthalpy and heat capacity of crystalline molybdenum. A graphical comparison of the NBS results with those of all the principal investigators and critical evaluation is also given in the publication. These results are linearly extrapolated from 2800 K to 3300 K. The high temperature heat capacity values adopted by Brewer,[10] based on IPTS–48, are within 0.1% of the NBS results between 298 and 900 K and are 0.2 to 0.3% higher between 1000 and 1400 K. Between 1500 and 1900 K, the difference is less than 0.1%. From 2000 to 2300 K, the values are 0.2 to 0.3% lower and are 0.1% low to 0.2% high between 2400 to 2700 K. The value at 2800 K is 0.5% lower than our adopted value. At 2800 K, the entropy difference is 0.004 $cal \cdot K^{-1} \cdot mol^{-1}$ with the JANAF value being smaller.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Eight sublimation studies are discussed on the ideal gas table.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.585	0.	0.	0.
100	13.495	7.026	47.961	−4.094	0.	0.	0.
200	21.507	19.478	30.735	−2.251	0.	0.	0.
250	23.074	24.462	28.995	−1.133	0.	0.	0.
298.15	23.933	28.605	28.605	0.	0.	0.	0.
300	23.958	28.753	28.606	0.044	0.	0.	0.
350	24.580	32.494	28.900	1.258	0.	0.	0.
400	25.080	35.810	29.560	2.500	0.	0.	0.
450	25.500	38.789	30.423	3.765	0.	0.	0.
500	25.850	41.494	31.397	5.049	0.	0.	0.
600	26.460	46.263	33.487	7.665	0.	0.	0.
700	26.980	50.382	35.613	10.338	0.	0.	0.
800	27.440	54.015	37.691	13.059	0.	0.	0.
900	27.890	57.272	39.689	15.825	0.	0.	0.
1000	28.370	60.235	41.597	18.638	0.	0.	0.
1100	28.900	62.963	43.417	21.501	0.	0.	0.
1200	29.490	65.502	45.153	24.419	0.	0.	0.
1300	30.140	67.888	46.811	27.400	0.	0.	0.
1400	30.860	70.148	48.398	30.450	0.	0.	0.
1500	31.650	72.304	49.920	33.575	0.	0.	0.
1600	32.500	74.373	51.384	36.782	0.	0.	0.
1700	33.420	76.371	52.796	40.078	0.	0.	0.
1800	34.420	78.309	54.160	43.469	0.	0.	0.
1900	35.490	80.198	55.481	46.964	0.	0.	0.
2000	36.650	82.048	56.763	50.570	0.	0.	0.
2100	37.900	83.866	58.010	54.297	0.	0.	0.
2200	39.240	85.659	59.226	58.152	0.	0.	0.
2300	40.670	87.435	60.414	62.147	0.	0.	0.
2400	42.210	89.198	61.577	66.290	0.	0.	0.
2500	43.890	90.954	62.717	70.594	0.	0.	0.
2600	45.880	92.713	63.837	75.079	0.	0.	0.
2700	48.370	94.490	64.939	79.786	0.	0.	0.
2800	51.570	96.304	66.027	84.777	0.	0.	0.
2896.000	54.835	98.098	67.060	89.885	--- CRYSTAL <--> LIQUID ---		
2900	54.970	98.173	67.103	90.104	−35.913	0.050	−0.001
3000	58.370	100.094	68.170	95.771	−34.012	1.258	−0.022
3100	61.770	102.064	69.232	101.778	−31.771	2.398	−0.040
3200	65.170	104.078	70.289	108.125	−29.189	3.460	−0.056
3300	68.570	106.136	71.344	114.812	−26.268	4.436	−0.070

PREVIOUS: December 1966 CURRENT: March 1978

$S°(298.15\ K) = [43.146]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2896 \pm 8\ K$

$\Delta_f H°(298.15\ K) = [41.568]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 36.0 \pm 5.4\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2896\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Enthalpy measurements via levitation calorimetry by Treverton and Margrave[3] were over a sufficient range of temperature, 2692–3112 K, to establish $C_p°(l) = 8.19\ cal·K^{-1}·mol^{-1}$. The enthalpy measurements of Berezin *et al.*[2] in the liquid region (14 pts., 2890–2925 K) are insufficient to define a liquid phase heat capacity value. Shaner *et al.*[5] and Dikhter and Lebedev[6] have reported $C_p°(l)$ values of 16.7 $cal·K^{-1}·mol^{-1}$ and 14.0 $cal·K^{-1}·mol^{-1}$, respectively, using pulse heating techniques.

We adopt $C_p°(l) = 9.0\ cal·K^{-1}·mol^{-1}$ as did Brewer.[9] This value implies a heavier weighting of the drop calorimetric studies rather than the pulse heating techniques. The magnitude of the difference of the $C_p°(l)$ values derived from the various studies[3,5,6] suggests further study in this area. A glass transition is assumed at 2150 K below which the heat capacity is assumed to be that of the crystal. The entropy is calculated in a manner analogous to the enthalpy of formation.

Fusion Data

The adopted melting point, $T_{fus} = 2896 \pm 8$ K, is derived from the recent experimental study and critical evaluation of earlier data by Kenisarin *et al.*[1]

Bererzin *et al.*[2] have measured the enthalpy of crystal and liquid molybdenum by levitation calorimetry in the range 1962–2869 K and 2890–2925 K, respectively. They reported $\Delta_{fus}H° = 8.741 \pm 0.314\ kcal·mol^{-1}$ at an assumed melting temperature of 2890 K. Correcting these results to $T_{fus} = 2896$ K yields $8.693 \pm 0.314\ kcal·mol^{-1}$. Shaner *et al.*,[5] using a pulse–heating technique, reported enthalpy measurements (1978–4450 K) which gave $\Delta_{fus}H° = 8.553\ kcal·mol^{-1}$ at a melting point of 2883 K.

Treverton and Margrave[3] also used levitation calorimetry to measure the liquid phase enthalpy of molybdenum in the range 2693–3115 K. Using the enthalpy value for the liquid at the melting point as determined by Treverton and Margrave[3] and the enthalpy value of the crystal at the melting point as determined by our adopted functions, we calculate $\Delta_{fus}H° = 7.264\ kcal·mol^{-1}$. Lebedev *et al.*[7] reported $\Delta_{fus}H° = 9.864\ kcal·mol^{-1}$ (exploding wire technique) while Kostikov *et al.*[8] found $\Delta_{fus}H° = 6.095\ kcal·mol^{-1}$ (drop technique).

We adopt $\Delta_{fus}H° = 8.6 \pm 1.3\ kcal·mol^{-1}$, which corresponds to $\Delta_{fus}S° = 2.97\ cal·K^{-1}·mol^{-1}$. This $\Delta_{fus}S°$ appears high for a metal with a bcc (A2) structure; however, this value is supported by the studies of Berezin *et al.*[2] and Shaner *et al.*[5] Brewer[9] selected a value of $\Delta_{fus}H° = 8.54 \pm 0.3\ kcal·mol^{-1}$ (IPTS–48).

Vaporization Data

The boiling point and enthalpy of vaporization are calculated from the adopted functions and enthalpy of sublimation in order to maintain proper themodynamic consistency.

Koch and Anable[4] have measured the vapor pressure of liquid molybdenum by a Langmuir free–evaporation method. They measured 16 data points in the range 2895–2995 K. A 2nd and 3th law analysis gives $\Delta_{vap}H°(298.15\ K)$ values of 136.8 ± 18.4 and $147.7 \pm 1.7\ kcal·mol^{-1}$, respectively. This corresponds to our adopted value of $\Delta_{vap}H°(298.15\ K) = 147.565\ kcal·mol^{-1}$. Note, however, that there is a significant difference between the 2nd and 3rd law results.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	23.932	43.146	43.146	0.	41.568	37.233	−6.523
300	23.958	43.294	43.146	0.044	41.568	37.206	−6.478
350	24.580	47.035	43.440	1.258	41.568	36.479	−5.444
400	25.080	50.351	44.101	2.500	41.568	35.752	−4.669
450	25.500	53.330	44.964	3.765	41.568	35.025	−4.066
500	25.850	56.035	45.938	5.049	41.568	34.298	−3.583
600	26.460	60.804	48.028	7.665	41.568	32.844	−2.859
700	26.980	64.922	50.154	10.338	41.568	31.390	−2.342
800	27.440	68.555	52.232	13.059	41.568	29.935	−1.955
900	27.890	71.813	54.230	15.825	41.568	28.481	−1.653
1000	28.370	74.776	56.138	18.638	41.568	27.027	−1.412
1100	28.900	77.504	57.958	21.501	41.568	25.573	−1.214
1200	29.490	80.043	59.694	24.419	41.568	24.119	−1.050
1300	30.140	82.429	61.352	27.400	41.568	22.665	−0.911
1400	30.860	84.689	62.939	30.450	41.568	21.211	−0.791
1500	31.650	86.845	64.461	33.575	41.568	19.757	−0.688
1600	32.500	88.914	65.925	36.782	41.568	18.303	−0.598
1700	33.420	90.912	67.337	40.078	41.568	16.849	−0.518
1800	34.420	92.850	68.701	43.469	41.568	15.395	−0.447
1900	35.490	94.739	70.021	46.964	41.568	13.940	−0.383
2000	36.650	96.589	71.304	50.570	41.568	12.486	−0.326
2100	37.900	98.407	72.551	54.297	41.568	11.032	−0.274
2150.000	38.550	99.306	73.163	56.208	GLASS <--> LIQUID		
2150.000	37.656	99.306	73.163	56.208	TRANSITION		
2200	37.656	100.172	73.767	58.091	41.506	9.579	−0.227
2300	37.656	101.846	74.952	61.856	41.277	8.132	−0.185
2400	37.656	103.448	76.106	65.622	40.900	6.699	−0.146
2500	37.656	104.985	77.231	69.387	40.362	5.284	−0.110
2600	37.656	106.462	78.327	73.153	39.642	3.894	−0.078
2700	37.656	107.884	79.395	76.919	38.700	2.537	−0.049
2800	37.656	109.253	80.437	80.684	37.475	1.219	−0.023
2896.000	37.656	110.522	81.414	84.299	--- CRYSTAL <--> LIQUID ---		
2900	37.656	110.574	81.454	84.450	0.	0.	0.
3000	37.656	111.851	82.446	88.215	0.	0.	0.
3100	37.656	113.086	83.414	91.981	0.	0.	0.
3200	37.656	114.281	84.360	95.747	0.	0.	0.
3300	37.656	115.440	85.285	99.512	0.	0.	0.
3400	37.656	116.564	86.188	103.278	0.	0.	0.
3500	37.656	117.656	87.072	107.043	0.	0.	0.
3600	37.656	118.716	87.936	110.809	0.	0.	0.
3700	37.656	119.748	88.782	114.575	0.	0.	0.
3800	37.656	120.752	89.610	118.340	0.	0.	0.
3900	37.656	121.731	90.421	122.106	0.	0.	0.
4000	37.656	122.684	91.216	125.871	0.	0.	0.
4100	37.656	123.614	91.995	129.637	0.	0.	0.
4200	37.656	124.521	92.759	133.403	0.	0.	0.
4300	37.656	125.407	93.508	137.168	0.	0.	0.
4400	37.656	126.273	94.243	140.934	0.	0.	0.
4500	37.656	127.119	94.964	144.699	0.	0.	0.
4600	37.656	127.947	95.672	148.465	0.	0.	0.
4700	37.656	128.757	96.367	152.231	0.	0.	0.
4800	37.656	129.549	97.050	155.996	0.	0.	0.
4900	37.656	130.326	97.721	159.762	0.	0.	0.
4951.969	37.656	130.723	98.066	161.719	----- FUGACITY = 1 bar -----		
5000	37.656	131.087	98.381	163.527	−591.385	5.731	−0.060
5100	37.656	131.832	99.030	167.293	−593.064	17.690	−0.181
5200	37.656	132.564	99.668	171.059	−594.890	29.683	−0.298
5300	37.656	133.281	100.295	174.824	−596.860	41.713	−0.411
5400	37.656	133.985	100.912	178.590	−598.972	53.781	−0.520
5600	37.656	135.354	102.118	186.121	−603.614	78.040	−0.728
5800	37.656	136.676	103.287	193.652	−608.795	102.474	−0.923
6000	37.656	137.952	104.422	201.183	−614.491	127.096	−1.106

PREVIOUS: December 1966 CURRENT: March 1978

0	to	2896 K	crystal
above		2896 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.585	0.	0.	0.
100	13.495	7.026	47.961	−4.094	0.	0.	0.
200	21.507	19.478	30.735	−2.251	0.	0.	0.
250	23.074	24.462	28.995	−1.133	0.	0.	0.
298.15	23.933	28.605	28.605	0.	0.	0.	0.
300	23.958	28.753	28.606	0.044	0.	0.	0.
350	24.580	32.494	28.900	1.258	0.	0.	0.
400	25.080	35.810	29.560	2.500	0.	0.	0.
450	25.500	38.789	30.423	3.765	0.	0.	0.
500	25.850	41.494	31.397	5.049	0.	0.	0.
600	26.460	46.263	33.487	7.665	0.	0.	0.
700	26.980	50.382	35.613	10.338	0.	0.	0.
800	27.440	54.015	37.691	13.059	0.	0.	0.
900	27.890	57.272	39.689	15.825	0.	0.	0.
1000	28.370	60.235	41.597	18.638	0.	0.	0.
1100	28.900	62.963	43.417	21.501	0.	0.	0.
1200	29.490	65.502	45.153	24.419	0.	0.	0.
1300	30.140	67.888	46.811	27.400	0.	0.	0.
1400	30.860	70.148	48.398	30.450	0.	0.	0.
1500	31.650	72.304	49.920	33.575	0.	0.	0.
1600	32.500	74.373	51.384	36.782	0.	0.	0.
1700	33.420	76.371	52.796	40.078	0.	0.	0.
1800	34.420	78.309	54.160	43.469	0.	0.	0.
1900	35.490	80.198	55.481	46.964	0.	0.	0.
2000	36.650	82.048	56.763	50.570	0.	0.	0.
2100	37.900	83.866	58.010	54.297	0.	0.	0.
2200	39.240	85.659	59.226	58.152	0.	0.	0.
2300	40.670	87.435	60.414	62.147	0.	0.	0.
2400	42.210	89.198	61.577	66.290	0.	0.	0.
2500	43.890	90.954	62.717	70.594	0.	0.	0.
2600	45.880	92.713	63.837	75.079	0.	0.	0.
2700	48.370	94.490	64.939	79.786	0.	0.	0.
2800	51.570	96.304	66.027	84.777	0.	0.	0.
2896.000	54.835	98.098	67.060	89.885	CRYSTAL <--> LIQUID TRANSITION		
2896.000	37.656	110.522	67.060	125.867			
2900	37.656	110.574	67.120	126.018	0.	0.	0.
3000	37.656	111.851	68.590	129.784	0.	0.	0.
3100	37.656	113.086	70.005	133.549	0.	0.	0.
3200	37.656	114.281	71.370	137.315	0.	0.	0.
3300	37.656	115.440	72.688	141.080	0.	0.	0.
3400	37.656	116.564	73.962	144.846	0.	0.	0.
3500	37.656	117.656	75.195	148.612	0.	0.	0.
3600	37.656	118.716	76.389	152.377	0.	0.	0.
3700	37.656	119.748	77.547	156.143	0.	0.	0.
3800	37.656	120.752	78.671	159.908	0.	0.	0.
3900	37.656	121.731	79.763	163.674	0.	0.	0.
4000	37.656	122.684	80.824	167.440	0.	0.	0.
4100	37.656	123.614	81.856	171.205	0.	0.	0.
4200	37.656	124.521	82.861	174.971	0.	0.	0.
4300	37.656	125.407	83.841	178.736	0.	0.	0.
4400	37.656	126.273	84.795	182.502	0.	0.	0.
4500	37.656	127.119	85.726	186.268	0.	0.	0.
4600	37.656	127.947	86.635	190.033	0.	0.	0.
4700	37.656	128.757	87.523	193.799	0.	0.	0.
4800	37.656	129.549	88.390	197.564	0.	0.	0.
4900	37.656	130.326	89.238	201.330	0.	0.	0.
4951.969	37.656	130.723	89.671	203.287	FUGACITY = 1 bar		
5000	37.656	131.087	90.068	205.096	−591.385	5.731	−0.060
5100	37.656	131.832	90.879	208.861	−593.064	17.690	−0.181
5200	37.656	132.564	91.674	212.627	−594.890	29.683	−0.298
5300	37.656	133.281	92.452	216.392	−596.860	41.713	−0.411
5400	37.656	133.985	93.215	220.158	−598.972	53.781	−0.520
5500	37.656	134.676	93.962	223.924	−601.224	65.889	−0.626
5600	37.656	135.354	94.695	227.689	−603.614	78.040	−0.728
5800	37.656	136.676	96.120	235.220	−608.795	102.475	−0.923
6000	37.656	137.952	97.494	242.752	−614.491	127.096	−1.106

PREVIOUS: CURRENT: March 1978

IP(Mo, g) = 57260 ± 50 cm^{-1}
$S°(298.15\ K)$ = 181.951 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 657.37 ± 3.8 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 658.98 ± 3.8 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^7S_3$	0	7
$^5S_2$	10768.33	5
$^5D_0$	10965.97	1
.	.	.
.	.	.
.	.	.
.	.	.
.	.	.
IP	57260	

Enthalpy of Formation

The enthalpy of formation at 298.15 K for Mo(g) is simply the enthalpy of sublimation at 298.15 K; i.e. Mo(cr) → Mo(g). The following table summarizes the analysis of the numerous sublimation studies by a 2nd and 3rd law calculation. All temperatures have been corrected to IPTS–68. All studies are based on the Langmuir effusion method.

Source	Data Points	T/K	$\Delta_{sub}H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
1	eqn	1201–2396	159.8	158.5	−0.7
2	9	2068–2500	162.2 ± 3.8	156.2 ± 1.4	−2.6 ± 1.6
3	12	2144–2537	158.4 ± 2.6	157.8 ± 0.8	−0.3 ± 1.1
4	9	2154–2466	146.8 ± 1.4	158.4 ± 1.2	5.1 ± 0.6
5	eqn	1601–2297	131.7	148.8	8.8
6	12	2089–2493	156.8 ± 1.6	156.9 ± 0.6	0.1 ± 0.7
7	10	2293–2673	152.4 ± 4.1	158.2 ± 1.4	2.3 ± 1.6

A mass spectrometric study of the enthalpy of sublimation of molybdenum[8] yielded , $\Delta_{sub}H°(2500\ K)$ = 144.1 ± 2.2 kcal·mol^{-1}; correcting to 298.15 K, we calculate $\Delta_{sub}H°(298.15\ K)$ = 149.8 kcal·mol^{-1}.

We adopt $\Delta_{sub}H°(298.15\ K)$ = 157.5 ± 0.9 kcal·mol^{-1} from a consideration of five studies.[1–3,6,7] Brewer[12] has adopted a value 0.2 kcal·mol^{-1} less positive; however his vapor pressure analysis is based on the 1948 temperature scale.

Heat Capacity and Entropy

The electronic energy levels are given in the compilations by Moore.[9,10] Although we have only listed the ground state, first excited state, highest observed excited state, and the ionization limit for Mo(g), all levels listed by Moore,[9,10] as well as estimated levels, are used in our calculations. The observed levels are too numerous to list completely. An examination of the estimates for missing levels suggests that they all lie above 20000 cm^{-1}. Our calculations indicate that for Mo(g) the thermochemical functions are independent of the estimated missing levels (for n = 5, 6, 7), the cut–off procedure, and the inclusion of n = 6, 7 levels up to 3000 K. The Gibbs energy function is essentially unaffected up to 4000 K. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic gas and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut–off procedures.[11] In fact, the inclusion of some higher states (n = 5, 6, 7) and consideration of various cut–off procedures leads to calculational differences in the Gibbs energy function of roughly 0.1 cal·K^{-1}·mol^{-1} or greater at temperatures in excess of 7600 K. The thermal functions adopted here are the same as those of Brewer.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−6.197	657.367	657.367	INFINITE
100	20.786	159.243	200.431	−4.119	658.955	643.733	−336.252
200	20.786	173.651	183.852	−2.040	659.191	628.357	−164.110
250	20.786	178.290	182.293	−1.001	659.112	620.655	−129.679
298.15	20.786	181.951	181.951	0.	658.980	613.260	−107.441
300	20.786	182.079	181.951	0.038	658.974	612.976	−106.729
350	20.786	185.283	182.204	1.078	658.800	605.323	−90.340
400	20.786	188.059	182.766	2.117	658.597	597.697	−78.051
450	20.786	190.507	183.493	3.156	658.372	590.098	−68.497
500	20.786	192.697	184.306	4.196	658.127	582.525	−60.856
600	20.786	196.487	186.030	6.274	657.589	567.455	−49.401
700	20.786	199.691	187.759	8.353	656.995	552.478	−41.226
800	20.786	202.467	189.427	10.431	656.352	537.591	−35.101
900	20.786	204.915	191.015	12.510	655.665	522.786	−30.342
1000	20.787	207.105	192.516	14.589	654.931	508.061	−26.538
1100	20.788	209.086	193.934	16.667	654.147	493.411	−23.430
1200	20.793	210.895	195.273	18.746	653.307	478.836	−20.843
1300	20.803	212.560	196.540	20.826	652.406	464.333	−18.657
1400	20.823	214.102	197.740	22.907	651.437	449.901	−16.786
1500	20.856	215.540	198.879	24.991	650.396	435.542	−15.167
1600	20.910	216.888	199.963	27.079	649.277	421.254	−13.753
1700	20.989	218.158	200.996	29.174	648.076	407.039	−12.507
1800	21.100	219.360	201.983	31.278	646.789	392.897	−11.402
1900	21.250	220.505	202.928	33.395	645.412	378.829	−10.415
2000	21.443	221.600	203.835	35.530	643.940	364.836	−9.529
2100	21.687	222.652	204.706	37.686	642.369	350.919	−8.729
2200	21.985	223.667	205.545	39.869	640.697	337.079	−8.003
2300	22.342	224.652	206.354	42.085	638.918	323.318	−7.343
2400	22.761	225.611	207.137	44.339	637.029	309.636	−6.739
2500	23.248	226.550	207.895	46.639	635.026	296.036	−6.185
2600	23.802	227.473	208.630	48.991	632.892	282.518	−5.676
2700	24.428	228.382	209.345	51.402	630.596	269.085	−5.206
2800	25.127	229.283	210.041	53.879	628.082	255.741	−4.771
2900	25.898	230.178	210.720	56.430	589.392	242.541	−4.369
3000	26.742	231.070	211.383	59.061	588.258	230.600	−4.015
3100	27.659	231.962	212.033	61.781	587.212	218.696	−3.685
3200	28.647	232.855	212.669	64.595	586.261	206.823	−3.376
3300	29.704	233.753	213.295	67.512	585.412	194.979	−3.086
3400	30.827	234.656	213.910	70.538	584.672	183.160	−2.814
3500	32.012	235.567	214.515	73.680	584.048	171.360	−2.557
3600	33.256	236.486	215.113	76.943	583.546	159.576	−2.315
3700	34.554	237.415	215.703	80.333	583.170	147.805	−2.087
3800	35.900	238.354	216.287	83.855	582.927	136.042	−1.870
3900	37.288	239.304	216.865	87.514	582.820	124.283	−1.665
4000	38.713	240.266	217.438	91.314	582.855	112.526	−1.469
4100	40.169	241.240	218.006	95.258	583.033	100.765	−1.284
4200	41.649	242.226	218.571	99.349	583.358	88.999	−1.107
4300	43.147	243.223	219.133	103.588	583.832	77.223	−0.938
4400	44.658	244.232	219.692	107.978	584.456	65.435	−0.777
4500	46.176	245.253	220.248	112.520	585.233	53.630	−0.623
4600	47.696	246.284	220.803	117.214	586.161	41.807	−0.475
4700	49.214	247.327	221.356	122.059	587.240	29.962	−0.333
4800	50.725	248.378	221.908	127.056	588.472	18.092	−0.197
4900	52.226	249.440	222.459	132.204	589.854	6.195	−0.066
4951.969	53.001	249.995	222.746	134.938	----- FUGACITY = 1 bar -----		
5000	53.713	250.510	223.010	137.501	0.	0.	0.
5100	55.185	251.588	223.560	142.946	0.	0.	0.
5200	56.640	252.674	224.109	148.537	0.	0.	0.
5300	58.072	253.766	224.658	154.272	0.	0.	0.
5400	59.485	254.865	225.207	160.150	0.	0.	0.
5500	60.874	255.969	225.757	166.168	0.	0.	0.
5600	62.239	257.078	226.306	172.323	0.	0.	0.
5700	63.577	258.191	226.856	178.613	0.	0.	0.
5800	64.887	259.308	227.406	185.035	0.	0.	0.
5900	66.164	260.428	227.956	191.585	0.	0.	0.
6000	67.413	261.550	228.506	198.263	0.	0.	0.

PREVIOUS: March 1978 (1 atm) CURRENT: March 1978 (1 bar)

IP(Mo^+, g) = 130300 ± 500 cm^{-1}
$S°$(298.15 K) = 180.669 ± 0.05 $J·K·mol^{-1}$

$\Delta_f H°$(0 K) = 1342.35 ± 4.0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1350.159] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0.00	6
$^6D_{1/2}$	11783.36	2
$^6D_{3/2}$	12034.06	4
$^6D_{5/2}$	12417.28	6
$^6D_{7/2}$	12900.33	8
$^6D_{9/2}$	13460.70	10

Enthalpy of Formation

$\Delta_f H°(Mo^+, g, 0 K)$ is calculated from $\Delta_f H°$(Mo, g, 0 K)[1]using the spectroscopic value of IP(Mo) = 57260 ± 50 cm^{-1} (684.982 ± 0.60 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Mo^+, g, 298.15 K)$ is calculated from $\Delta_f H°$(Mo, g, 0 K) by using IP(Mo) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Mo(g), Mo^+(g), and e^-(ref). $\Delta_f H°(Mo \rightarrow Mo^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for Mo^+(g), all levels listed by Moore, as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Mo^+(g), the thermodynamic functions are independent of the estimated missing levels (for n = 4, 5), the cut-off procedure, and the inclusion of n = 5 levels up to 4000 K; the Gibbs energy function showing variations of 0.4 $J·K^{-1}·mol^{-1}$ at this temperature. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>5), and use of different fill and cut-off procedures.[7]

References

[1]JANAF Thermochemical Tables: Mo(g), 3-31-78; e^-(ref), 3-31-82.
[2]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS-NBS-34, 8 pp.(1970).
[3]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
[4]H. M. Rosenstock, K. Draxl et al., J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[5]R. D. Levin and S. G. Lias, U. S. Natl. Bur. Stand. NSRDS-NBS-71, 634 pp. (1982).
[6]C. E. Moore, U.S. Nat. Bur. Stand., NSRDS-NBS-35, Volume III, (1970) [Reprint of NBS Circular 467, Volume III, 1958].
[7]J. R. Downey, Jr., The Dow Chemical Company, AFOSR-TR-78-0960, Contract No. F44620-75-1-0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1342.349		
100	20.786	157.962	199.149	−4.119			
200	20.786	172.369	182.570	−2.040			
250	20.786	177.008	181.011	−1.001			
298.15	20.786	180.669	180.669	0.	1350.159	1298.567	−227.503
300	20.786	180.798	180.669	0.038	1350.192	1298.246	−226.045
350	20.786	184.002	180.922	1.078	1351.057	1289.520	−192.450
400	20.786	186.777	181.485	2.117	1351.893	1280.672	−167.239
450	20.786	189.226	182.211	3.156	1352.707	1271.720	−147.617
500	20.786	191.416	183.024	4.196	1353.502	1262.679	−131.911
600	20.786	195.205	184.748	6.274	1355.043	1244.368	−108.332
700	20.786	198.409	186.477	8.353	1356.527	1225.804	−91.471
800	20.786	201.185	188.146	10.431	1357.963	1207.031	−78.811
900	20.786	203.633	189.733	12.510	1359.354	1188.081	−68.954
1000	20.786	205.823	191.235	14.589	1360.699	1168.978	−61.061
1100	20.787	207.804	192.652	16.667	1361.993	1149.742	−54.597
1200	20.789	209.613	193.992	18.746	1363.232	1130.392	−49.205
1300	20.794	211.277	195.258	20.825	1364.409	1110.940	−44.638
1400	20.804	212.819	196.458	22.905	1365.517	1091.401	−40.721
1500	20.824	214.255	197.597	24.986	1366.552	1071.784	−37.323
1600	20.860	215.600	198.681	27.070	1367.507	1052.102	−34.348
1700	20.917	216.866	199.714	29.159	1368.379	1032.362	−31.721
1800	21.004	218.064	200.700	31.255	1369.162	1012.573	−29.384
1900	21.128	219.202	201.644	33.361	1369.853	992.743	−27.292
2000	21.300	220.290	202.549	35.482	1370.446	972.879	−25.409
2100	21.526	221.335	203.419	37.623	1370.939	952.988	−23.704
2200	21.816	222.343	204.257	39.789	1371.328	933.076	−22.154
2300	22.176	223.320	205.064	41.988	1371.611	913.149	−20.738
2400	22.613	224.273	205.845	44.227	1371.785	893.212	−19.440
2500	23.131	225.206	206.601	46.514	1371.847	873.270	−18.246
2600	23.734	226.125	207.334	48.856	1371.783	853.327	−17.144
2700	24.423	227.033	208.047	51.263	1371.561	833.390	−16.123
2800	25.198	227.935	208.741	53.744	1371.129	813.465	−15.175
2900	26.060	228.834	209.418	56.306	1334.529	793.610	−14.294
3000	27.004	229.733	210.081	58.958	1335.495	774.941	−13.493
3100	28.028	230.635	210.729	61.709	1336.559	756.239	−12.743
3200	29.127	231.542	211.365	64.566	1337.729	737.500	−12.038
3300	30.296	232.456	211.991	67.537	1339.013	718.724	−11.376
3400	31.528	233.379	212.606	70.628	1340.416	699.906	−10.753
3500	32.817	234.311	213.213	73.844	1341.946	681.046	−10.164
3600	34.156	235.254	213.812	77.193	1343.607	662.140	−9.607
3700	35.541	236.209	214.404	80.677	1345.405	643.186	−9.080
3800	36.963	237.176	214.991	84.302	1347.343	624.181	−8.580
3900	38.419	238.155	215.572	88.071	1349.425	605.124	−8.105
4000	39.904	239.146	216.149	91.987	1351.653	586.011	−7.653
4100	41.412	240.150	216.722	96.053	1354.032	566.841	−7.222
4200	42.942	241.166	217.292	100.270	1356.563	547.611	−6.811
4300	44.491	242.195	217.859	104.642	1359.247	528.319	−6.418
4400	46.057	243.235	218.424	109.169	1362.087	508.962	−6.042
4500	47.638	244.288	218.987	113.853	1365.085	489.540	−5.682
4600	49.235	245.352	219.549	118.697	1368.242	470.049	−5.338
4700	50.847	246.429	220.109	123.701	1371.559	450.487	−5.007
4800	52.473	247.516	220.669	128.867	1375.037	430.853	−4.689
4900	54.112	248.615	221.228	134.196	1378.680	411.146	−4.383
5000	55.765	249.725	221.787	139.690	791.101	397.093	−4.148
5100	57.429	250.845	222.346	145.349	793.394	389.190	−3.986
5200	59.102	251.977	222.904	151.176	795.708	381.242	−3.830
5300	60.781	253.118	223.464	157.170	798.046	373.249	−3.679
5400	62.463	254.270	224.024	163.332	800.409	365.212	−3.533
5500	64.142	255.432	224.584	169.662	802.800	357.131	−3.392
5600	65.814	256.603	225.145	176.160	805.221	349.006	−3.255
5700	67.470	257.782	225.708	182.825	807.674	340.837	−3.123
5800	69.103	258.970	226.271	189.654	810.159	332.625	−2.996
5900	70.706	260.165	226.835	196.644	812.679	324.370	−2.872
6000	72.268	261.366	227.401	203.793	815.229	316.072	−2.752

PREVIOUS: March 1978 (1 atm) CURRENT: March 1984 (1 bar)

EA(Mo, g) = 0.746 ± 0.010 eV
$S°(298.15\ K) = 180.669 \pm 0.003\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 585.390 \pm 1.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [580.805]\ kJ \cdot mol^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0.0	6

Enthalpy of Formation

$\Delta_f H°(Mo^-, g, 0\ K)$ is calculated from $\Delta_f H°(Mo, g, 0\ K)$[1] using the adopted electron affinity of EA(Mo) = 0.746 ± 0.010 eV (71.978 ± 0.965 $kJ \cdot mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $Mo^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Mo^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Mo, g, 0\ K)$ by using EA(Mo) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, or $Mo^-(g)$, Mo(g), and e^-(ref). $\Delta_r H°(Mo^- \rightarrow Mo + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Mo^-(g)$ is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

[1]JANAF Thermochemical Tables: Mo(g), 3-31-78; e^-(ref), 3-31-82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
[3]C. S. Feigerle, R. R. Cordermann, S. V. Bobashev and W. C. Lineberger, J. Chem. Phys. **74**, 1580 (1981).
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[6]H. S. W. Massey, "Negative Ions," 3rd ed., Cambridge University Press, Cambridge, 741 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	585.390		
100	20.786	157.962	199.149	−4.119			
200	20.786	172.370	182.570	−2.040			
250	20.786	177.008	181.011	−1.001			
298.15	20.786	180.669	180.669	0.	580.805	541.722	−94.907
300	20.786	180.798	180.669	0.038	580.761	541.480	−94.280
350	20.786	184.002	180.923	1.078	579.547	535.028	−79.849
400	20.786	186.777	181.485	2.117	578.305	528.753	−69.048
450	20.786	189.226	182.212	3.156	577.040	522.635	−60.666
500	20.786	191.416	183.024	4.196	575.757	516.658	−53.975
600	20.786	195.205	184.748	6.274	573.140	505.083	−43.971
700	20.786	198.410	186.477	8.353	570.467	493.951	−36.859
800	20.786	201.185	188.146	10.431	567.746	483.205	−31.550
900	20.786	203.633	189.733	12.510	564.980	472.804	−27.441
1000	20.786	205.823	191.235	14.589	562.167	462.712	−24.170
1100	20.786	207.805	192.653	16.667	559.304	452.905	−21.507
1200	20.786	209.613	193.992	18.746	556.386	443.360	−19.299
1300	20.786	211.277	195.258	20.824	553.405	434.062	−17.441
1400	20.786	212.817	196.458	22.903	550.355	424.996	−15.857
1500	20.786	214.251	197.597	24.982	547.230	416.150	−14.492
1600	20.786	215.593	198.680	27.060	544.023	407.516	−13.304
1700	20.786	216.853	199.713	29.139	540.727	399.084	−12.262
1800	20.786	218.041	200.698	31.217	537.336	390.850	−11.342
1900	20.786	219.165	201.641	33.296	533.842	382.806	−10.524
2000	20.786	220.231	202.544	35.375	530.235	374.950	−9.793
2100	20.786	221.245	203.410	37.453	526.509	367.277	−9.136
2200	20.786	222.212	204.243	39.532	522.653	359.784	−8.542
2300	20.786	223.136	205.045	41.610	518.658	352.470	−8.005
2400	20.786	224.021	205.817	43.689	514.515	345.333	−7.516
2500	20.786	224.869	206.562	45.768	510.212	338.371	−7.070
2600	20.786	225.685	207.282	47.846	505.726	331.585	−6.662
2700	20.786	226.469	207.979	49.925	501.019	324.976	−6.287
2800	20.786	227.225	208.652	52.004	496.028	318.547	−5.943
2900	20.786	227.955	209.306	54.082	454.787	312.351	−5.626
3000	20.786	228.659	209.939	56.161	451.022	307.503	−5.354
3100	20.786	229.341	210.554	58.239	447.256	302.781	−5.102
3200	20.786	230.001	211.151	60.318	443.490	298.181	−4.867
3300	20.786	230.640	211.732	62.397	439.725	293.698	−4.649
3400	20.786	231.261	212.298	64.475	435.959	289.330	−4.445
3500	20.786	231.863	212.848	66.554	432.194	285.072	−4.254
3600	20.786	232.449	213.384	68.632	428.428	280.922	−4.076
3700	20.786	233.018	213.907	70.711	424.662	276.876	−3.909
3800	20.786	233.573	214.418	72.790	420.897	272.932	−3.752
3900	20.786	234.113	214.916	74.868	417.131	269.088	−3.604
4000	20.786	234.639	215.402	76.947	413.366	265.340	−3.465
4100	20.786	235.152	215.878	79.025	409.600	261.686	−3.334
4200	20.786	235.653	216.343	81.104	405.834	258.123	−3.210
4300	20.786	236.142	216.797	83.183	402.069	254.651	−3.093
4400	20.786	236.620	217.243	85.261	398.303	251.266	−2.983
4500	20.786	237.087	217.678	87.340	394.538	247.967	−2.878
4600	20.786	237.544	218.105	89.418	390.772	244.751	−2.779
4700	20.786	237.991	218.524	91.497	387.006	241.617	−2.685
4800	20.786	238.429	218.934	93.576	383.241	238.564	−2.596
4900	20.786	238.857	219.336	95.654	379.475	235.589	−2.511
5000	20.786	239.277	219.731	97.733	−215.675	238.422	−2.491
5100	20.786	239.689	220.118	99.811	−221.120	247.557	−2.536
5200	20.786	240.093	220.498	101.890	−226.712	256.802	−2.580
5300	20.786	240.488	220.872	103.969	−232.447	266.154	−2.623
5400	20.786	240.877	221.239	106.047	−238.325	275.617	−2.666
5500	20.786	241.258	221.599	108.126	−244.342	285.189	−2.709
5600	20.786	241.633	221.954	110.204	−250.498	294.873	−2.750
5700	20.786	242.001	222.302	112.283	−256.788	304.667	−2.792
5800	20.786	242.362	222.645	114.362	−263.210	314.573	−2.833
5900	20.786	242.718	222.982	116.440	−269.760	324.590	−2.874
6000	20.786	243.067	223.314	118.519	−276.437	334.720	−2.914

PREVIOUS: March 1978 (1 atm) CURRENT: March 1984 (1 bar)

$S°(298.15\ K) = 241.764 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 310.25 \pm 33.5\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 310.96 \pm 33.5\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[450]	[5]

$\omega_e = [1000 \pm 20]\ cm^{-1}$ $\omega_e x_e = [3.99]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.40604]\ cm^{-1}$ $\alpha_e = [0.00309]\ cm^{-1}$ $r_e = [1.74]$ Å

Enthalpy of Formation

The enthalpy of formation of MoO(g) is taken from the critical analysis of the Mo–O system by Brewer.[1] The adopted value is $\Delta_f H°(298.15\ K) = 74.32 \pm 8\ kcal \cdot mol^{-1}$. All the current JANAF Thermochemical Tables for molybdenum–oxygen species are based on the internally consistent values of Brewer.[1]

Choudary *et al.*[2] have reviewed earlier data and evaluations of $\Delta_f H°$ for MoO(g). They have also presented new data between 1462 and 1908 K. For the reaction $2\ MoO_2(g) = MoO(g) + MoO_3(g)$, the 3rd law values are mostly in the range −2.4 to −4.6 $kcal \cdot mol^{-1}$ compared to 2nd law values of −7.8 $kcal \cdot mol^{-1}$ or more negative. $\Delta_f H°/R = -2200 \pm 2000$ K was selected by Brewer[1] for the reaction as written.

Heat Capacity and Entropy

The ground state configuration is assumed to be similar to that for gaseous WO_3.[3] Swaminathan and Krisnamurthy[4] observed ten band systems which they attributed to molybdenum oxide with lower state values of $\omega_e = 950 \pm 10\ cm^{-1}$. Iorns and Stafford[5] also observed a band with a peak at 969 cm^{-1} in the vapor above MoO_3(cr). It is surprising that the observed vibrational frequency of MoO(g) is lower than 1055 cm^{-1} observed for WO(g). The latter comes not only from electronic spectra of the gas but also from infrared observation in matrix isolation; the former comes only from tentative assignments of electronic spectra presumably arising from MoO(g). It is possible that the observed states could be low lying excited states. We tentatively assume the fundamental vibrational frequency to be $1000 \pm 20\ cm^{-1}$. The anharmonicity correction x_e is estimated from the relation $x_e \mu^{1/2} = 0.014$ given by Barrow and Caunt.[6] The constant (0.014) is assumed to be the same as that for WO(g). The value of α_e is calculated from the Morse potential function. Schroder[7] gave a relationship between bond order and Mo–O internuclear distance which yields values of 1.74 Å for a bond order of two and 1.62 Å for a bond order of three. A value 1.74 ± 0.05 Å was used.

The suggestion of Hewett *et al.*,[8] that the electronic structure of MoO should be closer to that of CrO than WO, was followed in using the same treatment as for MoF_2[1] where $g = 3$ was taken for the ground state and $g = 5$ for a low-lying excited state at 450 cm^{-1}.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.636	310.249	310.249	INFINITE
100	29.997	205.390	272.530	−6.714	311.228	300.056	−156.733
200	34.472	227.640	245.025	−3.477	311.167	288.883	−75.449
250	35.531	235.461	242.355	−1.724	311.073	283.322	−59.197
298.15	36.002	241.764	241.764	0.	310.959	277.988	−48.702
300	36.014	241.987	241.765	0.067	310.954	277.783	−48.366
350	36.242	247.558	242.205	1.874	310.809	272.266	−40.633
400	36.376	252.407	243.183	3.689	310.635	266.771	−34.837
450	36.478	256.697	244.451	5.511	310.433	261.300	−30.331
500	36.567	260.545	245.871	7.337	310.205	255.852	−26.729
600	36.732	267.227	248.890	11.002	309.674	245.030	−21.332
700	36.879	272.901	251.925	14.683	309.054	234.304	−17.484
800	37.006	277.834	254.862	18.377	308.359	223.672	−14.604
900	37.114	282.199	257.662	22.083	307.596	213.131	−12.370
1000	37.207	286.114	260.314	25.799	306.769	202.679	−10.587
1100	37.287	289.664	262.824	29.524	305.876	192.313	−9.132
1200	37.357	292.911	265.198	33.256	304.916	182.031	−7.924
1300	37.418	295.904	267.446	36.995	303.882	171.832	−6.904
1400	37.473	298.679	269.579	40.740	302.770	161.715	−6.034
1500	37.522	301.266	271.606	44.490	301.574	151.681	−5.282
1600	37.568	303.689	273.537	48.244	300.288	141.730	−4.627
1700	37.610	305.968	275.378	52.003	298.905	131.862	−4.052
1800	37.649	308.119	277.138	55.766	297.419	122.078	−3.543
1900	37.686	310.155	278.822	59.533	295.821	112.380	−3.090
2000	37.721	312.089	280.438	63.303	294.104	102.769	−2.684
2100	37.754	313.931	281.989	67.077	292.259	93.247	−2.319
2200	37.786	315.688	283.481	70.854	290.276	83.816	−1.990
2300	37.817	317.368	284.918	74.634	288.146	74.479	−1.691
2400	37.846	318.978	286.304	78.417	285.859	65.237	−1.420
2500	37.875	320.524	287.642	82.203	283.405	56.094	−1.172
2600	37.903	322.010	288.936	85.992	280.760	47.054	−0.945
2700	37.931	323.441	290.187	89.784	277.886	38.119	−0.737
2800	37.958	324.821	291.400	93.578	274.720	29.295	−0.547
2900	37.985	326.153	292.575	97.376	235.298	20.640	−0.372
3000	38.011	327.441	293.716	101.175	233.344	13.272	−0.231
3100	38.036	328.688	294.824	104.978	231.383	5.969	−0.101
3200	38.062	329.896	295.901	108.783	229.415	−1.272	0.021
3300	38.087	331.068	296.949	112.590	227.441	−8.450	0.134
3400	38.112	332.205	297.970	116.400	225.462	−15.568	0.239
3500	38.136	333.310	298.964	120.212	223.477	−22.629	0.338
3600	38.161	334.385	299.933	124.027	221.486	−29.632	0.430
3700	38.185	335.431	300.878	127.844	219.491	−36.581	0.516
3800	38.209	336.449	301.801	131.664	217.491	−43.474	0.598
3900	38.233	337.442	302.702	135.486	215.486	−50.315	0.674
4000	38.257	338.410	303.583	139.311	213.477	−57.106	0.746
4100	38.280	339.355	304.444	143.138	211.464	−63.845	0.813
4200	38.304	340.278	305.286	146.967	209.447	−70.536	0.877
4300	38.327	341.180	306.110	150.798	207.426	−77.178	0.938
4400	38.350	342.061	306.917	154.632	205.402	−83.773	0.995
4500	38.374	342.923	307.708	158.468	203.373	−90.323	1.048
4600	38.397	343.767	308.483	162.307	201.341	−96.827	1.100
4700	38.420	344.593	309.242	166.148	199.305	−103.287	1.148
4800	38.443	345.402	309.987	169.991	197.265	−109.704	1.194
4900	38.466	346.195	310.718	173.836	195.221	−116.077	1.237
5000	38.489	346.972	311.435	177.684	−398.212	−116.678	1.219
5100	38.512	347.735	312.140	181.534	−401.945	−111.011	1.137
5200	38.534	348.483	312.831	185.386	−405.828	−105.269	1.057
5300	38.557	349.217	313.511	189.241	−409.860	−99.450	0.980
5400	38.580	349.938	314.179	193.098	−414.040	−93.555	0.905
5500	38.602	350.646	314.836	196.957	−418.366	−87.581	0.832
5600	38.625	351.342	315.481	200.818	−422.836	−81.526	0.760
5700	38.648	352.026	316.116	204.682	−427.446	−75.391	0.691
5800	38.670	352.698	316.741	208.548	−432.196	−69.173	0.623
5900	38.693	353.359	317.356	212.416	−437.081	−62.873	0.557
6000	38.715	354.010	317.962	216.286	−442.103	−56.488	0.492

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

Pearson Notation: mP12
$S°(298.15\ K) = 46.459 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -582.90 \pm 2.1\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -587.85 \pm 2.9\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation of MoO_2(cr) at 298.15 K is -140.5 ± 0.2 kcal·mol^{-1}. This value is chosen so as to be in agreement with Brewer[1] who has performed a critical analysis of all data pertaining to the molybdenum–oxygen system. However, Brewer[1] chose to adopt the value previously used by JANAF;[14] a value which was derived as a weighted average of two calorimetric determinations and seven equilibrium studies, the latter results based on $S°(298.15\ K) = 11.954$ cal·K^{-1}·mol^{-1}. In revising the $S°(298.15\ K)$ value to 11.04 cal·K^{-1}·mol^{-1} in this tabulation, the enthalpy of formation should also have been revised. With the exception of the data from Barbi[5] the following equilibrium studies suggest $\Delta_f H°(298.15\ K) = -141.20$ kcal·mol^{-1} in comparison with the calorimetric mean of $\Delta_f H°(298.15\ K) = -140.8$ kcal·mol^{-1} for MoO_2(cr). In addition, eight recent emf studies (published since the analysis by Brewer) also yield a value of $\Delta_f H°(298.15\ K) = -141.2$ kcal·mol^{-1}. Although there is some overlap in the values for $\Delta_f H°$ derived from equilibrium and calorimetric studies, the equilibrium studies appear to be more negative by 0.4 kcal·mol^{-1}. Brewer[1] noted (in reference to $\Delta_f H°(298.15\ K) = -140.5$ kcal·mol^{-1}, however, that a better overall fit of all Mo–O data would be obtained if the enthalpy of formation of MoO_2(cr) were made more negative by 0.5 kcal·mol^{-1} with a corresponding decrease of 0.5 kcal·mol^{-1} for MoO_2(g) and MoO(g) and 0.8 kcal·mol^{-1} for MoO_3 (g). Such a change could be accommodated in the MoO_2 tables.

Ignition of the bomb products from the calorimetric studies of Staskiewicz *et. al.*[2] indicated that oxidation was only about 70 percent complete. The authors also digested the products with NH_4OH to remove the trioxide. The residue was the dioxide, as indicated by both oxidation and reduction. This evidence does not necessarily eliminate the possibility of known intermediate oxides in the combustion products. Mah[3] found 72–75 percent conversion to trioxide by weighing the total combustion products; no additional analysis was performed.

Source	Method	Reaction	T/K	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Staskiewicz *et. al.*[2]	Calorimetric	A	–		−37.12		–	−140.86 ± 0.13**
Mah[3]	Calorimetric	A	–	–	−37.52		–	−140.64 ± 0.13**
Rapp[4]	emf	B	1023–1323	35	−13.26	−14.18	−0.8 ± 0.1	−141.46
		C	1023–1273	22	−25.64	−26.65	−0.9 ± 0.1	−141.25
Barbi[5]	emf	F	873–1073	Eqn.	−140.4	−139.45	0.9	−139.45
Gleiser and Chipman[6]	Equilibrium	D	1296–1341	9	+3.02	−6.57	−3.6 ± 1.5	−141.84
Gokcen[7]	Equilibrium	E	949–1344	Eqn.	−19.88	−25.50	−3.4	−141.11
Collins[8]	Equilibrium	E	973–1173	Eqn.	−22.18	−25.46	−1.5	−141.07
Tonosaki[9]	Equilibrium	E	981–1096	Eqn.	−18.86	−25.86	−3.0	−140.47

**Auxiliary data for MoO_3(cr) are taken from corresponding measurements of the same authors. See also JANAF.[13]

Reaction:

A. $MoO_2(cr) + 1/2\ O_2(g) = MoO_3(cr)$
B. $2\ Fe_xO(cr) + Mo(cr) = MoO_2(cr) + 2\ xFe(cr)$
C. $2\ NiO(cr) + Mo(cr) = MoO_2(cr) + 2\ Ni(cr)$
D. $Mo(cr) + 2\ CO_2(g) = MoO_2(cr) + 2\ CO(g)$
E. $Mo(cr) + 2\ H_2O(g) = MoO_2(cr) + 2\ H_2(g)$
F. $Mo(cr) + O_2(g) = MoO_2(cr)$ derived by the author from the cell reaction $2\ Fe_xO(cr) + Mo(cr) = MoO_2(cr) + 2\ xFe(cr)$ using $\Delta_f G°$ data for Fe_xO(cr)

Heat Capacity and Entropy

King[10] measured low temperature heat capacities from 53.3 to 296 K. King *et al.*[11] measured the high temperature enthalpy changes from 399 to 1801 K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that they join smoothly at 298.15 K. Deviations of the enthalpy data from the adopted values are −1.3 to +0.7%, excluding the point at 1801 K. This point at the highest temperature deviates by +2.3%, which suggests that the apparent heat capacity is rising very rapidly. No explanation for this rapid rise is available.

The entropy $S°(298.15\ K) = 11.104$ cal·K^{-1}·mol^{-1} is obtained from the low temperature heat capacity data, based on $S°(51\ K) = 0.36$ cal·K^{-1}·mol^{-1}. As discussed by Brewer,[1] Ghose *et. al.*[12] used neutron diffraction measurements to demonstrate the absence of a permanent magnetic moment. Thus no additional heat capacity or entropy contribution below 50 K due to a possible antiferromagnetic effect is necessary.

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Continued on page 1598

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.319	−582.903	−582.903	INFINITE
100	16.175	7.463	85.470	−7.801	−585.780	−568.493	296.951
200	41.363	26.960	51.165	−4.841	−587.574	−550.373	143.743
298.15	55.898	46.459	46.459	0.	−587.852	−532.011	93.206
300	56.095	46.806	46.460	0.104	−587.847	−531.664	92.571
400	63.551	64.076	48.764	6.125	−587.253	−513.011	66.992
500	67.936	78.758	53.333	12.713	−586.272	−494.558	51.666
600	71.174	91.441	58.651	19.674	−585.087	−476.324	41.468
700	73.935	102.623	64.150	26.932	−583.757	−458.300	34.199
800	76.488	112.664	69.597	34.454	−582.293	−440.476	28.760
900	78.965	121.816	74.898	42.227	−580.692	−422.843	24.541
1000	81.437	130.264	80.017	50.247	−578.946	−405.397	21.176
1100	83.948	138.143	84.947	58.515	−577.049	−388.132	18.431
1200	86.513	145.557	89.692	67.038	−574.994	−371.048	16.151
1300	89.148	152.585	94.262	75.820	−572.776	−354.141	14.230
1400	91.872	159.291	98.669	84.870	−570.389	−337.411	12.589
1500	94.680	165.725	102.926	94.197	−567.829	−320.858	11.173
1600	97.588	171.927	107.046	103.810	−565.090	−304.482	9.940
1700	100.588	177.933	111.040	113.718	−562.170	−288.282	8.858
1800	103.688	183.770	114.919	123.931	−559.064	−272.260	7.901
1900	106.893	189.461	118.694	134.459	−555.770	−256.416	7.049
2000	110.198	195.028	122.372	145.313	−552.285	−240.749	6.288
2100	113.608	200.487	125.962	156.502	−548.608	−225.262	5.603
2200	117.123	205.852	129.472	168.038	−544.736	−209.954	4.985
2300	120.742	211.138	132.908	179.930	−540.669	−194.828	4.425
2400	124.470	216.355	136.276	192.190	−536.405	−179.882	3.915
2500	128.302	221.514	139.583	204.827	−531.946	−165.118	3.450
2600	132.244	226.622	142.832	217.854	−527.301	−150.536	3.024
2700	136.290	231.689	146.030	231.280	−522.500	−136.135	2.634
2800	140.440	236.720	149.179	245.115	−517.593	−121.915	2.274
2900	144.704	241.722	152.284	259.371	−548.535	−107.822	1.942
3000	149.072	246.701	155.348	274.059	−541.590	−92.742	1.615

PREVIOUS: June 1967 CURRENT: September 1978

$\Delta_{at}H°(0\ K) = 1157.294 \pm 20.9\ kJ·mol^{-1}$
$S°(298.15\ K) = [276.990 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = -6.32 \pm 12.6\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = -8.31 \pm 12.6\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
900 (1)
[300] (1)
950 (1)

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[13000]	[6]
[25000]	[6]

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Mo–O = 1.73 Å
Bond Angle: O–Mo–O = 116°
Product of the Moments of Inertia: $I_AI_BI_C = 5.663388 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

The adopted enthalpy of formation for $MoO_2(g)$ at 298.15 K is -1.99 ± 3 kcal·mol^{-1}. This value was adopted by Brewer[1] who has performed a critical analysis of all data pertaining to the molybdenum–oxygen system. Brewer[1] adopted $\Delta_{sub}H°(298.15\ K)/R = 69700 \pm 1500$ K for the sublimation process $MoO_2(cr) = MoO_2(g)$. The vapor pressures of MoO_2 calculated from the adopted tabulation slightly exceed those of Burns *et al.*[2] and are 50% lower than those of Chizhikov *et al.*[6] The adopted ΔG values for the formation of $MoO_2(g)$ from Mo(cr) and $O_2(g)$ average 1 kcal·mol^{-1} more negative than those determined by Franklin and Stickney.[7] The only recent determination that deviates seriously is that of Belton and Jordan[8] who determined the volatility of molybdenum in steam–hydrogen mixtures at 1200 and 1500°C. The variation of their results with water partial pressure at 1383 to 1500°C indicate an intercept corresponding to non–hydrated species which they attribute to MoO_3 and MoO_2. They assumed the ratio of MoO_2 to MoO_3 to be that observed by Burns *et al.*[2] and obtained partial pressures of MoO_2 about six times higher than calculated from the adopted values. Their values would require that $\Delta_fH°(298.15\ K)/R$ of $Mo(cr) + O_2(g) = MoO_2(g)$ be made more negative by 3200 K. If both $\Delta_{sub}H°$ and $\Delta_fH°(cr)$ were shifted by their assigned uncertainties indicated, a change of 2000 K could be accomodated.

Burns *et al.*[2] have investigated mass–spectrometrically the vapor in equilibrium with powdered $MoO_2(cr)$ and also reported the partial pressures of $MoO_2(g)$, $MoO_3(g)$, $(MoO_3)_2(g)$ and $(MoO_3)_3(g)$. DeMaria *et al.*[3] have measured the partial pressures of gaseous oxides MoO, MoO_2, and O(g) in the Mo–Al_2O_3 system by mass spectrometry. Blackburn *et al.*[4] and Plante[5] have studied the vapor pressures above MoO_2 (cr) by the Knudsen effusion method. More recently there have been mass spectroscopic Knudsen cell studies of Chizhikov *et al.*[6] of the vapor over $MoO_2(cr)$ between 1500 and 1730 K and the Langmuir type studies of Franklin and Stickney[7] on the vapor resulting from oxygen on a molybdenum surface.

Source	Reaction	T/K	Data Points	$\Delta_fH°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°(298.15\ K)$ kcal·mol^{-1}
Burns *et al.*[2]	$MoO_2(cr) \rightarrow MoO_2(g)$	1598–1777	11*	137.6 ± 3.0	137.38	−0.7 ± 1.8	−1.67
DeMaria *et al.*[3]	$Mo(cr)+2O(g) \rightarrow MoO_2(g)$	2262–2466	9	−61.3 ± 32.0	138.83	−20.0 ± 13.6	+10.74
Blackburn *et al.*[4]	$MoO_2(cr) \rightarrow MoO_2(g)$	1818–2028	7	107.6 ± 6.8	126.55	−9.9 ± 3.5	−13.95
Plante[5]	$MoO_2(cr) \rightarrow MoO_2(g)$	1611–1802	6	151.1 ± 13.4	142.89	−5.0 ± 7.7	+1.89
Chizhikov *et al.*[6]	$MoO_2(cr) = MoO_2(g)$	1500–1750	Eqn	131.3 ± 0.2	136.88	3.4 ± 0.1	−3.6
Franklin and Stickney[7]	$Mo(cr)+O_2(g) = MoO_2(g)$	1900–2500	Eqn	−0.2 ± 1.3	−0.80	−0.3 ± 0.6	−0.80
Beltonand Jordan[8]	$Mo(cr)+2H_2O(g) = MoO_2(g)+2H_2(g)$	1473–1773	Eqn	−118.1 ± 0.1	109.91	−6.5 ± 0.0	−5.7

*2 points rejected due to failure of statistical test

Heat Capacity and Entropy

Hewett *et al.*[9] have reviewed the spectroscopic studies on $MoO_2(g)$. In addition they have studied spectroscopically MoO_2in neon and argon matrices at 4 K. The adopted bond distance and angle and two stretching frequencies are derived from this study. Brewer[1] adopted the same values. The bending frequency (300 cm^{-1}) is estimated by comparison with other transition metal dioxides.

Continued on page 1598

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_fH°$ (kJ·mol^{-1})	$\Delta_fG°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−11.278	−6.324	−6.324	INFINITE
100	35.387	234.266	313.300	−7.903	−6.346	−11.739	6.132
200	39.935	260.251	280.895	−4.129	−7.324	−16.782	4.383
250	42.110	269.395	277.706	−2.078	−7.849	−19.085	3.988
298.15	44.174	276.990	276.990	0.	−8.314	−21.206	3.715
300	44.250	277.264	276.991	0.082	−8.331	−21.286	3.706
350	46.212	284.235	277.537	2.344	−8.759	−23.410	3.494
400	47.922	290.521	278.774	4.699	−9.141	−25.477	3.327
450	49.371	296.251	280.402	7.132	−9.490	−27.498	3.192
500	50.583	301.518	282.254	9.632	−9.815	−29.481	3.080
600	52.431	310.914	286.267	14.788	−10.435	−33.355	2.904
700	53.723	319.099	290.385	20.100	−11.051	−37.127	2.770
800	54.644	326.336	294.435	25.521	−11.688	−40.809	2.665
900	55.317	332.813	298.346	31.020	−12.360	−44.409	2.577
1000	55.821	338.668	302.090	36.578	−13.077	−47.932	2.504
1100	56.206	344.008	305.662	42.180	−13.847	−51.380	2.440
1200	56.507	348.912	309.064	47.817	−14.678	−54.756	2.383
1300	56.747	353.444	312.306	53.480	−15.579	−58.060	2.333
1400	56.942	357.657	315.397	59.165	−16.557	−61.292	2.287
1500	57.104	361.591	318.347	64.867	−17.621	−64.451	2.244
1600	57.243	365.281	321.166	70.585	−18.778	−67.536	2.205
1700	57.365	368.755	323.864	76.315	−20.035	−70.545	2.168
1800	57.479	372.037	326.450	82.057	−21.400	−73.478	2.132
1900	57.587	375.148	328.932	87.811	−22.880	−76.331	2.098
2000	57.694	378.105	331.317	93.575	−24.485	−79.103	2.066
2100	57.805	380.922	333.613	99.350	−26.222	−81.792	2.034
2200	57.920	383.614	335.825	105.136	−28.100	−84.394	2.004
2300	58.043	386.191	337.959	110.934	−30.127	−86.908	1.974
2400	58.176	388.664	340.021	116.745	−32.313	−89.331	1.944
2500	58.318	391.042	342.014	122.569	−34.666	−91.659	1.915
2600	58.471	393.332	343.944	128.409	−37.208	−93.890	1.886
2700	58.634	395.542	345.815	134.264	−39.978	−96.017	1.858
2800	58.809	397.677	347.629	140.136	−43.035	−98.038	1.829
2900	58.994	399.744	349.391	146.026	−82.343	−99.894	1.799
3000	59.188	401.748	351.103	151.935	−84.176	−100.468	1.749
3100	59.392	403.692	352.768	157.864	−86.009	−100.980	1.702
3200	59.603	405.581	354.389	163.814	−87.838	−101.435	1.656
3300	59.822	407.418	355.968	169.785	−89.664	−101.832	1.612
3400	60.046	409.207	357.508	175.778	−91.484	−102.173	1.570
3500	60.276	410.951	359.010	181.794	−93.297	−102.461	1.529
3600	60.510	412.652	360.476	187.833	−95.103	−102.697	1.490
3700	60.746	414.313	361.909	193.896	−96.900	−102.884	1.452
3800	60.985	415.937	363.310	199.983	−98.687	−103.021	1.416
3900	61.225	417.524	364.679	206.093	−100.464	−103.111	1.381
4000	61.465	419.077	366.020	212.228	−102.231	−103.157	1.347
4100	61.704	420.598	367.333	218.386	−103.987	−103.158	1.314
4200	61.941	422.087	368.619	224.568	−105.731	−103.117	1.282
4300	62.177	423.548	369.879	230.774	−107.465	−103.034	1.252
4400	62.409	424.980	371.115	237.004	−109.187	−102.911	1.222
4500	62.638	426.385	372.328	243.256	−110.898	−102.750	1.193
4600	62.863	427.764	373.518	249.531	−112.599	−102.550	1.164
4700	63.083	429.118	374.687	255.828	−114.290	−102.313	1.137
4800	63.298	430.449	375.835	262.148	−115.971	−102.041	1.110
4900	63.507	431.756	376.963	268.488	−117.644	−101.733	1.084
5000	63.711	433.041	378.071	274.849	−710.695	−95.660	0.999
5100	63.909	434.305	379.162	281.230	−714.033	−83.326	0.853
5200	64.100	435.548	380.234	287.630	−717.513	−70.926	0.712
5300	64.285	436.770	381.289	294.050	−721.131	−58.457	0.576
5400	64.462	437.974	382.328	300.487	−724.890	−45.919	0.444
5500	64.633	439.158	383.350	306.942	−728.787	−33.310	0.316
5600	64.798	440.324	384.357	313.413	−732.823	−20.628	0.192
5700	64.954	441.472	385.349	319.901	−736.994	−7.874	0.072
5800	65.104	442.603	386.327	326.404	−741.301	4.956	−0.045
5900	65.247	443.717	387.290	332.922	−745.740	17.858	−0.158
6000	65.383	444.815	388.240	339.453	−750.314	30.840	−0.268

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

Pearson Notation: mP60
$S°(298.15\ K) = [69.936 \pm 1.7]\ J\ K^{-1}\cdot mol^{-1}$
$T_{trs} = 875 \pm 50\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -708.41 \pm 3.3\ kJ\cdot mol^{-1}$
$\Delta_{trs} H° = 0\ kJ\cdot mol^{-1}$

Enthalpy of Formation

For this oxide, the atomic ratio of oxygen to molybdenum is 2.750 or 11/4. The formula $MoO_{2.750}$ (upon which this tabulation is based) is more indicative of the oxygen content relative to MoO_2 and MoO_3, as opposed to Mo_4O_{11}. The thermochemical values describing $MoO_{2.750}$ are numerically 1/4 those of Mo_4O_{11}.

The high temperature emf measurements[1,2,3] on compositions between MoO_2 and MoO_3 gave widely divergent results, some of which are contradicted by the Mo–O phase diagram recommended by Brewer.[4] Brewer[4] found that it was more practical to determine a $\Delta_f H°(298.15\ K)$ value for Mo_4O_{11}(cr) by fixing the thermodynamic properties from the peritectic equilibrium together with the thermodynamic data for the liquid. From the phase diagram,[4] MoO_2 and Mo_4O_{11} solids are in equilibrium with the peritectic liquid of 74.2 ± 0.1 atomic % oxygen at 1091 ± 7 K. For Mo_4O_{11}(cr) = MoO_2(cr) + 3 MoO_3(l), Brewer[4] obtained $\Delta_r G°/RT = 0.863 \pm 0.05$ at 1091 K. This yielded, using auxiliary data,[5] $\Delta_r H°/R = 1280 \pm 400$ K for the disproportionation of Mo_4O_{11} to crystalline MoO_2 and MoO_3 at 298.15 K. This heat of reaction yields $\Delta_r H°(298.15\ K)/R = -85203 \pm 200$ K for Mo_4O_{11}, from which we calculate $\Delta_f H°(MoO_{2.750}, cr, 298.15\ K) = -169.315 \pm 0.4\ kcal\cdot mol^{-1}$. We increase the uncertainty in $\Delta_f H°$ to ± 0.8 kcal·mol^{-1} which better represents the effect of errors in reducing a $\Delta_r G°$ value at 1091 K to a $\Delta_f H°$ value at 298.15 K.

Heat Capacity and Entropy

Bousquet *et. al.*[6] used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for Mo_4O_{11}(cr), Mo_8O_{23}(cr), and Mo_9O_{26}(cr). Brewer[1] compared their values of MoO_2(cr) and MoO_3(cr) mixtures with the same composition. For Mo_4O_{11}(cr), the enthalpies were higher by 3% at 400 K, decreasing to 1.5% at 700 K. As these differences were within the scatter of the experimental measurements, Brewer[1] assumed $\Delta C_p° = 0$ and $\Delta S° = 0$ for the formation of Mo_4O_{11} from 3 MoO_3(cr) and MoO_2(cr). Bousquet *et. al.*[6] also measured the high temperature enthalpy data of MoO_3 fom 379 to 971 K. Their values agree with the adopted JANAF values for MoO_3[5] within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for Mo_4O_{11}(cr), based on the assumption $\Delta C_p° = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

Phase Data

Mo_4O_{11}(oP60) disproportionates to MoO_2 and liquid at 1091 ± 7 K, according to the phase diagram of Phillips and Chang.[7,8] Mo_4O_{11}(oP60) transforms on cooling below 875 ± 50 K to Mo_4O_{11}(mP60). Bousquet *et. al.*[6] did not interpret their enthalpy data to include a transition at 875 K. However, a graphical examination of their data suggests two comments. First, the data point at 670 K may be a typographical error; perhaps 62.58 cal g^{-1} should be 52.58 cal g^{-1}. Second, a transition at approximately 850 K with a corresponding heat of 0.7 kcal·mol^{-1} could be easily derived. To be consistent with Brewer,[4] we assume a transition at 875 ± 50 K with a corresponding zero heat of transition.

In addition to the discussion of the molybdenum oxygen system by Brewer,[4] Gmelin Handbuch der Anorganischen Chemie[9] has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley[10] have reviewed the work of Ekstrom as well as the earlier work of Kihlborg[11] on the phases in the Mo–O system.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	70.135	69.936	69.936	0.	−708.412	−636.633	111.535
300	70.354	70.370	69.937	0.130	−708.401	−636.188	110.770
400	78.208	91.763	72.800	7.585	−707.487	−612.239	79.950
500	82.797	109.722	78.438	15.642	−706.185	−588.572	61.488
600	86.626	125.158	84.968	24.114	−704.674	−565.189	49.204
700	90.344	138.790	91.701	32.962	−702.973	−542.073	40.450
800	94.145	151.100	98.369	42.185	−701.059	−519.215	33.901
900	98.072	162.414	104.864	51.795	−698.899	−496.612	28.823
1000	102.139	172.956	111.152	61.804	−696.462	−474.263	24.773
1100	106.331	182.887	117.226	72.227	−693.727	−452.173	21.472
1200	110.638	192.323	123.094	83.074	−690.678	−430.346	18.732
1300	115.050	201.352	128.769	94.358	−687.302	−408.786	16.425
1400	119.553	210.043	134.266	106.087	−683.591	−387.498	14.458
1500	124.139	218.447	139.599	118.271	−679.539	−366.489	12.762

PREVIOUS: CURRENT: September 1978

Molybdenum Oxide ($MoO_{2.875}$) CRYSTAL M_r = 141.9383

Pearson Notation: mP62

$S°(298.15\ K)$ = [73.849 ± 1.7] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K)$ = −727.13 ± 2.5 $kJ·mol^{-1}$

Enthalpy of Formation

For this oxide, the atomic ratio of oxygen to molybdenum is 2.875 or 23/8. The formula $MoO_{2.875}$ (upon which this tabulation is based) is more indicative of the oxygen content relative to MoO_2 and MoO_3, as opposed to Mo_8O_{23}. The thermochemical values describing $MoO_{2.875}$ are numerically 1/8 those of Mo_8O_{23}.

The high temperature emf measurements[1,2,3] on compositions between MoO_2 and MoO_3 gave widely divergent results, some of which are contradicted by the Mo–O phase diagram recommended by Brewer.[4] Brewer[4] found that it was more practical to determine a $\Delta_f H°(298.15\ K)$ value for $MoO_{2.875}$ by fixing the thermodynamic properties from the peritectic equilibria together with the thermodynamic data for the liquid. From the Mo–O phase diagram,[4] Mo_8O_{23} and Mo_4O_{11} solids are in equilibrium with the peritectic liquid of 74.45 ± 0.1 atomic % oxygen at 1058 ± 5 K. For the equilibrium $Mo_8O_{23}(cr) = Mo_4O_{11}(cr) + 4\ MoO_3(l)$, Brewer[4] calculated a $\Delta_r G°/RT$ value at 1058 K. This yielded, using auxiliary data,[5] $\Delta_r H°/R$ = 380 ± 200 K for the disproportionation of Mo_8O_{23} to crystalline Mo_4O_{11} and MoO_3 at 298.15 K. This enthalpy of reaction yields $\Delta_r H°(298.15\ K)/R = -87454 \pm 150$ K from which we calculate $\Delta_f H°(MoO_{2.875}, cr, 298.15\ K) = -173.788 \pm 0.3$ $kcal·mol^{-1}$. We increase the uncertainty in $\Delta_f H°$ to ± 0.6 $kcal·mol^{-1}$; a value which better represents the effect of uncertainties in reducing a $\Delta_r G°$ value at 1058 K to a $\Delta_f H°$ value at 298.15 K.

Heat Capacity and Entropy

Bousquet *et al.*[6] used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for $Mo_4O_{11}(cr)$, $Mo_8O_{23}(cr)$, and $Mo_9O_{26}(cr)$. Brewer[4] compared their values with values of $MoO_2(cr)$ and $MoO_3(cr)$ mixtures with the same composition. For $Mo_8O_{23}(cr)$, the enthalpies were lower by 15% at 400 K, lower by 3% at 500 K, and higher at higher temperatures, becoming 6% high at 700 K. As these differences were within the scalter of the expeirmental measurements, Brewer[4] assumed $\Delta C_p° = 0$ and $\Delta S° = 0$ for the formation of $Mo_4O(cr)$ from $3MoO_2(cr)$ and $MoO_2(cr)$.

Bousquet *et al.*[6] also measured high temperature enthalpy data of MoO_3 from 379 to 971 K. Their values agree with the adopted JANAF values[5] for $MoO_3(cr)$ within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for $Mo_8O_{23}(cr)$, based on the assumption $\Delta C_p° = 0$ as discussed in the preceding paragraph, may be less reliable at higher temperatures.

Phase Data

The phase Mo_8O_{23}(mP62) was found by Kihlborg[7] and Bousquet and Guillon[8] at temperatures up to 1058–1063 K. Bousquet and Guillon[8] observed Mo_8O_{23} to disproportionate to $Mo_4O_{11}(cr)$ and $MoO_3(g)$ at 1053 K by differential thermal analysis. Brewer[4] adopted Mo_8O_{23} as a stable phase which disproportionates to Mo_4O_{11} and liquid at a temperature, T_{dcm} = 1058 ± 5 K, which is slightly above the disproportionation temperature of Mo_9O_{26}.

In addition to the discussion of the molybdenum–oxygen system by Brewer,[4] Gmeli Handbuch der Anorganischen Chemie[9] has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley[10] have reviewed the work of Ekstrom as well as the earlier work of Kihlborg[11] on the phases in the Mo–O system.

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Molybdenum Oxide ($MoO_{2.875}$) $Mo_1O_{2.875}(cr)$

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	72.508	73.849	73.849	0.	−727.128	−652.662	114.344
300	72.730	74.298	73.850	0.134	−727.116	−652.200	113.558
400	80.651	96.385	76.807	7.831	−726.147	−627.358	81.925
500	85.274	114.891	82.625	16.133	−724.793	−602.813	62.975
600	89.201	130.786	89.358	24.857	−723.229	−578.561	50.368
700	93.079	144.826	96.297	33.970	−721.468	−554.586	41.384
800	97.088	157.515	103.169	43.477	−719.481	−530.878	34.663
900	101.256	169.189	109.864	53.393	−717.229	−507.435	29.451
1000	105.589	180.081	116.347	63.734	−714.679	−484.259	25.295
1100	110.062	190.353	122.612	74.516	−711.806	−461.353	21.908
1200	114.658	200.126	128.667	85.751	−708.592	−438.723	19.097
1300	119.366	209.489	134.527	97.451	−705.025	−416.376	16.730
1400	124.166	218.510	140.205	109.627	−701.096	−394.318	14.712
1500	129.049	227.243	145.718	122.287	−696.797	−372.553	12.973

PREVIOUS: CURRENT: September 1978

Pearson Notation: mP70
$S°(298.15\ K)$ = [74.281 ± 1.7] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K)$ = −729.16 ± 2.5 $kJ·mol^{-1}$

Enthalpy of Formation

For this oxide, the atomic ratio of oxygen to molybdenum is 2.889 or, more exactly, 26/9. The formula $MoO_{2.889}$ (upon which this tabulation is based) is more indicative of the oxygen content relative to MoO_2 and MoO_3, as opposed to Mo_9O_{26}. The thermochemical values describing $MoO_{2.889}$ are numerically 1/9 those of Mo_9O_{26}.

The high temperature emf measurements[1,2,3] on compositions between MoO_2 and MoO_3 gave widely divergent results, some of which are contradicted by the Mo–O phase diagram recommended by Brewer.[4] Brewer[4] found that it was more practical to determine a $\Delta_f H°(298.15\ K)$ value for $MoO_{2.889}$ by fixing the thermodynamic properties from the peritectic equilibria together with the thermodynamic data for the liquid. From the Mo–O phase diagram,[4] Mo_9O_{26} and Mo_8O_{23} solids are in equilibrium with the peritectic liquid of 74.6 ± 0.1 atomic % oxygen at 1053 ± 5 K. For the equilibrium $Mo_9O_{26}(cr) = Mo_8O_{23}(cr) + MoO_3(l)$, Brewer[4] calculated a $\Delta_r G°/RT$ value at 1053 K. This yielded, using auxiliary data[5], $\Delta_f H°/R$ = 50 ± 50 K for the disproportionation of Mo_9O_{26} to crystalline Mo_8O_{23} and MoO_3 at 298.15 K. This enthalpy of reaction yields $\Delta_f H°(298.15\ K)/R$ = −87699 ± 150 K from which we calculate $\Delta_f H°(MoO_{2.889}, cr, 298.15\ K)$ = −174.275 ± 0.3 $kcal·mol^{-1}$. We increase the uncertainty in $\Delta_f H°$ to ± 0.6 $kcal·mol^{-1}$; a value which better represents the effects of uncertainties in reducing a $\Delta_r G°$ value of 1053 K to a $\Delta_f H°$ value at 298.15 K.

Heat Capacity and Entropy

Bousquet *et al.*[6] used differential enthalpy analysis to obtain enthalpies between 379 and 971 K for $Mo_4O_{11}(cr)$, $Mo_8O_{23}(cr)$, and $Mo_9O_{26}(cr)$. Brewer[4] compared their values with values of $MoO_2(cr)$ and $MoO_3(cr)$ mixtures with the same composition. For $Mo_9O_{26}(cr)$, the enthalpies were lower by 10% at 400 K but crossed over between 500 and 600 K and were 3% higher at 700 K. As these differences were within the scatter of the experimental measurements, Brewer[4] assumed $\Delta C_p° = 0$ and $\Delta S° = 0$ for the formation of $Mo_9O_{25}(cr)$ from $MoO_2(cr)$ and 8 $MoO_3(cr)$.

Bousquet *et al.*[6] also measured high temperature enthalpy data of MoO_3 from 379 to 971 K. Their values agree with the adopted JANAF values[5] for $MoO_3(cr)$ within 2% below 500 K, but the deviations increase rapidly at higher temperatures becoming 10% high at 950 K. Thus, the adopted heat capacity values for $Mo_9O_{26}(cr)$, based on the assumption $\Delta C_p° = 0$ as discussed in the preceding paragraph, may be less reliable at hgher temperatures.

Phase Data

Mo_9O_{26} (mP70) disproportionates at 1053 ± 5 K to Mo_4O_{11} and liquid according to the phase diagram of Phillips and Chang.[7,8] Brewer[4] adopted a phase diagram which included Mo_8O_{23} which Phillips and Chang[7,8] did not have.

In addition to the discussion of the molybdenum–oxygen system by Brewer,[4] Gmelin Handbuch der Anorganischen Chemie[9] has recently presented a thorough summary of the literature dealing with the phase diagram and properties of the oxide phases. Ekstrom and Tilley[10] have reviewed the work of Ekstrom as well as the earlier work of Kihlborg[11] on the phases in the Mo–O system.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	72.772	74.281	74.281	0.	−729.165	−654.461	114.659
300	72.995	74.732	74.282	0.135	−729.153	−653.998	113.871
400	80.923	96.896	77.250	7.858	−728.175	−629.078	82.149
500	85.550	115.463	83.088	16.188	−726.812	−604.456	63.147
600	89.487	131.409	89.843	24.940	−725.239	−580.129	50.505
700	93.383	145.494	96.806	34.082	−723.469	−556.082	41.495
800	97.415	158.225	103.700	43.621	−721.470	−532.303	34.756
900	101.611	169.940	110.417	53.571	−719.204	−508.790	29.529
1000	105.973	180.870	116.922	63.949	−716.637	−485.545	25.362
1100	110.476	191.181	123.208	74.770	−713.746	−462.573	21.966
1200	115.105	200.991	129.284	86.048	−710.511	−439.879	19.147
1300	119.846	210.391	135.164	97.795	−706.919	−417.470	16.774
1400	124.679	219.449	140.863	110.021	−702.961	−395.351	14.751
1500	129.595	228.218	146.396	122.734	−698.631	−373.528	13.007

PREVIOUS: CURRENT: September 1978

Molybdenum Oxide (MoO_3) CRYSTAL M_r = 143.9382

Pearson Notation: oP16
$S°(298.15\ K) = 77.760 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1074 \pm 5\ K$

$\Delta_f H°(0\ K) = -740.15 \pm 0.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -745.17 \pm 0.4\ kJ·mol^{-1}$
$\Delta_{fus} H° = 48.534 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

lemThe adopted enthalpy of formation, $-178.1\ kcal·mol^{-1}$, is the weighted average of two calorimetric determinations.[1,2] The result of these and other calorimetric determinations, all for the reaction $Mo(cr) + 3/2\ O_2(g) \rightarrow MoO_3(cr)$, are given below. Staskiewicz *et al.*[1] found that oxidation was only about 80% complete and tentatively attributed this to formation of $MoO_2(cr)$. Using their analytical results and their value of enthalpy of combustion for the dioxide, we obtain $\Delta_f H°(MoO_3, cr, 298.15\ K) = -177.98\ kcal·mol^{-1}$. Subsequent discovery of oxides intermediate between MoO_2 and MoO_3 raises a possible uncertainty concerning the incomplete oxidation. Mah[2] also reported that combustion of the Mo(cr) sample ranged from 84 to 93 percent complete, as determined only by weight gain of the total combustion products upon prolonged low temperature ignition. In contrast, the earlier workers reported almost complete combustion. Neumann *et al.*[3] found about 97% completion using a wet analysis involving aqua regia. Moose and Parr[4] found that in several combustions, they obtained over 99% completion, based on the weight of the oxide formed.

Source	Year	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$
[1]	1955	−177.98
[2]	1957	−178.16
[3]	1934	−180.4
[4]	1924	−175.6

Heat Capacity and Entropy

Smith *et al.*[5] measured low temperature heat capacities from 18.3 to 299.8 K. King *et al.*[6] measured high temperature enthalpy data from 399.3 to 1063.9 K by drop calorimetry. The adopted heat capacities are derived from these two sets of data, subject to the constraint that they join smoothly near 300 K. Deviations of the enthalpy data from the adopted values are −0.65% to +0.17%. Seltz *et al.*[7] have also measured low temperature heat capacities from 70 to 298.7 K which are not in agreement with the values adopted; the discrepancy has been discussed by Smith. Cosgrove and Snyder[8] measured high temperture enthalpy data
from 273 to 1068 K by drop calorimetry. Their smooth values are about 2% higher than the values adopted in the tabulation. Bousquet *et al.*[9] also measured high temperature enthalpy data from 379 to 971 K. Their values agree with the adopted values within 2% below 500 K, but the deviations increase rapidly at higher temperature becoming +10% at 950 K.

The entropy, $S°(298.15\ K) = 18.585\ cal·K^{-1}·mol^{-1}$, is obtained from the low temperature heat capacity data of Smith *et al.*,[5] based on $S°(20\ K) = 0.197\ cal·K^{-1}·mol^{-1}$. This starting entropy was obtained by the authors from a T^2 extrapolation of the data. Recently, McBride and Westrum[10] have shown that the T^2 limiting law is inappropriate for MoS_2 and a T^3 law is suggested for this and other compounds with lamellar lattices. They have also shown that the heat capacity data of Smith *et al.* for MoS_2[5] was positively biased by $\sim 0.07\ cal·K^{-1}·mol^{-1}$ below 100 K. If the same bias is present in the $C_p°$ data of Smith *et al.* for MoO_3, and a T^3 extrapolation is used, our analysis suggests a reduction of $\sim 0.12\ cal·K^{-1}·mol^{-1}$ in $S°(298.15\ K)$. Other treatments result in estimated decreases in $S°(298.15\ K)$ ranging from 0.08 to 0.17 $cal·K^{-1}·mol^{-1}$. The increasing scatter in the $C_p°$ data below 40 K (indicative of a loss of calorimeter sensitivity) coupled with uncertainty due to bias suggests an uncertainty of $\pm 0.3\ cal·K^{-1}·mol^{-1}$ for $S°(298.15\ K)$. Therefore, we adopt the author's original interpretation while recognizing the need for new low temperature $C_p°$ measurements. It is surprising that the entropy of $MoO_3(cr)$ is larger than that of $WO_3(cr)$ by about $0.4\ cal·K^{-1}mol^{-1}$. This may be due to the difference in the crystal structures, MoO_3 being orthorhomibc (oP16) and WO_3 monoclinic, and also to uncertainty in the entropy extrapolation below 50 K for $WO_3(cr)$.

Fusion Data

The adopted melting point, 1074 ± 5 K, is obtained from King *et al.*[6] The enthalpy of fusion is calculated from the adopted enthalpies of the crystal and liquid based on the enthalpy data of King. Cosgrove and Snyder[8] found the melting point 1068 K by the cooling curve method and derived $\Delta_{fus} H° = 12.54\ kcal·mol^{-1}$ from their smooth enthalpy values at the melting point.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.590	−740.150	−740.150	INFINITE
100	31.648	19.553	132.814	−11.326	−743.735	−718.992	375.563
200	59.279	50.977	84.136	−6.632	−745.249	−693.504	181.125
298.15	74.881	77.760	77.760	0.	−745.170	−668.079	117.045
300	75.107	78.224	77.761	0.139	−745.158	−667.601	116.240
400	83.094	101.065	80.821	8.098	−744.111	−641.890	83.822
500	87.751	120.130	86.830	16.650	−742.696	−616.494	64.405
600	91.776	136.487	93.775	25.627	−741.074	−591.403	51.486
700	95.814	150.936	100.927	35.006	−739.250	−566.599	42.280
800	100.031	164.003	108.007	44.796	−737.186	−542.072	35.394
900	104.441	176.037	114.906	55.018	−734.839	−517.821	30.054
1000	109.039	187.278	121.587	65.691	−732.172	−493.847	25.796
1074.000	112.562	195.186	126.387	73.889	− − − CRYSTAL <− − > LIQUID − − −		
1100	113.792	197.894	128.046	76.833	−729.156	−470.158	22.326
1200	118.679	208.004	134.291	88.455	−725.775	−446.759	19.447
1300	123.683	217.700	140.336	100.573	−722.014	−423.657	17.023
1400	128.779	227.052	146.198	113.195	−717.862	−400.860	14.956
1500	133.959	236.113	151.892	126.331	−713.312	−378.374	13.176

PREVIOUS: June 1967 CURRENT: September 1978

$S°$(298.15 K) = [114.935] J·K^{-1}·mol^{-1}
T_{fus} = 1074 ± 5 K

$\Delta_f H°$(298.15 K) = [−703.727] kJ·mol^{-1}
$\Delta_{fus}H°$ = 48.534 ± 4.2 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(MoO_3, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1074\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is derived from the enthalpy data (1074–1392 K) measured by King *et al.*[1] The heat capacity is assumed constant above and below the measured range. At 750 K, a glass transition is assumed, below which the heat capacity is taken to be the same as that of the crystal. $S°(MoO_3, l, 298.15\ K)$ is calculated in a manner analogous to that used for the enthalpy of formation.

Cosgrove and Snyder[2] also measured enthalpy data for MoO_3(l) in the temperature range from 1068 to 1300 K. Their smooth values are 2.5 to 4.0 percent higher than our tabulated values.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

Effusion[3] and transpiration[4] measurements indicate that MoO_3(g) is not the major species found in the vapor above MoO_3condensed phases. Both sets of measurements indicate the presence of polymeric species $(MoO_3)_x$ where the predominant species near the normal boiling point are those for x = 3 and 4. At higher temperatures the equilibrium shifts toward lower x but MoO_3(l) will reach 1 atm at 1380 ± 30 K based primarily on the transpiration measurements of Ackermann *et al.*[4] Feiser,[6] using indirect methods, reported a normal boiling point of 1438 K. We adopt Brewer's estimate[5] and emphasize that this represents vaporization to a mixture of gases, $(MoO_3)_x$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	74.881	114.935	114.935	0.	−703.727	−637.719	111.726
300	75.107	115.399	114.936	0.139	−703.714	−637.310	110.966
400	83.094	138.240	117.996	8.098	−702.668	−615.317	80.352
500	87.751	157.305	124.005	16.650	−701.252	−593.638	62.017
600	91.776	173.661	130.949	25.627	−699.631	−572.264	49.820
700	95.814	188.110	138.102	35.006	−697.807	−551.178	41.129
750.000	97.898	194.791	141.660	39.848	GLASS <- -> LIQUID		
750.000	126.951	194.791	141.660	39.848	TRANSITION		
800	126.951	202.985	145.240	46.196	−694.343	−530.415	34.633
900	126.951	217.937	152.503	58.891	−689.523	−510.214	29.612
1000	126.951	231.313	159.727	71.586	−684.833	−490.544	25.623
1074.000	126.951	240.376	164.975	80.980	--- CRYSTAL <--> LIQUID ---		
1100	126.951	243.413	166.794	84.281	−680.265	−471.337	22.382
1200	126.951	254.459	173.645	96.976	−675.811	−452.541	19.699
1300	126.951	264.620	180.258	109.671	−671.472	−434.112	17.443
1400	126.951	274.028	186.624	122.366	−667.247	−416.012	15.522
1500	126.951	282.787	192.746	135.061	−663.139	−398.212	13.867
1600	126.951	290.980	198.633	147.757	−659.152	−380.680	12.428
1700	126.951	298.677	204.293	160.452	−655.290	−363.395	11.166
1800	126.951	305.933	209.740	173.147	−651.560	−346.333	10.050
1900	126.951	312.797	214.985	185.842	−647.968	−329.475	9.058
2000	126.951	319.309	220.040	198.537	−644.523	−312.801	8.170

PREVIOUS: June 1967 CURRENT: September 1978

0 to 1074 K crystal (oP16)
above 1074 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−12.590	−740.150	−740.150	INFINITE
100	31.648	19.553	132.814	−11.326	−743.735	−718.992	375.563
200	59.279	50.977	84.136	−6.632	−745.249	−693.504	181.125
298.15	74.881	77.760	77.760	0.	−745.170	−668.079	117.045
300	75.107	78.224	77.761	0.139	−745.158	−667.601	116.240
400	83.094	101.065	80.821	8.098	−744.111	−641.890	83.822
500	87.751	120.130	86.830	16.650	−742.696	−616.494	64.405
600	91.776	136.487	93.775	25.627	−741.074	−591.403	51.486
700	95.814	150.936	100.927	35.006	−739.250	−566.599	42.280
800	100.031	164.003	108.007	44.796	−737.186	−542.072	35.394
900	104.441	176.037	114.906	55.018	−734.839	−517.821	30.054
1000	109.039	187.278	121.587	65.691	−732.172	−493.847	25.796
1074.000	112.562	195.186	126.387	73.889	--- CRYSTAL <---> LIQUID ---		
1074.000	126.951	240.376	126.387	122.424	TRANSITION		
1100	126.951	243.413	129.118	125.724	−680.265	−471.337	22.382
1200	126.951	254.459	139.109	138.420	−675.811	−452.541	19.699
1300	126.951	264.620	148.378	151.115	−671.472	−434.112	17.443
1400	126.951	274.028	157.022	163.810	−667.247	−416.012	15.522
1500	126.951	282.787	165.117	176.505	−663.139	−398.212	13.867
1600	126.951	290.980	172.730	189.200	−659.152	−380.680	12.428
1700	126.951	298.677	179.915	201.895	−655.290	−363.395	11.166
1800	126.951	305.933	186.716	214.590	−651.560	−346.333	10.050
1900	126.951	312.797	193.173	227.285	−647.968	−329.475	9.058
2000	126.951	319.309	199.319	239.980	−644.523	−312.801	8.170

PREVIOUS: CURRENT: September 1978

$\Delta_{at}H°(0\ K) = 1740.126 \pm 21.3\ kJ·mol^{-1}$
$S°(298.15\ K) = [283.897 \pm 12.6]\ J·K^{-1}·mol^{-1}$

$\Delta_fH°(0\ K) = -342.22 \pm 20.9\ kJ·mol^{-1}$
$\Delta_fH°(298.15\ K) = -346.44 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
978 (1)	924 (2)
[340](1)	[310](2)

Ground State Quantum Weight: [1] $\sigma = 3$
Point Group: C_{3v}
Bond Distance: Mo–O = [1.73] Å
Bond Angle: O–Mo–O = 99°
Product of the Moments of Inertia: $I_AI_BI_C = [3.0307222 \times 10^{-114}]\ g^3·cm^6$

Enthalpy of Formation

Burns *et al.*[1] determined the partial pressures of gaseous oxides MoO_2, MoO_3, $(MoO_3)_2$ and $(MoO_3)_3$ in equilibrium with powdered MoO_2 by mass spectrometry. Plante,[2] Blackburn *et al.*[3] and Chizhikov *et al.*[4] also investigated the vapor pressures above molybdenum dioxide by the Knudsen effusion method. These studies[1–4] involve the disproportionation of MoO_2(cr) to Mo(cr) and MoO_3(g). DeMaria *et al.*[5] reported the partial pressures of MoO(g), MoO_2(g), MoO_3(g) and O(g) in the Mo–Al_2O_2system from mass spectrometry.

Source	Reaction	T/K	Data Points	$\Delta_fH°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_fH°$(298.15 K) kcal·mol^{-1}
1	1.5 MoO_2(cr) → MoO_3(g) + 0.5 Mo(cr)	1481–1777	34	131.7 ± 1.5	128.0 ± 0.8	−2.2 ± 0.9	−82.8
2	1.5 MoO_2(cr) → MoO_3(g) + 0.5 Mo(cr)	1592–1918	119	133.5 ± 1.4	124.0 ± 1.3	−6.3 ± 0.8	−86.8
3	1.5 MoO_2(cr) → MoO_3(g) + 0.5 Mo(cr)	1818–2028	7	108.8 ± 6.4	121.2 ± 1.6	6.3 ± 3.4	−89.5
4	1.5 MoO_2(cr) → MoO_3(g) + 0.5 Mo(cr)	1500–1730	Eqn	137.9	133.1 ± 0.5	−3.0	−77.6
5	Mo(cr) + 3 O(g) → MoO_3(g)	2281–2416	6	−210.5 ± 28.0	−253.7 ± 4.0	−18.6 ± 11.8	−75.0

The selected enthalpy of formation is −82.8 kcal·mol^{-1}, based on the 3rd law value of $\Delta_fH°$(298.15 K) of Burns *et al.*[1] The choice is made because there is serious doubt about the data of Blackburn[3] as discussed by Burns *et al.*[1] In addition, the assumption made by Plante[2] that they only vapor species of any importance is MoO_3 may be erroneous. The mass specrometric work of Burns *et al.*[1] is thus preferred. Our adopted value differs slightly from the value of −82.57 kcal·mol^{-1} adopted by Brewer,[7] which is also based on Burns *et al.*[1] The difference is a result of slight differences in Gibbs energy functions in the respective auxiliary data for Mo(cr).[6,7]

The heat of atomization calculated from the JANAF tables[6] is $\Delta_{at}H°(0\ K) = 415.9 \pm 5.1$ kcal·mol^{-1}.

Heat Capacity and Entropy

In a recent IR matrix isolation study, Hewett *et al.*[8] observed peaks at 976 and 922 cm^{-1} which they assigned to stretching modes of MoO_3(g). We add 2 cm^{-1} to these frequencies to correct for the matrix effect. The observation of two stretching modes in the infrared spectrum suggests a pyramidal C_{3v} structure for MoO_3(g). Hewett *et al.* performed a normal coordinate analysis using a bond distance of 1.8 Å and an estimated bending force constant (f_α) of 0.296 mdyn/Å. Variations of 20% in f_α changed the calculated stretching frequencies by only a few cm^{-1}. The calculated stretching frequencies were more sensitive to the estimated pyramidal angle (β) which was adjusted to obtain the best fit to the observed stretching frequencies of oxide molecules containing ^{16}O, ^{18}O, and mixed ^{16}O–^{18}O. The final results yielded β = 61.5 ± 2° and values of 261, 275 and 275 cm^{-1} for the bending frequencies of $Mo^{16}O_3$. Due to the insensitivity of the normal coordinate analysis to f_α these bending frequencies are useful only for comparing changes due to isotopic substitution. In contrast, we adopt bending frequencies of 310, 310 and 340 cm^{-1} and a bond distance of 1.73 Å as selected by Brewer[7] for consistency with other metal oxides. The pyramidal angle of 61.5° is adopted; the possible effect of using a shorter bond distance during the normal coordinate analysis is unknown. The pyramidal angle of 61.5° corresponds to an O–Mo–O bond angle of 99°. Based on the adopted structure, the principal moments of inertia are $I_A = I_B = [12.8372 \times 10^{-39}]$ and $I_C = [18.3909 \times 10^{-39}]$ g·cm^2. The thermochemical functions are consistent with those of Brewer.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_fH°$	$\Delta_fG°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−13.399	−342.225	−342.225	INFINITE
100	38.694	231.037	330.596	−9.956	−343.630	−340.035	177.616
200	50.906	261.923	289.070	−5.429	−345.312	−335.755	87.690
250	55.482	273.785	284.854	−2.767	−345.954	−333.289	69.637
298.15	59.378	283.897	283.897	0.	−346.435	−330.804	57.955
300	59.518	284.265	283.899	0.110	−346.451	−330.707	57.581
350	63.017	293.710	284.637	3.176	−346.814	−328.052	48.959
400	65.979	302.324	286.317	6.403	−347.071	−325.353	42.487
450	68.449	310.242	288.541	9.765	−347.249	−322.627	37.450
500	70.494	317.563	291.082	13.241	−347.370	−319.885	33.418
600	73.589	330.707	296.616	20.454	−347.512	−314.373	27.369
700	75.738	342.222	302.326	27.927	−347.594	−308.842	23.046
800	77.266	352.440	307.964	35.581	−347.666	−303.302	19.804
900	78.381	361.609	313.424	43.366	−347.756	−297.751	17.281
1000	79.214	369.912	318.664	51.248	−347.880	−292.189	15.262
1100	79.851	377.493	323.672	59.203	−348.051	−286.612	13.610
1200	80.348	384.463	328.452	67.214	−348.282	−281.017	12.232
1300	80.742	390.911	333.011	75.269	−348.582	−275.400	11.066
1400	81.059	396.906	337.364	83.359	−348.962	−269.756	10.065
1500	81.318	402.508	341.522	91.479	−349.430	−264.083	9.196
1600	81.532	407.763	345.500	99.622	−349.995	−258.376	8.435
1700	81.711	412.711	349.309	107.784	−350.665	−252.629	7.762
1800	81.862	417.386	352.962	115.963	−351.452	−246.841	7.163
1900	81.990	421.816	356.471	124.156	−352.363	−241.005	6.626
2000	82.100	426.024	359.844	132.360	−353.408	−235.117	6.141
2100	82.196	430.032	363.092	140.575	−354.598	−229.174	5.700
2200	82.278	433.858	366.222	148.799	−355.942	−223.170	5.299
2300	82.351	437.517	369.243	157.030	−357.451	−217.102	4.931
2400	82.415	441.023	372.161	165.269	−359.136	−210.965	4.592
2500	82.471	444.389	374.983	173.513	−361.007	−204.754	4.278
2600	82.521	447.624	377.716	181.763	−363.087	−198.463	3.987
2700	82.566	450.740	380.363	190.017	−365.416	−192.088	3.716
2800	82.606	453.743	382.930	198.276	−368.055	−185.621	3.463
2900	82.642	456.642	385.422	206.538	−406.969	−179.005	3.224
3000	82.675	459.445	387.843	214.804	−408.435	−171.118	2.979
3100	82.704	462.156	390.197	223.073	−409.925	−163.183	2.750
3200	82.731	464.782	392.487	231.345	−411.439	−155.200	2.533
3300	82.756	467.328	394.716	239.619	−412.977	−147.169	2.329
3400	82.778	469.799	396.889	247.896	−414.537	−139.090	2.137
3500	82.798	472.199	399.006	256.175	−416.120	−130.967	1.955
3600	82.817	474.532	401.072	264.456	−417.724	−122.796	1.782
3700	82.835	476.801	403.088	272.738	−419.348	−114.582	1.618
3800	82.851	479.010	405.057	281.023	−420.992	−106.322	1.462
3900	82.865	481.163	406.981	289.308	−422.655	−98.019	1.313
4000	82.879	483.261	408.862	297.596	−424.337	−89.675	1.171
4100	82.892	485.308	410.702	305.884	−426.037	−81.287	1.036
4200	82.904	487.305	412.502	314.174	−427.754	−72.858	0.906
4300	82.915	489.256	414.264	322.465	−429.489	−64.387	0.782
4400	82.925	491.162	415.990	330.757	−431.242	−55.877	0.663
4500	82.934	493.026	417.682	339.050	−433.011	−47.327	0.549
4600	82.943	494.849	419.339	347.344	−434.798	−38.737	0.440
4700	82.952	496.633	420.965	355.639	−436.603	−30.106	0.335
4800	82.960	498.379	422.560	363.934	−438.426	−21.438	0.233
4900	82.967	500.090	424.125	372.230	−440.267	−12.731	0.136
5000	82.974	501.766	425.661	380.528	−1033.511	1.744	−0.018
5100	82.981	503.409	427.169	388.825	−1037.070	22.485	−0.230
5200	82.987	505.021	428.651	397.124	−1040.796	43.295	−0.435
5300	82.993	506.602	430.107	405.423	−1044.686	64.181	−0.633
5400	82.998	508.153	431.538	413.722	−1048.742	85.140	−0.824
5500	83.004	509.676	432.945	422.022	−1052.961	106.176	−1.008
5600	83.009	511.172	434.328	430.323	−1057.343	127.292	−1.187
5700	83.013	512.641	435.689	438.624	−1061.885	148.485	−1.361
5800	83.018	514.085	437.028	446.926	−1066.587	169.761	−1.529
5900	83.022	515.504	438.347	455.228	−1071.446	191.116	−1.692
6000	83.026	516.899	439.644	463.530	−1076.463	212.559	−1.850

PREVIOUS: September 1978 (1 atm) CURRENT: September 1978 (1 bar)

Molybdenum Sulfide (MoS_2) CRYSTAL M_r = 160.06

Pearson Notation: hP6
$S°(298.15\ K) = 62.572 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2023 \pm 50\ K$ [p = 1 atm $S_2(g)$]

$\Delta_f H°(0\ K) = -273.31 \pm 2.5\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -276.14 \pm 2.5\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The adopted enthalpy of formation is from Brewer[1] and is a weighted average of calorimetric[2] and equilibrium[3] values. O'Hare *et. al.*[2] obtained $\Delta_f H°(298.15\ K) = 65.8 \pm 1.2\ kcal \cdot mol^{-1}$ using a fluorine bomb calorimeter. Larson and Elliott[3] studied the equilibrium $MoO_2(cr) + 2\ SO_2(g) = MoS_2(cr) + 3\ O_2(g)$ via emf technique (1051–1372 K); using auxiliary data[1,4] Brewer calculated $\Delta_f H°(MoS_2, 298.15\ K) = -66.64 \pm 0.6\ kcal \cdot mol^{-1}$ from their results. Thermodynamic analysis of other calorimetric and equilibrium measurements[5–7] are summarized by O'Hare *et. al.*[2] and Mills.[8]

Heat Capacity and Entropy

The adopted values of $C_p°$ are from Brewer[1] and are based on experimental $C_p°$ data (6–346 K) of McBride and Westrum[9] and high temperature enthalpy data (523–1204 K) of Fredrickson and Chasanov.[10] $C_p°$ values above 1200 K are extrapolated. The recent enthalpy data (500–1700 K) of Volovik *et. al.*[11] agrees with enthalpies in this table to within ±2% to 2000 K. Older $C_p°$ data of Smith *et. al.*[12] and Anderson[13] contain considerable scatter and are given no weight.

$S°(298.15\ K)$ is obtained from the appropriate integration of the adopted $C_p°$ data based on $S°(10\ K) = 0.012\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The crystal structure of MoS_2 is (hP6). Mering and Levialdi[14] have shown that nonstoichiometric sulfur–rich modifications (which have essentially the hP6 structure with expansion and distortion of the lattice) can be prepared as metastable compositions up to $MoS_{2.59}$; amorphous metastable phases are obtained with higher sulfur contents. For information on other metastable phases, refer to[1] and.[15] According to Brewer's[1] phase diagram the compositional range of stability decreases as the temperature increases.

Based on Cannon's evidence[16] of a melting point in excess of 2073 K, Brewer[1] adopted a congruent melting point of 2173 K. However, congruent melting is observed only at high sulfur pressures; the melting point of 2173 K corresponds to a $S_2(g)$ pressure of ~4 atm. Incongruent melting points up to 350 K lower may be obtained depending upon the pressure of $S_2(g)$. The adopted melting point is that selected by Brewer[1] for an $S_2(g)$ pressure of 1 atm. Mills[8] adopted a 1 atm value of 1458 K which appears much too low.

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Molybdenum Sulfide (MoS_2) Mo_1S_2(cr)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.579	−273.314	−273.314	INFINITE
100	24.050	12.991	110.098	−9.711	−274.317	−272.409	142.292
200	51.840	39.359	68.080	−5.744	−275.476	−269.998	70.516
298.15	63.555	62.572	62.572	0.	−276.144	−267.156	46.805
300	63.680	62.965	62.573	0.118	−276.155	−267.100	46.506
400	68.910	82.099	65.146	6.781	−281.141	−263.822	34.452
500	71.756	97.805	70.155	13.825	−284.502	−259.125	27.071
600	73.597	111.057	75.897	21.096	−287.017	−253.800	22.095
700	75.019	122.511	81.756	28.528	−288.951	−248.105	18.514
800	76.232	132.610	87.494	36.092	−290.530	−242.159	15.811
900	77.278	141.650	93.018	43.769	−398.134	−233.867	13.573
1000	78.241	149.842	98.297	51.545	−396.882	−215.682	11.266
1100	79.119	157.341	103.329	59.413	−395.620	−197.623	9.384
1200	79.998	164.263	108.122	67.370	−394.356	−179.680	7.821
1300	80.835	170.699	112.691	75.411	−393.101	−161.841	6.503
1400	81.672	176.721	117.052	83.537	−391.861	−144.098	5.376
1500	82.467	182.383	121.220	91.744	−390.646	−126.444	4.403
1600	83.262	187.730	125.211	100.030	−389.463	−108.869	3.554
1700	84.057	192.802	129.039	108.396	−388.317	−91.367	2.807
1800	84.810	197.628	132.717	116.839	−387.219	−73.931	2.145
1900	85.605	202.235	136.255	125.361	−386.171	−56.555	1.555
2000	86.358	206.645	139.665	133.959	−385.182	−39.233	1.025
2100	87.111	210.876	142.956	142.632	−384.261	−21.958	0.546
2200	87.906	214.947	146.137	151.383	−383.410	−4.726	0.112
2300	88.659	218.871	149.214	160.211	−382.640	12.469	−0.283
2400	89.412	222.660	152.196	169.115	−381.961	29.633	−0.645

PREVIOUS: CURRENT: June 1978

Molybdenum Sulfide (MoS_2) Mo_1S_2(cr)

Pearson notation: mP10
$S°(298.15\ K) = 114.976 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2080 \pm 20\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -407.103 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = -129.704 \pm 41.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation is taken from the critical review by Brewer.[1] His linear regression analysis of equilibrium data, which is based on Cubicciotti's sigma–plot method,[2] yields both $\Delta_f H°(298.15\ K)$ and $S°(298.15\ K)$. The data used in Brewer's analysis are outlined below. Auxiliary data are taken from the JANAF tables.[3]

Source	Reaction	T/K
McCabe[4]	A	1303 – 1425
Isakova[5]	B	1523 – 1738
Hager and Elliott[6]	C	1366 – 1612
Stubbles and Richardson[7]	C	1119 – 1467
Pouillard and Perrot[8]	C	1030 – 1280
Stubbles and Richardson[7]	D	1270 – 1470
Pouillard and Perrot[8]	D	1030 – 1280

Reactions: (A) $2\ Mo(cr) + 3/2\ S_2(g) = Mo_2S_3(cr)$ (C) $2\ Mo(cr) + 3\ H_2S(g) = Mo_2S_3(cr) + 3\ H_2(g)$
(B) $2\ MoS_2(cr) = Mo_2S_3(cr) + 1/2 S_2(g)$ (D) $2\ MoS_2(cr) + H_2(g) = Mo_2S_3(cr) + H_2S(g)$

Heat Capacity and Entropy

There are no experimental high temperature heat capacity or enthalpy studies. The adopted heat capacity, which is assumed to represent the high temperature crystal form, is based on the estimate of Gronvold and Westrum,[9] $C_p° = 26.36 + 7.88 \times 10^{-3} T = 2.30 \times 10^5 / T^2$. The value of $S°(298.15\ K)$ is taken from Brewer,[1] refer above.

Rastogi and Ray[10] measured the low temperature $C_p°(350\ K)$ but report only $C_p°(298.15\ K) = 33.2\ cal \cdot K^{-1} \cdot mol^{-1}$. This value apparently refers to the low temperature superstructure crystal form but is not expected to differ significantly from the high temperature form. The reason for the $7\ cal \cdot K^{-1} \cdot mol^{-1}$ discrepancy between the Rastogi–Ray value of $C_p°(298.15\ K)$ and that adopted here is not known but it should be mentioned that the Rastogi–Ray value is well above the classical limit of 15R. Insufficient information on sample preparation and calorimetric technique is available to assess the validity of the Rastogi–Ray data.

Phase Data

The crystal structure of Mo_2S_3 is monoclinic and belongs to space group $P2_1/m$ above 310 K.[11] Below 310 K all axes are doubled and a superstructure is formed. The heat of transition is reported to be $5\ cal \cdot K^{-1} \cdot mol^{-1}$.[10]

The stability region for Mo_2S_3 is from $900 \pm 40\ K$[1] to the melting point. Below 900 K the material is metastable with respect to disproportionation to Mo(cr) and MoS_2(cr). However equilibrium is established very slowly below 1100 K[11,12] and, once prepared, Mo_2S_3 may be quenched and stored indefinitely at room temperature. The enthalpy of decomposition at 900 K ($\Delta_{dcm} H°$) for the reaction $Mo_2S_3(cr) \rightarrow 1/2\ Mo(cr) + 3/2\ MoS_2(cr)$ is calculated from the JANAF tables.[3]

Fusion Data

We adopt the congruent melting point from Brewer.[1] The enthalpy of fusion is estimated assuming an entropy of fusion of $\sim 3\ cal \cdot K^{-1}$ g–atom^{-1} as suggested by Kubaschewski *et al.*[13] This gives a enthalpy of fusion of $31\ kcal \cdot mol^{-1}$ and the uncertainty is estimated to be $10\ kcal \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
298.15	109.294	114.976	114.976	0.	−407.103	−395.654	69.317
300	109.489	115.653	114.978	0.202	−407.116	−395.583	68.877
400	117.464	148.339	119.381	11.583	−414.437	−391.374	51.108
500	122.926	175.164	127.934	23.615	−419.287	−385.077	40.229
600	127.399	197.981	137.754	36.136	−422.753	−377.885	32.898
700	131.405	217.925	147.812	49.079	−425.196	−370.204	27.625
800	135.162	235.719	157.707	62.409	−426.942	−362.222	23.651
900	138.775	251.848	167.285	76.107	−587.548	−350.811	20.361
1000	142.297	266.652	176.491	90.161	−584.687	−324.658	16.958
1100	145.762	280.378	185.319	104.564	−581.623	−298.802	14.189
1200	149.186	293.208	193.781	119.312	−578.373	−273.233	11.894
1300	152.582	305.283	201.898	134.401	−574.954	−247.942	9.962
1400	155.957	316.714	209.695	149.828	−571.381	−222.920	8.317
1500	159.317	327.589	217.195	165.591	−567.668	−198.159	6.901
1600	162.666	337.978	224.421	181.691	−563.828	−173.650	5.669
1700	166.006	347.940	231.396	198.124	−559.873	−149.384	4.590
1800	169.339	357.523	238.138	214.892	−555.817	−125.354	3.638
1900	172.666	366.768	244.667	231.992	−551.674	−101.552	2.792
2000	175.989	375.709	250.996	249.425	−547.458	−77.970	2.036
2080.000	178.645	382.663	255.927	263.610	--- CRYSTAL <---> LIQUID ---		
2100	179.309	384.376	257.142	267.190	−543.184	−54.601	1.358
2200	182.625	392.794	263.118	285.286	−538.867	−31.436	0.746
2300	185.939	400.985	268.935	303.715	−534.523	−8.468	0.192
2400	189.251	408.968	274.604	322.474	−530.172	14.311	−0.311

PREVIOUS: CURRENT: June 1978

$S°(298.15\ K) = [181.170]\ J·K^{-1}·mol^{-1}$

$T_{fus} = 2080 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-270.304]\ kJ·mol^{-1}$

$\Delta_{fus} H° = 129.704 \pm 41.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Mo_2S_3, l, 298.15\ K)$ is calculated from that of the crystal by adding the enthalpy fusion, of $\Delta_{fus}H°$, and the difference in enthalpy, $H°(2080\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A constant liquid $C_p°$ of 7.5 $cal·K^{-1}·g–atom^{-1}$ is assumed which yields a $C_p°$ value of 37.5 $cal·K^{-1}·mol^{-1}$. This value is adopted above an assumed glass transition at 1450 K. The heat capacity of the crystal[1] is assumed below the glass transition.

$S°(Mo_2S_3, l, 298.15\ K)$ in calculated by a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.[1]

Decomposition Data

According to Brewer's phase diagram,[2] Mo_2S_3 has a very short liquid range at 1 atm $S_2(g)$. We adopt a decomposition temperature of 2140 ± 30 K based on the phase diagram.[2] Above this temperature $Mo_2S_3(l)$ decomposes to $S_2(g)$ plus a liquid poorer in sulfur than Mo_2S_3. At higher sulfur pressures, the liquid range is much more extensive.

References

[1]JANAF Thermochemical Tables: Mo_2S_3(cr) 6–30–78.

[2]L. Brewer, Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley; personal communication of preliminary draft of review to be submitted for publication in Atomic Energy Review, International Atomic Energy Agency, Vienna, Austria; (September 29, 1978).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	109.294	181.170	181.170	0.	−270.304	−278.590	48.808
300	109.489	181.847	181.172	0.202	−270.316	−278.641	48.516
400	117.464	214.533	185.575	11.583	−277.637	−281.052	36.702
500	122.926	241.358	194.129	23.615	−282.487	−281.374	29.395
600	127.399	264.175	203.948	36.136	−285.953	−280.802	24.446
700	131.405	284.119	214.006	49.079	−288.396	−279.740	20.874
800	135.162	301.913	223.901	62.409	−290.142	−278.377	18.176
900	138.775	318.042	233.479	76.107	−450.748	−273.586	15.878
1000	142.297	332.846	242.685	90.161	−447.887	−254.052	13.270
1100	145.762	346.572	251.513	104.564	−444.824	−234.816	11.150
1200	149.186	359.402	259.975	119.312	−441.574	−215.866	9.396
1300	152.582	371.477	268.092	134.401	−438.155	−197.195	7.923
1400	155.957	382.908	275.889	149.828	−434.582	−178.792	6.671
1450.000	157.639	388.410	279.674	157.668	GLASS <--> LIQUID TRANSITION		
1450.000	156.900	388.410	279.674	157.668			
1500	156.900	393.730	283.388	165.513	−430.947	−160.649	5.594
1600	156.900	403.856	290.604	181.203	−427.516	−142.743	4.660
1700	156.900	413.368	297.548	196.893	−424.305	−125.044	3.842
1800	156.900	422.336	304.234	212.583	−421.327	−107.527	3.120
1900	156.900	430.819	310.676	228.273	−418.594	−90.170	2.479
2000	156.900	438.867	316.886	243.963	−416.121	−72.949	1.905
2080.000	156.900	445.021	321.696	256.515	--- CRYSTAL <--> LIQUID ---		
2100	156.900	446.522	322.878	259.653	−413.922	−55.846	1.389
2200	156.900	453.821	328.665	275.343	−412.011	−38.841	0.922
2300	156.900	460.796	334.260	291.033	−410.406	−21.915	0.498
2400	156.900	467.473	339.672	306.723	−409.124	−5.053	0.110
2500	156.900	473.878	344.913	322.413	−408.188	11.763	−0.246
2600	156.900	480.032	349.992	338.103	−407.636	28.548	−0.574
2700	156.900	485.953	354.919	353.793	−407.546	45.321	−0.877
2800	156.900	491.659	359.701	369.483	−408.042	62.101	−1.159
2900	156.900	497.165	364.347	385.173	−481.053	79.010	−1.423
3000	156.900	502.484	368.863	400.863	−479.131	98.290	−1.711
3100	156.900	507.629	373.257	416.553	−477.222	117.506	−1.980
3200	156.900	512.610	377.535	432.243	−475.327	136.660	−2.231
3300	156.900	517.439	381.701	447.933	−473.444	155.756	−2.465
3400	156.900	522.122	385.763	463.623	−471.573	174.794	−2.685
3500	156.900	526.671	389.724	479.313	−469.716	193.778	−2.892

PREVIOUS: CURRENT: June 1978

298	to	2080*	K crystal
above		2080	K liquid

Refer to the individual tables for details.

*This material is reported to be metastable with respect to disproportionation to Mo(cr) and MoS_2(cr) below 900 K. However, disproportionation is very slow and the material may be quenched and stored at room temperature indefinitely.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	109.294	114.976	114.976	0.	−407.103	−395.654	69.317
300	109.489	115.653	114.978	0.202	−407.116	−395.583	68.877
400	117.464	148.339	119.381	11.583	−414.437	−391.374	51.108
500	122.926	175.164	127.934	23.615	−419.287	−385.077	40.229
600	127.399	197.981	137.754	36.136	−422.753	−377.885	32.898
700	131.405	217.925	147.812	49.079	−425.196	−370.204	27.625
800	135.162	235.719	157.707	62.409	−426.942	−362.222	23.651
900	138.775	251.848	167.285	76.107	−587.548	−350.811	20.361
1000	142.297	266.652	176.491	90.161	−584.687	−324.658	16.958
1100	145.762	280.378	185.319	104.564	−581.623	−298.802	14.189
1200	149.186	293.208	193.781	119.312	−578.373	−273.233	11.894
1300	152.582	305.283	201.898	134.401	−574.954	−247.942	9.962
1400	155.957	316.714	209.695	149.828	−571.381	−222.920	8.317
1500	159.317	327.589	217.195	165.591	−567.668	−198.159	6.901
1600	162.666	337.978	224.421	181.691	−563.828	−173.650	5.669
1700	166.006	347.940	231.396	198.124	−559.873	−149.384	4.590
1800	169.339	357.523	238.138	214.892	−555.817	−125.354	3.638
1900	172.666	366.768	244.667	231.992	−551.674	−101.552	2.792
2000	175.989	375.709	250.996	249.425	−547.458	−77.970	2.036
2080.000	178.645	382.663	255.927	263.610	CRYSTAL <−−> LIQUID TRANSITION		
2080.000	156.900	445.021	255.927	393.314			
2100	156.900	446.522	257.735	396.452	−413.922	−55.846	1.389
2200	156.900	453.821	266.484	412.142	−412.011	−38.841	0.922
2300	156.900	460.796	274.782	427.832	−410.406	−21.915	0.498
2400	156.900	467.473	282.672	443.522	−409.124	−5.053	0.110
2500	156.900	473.878	290.193	459.212	−408.187	11.763	−0.246
2600	156.900	480.032	297.377	474.902	−407.636	28.548	−0.574
2700	156.900	485.953	304.252	490.592	−407.546	45.321	−0.877
2800	156.900	491.659	310.844	506.282	−408.042	62.101	−1.159
2900	156.900	497.165	317.175	521.972	−481.053	79.010	−1.423
3000	156.900	502.484	323.264	537.662	−479.131	98.290	−1.711
3100	156.900	507.629	329.128	553.352	−477.222	117.506	−1.980
3200	156.900	512.610	334.785	569.042	−475.327	136.660	−2.231
3300	156.900	517.438	340.247	584.732	−473.443	155.756	−2.465
3400	156.900	522.122	345.528	600.422	−471.573	174.794	−2.685
3500	156.900	526.671	350.639	616.112	−469.716	193.778	−2.892

PREVIOUS: CURRENT: June 1978

Continued from Page 1585

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Continued from Page 1586

The electronic levels and quantum weights are estimated from the data reported by Weltner and McLeod[10] on WO_2. The ground state is assumed to be $^3A_1$ and the first excited level is assumed to lie close to the observed transitions at 7890 Å and 7806 Å in WO_2. Since both these states are presumed to be triplet, we have assigned a total degeneracy of 6. In addition, we expect from the electronic levels of Mo^{+4}(g)[11] that other electronic states will also be found and these are arbitrarily estimated in the level at 25000 cm^{-1}. The principal moments of inertia are: $I_A = 3.3489 \times 10^{-39}$, $I_B = 11.4373 \times 10^{-39}$, and $I_C = 14.7862 \times 10^{-39}$ g·cm^2.

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$S°(298.15\ K) = 26.712 \pm 0.042\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -130.187 \pm 6.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -132.214 \pm 6.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Pankratz *et. al.*[1] measured the enthalpy of combustion of vanadium subnitride at 303.15 K. The composition of their sample was $VN_{0.465}$ which corresponds to the nitrogen rich boundary of the subnitride phase (see Phase Data section). Chemical analysis also showed that the sample contained 0.74 weight percent VO and trace amounts of CaO and Mo as impurities. The composition of the combustion products fell between V_2O_4 and V_2O_5. JANAF data[2] for these two oxides are used to correct their combustion values to correspond to the formation of the pentoxide as the final state. Our values for this correction are roughly 3 $cal \cdot K^{-1} mol^{-1}$ subnitride greater than those used by Pankratz *et. al.*[1] Impurity corrections for VO and Mo are also based on JANAF[2] data and amount to 9.03 and 0.37 cal g^{-1} subnitride, respectively. For the process $VN_{0.465}(cr) + 1.25\ O_2(g) = 0.5\ V_2O_5(cr) + 0.2325\ N_2(g)$, we obtain $\Delta_c H° = 153.69 \pm 0.75\ kcal \cdot mol^{-1}$ at unit fugacities of oxygen and nitrogen. When this value is combined with $\Delta_f H°(V_2O_5, cr, 298.15\ K)$[2], that for vanadium subnitride is $\Delta_f H°(VN_{0.465}, cr, 298.15\ K) = -31.6 \pm 1.5\ kcal \cdot mol^{-1}$. We adopt this value and include in the overall uncertainty ($+1.5\ kcal \cdot mol^{-1}$) the error associated with correcting the combustion values to correspond to the pentoxide as the final state. The only other value for $\Delta_f H°$ is derived from dissociation pressure data for $VN_{0.43}$ which were reported by Brauer and Schnell[3] for the temperature range 1655–1879 K (corrected to IPTS 68). JANAF functions for $VN_{0.465}$ are used to analyze these pressures by the 3rd law method. These calculations lead to $\Delta_f H°$ for the subnitride phase of $-25.2 \pm 1.7\ kcal \cdot mol^{-1}$. The 2nd law value is $\Delta_f H°(298.15\ K) = -10.7\ kcal \cdot mol^{-1}$; the 3rd law drift is $8.3 \pm 1.1\ cal \cdot K^{-1} \cdot mol^{-1}$. These results show considerable scatter and are believed to be less reliable than those obtained by combustion calorimetry.

Heat Capacity and Entropy

Pankratz *et. al.*[1] have measured low temperature heat capacities (9 to 307 K) for $VN_{0.465}$ in an adiabatic calorimeter. The composition of the subnitride sample was similar to that employed in their combustion work. Their $C_p°$ data are adopted and used to obtain a value ($6.384\ cal \cdot K^{-1} \cdot mol^{-1}$) for $S°(298.15\ K)$. This latter value is based on $S°(9\ K) = 0.004\ cal \cdot K^{-1} \cdot mol^{-1}$.

In the same paper, Pankratz *et. al.*[1] reported measurements of the high temperature enthalpies (401–1794 K) for $VN_{0.465}$ which were obtained in a copper–block drop calorimeter. The subnitride sample was the same as that used in their combustion work and was contained in Pt–Rh alloy capsules during the "drop" experiments. Temperature measurements were based on the IPTS–68 scale. A technique employing orthogonal polynomials is used to fit their experimental enthalpies by computer. The curve is constrained to join smoothly with the low temperature $C_p°$ data near 298.15 K. The average deviation of the smoothed enthalpies from the experimental values is +0.46%; the maximum deviation is +0.73% at 702 K. $C_p°$ data above 1800 K are obtained by graphical extrapolation. No anomalies are observed in either the low temperature $C_p°$ data or the high temperature enthalpies.

Phase Data

In a review of vanadium binary systems, Rostoker and Yamamoto[4] have questioned the existence of a subnitride phase, since Muthmann *et. al.*[5] were unable to recognize its presence. However, several recent investigations[1,3,6,8] have reported the preparation of the subnitride at temperatures in excess of 1300 K. Using x–ray techniques, Brauer and Schnell[3] and Hahn[6] found that the phase had an extensive homogeneity range which extends from about $VN_{0.37}$ to $VN_{0.49}$ (27 to 33 atomic percent nitrogen). Pankratz *et. al.*[1] reported the composition of the nitrogen rich phase boundary as $VN_{0.465}$. These results are in agreement with the earlier x–ray work.[3,6] The structure of vanadium subnitride has been determined to be hexagonal.[6,7] Further information on the vanadium vanadium nitride system has been reviewed by Storms.[9]

Decomposition Data

No information is available on the melting behavior of $VN_{0.465}$ at elevated temperatures. Mass spectrometric evidence[10] has been presented which indicates that vanadium mononitride decomposes to its elements rather than melting. By analogy with VN, we assume the process $VN_{0.465}(cr) = V(l) + 0.2325\ N_2(g)$ to be the mode of decomposition upon heating the solid. $T_{dcm} = 2875$ K is the temperature at which the fugacity for the above process approaches 1 atm. $\Delta_{dcm} H° = 34.3\ kcal \cdot mol^{-1}$ is the negative of the enthalpy of formation of $VN_{0.465}$ at T_{dcm}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−4.623	−130.187	−130.187	INFINITE
100	10.647	4.977	47.673	−4.270	−130.995	−127.066	66.373
200	22.457	16.425	29.173	−2.550	−131.786	−122.808	32.074
298.15	28.877	26.712	26.712	0.	−132.214	−118.297	20.725
300	28.971	26.891	26.712	0.054	−132.219	−118.211	20.582
400	32.677	35.771	27.898	3.149	−132.365	−113.513	14.823
500	35.016	43.324	30.247	6.538	−132.318	−108.802	11.367
600	36.815	49.871	32.984	10.132	−132.138	−104.114	9.064
700	38.359	55.664	35.818	13.892	−131.860	−99.464	7.422
800	39.765	60.878	38.630	17.799	−131.508	−94.860	6.194
900	41.095	65.639	41.370	21.842	−131.104	−90.303	5.241
1000	42.376	70.036	44.020	26.016	−130.653	−85.793	4.481
1100	43.627	74.133	46.573	30.316	−130.165	−81.330	3.862
1200	44.852	77.982	49.032	34.740	−129.652	−76.913	3.348
1300	46.066	81.620	51.400	39.286	−129.119	−72.540	2.915
1400	47.262	85.078	53.683	43.953	−128.577	−68.208	2.545
1500	48.455	88.379	55.887	48.739	−128.026	−63.915	2.226
1600	49.643	91.544	58.017	53.644	−127.465	−59.659	1.948
1700	50.823	94.589	60.080	58.667	−126.904	−55.438	1.703
1800	51.999	97.529	62.079	63.810	−126.344	−51.251	1.487
1900	52.928	100.365	64.020	69.055	−125.814	−47.093	1.295
2000	53.974	103.106	65.906	74.401	−125.322	−42.963	1.122
2100	54.936	105.763	67.741	79.846	−124.880	−38.856	0.966
2200	55.940	108.342	69.528	85.390	−147.378	−34.665	0.823
2300	56.902	110.850	71.270	91.032	−147.199	−29.545	0.671
2400	57.907	113.293	72.971	96.774	−146.923	−24.435	0.532
2500	58.743	115.674	74.631	102.606	−146.560	−19.339	0.404
2600	59.622	117.995	76.255	108.524	−146.113	−14.258	0.286
2700	60.584	120.263	77.843	114.534	−145.576	−9.197	0.178
2800	61.505	122.483	79.398	120.639	−144.947	−4.157	0.078
2900	62.425	124.657	80.921	126.836	−144.227	0.859	−0.015
3000	63.304	126.789	82.414	133.123	−143.419	5.848	−0.102
3100	64.141	128.878	83.880	139.494	−142.527	10.809	−0.182
3200	65.019	130.928	85.318	145.952	−141.551	15.740	−0.257
3300	65.898	132.942	86.731	152.498	−140.488	20.639	−0.327
3400	66.777	134.923	88.119	159.132	−139.339	25.505	−0.392
3500	67.655	136.871	89.484	165.854	−138.103	30.336	−0.453

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 153.300 \pm 0.02\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 470.82 \pm 0.10\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 472.68 \pm 0.10\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4S°_{3/2}$	0.000	4
$^2D°_{5/2}$	19224.464	6
$^2D°_{3/2}$	19233.177	4
$^2P°_{1/2}$	28838.920	2
$^2P°_{3/2}$	28839.306	4

Enthalpy of Formation

$\Delta_f H°$ is based on the $D_0°$ value for N_2(g) adopted by the Committee on Data for Science and Technology (CODATA) of the International Council of Scientific Unions.[1] The adopted value for $\Delta_f H°$(N, 298.15, 0 K) is derived using $D_0°(N_2, g) = 78715 \pm 50\ cm^{-1}$ ($225.057 \pm 0.143\ kcal \cdot mol^{-1}$) from Buttenbender and Herzberg,[2] Tanaka, Ogawa, and Jursa,[3] and Telford, Vanderslice, and Wilkinson.[4] This is discussed further by Gaydon[5] and Lofthus and Krupenie.[6]

Heat Capacity and Entropy

The electronic levels for N(g) are given in the compilation by Moore.[7] Our calculations indicate that, except for the five states lying below 29000 cm^{-1}, the inclusion of levels up to $n = 12$ has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 83284.070 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic function (to 6000 K) we list only the lowest lying states ($\epsilon_i < 29000\ cm^{-1}$). The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures.[8]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	470.820	470.820	INFINITE
100	20.786	130.593	171.780	−4.119	471.448	466.379	−243.611
200	20.786	145.001	155.201	−2.040	472.071	461.070	−120.419
250	20.786	149.639	153.642	−1.001	472.383	458.283	−95.753
298.15	20.786	153.300	153.300	0.	472.683	455.540	−79.809
300	20.786	153.429	153.300	0.038	472.694	455.434	−79.298
350	20.786	156.633	153.554	1.078	473.005	452.533	−67.537
400	20.786	159.408	154.116	2.117	473.314	449.587	−58.710
450	20.786	161.857	154.843	3.156	473.621	446.603	−51.840
500	20.786	164.047	155.655	4.196	473.923	443.584	−46.341
600	20.786	167.836	157.379	6.274	474.510	437.461	−38.084
700	20.786	171.041	159.108	8.353	475.067	431.242	−32.180
800	20.786	173.816	160.777	10.431	475.591	424.945	−27.746
900	20.786	176.264	162.364	12.510	476.081	418.584	−24.294
1000	20.786	178.454	163.866	14.589	476.540	412.171	−21.530
1100	20.786	180.436	165.284	16.667	476.970	405.713	−19.266
1200	20.786	182.244	166.623	18.746	477.374	399.217	−17.377
1300	20.786	183.908	167.889	20.824	477.756	392.688	−15.778
1400	20.786	185.448	169.089	22.903	478.118	386.131	−14.407
1500	20.786	186.882	170.228	24.982	478.462	379.548	−13.217
1600	20.786	188.224	171.311	27.060	478.791	372.943	−12.175
1700	20.786	189.484	172.344	29.139	479.107	366.318	−11.256
1800	20.787	190.672	173.329	31.218	479.411	359.674	−10.437
1900	20.788	191.796	174.272	33.296	479.705	353.014	−9.705
2000	20.790	192.863	175.175	35.375	479.990	346.339	−9.045
2100	20.793	193.877	176.042	37.454	480.266	339.650	−8.448
2200	20.797	194.844	176.874	39.534	480.536	332.947	−7.905
2300	20.804	195.769	177.676	41.614	480.799	326.233	−7.409
2400	20.813	196.655	178.448	43.695	481.057	319.507	−6.954
2500	20.826	197.504	179.194	45.777	481.311	312.770	−6.535
2600	20.843	198.322	179.914	47.860	481.561	306.024	−6.148
2700	20.864	199.109	180.610	49.945	481.809	299.268	−5.790
2800	20.891	199.868	181.285	52.033	482.054	292.502	−5.457
2900	20.924	200.601	181.938	54.124	482.299	285.728	−5.147
3000	20.963	201.311	182.572	56.218	482.543	278.946	−4.857
3100	21.010	202.000	183.188	58.317	482.789	272.155	−4.586
3200	21.064	202.667	183.786	60.420	483.036	265.357	−4.332
3300	21.126	203.317	184.368	62.530	483.286	258.550	−4.093
3400	21.197	203.948	184.935	64.646	483.540	251.736	−3.867
3500	21.277	204.564	185.487	66.769	483.799	244.915	−3.655
3600	21.365	205.164	186.025	68.902	484.064	238.086	−3.455
3700	21.463	205.751	186.550	71.043	484.335	231.249	−3.265
3800	21.569	206.325	187.063	73.194	484.614	224.405	−3.085
3900	21.685	206.887	187.564	75.357	484.903	217.554	−2.914
4000	21.809	207.437	188.054	77.532	485.201	210.695	−2.751
4100	21.941	207.977	188.534	79.719	485.510	203.829	−2.597
4200	22.082	208.508	189.003	81.920	485.830	196.955	−2.449
4300	22.231	209.029	189.463	84.136	486.164	190.073	−2.309
4400	22.388	209.542	189.913	86.367	486.510	183.183	−2.175
4500	22.551	210.047	190.355	88.614	486.871	176.285	−2.046
4600	22.722	210.544	190.788	90.877	487.247	169.379	−1.923
4700	22.899	211.035	191.214	93.158	487.638	162.465	−1.806
4800	23.081	211.519	191.632	95.457	488.046	155.542	−1.693
4900	23.269	211.997	192.043	97.775	488.471	148.610	−1.584
5000	23.461	212.469	192.447	100.111	488.912	141.670	−1.480
5100	23.658	212.935	192.844	102.467	489.372	134.721	−1.380
5200	23.858	213.397	193.235	104.843	489.849	127.762	−1.283
5300	24.061	213.853	193.619	107.238	490.345	120.794	−1.190
5400	24.266	214.305	193.998	109.655	490.860	113.817	−1.101
5500	24.474	214.752	194.371	112.092	491.394	106.829	−1.015
5600	24.682	215.195	194.739	114.550	491.947	99.832	−0.931
5700	24.892	215.633	195.102	117.028	492.519	92.825	−0.851
5800	25.102	216.068	195.460	119.528	493.110	85.808	−0.773
5900	25.312	216.499	195.813	122.049	493.720	78.780	−0.697
6000	25.521	216.926	196.161	124.590	494.349	71.742	−0.625

PREVIOUS: March 1977 (1 atm) CURRENT: December 1982 (1 bar)

IP(N^+, g) = 238750.50 ± 1.3 cm^{-1}
$S°$(298.15 K) = 159.797 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1873.152 ± 0.42 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1882.130] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0.0	1
$^3P_1$	48.7	3
$^3P_2$	130.8	5
$^1D_2$	15316.2	5
$^1S_0$	32688.8	1
$^5S_2$	46784.6	5

Enthalpy of Formation

$\Delta_f H°(N^+, g, 0 K)$ is calculated from $\Delta_f H°(N, g, 0 K)$[1] using the spectroscopic value of IP(N) = 117225.7 ± 0.3 cm^{-1} (1402.331 ± 0.004 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(N^+, g, 298.15 K)$ is calculated from $\Delta_f H°(N, g, 0 K)$ by using IP(N) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for N(g), $N^+(g)$, and e^-(ref). $\Delta_f H°(N \rightarrow N^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first five excited states; the next excited state is 92237.2 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first five excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: N(g), 12–31–82 ; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.116	1873.152		
100	24.729	135.201	179.245	−4.404			
200	21.896	151.192	161.758	−2.113			
250	21.497	156.030	160.148	−1.030			
298.15	21.284	159.797	159.797	0.	1882.130	1856.796	−325.303
300	21.278	159.929	159.797	0.039	1882.181	1856.639	−323.270
350	21.146	163.198	160.056	1.100	1883.552	1852.273	−276.437
400	21.060	166.016	160.629	2.155	1884.917	1847.712	−241.286
450	21.002	168.492	161.368	3.206	1886.274	1842.979	−213.927
500	20.960	170.703	162.193	4.255	1887.626	1838.096	−192.025
600	20.906	174.519	163.939	6.348	1890.306	1827.938	−159.136
700	20.874	177.739	165.686	8.437	1892.952	1817.334	−135.611
800	20.853	180.525	167.371	10.523	1895.562	1806.353	−117.943
900	20.839	182.980	168.972	12.608	1898.137	1795.047	−104.182
1000	20.829	185.175	170.484	14.691	1900.679	1783.456	−93.158
1100	20.821	187.160	171.911	16.774	1903.191	1771.612	−84.127
1200	20.815	188.972	173.259	18.855	1905.677	1759.540	−76.591
1300	20.811	190.638	174.532	20.937	1908.140	1747.262	−70.206
1400	20.808	192.180	175.738	23.018	1910.583	1734.795	−64.726
1500	20.805	193.615	176.883	25.098	1913.008	1722.154	−59.971
1600	20.803	194.958	177.971	27.179	1915.418	1709.351	−55.805
1700	20.802	196.219	179.008	29.259	1917.814	1696.399	−52.124
1800	20.803	197.408	179.997	31.339	1920.198	1683.306	−48.848
1900	20.804	198.533	180.943	33.420	1922.572	1670.080	−45.914
2000	20.806	199.600	181.850	35.500	1924.937	1656.730	−43.269
2100	20.810	200.615	182.719	37.581	1927.294	1643.261	−40.874
2200	20.816	201.583	183.555	39.662	1929.644	1629.681	−38.694
2300	20.824	202.509	184.359	41.744	1931.988	1615.994	−36.700
2400	20.835	203.395	185.134	43.827	1934.327	1602.205	−34.871
2500	20.848	204.246	185.882	45.911	1936.661	1588.318	−33.186
2600	20.864	205.064	186.604	47.997	1938.992	1574.339	−31.629
2700	20.883	205.852	187.302	50.084	1941.320	1560.269	−30.185
2800	20.904	206.612	187.978	52.174	1943.646	1546.114	−28.843
2900	20.929	207.346	188.634	54.265	1945.970	1531.875	−27.592
3000	20.956	208.056	189.269	56.359	1948.293	1517.556	−26.423
3100	20.987	208.743	189.886	58.457	1950.616	1503.160	−25.328
3200	21.020	209.410	190.486	60.557	1952.938	1488.689	−24.300
3300	21.056	210.058	191.069	62.661	1955.261	1474.145	−23.334
3400	21.094	210.687	191.637	64.768	1957.585	1459.531	−22.423
3500	21.135	211.299	192.190	66.880	1959.910	1444.849	−21.563
3600	21.178	211.895	192.729	68.995	1962.237	1430.100	−20.750
3700	21.223	212.476	193.255	71.115	1964.566	1415.286	−19.980
3800	21.269	213.042	193.768	73.240	1966.897	1400.410	−19.250
3900	21.317	213.595	194.270	75.369	1969.231	1385.472	−18.556
4000	21.366	214.136	194.760	77.503	1971.567	1370.474	−17.897
4100	21.417	214.664	195.239	79.642	1973.906	1355.417	−17.268
4200	21.468	215.180	195.707	81.787	1976.248	1340.304	−16.669
4300	21.520	215.686	196.166	83.936	1978.594	1325.135	−16.097
4400	21.573	216.182	196.615	86.091	1980.943	1309.911	−15.551
4500	21.625	216.667	197.056	88.251	1983.296	1294.634	−15.028
4600	21.679	217.143	197.487	90.416	1985.652	1279.304	−14.527
4700	21.732	217.610	197.910	92.586	1988.011	1263.923	−14.047
4800	21.784	218.068	198.326	94.762	1990.374	1248.492	−13.586
4900	21.837	218.517	198.733	96.943	1992.741	1233.012	−13.144
5000	21.889	218.959	199.133	99.129	1995.111	1217.483	−12.719
5100	21.941	219.393	199.526	101.321	1997.485	1201.907	−12.310
5200	21.992	219.820	199.912	103.518	1999.862	1186.284	−11.916
5300	22.042	220.239	200.292	105.719	2002.242	1170.616	−11.537
5400	22.092	220.652	200.665	107.926	2004.626	1154.902	−11.171
5500	22.141	221.057	201.032	110.138	2007.013	1139.145	−10.819
5600	22.189	221.457	201.393	112.354	2009.404	1123.344	−10.478
5700	22.236	221.850	201.749	114.575	2011.797	1107.500	−10.149
5800	22.281	222.237	202.099	116.801	2014.192	1091.614	−9.831
5900	22.326	222.618	202.443	119.032	2016.591	1075.687	−9.523
6000	22.370	222.994	202.783	121.267	2018.991	1059.719	−9.226

PREVIOUS: March 1977 (1 atm) CURRENT: December 1982 (1 bar)

EA(N, g) = −0.07 ± 0.02 eV
$S°$(298.15 K) = 159.927 ± 0.001 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 477.574 ± 1.9 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [473.540] kJ·mol^{-1}

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0	5
$^3P_1$	[63]	3
$^3P_0$	[90]	1
$^1D_2$	[10800]	5
$^1S_0$	[22390]	1

Enthalpy of Formation

$\Delta_f H°(N^-, g, 0 K)$ is calculated from $\Delta_f H°(N, g, 0 K)$[1] using the adopted electron affinity of EA(N) = −0.07 ± 0.02 eV (−6.754 ± 1.930 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on a dissociative attachment of electrons study[3]. Additional information on N^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(N^-, g, 298.15 K)$ is obtained from $\Delta_f H°(N, g, 0 K)$ by using EA(N) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for N^-(g), N(g), and e^-(ref). $\Delta_r H°(N^- \rightarrow N + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if t is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state for N^-(g) is reported to be $2p^4\ ^3P$. We estimate the fine structure separations in the ground state by comparison of isoelectronic series based on N^-(g) [N^-, O, F^*, Ne^{++}, Na^{+++}] and C(g) [C, N^+, O^{++}, F^{+++}]. The unceratainty in $S°$(298.15 K) in part reflects this estimation. Massey[6] listed the hyperfine splitting of the ground state as 97 and 137 cm^{-1} based on a quadratic isoelectronic extrapolation. This technique led to high values in the case of O^-(g)[5] and is assumed to give high results for N^-(g).

A comparison of the isoelectronic sequence – N^-(g), O(g), F^+(g)–would suggest that stable electronic states may exist at low wave numbers. These states would greatly affect the entropy. We estimate two of these levels.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.498	477.574		
100	22.234	136.475	178.809	−4.233			
200	21.252	151.496	161.855	−2.072			
250	21.096	156.220	160.274	−1.014			
298.15	21.009	159.927	159.927	0.	473.540	460.677	−80.709
300	21.007	160.057	159.928	0.039	473.514	460.597	−80.197
350	20.951	163.291	160.183	1.088	472.795	458.501	−68.428
400	20.913	166.086	160.750	2.134	472.072	456.508	−59.614
450	20.888	168.548	161.483	3.179	471.345	454.606	−52.769
500	20.869	170.747	162.301	4.223	470.612	452.786	−47.302
600	20.844	174.550	164.035	6.309	469.128	449.360	−39.120
700	20.829	177.762	165.773	8.392	467.611	446.184	−33.295
800	20.819	180.542	167.449	10.475	466.060	443.229	−28.940
900	20.812	182.994	169.043	12.556	464.475	440.470	−25.564
1000	20.807	185.187	170.550	14.637	462.857	437.889	−22.873
1100	20.804	187.170	171.972	16.718	461.210	435.471	−20.679
1200	20.801	188.980	173.315	18.798	459.538	433.205	−18.857
1300	20.799	190.645	174.585	20.878	457.842	431.079	−17.321
1400	20.797	192.186	175.787	22.958	456.126	429.085	−16.009
1500	20.796	193.621	176.929	25.037	454.393	427.214	−14.877
1600	20.794	194.963	178.015	27.117	452.645	425.459	−13.890
1700	20.793	196.223	179.049	29.196	450.883	423.814	−13.022
1800	20.793	197.412	180.037	31.275	449.109	422.272	−12.254
1900	20.792	198.536	180.981	33.355	447.325	420.830	−11.569
2000	20.791	199.602	181.886	35.434	445.531	419.482	−10.956
2100	20.791	200.617	182.754	37.513	443.729	418.224	−10.403
2200	20.790	201.584	183.588	39.592	441.920	417.052	−9.902
2300	20.790	202.508	184.390	41.671	440.103	415.962	−9.447
2400	20.790	203.393	185.164	43.750	438.281	414.951	−9.031
2500	20.789	204.242	185.910	45.829	436.453	414.017	−8.650
2600	20.789	205.057	186.631	47.908	434.620	413.156	−8.300
2700	20.789	205.842	187.328	49.987	432.783	412.365	−7.978
2800	20.789	206.598	188.003	52.066	430.941	411.642	−7.679
2900	20.789	207.327	188.657	54.145	429.095	410.986	−7.403
3000	20.788	208.032	189.291	56.223	427.246	410.393	−7.146
3100	20.788	208.714	189.906	58.302	425.393	409.862	−6.906
3200	20.788	209.374	190.504	60.381	423.536	409.390	−6.683
3300	20.788	210.013	191.086	62.460	421.677	408.977	−6.474
3400	20.788	210.634	191.652	64.539	419.815	408.620	−6.278
3500	20.788	211.236	192.203	66.617	417.951	408.318	−6.094
3600	20.788	211.822	192.740	68.696	416.083	408.069	−5.921
3700	20.788	212.392	193.263	70.775	414.214	407.872	−5.758
3800	20.788	212.946	193.774	72.854	412.342	407.726	−5.605
3900	20.787	213.486	194.272	74.932	410.468	407.629	−5.460
4000	20.787	214.012	194.759	77.011	408.591	407.580	−5.322
4100	20.787	214.526	195.235	79.090	406.713	407.578	−5.193
4200	20.787	215.026	195.701	81.169	404.833	407.622	−5.070
4300	20.787	215.516	196.156	83.247	402.950	407.710	−4.953
4400	20.787	215.993	196.601	85.326	401.066	407.843	−4.842
4500	20.787	216.461	197.037	87.405	399.180	408.018	−4.736
4600	20.787	216.917	197.465	89.484	397.293	408.235	−4.636
4700	20.787	217.365	197.883	91.562	395.403	408.493	−4.540
4800	20.787	217.802	198.294	93.641	393.512	408.792	−4.449
4900	20.787	218.231	198.696	95.720	391.619	409.130	−4.361
5000	20.787	218.651	199.091	97.798	389.724	409.506	−4.278
5100	20.787	219.062	199.479	99.877	387.828	409.921	−4.198
5200	20.787	219.466	199.859	101.956	385.930	410.373	−4.122
5300	20.787	219.862	200.233	104.034	384.030	410.861	−4.049
5400	20.787	220.251	200.600	106.113	382.129	411.385	−3.979
5500	20.787	220.632	200.961	108.192	380.226	411.944	−3.912
5600	20.787	221.006	201.315	110.270	378.321	412.538	−3.848
5700	20.787	221.374	201.664	112.349	376.414	413.166	−3.786
5800	20.787	221.736	202.007	114.428	374.506	413.827	−3.727
5900	20.787	222.091	202.344	116.506	372.595	414.522	−3.670
6000	20.787	222.441	202.676	118.585	370.682	415.248	−3.615

PREVIOUS: March 1977 (1 atm) CURRENT: December 1982 (1 bar)

$S°(298.15\ K) = 210.758\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 89.775 \pm 0.17\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 90.291 \pm 0.17\ kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	2
	121.1	2

$\omega_e = 1903.60\ cm^{-1}$ $\omega_e x_e = 13.97\ cm^{-1}$ $\sigma = 1$

$B_e = 1.7042\ cm^{-1}$ $\alpha_e = 0.0178\ cm^{-1}$ $r_e = 1.1508$ Å

Enthalpy of Formation

Herzberg,[1] lists two $D_0°$(NO) values, 5.296 and 6.487 eV. Gaydon[2] lists $D_0°(NO) = 6.49 \pm 0.05$ eV. A Birge–Sponer extrapolation of the vibrational levels, up to $v = 18$, of the ground state leads to a $D_0°$ of about 6.5 eV. Gaydon's[2] analysis on the predissociation of NO also leads to the higher value for $D°$(NO).

Tanaka,[3] has observed and analyzed the emmission bands of NO in the vacuum ultraviolet region. Tanaka's,[3] observation and interpretation of the abrupt cutoff (predissociation) of certain v' values in the β, γ, and δ bands and of the complete non appearance of ε and β' bands strongly favors a $D°(NO) = 6.48$ eV. $\Delta_f H°$(NO, g, 298.15 K) was calculated on this basis to be $22.033 \pm 1\ kcal·mol^{-1}$.

More recently Frisch,[4] has calorimetrically determined the enthalpy of reaction for:

$$NO(g) + CO(g) \rightarrow CO_2(g) + 1/2N_2(g)$$

at 298.15 K, from which the author derives a $\Delta_f H°$(NO, g, 298.15 K) = $21.58 \pm 0.04\ kcal·mol^{-1}$. The auxiliary values used by Frisch to calculate the enthalpy of formation of nitric oxide were based upon the 1961 atomic weight scale. Recalculating $\Delta_f H°$(NO, g, 298.15 K) using auxiliary functions based on the 1956 atomic weight scale had a negligible effect on the final result.

The calorimetrically determined heat of formation for nitric oxide, $21.58 \pm 0.04\ kcal·mol^{-1}$, was selected as the best value.

Heat Capacity and Entropy

The spectroscopic constants were taken from Gillette and Eyster,[5] who measured and analyzed the fundamental rotation–vibration band of nitric oxide using a grating spectrometer. The constants used in this calculation were adjusted to correspond to the naturally occurring isotopic mixture.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.192	89.775	89.775	INFINITE
100	32.302	177.031	237.757	−6.073	89.991	88.944	−46.460
200	30.420	198.747	213.501	−2.951	90.202	87.800	−22.931
250	30.025	205.488	211.251	−1.441	90.256	87.193	−18.218
298.15	29.845	210.758	210.758	0.	90.291	86.600	−15.172
300	29.841	210.943	210.759	0.055	90.292	86.577	−15.074
350	29.823	215.540	211.122	1.546	90.316	85.955	−12.828
400	29.944	219.529	211.929	3.040	90.332	85.331	−11.143
450	30.175	223.068	212.974	4.542	90.343	84.705	−9.832
500	30.486	226.263	214.145	6.059	90.352	84.079	−8.784
600	31.238	231.886	216.646	9.144	90.366	82.822	−7.210
700	32.028	236.761	219.179	12.307	90.381	81.564	−6.086
800	32.767	241.087	221.652	15.548	90.398	80.303	−5.243
900	33.422	244.985	224.031	18.858	90.417	79.041	−4.587
1000	33.987	248.536	226.307	22.229	90.437	77.775	−4.063
1100	34.468	251.799	228.478	25.653	90.457	76.508	−3.633
1200	34.877	254.816	230.549	29.120	90.476	75.239	−3.275
1300	35.226	257.621	232.525	32.626	90.493	73.969	−2.972
1400	35.524	260.243	234.412	36.164	90.508	72.697	−2.712
1500	35.780	262.703	236.217	39.729	90.518	71.425	−2.487
1600	36.002	265.019	237.945	43.319	90.525	70.151	−2.290
1700	36.195	267.208	239.603	46.929	90.526	68.878	−2.116
1800	36.364	269.282	241.195	50.557	90.522	67.605	−1.962
1900	36.514	271.252	242.725	54.201	90.511	66.332	−1.824
2000	36.647	273.128	244.199	57.859	90.494	65.060	−1.699
2100	36.767	274.919	245.619	61.530	90.469	63.788	−1.587
2200	36.874	276.632	246.990	65.212	90.438	62.519	−1.484
2300	36.971	278.273	248.315	68.904	90.398	61.251	−1.391
2400	37.060	279.849	249.596	72.606	90.350	59.984	−1.306
2500	37.141	281.363	250.837	76.316	90.295	58.720	−1.227
2600	37.216	282.822	252.039	80.034	90.231	57.458	−1.154
2700	37.285	284.227	253.205	83.759	90.160	56.199	−1.087
2800	37.350	285.585	254.338	87.491	90.081	54.943	−1.025
2900	37.410	286.896	255.438	91.229	89.994	53.689	−0.967
3000	37.466	288.165	256.508	94.973	89.899	52.439	−0.913
3100	37.519	289.395	257.549	98.722	89.798	51.192	−0.863
3200	37.570	290.587	258.563	102.477	89.689	49.948	−0.815
3300	37.617	291.744	259.551	106.236	89.574	48.708	−0.771
3400	37.663	292.867	260.514	110.000	89.451	47.472	−0.729
3500	37.706	293.960	261.454	113.768	89.323	46.239	−0.690
3600	37.747	295.022	262.372	117.541	89.189	45.010	−0.653
3700	37.787	296.057	263.269	121.318	89.049	43.784	−0.618
3800	37.825	297.065	264.145	125.098	88.903	42.563	−0.585
3900	37.862	298.048	265.002	128.883	88.752	41.346	−0.554
4000	37.898	299.008	265.840	132.671	88.596	40.132	−0.524
4100	37.933	299.944	266.660	136.462	88.434	38.922	−0.496
4200	37.966	300.858	267.464	140.257	88.268	37.717	−0.469
4300	37.999	301.752	268.251	144.056	88.097	36.515	−0.444
4400	38.031	302.626	269.022	147.857	87.922	35.318	−0.419
4500	38.062	303.481	269.778	151.662	87.741	34.124	−0.396
4600	38.092	304.318	270.520	155.469	87.556	32.934	−0.374
4700	38.122	305.137	271.248	159.280	87.366	31.749	−0.353
4800	38.151	305.940	271.962	163.094	87.171	30.568	−0.333
4900	38.180	306.727	272.664	166.910	86.970	29.391	−0.313
5000	38.208	307.499	273.353	170.730	86.765	28.218	−0.295
5100	38.235	308.256	274.030	174.552	86.553	27.049	−0.277
5200	38.262	308.998	274.695	178.377	86.336	25.884	−0.260
5300	38.289	309.728	275.349	182.204	86.112	24.724	−0.244
5400	38.316	310.443	275.993	186.034	85.881	23.568	−0.228
5500	38.342	311.147	276.625	189.867	85.644	22.416	−0.213
5600	38.367	311.838	277.248	193.703	85.399	21.269	−0.198
5700	38.393	312.517	277.861	197.541	85.146	20.125	−0.184
5800	38.418	313.185	278.464	201.381	84.884	18.987	−0.171
5900	38.443	313.842	279.058	205.224	84.613	17.853	−0.158
6000	38.468	314.488	279.643	209.070	84.331	16.724	−0.146

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

Nitrogen Oxide, Ion (NO^+) — IDEAL GAS — $M_r = 30.00555$ — Nitrogen Oxide, Ion (NO_1^+) — $N_1O_1^+(g)$

$(298.15\ K) = 198.219\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 983.995 \pm 0.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 990.185 \pm 0.8\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 2377.1\ cm^{-1}$ $\omega_e x_e = 16.35\ cm^{-1}$ $\sigma = 1$

$B_e = 2.002\ cm^{-1}$ $\alpha_e = 0.0202\ cm^{-1}$ $r_e = 1.0619\ Å$

Enthalpy of Formation

Watanabe[1] and Walker and Weissler[2] have measured the ionization potential of NO(g) by photoionization, yielding IP = 9.25 ± 0.02 and 9.20 ± 0.03 eV, respectively. Hagstrum,[3] reported IP = 9.4 ± 0.2 eV by electron impact. Huber[4] determined spectroscopically the ionization potential for NO(g), IP = 9.267 ± 0.005 eV (213.72 ± 0.1 $kcal \cdot mol^{-1}$). The last value has been selected, and yields the enthalpy of formation of $NO^+(g)$, $\Delta_f H°(NO^+, g, 0\ K) = 235.18\ kcal \cdot mol^{-1}$, using $\Delta_f H°(NO, g, 0\ K) = 21.46 \pm 0.04\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The selected molecular constants were obtained from the ultraviolet spectra by Miescher.[5]

The tabulated thermodynamic functions are in reasonable agreement with those calculated by Hilsenrath and Messina,[6] who have used slightly different molecular constants.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.670	983.995		
100	29.104	166.421	224.100	−5.768			
200	29.107	186.595	200.882	−2.857			
250	29.111	193.091	198.698	−1.402			
298.15	29.123	198.219	198.219	0.	990.185	983.978	−172.389
300	29.124	198.399	198.219	0.054	990.224	983.939	−171.319
350	29.163	202.891	198.574	1.511	991.253	982.811	−146.676
400	29.244	206.790	199.363	2.971	992.275	981.535	−128.175
450	29.378	210.242	200.383	4.436	993.288	980.131	−113.771
500	29.568	213.346	201.527	5.910	994.293	978.615	−102.235
600	30.089	218.781	203.962	8.891	996.282	975.293	−84.907
700	30.728	223.466	206.421	11.931	998.252	971.639	−72.505
800	31.403	227.613	208.816	15.038	1000.214	967.703	−63.185
900	32.059	231.350	211.115	18.211	1002.175	963.521	−55.921
1000	32.666	234.760	213.312	21.448	1004.139	959.121	−50.099
1100	33.213	237.899	215.406	24.742	1006.109	954.524	−45.327
1200	33.697	240.810	217.403	28.088	1008.085	949.747	−41.341
1300	34.124	243.525	219.309	31.480	1010.066	944.805	−37.963
1400	34.497	246.067	221.131	34.911	1012.053	939.711	−35.061
1500	34.825	248.459	222.874	38.378	1014.043	934.474	−32.541
1600	35.112	250.716	224.544	41.875	1016.036	929.104	−30.332
1700	35.365	252.852	226.147	45.399	1018.030	923.610	−28.379
1800	35.588	254.880	227.687	48.947	1020.024	917.998	−26.640
1900	35.786	256.810	229.170	52.516	1022.017	912.276	−25.080
2000	35.963	258.650	230.598	56.103	1024.008	906.449	−23.674
2100	36.121	260.408	231.976	59.708	1025.995	900.522	−22.399
2200	36.263	262.092	233.307	63.327	1027.979	894.501	−21.238
2300	36.391	263.707	234.594	66.960	1029.959	888.389	−20.176
2400	36.507	265.258	235.839	70.605	1031.933	882.191	−19.200
2500	36.612	266.750	237.046	74.261	1033.902	875.911	−18.301
2600	36.709	268.188	238.216	77.927	1035.865	869.553	−17.470
2700	36.798	269.575	239.352	81.602	1037.823	863.119	−16.698
2800	36.880	270.915	240.456	85.286	1039.774	856.613	−15.980
2900	36.955	272.211	241.529	88.978	1041.720	850.037	−15.311
3000	37.025	273.465	242.572	92.677	1043.659	843.395	−14.685
3100	37.091	274.680	243.589	96.383	1045.593	836.687	−14.098
3200	37.152	275.858	244.579	100.095	1047.520	829.917	−13.547
3300	37.209	277.003	245.544	103.813	1049.442	823.087	−13.028
3400	37.263	278.114	246.486	107.537	1051.358	816.200	−12.539
3500	37.313	279.195	247.405	111.266	1053.269	809.255	−12.077
3600	37.361	280.247	248.303	114.999	1055.174	802.257	−11.640
3700	37.407	281.271	249.180	118.738	1057.074	795.205	−11.226
3800	37.450	282.269	250.038	122.481	1058.969	788.102	−10.833
3900	37.491	283.243	250.877	126.228	1060.860	780.950	−10.460
4000	37.531	284.192	251.698	129.979	1062.745	773.748	−10.104
4100	37.569	285.120	252.502	133.734	1064.626	766.500	−9.765
4200	37.605	286.025	253.289	137.492	1066.502	759.206	−9.442
4300	37.640	286.911	254.061	141.255	1068.374	751.867	−9.133
4400	37.673	287.776	254.817	145.020	1070.241	744.485	−8.838
4500	37.705	288.623	255.559	148.789	1072.103	737.060	−8.556
4600	37.737	289.452	256.287	152.561	1073.961	729.594	−8.285
4700	37.767	290.264	257.001	156.337	1075.814	722.088	−8.025
4800	37.796	291.060	257.702	160.115	1077.662	714.542	−7.776
4900	37.825	291.839	258.391	163.896	1079.505	706.959	−7.536
5000	37.853	292.604	259.068	167.680	1081.342	699.337	−7.306
5100	37.880	293.354	259.733	171.466	1083.174	691.679	−7.084
5200	37.906	294.089	260.386	175.256	1084.999	683.984	−6.871
5300	37.932	294.812	261.029	179.048	1086.819	676.255	−6.665
5400	37.957	295.521	261.661	182.842	1088.631	668.492	−6.466
5500	37.982	296.218	262.283	186.639	1090.436	660.694	−6.275
5600	38.006	296.902	262.895	190.438	1092.234	652.865	−6.090
5700	38.030	297.575	263.498	194.240	1094.023	645.003	−5.911
5800	38.053	298.237	264.091	198.044	1095.803	637.110	−5.738
5900	38.076	298.887	264.675	201.851	1097.574	629.186	−5.570
6000	38.098	299.528	265.251	205.660	1099.334	621.233	−5.408

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 240.034 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 35.93 \pm 0.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 33.10 \pm 0.8\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1357.8(1)
756.8(1)
1665.5(1)

Ground State Quantum Weight: 2 $\sigma = 2$

Point Group: C_{2v}

Bond Distance: N–O = 1.197 Å

Bond Angle: O–N–O = 134° 15'

Product of the Moments of Inertia: $I_A I_B I_C = 1.54229 \times 10^{-116}\ g^3 \cdot cm^6$

Enthalpy of Formation

The equilibrium constants for NO(g) + 1/2 $O_2 \rightarrow NO_2$(g) of Bodenstein and Lindner,[1] as given by Giauque and Kemp[2] were subjected to 2nd and 3rd law analysis. 3rd law analysis gave $\Delta_f H°(298.15\ K) = -13.67\ kcal \cdot mol^{-1}$ and 2nd law $\Delta_f H°(298.15\ K) = -13.52 \pm 0.01\ kcal \cdot mol^{-1}$. The 3rd law value had a very slight trend with temperature which was consistent with an entropy error of 0.25 $cal \cdot K^{-1} \cdot mol^{-1}$, the 2nd law entropy was also consistent with an entropy error of 0.25 $cal \cdot K^{-1} \cdot mol^{-1}$. However the functions for all three gases are well established to about 0.03 $cal \cdot K^{-1} \cdot mol^{-1}$ or better and so this must be interpreted as due to errors in the data. On this basis the 3rd law value was chosen and combined with JANAF auxiliary data to give $\Delta_f H°(298.15\ K) = 7.91 \pm 0.2\ kcal \cdot mol^{-1}$, where the uncertainty includes that due to the possible error in the equilibrium constants.

Heat Capacity and Entropy

Bird *et al.* have given a complete review of the microwave spectrum of NO_2. They also give a corrected infra-red vibrational assignment, adopted here, which is in excellent agreement with calculations from the microwave data. They report $I_A = 0.34981 \times 10^{-39}$, $I_B = 6.45446 \times 10^{-39}$, and $I_C = 6.81994 \times 10^{-39}\ g \cdot cm^2$. The bond length and angle were chosen to give the best fit of the moments of inertia.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.186	35.927	35.927	INFINITE
100	33.276	202.563	271.168	−6.861	34.898	39.963	−20.874
200	34.385	225.852	243.325	−3.495	33.897	45.422	−11.863
250	35.593	233.649	240.634	−1.746	33.460	48.355	−10.103
298.15	36.974	240.034	240.034	0.	33.095	51.258	−8.980
300	37.029	240.262	240.034	0.068	33.083	51.371	−8.944
350	38.583	246.086	240.491	1.958	32.768	54.445	−8.125
400	40.171	251.342	241.524	3.927	32.512	57.560	−7.517
450	41.728	256.164	242.886	5.975	32.310	60.703	−7.046
500	43.206	260.638	244.440	8.099	32.154	63.867	−6.672
600	45.834	268.755	247.830	12.555	31.959	70.230	−6.114
700	47.986	275.988	251.345	17.250	31.878	76.616	−5.717
800	49.708	282.512	254.840	22.138	31.874	83.008	−5.420
900	51.076	288.449	258.250	27.179	31.923	89.397	−5.188
1000	52.166	293.889	261.545	32.344	32.005	95.779	−5.003
1100	53.041	298.903	264.717	37.605	32.109	102.152	−4.851
1200	53.748	303.550	267.761	42.946	32.226	108.514	−4.724
1300	54.326	307.876	270.683	48.351	32.351	114.867	−4.615
1400	54.803	311.920	273.485	53.808	32.478	121.209	−4.522
1500	55.200	315.715	276.175	59.309	32.603	127.543	−4.441
1600	55.533	319.288	278.759	64.846	32.724	133.868	−4.370
1700	55.815	322.663	281.244	70.414	32.837	140.186	−4.307
1800	56.055	325.861	283.634	76.007	32.940	146.497	−4.251
1900	56.262	328.897	285.937	81.624	33.032	152.804	−4.201
2000	56.441	331.788	288.158	87.259	33.111	159.106	−4.155
2100	56.596	334.545	290.302	92.911	33.175	165.404	−4.114
2200	56.732	337.181	292.373	98.577	33.223	171.700	−4.077
2300	56.852	339.706	294.377	104.257	33.255	177.993	−4.042
2400	56.958	342.128	296.316	109.947	33.270	184.285	−4.011
2500	57.052	344.455	298.196	115.648	33.268	190.577	−3.982
2600	57.136	346.694	300.018	121.357	33.248	196.870	−3.955
2700	57.211	348.852	301.787	127.075	33.210	203.164	−3.930
2800	57.278	350.934	303.505	132.799	33.155	209.460	−3.908
2900	57.339	352.945	305.176	138.530	33.082	215.757	−3.886
3000	57.394	354.889	306.800	144.267	32.992	222.058	−3.866
3100	57.444	356.772	308.382	150.009	32.885	228.363	−3.848
3200	57.490	358.597	309.923	155.756	32.761	234.670	−3.831
3300	57.531	360.366	311.425	161.507	32.622	240.981	−3.814
3400	57.569	362.084	312.890	167.262	32.467	247.298	−3.799
3500	57.604	363.754	314.319	173.020	32.297	253.618	−3.785
3600	57.636	365.377	315.715	178.783	32.113	259.945	−3.772
3700	57.666	366.957	317.079	184.548	31.914	266.276	−3.759
3800	57.693	368.495	318.412	190.316	31.701	272.613	−3.747
3900	57.719	369.994	319.715	196.086	31.475	278.956	−3.736
4000	57.742	371.455	320.991	201.859	31.236	285.305	−3.726
4100	57.764	372.881	322.239	207.635	30.985	291.659	−3.716
4200	57.784	374.274	323.461	213.412	30.720	298.020	−3.706
4300	57.803	375.634	324.659	219.191	30.444	304.388	−3.698
4400	57.821	376.963	325.833	224.973	30.155	310.762	−3.689
4500	57.837	378.262	326.983	230.756	29.854	317.142	−3.681
4600	57.853	379.534	328.112	236.540	29.540	323.530	−3.674
4700	57.867	380.778	329.219	242.326	29.214	329.925	−3.667
4800	57.881	381.996	330.306	248.114	28.875	336.326	−3.660
4900	57.894	383.190	331.373	253.902	28.523	342.736	−3.654
5000	57.906	384.360	332.421	259.692	28.158	349.152	−3.648
5100	57.917	385.507	333.451	265.483	27.778	355.576	−3.642
5200	57.928	386.631	334.463	271.276	27.384	362.006	−3.636
5300	57.938	387.735	335.458	277.069	26.974	368.446	−3.631
5400	57.948	388.818	336.436	282.863	26.548	374.892	−3.626
5500	57.957	389.881	337.398	288.658	26.106	381.347	−3.622
5600	57.965	390.926	338.344	294.455	25.646	387.811	−3.617
5700	57.973	391.952	339.276	300.251	25.167	394.281	−3.613
5800	57.981	392.960	340.193	306.049	24.669	400.762	−3.609
5900	57.988	393.951	341.096	311.848	24.150	407.249	−3.606
6000	57.995	394.926	341.985	317.647	23.608	413.748	−3.602

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

$S°(298.15\ K) = 236.598 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -193.73 \pm 5.8\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -202.72 \pm 5.8\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^1A_1]$	[0]	[1]
$[^3B_1]$	[22000]	[3]
$[^1B_1]$	[27000]	[1]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1320](1)
[750](1)
1244 (1)

Point Group: C_{2v} $\sigma = 2$

Bond Distance: N–O = [1.23 ± 0.04] Å

Bond Angle: O–N–O = 115° ± 3°

Product of the Moments of Inertia: $I_A I_B I_C = [2.59592 \times 10^{-116}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The recent literature concerning the electron affinity of NO_2(g) is summarized in the following table.

Source	Technique	electron affinity NO_2(g), eV
[1]	magnetron technique, direct electron–capture process	3.99 ± 0.16
[2]	endothermic charge transfer reaction	>2.04, >3.063
[3]	endothermic charge transfer reaction	2.30 ± 0.15
[4]	photodetachment of e^- from NO_2^- in argon matrix	<3.9
[5]	reaction of NO_2^- with HCl and HBr in flowing after glow system	<2.6
[6]	correlation between heats of hydration and heterolytic bond dissociation energies	2.5
[7]	charge transfer reactions, flowing after glow system	2.38 ± 0.06

The early literature on the electron affinity of NO_2(g) is best summarized and referenced by Berkowitz *et al.*,[2] Ferguson, *et al.*[5] and Dunkin, *et al.*[7] Much of these early data are not only widely scattered but also conflicting.

The value chosen for the electron affinity of NO_2(g) is 2.38 ± 0.06 eV, based on the work of Dunkin *et al.*[7] This leads to $\Delta_f H°(NO_2^-, g, 298.15\ K) = -48.45 \pm 1.38\ kcal \cdot mol^{-1}$, using JANAF auxiliary data.

Heat Capacity and Entropy

The infrared spectrum of the NO_2^- ion isolated in an argon matrix was studied by Milligan *et al.*[4] and Milligan and Jacox.[8] They reported that the antisymmetric stretching fundamental was $\nu_3 = 1244\ cm^{-1}$.

Hochstrasser and Marchetti,[9] in combination with data from Sidman,[10] reported $\nu_1 = 1325\ cm^{-1}$, $\nu_2 = 831\ cm^{-1}$ and $\nu_3 = 1243\ cm^{-1}$ as the vibrational frequencies of the nitrite ion in solution. These frequencies are also very similar to the values reported for NO_2(g) by Herzberg.[12] The ν_1 and ν_2 vibrational frequencies of NO_2^-(g) were assumed to be the same as those for nitrite ion in solution.[11] The value adopted for ν_3 was that of Milligan, *et al.*[4,8]

Milligan, *et al.*,[4,8] via studies of the infrared spectrum of NO_2^- ion isolated in an argon matrix, concluded that the isotopic data were consistent with a O–N–O angle of 115°. Hochstrasser and Marchetti,[9] relying on crystallographic data for $NaNO_2$(cr) collected by other investigators, reported the N–O bond distance as 1.23 ± 0.04 Å and the O–N–O bond angle as 115° ± 3°. The N–O bond distance in NO_2^-(g) is assumed to be the same as that reported for $NaNO_2$(cr).

The electronic states are estimated by analogy with the electronic levels of the isoelectronic molecule SO_2.[12]

References

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Continued on page 1635

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−10.227	−193.726		
100	33.278	198.965	267.973	−6.901			
200	34.509	222.275	239.931	−3.531			
250	35.955	230.122	237.208	−1.771			
298.15	37.663	236.598	236.598	0.	−202.715	−177.273	31.057
300	37.733	236.831	236.599	0.070	−202.765	−177.115	30.838
350	39.645	242.791	237.065	2.004	−204.075	−172.735	25.779
400	41.538	248.209	238.124	4.034	−205.309	−168.173	21.961
450	43.317	253.206	239.526	6.156	−206.476	−163.460	18.974
500	44.933	257.855	241.129	8.363	−207.587	−158.621	16.571
600	47.641	266.297	244.635	12.997	−209.683	−148.628	12.939
700	49.714	273.804	248.275	17.870	−211.665	−138.295	10.320
800	51.291	280.550	251.895	22.924	−213.581	−127.682	8.337
900	52.496	286.664	255.424	28.116	−215.462	−116.831	6.781
1000	53.429	292.245	258.831	33.414	−217.324	−105.773	5.525
1100	54.160	297.373	262.105	38.795	−219.179	−94.527	4.489
1200	54.741	302.111	265.244	44.241	−221.035	−83.113	3.618
1300	55.208	306.512	268.251	49.739	−222.896	−71.545	2.875
1400	55.590	310.618	271.132	55.279	−224.764	−59.832	2.232
1500	55.904	314.464	273.894	60.855	−226.643	−47.986	1.671
1600	56.166	318.081	276.544	66.459	−228.534	−36.014	1.176
1700	56.387	321.493	279.089	72.087	−230.439	−23.923	0.735
1800	56.574	324.721	281.535	77.735	−232.360	−11.720	0.340
1900	56.734	327.784	283.889	83.400	−234.297	0.591	−0.016
2000	56.872	330.698	286.157	89.081	−236.252	13.004	−0.340
2100	56.992	333.476	288.345	94.774	−238.226	25.515	−0.635
2200	57.098	336.129	290.457	100.479	−240.218	38.121	−0.905
2300	57.191	338.670	292.498	106.193	−242.229	50.817	−1.154
2400	57.275	341.105	294.473	111.917	−244.260	63.602	−1.384
2500	57.351	343.445	296.386	117.648	−246.310	76.471	−1.598
2600	57.421	345.696	298.239	123.387	−248.380	89.424	−1.797
2700	57.487	347.864	300.037	129.132	−250.468	102.456	−1.982
2800	57.550	349.956	301.783	134.884	−252.574	115.566	−2.156
2900	57.612	351.977	303.479	140.642	−254.699	128.750	−2.319
3000	57.673	353.931	305.129	146.407	−256.840	142.010	−2.473
3100	57.735	355.823	306.733	152.177	−258.997	155.341	−2.617
3200	57.799	357.657	308.296	157.954	−261.169	168.740	−2.754
3300	57.866	359.436	309.819	163.737	−263.354	182.208	−2.884
3400	57.937	361.165	311.304	169.527	−265.553	195.744	−3.007
3500	58.012	362.845	312.753	175.324	−267.763	209.343	−3.124
3600	58.092	364.481	314.167	181.130	−269.983	223.006	−3.236
3700	58.178	366.074	315.548	186.943	−272.212	236.731	−3.342
3800	58.271	367.626	316.899	192.765	−274.449	250.517	−3.444
3900	58.370	369.141	318.219	198.597	−276.692	264.361	−3.541
4000	58.476	370.620	319.510	204.440	−278.940	278.262	−3.634
4100	58.590	372.066	320.775	210.293	−281.193	292.220	−3.723
4200	58.711	373.479	322.013	216.158	−283.448	306.233	−3.809
4300	58.840	374.862	323.226	222.035	−285.705	320.300	−3.891
4400	58.977	376.216	324.415	227.926	−287.963	334.419	−3.970
4500	59.121	377.543	325.581	233.831	−290.221	348.589	−4.046
4600	59.273	378.844	326.725	239.751	−292.478	362.809	−4.120
4700	59.432	380.121	327.847	245.686	−294.733	377.079	−4.191
4800	59.598	381.374	328.949	251.637	−296.987	391.397	−4.259
4900	59.771	382.604	330.032	257.606	−299.238	405.762	−4.325
5000	59.951	383.814	331.095	263.592	−301.486	420.173	−4.390
5100	60.136	385.003	332.141	269.596	−303.731	434.629	−4.452
5200	60.327	386.172	333.169	275.619	−305.973	449.127	−4.512
5300	60.523	387.323	334.179	281.662	−308.212	463.671	−4.570
5400	60.724	388.456	335.174	287.724	−310.448	478.255	−4.626
5500	60.930	389.573	336.153	293.807	−312.681	492.881	−4.681
5600	61.139	390.672	337.117	299.910	−314.913	507.548	−4.734
5700	61.351	391.756	338.066	306.035	−317.142	522.254	−4.786
5800	61.566	392.825	339.001	312.181	−319.371	537.001	−4.836
5900	61.783	393.879	339.922	318.348	−321.600	551.783	−4.885
6000	62.002	394.920	340.830	324.537	−323.831	566.606	−4.933

PREVIOUS: June 1972 (1 atm) CURRENT: June 1972 (1 bar)

$S°(298.15\ K) = [252.619]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 77.53 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 71.13 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[1158](2)
[940](1)
[704](2)
[765](1)

Ground State Quantum Weight: 2 σ = [6]
Point Group: [D_{3h}]
Bond Distance: O–N = [1.2] Å
Bond Angle: O–N–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.311350 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is based on equilibrium constants for the reaction $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$ obtained from shock wave studies by Schott and Davidson.[1] These equilibria give a 2nd law value of $\Delta_r H°(495\ K) = 21.5 \pm 1.4\ kcal·mol^{-1}$, corresponding to $\Delta_f H°(298.15\ K) = 22.2\ kcal·mol^{-1}$, and a 3rd law value of $\Delta_f H°(298.15\ K) = 22.2\ kcal·mol^{-1}$. The resulting enthalpy of formation is 17.0 $kcal·mol^{-1}$.

Guillory and Johnston[2] report an equilibrium constant based on estimated Beer's law constants for NO_3 and attributed to the reaction $O_2 + NO \rightarrow NO_3$. This gives a 3rd law heat of formation of 12 ± 2 $kcal·mol^{-1}$ which was not considered. A tentative value of 23 $kcal·mol^{-1}$ (or greater) may be derived from the $D°$ given by Ramsay.[3]

Heat Capacity and Entropy

The structure and frequencies are those estimated by Hisatsune.[4] A symmetry of D_{3h} was chosen on the basis of Walsh's[5] correlation, and the bond distance was taken as 2% longer than in the nitrate ion. The planar mode frequencies were calculated from estimated Urey–Bradley force constants, while the out-of-plane wagging frequency (765 cm^{-1}) was assumed the same as in HNO_3(g).

There are several conflicting bits of information concerning NO_3 radicals. Chantry *et al.*[6] studied the electron resonance and optical absorption spectra of what appears to be NO_3 radicals trapped in crystals of urea nitrate. The authors suggest a planar structure without a threefold axis (thus C_s or C_{2v} symmetry), at least for the trapped radicals. Guillory and Johnston[2] report for gaseous NO_3 radicals an infrared frequency at 1840 cm^{-1} which they assign as the N–O stretch. The similarity of this frequency to those in N–O and X–N–O molecules led the authors to suggest an OONO structure (thus C_s symmetry) rather than the nitrate structure. The remaining frequences for such a structure may be crudely estimated by analogy with those measured for $(NO)_2$ by Smith *et al.*[7] Based on such frequencies and reasonable bond distances, the room temperature entropy for the OONO structure would be 68–72 $cal·K^{-1}·mol^{-1}$. Such an entropy is quite inconsistent with the 2nd law $\Delta_r S°(495\ K) = 33.2 \pm 3\ cal·K^{-1}·mol^{-1}$ for $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$ obtained from the shock wave studies of Schott and Davidson. The Hisatsune functions based on the nitrate structure were selected because they are consistent with the experimental entropy. The principal moments of inertia for this structure are $I_A = I_B = 6.4277 \times 10^{-39}$ and $I_C = 12.8555 \times 10^{-39}\ g·cm^2$. A structure of C_{2v} symmetry would result if the nitrate structure were distorted to give one non-equivalent oxygen. Ramsay[3] suggests that such distortion can only be small, based on the high dispersion optical spectra of the gas phase.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.959	77.529	77.529	INFINITE
100	33.345	211.871	288.193	−7.632	75.048	87.847	−45.887
200	37.739	235.888	256.603	−4.143	72.715	101.581	−26.530
250	42.240	244.778	253.366	−2.147	71.797	108.909	−22.755
298.15	46.934	252.619	252.619	0.	71.128	116.121	−20.344
300	47.113	252.910	252.620	0.087	71.106	116.400	−20.267
350	51.765	260.527	253.211	2.561	70.637	123.989	−18.504
400	55.929	267.717	254.579	5.255	70.359	131.631	−17.189
450	59.533	274.519	256.420	8.144	70.240	139.299	−16.169
500	62.601	280.954	258.555	11.200	70.246	146.973	−15.354
600	67.380	292.815	263.295	17.712	70.527	162.297	−14.129
700	70.793	303.472	268.286	24.630	71.042	177.554	−13.249
800	73.266	313.095	273.296	31.840	71.691	192.726	−12.584
900	75.095	321.836	278.211	39.262	72.417	207.813	−12.061
1000	76.476	329.822	282.979	46.844	73.186	222.816	−11.639
1100	77.539	337.163	287.576	54.547	73.977	237.741	−11.289
1200	78.373	343.947	291.994	62.344	74.776	252.593	−10.995
1300	79.037	350.248	296.236	70.216	75.576	267.379	−10.743
1400	79.573	356.125	300.306	78.147	76.371	282.103	−10.525
1500	80.013	361.631	304.213	86.127	77.155	296.771	−10.334
1600	80.377	366.807	307.965	94.147	77.925	311.387	−10.166
1700	80.682	371.689	311.571	102.200	78.678	325.955	−10.015
1800	80.939	376.308	315.040	110.282	79.411	340.479	−9.880
1900	81.159	380.690	318.381	118.387	80.122	354.963	−9.759
2000	81.348	384.858	321.602	126.513	80.809	369.411	−9.648
2100	81.511	388.831	324.709	134.656	81.472	383.825	−9.547
2200	81.653	392.626	327.711	142.814	82.108	398.208	−9.455
2300	81.777	396.259	330.613	150.986	82.717	412.562	−9.370
2400	81.887	399.741	333.421	159.169	83.298	426.890	−9.291
2500	81.984	403.086	336.141	167.363	83.851	441.195	−9.218
2600	82.070	406.303	338.778	175.565	84.376	455.478	−9.151
2700	82.147	409.402	341.337	183.776	84.873	469.743	−9.088
2800	82.216	412.391	343.822	191.994	85.343	483.989	−9.029
2900	82.278	415.277	346.236	200.219	85.785	498.217	−8.974
3000	82.334	418.067	348.584	208.450	86.200	512.432	−8.922
3100	82.385	420.768	350.869	216.686	86.590	526.634	−8.874
3200	82.431	423.384	353.095	224.927	86.954	540.822	−8.828
3300	82.473	425.922	355.263	233.172	87.293	555.000	−8.785
3400	82.512	428.384	357.378	241.421	87.608	569.169	−8.744
3500	82.547	430.777	359.441	249.674	87.901	583.327	−8.706
3600	82.580	433.102	361.455	257.931	88.171	597.479	−8.669
3700	82.609	435.365	363.422	266.190	88.419	611.622	−8.635
3800	82.637	437.569	365.345	274.452	88.647	625.761	−8.602
3900	82.663	439.716	367.224	282.717	88.854	639.893	−8.570
4000	82.686	441.809	369.063	290.985	89.042	654.019	−8.541
4100	82.708	443.851	370.862	299.255	89.210	668.142	−8.512
4200	82.728	445.844	372.624	307.526	89.360	682.260	−8.485
4300	82.747	447.791	374.349	315.800	89.491	696.376	−8.459
4400	82.765	449.694	376.040	324.076	89.603	710.487	−8.435
4500	82.782	451.554	377.697	332.353	89.698	724.597	−8.411
4600	82.797	453.373	379.323	340.632	89.774	738.704	−8.388
4700	82.812	455.154	380.917	348.913	89.831	752.811	−8.367
4800	82.825	456.898	382.482	357.194	89.869	766.917	−8.346
4900	82.838	458.606	384.018	365.478	89.887	781.023	−8.326
5000	82.850	460.279	385.527	373.762	89.886	795.127	−8.307
5100	82.862	461.920	387.009	382.048	89.863	809.233	−8.288
5200	82.872	463.529	388.465	390.334	89.819	823.337	−8.271
5300	82.883	465.108	389.896	398.622	89.753	837.445	−8.254
5400	82.892	466.657	391.303	406.911	89.662	851.552	−8.237
5500	82.901	468.178	392.687	415.201	89.547	865.662	−8.221
5600	82.910	469.672	394.049	423.491	89.406	879.776	−8.206
5700	82.918	471.140	395.388	431.782	89.237	893.890	−8.192
5800	82.926	472.582	396.707	440.075	89.040	908.010	−8.178
5900	82.933	474.000	398.005	448.368	88.811	922.129	−8.164
6000	82.940	475.393	399.283	456.661	88.550	936.257	−8.151

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 211.137\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 105.77 \pm 5.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 104.78 \pm 5.0\ kJ·mol^{-1}$

Electronic Level and Multiplicity		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1

$\omega_e = 1337.24\ cm^{-1}$ $\omega_e x_e = 6.983\ cm^{-1}$ $\sigma = 1$
$B_e = 0.7862\ cm^{-1}$ $\alpha_e = 0.00557\ cm^{-1}$ $r_e = 1.4910$ Å

Enthalpy of Formation

The selected $\Delta_f H°(298.15\ K)$ was calculated from the $D_0° = 165.8 \pm 1.2$ kcal·mol^{-1} reported by Potter and DiStefano.[1] $D_0° = 163.7 \pm 1.2$ kcal·mol^{-1} was experimentally determined by Huffman *et al.*[2] The $D_0°$ reported by Huffman *et al.*[2] was derived using a pressure–composition method, i.e., measurement of equilibrium vapor pressure, at 1173 K for the reaction [PN(g) → P_2(g) + N_2(g)]. Potter and DiStefano[1] recalculated Huffman's results to obtain their $D_0°$ value. Gaydon[3] lists a $D_0° = 138.4 \pm 19$ kcal·mol^{-1}. The corresponding enthalpy of formation are:

Source	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
Potter and DiStefano[1]	25.0 ± 1.2
Huffman *et al.*[2]	27.1 ± 1.2
Gaydon[3]	53 ± 19

Heat Capacity and Entropy

The molecular constants are taken from Herzburg.[4]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.703	105.772	105.772	INFINITE
100	29.105	179.230	237.189	−5.796	106.341	98.177	−51.282
200	29.168	199.412	213.832	−2.884	105.534	90.075	−23.525
250	29.361	205.938	211.624	−1.422	105.177	86.251	−18.021
298.15	29.710	211.137	211.137	0.	104.780	82.641	−14.478
300	29.726	211.321	211.138	0.055	104.764	82.503	−14.365
350	30.230	215.940	211.501	1.553	103.598	78.899	−11.775
400	30.809	220.013	212.315	3.079	103.077	75.407	−9.847
450	31.409	223.677	213.378	4.635	102.584	71.978	−8.355
500	31.991	227.017	214.577	6.220	102.116	68.603	−7.167
600	33.033	232.944	217.157	9.473	101.244	61.983	−5.396
700	33.879	238.102	219.788	12.820	100.437	55.504	−4.142
800	34.548	242.672	222.369	16.242	99.673	49.138	−3.208
900	35.075	246.772	224.856	19.725	98.934	42.866	−2.488
1000	35.494	250.490	227.237	23.254	98.211	36.675	−1.916
1100	35.830	253.890	229.507	26.821	97.496	30.556	−1.451
1200	36.103	257.019	231.671	30.418	33.214	25.580	−1.113
1300	36.328	259.918	233.734	34.040	33.281	24.941	−1.002
1400	36.516	262.618	235.702	37.682	33.344	24.297	−0.907
1500	36.675	265.143	237.581	41.342	33.403	23.649	−0.824
1600	36.812	267.514	239.379	45.016	33.458	22.996	−0.751
1700	36.930	269.749	241.100	48.704	33.509	22.341	−0.686
1800	37.033	271.863	242.751	52.402	33.556	21.683	−0.629
1900	37.124	273.868	244.336	56.110	33.600	21.022	−0.578
2000	37.206	275.774	245.861	59.826	33.642	20.359	−0.532
2100	37.279	277.591	247.329	63.551	33.680	19.694	−0.490
2200	37.346	279.327	248.744	67.282	33.716	19.027	−0.452
2300	37.407	280.988	250.110	71.020	33.750	18.358	−0.417
2400	37.463	282.582	251.430	74.763	33.781	17.688	−0.385
2500	37.515	284.112	252.707	78.512	33.811	17.017	−0.356
2600	37.563	285.584	253.944	82.266	33.839	16.345	−0.328
2700	37.608	287.003	255.142	86.024	33.866	15.672	−0.303
2800	37.651	288.371	256.304	89.787	33.891	14.997	−0.280
2900	37.692	289.693	257.433	93.555	33.915	14.322	−0.258
3000	37.730	290.972	258.530	97.326	33.937	13.646	−0.238
3100	37.767	292.210	259.596	101.101	33.959	12.969	−0.219
3200	37.802	293.409	260.634	104.879	33.979	12.292	−0.201
3300	37.836	294.573	261.645	108.661	33.999	11.614	−0.184
3400	37.869	295.703	262.630	112.446	34.018	10.935	−0.168
3500	37.900	296.801	263.591	116.235	34.036	10.256	−0.153
3600	37.931	297.869	264.529	120.026	34.053	9.577	−0.139
3700	37.961	298.909	265.444	123.821	34.069	8.896	−0.126
3800	37.990	299.922	266.338	127.618	34.085	8.216	−0.113
3900	38.018	300.909	267.212	131.419	34.100	7.535	−0.101
4000	38.046	301.872	268.066	135.222	34.115	6.854	−0.089
4100	38.073	302.811	268.902	139.028	34.129	6.172	−0.079
4200	38.099	303.729	269.721	142.836	34.143	5.490	−0.068
4300	38.125	304.626	270.522	146.648	34.156	4.807	−0.058
4400	38.151	305.503	271.307	150.461	34.168	4.125	−0.049
4500	38.176	306.360	272.076	154.278	34.180	3.442	−0.040
4600	38.201	307.200	272.831	158.097	34.192	2.759	−0.031
4700	38.226	308.022	273.571	161.918	34.203	2.075	−0.023
4800	38.250	308.827	274.297	165.742	34.214	1.391	−0.015
4900	38.274	309.616	275.010	169.568	34.224	0.708	−0.008
5000	38.298	310.389	275.710	173.397	34.234	0.023	−0.000
5100	38.321	311.148	276.397	177.228	34.243	−0.661	0.007
5200	38.345	311.892	277.073	181.061	34.251	−1.345	0.014
5300	38.368	312.623	277.737	184.897	34.259	−2.030	0.020
5400	38.391	313.340	278.389	188.735	34.267	−2.715	0.026
5500	38.414	314.045	279.031	192.575	34.274	−3.400	0.032
5600	38.436	314.737	279.663	196.417	34.280	−4.085	0.038
5700	38.459	315.418	280.284	200.262	34.285	−4.770	0.044
5800	38.481	316.087	280.895	204.109	34.290	−5.455	0.049
5900	38.503	316.745	281.497	207.958	34.294	−6.140	0.054
6000	38.525	317.392	282.090	211.810	34.296	−6.826	0.059

PREVIOUS: September 1962 (1 atm) CURRENT: September 1962 (1 bar)

$S°(298.15\ K) = 222.087\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 262.9 \pm 105\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 263.6 \pm 105\ kJ·mol^{-1}$

Electronic Levels and Multiplicities		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_r$	0	2
	223	2

$\omega_e = 1220.0\ cm^{-1}$ $\omega_e x_e = 7.75\ cm^{-1}$ $\sigma = 1$
$B_e = [0.7762]\ cm^{-1}$ $\alpha_e = [0.0064]\ cm^{-1}$ $r_e = 1.495(7)$ Å

Enthalpy of Formation

The dissociation energy is listed by Gaydon.[1]

Heat Capacity and Entropy

The spectroscopic constants other than B_e and α_e are from Herzberg.[2] r_e is from Bowen[3] and has been used, together with the equation $\alpha_e = 6(\sqrt{\omega_e x_e B_e^3} - 6B_e^2)\omega_e$ to calculate B_e and α_e.[2]

References

[1]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London (1953).
[2]G. Herzberg, "Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Company, New York (1950).
[3]H. J. M. Bowen, Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London (1958).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.397	262.942	262.942	INFINITE
100	32.301	186.768	250.632	−6.386	263.812	254.378	−132.873
200	32.201	209.348	224.999	−3.130	263.971	244.827	−63.942
250	31.833	216.488	222.611	−1.531	263.823	240.056	−50.157
298.15	31.793	222.087	222.087	0.	263.592	235.498	−41.258
300	31.797	222.284	222.088	0.059	263.582	235.324	−40.974
350	32.020	227.200	222.476	1.653	263.282	230.637	−34.421
400	32.391	231.498	223.340	3.263	260.731	226.084	−29.524
450	32.824	235.338	224.464	4.894	259.703	221.806	−25.747
500	33.267	238.820	225.728	6.546	258.615	217.656	−22.738
600	34.081	244.959	228.435	9.914	256.907	209.632	−18.250
700	34.751	250.265	231.183	13.357	255.482	201.868	−15.064
800	35.284	254.941	233.866	16.860	254.219	194.297	−12.686
900	35.704	259.122	236.444	20.410	199.924	187.958	−10.909
1000	36.039	262.902	238.904	23.998	200.036	186.622	−9.748
1100	36.308	266.350	241.245	27.616	200.133	185.276	−8.798
1200	36.529	269.519	243.471	31.258	200.214	183.922	−8.006
1300	36.713	272.450	245.589	34.920	200.277	182.562	−7.335
1400	36.867	275.177	247.606	38.600	200.322	181.197	−6.761
1500	36.999	277.725	249.530	42.293	200.348	179.830	−6.262
1600	37.114	280.117	251.367	45.999	200.356	178.462	−5.826
1700	37.214	282.370	253.125	49.715	200.347	177.094	−5.441
1800	37.303	284.499	254.810	53.441	200.322	175.726	−5.099
1900	37.383	286.519	256.426	57.176	200.282	174.361	−4.794
2000	37.455	288.438	257.979	60.918	200.228	172.998	−4.518
2100	37.521	290.267	259.473	64.667	200.162	171.638	−4.269
2200	37.582	292.014	260.913	68.422	200.085	170.282	−4.043
2300	37.639	293.686	262.302	72.183	199.997	168.929	−3.836
2400	37.691	295.289	263.643	75.949	199.900	167.580	−3.647
2500	37.741	296.828	264.940	79.721	199.795	166.236	−3.473
2600	37.788	298.310	266.195	83.498	199.683	164.895	−3.313
2700	37.833	299.737	267.411	87.279	199.564	163.560	−3.164
2800	37.875	301.113	268.590	91.064	199.439	162.228	−3.026
2900	37.916	302.443	269.735	94.854	199.309	160.902	−2.898
3000	37.955	303.729	270.847	98.647	199.174	159.580	−2.779
3100	37.993	304.974	271.928	102.445	199.035	158.262	−2.667
3200	38.030	306.181	272.979	106.246	198.892	156.949	−2.562
3300	38.066	307.352	274.003	110.051	198.746	155.641	−2.464
3400	38.101	308.489	275.001	113.859	198.596	154.337	−2.371
3500	38.135	309.594	275.974	117.671	198.442	153.037	−2.284
3600	38.168	310.669	276.922	121.486	198.286	151.742	−2.202
3700	38.201	311.715	277.849	125.304	198.126	150.451	−2.124
3800	38.233	312.734	278.753	129.126	197.963	149.165	−2.050
3900	38.265	313.727	279.637	132.951	197.796	147.883	−1.981
4000	38.296	314.697	280.502	136.779	197.626	146.605	−1.914
4100	38.326	315.643	281.347	140.610	197.452	145.332	−1.852
4200	38.357	316.567	282.175	144.444	197.275	144.063	−1.792
4300	38.386	317.469	282.985	148.281	197.093	142.798	−1.735
4400	38.416	318.352	283.779	152.122	196.907	141.538	−1.680
4500	38.445	319.216	284.557	155.965	196.717	140.281	−1.628
4600	38.474	320.061	285.320	159.811	196.523	139.029	−1.579
4700	38.503	320.889	286.068	163.660	196.323	137.782	−1.531
4800	38.532	321.700	286.802	167.511	196.119	136.538	−1.486
4900	38.560	322.495	287.522	171.366	195.909	135.299	−1.442
5000	38.588	323.274	288.229	175.223	195.694	134.064	−1.401
5100	38.616	324.038	288.924	179.083	195.474	132.834	−1.360
5200	38.644	324.789	289.607	182.946	195.247	131.608	−1.322
5300	38.671	325.525	290.277	186.812	195.015	130.386	−1.285
5400	38.699	326.248	290.937	190.681	194.776	129.169	−1.249
5500	38.726	326.958	291.585	194.552	194.532	127.956	−1.215
5600	38.753	327.656	292.223	198.426	194.281	126.748	−1.182
5700	38.780	328.343	292.851	202.303	194.023	125.544	−1.150
5800	38.807	329.017	293.469	206.182	193.759	124.345	−1.120
5900	38.834	329.681	294.077	210.064	193.488	123.151	−1.090
6000	38.861	330.334	294.676	213.949	193.211	121.961	−1.062

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 216.812\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 371.20 \pm 62.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 372.38 \pm 62.8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Sigma^+$	0	2
	[6000]	4
	24299.4	2
	[31000]	4

$\omega_e = 1150.8\ cm^{-1}$ $\omega_e x_e = 6.55\ cm^{-1}$ $\sigma = 1$

$B_e = 0.7299\ cm^{-1}$ $\alpha_e = 0.00567\ cm^{-1}$ $r_e = 1.5718$ Å

Enthalpy of Formation

A linear Birge–Sponer extrapolation of the ground state gives a dissociation energy of 142.9 $kcal·mol^{-1}$. The ground state cancorrelate with normal atoms $Si(^3P) + N(^4S)$ or with $Si(^3P) + N(^2D)$; in this latter case D_0° would be 88 $kcal·mol^{-1}$. The uncertainty in the extrapolation is quite large, ± 30 $kcal·mol^{-1}$, since only 6 levels, of the estimated total of 87 levels, are observed.

A dissociation energy can also be calculated from the $B^2\Sigma^+$ state by a much shorter extrapolation. This extrapolation is done graphically since some curvature is evident in the first six levels. A value of $D_0^\circ(B^2\Sigma) = 50.4\ kcal·mol^{-1}$ is obtained. This corresponds to $D_0^\circ(X^2\Sigma) = 119.9\ kcal·mol^{-1}$ for normal products or $D_0^\circ(X^2\Sigma) = 65\ kcal·mol^{-1}$ for excited nitrogen as a product. The uncertainty in this extrapolation is less than the ground state and is probably ± 20 $kcal·mol^{-1}$.

An estimate of D_0° (SiN) may be obtained by equating $D_0^\circ(SiN)/D_0^\circ(SiO) = D_0^\circ(CN)/D_0^\circ(CO)$; this yields $D_0^\circ(SiN) = 135\ kcal·mol^{-1}$.

A comparison of the isoelectronic molecules CP, BS and BeCl and the related molecules CN, BO, BeF indicates $D_0^\circ(SiN) > 115\ kcal·mol^{-1}$.

A value of $D_0^\circ(SiN) = 130 \pm 15\ kcal·mol^{-1}$ is in agreement within the uncertainties of both ground state and B state extrapolations assuming normal atoms as products, and is in agreement with the other estimates. This value is adopted and yields $\Delta_f H°(SiN, g, 298.15\ K) = 89\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The B–X transition has been reported by Jenkins and de Laszlo.[1] The rotational and vibrational constants are derived from their work and adjusted to normal isotopic abundance. The $A^2\Pi$–$C^2\Pi$ transition has been observed by Shetlar.[2] The height of the A state is estimated by correlation with CP(g). The level of the B state is taken from Herzberg.[3]

References

[1]F. A. Jenkins and H. de Laszlo, Proc. Roy. Soc. (London) **122**, 103 (1929).

[2]M. D. Shetlar, Ph.D. Thesis, Univ. of California, Berkeley (1965).

[3]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., 2nd Edition, New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.733	371.197	371.197	INFINITE
100	29.106	184.787	243.038	−5.825	372.387	362.282	−189.237
200	29.267	204.984	219.537	−2.910	372.667	352.002	−91.934
250	29.630	211.550	217.306	−1.439	372.561	346.845	−72.469
298.15	30.168	216.812	216.812	0.	372.376	341.909	−59.901
300	30.191	216.999	216.813	0.056	372.368	341.720	−59.499
350	30.859	221.703	217.183	1.582	372.130	336.630	−50.239
400	31.551	225.868	218.013	3.142	371.874	331.576	−43.299
450	32.213	229.623	219.098	4.736	371.611	326.554	−37.905
500	32.818	233.049	220.324	6.362	371.347	321.562	−33.593
600	33.832	239.126	222.964	9.697	370.814	311.655	−27.132
700	34.616	244.403	225.658	13.121	370.269	301.838	−22.523
800	35.234	249.067	228.298	16.615	369.698	292.101	−19.072
900	35.752	253.248	230.842	20.165	369.098	282.437	−16.392
1000	36.222	257.039	233.275	23.764	368.466	272.841	−14.252
1100	36.683	260.513	235.596	27.409	367.807	263.311	−12.504
1200	37.156	263.725	237.808	31.101	367.125	253.841	−11.049
1300	37.652	266.718	239.918	34.841	366.428	244.429	−9.821
1400	38.173	269.528	241.933	38.632	365.720	235.071	−8.771
1500	38.713	272.180	243.862	42.476	365.006	225.764	−7.862
1600	39.264	274.696	245.711	46.375	364.289	216.504	−7.068
1700	39.814	277.093	247.487	50.329	313.395	207.736	−6.383
1800	40.355	279.384	249.196	54.338	312.910	201.535	−5.848
1900	40.877	281.580	250.843	58.399	312.467	195.360	−5.371
2000	41.372	283.689	252.433	62.512	312.066	189.207	−4.942
2100	41.834	285.719	253.970	66.673	311.705	183.073	−4.554
2200	42.258	287.675	255.458	70.878	311.380	176.956	−4.201
2300	42.642	289.562	256.900	75.123	311.089	170.852	−3.880
2400	42.984	291.384	258.299	79.405	310.829	164.760	−3.586
2500	43.285	293.145	259.658	83.719	310.595	158.679	−3.315
2600	43.544	294.848	260.979	88.060	310.384	152.607	−3.066
2700	43.765	296.496	262.264	92.426	310.192	146.542	−2.835
2800	43.948	298.091	263.515	96.812	310.016	140.484	−2.621
2900	44.097	299.636	264.734	101.215	309.853	134.433	−2.421
3000	44.215	301.133	265.923	105.630	309.699	128.386	−2.235
3100	44.304	302.584	267.082	110.057	309.553	122.345	−2.061
3200	44.368	303.992	268.214	114.490	309.411	116.308	−1.899
3300	44.409	305.358	269.319	118.929	309.271	110.276	−1.746
3400	44.430	306.684	270.398	123.372	309.131	104.248	−1.602
3500	44.435	307.972	271.453	127.815	308.990	98.224	−1.466
3600	44.425	309.224	272.485	132.258	−75.306	102.665	−1.490
3700	44.402	310.440	273.495	136.699	−75.040	107.605	−1.519
3800	44.370	311.624	274.483	141.138	−74.781	112.538	−1.547
3900	44.330	312.776	275.450	145.573	−74.529	117.464	−1.573
4000	44.283	313.898	276.397	150.004	−74.284	122.383	−1.598
4100	44.231	314.991	277.325	154.430	−74.047	127.297	−1.622
4200	44.176	316.056	278.235	158.850	−73.819	132.205	−1.644
4300	44.118	317.095	279.126	163.265	−73.598	137.108	−1.666
4400	44.059	318.108	280.001	167.673	−73.384	142.006	−1.686
4500	44.000	319.098	280.859	172.076	−73.178	146.898	−1.705
4600	43.941	320.064	281.700	176.473	−72.980	151.787	−1.724
4700	43.883	321.009	282.527	180.865	−72.789	156.671	−1.741
4800	43.827	321.932	283.338	185.250	−72.605	161.551	−1.758
4900	43.772	322.835	284.135	189.630	−72.428	166.428	−1.774
5000	43.721	323.719	284.918	194.005	−72.257	171.300	−1.790
5100	43.672	324.584	285.687	198.374	−72.093	176.170	−1.804
5200	43.626	325.432	286.443	202.739	−71.935	181.036	−1.819
5300	43.584	326.262	287.187	207.100	−71.783	185.900	−1.832
5400	43.544	327.077	287.918	211.456	−71.637	190.760	−1.845
5500	43.508	327.875	288.637	215.808	−71.496	195.618	−1.858
5600	43.476	328.659	289.345	220.158	−71.360	200.474	−1.870
5700	43.447	329.428	290.042	224.504	−71.230	205.327	−1.882
5800	43.422	330.184	290.727	228.847	−71.106	210.177	−1.893
5900	43.400	330.926	291.402	233.188	−70.986	215.026	−1.904
6000	43.382	331.655	292.067	237.528	−70.872	219.873	−1.914

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K)$ = [256.487 ± 8.4] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 396.43 ± 20.9 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 397.48 ± 20.9 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[4]
[24000]	[4]
[28000]	[2]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[600](1)
[240](2)
[1000](1)

Point Group: [$D_{\infty h}$] σ = 2
Bond Distance: Si–N = [170] Å
Bond Angle: Si–N–Si = [180]°
Rotational Constant: B_0 = [0.103845] cm^{-1}

Enthalpy of Formation

Zmbov and Margrave[1] have identified Si_2N(g) in a mass spectrometer. They also determined partial pressures of Si_2N(g) in equilibrium with Si(g) and N_2(g). From four of these measurements, in the temperature range 1742–1846 K, we obtain a 2nd law $\Delta_f H°(298.15\ K)$ = 99.6 ± 6 $kcal·mol^{-1}$ for the reaction $Si_2N(g) = 2\ Si(g) + 0.5\ N_2(g)$; and a 3rd law $\Delta_f H°(298.15\ K)$ = 120.2 $kcal·mol^{-1}$ with a drift of −11.4 ± 3.4 $cal·K^{-1}·mol^{-1}$. Considering the small temperature range and the uncertainties in the free energy functions, the data appear consistent. We adopt the 3rd law enthalpy of reaction which yields $\Delta_f H°(Si_2N, g, 298.15\ K)$ = 95 $kcal·mol^{-1}$.

Heat Capacity and Entropy

Si_2N(g) is considered to be closely related to C_2N(g), and its structure and electronic configuration are adopted by analogy to this species. The bond length was obtained by adding the difference between the bond distances of SiN(g) and CN(g) to the bond length in CNC(g). The vibrational frequencies were estimated by comparison with several molecules, CNC(g); ^{1} state of C_3 (g); NCN(g); and Si_2C(g). It should be noted that there is a wide variation in observed frequencies for these molecules and ν_1 and ν_3 may be significantly different from the chosen values.

The electronic ground state is considered to be $^2\pi g$ with excited states of $^2\Delta_u$ and $^2\Sigma_u^-$ as in the case of CNC(g). The levels are obtained from those in CNC(g) by use of the shift between C_3(g) and SiCSi(g).

Reference

[1] K. F. Zmbov and J. L. Margrave, Rice University, personal communication, (March 1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.822	396.430	396.430	INFINITE
100	35.904	209.763	296.993	−8.723	397.545	385.325	−201.273
200	44.596	237.627	260.893	−4.653	397.802	372.941	−97.402
250	47.543	247.906	257.295	−2.347	397.680	366.736	−76.625
298.15	49.884	256.487	256.487	0.	397.480	360.795	−63.210
300	49.965	256.795	256.488	0.092	397.471	360.567	−62.780
350	51.951	264.652	257.104	2.642	397.223	354.436	−52.897
400	53.570	271.699	258.495	5.281	396.959	348.341	−45.489
450	54.886	278.087	260.323	7.994	396.690	342.280	−39.731
500	55.958	283.927	262.395	10.766	396.418	336.249	−35.128
600	57.554	294.280	266.869	16.447	395.855	324.268	−28.230
700	58.648	303.239	271.439	22.260	395.251	312.384	−23.310
800	59.420	311.124	275.917	28.166	394.584	300.590	−19.627
900	59.981	318.156	280.226	34.137	393.843	288.885	−16.766
1000	60.399	324.499	284.342	40.157	393.021	277.266	−14.483
1100	60.718	330.271	288.259	46.214	392.117	265.734	−12.619
1200	60.966	335.565	291.983	52.298	391.130	254.287	−11.069
1300	61.163	340.453	295.526	58.405	390.059	242.926	−9.761
1400	61.321	344.992	298.899	64.529	388.902	231.651	−8.643
1500	61.450	349.227	302.115	70.668	387.658	220.462	−7.677
1600	61.557	353.196	305.185	76.819	386.327	209.359	−6.835
1700	61.646	356.931	308.120	82.979	284.554	199.235	−6.122
1800	61.721	360.457	310.930	89.147	283.509	194.246	−5.637
1900	61.785	363.795	313.626	95.323	282.460	189.316	−5.205
2000	61.840	366.966	316.214	101.504	281.408	184.440	−4.817
2100	61.887	369.984	318.703	107.690	280.353	179.618	−4.468
2200	61.928	372.864	321.100	113.881	279.295	174.846	−4.151
2300	61.965	375.618	323.411	120.076	278.233	170.122	−3.864
2400	61.997	378.256	325.642	126.274	277.170	165.444	−3.601
2500	62.025	380.787	327.797	132.475	276.103	160.811	−3.360
2600	62.051	383.220	329.882	138.679	275.035	156.220	−3.139
2700	62.075	385.563	331.902	144.885	273.964	151.671	−2.934
2800	62.097	387.821	333.859	151.094	272.891	147.161	−2.745
2900	62.118	390.000	335.757	157.305	271.817	142.690	−2.570
3000	62.137	392.106	337.601	163.517	270.741	138.255	−2.407
3100	62.156	394.144	339.392	169.732	269.663	133.857	−2.255
3200	62.175	396.118	341.134	175.949	268.584	129.493	−2.114
3300	62.194	398.031	342.829	182.167	267.504	125.163	−1.981
3400	62.214	399.888	344.480	188.388	266.423	120.866	−1.857
3500	62.234	401.692	346.089	194.610	265.341	116.601	−1.740
3600	62.255	403.445	347.658	200.834	−504.045	133.288	−1.934
3700	62.278	405.151	349.189	207.061	−504.299	150.995	−2.132
3800	62.302	406.813	350.684	213.290	−504.557	168.709	−2.319
3900	62.327	408.431	352.144	219.521	−504.817	186.430	−2.497
4000	62.355	410.010	353.571	225.755	−505.079	204.158	−2.666
4100	62.384	411.550	354.966	231.992	−505.342	221.892	−2.827
4200	62.416	413.053	356.331	238.232	−505.604	239.633	−2.980
4300	62.450	414.522	357.668	244.476	−505.866	257.379	−3.127
4400	62.486	415.959	358.976	250.722	−506.126	275.132	−3.266
4500	62.524	417.363	360.258	256.973	−506.384	292.891	−3.400
4600	62.566	418.738	361.515	263.227	−506.639	310.656	−3.528
4700	62.609	420.084	362.746	269.486	−506.891	328.426	−3.650
4800	62.655	421.402	363.955	275.749	−507.139	346.201	−3.767
4900	62.704	422.695	365.140	282.017	−507.384	363.981	−3.880
5000	62.755	423.962	366.304	288.290	−507.625	381.767	−3.988
5100	62.809	425.205	367.447	294.568	−507.861	399.557	−4.092
5200	62.865	426.426	368.569	300.852	−508.093	417.352	−4.192
5300	62.923	427.624	369.672	307.141	−508.321	435.151	−4.289
5400	62.984	428.800	370.756	313.437	−508.544	452.954	−4.381
5500	63.047	429.957	371.822	319.738	−508.761	470.762	−4.471
5600	63.112	431.093	372.871	326.046	−508.976	488.573	−4.557
5700	63.179	432.211	373.902	332.361	−509.187	506.388	−4.641
5800	63.248	433.310	374.917	338.682	−509.395	524.207	−4.721
5900	63.318	434.392	375.916	345.010	−509.600	542.030	−4.799
6000	63.391	435.457	376.899	351.346	−509.801	559.856	−4.874

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 30.235 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3220 \pm 50\ K$

$\Delta_f H°(0\ K) = -333.971 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -337.649 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = [66.944]\ kJ·mol^{-1}$

Enthalpy of Formation

Humphrey[1] and Neumann *et al.*[2] determined the enthalpy of combustion of titanium nitride by burning the material in an oxygen bomb calorimeter. For reaction (a) Humphrey obtained $\Delta_f H°(298.15\ K) = -145.05 \pm 0.14\ kcal·mol^{-1}$ and Neumann *et al.*, $\Delta_f H°(298.15\ K) = -145.0\ kcal·mol^{-1}$. From an examination of the combustion products Humphrey reported that the TiO_2 was >95 percent rutile and <5 percent anatase, but made no correction for the anatase. The adopted $\Delta_f H°(298.15\ K) = -80.7\ kcal·mol^{-1}$ is the average of three values, two from Humphrey (−80.75, −80.61) one as reported and one corrected for anatase and one from Neumann *et al.* (−80.8). The uncertainty in the adopted enthalpy is due mainly to the uncertainty in the enthalpy of formation of rutile. Hoch *et al.*[3] determined the vapor pressure of reaction (b), in the temperature range 1987–2241 K, using a Knudsen effusion method. 3rd law analysis of the data yields $\Delta_f H°(298.15\ K) = -79.5\ kcal·mol^{-1}$. Linevsky[4] obtained the titanium partial pressures of reaction (C) at fixed nitrogen pressures using atomic absorption spectroscopy. 3rd law analysis of the data gives a $\Delta_f H°(298.15\ K) = -81 \pm 18\ kcal·mol^{-1}$. These equilibrium measurements were not considered in deriving the heat of formation due to their large uncertainties in comparison to the calorimetric data.

Source	Method	Reaction	T/K	$\Delta_r H°(298.15\ K)$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
1	Calorimeter	(a) $TiN(cr) + O_2(g) \rightarrow TiO_2(rutile) + 1/2\ N_2(g)$	298	−145.05 ± .14			−80.75
1	Calorimeter	(a) $TiN(cr) + O_2(g) \rightarrow TiO_2(rutile) + 1/2\ N_2(g)$	298	−14505 ± .14			−80.61*
2	Calorimeter	(a) $TiN(cr) + O_2(g) \rightarrow TiO_2(rutile) + 1/2\ N_2(g)$	298	−145.0			−80.80
3	Equilibrium	(b) $TiN(cr) \rightarrow Ti(g) + 1/2\ N_2(g)$	1987−2241	212 ± 9	192.5	−9.3 ± 4.3	−79.5
4	Equilibrium	(c) $TiN(cr) \rightarrow Ti(g) + 1/2\ N_2(g)$	2088−2141	230 ± 17	194.2	−17 ± 8	−81.2

*Assumes that the product TiO_2 is 95 percent rutile and 5 percent anatase.

Heat Capacity and Entropy

Low temperature heat capacities are from the data (52–296 K) of Shomate.[5] Naylor[6] measured high temperature heat contents (388–1738 K). High temperature heat capacities are derived from the enthalpies by a fitting technique which constrains the curve to join smoothly with the low temperature values. Above 1738 K the heat capacity is graphically extrapolated. The entropy is based on $S°(50;0) = 0.138\ cal·K^{-1}·mol^{-1}$.

Fusion Data

Refer to the liquid table for details.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$	$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$		$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−5.487	−333.971	−333.971	INFINITE
100	10.761	4.422	56.044	−5.162	−335.658	−327.283	170.955
200	27.330	17.338	33.350	−3.202	−337.070	−318.294	83.130
298.15	37.079	30.235	30.235	0.	−337.649	−308.929	54.123
300	37.238	30.465	30.236	0.069	−337.654	−308.750	53.758
400	43.811	42.171	31.787	4.154	−337.641	−299.104	39.059
500	47.057	52.338	34.906	8.716	−337.289	−289.506	30.245
600	48.723	61.074	38.557	13.510	−336.812	−279.993	24.376
700	49.781	68.667	42.328	18.437	−336.294	−270.564	20.190
800	50.618	75.370	46.048	23.458	−335.753	−261.211	17.055
900	51.384	81.376	49.645	28.558	−335.232	−251.925	14.621
1000	52.145	86.829	53.095	33.734	−334.797	−242.693	12.677
1100	52.919	91.835	56.392	38.987	−334.508	−233.498	11.088
1200	53.718	96.474	59.542	44.319	−338.345	−224.203	9.759
1300	54.538	100.806	62.551	49.731	−337.610	−214.721	8.628
1400	55.384	104.878	65.430	55.227	−336.890	−205.295	7.660
1500	56.246	108.729	68.190	60.809	−336.193	−195.920	6.823
1600	57.128	112.387	70.839	66.477	−335.528	−186.591	6.092
1700	58.020	115.877	73.386	72.235	−334.906	−177.301	5.448
1800	58.927	119.219	75.840	78.082	−334.337	−168.047	4.877
1900	59.848	122.430	78.208	84.020	−333.831	−158.823	4.366
2000	60.777	125.523	80.497	90.052	−348.087	−149.170	3.896
2100	61.710	128.511	82.713	96.176	−348.489	−139.214	3.463
2200	62.655	131.403	84.861	102.394	−348.804	−129.240	3.069
2300	63.605	134.209	86.946	108.707	−349.031	−119.255	2.708
2400	64.559	136.937	88.972	115.115	−349.170	−109.261	2.378
2500	65.517	139.591	90.944	121.619	−349.218	−99.264	2.074
2600	66.480	142.180	92.865	128.219	−349.175	−89.266	1.793
2700	67.446	144.707	94.738	134.915	−349.040	−79.272	1.534
2800	68.413	147.177	96.567	141.708	−348.813	−69.284	1.293
2900	69.387	149.595	98.354	148.598	−348.493	−59.307	1.068
3000	70.362	151.964	100.102	155.586	−348.079	−49.341	0.859
3100	71.337	154.287	101.812	162.670	−347.571	−39.392	0.664
3200	72.316	156.567	103.488	169.853	−346.969	−29.460	0.481
3220.000	72.513	157.018	103.819	171.301	− − − CRYSTAL <− −> LIQUID − − −		
3300	73.295	158.807	105.130	177.134	−346.271	−19.548	0.309
3400	74.279	161.010	106.742	184.512	−345.478	−9.659	0.148
3500	75.262	163.177	108.323	191.989	−344.590	0.205	−0.003
3600	76.244	165.311	109.877	199.565	−343.606	10.043	−0.146
3700	77.228	167.414	111.403	207.238	−751.624	27.640	−0.390
3800	78.215	169.486	112.905	215.010	−749.214	48.669	−0.669
3900	79.203	171.531	114.382	222.881	−746.762	69.634	−0.933
4000	80.193	173.549	115.836	230.851	−744.267	90.536	−1.182
4100	81.182	175.541	117.268	238.920	−741.729	111.375	−1.419
4200	82.171	177.509	118.679	247.087	−739.144	132.151	−1.644
4300	83.161	179.454	120.069	255.354	−736.511	152.865	−1.857
4400	84.152	181.377	121.441	263.720	−733.829	173.517	−2.060
4500	85.144	183.280	122.794	272.185	−731.095	194.108	−2.253

PREVIOUS: December 1960 CURRENT: June 1968

$S°(298.15\ K) = [52.733]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3220 \pm 50\ K$

$\Delta_f H°(298.15\ K) = [-265.813]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [66.944]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(TiN, I, 298.15 K) is calculated from $\Delta_f H°$(TiN, cr, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(3220\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2200 K. Below 2200 K the heat capacity is obtained from the heat capacity of the crystal. Above 2200 K it is assumed constant and estimated as 15 $cal·K^{-1}·mol^{-1}$ or 7.5 $cal·K^{-1}$ g–atom. $S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

T_{fus} is taken from Agte and Moers.[1] $\Delta_{fus}H°$ is derived from an estimated $\Delta_{fus}S° = 2.5\ cal·K^{-1}$ g–atom as suggested by Kubaschewski *et al.*[2]

References

[1]C. Agte and K. Moers, Z. Anorg. Allg. Chem. **198**, 233–43 (1931).
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	37.079	52.733	52.733	0.	−265.813	−243.800	42.713
300	37.238	52.963	52.734	0.069	−265.818	−243.664	42.426
400	43.811	64.670	54.285	4.154	−265.805	−236.267	30.853
500	47.057	74.836	57.404	8.716	−265.453	−228.919	23.915
600	48.723	83.572	61.056	13.510	−264.976	−221.656	19.297
700	49.781	91.165	64.827	18.437	−264.458	−214.477	16.004
800	50.618	97.868	68.546	23.458	−263.917	−207.374	13.540
900	51.384	103.874	72.143	28.558	−263.396	−200.337	11.627
1000	52.145	109.327	75.593	33.734	−262.961	−193.355	10.100
1100	52.919	114.333	78.891	38.987	−262.672	−186.410	8.852
1200	53.718	118.972	82.040	44.319	−266.509	−179.365	7.808
1300	54.538	123.304	85.049	49.731	−265.774	−172.133	6.916
1400	55.384	127.377	87.929	55.227	−265.054	−164.957	6.155
1500	56.246	131.227	90.688	60.809	−264.357	−157.831	5.496
1600	57.128	134.885	93.337	66.477	−263.692	−150.751	4.922
1700	58.020	138.375	95.884	72.235	−263.070	−143.712	4.416
1800	58.927	141.717	98.338	78.082	−262.501	−136.708	3.967
1900	59.848	144.928	100.706	84.020	−261.995	−129.733	3.567
2000	60.777	148.021	102.995	90.052	−276.251	−122.330	3.195
2100	61.710	151.009	105.211	96.176	−276.653	−114.624	2.851
2200	62.655	153.901	107.359	102.394	−276.968	−106.900	2.538
2200.000	62.655	153.901	107.359	102.394	GLASS <--> LIQUID TRANSITION		
2200.000	62.760	153.901	107.359	102.394			
2300	62.760	156.691	109.443	108.670	−277.232	−99.164	2.252
2400	62.760	159.362	111.468	114.946	−277.503	−91.416	1.990
2500	62.760	161.924	113.436	121.222	−277.779	−83.657	1.748
2600	62.760	164.386	115.348	127.498	−278.060	−75.886	1.525
2700	62.760	166.754	117.208	133.774	−278.345	−68.105	1.318
2800	62.760	169.037	119.019	140.050	−278.635	−60.313	1.125
2900	62.760	171.239	120.782	146.326	−278.929	−52.511	0.946
3000	62.760	173.367	122.499	152.602	−279.227	−44.698	0.778
3100	62.760	175.425	124.174	158.878	−279.527	−36.876	0.621
3200	62.760	177.417	125.807	165.154	−279.832	−29.043	0.474
3220.000	62.760	177.808	126.128	166.409	--- CRYSTAL <--> LIQUID ---		
3300	62.760	179.348	127.400	171.430	−280.139	−21.201	0.336
3400	62.760	181.222	128.956	177.706	−280.449	−13.350	0.205
3500	62.760	183.041	130.475	183.982	−280.761	−5.490	0.082
3600	62.760	184.809	131.960	190.258	−281.076	2.379	−0.035
3700	62.760	186.529	133.412	196.534	−690.492	18.046	−0.255
3800	62.760	188.203	134.832	202.810	−689.578	37.183	−0.511
3900	62.760	189.833	136.221	209.086	−688.721	56.297	−0.754
4000	62.760	191.422	137.581	215.362	−687.920	75.390	−0.984
4100	62.760	192.971	138.913	221.638	−687.174	94.463	−1.203
4200	62.760	194.484	140.219	227.914	−686.481	113.519	−1.412
4300	62.760	195.961	141.498	234.190	−685.839	132.559	−1.610
4400	62.760	197.403	142.752	240.466	−685.247	151.585	−1.800
4500	62.760	198.814	143.982	246.742	−684.701	170.597	−1.980

PREVIOUS: December 1960 CURRENT: June 1968

0 to 3220 K crystal
above 3220 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.487	−333.971	−333.971	INFINITE
100	10.761	4.422	56.044	−5.162	−335.658	−327.283	170.955
200	27.330	17.338	33.350	−3.202	−337.070	−318.294	83.130
298.15	37.079	30.235	30.235	0.	−337.649	−308.929	54.123
300	37.238	30.465	30.236	0.069	−337.654	−308.750	53.758
400	43.811	42.171	31.787	4.154	−337.641	−299.104	39.059
500	47.057	52.338	34.906	8.716	−337.289	−289.506	30.245
600	48.723	61.074	38.557	13.510	−336.812	−279.993	24.376
700	49.781	68.667	42.328	18.437	−336.294	−270.564	20.190
800	50.618	75.370	46.048	23.458	−335.753	−261.211	17.055
900	51.384	81.376	49.645	28.558	−335.232	−251.925	14.621
1000	52.145	86.829	53.095	33.734	−334.797	−242.693	12.677
1100	52.919	91.835	56.392	38.987	−334.508	−233.498	11.088
1200	53.718	96.474	59.542	44.319	−338.345	−224.203	9.759
1300	54.538	100.806	62.551	49.731	−337.610	−214.721	8.628
1400	55.384	104.878	65.430	55.227	−336.890	−205.295	7.660
1500	56.246	108.729	68.190	60.809	−336.193	−195.920	6.823
1600	57.128	112.387	70.839	66.477	−335.528	−186.591	6.092
1700	58.020	115.877	73.386	72.235	−334.906	−177.301	5.448
1800	58.927	119.219	75.840	78.082	−334.337	−168.047	4.877
1900	59.848	122.430	78.208	84.020	−333.831	−158.823	4.366
2000	60.777	125.523	80.497	90.052	−348.087	−149.170	3.896
2100	61.710	128.511	82.713	96.176	−348.489	−139.214	3.463
2200	62.655	131.403	84.861	102.394	−348.804	−129.240	3.069
2300	63.605	134.209	86.946	108.707	−349.031	−119.255	2.708
2400	64.559	136.937	88.972	115.115	−349.170	−109.261	2.378
2500	65.517	139.591	90.944	121.619	−349.218	−99.264	2.074
2600	66.480	142.180	92.865	128.219	−349.175	−89.266	1.793
2700	67.446	144.707	94.738	134.915	−349.040	−79.272	1.534
2800	68.413	147.177	96.567	141.708	−348.813	−69.284	1.293
2900	69.387	149.595	98.354	148.598	−348.493	−59.307	1.068
3000	70.362	151.964	100.102	155.586	−348.079	−49.341	0.859
3100	71.337	154.287	101.812	162.670	−347.571	−39.392	0.664
3200	72.316	156.567	103.488	169.853	−346.969	−29.460	0.481
3220.000	72.513	157.018	103.819	171.301	CRYSTAL <--> LIQUID TRANSITION		
3220.000	62.760	177.808	103.819	238.245			
3300	62.760	179.348	105.631	243.266	−280.139	−21.201	0.336
3400	62.760	181.222	107.827	249.542	−280.449	−13.350	0.205
3500	62.760	183.041	109.950	255.818	−280.761	−5.490	0.082
3600	62.760	184.809	112.005	262.094	−281.076	2.379	−0.035
3700	62.760	186.529	113.996	268.370	−690.492	18.046	−0.255
3800	62.760	188.203	115.927	274.646	−689.578	37.183	−0.511
3900	62.760	189.833	117.801	280.922	−688.721	56.297	−0.754
4000	62.760	191.422	119.622	287.198	−687.920	75.390	−0.984
4100	62.760	192.971	121.392	293.474	−687.174	94.463	−1.203
4200	62.760	194.484	123.115	299.750	−686.481	113.519	−1.412
4300	62.760	195.961	124.792	306.026	−685.839	132.559	−1.610
4400	62.760	197.403	126.426	312.302	−685.247	151.585	−1.800
4500	62.760	198.814	128.019	318.578	−684.701	170.597	−1.980

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = 37.264 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -214.403 \pm 5.0\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -217.150 \pm 5.0\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Mah[1] measured the enthalpy of combustion of vanadium mononitride at 303.15 K. The composition of the sample was $VN_{1.00}$ which corresponds to the nitrogen-rich boundary of the mononitride phase (see Phase Data section). Chemical analysis also showed that the sample contained 0.07 weight percent of unreacted vanadium. The composition of the combustion products ranged from $VO_{2.231}$ to $VO_{2.296}$. X-ray diffraction patterns showed the solid combustion products to be a mixture of V_2O_4 and V_2O_5. JANAF enthalpy of formation data[2] for these two oxides are used to correct Mah's combustion values to correspond to the formation of the pentoxide as the final state. Our values for this correction agree with those of Mah[1] to within 0.1 $cal \cdot K^{-1} \cdot mol^{-1}$ mononitride. For the process $VN(cr) + 1.25\ O_2(g) = 0.5\ V_2O_5(cr) + 0.5\ N_2(g)$, we obtain $\Delta_c H° = -133.41 \pm 0.43\ kcal \cdot mol^{-1}$ at unit fugacities of oxygen and nitrogen. When this value is combined with the enthalpy of formation of V_2O_5,[2] that for vanadium mononitride is $\Delta_f H°(VN, cr, 298.15\ K) = -51.9 \pm 1.2\ kcal \cdot mol^{-1}$. We adopt this value and include in the overall uncertainty ($\pm 1.2\ kcal \cdot mol^{-1}$) the error associated with correcting the combustion values for the V_2O_4(cr) formed to V_2O_5(cr) as the final state.

Other values for $\Delta_f H°$ can be derived from the results of dissociation pressure measurements,[3] emf data,[4] and equilibrium data[5] obtained by an effusion-mass spectrometric technique. Analyses of these data are summarized below.

Source	Method	Reaction	Data Points	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$-\Delta_f H°$(298.15 K) kcal·mol^{-1}
Slade and Higson[3]	Static	A	2	1476–1544	−68.8	−41.1 ± 1.8	−18.3	41.1
Voleinik and Shabdenov[4]	emf	A	Equation	363–403	−54.4	−55.5 ± 0.1	−2.7	55.5 ± 0.1
Farber and Srivastava[5]	Mass Spec.	B	13	1900–2412	173.5	181.7 ± 1.6	3.8 ± 0.8	58.5 ± 3.6

Reactions: A) $V(cr) + 0.5\ N_2(g) = VN(cr)$ B) $VN(cr) = V(g) + 0.5\ N_2(g)$

Results obtained from the dissociation pressures of Slade and Higson[3] are obviously not reliable. Two other more extensive sets of dissociation pressure data[6,7] have been reported for the mononitride phase. Brauer and Schnell[6] measured the nitrogen dissociation pressures for $VN_{0.72}$ between 1573 and 1873 K, while Kozheurov *et al.*[7] determined equilibrium pressures for VN_x (x = 0.55–0.9) at temperatures in the range 1573–1923 K. Unfortunately, these compositions are significantly different from $VN_{1.00}$, and thus the data are probably of no use in defining the enthalpy of formation of the mononitride at its nitrogen-rich phase boundary. The 3rd law values of $\Delta_f H°$ obtained from the emf[4] and mass spectral[5] data are 3.6 and 6.6 $kcal \cdot mol^{-1}$, respectively, more negative than our adopted value. However, since the thermal functions used in the analysis of the mass spectral data[5] are based on extrapolated data, the 2nd law value, $\Delta_f H°(298.15\ K) = -50.3\ kcal \cdot mol^{-1}$, is probably more reliable. This value is in much better agreement with that obtained by combustion calorimetry.

Heat Capacity and Entropy

Shomate and Kelley,[8] (52.6–296.3 K) measured the low temperature heat capacities for VN. The purity of the mononitride sample based on an analysis for vanadium by permanganate titration was found to be 99.76 weight percent. Their $C_p°$ data corrected to 1969 Atomic Weight Scale are adopted. $S°(298.15\ K)$ is obtained from the adopted $C_p°$ data and is based on $S°(52\ K) = 0.47\ cal \cdot K^{-1} \cdot mol^{-1}$. This latter value is calculated from the Debye function D(351/T) which was suggested by Shomate and Kelley.[8]

High temperature enthalpies for VN have been reported by King[9] for the temperature range 408–1611 K. The sample was identical to that employed by Shomate and Kelley[8] and was contained in platinum-rhodium alloy capsules for the "drop" experiments. His experimental enthalpies are corrected to refer to the 1969 Atomic Weight Scale. Also, his reported temperatures are corrected to the IPTS-68 scale. A technique based on orthogonal polynomials is used to fit the corrected enthalpies by computer. The curve is constrained to join smoothly with the low temperature $C_p°$ data[8] near 298 K. Our smoothed enthalpies show an average deviation of ±0.4% from the experimental values.[9] The maximum deviation is +2.1% at 408 K. No anomalies are observed in either the low temperature $C_p°$ data[8] or the high temperature enthalpies.[9] $C_p°$ data above 1613 K are obtained by graphical extrapolation. Satoh[10] has measured the mean specific heats of VN over three temperature intervals by means of an ice calorimeter. However, the sample used in his study was impure (97.93% VN), and we believe the results are probably not reliable. They do show considerable scatter from our adopted results; deviations are in the range of ±1–5%.

Phase Data

The mononitride phase has been prepared by several workers[1,5–8,and11–13] at temperatures as high as 1600 K. X-ray data[6,11] and dissociation pressure measurements[7] have shown that the phase has an extensive homogeneity range. Although Kozeurov *et al.*[7] were unable to obtain $VN_{1.00}$ at 1273 K, Brauer and Schnell[6] and Hahn[11] reported that the composition of the mononitride phase extends from $VN_{0.72}$ to $VN_{1.00}$ (42 to 50 atomic percent nitrogen) at 1273–1873 K. The dissociation pressure data of Kozheurov *et al.*[7] indicate that the vanadium-rich phase boundary decreases from $VN_{0.7}$ at 1573 K to $VN_{0.56}$ at 1923 K. The structure of the mononitride is face-centered cubic.[6,11] Further information on the vanadium-vanadium nitride system has been reviewed by Storms.[14]

Continued on page 1635

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}mol^{-1}	$S°$ J·K^{-1}mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−6.228	−214.403	−214.403	INFINITE
100	15.111	8.354	64.935	−5.658	−215.773	−207.899	108.595
200	29.675	23.719	40.504	−3.357	−216.763	−199.597	52.129
298.15	37.981	37.264	37.264	0.	−217.150	−191.068	33.474
300	38.200	37.499	37.264	0.070	−217.152	−190.907	33.240
400	43.296	49.239	38.830	4.164	−217.082	−182.158	23.787
500	46.183	59.227	41.937	8.645	−216.731	−173.464	18.122
600	48.208	67.832	45.553	13.368	−216.221	−164.856	14.352
700	49.819	75.387	49.286	18.271	−215.615	−156.342	11.666
800	51.212	82.132	52.978	23.324	−214.951	−147.919	9.658
900	52.480	88.238	56.561	28.509	−214.256	−139.582	8.101
1000	53.668	93.829	60.013	33.817	−213.540	−131.323	6.860
1100	54.806	98.998	63.325	39.241	−212.812	−123.137	5.847
1200	55.907	103.814	66.500	44.777	−212.084	−115.017	5.007
1300	56.986	108.332	69.546	50.421	−211.362	−106.957	4.298
1400	58.045	112.594	72.470	56.173	−210.655	−98.952	3.692
1500	59.091	116.634	75.281	62.030	−209.963	−90.998	3.169
1600	60.124	120.481	77.987	67.990	−209.284	−83.089	2.713
1700	61.170	124.158	80.595	74.057	−208.625	−75.222	2.311
1800	62.049	127.679	83.114	80.217	−207.999	−67.393	1.956
1900	62.969	131.058	85.549	86.468	−207.420	−59.598	1.638
2000	63.932	134.313	87.906	92.813	−206.890	−51.832	1.354
2100	64.852	137.454	90.191	99.252	−206.420	−44.091	1.097
2200	65.772	140.493	92.409	105.784	−228.900	−36.266	0.861
2300	66.651	143.436	94.564	112.405	−228.716	−27.514	0.625
2400	67.530	146.291	96.660	119.114	−228.450	−18.771	0.409
2500	68.408	149.065	98.701	125.911	−228.102	−10.041	0.210
2600	69.287	151.766	100.690	132.796	−227.671	−1.327	0.027
2700	70.166	154.397	102.631	139.768	−227.156	7.369	−0.143
2800	71.044	156.965	104.526	146.829	−226.558	16.044	−0.299
2900	71.923	159.473	106.377	153.977	−225.877	24.697	−0.445
3000	72.802	161.926	108.188	161.214	−225.110	33.325	−0.580
3100	73.638	164.327	109.961	168.536	−224.262	41.925	−0.706
3200	74.475	166.678	111.696	175.941	−223.333	50.497	−0.824
3300	75.312	168.983	113.398	183.430	−222.323	59.039	−0.935
3400	76.191	171.244	115.066	191.006	−221.231	67.549	−1.038
3500	77.027	173.465	116.703	198.667	−220.055	76.026	−1.135

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [233.384 \pm 8.4]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 523.18 \pm 20.9\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 523.00 \pm 20.9\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	[6]	[12000]	[2]	[16000]	[6]	[21000]	[2]
[1000]	[2]	[13000]	[3]	[18000]	[2]	[22000]	[6]
[3000]	[1]	[14000]	[6]	[19000]	[2]	[24000]	[2]
[10000]	[6]	[15000]	[1]	[20000]	[6]	[25000]	[6]
						[28000]	[6]

Ground State Configuration: $[^3\Delta]$

$\omega_e = [1025]\ cm^{-1}$ $\omega_e x_e = [4.41]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.5905]\ cm^{-1}$ $\alpha_e = [0.00354]\ cm^{-1}$ $r_e = [1.612]$ Å

Enthalpy of Formation

Dissociation energies for the diatomic group III–VI transition–metal nitrides have been estimated by Gingerich[1] and provide support for the existence of these gaseous molecules. Very recently, mass-spectrometric evidence[2] has been presented which verifies the existence of VN(g). Using an effusion–mass spectrometric technique, Farber and Srivastava[2] observed the VN^+ion as one of the vapor species in equilibrium with solid VN in the temperature range 1900–2412 K. The molecular precursor of this ion is assumed to be VN(g). Results of effusion weight loss and mass spectrometric experiments[2] were combined to yield partial pressures for the species involved in the following two reactions: (A) VN(cr) = VN(g) and (B) VN(g) = V(g) + 0.5 N_2(g). During the course of these experiments, the ion intensities for each species did not show any variation with time. This implies that the mononitride phase remained at near unit activity during their measurements.

Source	Reaction	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Dift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
2	A	1900–2412	13	174.3	185.4 ± 2.4	5.2 ± 1.4	133.5 ± 3.6
2	B	1900–2412	12*	−1.9	−3.6 ± 1.6	−0.8 ± 1.4	126.8 ± 3.6

*One point rejected due to failure of a statistical test.

The 3rd law value of 126.8 ± 3.6 kcal·mol^{-1} for $\Delta_f H°$ is considered to be more reliable than that (133.5 kcal·mol^{-1}) derived from the sublimation data, since the results for the gas phase reaction (B) show the least drift. Also, Farber and Srivastava[2] reported a 2nd law value determined from ion intensity plots of $\Delta_r H° = 3 \pm 5$ kcal·mol^{-1} for reaction (B) at 2162 K. Using auxiliary data,[3] this value leads to $\Delta_f H°$(VN, g, 298.15 K) = 122.0 ± 7.0 kcal·mol^{-1}. We adopt $\Delta_f H°$(VN, g, 298.15 K) = 125.0 ± 5.0 kcal·mol^{-1}which is a weighted average of the 3rd law value derived from reaction (B) and the 2nd law value based on ion intensity plots. The adopted $\Delta_f H°$ value corresponds to a bond dissociation energy, $D°$(298.5 K), of 111.2 kcal·mol^{-1}. This compares favorably with the value (116 kcal·mol^{-1}) estimated by Gingerich.[1]

Heat Capacity and Entropy

The value of r_e(VN) is obtained from the expression r_e(MO)–r_e(MN) = −0.023 A with r_e(VO) = 1.589 A.[3] Differences in the bond lengths[4] for the oxides and nitrides of As, B, P, Si, and Ti are used to establish the value −0.023. B_e is calculated from the estimated value for r_e. The value of α_e is obtained from the other constants assuming a Morse potential function. The values of ω_e and $\omega_e x_e$ are assumed to lie between those for TiO(g) and AsN(g)[4]. VN is isoelectronic with TiO. Farber and Srivastava[2] have estimated a somewhat higher value (1065 cm^{-1}) for ω_e. However, their estimate is based partially on estimated JANAF data[3] for ZrN(g).

The ground state electronic configuration ($^3\Delta$), upper electronic levels and quantum weights are estimated by analogy with those for TiO.[3,5] It is possible, however, that the ground state for VN is $^1\Delta$. VN is also isoelectronic with ScF and ZrO which both have singlet ground states.[5] If the adopted ground state and first excited state are interchanged, then the value of $S°$(298.15 K) is reduced by 1.94 cal·K^{-1}·mol^{-1}. Our adopted upper levels and quantum weights contribute 0.61 and 1.11 cal·K^{-1}·mol^{-1} to the entropy of VN(g) at 2000 and 4000 K, respectively.

References

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[3] JANAF Thermochemical Tables: VN(cr), VO(g) and TiO(g), 12–31–73; V(g), 6–30–73; N_2(g), 9–30–65; ZrN(g), 6–30–63.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.800	523.175	523.175	INFINITE
100	29.107	201.085	260.002	−5.892	524.143	512.744	−267.830
200	29.518	221.325	236.173	−2.970	523.774	501.419	−130.957
250	30.234	227.982	233.891	−1.477	523.395	495.873	−103.607
298.15	31.147	233.384	233.384	0.	523.000	490.608	−85.952
300	31.184	233.577	233.384	0.058	522.985	490.407	−85.387
350	32.193	238.460	233.768	1.642	522.574	485.010	−72.384
400	33.143	242.821	234.632	3.276	522.180	479.671	−62.639
450	33.983	246.775	235.765	4.955	521.804	474.380	−55.065
500	34.699	250.393	237.049	6.672	521.446	469.130	−49.010
600	35.799	256.823	239.823	10.200	520.761	458.732	−39.936
700	36.560	262.402	242.659	13.821	520.084	448.447	−33.464
800	37.092	267.321	245.440	17.505	519.380	438.260	−28.615
900	37.472	271.713	248.120	21.234	518.619	428.165	−24.850
1000	37.750	275.676	250.680	24.996	517.789	418.159	−21.842
1100	37.959	279.284	253.119	28.782	516.879	408.239	−19.386
1200	38.118	282.594	255.439	32.586	515.875	398.406	−17.342
1300	38.245	285.651	257.647	36.404	514.771	388.661	−15.617
1400	38.349	288.489	259.750	40.234	513.556	379.005	−14.141
1500	38.441	291.138	261.755	44.074	512.231	369.440	−12.865
1600	38.527	293.622	263.670	47.922	510.798	359.967	−11.752
1700	38.614	295.960	265.501	51.779	509.248	350.587	−10.772
1800	38.706	298.169	267.256	55.645	507.579	341.301	−9.904
1900	38.807	300.265	268.938	59.521	505.783	332.112	−9.130
2000	38.921	302.258	270.555	63.407	503.853	323.021	−8.436
2100	39.048	304.160	272.110	67.305	501.783	314.029	−7.811
2200	39.192	305.980	273.609	71.217	476.683	305.245	−7.247
2300	39.353	307.726	275.054	75.144	474.173	297.508	−6.757
2400	39.531	309.404	276.451	79.088	471.674	289.881	−6.309
2500	39.727	311.022	277.801	83.051	469.188	282.357	−5.900
2600	39.940	312.584	279.109	87.034	466.717	274.933	−5.523
2700	40.171	314.096	280.377	91.040	464.265	267.603	−5.177
2800	40.417	315.561	281.608	95.069	461.831	260.364	−4.857
2900	40.678	316.984	282.803	99.124	459.419	253.211	−4.561
3000	40.954	318.367	283.966	103.205	457.031	246.142	−4.286
3100	41.242	319.715	285.097	107.315	454.667	239.151	−4.030
3200	41.541	321.029	286.200	111.454	452.329	232.236	−3.791
3300	41.850	322.312	287.275	115.623	450.019	225.394	−3.568
3400	42.167	323.566	288.324	119.824	447.737	218.622	−3.359
3500	42.492	324.793	289.348	124.057	445.485	211.916	−3.163
3600	42.821	325.995	290.350	128.323	443.263	205.274	−2.978
3700	43.154	327.173	291.329	132.621	−5.736	199.894	−2.822
3800	43.490	328.328	292.287	136.954	−6.210	205.458	−2.824
3900	43.827	329.462	293.226	141.320	−6.703	211.035	−2.826
4000	44.163	330.576	294.146	145.719	−7.216	216.624	−2.829
4100	44.498	331.670	295.048	150.152	−7.752	222.227	−2.831
4200	44.829	332.747	295.933	154.618	−8.309	227.843	−2.834
4300	45.157	333.805	296.801	159.118	−8.891	233.472	−2.836
4400	45.479	334.847	297.654	163.650	−9.497	239.115	−2.839
4500	45.795	335.873	298.492	168.213	−10.129	244.773	−2.841
4600	46.104	336.883	299.316	172.808	−10.788	250.445	−2.844
4700	46.405	337.877	300.126	177.434	−11.475	256.131	−2.847
4800	46.698	338.858	300.922	182.089	−12.192	261.832	−2.849
4900	46.981	339.823	301.706	186.773	−12.939	267.549	−2.852
5000	47.254	340.775	302.478	191.485	−13.718	273.281	−2.855
5100	47.517	341.714	303.238	196.224	−14.531	279.029	−2.858
5200	47.770	342.639	303.987	200.988	−15.378	284.793	−2.861
5300	48.011	343.551	304.725	205.777	−16.262	290.574	−2.864
5400	48.241	344.451	305.452	210.590	−17.184	296.372	−2.867
5500	48.459	345.338	306.170	215.425	−18.145	302.187	−2.870
5600	48.665	346.213	306.877	220.281	−19.148	308.020	−2.873
5700	48.860	347.076	307.575	225.158	−20.194	313.872	−2.876
5800	49.043	347.927	308.263	230.053	−21.285	319.742	−2.880
5900	49.214	348.767	308.942	234.966	−22.422	325.631	−2.883
6000	49.374	349.596	309.613	239.895	−23.608	331.541	−2.886

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 38.861 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = [3225\ K]$

$\Delta_f H°(0\ K) = -362.020 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -365.263 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [67.362]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of reaction I, -174.25 ± 0.30 kcal·mol^{-1}, was measured by Mah and Gelbert.[7] The $\Delta_f H°$(298.15 K) of ZrN was obtained using 261.5 ± 0.2 kcal·mol^{-1} for $\Delta_f H°$(298.15 K) of ZrO_2. For the same reaction, Neumann *et al.*[1] obtain -176.0 kcal·mol^{-1} on a sample of unspecified purity. Vapor pressure measurements of Hoch *et al.*[2] lead to 81 kcal·mol^{-1} for the $\Delta_f H°$(298.15 K) of ZrN. However, this value is uncertain by 10% as evidenced by the work on ZrO_2 by Chupka *et al.*[3]

(I) $ZrN(cr) + O_2(g) = ZrO_2(cr) + 1/2\ N_2(g)$

Heat Capacity and Entropy

Low temperature measurements, 53 297 K, of Todd[4] were smoothly joined to those of Coughlin and King,[5] 298 1073 K.

Fusion Data

Estimated by Henderson and Scheffee.[6]

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[6]C. B. Henderson and R. S. Scheffee, Alexandria, Va., "Survey of Thermochemical Data," Atlantic Research Corp., (January 1960).
[7]A. D. Mah and N. L. Gelbert, J. Am. Chem. Soc. **78**, 3261 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.590	−362.020	−362.020	INFINITE
100	15.548	8.134	68.383	−6.025	−363.793	−355.210	185.543
200	31.765	24.376	42.325	−3.590	−365.006	−346.073	90.385
298.15	40.443	38.861	38.861	0.	−365.263	−336.697	58.988
300	40.556	39.112	38.862	0.075	−365.262	−336.519	58.593
400	44.756	51.399	40.508	4.356	−364.999	−326.969	42.698
500	47.078	61.649	43.741	8.954	−364.495	−317.516	33.171
600	48.660	70.378	47.471	13.744	−363.888	−308.176	26.829
700	49.894	77.974	51.298	18.673	−363.247	−298.942	22.307
800	50.940	84.706	55.061	23.716	−362.609	−289.799	18.922
900	51.882	90.760	58.697	28.857	−362.003	−280.734	16.293
1000	52.752	96.272	62.183	34.089	−361.447	−271.735	14.194
1100	53.580	101.339	65.515	39.406	−360.950	−262.788	12.479
1200	54.379	106.036	68.698	44.804	−364.228	−253.662	11.042
1300	55.153	110.419	71.741	50.281	−363.317	−244.485	9.824
1400	55.915	114.534	74.652	55.835	−362.391	−235.379	8.782
1500	56.668	118.418	77.442	61.464	−361.459	−226.339	7.882
1600	57.409	122.099	80.119	67.168	−360.532	−217.362	7.096
1700	58.141	125.601	82.692	72.945	−359.618	−208.442	6.405
1800	58.873	128.945	85.169	78.796	−358.727	−199.575	5.792
1900	59.597	132.147	87.558	84.720	−357.869	−190.757	5.244
2000	60.321	135.223	89.865	90.716	−357.054	−181.983	4.753
2100	60.973	138.181	92.096	96.780	−356.296	−173.248	4.309
2200	61.756	141.036	94.256	102.917	−376.922	−163.802	3.889
2300	62.471	143.797	96.350	109.128	−376.712	−154.119	3.500
2400	63.187	146.471	98.383	115.411	−376.435	−144.447	3.144
2500	63.898	149.065	100.359	121.765	−376.093	−134.788	2.816
2600	64.614	151.585	102.281	128.191	−375.685	−125.143	2.514
2700	65.321	154.037	104.152	134.688	−375.210	−115.516	2.235
2800	66.032	156.425	105.977	141.255	−374.669	−105.907	1.976
2900	66.743	158.755	107.757	147.894	−374.060	−96.319	1.735
3000	67.450	161.029	109.495	154.604	−373.384	−86.754	1.511
3100	68.157	163.252	111.193	161.384	−372.641	−77.211	1.301
3200	68.864	165.428	112.854	168.235	−371.830	−67.694	1.105
3225.000	69.041	165.964	113.264	169.959	− − − CRYSTAL <− −> LIQUID − − −		
3300	69.572	167.557	114.480	175.157	−370.952	−58.203	0.921
3400	70.279	169.645	116.072	182.149	−370.005	−48.740	0.749
3500	70.986	171.692	117.632	189.213	−368.991	−39.306	0.587
3600	71.693	173.702	119.161	196.347	−367.908	−29.901	0.434
3700	72.396	175.676	120.662	203.551	−366.758	−20.528	0.290
3800	73.103	177.616	122.135	210.826	−365.539	−11.186	0.154
3900	73.810	179.524	123.582	218.172	−364.252	−1.878	0.025
4000	74.517	181.402	125.005	225.588	−362.896	7.397	−0.097

PREVIOUS: CURRENT: June 1961

Zirconium Nitride (ZrN) LIQUID M_r = 105.2267

$S°(298.15\ K) = [62.342]\ J·K^{-1}·mol^{-1}$
$T_{fus} = [3225]\ K$

$\Delta_f H°(298.15\ K) = [-290.749]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [67.362]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(ZrN, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion, $\Delta_{fus} H°$, and the difference in enthalpy, $H°$(3225 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

Calculated from the solid. The heat capacity function of the solid was assumed to approximate those of the liquid up to the estimated glass point of 2150 K. Above the glass point the heat capacity was estimated.

$S°$(ZrN, l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	40.443	62.342	62.342	0.	−290.749	−269.183	47.160
300	40.556	62.592	62.342	0.075	−290.747	−269.049	46.846
400	44.756	74.880	63.989	4.356	−290.484	−261.846	34.194
500	47.078	85.130	67.222	8.954	−289.981	−254.742	26.613
600	48.660	93.858	70.952	13.744	−289.374	−247.750	21.569
700	49.894	101.454	74.778	18.673	−288.732	−240.864	17.973
800	50.940	108.186	78.542	23.716	−288.094	−234.069	15.283
900	51.882	114.241	82.177	28.857	−287.489	−227.353	13.195
1000	52.752	119.753	85.663	34.089	−286.932	−220.701	11.528
1100	53.580	124.820	88.996	39.406	−286.436	−214.103	10.167
1200	54.379	129.516	92.179	44.804	−289.714	−207.325	9.025
1300	55.153	133.900	95.222	50.281	−288.802	−200.496	8.056
1400	55.915	138.015	98.133	55.835	−287.876	−193.738	7.228
1500	56.668	141.898	100.922	61.464	−286.945	−187.046	6.514
1600	57.409	145.579	103.599	67.168	−286.017	−180.416	5.890
1700	58.141	149.082	106.173	72.945	−285.103	−173.844	5.342
1800	58.873	152.426	108.650	78.796	−284.213	−167.326	4.856
1900	59.597	155.628	111.039	84.720	−283.355	−160.856	4.422
2000	60.321	158.704	113.346	90.716	−282.539	−154.430	4.033
2100	60.973	161.663	115.577	96.781	−281.780	−148.043	3.682
2150.000	61.273	163.101	116.665	99.838	GLASS <--> LIQUID TRANSITION		
2150.000	58.576	163.101	116.665	99.838			
2200	58.576	164.448	117.736	102.766	−302.558	−140.944	3.346
2300	58.576	167.052	119.824	108.624	−302.701	−133.594	3.034
2400	58.576	169.545	121.844	114.482	−302.850	−126.239	2.748
2500	58.576	171.936	123.800	120.339	−303.005	−118.877	2.484
2600	58.576	174.233	125.696	126.197	−303.164	−111.509	2.240
2700	58.576	176.444	127.535	132.054	−303.329	−104.134	2.015
2800	58.576	178.574	129.320	137.912	−303.497	−96.753	1.805
2900	58.576	180.630	131.054	143.770	−303.670	−89.367	1.610
3000	58.576	182.615	132.740	149.627	−303.846	−81.974	1.427
3100	58.576	184.536	134.380	155.485	−304.025	−74.575	1.257
3200	58.576	186.396	135.976	161.342	−304.208	−67.171	1.096
3225.000	58.576	186.852	136.369	162.807	--- CRYSTAL <--> LIQUID ---		
3300	58.576	188.198	137.532	167.200	−304.394	−59.760	0.946
3400	58.576	189.947	139.048	173.058	−304.583	−52.345	0.804
3500	58.576	191.645	140.526	178.915	−304.774	−44.923	0.670
3600	58.576	193.295	141.969	184.773	−304.968	−37.496	0.544
3700	58.576	194.900	143.378	190.630	−305.164	−30.063	0.424
3800	58.576	196.462	144.755	196.488	−305.362	−22.626	0.311
3900	58.576	197.984	146.100	202.346	−305.563	−15.183	0.203
4000	58.576	199.467	147.416	208.203	−305.766	−7.734	0.101
4100	58.576	200.913	148.703	214.061	−305.971	−0.281	0.004
4200	58.576	202.325	149.963	219.918	−306.178	7.177	−0.089
4300	58.576	203.703	151.197	225.776	−306.387	14.641	−0.178
4400	58.576	205.050	152.406	231.634	−306.597	22.109	−0.262
4500	58.576	206.366	153.590	237.491	−306.810	29.582	−0.343
4600	58.576	207.653	154.752	243.349	−307.024	37.059	−0.421
4700	58.576	208.913	155.891	249.206	−307.240	44.542	−0.495
4800	58.576	210.146	157.008	255.064	−868.394	63.646	−0.693
4900	58.576	211.354	158.105	260.922	−868.265	83.062	−0.885
5000	58.576	212.538	159.182	266.779	−868.155	102.476	−1.071
5100	58.576	213.698	160.239	272.637	−868.062	121.888	−1.248
5200	58.576	214.835	161.278	278.494	−867.986	141.298	−1.419
5300	58.576	215.951	162.299	284.352	−867.923	160.706	−1.584
5400	58.576	217.046	163.303	290.210	−867.875	180.114	−1.742
5500	58.576	218.120	164.290	296.067	−867.838	199.521	−1.895
5600	58.576	219.176	165.261	301.925	−867.811	218.927	−2.042
5700	58.576	220.213	166.216	307.782	−867.795	238.333	−2.184
5800	58.576	221.231	167.156	313.640	−867.787	257.739	−2.321
5900	58.576	222.233	168.081	319.498	−867.786	277.144	−2.454
6000	58.576	223.217	168.991	325.355	−867.792	296.550	−2.582

PREVIOUS: CURRENT: June 1961

0 to 3225 K crystal
above 3225 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.590	−362.020	−362.020	INFINITE
100	15.548	8.134	68.383	−6.025	−363.793	−355.210	185.543
200	31.765	24.376	42.325	−3.590	−365.006	−346.073	90.385
298.15	40.443	38.861	38.861	0.	−365.263	−336.697	58.988
300	40.556	39.112	38.862	0.075	−365.262	−336.519	58.593
400	44.756	51.399	40.508	4.356	−364.999	−326.969	42.698
500	47.078	61.649	43.741	8.954	−364.495	−317.516	33.171
600	48.660	70.378	47.471	13.744	−363.888	−308.176	26.829
700	49.894	77.974	51.298	18.673	−363.247	−298.942	22.307
800	50.940	84.706	55.061	23.716	−362.609	−289.799	18.922
900	51.882	90.760	58.697	28.857	−362.003	−280.734	16.293
1000	52.752	96.272	62.183	34.089	−361.447	−271.735	14.194
1100	53.580	101.339	65.515	39.406	−360.950	−262.788	12.479
1200	54.379	106.036	68.698	44.804	−364.228	−253.662	11.042
1300	55.153	110.419	71.741	50.281	−363.317	−244.485	9.824
1400	55.915	114.534	74.652	55.835	−362.391	−235.379	8.782
1500	56.668	118.418	77.442	61.464	−361.459	−226.339	7.882
1600	57.409	122.099	80.119	67.168	−360.532	−217.362	7.096
1700	58.141	125.601	82.692	72.945	−359.618	−208.442	6.405
1800	58.873	128.945	85.169	78.796	−358.727	−199.575	5.792
1900	59.597	132.147	87.558	84.720	−357.869	−190.757	5.244
2000	60.321	135.223	89.865	90.716	−357.054	−181.983	4.753
2100	60.973	138.181	92.096	96.780	−356.296	−173.248	4.309
2200	61.756	141.036	94.256	102.917	−376.922	−163.802	3.889
2300	62.471	143.797	96.350	109.128	−376.712	−154.119	3.500
2400	63.187	146.471	98.383	115.411	−376.435	−144.447	3.144
2500	63.898	149.065	100.359	121.765	−376.093	−134.788	2.816
2600	64.614	151.585	102.281	128.191	−375.685	−125.143	2.514
2700	65.321	154.037	104.152	134.688	−375.210	−115.516	2.235
2800	66.032	156.425	105.977	141.255	−374.669	−105.907	1.976
2900	66.743	158.755	107.757	147.894	−374.060	−96.319	1.735
3000	67.450	161.029	109.495	154.604	−373.384	−86.754	1.511
3100	68.157	163.252	111.193	161.384	−372.641	−77.211	1.301
3200	68.864	165.428	112.854	168.235	−371.830	−67.694	1.105
3225.000	69.041	165.964	113.264	169.959	CRYSTAL <--> LIQUID TRANSITION		
3225.000	58.576	186.852	113.264	237.321			
3300	58.576	188.198	114.952	241.715	−304.394	−59.760	0.946
3400	58.576	189.947	117.132	247.572	−304.583	−52.345	0.804
3500	58.576	191.645	119.236	253.430	−304.774	−44.923	0.670
3600	58.576	193.295	121.271	259.287	−304.968	−37.496	0.544
3700	58.576	194.900	123.239	265.145	−305.164	−30.063	0.424
3800	58.576	196.462	125.146	271.003	−305.362	−22.626	0.311
3900	58.576	197.984	126.994	276.860	−305.563	−15.183	0.203
4000	58.576	199.467	128.787	282.718	−305.766	−7.734	0.101
4100	58.576	200.913	130.529	288.575	−305.971	−0.281	0.004
4200	58.576	202.325	132.222	294.433	−306.178	7.177	−0.089
4300	58.576	203.703	133.868	300.291	−306.387	14.641	−0.178
4400	58.576	205.050	135.470	306.148	−306.597	22.109	−0.262
4500	58.576	206.366	137.031	312.006	−306.810	29.582	−0.343
4600	58.576	207.653	138.553	317.863	−307.024	37.059	−0.421
4700	58.576	208.913	140.036	323.721	−307.240	44.542	−0.495
4800	58.576	210.146	141.484	329.579	−868.394	63.646	−0.693
4900	58.576	211.354	142.898	335.436	−868.265	83.062	−0.885
5000	58.576	212.538	144.279	341.294	−868.155	102.476	−1.071
5100	58.576	213.698	145.629	347.151	−868.062	121.888	−1.248
5200	58.576	214.835	146.949	353.009	−867.986	141.298	−1.419
5300	58.576	215.951	148.240	358.867	−867.923	160.706	−1.584
5400	58.576	217.046	149.504	364.724	−867.875	180.114	−1.742
5500	58.576	218.120	150.742	370.582	−867.838	199.521	−1.895
5600	58.576	219.176	151.955	376.439	−867.811	218.927	−2.042
5700	58.576	220.213	153.143	382.297	−867.795	238.333	−2.184
5800	58.576	221.231	154.308	388.155	−867.787	257.739	−2.321
5900	58.576	222.233	155.451	394.012	−867.786	277.144	−2.454
6000	58.576	223.217	156.572	399.870	−867.792	296.550	−2.582

PREVIOUS: CURRENT: June 1961

$S°(298.15\ K)$ = [233.487] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [714.342] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [713.372] $kJ·mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^2\Sigma]$	0	[2]

ω_e = [840] cm^{-1} $\omega_e x_e$ = [5] cm^{-1} σ = 1
B_e = [0.4146] cm^{-1} α_e = [0.0025] cm^{-1} r_e = [1.83] Å

Enthalpy of Formation

$\Delta_f H°(0\ K)$ was estimated as 170.7 $kcal·mol^{-1}$ by Gordon.[1] $\Delta_f H°(298.15\ K)$ was then calculated.

Heat Capacity and Entropy

Molecular constants were estimated by Gordon.[1] r_e was calculated from the relationship $r_e = (16.858778/\mu B_e)^{1/2}$ Å.

Reference

[1]J. S. Gordon, Astrosystems International, Livingston, New Jersey, personal communication, (January 10, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.863	714.342	714.342	INFINITE
100	29.114	200.910	260.451	−5.954	714.913	704.218	−367.846
200	29.877	221.235	236.323	−3.018	714.201	693.763	−181.192
250	30.752	227.993	234.003	−1.503	713.772	688.703	−143.897
298.15	31.661	233.487	233.487	0.	713.372	683.911	−119.818
300	31.695	233.683	233.488	0.059	713.357	683.728	−119.048
350	32.569	238.636	233.877	1.666	712.965	678.821	−101.309
400	33.326	243.036	234.752	3.314	712.594	673.969	−88.011
450	33.961	246.999	235.896	4.996	712.239	669.162	−77.674
500	34.488	250.605	237.189	6.708	711.893	664.395	−69.409
600	35.286	256.968	239.970	10.199	711.202	654.960	−57.019
700	35.845	262.452	242.799	13.757	710.472	645.643	−48.178
800	36.248	267.266	245.562	17.363	709.673	636.435	−41.555
900	36.549	271.554	248.217	21.003	708.778	627.333	−36.409
1000	36.781	275.417	250.747	24.670	707.769	618.336	−32.299
1100	36.964	278.931	253.151	28.358	706.637	609.447	−28.940
1200	37.114	282.154	255.436	32.062	701.665	600.888	−26.156
1300	37.239	285.130	257.607	35.780	700.817	592.524	−23.808
1400	37.345	287.894	259.673	39.509	699.919	584.227	−21.798
1500	37.437	290.474	261.641	43.248	698.960	575.996	−20.058
1600	37.519	292.892	263.520	46.996	697.932	567.832	−18.538
1700	37.592	295.169	265.315	50.752	696.824	559.734	−17.199
1800	37.659	297.320	267.034	54.515	695.626	551.704	−16.010
1900	37.720	299.358	268.682	58.283	694.330	543.743	−14.949
2000	37.776	301.294	270.265	62.058	692.923	535.853	−13.995
2100	37.829	303.138	271.786	65.839	691.398	528.037	−13.134
2200	37.880	304.899	273.252	69.624	668.420	521.042	−12.371
2300	37.927	306.584	274.665	73.414	666.210	514.392	−11.682
2400	37.973	308.199	276.029	77.209	663.998	507.839	−11.053
2500	38.017	309.750	277.347	81.009	661.786	501.378	−10.476
2600	38.059	311.242	278.622	84.813	659.572	495.005	−9.945
2700	38.100	312.679	279.857	88.621	657.358	488.717	−9.455
2800	38.140	314.066	281.054	92.433	655.144	482.512	−9.001
2900	38.179	315.405	282.215	96.249	652.930	476.386	−8.581
3000	38.218	316.700	283.343	100.069	650.716	470.336	−8.189
3100	38.255	317.953	284.440	103.892	648.503	464.359	−7.824
3200	38.292	319.169	285.506	107.720	646.290	458.455	−7.484
3300	38.328	320.347	286.544	111.551	644.077	452.619	−7.164
3400	38.364	321.492	287.555	115.385	641.866	446.850	−6.865
3500	38.399	322.605	288.541	119.224	639.655	441.147	−6.584
3600	38.434	323.687	289.502	123.065	637.445	435.507	−6.319
3700	38.469	324.740	290.440	126.910	635.237	429.927	−6.069
3800	38.503	325.767	291.357	130.759	633.029	424.408	−5.834
3900	38.537	326.767	292.252	134.611	630.823	418.947	−5.611
4000	38.571	327.744	293.127	138.466	628.618	413.542	−5.400
4100	38.604	328.696	293.983	142.325	626.414	408.193	−5.200
4200	38.638	329.627	294.821	146.187	624.212	402.897	−5.011
4300	38.671	330.537	295.641	150.053	622.011	397.653	−4.831
4400	38.704	331.426	296.444	153.921	619.811	392.461	−4.659
4500	38.736	332.296	297.231	157.793	617.613	387.319	−4.496
4600	38.769	333.148	298.003	161.669	615.417	382.226	−4.340
4700	38.801	333.982	298.759	165.547	613.222	377.180	−4.192
4800	38.834	334.799	299.502	169.429	50.092	383.798	−4.177
4900	38.866	335.600	300.230	173.314	48.248	390.769	−4.166
5000	38.898	336.386	300.945	177.202	46.389	397.778	−4.156
5100	38.930	337.156	301.648	181.093	44.515	404.825	−4.146
5200	38.962	337.913	302.338	184.988	42.629	411.908	−4.138
5300	38.994	338.655	303.016	188.886	40.731	419.028	−4.130
5400	39.026	339.384	303.683	192.787	38.823	426.183	−4.123
5500	39.057	340.101	304.339	196.691	36.907	433.374	−4.116
5600	39.089	340.805	304.984	200.598	34.983	440.600	−4.110
5700	39.121	341.497	305.618	204.509	33.052	447.860	−4.104
5800	39.152	342.178	306.243	208.423	31.116	455.155	−4.099
5900	39.184	342.847	306.857	212.339	29.176	462.482	−4.095
6000	39.215	343.506	307.463	216.259	27.233	469.843	−4.090

PREVIOUS: June 1963 (1 atm) CURRENT: June 1963 (1 bar)

$S°(298.15\ K) = 191.609 \pm 0.020\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$

Vibrational and Rotational Levels (cm^{-1})

Direct Summation of Electronic Ground State:

$E = G - G_o + F = G - G_o + BZ - DZ^2 + ... \approx G - G_o + B^2Z/(B + DZ)$,
where $Z = J(J + 1)$, $Y = v + 1/2$, and we omit subscript v on G, F, B, and D
$G = 2358.583Y - 14.33594Y^2 - 3.767755 \times 10^{-3}Y^3 + 2.753652 \times 10^{-4}Y^4 - 2.701198 \times 10^{-5}Y^5 + 1.749062 \times 10^{-7}Y^6$
$B = 1.998197 - 0.017279Y - 3.283 \times 10^{-5}Y^2$, $D = 5.74 \times 10^{-6}$
$v_{max} = 58$, $J_{max} = 260 - 250v/v_{max}$

Ground State Configuration, $^1\Sigma_g^+$ $\sigma = 2$

Excited Electronic States – Contributions at 4800 – 6000 K Calculated Using First–Order Corrections:

State	ϵ_i/cm^{-1}	g_i	B_e/cm^{-1}	α_e/cm^{-1}	ω_e/cm^{-1}	$\omega_e x_e/cm^{-1}$
$A^3\Sigma_u^+$	49754.78	3	1.4546	0.01799	1460.638	13.8723
$B^3\Pi_g$	59306.81	6	1.63745	0.017906	1733.391	14.1221
$W^3\Delta_g$	59380.	6	[1.47327]	[0.016656]	1501.4	11.6

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

These are calculated by combining direct summation of vibrational–rotational energy levels of the electronic ground state with an approximate correction for the contribution of three excited states. All spectroscopic constants are from Lofthus and Krupenie[1] except the vibrational polynomial G used in direct summation of the ground state. We revise the G equation[1] so that is converges near $D_0^o = 78715\ cm^{-1}$.[2,1] Experimental data are limited to $v \leq 27$ and there is uncertainty in the extrapolation to high v values. Methods proposed by Khachkuruzov[3] are used to approximate the infinite–series (F) equation for rotational levels and the limiting values (J_{max}) of rotational quantum number. Values in the J_{max} equation are estimated by comparison with Khachkuruzov[3] and Gurvich *et al.*[4]

Contributions of excited states begin to appear in C_p^o at ~4800 K. We obtain these contributions using the difference between approximate calculations for four states (X, A, B, and W) and one state (ground state). These approximate calculations used first–order corrections for anharmonicity and vibrational–rotational interaction. The excited state contribution to C_p^o is 0.019 $cal^{-1}\ K^{-1} \cdot mol^{-1}$ at 5000 K.

Values and uncertainties at 298.15 K are the same as those selected by CODATA.[2] Uncertainties at 6000 K are considerably larger due to uncertainty in the extrapolation of G and F. Comparing our approximate calculation (a) with our adopted values (b) and those (c) of Gurvich *et al.*,[4] we have $S°(600\ K)$ = 69.981, 69.999 and 70.005 $cal^{-1} \cdot mol^{-1}$ and H(T) – H(0 K) = 51.196, 51.271, and 51.289 $J \cdot K \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−8.670	0.	0.	0.
100	29.104	159.811	217.490	−5.768	0.	0.	0.
200	29.107	179.985	194.272	−2.857	0.	0.	0.
250	29.111	186.481	192.088	−1.402	0.	0.	0.
298.15	29.124	191.609	191.609	0.	0.	0.	0.
300	29.125	191.789	191.610	0.054	0.	0.	0.
350	29.165	196.281	191.964	1.511	0.	0.	0.
400	29.249	200.181	192.753	2.971	0.	0.	0.
450	29.387	203.633	193.774	4.437	0.	0.	0.
500	29.580	206.739	194.917	5.911	0.	0.	0.
600	30.110	212.176	197.353	8.894	0.	0.	0.
700	30.754	216.866	199.813	11.937	0.	0.	0.
800	31.433	221.017	202.209	15.046	0.	0.	0.
900	32.090	224.757	204.510	18.223	0.	0.	0.
1000	32.697	228.170	206.708	21.463	0.	0.	0.
1100	33.241	231.313	208.804	24.760	0.	0.	0.
1200	33.723	234.226	210.802	28.109	0.	0.	0.
1300	34.147	236.943	212.710	31.503	0.	0.	0.
1400	34.518	239.487	214.533	34.936	0.	0.	0.
1500	34.843	241.880	216.277	38.405	0.	0.	0.
1600	35.128	244.138	217.948	41.904	0.	0.	0.
1700	35.378	246.275	219.552	45.429	0.	0.	0.
1800	35.600	248.304	221.094	48.978	0.	0.	0.
1900	35.796	250.234	222.577	52.548	0.	0.	0.
2000	35.971	252.074	224.006	56.137	0.	0.	0.
2100	36.126	253.833	225.385	59.742	0.	0.	0.
2200	36.268	255.517	226.717	63.361	0.	0.	0.
2300	36.395	257.132	228.004	66.995	0.	0.	0.
2400	36.511	258.684	229.250	70.640	0.	0.	0.
2500	36.616	260.176	230.458	74.296	0.	0.	0.
2600	36.713	261.614	231.629	77.963	0.	0.	0.
2700	36.801	263.001	232.765	81.639	0.	0.	0.
2800	36.883	264.341	233.869	85.323	0.	0.	0.
2900	36.959	265.637	234.942	89.015	0.	0.	0.
3000	37.030	266.891	235.986	92.715	0.	0.	0.
3100	37.096	268.106	237.003	96.421	0.	0.	0.
3200	37.158	269.285	237.993	100.134	0.	0.	0.
3300	37.216	270.429	238.959	103.852	0.	0.	0.
3400	37.271	271.541	239.901	107.577	0.	0.	0.
3500	37.323	272.622	240.821	111.306	0.	0.	0.
3600	37.373	273.675	241.719	115.041	0.	0.	0.
3700	37.420	274.699	242.596	118.781	0.	0.	0.
3800	37.465	275.698	243.454	122.525	0.	0.	0.
3900	37.508	276.671	244.294	126.274	0.	0.	0.
4000	37.550	277.622	245.115	130.027	0.	0.	0.
4100	37.590	278.549	245.919	133.784	0.	0.	0.
4200	37.629	279.456	246.707	137.545	0.	0.	0.
4300	37.666	280.341	247.479	141.309	0.	0.	0.
4400	37.702	281.208	248.236	145.078	0.	0.	0.
4500	37.738	282.056	248.978	148.850	0.	0.	0.
4600	37.773	282.885	249.706	152.625	0.	0.	0.
4700	37.808	283.698	250.420	156.405	0.	0.	0.
4800	37.843	284.494	251.122	160.187	0.	0.	0.
4900	37.878	285.275	251.811	163.973	0.	0.	0.
5000	37.912	286.041	252.488	167.763	0.	0.	0.
5100	37.947	286.792	253.153	171.556	0.	0.	0.
5200	37.981	287.529	253.807	175.352	0.	0.	0.
5300	38.013	288.253	254.451	179.152	0.	0.	0.
5400	38.046	288.964	255.083	182.955	0.	0.	0.
5500	38.080	289.662	255.705	186.761	0.	0.	0.
5600	38.116	290.348	256.318	190.571	0.	0.	0.
5700	38.154	291.023	256.921	194.384	0.	0.	0.
5800	38.193	291.687	257.515	198.201	0.	0.	0.
5900	38.234	292.341	258.099	202.023	0.	0.	0.
6000	38.276	292.984	258.675	205.848	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1977 (1 bar)

$S°(298.15\ K) = 197.660 \pm 0.04\ kJ \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1503.303 \pm 0.04\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1509.499]\ kJ \cdot mol^{-1}$

		Electronic and Molecular Constants (σ = 2)						
State	g_i	T_o, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	$\omega_e y_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Sigma_g^+$	2	0.0	2207.00	16.10	−0.040	1.9319	0.0190	1.116384
$A^2\Pi_{ui}$	4	9016.4	1903.53	15.011		1.748	0.020	1.17364
$B^2\Sigma_u^+$	2	25566.0	2419.84	23.19		2.073	0.020	1.07772

Enthalpy of Formation

The adopted value for the enthalpy of formation of N_2^+(g), $\Delta_f H°(0\ K) = 359.298 \pm 0.01\ kcal \cdot mol^{-1}$ is recommended in a critical review on the energetics of gaseous ions by Rosenstock *et al.*[1] This value is derived from ionization potentials determined in the spectroscopic studies of Worley[2] and Ogawa and Tanaka.[3] The IP values are 125665.8 and 125666.8 cm^{-1} respectively.

$\Delta_f H°(N_2^+, 298.15\ K)$ is obtained from $\Delta_f H°(N_2, g, 0\ K)$ by using IP (N_2, g, 0 K) with JANAF[7] enthalpies $H°(0\ K) - H°(298.15)$ for N_2(g), N_2(g), and e^-(ref). $\Delta_f H°(298.15)$ for the reaction $N_2(g) = N_2^+(g) + e^-$(ref) differs from a room temperature threshold energy due to the inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[1] $\Delta_f H°(298.15)$ should be changed by $-6.197\ kJ \cdot mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The thermal functions are calculated using the program of McBride and Gordon.[4] The contributions of vibrational anharmonicity and rotation–vibration interaction are calculated via the procedures given by Pennington and Kobe.[5] In this procedure the energy levels are calculated as follows: $\epsilon_l = T_o + G(v) - G(o) + B_v J(J+1) - D_e J^2(J+1)^2$ where $G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3$ and $B_v = B_e - \alpha_e(v + 1/2)$. When a value of D_e is not available, it is calculated to be $D_e = 4B_e^3/\omega_e$.[2] Molecular constant data in the table are from the critical review of Lofthus and Krupenie.[6] Electronic levels above 5000 cm^{-1} given by Lofthus and Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.669	1503.303		
100	29.104	165.859	223.544	−5.768			
200	29.137	197.660	211.948	−2.858			
298.15	29.137	197.660	197.660	0.	1509.499	1501.440	−263.046
300	29.139	197.840	197.660	0.054	1509.538	1501.390	−261.415
400	29.321	206.242	198.804	2.975	1511.620	1498.361	−195.666
500	29.752	212.827	200.973	5.927	1513.711	1494.804	−156.161
600	30.379	218.305	203.418	8.933	1515.812	1490.826	−129.788
700	31.097	223.042	205.890	12.006	1517.922	1486.495	−110.924
800	31.819	227.242	208.302	15.153	1520.037	1481.861	−96.756
900	32.495	231.030	210.620	18.369	1522.155	1476.962	−85.721
1000	33.108	234.486	212.836	21.650	1524.275	1471.826	−76.880
1100	33.657	237.668	214.951	24.988	1526.395	1466.479	−69.637
1200	34.148	240.617	216.968	28.379	1528.515	1460.939	−63.593
1300	34.597	243.369	218.894	31.816	1530.637	1455.221	−58.472
1400	35.018	245.948	220.736	35.297	1532.763	1449.340	−54.076
1500	35.422	248.378	222.498	38.819	1534.895	1443.307	−50.260
1600	35.822	250.677	224.188	42.381	1537.037	1437.131	−46.918
1700	36.225	252.860	225.811	45.984	1539.193	1430.821	−43.964
1800	36.636	254.943	227.372	49.627	1541.365	1424.384	−41.335
1900	37.059	256.935	228.876	53.311	1543.559	1417.825	−38.979
2000	37.496	258.847	230.327	57.039	1545.776	1411.150	−36.855
2100	37.944	260.687	231.729	60.811	1548.022	1404.364	−34.932
2200	38.403	262.463	233.086	64.628	1550.298	1397.470	−33.180
2300	38.869	264.180	234.401	68.492	1552.607	1390.472	−31.579
2400	39.339	265.844	235.676	72.402	1554.951	1383.372	−30.108
2500	39.809	267.459	236.916	76.360	1557.330	1376.174	−28.754
2600	40.275	269.030	238.121	80.364	1559.746	1368.880	−27.501
2700	40.733	270.559	239.294	84.414	1562.200	1361.493	−26.340
2800	41.181	272.048	240.437	88.510	1564.690	1354.014	−25.259
2900	41.615	273.501	241.552	92.650	1567.216	1346.445	−24.252
3000	42.032	274.919	242.641	96.833	1569.778	1338.789	−23.310
3100	42.433	276.304	243.705	101.056	1572.374	1331.047	−22.428
3200	42.811	277.657	244.745	105.318	1575.002	1323.220	−21.599
3300	43.165	278.980	245.762	109.617	1577.661	1315.311	−20.820
3400	43.496	280.273	246.758	113.951	1580.348	1307.321	−20.085
3500	43.804	281.538	247.734	118.316	1583.062	1299.251	−19.390
3600	44.084	282.776	248.690	122.710	1585.801	1291.103	−18.733
3700	44.343	283.988	249.628	127.132	1588.561	1282.879	−18.111
3800	44.581	285.174	250.548	131.578	1591.342	1274.580	−17.520
3900	44.798	286.335	251.451	136.048	1594.141	1266.208	−16.959
4000	44.994	287.471	252.337	140.537	1596.957	1257.764	−16.425
4100	45.158	288.584	253.207	145.045	1599.786	1249.249	−15.916
4200	45.307	289.674	254.063	149.568	1602.627	1240.665	−15.430
4300	45.439	290.742	254.903	154.106	1605.478	1232.013	−14.966
4400	45.556	291.788	255.730	158.656	1608.338	1223.295	−14.522
4500	45.656	292.813	256.543	163.216	1611.205	1214.512	−14.098
4600	45.730	293.817	257.342	167.786	1614.078	1205.665	−13.691
4700	45.794	294.801	258.129	172.362	1616.954	1196.755	−13.300
4800	45.846	295.766	258.903	176.944	1619.832	1187.784	−12.926
4900	45.889	296.712	259.665	181.531	1622.711	1178.753	−12.566
5000	45.920	297.639	260.415	186.122	1625.591	1169.664	−12.219
5100	45.933	298.549	261.154	190.714	1628.469	1160.517	−11.886
5200	45.939	299.441	261.881	195.308	1631.345	1151.313	−11.565
5300	45.939	300.316	262.598	199.902	1634.218	1142.054	−11.256
5400	45.932	301.174	263.305	204.495	1637.087	1132.741	−10.957
5500	45.919	302.017	264.001	209.088	1639.952	1123.375	−10.669
5600	45.900	302.844	264.687	213.679	1642.812	1113.957	−10.391
5700	45.875	303.657	265.364	218.268	1645.666	1104.488	−10.121
5800	45.843	304.454	266.031	222.854	1648.513	1094.969	−9.861
5900	45.805	305.237	266.689	227.436	1651.353	1085.400	−9.609
6000	45.761	306.007	267.338	232.015	1654.184	1075.784	−9.366

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 204.54 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 155 \pm 96\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [148.615]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi_g$	0	4

$\omega_e = [1900]\ cm^{-1}$ $\omega_e x_e = [12.0]\ cm^{-1}$ $\sigma = 2$
$B_e = [1.691]\ cm^{-1}$ $\alpha_e = [0.015]\ cm^{-1}$ $r_e = [1.193 \pm 0.003]$Å

Enthalpy of Formation

The enthalpy of formation at 0 K for N_2^-(g) is based on the electron affinity value derived from the Rydberg–Klein–type calculations of Gilmore.[1] Use of this adopted value, $EA(N_2) = -1.6 \pm 1.0$ eV and auxiliary data[2] leads to $\Delta_f H° = 37 \pm 23\ kJ \cdot mol^{-1}$ and $D_0°(N_2^-) = 190 \pm 30\ kJ \cdot mol^{-1}$. Additional discussion on N_2^-(g) may be found in the reviews by Lofthus and Krupenie[3] and Massey.[4]

The adopted EA is the only tabulated value for the ground state given in a recent compilation by Rosenstock *et al.*[5] This compilation contains results through the end of 1973. In support of the adopted value there are two additional studies to consider. First, Massey[4] discusses qualitatively the electronic and molecular structure as follows. The ground state of N_2 has a closed shell configuration. The corresponding configuration for N_2^- is obtained by adding an additional electron in an antibonding Πg 2p orbital. According to Mulliken's rule this reduces the binding energy by about 1.25 eV (~29 $kJ \cdot mol^{-1}$). In contrast to O_2^-(g), in the separated atom limit the ion N_2^- is not stable so that we expect the lowest level of N_2^- will be at least 1.25 eV above that for N_2 as well as occurring at a larger nuclear separation. Second, Birtwistle and Herzenberg[6] developed a theory of vibrational excitation through an intermediate state which predicts that the lowest energies of N_2^- and N_2 are separated by 1.925 eV (~44 $kJ \cdot mol^{-1}$). Comparable results were obtained by Krauss and Mies[7] using a variational method.

$\Delta_f H°(0\ K)$ is converted to $\Delta_f H°(298.15\ 0\ K)$ by use of JANAF[2] enthalpies $H°(0\ K) - H°(298.15\ K)$ for N_2(g), N_2^-(g), and e^-(ref). $\Delta_f H°(298.15\ K)$ should be changed by + 1.481 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The vibrational constants are estimated based on trends implied in isoelectronic sequences involving (N_2^-,NO, and O_2^+) and N_2 and NO^+). The value adopted for ω_e is ~35 cm^{-1} and 65 cm^{-1} lower than those calculated by Krauss and Mies[7] and Birtwistle and Herzenberg,[6] respectively.

We adopt the $r_e = 1.193 \pm 0.003$ Å value calculated by Birtwistle and Herzenberg[6] as it agrees with the value suggested from the above isoelectronic series. The calculations of Krauss and Mies[7] suggest $r_e = 1.22$ Å which, in our estimation, is too high. B_e is calculated from r_e while α_e is estimated from the aforementioned isoelectronic series. This α_e value is the same as one would calculate assuming a Morse potential for the electronic ground state.

No low lying excited states are assumed to exist.[3,4]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−8.674	154.808		
100	29.105	172.727	230.434	−5.771			
200	29.111	192.903	207.202	−2.860			
250	29.131	199.400	205.016	−1.404			
298.15	29.194	204.536	204.536	0.	148.615	151.015	−26.457
300	29.198	204.716	204.536	0.054	148.576	151.030	−26.297
350	29.339	209.227	204.892	1.517	147.543	151.521	−22.613
400	29.567	213.158	205.685	2.989	146.516	152.160	−19.870
450	29.874	216.658	206.713	4.475	145.497	152.926	−17.751
500	30.240	219.824	207.869	5.978	144.486	153.806	−16.068
600	31.062	225.409	210.339	9.042	142.489	155.858	−13.569
700	31.895	230.260	212.845	12.190	140.516	158.243	−11.808
800	32.661	234.570	215.297	15.419	138.556	160.909	−10.506
900	33.333	238.457	217.657	18.719	136.601	163.820	−9.508
1000	33.909	241.999	219.917	22.082	134.646	166.950	−8.721
1100	34.398	245.255	222.075	25.498	132.686	170.275	−8.086
1200	34.813	248.266	224.133	28.959	130.719	173.779	−7.564
1300	35.165	251.067	226.099	32.459	128.746	177.447	−7.130
1400	35.465	253.684	227.977	35.991	126.766	181.268	−6.763
1500	35.723	256.140	229.773	39.550	124.779	185.230	−6.450
1600	35.946	258.453	231.494	43.134	122.785	189.325	−6.181
1700	36.139	260.638	233.145	46.739	120.785	193.545	−5.947
1800	36.308	262.709	234.730	50.361	118.780	197.883	−5.742
1900	36.457	264.676	236.255	54.000	116.770	202.332	−5.562
2000	36.590	266.549	237.723	57.652	114.755	206.887	−5.403
2100	36.708	268.337	239.139	61.317	112.737	211.544	−5.262
2200	36.814	270.047	240.505	64.993	110.715	216.296	−5.136
2300	36.910	271.686	241.825	68.680	108.689	221.141	−5.022
2400	36.997	273.259	243.103	72.375	106.661	226.073	−4.920
2500	37.077	274.771	244.339	76.079	104.629	231.090	−4.828
2600	37.150	276.226	245.538	79.790	102.596	236.189	−4.745
2700	37.218	277.630	246.701	83.509	100.560	241.366	−4.670
2800	37.280	278.984	247.830	87.234	98.522	246.618	−4.601
2900	37.339	280.294	248.927	90.964	96.482	251.943	−4.538
3000	37.393	281.560	249.993	94.701	94.441	257.339	−4.481
3100	37.444	282.787	251.032	98.443	92.397	262.803	−4.428
3200	37.493	283.977	252.043	102.190	90.353	268.332	−4.380
3300	37.538	285.131	253.028	105.941	88.307	273.926	−4.336
3400	37.582	286.253	253.989	109.697	86.260	279.581	−4.295
3500	37.623	287.343	254.926	113.458	84.212	285.297	−4.258
3600	37.662	288.403	255.841	117.222	82.163	291.071	−4.223
3700	37.700	289.436	256.735	120.990	80.113	296.902	−4.192
3800	37.736	290.441	257.609	124.762	78.062	302.789	−4.162
3900	37.771	291.422	258.464	128.537	76.010	308.730	−4.135
4000	37.805	292.379	259.300	132.316	73.957	314.723	−4.110
4100	37.837	293.313	260.118	136.098	71.904	320.767	−4.087
4200	37.869	294.225	260.919	139.884	69.849	326.862	−4.065
4300	37.899	295.116	261.704	143.672	67.795	333.006	−4.045
4400	37.929	295.988	262.474	147.463	65.739	339.197	−4.027
4500	37.958	296.841	263.228	151.258	63.683	345.435	−4.010
4600	37.986	297.675	263.968	155.055	61.626	351.719	−3.994
4700	38.014	298.492	264.693	158.855	59.568	358.048	−3.979
4800	38.041	299.293	265.406	162.658	57.510	364.420	−3.966
4900	38.067	300.078	266.106	166.463	55.450	370.835	−3.953
5000	38.093	300.847	266.793	170.271	53.390	377.293	−3.942
5100	38.118	301.602	267.468	174.082	51.329	383.791	−3.931
5200	38.143	302.342	268.131	177.895	49.267	390.330	−3.921
5300	38.168	303.069	268.784	181.710	47.205	396.909	−3.912
5400	38.192	303.782	269.425	185.528	45.141	403.526	−3.903
5500	38.216	304.483	270.056	189.349	43.077	410.182	−3.896
5600	38.239	305.172	270.677	193.171	41.011	416.875	−3.888
5700	38.263	305.849	271.289	196.996	38.944	423.606	−3.882
5800	38.286	306.515	271.890	200.824	36.875	430.372	−3.876
5900	38.308	307.170	272.483	204.654	34.805	437.174	−3.870
6000	38.331	307.814	273.066	208.486	32.733	444.012	−3.865

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

Nitrogen Oxide (N_2O) IDEAL GAS $M_r = 44.0128$

$S°(298.15\ K) = 219.957\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 85.48 \pm 0.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 82.05 \pm 0.4\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1276.5(1)
589.2(2)
2223.7(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: $C_{\infty v}$
Bond Distances: N–N = 1.1282 Å N–O = 1.1842 Å
Bond Angle: N–N–O = 180°
Rotational Constant: $B_o = 0.421019\ cm^{-1}$

Enthalpy of Formation

An analysis of the enthalpy of reaction data is summarized below. Carlton–Sutton *et al.*[1] studied the direct decomposition at pressures of 40 to 50 atmospheres and made *P–V–T* measurements in order to reduce the data. They obtained a similar but less certain enthalpy of formation by combustion of N_2O in CO. Flame calorimetric measurements of the combustion by Awberry and Griffiths[2] are in good agreement, but the bomb calorimetry of Fenning and Cotton[3] gives a enthalpy of formation about 0.2 $kcal·mol^{-1}$ larger. The selected enthalpy of formation is a weighted average of these values.

Source	Method	Reaction	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$
[1]	Bomb calorimetry	$N_2O(g) \rightarrow N_2(g) + 0.5\ O_2(g)$	-19.52 ± 0.10	19.52
[1]	Bomb calorimetry	$N_2O(g) + CO(g) \rightarrow CO_2(g) + N_2(g)$	-87.10 ± 0.30	19.46*
[2]	Flame calorimetry	$N_2O(g) + CO(g) \rightarrow CO_2(g) + N_2(g)$	-87.09 ± 0.22	19.45*
[3]	Bomb calorimetry	$N_2O(g) + CO(g) \rightarrow CO_2(g) + N_2(g)$	-87.37 ± 0.12	19.73*
[3]	Bomb calorimetry	$N_2O(g) + H_2(g) \rightarrow H_2O(l) + N_2(g)$	-88.03 ± 0.12	19.71*

*Based on $\Delta_f H°(298.15\ K) = -68.32\ (H_2O, l), -94.054\ (CO_2, g), -26.417\ (CO, g)$

Heat Capacity and Entropy

The functions are based on the rotational constants of Pliva[4] and the frequencies determined by Tidwell *et al.*[5] The bond distances reported by Pliva were obtained from measurements of isotopic shifts in the infrared. They include higher–order corrections for vibration–rotation interaction and are in satisfactory agreement with the infrared and microwave studies of Douglas and Moller[6] and the electron diffraction data of Schomaker and Spurr.[7]

References

[1]T. Carlton–Sutton, H. R. Ambler, G. W. Williams, Proc. Phys. Soc. (London) **48**, 189 (1936).
[2]J. H. Awberry, E. Giffiths, Proc. Roy. Soc. (London) **A141**, 17 (1933).
[3]R. W. Fenning, F. T. Cotton, Proc. Roy. Soc. (London) **A141**, 1 (1933).
[4]Pliva, J. Mol. Spectrosc. **12**, 360 (1964).
[5]Tidwell, Plyler and Benedict, J. Opt. Soc. Am. **50**, 1243 (1960).
[6]Douglas and Moller, J. Chem. Phys. **22**, 275 (1954).
[7]Schomaker and Spurr, J. Amer. Chem. Soc. **64**, 1184 (1942).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−9.579	85.481	85.481	INFINITE
100	29.349	184.150	250.829	−6.668	84.038	90.269	−47.152
200	33.610	205.571	223.335	−3.553	82.787	97.018	−25.338
250	36.290	213.362	220.580	−1.805	82.351	100.629	−21.025
298.15	38.617	219.957	219.957	0.	82.048	104.179	−18.252
300	38.701	220.196	219.958	0.072	82.039	104.316	−18.163
350	40.817	226.324	220.437	2.061	81.832	108.046	−16.125
400	42.680	231.899	221.526	4.149	81.713	111.800	−14.600
450	44.338	237.023	222.967	6.325	81.665	115.565	−13.414
500	45.826	241.773	224.613	8.580	81.675	119.331	−12.466
600	48.389	250.363	228.204	13.295	81.827	126.851	−11.043
700	50.500	257.986	231.924	18.243	82.105	134.334	−10.024
800	52.241	264.846	235.618	23.383	82.467	141.772	−9.257
900	53.678	271.085	239.217	28.681	82.886	149.160	−8.657
1000	54.865	276.804	242.694	34.110	83.344	156.500	−8.175
1100	55.848	282.081	246.038	39.647	83.829	163.792	−7.778
1200	56.665	286.976	249.248	45.274	84.333	171.039	−7.445
1300	57.349	291.540	252.328	50.976	84.849	178.244	−7.162
1400	57.924	295.811	255.283	56.740	85.373	185.408	−6.918
1500	58.410	299.825	258.120	62.557	85.902	192.535	−6.705
1600	58.825	303.608	260.846	68.420	86.432	199.627	−6.517
1700	59.180	307.185	263.467	74.320	86.961	206.685	−6.351
1800	59.486	310.577	265.991	80.254	87.488	213.713	−6.202
1900	59.752	313.800	268.423	86.216	88.010	220.711	−6.068
2000	59.983	316.871	270.769	92.203	88.527	227.682	−5.946
2100	60.186	319.803	273.035	98.212	89.038	234.627	−5.836
2200	60.365	322.607	275.225	104.240	89.542	241.548	−5.735
2300	60.523	325.294	277.344	110.284	90.038	248.446	−5.642
2400	60.663	327.873	279.396	116.344	90.526	255.323	−5.557
2500	60.788	330.352	281.385	122.417	91.005	262.179	−5.478
2600	60.900	332.738	283.314	128.501	91.474	269.017	−5.405
2700	61.001	335.038	285.188	134.596	91.935	275.837	−5.336
2800	61.091	337.258	287.008	140.701	92.387	282.640	−5.273
2900	61.173	339.404	288.778	146.814	92.829	289.427	−5.213
3000	61.248	341.479	290.500	152.935	93.262	296.199	−5.157
3100	61.315	343.488	292.177	159.063	93.686	302.956	−5.105
3200	61.377	345.436	293.811	165.198	94.101	309.700	−5.055
3300	61.434	347.325	295.405	171.339	94.508	316.431	−5.009
3400	61.486	349.160	296.959	177.485	94.905	323.150	−4.965
3500	61.533	350.943	298.476	183.636	95.295	329.857	−4.923
3600	61.577	352.677	299.957	189.791	95.676	336.554	−4.883
3700	61.618	354.365	301.405	195.951	96.049	343.240	−4.846
3800	61.655	356.009	302.821	202.115	96.414	349.916	−4.810
3900	61.690	357.611	304.205	208.282	96.772	356.583	−4.776
4000	61.722	359.173	305.560	214.453	97.121	363.240	−4.743
4100	61.752	360.697	306.886	220.626	97.464	369.888	−4.712
4200	61.780	362.186	308.185	226.803	97.799	376.529	−4.683
4300	61.806	363.640	309.458	232.982	98.127	383.162	−4.654
4400	61.830	365.061	310.705	239.164	98.447	389.786	−4.627
4500	61.853	366.451	311.929	245.348	98.760	396.404	−4.601
4600	61.874	367.810	313.129	251.534	99.066	403.015	−4.576
4700	61.894	369.141	314.307	257.723	99.364	409.619	−4.552
4800	61.913	370.445	315.463	263.913	99.654	416.217	−4.529
4900	61.931	371.721	316.598	270.106	99.937	422.810	−4.507
5000	61.947	372.973	317.713	276.299	100.211	429.396	−4.486
5100	61.963	374.200	318.808	282.495	100.476	435.977	−4.465
5200	61.978	375.403	319.885	288.692	100.732	442.553	−4.445
5300	61.992	376.584	320.944	294.891	100.980	449.124	−4.426
5400	62.005	377.743	321.985	301.090	101.218	455.690	−4.408
5500	62.018	378.880	323.009	307.292	101.445	462.252	−4.390
5600	62.030	379.998	324.017	313.494	101.662	468.811	−4.373
5700	62.041	381.096	325.009	319.697	101.868	475.365	−4.356
5800	62.052	382.175	325.985	325.902	102.061	481.916	−4.340
5900	62.062	383.236	326.946	332.108	102.242	488.463	−4.325
6000	62.072	384.279	327.893	338.314	102.409	495.009	−4.309

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 233.856 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1329.592 \pm 0.63\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 1333.399 \pm 0.63\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\pi_{3/2}$	0	2
$X^2\pi_{1/2}$	132.4	2
$A^2\Sigma^+$	28229	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
1736.6(1)
461.2(2)
1126.4(1)

Point Group: $C_{\infty v}$ $\sigma = 1$
Bond Distances: N–N = 1.155 Å N–O = 1.185 Å
Bond Angle: N–N–O = 180°
Rotational Constant: $B_0 = 0.411407\ cm^{-1}$

Enthalpy of Formation

The ionization potential of 104000 cm^{-1} (297.35 $kcal \cdot mol^{-1}$) has been obtained by Tanaka *et al.*[1] from a Rydberg series terminating on $X^2\pi_{3/2}$ Other Rydberg series terminating on $X\ ^2\pi_{1/2}$ and $A^2\Sigma^+$ were also obtained and confirm the adopted value. This value in conjunction with the enthalpy of formation of $N_2O(g)$[2] was used to calculate the adopted enthalpy of formation.

Heat Capacity and Entropy

The electronic, vibrational and rotational constants are those reported by Herzberg[3] from the work of Callomon and Creutzberg.[4]

References

[1]Y. Tanaka, A. S. Jura and F. L. LeBlanc, J. Chem. Phys. **28**, 350 (1958).
[2]JANAF Thermochemical Tables: $N_2O(g)$, 12–31–64.
[3]G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Von Nostrand Co., Inc., New York, (1966).
[4]J. H. Callomon and F. C. Creutzberg, Proc. Int. Conf. Spectrosc., 1st Bombay **1**, 171 (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.622	1329.592		
100	33.467	193.445	268.380	−7.494			
200	37.926	217.872	237.588	−3.943			
250	40.258	226.590	234.540	−1.988			
298.15	42.262	233.856	233.856	0.	1333.399	1345.131	−235.661
300	42.335	234.117	233.856	0.078	1333.435	1345.203	−234.221
350	44.212	240.787	234.379	2.243	1334.443	1347.086	−201.042
400	45.924	246.804	235.562	4.497	1335.529	1348.819	−176.138
450	47.485	252.304	237.121	6.833	1336.680	1350.412	−156.752
500	48.903	257.382	238.896	9.243	1337.885	1351.874	−141.229
600	51.329	266.520	242.756	14.259	1340.416	1354.436	−117.914
700	53.267	274.584	246.738	19.492	1343.058	1356.565	−101.228
800	54.801	281.801	250.678	24.899	1345.765	1358.310	−88.689
900	56.016	288.329	254.504	30.442	1348.508	1359.714	−78.916
1000	56.983	294.283	258.189	36.094	1351.267	1360.811	−71.081
1100	57.759	299.751	261.722	41.832	1354.032	1361.632	−64.659
1200	58.387	304.805	265.104	47.641	1356.796	1362.201	−59.295
1300	58.900	309.499	268.341	53.506	1359.554	1362.539	−54.747
1400	59.324	313.880	271.439	59.418	1362.305	1362.666	−50.842
1500	59.677	317.985	274.407	65.368	1365.045	1362.596	−47.450
1600	59.973	321.847	277.252	71.351	1367.774	1362.343	−44.476
1700	60.225	325.490	279.984	77.361	1370.491	1361.921	−41.847
1800	60.439	328.939	282.608	83.395	1373.196	1361.338	−39.505
1900	60.623	332.212	285.134	89.448	1375.889	1360.606	−37.406
2000	60.783	335.325	287.566	95.519	1378.568	1359.732	−35.513
2100	60.922	338.294	289.912	101.604	1381.234	1358.725	−33.796
2200	61.043	341.131	292.176	107.702	1383.887	1357.591	−32.233
2300	61.150	343.847	294.364	113.812	1386.527	1356.336	−30.803
2400	61.245	346.452	296.480	119.932	1389.154	1354.967	−29.490
2500	61.329	348.954	298.529	126.061	1391.767	1353.489	−28.280
2600	61.404	351.361	300.515	132.197	1394.368	1351.907	−27.160
2700	61.471	353.679	302.442	138.341	1396.956	1350.224	−26.122
2800	61.532	355.916	304.312	144.491	1399.532	1348.447	−25.156
2900	61.587	358.076	306.129	150.647	1402.095	1346.576	−24.254
3000	61.636	360.165	307.895	156.809	1404.647	1344.619	−23.412
3100	61.681	362.187	309.614	162.975	1407.187	1342.576	−22.622
3200	61.723	364.146	311.288	169.145	1409.717	1340.451	−21.881
3300	61.761	366.046	312.919	175.319	1412.235	1338.247	−21.183
3400	61.796	367.890	314.508	181.497	1414.743	1335.968	−20.525
3500	61.828	369.682	316.059	187.678	1417.242	1333.614	−19.903
3600	61.859	371.424	317.573	193.862	1419.730	1331.190	−19.315
3700	61.887	373.119	319.052	200.050	1422.209	1328.696	−18.758
3800	61.914	374.770	320.496	206.240	1424.680	1326.136	−18.229
3900	61.939	376.378	321.908	212.433	1427.141	1323.511	−17.726
4000	61.964	377.947	323.290	218.628	1429.594	1320.822	−17.248
4100	61.987	379.477	324.642	224.825	1432.039	1318.073	−16.792
4200	62.009	380.971	325.965	231.025	1434.476	1315.263	−16.358
4300	62.031	382.431	327.261	237.227	1436.905	1312.397	−15.942
4400	62.053	383.857	328.532	243.431	1439.326	1309.473	−15.545
4500	62.073	385.252	329.777	249.638	1441.740	1306.494	−15.165
4600	62.094	386.616	330.997	255.846	1444.147	1303.462	−14.801
4700	62.115	387.952	332.195	262.056	1446.545	1300.378	−14.452
4800	62.135	389.260	333.370	268.269	1448.936	1297.243	−14.117
4900	62.155	390.541	334.524	274.483	1451.319	1294.058	−13.795
5000	62.176	391.797	335.657	280.700	1453.695	1290.824	−13.485
5100	62.197	393.028	336.770	286.919	1456.062	1287.544	−13.187
5200	62.217	394.236	337.863	293.139	1458.420	1284.216	−12.900
5300	62.238	395.422	338.938	299.362	1460.771	1280.844	−12.623
5400	62.260	396.585	339.995	305.587	1463.112	1277.427	−12.357
5500	62.281	397.728	341.034	311.814	1465.444	1273.966	−12.099
5600	62.303	398.850	342.057	318.043	1467.767	1270.464	−11.850
5700	62.326	399.953	343.063	324.275	1470.079	1266.920	−11.610
5800	62.348	401.037	344.053	330.508	1472.380	1263.336	−11.378
5900	62.371	402.103	345.028	336.744	1474.670	1259.712	−11.153
6000	62.395	403.152	345.988	342.983	1476.947	1256.050	−10.935

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = 308.54 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = 82.843 \pm 0.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1863(1)	783(1)	313(1)
1589(1)	627(1)	253(1)
1297(1)	407(1)	[Rotation]

Ground State Quantum Weight: 1 σ = 1
Point Group: C_s
Bond Distances: N–N = 2.08 Å N–O (nitroso) = 1.12 Å N–O(nitro) = 1.18 Å
Bond Angles: O–N–N (nitroso) = 110° O–N–O = 134°
Product of Moments of Inertia: $I_A I_B I_C = 4.6201 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

Equilibria for the reaction $N_2O_3(g) \rightarrow NO(g) + NO_2(g)$ have been studied by Beattie and Bell,[1] Verhoek and Daniels,[2] and Abel and Proisl.[3] The results of Beattie and Bell are the most extensive, but they depend on the early analysis of Giauque and Kemp[4] for the simultaneous equilbrium $N_2O_4(g) \rightarrow 2\ NO_2(g)$. The JANAF analysis of the tetroxide dissociation has been used to recalculate the data of Beattie and Bell. Non–ideality of N_2O_4 and NO_2 was allowed for by use of the equations of state of Giauque and Kemp, while non–ideality of NO and N_2O_3 was removed by extrapolation of the equilibrium constants to zero pressure in a manner similar to that of Beattie and Bell. The data of Verhoek and Daniels and of Abel and Proisl have not been recalculated. 2nd and 3rd law analyses of the results are summarized below. The enthalpy of formation was obtained from $\Delta_f H°(298.15\ K) = 9.70\ kcal·mol^{-1}$.

Source	Temp. Range	T/K	$\Delta_r S°$, $cal·K^{-1}·mol^{-1}$ 2nd law	$\Delta_r S°$ 3rd law	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	$\Delta_f H°$ 3rd law
[1a]	278–318	298	33.25 ± 0.35	—	9.527 ± 0.096	—
[1b]	278–318	298	33.04 ± 0.31	33.77	9.476 ± 0.093	9.695
[1c]	278–318	298	33.56 ± 0.52	33.77	9.642 ± 0.155	9.706
[2]	298–318	308	38.8 ± 1.9	33.78	11.1 ± 0.6	9.59
[3]	291–308	294	32.9	33.77	9.60	9.86

a) given by authors b) from author's K_p values c) from recalculated K_p values

Heat Capacity and Entropy

The functions are similar to those calculated by Hisatsune[5] based on the analysis of Devlin and Hisatsune[6] of the Raman and infrared spectra in terms of Urey–Bradley force constants. Devlin and Hisatsune used observed isotopic shifts in the spectra along with force constants transferred from nitrogen oxides and oxyhalides in order to select the N–N bond distance and the O–N–N bond angle.

The unobserved mode was assumed to be free internal rotation around the N–N bond, leading to $S°(298.15\ K) = 73.91\ cal·K^{-1}·mol^{-1}$ which is in good agreement with $74.13 \pm 0.52\ cal·K^{-1}·mol^{-1}$ obtained from the recalculated 2nd law of Beattie and Bell. The principal moments of inertia are $I_A = 22.694 \times 10^{-39}$, $I_B = 29.577 \times 10^{-39}$, and $I_C = 6.883 \times 10^{-39}\ g·cm^2$, while the reduced moment for internal rotation was calculated as $I_r = 0.990 \times 10^{-39}\ g·cm^2$.

References

[1]Beattie and Bell, J. Chem. Soc. **1957**, 1681 (1957).
[2]Verhoek and Daniels, J. Amer. Chem. Soc. **53**, 1250 (1931).
[3]Abel and Proisl, Z. Elektrochem. **35**, 712 (1929).
[4]Giauque and Kemp, J. Chem. Phys. **6**, 40 (1938).
[5]I. C. Hisatsune, J. Phys. Chem. **65**, 2249 (1961).
[6]Devlin and Hisatsune, Spectrochim. Acta **17**, 218 (1961).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	4.157	0.	INFINITE	−14.920	89.618	89.618	INFINITE
100	43.290	249.899	360.299	−11.040	86.239	103.226	−53.920
200	56.497	284.180	314.268	−6.018	83.984	121.191	−31.652
250	61.524	297.344	309.597	−3.063	83.297	130.577	−27.283
298.15	65.615	308.539	308.539	0.	82.843	139.727	−24.480
300	65.761	308.946	308.541	0.122	82.829	140.080	−24.390
350	69.450	319.366	309.355	3.504	82.540	149.647	−22.334
400	72.738	328.858	311.208	7.060	82.394	159.246	−20.795
450	75.698	337.599	313.661	10.772	82.365	168.855	−19.600
500	78.370	345.715	316.466	14.625	82.431	178.462	−18.644
600	82.931	360.422	322.592	22.698	82.781	197.640	−17.206
700	86.579	373.491	328.947	31.181	83.339	216.741	−16.173
800	89.478	385.248	335.262	39.989	84.033	235.752	−15.393
900	91.780	395.925	341.418	49.056	84.815	254.671	−14.781
1000	93.617	405.694	347.364	58.330	85.656	273.499	−14.286
1100	95.095	414.688	353.081	67.768	86.533	292.242	−13.877
1200	96.294	423.016	358.567	77.339	87.432	310.903	−13.533
1300	97.276	430.764	363.826	87.019	88.344	329.489	−13.239
1400	98.087	438.003	368.868	96.789	89.259	348.004	−12.984
1500	98.764	444.794	373.706	106.632	90.173	366.453	−12.761
1600	99.333	451.187	378.351	116.538	91.079	384.843	−12.564
1700	99.816	457.224	382.815	126.496	91.974	403.175	−12.388
1800	100.228	462.941	387.109	136.499	92.854	421.455	−12.230
1900	100.583	468.370	391.244	146.540	93.716	439.688	−12.088
2000	100.890	473.537	395.230	156.614	94.557	457.875	−11.958
2100	101.157	478.466	399.078	166.716	95.377	476.021	−11.840
2200	101.391	483.178	402.794	176.844	96.172	494.129	−11.732
2300	101.598	487.689	406.388	186.994	96.943	512.200	−11.632
2400	101.780	492.017	409.866	197.163	97.687	530.238	−11.540
2500	101.942	496.175	413.236	207.349	98.405	548.246	−11.455
2600	102.087	500.177	416.503	217.551	99.095	566.226	−11.376
2700	102.216	504.032	419.674	227.766	99.759	584.180	−11.302
2800	102.333	507.751	422.754	237.993	100.396	602.110	−11.233
2900	102.438	511.344	425.747	248.232	101.006	620.017	−11.168
3000	102.533	514.819	428.658	258.481	101.589	637.904	−11.107
3100	102.619	518.182	431.492	268.738	102.147	655.773	−11.050
3200	102.698	521.441	434.253	279.004	102.680	673.622	−10.996
3300	102.770	524.603	436.943	289.278	103.188	691.456	−10.945
3400	102.836	527.672	439.566	299.558	103.672	709.275	−10.897
3500	102.896	530.653	442.126	309.845	104.133	727.080	−10.851
3600	102.952	533.553	444.626	320.137	104.572	744.872	−10.808
3700	103.003	536.374	447.068	330.435	104.989	762.652	−10.767
3800	103.050	539.122	449.454	340.738	105.385	780.423	−10.728
3900	103.094	541.799	451.788	351.045	105.760	798.182	−10.690
4000	103.135	544.410	454.071	361.356	106.115	815.931	−10.655
4100	103.173	546.957	456.305	371.672	106.451	833.673	−10.621
4200	103.208	549.444	458.494	381.991	106.767	851.406	−10.589
4300	103.240	551.873	460.637	392.313	107.064	869.133	−10.558
4400	103.271	554.246	462.738	402.639	107.342	886.851	−10.528
4500	103.300	556.568	464.797	412.967	107.602	904.564	−10.500
4600	103.326	558.838	466.817	423.299	107.842	922.271	−10.473
4700	103.352	561.061	468.798	433.633	108.063	939.974	−10.447
4800	103.375	563.237	470.743	443.969	108.265	957.672	−10.422
4900	103.397	565.369	472.653	454.308	108.446	975.367	−10.398
5000	103.418	567.458	474.528	464.648	108.606	993.057	−10.374
5100	103.438	569.506	476.370	474.991	108.744	1010.746	−10.352
5200	103.456	571.515	478.181	485.336	108.860	1028.429	−10.331
5300	103.474	573.485	479.960	495.682	108.952	1046.114	−10.310
5400	103.491	575.420	481.710	506.031	109.020	1063.794	−10.290
5500	103.506	577.319	483.432	516.380	109.062	1081.474	−10.271
5600	103.521	579.184	485.125	526.732	109.077	1099.156	−10.253
5700	103.535	581.016	486.791	537.085	109.063	1116.835	−10.235
5800	103.549	582.817	488.431	547.439	109.018	1134.517	−10.217
5900	103.561	584.587	490.046	557.794	108.942	1152.196	−10.201
6000	103.574	586.328	491.636	568.151	108.831	1169.881	−10.185

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = 150.290\ J·K^{-1}·mol^{-1}$
$T_{fus} = 261.95 \pm 0.05\ K$

$\Delta_f H°(0\ K) = -30.399 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -35.046 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{fus} H° = 14.652 \pm 0.013\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from that of the liquid using the measured enthalpy of melting and the enthalpy of the crystal and liquid.

Heat Capacity and Entropy

Giauque and Kemp[1] measured the low temperature heat capacity from 15–295 K. The entropy was obtained by integration of these data using $S°(15\ K) = 0.34\ cal·K^{-1}·mol^{-1}$.

Fusion Data

The temperature and enthalpy of fusion were also measured by Giauque and Kemp.[1]

Reference

[1]W. F. Giauque and J. D. Kemp, J. Chem. Phys. **6**, 40 (1938).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.390	−30.399	−30.399	INFINITE
100	60.702	56.130	237.659	−18.153	−35.874	9.156	−4.783
200	91.701	108.002	160.472	−10.494	−36.947	54.843	−14.324
261.950	110.918	135.224	151.325	−4.218	--- CRYSTAL <--> LIQUID ---		
298.15	122.103	150.290	150.290	0.	−35.046	99.603	−17.450
300	122.675	151.047	150.292	0.226	−34.982	100.438	−17.488
400	153.636	190.991	155.526	14.186	−29.882	144.891	−18.921
500	167.360	227.068	166.310	30.379	−22.746	187.782	−19.617

PREVIOUS: June 1961 CURRENT: September 1964

$S°(298.15\ K) = 209.198\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = -19.564 \pm 1.7\ kJ·mol^{-1}$

$T_{fus} = 261.95 \pm 0.05\ K$ $\Delta_{fus} H° = 14.652 \pm 0.013\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation was calculated from that of the gas using the calorimetrically measured enthalpy of vaporization to the equilibrium mixture, in conjunction with the fraction of NO_2 dimerized $\alpha = 0.161$.

Heat Capacity and Entropy

Giauque and Kemp[1] measured the low temperature heat capacity from 15–295 K. Above 295 K the heat capacity was smoothly extrapolated. $S°(l, 298.15\ K)$ is calculated from $C_p°$.

Fusion and Vaporization Data

Giauque and Kemp[1] measured the temperature and enthalpy of fusion and also the boiling point and the calorimetric value of the enthalpy of vaporization to the equilibrium mixture. The enthalpy of vaporization (f = 1 atm) to a hypothetical pure N_2O_4 gas at 294.25 K was calculated to be 6.91 kcal·mol^{-1}.

References

[1]W. F. Giauque and J. D. Kemp, J. Chem. Phys. **6**, 40 (1938).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100	112.884	72.843	325.324	−25.248	−27.487	15.871	−8.290
200	127.528	155.582	221.720	−13.227	−24.199	58.075	−15.168
261.950	136.843	191.160	210.426	−5.047	--- CRYSTAL <---> LIQUID ---		
298.15	142.509	209.198	209.198	0.	−19.564	97.521	−17.085
300	142.842	210.081	209.201	0.264	−19.463	98.247	−17.106
400	160.833	253.638	215.019	15.448	−13.139	136.576	−17.835
500	178.824	291.459	226.598	32.431	−5.213	173.120	−18.086

PREVIOUS: September 1964 CURRENT: December 1964

0	to	261.95 K crystal
above		261.95 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−36.872	−30.399	−30.399	INFINITE
100	60.702	56.130	392.476	−33.635	−35.874	9.156	−4.783
200	91.701	108.002	237.881	−25.976	−36.947	54.843	−14.324
261.950	110.918	135.224	210.426	−19.699	CRYSTAL <--> LIQUID TRANSITION		
261.950	136.843	191.160	210.426	−5.047			
298.15	142.509	209.198	209.198	0.	−19.564	97.521	−17.085
300	142.842	210.081	209.201	0.264	−19.463	98.247	−17.106
400	160.833	253.638	215.019	15.448	−13.139	136.576	−17.835
500	178.824	291.459	226.598	32.431	−5.213	173.120	−18.086

PREVIOUS: CURRENT: December 1964

$S°(298.15\ K) = 304.376\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 18.72 \pm 1.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 9.08 \pm 1.7\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1373 (1)	1710(1)	1748(1)
823 (1)	480(1)	385(1)
260 (1)	430(1)	1261(1)
[50](1)	675(1)	750(1)

Ground State Quantum Weight: 1 $\sigma = 4$
Point Group: D_{2h}
Bond Distances: N–N = 1.750 Å N–O = 1.180 Å
Bond Angle: O–N–O = 133.7°
Product of the Moments of Inertia: $I_A I_B I_C = 9.935917 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

Giauque and Kemp[1] calculated idealized equilibrium constants for the reaction $N_2O_4(g) = 2\ NO_2(g)$ from the work of Bodenstein and Boes,[2] Verhoek and Daniels[3] and Wourtzel.[4] The 2nd and 3rd law analysis of these equilibrium constants has been repeated using more recent functions. The results are shown below.

Source	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law
[2]	13.634 ± 0.015*	13.644
[3]	14.429 ± 0.126	13.672
[4]	13.599 ± 0.019**	13.657

*Ten points rejected because of statistically significant scatter.
**One point rejected.

The 2nd law value of Verhoek and Daniels[3] was not considered significant due to the extremely small temperature range and the use of only three temperatures. The adopted value was 13.65 ± 0.03 $kcal·mol^{-1}$ which leads to 2.17 $kcal·mol^{-1}$ for the enthalpy of formation of $N_2O_4(g)$.

Heat Capacity and Entropy

The structural parameters were taken from the electron diffraction measurements of Smith and Hedberg.[5] The vibrational frequencies are those chosen by Hitsatsune *et al.*[6] The torsional frequency of 50 cm^{-1} was estimated in order to bring the entropy of the gas into agreement with that determined by Giauque and Kemp[1] from low temperature heat capacities and heats of fusion and vaporization. The principal moments of inertia are: $I_A = 12.5103 \times 10^{-39}$, $I_B = 22.6126 \times 10^{-39}$, and $I_C = 35.1229 \times 10^{-39}\ g·cm^2$.

References

[1]W. F. Guauque and J. D. Kemp, J. Chem. Phys. **6**, 40 (1938).
[2]Bodenstein and Boes, Zeits. fur physik. Chem. **100**, 75 (1922).
[3]Verhoek and Daniels, J. Amer. Chem. Soc. **53**, 1250 (1931).
[4]Wourtzel, Compt. Rend. **169**, 1397 (1919).
[5]D. W. Smith and K. Hedberg, J. Chem. Phys. **25**, 1282 (1956).
[6]I. C. Hitsatsune, J. P. Devlin and V. Wada, J. Chem. Phys. **33**, 714 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−16.398	18.718	18.718	INFINITE
100	46.262	239.166	363.098	−12.393	14.011	40.737	−21.279
200	63.206	276.398	311.015	−6.923	10.749	68.860	−17.984
250	70.825	291.339	305.613	−3.568	9.732	83.513	−17.449
298.15	77.256	304.376	304.376	0.	9.079	97.787	−17.132
300	77.487	304.854	304.377	0.143	9.060	98.338	−17.122
350	83.340	317.248	305.343	4.167	8.673	113.251	−16.902
400	88.521	328.722	307.557	8.466	8.523	128.204	−16.742
450	93.121	339.419	310.509	13.009	8.567	143.163	−16.618
500	97.204	349.446	313.907	17.769	8.769	158.109	−16.518
600	104.012	367.795	321.388	27.844	9.542	187.911	−16.359
700	109.314	384.244	329.213	38.522	10.667	217.555	−16.234
800	113.439	399.122	337.037	49.668	12.030	247.019	−16.129
900	116.665	412.677	344.700	61.180	13.554	276.303	−16.036
1000	119.208	425.106	352.127	72.978	15.189	305.410	−15.953
1100	121.235	436.566	359.290	85.004	16.899	334.350	−15.877
1200	122.867	447.187	366.177	97.212	18.661	363.132	−15.807
1300	124.196	457.076	372.794	109.567	20.456	391.765	−15.741
1400	125.290	466.321	379.148	122.044	22.272	420.259	−15.680
1500	126.198	474.997	385.251	134.619	24.097	448.623	−15.622
1600	126.959	483.167	391.118	147.278	25.922	476.865	−15.568
1700	127.603	490.884	396.762	160.007	27.742	504.994	−15.517
1800	128.152	498.193	402.196	172.796	29.550	533.014	−15.468
1900	128.623	505.135	407.432	185.635	31.340	560.936	−15.421
2000	129.030	511.743	412.484	198.518	33.110	588.764	−15.377
2100	129.385	518.047	417.362	211.439	34.855	616.503	−15.335
2200	129.694	524.074	422.077	224.394	36.573	644.162	−15.294
2300	129.967	529.845	426.638	237.377	38.262	671.741	−15.256
2400	130.208	535.381	431.054	250.386	39.920	699.247	−15.219
2500	130.421	540.701	435.334	263.418	41.545	726.685	−15.183
2600	130.612	545.820	439.486	276.469	43.138	754.059	−15.149
2700	130.783	550.753	443.516	289.539	44.698	781.373	−15.117
2800	130.936	555.512	447.431	302.625	46.224	808.630	−15.085
2900	131.074	560.109	451.238	315.726	47.718	835.831	−15.055
3000	131.200	564.555	454.942	328.840	49.178	862.983	−15.026
3100	131.313	568.859	458.547	341.966	50.606	890.087	−14.998
3200	131.417	573.029	462.060	355.102	52.002	917.144	−14.971
3300	131.511	577.075	465.484	368.249	53.368	944.157	−14.945
3400	131.597	581.002	468.824	381.404	54.703	971.132	−14.920
3500	131.677	584.818	472.084	394.568	56.010	998.066	−14.895
3600	131.750	588.528	475.268	407.739	57.288	1024.964	−14.872
3700	131.817	592.139	478.378	420.918	58.538	1051.826	−14.849
3800	131.879	595.655	481.418	434.102	59.762	1078.657	−14.827
3900	131.936	599.082	484.391	447.293	60.960	1105.455	−14.806
4000	131.990	602.423	487.300	460.490	62.132	1132.220	−14.785
4100	132.039	605.683	490.148	473.691	63.279	1158.958	−14.765
4200	132.085	608.865	492.937	486.897	64.402	1185.669	−14.746
4300	132.128	611.973	495.669	500.108	65.501	1212.353	−14.727
4400	132.168	615.011	498.347	513.323	66.575	1239.011	−14.709
4500	132.206	617.982	500.973	526.542	67.626	1265.644	−14.691
4600	132.241	620.888	503.548	539.764	68.653	1292.255	−14.674
4700	132.274	623.733	506.075	552.990	69.654	1318.845	−14.657
4800	132.305	626.518	508.555	566.219	70.630	1345.413	−14.641
4900	132.334	629.246	510.991	579.451	71.581	1371.962	−14.625
5000	132.361	631.920	513.383	592.685	72.504	1398.491	−14.610
5100	132.387	634.541	515.733	605.923	73.400	1425.003	−14.595
5200	132.411	637.112	518.042	619.163	74.267	1451.494	−14.580
5300	132.434	639.635	520.313	632.405	75.104	1477.973	−14.566
5400	132.456	642.110	522.545	645.649	75.908	1504.434	−14.553
5500	132.476	644.541	524.742	658.896	76.680	1530.880	−14.539
5600	132.496	646.928	526.902	672.145	77.417	1557.315	−14.526
5700	132.514	649.273	529.029	685.395	78.116	1583.734	−14.513
5800	132.532	651.578	531.122	698.648	78.776	1610.145	−14.501
5900	132.549	653.844	533.183	711.902	79.394	1636.539	−14.489
6000	132.564	656.072	535.212	725.157	79.968	1662.928	−14.477

PREVIOUS: September 1964 (1 atm) CURRENT: September 1964 (1 bar)

$S°(298.15\ K) = 346.548 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = 11.297 \pm 1.3\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies				
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
1728(1)	614 (1)	[614](1)	[Rotation]	860(1)
1338(1)	353 (1)	[Rotation]	1728(1)	743(1)
743(1)	[85](1)	577 (1)	1247(1)	353(1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distances: O–N = 1.21 Å N–O' = 1.46 Å
Bond Angles: O–N–O = 134° N–O'–N = 95°
O–N–O planes perpendicular to N–O'–N plane
Product of the Moments of Inertia: $I_A I_B I_C = 2.066 \times 10^{-113}\ g^3 \cdot cm^6$

Enthalpy of Formation

The enthalpy of formation was obtained by recalculation of the calorimetric data of Ray and Ogg for the reaction of N_2O_5(g) with NO. The stoichiometry of the reaction products, originally based on the results for $N_2O_4 \rightarrow 2\ NO_2$ from Giauque and Kemp[1] was based on the JANAF analysis of this simultaneous equilibrium. A correction of 0.29 kcal·mol^{-1} was made in the enthalpy of reaction because of the additional formation of N_2O_3 from NO and NO_2.

Confirmation of the enthalpy of formation was obtained by combination of the enthalpies of hydrolysis and sublimation of N_2O_5(cr). The results are summarized below. 2nd law values are given for the enthalpies of sublimation, but 3rd law analyses suggest that the value from Russ and Pokorny[4] is more reliable. Most of the uncertainty in this path, however, arises from the enthalpy of hydrolysis.

Source	Method	Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
[2]	Calorimetric	$N_2O_5(g) + NO(g) \rightarrow 0.724\ NO_2(g) + 1.138\ N_2O_4(g)$	-16.05 ± 0.20	2.67
[3]	Calorimetric	$N_2O_5(cr) + H_2O(l) \rightarrow 2\ HNO_3(aq)$	-20.2 ± 0.5	--
[4]	Vapor Pressure	$N_2O_5(cr) \rightarrow N_2O_5(g)$	13.37 ± 0.06	2.79*
[5]	Vapor Pressure	$N_2O_5(cr) \rightarrow N_2O_5(g)$	13.25 ± 0.12	2.67*

*Using reaction 2 and $\Delta_f H°(298.15\ K) = -68.32(H_2O, l), -49.55(HNO_3, aq)$.

Heat Capacity and Entropy

Ray and Ogg[6] reported $S°(298.15\ K) = 85 \pm 0.5$ cal·K^{-1}·mol^{-1} from combination of kinetic and thermochemical values. This entropy was recalculated as follows. The rate data of Ray and Ogg[6] and of Daniels and Johnston[7] give for the reaction $N_2O_5(g) \rightarrow NO(g) + NO_2(g) + O_2(g)$ at 25°C the equilibrium constant $K = 5.15 \times 10^{-7}$ moles^2 liter^{-2} $= 3.08 \times 10^{-4}$ atm^2. The resulting value of $\Delta_r H°(298.15\ K) = 4.79$ kcal·mol^{-1} leads to $S°(298.15\ K) = 82.8$ cal·K^{-1}·mol^{-1} for N_2O_5(g) when combined with the JANAF entropies and heats of formation of the components of the reaction.

The molecular structure is the nonplanar configuration from the electron diffraction study of Akishin *et al.*[8] A planar model (also point group C_{2v}) was assumed by Hisatsune *et al.*[9] in their approximate normal coordinate analysis of the infrared and Raman spectra. The frequency assignments of these authors are listed above in the order for the planar model, although the vibrations for the nonplanar form will separate differently into the species $5A_1$, $3A_2$, $3B_1$ and $4B_2$. Hisatsune *et al.*[9] estimated the N–O'–N deformation frequency (8 cm^{-1}) from combination bands in the solid and gas phase spectra. The JANAF thermodynamic functions were obtained using these frequencies and assuming the two NO_2 groups to be hindered internal rotators. Barriers to internal rotation of 4.4 kcal·mol^{-1} (corresponding to torsional vibratons of about 55 cm^{-1}) were selected in order to give the observed entropy at room temperature. The principal moments of inertia for the nonplanar model were taken as $I_A = 30.60 \times 10^{-39}$, $I_B = 40.15 \times 10^{-39}$, and $I_C = 16.82 \times 10^{-39}$ g·cm^2, while $I_r = 4.693 \times 10^{-39}$ g·cm^2 was used for the reduced moment of inertia of the O_2 tops.

References

[1]Giauque and Kemp, J. Chem. Phys. **6**, 40 (1938).
[2]J. D. Ray and R. A. Ogg, J. Phys. Chem. **61**, 1087 (1957).
[3]R. A. Ogg, J. Chem. Phys. **15**, 337 (1947).
[4]Russ and Pokorny, Monatsh. **34**, 1027 (1913).
[5]F. Daniels and A. C. Bright, J. Amer. Chem. Soc. **42**, 1131 (1920).
[6]J. D. Ray and R. A. Ogg, J. Chem. Phys. **26**, 984 (1957).
[7]F. Daniels and Johnston, J. Amer. Chem. Soc. **43**, 53 (1921).
[8]Akishin, Vilkov and Rosolovskii, Zhur. Strukt. Khim. **1**, 1 (1960).
[9]Hisatsune, Devlin and Wada, Spectrochim. Acta **18**, 1641 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200	78.203	311.842	354.795	−8.591	12.733	83.104	−21.704
298.15	96.303	346.548	346.548	0.	11.297	118.013	−20.675
300	96.604	347.145	346.550	0.178	11.285	118.675	−20.663
400	110.851	376.991	350.523	10.587	11.349	154.497	−20.175
500	121.190	402.904	358.466	22.219	12.395	190.178	−19.868
600	128.382	425.677	367.809	34.720	14.013	225.590	−19.639
700	133.432	445.869	377.546	47.826	15.940	260.703	−19.454
800	137.001	463.930	387.235	61.356	18.018	295.528	−19.296
900	139.599	480.224	396.677	75.192	20.164	330.089	−19.158
1000	141.444	495.031	405.784	89.248	22.324	364.409	−19.035
1100	142.829	508.579	414.522	103.463	24.470	398.514	−18.924
1200	143.971	521.058	422.886	117.805	26.591	432.424	−18.823
1300	144.816	532.616	430.888	132.246	28.680	466.158	−18.730
1400	145.528	543.375	438.543	146.764	30.731	499.734	−18.645
1500	146.078	553.434	445.871	161.345	32.741	533.163	−18.566
1600	146.553	562.877	452.892	175.977	34.706	566.460	−18.493
1700	146.879	571.772	459.626	190.649	36.623	599.636	−18.425
1800	147.179	580.176	466.091	205.352	38.487	632.699	−18.360
1900	147.454	588.141	472.307	220.084	40.300	665.662	−18.300
2000	147.704	595.711	478.290	234.842	42.064	698.530	−18.244
2100	147.846	602.921	484.054	249.620	43.773	731.311	−18.190
2200	147.981	609.802	489.615	264.411	45.424	764.013	−18.140
2300	148.109	616.383	494.985	279.216	47.018	796.640	−18.092
2400	148.230	622.689	500.175	294.033	48.558	829.198	−18.047
2500	148.344	628.742	505.198	308.861	50.043	861.694	−18.004
2600	148.450	634.562	510.062	323.701	51.475	894.131	−17.963
2700	148.549	640.167	514.777	338.551	52.857	926.516	−17.925
2800	148.641	645.571	519.353	353.411	54.188	958.850	−17.888
2900	148.726	650.788	523.796	368.279	55.470	991.134	−17.852
3000	148.804	655.832	528.113	383.156	56.704	1023.378	−17.819
3100	148.851	660.712	532.312	398.038	57.892	1055.582	−17.786
3200	148.896	665.438	536.399	412.926	59.032	1087.746	−17.756
3300	148.939	670.021	540.379	427.818	60.127	1119.875	−17.726
3400	148.980	674.468	544.258	442.714	61.180	1151.974	−17.698
3500	149.019	678.787	548.040	457.614	62.190	1184.041	−17.671
3600	149.057	682.985	551.730	472.517	63.161	1216.080	−17.645
3700	149.092	687.070	555.333	487.425	64.094	1248.092	−17.620
3800	149.125	691.046	558.853	502.336	64.989	1280.082	−17.596
3900	149.156	694.920	562.292	517.250	65.849	1312.047	−17.573
4000	149.185	698.697	565.655	532.167	66.674	1343.989	−17.551
4100	149.206	702.381	568.945	547.086	67.465	1375.912	−17.529
4200	149.227	705.977	572.165	562.008	68.223	1407.816	−17.509
4300	149.247	709.488	575.318	576.932	68.948	1439.704	−17.489
4400	149.267	712.920	578.407	591.858	69.640	1471.572	−17.470
4500	149.285	716.274	581.433	606.785	70.301	1503.426	−17.451
4600	149.303	719.556	584.400	621.715	70.929	1535.266	−17.433
4700	149.319	722.767	587.310	636.646	71.525	1567.093	−17.416
4800	149.335	725.911	590.165	651.578	72.088	1598.908	−17.400
4900	149.350	728.990	592.967	666.513	72.616	1630.713	−17.384
5000	149.365	732.007	595.718	681.448	73.111	1662.506	−17.368
5100	149.378	734.965	598.419	696.386	73.569	1694.290	−17.353
5200	149.391	737.866	601.073	711.324	73.990	1726.062	−17.339
5300	149.402	740.712	603.681	726.264	74.373	1757.831	−17.324
5400	149.413	743.505	606.244	741.204	74.714	1789.590	−17.311
5500	149.423	746.246	608.765	756.146	75.014	1821.343	−17.298
5600	149.432	748.939	611.244	771.089	75.269	1853.094	−17.285
5700	149.441	751.584	613.683	786.033	75.477	1884.838	−17.273
5800	149.448	754.183	616.083	800.977	75.635	1916.581	−17.261
5900	149.455	756.738	618.446	815.922	75.741	1948.317	−17.249
6000	149.461	759.250	620.772	830.868	75.791	1980.057	−17.238

PREVIOUS: December 1964 (1 atm) CURRENT: December 1964 (1 bar)

$S°(298.15\ K) = [226.469 \pm 2.1]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 416.97 \pm 20.9\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 414.22 \pm 20.9\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{g3/2}$	0	2
$X^2\Pi_{g1/2}$	71.3	2
$A^2\Sigma_u^+$	36811	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[1800](1)
[500](2)
[1200](1)

Point Group: $D_{\infty h}$ $\sigma = 2$
Bond Distance: N–N = 1.1815 Å
Bond Angle: N–N–N = 180°
Rotational Constant: $B_0 = 0.431085\ cm^{-1}$

Enthalpy of Formation

Okabe and Mele[1] have measured the photodissociation onset of the process

$$CN\cdot N_3(g) \rightarrow CN(g) + N_3(g) \qquad \Delta H°(0\ K) = 96 \pm 2.5\ kcal\cdot mol^{-1}$$

Using a value of $\Delta_f H°(CN\cdot N_3, g, 298.15\ K) = 107 \pm 3\ kcal\cdot mol^{-1}$ and $\Delta_f H°(CN, g, 298.15\ K) = 104 \pm 2.5\ kcal\cdot mol^{-1}$,[1,2] we derive $\Delta_f H°(N_3, g, 298.15\ K) = 99 \pm 5\ kcal\cdot mol^{-1}$. The enthalpy of formation of $CN\cdot N_3$ is obtained from $\Delta_f H°(CN\cdot N_3, cr, 298.15\ K) = 92.6 \pm 3\ kcal\cdot mol^{-1}$[3] and an estimated $\Delta_{sub}H°(298.15\ K) = 14.4 \pm 3\ kcal\cdot mol^{-1}$. The enthalpy of sublimation is similar to that for ICN(cr).[2] A rough confirmation of $\Delta_{sub}H°$ can be made by assuming a boiling point of 227°C (500 K), from the facts that $CN\cdot N_3$ sublimes in vacuo at 40°C and can be heated as a liquid to 170°C. Thus, using the Trouton rule, $\Delta_{vap}H° = 11\ kcal\cdot mol^{-1}$, in addition the enthalpy of melting would be expected to be about 3.6 $kcal\cdot mol^{-1}$ for this 5 atom molecule, thus $\Delta_{sub}H° = 14.6\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The electronic levels and rotational constants have been reported by Douglas and Jones[4] and Thrush.[5] The vibrational frequencies were estimated from the isoelectronic species NCO, NNO^+, and the related molecules NCN and NNO.[2]

References

[1] H. Okabe and A. Mele, J. Chem. Phys. **51**, 2100 (1959).
[2] JANAF Thermochemical Tables: CN(g), 6–30–69; ICN(g), 6–30–69; NCO(g), 12–31–70; NNO^+(g), 12–31–70; NCN(g), 12–31–70; N_2O(g), 12–31–64.
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[5] B. A. Thrush, Proc. Roy. Soc. (London) **235A**, 143 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.253	416.969	416.969	INFINITE
100	31.448	188.244	259.348	−7.110	415.757	420.905	−219.858
200	35.960	211.175	230.051	−3.775	414.727	426.487	−111.387
250	38.562	219.485	227.128	−1.911	414.408	429.467	−89.732
298.15	40.762	226.469	226.469	0.	414.216	432.387	−75.752
300	40.842	226.721	226.470	0.075	414.211	432.499	−75.305
350	42.864	233.172	226.974	2.169	414.119	435.556	−65.003
400	44.686	239.016	228.120	4.359	414.118	438.620	−57.278
450	46.339	244.377	229.633	6.635	414.196	441.679	−51.269
500	47.838	249.338	231.358	8.990	414.340	444.725	−46.460
600	50.407	258.295	235.117	13.907	414.782	450.764	−39.242
700	52.470	266.226	239.006	19.054	415.365	456.716	−34.081
800	54.113	273.344	242.861	24.387	416.033	462.578	−30.203
900	55.421	279.796	246.612	29.866	416.748	468.354	−27.183
1000	56.467	285.691	250.229	35.462	417.484	474.048	−24.762
1100	57.308	291.114	253.703	41.152	418.228	479.669	−22.778
1200	57.992	296.131	257.032	46.919	418.971	485.222	−21.121
1300	58.552	300.796	260.221	52.747	419.709	490.712	−19.717
1400	59.015	305.152	263.277	58.626	420.437	496.147	−18.511
1500	59.402	309.238	266.206	64.547	421.156	501.530	−17.465
1600	59.727	313.082	269.017	70.504	421.865	506.865	−16.547
1700	60.003	316.711	271.717	76.491	422.563	512.156	−15.737
1800	60.239	320.148	274.313	82.503	423.252	517.406	−15.015
1900	60.442	323.410	276.812	88.538	423.932	522.618	−14.368
2000	60.617	326.515	279.220	94.591	424.602	527.795	−13.785
2100	60.770	329.477	281.543	100.660	425.264	532.938	−13.256
2200	60.904	332.307	283.787	106.744	425.918	538.050	−12.775
2300	61.022	335.017	285.956	112.841	426.565	543.132	−12.335
2400	61.127	337.616	288.054	118.948	427.204	548.187	−11.931
2500	61.219	340.113	290.087	125.066	427.837	553.215	−11.559
2600	61.302	342.516	292.058	131.192	428.464	558.217	−11.215
2700	61.376	344.831	293.970	137.326	429.084	563.196	−10.896
2800	61.443	347.064	295.826	143.467	429.699	568.152	−10.599
2900	61.503	349.221	297.630	149.614	430.308	573.086	−10.322
3000	61.558	351.307	299.385	155.767	430.912	577.999	−10.064
3100	61.607	353.327	301.093	161.926	431.510	582.892	−9.822
3200	61.652	355.283	302.756	168.089	432.104	587.766	−9.594
3300	61.693	357.181	304.376	174.256	432.693	592.621	−9.380
3400	61.731	359.024	305.957	180.427	433.278	597.459	−9.179
3500	61.766	360.813	307.499	186.602	433.858	602.279	−8.989
3600	61.798	362.554	309.004	192.780	434.434	607.083	−8.809
3700	61.827	364.248	310.474	198.962	435.006	611.871	−8.638
3800	61.855	365.897	311.911	205.146	435.574	616.643	−8.476
3900	61.880	367.504	313.316	211.332	436.138	621.401	−8.323
4000	61.904	369.071	314.690	217.522	436.697	626.144	−8.177
4100	61.926	370.600	316.035	223.713	437.253	630.874	−8.037
4200	61.946	372.092	317.352	229.907	437.806	635.589	−7.905
4300	61.966	373.550	318.642	236.102	438.354	640.292	−7.778
4400	61.984	374.975	319.907	242.300	438.899	644.982	−7.657
4500	62.001	376.368	321.146	248.499	439.440	649.660	−7.541
4600	62.018	377.731	322.361	254.700	439.978	654.325	−7.430
4700	62.033	379.065	323.553	260.903	440.512	658.979	−7.324
4800	62.048	380.371	324.724	267.107	441.042	663.622	−7.222
4900	62.063	381.650	325.872	273.312	441.568	668.253	−7.124
5000	62.077	382.904	327.001	279.519	442.091	672.874	−7.029
5100	62.090	384.134	328.109	285.728	442.610	677.485	−6.939
5200	62.103	385.340	329.198	291.937	443.125	682.085	−6.852
5300	62.116	386.523	330.268	298.148	443.637	686.676	−6.768
5400	62.128	387.684	331.321	304.360	444.144	691.256	−6.687
5500	62.141	388.824	332.356	310.574	444.649	695.828	−6.608
5600	62.153	389.944	333.374	316.788	445.149	700.390	−6.533
5700	62.165	391.044	334.377	323.004	445.644	704.944	−6.460
5800	62.177	392.125	335.363	329.222	446.135	709.489	−6.390
5900	62.189	393.188	336.334	335.440	446.622	714.025	−6.321
6000	62.202	394.234	337.290	341.659	447.103	718.553	−6.256

PREVIOUS: December 1970 (1 atm) CURRENT: December 1970 (1 bar)

$S°(298.15\ K) = [112.967 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -744.752 \pm 29.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The equilibria (A) $Si_3N_4(cr) = 3\ Si(l) + 2\ N_2(g)$ and (B) $Si_3N_4(cr) = 3\ Si(cr) + 2\ N_2(g)$ have been investigated by three groups. Pehlke and Elliott[1] made four series of measurements which mainly concerned reaction (A). Hincke and Brantley[2] made a single series of measurements which covered reactions (A) and (B). Matignon[3] also gave a single equilibrium point for reaction (C) $3\ SiO_2(cr) + 6\ C + 2\ N_2 = Si_3N_4(cr) + 6\ CO(g)$. Below are shown 2nd and 3rd law analyses of the data. It should be noted that these analyses are based on the estimated enthalpy capacities above 900 K and on an estimated entropy. The uncertainty due to these estimates is estimated as $\pm 7\ kcal \cdot mol^{-1}$ in $\Delta_f H°(298.15\ K)$.

Source	Data Points	T/K	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
Pehlke – 1	9	1699–1934	A	190.1 ± 7.6	211.79	11.8 ± 4.3	−177.04
Pehlke – 2	9	1691–1939	A	210.7 ± 8.6	213.29	1.8 ± 4.9	−178.53
Pehlke – 3	10	1692–1966	A	212.3 ± 3.3	212.61	0.1 ± 1.9	−177.85
Pehlke – 4	6	1690–1872	A	207.0 ± 7.5	212.47	2.6 ± 4.3	−177.71
Pehlke	30**	1690–1966	A	212.8 ± 3.2	212.67	−0.2 ± 1.8	−177.91
Hinke	4	1709–1802	A	196.0 ± 18.5	213.43	10.3 ± 10.4	−178.67
Pehlke	4	1659–1666	B		177.41		−177.41
Hinke	3	1606–1675	B		177.82	22.8 ± 11.8	−177.82
Matignon	1	1700	C		318.9		−175.1

**Four points rejected due to failure of a statistical test; this set is a combination of the first four sets.

The adopted $\Delta_f H°(\alpha\text{–}Si_3N_4, 298.15\ K) = -178 \pm 7\ kcal \cdot mol^{-1}$.

McClaine and Coppel[4] have investigated the decomposition reaction (B). The conclude that at 1618 K the equilibrium pressure is roughly 0.15 mm. This corresponds to $\Delta_f H°(298.15\ K) = 182.3\ kcal \cdot mol^{-1}$, and was not given any weight in the adopted value.

Heat Capacity and Entropy

The enthalpy of α–Si_3N_4 has been measured at three temperatures, in the range 373–858 K, by Sato.[5] The heat capacity is calculated from the data assuming that a limit of $45\ cal \cdot K^{-1} \cdot mol^{-1}$ is attained by 3000 K. The entropy is obtained from the equilibrium data of Pehlke and Elliott.[1]

Decomposition Data

The temperature of decomposition, $T_{dcm} = 2151$ K, is calculated as the point at which the decomposition pressure of nitrogen reaches a fugacity of 1 atm.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	99.533	112.967	112.967	0.	−744.752	−647.343	113.412
300	99.788	113.583	112.969	0.184	−744.787	−646.739	112.607
400	110.667	143.790	117.014	10.711	−746.459	−613.792	80.153
500	120.708	169.582	125.007	22.288	−747.595	−580.482	60.643
600	129.704	192.417	134.374	34.826	−748.151	−546.998	47.620
700	138.072	213.048	144.162	48.220	−748.186	−513.462	38.315
800	145.812	232.003	153.973	62.424	−747.729	−479.956	31.338
900	152.298	249.566	163.631	77.342	−746.850	−446.533	25.916
1000	158.155	265.920	173.051	92.869	−745.635	−413.227	21.585
1100	163.678	281.258	182.198	108.966	−744.100	−380.058	18.047
1200	168.490	295.712	191.061	125.581	−742.280	−347.041	15.106
1300	172.531	309.362	199.641	142.637	−740.233	−314.187	12.624
1400	175.920	322.276	207.944	160.065	−738.019	−281.496	10.503
1500	178.657	334.510	215.977	177.799	−735.694	−248.968	8.670
1600	180.548	346.102	223.751	195.762	−733.327	−216.597	7.071
1700	182.171	357.098	231.274	213.900	−881.495	−183.033	5.624
1800	183.452	367.548	238.557	232.183	−878.469	−142.034	4.122
1900	184.539	377.496	245.610	250.584	−875.367	−101.205	2.782
2000	185.435	386.986	252.444	269.084	−872.202	−60.541	1.581
2100	185.780	396.041	259.068	287.645	−869.010	−20.037	0.498
2200	186.111	404.692	265.492	306.240	−865.814	20.316	−0.482
2300	186.429	412.972	271.725	324.867	−862.612	60.523	−1.375
2400	186.734	420.913	277.777	343.525	−859.403	100.590	−2.189
2500	187.025	428.541	283.656	362.213	−856.187	140.524	−2.936
2600	187.303	435.882	289.371	380.930	−852.962	180.329	−3.623
2700	187.567	442.956	294.929	399.673	−849.729	220.009	−4.256
2800	187.818	449.782	300.338	418.443	−846.487	259.570	−4.842
2900	188.056	456.377	305.606	437.236	−843.236	299.015	−5.386
3000	188.280	462.756	310.738	456.053	−839.977	338.347	−5.891

PREVIOUS: December 1960 CURRENT: March 1967

$S°(298.15\ K) = [184.096 \pm 25.1]\ J \cdot K^{-1}\ mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -320.155 \pm 20.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is based on the work of Stock and Wrede[1] who burned P_3N_5 in oxygen. They report a $\Delta_f H°(298.15\ K) = -949.4$ kcal·mol^{-1} for the reaction 2 P_3N_5(cr) + 7.5 O_2(g) = 1.5 P_4O_{10}(amorph) + 5 N_2(g). In[2] a value of −947.7 kcal·mol^{-1} is used for the above reaction and we adopt this value. Using the JANAF value of P_4O_{10}(cr) and correcting this to P_4O_{10}(amorph) by adding 13.8 kcal·mol^{-1}, from[2] we obtain $\Delta_f H°(298.15\ K)$ P_4O_{10}(amorph) = −716.5 kcal·mol^{-1}. Thus, we derive $\Delta_f H°(P_3N_5, cr, 298.15\ K) = -63.525$ kcal·mol^{-1}; however, because of the uncertainties in the enthalpy of reaction and correction for amorphous P_4O_{10}, we round the value to −64 ± 5 kcal·mol^{-1}.

Heat Capacity and Entropy

Sato[3] gave an equation for the heat capacity in the range 273–578 K. Judging from his results for Be_3N_2(cr) in the same paper, we believe his values will be slightly high at the upper end of the range. Thus, taking 8.2 cal·K^{-1} g atom as the limiting value, a curve was drawn through Sato's values at the low end and approaching the limit asympototically. The entropy was estimated from that of Si_3N_4(cr) by assuming that the ratio $C_p°(298.15\ K)/S°(298.15\ K)$ on a gram atom basis would be the same for P_3N_5(cr).

Decomposition Data

T_{dcm} = 730 K is calculated as the point at which the total pressure reaches a fugacity of 1 atm. This corresponds to log $K_p°$ = 0.76 for the reaction P_3N_5(cr) = 0.75 P_4(g) + 2.5 N_2(g). The temperature of decomposition has been reported by Postnikov and Kuzmin[4] as 1073 K. This has been confirmed by Moreau and Rocquet[5] and Huffman *et. al.*[6] However, it was also noted that P_3N_5(cr) is not reformed on cooling the decomposition products; thus the decomposition is non equilibrium. It is known that the decomposition of AlN, BN and Be_3N_2 is kinetically limited and the equilibrium pressure is not attained until the average energy is greater than the activation energy. It appears that this is also the case for P_3N_5 and a high activation energy is expected.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	148.950	184.096	184.096	0.	−320.155	−195.482	34.248
300	149.787	185.020	184.099	0.276	−320.146	−194.708	33.902
400	192.464	234.376	190.538	17.535	−319.936	−152.610	19.929
500	217.568	280.175	203.962	38.107	−314.612	−111.344	11.632
600	234.304	321.385	220.160	60.735	−307.339	−71.348	6.211
700	246.856	358.500	237.317	84.828	−298.751	−32.680	2.439
800	255.224	392.032	254.596	109.949	−289.301	4.694	−0.306
900	261.500	422.480	271.584	135.807	−279.283	40.846	−2.371
1000	265.266	450.236	288.083	162.153	−268.934	75.864	−3.963
1100	267.888	475.646	303.995	188.816	−258.412	109.835	−5.216
1200	269.868	499.045	319.287	215.709	−438.505	146.079	−6.359
1300	271.207	520.703	333.958	242.768	−425.504	194.267	−7.806
1400	271.904	540.831	348.025	269.929	−412.515	241.454	−9.009
1500	271.960	559.596	361.511	297.128	−399.588	287.715	−10.019

PREVIOUS: September 1962 CURRENT: March 1967

Continued from page 1606

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Continued from page 1615

Decomposition Data

The melting point of VN has been reported to be approximately 2323 K by Rostoker and Yamamoto.[15] However, Farber and Srivastava[5] in their mass spectrometric studies observed solid nitride at temperatures as high as 2412 K. Liquid vanadium metal, presumably formed from decomposition of the nitride, was deposited in the sample. We assume that VN decomposes to its elements prior to melting. $T_{dcm} = 2619$ K is the temperature at which the fugacity is 1 atm for the decomposition reaction $VN(cr) \rightarrow V(l) + 0.5\ N_2(g)$ approaches zero. $\Delta_{dcm}H°$ is the negative of the heat of formation of VN(cr) at T_{dcm}.

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REFERENCE STATE

0	to	370.98	K crystal
370.98	to	1170.525	K liquid
above		117.525	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.447	0.	0.	0.
55.120	18.800	11.738	121.072	−6.027	C_p HUMP MAXIMUM TRANSITION		
55.120	18.791	11.738	121.072	−6.027			
100	22.451	23.814	74.885	−5.107	0.	0.	0.
200	25.987	40.697	53.954	−2.651	0.	0.	0.
250	27.008	46.604	51.911	−1.327	0.	0.	0.
298.15	28.154	51.455	51.455	0.	0.	0.	0.
300	28.204	51.629	51.455	0.052	0.	0.	0.
370.980	31.583	57.898	52.098	2.152	CRYSTAL <--> LIQUID TRANSITION		
370.980	31.827	64.915	52.098	4.755			
400	31.510	67.301	53.116	5.674	0.	0.	0.
500	30.552	74.225	56.675	8.775	0.	0.	0.
600	29.807	79.726	60.074	11.791	0.	0.	0.
700	29.271	84.278	63.216	14.743	0.	0.	0.
800	28.945	88.163	66.097	17.652	0.	0.	0.
900	28.836	91.564	68.742	20.540	0.	0.	0.
1000	28.945	94.606	71.179	23.427	0.	0.	0.
1100	29.259	97.377	73.436	26.335	0.	0.	0.
1170.525	29.613	99.206	74.934	28.411	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1170.525	20.786	182.094	74.934	125.433			
1200	20.786	182.611	77.573	126.046	0.	0.	0.
1300	20.786	184.275	85.717	128.124	0.	0.	0.
1400	20.786	185.815	92.813	130.203	0.	0.	0.
1500	20.787	187.249	99.061	132.282	0.	0.	0.
1600	20.787	188.591	104.616	134.360	0.	0.	0.
1700	20.789	189.851	109.593	136.439	0.	0.	0.
1800	20.792	191.039	114.085	138.518	0.	0.	0.
1900	20.797	192.164	118.165	140.598	0.	0.	0.
2000	20.805	193.231	121.892	142.678	0.	0.	0.
2100	20.816	194.246	125.313	144.759	0.	0.	0.
2200	20.833	195.215	128.469	146.841	0.	0.	0.
2300	20.856	196.141	131.391	148.925	0.	0.	0.
2400	20.886	197.029	134.108	151.012	0.	0.	0.
2500	20.924	197.883	136.642	153.103	0.	0.	0.
2600	20.973	198.704	139.013	155.198	0.	0.	0.
2700	21.032	199.497	141.238	157.298	0.	0.	0.
2800	21.104	200.263	143.333	159.405	0.	0.	0.
2900	21.189	201.005	145.309	161.519	0.	0.	0.
3000	21.289	201.725	147.177	163.643	0.	0.	0.
3100	21.403	202.425	148.948	165.777	0.	0.	0.
3200	21.535	203.106	150.630	167.924	0.	0.	0.
3300	21.680	203.771	152.230	170.084	0.	0.	0.
3400	21.845	204.421	153.756	172.260	0.	0.	0.
3500	22.030	205.057	155.213	174.454	0.	0.	0.
3600	22.234	205.680	156.606	176.667	0.	0.	0.
3700	22.460	206.292	157.941	178.901	0.	0.	0.
3800	22.709	206.894	159.221	181.160	0.	0.	0.
3900	22.981	207.488	160.451	183.444	0.	0.	0.
4000	23.278	208.073	161.634	185.757	0.	0.	0.
4100	23.602	208.652	162.774	188.100	0.	0.	0.
4200	23.945	209.224	163.873	190.475	0.	0.	0.
4300	24.324	209.792	164.934	192.889	0.	0.	0.
4400	24.611	210.345	165.959	195.298	0.	0.	0.
4500	24.992	210.901	166.952	197.769	0.	0.	0.
4600	25.421	211.454	167.913	200.289	0.	0.	0.
4700	25.876	212.006	168.846	202.854	0.	0.	0.
4800	26.359	212.556	169.750	205.466	0.	0.	0.
4900	26.868	213.104	170.630	208.127	0.	0.	0.
5000	27.388	213.651	171.484	210.832	0.	0.	0.
5200	28.537	214.747	173.127	216.423	0.	0.	0.
5400	29.789	215.847	174.689	222.254	0.	0.	0.
5600	31.141	216.955	176.179	228.346	0.	0.	0.
5800	32.583	218.073	177.604	234.717	0.	0.	0.
6000	33.880	219.173	178.969	241.226	0.	0.	0.

PREVIOUS: June 1962 (1 atm) CURRENT: June 1962 (1 bar)

$S°(298.15\ K) = 51.455\ J·K^{-1}·mol^{-1}$
$T_{fus} = 370.98 \pm 0.02\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 2.602\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Martin[1] reports that the low temperature heat capacity of sodium depends on the thermal history of the sample and ascribes this to a martensitic transformation. The effect is most pronounced in the range 40–80 K, where the graph of C_p against T increases continuously for some samples and rises to a peak at 55 K for others. Martin[1] lists heat capacities obtained in several runs on "high purity" sodium at 21 to 300 K and the higher values, those defining the peak at 55 K, have been selected here. The heat capacities reported by Dauphinee *et al.*,[2] have not been used, since one of the authors in a later publication, Martin[1] questions the accuracy of the measurements above 100 K, and at lower temperatures there is no rise to a peak at 55 K. In the range 1.5 to 20 K, Roberts[3] and Parkinson and Quarrington[4] have measured the heat capacity of very high purity sodium. The values of Parkinson and Quarrington[4] are somewhat higher than those of Roberts[3] and have been given greater weight, since they show better continuity with Martin's[1] results. The results of Pickard and Simon[5] have been rejected below 10 K, since they show a peak between 5 and 8 K, a feature not verified by other workers; between 10 and 25 K they agree exactly with the results of Parkinson and Quarrington.[4] Rayne[6] states that the graph of C_p against T has a small peak at about 0.9 K. This peak has not been observed in the work of Lien and Phillips[7] from 0.15 to 1 K; Gaumer and Heer from 0.4 to 2 K and Martin[9] from 0.4 to 1.5 K.

Douglas *et al.*[10] report heat capacities in the range 273 to 1173 K on a sample of not less than 99.9% purity. These values agree to within 1% with those of Martin[1] in the range 273 to 300 K, and the two sets of dates have been smoothly joined.

Fusion Data

Douglas *et al.*[10] have determined the triple point to be 97.82 ± 0.02°C, from which the melting point is calculated to be 97.83 ± 0.02°C, and have measured the enthalpy of fusion.

Sublimation Data

At the boiling point and higher temperatures sodium vapor contains an appreciable proportion of diatomic moleculses. Thompson and Garelis[11] have made a careful analysis of the available vapor pressure data. Their results are consistent with the Gibbs energy functions calculated in the present work and have been adopted.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−6.447	0.	0.	0.
55.120	18.800	11.738	121.072	−6.027	C_p HUMP MAXIMUM		
55.120	18.791	11.738	121.072	−6.027	TRANSITION		
100	22.451	23.814	74.885	−5.107	0.	0.	0.
200	25.987	40.697	53.954	−2.651	0.	0.	0.
250	27.008	46.604	51.911	−1.327	0.	0.	0.
298.15	28.154	51.455	51.455	0.	0.	0.	0.
300	28.204	51.629	51.455	0.052	0.	0.	0.
350	30.142	56.104	51.805	1.505	0.	0.	0.
370.980	31.583	57.898	52.098	2.152	--- CRYSTAL <--> LIQUID ---		
400	32.489	60.315	52.608	3.083	−2.591	0.203	−0.027
450	33.103	64.180	53.683	4.724	−2.513	0.548	−0.064
500	33.472	67.689	54.910	6.389	−2.386	0.882	−0.092
600	33.472	73.792	57.564	9.736	−2.055	1.506	−0.131
700	33.472	78.951	60.260	13.084	−1.660	2.069	−0.154
800	33.472	83.421	62.882	16.431	−1.222	2.572	−0.168
900	33.472	87.363	65.388	19.778	−0.762	3.019	−0.175
1000	33.472	90.890	67.765	23.125	−0.302	3.414	−0.178

PREVIOUS: CURRENT: June 1962

$S°(298.15\ K)$ = [57.862] $J·K^{-1}·mol^{-1}$
T_{fus} = 370.98 ± 0.02 K

$\Delta_f H°(298.15\ K)$ = [2.406] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 2.602 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(Na, l, 298.15 K) is calculated from that of the crystal by adding the enthalpy of fusion and the difference in enthalpy, $H°$(370.98 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The liquid heat capacity values are derived from the enthalpy measurements of Douglas *et al.*[1] The heat capacity curve was extrapolated to 298.15 K and 2000 K in a reasonable manner.

The entropy is calculated in a manner anologous to that used for the enthalpy of formation.

Fusion Data

The enthalpy of fusion and the melting point were measured by Douglas *et al.*[1]

Vaporization Data

Sodium vaporizes to a mixture of monatomic and diatomic gas. The total vapor pressure reaches 1 atm at 1156 K. The vapor pressure of the monatomic gas reaches 1 atm at 1176.9 K and the enthalpy of vaporization to monatomic gas is 23.285 $kcal·mol^{-1}$.

Reference

[1]T. B. Douglas, A. F. Ball, D. C. Ginnings and W. D. Davis, J. Am. Chem. Soc. **74**, 2472 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	32.706	57.862	57.862	0.	2.406	0.495	−0.087
300	32.685	58.064	57.863	0.060	2.414	0.483	−0.084
350	32.068	63.056	58.258	1.679	2.580	0.147	−0.022
370.9180	31.827	64.915	58.583	2.349	--- CRYSTAL <--> LIQUID ---		
400	31.510	67.301	59.130	3.268	0.	0.	0.
450	31.004	70.982	60.247	4.831	0.	0.	0.
500	30.552	74.225	61.486	6.370	0.	0.	0.
600	29.807	79.726	64.083	9.386	0.	0.	0.
700	29.271	84.278	66.652	12.338	0.	0.	0.
800	28.945	88.163	69.104	15.247	0.	0.	0.
900	28.836	91.564	71.415	18.134	0.	0.	0.
1000	28.945	94.606	73.584	21.021	0.	0.	0.
1100	29.259	97.377	75.623	23.930	0.	0.	0.
1170.525	29.613	99.206	76.989	26.005	----- FUGACITY = 1 bar -----		
1200	29.790	99.945	77.544	26.881	−96.760	2.440	−0.106
1300	30.514	102.357	79.361	29.895	−95.824	10.669	−0.429
1400	31.351	104.649	81.086	32.988	−94.809	18.823	−0.702
1500	32.188	106.840	82.730	36.165	−93.711	26.902	−0.937
1600	33.024	108.944	84.303	39.426	−92.529	34.905	−1.140

PREVIOUS: CURRENT: June 1962

0 to 370.98 K crystal
above 370.98 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−6.447	0.	0.	0.
55.120	18.800	11.738	121.072	−6.027	——— C_p HUMP MAXIMUM ———		
55.120	18.791	11.738	121.072	−6.027	TRANSITION		
100	22.451	23.814	74.885	−5.107	0.	0.	0.
200	25.987	40.697	53.954	−2.651	0.	0.	0.
250	27.008	46.604	51.911	−1.327	0.	0.	0.
298.15	28.154	51.455	51.455	0.	0.	0.	0.
300	28.204	51.629	51.455	0.052	0.	0.	0.
350	30.142	56.104	51.805	1.505	0.	0.	0.
370.980	31.583	57.898	52.098	2.152	——— CRYSTAL <--> LIQUID ———		
370.980	31.827	64.915	52.098	4.755	TRANSITION		
400	31.510	67.301	53.116	5.674	0.	0.	0.
450	31.004	70.982	54.901	7.236	0.	0.	0.
500	30.552	74.225	56.675	8.775	0.	0.	0.
600	29.807	79.726	60.074	11.791	0.	0.	0.
700	29.271	84.278	63.216	14.743	0.	0.	0.
800	28.945	88.163	66.097	17.652	0.	0.	0.
900	28.836	91.564	68.742	20.540	0.	0.	0.
1000	28.945	94.606	71.179	23.427	0.	0.	0.
1100	29.259	97.377	73.436	26.335	0.	0.	0.
1170.525	29.613	99.206	74.934	28.411	----- FUGACITY = 1 bar -----		
1200	29.790	99.945	75.539	29.286	−96.760	2.440	−0.106
1300	30.514	102.357	77.510	32.300	−95.824	10.669	−0.429
1400	31.351	104.649	79.368	35.394	−94.809	18.823	−0.702
1500	32.188	106.840	81.127	38.571	−93.711	26.902	−0.937
1600	33.024	108.944	82.800	41.831	−92.529	34.905	−1.140

PREVIOUS: CURRENT: June 1962

IP(Na, g) = 41449.44 ± 0.03 cm^{-1}
$S°(298.15\ K)$ = 153.667 ± 0.025 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 107.5 ± 0.7 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 107.3 ± 0.7 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2
$^2P_{1/2}$	16956.172	2
$^2P_{3/2}$	16973.368	4
$^2S_{1/2}$	25739.991	2
.	.	.
.	.	.
.	.	.
$^2P_{3/2}$	41404.006	4
IP	41449.44	

Enthalpy of Formation

The enthalpy of formation of sodium gas, $\Delta_f H°(298.15\ K)$ = 107.5 ± 0.7 $kJ·mol^{-1}$, is chosen to be the value recommended by CODATA.[1] This value was obtained from 2nd and 3rd law treatment of vapor pressure data. The reported vapor pressures were corrected for the effects of $Na_2(g)$, using $D_0°$ = 70.63 $kJ·mol^{-1}$. At higher pressures, an alternate virial treatment was employed.

As stated by CODATA,[1] the selected value is the weighted average of the 3rd law values of $\Delta_{sub}H°(298.15\ K)$ calculated from the following:

Source	$\Delta_{sub}H°(298.15\ K)$, $kJ·mol^{-1}$
Haycock and Lamplough[2]	107.52 ± 0.68
Rodebush and Devries[3]	107.37 ± 0.60
Thiele[4]	107.99 ± 0.60
Kis Tiakowsky[5]	107.38 ± 0.70
Makansi *et al.*[6]	107.18 ± 0.95
Shpil'rain and Belova[7]	107.26 ± 0.78
Sowa[8]	107.60 ± 1.35
Stone *et al.*[9]	107.68 ± 1.33
Achener and Jouthas[10]	107.85 ± 0.80
Vinogradov and Volyak[11]	107.44 ± 0.60
Bohdansky and Schins[12]	107.47 ± 1.00
Schins *et al.*[13]	107.36 ± 1.22

The 2nd law calculations from the above sources led to somewhat more positive values.[1]

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP–kT) technique as the cutoff procedure in the energy level summation.[15]

The lowest lying levels for these metals [14904 cm^{-1} (Li), 16956 cm^{-1} (Na), 12985 cm^{-1} (K), 12578 cm^{-1} (Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm^{-1} for Li to 31406.1 cm^{-1} for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.[15]

The atomic energy levels have been taken from the compilation of Martin and Zalubas.[14] Our calculated values for the thermal functions are similar to those recommended by CODATA.[1] They do differ for two reasons, however. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 $J·K^{-1}·mol^{-1}$, presumably due to the use of slightly different values for auxiliary data.

Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	107.549	107.549	INFINITE
100	20.786	130.960	172.147	−4.119	108.288	97.574	−50.967
200	20.786	145.367	155.568	−2.040	107.911	86.977	−22.716
250	20.786	150.006	154.009	−1.001	107.626	81.776	−17.086
298.15	20.786	153.667	153.667	0.	107.300	76.825	−13.460
300	20.786	153.795	153.667	0.038	107.286	76.636	−13.344
350	20.786	157.000	153.920	1.078	106.873	71.560	−10.680
400	20.786	159.775	154.482	2.117	103.743	66.753	−8.717
450	20.786	162.223	155.209	3.156	103.220	62.161	−7.216
500	20.786	164.413	156.022	4.196	102.721	57.626	−6.020
600	20.786	168.203	157.746	6.274	101.783	48.697	−4.239
700	20.786	171.407	159.475	8.353	100.909	39.919	−2.979
800	20.786	174.183	161.144	10.431	100.079	31.263	−2.041
900	20.786	176.631	162.731	12.510	99.270	22.710	−1.318
1000	20.786	178.821	164.232	14.589	98.462	14.246	−0.744
1100	20.786	180.802	165.650	16.667	97.632	5.865	−0.278
1170.525	20.786	182.094	166.602	18.133	----- FUGACITY = 1 bar -----		
1200	20.786	182.611	166.989	18.746	0.	0.	0.
1300	20.786	184.275	168.256	20.824	0.	0.	0.
1400	20.786	185.815	169.456	22.903	0.	0.	0.
1500	20.787	187.249	170.595	24.982	0.	0.	0.
1600	20.787	188.591	171.678	27.060	0.	0.	0.
1700	20.789	189.851	172.710	29.139	0.	0.	0.
1800	20.792	191.039	173.696	31.218	0.	0.	0.
1900	20.797	192.164	174.639	33.298	0.	0.	0.
2000	20.805	193.231	175.542	35.378	0.	0.	0.
2100	20.816	194.246	176.408	37.459	0.	0.	0.
2200	20.833	195.215	177.241	39.541	0.	0.	0.
2300	20.856	196.141	178.043	41.626	0.	0.	0.
2400	20.886	197.029	178.816	43.713	0.	0.	0.
2500	20.924	197.883	179.562	45.803	0.	0.	0.
2600	20.973	198.704	180.282	47.898	0.	0.	0.
2700	21.032	199.497	180.979	49.998	0.	0.	0.
2800	21.104	200.263	181.654	52.105	0.	0.	0.
2900	21.189	201.005	182.309	54.219	0.	0.	0.
3000	21.289	201.725	182.944	56.343	0.	0.	0.
3100	21.403	202.425	183.561	58.477	0.	0.	0.
3200	21.535	203.106	184.161	60.624	0.	0.	0.
3300	21.680	203.771	184.746	62.784	0.	0.	0.
3400	21.845	204.421	185.315	64.960	0.	0.	0.
3500	22.030	205.057	185.870	67.154	0.	0.	0.
3600	22.234	205.680	186.411	69.367	0.	0.	0.
3700	22.460	206.292	186.941	71.601	0.	0.	0.
3800	22.709	206.894	187.458	73.860	0.	0.	0.
3900	22.981	207.488	187.964	76.144	0.	0.	0.
4000	23.278	208.073	188.459	78.457	0.	0.	0.
4100	23.602	208.652	188.945	80.800	0.	0.	0.
4200	23.945	209.224	189.421	83.175	0.	0.	0.
4300	24.324	209.792	189.888	85.589	0.	0.	0.
4400	24.611	210.345	190.346	87.998	0.	0.	0.
4500	24.992	210.901	190.796	90.469	0.	0.	0.
4600	25.421	211.454	191.239	92.990	0.	0.	0.
4700	25.876	212.006	191.675	95.554	0.	0.	0.
4800	26.359	212.556	192.105	98.166	0.	0.	0.
4900	26.868	213.104	192.528	100.827	0.	0.	0.
5000	27.388	213.651	192.944	103.533	0.	0.	0.
5100	27.949	214.199	193.356	106.299	0.	0.	0.
5200	28.537	214.747	193.762	109.123	0.	0.	0.
5300	29.150	215.297	194.163	112.007	0.	0.	0.
5400	29.789	215.847	194.560	114.954	0.	0.	0.
5500	30.453	216.400	194.952	117.966	0.	0.	0.
5600	31.141	216.955	195.340	121.046	0.	0.	0.
5700	31.851	217.512	195.724	124.195	0.	0.	0.
5800	32.583	218.073	196.104	127.417	0.	0.	0.
5900	33.334	218.636	196.481	130.712	0.	0.	0.
6000	33.880	219.173	196.852	133.926	0.	0.	0.

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

IP(Na^+, g) = 381390 ± 50 eV
$S°$(298.15 K) = 147.953 ± 0.025 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 603.4 ± 0.7 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [609.343] kJ·mol^{-1}

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

$\Delta_f H°(Na^+, g, 0 K)$ is calculated from $\Delta_f H°(Na, g, 0 K)$[1] using the spectroscopic value of IP(Na) = 41449.44 ± 0.03 cm^{-1} (495.846 ± 0.0000 kJ·mol^{-1}) from Martin and Zolubas.[2] The ionization limit is converted from cm^{-1} to kJ·mol^{-1} using the factor, 1 cm^{-1} = 0.01196266 kJ·mol^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Na^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Na, g, 0 K)$ by using IP(Na) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Na(g), $Na^+(g)$, and e^-(ref). $\Delta_r H°(Na \rightarrow Na^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Martin and Zolubas,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[6] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state; the first excited state is approximately 264924 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[6]

References

[1]JANAF Thermochemical Tables: Na(g), 12–31–83; e^-(ref), 3–31–82.
[2]W. C. Martin and R. Zolubas, J. Phys. Chem. Ref. Data **10**, 153 (1981).
[3]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
[4]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1 (1977).
[5]R. D. Levin and S. G. Lias, U. S. Nat. Bur. Stand., NSRDS–NBS–71, (1982).
[6]J. R. Downey, The Dow Chemical Company, AFOSR–TR–78–960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	603.395		
100	20.786	125.246	166.434	−4.119			
200	20.786	139.654	149.855	−2.040			
250	20.786	144.292	148.296	−1.001			
298.15	20.786	147.953	147.953	0.	609.343	574.317	−100.618
300	20.786	148.082	147.954	0.038	609.368	574.100	−99.960
350	20.786	151.286	148.207	1.078	609.994	568.171	−84.795
400	20.786	154.062	148.769	2.117	607.903	562.364	−73.437
450	20.786	156.510	149.496	3.156	608.419	556.641	−64.613
500	20.786	158.700	150.309	4.196	608.959	550.859	−57.548
600	20.786	162.490	152.033	6.274	610.100	539.133	−46.936
700	20.786	165.694	153.761	8.353	611.305	527.211	−39.341
800	20.786	168.470	155.430	10.431	612.553	515.112	−33.633
900	20.786	170.918	157.018	12.510	613.823	502.856	−29.185
1000	20.786	173.108	158.519	14.589	615.093	490.458	−25.619
1100	20.786	175.089	159.937	16.667	616.342	477.934	−22.695
1200	20.786	176.898	161.276	18.746	520.789	467.738	−20.360
1300	20.786	178.561	162.542	20.824	522.867	463.232	−18.613
1400	20.786	180.102	163.742	22.903	524.946	458.567	−17.109
1500	20.786	181.536	164.881	24.982	527.025	453.753	−15.801
1600	20.786	182.877	165.965	27.060	529.103	448.801	−14.652
1700	20.786	184.137	166.997	29.139	531.181	443.718	−13.634
1800	20.786	185.326	167.982	31.217	533.260	438.513	−12.725
1900	20.786	186.449	168.925	33.296	535.337	433.193	−11.909
2000	20.786	187.516	169.828	35.375	537.415	427.763	−11.172
2100	20.786	188.530	170.695	37.453	539.491	422.229	−10.502
2200	20.786	189.497	171.528	39.532	541.566	416.597	−9.891
2300	20.786	190.421	172.329	41.610	543.638	410.870	−9.331
2400	20.786	191.305	173.102	43.689	545.709	405.053	−8.816
2500	20.786	192.154	173.847	45.768	547.775	399.150	−8.340
2600	20.786	192.969	174.567	47.846	549.838	393.164	−7.899
2700	20.786	193.754	175.263	49.925	551.895	387.099	−7.489
2800	20.786	194.509	175.937	52.004	553.945	380.958	−7.107
2900	20.786	195.239	176.590	54.082	555.988	374.744	−6.750
3000	20.786	195.944	177.223	56.161	558.021	368.460	−6.415
3100	20.786	196.625	177.838	58.239	560.044	362.107	−6.101
3200	20.786	197.285	178.436	60.318	562.055	355.690	−5.806
3300	20.786	197.925	179.017	62.397	564.052	349.210	−5.528
3400	20.786	198.545	179.582	64.475	566.033	342.670	−5.264
3500	20.786	199.148	180.132	66.554	567.997	336.072	−5.016
3600	20.786	199.733	180.669	68.632	569.941	329.418	−4.780
3700	20.786	200.303	181.192	70.711	571.863	322.710	−4.556
3800	20.786	200.857	181.702	72.790	573.762	315.951	−4.343
3900	20.786	201.397	182.200	74.868	575.635	309.142	−4.140
4000	20.786	201.923	182.687	76.947	577.480	302.285	−3.947
4100	20.786	202.437	183.162	79.025	579.293	295.383	−3.763
4200	20.786	202.937	183.627	81.104	581.075	288.437	−3.587
4300	20.786	203.427	184.082	83.183	582.819	281.448	−3.419
4400	20.786	203.904	184.527	85.261	584.567	274.417	−3.258
4500	20.786	204.372	184.963	87.340	586.253	267.348	−3.103
4600	20.786	204.828	185.390	89.418	587.890	260.243	−2.955
4700	20.786	205.275	185.808	91.497	589.483	253.103	−2.813
4800	20.786	205.713	186.218	93.576	591.028	245.929	−2.676
4900	20.786	206.142	186.620	95.654	592.524	238.724	−2.545
5000	20.786	206.562	187.015	97.733	593.976	231.488	−2.418
5100	20.786	206.973	187.402	99.811	595.366	224.225	−2.297
5200	20.786	207.377	187.783	101.890	596.700	216.934	−2.179
5300	20.786	207.773	188.156	103.969	597.973	209.619	−2.066
5400	20.786	208.161	188.523	106.047	599.183	202.280	−1.957
5500	20.786	208.543	188.883	108.126	600.328	194.919	−1.851
5600	20.786	208.917	189.238	110.204	601.406	187.539	−1.749
5700	20.786	209.285	189.586	112.283	602.414	180.139	−1.651
5800	20.786	209.647	189.929	114.362	603.349	172.722	−1.556
5900	20.786	210.002	190.266	116.440	604.211	165.290	−1.463
6000	20.786	210.351	190.598	118.519	605.155	157.826	−1.374

PREVIOUS: March 1965 (1 atm) CURRENT: December 1983 (1 bar)

EA(Na, g) = 0.547930 ± 0.000025 eV
$S°$(298.15 K) = 147.954 ± 0.005 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 54.68 ± 0.1 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [48.236] kJ·mol^{-1}

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for Na^-(g) is calculated from the adopted electron affinity, EA(Na, g) = 0.547930 ± 0.000025 eV (52.867 ± 0.002 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[6] was measured by a tunable laser detachment threshold technique.[2] Additional discussion on Na^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[1,6] Rosenstock *et al.*,[3] and Massey.[4]

$\Delta_f H°(Na^-, g, 298.15\ K)$ is obtained from $\Delta_f H°$(Na, g, 0 K) by using EA(Na, g) with JANAF[5] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for Na^-(g), Na(g), and e^-(ref). $\Delta_r H°(Na^- \rightarrow Na + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Na^-(g) is given by Hotop and Lineberger[1,6] and Rosenstock *et al.*[3] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

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[5]JANAF Thermochemical Tables: Na(g), 3–31–82; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−6.197	54.683		
100	20.786	125.247	166.434	−4.119			
200	20.786	139.655	149.855	−2.040			
250	20.786	144.293	148.296	−1.001			
298.15	20.786	147.954	147.954	0.	48.236	25.719	−4.506
300	20.786	148.083	147.954	0.038	48.184	25.580	−4.454
350	20.786	151.287	148.207	1.078	46.731	21.926	−3.272
400	20.786	154.062	148.770	2.117	42.562	18.692	−2.441
450	20.786	156.511	149.496	3.156	40.999	15.803	−1.834
500	20.786	158.701	150.309	4.196	39.461	13.086	−1.367
600	20.786	162.490	152.033	6.274	36.445	8.095	−0.705
700	20.786	165.695	153.762	8.353	33.492	3.604	−0.269
800	20.786	168.470	155.431	10.431	30.583	−0.467	0.030
900	20.786	170.918	157.018	12.510	27.696	−4.174	0.242
1000	20.786	173.108	158.520	14.589	24.809	−7.561	0.395
1100	20.786	175.090	159.937	16.667	21.900	−10.657	0.506
1200	20.786	176.898	161.277	18.746	−77.810	−11.047	0.481
1300	20.786	178.562	162.543	20.824	−79.889	−5.400	0.217
1400	20.786	180.102	163.743	22.903	−81.967	0.408	−0.015
1500	20.786	181.536	164.882	24.982	−84.046	6.365	−0.222
1600	20.786	182.878	165.965	27.060	−86.125	12.460	−0.407
1700	20.786	184.138	166.998	29.139	−88.203	18.685	−0.574
1800	20.786	185.326	167.983	31.217	−90.282	25.033	−0.726
1900	20.786	186.450	168.926	33.296	−92.362	31.496	−0.866
2000	20.786	187.516	169.829	35.375	−94.442	38.069	−0.994
2100	20.786	188.530	170.695	37.453	−96.523	44.745	−1.113
2200	20.786	189.497	171.528	39.532	−98.605	51.521	−1.223
2300	20.786	190.421	172.330	41.610	−100.690	58.392	−1.326
2400	20.786	191.306	173.102	43.689	−102.777	65.353	−1.422
2500	20.786	192.154	173.847	45.768	−104.867	72.401	−1.513
2600	20.786	192.970	174.567	47.846	−106.962	79.533	−1.598
2700	20.786	193.754	175.263	49.925	−109.062	86.746	−1.678
2800	20.786	194.510	175.937	52.004	−111.169	94.037	−1.754
2900	20.786	195.239	176.590	54.082	−113.283	101.403	−1.826
3000	20.786	195.944	177.224	56.161	−115.407	108.842	−1.895
3100	20.786	196.626	177.839	58.239	−117.541	116.352	−1.961
3200	20.786	197.286	178.436	60.318	−119.688	123.931	−2.023
3300	20.786	197.925	179.017	62.397	−121.848	131.578	−2.083
3400	20.786	198.546	179.583	64.475	−124.024	139.290	−2.140
3500	20.786	199.148	180.133	66.554	−126.218	147.066	−2.195
3600	20.786	199.734	180.669	68.632	−128.431	154.906	−2.248
3700	20.786	200.303	181.192	70.711	−130.665	162.807	−2.298
3800	20.786	200.858	181.703	72.790	−132.924	170.769	−2.347
3900	20.786	201.398	182.201	74.868	−135.208	178.790	−2.395
4000	20.786	201.924	182.687	76.947	−137.521	186.871	−2.440
4100	20.786	202.437	183.163	79.025	−139.865	195.010	−2.484
4200	20.786	202.938	183.628	81.104	−142.239	203.206	−2.527
4300	20.786	203.427	184.082	83.183	−144.653	211.459	−2.569
4400	20.786	203.905	184.528	85.261	−147.062	219.766	−2.609
4500	20.786	204.372	184.963	87.340	−149.533	228.130	−2.648
4600	20.786	204.829	185.390	89.418	−152.054	236.550	−2.686
4700	20.786	205.276	185.809	91.497	−154.618	245.026	−2.723
4800	20.786	205.714	186.219	93.576	−157.230	253.556	−2.759
4900	20.786	206.142	186.621	95.654	−159.891	262.142	−2.794
5000	20.786	206.562	187.016	97.733	−162.597	270.781	−2.829
5100	20.786	206.974	187.403	99.811	−165.363	279.476	−2.862
5200	20.786	207.377	187.783	101.890	−168.187	288.226	−2.895
5300	20.786	207.773	188.157	103.969	−171.071	297.031	−2.927
5400	20.786	208.162	188.524	106.047	−174.018	305.890	−2.959
5500	20.786	208.543	188.884	108.126	−177.030	314.805	−2.990
5600	20.786	208.918	189.239	110.204	−180.110	323.775	−3.020
5700	20.786	209.286	189.587	112.283	−183.259	332.801	−3.050
5800	20.786	209.647	189.930	114.362	−186.481	341.883	−3.079
5900	20.786	210.003	190.267	116.440	−189.776	351.020	−3.108
6000	20.786	210.352	190.599	118.519	−192.990	360.197	−3.136

PREVIOUS: CURRENT: December 1983 (1 bar)

$S°(298.15\ K) = [229.13 \pm 2.1]\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = [85.04 \pm 41.8]\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [83.68 \pm 41.8]\ kJ\cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^2\Pi]$	0	[4]

$\omega_e = [440]\ cm^{-1}$ $\omega_e x_e = [3.0]\ cm^{-1}$ $\sigma = 1$

$B_e = [0.4467]\ cm^{-1}$ $\alpha_e = [0.0043]\ cm^{-1}$ $r_e = [2.0]$ Å

Enthalpy of Formation

Bawn and Evans[1] studied the reaction rate of sodium vapor with nitrous oxide, nitrogen peroxide, nitromethane, ethyl nitrate and amyl nitrite, using the diffusion flame method. On the evidence of reaction rate measurements they estimated the value, $\Delta_f H°(298.15\ K) < 0$, for the reaction $Na(g) + NO_2(g) = NaO(g) + NO(g)$. Based on this result, we calculate $\Delta_f H°(NaO, g, 298.15\ K) > 12\ kcal\cdot mol^{-1}$, using $\Delta_f H°(298.15\ K) = 25.8$, 7.9 and 21.6 $kcal\cdot mol^{-1}$ for Na(g), NO_2(g) and NO(g), respectively.

Assuming that $D_0°(NaO) = 1/2\ [D_0°(Na_2) + D_0°(O_2)]$, or $\Delta_f H°(0\ K) = 68.1\ kcal\cdot mol^{-1}$ for the reaction $NaO(g) = Na(g) + O(g)$, we derive $\Delta_f H° = 16.7$ and $\Delta_f H°(298.15\ K) = 16.4\ kcal\cdot mol^{-1}$, using $\Delta_f H°(0\ K) = 25.8$ and 59.0 $kcal\cdot mol^{-1}$ for Na(g) and O(g), respectively.

Somayajulu[2] found that in a sequence of similar diatomic molecules the force constant (k_e), dissociation energy ($D_0°$ and equilibrium bond distance (r_e) are related by the expression $k_e r_e(D_0° = \text{constant}$. Using $r_e = 1.62$ Å, $D_0° = 77.9\ kcal\cdot mol^{-1}$ for LiO(g), $r_e = 2.0$ Å for NaO(g) and $k_e(NaO)/k_e(LiO) = 0.4827$, we evaluate $D_0° = 65.4\ kcal\cdot mol^{-1}$ for NaO(g), yielding $\Delta_f H°(NaO, g, 298.15\ K) = 19.4\ kcal\cdot mol^{-1}$. The value k_e is calculated from the relation $k_e = 4\ ^2\mu^2$where is the vibrational frequency of the diatomic molecule and μ is the reduced mass.

The value of $\Delta_f H°(NaO, g, 298.15\ K)$ is tentatively adopted as $20 \pm 10\ kcal\cdot mol^{-1}$. The corresponding $D_0°(NaO)$ is $65 \pm 10\ kcal\cdot mol^{-1}$.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that for OH(g) which has the same number of valence electrons as NaO(g). The values of ω_e and $\omega_e x_e$ are estimated by comparison with those for LiO(g), LiF(g) and NaF(g). The value of r_e is estimated from those for OH(g), HF(g) and NaF(g). B_e and α_e are derived from r_e, ω_e and $\omega_e x_e$ by the method suggested by Herzberg.[3]

References

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[2]G. R. Somayajulu, J. Chem. Phys. **33**, 1541 (1960).

[3]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.427	85.042	85.042	INFINITE
100	29.760	193.820	258.890	−6.507	85.169	76.834	−40.134
200	33.116	215.486	232.293	−3.361	84.404	68.794	−17.967
250	34.324	223.013	229.708	−1.674	84.038	64.935	−13.567
298.15	35.147	229.133	229.133	0.	83.680	61.287	−10.737
300	35.173	229.351	229.134	0.065	83.666	61.149	−10.647
350	35.777	234.821	229.565	1.840	83.249	57.428	−8.571
400	36.218	239.628	230.528	3.640	80.133	53.977	−7.049
450	36.550	243.914	231.782	5.460	79.632	50.738	−5.889
500	36.809	247.779	233.191	7.294	79.157	47.553	−4.968
600	37.189	254.526	236.201	10.995	78.262	41.317	−3.597
700	37.457	260.280	239.240	14.728	77.415	35.227	−2.629
800	37.664	265.295	242.190	18.484	76.594	29.256	−1.910
900	37.833	269.742	245.009	22.259	75.779	23.388	−1.357
1000	37.979	273.736	247.685	26.050	74.952	17.611	−0.920
1100	38.109	277.362	250.221	29.855	74.093	11.918	−0.566
1200	38.228	280.683	252.623	33.672	−23.575	8.745	−0.381
1300	38.339	283.747	254.901	37.500	−23.616	11.440	−0.460
1400	38.445	286.592	257.064	41.339	−23.662	14.139	−0.528
1500	38.546	289.248	259.122	45.189	−23.712	16.840	−0.586
1600	38.645	291.739	261.084	49.049	−23.765	19.546	−0.638
1700	38.740	294.085	262.956	52.918	−23.820	22.254	−0.684
1800	38.834	296.302	264.748	56.797	−23.878	24.966	−0.724
1900	38.926	298.404	266.464	60.685	−23.940	27.681	−0.761
2000	39.017	300.403	268.112	64.582	−24.004	30.400	−0.794
2100	39.107	302.309	269.695	68.488	−24.071	33.122	−0.824
2200	39.196	304.130	271.219	72.403	−24.142	35.847	−0.851
2300	39.285	305.874	272.688	76.327	−24.218	38.575	−0.876
2400	39.373	307.548	274.106	80.260	−24.299	41.307	−0.899
2500	39.460	309.157	275.476	84.202	−24.385	44.043	−0.920
2600	39.547	310.706	276.802	88.152	−24.477	46.781	−0.940
2700	39.633	312.201	278.085	92.111	−24.577	49.524	−0.958
2800	39.720	313.643	279.330	96.079	−24.685	52.271	−0.975
2900	39.806	315.039	280.537	100.055	−24.802	55.021	−0.991
3000	39.891	316.390	281.710	104.040	−24.930	57.776	−1.006
3100	39.977	317.699	282.850	108.033	−25.068	60.535	−1.020
3200	40.062	318.970	283.959	112.035	−25.220	63.298	−1.033
3300	40.147	320.204	285.038	116.046	−25.385	66.067	−1.046
3400	40.233	321.404	286.090	120.065	−25.566	68.841	−1.058
3500	40.317	322.571	287.116	124.092	−25.764	71.621	−1.069
3600	40.402	323.708	288.117	128.128	−25.981	74.406	−1.080
3700	40.487	324.816	289.094	132.173	−26.218	77.198	−1.090
3800	40.572	325.897	290.048	136.226	−26.478	79.996	−1.100
3900	40.656	326.952	290.981	140.287	−26.761	82.802	−1.109
4000	40.741	327.982	291.893	144.357	−27.072	85.615	−1.118
4100	40.825	328.989	292.786	148.435	−27.412	88.436	−1.127
4200	40.909	329.974	293.659	152.522	−27.781	91.266	−1.135
4300	40.994	330.938	294.515	156.617	−28.186	94.106	−1.143
4400	41.078	331.881	295.354	160.721	−28.585	96.951	−1.151
4500	41.162	332.805	296.176	164.833	−29.043	99.808	−1.159
4600	41.246	333.711	296.982	168.953	−29.548	102.677	−1.166
4700	41.330	334.599	297.773	173.082	−30.095	105.557	−1.173
4800	41.415	335.470	298.549	177.219	−30.687	108.450	−1.180
4900	41.499	336.325	299.311	181.365	−31.326	111.355	−1.187
5000	41.583	337.164	300.060	185.519	−32.008	114.273	−1.194
5100	41.667	337.988	300.796	189.681	−32.749	117.206	−1.200
5200	41.751	338.798	301.519	193.852	−33.547	120.154	−1.207
5300	41.835	339.594	302.230	198.032	−34.403	123.118	−1.213
5400	41.918	340.377	302.929	202.219	−35.321	126.098	−1.220
5500	42.002	341.147	303.617	206.415	−36.304	129.096	−1.226
5600	42.086	341.904	304.294	210.620	−37.355	132.114	−1.232
5700	42.170	342.650	304.960	214.832	−38.476	135.149	−1.239
5800	42.254	343.384	305.616	219.054	−39.670	138.206	−1.245
5900	42.338	344.107	306.263	223.283	−40.940	141.283	−1.251
6000	42.422	344.819	306.899	227.521	−42.130	144.365	−1.257

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

$S°(298.15\ K) = [217.49 \pm 2.1]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-113.76 \pm 83.7]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [-121.34 \pm 83.7]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$[^1\Sigma]$	0	[1]

$\omega_e = [450]\ cm^{-1}$ $\omega_e x_e = [3.2]\ cm^{-1}$ $\sigma = 1$
$B_e = [0.4467]\ cm^{-1}$ $\alpha_e = [0.00495]\ cm^{-1}$ $r_e = [2.0]$ Å

Enthalpy of Formation

The electron affinity of NaO^-(g) is unavailable, therefore the value of $\Delta_f H°(NaO^-, g, 298.15\ K)$ is estimated. We first assume that the enthalpy change $\Delta_r H°(0\ K)$ of the reaction (1) $NaO^-(g) = Na(g) + O^-(g)$ is close to the average of the $\Delta_r H°(0\ K)$uccircl values for the reactions (2) NaO(g) = Na(g) + O(g) and (3) NaF(g) = Na(g) + F(g). The atom F(g) is isoelectronic with O^-(g). In other words, the $\Delta_r H°(0\ K)$ for reaction (1) is approximately 1/2 (64.8 + 113.9) = 89.3 $kcal \cdot mol^{-1}$. Then we compare the $\Delta_r H°(0\ K)$ values for the reactions (4) HO(g) = H(g) + O(g), (5) $HO^-(g) = H(g) + O^-(g)$, and (6) HF(g) = H(g) + F(g), and find that $\Delta_r H°(0\ K)$ for reaction (5) is experimentally determined as 109.7 $kcal \cdot mol^{-1}$ which is about 8 $kcal \cdot mol^{-1}$ more negative than the average of $\Delta_r H°(0\ K)$ values for reactions (4) and (6). Based on this fact we estimate $\Delta_r H°(0\ K) = 80\ kcal \cdot mol^{-1}$ for reaction (1), yielding $\Delta_f H°(NaO^-, g, 298.15\ K) = -29\ kcal \cdot mol^{-1}$ which is tenatively adopted. The uncertainty of this value may be ±20 $kcal \cdot mol^{-1}$. Based on this $\Delta_f H°(298.15\ K)$ value we calculate E. A. = 2.1 ± 0.9 eV. The corresponding value for HO(g) is 1.8 ± 0.1 eV.

Heat Capacity and Entropy

The ground state configuration is assumed to be the same as that of NaF(g) which is isoelectronic with NaO^-(g). The values of ω_e, $\omega_e x_e$ and r_e are estimated by comparison with the observed data for NaF(g). The values of B_e and α_e are calculated from r_e, ω_e and $\omega_e x_e$ using the method recommended by Herzberg.[1]

Reference

[1]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1950).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.405	−113.755		
100	29.702	182.286	247.150	−6.486			
200	32.996	203.881	220.638	−3.351			
250	34.222	211.383	218.060	−1.669			
298.15	35.064	217.487	217.487	0.	−121.336	−134.001	23.476
300	35.091	217.704	217.488	0.065	−121.389	−134.080	23.345
350	35.712	223.163	217.917	1.836	−122.848	−136.081	20.309
400	36.168	227.963	218.879	3.633	−127.006	−137.662	17.977
450	36.513	232.243	220.131	5.451	−128.549	−138.901	16.123
500	36.781	236.105	221.538	7.283	−130.066	−139.970	14.623
600	37.175	242.848	224.544	10.982	−133.041	−141.670	12.333
700	37.455	248.601	227.580	14.715	−135.967	−142.876	10.662
800	37.670	253.617	230.527	18.471	−138.866	−143.665	9.380
900	37.846	258.064	233.345	22.247	−141.759	−144.091	8.363
1000	37.997	262.059	236.020	26.040	−144.663	−144.195	7.532
1100	38.132	265.687	238.554	29.846	−147.598	−144.006	6.838
1200	38.256	269.011	240.956	33.666	−247.342	−141.109	6.142
1300	38.371	272.077	243.233	37.497	−249.460	−132.170	5.311
1400	38.481	274.925	245.397	41.340	−251.581	−123.068	4.592
1500	38.586	277.584	247.455	45.193	−253.705	−113.815	3.963
1600	38.688	280.077	249.417	49.057	−255.833	−104.419	3.409
1700	38.788	282.426	251.290	52.931	−257.962	−94.891	2.916
1800	38.885	284.645	253.082	56.814	−260.094	−85.237	2.474
1900	38.981	286.750	254.799	60.708	−262.228	−75.465	2.075
2000	39.075	288.752	256.447	64.611	−264.366	−65.580	1.713
2100	39.168	290.661	258.031	68.523	−266.506	−55.588	1.383
2200	39.261	292.485	259.556	72.444	−268.649	−45.493	1.080
2300	39.352	294.232	261.026	76.375	−270.797	−35.302	0.802
2400	39.443	295.909	262.445	80.315	−272.949	−25.017	0.544
2500	39.534	297.521	263.816	84.264	−275.107	−14.642	0.306
2600	39.624	299.074	265.142	88.221	−277.270	−4.181	0.084
2700	39.714	300.571	266.427	92.188	−279.441	6.364	−0.123
2800	39.803	302.017	267.672	96.164	−281.619	16.989	−0.317
2900	39.892	303.415	268.881	100.149	−283.806	27.692	−0.499
3000	39.981	304.769	270.055	104.143	−286.004	38.471	−0.670
3100	40.070	306.081	271.196	108.145	−288.212	49.323	−0.831
3200	40.158	307.355	272.306	112.157	−290.433	60.246	−0.983
3300	40.247	308.592	273.387	116.177	−292.667	71.239	−1.128
3400	40.335	309.795	274.440	120.206	−294.916	82.301	−1.264
3500	40.423	310.965	275.467	124.244	−297.182	93.428	−1.394
3600	40.511	312.105	276.469	128.290	−299.467	104.621	−1.518
3700	40.598	313.216	277.447	132.346	−301.772	115.877	−1.636
3800	40.686	314.300	278.403	136.410	−304.099	127.196	−1.748
3900	40.774	315.358	279.337	140.483	−306.450	138.577	−1.856
4000	40.861	316.391	280.250	144.565	−308.827	150.018	−1.959
4100	40.949	317.402	281.144	148.655	−311.233	161.519	−2.058
4200	41.036	318.389	282.019	152.755	−313.668	173.079	−2.153
4300	41.124	319.356	282.876	156.863	−316.139	184.697	−2.244
4400	41.211	320.302	283.716	160.979	−318.603	196.370	−2.331
4500	41.298	321.229	284.539	165.105	−321.126	208.101	−2.416
4600	41.385	322.138	285.347	169.239	−323.696	219.890	−2.497
4700	41.473	323.029	286.139	173.382	−326.308	231.735	−2.575
4800	41.560	323.903	286.917	177.534	−328.964	243.636	−2.651
4900	41.647	324.761	287.681	181.694	−331.667	255.594	−2.725
5000	41.734	325.603	288.431	185.863	−334.413	267.606	−2.796
5100	41.821	326.431	289.168	190.041	−337.217	279.674	−2.864
5200	41.908	327.243	289.892	194.227	−340.078	291.797	−2.931
5300	41.995	328.043	290.604	198.422	−342.997	303.977	−2.996
5400	42.082	328.828	291.305	202.626	−345.978	316.211	−3.059
5500	42.169	329.601	291.994	206.839	−349.023	328.502	−3.120
5600	42.256	330.362	292.673	211.060	−352.135	340.849	−3.179
5700	42.343	331.111	293.340	215.290	−355.318	353.252	−3.237
5800	42.430	331.848	293.998	219.529	−358.573	365.711	−3.294
5900	42.517	332.574	294.646	223.776	−361.903	378.227	−3.349
6000	42.604	333.289	295.284	228.032	−365.154	390.782	−3.402

PREVIOUS: December 1967 (1 atm) CURRENT: December 1967 (1 bar)

Sodium Superoxide (NaO_2) CRYSTAL $M_r = 54.98857$

$S°(298.15\ K) = 115.90 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 196.5\ K$
$T_{trs2} = 223.3\ K$
$T_{fus} = 825 \pm 10\ K$

$\Delta_f H°(0\ K) = -263.88 \pm 2.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -260.66\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 1464.400\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 1548.080\ kJ·mol^{-1}$
$\Delta_{fus} H° = Unknown$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ was obtained from Wagman.[1] Giles and Margrave[2] measured the enthalpy of decomposition of NaO_2(cr) in H_2O, yielding $\Delta_f H°(298.15\ K) = -62.1 \pm 0.7\ kcal·mol^{-1}$. From the original experimental data by de Forcrand,[3] the value of $\Delta_f H°(298.15\ K)$ was recalculated to be $-65.0\ kcal·mol^{-1}$ by Gilles and Margrave.[2]

Heat Capacity and Entropy

The low temperature heat capacities, 52.13–296.46 K, were measured by Todd.[4] The heat capacities above 298.15 K were estimated by comparison with those for Na_2O(cr). $S°(298.15\ K)$ was given by Todd[4] using $S°(51\ K) = 2.23\ cal·K^{-1}·mol^{-1}$(extrap.).

Transition Data

T_{trs1}, T_{trs2}, $\Delta_{trs1} H°$ and $\Delta_{trs2} H°$ were calculated from the data reported by Todd.[4]

Fusion Data

The melting temperature was obtained from Margrave.[5]

References

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[3]R. de Forcrand, Compt. Rend. **127**, 514 (1898); **158**, 843, 991 (1914).
[4]S. S. Todd, J. Amer. Chem. Soc. **75**, 1229 (1953).
[5]J. L. Margrave, University of Wisconsin, personal communication, (May 21, 1963).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−18.351	−263.884	−263.884	INFINITE
100	45.564	30.585	194.891	−16.431	−266.208	−249.554	130.354
200	78.450	78.241	118.679	−8.088	−263.232	−232.044	60.604
298.15	72.141	115.897	115.897	0.	−260.663	−218.712	38.317
300	72.216	116.343	115.898	0.134	−260.636	−218.452	38.036
400	76.274	137.673	118.779	7.558	−261.805	−204.405	26.693
500	80.375	155.134	124.354	15.390	−260.133	−190.240	19.874
600	84.475	170.151	130.763	23.633	−258.066	−176.450	15.361
700	88.502	183.474	137.358	32.281	−255.625	−163.035	12.166
800	92.634	195.560	143.889	41.337	−252.814	−149.996	9.794
900	96.962	206.721	150.258	50.817	−249.627	−137.331	7.970
1000	101.211	217.158	156.431	60.726	−246.067	−125.041	6.531
1100	105.186	226.991	162.403	71.046	−242.164	−113.124	5.372
1200	109.177	236.314	168.177	81.764	−334.706	−99.137	4.315
1300	113.186	245.211	173.763	92.882	−329.249	−79.725	3.203
1400	117.211	253.746	179.173	104.402	−323.422	−60.747	2.267
1500	121.252	261.971	184.421	116.325	−317.219	−42.199	1.470
1600	125.311	269.925	189.517	128.653	−310.637	−24.077	0.786
1700	129.386	277.645	194.475	141.388	−303.672	−6.378	0.196
1800	133.478	285.156	199.305	154.531	−296.324	10.899	−0.316
1900	137.587	292.483	204.017	168.084	−288.590	27.758	−0.763
2000	141.712	299.645	208.620	182.048	−280.468	44.200	−1.154

PREVIOUS: CURRENT: June 1963

$D_0^\circ = 71.113 \pm 0.072$ kJ·mol^{-1}
$S^\circ(298.15\ K) = 230.243 \pm 0.030$ J·K^{-1}·mol^{-1}

$\Delta_f H^\circ(0\ 144.56 \pm 1.20$ kJ·mol^{-1}
$\Delta_f H^\circ(298.15\ K) = 142.07 \pm 1.20$ kJ·mol^{-1}

State	T_e	D_0°	Spectroscopic Data for Na_2 in cm^{-1} ω_e	$\omega_e x_e$	B_e	$10^3\ \alpha_e$	$10^6\ D_e$	r_e, Å	Reference
$^1\Sigma_g^+$	0	6024	159.11	0.72142[a]	0.15474	0.86827[b]	0.58972[c]	3.07857	d[2], e[6]
$^1\Sigma_u^+$	14681	22900[f]	117.32	0.35758[g]	0.11078	0.54884[h]	0.38816	3.6384	[5]

(a) $-1.5354 \times 10^{-3}(v + 1/2)^3 - 2.3576 \times 10^{-5}(v + 1/2)^4$
(b) $-4.2855 \times 10^{-6}(v + 1/2)^2 - 1.4784 \times 10^{-7}(v + 1/2)^3$
(c) $-3.9068 \times 10^{-9}(v + 1/2) + 9.1188 \times 10^{-11}(v + 1/2)^2$
(d) Reference for D_0°
(e) Reference for constants
(f) This value was estimated based on the estimate of Konowalow, et al[4], $D_e = 8275$ cm^{-1}
(g) $+ 5.1671 \times 10^{-5}(v + 1/2)^3 + 9.2770 \times 10^{-6}(v + 1/2)^4$
(h) $+ 1.6252 \times 10^{-8}(v + 1/2)^2 + 3.1645 \times 10^{-8}(v + 1/2)^3$

Enthalpy of Formation

Using the adopted value of the dissociation energy for Na_2(g), $D_0^\circ = 71.113$ kJ·mol^{-1},[2] and the recommended $\Delta_f H^\circ$(Na, g, 0 K) = 107.32 kJ·mol^{-1} from NBS,[7] we calculate $\Delta_f H^\circ(Na_2, g, 0\ K) = 143.51$ kJ·mol^{-1}. Since this value is only 1.05 kJ·mol^{-1}smaller than the NBS recommended value of 144.56 kJ·mol^{-1}[7] we adopt the NBS result. Correcting this value to 298.15 K using the current value of $H^\circ(298.15\ K) - H^\circ(0\ K) = 10403.27$ J·K^{-1}·mol^{-1} for Na_2 and the NBS value of $H^\circ(298.15\ K) - H^\circ(0\ K)$ for Na(cr)[1] we obtain $\Delta_f H^\circ(Na_2, g, 298.15\ K) = 142.05$ kJ·mol^{-1}.

Heat Capacity and Entropy

The heat capacity and entropy were calculated using a direct summation technique similar to the Li_2(g) calculation (refer to Li_2(g) table) using data recommended by Stwalley[1, 2] for the ground state. Reliable spectroscopic data for the lower lying excited states of Na_2 is sparse. Only the $^1\Sigma_u^+$ state at $T_e = 14680.6$ cm^{-1} has been experimentally characterized with any degree of confidence.[3, 6] Theoretical calculations by Konowalow, Rosenkrantz and Olson[4] show that the relative ordering of states is equivalent to that of Li_2(g) (see Li_2(g) table). Since the excited state contribution to all thermodynamic functions (except for the heat capacity) for Li_2(g) was small (~0.2% at 6000 K) we decided to treat the excited states for Na_2(g) in an approximate way as follows. First, the $^3\Sigma_u^+$ state was neglected entirely due to the extremely shallow potential well (The $^3\Sigma_u^+$ state of Li_2(g) contributes insignificantly to the thermodynamic functions.) Second, the $^3\Pi_u$, $^1\Sigma_u^+$, and $^3\Sigma_g^+$ states were combined as a single $^1\Sigma_u^+$ state using the spectroscopic constants of Kamimsky[5] and an artifical degeneracy of 10 (6 for the $^3\Pi_u$, 1 for the $^1\Sigma_u^+$, and 3 for the $^3\Sigma_g^+$ state). This procedure certainly overestimates the $^3\Sigma_g^+$ contribution (which lies above the $^1\Sigma_u^+$ state by ca. 3300 cm^{-1}) but at the same time underestimates the $^3\Pi_u$ contribution (which lies below the $^1\Sigma_u^+$ state by ca 1100 cm^{-1}).[4] In any case the contribution to the Gibbs energy function is very small (< 0.01 J·K^{-1}·mol^{-1}) at temperatures below 2500 K and only contributes ca. 3 J·mol^{-1} K^{-1} at 6000 K. Note also that the Dunham coefficients for the ground state are reported to higher order in[6] than used in the calculation. The neglect of these higher order terms results in uncertainties similar to the Li_2(g) calculation (the Gibbs energy function at 6000 K is probably only 0.3 J·K^{-1}·mol^{-1} smaller than the truncated rovib expression method). The rotational levels of the ground state were weighted in accordance with the nuclear spin of 3/2 (even J weight = 0.625, odd J weight = 0.375). The adopted value of $S^\circ(298.15\ K)$ is only 0.1 J·K^{-1}·mol^{-1} lower than that adopted by NBS.[7]

Reference

[1]W. C. Stwalley, Director, Iowa Laser Facility and Professor of Chemistry and Physics, University of Iowa, personal communication, (1982).
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[5]M. E. Kaminsky, J. Chem. Phys, **66**, 4951 (1977).
[6]P. Kusch and M. M. Hessel, J. Chem. Phys. **68**, 2591 (1978).
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p° (J·K^{-1}·mol^{-1})	S° (J·K^{-1}·mol^{-1})	$-[G^\circ - H^\circ(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H^\circ - H^\circ(T_r)$ (kJ·mol^{-1})	$\Delta_f H^\circ$ (kJ·mol^{-1})	$\Delta_f G^\circ$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−10.403	144.560	144.560	INFINITE
100	34.747	190.419	263.127	−7.271	145.013	130.734	−68.288
200	36.922	215.363	233.663	−3.660	143.713	116.919	−30.536
250	37.315	223.647	230.860	−1.803	142.920	110.310	−23.048
298.15	37.577	230.243	230.243	0.	142.070	104.105	−18.239
300	37.585	230.476	230.244	0.070	142.035	103.870	−18.085
350	37.799	236.286	230.702	1.954	141.014	97.587	−14.564
400	37.984	241.346	231.723	3.849	134.571	91.873	−11.997
450	38.157	245.830	233.046	5.752	133.349	86.610	−10.053
500	38.327	249.859	234.529	7.665	132.184	81.480	−8.512
600	38.667	256.876	237.686	11.514	130.002	71.547	−6.229
700	38.998	262.862	240.865	15.398	127.981	61.966	−4.624
800	39.269	268.088	243.949	19.312	126.077	52.667	−3.439
900	39.411	272.723	246.893	23.247	124.238	43.601	−2.531
1000	39.369	276.875	249.687	27.188	122.404	34.740	−1.815
1100	39.123	280.618	252.332	31.114	120.513	26.064	−1.238
1200	38.680	284.004	254.833	35.006	−75.016	22.445	−0.977
1300	38.074	287.077	257.197	38.845	−75.334	30.579	−1.229
1400	37.347	289.873	259.432	42.617	−75.720	38.741	−1.445
1500	36.546	292.423	261.548	46.312	−76.182	46.932	−1.634
1600	35.714	294.755	263.552	49.925	−76.726	55.157	−1.801
1700	34.891	296.895	265.451	53.455	−77.354	63.418	−1.949
1800	34.110	298.867	267.253	56.904	−78.062	71.719	−2.081
1900	33.399	300.692	268.966	60.279	−78.846	80.061	−2.201
2000	32.782	302.389	270.595	63.587	−79.698	88.447	−2.310
2100	32.280	303.976	272.147	66.840	−80.608	96.876	−2.410
2200	31.908	305.468	273.628	70.048	−81.565	105.350	−2.501
2300	31.681	306.881	275.044	73.226	−82.555	113.868	−2.586
2400	31.610	308.227	276.398	76.389	−83.566	122.430	−2.665
2500	31.700	309.519	277.698	79.553	−84.583	131.034	−2.738
2600	31.957	310.767	278.946	82.735	−85.591	139.678	−2.806
2700	32.381	311.980	280.147	85.950	−86.575	148.361	−2.870
2800	32.968	313.168	281.305	89.217	−87.523	157.080	−2.930
2900	33.712	314.337	282.424	92.549	−88.419	165.832	−2.987
3000	34.601	315.495	283.507	95.964	−89.252	174.614	−3.040
3100	35.624	316.646	284.557	99.474	−90.011	183.422	−3.091
3200	36.761	317.794	285.578	103.092	−90.686	192.253	−3.138
3300	37.996	318.944	286.572	106.830	−91.269	201.105	−3.183
3400	39.305	320.098	287.541	110.694	−91.756	209.972	−3.226
3500	40.666	321.257	288.488	114.692	−92.145	218.852	−3.266
3600	42.055	322.422	289.414	118.828	−92.435	227.742	−3.304
3700	43.449	323.593	290.322	123.103	−92.629	236.639	−3.341
3800	44.823	324.770	291.213	127.517	−92.732	245.540	−3.375
3900	46.156	325.952	292.088	132.067	−92.751	254.442	−3.408
4000	47.426	327.136	292.950	136.746	−92.697	263.344	−3.439
4100	48.616	328.322	293.798	141.549	−92.582	272.243	−3.468
4200	49.710	329.507	294.634	146.466	−92.414	281.139	−3.496
4300	50.695	330.689	295.459	151.488	−92.220	290.031	−3.523
4400	51.560	331.864	296.273	156.601	−91.925	298.911	−3.549
4500	52.299	333.032	297.077	161.795	−91.673	307.789	−3.573
4600	52.908	334.188	297.871	167.057	−91.452	316.664	−3.596
4700	53.386	335.331	298.656	172.373	−91.266	325.534	−3.618
4800	53.733	336.459	299.432	177.730	−91.132	334.401	−3.639
4900	53.952	337.569	300.199	183.115	−91.069	343.265	−3.659
5000	54.050	338.660	300.957	188.516	−91.079	352.128	−3.679
5100	54.032	339.731	301.707	193.921	−91.207	360.993	−3.697
5200	53.906	340.779	302.448	199.319	−91.458	369.862	−3.715
5300	53.681	341.804	303.181	204.699	−91.846	378.737	−3.733
5400	53.366	342.804	303.906	210.052	−92.386	387.620	−3.749
5500	52.971	343.780	304.622	215.370	−93.093	396.516	−3.766
5600	52.504	344.731	305.330	220.644	−93.977	405.425	−3.782
5700	51.976	345.655	306.029	225.868	−95.052	414.353	−3.797
5800	51.395	346.554	306.720	231.037	−96.326	423.300	−3.812
5900	50.769	347.428	307.403	236.146	−97.809	432.272	−3.827
6000	50.107	348.275	308.077	241.190	−99.192	441.234	−3.841

PREVIOUS: June 1962 (1 atm) CURRENT: December 1983 (1 bar)

$S°(298.15\ K) = 75.042\ J·K^{-1}·mol^{-1}$
$T_{trs}(\gamma \rightarrow \beta) = 1023.2\ K$
$T_{trs}(\beta \rightarrow \alpha) = 1243.2\ K$
$T_{fus} = 1405.2\ K$

$\Delta_f H°(0\ K) = -413.15 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -417.98 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{trs} H°(\gamma \rightarrow \beta) = 1.757\ kJ·mol^{-1}$
$\Delta_{trs} H°(\beta \rightarrow \alpha) = 11.924\ kJ·mol^{-1}$
$\Delta_{fus} H° = 47.698\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy change of the reaction $Na_2O(cr) + H_2O(l) = 2\ NaOH(aq)$ has been determined by Matsui and Oka[1,2] Roth and Kaule[3,4] and Rengade.[5] Based on their reported $\Delta_r H°$ values, the corresponding $\Delta_f H°(298.15\ K)$ for $Na_2O(cr)$ are calculated, using $\Delta_f H°(H_2O, l, 298.15\ K) = -68.315\ kcal·mol^{-1}$ obtained from,[6] and $\Delta_f H°(NaOH, nH_2O, 298.15\ K)$ derived from JANAF $\Delta_f H°(NaOH, cr, 298.15\ K)$ and $\Delta_{sln} H°$ and $\Delta_{dil} H°$ reported by Parker.[7] The sample employed by Matsui and Oka was prepared by the method of Rengade[9] and contains $Na_2O(cr)$ and Na(cr) as impurities. The sample used by Roth also contains 3.96% (by weight) $Na_2O_2(cr)$. Corrections in the reported results for such impurities have been made by the authors. However, in order to obtain better results, more measurements using purer samples are necessary. The enthalpy change of the reaciton $2\ Na(cr) + H_2O(l) = Na_2O(cr) + H_2(g)$ was calculated by Rengade[5] from his measurements incorporating with $\Delta_r H° = -85.2\ kcal·mol^{-1}$ for the reaction $2\ Na(cr) + 2\ H_2O(l) = 2\ NaOH(aq) + H_2(g)$ determined by Joannis.[10] The value $\Delta_f H°(298.15\ K) = -94.9\ kcal·mol^{-1}$ is derived from the data of Forcrand[8] using $\Delta_f H°(Na_2O_2, cr, 298.15\ K) = -122.66\ kcal·mol^{-1}$. The results are presented in the table below.

Brewer and Margrave[13] determined the equilibrium constants, 918 1467 K, for the vaporization of $Na_2O(cr)$, using an effusion method. The Na_2O vapor consists predominately of Na(g) and $O_2(g)$ molecules with any oxide molecules being not important. The Na/O ratio was not measured and assumed to be 2/1 in all calculations on Na_2O. Based on the reported data, we derive the equilibrium constants for the reaction $Na_2O(cr) = 2\ Na(g) + 1/2\ O_2(g)$ and evaluate the 3rd law $\Delta_r H°(298.15\ K)$ as $117.1 \pm 10\ kcal·mol^{-1}$.From this $\Delta_r H°(298.15\ K)$ value, we obtain $\Delta_f H°(Na_2O, cr, 298.15\ K) = -65.6 \pm 10\ kcal·mol^{-1}$, employing $\Delta_f H°(298.15\ K)$ for Na(g). The value $-65.6\ kcal·mol^{-1}$ is not consistent with the other values described above. This may be caused by an invalid assumption used in the calculation.

The enthalpy of formation at 298.15 K for $Na_2O(cr)$ is tentatively selected as $-99.90 \pm 1.0\ kcal·mol^{-1}$.

Source	Reaction	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[1]	$Na_2O(cr) + H_2O(l) = 2\ NaOH(7890\ H_2O)$	-56.61 ± 0.16	-100.08
[2]	$Na_2O(cr) + H_2O(l) = 2\ NaOH(4600\ H_2O)$	-56.70 ± 0.07	-99.89
[3]	$Na_2O(cr) + H_2O(l) = 2\ NaOH(825\ H_2O)$	-56.03 ± 0.13	-100.55
[4]	$Na_2O(cr) + H_2O(l) = 2\ NaOH(825\ H_2O)$	-55.98 ± 0.13	-100.60
[5]	$Na_2O(cr) + H_2O(l) = 2\ NaOH(aq)$	-56.50	-100.09
	$2\ Na(cr) + H_2O(l) = Na_2O(cr) + H_2(g)$	-28.70	-97.02
[8]	$Na_2O(cr) + 1/2\ O_2(g) = Na_2O_2(cr)$	-27.76	-94.90

Heat Capacity and Entropy

The low temperature heat capacities, 15–380 K, were obtained from Furukawa.[11] We make the corrections in the reported $C_p°$ values for impurity $Na_2CO_3(cr)$ 2.33% (by weight), analyzed by Grimley and Margrave.[12] The effect on heat capacity due to the presence of Na_2O_2(0.91%) impurity is insignificant. Using the smoothed low temperature $C_p°$ data, the $S°(298.15\ K)$ is calculated, based on $S°(15\ K) = 0.0122\ cal·K^{-1}·mol^{-1}$.

Grimley and Margrave[12] measured the high temperature enthalpies, 380.1–1174.6 K, with a copper block drop type calorimeter. The enthalpies for the γ phase, 380.1–980.4 K, are joined smoothly with the low temperature data and extrapolated to 1023.2 K (the $\gamma \rightarrow \beta$ transition temperature. The enthalpies above 1023.2 K are obtained by extrapolation. The enthalpies measured at 1078.3 and 1174.6 K by Grimley are unreasonably large, and are not adopted.

Transition Data

The transition temperature and heats of transition were determined calorimetrically by Bouaziz *et al.*[14] who used a very pure sample. The adopted $\Delta_{trs} H° = 0.42$ and 2.85 kcal·mol^{-1}, are averages of the derived values, 0.36–0.48 and 2.7–3.0 kcal·mol^{-1}, respectively.

Fusion Data

T_{fus} and $\Delta_{fus} H°$ were obtained from Bouaziz *et al.*[14] The adopted $\Delta_{fus} H°$ is an average of the reported 10.8–12.0 kcal·mol^{-1}. T_{fus} has been reported as 1193 and 1190 ± 10 K by Bunzel and Kohlmeyer[15] and Brewer and Margrave,[13] respectively, which are not adopted.

References

[1] M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) **32**, 79 (1929).
[2] M. Matsui and S. Oka, J. Soc. Chem. Ind. (Japan) **32**, 83 (1929).
[3] W. A. Roth and H. L. Kaule, Z. Anorg. Chem. **253**, 352 (1947).
[4] W. A. Roth, Z. Anorg. Chem. **255**, 324 (1948).

Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−12.399	−413.146	−413.146	INFINITE
100	32.752	16.649	128.981	−11.233	−416.111	−404.348	211.210
200	59.551	49.209	81.114	−6.381	−417.626	−391.841	102.338
298.15	69.103	75.042	75.042	0.	−417.982	−379.090	66.415
300	69.245	75.470	75.043	0.128	−417.985	−378.849	65.964
400	75.776	96.304	77.840	7.386	−423.456	−365.363	47.712
500	81.496	113.855	83.332	15.262	−423.312	−350.842	36.652
600	85.709	129.103	89.717	23.631	−422.555	−336.410	29.287
700	88.851	142.560	96.324	32.365	−421.353	−322.142	24.039
800	91.291	154.589	102.869	41.376	−419.828	−308.070	20.115
900	93.266	165.458	109.229	50.607	−418.075	−294.204	17.075
1000	94.918	175.373	115.355	60.018	−416.169	−280.541	14.654
1023.150	95.264	177.549	116.737	62.219	GAMMA <--> BETA		
1023.150	95.265	179.266	116.737	63.977	TRANSITION		
1100	96.353	186.205	121.351	71.340	−412.418	−267.206	12.689
1200	97.629	194.645	127.111	81.040	−603.913	−249.215	10.848
1243.150	98.140	198.103	129.516	85.264	BETA <--> ALPHA		
1243.150	98.142	207.695	129.516	97.188	TRANSITION		
1300	98.788	212.098	133.031	102.786	−588.116	−220.358	8.854
1400	99.860	219.459	138.945	112.719	−584.147	−192.218	7.172
1405.200	99.913	219.829	139.243	113.239	ALPHA <--> LIQUID		
1500	100.868	226.383	144.545	122.756	−580.088	−164.364	5.724
1600	101.822	232.923	149.866	132.891	−575.944	−136.784	4.466
1700	102.734	239.124	154.936	143.119	−571.720	−109.465	3.363
1800	103.617	245.021	159.778	153.437	−567.418	−82.398	2.391
1900	104.470	250.646	164.414	163.841	−563.042	−55.571	1.528
2000	105.307	256.026	168.861	174.330	−558.594	−28.977	0.757

PREVIOUS: June 1962 CURRENT: June 1968

$S°$(298.15 K) = [91.607] J·K^{-1}·mol^{-1}
T_{fus} = 1405.2 K

$\Delta_f H°$(298.15 K) = [−372.843] kJ·mol^{-1}
$\Delta_{fus} H°$ = 47.698 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(Na_2O, l, 298.15\ K)$ is calculated from $\Delta_f H°(Na_2O, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1405.2\ K) - H°(298.15\ K)$, between Na_2O(cr) and Na_2O(l).

Heat Capacity and Entropy

The heat capacity is estimated by comparison with those for Na_2SiO_3(l) and SiO_2(l). $S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

T_{dcm} = 2223 K is the temperature at $\Delta_r G° = 0$ for the decomposition reaction $Na_2O(l) = 2\ Na(g) + 1/2\ O_2(g)$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	104.600	91.607	91.607	0.	−372.843	−338.890	59.372
300	104.600	92.254	91.609	0.194	−372.780	−338.680	58.969
400	104.600	122.346	95.712	10.654	−375.049	−327.373	42.751
500	104.600	145.687	103.460	21.114	−372.321	−315.766	32.988
600	104.600	164.757	112.135	31.574	−369.474	−304.721	26.528
700	104.600	180.882	120.834	42.034	−366.545	−294.160	21.950
800	104.600	194.849	129.232	52.494	−363.572	−284.022	18.545
900	104.600	207.169	137.221	62.954	−360.589	−274.257	15.917
1000	104.600	218.190	144.776	73.414	−357.635	−264.824	13.833
1100	104.600	228.159	151.911	83.874	−354.746	−255.683	12.141
1200	104.600	237.261	158.649	94.334	−545.481	−241.922	10.531
1300	104.600	245.633	165.023	104.794	−540.970	−216.808	8.711
1400	104.600	253.385	171.061	115.254	−536.474	−192.041	7.165
1405.200	104.600	253.773	171.366	115.797	---- ALPHA <--> LIQUID ----		
1500	104.600	260.601	176.792	125.714	−531.992	−167.596	5.836
1600	104.600	267.352	182.244	136.174	−527.523	−143.448	4.683
1700	104.600	273.693	187.438	146.634	−523.066	−119.580	3.674
1800	104.600	279.672	192.398	157.094	−518.622	−95.974	2.785
1900	104.600	285.328	197.142	167.554	−514.191	−72.614	1.996
2000	104.600	290.693	201.686	178.014	−509.772	−49.488	1.292
2100	104.600	295.796	206.047	188.474	−505.367	−26.582	0.661
2200	104.600	300.662	210.238	198.934	−500.976	−3.886	0.092
2300	104.600	305.312	214.271	209.394	−496.600	18.611	−0.423
2400	104.600	309.764	218.158	219.854	−492.240	40.918	−0.891
2500	104.600	314.034	221.908	230.314	−487.899	63.044	−1.317
2600	104.600	318.136	225.531	240.774	−483.576	84.996	−1.708
2700	104.600	322.084	229.034	251.234	−479.275	106.783	−2.066
2800	104.600	325.888	232.426	261.694	−474.998	128.410	−2.396
2900	104.600	329.559	235.712	272.154	−470.745	149.885	−2.700
3000	104.600	333.105	238.900	282.614	−466.522	171.214	−2.981

PREVIOUS: June 1962 CURRENT: June 1968

0	to	1023.2	K crystal, gamma
1023.2	to	1243.2	K crystal, beta
1243.2	to	1405.2	K crystal, alpha
above		1405.2	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−12.399	−413.146	−413.146	INFINITE
100	32.752	16.649	128.981	−11.233	−416.111	−404.348	211.210
200	59.551	49.209	81.114	−6.381	−417.626	−391.841	102.338
298.15	69.103	75.042	75.042	0.	−417.982	−379.090	66.415
300	69.245	75.470	75.043	0.128	−417.985	−378.849	65.964
400	75.776	96.304	77.840	7.386	−423.456	−365.363	47.712
500	81.496	113.855	83.332	15.262	−423.312	−350.842	36.652
600	85.709	129.103	89.717	23.631	−422.555	−336.410	29.287
700	88.851	142.560	96.324	32.365	−421.353	−322.142	24.039
800	91.291	154.589	102.869	41.376	−419.828	−308.070	20.115
900	93.266	165.458	109.229	50.607	−418.075	−294.204	17.075
1000	94.918	175.373	115.355	60.018	−416.169	−280.541	14.654
1023.150	95.264	177.549	116.737	62.219	GAMMA <--> BETA TRANSITION		
1023.150	95.265	179.266	116.737	63.977			
1100	96.353	186.205	121.351	71.340	−412.418	−267.206	12.689
1200	97.629	194.645	127.111	81.040	−603.913	−249.215	10.848
1243.150	98.140	198.103	129.516	85.264	BETA <--> ALPHA TRANSITION		
1243.150	98.142	207.695	129.516	97.188			
1300	98.788	212.098	133.031	102.786	−588.116	−220.358	8.854
1400	99.860	219.459	138.945	112.719	−584.147	−192.218	7.172
1405.200	99.913	219.829	139.243	113.239	ALPHA <--> LIQUID TRANSITION		
1405.200	104.600	253.773	139.243	160.936			
1500	104.600	260.601	146.700	170.853	−531.992	−167.596	5.836
1600	104.600	267.352	154.032	181.313	−527.523	−143.448	4.683
1700	104.600	273.693	160.886	191.773	−523.066	−119.580	3.674
1800	104.600	279.672	167.321	202.233	−518.622	−95.974	2.785
1900	104.600	285.328	173.384	212.693	−514.191	−72.614	1.996
2000	104.600	290.693	179.117	223.153	−509.772	−49.488	1.292
2100	104.600	295.796	184.552	233.613	−505.367	−26.582	0.661
2200	104.600	300.662	189.720	244.073	−500.976	−3.886	0.092
2300	104.600	305.312	194.646	254.533	−496.600	18.611	−0.423
2400	104.600	309.764	199.350	264.993	−492.240	40.918	−0.891
2500	104.600	314.034	203.853	275.453	−487.899	63.044	−1.317
2600	104.600	318.136	208.170	285.913	−483.576	84.996	−1.708
2700	104.600	322.084	212.316	296.373	−479.275	106.783	−2.066
2800	104.600	325.888	216.305	306.833	−474.998	128.410	−2.396
2900	104.600	329.559	220.147	317.293	−470.745	149.885	−2.700
3000	104.600	333.105	223.854	327.753	−466.522	171.214	−2.981

PREVIOUS: CURRENT: June 1968

$S°(298.15\ K) = 94.80 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{trs} = 785 \pm 1\ K$
$T_{fus} = 948\ K$

$\Delta_f H°(0\ K) = -507.34 \pm 5.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -513.21 \pm 5.0\ kJ·mol^{-1}$
$\Delta_{trs} H° = 5.732\ kJ·mol^{-1}$
$\Delta_{fus} H°$ = Unknown

Enthalpy of Formation

The enthalpy change of the reaction $Na_2O_2(cr) + H_2O(l) = 2\ NaOH(aq, 1200\ H_2O) + 1/2\ O_2(g)$ was measured at 18.5°C by Roth and Kaule.[1] He employed a sample with composition 96.81% Na_2O_2 and 3.4% Na_2O by weight. Using $\Delta_{sln}H°(Na_2O_2, cr) = -56.02\ kcal·mol^{-1}$, Roth derived the value $\Delta_{sln}H°(Na_2O_2, cr) = -34.85\ kcal·mol^{-1}$. This value was later corrected to $-35.75\ kcal·mol^{-1}$ by Roth.[2] From these data we calculate the enthalpy of formation (298.15 K) of $Na_2O_2(cr)$ as $-121.0\ kcal·mol^{-1}$. Forcrand obtained $\Delta_{sln}H° = -36.65\ kcal·mol^{-1}$ for the same reaction, quoted by Roth and Kaule,[1] yielding $\Delta_f H°(Na_2O_2, cr, 298.15\ K) = -120.0\ kcal·mol^{-1}$. The auxiliary data $\Delta_f H°(H_2O, l, 298.15\ K)$[3] $= -68.315\ kcal·mol^{-1}$; and $\Delta_f H°(NaOH·aq, 1200\ H_2O, 298.15\ K) = 112.458\ kcal·mol^{-1}$ is derived based on $\Delta_f H°(NaOH, cr, 298.15\ K) = -101.90\ kcal·mol^{-1}$ from JANAF Table and $\Delta_{sol}H°(aq, \infty) = -10.637\ kcal·mol^{-1}$ and $\Delta_{dil}H°(aq, 1200\ H_2O \rightarrow aq, \infty) = -0.079\ kcal·mol^{-1}$ from Parker.[4]

Gilles and Margrave[5] determined the enthalpy change of the reaction $Na_2O_2(cr) + H_2O(l) = 2\ NaOH(aq, 3800\ H_2O) + 1/2\ O_2(g)$, using a purer sample ($Na_2O_2$, 99.2%; Na_2O, 0.8%). Based on the reported value $\Delta_f H°(298.15\ K) = -34.0 \pm 0.3\ kcal·mol^{-1}$ and derived $\Delta_f H°(NaOH·aq, 3800\ H_2O, 298.15\ K) = -112.487\ kcal·mol^{-1}$, we calculate $\Delta_f H°(298.15\ K) = -122.66 \pm 1.2\ kcal·mol^{-1}$ for $Na_2O_2(cr)$.

Leffler and Wiederhorn[6] studied the oxygen pressure melt composition for the liquid sodium oxygen system between 780 and 980 °C. These results, together with the thermodynamic data for Na_2O_2, were used to calculate the enthalpies and Gibbs energies of formation of melt compositions between $NaO_{1.0}$ and $NaO_{0.5}$. However, there are no numerical results reported. Therefore these data are not used for evaluation.

The enthalpy of formation at 298.15 K is adopted as $-122.66 \pm 1.2\ kcal·mol^{-1}$.

Heat Capacity and Entropy

The low temperature heat capacities, 52.31 296.22 K, were measured by Todd.[7] His sample contains (percent) 94 $Na_2O_2(cr)$, 3.6 $Na_2O(cr)$ and 2.4 Na_2CO_3. Corrections in the reported results have been made for Na_2CO_3 content, but not for Na_2O content which was estimated to be small. The $C_p°$ values below 52.31 K are calculated using the equation $C_p° = D(252/T) + 3E(399/T)$ reported by Todd. $S°(298.15\ K)$ is derived from the adopted $C_p°$, based on $S°(50\ K) = 1.012\ cal·K^{-1}·mol^{-1}$.

The high temperature enthalpies, 375.4–869.2 K, were determined by Chandrasekharaiah *et al.*,[8] using drop calorimetry. Corrections were made for the contributions from impurities (Na_2CO_3, 1.5 and Na_2O, 0.2%). A discontinuity was observed in the enthalpies between 773 and 793 K, indicating some kind of transition (see Transition Data). The $C_p°$ for $Na_2O_2(\alpha)$ at temperatures 298–769.5 K are derived from the enthalpy measurements, 375.4–769.5 K, and joined smoothly with the low temperature data at 298.15 K, and extrapolated to 785 K(T_{trs}). The $C_p°$ for $Na_2O_2(\beta)$ is derived from the enthalpy data, 794–869.2 K, as constant, 27.15 $cal·K^{-1}·mol^{-1}$, and extrapolated to 2500 K.

Vedeneev and Skuratov[9] measured the high temperature specific heat of $Na_2O_2(cr)$ in the temperature interval 292–373 K using adiabatic calorimetry. The reported average value, 21.46 $cal·K^{-1}·mol^{-1}$, is in fair agreement with the adopted ones.

Transition Data

T_{trs} was reported by Tallman and Margrave,[10] who measured the X–ray power diffraction pattern by a Geiger counter diffractometer and found that at about 510°C the pattern changes entirely and a new set of peaks indicates a new phase. Separate thermal analysis measurements[10] confirm the transition temperature ($\alpha \rightarrow \beta$) is 512 ± 1°C or 785 ± 1 K, which is adopted here. Foppl[11] found a thermal anomaly at 485°C in both heating and cooling curves. $\Delta_{trs}H°$ is derived from the adopted enthalpy and $C_p°$ data on $Na_2O_2(\alpha)$ and $Na_2O_2(\beta)$.

Fusion Data

T_{fus} is obtained from Bunzel and Kohlmeyer.[12] T_{fus} = 733 and 783 K were reported by Blumenthal[13] and Rode and Gol'der,[14] respectively, which are not adopted.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−15.707	−507.339	−507.339	INFINITE
100	40.689	20.882	163.515	−14.263	−511.480	−491.475	256.720
200	75.479	61.785	102.600	−8.163	−513.202	−470.583	122.904
298.15	89.266	94.801	94.801	0.	−513.209	−449.627	78.773
300	89.408	95.354	94.803	0.165	−513.203	−449.233	78.218
400	97.721	122.268	98.416	9.541	−518.042	−427.560	55.834
500	103.767	144.748	105.495	19.626	−517.218	−405.020	42.312
600	108.445	164.093	113.687	30.244	−515.792	−382.706	33.318
700	112.332	181.108	122.127	41.287	−513.908	−360.668	26.913
785.000	115.253	194.149	129.230	50.961	ALPHA <--> BETA		
785.000	113.596	201.451	129.230	56.694	TRANSITION		
800	113.596	203.601	130.604	58.397	−505.952	−339.036	22.137
900	113.596	216.981	139.473	69.757	−503.773	−318.303	18.474
1000	113.596	228.949	147.833	81.117	−501.650	−297.810	15.556
1100	113.596	239.776	155.707	92.476	−499.616	−277.525	13.179
1200	113.596	249.660	163.130	103.836	−691.226	−252.540	10.993
1300	113.596	258.753	170.141	115.195	−687.607	−216.130	8.684
1400	113.596	267.171	176.775	126.555	−684.018	−179.997	6.716
1500	113.596	275.008	183.065	137.914	−680.457	−144.121	5.019
1600	113.596	282.340	189.043	149.274	−676.922	−108.480	3.542
1700	113.596	289.226	194.736	160.634	−673.412	−73.060	2.245
1800	113.596	295.719	200.168	171.993	−669.926	−37.846	1.098
1900	113.596	301.861	205.360	183.353	−666.465	−2.825	0.078
2000	113.596	307.688	210.332	194.712	−663.028	32.014	−0.836
2100	113.596	313.230	215.101	206.072	−659.616	66.682	−1.659
2200	113.596	318.515	219.682	217.431	−656.229	101.189	−2.403
2300	113.596	323.564	224.090	228.791	−652.869	135.542	−3.078
2400	113.596	328.399	228.336	240.150	−649.537	169.748	−3.694
2500	113.596	333.036	232.432	251.510	−646.233	203.817	−4.259

PREVIOUS: June 1963 CURRENT: June 1968

$S°(298.15\ K) = 113.847 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1362 \pm 0.5\ K$

$\Delta_f H°(0\ K) = -1551.20 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1561.43 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 51.798\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of NaCl(cr), Na_2SO_4(cr), SiO_2(quartz), Na_2SiO_3(cr), HCl(aq) and H_2SO_4(aq) in 20% hydrofluoric acid at 74.7°C were measured by Kracek.[1] The author derived two values of $\Delta_{sln} H°$ of Na_2O(cr) from those of NaCl(cr), Na_2SO_4(cr), HCl(aq) and H_2SO_4(aq) presumably employing auxiliary data from.[2] We recalculate $\Delta_{sln} H°$ of Na_2O(cr) in the calorimetric solution as −87.50 (chloride scheme, originally −87.66) and −88.74 kcal·mol^{-1} (sulfate scheme, originally −89.19), using recent $\Delta_f H°$(298.15 K) values for NaCl(cr), Na_2SO_4(cr), HCl(aq), H_2SO_4(aq), and Na_2O(cr). The corresponding enthalpy changes, $\Delta_r H°$(298.15 K), for the reaction Na_2O(cr) + SiO_2(quartz) = Na_2SiO_3(cr) are derived as −55.20 and −56.38 kcal·mol^{-1}. Adopting the weighted average $\Delta_r H°$(298.15 K) = −55.59 kcal·mol^{-1} with $\Delta_f H°(Na_2O, cr, 298.15\ K)$ = −99.9 kcal·mol^{-1} and $\Delta_f H°(SiO_2, quartz, 298.15\ K)$ = −217.7 kcal·mol^{-1}, we obtain $\Delta_f H°$(298.15 K) = −373.19 kcal·mol^{-1} for Na_2SiO_3(cr). This $\Delta_f H°(Na_2SiO_3, cr, 298.15\ K)$ value is independent of future changes in $\Delta_f H°$(298.15 K) of Na_2O(cr) but the values of $\Delta_{sln} H°$ and $\Delta_r H°$ are not independent. The adopted value of $\Delta_f H°(Na_2, cr, 298.15\ K)$ is the average of −100.1 and −99.7 kcal·mol^{-1} reported by Roth and Kaule[3] and Matsui and Oka,[4] respectively.

Roth and Troitzsch[5] have measured the enthalpies of solution of SiO_2(quartz), Na_2SiO_3(cr) and Na_2O(cr) in 10.3% HF at 22°C to be −32.85, −67.96 and −89.9 kcal·mol^{-1}, respectively. Using these results, we calculate the enthalpy change of the reaction Na_2O(cr) + SiO_2(quartz) = Na_2SiO_3(cr) as −53.79 kcal·mol^{-1} and $\Delta_f H°(Na_2SiO_3, cr, 298.15\ K)$ = −371.39 kcal·mol^{-1}.

By use of high temperature reaction calorimetry, Kroger and Janetzko[6] have determined the enthalpy change of the reaction Na_2C_3(cr) + $Na_2Si_2O_5$(g, l) = 2 Na_2SiO_3(cr) + CO_2(g) as 17.99 kcal·mol^{-1}. Based on $\Delta_f H°$(298.15 K) = −270.26, −582.92 and −94.05 kcal·mol^{-1} for Na_2SiO_3(cr).

The enthalpies of solution of Na_2CO_3(cr), SiO_2(quartz) and Na_2SiO_3(cr) in 39% HF at 26.5°C were measured to be −244.1, −564.5 and −673.6 cal·g^{-1} by Hummel and Schwiete.[7] From these results we calculate the enthalpy change to be 22.43 kcal·mol^{-1} for the reaction Na_2CO_3(cr) + SiO_2(quartz) = Na_2SiO_3(cr) + CO_2(g), yielding $\Delta_f H°(Na_2SiO_3, cr, 298.15\ K)$ = −371.48 kcal·mol^{-1}.

Many other older calorimetric measurements have been made in order to derive the enthalpies of formation for Na_2SiO_2(cr), but most of these are of questionable accuracy and in some cases the products of the reaction are uncertain. For further details, refer to the review by McCready.[8]

Heat Capacity and Entropy

The low temperature heat capacities, 53.6–294.5 K, were measured by Kelley,[9] and high temperature enthalpies, 360.5–1747 K were determined by Naylor.[10] The high temperature heat capacities are derived from the measured enthalpy data and joined smoothly with the low temperature $C_p°$ values. The entropy at 298.15 K is calculated using the adopted low temperature heat capacities, based on $S°(50\ K)$ = 1.195 cal K^{-1}·mol^{-1}.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.913	−1551.203	−1551.203	INFINITE
100	48.308	25.568	196.995	−17.143	−1556.736	−1528.150	798.224
200	89.743	73.542	123.451	−9.982	−1560.031	−1498.083	391.259
298.15	111.880	113.847	113.847	0.	−1561.427	−1467.330	257.070
300	112.395	114.540	113.849	0.207	−1561.442	−1466.746	255.383
400	127.779	149.118	118.459	12.264	−1567.208	−1434.679	187.350
500	138.716	178.865	127.635	25.615	−1566.925	−1401.558	146.420
600	147.114	204.926	138.390	39.922	−1565.766	−1368.581	119.146
700	153.946	228.133	149.583	54.985	−1563.937	−1335.853	99.683
800	159.749	249.078	160.732	70.677	−1561.578	−1303.425	85.105
900	164.841	268.193	171.625	86.911	−1558.788	−1271.319	73.785
1000	169.423	285.801	182.174	103.628	−1555.650	−1239.544	64.747
1100	173.628	302.149	192.346	120.783	−1552.231	−1208.096	57.368
1200	177.540	317.425	202.140	138.343	−1742.114	−1172.091	51.020
1300	181.230	331.783	211.566	156.283	−1736.446	−1124.817	45.196
1362.000	183.407	340.278	217.233	167.587	--- CRYSTAL <--> LIQUID ---		
1400	184.736	345.343	220.641	174.582	−1730.507	−1077.989	40.220
1500	188.100	358.203	229.387	193.224	−1724.308	−1031.596	35.923
1600	191.347	370.441	237.824	212.187	−1717.869	−985.624	32.177
1700	195.748	382.186	245.972	231.564	−1761.273	−939.617	28.871
1800	197.560	393.420	253.854	251.219	−1754.069	−891.492	25.870
1900	200.556	404.182	261.485	271.125	−1746.650	−843.772	23.197
2000	203.489	414.544	268.880	291.328	−1738.971	−796.449	20.801
2100	206.376	424.543	276.056	311.822	−1731.037	−749.517	18.643
2200	209.213	434.209	283.026	332.601	−1722.854	−702.968	16.691
2300	212.016	443.571	289.804	353.663	−1714.427	−656.798	14.916
2400	214.781	452.653	296.401	375.003	−1705.760	−611.000	13.298
2500	217.518	461.476	302.829	396.618	−1696.857	−565.567	11.817

PREVIOUS: June 1965 CURRENT: September 1967

$S°$(298.15 K) = [150.496] J·K^{-1}·mol^{-1}
T_{fus} = 1362 ± 0.5 K

$\Delta_f H°$(298.15 K) = [−1510.875] kJ·mol^{-1}
$\Delta_{fus}H°$ = 51.798 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(Na_2SiO_3, l, 298.15\ K)$ is calculated from $\Delta_f H°(Na_2SiO_3, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1362\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity above 900 K is derived as constant from the high temperature enthalpy data, 1414–1747 K, measured by Naylor.[1] A glass transition temperature is assumed at 900 K, i.e., the heat capacities below 900 K are taken to be those for Na_2SiO_3(cr).

$S°$(l, 298.15 K) is calculated in a manner analogous to that used for the enthalpy of formation. The low temperature heat capacities, 63.74–162.48 K, have been measured by Tarasov and Savitskaya;[2] however, these are not adequate to be used to evaluate $S°$(298.15 K).

Fusion Data

The adopted T_{fus} = 1362 K, determined by Kracek,[3] is in good agreement with the value 1261 K reported by Jaeger[4] and later confirmed by Morey and Bowen.[5]

Other reported T_{fus} values are 1280, 1291, and 1329 K by Kultascheff,[6] Wallace[7] and van Klooster,[8] respectively. These values are all lower than the adopted T_{fus} value, probably because the sample compositions were not the exact composition of metasilicate.

The value of $\Delta_{fus}H°$ is evaluated from the adopted heat capacities for Na_2SiO_3(cr) and Na_2SiO_3(l), and the enthalpy data reported by Naylor,[1] assuming the final state of the calorimetric sample to be Na_2SiO_3(cr). From the phase diagrams of Na_2SiO_3 with other compounds, Kelley[9] derived the values of $\Delta_{fus}H°$ of 9.8–10.5 kcal·mol^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	111.880	150.496	150.496	0.	−1510.875	−1427.704	250.128
300	112.395	151.189	150.498	0.207	−1510.890	−1427.188	248.496
400	127.779	185.767	155.108	12.264	−1516.655	−1398.786	182.663
500	138.716	215.514	164.284	25.615	−1516.373	−1369.330	143.053
600	147.114	241.575	175.039	39.922	−1515.214	−1340.018	116.659
700	153.946	264.782	186.232	54.985	−1513.385	−1310.955	97.825
800	159.749	285.727	197.381	70.677	−1511.025	−1282.192	83.719
900	164.842	304.843	208.274	86.912	−1508.235	−1253.751	72.766
900.000	164.842	304.843	208.274	86.912	GLASS <--> LIQUID		
900.000	177.318	304.843	208.274	86.912	TRANSITION		
1000	177.318	323.525	218.882	104.644	−1504.081	−1225.699	64.024
1100	177.318	340.425	229.175	122.375	−1500.086	−1198.055	56.891
1200	177.318	355.854	239.098	140.107	−1689.797	−1165.888	50.750
1300	177.318	370.047	248.632	157.839	−1684.338	−1122.451	45.101
1362.000	177.318	378.308	254.349	168.833	--- CRYSTAL <--> LIQUID ---		
1400	177.318	383.188	257.780	175.571	−1678.966	−1079.431	40.274
1500	177.318	395.421	266.553	193.303	−1673.677	−1036.792	36.104
1600	177.318	406.865	274.969	211.034	−1668.470	−994.504	32.467
1700	177.318	417.615	283.047	228.766	−1713.518	−952.091	29.254
1800	177.318	427.750	290.807	246.498	−1708.238	−907.454	26.334
1900	177.318	437.337	298.269	264.230	−1702.994	−863.110	23.729
2000	177.318	446.433	305.452	281.962	−1697.785	−819.040	21.391
2100	177.318	455.084	312.373	299.693	−1692.613	−775.230	19.283
2200	177.318	463.333	319.049	317.425	−1687.478	−731.665	17.372
2300	177.318	471.215	325.495	335.157	−1682.381	−688.333	15.633
2400	177.318	478.762	331.725	352.889	−1677.322	−645.223	14.043
2500	177.318	486.000	337.752	370.621	−1672.303	−602.322	12.585

PREVIOUS: June 1965 CURRENT: September 1967

0 to 1362 K crystal
above 1362 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−18.913	−1551.203	−1551.203	INFINITE
100	48.308	25.568	196.995	−17.143	−1556.736	−1528.150	798.224
200	89.743	73.542	123.451	−9.982	−1560.031	−1498.083	391.259
298.15	111.880	113.847	113.847	0.	−1561.427	−1467.330	257.070
300	112.395	114.540	113.849	0.207	−1561.442	−1466.746	255.383
400	127.779	149.118	118.459	12.264	−1567.208	−1434.679	187.350
500	138.716	178.865	127.635	25.615	−1566.925	−1401.558	146.420
600	147.114	204.926	138.390	39.922	−1565.766	−1368.581	119.146
700	153.946	228.133	149.583	54.985	−1563.937	−1335.853	99.683
800	159.749	249.078	160.732	70.677	−1561.578	−1303.425	85.105
900	164.841	268.193	171.625	86.911	−1558.788	−1271.319	73.785
1000	169.423	285.801	182.174	103.628	−1555.650	−1239.544	64.747
1100	173.628	302.149	192.346	120.783	−1552.231	−1208.096	57.368
1200	177.540	317.425	202.140	138.343	−1742.114	−1172.091	51.020
1300	181.230	331.783	211.566	156.283	−1736.446	−1124.817	45.196
1362.000	183.407	340.278	217.233	167.587	CRYSTAL <--> LIQUID		
1362.000	177.318	378.308	217.233	219.385	TRANSITION		
1400	177.318	383.188	221.671	226.123	−1678.966	−1079.431	40.274
1500	177.318	395.421	232.851	243.855	−1673.677	−1036.792	36.104
1600	177.318	406.865	243.374	261.587	−1668.470	−994.504	32.467
1700	177.318	417.615	253.310	279.319	−1713.518	−952.091	29.254
1800	177.318	427.750	262.722	297.050	−1708.238	−907.454	26.334
1900	177.318	437.337	271.663	314.782	−1702.994	−863.110	23.729
2000	177.318	446.433	280.176	332.514	−1697.785	−819.040	21.391
2100	177.318	455.084	288.300	350.246	−1692.613	−775.230	19.283
2200	177.318	463.333	296.070	367.978	−1687.478	−731.665	17.372
2300	177.318	471.215	303.515	385.709	−1682.381	−688.334	15.633
2400	177.318	478.762	310.661	403.441	−1677.322	−645.223	14.043
2500	177.318	486.000	317.531	421.173	−1672.303	−602.322	12.585

PREVIOUS: CURRENT: September 1967

$S°(298.15\ K)$ = [163.212] $J·K^{-1}·mol^{-1}$
$T_{trs}(I \rightarrow \delta)$ = [986] K
$T_{fus}(\delta \rightarrow l)$ = [1170] K

$\Delta_f H°(298.15\ K)$ = [−1379.294] $kJ·mol^{-1}$
$\Delta_{trs}H°(I \rightarrow \delta)$ = [0.502] $kJ·mol^{-1}$
$\Delta_{fus}H°(\delta \rightarrow l)$ = [21.338] $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation adopted in this tabulation is obtained from $\Delta_f H°(298.15\ K)$ for Na_2SO_4(cr, I) by adding $\Delta_{trs}H°(I \rightarrow \delta)$ and the difference between $H°(986\ K)$ $H°(298.15\ K)$ for Na_2SO_4(cr, I) and Na_2SO_4(cr, δ).[2]

Heat Capacity and Entropy

Heat capacities in the range 900–1010 K were measured by Shmidt and Sokolov[1] in an adiabatic calorimeter. We have graphically extrapolated these data down to 298.15 K, paralleling the $C_p°$ data of Na_2SO_4(cr, I), and extended the data smoothly to 1500 K. Our calculated enthalpies are biased by some 300 $cal·K^{-1}·mol^{-1}$ above the experimental results (for the I phase) of Denielou *et al.*[3] and Coughlin.[4] See the discussion in the Na_2SO_4(cr, I) table.[2]

Transition Data

The existence of Na_2SO_4(cr, δ) is based on the work of Shmidt and Sokolov[1] who found an anomolous region in the heat capacity curve of Na_2SO_4(cr, I) between 963–993 K. Popov and Ginzburg[5] also observed a sharp change in the heat capacity above 837.6 K. Simanov and Kirkina[6] have observed an orthorhombic modification of Na_2SO_4 at 993 K by X-ray diffraction. As noted above, our calculated enthalpies do not agree with measured enthalpies above 980 K. The evidence for the existence of the δ phase is not conclusive. We have deleted the δ phase from our combined phase table for Na_2SO_4. The heat of transition $\Delta_{trs}H°(I \rightarrow \delta, 986\ K)$ = 120 ± 10 $cal·mol^{-1}$ is obtained by graphical integration of the area between the measured $C_p°$ curve from[1] and the adopted $C_p°$ curve for Na_2SO_4(cr, I).[2] The temperature of the transition is assumed to be 986 K.

Fusion Data

Based on our selected $C_p°$ values for Na_2SO_4(cr, δ) and Na_2SO_4(l), we derive $\Delta_{fus}H°(\delta \rightarrow l)$ = 5.10 ± 0.10 $kcal·mol^{-1}$ using the experimental liquid enthalpies from Denielou *et al.*[3] and Coughlin.[4] $T_{fus}(\delta \rightarrow l)$ = 1170 K is the calculated temperature at which $\Delta_r G°$ = 0 for Na_2SO_4(cr, δ) → Na_2SO_4(l).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	155.812	163.212	163.212	0.	−1379.294	−1265.387	221.690
300	155.896	164.176	163.215	0.288	−1379.261	−1264.680	220.200
400	163.050	210.099	169.427	16.269	−1385.063	−1226.248	160.132
500	166.251	246.782	181.355	32.714	−1384.866	−1186.573	123.960
600	171.816	277.574	194.889	49.611	−1383.905	−1146.990	99.854
700	178.113	304.516	208.664	67.097	−1382.180	−1107.631	82.652
800	185.707	328.766	222.184	85.266	−1379.714	−1068.569	69.770
900	195.979	351.212	235.287	104.333	−1429.489	−1028.786	59.709
1000	208.112	372.490	247.951	124.539	−1423.838	−984.557	51.428
1100	220.413	392.907	260.207	145.970	−1417.113	−940.945	44.682
1200	232.086	412.592	272.090	168.602	−1602.887	−893.112	38.876
1300	242.881	431.600	283.633	192.357	−1592.358	−834.384	33.526
1400	252.923	449.977	294.862	217.160	−1580.856	−776.504	28.972
1500	261.333	467.723	305.798	242.887	−1568.503	−719.477	25.054

PREVIOUS: December 1966 CURRENT: June 1978

$S°(298.15\ K) = [160.132 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(III \rightarrow I) = 509 \pm 1\ K$
$T_{trs}(IV \rightarrow I) = 514 \pm 1\ K$
$T_{fus}(I \rightarrow l) = 1157 \pm 1\ K$

$\Delta_f H°(298.15\ K) = [-1380.899 \pm 0.8]\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(III \rightarrow I) = 6.887 \pm 0.084\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(IV \rightarrow I) = 10.908 \pm 0.084\ kJ \cdot mol^{-1}$
$\Delta_{fus} H°(I \rightarrow l) = 23.849 \pm 0.42\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation adopted in this tabulation is obtained from $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K)$ by adding $\Delta_{trs} H°(III \rightarrow I, 509\ K) = 1646\ cal \cdot K^{-1} \cdot mol^{-1}$ [1,2] and the difference between $H°(509\ K)$ $H°(298.15\ K)$ for Na_2SO_4(cr, III) and Na_2SO_4(cr, I).[2]

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(cr, I) have been measured by Shmidt and Sokolov[3] in an adiabatic calorimeter over the temperature range 538.65–1021.75 K. The direct heating measurements of Popov and Galchenko[4] using a heat flow calorimeter are in substantial agreement. Enthalpy measurements by drop calorimetry have been carried out by Coughlin,[5] 515–1143 K, Popov and Ginzburg,[6] 1173–1290 K, May,[7] (520–1157 K), and by Denielou *et. al.*,[8] 516–1154 K.

The data of May[7] are not in agreement with the other enthalpy results. The enthalpy data of references[5, 6, 8] are in general agreement but our derived $C_p°$ values are lower than the calorimetric $C_p°$[3] results below 800 K but show the proper slope. Derived $C_p°$ values from Denielou *et. al.*[8] are in agreement with the calorimetric results above 930 K. All of the experiments seem to show a change in the slope of the $C_p°$ curve near 900 K. We adopt $C_p°$ from 530–880 K from[3] and extrapolate smoothly to 1500 K. $C_p°$ values below 530 K are obtained by graphical extrapolation. The entropy, $S°(298.15\ K)$, is calculated in a manner analogous to that of the heat of formation.

Transition Data

Na_2SO_4(cr, I) is the hexagonal modification (space group D_{3d}^3 or C3ml)[9, 10] of anhydrous sodium sulfate stable from 514–1157 K. All the low temperature modifications (III, IV, V) are converted to the high temperature form between 500–530 K;[2] $\Delta_{trs} H°(IV \rightarrow I, 514\ K) = 2607\ cal \cdot mol^{-1}$, [1, 2] $\Delta_{trs} H°(V \rightarrow I, 512\ K) = 2663\ cal \cdot mol^{-1}$, [1, 2] and $\Delta_{trs} H°(III \rightarrow I, 509\ K) = 1646\ cal \cdot mol^{-1}$. [1, 2]

A small anomalous region between 963.15–993.15 K on the $C_p°$ curve for Na_2SO_4(cr, I) was reported by Shmidt and Sokolov,[3] who attributed the anomaly to a transition to another phase of Na_2SO_4 which they referred to as the δ phase. There is not sufficient evidence to warrant our inclusion of the δ phase.

Fusion Data

The enthalpy of melting of Na2SO4(cr, I) → Na2SO4 (l) has been derived from drop calorimetry data by Denielou *et. al.*,[8] 5.58 ± 0.13 kcal·mol^{-1}, Coughlin,[5] 5.67 ± 0.1 kcal·mol^{-1}, Popov and Ginzburg,[6] 5.77 ± 0.2 kcal·mol^{-1}, and May,[7] 5.8 ± 0.2 kcal·mol^{-1}. No mention was made of the δ phase. Based on our selected $C_p°$ values for Na_2SO_4(cr, I) and Na_2SO_4(l), we derive $\Delta_{fus} H°(I \rightarrow l) = 5.70 \pm 0.10\ kcal \cdot mol^{-1}$, using the enthalpy data of Coughlin.[5] There is good agreement on the melting temperature which we take as $T_{fus}(I \rightarrow l) = 1157 \pm 1\ K$.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	159.620	160.132	160.132	0.	−1380.899	−1266.074	221.811
300	159.724	161.120	160.135	0.295	−1380.859	−1265.361	220.319
400	164.758	207.754	166.460	16.518	−1386.419	−1226.666	160.186
500	170.017	245.088	178.571	33.258	−1385.927	−1186.787	123.983
514.000	170.732	249.793	180.447	35.644	- - - - - - - - IV <- - > I - - - - - - -		
600	175.331	276.549	192.345	50.522	−1384.599	−1147.069	99.861
700	181.042	303.999	206.375	68.337	−1382.545	−1107.634	82.653
800	187.276	328.577	220.140	86.750	−1379.835	−1068.539	69.768
900	193.845	351.015	233.452	105.807	−1429.621	−1028.740	59.707
1000	200.309	371.773	246.259	125.515	−1424.467	−984.470	51.423
1100	206.731	391.167	258.560	145.867	−1418.821	−940.739	44.672
1157.000	210.367	401.702	265.354	157.755	- - - - - I <- - > LIQUID - - - - - -		
1200	213.133	409.428	270.379	166.860	−1606.234	−892.663	38.857
1300	219.447	426.739	281.746	188.490	−1597.830	−833.536	33.492
1400	225.598	443.227	292.696	210.744	−1588.878	−775.076	28.918
1500	231.584	458.997	303.261	233.604	−1579.391	−717.276	24.978

PREVIOUS: December 1966 CURRENT: June 1978

$S°(298.15\ K) = 154.908 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(III \rightarrow I) = 509 \pm 1\ K$

$\Delta_f H°(0\ K) = -1373.71 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1384.85 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(III \rightarrow I) = 6.887 \pm 0.084\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Brodale and Giauque[1] determined the enthalpy of solution at infinite dilution $\Delta_{sln}H°(Na_2SO_4, cr, III, 298.15\ K) = -1273 \pm 4\ cal \cdot K^{-1} \cdot mol^{-1}$ for the process $Na_2SO_4(cr, III) \rightarrow Na_2SO_4(aq, \infty)$. When this result is combined with the enthalpies of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(Na_2SO_4, aq, \infty, 298.15\ K) = -332.266 \pm 0.13\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.993 \pm 0.15\ kcal \cdot mol^{-1}$. Coughlin[3] also measured the enthalpy of solution, $\Delta_{sln}H°(Na_2SO_4, cr, III, 303\ K) = -1363 \pm 4\ cal \cdot K^{-1} \cdot mol^{-1}$ for the process $Na_2SO_4(cr, III) \rightarrow Na_2SO_4(aq, 1068\ H_2O)$. Using $\Delta C_p°$ as determined by Coughlin to extrapolate the heat of solution to 298 K gives $\Delta_{sln}H°(Na_2SO_4, cr, III, 298.15\ K) = -1037 \pm 20\ cal \cdot K^{-1} \cdot mol^{-1}$. Extrapolating to infinite dilution using the data of Lange and Streeck[4] and Wallace and Robinson[5] gives $\Delta_{sln}H°(Na_2SO_4, cr, III, 298.15\ K) = -1282 \pm 20\ cal \cdot K^{-1} \cdot mol^{-1}$. Using the same auxiliary data as above[2] $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.984 \pm 0.15\ kcal \cdot mol^{-1}$. The enthalpy of solution data of Coughlin[3] as corrected by Brodale and Giauque[1] leads to $\Delta_r H°(V \rightarrow III, 298.15\ K) = 716 \pm 8\ cal \cdot K^{-1} \cdot mol^{-1}$. When this is combined with auxiliary data for Na_2SO_4(cr, V),[6] we obtain $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.980 \pm 0.2\ kcal \cdot mol^{-1}$. We adopt an intermediate value $\Delta_f H°(Na_2SO_4, cr, III, 298.15\ K) = -330.988 \pm 0.15\ kcal \cdot mol^{-1}$ for this tabulation.

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(cr, III) have been measured by Brodale and Giauque[1] over the ragne 13.16–297.71 K and by Shmidt and Sokolov[7] in an adiabatic calorimeter over the temperature range 319.03–520.56 K. Paukov and Lavrent'eva[8] also measured the low temperature heat capacity of Na_2SO_4(cr, III) but their results are intermediate between Na_2SO_4(cr, V) and Na_2SO_4(cr, III) indicating that their sample may have been converted to as much as two–thirds of the V modification. Coughlin[3] measured enthalpies of Na_2SO_4(cr, III) from 370.2–514.9 K by drop calorimetry, but his data appear high by 2% at 450 K. Enthalpy measurements of Denielou *et al.*[9] are in very good agreement with the $C_p°$ measurements of Shmidt and Sokolov.[7] We combine the three sets of experimental data[1, 7, 9] by graphical smoothing and by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. $C_p°$ is smoothly extrapolated to 1000 K. $S°(298.15\ K)$ is derived from our combined smooth fit based on $S°(14\ K) = 0.100\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(14\ K) - H°(0\ K) = 1.051\ cal \cdot K^{-1} \cdot mol^{-1}$ derived from a Debye T^3–law extrapolation.

Transition Data

Na_2SO_4(cr, III) is the meltable low–temperature orthorhombic modification of anhydrous sodium sulfate which is obtained on cooling, in the absence of moisture, the high–temperature hexagonal form Na_2SO_4(cr, I). Na_2SO_4(cr, III) is metastable with respect to the two other low–temperature orthorhombic forms Na_2SO_4(cr, V) and Na_2SO_4(cr, IV). The space group of Na_2SO_4(cr, III) has been given as Cmcm.[10]

The second–order transformation from Na_2SO_4(cr, III) to Na_2SO_4(cr, I) in which both phases are metastable, has been observed by Shmidt and Sokolov[7] at 521.5 K, $\Delta_{trs}H°(III \rightarrow I) = 1642 \pm 20\ cal \cdot mol^{-1}$; by Coughlin[3] at 514 K, $\Delta_{trs}H°(III \rightarrow I) = 1680\ cal \cdot mol^{-1}$, by Denielou *et al.*[9] at 515 ± 1 K, $\Delta_{trs}H°(III \rightarrow I) = 1650 \pm 90\ cal \cdot mol^{-1}$; and by May[11] at 520 ± 5 K, $\Delta_{trs}H°(III \rightarrow I) = 1150\ cal \cdot mol^{-1}$. We adopt the transition temperature from the analysis of Brodale and Giauque.[1] This is consistent with our analysis which yields $\Delta_{trs}H°(III \rightarrow I, 298.15\ K) = 1646 \pm 20\ cal \cdot mol^{-1}$. The heat of transition from metastable Na_2SO_4(cr, V) to metastable Na_2SO_4(cr, III) has been measured by heat of solution measurements on the separate crystalline forms by Coughlin,[3] Brodale and Giauque[1] and Pickering.[12] $\Delta_r H°(V \rightarrow III, 298.15\ K) = 716 \pm 8\ cal\ mol\ l^{-1}$,[1, 3] $699 \pm 10\ cal \cdot mol^{-1}$,[1] $709 \pm 10\ cal \cdot mol^{-1}$[1, 13] and $\Delta_r H°(V \rightarrow III, 294\ K) = 708 \pm 20\ cal \cdot mol^{-1}$.[12] Using the heat of transition value from[1] and the difference between $H°(517\ K) - H°(298.15\ K)$ for Na_2SO_4(cr, III) and Na_2SO_4(cr, V),[6] we obtain $\Delta_{trs}H°(V \rightarrow III, 517\ K) = 1041 \pm 20\ cal \cdot mol^{-1}$. The heat of transition from metastable Na_2SO_4(cr, IV) to metastable Na_2SO_4(cr, III) is discussed on the table for Na_2SO_4(cr, IV). Our analysis yields $\Delta_{trs}H°(IV \rightarrow III, 519\ K) = 988 \pm 20\ cal \cdot mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.527	−1373.708	−1373.708	INFINITE
100	68.216	47.861	252.668	−20.481	−1379.841	−1343.950	702.008
200	105.621	108.169	165.992	−11.565	−1383.300	−1306.534	341.232
298.15	129.168	154.908	154.908	0.	−1384.854	−1268.471	222.231
300	129.570	155.709	154.911	0.239	−1384.870	−1267.748	220.735
400	150.143	195.743	160.231	14.205	−1392.687	−1228.129	160.377
500	173.167	231.587	170.966	30.311	−1392.829	−1186.938	123.999
600	200.091	265.539	183.916	48.973	−1390.103	−1145.967	99.765
700	227.011	298.405	197.935	70.329	−1384.508	−1105.681	82.507
800	253.935	330.475	212.505	94.376	−1376.164	−1066.386	69.628
900	280.859	361.939	227.366	121.116	−1418.266	−1027.217	59.618
1000	307.779	392.924	242.376	150.548	−1403.389	−984.542	51.427

PREVIOUS: December 1966 CURRENT: June 1978

$S°(298.15\ K) = [150.157 \pm 0.4]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(V \rightarrow IV) = 458 \pm 1\ K$
$T_{trs}(IV \rightarrow I) = 514 \pm 1\ K$

$\Delta_f H°(0\ K) = [-1380.09]\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1387.559 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(V \rightarrow IV) = 0.255 \pm 0.063\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(IV \rightarrow I) = 10.908 \pm 0.084\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Brodale and Giauque[1] determined the enthalpy of solution at infinite dilution $\Delta_{sln} H°(Na_2SO_4, cr, IV, 298.15\ K) = 635 \pm 1\ kcal \cdot mol^{-1}$ for the process $Na_2SO_4(cr, IV) \rightarrow Na_2SO_4(aq, \infty)$. When this result is combined with the enthalpies of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(Na_2SO_4, aq, \infty, 298.15\ K) = 332.266 \pm 0.13\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Na_2SO_4, cr, IV, 298.15\ K) = -331.631 \pm 0.15\ kcal \cdot mol^{-1}$. Brodale and Giauque[1] have also determined the difference in $\Delta_f H°(298.15\ K)$ between $Na_2SO_4(cr, IV)$ and $Na_2SO_4(cr, V)$ by direct heat of solution experiments. We prefer to give complete weight to these results using the same calorimeter. $\Delta_{sln} H°(Na_2SO_4, cr, V, 298.15\ K) = -574\ cal \cdot K^{-1} \cdot mol^{-1}$ [1] which leads to $\Delta_f H°(V \rightarrow IV, 298.15\ K) = 61 \pm 15\ cal \cdot K^{-1} \cdot mol^{-1}$. When this is combined with auxiliary data for $Na_2SO_4(cr, V)$,[3] we obtain $\Delta_f H°(Na_2SO_4, cr, IV, 298.15\ K) = -331.635 \pm 0.15\ kcal \cdot mol^{-1}$. This value of $\Delta_f H°(298.15\ K)$ is adopted in this tabulation.

Heat Capacity and Entropy

The heat capacity of $Na_2SO_4(cr, IV)$ has been taken equal to the heat capacity of the V form from 298–514 K.[1, 3] The heat of transition ($V \rightarrow IV$) adopted here leads to a calculated entropy of transition of $0.133\ cal \cdot K^{-1} \cdot mol^{-1}$ and $S°(Na_2SO_4, cr, IV, 458\ K) = 50.304\ cal \cdot K^{-1} \cdot mol^{-1}$. Brodale and Giauque[1] state that the small difference in entropy (between IV and V) means that on the average the heat capacity of $Na_2SO_4(cr, IV)$ should exceed the heat capacity of $Na_2SO_4(cr, V)$ by only about 0.3% over the range 298–514 K. We calculate $S°(Na_2SO_4, cr, IV, 298.15\ K) = 35.887\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

$Na_2SO_4(cr, IV)$ is the orthorhombic modification of anhydrous sodium sulfate stable from 458 514 K.[1, 4] This form can persist down to low temperatures. The presence of moisture enhances the achievement of equilibrium. A recent Raman and DSC study has failed to observe the IV modification.[8] The ($V \rightarrow IV$) transition at 458 K has been discussed previously (see [3] and above), $\Delta_f H°(V \rightarrow IV, 298.15\ K) = 61 \pm 15\ cal \cdot mol^{-1}$. Since $\Delta C_p° = 0$,[1, 3] $\Delta_{trs} H°(V \rightarrow IV, 458\ K) = 61 \pm 15\ cal \cdot mol^{-1}$. The temperature of 458 K for the transition is taken from Kracek[4] and Brodale and Giauque.[1]

The transition from $Na_2SO_4(cr, IV)$ to $Na_2SO_4(cr, I)$ has been found to occur at 514 K.[1, 4] The heat of the transition has not been directly measured although Shmidt and Sokolov[5] obtained $\Delta_{trs} H°(516\ K) = 2584 \pm 15\ cal \cdot mol^{-1}$ for a sample of ground Na_2SO_4 which could have been $Na_2SO_4(cr, IV)$ (see [1]). We adopt the value of the heat of transition $\Delta_{trs} H°(IV \rightarrow I, 514\ K) = 2607 \pm 20\ cal \cdot mol^{-1}$. This is obtained by summation of $\Delta_{trs} H°(IV \rightarrow III)$[1, 3] and $\Delta_{trs} H°(III \rightarrow I)$,[1, 3] all reduced to 514 K. Other measurements include that of Kreidl and Simon[6] who found $\Delta_{trs} H°(IV \rightarrow I, 511\ K) = 2300\ cal \cdot mol^{-1}$ and Popov and Galchenko[7] who found $\Delta_{trs} H°(518\ K) = 2586 \pm 64\ cal \cdot mol^{-1}$ on first heating. Later heating apparently converted some sample over to the III modification. Brodale and Giauque[1] give $\Delta_{trs} H°(IV \rightarrow I, 514\ K) = 2611\ cal \cdot mol^{-1}$.

The heat of transition from metastable $Na_2SO_4(cr, IV)$ to metastable $Na_2SO_4(cr, III)$ is obtained from heat of solution measurements on the separate crystalline forms. Brodale and Giauque[1] obtained $\Delta_{sln} H°(Na_2SO_4, cr, IV, 298.15\ K) = -635 \pm 1\ cal \cdot mol^{-1}$ and $\Delta_{sln} H°(Na_2SO_4, cr, III, 298.15\ K) = -1273 \pm 4\ cal \cdot mol^{-1}$ from which $\Delta_f H°(IV \rightarrow III, 298.15\ K) = 638 \pm 10\ cal \cdot mol^{-1}$. Combining this result with the difference between $H°(519\ K) - H°(298.15\ K)$ for $Na_2SO_4(cr, IV)$ and $Na_2SO_4(cr, III)$ we obtain $\Delta_{trs} H°(IV \rightarrow III, 519\ K) = 988 \pm 20\ cal \cdot mol^{-1}$. Shmidt and Sokolov[5] have measured the heats of transformation of Na_2SO_4(thenardite) $\rightarrow Na_2SO_4$,cr, I) and $Na_2SO_4(cr, III) \rightarrow Na_2SO_4(cr, I)$ calorimetrically from which we obtain $\Delta_{trs} H°$(thenardite $\rightarrow$ III, 516 K) = $954 \pm 20\ cal \cdot mol^{-1}$. Brodale and Giauque[1] have speculated that the "ground thenardite" of Shmidt and Sokolov[5] was actually the IV modification of Na_2SO_4.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	128.143	150.157	150.157	0.	−1387.559	−1269.759	222.456
300	128.495	150.950	150.159	0.237	−1387.577	−1269.028	220.957
400	145.101	190.263	155.407	13.943	−1395.654	−1228.904	160.478
458.000	153.331	210.462	161.117	22.600	-------- V <--> IV --------		
500	158.908	224.159	165.842	29.158	−1396.687	−1187.082	124.014
514.000	160.712	228.572	167.491	31.396	-------- IV <--> I --------		
600	171.322	254.242	178.113	45.677	−1396.104	−1145.190	99.698
700	182.933	281.530	190.967	63.394	−1394.148	−1103.508	82.345
800	194.046	306.686	203.879	82.246	−1390.999	−1062.190	69.354
900	204.828	330.166	216.620	102.191	−1439.895	−1020.251	59.214
1000	215.371	352.295	229.091	123.203	−1433.438	−973.962	50.875

PREVIOUS: CURRENT: June 1978

$S°(298.15\ K) = 149.595 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(V \rightarrow IV) = 458 \pm 1\ K$

$\Delta_f H°(0\ K) = -1376.361 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1387.816 \pm 0.63\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°(V \rightarrow IV) = 0.255 \pm 0.063\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Shibata *et. al.*[1] measured the emf of the cell: Na(amalgam, 0.2077%)|Na_2SO_4(sat. soln), Hg_2SO_4|Hg at 306–310 K. Extrapolating their results to 298 K, correcting the observed voltage for the formation of the Na amalgam, and converting to absolute volts, we have E_{cell} = 3.33404 volts for the reaction at 298 K, 2 Na(cr) + Hg_2SO_4(cr) = 2 Hg(l) + Na_2SO_4(cr, V). From this voltage we calculate $\Delta_f G°(298.15\ K) = -153.77\ kcal \cdot mol^{-1}$. Taking $\Delta_f G°(Hg_2SO_4, cr, 298.15\ K) = -149.66\ kcal \cdot mol^{-1}$ [2] and reference entropies from,[3] we calculate $\Delta_f G°(Na_2SO_4, cr, V, 298.15\ K) = -303.43\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Na_2SO_4, cr, V, 298.15\ K) = -331.60 \pm 0.2\ kcal \cdot mol^{-1}$.

The enthalpy of solution at infinite dilution, $\Delta_{sln} H°(Na_2SO_4, cr, V, 298.15\ K) = -570 \pm 10\ cal \cdot K^{-1} \cdot mol^{-1}$ adopted in this tabulation is based on our reanalysis of the enthalpy of solution measurements of Gardner *et al.*,[4] Brodale and Giauque,[5] Pitzer and Coulter,[6] Coughlin[7] as corrected in,[5] and Readnour and Cobble.[8] When this result is combined with heats of formation of the infinitely dilute ions from CODATA,[2] we obtain $\Delta_f H°(Na_2SO_4, aq, \infty, 298.15\ K) = -332.266 \pm 0.13\ kcal \cdot mol^{-1}$ and $\Delta_f H°(Na_2SO_4, cr, V, 298.15\ K) = -331.696 \pm 0.15\ kcal \cdot mol^{-1}$. The experimental $\Delta_{sln} H°$ values and the number of determinations are $-582 \pm 5\ cal \cdot K^{-1} \cdot mol^{-1}$, 6,[4] $-574\ cal \cdot K^{-1} \cdot mol^{-1}$, 1,[5] $-564 \pm 10\ cal \cdot K^{-1} \cdot mol^{-1}$, 2,[6] $-565 \pm 30\ cal \cdot K^{-1} \cdot mol^{-1}$, 5,[7,5] and $-567 \pm 12\ cal \cdot K^{-1} \cdot mol^{-1}$, 9.[8]

We adopt $\Delta_f H°(Na_2SO_4, cr, V, 298.15\ K) = -331.696 \pm 0.5\ kcal \cdot mol^{-1}$ from the heat of solution results for consistency with the other modifications of Na_2SO_4(cr).[3]

Heat Capacity and Entropy

Heat capacities of Na_2SO_4(cr, V) have been measured by Pitzer and Coulter[6] over the range 13.74–313.44 K and by Shmidt and Sokolov[9] in an adiabatic calorimeter over the temperature range 324.62–503.06 K. Shmidt[10] later carried out additional measurements which he combined with the earlier measurements of Shmidt and Sokolov[9] and reported $C_p°$ values extending from 298.5–503.1 K. We have smoothed the experimental data[6, 9, 10] by fitting the data with orthogonal polynomials over selected overlapping temperature intervals. The data have been smoothly extrapolated to 1000 K. We have given no weight to the calorimetry enthalpy differences measured by Coughlin,[7] May,[11] and Denielou *et. al.*[12] These measured enthalpies are higher than our calculated enthalpies by 6%, 9% and 2%, respectively at 400 K. The $C_p°$ measurements of Popov and Galchenko[13] from 373–468 K appear to be biased, being too low at 373 K and too high at 468 K. $S°(298.15\ K)$ is derived from our combined smooth fit based on $S°(14\ K) = 0.059\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(14\ K) - H°(0\ K) = 0.620\ cal \cdot mol^{-1}$ derived from a T^3 law extrapolation.

Transition Data

Na_2SO_4(cr, V) is the stable low temperature modification of anhydrous sodium sulfate which is obtained by crystallization from aqueous solution above 305.65 K under ordinary pressure. The mineral is known as thenardite and exists in the form of orthorhombic crystals (space group Fddd).[15]

Polymorphism studies by Kracek[14] indicated five distinct modifications of anhydrous sodium sulfate, i.e., V, IV, III, II, I. Calorimetric studies by Shmidt and Sokolov[9] as well as the X-ray work of Simanov and Kirkina[15] suggested another form, stable at high temperatures which is labeled as δ. Brodale and Giauque[5] have recently reviewed the relationships among the various crystalline forms of Na_2SO_4(cr). Their analysis shows that Na_2SO_4(cr, V) is the stable form from 0 to 458 K; Na_2SO_4(cr, IV) rather than Na_2SO_4 (cr, III) is the stable form from 458 to 514 K; Na_2SO_4(cr, I) is the form stable from 514 K to the melting point. Na_2SO_4(cr, III) is metastable at all temperatures from 0 to 517 K. Na_2SO_4(cr, II) is a meta stable phase intermediate between forms III and I. The phase transitions are sluggish and subject to hysteresis. Forms V, IV and III can all persist far beyond their stable regions.

The heat of transition $\Delta_{trs} H°(V \rightarrow IV, 458\ K) = 61 \pm 15\ cal \cdot mol^{-1}$ is discussed on the table for Na_2SO_4(cr, IV).[3] The temperature of the transition is taken from the work of Kracek[14] and Brodale and Giauque.[5] The heat of transition from metastable Na_2SO_4(cr, V) to metastable Na_2SO_4(cr, III) $\Delta_{trs} H°(V \rightarrow III, 517\ K) = 1041 \pm 20\ cal \cdot mol^{-1}$ has been discussed on the table for Na_2SO_4(cr, III).[3] This compares to $\Delta_{trs} H°(V \rightarrow III, 521\ K) = 1030 \pm 25\ cal \cdot mol^{-1}$ from Shmidt and Sokolov[9] and $\Delta_{trs} H°(V \rightarrow III, 514\ K) = 1040 \pm 20\ cal \cdot mol^{-1}$ from.[5] The heat of transition from metastable Na_2SO_4(cr, V) to metastable Na_2SO_4(cr, I) at 512 ± 1 K is obtained by summation of $\Delta_{trs} H°(V \rightarrow III) = 1021\ cal \cdot mol^{-1}$ and $\Delta_{trs} H°(III \rightarrow I) = 1642\ cal \cdot mol^{-1}$ [5] to yield $\Delta_{trs} H°(V \rightarrow I, 512\ K) = 2663 \pm 25\ cal \cdot mol^{-1}$, in good agreement with the value measured by Shmidt and Sokolov,[9] $\Delta_{trs} H°(V \rightarrow I, 521\ K) = 2673 \pm 5\ cal \cdot mol^{-1}$. Brodale and Giauque[5] give $\Delta_{trs} H°(V \rightarrow I, 512\ K) = 2681 \pm 20\ cal \cdot mol^{-1}$.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$	$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹		kJ·mol⁻¹			
0	0.	0. INFINITE	−23.217	−1376.361	−1376.361	INFINITE
100	66.542	43.120 247.007	−20.389	−1382.711	−1346.347	703.259
200	105.667	103.010 160.624	−11.523	−1386.221	−1308.422	341.725
298.15	128.143	149.595 149.595	0.	−1387.816	−1269.849	222.472
300	128.495	150.388 149.597	0.237	−1387.834	−1269.117	220.973
400	145.101	189.702 154.845	13.943	−1395.911	−1228.937	160.483
458.000	153.331	209.905 160.555	22.602	-------- V <--> IV --------		
500	158.908	223.596 165.280	29.158	−1396.944	−1187.058	124.011
600	171.322	253.678 177.551	45.676	−1396.362	−1145.110	99.691
700	182.933	280.966 190.404	63.393	−1394.406	−1103.372	82.335
800	194.046	306.122 203.316	82.245	−1391.257	−1061.997	69.341
900	204.828	329.602 216.057	102.190	−1440.154	−1020.002	59.199
1000	215.371	351.731 228.529	123.202	−1433.696	−973.656	50.859

PREVIOUS: December 1966 CURRENT: June 1978

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Continued on page 1673

$S°(298.15\ K) = [181.172]\ J·K^{-1}·mol^{-1}$
$T_{fus}(I \rightarrow l) = 1157 \pm 1\ K$
$T_{dcm} = 2500\ K$

$\Delta_f H°(298.15\ K) = [-1356.385]\ kJ·mol^{-1}$
$\Delta_{fus}H°(I \rightarrow l) = 238.49 \pm 0.42\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°(Na_2SO_4$, cr, I, 298.15 K) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(1157 K)–$H°$(298.15 K), between Na_2SO_4(cr, I) and Na_2SO_4(l).[5]

Heat Capacity and Entropy

The enthalpies for Na_2SO_4(l) have been measured by drop calorimetry in the temperature range 1164.7–1826.2 K by Coughlin[1], 1173.3–1502.6 K by Denielou,[2] 1157–1500 K by May[3] and 1173.4–1290.2 K by Popov and Ginzburg.[4] The more recent studies[1, 2, 4] are in very good agreement. The study of May[4] appears biased, being 1% low at 1200 K and 2% high at 1500 K. We have adopted heat capacities derived from the enthalpy data of Coughlin[1] over the range 1157–1800 K. The data have been extended to 800 K and 3000 K. Below an assumed glass transition temperature of 800 K, the heat capacities are taken to be identical to those of the I phase. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The enthalpy of melting of Na_2SO_4(cr, I) → Na_2SO_4(l) has been discussed in the Na_2SO_4(cr, I) table.[5] Kelley[6] had previously reported $\Delta_{fus}H°(1157\ K) = 5.83\ kcal·mol^{-1}$ from data on binary systems. We prefer the results from direct calorimetric measurements.

Vaporization and Decomposition Data

Vaporization data on Na_2SO_4(l) is discordant due primarily to the extent to which the vapor is dissociated. Na_2SO_4(l) can decompose according to various mechanisms, the most significant of which is the reaction $Na_2SO_4(l) = 2\ Na(g) + SO_2(g) + O_2(g)$. Recent experimental data[7,8,9] are in good agreement with dissociation pressures and the heat of reaction calculated from the JANAF Thermochemical Tables.[5] Decomposition to the oxides of sodium produces lower decomposition pressures than decomposition to the metal. In the presence of water vapor, significant decomposition can occur according to $Na_2SO_4(l) + H_2O(g) = 2\ NaOH(g) + SO_2(g) + 1/2\ O_2(g)$.[10] Molecular vaporization data are discussed in the Na_2SO_4(g) table.[5] $T_{dec} = 2500$ K is the calculated temperature at which the Gibbs energy difference is zero for the reaction $Na_2SO_4(l) = 2\ Na(g) + SO_2(g) + O_2(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	159.620	181.172	181.172	0.	−1356.385	−1247.832	218.615
300	159.724	182.160	181.175	0.295	−1356.345	−1247.159	217.150
400	164.758	228.794	187.500	16.518	−1361.905	−1210.568	158.084
500	170.017	266.128	199.611	33.258	−1361.412	−1172.792	122.521
600	175.331	297.589	213.385	50.522	−1360.085	−1135.179	98.826
700	181.042	325.038	227.415	68.337	−1358.031	−1097.848	81.922
800	187.276	349.614	241.179	86.748	−1355.323	−1060.856	69.267
800.000	187.276	349.614	241.179	86.748	GLASS <- -> LIQUID		
800.000	197.033	349.614	241.179	86.748	TRANSITION		
900	197.033	372.822	254.542	106.451	−1404.461	−1023.207	59.385
1000	197.033	393.581	267.426	126.155	−1399.313	−981.123	51.249
1100	197.033	412.360	279.762	145.858	−1394.316	−939.547	44.615
1157.000	197.033	422.314	286.541	157.089	----- I <--> LIQUID ------		
1200	197.033	429.504	291.537	165.561	−1583.018	−893.538	38.895
1300	197.033	445.275	302.764	185.265	−1576.541	−836.345	33.605
1400	197.033	459.877	313.471	204.968	−1570.140	−779.647	29.089
1500	197.033	473.471	323.690	224.671	−1563.809	−723.405	25.191
1600	197.033	486.187	333.453	244.374	−1557.546	−667.583	21.794
1700	197.033	498.132	342.792	264.078	−1551.347	−612.150	18.809
1800	197.033	509.394	351.738	283.781	−1545.210	−557.082	16.166
1900	197.033	520.047	360.319	303.484	−1539.134	−502.351	13.811
2000	197.033	530.154	368.560	323.188	−1533.117	−447.939	11.699
2100	197.033	539.767	376.486	342.891	−1527.159	−393.827	9.796
2200	197.033	548.933	384.118	362.594	−1521.259	−339.997	8.073
2300	197.033	557.692	391.475	382.298	−1515.418	−286.435	6.505
2400	197.033	566.077	398.577	402.001	−1509.635	−233.125	5.074
2500	197.033	574.120	405.439	421.704	−1503.912	−180.055	3.762
2600	197.033	581.848	412.076	441.407	−1498.246	−127.213	2.556
2700	197.033	589.284	418.503	461.111	−1492.640	−74.587	1.443
2800	197.033	596.450	424.731	480.814	−1487.093	−22.168	0.414
2900	197.033	603.364	430.772	500.517	−1481.607	30.053	−0.541
3000	197.033	610.044	436.637	520.221	−1476.185	82.087	−1.429

PREVIOUS: December 1966 CURRENT: June 1978

0	to	458	K crystal, V
458	to	514	K crystal, IV
514	to	1157	K crystal, I
above		1157	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−23.217	−1376.361	−1376.361	INFINITE
100	66.542	43.120	247.007	−20.389	−1382.711	−1346.347	703.259
200	105.667	103.010	160.624	−11.523	−1386.221	−1308.422	341.725
298.15	128.143	149.595	149.595	0.	−1387.816	−1269.849	222.472
300	128.495	150.388	149.597	0.237	−1387.834	−1269.117	220.973
400	145.101	189.702	154.845	13.943	−1395.911	−1228.937	160.483
458.000	153.331	209.905	160.555	22.602	V <--> IV		
458.000	153.331	210.462	160.555	22.857	TRANSITION		
500	158.908	224.159	165.328	29.415	−1396.687	−1187.082	124.014
514.000	160.712	228.572	166.990	31.653	IV <--> I		
514.000	170.732	249.793	166.990	42.560	TRANSITION		
600	175.331	276.549	180.817	57.439	−1384.599	−1147.069	99.861
700	181.042	303.999	196.494	75.253	−1382.545	−1107.634	82.653
800	187.276	328.577	211.494	93.666	−1379.835	−1068.539	69.768
900	193.845	351.015	225.767	112.723	−1429.621	−1028.740	59.707
1000	200.309	371.773	239.342	132.431	−1424.467	−984.470	51.423
1100	206.731	391.166	252.272	152.784	−1418.821	−940.739	44.672
1157.000	210.367	401.702	259.376	164.671	I <--> LIQUID		
1157.000	197.033	422.314	259.376	188.520	TRANSITION		
1200	197.033	429.504	265.344	196.992	−1583.018	−893.538	38.895
1300	197.033	445.275	278.586	216.696	−1576.541	−836.345	33.605
1400	197.033	459.877	291.021	236.399	−1570.140	−779.647	29.089
1500	197.033	473.471	302.736	256.102	−1563.809	−723.405	25.191
1600	197.033	486.187	313.809	275.806	−1557.546	−667.583	21.794
1700	197.033	498.132	324.303	295.509	−1551.347	−612.150	18.809
1800	197.033	509.394	334.276	315.212	−1545.210	−557.081	16.166
1900	197.033	520.047	343.776	334.916	−1539.134	−502.351	13.811
2000	197.033	530.154	352.844	354.619	−1533.117	−447.939	11.699
2100	197.033	539.767	361.518	374.322	−1527.159	−393.827	9.796
2200	197.033	548.933	369.831	394.025	−1521.259	−339.997	8.073
2300	197.033	557.692	377.809	413.729	−1515.418	−286.435	6.505
2400	197.033	566.077	385.480	433.432	−1509.635	−233.125	5.074
2500	197.033	574.120	392.866	453.135	−1503.912	−180.055	3.762
2600	197.033	581.848	399.987	472.839	−1498.246	−127.213	2.556
2700	197.033	589.284	406.861	492.542	−1492.640	−74.587	1.443
2800	197.033	596.450	413.505	512.245	−1487.093	−22.168	0.414
2900	197.033	603.364	419.934	531.948	−1481.607	30.053	−0.541
3000	197.033	610.044	426.160	551.652	−1476.185	82.087	−1.429

PREVIOUS: CURRENT: June 1978

$S°(298.15\ K) = [346.854 \pm 16.7]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -1020.106 \pm 25.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -1033.615 \pm 25.1\ kJ \cdot mol^{-1}$

Vibrational Frequencies, Symmetries and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
A_1 961 (1)	B_1[460] (1)	E 1101 (2)
[510](1)	$B_2$1131 (1)	610 (2)
[160](1)	640 (1)	[333](2)
[391](1)	[81](2)	

Ground State Quantum Weight: [1] σ = [4]
Point Group: [D_{2d}]
Bond Distances: S–O = [1.48] Å Na–O = [2.21] Å
Bond Angles: O–S–O = [109.47]° O–Na–O = [66.205]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.9153 \times 10^{-113}]\ g^3 \cdot cm^6$

Enthalpy of Formation

The adopted value of the enthalpy of formation, $\Delta_f H°(Na_2SO_4, g, 298.15\ K) = -247.04 \pm 6.0\ kcal \cdot mol^{-1}$, is based on JANAF analyses of the vaporization data given below. Early studies of the vaporization of sodium sulfate failed to take dissociation into account. The many of the effusion and transpiration results in the literature are in error. The dissociation is retarded in the presence of SO_2, O_2 mixtures as in the study of Cubicciotti and Kenesha[1] or in the presence of air (O_2) as in the study of Fryxell *et al.*[4] We have "corrected" some of the original data by subtracting the calculated dissociation pressures[15] from the total pressure to give molecular vaporization pressures. These "corrected data sets" are explicitly noted. Mass spectrometric experiments[2, 3, 5, and 14] can lead to direct molecular vaporization data provided the $Na_2SO_4^+$ ion is directly measured. Results from the Knudsen effusion experiments[5, 14] are in reasonable agreement with the most reliable transpiration experiments.[1, 4] The calculated 3rd law $\Delta_f H°(298.15\ K)$ may have an uncertainty of 4 $kcal \cdot mol^{-1}$ since the JANAF free energy functions are partially based on the estimated molecular constants of Na_2SO_4(g). Vapor pressures from[1, 4 and 5] are in general agreement. Our adopted heat of formation is based on a weighted average of the 2nd or 3rd law results from.[1, 4, 5, 14]

Source	Method	Reaction[a]	T/K	Points	δS[b] $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$ 2nd law	3rd law	$\Delta_f H°(298.15\ K)$ $kcal \cdot mol^{-1}$
1b	Transpiration (N_2)	A	1400–1624	8	9.24 ± 2.8	90.36 ± 4.2	76.31 ± 2.0	−247.86 ± 6
1	Transpiration ($SO_2 + O_2$)	A	1305–1663	12	4.69 ± 1.2	84.26 ± 1.8	77.06 ± 1.1	−247.11 ± 4
4b	Transpiration (air)	A	1283–1477	20	0.23 ± 1.1	78.51 ± 1.5	78.20 ± 0.6	−245.97 ± 4
4	Transpiration (air)	A	1339–1477	16	3.70 ± 1.1	83.18 ± 1.5	78.05 ± 0.6	−246.12 ± 3
13	Transpiration ($SO_2 + O_2$)	A	1289–1412	6	5.60 ± 1.4	81.39 ± 1.8	73.81 ± 0.6	−250.36 ± 6
13b	Transpiration (N_2)	A	1301–1426	4	17.3 ± 2.5	98.78 ± 3.5	75.05 ± 2.0	−249.12 ± 6
5	Knudsen mass spec	A	1180–1370	2	——	75.76 ± 4.0	——	−248.41 ± 4
5	Knudsen mass spec	A	1196–1349	19	−1.89 ± 0.9	78.36 ± 0.9	78.76 ± 0.4	−245.41 ± 2
14	Knudsen mass spec	A,B	1069–1281	?	——	74.93 ± 2.5	——	−249.24 ± 4
14	Knudsen mass spec	A	1440–1540	?	——	77.41 ± 4.0	——	−246.76 ± 4

[a] A) $Na_2SO_4(l) = Na_2SO_4(g)$ B) $Na_2SO_4(cr) = Na_2SO_4(g)$
[b] data corrected for dissociation.

Heat Capacity and Entropy

The adopted structure (D_{2d} symmetry) is based on the similar symmetry assigned to Cs_2SO_4(g) and to K_2SO_4(g) in the high temperature electron diffraction studies of Ugarov *et al.*[6] and Spiridonov and Lutoshkin.[7] This symmetry is supported by the IR and Raman study of Atkins and Gingerich[9] on Na_2SO_4 and K_2SO_4. The molecule can be pictured as having a central sulfur atom surrounded at the corners of a tetrahedron by four oxygen atoms with bridging sodium atoms between two pairs of oxygens. The internuclear distance of 1.48 Å for S–O is taken from data on other sulphates[6, 7, 8] while Na–O = 2.21 Å is an estimate from.[7] The principal moments of inertia are $I_A = 15.518 \times 10^{-39}$ and $I_B = I_C = 71.418 \times 10^{-39}\ g \cdot cm^2$.

Atkins and Gingerich[9] have observed the infrared and Raman spectra of Na_2SO_4 and K_2SO_4 isolated in oxygen and nitrogen matrices at 12 K. Five of the eleven fundamental frequencies were observed in this work. The two other sulphate–ion group fundamentals are estimates taken from Gurvich *et al.*[10] The four fundamentals involving the metal atoms are based on the Raman single–crystal study of Montero[11] and comparisons involving K_2SO_4, Cs_2SO_4,[10] LiO_2 and NaO_2.[12] Uncertainties in the estimates of the gas phase frequencies may contribute an uncertainty of 4 $cal \cdot K^{-1} \cdot mol^{-1}$ to $S°(298.15\ K)$.

Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−21.163	−1020.106	−1020.106	INFINITE
100	58.797	259.777	426.257	−16.648	−1024.770	−1010.071	527.607
200	85.280	308.790	355.907	−9.423	−1029.920	−993.278	259.418
250	96.480	329.057	348.544	−4.872	−1031.953	−983.875	205.569
298.15	105.619	346.854	346.854	0.	−1033.615	−974.461	170.721
300	105.940	347.509	346.856	0.196	−1033.675	−974.094	169.605
350	113.834	364.451	348.176	5.696	−1035.199	−964.041	143.875
400	120.370	380.092	351.201	11.556	−1044.097	−953.279	124.485
450	125.760	394.591	355.226	17.714	−1046.024	−941.817	109.323
500	130.203	408.078	359.845	24.117	−1047.785	−930.140	97.171
600	136.924	432.449	369.960	37.494	−1050.344	−906.354	78.905
700	141.606	453.929	380.452	51.434	−1052.164	−882.204	65.831
800	144.949	473.068	390.854	65.771	−1053.531	−857.827	56.010
900	147.397	490.289	400.962	80.394	−1107.749	−832.215	48.301
1000	149.234	505.918	410.688	95.230	−1107.468	−801.615	41.872
1100	150.641	520.211	420.005	110.227	−1107.178	−771.044	36.614
1200	151.741	533.367	428.911	125.348	−1300.462	−735.618	32.021
1300	152.614	545.549	437.420	140.567	−1298.469	−688.628	27.669
1400	153.319	556.885	445.553	155.865	−1296.473	−641.792	23.946
1500	153.895	567.483	453.332	171.227	−1294.484	−595.099	20.723
1600	154.371	577.431	460.781	186.641	−1292.511	−548.538	17.908
1700	154.769	586.802	467.921	202.098	−1290.557	−502.099	15.428
1800	155.106	595.658	474.774	217.592	−1288.629	−455.776	13.226
1900	155.392	604.052	481.359	233.118	−1286.731	−409.558	11.260
2000	155.638	612.029	487.695	248.670	−1284.865	−363.439	9.492
2100	155.851	619.628	493.798	264.244	−1283.036	−317.413	7.895
2200	156.036	626.883	499.683	279.839	−1281.245	−271.472	6.446
2300	156.198	633.822	505.366	295.451	−1279.496	−225.613	5.124
2400	156.340	640.473	510.858	311.078	−1277.789	−179.830	3.914
2500	156.467	646.858	516.171	326.718	−1276.128	−134.116	2.802
2600	156.579	652.997	521.316	342.371	−1274.513	−88.467	1.777
2700	156.679	658.908	526.303	358.034	−1272.947	−42.879	0.830
2800	156.769	664.608	531.141	373.706	−1271.431	2.652	−0.049
2900	156.849	670.111	535.839	389.387	−1269.968	48.127	−0.867
3000	156.922	675.429	540.404	405.076	−1268.560	93.555	−1.629
3100	156.988	680.576	544.843	420.771	−1267.208	138.938	−2.341
3200	157.049	685.561	549.163	436.473	−1265.915	184.275	−3.008
3300	157.103	690.394	553.370	452.181	−1264.681	229.573	−3.634
3400	157.153	695.085	557.469	467.894	−1263.512	274.837	−4.222
3500	157.199	699.641	561.467	483.611	−1262.410	320.066	−4.777
3600	157.241	704.070	565.367	499.333	−1261.377	365.265	−5.300
3700	157.280	708.379	569.174	515.059	−1260.416	410.435	−5.794
3800	157.316	712.574	572.893	530.789	−1259.533	455.583	−6.262
3900	157.349	716.661	576.527	546.523	−1258.729	500.708	−6.706
4000	157.380	720.645	580.080	562.259	−1258.011	545.811	−7.128
4100	157.408	724.531	583.556	577.998	−1257.383	590.899	−7.528
4200	157.435	728.325	586.958	593.741	−1256.844	635.972	−7.909
4300	157.459	732.030	590.289	609.485	−1256.410	681.034	−8.273
4400	157.482	735.650	593.552	625.232	−1255.996	726.079	−8.620
4500	157.504	739.189	596.749	640.982	−1255.731	771.121	−8.951
4600	157.524	742.651	599.883	656.733	−1255.594	816.159	−9.268
4700	157.543	746.039	602.957	672.486	−1255.573	861.198	−9.571
4800	157.560	749.356	605.972	688.242	−1255.676	906.236	−9.862
4900	157.577	752.605	608.932	703.999	−1255.908	951.280	−10.141
5000	157.593	755.789	611.837	719.757	−1256.261	996.327	−10.409
5100	157.608	758.910	614.691	735.517	−1256.767	1041.384	−10.666
5200	157.621	761.970	617.494	751.278	−1257.422	1086.450	−10.914
5300	157.635	764.973	620.248	767.041	−1258.231	1131.533	−11.152
5400	157.647	767.919	622.955	782.805	−1259.203	1176.631	−11.382
5500	157.659	770.812	625.618	798.571	−1260.343	1221.748	−11.603
5600	157.670	773.653	628.236	814.337	−1261.658	1266.891	−11.817
5700	157.680	776.444	630.811	830.105	−1263.155	1312.055	−12.024
5800	157.690	779.186	633.346	845.873	−1264.839	1357.250	−12.223
5900	157.700	781.882	635.841	861.643	−1266.717	1402.471	−12.417
6000	157.709	784.533	638.297	877.413	−1268.480	1447.695	−12.603

PREVIOUS: June 1978 (1 atm) CURRENT: June 1978 (1 bar)

$S°(298.15\ K) = 160.331 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1} = 862.0\ K$
$T_{trs2} = 860.8\ K$
$T_{fus} = 968.7\ K$

$\Delta_f H°(0\ K) = -1534.79 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1544.73 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H° = 4.113\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H° = 30.849\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 23.799\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -369.2\ kcal \cdot mol^{-1}$, is calculated from $\Delta_r H°(303.15\ K) = 19.44 \pm 0.08\ kcal \cdot mol^{-1}$ for the reaction of $H_2WO_4(cr) + 2\ NaCl(cr) = Na_2WO_4(cr) + 2\ HCl(aq, 12.731\ H_2O)$, using the JANAF value of $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -270.5\ kcal \cdot mol^{-1}$ and $\Delta_f H°(NaCl, cr, 298.15\ K) = -98.26\ kcal \cdot mol^{-1}$, and auxiliary data for HCl(aq).[11] The value of $\Delta_r H°(303.15\ K)$ was determined by solution calorimetry by Koehler *et al.*[1]

Sherfey and Brenner[2] measured by electrochemical calorimetry the enthalpy of reaction $\Delta_r H°(298.15\ K) = -7 \pm 1.5\ kcal \cdot mol^{-1}$ for $W(cr) + 2\ NaOH(aq, 55.55\ H_2O) + 2\ H_2O(l) = Na_2WO_4(aq, \infty) + 3\ H_2(g)$. This value, combined with the heat of solution,[1,3,9] $\Delta_{sln} H° = 1.7 \pm 0.1\ kcal \cdot mol^{-1}$ for $Na_2WO_4(cr) = Na_2WO_4(aq, \infty)$, gives $\Delta_f H°(298.15\ K)(Na_2WO_4, cr) = -368.4\ kcal \cdot mol^{-1}$, which is in good agreement with the value adopted.

The previously accepted value,[1,3] $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -379 \pm 0.5\ kcal \cdot mol^{-1}$, was based on the unreliable $\Delta_f H°(H_2WO_4, cr, 298.15\ K) = -280.2 \pm 0.4\ kcal \cdot mol^{-1}$. (See JANAF H_2WO_4, cr, table of March 31, 1967.) The other quoted value,[4] $\Delta_f H°(Na_2WO_4, cr, 298.15\ K) = -395\ kcal \cdot mol^{-1}$, was obtained from Mixter's[5] measurement of the heat of reaction of tungsten powder with excess Na_2O_2. This value was probably in error because the complex tungstate and peroxytungstates were formed in the reaction.

Heat Capacity and Entropy

Low temperature heat capacities (52–299.87 K) were measured calorimetrically by King and Weller.[6] The heat capacities above 300 K are estimated by extrapolation of the low temperature heat capacity curve to $C_p°(860\ K) = 49.0\ cal \cdot K^{-1} \cdot mol^{-1}$. The latter is obtained from an estimate of $C_p°$ equal to 7 $cal \cdot K^{-1}$ g–atom at the first transition temperature.

The entropy, $S°(298.15\ K) = 38.32 \pm 0.5\ cal \cdot K^{-1} \cdot mol^{-1}$, is calculated from low temperature heat capacity data of King and Weller,[6] based on an extrapolation of $S°(51\ K) = 2.77 \pm 0.5\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition Data

Transition temperatures and heats were obtained from differential heating and cooling curves both at atmospheric and higher pressures by Goranson and Kracek.[7] Existence of three phases is confirmed by the earlier birefringence studies of Boeke.[8]

Riccardi and Sinistri[10] found only one transition at 864 K with $\Delta_{trs} H° = 8.23\ kcal \cdot mol^{-1}$ by differential thermal analysis. This heat is apparently the sum of the two adopted heats of transition.

Fusion Data

The adopted melting data were measured by the differential heating and cooling curve method by Goranson and Kracek.[7] Riccardi and Sinistri[10] found the melting point at 971 K with $\Delta_{fus} H° = 7.52\ kcal \cdot mol^{-1}$ by differential thermal analysis.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−25.286	−1534.786	−1534.786	INFINITE
100	69.860	43.482	267.673	−22.419	−1541.060	−1505.022	786.143
200	117.244	108.962	172.462	−12.700	−1544.082	−1467.547	383.284
298.15	139.775	160.331	160.331	0.	−1544.733	−1429.786	250.493
300	140.122	161.197	160.334	0.259	−1544.732	−1429.073	248.824
400	155.335	203.750	166.032	15.087	−1549.553	−1390.158	181.536
500	167.360	239.748	177.264	31.242	−1548.233	−1350.438	141.079
600	178.238	271.237	190.355	48.529	−1545.854	−1311.086	114.140
700	188.698	299.500	203.961	66.877	−1542.521	−1272.209	94.933
800	198.740	325.351	217.541	86.248	−1538.287	−1233.871	80.564
860.800	205.101	340.137	225.682	98.524	I <--> II		
860.800	205.099	375.975	225.682	129.372	TRANSITION		
862.000	205.226	376.260	225.891	129.618	II <--> III		
862.000	205.224	381.032	225.891	133.731	TRANSITION		
900	209.200	389.971	232.631	141.606	−1498.203	−1197.704	69.513
1000	219.242	412.530	249.504	163.026	−1492.216	−1164.628	60.834
1100	229.492	433.907	265.304	185.463	−1485.393	−1132.192	53.763
1200	239.743	454.314	280.211	208.923	−1671.275	−1095.535	47.687
1300	250.120	473.913	294.362	233.417	−1660.975	−1047.968	42.108
1400	260.454	492.828	307.866	258.946	−1649.746	−1001.228	37.356
1500	270.705	511.147	320.811	285.505	−1637.590	−955.325	33.267

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 164.055 \pm 4.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs}(B \rightarrow A\beta) = 951\ K$
$T_{trs}(A\beta \rightarrow A\alpha) = 980\ K$
$T_{fus} = 1147\ K$

$\Delta_f H°(0\ K) = -2455.46 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2470.07 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.418\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.628\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 35.564\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpies of solution of NaCl(cr), Na_2SO_4(cr) SiO_2(quartz), $Na_2Si_2O_5$(cr), HCl(aq) and H_2SO_4(aq), in 20% hydrofluoric acid at 74.7°C were measured by Kracek.[1] The author derived two values of $\Delta_{sln}H°$ of Na_2O(cr) from those of NaCl(cr), Na_2SO_4(cr), HCl(aq) and H_2SO_4(aq), presumably employing auxiliary data from.[2] We recalculate $\Delta_{sln}H°$ of Na_2O(cr) in the calorimetric solution as −87.50 (chlorine scheme, originally −87.66) and −88.74 kcal·mol^{-1} (sulfate scheme, originally −89.19), using recent $\Delta_f H°$(298.15 K) values[16,17,18] for NaCl(cr), HCl(aq), H_2SO_4(aq), Na_2SO_4(cr), and Na_2O(cr). The corresponding enthalpy changes, $\Delta_r H°$(298.15 K), for the reaction Na_2O(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(cr) are derived as −54.65 and −55.89 kcal·mol^{-1}. Adopting the weighted average $\Delta_r H°$(298.15 K) = −55.06 kcal·mol^{-1} with $\Delta_f H°$(Na_2O, cr, 298.15 K) = −99.9 kcal·mol^{-1} and $\Delta_f H°$(SiO_2, quartz, 298.15 K) = −217.7 kcal·mol^{-1}, we obtain $\Delta_f H°$(298.15 K) = −590.36 kcal·mol^{-1} for $Na_2Si_2O_5$(cr). This $\Delta_f H°$($Na_2Si_2O_5$, cr, 298.15 K) value is independent of future changes in $\Delta_f H°$(298.15 K) of Na_2O(cr), but the values of $\Delta_{sln}H°$ and $\Delta_r H°$ are not independent.

Stevens *et al.*[3] measured the enthalpies of solution of $Na_2Si_2O_5$(cr), Na_2O(cr) and SiO_2(quartz) in HF(aq) at 25°C. Based on the reported results, the enthalpy change for the reaction Na_2O(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(cr) is calculated as −53.25 ± 0.32 kcal·mol^{-1}, yielding $\Delta_f H°$($Na_2Si_2O_5$, cr, 298.15 K) = −588.55 kcal·mol^{-1}.

Hummel[4] determined the enthalpies of solution of $Na_2Si_2O_5$(cr), SiO_2(quartz) and Na_2CO_3(cr) in 39% HF at 26.5°C. From the data reported we derive the enthalpy change to be 20.88 kcal·mol^{-1} for the reaction Na_2CO_3(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(cr) + CO_2(g). Employing $\Delta_f H°$(298.15 K) = −270.26, −217.7 and −94.05 kcal·mol^{-1} for Na_2CO_3(cr), SiO_2(quartz) and CO_2(g), respectively, we obtain $\Delta_f H°$(298.15 K) = −590.78 kcal·mol^{-1} for $Na_2Si_2O_5$(cr) which is in good agreement with the adopted one.

Heat Capacity and Entropy

The low temperature heat capacities, 54.3–294.7 K, have been measured by Kelley[5] and the high temperature enthalpies, 376.8–1100.2 K, by Naylor.[6] The derived high temperature heat capacities are joined smoothly with the low temperature ones at 298.15 K. An approximate $C_p°$ of 70 cal·K^{-1}·mol^{-1} is derived from the enthalpies above 980 K; this value is extrapolated to 2000 K. The value of $S°$(298.15 K) is calculated from the adopted low temperature heat capacities based on $S°$(50 K) = 2.945 cal·K^{-1}mol^{-1}. The entropy extrapolation derives from the Debye–Einstein extrapolation of Kelley[5] which yields a $C_p°$ curve with an extra inflection in the region from 15 to 50 K. A more normal extrapolation would lead to a value of $S°$(50 K) which is lower by 0.5 cal·K^{-1}·mol^{-1}.

Transition Data

There are six slowly inverting polymorphous phases,[1,7-9] namely A, B, C, D, E and F, of which only the first two phases are stable. Two rapid transitions have been reported at 951 and 980 K.[1, 10] Phase A, which has two subphases, Aα and Aβ, is stable above 951 K. The stable phase below 951 K is known as phase B, previously called β–$Na_2Si_2O_5$. The $\Delta_{trs}H°$ values are derived from the enthalpy data of Naylor[6] using the adopted $C_p°$ values. Three more rapid transitions have been reported at 822, 846 and 866 K[1,10] in E, previously called γ–$Na_2Si_2O_5$. Willgallis and Range[10] have examined these transitions.

Fusion Data

T_{fus} is obtained from Morey.[11] The selected value of $\Delta_{fus}H°$ is based on the following $\Delta_{fus}H°$ values derived from four different kinds of measurements.

Source	$\Delta_{fus}H°$, kcal·mol^{-1}* 298.15 K	1147 K	Method**
12	(7.51)	8.46	I
1	5.25	(6.20)	II
13	8.81	(9.76)	III
14	8.83	(9.78)	II
15	(7.50)	8.45	IV
4	8.09	(9.04)	II

* The numbers in parentheses are derived from the measured ones at the other listed temperatures.
**I = phase diagram, II = solution calorimetry; III = high temperature reaction calorimetry; and IV = dynamic–differential calorimetric method.

Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−26.430	−2455.459	−2455.459	INFINITE
100	66.906	42.058	279.416	−23.736	−2463.238	−2418.587	1263.340
200	124.081	107.976	177.452	−13.895	−2467.943	−2371.851	619.464
298.15	156.984	164.055	164.055	0.	−2470.066	−2324.163	407.184
300	157.494	165.027	164.058	0.291	−2470.090	−2323.258	404.515
400	183.401	214.007	170.560	17.379	−2475.916	−2273.781	296.925
500	203.246	257.178	183.653	36.762	−2474.938	−2223.325	232.269
600	217.576	295.572	199.168	57.843	−2472.541	−2173.208	189.195
700	227.840	329.925	215.438	80.141	−2469.179	−2123.575	158.463
800	235.162	360.855	231.715	103.312	−2465.186	−2074.470	135.449
900	240.325	388.869	247.645	127.102	−2460.809	−2025.890	117.580
951.000	242.313	402.170	255.578	139.409	I <--> II		
951.000	242.316	402.610	255.578	139.828	TRANSITION		
980.000	243.275	409.903	260.037	146.869	II <--> III		
980.000	292.880	410.544	260.037	147.497	TRANSITION		
1000	292.880	416.461	263.107	153.354	−2454.208	−1977.854	103.312
1100	292.880	444.375	278.337	182.642	−2444.821	−1930.674	91.680
1147.000	292.880	456.629	285.393	196.408	----- III <--> LIQUID -----		
1200	292.880	469.859	293.251	211.930	−2629.223	−1879.459	81.811
1300	292.880	493.302	307.750	241.218	−2618.531	−1817.413	73.025
1400	292.880	515.007	321.788	270.506	−2607.999	−1756.184	65.524
1500	292.880	535.213	335.351	299.794	−2597.620	−1695.704	59.050
1600	292.880	554.115	348.439	329.082	−2587.389	−1635.911	53.407
1700	292.880	571.871	361.065	358.370	−2677.658	−1575.859	48.420
1800	292.880	588.612	373.246	387.658	−2667.257	−1511.349	43.858
1900	292.880	604.447	385.002	416.946	−2656.916	−1447.414	39.792
2000	292.880	619.470	396.353	446.234	−2646.633	−1384.022	36.147

PREVIOUS: June 1965 CURRENT: September 1967

$S°$(298.15 K) = [188.705] J·K^{-1}·mol^{-1}
T_{fus} = 1147 K

$\Delta_f H°$(298.15 K) = [−2438.485] kJ·mol^{-1}
$\Delta_{fus} H°$ = 35.564 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°$(1147 K)–$H°$(298.15 K), between the crystal and liquid.

The enthalpies of solution of NaCl(cr), Na_2SO_4(cr), HCl(aq), H_2SO_4(aq), SiO_2(quartz) and $Na_2Si_2O_5$(g, l) in 20% hydrofluoric acid at 74.7°C were measured by Kracek.[1] Following the same procedure as described in the $Na_2Si_2O_5$(cr) table, we derive the enthalpy changes, $\Delta_r H°$(298.15 K), for the reaction Na_2O(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(g, l) as −49.40 and −50.64 kcal·mol^{-1} using the heats of solution of Na_2O(cr) as −87.50 (chloride scheme) and −88.74 kcal·mol^{-1} (sulfate scheme), respectively. Adopting the weighted average $\Delta_r H°$(298.15 K) = −49.81 kcal·mol^{-1} with $\Delta_f H°$(Na_2O, cr, 298.15 K) = −99.9 kcal·mol^{-1} and $\Delta_f H°$(SiO_2, quartz, 298.15 K) = −217.7 kcal·mol^{-1}, we obtain $\Delta_f H°$(298.15 K) = −585.113 kcal·mol^{-1} for $Na_2Si_2O_5$(g, l).

Using high temperature reaction calorimetry, Kroger[2] determined the enthalpy changes as 25.28 ± 0.22 and −18.58 ± 0.36 kcal·mol^{-1} for the reactions Na_2CO_3(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(g, l) + CO_2(g) and 2 NaOH(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(g, l) + H_2O(l), respectively. From the given results, we calculate the corresponding values of $\Delta_f H°$($Na_2Si_2O_5$, g, l, 298.15 K) to be −586.32 and −589.46 kcal·mol^{-1}, using $\Delta_f H°$(298.15 K) = −270.26, −217.70, −94.05, −101.90 and −68.32 kcal·mol^{-1} for Na_2CO_3(cr), SiO_2(quartz, CO_2(g), NaOH(cr) and H_2O(l), respectively. These two $\Delta_f H°$($Na_2Si_2O_5$, l, 298.15 K) values, as well as the value −585.113 kcal·mol^{-1} based on Kracek's data, are not adopted, because incorporating these $\Delta_f H°$(g, l, 298.15 K) values with the value of $\Delta_f H°$(cr, 298.15 K), gives values of the enthalpy of melting at 298.15 K which are too low in comparison with the other values (see the $Na_2Si_2O_5$, cr, table).

Hummel[3] measured the enthalpies of solution of Na_2CO_3(cr), SiO_2(quartz) and $Na_2Si_2O_5$(g, l) in 39% hydrofluoric acid at 26.5°C, as −244.1, −564.5 and −673.7 cal·g^{-1}, respectively. Based on these results, we derive the enthalpy change for the reaction Na_2CO_3(cr) + 2 SiO_2(quartz) = $Na_2Si_2O_5$(g, l) + CO_2(g) to be 29.01 kcal·mol^{-1}, yielding $\Delta_f H°$($Na_2Si_2O_5$, g, l, 298.15 K) = −582.6 kcal·mol^{-1} which is in good agreement with the adopted value.

Heat Capacity and Entropy

Using drop calorimetry, Naylor[4] has measured the enthalpies of $Na_2Si_2O_5$(g, l), 445.5–1120.7 K, and $Na_2Si_2O_5$(l), 1173.2–1744 K. Based on the liquid enthalpy data, we evaluate the heat capacity of $Na_2Si_2O_5$(l) to be 62.43 cal·K^{-1}·mol^{-1}. The $C_p°$ values below 1147 K are derived from the enthalpies measured at 445.5–1120.7 K by Naylor.[4] Below 600 K, $C_p°$ is identical with that of the crystal. The adopted curve rises rapidly to a maximum in the glass transition region, 650–950 K, then smoothly approaches the value of the real liquid near T_{fus}. The heat capacity of $Na_2Si_2O_5$(l) is assumed to be constant in the temperature range 1147 to 2500 K.

$S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

References

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[3]C. Hummel and H. E. Schwiete, Glastech. Ber. **32**, 327 (1959).
[4]B. F. Naylor, J. Amer. Chem. Soc. **67**, 466 (1945).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	156.984	188.705	188.705	0.	−2438.485	−2299.931	402.938
300	157.494	189.678	188.708	0.291	−2438.508	−2299.071	400.304
400	183.401	238.657	195.210	17.379	−2444.334	−2252.060	294.089
500	203.246	281.828	208.304	36.762	−2443.356	−2204.069	230.258
600	217.576	320.191	223.817	57.825	−2440.978	−2156.416	187.733
700	245.810	355.525	240.121	80.783	−2436.956	−2109.271	157.396
800	272.169	390.353	256.734	106.895	−2430.022	−2062.904	134.694
900	276.228	422.809	273.415	134.455	−2421.874	−2017.501	117.093
1000	267.776	451.569	289.825	161.744	−2414.237	−1972.990	103.058
1100	261.207	476.706	305.694	188.113	−2407.769	−1929.186	91.609
1147.000	261.207	487.635	312.927	200.390	----- III <--> LIQUID -----		
1200	261.207	499.434	320.906	214.234	−2595.338	−1881.064	81.881
1300	261.207	520.342	335.454	240.355	−2587.813	−1821.847	73.203
1400	261.207	539.700	349.360	266.475	−2580.448	−1763.204	65.786
1500	261.207	557.721	362.657	292.596	−2573.236	−1705.082	59.376
1600	261.207	574.579	375.381	318.717	−2566.173	−1647.437	53.783
1700	261.207	590.415	387.569	344.838	−2659.609	−1589.334	48.834
1800	261.207	605.345	399.257	370.958	−2652.376	−1526.587	44.300
1900	261.207	619.468	410.479	397.079	−2645.202	−1464.239	40.255
2000	261.207	632.866	421.266	423.200	−2638.086	−1402.267	36.623
2100	261.207	645.610	431.648	449.320	−2631.031	−1340.650	33.347
2200	261.207	657.761	441.652	475.441	−2624.034	−1279.366	30.376
2300	261.207	669.373	451.302	501.562	−2617.098	−1218.401	27.671
2400	261.207	680.489	460.622	527.683	−2610.223	−1157.736	25.197
2500	261.207	691.152	469.631	553.803	−2603.410	−1097.356	22.928

PREVIOUS: June 1965 CURRENT: September 1967

Sodium Silicate ($Na_2Si_2O_5$) **CRYSTAL(B–Aβ–Aα)-LIQUID**

0	to	951 K	crystal, B
951	to	980 K	crystal, Aβ
980	to	1147 K	crystal, Aα
above		1147 K	liquid

Refer to the individual tables for details.

M_r = 182.14754 Sodium Silicate ($Na_2Si_2O_5$) **$Na_2O_5Si_2$(cr,l)**

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−26.430	−2455.459	−2455.459	INFINITE
100	66.906	42.058	279.416	−23.736	−2463.238	−2418.587	1263.340
200	124.081	107.976	177.452	−13.895	−2467.943	−2371.851	619.464
298.15	156.984	164.055	164.055	0.	−2470.066	−2324.163	407.184
300	157.494	165.027	164.058	0.291	−2470.090	−2323.258	404.515
400	183.401	214.007	170.560	17.379	−2475.916	−2273.781	296.925
500	203.246	257.178	183.653	36.762	−2474.938	−2223.325	232.269
600	217.576	295.572	199.168	57.843	−2472.541	−2173.208	189.195
700	227.840	329.925	215.438	80.141	−2469.179	−2123.575	158.463
800	235.162	360.855	231.715	103.312	−2465.186	−2074.470	135.449
900	240.325	388.869	247.645	127.102	−2460.809	−2025.890	117.580
951.000	242.313	402.170	255.578	139.409	I <−−> II		
951.000	242.316	402.610	255.578	139.828	TRANSITION		
980.000	243 .275	409.903	260.037	146.869	II <−−> III		
980.000	292 .880	410.544	260.037	147.497	TRANSITION		
1000	292.880	416.461	263.107	153.354	−2454.208	−1977.854	103.312
1100	292.880	444.375	278.337	182.642	−2444.821	−1930.674	91.680
1147.000	292.880	456.629	285.393	196.408	III <−−> LIQUID		
1147.000	261.207	487.635	285.393	231.972	TRANSITION		
1200	261.207	499.434	294.588	245.816	−2595.338	−1881.064	81.881
1300	261.207	520.342	311.160	271.936	−2587.813	−1821.847	73.203
1400	261.207	539.700	326.802	298.057	−2580.448	−1763.204	65.786
1500	261.207	557.721	341.603	324.178	−2573.236	−1705.082	59.376
1600	261.207	574.579	355.643	350.298	−2566.173	−1647.437	53.783
1700	261.207	590.415	368.992	376.419	−2659.609	−1589.334	48.834
1800	261.207	605.345	381.712	402.540	−2652.376	−1526.587	44.300
1900	261.207	619.468	393.857	428.661	−2645.202	−1464.239	40.255
2000	261.207	632.866	405.475	454.781	−2638.086	−1402.267	36.623
2100	261.207	645.610	416.609	480.902	−2631.031	−1340.650	33.347
2200	261.207	657.761	427.297	507.023	−2624.035	−1279.366	30.376
2300	261.207	669.373	437.571	533.143	−2617.098	−1218.401	27.671
2400	261.207	680.489	447.463	559.264	−2610.223	−1157.736	25.197
2500	261.207	691.152	456.999	585.385	−2603.410	−1097.356	22.928

PREVIOUS: CURRENT: September 1967

$S°$(298.15 K) = 96.232 ± 16.7 J·K^{-1}·mol^{-1}
T_{trs} = [1276 ± 20 K] (lambda transition)
T_{fus} = 1445 ± 10 K

$\Delta_f H°$(0 K) = Unknown
$\Delta_f H°$(298.15 K) = −366.10 ± 12.6 kJ·mol^{-1}
$\Delta_{trs} H°$ = 0
$\Delta_{fus} H°$ = [19.246 ± 4.2] kJ·mol^{-1}

Enthalpy of Formation

We adopt the average value, $\Delta_f H°$(298.15 K) = −87.5 kcal·mol^{-1}, derived from the experimental results summarized below.

Source	Reaction	$\Delta_f H°$(298.15 K), kcal·mol^{-1}
[1]	$\Delta_{sln} H°$ Na_2S(cr) and Na(cr), $\Delta_n H°$ NaOH(aq) + H_2S(aq)	−88.2
[2]		−89.7
[3]	Na (in NH_3) + S(cr) = Na_2S(cr)	−87.0
[4]	H_2SO_4(aq, 1100 H_2O) + Na_2S(cr) = Na_2SO_4(soln.) + H_2S(g)	−85.1*

* The author's value of −84.35 ± 0.9 kcal·mol^{-1} is corrected for newer values for $\Delta_f H°$(298.15 K) of Na_2SO_4(c, V) and H_2S(g).[5,11]

The adopted value is reasonably consistent with −86.6 ± 1 kcal·mol^{-1} calculated from the 2nd law analysis of Uusitalo's equilibrium data[10] described in the following section.

Heat Capacity and Entropy

The heat capacity is based on the drop calorimetry of May[6] (400–1500 K). The pre–melt S–shaped enthalpy curve is reinterpreted as incorporating a lambda transition in view of the enthalpy measurements on K_2S by Dworkin and Bredig[7] and the occurrence of lambda transitions in other materials having the fluorite or anti flourite type of structure.[8] The adopted heat capacity shows the maximum of the lambda transition at 50.65 cal·K^{-1}·mol^{-1} and 1276 K. The heat capacity then falls to a constant value of 32 cal·K^{-1}·mol^{-1} at 1420 K. This interpretation along with the adopted melting point, heat of melting, and liquid heat capacity (22 cal·K^{-1}·mol^{-1},[9] leads to an enthalpy of the liquid consistent with May's measurement.

May,[6] (648–656 K) and Uusitalo,[10] (462–763 K) have measured equilibrium pressures for the reaction Na_2SO_4(cr) + 2 C(solid) = Na_2S(cr) + 2 CO_2(g) and have derived $S°$(Na_2S, cr, 298.15 K) = 18.6 and 18.5 cal·K^{-1}·mol^{-1}. These derivations are open to question because of the uncertainty of the crystalline form of Na_2SO_4 used in the reaction (forward direction) or resulting from the reaction (reverse direction). Five crystalline forms of Na_2SO_4 have been identified.[11, 12] $S°$(298.15 K) for form V, stable at room temperature, has erroneously been used to derive $S°$(Na_2S, cr, 298.15 K) rather than $S°$(298.15 K) for form I which is the form stable at the equilibrium measurement temperature. Furthermore, Uusitalo[10] used charcoal which probably deviates from graphite, the standard reference state. Our 2nd law treatment of Uusitalo's data[10] with auxiliary data for Na_2SO_4(cr, I) and C(graphite),[11] which is still questionable, leads to $S°$(Na_2S, cr, 298.15 K) = 23.2 cal·K^{-1}·mol^{-1}. The agreement of this derivation with the estimate below is almost surely fortuitous.

Kubaschewski *et. al.*[13] have estimated the entropy as 23.5 ± 2.5 cal·K^{-1}·mol^{-1}. Voronin's[14] estimate is 21.6 cal·K^{-1}mol^{-1}. The summation of Kelley's additive entropy constants[15] gives 23.0 cal·K^{-1}·mol^{-1}. We adopt $S°$(Na_2S, cr, 298.15 K) = 23.0 ± 4 cal·K^{-1}·mol^{-1}.

Fusion Data

Tegman[16] indicated that many of the early measurements of the melting point of Na_2S were made on impure brown material. Several measurements on white or light pink material are in reasonable agreement: in °C, 1200,[17] 1180 ± 10,[18] 1180,[19] 1160 ± 5,[20,21] 1175 ± 10,[22] and 1168 ± 10.[23] We adopt a melting point of 1445 ± 10 K (1172 ± 10°C). This is consistent with May's[6] enthalpy measurements.

In an examination of May's enthalpy data, Wagman[24] has used an entropy of fusion of 3.21 cal·K^{-1}·mol^{-1} —the entropy of fusion of K_2S is 3.16 cal·K^{-1}·mol^{-1} —which leads to an entahlpy of fusion of 4.8 kcal·mol^{-1} at the adopted melting point of 1445 K. From the Na_2S–S phase diagram work of Rosen and Tegman,[23] Wagman[24] calculates an average enthalpy of fusion of 5.7 kcal·mol^{-1} and recommends $\Delta_{fus} H°$ = 5 ± 1 kcal·mol^{-1}. We adopt $\Delta_{fus} H°$ = 4.8 kcal·mol^{-1} to remain consistent with our incorporation of a lambda transition in the evaluation of May's[6] enthalpy measurements.

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Continued on page 1673

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	82.801	96.232	96.232	0.	−366.100	−354.552	62.116
300	82.843	96.744	96.234	0.153	−366.093	−354.480	61.720
400	84.308	120.780	99.501	8.512	−373.575	−350.129	45.722
500	85.772	139.753	105.719	17.017	−375.200	−344.086	35.946
600	87.236	155.522	112.742	25.668	−376.166	−337.761	29.405
700	88.701	169.081	119.844	34.466	−376.619	−331.319	24.723
800	90.165	181.023	126.760	43.411	−376.704	−324.838	21.210
900	91.337	191.717	133.394	52.491	−429.655	−317.282	18.415
1000	92.843	201.418	139.718	61.700	−428.077	−304.880	15.925
1100	110.458	210.823	145.749	71.581	−425.884	−292.653	13.897
1200	159.494	222.269	151.627	84.771	−614.002	−275.864	12.008
1276.000	211.921	233.718	156.162	98.962	C_p LAMBDA MAXIMUM		
1276.000	211.939	233.718	156.162	98.962	TRANSITION		
1300	187.652	237.411	157.629	103.718	−601.115	−248.179	9.972
1400	137.152	249.134	163.773	119.505	−591.403	−221.426	8.262
1445.000	133.888	253.390	166.498	125.559	--- CRYSTAL <---> LIQUID ---		
1500	133.888	258.392	169.777	132.923	−584.076	−195.256	6.799
1600	133.888	267.033	175.588	146.312	−576.793	−169.572	5.536
1700	133.888	275.150	181.208	159.700	−569.524	−144.343	4.435
1800	133.888	282.802	186.642	173.089	−562.270	−119.542	3.469
1900	133.888	290.041	191.895	186.478	−555.029	−95.144	2.616
2000	133.888	296.909	196.976	199.867	−547.802	−71.126	1.858

PREVIOUS: December 1960 CURRENT: March 1978

$S°(298.15\ K) = [127.656]\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 1445 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-323.940]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = [19.246 \pm 4.2]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_2S, l, 298.15\ K)$ is calculated from $\Delta_f H°(Na_2S, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1445\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of 22 cal $K^{-1}\cdot mol^{-1}$ is from the estimated value of Barin *et al.* [1] and is assumed to be constant above the assumed glass transition at 970 K. Below the glass transition, the heat capacity is that of the crystal.

The entropy at 298.15 K is calculated in a manner similar to that used for the enthalpy of formation.

Reference

[1] I. Barin, D. Knacke, and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances," Supplement, Springer Verlag, Berlin, (1977).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	82.801	127.656	127.656	0.	−323.940	−321.761	56.371
300	82.843	128.169	127.658	0.153	−323.933	−321.747	56.021
400	84.308	152.205	130.925	8.512	−331.415	−320.539	41.858
500	85.772	171.177	137.143	17.017	−333.040	−317.638	33.183
600	87.236	186.947	144.166	25.668	−334.006	−314.455	27.376
700	88.701	200.506	151.268	34.466	−334.459	−311.156	23.219
800	90.165	212.447	158.184	43.411	−334.544	−307.817	20.098
900	91.337	223.141	164.818	52.491	−387.495	−303.404	17.609
970.010	92.425	230.023	169.278	58.923	GLASS <--> LIQUID TRANSITION		
970.010	92.048	230.023	169.278	58.923			
1000	92.048	232.826	171.142	61.684	−385.933	−294.144	15.365
1100	92.048	241.599	177.155	70.888	−384.416	−285.039	13.535
1200	92.048	249.608	182.864	80.093	−576.519	−271.189	11.805
1300	92.048	256.976	188.285	89.298	−573.374	−245.872	9.879
1400	92.048	263.798	193.438	98.503	−570.245	−220.797	8.238
1445.000	92.048	266.710	195.675	102.645	--- CRYSTAL <--> LIQUID ---		
1500	92.048	270.148	198.343	107.708	−567.131	−195.945	6.823
1600	92.048	276.089	203.019	116.912	−564.031	−171.301	5.592
1700	92.048	281.669	207.483	126.117	−560.947	−146.849	4.512
1800	92.048	286.930	211.752	135.322	−557.877	−122.579	3.557
1900	92.048	291.907	215.841	144.527	−554.820	−98.480	2.707
2000	92.048	296.629	219.763	153.732	−551.777	−74.541	1.947
2100	92.048	301.120	223.531	162.936	−548.747	−50.753	1.262
2200	92.048	305.402	227.156	172.141	−545.729	−27.110	0.644
2300	92.048	309.494	230.647	181.346	−542.725	−3.604	0.082
2400	92.048	313.411	234.015	190.551	−539.735	19.772	−0.430
2500	92.048	317.169	237.266	199.756	−536.760	43.024	−0.899
2600	92.048	320.779	240.409	208.960	−533.800	66.157	−1.329
2700	92.048	324.253	243.451	218.165	−530.858	89.176	−1.725
2800	92.048	327.600	246.397	227.370	−527.934	112.087	−2.091
2900	92.048	330.830	249.253	236.575	−525.032	134.893	−2.430
3000	92.048	333.951	252.024	245.780	−522.153	157.600	−2.744

PREVIOUS: December 1960 CURRENT: March 1978

0	to	1276*	K crystal
1276	to	1445	K crystal
above		1445	K liquid

*There is a lambda transition at 1276 K.

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	82.801	96.232	96.232	0.	−366.100	−354.552	62.116
300	82.843	96.744	96.234	0.153	−366.093	−354.480	61.720
400	84.308	120.780	99.501	8.512	−373.575	−350.129	45.722
500	85.772	139.753	105.719	17.017	−375.200	−344.086	35.946
600	87.236	155.522	112.742	25.668	−376.166	−337.761	29.405
700	88.701	169.081	119.844	34.466	−376.619	−331.319	24.723
800	90.165	181.023	126.760	43.411	−376.704	−324.838	21.210
900	91.337	191.717	133.394	52.491	−429.655	−317.282	18.415
1000	92.843	201.418	139.718	61.700	−428.077	−304.880	15.925
1100	110.458	210.823	145.749	71.581	−425.884	−292.653	13.897
1200	159.494	222.269	151.627	84.771	−614.002	−275.864	12.008
1276.000	211.921	233.718	156.162	98.962	____ C_p LAMBDA MAXIMUM ____		
1276.000	211.939	233.718	156.162	98.962	TRANSITION		
1300	187.652	237.411	157.629	103.718	−601.115	−248.179	9.972
1400	137.152	249.134	163.773	119.505	−591.403	−221.426	8.262
1445.000	133.888	253.390	166.498	125.559	____ CRYSTAL <--> LIQUID ____		
1445.000	92.048	266.710	166.498	144.805	TRANSITION		
1500	92.048	270.148	170.236	149.868	−567.131	−195.945	6.823
1600	92.048	276.089	176.668	159.073	−564.031	−171.301	5.592
1700	92.048	281.669	182.682	168.278	−560.947	−146.849	4.512
1800	92.048	286.931	188.329	177.482	−557.877	−122.579	3.557
1900	92.048	291.907	193.651	186.687	−554.820	−98.480	2.707
2000	92.048	296.629	198.683	195.892	−551.777	−74.541	1.947
2100	92.048	301.120	203.455	205.097	−548.747	−50.753	1.262
2200	92.048	305.402	207.992	214.302	−545.729	−27.110	0.644
2300	92.048	309.494	212.317	223.506	−542.725	−3.604	0.082
2400	92.048	313.411	216.448	232.711	−539.735	19.772	−0.430
2500	92.048	317.169	220.402	241.916	−536.760	43.024	−0.899
2600	92.048	320.779	224.194	251.121	−533.800	66.157	−1.329
2700	92.048	324.253	227.836	260.326	−530.858	89.176	−1.725
2800	92.048	327.600	231.339	269.530	−527.934	112.087	−2.091
2900	92.048	330.830	234.715	278.735	−525.032	134.893	−2.430
3000	92.048	333.951	237.971	287.940	−522.153	157.600	−2.744

PREVIOUS: CURRENT: March 1978

$S°(298.15\ K) = 150.6 \pm 24\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 423 - 523\ K$
$T_{fus} = 753 \pm 5\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -397.1 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_{trs} H°$ = Unknown
$\Delta_{fus} H° = [18.91 \pm 1.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Kraus and Ridderhof[1] determined $\Delta_f H°(Na_2S_2, cr, 298.15\ K) = -96.2\ kcal \cdot mol^{-1}$ from the enthalpy of reaction of Na(in NH_3) and S(cr) to form Na_2S_2(cr) in liquid ammonia. Letoffe *et al.*[2] derived $\Delta_f H°(Na_2S_2, cr, 298.15\ K) = -92.7\ kcal \cdot mol^{-1}$ from the enthalpy of reaction of Na_2S_2(cr) and H_2SO_4(1100 H_2O) to form Na_2SO_4(acid solution), H_2S(g), and S(cr). With newer values for the enthalpies of formation of H_2SO_4(1100 H_2O),[3] Na_2SO_4(cr),[4] and H_2S(g),[4] the value of Letoffe *et al.* corrects to $-93.6\ kcal \cdot mol^{-1}$. We adopt the average of $\Delta_f H°(Na_2S_2, cr, 298.15\ K) = -94.9 \pm 2\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The heat capacities are those estimated by Barin *et al.*[5]

Mills[6] gives $S°(298.15\ K) = 21.4 \pm 5\ cal \cdot K^{-1} \cdot mol^{-1}$ derived from the dissociation pressure measurements of Teder and Tiberg;[7] the path of the derivation is not clear. Tegman[8] has measured the vapor pressure of sulfur over sodium polysulfide melts which he has supplemented with other measurements from the literature to form an extensive data set covering a composition range of $Na_2S_{1.3}$–$Na_2S_{6.0}$ and a temperature range of 523–1273 K. His analysis of this data set via computer modeling gave, among other things, the entropy changes for the reactions: $Na_2S(l) + 1/2\ S_2(g) = Na_2S_2(l)$; $\Delta S° = -9.00\ cal \cdot K^{-1} \cdot mol^{-1}$ and $Na_2S_2(cr) = Na_2S_2(l)$; $\Delta S° = 4.43\ cal \cdot K^{-1} \cdot mol^{-1}$. It had been assumed these values are independent of temperature, but for our calculation of $S°(Na_2S_2, cr, 298.15\ K)$ we have used a temperature of 900 K, near the mid-point of the experimental range. With auxiliary data for $Na_2S(l)$ and $S_2(g)$[4] and $S°(900\ K)$–$S°(298.15\ K)$ for Na_2S_2(cr) from a preliminary table, we derive $S°(Na_2S_2, cr, 298.15\ K) = 42.1\ cal \cdot K^{-1} \cdot mol^{-1}$.

A graphical comparison of the standard entropies of K_2S(cr),[5] K_2S_3(cr),[19] K_2S_5(cr),[19] and Na_2S(cr)[5] indicates that $21.4\ cal \cdot K^{-1} \cdot mol^{-1}$ is probably too low and $42.1\ cal \cdot K^{-1} \cdot mol^{-1}$ is probably too high for $S°(Na_2S_2, cr, 298.15\ K)$. We adopt $S°(Na_2S_2, cr, 298.15\ K) = 36 \pm 6\ cal \cdot K^{-1} \cdot mol^{-1}$.

Transition and Fusion Data

The existence of two forms of Na_2S_2 is well established,[9–13] but the α–β transition is sluggish. Some indicate the transition is irreversible[9–12] while others find it reversible.[13] On heating the α-form, it changes to the β-form in the 150–250° range[9, 12,13] (423–523 K).

The melting point of the β-form has been determined as 473.9,[14] ~490,[9] 482 ± 2,[15] 478 ± 5,[16] 475,[17] 475,[12] 455,[13] and 484°C.[18] We adopt 480 ± 5°C (753 ± 5 K).

The adopted $\Delta_{fus} H° = 4.52\ kcal \cdot mol^{-1}$ is taken from the tabulation of Barin *et al.*,[5] referenced to private communications from Mills.[6] It is not known if this is a measured or an estimated value. Tegman[8] derived a $\Delta_{fus} H° = 4.62\ kcal \cdot mol^{-1}$ from liquid–vapor and solid–liquid equilibria data via complex computer modeling. This indirectly calculated figure apparently corresponds to an average temperature of approximately 1000 K so that $\Delta_{fus} H°(753\ K)$ ~4.8 $kcal \cdot mol^{-1}$; this value tends to confirm the adopted value and is used in estimating an uncertainty of ±0.4 $kcal \cdot mol^{-1}$.

References

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[3] U. S. Nat. Bur. Stand. Tech. Note 270–3, (1968).
[4] JANAF Thermochemical Tables: Na_2SO_4, V(cr), 6–30–78; H_2S(g), 6–30–77; Na_2S(cr), Na_2S(l), K_2S(cr), 3–31–78; S_2(g), 9–30–77.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	98.625	150.624	150.624	0.	−397.062	−392.173	68.707
300	98.726	151.234	150.626	0.183	−397.067	−392.142	68.278
400	104.299	180.399	154.565	10.334	−407.354	−389.839	50.908
500	109.872	204.272	162.187	21.042	−410.704	−385.082	40.229
600	115.445	224.796	170.949	32.308	−412.640	−379.752	33.060
700	121.018	243.011	179.966	44.131	−413.415	−374.196	27.923
753.000	123.972	251.950	184.720	50.624	---- BETA <--> LIQUID ----		
800	126.591	259.534	188.894	56.512	−413.275	−368.593	24.067
900	132.164	274.766	197.600	69.450	−518.625	−360.893	20.946
1000	137.737	288.979	206.035	82.945	−514.617	−343.578	17.947

PREVIOUS: CURRENT: December 1983

$S°(298.15\ K) = [172.365]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 753 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [-380.114]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [18.91 \pm 1.7]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Na_2S_2, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(753\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of 29.8 $cal·K^{-1}·mol^{-1}$ is from the estimated value of Barin *et al.*[1] and is assumed to be constant above an assumed glass transition at 500 K. Below the glass transition, the heat capacity is that of the crystal.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the β–crystal table for details.

References

[1] I. Barin, O. Knacke, and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances," Supplement, Springer–Verlag, Berlin, (1977).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹		kJ·mol⁻¹			
0							
100							
200							
250							
298.15	98.625	172.365	172.365	0.	−380.114	−381.707	66.873
300	98.726	172.975	172.367	0.183	−380.119	−381.717	66.463
400	104.299	202.140	176.305	10.334	−390.405	−381.587	49.830
500	109.872	226.012	183.928	21.042	−393.756	−379.005	39.594
500.000	109.872	226.012	183.928	21.042	GLASS <--> LIQUID TRANSITION		
500.000	124.683	226.012	183.928	21.042			
600	124.683	248.745	192.894	33.511	−394.489	−375.971	32.731
700	124.683	267.965	202.280	45.979	−394.619	−372.868	27.824
753.000	124.683	277.065	207.228	52.587	---- BETA <--> LIQUID ----		
800	124.683	284.614	211.555	58.447	−394.391	−369.773	24.144
900	124.683	299.299	220.504	70.916	−500.211	−364.559	21.158
1000	124.683	312.436	229.052	83.384	−497.229	−349.647	18.264
1100	124.683	324.320	237.181	95.852	−494.321	−335.030	15.909
1200	124.683	335.168	244.901	108.321	−685.047	−315.794	13.746
1300	124.683	345.148	252.234	120.789	−680.541	−285.206	11.460
1400	124.683	354.388	259.205	133.257	−676.066	−254.963	9.513
1500	124.683	362.991	265.840	145.726	−671.622	−225.040	7.837

PREVIOUS: CURRENT: December 1983

298 to 753 K crystal, beta
above 753 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	98.625	150.624	150.624	0.	−397.062	−392.173	68.707
300	98.726	151.234	150.626	0.183	−397.067	−392.142	68.278
400	104.299	180.399	154.565	10.334	−407.354	−389.839	50.908
500	109.872	204.272	162.187	21.042	−410.704	−385.082	40.229
600	115.445	224.796	170.949	32.308	−412.640	−379.752	33.060
700	121.018	243.011	179.966	44.131	−413.415	−374.196	27.923
753.000	123.972	251.950	184.720	50.624	BETA <--> LIQUID TRANSITION		
753.000	124.683	277.065	184.720	69.535			
800	124.683	284.614	190.370	75.395	−394.391	−369.773	24.144
900	124.683	299.299	201.673	87.864	−500.211	−364.559	21.158
1000	124.683	312.436	212.104	100.332	−497.229	−349.647	18.264
1100	124.683	324.320	221.774	112.800	−494.321	−335.030	15.909
1200	124.683	335.168	230.778	125.269	−685.047	−315.794	13.746
1300	124.683	345.148	239.197	137.737	−680.541	−285.206	11.460
1400	124.683	354.388	247.099	150.205	−676.066	−254.963	9.513
1500	124.683	362.991	254.542	162.674	−671.622	−225.040	7.837

PREVIOUS: CURRENT: December 1983

Continued from page 1641

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REFERENCE STATE

0	to	2750 K	crystal
2750	to	5130.824 K	liquid
above		5130.824 K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.241	0.	0.	0.
100	17.439	12.558	57.153	−4.460	0.	0.	0.
200	23.091	26.878	38.685	−2.361	0.	0.	0.
250	24.154	32.159	36.867	−1.177	0.	0.	0.
298.15	24.694	36.464	36.464	0.	0.	0.	0.
300	24.711	36.616	36.464	0.046	0.	0.	0.
400	25.393	43.826	37.442	2.553	0.	0.	0.
500	25.899	49.548	39.311	5.118	0.	0.	0.
600	26.347	54.309	41.424	7.731	0.	0.	0.
700	26.769	58.403	43.564	10.387	0.	0.	0.
800	27.183	62.004	45.649	13.084	0.	0.	0.
900	27.593	65.230	47.648	15.823	0.	0.	0.
1000	27.999	68.158	49.555	18.603	0.	0.	0.
1100	28.405	70.846	51.370	21.423	0.	0.	0.
1200	28.798	73.334	53.098	24.284	0.	0.	0.
1300	29.179	75.654	54.745	27.182	0.	0.	0.
1400	29.589	77.831	56.317	30.120	0.	0.	0.
1500	30.062	79.888	57.820	33.102	0.	0.	0.
1600	30.606	81.846	59.261	36.135	0.	0.	0.
1700	31.221	83.719	60.645	39.226	0.	0.	0.
1800	31.903	85.523	61.977	42.381	0.	0.	0.
1900	32.639	87.267	63.263	45.608	0.	0.	0.
2000	33.430	88.961	64.506	48.911	0.	0.	0.
2100	34.275	90.612	65.710	52.296	0.	0.	0.
2200	35.187	92.228	66.878	55.768	0.	0.	0.
2300	36.192	93.813	68.015	59.336	0.	0.	0.
2400	37.317	95.377	69.123	63.010	0.	0.	0.
2500	38.635	96.926	70.204	66.805	0.	0.	0.
2600	40.233	98.471	71.261	70.745	0.	0.	0.
2700	42.283	100.027	72.298	74.868	0.	0.	0.
2750.000	43.423	100.813	72.809	77.011	CRYSTAL <--> LIQUID TRANSITION		
2750.000	33.472	110.596	72.809	103.914			
2800	33.472	111.199	73.489	105.587	0.	0.	0.
2900	33.472	112.374	74.810	108.935	0.	0.	0.
3000	33.472	113.508	76.081	112.282	0.	0.	0.
3100	33.472	114.606	77.306	115.629	0.	0.	0.
3200	33.472	115.669	78.489	118.976	0.	0.	0.
3300	33.472	116.699	79.631	122.323	0.	0.	0.
3400	33.472	117.698	80.736	125.671	0.	0.	0.
3500	33.472	118.668	81.806	129.018	0.	0.	0.
3600	33.472	119.611	82.843	132.365	0.	0.	0.
3700	33.472	120.528	83.849	135.712	0.	0.	0.
3800	33.472	121.421	84.826	139.059	0.	0.	0.
3900	33.472	122.290	85.776	142.407	0.	0.	0.
4000	33.472	123.138	86.699	145.754	0.	0.	0.
4100	33.472	123.964	87.598	149.101	0.	0.	0.
4200	33.472	124.771	88.474	152.448	0.	0.	0.
4300	33.472	125.558	89.327	155.795	0.	0.	0.
4400	33.472	126.328	90.159	159.143	0.	0.	0.
4500	33.472	127.080	90.971	162.490	0.	0.	0.
4600	33.472	127.816	91.764	165.837	0.	0.	0.
4700	33.472	128.536	92.539	169.184	0.	0.	0.
4800	33.472	129.240	93.296	172.531	0.	0.	0.
4900	33.472	129.930	94.037	175.879	0.	0.	0.
5000	33.472	130.607	94.762	179.226	0.	0.	0.
5100	33.472	131.270	95.471	182.573	0.	0.	0.
5130.824	33.472	131.471	95.687	183.605	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
5130.824	36.434	266.042	95.686	874.064			
5200	36.642	266.531	97.956	876.592	0.	0.	0.
5300	36.943	267.232	101.143	880.271	0.	0.	0.
5400	37.115	267.914	104.225	883.923	0.	0.	0.
5600	37.678	269.274	110.095	891.403	0.	0.	0.
5800	38.251	270.606	115.607	898.995	0.	0.	0.
6000	38.839	271.913	120.795	906.704	0.	0.	0.

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 36.46 \pm 0.4\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2750 \pm 10\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 26.90 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for $T < 10$ are chosen to be the same as those adopted by Hultgren *et al.*[1] A graphical integration of these $C_p°$ data yields $S°(10\ K) = 0.029\ J·K^{-1}·mol^{-1}$ and $H°(10\ K) = 0.19\ cal·mol^{-1}$. The work by DaSilva *et al.*[2,3] on the low temperature (1–10 K) heat capacity of annealed and unannealed niobium wires in magnetic fields supports this choice. Clusius *et al.*[4] measured the heat capacity (61 pts.) in the region 11–274 K. This data is smoothed graphically and is constrained to join smoothly with the $C_p°$ values for $T \leq 10$ K. Deviations up to 4% occur between the observed and adopted $C_p°$ values for $T < 80$ K. The deviations here parallel the deviations obtained in our analysis of the heat capacity for Ta.[5] The deviations decrease steadily with increasing temperature up to 274 K.

There are numerous high temperature heat capacity and enthalpy measurements for Nb(cr). The various studies are listed below.

Source	T/K	Method
[6]	273–1873	drop
[7]	454–1882	drop
[8]	433–1840	drop
[9]	1400–2350	modul
[10]	1300–2700	modul
[11]	358–1415	drop
[12]	600–2600	drop
[13]	1273–2593	drop
[14]	1100–2400	pulse
[15]	1500–2700	pulse
[16]	1650–2707	drop

The adopted $C_p°$ values for $T > 298.15$ K are obtained by a combination of graphical and polynomial curve fitting techniques. A polynomial curve fit procedure is used on the enthalpy data of Hawkins and Orr[11] with the constraint that it join smoothly in the 298.15 K region with the enthalpy derived from the Clusius *et al.*[4] heat capacity data. Above 1300 K, a heat capacity curve is adopted through graphical procedures. The adopted curve is chosen so as to be intermediate between the $C_p°$ values of Cezairliyan[15] and the higher $C_p°$ values implied from the enthalpy data of Kirillin *et al.*[12] and Sheindlin *et al.*[16] In general there is good agreement between the various sets of data.

The heat capacity values near T_{fus} are the smoothed values suggested by Cezairliyan.[15] In comparison with the adopted $C_p°$ values, Cezairliyan's smoothed data lies low by 1.9% at 1500 K with the difference steadily decreasing to zero at 2600 K. The smoothed results of Cezairliyan[15] are used for extrapolation to 3200 K. The $C_p°$ values reported by Makarenko and Trukhanov[14] are linear in the region 1100–2400 K whereas the adopted $C_p°$ values are nonlinear; the $C_p°$–T curve being concave upward in this region. The $C_p°$ values of Makarenko *et al.*[14] are within −0.4% to +0.8% of the adopted values in the region 1400– 2100 K but drift to −3% at 1100 K and 2400 K. In comparing enthalpies, Kirillin *et al.*[12] reported smoothed values[2] which are 15 cal·mol^{-1} or 0.8% lower than our tabulated values at 600 K and drift to 849 cal·mol^{-1} or 4.5% higher at 2700 K. The enthalpy results of Sheindlin *et al.*[16] lie above the JANAF values by 0.9% in the region 1700–2700 K (82 cal·mol^{-1} at 1700 K and 181 cal·mol^{-1} at 2700 K).

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K)$ for Nb(cr) = Nb(g) is simply $\Delta_f H°(298.15\ K)$ for Nb(g). Refer to the ideal gas table for details.

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Continued on page 1693

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
0	0.	0.	INFINITE	−5.241	0.	0.	0.
100	17.439	12.558	57.153	−4.460	0.	0.	0.
200	23.091	26.878	38.685	−2.361	0.	0.	0.
250	24.154	32.159	36.867	−1.177	0.	0.	0.
298.15	24.694	36.464	36.464	0.	0.	0.	0.
300	24.711	36.616	36.464	0.046	0.	0.	0.
350	25.088	40.455	36.766	1.291	0.	0.	0.
400	25.393	43.826	37.442	2.553	0.	0.	0.
450	25.653	46.832	38.322	3.830	0.	0.	0.
500	25.899	49.548	39.311	5.118	0.	0.	0.
600	26.347	54.309	41.424	7.731	0.	0.	0.
700	26.769	58.403	43.564	10.387	0.	0.	0.
800	27.183	62.004	45.649	13.084	0.	0.	0.
900	27.593	65.230	47.648	15.823	0.	0.	0.
1000	27.999	68.158	49.555	18.603	0.	0.	0.
1100	28.405	70.846	51.370	21.423	0.	0.	0.
1200	28.798	73.334	53.098	24.284	0.	0.	0.
1300	29.179	75.654	54.745	27.182	0.	0.	0.
1400	29.589	77.831	56.317	30.120	0.	0.	0.
1500	30.062	79.888	57.820	33.102	0.	0.	0.
1600	30.606	81.846	59.261	36.135	0.	0.	0.
1700	31.221	83.719	60.645	39.226	0.	0.	0.
1800	31.903	85.523	61.977	42.381	0.	0.	0.
1900	32.639	87.267	63.263	45.608	0.	0.	0.
2000	33.430	88.961	64.506	48.911	0.	0.	0.
2100	34.275	90.612	65.710	52.296	0.	0.	0.
2200	35.187	92.228	66.878	55.768	0.	0.	0.
2300	36.192	93.813	68.015	59.336	0.	0.	0.
2400	37.317	95.377	69.123	63.010	0.	0.	0.
2500	38.635	96.926	70.204	66.805	0.	0.	0.
2600	40.233	98.471	71.261	70.745	0.	0.	0.
2700	42.283	100.027	72.298	74.868	0.	0.	0.
2750.000	43.423	100.813	72.809	77.011	--- CRYSTAL <---> LIQUID ---		
2800	44.643	101.606	73.316	79.212	−26.375	0.484	−0.009
2900	47.342	103.219	74.319	83.808	−25.126	1.423	−0.026
3000	50.410	104.874	75.310	88.692	−23.589	2.313	−0.040
3100	53.879	106.583	76.291	93.903	−21.725	3.146	−0.053
3200	57.777	108.354	77.265	99.483	−19.494	3.914	−0.064

PREVIOUS: June 1972 CURRENT: December 1973

$S°(298.15\ K) = [47.302]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2750 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [29.647]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 26.90 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Nb(l) at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2750\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The enthalpy measurements on Nb(l) by Sheindlin *et al.*[7] and Margrave[8] do not extend over a sufficiently wide temperature range such that a heat capacity value could be derived. Therefore, the heat capacity for Nb(l) is estimated as 8.0 $cal·K^{-1}·mol^{-1}$ by analogy with other monatomic metals. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation. A glass transition is assumed at 1750 K. The heat capacity values used below 1750 K are those of Nb(cr).

Fusion Data

Melting point determinations for Nb have been numerous, with most reported values in the range 2680–2795 K (IPTS–68 scale). A prime cause for diversity in the results is that the melting point is quite sensitive to impurities, especially gases such as oxygen and nitrogen. These effects have been documented by Schofield[1] and Pemsler.[2] The value chosen is 2750 ± 10 K as reported by Cezairliyan[3] using a subsecond pulse heating method. This value is consistent with the heat capacity values near T_{fus} which are also based on related work by Cezairliyan.[4] Other values in this range (corrected to IPTS–68 scale) are 2746 K by Schofield,[1] 2745 K by Pemsler,[2] and 2738 K by Buehler.[5] Kocherzhinskii and Kobzenko[6] have reported a T_{fus} value of 2793 K, using a sample purified by electron zone fusion.

The value chosen for $\Delta_{fus}H°$ is 6.43 ± 0.20 $kcal·mol^{-1}$ as determined by Cezairliyan[3] using a pulse heating technique. Adopting this value gives consistency between the $C_p°$ values near T_{fus}, $\Delta_{fus}H°$, and T_{fus} as all these values are dependent upon the same heating technique. Sheindlin *et al.*[7] reported $\Delta_{fus}H° = 6.597 \pm 0.170\ kcal·mol^{-1}$ based on enthalpy measurements on Nb(cr) and Nb(l) obtained from levitation calorimetry techniques. In the vicinity of T_{fus}, the adopted enthalpy vlaues for Nb(cr) and Nb(l) lie roughly 200 $cal·mol^{-1}$ lower than those reported by Sheindlin *et al.*[7] Margrave,[8] also using levitation techniques, reported a value $\Delta_{fus}H° = 7.9\ kcal·mol^{-1}$. It is felt that Margrave's value was calculated from a measured enthalpy of Nb(l) at T_{fus} and the enthalpy of Nb(cr) at T_{fus} as suggested by Hultgren *et al.*[9] Our enthalpy vlaues at T_{fus} for Nb(cr) would reduce Margrave's value to roughly 7.4 $kcal·mol^{-1}$ for $\Delta_{fus}H°$.

Martynyuk and Tsapkov[10] measured the enthalpies of Nb(cr) and Nb(l) at the melting point using the method of pulse heating. They reported enthalpy of melting value of 7.98 $kcal·mol^{-1}$ for an Nb sample which was reported to be 99.94% pure. No T_{fus} value was reported.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the reaction Nb(l) = Nb(g) is zero. The difference between $\Delta_f H°$(Nb, g) and $\Delta_f H°$(Nb, l) at T_{vap} is $\Delta_{vap}H°$. The uncertainty in the boiling point is probably of the order of ± 100 K. Also refer to Nb(g) table.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$		$kJ·mol^{-1}$			
0						
100						
200						
250						
298.15	24.694	47.302	0.	29.647	26.415	−4.628
300	24.711	47.455	0.046	29.647	26.395	−4.596
350	25.088	51.293	1.291	29.647	25.853	−3.858
400	25.393	54.664	2.553	29.647	25.311	−3.305
450	25.653	57.670	3.830	29.647	24.770	−2.875
500	25.899	60.386	5.118	29.647	24.228	−2.531
600	26.347	65.148	7.731	29.647	23.144	−2.015
700	26.769	69.241	10.387	29.647	22.060	−1.646
800	27.183	72.842	13.084	29.647	20.976	−1.370
900	27.593	76.068	15.823	29.647	19.892	−1.155
1000	27.999	78.996	18.603	29.647	18.808	−0.982
1100	28.405	81.684	21.423	29.647	17.725	−0.842
1200	28.798	84.172	24.284	29.647	16.641	−0.724
1300	29.179	86.492	27.182	29.647	15.557	−0.625
1400	29.589	88.669	30.120	29.647	14.473	−0.540
1500	30.062	90.727	33.102	29.647	13.389	−0.466
1600	30.606	92.684	36.135	29.647	12.306	−0.402
1700	31.221	94.557	39.226	29.647	11.222	−0.345
1750.000	31.559	95.467	40.795	GLASS <--> LIQUID TRANSITION		
1750.000	33.472	95.467	72.156	40.795		
1800	33.472	96.410	72.816	42.469	29.734	10.137	−0.294
1900	33.472	98.220	74.106	45.816	29.854	9.044	−0.249
2000	33.472	99.937	75.355	49.163	29.899	7.948	−0.208
2100	33.472	101.570	76.565	52.510	29.861	6.851	−0.170
2200	33.472	103.127	77.737	55.857	29.736	5.757	−0.137
2300	33.472	104.615	78.874	59.205	29.515	4.672	−0.106
2400	33.472	106.039	79.976	62.552	29.188	3.599	−0.078
2500	33.472	107.406	81.046	65.899	28.740	2.541	−0.053
2600	33.472	108.718	82.085	69.246	28.148	1.504	−0.030
2700	33.472	109.982	83.095	72.593	27.372	0.494	−0.010
2750.000	33.472	110.596	83.590	74.267	--- CRYSTAL <--> LIQUID ---		
2800	33.472	111.199	84.077	75.941	0.	0.	0.
2900	33.472	112.374	85.033	79.288	0.	0.	0.
3000	33.472	113.508	85.963	82.635	0.	0.	0.
3100	33.472	114.606	86.870	85.982	0.	0.	0.
3200	33.472	115.669	87.753	89.329	0.	0.	0.
3300	33.472	116.699	88.615	92.677	0.	0.	0.
3400	33.472	117.698	89.456	96.024	0.	0.	0.
3500	33.472	118.668	90.276	99.371	0.	0.	0.
3600	33.472	119.611	91.078	102.718	0.	0.	0.
3700	33.472	120.528	91.862	106.065	0.	0.	0.
3800	33.472	121.421	92.628	109.413	0.	0.	0.
3900	33.472	122.290	93.377	112.760	0.	0.	0.
4000	33.472	123.138	94.111	116.107	0.	0.	0.
4100	33.472	123.964	94.829	119.454	0.	0.	0.
4200	33.472	124.771	95.532	122.801	0.	0.	0.
4300	33.472	125.558	96.221	126.149	0.	0.	0.
4400	33.472	126.328	96.897	129.496	0.	0.	0.
4500	33.472	127.080	97.559	132.843	0.	0.	0.
4600	33.472	127.816	98.209	136.190	0.	0.	0.
4700	33.472	128.536	98.847	139.537	0.	0.	0.
4800	33.472	129.240	99.473	142.885	0.	0.	0.
4900	33.472	129.931	100.087	146.232	0.	0.	0.
5000	33.472	130.607	100.691	149.579	0.	0.	0.
5100	33.472	131.270	101.284	152.926	0.	0.	0.
5130.824	33.472	131.471	101.465	153.958	----- FUGACITY = 1 bar -----		
5200	33.472	131.920	101.867	156.273	−690.672	9.309	−0.094
5300	33.472	132.557	102.440	159.621	−691.004	22.774	−0.224
5400	33.472	133.183	103.004	162.968	−691.309	36.240	−0.351
5600	33.472	134.400	104.103	169.662	−692.094	63.200	−0.590
5800	33.472	135.575	105.168	176.357	−692.992	90.191	−0.812
6000	33.472	136.709	106.201	183.051	−694.007	117.214	−1.020

PREVIOUS: June 1972 CURRENT: December 1973

0 to 2750 K crystal
above 2750 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.241	0	0.	0.
100	17.439	12.558	57.153	−4.460	0.	0.	0.
200	23.091	26.878	38.685	−2.361	0.	0.	0.
250	24.154	32.159	36.867	−1.177	0.	0.	0.
298.15	24.694	36.464	36.464	0.	0.	0.	0.
300	24.711	36.616	36.464	0.046	0.	0.	0.
350	25.088	40.455	36.766	1.291	0.	0.	0.
400	25.393	43.826	37.442	2.553	0.	0.	0.
450	25.653	46.832	38.322	3.830	0.	0.	0.
500	25.899	49.548	39.311	5.118	0.	0.	0.
600	26.347	54.309	41.424	7.731	0.	0.	0.
700	26.769	58.403	43.564	10.387	0.	0.	0.
800	27.183	62.004	45.649	13.084	0.	0.	0.
900	27.593	65.230	47.648	15.823	0.	0.	0.
1000	27.999	68.158	49.555	18.603	0.	0.	0.
1100	28.405	70.846	51.370	21.423	0.	0.	0.
1200	28.798	73.334	53.098	24.284	0.	0.	0.
1300	29.179	75.654	54.745	27.182	0.	0.	0.
1400	29.589	77.831	56.317	30.120	0.	0.	0.
1500	30.062	79.888	57.820	33.102	0.	0.	0.
1600	30.606	81.846	59.261	36.135	0.	0.	0.
1700	31.221	83.719	60.645	39.226	0.	0.	0.
1800	31.903	85.523	61.977	42.381	0.	0.	0.
1900	32.639	87.267	63.263	45.608	0.	0.	0.
2000	33.430	88.961	64.506	48.911	0.	0.	0.
2100	34.275	90.612	65.710	52.296	0.	0.	0.
2200	35.187	92.228	66.878	55.768	0.	0.	0.
2300	36.192	93.813	68.015	59.336	0.	0.	0.
2400	37.317	95.377	69.123	63.010	0.	0.	0.
2500	38.635	96.926	70.204	66.805	0.	0.	0.
2600	40.233	98.471	71.261	70.745	0.	0.	0.
2700	42.283	100.027	72.298	74.868	0.	0.	0.
2750.000	43.423	100.813	72.809	77.011	CRYSTAL <--> LIQUID TRANSITION		
2750.000	33.472	110.596	72.809	103.914			
2800	33.472	111.199	73.489	105.587	0.	0.	0.
2900	33.472	112.374	74.810	108.935	0.	0.	0.
3000	33.472	113.508	76.081	112.282	0.	0.	0.
3100	33.472	114.606	77.306	115.629	0.	0.	0.
3200	33.472	115.669	78.489	118.976	0.	0.	0.
3300	33.472	116.699	79.631	122.323	0.	0.	0.
3400	33.472	117.698	80.736	125.671	0.	0.	0.
3500	33.472	118.668	81.806	129.018	0.	0.	0.
3600	33.472	119.611	82.843	132.365	0.	0.	0.
3700	33.472	120.528	83.849	135.712	0.	0.	0.
3800	33.472	121.421	84.826	139.059	0.	0.	0.
3900	33.472	122.290	85.776	142.407	0.	0.	0.
4000	33.472	123.138	86.699	145.754	0.	0.	0.
4100	33.472	123.964	87.598	149.101	0.	0.	0.
4200	33.472	124.771	88.474	152.448	0.	0.	0.
4300	33.472	125.558	89.327	155.795	0.	0.	0.
4400	33.472	126.328	90.159	159.143	0.	0.	0.
4500	33.472	127.080	90.971	162.490	0.	0.	0.
4600	33.472	127.816	91.764	165.837	0.	0.	0.
4700	33.472	128.536	92.539	169.184	0.	0.	0.
4800	33.472	129.240	93.296	172.531	0.	0.	0.
4900	33.472	129.930	94.037	175.879	0.	0.	0.
5000	33.472	130.607	94.762	179.226	0.	0.	0.
5100	33.472	131.270	95.471	182.573	0.	0.	0.
5130.824	33.472	131.471	95.687	183.605	----- FUGACITY = 1 bar -----		
5200	33.472	131.920	96.166	185.920	−690.672	9.310	−0.094
5300	33.472	132.557	96.846	189.267	−691.004	22.774	−0.224
5400	33.472	133.183	97.513	192.615	−691.309	36.240	−0.351
5600	33.472	134.400	98.809	199.309	−692.094	63.200	−0.590
5800	33.472	135.575	100.057	206.003	−692.992	90.191	−0.812
6000	33.472	136.709	101.260	212.698	−694.007	117.214	−1.020

PREVIOUS: CURRENT: December 1973

IP(Nb, g) = 55511 ± 1 cm^{-1}
$S°(298.15\ K)$ = 186.26 ± 0.4 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 729.9 ± 8 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 733.0 ± 8 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6D_{1/2}$	0.00	2
$^6D_{3/2}$	154.19	4
$^6D_{5/2}$	391.99	6
$^6D_{7/2}$	695.25	8
$^6D_{9/2}$	1050.26	10

Enthalpy of Formation

A 2nd and 3rd law analysis of six reported vapor pressure studies is tabulated below. Five studies[1-5] used the Langmuir free evaporation method while one study[6] used the integral variation of the Knudsen method.

Source	Reaction	T/K (IPTS–68)	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$ (298.15 K) kcal·mol^{-1}
1	A	2744–3146	15*	146.2	168.4	7.5 ± 1.5	175.5
2	B	2307–2600	14**	175.8	172.5	−1.3 ± 1.6	172.5
3	B	2456–2691	8	182.8	175.7	−2.8 ± 5.3	175.7
4	B	2253–260	eqn	183.4	174.8	−3.6	174.8
5	B	2370–2685	eqn	175.0	177.7	1.1	177.7
6	B	2553–2684	4	143.1	191.4	18.4 ± 4.8	191.4

* 2939.9 K point deleted due to a statistical test.
** 2307, 2328, 2584 K points deleted due to a statistical test.
A = vaporization
B = sublimation

We adopt $\Delta_f H°(298.15\ K)$ = 175.2 kcal·mol^{-1} for Nb(g) which is a rounded average of four results.[2-5] With a drift of 7.5 cal·K^{-1}·mol^{-1} in that data, Shchukarev *et al.*[7] reported an enthalpy of sublimation of Nb(cr), determined at 2243–2393 K,of 172 ± 5 kcal·mol^{-1}. Our tabulations give $\Delta_{sub}H°(2300\ K)$ = 173.5 kcal·mol^{-1}. The same workers[7] later reported $\Delta_{sub}H°(298.15K)$ = 173 kcal·mol^{-1} based on a 2nd law analysis of Nb^+ ion currents at temperatures above 2573 K.

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore.[8] Only a few of the levels are listed above. All levels reported by Moore[8] are considered in the calculation. There are predicted electronic levels which have not beenobserved.[8] These levels are assumed to lie above 20,000 cm^{-1} and thus will not significantly affect the entropy attemperatures below 3000 K. The heat capacity and entropy values are very similar to those adopted by Hultgren *et al.*,[9] being the sameat 298.15 K and differing by 0.39 cal·K^{-1}·mol^{-1} in C_p at 5500 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.354	729.923	729.923	INFINITE
100	28.819	153.823	212.891	−5.907	731.590	717.463	−374.764
200	29.932	174.240	189.016	−2.955	732.443	702.971	−183.597
250	30.144	180.945	186.756	−1.453	732.761	695.565	−145.330
298.15	30.159	186.259	186.259	0.	733.037	688.375	−120.600
300	30.155	186.446	186.260	0.056	733.047	688.098	−119.809
350	29.969	191.082	186.626	1.560	733.305	680.586	−101.572
400	29.646	195.064	187.438	3.050	733.534	673.039	−87.890
450	29.253	198.534	188.482	4.523	733.730	665.464	−77.245
500	28.840	201.594	189.644	5.975	733.894	657.870	−68.727
600	28.050	206.781	192.083	8.819	734.125	642.642	−55.947
700	27.365	211.052	194.497	11.589	734.239	627.384	−46.816
800	26.785	214.668	196.798	14.296	734.248	612.117	−39.967
900	26.294	217.793	198.961	16.949	734.162	596.855	−34.641
1000	25.880	220.542	200.984	19.557	733.991	581.607	−30.380
1100	25.533	222.991	202.876	22.127	733.741	566.380	−26.895
1200	25.248	225.200	204.646	24.666	733.419	551.179	−23.992
1300	25.023	227.212	206.305	27.179	733.033	536.008	−21.537
1400	24.857	229.060	207.866	29.672	732.589	520.869	−19.434
1500	24.748	230.771	209.336	32.152	732.087	505.763	−17.612
1600	24.696	232.366	210.726	34.624	731.526	490.693	−16.019
1700	24.700	233.863	212.044	37.093	730.904	475.659	−14.615
1800	24.759	235.276	213.296	39.566	730.221	460.664	−13.368
1900	24.872	236.618	214.488	42.047	729.475	445.709	−12.253
2000	25.034	237.898	215.627	44.542	728.667	430.794	−11.251
2100	25.244	239.124	216.717	47.055	727.796	415.922	−10.345
2200	25.496	240.304	217.762	49.592	726.860	401.092	−9.523
2300	25.788	241.444	218.767	52.156	725.856	386.307	−8.773
2400	26.115	242.548	219.735	54.751	724.777	371.567	−8.087
2500	26.472	243.621	220.669	57.380	723.611	356.873	−7.456
2600	26.854	244.667	221.572	60.046	722.338	342.229	−6.875
2700	27.256	245.688	222.446	62.751	720.920	327.635	−6.338
2800	27.675	246.686	223.294	65.498	692.947	313.582	−5.850
2900	28.105	247.665	224.118	68.287	692.389	300.044	−5.404
3000	28.544	248.625	224.919	71.119	691.874	286.523	−4.989
3100	28.986	249.568	225.699	73.995	691.403	273.020	−4.600
3200	29.430	250.496	226.459	76.916	690.977	259.530	−4.236
3300	29.871	251.408	227.202	79.881	690.595	246.054	−3.895
3400	30.309	252.306	227.927	82.890	690.257	232.588	−3.573
3500	30.740	253.191	228.636	85.943	689.962	219.131	−3.270
3600	31.162	254.063	229.330	89.038	689.710	205.683	−2.984
3700	31.576	254.922	230.010	92.175	689.500	192.241	−2.714
3800	31.979	255.770	230.677	95.353	689.330	178.804	−2.458
3900	32.371	256.606	231.331	98.570	689.201	165.370	−2.215
4000	32.751	257.430	231.973	101.827	689.110	151.940	−1.984
4100	33.120	258.243	232.604	105.120	689.056	138.512	−1.765
4200	33.479	259.046	233.224	108.450	689.039	125.084	−1.556
4300	33.826	259.838	233.834	111.816	689.057	111.656	−1.356
4400	34.164	260.619	234.434	115.215	689.110	98.228	−1.166
4500	34.493	261.391	235.024	118.648	689.195	84.798	−0.984
4600	34.814	262.152	235.606	122.114	689.313	71.365	−0.810
4700	35.127	262.904	236.179	125.611	689.463	57.930	−0.644
4800	35.436	263.647	236.743	129.139	689.644	44.492	−0.484
4900	35.740	264.381	237.300	132.698	689.856	31.049	−0.331
5000	36.041	265.106	237.849	136.287	690.098	17.601	−0.184
5100	36.342	265.823	238.390	139.906	690.370	4.149	−0.042
5130.824	36.434	266.042	238.556	141.028	------ FUGACITY = 1 bar ------		
5200	36.642	266.531	238.925	143.555	0.	0.	0.
5300	36.943	267.232	239.452	147.234	0.	0.	0.
5400	37.115	267.914	239.972	150.887	0.	0.	0.
5500	37.396	268.598	240.486	154.612	0.	0.	0.
5600	37.678	269.274	240.994	158.366	0.	0.	0.
5700	37.963	269.943	241.496	162.148	0.	0.	0.
5800	38.251	270.606	241.993	165.959	0.	0.	0.
5900	38.543	271.263	242.483	169.798	0.	0.	0.
6000	38.839	271.913	242.968	173.667	0.	0.	0.

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

IP(Nb^+, g) = 115500 ± 100 cm^{-1}
$S°(298.15\ K) = 183.333 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1394.0 \pm 8\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1402.954]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5D_0$	0.00	1
$^5D_1$	158.38	3
$^5D_2$	438.99	5
$^5D_3$	801.38	7
$^5D_4$	1224.87	9

Enthalpy of Formation

$\Delta_f H°(Nb^+, g, 0\ K)$ is calculated from $\Delta_f H°(Nb, g, 0\ K)$[1] using the spectroscopic value of IP(Nb) = 55511 ± 1 cm^{-1} (664.059 ± 0.01 $kJ \cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Nb^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Nb, g, 0\ K)$ by using IP(Nb) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for Nb(g), $Nb^+(g)$, and e^-(ref). $\Delta_f H°(Nb \rightarrow Nb^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first excited state, the highest observed excited state, and the ionization potential for $Nb^+(g)$, all levels listed by Moore[6] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for $Nb^+(g)$, the thermodynamic functions are independent of the estimated missing levels (for $n = 4, 5$), the cut–off procedure, and the inclusion of $n = 5$ levels up to 6000 K; the Gibbs energy function showing variations of 0.2% at this temperature. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states ($n > 5$), and use of different fill and cut–off procedures.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.015	1393.983		
100	26.964	152.351	209.002	−5.665			
200	28.783	171.684	186.012	−2.866			
250	29.250	178.162	183.816	−1.414			
298.15	29.421	183.333	183.333	0.	1402.954	1352.911	−237.024
300	29.423	183.515	183.333	0.054	1403.002	1352.600	−235.509
350	29.331	188.046	183.691	1.524	1404.265	1344.099	−200.596
400	29.059	191.947	184.485	2.985	1405.503	1335.419	−174.388
450	28.698	195.349	185.507	4.429	1406.710	1326.586	−153.986
500	28.323	198.353	186.645	5.854	1407.886	1317.620	−137.651
600	27.697	203.458	189.036	8.653	1410.151	1299.353	−113.119
700	27.316	207.696	191.407	11.402	1412.322	1280.714	−95.568
800	27.143	211.330	193.676	14.123	1414.425	1261.768	−82.385
900	27.099	214.524	195.819	16.835	1416.476	1242.562	−72.116
1000	27.118	217.380	197.834	19.545	1418.485	1223.131	−63.890
1100	27.159	219.966	199.731	22.259	1420.457	1203.499	−57.149
1200	27.203	222.331	201.517	24.977	1422.394	1183.690	−51.525
1300	27.242	224.510	203.203	27.700	1424.296	1163.721	−46.759
1400	27.281	226.530	204.798	30.426	1426.163	1143.606	−42.668
1500	27.324	228.414	206.310	33.156	1427.990	1123.360	−39.119
1600	27.378	230.179	207.747	35.891	1429.771	1102.993	−36.009
1700	27.448	231.841	209.116	38.632	1431.500	1082.516	−33.262
1800	27.537	233.412	210.423	41.381	1433.171	1061.939	−30.817
1900	27.647	234.904	211.672	44.140	1434.782	1041.271	−28.627
2000	27.780	236.325	212.870	46.911	1436.329	1020.519	−26.653
2100	27.934	237.684	214.019	49.697	1437.809	999.692	−24.866
2200	28.108	238.988	215.125	52.499	1439.217	978.796	−23.240
2300	28.300	240.242	216.190	55.319	1440.548	957.838	−21.753
2400	28.507	241.450	217.217	58.159	1441.793	936.823	−20.389
2500	28.726	242.618	218.210	61.021	1442.938	915.759	−19.134
2600	28.956	243.750	219.171	63.905	1443.961	894.651	−17.974
2700	29.193	244.847	220.101	66.812	1444.823	873.507	−16.899
2800	29.437	245.913	221.004	69.744	1419.114	852.819	−15.910
2900	29.686	246.950	221.881	72.700	1420.802	832.564	−14.996
3000	29.939	247.961	222.734	75.681	1422.514	812.251	−14.143
3100	30.196	248.947	223.563	78.688	1424.252	791.880	−13.343
3200	30.457	249.909	224.372	81.720	1426.016	771.453	−12.593
3300	30.723	250.851	225.160	84.779	1427.807	750.970	−11.887
3400	30.996	251.772	225.929	87.865	1429.624	730.433	−11.222
3500	31.276	252.674	226.680	90.979	1431.469	709.842	−10.594
3600	31.566	253.560	227.415	94.121	1433.343	689.197	−10.000
3700	31.868	254.429	228.133	97.292	1435.246	668.500	−9.438
3800	32.183	255.283	228.837	100.495	1437.179	647.752	−8.904
3900	32.513	256.123	229.525	103.729	1439.145	626.952	−8.397
4000	32.861	256.950	230.201	106.998	1441.145	606.101	−7.915
4100	33.229	257.766	230.863	110.302	1443.181	585.200	−7.456
4200	33.617	258.571	231.513	113.644	1445.255	564.248	−7.017
4300	34.027	259.367	232.152	117.027	1447.368	543.247	−6.599
4400	34.461	260.154	232.779	120.451	1449.524	522.196	−6.199
4500	34.917	260.934	233.396	123.919	1451.724	501.096	−5.817
4600	35.398	261.707	234.003	127.435	1453.971	479.946	−5.450
4700	35.902	262.473	234.601	131.000	1456.267	458.747	−5.098
4800	36.428	263.235	235.190	134.616	1458.615	437.498	−4.761
4900	36.977	263.991	235.770	138.286	1461.016	416.200	−4.437
5000	37.546	264.744	236.342	142.012	1463.473	394.853	−4.125
5100	38.133	265.493	236.906	145.796	1465.989	373.456	−3.825
5200	38.737	266.240	237.463	149.639	777.892	361.318	−3.629
5300	39.356	266.983	238.013	153.544	780.196	353.285	−3.482
5400	39.985	267.725	238.556	157.511	782.589	345.204	−3.339
5500	40.624	268.464	239.093	161.541	784.972	337.082	−3.201
5600	41.268	269.202	239.624	165.636	787.392	328.917	−3.068
5700	41.915	269.938	240.150	169.795	789.847	320.708	−2.939
5800	42.561	270.673	240.670	174.019	792.339	312.456	−2.814
5900	43.203	271.406	241.184	178.307	794.866	304.160	−2.693
6000	43.839	272.137	241.694	182.659	797.428	295.822	−2.575

PREVIOUS: CURRENT: March 1984 (1 bar)

EA(Nb, g) = 0.893 ± 0.025 eV
$S°(298.15\ K)$ = 186.095 ± 0.002 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 643.763 ± 4.5 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [640.978] $kJ·mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5D_0$	0	1
$^5D_1$	110	3
$^5D_2$	310	5
$^5D_3$	560	7
$^5D_4$	870	9

Enthalpy of Formation

$\Delta_f H°(Nb^-, g, 0\ K)$ is calculated from $\Delta_f H°(Nb, g, 0\ K)$[1] using the adopted electron affinity of EA(Nb) = 0.893 ± 0.025 eV (86.161 ± 2.412 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $Nb^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Nb^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Nb, g, 0\ K)$ by using EA(Nb) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, or $Nb^-(g)$, Nb(g), and e^-(ref). $\Delta_r H°(Nb^- \rightarrow Nb + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Nb^-(g)$ is given by Hotop and Lineberger,[2, 4] Rosenstock *et al.*,[5] and Massey.[6] The fine structure separation has been calculated by an isoelectronic extrapolation of ratios of fine structure separations[3] and is that recommended by Hotop and Lineberger.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.654	643.763		
100	30.251	153.166	212.710	−5.954			
200	30.317	174.205	188.796	−2.918			
250	29.768	180.919	186.576	−1.414			
298.15	28.948	186.095	186.095	0.	640.978	602.621	−105.577
300	28.913	186.274	186.095	0.054	640.948	602.383	−104.884
350	27.956	190.659	186.444	1.475	640.085	596.023	−88.952
400	27.029	194.331	187.207	2.850	639.158	589.790	−77.019
450	26.196	197.465	188.177	4.180	638.172	583.678	−67.752
500	25.474	200.187	189.245	5.471	637.135	577.678	−60.350
600	24.342	204.725	191.461	7.959	634.932	565.991	−49.274
700	23.538	208.414	193.627	10.350	632.589	554.685	−41.391
800	22.962	211.517	195.675	12.674	630.136	543.722	−35.501
900	22.541	214.196	197.587	14.948	627.593	533.072	−30.939
1000	22.227	216.554	199.368	17.186	624.972	522.709	−27.304
1100	21.988	218.661	201.028	19.396	622.284	512.613	−24.342
1200	21.803	220.566	202.578	21.585	619.534	502.764	−21.885
1300	21.656	222.305	204.030	23.758	616.729	493.146	−19.815
1400	21.539	223.905	205.393	25.917	613.872	483.746	−18.049
1500	21.443	225.388	206.677	28.066	610.961	474.553	−16.525
1600	21.364	226.769	207.890	30.206	607.990	465.556	−15.199
1700	21.299	228.062	209.039	32.339	604.953	456.746	−14.034
1800	21.243	229.278	210.130	34.466	601.846	448.117	−13.004
1900	21.197	230.425	211.168	36.588	598.663	439.663	−12.087
2000	21.157	231.512	212.159	38.706	595.399	431.379	−11.266
2100	21.122	232.543	213.105	40.820	592.049	423.260	−10.528
2200	21.092	233.525	214.011	42.931	588.609	415.303	−9.861
2300	21.066	234.462	214.880	45.038	585.070	407.504	−9.255
2400	21.043	235.358	215.715	47.144	581.423	399.862	−8.703
2500	21.023	236.217	216.518	49.247	577.653	392.374	−8.198
2600	21.005	237.041	217.291	51.349	573.736	385.039	−7.736
2700	20.989	237.833	218.038	53.448	569.634	377.859	−7.310
2800	20.975	238.596	218.758	55.546	538.934	371.319	−6.927
2900	20.962	239.332	219.455	57.643	535.605	365.391	−6.581
3000	20.950	240.043	220.130	59.739	532.275	359.579	−6.261
3100	20.940	240.729	220.783	61.833	528.944	353.877	−5.963
3200	20.930	241.394	221.417	63.927	525.611	348.283	−5.685
3300	20.922	242.038	222.032	66.019	522.278	342.793	−5.426
3400	20.914	242.662	222.630	68.111	518.944	337.404	−5.184
3500	20.906	243.268	223.211	70.202	515.609	332.113	−4.957
3600	20.900	243.857	223.776	72.293	512.274	326.918	−4.743
3700	20.894	244.430	224.327	74.382	508.938	321.815	−4.543
3800	20.888	244.987	224.863	76.471	505.601	316.802	−4.355
3900	20.883	245.530	225.386	78.560	502.264	311.877	−4.177
4000	20.878	246.058	225.896	80.648	498.926	307.038	−4.010
4100	20.874	246.574	226.394	82.735	495.588	302.282	−3.851
4200	20.869	247.077	226.881	84.823	492.249	297.608	−3.701
4300	20.866	247.568	227.356	86.909	488.910	293.013	−3.559
4400	20.862	248.047	227.821	88.996	485.570	288.496	−3.425
4500	20.859	248.516	228.276	91.082	482.231	284.054	−3.297
4600	20.855	248.974	228.721	93.167	478.891	279.687	−3.176
4700	20.853	249.423	229.156	95.253	475.550	275.393	−3.061
4800	20.850	249.862	229.583	97.338	472.210	271.169	−2.951
4900	20.847	250.292	230.001	99.423	468.869	267.016	−2.846
5000	20.845	250.713	230.412	101.507	465.527	262.930	−2.747
5100	20.842	251.126	230.814	103.592	462.186	258.911	−2.652
5200	20.840	251.530	231.208	105.676	−231.828	264.268	−2.655
5300	20.838	251.927	231.595	107.760	−235.501	273.843	−2.699
5400	20.836	252.317	231.975	109.844	−239.149	283.483	−2.742
5500	20.834	252.699	232.349	111.927	−242.869	293.196	−2.785
5600	20.833	253.075	232.716	114.010	−246.618	302.977	−2.826
5700	20.831	253.443	233.076	116.094	−250.396	312.824	−2.867
5800	20.830	253.806	233.430	118.177	−254.202	322.738	−2.907
5900	20.828	254.162	233.779	120.260	−258.037	332.718	−2.946
6000	20.827	254.512	234.121	122.342	−261.902	342.764	−2.984

PREVIOUS: CURRENT: March 1984 (1 bar)

$S°(298.15\ K) = [46.024 \pm 8.4]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2210 \pm 15\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -419.66 \pm 12.6\ kJ·mol^{-1}$
$\Delta_{fus} H° = 85.354 \pm 20.9\ kJ·mol^{-1}$
$\Delta_{sub} H°(298.15\ K) = 618.395 \pm 20.9\ kJ·mol^{-1}$

Enthalpy of Formation

There are two reported oxygen bomb calorimetric studies for NbO(cr). The results must be interpreted in light of impure samples, incomplete combustion to Nb_2O_5(cr), and the possible nonstoichiometry of the reactants and products. Morozova and Getskina[1] reported $\Delta_c H°(291\ K) = 255.0\ kcal·mol^{-1}$ while Kusenko and Gel'd[2] reported $\Delta_c H°(298.15\ K) = 263.2\ kcal·mol^{-1}$ for the combustion of NbO(cr). Using auxiliary data,[3] we calculate $\Delta_f H°(298.15\ K) = -99.5$ and $-95.4\ kcal·mol^{-1}$ for NbO(cr).Schaefer and Liedmeier,[4] using Cl_2 bomb calorimetry, reported a value of $-97 \pm 1\ kcal·mol^{-1}$, based on $\Delta_f H°(NbOCl_3, cr, 298.15\ K) = -210.2\ kcal·mol^{-1}$.

A 2nd and 3rd law analysis of the majority of the reported smoothed emf data is tabulated below. Note that the enthalpy of formation for NbO(cr) calculated from the 3rd law $\Delta_r H°$ values are roughly 3 $kcal·mol^{-1}$ more negative than the adopted value. There is, however, excellent agreement within the equilibrium data; the 3rd law $\Delta_f H°(298.15\ K)$ values average $-100.3\ kcal·mol^{-1}$ with a spread of only 1.8 $kcal·mol^{-1}$. We adopt $\Delta_f H°(298.15\ K) = 100.3 \pm 3.0\ kcal·mol^{-1}$ based on an average of the equilibrium studies.[5-11] The reason for the discrepancy between the equilbrium and combustion results is not known at this time.[8]

Source	T/K	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
5	1245–1379	A	−35.56	−36.38	−0.63	−100.02
6	1115–1347	A	−35.34	−37.60	−1.80	−101.24
7	1123–1323	A	−38.62	−36.20	1.98	−99.84
8	1030–1300	B	−11.17	3.19	6.62	−100.99
9	1000–1400	A	−37.82	−35.91	1.60	−99.55
10	1073–1373	A	−36.95	−36.46	0.40	−100.10
11	1177–1388	C	−9.69	−9.72	−0.03	−100.12

A) $Nb(cr) + Fe_{0.95}O = NbO(cr) + 0.95\ Fe(cr)$
B) $Nb(cr) + 0.2\ Ta_2O_5(cr) = 0.4\ Ta(cr) + NbO(cr)$
C) $Nb(cr) + 1/3\ Cr_2O_3(cr) = NbO(cr) + 2/3\ Cr(cr)$

Heat Capacity and Entropy

Gel'd and Kusenko[12] measured the enthalpy of NbO(cr) and reported fourteen data points in the range 420–1702 K (IPTS–68). A Shomate type equation is used to represent the data. The average deviation between the data and calculated values is 0.31%; the maximum deviation of 0.62% occurs at 1518 K. This equation is used to obtain extrapolated values of $C_p°$ up to T_{fus}.

There is no low temperature heat capacity data reported in the literature for $T < 298$ K. In order to have the 3rd law results of the equilibrium data agree with the combustion data, an entropy value of the order of 13–14 $cal·K^{-1}·mol^{-1}$ would be necessary. At this point, however, the 3rd law drifts would be all positive. $S°(298.15\ K) = 10.2\ cal·K^{-1}·mol^{-1}$ would lead to a more satisfying variation in the 3rd law drifts for the condensed phase equilibrium data but an intermediate value $S°(298.15\ K) = 11.0\ cal·K^{-1}·mol^{-1}$ gives better consistency with the vapor pressure data. For more details refer to the NbO(g) and NbO_2(g) tables.[3]

Phase Data

Brauer[13] reported a homogeneity range of $x = 0.89–1.04$ for NbO_x. NbO(cr) has a cubic structure, a NaCl type with ordered vacancies.[13,14] Further information may be found in the review of the Nb–O system by Elliott.[15]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The mass spectrometric study by Shchukarev *et al.*[16] indicated that NbO(cr) at elevated temperatures yields NbO(g) and NbO_2(g). In the range 1873–2473 K, the concentration of NbO in the vapor phase over NbO(cr, l) varied in the range 5–30%.[16] $\Delta_{sub} H°(298.15\ K) = 147.8 \pm 5.0\ kcal·mol^{-1}$ is calculated as the difference between the $\Delta_f H°(298.15\ K)$ values for NbO(g) and NbO(cr).

References

[1] M. P. Morozova and L. L. Getskina, J. Gen. Chem. USSR **29**, 1019 (1959).
[2] F. G. Kusenko and P. V. Gel'd, Izv. Sibir. Otdel. Akad. Nauk SSSR, No. 2, 46 (1960); Chem. Abstr. **54**, 16160 (1960).
[3] JANAF Thermochemical Tables: Nb_2O_5(cr), 6–30–72; O_2(g), 9–30–65, NbO(g) and NbO_2(g), 12–31–73.
[4] H. Schaefer and F. Liedmeier, Z. Anorg. Chem. **329**, 225 (1964).

Continued on page 1693

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	41.112	46.024	46.024	0.	−419.655	−391.923	68.663
300	41.187	46.279	46.025	0.076	−419.652	−391.751	68.210
400	44.032	58.555	47.679	4.350	−419.371	−382.488	49.948
500	45.827	68.584	50.888	8.848	−418.968	−373.313	39.000
600	47.204	77.064	54.562	13.501	−418.507	−364.224	31.709
700	48.369	84.429	58.314	18.280	−418.011	−355.216	26.507
800	49.467	90.960	61.994	23.173	−417.485	−346.281	22.610
900	50.481	96.845	65.545	28.170	−416.929	−337.414	19.583
1000	51.467	102.215	68.947	33.268	−416.342	−328.610	17.165
1100	52.418	107.165	72.199	38.462	−415.722	−319.866	15.189
1200	53.359	111.766	75.307	43.751	−415.068	−311.181	13.545
1300	54.287	116.074	78.279	49.134	−414.376	−302.551	12.157
1400	55.208	120.131	81.125	54.608	−413.646	−293.976	10.968
1500	56.117	123.971	83.855	60.175	−412.882	−285.455	9.940
1600	57.024	127.622	86.477	65.832	−412.091	−276.986	9.043
1700	57.929	131.106	89.000	71.579	−411.280	−268.566	8.252
1800	58.831	134.443	91.433	77.417	−410.456	−260.195	7.551
1900	59.730	137.647	93.781	83.345	−409.624	−251.870	6.924
2000	60.626	140.734	96.052	89.363	−408.791	−243.589	6.362
2100	61.526	143.714	98.251	95.471	−407.960	−235.349	5.854
2200	62.413	146.596	100.384	101.668	−407.140	−227.148	5.393
2210.000	62.501	146.880	100.593	102.293	--- CRYSTAL <--> LIQUID ---		
2300	63.306	149.391	102.454	107.954	−406.337	−218.985	4.973
2400	64.199	152.104	104.466	114.329	−405.562	−210.856	4.589
2500	65.091	154.743	106.425	120.794	−404.831	−202.759	4.236
2600	65.982	157.313	108.333	127.347	−404.165	−194.689	3.911
2700	66.871	159.820	110.194	133.990	−403.604	−186.644	3.611
2800	67.760	162.268	112.010	140.722	−429.560	−178.131	3.323

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [83.233]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2210 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-336.743]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 85.354 \pm 20.9\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(NbO, l, 298.15 K) is calculated from $\Delta_f H°$(NbO, cr, 298.15K) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°$(2210 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

There is no data reported in the literature concerning the heat capacity or enthalpy of NbO(l). We estimate a constant value of $C_p° = 15.0$ cal·K^{-1}·mol^{-1} for the liquid phase. A glass transition is also assumed at 1500 K, so as to insure the proper thermodynamic relationship between the crystal values and extrapolated liquid values. At temperatures below 1500 K, $C_p°$ values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Elliott[1] reported the melting point of NbO(cr) as T_{fus} = 2222 K (IPTS–68). Measurements by Kolchin and Sumarokova[2] gave T_{fus} = 2212 K (IPTS–68). The vapor pressure study of NbO(cr, l) by Shchukarev *et al.*[3] gave T_{fus} = 2207 K. We adopt $T_{fus} = 2210 \pm 15$ K in order to maintain good consistency with the vapor pressure data. Since the crystal structure of NbO(cr) is a defect NaCl structure, we can estimate $\Delta_{fus} H° = 13.9$ kcal·mol^{-1} based on $\Delta_{fus} S° = 6.27$ cal·K^{-1}·mol^{-1} as observed for NaCl.[4] The data of Shchukarev *et al.*[3] are more consistent with $\Delta_{fus} H° = 20.4$ kcal·mol^{-1}, as determined from our analysis of the vapor pressures over NbO(cr, l).[4] We adopt $\Delta_{fus} H° = 20.4 \pm 5.0$ kcal·mol^{-1}. This leads to $\Delta_{fus} S° = 9.23$ cal·K^{-1}·mol^{-1} which is roughly 3 cal·K^{-1}·mol^{-1} greater than the NaCl value.[4]

Vaporization Data

The vapors over NbO(l) have been shown by Shchukarev *et al.*[3] to be NbO(g) and NbO_2(g). At 2300 K, the rates of the vapor pressures NbO_2(g):NbO(g) is 1.00:0.23.[3]

References

[1]R. P. Elliott, Trans. Amer. Soc. Metals **52**, 999 (1960).
[2]O. Kolchin and N. Sumarokova, Atomnaya Energ. **10**, 168 (1961).
[3]S. A. Shchukarev, G. A. Semenoo, and K. E. Frantseva, Russ. J. Inorg. Chem. **11**, 129 (1966).
[4]JANAF Thermochemical Tables: NaCl(cr), 9–30–64; NbO(g), 12–31–73.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	41.112	83.233	83.233	0.	−336.743	−320.105	56.081
300	41.187	83.488	83.234	0.076	−336.740	−320.002	55.717
400	44.032	95.764	84.888	4.350	−336.459	−314.460	41.064
500	45.827	105.793	88.097	8.848	−336.056	−309.005	32.282
600	47.204	114.273	91.771	13.501	−335.595	−303.638	26.434
700	48.369	121.638	95.523	18.280	−335.099	−298.351	22.263
800	49.467	128.169	99.203	23.173	−334.573	−293.136	19.140
900	50.481	134.054	102.754	28.170	−334.017	−287.990	16.714
1000	51.467	139.424	106.156	33.268	−333.430	−282.907	14.778
1100	52.418	144.374	109.408	38.462	−332.810	−277.884	13.196
1200	53.359	148.975	112.516	43.751	−332.156	−272.920	11.880
1300	54.287	153.283	115.488	49.134	−331.464	−268.011	10.769
1400	55.208	157.340	118.334	54.608	−330.734	−263.157	9.819
1500	56.120	161.180	121.063	60.175	−329.970	−258.357	8.997
1500.000	56.120	161.180	121.063	60.175	GLASS <--> LIQUID TRANSITION		
1500.000	62.760	161.180	121.063	60.175			
1600	62.760	165.231	123.699	66.451	−328.560	−253.629	8.280
1700	62.760	169.035	126.255	72.727	−327.221	−248.987	7.650
1800	62.760	172.623	128.732	79.003	−325.959	−244.422	7.093
1900	62.760	176.016	131.132	85.279	−324.779	−239.925	6.596
2000	62.760	179.235	133.458	91.555	−323.687	−235.487	6.150
2100	62.760	182.297	135.711	97.831	−322.689	−231.102	5.748
2200	62.760	185.217	137.895	104.107	−321.789	−226.762	5.384
2210.000	62.760	185.501	138.110	104.734	--- CRYSTAL <--> LIQUID ---		
2300	62.760	188.006	140.014	110.383	−320.997	−222.461	5.052
2400	62.760	190.677	142.070	116.659	−320.321	−218.192	4.749
2500	62.760	193.239	144.066	122.935	−319.778	−213.948	4.470
2600	62.760	195.701	146.004	129.211	−319.389	−209.723	4.213
2700	62.760	198.070	147.889	135.487	−319.195	−205.510	3.976
2800	62.760	200.352	149.722	141.763	−345.607	−200.815	3.746
2900	62.760	202.554	151.506	148.039	−344.657	−195.661	3.524
3000	62.760	204.682	153.244	154.315	−343.717	−190.539	3.318

PREVIOUS: CURRENT: December 1973

0 to 2210 K crystal
above 2210 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	41.112	46.024	46.024	0.	−419.655	−391.923	68.663
300	41.187	46.279	46.025	0.076	−419.652	−391.751	68.210
400	44.032	58.555	47.679	4.350	−419.371	−382.488	49.948
500	45.827	68.584	50.888	8.848	−418.968	−373.313	39.000
600	47.204	77.064	54.562	13.501	−418.507	−364.224	31.709
700	48.369	84.429	58.314	18.280	−418.011	−355.216	26.507
800	49.467	90.960	61.994	23.173	−417.485	−346.281	22.610
900	50.481	96.845	65.545	28.170	−416.929	−337.414	19.583
1000	51.467	102.215	68.947	33.268	−416.342	−328.610	17.165
1100	52.418	107.165	72.199	38.462	−415.722	−319.866	15.189
1200	53.359	111.766	75.307	43.751	−415.068	−311.181	13.545
1300	54.287	116.074	78.279	49.134	−414.376	−302.551	12.157
1400	55.208	120.131	81.125	54.608	−413.646	−293.976	10.968
1500	56.117	123.971	83.855	60.175	−412.882	−285.455	9.940
1600	57.024	127.622	86.477	65.832	−412.091	−276.986	9.043
1700	57.929	131.106	89.000	71.579	−411.280	−268.566	8.252
1800	58.831	134.443	91.433	77.417	−410.456	−260.195	7.551
1900	59.730	137.647	93.781	83.345	−409.624	−251.870	6.924
2000	60.626	140.734	96.052	89.363	−408.791	−243.589	6.362
2100	61.526	143.714	98.251	95.471	−407.960	−235.349	5.854
2200	62.413	146.596	100.384	101.668	−407.140	−227.148	5.393
2210.000	62.501	146.880	100.593	102.293	CRYSTAL <--> LIQUID TRANSITION		
2210.000	62.760	185.501	100.593	187.646			
2300	62.760	188.006	103.965	193.295	−320.997	−222.461	5.052
2400	62.760	190.677	107.523	199.571	−320.321	−218.192	4.749
2500	62.760	193.239	110.901	205.847	−319.778	−213.948	4.470
2600	62.760	195.701	114.115	212.123	−319.389	−209.723	4.213
2700	62.760	198.070	117.181	218.399	−319.195	−205.510	3.976
2800	62.760	200.352	120.111	224.675	−345.607	−200.815	3.746
2900	62.760	202.554	122.916	230.951	−344.657	−195.661	3.524
3000	62.760	204.682	125.606	237.227	−343.717	−190.539	3.318

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 238.976 \pm 3.56\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 199.54 \pm 20.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 198.74 \pm 20.9\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X[^4\Sigma^-]$	0	4
$[^4\Pi]$	15000	8
$[^4\Sigma^-]$	21316.2	4

$\omega_e = 989.03\ cm^{-1}$ $\omega_e x_e = 3.83\ cm^{-1}$ $\sigma = 1$

$B_e = 0.432\ cm^{-1}$ $\alpha_e = 2.1 \times 10^{-3}\ cm^{-1}$ $r_e = 1.691$ Å

Enthalpy of Formation

Using the adopted vibrational constants [ω_e and $\omega_e x_e$], we calculate $D_0^\circ = 7.855$ eV as the dissociation energy of NbO(g) based on the linear Birge–Sponer extrapolation of the ground state. Applying a correction for the ionicity in the Nb–O bond as suggested by Hildenbrand and Murad,[1] we recalculate $D_0^\circ = 8.032$ eV. This latter value corresponds to $\Delta_f H°$(NbO, g, 298.15 K) = 48.03 kcal·mol^{-1}, assuming dissociation to normal atoms, while the former yields 52.11 kcal·mol^{-1}.

Shchukarev *et al.*[2,3] have investigated mass spectrometrically the composition of the vapors over NbO(cr, l) and NbO_2(cr, l). In their first work,[2] the authors reported that, besides NbO sublimation at 1773–1923 K, the reaction 2 NbO(cr) = Nb(cr) + NbO_2(g) occurs. A 2nd law $\Delta_{sub}H° = 138 \pm 3$ kcal·mol^{-1} was reported for the range 1773–1923 K. Using auxiliary data,[5] we calculate $\Delta_f H°$(NbO, g, 298.15 K) = 47.2 ± 3.0 kcal·mol^{-1}, assuming the $\Delta_{sub}H°$ reported value refers to 1900 K.

Shchukarev *et al.*[3] measured the vapor pressures of NbO and NbO_2(cr, l) and NbO_2(cr, l) by the effusion method coupled with a mass spectrometer. The results are summarized in the following table.

Reaction	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law
NbO(cr) = NbO(g)	1773–2210	148.0	147.5	−0.24	47.7	47.2
NbO(l) = NbO(g)	2210–2473	128.1	128.0	−0.04	47.6	47.5

We adopt $\Delta_f H°(298.15\ K) = 47.5 \pm 5.0$ kcal·mol^{-1} for NbO(g). The adopted value is an average value based on the 2nd and 3rd law results tabulated above. It is interesting to note that the adjusted Birge–Sponer result shows excellent agreement with the adopted $\Delta_f H°(298.15\ K)$. The adopted $\Delta_f H°(298.15\ K)$ leads to a dissociation energy $D_0^\circ = 8.05$ eV.

Heat Capacity and Entropy

The spectroscopic work involving NbO(g) has been reviewed and referenced by Rosen.[4] The adopted vibrational and rotational constants as well as the electronic levels are those tabulated by Rosen.[4] As indicated in Rosen,[4] the data suggest a $^4\Sigma^-$ ground state as in VO(g).[5] However, a possible ground state $^2\Delta$ as in TaO(g)[5] is not definitely excluded. The recent reviews by Cheetham and Barrow[6] and Weltner[7] favor a $^2\Delta$ ground state. Using a $^2\Delta$ ground state and $^2\Delta$–$^2\Delta$ transition at 21316.2 cm^{-1} produces the same thermodynamic functions as does a $^4\Sigma^-$ ground state and a $^4\Sigma$–$^4\Sigma$ transition at 21316.2 cm^{-1}. Green *et al.*[9] studied the infrared absorption spectra of isotopic NbO isolated in an Ar matrix. Green *et al.*[9] reported that a partial analysis of the observed bands supported the assignment of a $^4\Sigma^-$ electronic ground state for NbO.

The Gibbs energy functions used here are approximately 0.85 cal·K^{-1}·mol^{-1} at 298 K and 2.90 cal·K^{-1}·mol^{-1} at 3000 K lower than those proposed by Brewer and Rosenblatt.[8] The difference arises from the fact that Brewer and Rosenblatt[8] approximated the NbO electronic levels by using Nb^{++} electronic levels (which included low lying levels) whereas we have used the observed NbO electronic levels.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.781	199.541	199.541	INFINITE
100	29.106	206.753	265.477	−5.872	200.216	189.462	−98.965
200	29.467	226.986	241.744	−2.952	199.584	178.910	−46.727
250	30.057	233.620	239.478	−1.464	199.157	173.791	−36.312
298.15	30.788	238.976	238.976	0.	198.740	168.943	−29.598
300	30.818	239.166	238.976	0.057	198.724	168.758	−29.383
350	31.614	243.977	239.354	1.618	198.301	163.798	−24.445
400	32.364	248.248	240.204	3.218	197.891	158.897	−20.750
450	33.033	252.099	241.315	4.853	197.492	154.047	−17.881
500	33.613	255.610	242.572	6.519	197.099	149.241	−15.591
600	34.531	261.824	245.276	9.929	196.316	139.742	−12.166
700	35.197	267.200	248.033	13.417	195.521	130.376	−9.729
800	35.687	271.934	250.730	16.963	194.700	121.125	−7.909
900	36.054	276.159	253.325	20.550	193.847	111.979	−6.499
1000	36.336	279.973	255.803	24.171	192.956	102.930	−5.377
1100	36.557	283.447	258.160	27.816	192.026	93.972	−4.462
1200	36.735	286.636	260.402	31.481	191.056	85.101	−3.704
1300	36.880	289.582	262.535	35.161	190.047	76.312	−3.066
1400	37.002	292.320	264.566	38.856	188.997	67.602	−2.522
1500	37.106	294.876	266.502	42.561	187.900	58.969	−2.053
1600	37.196	297.274	268.351	46.277	186.749	50.411	−1.646
1700	37.277	299.531	270.120	50.000	185.536	41.926	−1.288
1800	37.352	301.664	271.813	53.732	184.254	33.515	−0.973
1900	37.423	303.686	273.438	57.471	182.896	25.177	−0.692
2000	37.493	305.607	274.999	61.216	181.457	16.913	−0.442
2100	37.564	307.438	276.500	64.969	179.933	8.723	−0.217
2200	37.638	309.187	277.947	68.729	178.316	0.608	−0.014
2300	37.717	310.862	279.342	72.497	176.601	−7.432	0.169
2400	37.802	312.469	280.689	76.273	174.776	−15.394	0.335
2500	37.895	314.014	281.991	80.057	172.828	−23.279	0.486
2600	37.997	315.502	283.251	83.852	170.735	−31.082	0.624
2700	38.108	316.938	284.473	87.657	168.458	−38.802	0.751
2800	38.230	318.326	285.657	91.474	139.587	−45.948	0.857
2900	38.362	319.670	286.807	95.303	138.091	−52.549	0.947
3000	38.506	320.973	287.924	99.147	136.598	−59.097	1.029
3100	38.660	322.238	289.011	103.005	135.111	−65.595	1.105
3200	38.825	323.468	290.068	106.879	133.631	−72.046	1.176
3300	39.000	324.665	291.099	110.770	132.160	−78.451	1.242
3400	39.185	325.832	292.103	114.679	130.698	−84.811	1.303
3500	39.380	326.971	293.083	118.607	129.247	−91.128	1.360
3600	39.583	328.083	294.040	122.556	127.808	−97.404	1.413
3700	39.794	329.171	294.975	126.524	126.383	−103.641	1.463
3800	40.012	330.235	295.889	130.515	124.972	−109.838	1.510
3900	40.236	331.277	296.783	134.527	123.576	−115.999	1.554
4000	40.466	332.299	297.658	138.562	122.196	−122.125	1.595
4100	40.700	333.301	298.515	142.620	120.833	−128.216	1.633
4200	40.937	334.284	299.355	146.702	119.487	−134.274	1.670
4300	41.177	335.250	300.179	150.808	118.158	−140.300	1.704
4400	41.418	336.200	300.987	154.938	116.848	−146.296	1.737
4500	41.661	337.133	301.780	159.091	115.556	−152.262	1.767
4600	41.903	338.052	302.558	163.270	114.281	−158.199	1.796
4700	42.144	338.955	303.323	167.472	113.025	−164.109	1.824
4800	42.384	339.845	304.075	171.699	111.787	−169.992	1.850
4900	42.622	340.722	304.814	175.949	110.566	−175.850	1.875
5000	42.856	341.585	305.540	180.223	109.363	−181.683	1.898
5100	43.087	342.436	306.256	184.520	108.175	−187.492	1.920
5200	43.313	343.275	306.959	188.840	−583.668	−183.969	1.848
5300	43.535	344.102	307.652	193.182	−585.156	−176.268	1.737
5400	43.752	344.918	308.335	197.547	−586.603	−168.543	1.630
5500	43.963	345.722	309.007	201.933	−588.110	−160.788	1.527
5600	44.168	346.516	309.670	206.339	−589.633	−153.004	1.427
5700	44.366	347.300	310.323	210.766	−591.173	−145.194	1.331
5800	44.559	348.073	310.968	215.212	−592.731	−137.356	1.237
5900	44.744	348.837	311.603	219.677	−594.309	−129.492	1.146
6000	44.922	349.590	312.230	224.161	−595.909	−121.600	1.059

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 54.506 \pm 0.29\ J·K^{-1}·mol^{-1}$
$T_{trs1} \approx 1090 \pm 20\ K$
$T_{trs2} \approx 1200\ K$
$T_{fus} = 2175 \pm 15\ K$

$\Delta_f H°(0\ K) = -790.31 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) \approx -794.96 \pm 8.4\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 3.423\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 0.000\ kJ·mol^{-1}$
$\Delta_{fus} H° = 92.048 \pm 20.9\ kJ·mol^{-1}$

Enthalpy of Formation

There are three oxygen bomb calorimetric studies for NbO_2(cr). As with NbO(cr), the combustion results must be interpreted inlight of impure samples, possible incomplete combustion, and possible nonstoichiometry. The following $\Delta_c H°$ results have been reported for the oxygen combustion of one mole of NbO_2(cr) to yield Nb_2O_5(cr): 37.0 ± 0.4 kcal·mol^{-1} (291 K) by Morozova and Getskina,[1] 37.6 ± 2.6 kcal·mol^{-1} (298 K) by Kusenko and Gel'd,[2] and 36.67 ± 0.10 kcal·mol^{-1} (298 K) by Mah.[3] Using the value $\Delta_c H°(298.15\ K) = 37.0 \pm 2.0$ kcal·mol^{-1} and JANAF auxiliary data,[4] we calculate and adopt $\Delta_f H°(NbO_2, cr, 298.15\ K) = -190.0 \pm 2.0$ kcal·mol^{-1}.

There are numerous equilibrium studies involving NbO_2. Early work involved the reduction of niobium oxides with hydrogen by Grube *et al.*,[5] Sue,[6] and Schaefer and Breil,[7] and the carbon reduction of Nb_2O_5 by Sue.[8] The more recent emf equilbrium studies are analyzed and tabulated in the following table.

Source	T/K	Reaction	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[9]	1673–1823	$NbO_2(cr)+H_2(g)=NbO(cr)+H_2O(g)$	36.35	32.30	−2.3	−190.4
[10]	1100–1300	$NbO_2(cr)+Nb(cr)=2\ NbO(cr)$	−11.96	−9.59	2.0	−187.8
[11]	1074–1175	$Nb_2O_5(cr)+C(cr)=2\ NbO_2(cr)+CO(g)$	38.43	45.87	6.6	−190.9
[12]	1177–1361	$NbO(cr)+1/3\ Cr_2O_3(cr)=NbO_2(cr)+2/3\ Cr(cr)$	2.32	1.78	−0.4	−188.9

Heat Capacity and Entropy

King (53–296 K)[13] measured the heat capacity of NbO_2(cr). Using the combination of Debye and Einstein functions suggested by King,[13] we calculate $S°(51\ K) = 0.616$ cal·K^{-1}·mol^{-1} and $H°(51\ K)-H°(0\ K) = 23$ cal·K^{-1}·mol^{-1}. The enthalpy data of Gel'd and Kusenko,[14] and King and Christensen,[15] indicated a transition in the region 1000–1200 K. We adopt the reported enthalpy equations of King and Christensen[15] for the ranges 1090–1200 K and 1200–1800 K. The latter equation is extrapolated to T_{fus}. For the region 298–1090 K, we use a five term polynomial to fit the enthalpy data of King and Christensen[15] with constraints to join smoothly with the enthalpy derived from the King data:[13] the deviations are +0.34 to −0.67% in this range 298–1090 K. In the same range, the Gel'd and Kusenko data[14] lies approximately 2–3% higher; for $T > 1200$ K, it is 0.6–2.5% high.

Phase Data

Brauer[16] reported a homogeneity range of $x = 1.95$ to 2.05 for NbO_2. A recent study by Janninck and Whitmore,[17] using isopiestic reduction techniques at 1373 K, reported $x = 1.9975$ to 2.003.

Brauer,[16] Magneli *et al.*,[18] Terao,[19] and Marinder[20] have shown that at room temperature NbO_2 has a deformed rutile structure. NbO_2 is similar to V_2O_4 in terms of crystal structure.[21]

TransitionData

Electric conductivity and thermoelectric power measurements and a DTA and x-ray diffraction study indicated a phase transition in the region 1068–1173 K.[17,21,22] In this region, the structure of NbO_2 transforms from a deformed rutile to a rutile structure. The evidence suggested that the transition is not sharp but is actually spread over at least 50°.[21]

The enthalpy data of King and Christensen[15] and Gel'd and Kusenko[14] are consistent with the above interpretation. We treat this transition as first order with $T_{trs1} \approx 1090 \pm 20$ K and add an artificial transition $T_{trs2} = 1200$ K as in King and Christensen.[15] This combination reduces the reported enthalpy data.[15] The value $\Delta_{trs1} H° = 0.818$ kcal·mol^{-1} is calculated as the difference between the enthalpies of the two "phases" at 1090 K associated with the transition at T_{trs1}.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K) = 142.1 \pm 5.0$ kcal·mol^{-1} is calculated as the $\Delta_f H°(298.15\ K)$ differences for NbO_2(g) and NbO_2(cr).

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Continued on page 1693

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−9.271	−790.308	−790.308	INFINITE
100	21.143	11.275	96.297	−8.502	−793.224	−775.765	405.218
200	44.918	33.967	59.417	−5.090	−794.821	−757.542	197.850
298.15	57.452	54.506	54.506	0.	−794.960	−739.175	129.500
300	57.605	54.862	54.507	0.106	−794.954	−738.829	128.642
400	63.547	72.327	56.848	6.191	−794.348	−720.199	94.048
500	67.739	86.967	61.447	12.760	−793.403	−701.766	73.313
600	71.651	99.665	66.781	19.730	−792.205	−683.547	59.508
700	75.555	111.003	72.302	27.090	−790.755	−665.549	49.664
800	79.496	121.348	77.795	34.843	−789.037	−647.776	42.295
900	83.479	130.941	83.173	42.991	−787.033	−630.236	36.578
1000	87.500	139.945	88.405	51.540	−784.726	−612.934	32.016
1090.000	91.144	147.640	92.980	59.579	I <--> II		
1090.000	92.885	150.780	92.980	63.001	TRANSITION		
1100	92.885	151.628	93.510	63.930	−778.665	−595.911	28.297
1200	92.885	159.710	98.694	73.219	−775.786	−579.425	25.222
1200.000	92.885	159.710	98.694	73.219	II <--> III		
1200.000	83.052	159.710	98.694	73.219	TRANSITION		
1300	83.052	166.358	103.647	81.524	−773.962	−563.136	22.627
1400	83.052	172.513	108.349	89.829	−772.208	−546.984	20.408
1500	83.052	178.243	112.820	98.135	−770.526	−530.956	18.490
1600	83.052	183.603	117.078	106.440	−768.921	−515.038	16.814
1700	83.052	188.638	121.141	114.745	−767.398	−499.217	15.339
1800	83.052	193.385	125.024	123.050	−765.965	−483.484	14.030
1900	83.052	197.875	128.741	131.355	−764.626	−467.827	12.861
2000	83.052	202.135	132.305	139.661	−763.386	−452.239	11.811
2100	83.052	206.188	135.728	147.966	−762.251	−436.710	10.863
2175.000	83.052	209.102	138.208	154.195	----- III <--> LIQUID -----		
2200	83.052	210.051	139.019	156.271	−761.226	−421.232	10.001
2300	83.052	213.743	142.188	164.576	−760.320	−405.799	9.216
2400	83.052	217.278	145.244	172.882	−759.541	−390.402	8.497
2500	83.052	220.668	148.193	181.187	−758.906	−375.035	7.836
2600	83.052	223.925	151.044	189.492	−758.437	−359.690	7.226
2700	83.052	227.060	153.802	197.797	−758.172	−344.359	6.662
2800	83.052	230.080	156.472	206.103	−784.523	−328.549	6.129

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [92.835]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2175 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-710.872]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 92.048 \pm 20.9\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(NbO_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(NbO_2, cr, 298.15\ K)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2175\ K) - H(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

There is no data reported in the literature concerning the heat capacity or enthalpy of NbO_2(l). We estimate a constant value of $C_p° = 7.5\ cal·K^{-1}·g\text{–}atom^{-1}$ or $22.5\ cal·K^{-1}·mol^{-1}$ for the liquid phase. A glass transition is assumed at 1000 K below which the $C_p°$ values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation.

Fusion Data

Elliott[1] reported the melting point of NbO_2(cr) as T_{fus} = 2191 K (IPTS–68) and stated that NbO_2(cr) melts without decomposition. The vapor pressure study on NbO_2(cr, l) by Shchukarev *et al.*[2] gave T_{fus} = 2173 K (IPTS–68) with congruent melting. We adopt $T_{fus} = 2175 \pm 15$ K in order to maintain good consistency with the vapor pressure data. A value of T_{fus} = 2357 K reported by Kolchin and Sumarokova[3] appears too high.

The vapor pressure data of Shchukarev *et al.*[2] suggests $\Delta_{fus}H° = 22.0\ kcal·mol^{-1}$ which we adopt. This leads to $\Delta_{fus}S° = 10.11\ cal·K^{-1}·mol^{-1}$.

Vaporization Data

The vapors over NbO_2(l) have been shown by Shchukarev *et al.*[2] to be NbO(g), NbO_2(g), and O(g). At 2300 K, the ratio of the vapor pressures NbO_2(g):NbO(g) is 1.00:0.07.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	57.450	92.835	92.835	0.	−710.872	−666.514	116.771
300	57.605	93.191	92.836	0.106	−710.865	−666.239	116.003
400	63.547	110.656	95.177	6.191	−710.259	−651.442	85.070
500	67.739	125.296	99.776	12.760	−709.314	−636.842	66.530
600	71.651	137.993	105.109	19.730	−708.116	−622.456	54.190
700	75.555	149.331	110.631	27.090	−706.667	−608.290	45.391
800	79.496	159.677	116.124	34.843	−704.949	−594.351	38.807
900	83.479	169.270	121.502	42.991	−702.945	−580.643	33.700
1000	87.500	178.273	126.733	51.540	−700.637	−567.175	29.626
1000.000	87.500	178.273	126.733	51.540	GLASS <--> LIQUID		
1000.000	94.140	178.273	126.733	51.540	TRANSITION		
1100	94.140	187.246	131.833	60.954	−697.553	−553.978	26.306
1200	94.140	195.437	136.797	70.368	−694.548	−541.059	23.552
1300	94.140	202.972	141.602	79.782	−691.616	−528.388	21.231
1400	94.140	209.949	146.237	89.196	−688.753	−515.940	19.250
1500	94.140	216.444	150.704	98.610	−685.962	−503.694	17.540
1600	94.140	222.520	155.005	108.024	−683.248	−491.632	16.050
1700	94.140	228.227	159.146	117.438	−680.617	−479.737	14.741
1800	94.140	233.608	163.134	126.852	−678.075	−467.994	13.581
1900	94.140	238.698	166.979	136.266	−675.627	−456.390	12.547
2000	94.140	243.526	170.686	145.680	−673.278	−444.913	11.620
2100	94.140	248.119	174.265	155.094	−671.034	−433.550	10.784
2175.000	94.140	251.423	176.869	162.154	----- III <--> LIQUID -----		
2200	94.140	252.499	177.722	164.508	−668.901	−422.291	10.026
2300	94.140	256.683	181.065	173.922	−666.886	−411.128	9.337
2400	94.140	260.690	184.300	183.336	−664.998	−400.049	8.707
2500	94.140	264.533	187.433	192.750	−663.254	−389.046	8.129
2600	94.140	268.225	190.470	202.164	−661.676	−378.109	7.596
2700	94.140	271.778	193.416	211.578	−660.303	−367.229	7.104
2800	94.140	275.202	196.276	220.992	−685.546	−355.912	6.640
2900	94.140	278.505	199.055	230.406	−683.437	−344.177	6.199
3000	94.140	281.697	201.757	239.820	−681.347	−332.514	5.790

PREVIOUS: CURRENT: December 1973

0	to	1090 K	crystal, I
1090	to	1200 K	crystal, II
1200	to	2175 K	crystal, III
above		2175 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−9.271	−790.308	−790.308	INFINITE
100	21.143	11.275	96.297	−8.502	−793.224	−775.765	405.218
200	44.918	33.967	59.417	−5.090	−794.821	−757.542	197.850
298.15	57.452	54.506	54.506	0.	−794.960	−739.175	129.500
300	57.605	54.862	54.507	0.106	−794.954	−738.829	128.642
400	63.547	72.327	56.848	6.191	−794.348	−720.199	94.048
500	67.739	86.967	61.447	12.760	−793.403	−701.766	73.313
600	71.651	99.665	66.781	19.730	−792.205	−683.547	59.508
700	75.555	111.003	72.302	27.090	−790.755	−665.549	49.664
800	79.496	121.348	77.795	34.843	−789.037	−647.776	42.295
900	83.479	130.941	83.173	42.991	−787.033	−630.236	36.578
1000	87.500	139.945	88.405	51.540	−784.726	−612.934	32.016
1090.000	91.144	147.640	92.980	59.579	I <--> II		
1090.000	92.885	150.780	92.980	63.001	TRANSITION		
1100	92.885	151.628	93.510	63.930	−778.665	−595.911	28.297
1200	92.885	159.710	98.694	73.219	−775.786	−579.425	25.222
1200.000	92.885	159.710	98.694	73.219	II <--> III		
1200.000	83.052	159.710	98.694	73.219	TRANSITION		
1300	83.052	166.358	103.647	81.524	−773.962	−563.136	22.627
1400	83.052	172.513	108.349	89.829	−772.208	−546.984	20.408
1500	83.052	178.243	112.820	98.135	−770.526	−530.956	18.490
1600	83.052	183.603	117.078	106.440	−768.921	−515.038	16.814
1700	83.052	188.638	121.141	114.745	−767.398	−499.217	15.339
1800	83.052	193.385	125.024	123.050	−765.965	−483.484	14.030
1900	83.052	197.875	128.741	131.355	−764.626	−467.827	12.861
2000	83.052	202.135	132.305	139.661	−763.386	−452.239	11.811
2100	83.052	206.188	135.728	147.966	−762.251	−436.710	10.863
2175.000	83.052	209.102	138.208	154.195	III <--> LIQUID		
2175.000	94.140	251.423	138.208	246.243	TRANSITION		
2200	94.140	252.499	139.500	248.596	−668.901	−422.291	10.026
2300	94.140	256.683	144.505	258.010	−666.886	−411.128	9.337
2400	94.140	260.690	149.263	267.424	−664.998	−400.049	8.707
2500	94.140	264.533	153.798	276.838	−663.254	−389.046	8.129
2600	94.140	268.225	158.128	286.252	−661.676	−378.109	7.596
2700	94.140	271.778	162.272	295.666	−660.303	−367.229	7.104
2800	94.140	275.202	166.245	305.080	−685.546	−355.912	6.640
2900	94.140	278.505	170.059	314.494	−683.437	−344.177	6.199
3000	94.140	281.697	173.727	323.908	−681.347	−332.514	5.790

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [272.921 \pm 8.4]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -197.33 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -200.00 \pm 20.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[970](1)
[300](1)
[930](1)

Ground State Quantum Weight: [2] σ = [2]
Point Group: [C_{2v}]
Bond Distance: Nb–O = [1.691] Å
Bond Angle: O–Nb–O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.274350 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

Shchukarev *et al.*[1–4] measured the vapor pressures of NbO and NbO_2 over NbO(cr, l) and NbO_2(cr, l) by the effusion method coupled with a mass spectrometer. An analysis of the reported smoothed results is presented in the following table.[4]

Reaction	T/K	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law
$NbO_2(cr) = NbO_2(g)$	1773–2175	142.0	143.4	0.69	−48.0	−46.6
$NbO_2(l) = NbO_2(g)$	2175–2473	124.2	123.7	−0.22	−46.8	−46.3
$2\ NbO(cr) = NbO_2(g) + Nb(cr)$	1773–2210	147.8	149.9	1.03	−52.8	−50.7
$2\ NbO(l) = NbO_2(g) + Nb(cr)$	2210–2473	119.7	111.1	−3.73	−41.3	−49.9

We adopt $\Delta_f H°(NbO_2, g, 298.15\ K) = -47.8 \pm 5.0$ kcal·mol^{-1}. This value is an average value of the 2nd and 3rd law results for the sublimation and vaporization of NbO_2. This adopted $\Delta_f H°(298.15\ K)$ value leads to $D_0° = 14.73$ eV for the process $NbO_2(g) = Nb(g) + 2\ O(g)$. The $\Delta_{at} H°(0\ K)$ value is 1.83 times as great as the dissociation energy of NbO(g) ($D_0°$=8.05 eV).[2]

The earlier less complete studies by Shchukarev *et al.*[1–3] are in fair agreement with the above conclusions. Using a platinum strip to vaporize NbO_2(cr) in a mass spectrometer at temperatures of 1500 to 1880 K, Shchukarev *et al.*[1] reported a 2nd law sublimation heat, $\Delta_{sub} H°(1700\ K) = 142 \pm 3$ kcal·mol^{-1}. Using auxiliary data,[6] we calculate $\Delta_f H°(NbO_2, g, 298.15\ K) = -38.8$ kcal·mol^{-1}. The mass spectrometric investigation of the NbO(cr) evaporation by Shchukarev *et al.*[2] led to a reported value $\Delta_f H°(1800\ K) = 140 \pm 3$ kcal·mol^{-1} for the process $2\ NbO(cr) = Nb(cr) + NbO_2(g)$. Using auxiliary data,[6] we calculate $\Delta_f H°(NbO_2, g, 298.15\ K) = -53.3$ kcal·mol^{-1}. NbO_2 pressures were obtained (1938–2122 K) by the differential effusion method using the radioactive tracer ^{95}Nb.[3] The pressures agree within 5% of those obtained in the more complete study.[4] Golubtsov *et al.*[5] also measured the vapor pressure of $NbO_2(g)$ over NbO_2(cr) in the range 1489–1905 K by using labelled atoms in a Knudsen cell. The same authors also studied the dissociation of Nb_2O_5 in vacuo in the range 1432–1756 K, the process being $Nb_2O_5(cr) \rightarrow 2\ NbO_2(g) + 1/2\ O_2(g)$. These latter data[5] are not considered.

Heat Capacity and Entropy

The vibrational frequencies and geometry of $NbO_2(g)$ are estimated based on existing and estimated data for related metal dioxides such as $TiO_2(g)$, $TaO_2(g)$, and $WO_2(g)$.[6] The Nb–O bond distance is assumed to be the same as in NbO(g).[6] The ground state quantum weight of 2 is adopted so as to be consistent with $TaO_2(g)$.[6] The principal moments of inertia are calculated as $I_A = 3.7181 \times 10^{-39}$, $I_B = 10.1954 \times 10^{-39}$, and $I_C = 13.9136 \times 10^{-39}$ g·cm^2.

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[6]JANAF Thermochemical Tables: NbO_2(cr), NbO(cr, g), Nb(cr), $TaO_2(g)$ and $TiO_2(g)$, 12–31–73; $WO_2(g)$, 9–30–66.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.254	−197.325	−197.325	INFINITE
100	35.385	230.299	309.095	−7.880	−197.637	−202.080	105.556
200	39.819	256.260	276.805	−4.109	−198.875	−206.055	53.816
250	41.903	265.368	273.633	−2.066	−199.475	−207.779	43.413
298.15	43.907	272.921	272.921	0.	−199.995	−209.330	36.674
300	43.982	273.193	272.922	0.081	−200.014	−209.388	36.458
350	45.916	280.121	273.465	2.330	−200.488	−210.912	31.477
400	47.622	286.366	274.693	4.669	−200.905	−212.373	27.733
450	49.082	292.062	276.311	7.088	−201.280	−213.783	24.815
500	50.311	297.299	278.152	9.573	−201.625	−215.154	22.477
600	52.201	306.649	282.141	14.705	−202.266	−217.799	18.961
700	53.531	314.801	286.237	19.995	−202.886	−220.338	16.442
800	54.485	322.015	290.267	25.398	−203.517	−222.789	14.547
900	55.184	328.475	294.160	30.884	−204.176	−225.159	13.068
1000	55.708	334.317	297.888	36.429	−204.872	−227.453	11.881
1100	56.110	339.647	301.446	42.021	−205.609	−229.676	10.906
1200	56.424	344.543	304.836	47.649	−206.391	−231.829	10.091
1300	56.674	349.070	308.067	53.304	−207.217	−233.916	9.399
1400	56.875	353.277	311.147	58.982	−208.091	−235.937	8.803
1500	57.039	357.207	314.088	64.678	−209.018	−237.895	8.284
1600	57.175	360.893	316.900	70.388	−210.007	−239.788	7.828
1700	57.288	364.362	319.591	76.112	−211.067	−241.617	7.424
1800	57.384	367.640	322.170	81.846	−212.205	−243.382	7.063
1900	57.466	370.744	324.645	87.588	−213.428	−245.081	6.738
2000	57.536	373.694	327.025	93.338	−214.743	−246.713	6.443
2100	57.597	376.503	329.314	99.095	−216.157	−248.277	6.176
2200	57.649	379.183	331.521	104.857	−217.675	−249.771	5.930
2300	57.695	381.747	333.649	110.625	−219.306	−251.194	5.705
2400	57.736	384.203	335.705	116.396	−221.062	−252.544	5.496
2500	57.772	386.561	337.692	122.172	−222.956	−253.817	5.303
2600	57.804	388.827	339.616	127.951	−225.013	−255.012	5.123
2700	57.832	391.009	341.479	133.732	−227.272	−256.123	4.955
2800	57.858	393.113	343.286	139.517	−256.144	−256.662	4.788
2900	57.881	395.144	345.039	145.304	−257.662	−256.655	4.623
3000	57.902	397.106	346.742	151.093	−259.197	−256.593	4.468
3100	57.921	399.005	348.398	156.884	−260.749	−256.480	4.322
3200	57.938	400.845	350.008	162.677	−262.317	−256.318	4.184
3300	57.953	402.628	351.576	168.472	−263.901	−256.107	4.054
3400	57.967	404.358	353.103	174.268	−265.500	−255.846	3.931
3500	57.981	406.038	354.591	180.065	−267.113	−255.539	3.814
3600	57.992	407.672	356.043	185.864	−268.741	−255.185	3.703
3700	58.004	409.261	357.460	191.664	−270.382	−254.787	3.597
3800	58.014	410.808	358.844	197.465	−272.037	−254.342	3.496
3900	58.023	412.315	360.196	203.266	−273.705	−253.854	3.400
4000	58.032	413.784	361.517	209.069	−275.385	−253.325	3.308
4100	58.040	415.217	362.809	214.873	−277.077	−252.752	3.220
4200	58.047	416.616	364.074	220.677	−278.781	−252.138	3.136
4300	58.055	417.982	365.312	226.482	−280.497	−251.483	3.055
4400	58.061	419.317	366.524	232.288	−282.224	−250.789	2.977
4500	58.067	420.622	367.712	238.094	−283.963	−250.056	2.903
4600	58.073	421.898	368.876	243.901	−285.713	−249.283	2.831
4700	58.078	423.147	370.017	249.709	−287.476	−248.472	2.761
4800	58.083	424.370	371.137	255.517	−289.250	−247.623	2.695
4900	58.088	425.567	372.236	261.326	−291.036	−246.737	2.630
5000	58.092	426.741	373.314	267.135	−292.835	−245.815	2.568
5100	58.097	427.891	374.373	272.944	−294.647	−244.856	2.508
5200	58.101	429.020	375.413	278.754	−987.145	−234.553	2.356
5300	58.104	430.126	376.435	284.564	−989.316	−220.059	2.169
5400	58.108	431.212	377.439	290.375	−991.477	−205.529	1.988
5500	58.111	432.279	378.427	296.186	−993.725	−190.954	1.814
5600	58.114	433.326	379.398	301.997	−996.019	−176.337	1.645
5700	58.117	434.354	380.353	307.809	−998.359	−161.679	1.482
5800	58.120	435.365	381.293	313.621	−1000.745	−146.979	1.324
5900	58.123	436.359	382.218	319.433	−1003.180	−132.240	1.171
6000	58.126	437.336	383.128	325.245	−1005.664	−117.456	1.023

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 137.30 \pm 1.3\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1785 \pm 30\ K$

$\Delta_f H°(0\ K) = -1889.616 \pm 4.2\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1899.536 \pm 4.2\ kJ·mol^{-1}$
$\Delta_{fus} H° = 104.265 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The $\Delta_f H°(Nb_2O_5, cr, 298.15\ K)$ investigations suffer from uncertainties concerning the polymorphic state of the samples employed and the oftentimes incomplete impurity analysis of the samples.[1] There is considerable scatter in the following tabulation for the enthalpy of formation values, all of which are based on enthalpy of combustion studies.

Source	Nb(cr) purity, %	% completion*	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
2			−442.8
3	98.8	96.34–96.94	−459.9 ± 0.7**
4	99.69	97.63–99.38	−454.0 ± 0.6**
5			−472.6 ± 1.0
6	99.49		−454.8 ± 0.8
7			−458.6 ± 5.0
8	99.01	99.1–99.33	−455.1 ± 0.5
9	99.45	98.78–100	−454.4 ± 1.6
10	98.47–99.35	99.48–99.96	−453.5 ± 0.4
11	98.47–99.35	99.48–99.96	−453.5 ± 0.4
12			−456.9

* Percent completion refers to extent of reaction 2 Nb(cr) + 2.5 O_2(g) = Nb_2O_5(cr).
** Values adjusted by Kubaschewski and Catterall[13] to more satisfactorily correct for incomplete reaction.

The value chosen for $\Delta_f H°(Nb_2O_5, cr, 298.15\ K)$ is 454.0 ± 1 kcal·mol^{-1}. This value is representative of the work by Humphrey,[4] Kornilov *et al.*,[10, 11] Huber *et al.*,[9] Kusenko and Gel'd[8] and Morozova and Stolyarova.[6] These works have discussed sample purity and have percentage conversions of Nb(cr) to Nb_2O_5(cr) of the order of 97% or better. Based on the discussion by Reisman and Holtzberg,[1] this $\Delta_f H°(298.15\ K)$ value is for the high temperature α–phase of Nb_2O_5(cr). The heat capacity and enthalpy work, also dealing with Nb_2O_5(cr, α), indicated no phase changes for 53–297 K and 381–1785 K.[14, 16]

$\Delta_f G°$ values for Nb_2O_5(cr) in the range 1050 1300 K were calculated from measured emf values in an oxygen concentration cell and the known $\Delta_f G°$ values of Cr_2O_3.[17] The reported smoothed $\Delta_f G°$ values were treated by a 3rd law analysis, yielding $\Delta_f H°(Nb_2O_5, cr, 298.15\ K) = 451.6$ kcal·mol^{-1} with a drift equivalent to an entropy error of 4.8 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

King[14] measured the heat capacity of the high temperature α–phase Nb_2O_5 from 53.24 to 296.64 K and fitted the data (29 data points) with a combination of Debye and Einstein functions. These functions fit the data over the entire measured temperature range with a maximum deviation of 0.6%[14] and are used to calculate $S°(50\ K) = 2.42$ cal·K^{-1}·mol^{-1}.

Orr[15] using the same material as King,[14] measured the enthalpy from 381.4 to 1809.2 K. Gel'd and Kusenko[16] also measured the enthalpy from 461 to 1828 K. Combining these data[15,16] with a portion of the King data (a $C_p°$ fit, then integrated), a six term polynomial fit is used to represent the enthalpy data, yielding a deviation of 0.99% to +0.81% for the Orr data and 0.64% to + 1.10% for the Gel'd and Kusenko data. Two points (644 K, 734 K) of the Gel'd and Kusenko data are not used as they deviate from the polynomial fitted values by 2–3%. Entahlpy values corresponding to temperatures greater than 1750 K but less than T_{fus} are considered to be involved in premelting.[15] Enthalpy values for $1785 \leq T \leq 2300$ K are obtained by extrapolating the values obtained from the polynomial fit. The chosen heat capacity values are obtained by differentiating the enthalpy polynomial fit for the range 298–2300 K. For temperatures 50 298 K, the King data were fit to a six term polynomial.

The existing experimental data[14,15,16] did not indicate any transitions other than a crystal liquid transition. Lacking thermodynamic information for the other crystal phases of Nb_2O_5,[1] we assume that there is little difference in the heat capacity and enthalpy values for the various crystal phases. Thus the values tabulated here apply to all crystal Nb_2O_5 phases. The data for Ta_2O_5(cr) presented in these tables are treated in the same manner as discussed here so as to maintain consistency between Nb_2O_5(cr, l) and Ta_2O_5(cr, l).

Fusion Data

Refer to the liquid table for details.

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Continued on page 1693

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.287	−1889.634	−1889.634	INFINITE
100	54.455	34.317	235.233	−20.092	−1896.262	−1853.855	968.355
200	105.922	89.529	148.666	−11.827	−1899.472	−1809.884	472.693
298.15	131.988	137.298	137.298	0.	−1899.536	−1765.817	309.364
300	132.320	138.115	137.300	0.244	−1899.519	−1764.987	307.312
400	144.992	178.096	142.666	14.172	−1898.035	−1720.341	224.653
500	153.841	211.441	153.178	29.131	−1895.852	−1676.159	175.107
600	160.737	240.126	165.334	44.875	−1893.233	−1632.460	142.118
700	166.013	265.318	177.855	61.225	−1890.331	−1589.225	118.589
800	170.038	287.760	190.216	78.035	−1887.259	−1546.418	100.971
900	173.117	307.972	202.195	95.199	−1884.086	−1504.003	87.290
1000	175.502	326.340	213.706	112.634	−1880.865	−1461.944	76.364
1100	177.360	343.157	224.720	130.280	−1877.632	−1420.207	67.440
1200	178.828	358.654	235.244	148.092	−1874.413	−1378.766	60.016
1300	179.991	373.016	245.296	166.035	−1871.225	−1337.591	53.745
1400	180.920	386.390	254.902	184.082	−1868.087	−1296.661	48.379
1500	181.665	398.898	264.090	202.213	−1865.024	−1255.953	43.736
1600	182.263	410.642	272.886	220.410	−1862.060	−1215.445	39.680
1700	182.745	421.707	281.318	238.661	−1859.220	−1175.119	36.107
1785.000	183 .075	430.631	288.217	254.209	--- CRYSTAL <--> LIQUID ---		
1800	183.129	432.163	289.410	256.956	−1856.527	−1134.957	32.936
1900	183.435	442.073	297.187	275.284	−1854.000	−1094.939	30.102
2000	183.678	451.489	304.668	293.640	−1851.656	−1055.050	27.555
2100	183.862	460.455	311.875	312.018	−1849.512	−1015.273	25.254
2200	184.004	469.012	318.825	330.411	−1847.584	−975.592	23.164
2300	184.109	477.193	325.534	348.817	−1845.891	−935.996	21.257

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K)$ = [171.488] $J·K^{-1}·mol^{-1}$
T_{fus} = 1785 ± 30 K

$\Delta_f H°(298.15\ K)$ = [−1830.873] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 104.265 ± 2.1 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Nb_2O_5, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in $H°(1785\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Orr[1] and Gel'd and Kusenko[2] reported enthalpy measurements at temperatures greater than T_{fus}. The work of Orr[1] indicates a $C_p°$ value of 57.90 $cal·K^{-1}·mol^{-1}$ based on two enthalpy points in the liquid region. The three enthalpy points of Gel'd and Kusenko[2] deviate by +0.06%, −0.86%, and −0.37% from the linear representation of the Orr data. Thus, the constant $C_p°$ value of 57.90 $cal·K^{-1}·mol^{-1}$ is chosen for the liquid phase. A glass transition is also chosen at 1200 K so as to ensure the proper thermodynamic relationship between crystal values and extrapolated liquid value. At temperatures below 1200 K, the heat capacity values of the crystal are used. The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation.

Fusion Data

The enthalpy work of Orr[1] and Gel'd and Kusenko[2] provide information as to the heat of fusion. The heat capacity discussion for Nb_2O_5(cr) and Nb_2O_5(l) provide details as to the fitting of the data in the crystal and liquid regions. The heat of fusion is then calculated to be $\Delta_{fus}H°$ = 24.31 ± 0.5 $kcal·mol^{-1}$ at a melting point of 1785 K [$H°(1785\ K)-H°(298.15\ K)$ = −60.759 $kcal·mol^{-1}$ for the crystal]. This melting point, although it is consistent with the enthalpy work,[1,2] is 21 K greater than the value reported by Holtzberg *et al.*[3] and is greater than most T_{fus} values cited by Charlesworth[4] and Schneider.[5] Reisman and Holtzberg[6] attributed this high value of 1785 K to an impure sample. The melting point, T_{fus}, is chosen to be 1785 K strictly on the basis of being consistent with the two sets of enthalpy data. More data are necessary to accurately define consistent values for T_{fus}, $\Delta_{fus}H°$, and enthalpy values in the liquid and crystal regions.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	131.988	171.488	171.488	0.	−1830.873	−1707.347	299.120
300	132.320	172.306	171.491	0.244	−1830.856	−1706.581	297.142
400	144.992	212.286	176.857	14.172	−1829.371	−1665.354	217.473
500	153.841	245.631	187.368	29.131	−1827.189	−1624.591	169.720
600	160.737	274.316	199.524	44.875	−1824.569	−1584.311	137.927
700	166.013	299.509	212.045	61.225	−1821.668	−1544.495	115.252
800	170.038	321.950	224.406	78.035	−1818.595	−1505.107	98.273
900	173.117	342.162	236.386	95.199	−1815.423	−1466.111	85.091
1000	175.502	360.530	247.896	112.634	−1812.202	−1427.470	74.563
1100	177.360	377.347	258.910	130.280	−1808.969	−1389.153	65.965
1200	178.828	392.845	269.434	148.093	−1805.749	−1351.131	58.813
1200.000	178.828	392.845	269.434	148.093	GLASS <--> LIQUID		
1200.000	242.254	392.845	269.434	148.093	TRANSITION		
1300	242.254	412.236	279.683	172.318	−1796.279	−1313.631	52.782
1400	242.254	430.189	289.800	196.544	−1786.963	−1276.855	47.640
1500	242.254	446.902	299.723	220.769	−1777.804	−1240.739	43.206
1600	242.254	462.537	309.416	244.994	−1768.813	−1205.229	39.347
1700	242.254	477.224	318.859	269.220	−1759.998	−1170.276	35.958
1785.000	242 .254	489.043	326.684	289.811	--- CRYSTAL <--> LIQUID ---		
1800	242.254	491.070	328.045	293.445	−1751.374	−1135.837	32.961
1900	242.254	504.168	336.973	317.670	−1742.951	−1101.871	30.293
2000	242.254	516.594	345.646	341.896	−1734.738	−1068.343	27.902
2100	242.254	528.414	354.071	366.121	−1726.746	−1035.221	25.750
2200	242.254	539.684	362.253	390.347	−1718.985	−1002.472	23.802
2300	242.254	550.452	370.204	414.572	−1711.473	−970.074	22.031
2400	242.254	560.762	377.930	438.797	−1704.227	−937.996	20.415
2500	242.254	570.652	385.443	463.023	−1697.280	−906.214	18.934
2600	242.254	580.153	392.750	487.248	−1690.674	−874.703	17.573
2700	242.254	589.296	399.861	511.473	−1684.489	−843.437	16.317
2800	242.254	598.106	406.785	535.699	−1731.546	−811.424	15.137
2900	242.254	606.607	413.530	559.924	−1723.909	−778.699	14.026
3000	242.254	614.820	420.103	584.149	−1716.320	−746.234	12.993
3100	242.254	622.763	426.513	608.375	−1708.778	−714.021	12.031
3200	242.254	630.455	432.767	632.600	−1701.282	−682.053	11.133
3300	242.254	637.909	438.871	656.826	−1693.829	−650.319	10.294
3400	242.254	645.141	444.832	681.051	−1686.417	−618.807	9.507
3500	242.254	652.163	450.656	705.276	−1679.046	−587.515	8.768
3600	242.254	658.988	456.349	729.502	−1671.713	−556.432	8.074
3700	242.254	665.625	461.915	753.727	−1664.417	−525.554	7.419
3800	242.254	672.086	467.362	777.952	−1657.157	−494.869	6.802
3900	242.254	678.379	472.692	802.178	−1649.932	−464.376	6.220
4000	242.254	684.512	477.911	826.403	−1642.740	−434.070	5.668
4100	242.254	690.494	483.023	850.628	−1635.580	−403.942	5.146
4200	242.254	696.331	488.033	874.854	−1628.452	−373.988	4.651
4300	242.254	702.032	492.944	899.079	−1621.355	−344.203	4.181
4400	242.254	707.601	497.759	923.304	−1614.289	−314.585	3.735
4500	242.254	713.045	502.483	947.530	−1607.253	−285.126	3.310
4600	242.254	718.370	507.119	971.755	−1600.248	−255.824	2.905
4700	242.254	723.580	511.669	995.981	−1593.273	−226.671	2.519
4800	242.254	728.680	516.137	1020.206	−1586.330	−197.668	2.151
4900	242.254	733.675	520.526	1044.431	−1579.418	−168.808	1.800
5000	242.254	738.569	524.838	1068.657	−1572.540	−140.089	1.464

PREVIOUS: CURRENT: December 1972

0 to 1785 K crystal
above 1785 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−22.287	−1889.634	−1889.634	INFINITE
100	54.455	34.317	235.233	−20.092	−1896.262	−1853.855	968.355
200	105.922	89.529	148.666	−11.827	−1899.472	−1809.884	472.693
298.15	131.988	137.298	137.298	0.	−1899.536	−1765.817	309.364
300	132.320	138.115	137.300	0.244	−1899.519	−1764.987	307.312
400	144.992	178.096	142.666	14.172	−1898.035	−1720.341	224.653
500	153.841	211.441	153.178	29.131	−1895.852	−1676.159	175.107
600	160.737	240.126	165.334	44.875	−1893.233	−1632.460	142.118
700	166.013	265.318	177.855	61.225	−1890.331	−1589.225	118.589
800	170.038	287.760	190.216	78.035	−1887.259	−1546.418	100.971
900	173.117	307.972	202.195	95.199	−1884.086	−1504.003	87.290
1000	175.502	326.340	213.706	112.634	−1880.865	−1461.944	76.364
1100	177.360	343.157	224.720	130.280	−1877.632	−1420.207	67.440
1200	178.828	358.654	235.244	148.092	−1874.413	−1378.766	60.016
1300	179.991	373.016	245.296	166.035	−1871.225	−1337.591	53.745
1400	180.920	386.390	254.902	184.082	−1868.087	−1296.661	48.379
1500	181.665	398.898	264.090	202.213	−1865.024	−1255.953	43.736
1600	182.263	410.642	272.886	220.410	−1862.060	−1215.445	39.680
1700	182.745	421.707	281.318	238.661	−1859.220	−1175.119	36.107
1785.000	183.075	430.631	288.217	254.209	CRYSTAL <--> LIQUID TRANSITION		
1785.000	242.254	489.043	288.217	358.475			
1800	242.254	491.070	289.899	362.108	−1751.374	−1135.837	32.961
1900	242.254	504.168	300.835	386.334	−1742.951	−1101.871	30.293
2000	242.254	516.594	311.315	410.559	−1734.738	−1068.343	27.902
2100	242.254	528.414	321.374	434.784	−1726.746	−1035.221	25.750
2200	242.254	539.684	331.043	459.010	−1718.985	−1002.472	23.802
2300	242.254	550.452	340.350	483.235	−1711.473	−970.074	22.031
2400	242.254	560.762	349.321	507.461	−1704.227	−937.996	20.415
2500	242.254	570.652	357.977	531.686	−1697.280	−906.214	18.934
2600	242.254	580.153	366.341	555.911	−1690.674	−874.703	17.573
2700	242.254	589.296	374.430	580.137	−1684.489	−843.437	16.317
2800	242.254	598.106	382.262	604.362	−1731.546	−811.424	15.137
2900	242.254	606.607	389.853	628.587	−1723.909	−778.699	14.026
3000	242.254	614.820	397.216	652.813	−1716.320	−746.234	12.993
3100	242.254	622.763	404.364	677.038	−1708.778	−714.021	12.031
3200	242.254	630.455	411.310	701.263	−1701.282	−682.053	11.133
3300	242.254	637.909	418.064	725.489	−1693.829	−650.319	10.294
3400	242.254	645.141	424.637	749.714	−1686.417	−618.807	9.507
3500	242.254	652.163	431.038	773.940	−1679.046	−587.515	8.768
3600	242.254	658.988	437.275	798.165	−1671.713	−556.432	8.074
3700	242.254	665.625	443.358	822.390	−1664.417	−525.554	7.419
3800	242.254	672.086	449.292	846.616	−1657.157	−494.869	6.802
3900	242.254	678.379	455.086	870.841	−1649.932	−464.376	6.220
4000	242.254	684.512	460.745	895.066	−1642.740	−434.070	5.668
4100	242.254	690.494	466.276	919.292	−1635.580	−403.942	5.146
4200	242.254	696.331	471.685	943.517	−1628.452	−373.988	4.651
4300	242.254	702.032	476.975	967.742	−1621.355	−344.203	4.181
4400	242.254	707.601	482.154	991.968	−1614.289	−314.585	3.735
4500	242.254	713.045	487.225	1016.193	−1607.253	−285.126	3.310
4600	242.254	718.370	492.192	1040.418	−1600.248	−255.824	2.905
4700	242.254	723.580	497.060	1064.644	−1593.273	−226.671	2.519
4800	242.254	728.680	501.832	1088.869	−1586.330	−197.668	2.151
4900	242.254	733.675	506.513	1113.095	−1579.418	−168.808	1.800
5000	242.254	738.569	511.105	1137.320	−1572.540	−140.089	1.464

PREVIOUS: CURRENT: December 1972

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0 to 6000 K Ideal Monatomic Gas

IP(Ne, g) = 173929.70 ± 0.1 cm^{-1}
$S°(298.15\ K)$ = 146.327 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 0 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[1,9] All predicted levels have been observed for n=2 and 3 but above that many predicted levels are missing. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[2] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 134000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.[2]

The thermodynamic functions at 298.15 K agree exactly with recent CODATA recommendations[3] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard–state pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the rare gases arise due to the use of slightly different values for R; this table uses R = 8.31441 $J·K^{-1}·mol^{-1}$. Considering these minor changes, this table agrees within the estimated uncertainty with those by Hultgren *et al.*,[4] McBride *et al.*,[5] Gurvich *et al.*,[8] and Wagman *et al.*[12] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants, which are based on the 1981 scale[6] and the 1973 values,[7] respectively.

Phase Data

The triple point, 24.561 K, and boiling point, 27.102 K, are a secondary reference point and a defining fixed–point, respectively, of IPTS–68.[10,11] Hultgren *et al.*[4] had recommended a triple point of 24.533 K (0.4277 atm) and a boiling point of 27.096 K (1 atm). These values are provided for the convenience of the reader and have not been evaluated by the present authors. As a result of these low values, the reference state for neon is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	0.	0.	0.
100	20.786	123.620	164.808	−4.119	0.	0.	0.
200	20.786	138.028	148.229	−2.040	0.	0.	0.
250	20.786	142.666	146.670	−1.001	0.	0.	0.
298.15	20.786	146.327	146.327	0.	0.	0.	0.
300	20.786	146.456	146.328	0.038	0.	0.	0.
350	20.786	149.660	146.581	1.078	0.	0.	0.
400	20.786	152.436	147.143	2.117	0.	0.	0.
450	20.786	154.884	147.870	3.156	0.	0.	0.
500	20.786	157.074	148.683	4.196	0.	0.	0.
600	20.786	160.864	150.407	6.274	0.	0.	0.
700	20.786	164.068	152.135	8.353	0.	0.	0.
800	20.786	166.843	153.804	10.431	0.	0.	0.
900	20.786	169.292	155.392	12.510	0.	0.	0.
1000	20.786	171.482	156.893	14.589	0.	0.	0.
1100	20.786	173.463	158.311	16.667	0.	0.	0.
1200	20.786	175.271	159.650	18.746	0.	0.	0.
1300	20.786	176.935	160.916	20.824	0.	0.	0.
1400	20.786	178.476	162.116	22.903	0.	0.	0.
1500	20.786	179.910	163.255	24.982	0.	0.	0.
1600	20.786	181.251	164.339	27.060	0.	0.	0.
1700	20.786	182.511	165.371	29.139	0.	0.	0.
1800	20.786	183.699	166.356	31.217	0.	0.	0.
1900	20.786	184.823	167.299	33.296	0.	0.	0.
2000	20.786	185.889	168.202	35.375	0.	0.	0.
2100	20.786	186.904	169.069	37.453	0.	0.	0.
2200	20.786	187.871	169.902	39.532	0.	0.	0.
2300	20.786	188.795	170.703	41.610	0.	0.	0.
2400	20.786	189.679	171.475	43.689	0.	0.	0.
2500	20.786	190.528	172.221	45.768	0.	0.	0.
2600	20.786	191.343	172.941	47.846	0.	0.	0.
2700	20.786	192.127	173.637	49.925	0.	0.	0.
2800	20.786	192.883	174.311	52.004	0.	0.	0.
2900	20.786	193.613	174.964	54.082	0.	0.	0.
3000	20.786	194.317	175.597	56.161	0.	0.	0.
3100	20.786	194.999	176.212	58.239	0.	0.	0.
3200	20.786	195.659	176.810	60.318	0.	0.	0.
3300	20.786	196.299	177.391	62.397	0.	0.	0.
3400	20.786	196.919	177.956	64.475	0.	0.	0.
3500	20.786	197.522	178.506	66.554	0.	0.	0.
3600	20.786	198.107	179.043	68.632	0.	0.	0.
3700	20.786	198.677	179.566	70.711	0.	0.	0.
3800	20.786	199.231	180.076	72.790	0.	0.	0.
3900	20.786	199.771	180.574	74.868	0.	0.	0.
4000	20.786	200.297	181.061	76.947	0.	0.	0.
4100	20.786	200.811	181.536	79.025	0.	0.	0.
4200	20.786	201.311	182.001	81.104	0.	0.	0.
4300	20.786	201.801	182.456	83.183	0.	0.	0.
4400	20.786	202.278	182.901	85.261	0.	0.	0.
4500	20.786	202.745	183.337	87.340	0.	0.	0.
4600	20.786	203.202	183.764	89.418	0.	0.	0.
4700	20.786	203.649	184.182	91.497	0.	0.	0.
4800	20.786	204.087	184.592	93.576	0.	0.	0.
4900	20.786	204.516	184.994	95.654	0.	0.	0.
5000	20.786	204.936	185.389	97.733	0.	0.	0.
5100	20.786	205.347	185.776	99.811	0.	0.	0.
5200	20.786	205.751	186.157	101.890	0.	0.	0.
5300	20.786	206.147	186.530	103.969	0.	0.	0.
5400	20.786	206.535	186.897	106.047	0.	0.	0.
5500	20.786	206.917	187.257	108.126	0.	0.	0.
5600	20.786	207.291	187.612	110.204	0.	0.	0.
5700	20.786	207.659	187.960	112.283	0.	0.	0.
5800	20.786	208.021	188.303	114.362	0.	0.	0.
5900	20.786	208.376	188.640	116.440	0.	0.	0.
6000	20.786	208.725	188.972	118.519	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

IP(Ne^+, g) = 330391.0 ± 0.1 cm^{-1}
$S°(298.15\ K) = 158.307 \pm 0.003\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 2080.662 \pm 0.001\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [2086.966]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	780.45	2

Heat of Formation

The ionization limit of neutral neon (173929.70 ± 0.1 cm^{-1}) reported by Moore[1] is adopted as $\Delta_f H°(0\ K)$ for $Ne^+(g)$. The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the latest CODATA fundamental constants.[2] The uncertainty in the ionization limit is estimated to be ±0.1 cm^{-1} which corresponds to an uncertainty of ±0.001 $kJ \cdot mol^{-1}$ in the heat of formation. Rosenstock *et al.*[9] and Levin and Lias[11] have summarized additional ionization potential and appearance potential data. Gurvich *et al.*[8] and Wagman *et al.*[10] adopted the same ionization potential, but the use of slightly different fundamental constants by Wagman *et al.*[10] resulted in a heat of formation difference of 0.017 $kJ \cdot mol^{-1}$.

$\Delta_f H°(Ne^+, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ne, g, 0\ K)$ by using IP(Ne) with JANAF[3] enthalpies $H°(0\ K) - H°(298.15\ K)$ for $Ne^+(g)$, Ne(r), and $e^-(r)$. $\Delta_r H°(Ne \rightarrow Ne^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights given by Moore[4] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[5] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 217000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore.[1] The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[5]

The thermodynamic functions reported here agree with those of Green *et al.*,[6] Hilsenrath *et al.*,[7] and Gurvich *et al.*[8] except for one or two minor differences. First, the entropy differs by 0.1094 $J \cdot K^{-1} \cdot mol^{-1}$ because this table uses a standard-state pressure of 1 bar, whereas the cited references used a pressure of 1 atm. Second, smaller differences arise from the use of slightly different values for the fundamental constants, the relative ionic mass, and the position of the $^2P_{1/2}$ electronic level.

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.304	2080.662		
100	20.793	135.147	177.401	−4.225			
200	21.262	149.654	160.304	−2.130			
250	21.715	154.447	158.669	−1.056			
298.15	22.119	158.307	158.307	0.	2086.966	2077.139	−363.906
300	22.133	158.444	158.307	0.041	2087.007	2077.078	−361.651
350	22.448	161.881	158.578	1.156	2088.122	2075.336	−309.727
400	22.650	164.893	159.183	2.284	2089.250	2073.432	−270.762
450	22.755	167.567	159.969	3.419	2090.385	2071.387	−240.440
500	22.788	169.967	160.851	4.558	2091.524	2069.215	−216.169
600	22.718	174.118	162.727	6.835	2093.801	2064.539	−179.734
700	22.562	177.609	164.610	9.099	2096.065	2059.483	−153.681
800	22.382	180.610	166.427	11.346	2098.312	2054.103	−134.119
900	22.207	183.236	168.152	13.576	2100.542	2048.443	−118.889
1000	22.048	185.567	169.779	15.788	2102.754	2042.536	−106.691
1100	21.907	187.662	171.311	17.986	2104.952	2036.408	−96.701
1200	21.784	189.562	172.754	20.170	2107.136	2030.080	−88.367
1300	21.678	191.302	174.115	22.343	2109.309	2023.570	−81.308
1400	21.586	192.905	175.400	24.506	2111.472	2016.894	−75.251
1500	21.507	194.391	176.617	26.661	2113.627	2010.063	−69.997
1600	21.438	195.777	177.772	28.808	2115.774	2003.089	−65.394
1700	21.378	197.075	178.870	30.949	2117.915	1995.980	−61.329
1800	21.325	198.295	179.915	33.084	2120.050	1988.746	−57.712
1900	21.279	199.447	180.913	35.214	2122.180	1981.393	−54.472
2000	21.239	200.537	181.868	37.340	2124.306	1973.928	−51.554
2100	21.203	201.573	182.781	39.462	2126.428	1966.357	−48.910
2200	21.171	202.558	183.658	41.580	2128.546	1958.685	−46.505
2300	21.142	203.499	184.501	43.696	2130.662	1950.917	−44.307
2400	21.117	204.398	185.311	45.809	2132.775	1943.057	−42.290
2500	21.094	205.260	186.092	47.919	2134.885	1935.108	−40.432
2600	21.073	206.086	186.845	50.028	2136.994	1927.076	−38.715
2700	21.054	206.881	187.573	52.134	2139.100	1918.962	−37.125
2800	21.037	207.647	188.276	54.239	2141.205	1910.770	−35.646
2900	21.022	208.385	188.957	56.341	2143.307	1902.503	−34.268
3000	21.008	209.097	189.616	58.443	2145.409	1894.164	−32.980
3100	20.995	209.786	190.256	60.543	2147.509	1885.754	−31.775
3200	20.983	210.452	190.877	62.642	2149.608	1877.277	−30.643
3300	20.972	211.098	191.480	64.740	2151.706	1868.734	−29.580
3400	20.962	211.724	192.066	66.836	2153.802	1860.128	−28.577
3500	20.953	212.331	192.636	68.932	2155.898	1851.460	−27.632
3600	20.945	212.921	193.192	71.027	2157.993	1842.732	−26.737
3700	20.937	213.495	193.733	73.121	2160.087	1833.946	−25.891
3800	20.930	214.053	194.260	75.215	2162.181	1825.103	−25.088
3900	20.923	214.597	194.775	77.307	2164.273	1816.206	−24.325
4000	20.916	215.126	195.277	79.399	2166.365	1807.254	−23.600
4100	20.910	215.643	195.767	81.490	2168.456	1798.250	−22.910
4200	20.905	216.147	196.246	83.581	2170.547	1789.196	−22.252
4300	20.900	216.639	196.715	85.671	2172.637	1780.091	−21.624
4400	20.895	217.119	197.173	87.761	2174.727	1770.938	−21.024
4500	20.890	217.589	197.622	89.850	2176.816	1761.737	−20.450
4600	20.886	218.048	198.061	91.939	2178.905	1752.490	−19.900
4700	20.882	218.497	198.491	94.028	2180.994	1743.198	−19.373
4800	20.878	218.936	198.912	96.116	2183.082	1733.861	−18.868
4900	20.875	219.367	199.325	98.203	2185.169	1724.481	−18.383
5000	20.872	219.789	199.730	100.291	2187.257	1715.058	−17.917
5100	20.868	220.202	200.128	102.378	2189.344	1705.593	−17.469
5200	20.865	220.607	200.518	104.464	2191.430	1696.087	−17.037
5300	20.863	221.004	200.900	106.551	2193.517	1686.542	−16.622
5400	20.860	221.394	201.276	108.637	2195.603	1676.957	−16.221
5500	20.857	221.777	201.646	110.723	2197.689	1667.333	−15.835
5600	20.855	222.153	202.009	112.808	2199.774	1657.671	−15.462
5700	20.853	222.522	202.365	114.894	2201.860	1647.972	−15.102
5800	20.850	222.885	202.716	116.979	2203.945	1638.237	−14.754
5900	20.848	223.241	203.061	119.064	2206.030	1628.465	−14.417
6000	20.846	223.591	203.400	121.149	2208.115	1618.658	−14.092

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

REFERENCE STATE

0	to	1728	K	crystal
1728	to	3156.584	K	liquid
above		3156.584	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.786	0.	0.	0.
100	13.631	7.454	50.235	−4.278	0.	0.	0.
200	22.468	20.200	32.143	−2.389	0.	0.	0.
298.15	25.987	29.870	29.870	0.	0.	0.	0.
300	26.024	30.031	29.871	0.048	0.	0.	0.
400	28.493	37.863	30.922	2.776	0.	0.	0.
500	31.045	44.473	32.986	5.743	0.	0.	0.
600	34.853	50.440	35.404	9.022	0.	0.	0.
631.000	39.832	52.263	36.187	10.144	____ C_p LAMBDA MAXIMUM ____		
631.000	39.832	52.263	36.187	10.144	TRANSITION		
700	30.794	55.575	37.941	12.344	0.	0.	0.
800	31.003	59.697	40.408	15.431	0.	0.	0.
900	31.589	63.382	42.759	18.560	0.	0.	0.
1000	32.217	66.742	44.992	21.750	0.	0.	0.
1100	32.928	69.845	47.112	25.007	0.	0.	0.
1200	33.681	72.742	49.128	28.336	0.	0.	0.
1300	34.518	75.471	51.051	31.746	0.	0.	0.
1400	35.397	78.061	52.888	35.241	0.	0.	0.
1500	36.317	80.534	54.649	38.827	0.	0.	0.
1600	37.279	82.908	56.342	42.506	0.	0.	0.
1700	38.284	85.199	57.972	46.286	0.	0.	0.
1728.000	38.535	85.827	58.419	47.361	____ CRYSTAL <-- --> LIQUID ____		
1728.000	38.911	95.754	58.419	64.516	TRANSITION		
1800	38.911	97.343	59.944	67.317	0.	0.	0.
1900	38.911	99.446	61.968	71.208	0.	0.	0.
2000	38.911	101.442	63.893	75.099	0.	0.	0.
2100	38.911	103.341	65.726	78.991	0.	0.	0.
2200	38.911	105.151	67.477	82.882	0.	0.	0.
2300	38.911	106.881	69.153	86.773	0.	0.	0.
2400	38.911	108.537	70.760	90.664	0.	0.	0.
2500	38.911	110.125	72.303	94.555	0.	0.	0.
2600	38.911	111.651	73.787	98.446	0.	0.	0.
2700	38.911	113.120	75.217	102.337	0.	0.	0.
2800	38.911	114.535	76.596	106.228	0.	0.	0.
2900	38.911	115.900	77.928	110.120	0.	0.	0.
3000	38.911	117.219	79.216	114.011	0.	0.	0.
3100	38.911	118.495	80.462	117.902	0.	0.	0.
3156.584	38.911	119.199	81.151	120.104	____ LIQUID <-- --> IDEAL GAS ____		
3156.584	22.396	238.807	81.151	497.656	FUGACITY = 1 bar		
3200	22.388	239.113	83.292	498.628	0.	0.	0.
3300	22.373	239.802	88.024	500.866	0.	0.	0.
3400	22.366	240.469	92.498	503.103	0.	0.	0.
3500	22.368	241.118	96.735	505.339	0.	0.	0.
3600	22.377	241.748	100.755	507.576	0.	0.	0.
3700	22.395	242.361	104.573	509.815	0.	0.	0.
3800	22.421	242.959	108.207	512.056	0.	0.	0.
3900	22.456	243.542	111.670	514.299	0.	0.	0.
4000	22.499	244.111	114.974	516.547	0.	0.	0.
4100	22.551	244.667	118.130	518.799	0.	0.	0.
4200	22.611	245.211	121.150	521.058	0.	0.	0.
4300	22.681	245.744	124.041	523.322	0.	0.	0.
4400	22.761	246.266	126.813	525.594	0.	0.	0.
4500	22.850	246.779	129.473	527.875	0.	0.	0.
4600	22.949	247.282	132.029	530.164	0.	0.	0.
4700	23.058	247.777	134.486	532.465	0.	0.	0.
4800	23.178	248.263	136.852	534.776	0.	0.	0.
4900	23.309	248.743	139.130	537.101	0.	0.	0.
5000	23.451	249.215	141.327	539.439	0.	0.	0.
5200	23.769	250.141	145.495	544.160	0.	0.	0.
5400	24.136	251.045	149.387	548.950	0.	0.	0.
5600	24.555	251.930	153.034	553.818	0.	0.	0.
5800	25.028	252.799	156.459	558.775	0.	0.	0.
6000	25.560	253.657	159.685	563.833	0.	0.	0.

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = 29.870 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_t = 631 \pm 1\ K$
$T_{fus} = 1728 \pm 4\ K$

$\Delta_f H°(0\ K) = 0\ k\ J \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_t H° = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 17.15 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The low temperature heat capacity values are based primarily on the studies by Keesom and Clark[1] and Busey and Giaque.[2] The adopted values are actually those suggested by Busey and Giauque[2] with slight changes above 280 K so as to smoothly join the high temperature heat capacity data.

There are numerous heat capacity studies in the vicinity of the Curie point. The studies upon which our adopted values are based are as follows:

Source	Year	T, K
[3]	1938	343–1123
[4]	1955	453–1437
[5]	1965	323–883
[6]	1966	300–1728
[7]	1966	571–681
[8]	1970	333–1500
[9]	1971	580–680

The adoped value for the Curie point, $T_c = 631$ K, is from the study of Connelly *et al.*,[9] using an AC calorimetric method to measure relative heat capacity values, and Vollmer *et al.*[6] using a high temperature adiabatic calorimeter.

Above 700 K, the adopted heat capacity values are those reported by Vollmer *et al.*[6] Below the Curie point, the above studies and that of Bronson and Wilson (203–383 K)[10] are used to construct a curve which joins smoothly with the low temperature values. The adopted table is identical (purposely) to that suggested by Mah and Pankatz.[11]

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub} H°(298.15\ K)$, is calculated as the difference between $\Delta_f H°(298.15\ K)$ for Ni(g) and Ni(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−4.786	0.	0.	0.
100	13.631	7.454	50.235	−4.278	0.	0.	0.
200	22.468	20.200	32.143	−2.389	0.	0.	0.
250	24.397	25.432	30.290	−1.215	0.	0.	0.
298.15	25.987	29.870	29.870	0.	0.	0.	0.
300	26.024	30.031	29.871	0.048	0.	0.	0.
350	27.294	34.139	30.192	1.381	0.	0.	0.
400	28.493	37.863	30.922	2.776	0.	0.	0.
450	29.623	41.281	31.886	4.228	0.	0.	0.
500	31.045	44.473	32.986	5.743	0.	0.	0.
600	34.853	50.440	35.404	9.022	0.	0.	0.
631.000	39.832	52.263	36.187	10.144	____ C_p LAMBDA MAXIMUM ____		
631.000	39.832	52.263	36.187	10.144	TRANSITION		
700	30.794	55.575	37.941	12.344	0.	0.	0.
800	31.003	59.697	40.408	15.431	0.	0.	0.
900	31.589	63.382	42.759	18.560	0.	0.	0.
1000	32.217	66.742	44.992	21.750	0.	0.	0.
1100	32.928	69.845	47.112	25.007	0.	0.	0.
1200	33.681	72.742	49.128	28.336	0.	0.	0.
1300	34.518	75.471	51.051	31.746	0.	0.	0.
1400	35.397	78.061	52.888	35.241	0.	0.	0.
1500	36.317	80.534	54.649	38.827	0.	0.	0.
1600	37.279	82.908	56.342	42.506	0.	0.	0.
1700	38.284	85.199	57.972	46.286	0.	0.	0.
1728.000	38.535	85.827	58.419	47.361	--- CRYSTAL <---> LIQUID ---		
1800	39.330	87.411	59.547	50.156	−17.161	0.715	−0.021
1900	42.677	89.637	61.072	54.275	−16.933	1.704	−0.047
2000	43.806	91.855	62.556	58.599	−16.501	2.674	−0.070
2100	44.978	94.021	64.003	63.038	−15.953	3.620	−0.090
2200	46.191	96.141	65.415	67.596	−15.286	4.536	−0.108
2300	47.447	98.222	66.797	72.278	−14.495	5.420	−0.123
2400	48.702	100.268	68.149	77.085	−13.579	6.267	−0.136
2500	49.957	102.281	69.474	82.018	−12.537	7.073	−0.148

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = [41.487] J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [17.479]\ kJ·mol^{-1}$
$T_{fus} = 1728 \pm 4\ K$ $\Delta_{fus}H° = 17.15 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Ni(l) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1728–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Vollmer *et al.*,[1] using an adiabatic high temperature calorimeter with an inert gas atmosphere, measured the heat capcity of nickel in the liquid region (1728–1822 K) and reported $C_p°(l) = 9.32\ kcal·mol^{-1}$. Other studies yielding liquid phase heat capacity values are: 7.86 $kcal·mol^{-1}$ by Wüst *et al.*,[2] 9.2 $kcal·mol^{-1}$ by Umino,[3] 10.3 $kcal·mol^{-1}$ by Geoffray *et al.*,[4] and 2.58 $kcal·mol^{-1}$ by Margrave.[5] This latter value[5] is undoubtedly a misprint.

We adopt a constant value, $C_p°(l) = 9.3\ kcal·mol^{-1}$ based on the heat capacity measurements of Vollmer *et al.*[1] The enthalpy study of Geoffray *et al.*[4] (1393–2192 K) leads to a reported heat capacity whilch is roughly 10% higher than our adopted value. The adopted value is identical to that chosen by Mah and Pankratz.[6]

The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The adopted melting point, $T_{fus} = 1728 \pm 4$ K (based on IPTS–68), is selected from the studies of Vollmer *et al.* (1727 K),[1] Geoffray *et al.*[4] (1728 K), Oriani and Jones (1727 K),[7] and Kubachewski (1730 K).[8]

The adopted enthalpy of melting, $\Delta_{fus}H° = 4.10 \pm 0.1\ kcal·mol^{-1}$, is based on the calorimetric studies by Vollmer *et al.* (4.039 ± 0.060 $kcal·mol^{-1}$) and Geoffray *et al.* (4.176 ± 054 $kcal·mol^{-1}$). Other reported results are 3.31 $kcal·mol^{-1}$ by Wüst *et al.*,[2] 4.21 $kcal·mol^{-1}$ by Umino,[3] 3.32 $kcal·mol^{-1}$ by Margrave,[5] and 4.4 $kcal·mol^{-1}$ by Lebedev *et al.*[9]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	26.133	41.487	41.487	0.	17.479	14.016	−2.456
300	26.150	41.648	41.487	0.048	17.480	13.994	−2.437
350	26.568	45.711	41.807	1.366	17.464	13.414	−2.002
400	26.987	49.286	42.523	2.705	17.408	12.839	−1.677
450	27.405	52.489	43.455	4.065	17.316	12.273	−1.425
500	27.824	55.398	44.506	5.446	17.182	11.719	−1.224
600	28.660	60.544	46.761	8.270	16.728	10.665	−0.928
700	29.497	65.025	49.057	11.178	16.313	9.698	−0.724
800	30.334	69.019	51.307	14.169	16.218	8.760	−0.572
900	31.171	72.640	53.479	17.245	16.164	7.831	−0.455
1000	32.008	75.967	55.564	20.404	16.133	6.907	−0.361
1100	32.844	79.057	57.561	23.646	16.119	5.986	−0.284
1200	33.681	81.951	59.474	26.972	16.115	5.065	−0.220
1300	34.518	84.680	61.309	30.382	16.116	4.144	−0.166
1300.000	34.518	84.680	61.309	30.382	____ GLASS <--> LIQUID ____		
1300.000	38.911	84.680	61.309	30.382	TRANSITION		
1400	38.911	87.564	63.083	34.273	16.511	3.207	−0.120
1500	38.911	90.248	64.805	38.165	16.817	2.246	−0.078
1600	38.911	92.759	66.475	42.056	17.029	1.267	−0.041
1700	38.911	95.118	68.091	45.947	17.140	0.278	−0.009
1728.000	38.911	95.754	68.534	47.036	--- CRYSTAL <--> LIQUID ---		
1800	38.911	97.343	69.655	49.838	0.	0.	0.
1900	38.911	99.446	71.168	53.729	0.	0.	0.
2000	38.911	101.442	72.632	57.620	0.	0.	0.
2100	38.911	103.341	74.050	61.511	0.	0.	0.
2200	38.911	105.151	75.423	65.402	0.	0.	0.
2300	38.911	106.881	76.753	69.294	0.	0.	0.
2400	38.911	108.537	78.043	73.185	0.	0.	0.
2500	38.911	110.125	79.295	77.076	0.	0.	0.
2600	38.911	111.651	80.510	80.967	0.	0.	0.
2700	38.911	113.120	81.691	84.858	0.	0.	0.
2800	38.911	114.535	82.839	88.749	0.	0.	0.
2900	38.911	115.900	83.955	92.640	0.	0.	0.
3000	38.911	117.219	85.042	96.531	0.	0.	0.
3100	38.911	118.495	86.101	100.423	0.	0.	0.
3156.584	38.911	119.199	86.688	102.624	----- FUGACITY = 1 bar -----		
3200	38.911	119.731	87.133	104.314	−376.835	5.189	−0.085
3300	38.911	120.928	88.139	108.205	−375.182	17.101	−0.271
3400	38.911	122.090	89.120	112.096	−373.527	28.964	−0.445
3500	38.911	123.218	90.078	115.987	−371.873	40.778	−0.609
3600	38.911	124.314	91.014	119.878	−370.219	52.544	−0.762

PREVIOUS: CURRENT: December 1976

CRYSTAL-LIQUID

0 to 1728 K crystal
above 1728 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.786	0.	0.	0.
100	13.631	7.454	50.235	−4.278	0.	0.	0.
200	22.468	20.200	32.143	−2.389	0.	0.	0.
250	24.397	25.432	30.290	−1.215	0.	0.	0.
298.15	25.987	29.870	29.870	0.	0.	0.	0.
300	26.024	30.031	29.871	0.048	0.	0.	0.
350	27.294	34.139	30.192	1.381	0.	0.	0.
400	28.493	37.863	30.922	2.776	0.	0.	0.
450	29.623	41.281	31.886	4.228	0.	0.	0.
500	31.045	44.473	32.986	5.743	0.	0.	0.
600	34.853	50.440	35.404	9.022	0.	0.	0.
631.000	39.832	52.263	36.187	10.144	____ C_p LAMBDA MAXIMUM ____		
631.000	39.832	52.263	36.187	10.144	TRANSITION		
700	30.794	55.575	37.941	12.344	0.	0.	0.
800	31.003	59.697	40.408	15.431	0.	0.	0.
900	31.589	63.382	42.759	18.560	0.	0.	0.
1000	32.217	66.742	44.992	21.750	0.	0.	0.
1100	32.928	69.845	47.112	25.007	0.	0.	0.
1200	33.681	72.742	49.128	28.336	0.	0.	0.
1300	34.518	75.471	51.051	31.746	0.	0.	0.
1400	35.397	78.061	52.888	35.241	0.	0.	0.
1500	36.317	80.534	54.649	38.827	0.	0.	0.
1600	37.279	82.908	56.342	42.506	0.	0.	0.
1700	38.284	85.199	57.972	46.286	0.	0.	0.
1728.000	38.535	85.827	58.419	47.361	____ CRYSTAL <--> LIQUID ____		
1728.000	38.911	95.754	58.419	64.516	TRANSITION		
1800	38.911	97.343	59.944	67.317	0.	0.	0.
1900	38.911	99.446	61.968	71.208	0.	0.	0.
2000	38.911	101.442	63.893	75.099	0.	0.	0.
2100	38.911	103.341	65.726	78.991	0.	0.	0.
2200	38.911	105.151	67.477	82.882	0.	0.	0.
2300	38.911	106.881	69.153	86.773	0.	0.	0.
2400	38.911	108.537	70.760	90.664	0.	0.	0.
2500	38.911	110.125	72.303	94.555	0.	0.	0.
2600	38.911	111.651	73.787	98.446	0.	0.	0.
2700	38.911	113.120	75.217	102.337	0.	0.	0.
2800	38.911	114.535	76.596	106.228	0.	0.	0.
2900	38.911	115.900	77.928	110.120	0.	0.	0.
3000	38.911	117.219	79.216	114.011	0.	0.	0.
3100	38.911	118.495	80.462	117.902	0.	0.	0.
3156.584	38.911	119.199	81.151	120.104	----- FUGACITY = 1 bar -----		
3200	38.911	119.731	81.670	121.793	−376.835	5.189	−0.085
3300	38.911	120.928	82.842	125.684	−375.182	17.101	−0.271
3400	38.911	122.090	83.979	129.575	−373.527	28.964	−0.445
3500	38.911	123.218	85.084	133.466	−371.873	40.778	−0.609
3600	38.911	124.314	86.159	137.357	−370.219	52.544	−0.762

PREVIOUS: CURRENT: December 1976

IP(Ni, g) = 61579 ± 10 cm^{-1}
$S°(298.15\ K)$ = 182.190 ± 0.08 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 428.1 ± 8.4 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 430.1 ± 8.4 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_4$	0.00	9
$^3D_3$	204.786	7
$^3D_2$	879.813	5
$^3F_3$	1332.153	7
$^3D_1$	1713.080	3
$^3F_2$	2216.519	5

Enthalpy of Formation

The enthalpy of formation for Ni(g) is obtained by an analysis of the vapor pressure data of Morris *et al.*[1] In this study a gas–transport method was used to measure vapor pressures (16 points) over liquid nickel in the range 1816–1895 K. For this vaporization process, we obtain $\Delta_{vap}H°(298.15\ K)$ = 99.33 ± 1.23 $kcal·mol^{-1}$ (2nd law) and 98.54 ± 0.12 $cal·mol^{-1}$ (3rd law). The entropy difference (2nd law–3rd law) is only −0.04 ± 0.7 $cal·K^{-1}·mol^{-1}$ which suggests good consistency between our adopted functions and the vapor pressure data. Using the 3rd law $\Delta_{vap}H°(298.15\ K)$ and $\Delta_f H°(Ni, l, 298.15\ K)$,[2] we calculate and adopt $\Delta_f H°(Ni, g, 298.15\ K)$ = 102.8 $kcal·mol^{-1}$. [This is the same value chosen by Hultgren *et al.*[4] and Mah and Pankratz.[5] Thus we maintain closer similarity with the most recent tabulations.]

Using mass specrometric intensity data, Farber and Srivastava[3] obtained a 2nd law enthalpy of sublimation of 99.4 $kcal·mol^{-1}$ at an average temperature of 1653 K and a 2nd law enthalpy of vaporization of 92.2 $kcal·mol^{-1}$ at an average temperature of 1863 K. Using auxiliary data,[2] we calculate $\Delta_f H°(Ni, l, 298.15\ K)$ = 102.1 $kcal·mol^{-1}$ and 99.8 $kcal·mol^{-1}$ respectively. Rutner and Haury[6] measured vapor pressures over Ni (28 points in the range 1277–1658 K), using the Langmuir technique. Their results yield a 2nd law value of 107.0 ± 5.8 $kcal·mol^{-1}$ and a 3rd law value of 103.2 ± 4.0 $kcal·mol^{-1}$. The drift is −2.5 ± 3.9 $cal·K^{-1}·mol^{-1}$. In addition Rutner and Haury[6] determined the best values of the heat of sublimation and vaporization and the parameters in a vapor pressure equation by statistically weighting nine sets of data. Although the results of this statistical treatment lead to enthalpies of formation for Ni(g) consistent with the adopted value, the results are not consistent with the melting data. Other vapor pressure studies are discussed by Hultgren *et al.*[4]

Heat Capacity and Entropy

The electronic energy levels and quantum weights used in the calculation are from Moore[7] and Roth.[8] Not all levels are listed above. The tabulated entropy values agree within 0.001 $cal·K^{-1}·mol^{-1}$ with the recent tabulation by Hultgren *et al.*[4] and Mah and Pankratz.[5] There are predicted levels which have not been observed and/or classified. It is not expected that $S°(298.15\ K)$ would be affected by these states, but that in the range 3000–6000 K, an error of 0.2–0.3 $cal·K^{-1}·mol^{-1}$ might result. In our present tabulation, the levels above 20000 cm^{-1} contribute 0.0005 $cal·K^{-1}·mol^{-1}$ at 3000 K and 0.15 $cal·K^{-1}·mol^{-1}$ at 6000 K to the entropy.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.825	428.076	428.076	INFINITE
100	23.510	156.498	203.000	−4.650	429.743	414.839	−216.690
200	23.396	172.882	184.321	−2.288	430.216	399.680	−104.386
250	23.275	178.085	182.574	−1.122	430.208	392.044	−81.913
298.15	23.360	182.190	182.190	0.	430.115	384.701	−67.398
300	23.367	182.334	182.190	0.043	430.110	384.419	−66.933
350	23.587	185.952	182.475	1.217	429.951	376.816	−56.237
400	23.859	189.119	183.112	2.403	429.742	369.239	−48.218
450	24.131	191.945	183.939	3.603	429.490	361.691	−41.984
500	24.374	194.500	184.870	4.815	429.187	354.174	−37.000
600	24.734	198.979	186.858	7.272	428.366	339.243	−29.534
700	24.925	202.808	188.870	9.756	427.528	324.465	−24.212
800	24.981	206.141	190.825	12.253	426.937	309.782	−20.227
900	24.942	209.082	192.693	14.749	426.305	295.174	−17.131
1000	24.841	211.705	194.466	17.239	425.605	280.641	−14.659
1100	24.701	214.066	196.142	19.716	424.825	266.182	−12.640
1200	24.538	216.209	197.726	22.178	423.957	251.797	−10.960
1300	24.364	218.166	199.225	24.624	422.993	237.489	−9.542
1400	24.187	219.965	200.643	27.051	421.925	223.259	−8.330
1500	24.012	221.628	201.987	29.461	420.750	209.109	−7.282
1600	23.842	223.172	203.263	31.854	419.463	195.041	−6.367
1700	23.679	224.612	204.477	34.230	418.059	181.057	−5.563
1800	23.524	225.961	205.634	36.590	399.388	167.874	−4.872
1900	23.380	227.229	206.737	38.935	397.842	155.054	−4.263
2000	23.245	228.425	207.792	41.266	396.282	142.316	−3.717
2100	23.121	229.556	208.802	43.584	394.709	129.656	−3.225
2200	23.007	230.629	209.770	45.891	393.124	117.072	−2.780
2300	22.903	231.650	210.699	48.186	391.528	104.560	−2.375
2400	22.810	232.622	211.592	50.472	389.923	92.117	−2.005
2500	22.725	233.552	212.452	52.748	388.308	79.742	−1.666
2600	22.651	234.441	213.281	55.017	386.686	67.431	−1.355
2700	22.585	235.295	214.081	57.279	385.057	55.183	−1.068
2800	22.529	236.115	214.853	59.534	383.421	42.996	−0.802
2900	22.481	236.905	215.600	61.785	381.780	30.866	−0.556
3000	22.441	237.667	216.323	64.031	380.135	18.794	−0.327
3100	22.410	238.402	217.023	66.273	378.487	6.776	−0.114
3156.584	22.396	238.807	217.410	67.541	----- FUGACITY = 1 bar -----		
3200	22.388	239.113	217.703	68.513	0.	0.	0.
3300	22.373	239.802	218.362	70.751	0.	0.	0.
3400	22.366	240.469	219.002	72.988	0.	0.	0.
3500	22.368	241.118	219.625	75.225	0.	0.	0.
3600	22.377	241.748	220.231	77.462	0.	0.	0.
3700	22.395	242.361	220.821	79.700	0.	0.	0.
3800	22.421	242.959	221.395	81.941	0.	0.	0.
3900	22.456	243.542	221.956	84.185	0.	0.	0.
4000	22.499	244.111	222.503	86.433	0.	0.	0.
4100	22.551	244.667	223.036	88.685	0.	0.	0.
4200	22.611	245.211	223.558	90.943	0.	0.	0.
4300	22.681	245.744	224.068	93.208	0.	0.	0.
4400	22.761	246.266	224.566	95.480	0.	0.	0.
4500	22.850	246.779	225.054	97.760	0.	0.	0.
4600	22.949	247.282	225.532	100.050	0.	0.	0.
4700	23.058	247.777	226.000	102.350	0.	0.	0.
4800	23.178	248.263	226.459	104.662	0.	0.	0.
4900	23.309	248.743	226.909	106.986	0.	0.	0.
5000	23.451	249.215	227.350	109.324	0.	0.	0.
5100	23.604	249.681	227.783	111.677	0.	0.	0.
5200	23.769	250.141	228.209	114.045	0.	0.	0.
5300	23.947	250.595	228.627	116.431	0.	0.	0.
5400	24.136	251.045	229.038	118.835	0.	0.	0.
5500	24.339	251.489	229.442	121.258	0.	0.	0.
5600	24.555	251.930	229.840	123.703	0.	0.	0.
5700	24.784	252.366	230.231	126.170	0.	0.	0.
5800	25.028	252.799	230.617	128.660	0.	0.	0.
5900	25.287	253.229	230.996	131.176	0.	0.	0.
6000	25.560	253.657	231.370	133.718	0.	0.	0.

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

IP(Ni^+, g) = 146541.56 ± 0.02 cm^{-1}
$S°$(298.15 K) = 199.72 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1164.98 ± 8.4 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1179.003] $kJ·mol^{-1}$

Electronic Level and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2D_{5/2}$	0.00	6
$^2D_{3/2}$	1606.94	4

Enthalpy of Formation

$\Delta_f H°(Ni^+, g, 0 K)$ is calculated from $\Delta_f H°(Ni, g, 0 K)$[1] using the spectroscopic value of IP(Ni) = 61600 ± 10 cm^{-1} (736.90 ± 0.12 $kJ·mol^{-1}$) from Corliss and Sugar.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ni^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Ni, g, 0 K)$ by using IP(Ni) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for Ni(g), Ni^+(g), and e^-(ref). $\Delta_f H°(Ni \rightarrow Ni^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Corliss and Sugar,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground state for Ni^+(g), all levels listed by Corliss and Sugar[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Ni^+(g), the thermodynamic functions are dependent of the estimated missing levels (for n > 3) and the cut–off procedure, the Gibbs energy function shows variations of ~20% at 1000 K. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations aboue 6000 K may require consideration of the higher excited states (n > 5), and use of different fill and cut–off procedures.[6]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.615	1164.976		
100	20.787	151.833	257.198	−10.537			
200	35.551	167.752	208.658	−8.181			
250	86.780	180.587	201.615	−5.257			
298.15	121.588	199.724	199.724	0.	1179.003	1122.106	−196.588
300	121.596	200.476	199.726	0.225	1179.218	1121.752	−195.314
350	96.043	217.764	201.149	5.815	1184.514	1111.737	−165.918
400	62.862	228.293	203.945	9.739	1188.082	1101.076	−143.786
450	43.263	234.441	207.020	12.339	1190.270	1090.058	−126.531
500	33.285	238.423	209.973	14.225	1191.680	1078.842	−112.706
600	25.407	243.650	215.183	17.080	1193.335	1056.100	−91.942
700	22.887	247.345	219.525	19.474	1194.485	1033.143	−77.094
800	21.897	250.327	223.195	21.706	1195.709	1010.009	−65.947
900	21.442	252.877	226.354	23.870	1196.823	986.729	−57.268
1000	21.206	255.122	229.121	26.002	1197.843	963.329	−50.319
1100	21.072	257.137	231.578	28.115	1198.778	939.832	−44.629
1200	20.991	258.967	233.785	30.218	1199.630	916.253	−39.883
1300	20.939	260.645	235.788	32.314	1200.395	892.607	−35.865
1400	20.904	262.195	237.619	34.406	1201.070	868.905	−32.419
1500	20.879	263.636	239.306	36.495	1201.653	845.158	−29.431
1600	20.862	264.983	240.869	38.582	1202.139	821.375	−26.815
1700	20.849	266.248	242.325	40.668	1202.523	797.565	−24.506
1800	20.840	267.439	243.688	42.752	1185.655	774.450	−22.474
1900	20.833	268.566	244.968	44.836	1185.926	751.598	−20.663
2000	20.828	269.634	246.175	46.919	1186.197	728.732	−19.033
2100	20.824	270.650	247.316	49.002	1186.467	705.852	−17.557
2200	20.821	271.619	248.399	51.084	1186.737	682.959	−16.216
2300	20.819	272.544	249.429	53.166	1187.006	660.054	−14.990
2400	20.818	273.430	250.410	55.248	1187.275	637.137	−13.867
2500	20.817	274.280	251.348	57.329	1187.545	614.209	−12.833
2600	20.816	275.097	252.246	59.411	1187.814	591.271	−11.879
2700	20.816	275.882	253.107	61.493	1188.083	568.321	−10.995
2800	20.815	276.639	253.934	63.574	1188.352	545.362	−10.174
2900	20.815	277.370	254.730	65.656	1188.621	522.394	−9.409
3000	20.816	278.075	255.496	67.737	1188.890	499.416	−8.696
3100	20.816	278.758	256.236	69.819	1189.159	476.429	−8.028
3200	20.816	279.419	256.950	71.900	812.593	458.622	−7.486
3300	20.817	280.059	257.640	73.982	814.515	447.531	−7.084
3400	20.817	280.681	258.309	76.064	816.439	436.381	−6.704
3500	20.817	281.284	258.957	78.145	818.363	425.175	−6.345
3600	20.818	281.871	259.585	80.227	820.286	413.914	−6.006
3700	20.819	282.441	260.195	82.309	822.208	402.599	−5.684
3800	20.819	282.996	260.788	84.391	824.127	391.233	−5.378
3900	20.820	283.537	261.364	86.473	826.044	379.816	−5.087
4000	20.820	284.064	261.925	88.555	827.957	368.349	−4.810
4100	20.821	284.578	262.472	90.637	829.865	356.836	−4.546
4200	20.822	285.080	263.004	92.719	831.768	345.275	−4.294
4300	20.822	285.570	263.523	94.801	833.664	333.670	−4.053
4400	20.823	286.049	264.030	96.883	835.553	322.020	−3.823
4500	20.823	286.517	264.524	98.966	837.434	310.328	−3.602
4600	20.824	286.974	265.007	101.048	839.305	298.594	−3.391
4700	20.824	287.422	265.479	103.131	841.165	286.819	−3.188
4800	20.825	287.861	265.941	105.213	843.015	275.005	−2.993
4900	20.826	288.290	266.393	107.296	844.852	263.152	−2.805
5000	20.826	288.711	266.835	109.378	846.675	251.262	−2.625
5100	20.827	289.123	267.268	111.461	848.483	239.336	−2.451
5200	20.827	289.528	267.692	113.543	850.276	227.374	−2.284
5300	20.828	289.924	268.108	115.626	852.052	215.379	−2.123
5400	20.828	290.314	268.516	117.709	853.809	203.349	−1.967
5500	20.829	290.696	268.915	119.792	855.547	191.288	−1.817
5600	20.829	291.071	269.308	121.875	857.264	179.195	−1.671
5700	20.830	291.440	269.693	123.958	858.959	167.071	−1.531
5800	20.830	291.802	270.071	126.041	860.630	154.918	−1.395
5900	20.831	292.158	270.442	128.124	862.276	142.737	−1.264
6000	20.831	292.508	270.807	130.207	863.896	130.527	−1.136

PREVIOUS: CURRENT: June 1984 (1 bar)

EA(Ni, g) = 1.156 ± 0.010 eV
$S°(298.15\ K)$ = 174.577 ± 0.005 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 316.5 ± 1 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [311.764] $kJ·mol^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2D_{5/2}$	0	6
$^1D_{3/2}$	1470	4

Enthalpy of Formation

$\Delta_f H°(N_i^-, g, 0\ K)$ is calculated from $\Delta_f H°(Ni, g, 0\ K)$[1] using the adopted electron affinity of EA (Ni) = 1.156 ± 0.010 eV (111.546 ± 0.965 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3]

Additional information on Ni^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2, 4] Rosenstock *et al.*[5] and Massey.[6] $\Delta_f H°(Ni^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ni, g, 0\ K)$ by using EA(Ni) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for Ni^-(g), Ni(g), and e^-(ref). $\Delta_r H°(Ni^- \rightarrow Ni + e^-, 298.15\ K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Ni^-(g) is given by Hotop and Lineberger[2, 4] and Rosenstock *et al.*[5] and Masey.[6] The fine structure separation has been measured experimentally be laser photodetachment electron spectrometry[3] and is that recommended by Hotop and Lineberger.[2]

References

[1]JANAF Thermochemical Tables: Ni(g), 12–31–76; e ($^-$g), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.207	316.540		
100	20.786	151.833	193.117	−4.128			
200	20.802	166.242	176.490	−2.050			
250	20.870	170.890	174.922	−1.008			
298.15	21.017	174.577	174.577	0.	311.764	274.874	−48.157
300	21.025	174.707	174.578	0.039	311.716	274.646	−47.820
350	21.265	177.965	174.834	1.096	310.401	268.570	−40.082
400	21.564	180.824	175.408	2.166	309.037	262.687	−34.303
450	21.886	183.382	176.154	3.253	307.632	256.977	−29.829
500	22.202	185.705	176.995	4.355	306.180	251.427	−26.266
600	22.737	189.802	178.797	6.603	303.071	240.763	−20.960
700	23.099	193.337	180.627	8.896	299.963	230.634	−17.210
800	23.297	196.436	182.414	11.217	297.119	220.923	−14.425
900	23.367	199.185	184.127	13.552	294.245	211.571	−12.279
1000	23.348	201.646	185.758	15.888	291.313	202.542	−10.580
1100	23.274	203.869	187.305	18.219	288.309	193.809	−9.203
1200	23.165	205.889	188.771	20.541	285.223	185.354	−8.068
1300	23.040	207.738	190.160	22.852	282.045	177.160	−7.118
1400	22.908	209.441	191.477	25.149	278.769	169.214	−6.313
1500	22.776	211.017	192.728	27.433	275.389	161.506	−5.624
1600	22.648	212.483	193.918	29.705	271.902	154.027	−5.028
1700	22.526	213.852	195.050	31.963	268.302	146.769	−4.510
1800	22.411	215.136	196.131	34.210	247.439	140.441	−4.076
1900	22.304	216.345	197.163	36.446	243.705	134.599	−3.700
2000	22.206	217.487	198.151	38.671	239.961	128.953	−3.368
2100	22.114	218.568	199.098	40.887	236.207	123.495	−3.072
2200	22.030	219.595	200.006	43.094	232.444	118.216	−2.807
2300	21.952	220.572	200.880	45.293	228.674	113.108	−2.569
2400	21.881	221.505	201.720	47.485	224.896	108.165	−2.354
2500	21.815	222.397	202.529	49.670	221.111	103.379	−2.160
2600	21.755	223.251	203.310	51.848	217.320	98.744	−1.984
2700	21.699	224.071	204.064	54.021	213.522	94.256	−1.823
2800	21.648	224.860	204.792	56.188	209.720	89.908	−1.677
2900	21.600	225.618	205.497	58.350	205.913	85.696	−1.544
3000	21.556	226.350	206.180	60.508	202.101	81.616	−1.421
3100	21.516	227.056	206.843	62.662	198.285	77.662	−1.309
3200	21.478	227.739	207.485	64.811	−182.370	79.021	−1.290
3300	21.443	228.399	208.109	66.958	−184.541	87.223	−1.381
3400	21.411	229.039	208.715	69.100	−186.714	95.491	−1.467
3500	21.380	229.659	209.305	71.240	−188.889	103.823	−1.549
3600	21.352	230.261	209.878	73.376	−191.069	112.217	−1.628
3700	21.326	230.845	210.437	75.510	−193.252	120.671	−1.704
3800	21.301	231.414	210.982	77.642	−195.440	129.185	−1.776
3900	21.278	231.967	211.513	79.770	−197.633	137.756	−1.845
4000	21.257	232.505	212.031	81.897	−199.833	146.384	−1.912
4100	21.237	233.030	212.537	84.022	−202.039	155.067	−1.976
4200	21.218	233.541	213.031	86.145	−204.253	163.803	−2.037
4300	21.200	234.040	213.513	88.265	−206.475	172.593	−2.097
4400	21.183	234.528	213.986	90.385	−208.707	181.434	−2.154
4500	21.167	235.003	214.447	92.502	−210.948	190.326	−2.209
4600	21.152	235.468	214.899	94.618	−213.201	199.268	−2.263
4700	21.138	235.923	215.342	96.733	−215.465	208.259	−2.315
4800	21.125	236.368	215.775	98.846	−217.742	217.299	−2.365
4900	21.113	236.804	216.200	100.958	−220.033	226.386	−2.413
5000	21.101	237.230	216.616	103.068	−222.339	235.520	−2.460
5100	21.090	237.648	217.025	105.178	−224.661	244.700	−2.506
5200	21.079	238.057	217.425	107.286	−227.000	253.926	−2.551
5300	21.069	238.459	217.818	109.394	−229.357	263.197	−2.594
5400	21.059	238.852	218.204	111.500	−231.733	272.513	−2.636
5500	21.050	239.239	218.583	113.606	−234.129	281.873	−2.677
5600	21.041	239.618	218.955	115.710	−236.548	291.276	−2.717
5700	21.033	239.990	219.321	117.814	−238.990	300.723	−2.756
5800	21.025	240.356	219.681	119.917	−241.456	310.213	−2.794
5900	21.018	240.715	220.034	122.019	−243.948	319.746	−2.831
6000	21.010	241.068	220.382	124.120	−246.467	329.322	−2.867

PREVIOUS: CURRENT: June 1984 (1 bar)

$S°(298.15\ K) = 52.992 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 652 \pm 3\ K$
$T_{fus} = 1249 \pm 3\ K$

$\Delta_f H°(0\ K) = -87.13 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -87.86 \pm 6.3\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 6.443 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 30.125 \pm 2.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Rosenqvist[1] studied the sulfur vapor pressure above solid nickel sulfides using the N_2/H_2S equilibrium. Combining his data for several equilibria we calculate 2nd and 3rd law values of $\Delta_f H°(298.15\ K)$ for NiS(cr) to be 20.5 ± 0.7 kcal·mol^{-1} and -22.6 ± 3.6 kcal·mol^{-1}, respectively. The stoichiometry of NiS varies from at least $NiS_{.98}$ to $NiS_{1.06}$ and Ariya *et al.*[2] investigated $\Delta_f H°(298.15\ K)$ in the composition range by calorimetric methods. These authors found $\Delta_f H°(298.15\ K) = -20.3 \pm 0.6$ kcal·mol^{-1} for stoichiometric NiS with an ill–defined trend toward more exothermic values at higher sulfur content. DeRanter and Breckpot[3] obtained a value of 20.08 kcal·mol^{-1} for amorphous $Ni_{.98}S$ from an enthalpometric titration. We calculate $\Delta_f H°(298.15\ K) = -21.3$ kcal·mol^{-1} for the same material based on a 3rd law analysis of DeRanter and Breckpot's emf data.[3]

In view of the rather large uncertainties and variations due to stoichiometry we choose to adopt the average of the five values above, $\Delta_f H°(298.15\ K) = -21.0 \pm 1.5$ kcal·mol^{-1}. This value is somewhat less negative than values of -22.1 and -22.5 kcal·mol^{-1} adopted by Mah and Pankrantz[4] and Mills,[5] respectively.

Heat Capacity and Entropy

The low temperature heat capacity data (52–296 K) are taken from Weller and Kelley.[6] High temperature enthalpies of $NiS_{1.03}$ were measured by Conard *et al.*[7] via drop calorimetry. We have joined these values smoothly with the low temperature $C_p°$ measurements of Weller and Kelley[6] to derive the $C_p°$ values from 298 652 K. Values of $C_p°$ above the transition are also taken from our analysis of Conard's *et al.*[7] enthalpy data, disregarding the points above 1000 K to avoid problems due to incongruent melting. Values above 1000 K are extrapolated.

Phase Data

Both the low (β) and high (α) temperature polymorphs of NiS dissolve excess sulfur to form solid solutions. The β phase shows a limited range of homogeneity but the α phase shows a broad limit extending to approximately $NiS_{1.10}$.[8] The α phase is normally designated α $Ni_{1-x}S$ to emphasize this feature. However, the sulfur–poor limit of this phase has the stoichiometric composition to at least 873 K; at 1070 K the deviation from stoichiometry is less than 0.05 weight % nickel.[8] Above 1079 K the deviation of the sulfur–poor limit from stoichiometry increases more rapidly and a material of stoichiometry NiS will exist as an equilibrium mixture of liquid Ni_yS_z and solid α $Ni_{1-x}S$.[8] Thus, NiS melts incongruently.

Transition Data

We adopt 652 ± 3 K as the transition temperature of stoichiometric NiS from rhombohedral (β) to hexagonal (α) form base on the phase diagram of Kullerud and Yund.[8] The temperature of this transition is very dependent on the exact stoichiometry of the material.[8] The transition enthalpy has been measured via a DTA technique by Conard *et al.*[7] and we adopt their value of 1.54 ± 0.1 kcal·mol^{-1}. This is considerably higher than an older value of 0.63 kcal·mol^{-1} measured by Biltz *et al.*[9,5] but should be much more accurate due to the calibration technique used. Mah and Pankrantz[4] estimated 0.7 kcal·mol^{-1}. This transition enthalpy cannot be measured by drop calorimetry since the α form does not revert to the β form on cooling.

Fusion Data

As stated above, stoichiometric NiS will begin to form a liquid at 1079 K. The conversion to stoichiometric liquid NiS is complete at 1249 K.[8] We adopt the latter as the melting point of NiS with an uncertainty estimated to be ±3 K. The adopted heat of melting, $\Delta_{fus} H° = 7.20 \pm 0.7$ kcal·mol^{-1}, is from our analysis of the high temperature enthalpy data of Conard *et al.*[7] This value compares favorably with estimated values of 7.4 and 7.0 kcal·mol^{-1} due to Nagamori and Ingraham[10] and Mah and Pankrantz.[4]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.465	−87.131	−87.131	INFINITE
100	23.187	12.857	89.876	−7.702	−87.566	−86.854	45.368
200	40.626	35.370	57.135	−4.353	−87.748	−86.055	22.475
298.15	47.112	52.992	52.992	0.	−87.864	−85.200	14.927
300	47.196	53.284	52.993	0.087	−87.867	−85.184	14.832
400	50.501	67.332	54.886	4.978	−90.301	−84.172	10.992
500	53.053	78.880	58.563	10.158	−92.016	−82.453	8.614
600	55.312	88.757	62.792	15.579	−93.458	−80.402	7.000
652.000	56.372	93.399	65.050	18.483	BETA <--> ALPHA TRANSITION		
652.000	53.152	103.281	65.050	24.927			
700	54.518	107.105	67.804	27.511	−88.196	−78.598	5.865
800	57.363	114.570	73.189	33.105	−88.900	−77.175	5.039
900	60.208	121.491	78.176	38.983	−142.408	−74.603	4.330
1000	63.053	127.982	82.835	45.146	−141.290	−67.127	3.506
1100	65.898	134.125	87.221	51.594	−139.971	−59.773	2.838
1200	68.743	139.980	91.375	58.326	−138.456	−52.547	2.287
1249.000	70.137	142.759	93.337	61.728	---- ALPHA <--> LIQUID ----		
1300	71.588	145.595	95.332	65.342	−136.751	−45.456	1.826
1400	74.433	151.005	99.116	72.644	−134.864	−38.503	1.437
1500	77.278	156.237	102.751	80.229	−132.797	−31.691	1.104
1600	80.124	161.315	106.253	88.099	−130.554	−25.023	0.817
1700	82.969	166.258	109.638	96.254	−128.142	−18.500	0.568

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K)$ = [72.441] $J·K^{-1}·mol^{-1}$
T_{fus} = 1249 ± 3 K

$\Delta_f H°(298.15\ K)$ = [−62.474] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 30.125 ± 2.9 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from that of NiS(cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, H°(1249 K)–H°(298.15 K), between the crystal and liquid. Our 2nd and 3rd law analyses of Nagamori and Ingraham's[1] sulfur vapor pressure data yields $\Delta_f H°(298.15\ K)$ = 14.4 ± 0.4 and 16.7 ± 0.4 $kcal·mol^{-1}$, respectively. These values agree with the adopted value within the estimated uncertainty. Meyer *et al.*[2] and Rosenqvist[3] conducted similar vapor pressure studies at higher and lower temperatures, respectively. Both studies qualitatively show good agreement with Nagamori at overlapping temperatures.[2] However, Meyer's data are presented graphically only and Rosenqvist's data cover only compositions near Ni_3S_2(l) and is not of high enough quality to extrapolate to the proper composition.

Heat Capacity and Entropy

The heat capacity of liquid NiS above an assumed glass transition at 860 K is taken from our analysis of the enthalpy data of Conard *et al.*[4] This value has a fairly high uncertainty because of the limited temperature range of the data (35 K). It is in reasonable agreement with the estimated C_p° = 17 $cal·K^{-1}·mol^{-1}$ of Mah and Pankrantz.[5] The heat capacity below the glass transition is that of the crystal. $S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

The Gibbs energy data indicates that NiS(l) will decompose to the elements, Ni(l) + 1/2 S_2(g), at a temperature of 2350 ± 200 K and a fugacity of 1 atm. In view of the uncertainty in the Gibbs free energy data, computation of the exact zero point does not seem justified. Since the Gibbs energy data for NiS(l) and NiS(g)[6] intersect at 2990 ± 220 K, it seems clear that decomposition will occur rather than boiling.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	C_p°	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	47.112	72.441	72.441	0.	−62.474	−65.609	11.494
300	47.196	72.732	72.442	0.087	−62.477	−65.629	11.427
400	50.501	86.780	74.334	4.978	−64.911	−66.561	8.692
500	53.053	98.329	78.012	10.158	−66.627	−66.788	6.977
600	55.312	108.206	82.240	15.579	−68.069	−66.681	5.805
652.000	56.372	112.847	84.498	18.483	BETA <--> ALPHA TRANSITION		
652.000	53.152	122.729	84.498	24.927			
700	54.518	126.553	87.252	27.511	−62.807	−66.823	4.986
800	57.363	134.019	92.638	33.105	−63.511	−67.344	4.397
860.000	59.070	138.228	95.673	36.598	GLASS <--> LIQUID TRANSITION		
860.000	76.776	138.228	95.673	36.598			
900	76.776	141.719	97.642	39.669	−116.333	−66.733	3.873
1000	76.776	149.808	102.461	47.346	−113.701	−61.363	3.205
1100	76.776	157.125	107.103	55.024	−111.151	−56.254	2.671
1200	76.776	163.806	111.554	62.702	−108.690	−51.372	2.236
1249.000	76.776	166.878	113.665	66.464	---- ALPHA <--> LIQUID ----		
1300	76.776	169.951	115.813	70.379	−106.325	−46.692	1.876
1400	76.776	175.641	119.886	78.057	−104.061	−42.191	1.574
1500	76.776	180.938	123.781	85.735	−101.902	−37.847	1.318
1600	76.776	185.893	127.510	93.412	−99.852	−33.645	1.098
1700	76.776	190.547	131.083	101.090	−97.916	−29.567	0.908
1800	76.776	194.936	134.509	108.768	−113.247	−24.884	0.722
1900	76.776	199.087	137.800	116.445	−111.450	−20.024	0.551
2000	76.776	203.025	140.964	124.123	−109.664	−15.259	0.399
2100	76.776	206.771	144.009	131.800	−107.890	−10.582	0.263
2200	76.776	210.343	146.944	139.478	−106.126	−5.990	0.142
2300	76.776	213.755	149.775	147.156	−104.372	−1.477	0.034
2400	76.776	217.023	152.509	154.833	−102.626	2.959	−0.064
2500	76.776	220.157	155.153	162.511	−100.888	7.322	−0.153
2600	76.776	223.168	157.711	170.189	−99.158	11.617	−0.233
2700	76.776	226.066	160.190	177.866	−97.433	15.845	−0.307
2800	76.776	228.858	162.593	185.544	−95.714	20.009	−0.373
2900	76.776	231.552	164.924	193.222	−94.001	24.111	−0.434
3000	76.776	234.155	167.189	200.899	−92.294	28.155	−0.490
3100	76.776	236.673	169.390	208.577	−90.590	32.142	−0.542
3200	76.776	239.110	171.531	216.254	−465.726	41.262	−0.674
3300	76.776	241.473	173.615	223.932	−462.379	57.054	−0.903
3400	76.776	243.765	175.644	231.610	−459.034	72.744	−1.118

PREVIOUS: CURRENT: December 1976

0	to 652	K	crystal, rhombohedral (β)
652	to 1249	K	crystal, hexagonal (α)
above	1249	K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−8.465	−87.131	−87.131	INFINITE
100	23.187	12.857	89.876	−7.702	−87.566	−86.854	45.368
200	40.626	35.370	57.135	−4.353	−87.748	−86.055	22.475
298.15	47.112	52.992	52.992	0.	−87.864	−85.200	14.927
300	47.196	53.284	52.993	0.087	−87.867	−85.184	14.832
400	50.501	67.332	54.886	4.978	−90.301	−84.172	10.992
500	53.053	78.880	58.563	10.158	−92.016	−82.453	8.614
600	55.312	88.757	62.792	15.579	−93.458	−80.402	7.000
652.000	56.372	93.399	65.050	18.483	BETA <--> ALPHA TRANSITION		
652.000	53.152	103.281	65.050	24.927			
700	54.518	107.105	67.804	27.511	−88.196	−78.598	5.865
800	57.363	114.570	73.189	33.105	−88.900	−77.175	5.039
900	60.208	121.491	78.176	38.983	−142.408	−74.603	4.330
1000	63.053	127.982	82.835	45.146	−141.290	−67.127	3.506
1100	65.898	134.125	87.221	51.594	−139.971	−59.773	2.838
1200	68.743	139.980	91.375	58.326	−138.456	−52.547	2.287
1249.000	70.137	142.759	93.337	61.728	ALPHA <--> LIQUID TRANSITION		
1249.000	76.776	166.878	93.337	91.853			
1300	76.776	169.951	96.283	95.769	−106.325	−46.692	1.876
1400	76.776	175.641	101.751	103.447	−104.061	−42.191	1.574
1500	76.776	180.938	106.855	111.124	−101.902	−37.848	1.318
1600	76.776	185.893	111.642	118.802	−99.852	−33.645	1.098
1700	76.776	190.547	116.148	126.479	−97.916	−29.567	0.908
1800	76.776	194.936	120.404	134.157	−113.247	−24.884	0.722
1900	76.776	199.087	124.437	141.835	−111.450	−20.024	0.551
2000	76.776	203.025	128.269	149.512	−109.664	−15.259	0.399
2100	76.776	206.771	131.919	157.190	−107.890	−10.582	0.263
2200	76.776	210.343	135.403	164.868	−106.126	−5.990	0.142
2300	76.776	213.756	138.736	172.545	−104.372	−1.477	0.034
2400	76.776	217.023	141.930	180.223	−102.626	2.959	−0.064
2500	76.776	220.157	144.997	187.901	−100.888	7.322	−0.153
2600	76.776	223.168	147.946	195.578	−99.158	11.617	−0.233
2700	76.776	226.066	150.786	203.256	−97.433	15.845	−0.307
2800	76.776	228.858	153.525	210.933	−95.714	20.008	−0.373
2900	76.776	231.552	156.169	218.611	−94.001	24.111	−0.434
3000	76.776	234.155	158.726	226.289	−92.294	28.155	−0.490
3100	76.776	236.673	161.200	233.966	−90.590	32.142	−0.542
3200	76.776	239.110	163.597	241.644	−465.726	41.262	−0.674
3300	76.776	241.473	165.921	249.322	−462.379	57.054	−0.903
3400	76.776	243.765	168.177	256.999	−459.034	72.744	−1.118

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = [252.282 \pm 8.4]\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 357.40 \pm 16.7\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 357.42 \pm 16.7\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
[0]	[9]
[1360.7]	[7]
[2269.6]	[5]
[16661.6]	[5]
[16977.8]	[3]
[17230.7]	[1]

$\omega_e = 544\ cm^{-1}$ $\omega_e x_e = 2.6\ cm^{-1}$ $\sigma = 1$

$B_e = [0.191]\ cm^{-1}$ $\alpha_e = [0.0011]\ cm^{-1}$ $r_e = [2.07]$ Å

Enthalpy of Formation

Drowart *et al.*[1] used a modified Knudsen cell and a mass spectrometric technique to study the equilibrium NiS(g) + Mn(g) = MnS(g) + Ni(g). Since they report no data, we adopt their value of $D_0^\circ = 81.5 \pm 3.5$ kcal·mol^{-1} based on their 3rd law analysis of this equilibrium. With auxiliary JANAF data[2] this yields $\Delta_f H°(298.15\ K) = 85.4 \pm 4.0$ kcal·mol^{-1}. Trevedi[3] studied the absorption spectrum of NiS and determined $D_0^\circ = 101.6$ kcal·mol^{-1} from the onset of continuous absorption due to photodissociation. This value is likely to be too high in view of the experimental difficulties in determining the exact position of the onset of continuous absorption. Complications arise because of background emission from the furnace. A Birge–Sponer extrapolation of the vibrational data to determine D_0° is not meaningful since DeVore and Franzen[4] used the reverse procedure to arrive at the reported value of $\omega_e x_e$.

Heat Capacity and Entropy

No experimental information is available on the electronic structure of NiS. The electronic states are estimated to be identical to those of the Ni^{2+} ion[5] following the procedure of Brewer and Rosenblatt[6] for the transition metal oxides. As stated by Brewer and Robenblatt,[6] this procedure usually overestimates the contribution of electronic states. Nevertheless, it appears to be the best method available. The uncertainty assigned to $S°(298.15\ K)$ is based mainly on the uncertainties in this approximation since the presence of the sulfide ion will undoubtedly alter the electronic structure of the nickel ion. Levels above 50,000 cm^{-1} are not included since they have a negligible effect on the thermodynamic properties. The vibrational constants are taken from a study of the matrix isolation spectrum by DeVore and Franzen.[4] The rotational constants are estimated based on an oxide–sulfide correlation due to Barrow and Cousins,[7] $r(NiS) = 0.237 + 1.116\ r(NiO)$. The value $r(NiO) = 1.64$ Å is taken from Brewer and Chandraskharaiah.[8] The value of α_e is estimated assuming a Morse potential function using the expression given by Herzberg.[9]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.218	357.398	357.398	INFINITE
100	29.323	218.044	281.104	−6.306	359.113	339.306	−177.235
200	31.871	239.056	255.355	−3.260	358.628	319.584	−83.467
250	33.262	246.320	252.843	−1.631	358.063	309.886	−64.747
298.15	34.452	252.282	252.282	0.	357.419	300.664	−52.675
300	34.495	252.496	252.283	0.064	357.392	300.312	−52.289
350	35.599	257.897	252.707	1.817	356.646	290.857	−43.408
400	36.597	262.717	253.663	3.622	353.625	281.600	−36.773
450	37.497	267.081	254.915	5.475	352.101	272.680	−31.652
500	38.297	271.074	256.334	7.370	350.478	263.944	−27.574
600	39.598	278.177	259.397	11.268	347.513	246.918	−21.496
700	40.520	284.355	262.531	15.277	344.853	230.375	−17.191
800	41.118	289.808	265.607	19.361	342.639	214.174	−13.984
900	41.463	294.673	268.571	23.492	287.384	199.325	−11.569
1000	41.624	299.051	271.404	27.648	286.494	189.588	−9.903
1100	41.658	303.021	274.100	31.813	285.530	179.943	−8.545
1200	41.608	306.644	276.664	35.977	284.477	170.390	−7.417
1300	41.507	309.971	279.099	40.133	283.321	160.929	−6.466
1400	41.377	313.042	281.416	44.277	282.052	151.561	−5.655
1500	41.234	315.892	283.620	48.408	280.664	142.287	−4.955
1600	41.087	318.549	285.721	52.524	279.153	133.111	−4.346
1700	40.944	321.035	287.726	56.625	277.512	124.033	−3.811
1800	40.807	323.371	289.642	60.713	258.592	115.770	−3.360
1900	40.679	325.574	291.476	64.787	256.785	107.885	−2.966
2000	40.562	327.658	293.233	68.849	254.955	100.095	−2.614
2100	40.456	329.634	294.920	72.900	253.102	92.397	−2.298
2200	40.362	331.514	296.541	76.940	251.229	84.789	−2.013
2300	40.278	333.306	298.101	80.972	249.338	77.265	−1.755
2400	40.206	335.019	299.604	84.996	247.430	69.825	−1.520
2500	40.144	336.659	301.053	89.014	245.508	62.464	−1.305
2600	40.092	338.232	302.453	93.026	243.572	55.181	−1.109
2700	40.049	339.745	303.807	97.032	241.626	47.972	−0.928
2800	40.015	341.200	305.116	101.036	239.670	40.835	−0.762
2900	39.990	342.604	306.385	105.036	237.706	33.768	−0.608
3000	39.973	343.960	307.615	109.034	235.734	26.770	−0.466
3100	39.963	345.270	308.809	113.031	233.756	19.837	−0.334
3200	39.961	346.539	309.968	117.027	−145.061	18.156	−0.296
3300	39.964	347.769	311.095	121.023	−145.395	23.262	−0.368
3400	39.974	348.962	312.191	125.020	−145.731	28.378	−0.436
3500	39.990	350.121	313.258	129.018	−146.070	33.504	−0.500
3600	40.011	351.248	314.298	133.018	−146.411	38.639	−0.561
3700	40.036	352.344	315.312	137.020	−146.756	43.784	−0.618
3800	40.066	353.412	316.300	141.025	−147.105	48.938	−0.673
3900	40.100	354.453	317.265	145.034	−147.457	54.102	−0.725
4000	40.138	355.469	318.208	149.046	−147.815	59.275	−0.774
4100	40.178	356.461	319.129	153.061	−148.178	64.457	−0.821
4200	40.222	357.429	320.029	157.081	−148.547	69.647	−0.866
4300	40.269	358.376	320.910	161.106	−148.923	74.847	−0.909
4400	40.318	359.303	321.772	165.135	−149.308	80.055	−0.950
4500	40.369	360.209	322.616	169.169	−149.701	85.272	−0.990
4600	40.422	361.097	323.443	173.209	−150.104	90.498	−1.028
4700	40.476	361.967	324.253	177.254	−150.518	95.733	−1.064
4800	40.532	362.820	325.048	181.304	−150.944	100.977	−1.099
4900	40.589	363.656	325.828	185.360	−151.384	106.230	−1.132
5000	40.647	364.477	326.592	189.422	−151.838	111.492	−1.165
5100	40.706	365.282	327.343	193.490	−152.307	116.763	−1.196
5200	40.765	366.073	328.080	197.563	−152.793	122.044	−1.226
5300	40.825	366.850	328.804	201.643	−153.298	127.334	−1.255
5400	40.886	367.614	329.516	205.728	−153.822	132.634	−1.283
5500	40.946	368.365	330.216	209.820	−154.366	137.943	−1.310
5600	41.007	369.103	330.904	213.918	−154.933	143.263	−1.336
5700	41.067	369.829	331.580	218.021	−155.524	148.593	−1.362
5800	41.128	370.544	332.246	222.131	−156.139	153.934	−1.386
5900	41.188	371.248	332.901	226.247	−156.781	159.286	−1.410
6000	41.249	371.941	333.546	230.369	−157.451	164.648	−1.433

PREVIOUS: December 1976 (1 atm) CURRENT: December 1976 (1 bar)

$S°(298.15\ K) = [71.965 \pm 8.4]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1280 \pm 5\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -131.38 \pm 16.7\ kJ·mol^{-1}$
$\Delta_{fus} H° = [65.689 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

Our analysis of equilibrium data involving NiS_2 is summarized below.

Source	Reaction*	T/K	Data Points	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
[1]	A	298.15	1	calorimetric	−35.1	
[2]	B	923–1033	5	−46.3 ± 0.4	−47.1 ± 0.1	−0.8 ± 0.4
[3]	B	673–873	equation	−49.2	−48.7	0.7
[4]	C	500–723	2	13.9	−5.1 ± 9.9	−31.4
[5]	C	673–873	20	−2.9 ± 0.2	−7.5 ± 2.4	−14.1 ± 0.3
[6]	A	298.15	1	emf[$\Delta G°(298.15\ K) = -24.3$)]	−25.9	

*A) $Ni(cr) + 2\ S(cr) = NiS_2(cr)$
B) $2\ Ni_{1-x}S(cr) + S_2(g) = 2\ NiS_2(cr)$
C) $Ni_{1-x}S(cr) + H_2S(g) = NiS_2(cr) + H_2(g)$

The studies due to Delafosse and Barret[4] and Rosenqvist[5] show poor agreement between 2nd and 3rd law values of $\Delta_f H°$ as well as a large 3rd law drift and are not considered further. Kullerud and Yund[7] mention that a coating of $NiS_2(cr)$ often forms on $Ni_{1-x}S(cr)$ and it seems possible that this may lead to a slow establishment of equilibrium in this system. DeRanter and Breckpot[6] state that their results may be biased for $NiS_2(cr)$ since it is a semiconductor and this may interfere in emf measurements. Consequently their results are not considered further. 3rd law results of Biltz *et al.*[2] and Leegaard and Rosenquist[3] yield values of $\Delta_f H°(298.15\ K) = -29.1 \pm 1.6$ and -29.8 ± 1.7 kcal·mol^{-1}, respectively, when combined with auxiliary JANAF data.[8] These values are averaged with the calorimetric value due to Ariya[1] of −35.1 kcal·mol^{-1} to yield the adopted value of −31.4 kcal·mol^{-1}. An uncertainty of ±4 kcal·mol^{-1} is assigned due mainly to the variation in stoichiometry of one of the reactants, $Ni_{1-x}S$. The adopted value compares favorably with a value of −32.0 kcal·mol^{-1} obtained by Mills[9] in a recent critical evaluation. It also compares favorably with a value of −31.3 kcal·mol^{-1} calculated assuming the same contribution per gram–atom as in NiS and Ni_3S_2.[8]

Heat Capacity and Entropy

The only heat capacity measurements on NiS_2 are those of Winterberger and Bonnerot[10] at low temperature (5–10 K). Consequently the heat capacity is estimated via the following procedure. The value at 298.15 K is estimated assuming the same contribution per gram–atom as in NiS and Ni_3S_2[8] yielding $C_p°(298.15\ K) = 16.88$ cal·K^{-1}·mol^{-1}. The temperature dependence is estimated using method A of Kubaschewski *et al.*[11] This yields $C_p° = 15.401 + 4.960 \times 10^{-3}\ T$.

2nd law analyses of equilibrium data of Leegaard and Rosenqvist[3] and Biltz *et al.*[2] combined with auxiliary JANAF data[8] yield $S°(298.15\ K) = 16.89$ and 17.60 cal·K^{-1}·mol^{-1}, respectively. We adopt the average of these values, 17.2 cal·K^{-1}·mol^{-1}, with an uncertainty estimated to be ±2 cal K^{-1}·mol^{-1}. Similar analyses of studies of Delafosse and Barret[4] and Rosenqvist[5] give values of 13.10 and 29.96 cal·K^{-1}·mol^{-1}, respectively, but as mentioned above, these studies do not appear to be reliable since equilibrium may not have been established. A value of 19.10 cal·K^{-1}·mol^{-1} is obtained assuming the same contribution per gram–atom as in NiS and Ni_3S_2.[8] This is somewhat higher than the adopted value but this may be reasonable since the crystal symmetry of NiS_2 is higher (cubic) than that of NiS and Ni_3S_2 (hexagonal).[7]

Fusion Data

The melting point of $NiS_2(cr)$ is taken from the phase study by Kullerud and Yund.[7] The enthalpy of melting of NiS_2 is unknown and is estimated as follows. Lewis and Randall[12] point out that the sum of the entropy of transition(s) plus the entropy of fusion is approximately constant, on a gram–atom basis, for compounds of similar structure. Using NiS and Ni_3S_2[8] as base compounds, we calculate the above sums to be 4.06 and 4.13 cal·K^{-1} g–atom^{-1}, respectively. Since NiS_2 has no known transition, we use the average value of 4.10 cal·K^{-1}·g–atom^{-1} to calculate $\Delta_{fus} S°(NiS_2) = 12.3$ cal·K^{-1}·mol^{-1} which yields $\Delta_{fus} H° = 15.7$ kcal·mol^{-1} with an estimated uncertainty of ±2.0 kcal·mol^{-1}.

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Continued on page 1715

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	70.626	71.965	71.965	0.	−131.378	−124.813	21.867
300	70.664	72.402	71.966	0.131	−131.379	−124.772	21.725
400	72.739	93.015	74.763	7.301	−136.131	−122.358	15.978
500	74.814	109.469	80.112	14.678	−139.577	−118.542	12.384
600	76.889	123.292	86.186	22.264	−142.439	−114.057	9.930
700	78.965	135.301	92.363	30.056	−144.663	−109.134	8.144
800	81.040	145.981	98.410	38.057	−146.172	−103.951	6.787
900	83.115	155.646	104.241	46.264	−253.607	−96.438	5.597
1000	85.190	164.510	109.830	54.680	−252.093	−79.055	4.129
1100	87.266	172.727	115.179	63.302	−250.470	−61.829	2.936
1200	89.341	180.409	120.298	72.133	−248.744	−44.755	1.948
1280.000	91.001	186.228	124.238	79.346	--- CRYSTAL <--> LIQUID ---		
1300	91.416	187.642	125.203	81.171	−246.921	−27.829	1.118
1400	93.491	194.493	129.910	90.416	−245.007	−11.047	0.412
1500	95.567	201.014	134.434	99.869	−243.006	5.595	−0.195
1600	97.642	207.248	138.792	109.529	−240.921	22.101	−0.722
1700	99.717	213.229	142.996	119.397	−238.758	38.474	−1.182
1800	101.793	218.988	147.058	129.473	−253.667	55.432	−1.609

PREVIOUS: CURRENT: March 1977

$S°(298.15\ K) = [122.427]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1280 \pm 5\ K$

$\Delta_f H°(298.15\ K) = [-66.568]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [65.689 \pm 8.4]\ kJ·mol^{-1}$

Enthalpy of Formation

There are no experimental studies of the enthalpy of formation of NiS_2(l). Therefore, $\Delta_f H°(NiS_2, l, 298.15\ K)$ is calculated from that of NiS_2(cr)[1] by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1280\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity is assumed to remain constant at 21.75 $cal·K^{-1}·mol^{-1}$ (the value of NiS_2(cr) at the melting point) above an assumed glass transition point of 960 K. Below that temperature the crystal heat capacity[1] is assumed to be valid.

$S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

Under standard conditions (1 atm. pressure) the use of auxiliary JANAF data[1] indicates that NiS_2(l) will decompose spontaneously to NiS(l) + 1/2 S_2(g) at all temperatures above the normal melting point. This appears to be at variance with the phase diagram of Kullerud and Yund[2] which indicates the presence of a liquid of variable composition in the Ni S system from a stoichiometry less than Ni_3S_2 to just above NiS_2 at temperatures slightly above the melting point. However, the authors point out that this diagram does not refer to a constant pressure system and give a short discussion of the loss of sulfur to the vapor from NiS_2(cr). From the sealed tube experiments of Kullerud and Yund[2] it does appear that NiS_2(l) will be stable under its own vapor pressure in a sealed tube.

References

[1]JANAF Thermochemical Tables: NiS_2(cr), 3–31–77; NiS(l), 12–31–76; S_2(g), 12–31–65.
[2]G. Kullerud and R. A. Yund, J. Petrology **3**, 126 (1962).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	70.626	122.427	122.427	0.	−66.568	−75.048	13.148
300	70.664	122.864	122.428	0.131	−66.569	−75.101	13.076
400	72.739	143.477	125.225	7.301	−71.321	−77.733	10.151
500	74.814	159.931	130.574	14.678	−74.767	−78.963	8.249
600	76.889	173.754	136.648	22.264	−77.629	−79.524	6.923
700	78.965	185.763	142.825	30.056	−79.853	−79.647	5.943
800	81.040	196.443	148.872	38.057	−81.362	−79.511	5.192
900	83.115	206.108	154.703	46.264	−188.797	−77.044	4.471
960.000	84.360	211.511	158.086	51.289	GLASS <--> LIQUID		
960.000	91.002	211.511	158.086	51.289	TRANSITION		
1000	91.002	215.226	160.298	54.929	−187.034	−64.712	3.380
1100	91.002	223.900	165.692	64.029	−184.934	−52.582	2.497
1200	91.002	231.818	170.877	73.129	−182.937	−40.639	1.769
1280.000	91.002	237.691	174.871	80.409	--- CRYSTAL <--> LIQUID ---		
1300	91.002	239.102	175.849	82.229	−181.052	−28.858	1.160
1400	91.002	245.846	180.611	91.329	−179.283	−17.218	0.642
1500	91.002	252.124	185.171	100.430	−177.635	−5.700	0.199
1600	91.002	257.998	189.541	109.530	−176.111	5.712	−0.186
1700	91.002	263.515	193.732	118.630	−174.715	17.032	−0.523
1800	91.002	268.716	197.755	127.730	−190.600	28.989	−0.841

PREVIOUS: CURRENT: March 1977

0 to 1280 K crystal
above 1280 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	70.626	71.965	71.965	0.	−131.378	−124.813	21.867
300	70.664	72.402	71.966	0.131	−131.379	−124.772	21.725
400	72.739	93.015	74.763	7.301	−136.131	−122.358	15.978
500	74.814	109.469	80.112	14.678	−139.577	−118.542	12.384
600	76.889	123.292	86.186	22.264	−142.439	−114.057	9.930
700	78.965	135.301	92.363	30.056	−144.663	−109.134	8.144
800	81.040	145.981	98.410	38.057	−146.172	−103.951	6.787
900	83.115	155.646	104.241	46.264	−253.607	−96.438	5.597
1000	85.190	164.510	109.830	54.680	−252.093	−79.055	4.129
1100	87.266	172.727	115.179	63.302	−250.470	−61.829	2.936
1200	89.341	180.409	120.298	72.133	−248.744	−44.755	1.948
1280.000	91.001	186.228	124.238	79.346	CRYSTAL <-- --> LIQUID		
1280.000	91.002	237.691	124.238	145.219	TRANSITION		
1300	91.002	239.102	125.995	147.039	−181.052	−28.858	1.160
1400	91.002	245.846	134.318	156.140	−179.283	−17.218	0.642
1500	91.002	252.124	141.965	165.240	−177.635	−5.700	0.199
1600	91.002	257.998	149.035	174.340	−176.111	5.712	−0.186
1700	91.002	263.515	155.609	183.440	−174.715	17.032	−0.523
1800	91.002	268.716	161.749	192.540	−190.600	28.989	−0.841

PREVIOUS: CURRENT: March 1977

$S°(298.15\ K) = 133.887 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 829 \pm 3\ K$
$T_{fus} = 1062 \pm 3\ K$

$\Delta_f H°(0\ K) = -214.29 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -216.31 \pm 5.0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 56.233 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 19.748 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Three sets of authors studied the phase equilibrium between Ni_3S_2(cr) and Ni(cr) by use of the $H_2(g)/H_2S(g)$ method.[1,2,3] Our 3rd law analyses of the data due to Rosenqvist,[1] Sudo[2] and Line and Laffitte[3] yield $\Delta_f H°(298.15\ K = -51.6 \pm 1.0, -50.1 \pm 1.6$, and -53.4 ± 1.8 kcal·mol^{-1}, respectively. We adopt the average of the values, $\Delta_f H°(298.15\ K) = -51.7 \pm 1.7$ kcal·mol^{-1}. Ariya *et al.*[4] and Vanyukov and Kiseleva[5] reported calorimetric values of -48.3 ± 0.9 and -43.3 kcal·mol^{-1}, respectively. Vanuykov's value is undoubtedly incorrect since Mills[6] determined that values for Fes and MnS from the same study are approximately 25% too low. A 3rd law analysis of the emf value reported by DeRanter and Breckpot[7] yields $\Delta_f H°(298.15\ K) = -38.7$ kcal·mol^{-1}. This value, however, refers to an amorphous material. At least part of the variation in values of the enthalpy of formation apparently is a result of the very wide range of stoichiometry for the high temperature phase of Ni_3S_2.[8,9]

Heat Capacity and Entropy

The low temperature heat capacities (52–296 K) are from Weller and Kelley.[10] The high heat capacities are from our analysis of the high temperature enthalpy (298.15–1050 K) data of Conard *et al.*[11] Our analysis differs slightly from that of Conard *et al.*[11] since we have forced the high and low temperature heat capacities to join smoothly at 298.15 K. Data above 1050 K are extrapolated assuming a constant heat capacity for the high temperature phase of Ni_3S_2. The thermodynamic functions show good agreement with those reported by Mah and Pankrantz.[12]

The entropy at 298.15 is calculated based on an extrapolation of $S°(51\ K) = 2.06$ cal·K^{-1}·mol^{-1} by Weller and Kelley.[10]

Phase Data

A phase transition is observed at 829 K for Ni_3S_2.[8] Below the transition, Kullerud and Yund[8] reported the material to be stoichiometric within the limits of ±0.3 weight percent while Rau[9] reported the homogeneity range to extend over a smaller range and to the sulfur rich side only. Above the phase transition, a wide range of homogeneity exists for $Ni_{3\pm x}S_2$ from approximately $Ni_{2.5}S_2$ to $Ni_{3.7}S_2$.[1,8,9] The phase diagram indicates that upon heating stoichiometric Ni_3S_2, a two phase region [Ni_yS_z(l) + $Ni_{3\pm x}S_2$(cr)] will be encountered within a few degrees of the formation of stoichiometric liquid Ni_3S_2.[8,9]

Transition Data

We adopt a value of 829 ± 3 K for the phase transition from Ni_3S_2 to $Ni_{3\pm x}S_2$ based on the detailed study by Kullerud and Yund.[8] This value is in fair agreement with values of 838 and 828 ± 5 reported by Rau[9] and Rosenqvist,[1] respectively. The adopted heat of transition is from our analysis of the high temperature enthalpy data of Conard *et al.*[11] Mah and Pankrantz[12] reported the transition at 840 K with $\Delta_f H° = 13.38$ kcal·mol^{-1} in excellent agreement with the adopted $\Delta_{trs} H°$.

Fusion Data

Kullerud and Yung[8] reported that stoichiometric Ni_3S_2 begins to melt at 1055 K with melting completed at 1062 K. The cooling curve yielded identical results. In view of the two phase region in the phase diagram, we adopt the latter temperature as the melting point with an estimated uncertainty of ±3 K. The adopted heat of melting is from our analysis of Conard's *et al.* high temperature enthalpy data[11] and is in good agreement with a value of 4.70 kcal·mol^{-1} reported by Mah and Pankrantz.[12]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.156	−214.288	−214.288	INFINITE
100	58.116	33.666	225.939	−19.227	−215.261	−213.887	111.723
200	101.489	89.917	144.221	−10.861	−215.847	−212.256	55.436
298.15	117.738	133.887	133.887	0.	−216.313	−210.399	36.861
300	117.947	134.616	133.889	0.218	−216.323	−210.362	36.627
400	127.110	169.857	138.632	12.490	−221.430	−208.103	27.175
500	133.972	198.975	147.871	25.552	−225.126	−204.371	21.350
600	139.913	223.932	158.516	39.249	−228.432	−199.906	17.403
700	145.436	245.918	169.462	53.519	−230.824	−194.922	14.545
800	150.708	265.685	180.275	68.328	−231.697	−189.725	12.388
829.000	152 .190	271.078	183.357	72.720	I <--> II		
829.000	188 .615	338.910	183.357	128.953	TRANSITION		
900	188.615	354.410	196.248	142.345	−279.582	−187.213	10.866
1000	188.615	374.282	213.076	161.206	−274.001	−177.251	9.259
1062.000	188 .615	385.628	222.821	172.901	------ II <--> LIQUID -----		
1100	188.615	392.259	228.561	180.068	−268.653	−167.837	7.970
1200	188.615	408.671	242.896	198.929	−263.555	−158.899	6.917
1300	188.615	423.768	256.236	217.791	−258.727	−150.376	6.042
1400	188.615	437.746	268.708	236.652	−254.188	−142.213	5.306
1500	188.615	450.759	280.416	255.514	−249.949	−134.365	4.679
1600	188.615	462.932	291.447	274.375	−246.023	−126.789	4.139

PREVIOUS: CURRENT: December 1976

Nickel Sulfide (Ni_3S_2) LIQUID M_r = 240.19

$S°(298.15\ K) = [215.930]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1062 \pm 3\ K$

$\Delta_f H°(298.15\ K) = [-143.926]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 19.748 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is derived from that of Ni_3S_2(cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1062\ K)-H°(298.15\ K)$, between crystal and liquid. Our 2nd and 3rd law analyses of Nagamori and Ingraham's equilibrium data[1] yield $\Delta_f H°(298.15\ K) = -33.7 \pm 6$ and $-33.9 \pm 0.3\ kcal·mol^{-1}$, respectively, in good agreement with the adopted value. Meyer *et al.*[2] and Rosenqvist[3] conducted similar studies at higher and lower temperatures, respectively. Both studies qualitatively show good agreement with Nagamori and Ingraham at overlapping temperatures,[2] but Meyer's data are only presented graphically so a re analysis is not feasible. Rosenqvist's study included compositions near, but not exactly at, the Ni_3S_2 stoichiometry. Our extrapolation of his data to the proper stoichiometry leads to a higher value of $K_p°$ at 900 K than at 800 or 1000 K. We conclude that Rosenqvist's data are not of sufficient precision for the small number of points at each temperature (3 or 4) to yield meaningful results when extrapolated.

Heat Capacity and Entropy

The enthalpy of Ni_3S_2(l) from the melting point to 1250 K was measured by Conard *et al.*[4] Our analysis of these data yields the adopted constant heat capacity of $45.84\ cal·K^{-1}·mol^{-1}$. Above 1250 K the heat capacity is assumed to remain constant. This value is in good agreement with a value of $45.20\ cal·K^{-1}·mol^{-1}$ reported by Mah and Pankrantz.[5]

$S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Decomposition Data

There is no evidence for the existence of Ni_3S_2(g). In the absence of such information we can only point out that Ni_3S_2(l) will decompose to the gaseous elements at 3240 ± 15 K according to the Gibbs energy of formation in this table. This seems to yield an excessively long liquid range for Ni_3S_2.

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[5] A. D. Mah and L. B. Pankrantz, U. S. Bur. Mines Bull. 668, 125 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	117.738	215.930	215.930	0.	−143.926	−162.473	28.465
300	117.947	216.659	215.932	0.218	−143.937	−162.588	28.309
400	127.110	251.900	220.675	12.490	−149.043	−168.534	22.008
500	133.972	281.018	229.914	25.552	−152.739	−173.006	18.074
600	139.913	305.975	240.560	39.249	−156.045	−176.745	15.387
700	145.436	327.963	251.505	53.520	−158.436	−179.966	13.429
760.000	148.549	340.051	258.024	62.341	GLASS <--> LIQUID TRANSITION		
760.000	191 .795	340.051	258.024	62.341			
800	191.795	349.889	262.373	70.012	−157.626	−183.018	11.950
900	191.795	372.479	273.377	89.192	−260.348	−184.242	10.693
1000	191.795	392.686	284.315	108.371	−254.450	−176.104	9.199
1062.000	191.795	404.224	290.982	120.263	----- II <--> LIQUID -----		
1100	191.795	410.966	295.011	127.551	−248.784	−168.546	8.004
1200	191.795	427.655	305.379	146.730	−243.368	−161.493	7.030
1300	191.795	443.006	315.383	165.910	−238.222	−154.880	6.223
1400	191.795	457.220	325.013	185.089	−233.365	−148.654	5.546
1500	191.795	470.452	334.273	204.269	−228.808	−142.764	4.971
1600	191.795	482.830	343.175	223.448	−224.564	−137.168	4.478
1700	191.795	494.458	351.736	242.628	−220.648	−131.827	4.051
1800	191.795	505.421	359.972	261.807	−268.516	−124.563	3.615
1900	191.795	515.790	367.903	280.987	−264.989	−116.662	3.207
2000	191.795	525.628	375.545	300.166	−261.486	−108.946	2.845
2100	191.795	534.986	382.917	319.345	−258.004	−101.404	2.522
2200	191.795	543.908	390.033	338.525	−254.543	−94.028	2.233
2300	191.795	552.434	396.910	357.704	−251.101	−86.809	1.972
2400	191.795	560.596	403.562	376.884	−247.677	−79.740	1.735
2500	191.795	568.426	410.001	396.063	−244.268	−72.812	1.521
2600	191.795	575.948	416.240	415.243	−240.874	−66.021	1.326
2700	191.795	583.187	422.290	434.422	−237.491	−59.360	1.148
2800	191.795	590.162	428.161	453.602	−234.121	−52.825	0.985
2900	191.795	596.892	433.864	472.781	−230.762	−46.409	0.836
3000	191.795	603.394	439.407	491.961	−227.413	−40.109	0.698
3100	191.795	609.683	444.799	511.140	−224.074	−33.921	0.572
3200	191.795	615.772	450.048	530.319	−1351.248	−12.274	0.200
3300	191.795	621.674	455.159	549.499	−1342.966	29.440	−0.466
3400	191.795	627.400	460.141	568.678	−1334.689	70.904	−1.089
3500	191.795	632.959	465.000	587.858	−1326.421	112.125	−1.673
3600	191.795	638.362	469.741	607.037	−1318.162	153.109	−2.222
3700	191.795	643.617	474.370	626.217	−1309.915	193.864	−2.737
3800	191.795	648.732	478.891	645.396	−1301.683	234.397	−3.222

PREVIOUS: CURRENT: December 1976

0	to	829	K crystal, I
829	to	1062	K crystal, II
above		1062	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−21.156	−214.288	−214.288	INFINITE
100	58.116	33.666	225.939	−19.227	−215.261	−213.887	111.723
200	101.489	89.917	144.221	−10.861	−215.847	−212.256	55.436
298.15	117.738	133.887	133.887	0.	−216.313	−210.399	36.861
300	117.947	134.616	133.889	0.218	−216.323	−210.362	36.627
400	127.110	169.857	138.632	12.490	−221.430	−208.103	27.175
500	133.972	198.975	147.871	25.552	−225.126	−204.371	21.350
600	139.913	223.932	158.516	39.249	−228.432	−199.906	17.403
700	145.436	245.918	169.462	53.519	−230.824	−194.922	14.545
800	150.708	265.685	180.275	68.328	−231.697	−189.725	12.388
829.000	152.190	271.078	183.357	72.720	I <--> II		
829.000	188.615	338.910	183.357	128.953	TRANSITION		
900	188.615	354.410	196.248	142.345	−279.582	−187.213	10.866
1000	188.615	374.282	213.076	161.206	−274.001	−177.251	9.259
1062.000	188.615	385.628	222.821	172.901	II <--> LIQUID		
1062.000	191.795	404.224	222.821	192.649	TRANSITION		
1100	191.795	410.966	229.205	199.937	−248.784	−168.546	8.004
1200	191.795	427.655	245.057	219.117	−243.368	−161.493	7.030
1300	191.795	443.006	259.702	238.296	−238.222	−154.880	6.223
1400	191.795	457.220	273.309	257.476	−233.365	−148.654	5.546
1500	191.795	470.452	286.016	276.655	−228.808	−142.764	4.971
1600	191.795	482.830	297.934	295.834	−224.564	−137.168	4.478
1700	191.795	494.458	309.156	315.014	−220.648	−131.827	4.051
1800	191.795	505.421	319.758	334.193	−268.516	−124.563	3.615
1900	191.795	515.790	329.805	353.373	−264.989	−116.662	3.207
2000	191.795	525.628	339.352	372.552	−261.486	−108.946	2.845
2100	191.795	534.986	348.447	391.732	−258.004	−101.404	2.522
2200	191.795	543.908	357.130	410.911	−254.543	−94.028	2.233
2300	191.795	552.434	365.438	430.091	−251.101	−86.809	1.972
2400	191.795	560.596	373.401	449.270	−247.677	−79.740	1.735
2500	191.795	568.426	381.046	468.450	−244.268	−72.812	1.521
2600	191.795	575.948	388.399	487.629	−240.874	−66.021	1.326
2700	191.795	583.187	395.480	506.809	−237.491	−59.360	1.148
2800	191.795	590.162	402.309	525.988	−234.121	−52.825	0.985
2900	191.795	596.892	408.903	545.167	−230.762	−46.409	0.836
3000	191.795	603.394	415.279	564.347	−227.413	−40.109	0.698
3100	191.795	609.683	421.449	583.526	−224.074	−33.921	0.572
3200	191.795	615.772	427.427	602.706	−1351.248	−12.274	0.200
3300	191.795	621.674	433.224	621.885	−1342.966	29.440	−0.466
3400	191.795	627.400	438.851	641.065	−1334.689	70.904	−1.089
3500	191.795	632.959	444.318	660.244	−1326.421	112.125	−1.673
3600	191.795	638.362	449.634	679.424	−1318.162	153.109	−2.222
3700	191.795	643.617	454.806	698.603	−1309.915	193.864	−2.737
3800	191.795	648.732	459.842	717.783	−1301.683	234.397	−3.222

PREVIOUS: CURRENT: December 1976

$S°(298.15\ K) = 186.48 \pm 16.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -301.11 \pm 25.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The only measured value of $\Delta_f H°(298.15\ K)$ for Ni_3S_4 is based on the emf data of DeRanter and Breckpot.[1] Our 3rd law analysis of their data yields $\Delta_f H°(298.15\ K) = -71.0\ kcal \cdot mol^{-1}$. A value of $-72.9\ kcal \cdot mol^{-1}$ can be estimated assuming the same contribution per gram atom in NiS and Ni_3S_2.[2] The adopted value, $\Delta_f H°(298.15\ K) = -72.0 \pm 6.0\ kcal \cdot mol^{-1}$, lies approximately midway between the above values and is chosen so that $\Delta_r G(629\ K) = 0$ for reaction $Ni_3S_4(cr) = 2\ NiS(cr) + NiS_2(cr)$.[2] This temperature represents the decomposition point of Ni_3S_4(cr).[3,4]

Heat Capacity and Entropy

Since there are no measured values for the heat capacity of Ni_3S_4 it is estimated as follows. The value of $C_p°(298.15\ K)$ is estimated assuming the same contribution per gram atom as in NiS and Ni_3S_2,[2] yielding a value of $39.39\ cal \cdot K^{-1} \cdot mol^{-1}$. The value at the melting point is estimated assuming a contribution of $7.25\ cal \cdot K^{-1} \cdot g\text{-}atom^{-1}$ and the heat capacity is assumed to be linear between these two points.[5] This leads to $C_p°(cal \cdot K^{-1} \cdot mol^{-1}) = 29.153 \pm 0.03434\ T$.

The value of $S°(298.15\ K)$ is estimated assuming the same contribution per gram atom as in NiS and Ni_3S_2.[2] This estimate is subject to a rather large uncertainty since Ni_3S_4 has a spinel structure.[6] Navrotsky and Kleppa[7] showed that the entropies of oxide spinels vary by $\pm 3.7\ cal \cdot K^{-1} \cdot mol^{-1}$ depending on the distribution of cations among the available octahedral and tetrahedral sites.

Decomposition Data

The decomposition temperature of Ni_3S_4 is $629 \pm 3\ K$.[3,4] It decomposes according to $Ni_3S_4(cr) = 2\ Ni_{1-x}S(cr) + NiS_2(cr)$. As mentioned above, $\Delta_f H°(298.15\ K)$ for Ni_3S_4(cr) was chosen so that $\Delta_r G°(629\ K)$ for this reaction is zero. The value of $\Delta_r H°(629\ K)$ for this reaction, as calculated using auxiliary JANAF data,[2] is $2.2\ kcal \cdot mol^{-1}$. Kullerud and Yund[4] calculate $\Delta_r H°(629\ K) = +7.0\ kcal \cdot mol^{-1}$ for this reaction based on the volume change as calculated from cell dimensions for the three compounds.

Phase Data

The known crystal species in the Ni–S system include NiS, Ni_3S_2, Ni_3S_4, NiS_2, and Ni_7S_6.[3] The first four species occur naturally as minerals and we have prepared JANAF Thermochemical Tables for these species.[2] The species Ni_7S_6 (sometimes reported as Ni_9S_8 or Ni_6S_5) does not occur as a mineral and we have not prepared a table since there is a lack of thermochemical data. It is interesting to note that Ni_2S_3 does not occur as a stable species even though stable M_2S_3 species have been observed for Cr, Fe, and Co.[8] Estimates of $\Delta_f H°(298.15\ K)$ for Ni_2S_3 range from +225 to +484 $kcal \cdot mol^{-1}$.[9] Although Moody and Thomas[9] acknowledge large uncertainties in their calculations, they are unlikely to be in error to the extent necessary to predict stability for Ni_2S_3(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	164.808	186.481	186.481	0.	−301.115	−291.767	51.116
300	165.076	187.501	186.484	0.305	−301.122	−291.709	50.791
400	179.439	236.957	193.130	17.531	−310.469	−288.149	37.628
500	193.807	278.542	206.155	36.193	−316.421	−281.917	29.452
600	208.171	315.147	221.326	56.292	−320.495	−274.604	23.906
700	222.539	348.315	237.133	77.828	−322.315	−266.754	19.905
800	236.906	378.969	252.969	100.800	−321.447	−258.855	16.902
900	251.270	407.702	268.581	125.209	−531.454	−246.842	14.326
1000	265.638	434.919	283.865	151.054	−522.601	−215.682	11.266
1100	280.002	460.911	298.787	178.336	−512.576	−185.466	8.807

PREVIOUS: CURRENT: March 1977

Continued from page 1708

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IP(O, g) = 109837.02 ± 0.06 cm^{-1}
$S°$(298.15 K) = 161.058 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 246.79 ± 0.10 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 249.17 ± 0.10 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0	5
$^3P_1$	158.265	3
$^3P_0$	226.977	1
$^1D_2$	15867.862	5
$^1S_0$	33792.583	1

Enthalpy of Formation

The enthalpy of formation is based on the dissociation energy of O_2(g), 41260 ± 15 cm^{-1} (493.579 ± 0.18 $kJ·mol^{-1}$), as recommended by CODATA.[1] This value is derived from the spectroscopic study of Brix and Herzberg.[2] The products of dissociation are assumed to be oxygen atoms in their ground states. The justification for this is discussed by Gaydon[3] and Krupenie.[4]

Heat Capacity and Entropy

The electronic levles for O(g) are given in the compilation by Moore.[5] Our calcualtions indicate that, except for the five states lying below 34000 cm^{-1}, the inclusion of levels up to n=12 has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of these levels; the fifth excited state lies at 73768.20 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the lowest lying status (ϵ_i< 34000 cm^{-1}). The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative atomic mass, the fundamental constants, and the position of the low lying electronic levles. The calculated value of S(298.15 K) is 0.0094 $J·K^{-1}·mol^{-1}$ greater than that recommended by CODATA[1] due to the use of a 1 bar standard state pressure (CODATA used 1 atm). The difference is due to our use of the current CODATA fundamental constants.[6] Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cut off procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.725	246.790	246.790	INFINITE
100	23.703	135.947	181.131	−4.518	247.544	242.615	−126.729
200	22.734	152.153	163.085	−2.186	248.421	237.339	−61.986
250	22.246	157.170	161.421	−1.063	248.816	234.522	−49.001
298.15	21.911	161.058	161.058	0.	249.173	231.736	−40.599
300	21.901	161.194	161.059	0.041	249.187	231.628	−40.330
350	21.657	164.551	161.324	1.129	249.537	228.673	−34.128
400	21.482	167.430	161.912	2.207	249.868	225.670	−29.469
450	21.354	169.953	162.668	3.278	250.180	222.626	−25.842
500	21.257	172.197	163.511	4.343	250.474	219.549	−22.936
600	21.124	176.060	165.291	6.462	251.013	213.312	−18.570
700	21.040	179.310	167.067	8.570	251.494	206.990	−15.446
800	20.984	182.116	168.777	10.671	251.926	200.602	−13.098
900	20.944	184.585	170.399	12.767	252.320	194.163	−11.269
1000	20.915	186.790	171.930	14.860	252.682	187.681	−9.803
1100	20.893	188.782	173.373	16.950	253.018	181.165	−8.603
1200	20.877	190.599	174.734	19.039	253.332	174.619	−7.601
1300	20.864	192.270	176.019	21.126	253.627	168.047	−6.752
1400	20.853	193.816	177.236	23.212	253.906	161.453	−6.024
1500	20.845	195.254	178.390	25.296	254.171	154.840	−5.392
1600	20.838	196.599	179.486	27.381	254.421	148.210	−4.839
1700	20.833	197.862	180.530	29.464	254.659	141.564	−4.350
1800	20.830	199.053	181.527	31.547	254.884	134.905	−3.915
1900	20.827	200.179	182.479	33.630	255.097	128.234	−3.525
2000	20.826	201.247	183.391	35.713	255.299	121.552	−3.175
2100	20.827	202.263	184.266	37.796	255.488	114.860	−2.857
2200	20.830	203.232	185.106	39.878	255.667	108.159	−2.568
2300	20.835	204.158	185.914	41.962	255.835	101.450	−2.304
2400	20.841	205.045	186.693	44.045	255.992	94.734	−2.062
2500	20.851	205.896	187.444	46.130	256.139	88.012	−1.839
2600	20.862	206.714	188.170	48.216	256.277	81.284	−1.633
2700	20.877	207.502	188.871	50.303	256.405	74.551	−1.442
2800	20.894	208.261	189.550	52.391	256.525	67.814	−1.265
2900	20.914	208.995	190.208	54.481	256.637	61.072	−1.100
3000	20.937	209.704	190.846	56.574	256.741	54.327	−0.946
3100	20.963	210.391	191.466	58.669	256.838	47.578	−0.802
3200	20.991	211.057	192.068	60.767	256.929	40.826	−0.666
3300	21.022	211.704	192.653	62.867	257.014	34.071	−0.539
3400	21.056	212.332	193.223	64.971	257.094	27.315	−0.420
3500	21.092	212.943	193.777	67.079	257.169	20.555	−0.307
3600	21.130	213.537	194.318	69.190	257.241	13.794	−0.200
3700	21.170	214.117	194.845	71.305	257.309	7.030	−0.099
3800	21.213	214.682	195.360	73.424	257.373	0.265	−0.004
3900	21.257	215.234	195.862	75.547	257.436	−6.501	0.087
4000	21.302	215.772	196.353	77.675	257.496	−13.270	0.173
4100	21.349	216.299	196.834	79.808	257.554	−20.040	0.255
4200	21.397	216.814	197.303	81.945	257.611	−26.811	0.333
4300	21.445	217.318	197.763	84.087	257.666	−33.583	0.408
4400	21.495	217.812	198.213	86.234	257.720	−40.358	0.479
4500	21.545	218.295	198.654	88.386	257.773	−47.133	0.547
4600	21.596	218.769	199.086	90.543	257.825	−53.909	0.612
4700	21.647	219.234	199.510	92.705	257.876	−60.687	0.674
4800	21.697	219.690	199.925	94.872	257.926	−67.465	0.734
4900	21.748	220.138	200.333	97.045	257.974	−74.244	0.791
5000	21.799	220.578	200.734	99.222	258.021	−81.025	0.846
5100	21.849	221.010	201.127	101.405	258.066	−87.806	0.899
5200	21.899	221.435	201.514	103.592	258.110	−94.589	0.950
5300	21.949	221.853	201.893	105.784	258.150	−101.371	0.999
5400	21.997	222.264	202.267	107.982	258.189	−108.155	1.046
5500	22.045	222.668	202.634	110.184	258.224	−114.940	1.092
5600	22.093	223.065	202.995	112.391	258.255	−121.725	1.135
5700	22.139	223.457	203.351	114.602	258.282	−128.510	1.178
5800	22.184	223.842	203.701	116.818	258.304	−135.296	1.218
5900	22.229	224.222	204.046	119.039	258.321	−142.083	1.258
6000	22.273	224.596	204.385	121.264	258.332	−148.869	1.296

PREVIOUS: March 1977 (1 atm) CURRENT: September 1982 (1 bar)

$IP(O^+, g) = 283240 \pm 10\ cm^{-1}$
$S°(298.15\ K) = 154.959 \pm 0.02\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1560.733 \pm 0.10\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [1568.786]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4S_{3/2}$	0.0	4
$^2D_{5/2}$	26810.7	6
$^2D_{3/2}$	26830.5	4
$^2P_{3/2}$	40466.9	4
$^2P_{1/2}$	40468.4	2

Enthalpy of Formation

$\Delta_f H°(O^+, g, 0\ K)$ is calculated from $\Delta_f H°(O, g, 0\ K)$[1] using the spectroscopic value of IP(O) = 109837.02 ± 0.06 cm^{-1}(314.040 ± 0.001 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(O^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(O, g, 0\ K)$ by using IP(O) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for O(g), $O^+(g)$, and e^-(ref). $\Delta_f H°(O \rightarrow O^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is 119837.7 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	1560.733		
100	20.786	132.251	173.439	−4.119			
200	20.786	146.659	156.860	−2.040			
250	20.786	151.297	155.301	−1.001			
298.15	20.786	154.959	154.959	0.	1568.786	1546.912	−271.013
300	20.786	155.087	154.959	0.038	1568.835	1546.776	−269.318
350	20.786	158.291	155.212	1.078	1570.176	1542.994	−230.279
400	20.786	161.067	155.774	2.117	1571.507	1539.020	−200.975
450	20.786	163.515	156.501	3.156	1572.827	1534.879	−178.164
500	20.786	165.705	157.314	4.196	1574.135	1530.593	−159.900
600	20.786	169.495	159.038	6.274	1576.712	1521.642	−132.471
700	20.786	172.699	160.766	8.353	1579.242	1512.262	−112.846
800	20.786	175.475	162.435	10.431	1581.731	1502.524	−98.105
900	20.786	177.923	164.023	12.510	1584.185	1492.475	−86.621
1000	20.786	180.113	165.524	14.589	1586.612	1482.155	−77.420
1100	20.786	182.094	166.942	16.667	1589.014	1471.593	−69.880
1200	20.786	183.903	168.281	18.746	1591.397	1460.813	−63.588
1300	20.786	185.566	169.548	20.824	1593.763	1449.834	−58.255
1400	20.786	187.107	170.748	22.903	1596.113	1438.675	−53.678
1500	20.786	188.541	171.887	24.982	1598.450	1427.347	−49.705
1600	20.786	189.882	172.970	27.060	1600.773	1415.865	−46.223
1700	20.786	191.143	174.002	29.139	1603.085	1404.237	−43.147
1800	20.786	192.331	174.988	31.217	1605.384	1392.474	−40.409
1900	20.786	193.455	175.930	33.296	1607.671	1380.583	−37.955
2000	20.786	194.521	176.833	35.375	1609.947	1368.572	−35.743
2100	20.786	195.535	177.700	37.453	1612.212	1356.448	−33.740
2200	20.786	196.502	178.533	39.532	1614.465	1344.216	−31.916
2300	20.786	197.426	179.334	41.611	1616.707	1331.881	−30.248
2400	20.787	198.310	180.107	43.689	1618.938	1319.450	−28.717
2500	20.787	199.159	180.852	45.768	1621.157	1306.925	−27.307
2600	20.788	199.974	181.572	47.847	1623.367	1294.312	−26.003
2700	20.789	200.759	182.268	49.925	1625.565	1281.615	−24.794
2800	20.790	201.515	182.942	52.004	1627.754	1268.836	−23.670
2900	20.792	202.245	183.595	54.083	1629.933	1255.979	−22.623
3000	20.795	202.949	184.229	56.163	1632.102	1243.047	−21.643
3100	20.799	203.631	184.844	58.242	1634.263	1230.043	−20.726
3200	20.804	204.292	185.441	60.323	1636.415	1216.969	−19.865
3300	20.810	204.932	186.022	62.403	1638.558	1203.828	−19.055
3400	20.818	205.553	186.587	64.485	1640.695	1190.622	−18.292
3500	20.827	206.157	187.138	66.567	1642.823	1177.354	−17.571
3600	20.839	206.744	187.674	68.650	1644.946	1164.025	−16.890
3700	20.853	207.315	188.198	70.735	1647.062	1150.636	−16.244
3800	20.870	207.871	188.708	72.821	1649.172	1137.192	−15.632
3900	20.890	208.414	189.206	74.909	1651.278	1123.691	−15.050
4000	20.912	208.943	189.693	76.999	1653.379	1110.136	−14.497
4100	20.938	209.460	190.169	79.091	1655.476	1096.529	−13.970
4200	20.968	209.964	190.634	81.187	1657.569	1082.871	−13.467
4300	21.001	210.458	191.090	83.285	1659.659	1069.163	−12.988
4400	21.038	210.941	191.535	85.387	1661.747	1055.406	−12.529
4500	21.079	211.415	191.972	87.493	1663.832	1041.602	−12.091
4600	21.125	211.879	192.400	89.603	1665.916	1027.752	−11.670
4700	21.174	212.333	192.819	91.718	1667.998	1013.856	−11.268
4800	21.229	212.780	193.230	93.838	1670.079	999.916	−10.881
4900	21.287	213.218	193.634	95.964	1672.160	985.933	−10.510
5000	21.351	213.649	194.030	98.096	1674.240	971.908	−10.153
5100	21.418	214.072	194.418	100.234	1676.319	957.841	−9.810
5200	21.491	214.489	194.800	102.380	1678.399	943.732	−9.480
5300	21.568	214.899	195.176	104.532	1680.479	929.584	−9.162
5400	21.649	215.303	195.545	106.693	1682.560	915.397	−8.855
5500	21.735	215.701	195.908	108.862	1684.640	901.171	−8.559
5600	21.826	216.093	196.265	111.040	1686.721	886.907	−8.273
5700	21.921	216.480	196.616	113.228	1688.803	872.606	−7.997
5800	22.020	216.862	196.962	115.425	1690.885	858.269	−7.730
5900	22.123	217.240	197.302	117.632	1692.967	843.895	−7.471
6000	22.231	217.612	197.638	119.850	1695.049	829.487	−7.221

PREVIOUS: March 1977 (1 atm) CURRENT: September 1982 (1 bar)

EA(O, g) = 1.4611215 ± 0.0000010 eV
$S°$(298.15 K) = 157.790 ± 0.001 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 105.814 ± 0.1 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [101.846] kJ·mol^{-1}

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_3$	0.0	4
$^2P_1$	177.08	2

Enthalpy of Formation

$\Delta_f H°(O^-, g, 0 K)$ is calculated from $\Delta_f H°(O, g, 0 K)$[1] using the adopted electron affinity of EA(O) = 1.4611215 ± 0.0000010 eV (140.9757 ± 0.0001 kJ·mol^{-1}). This value, is assumed to be the same as that recommended by Hotop and Lineberger,[2] is based on a tunable laser photodetachment threshold study.[3] Additional information on O^-(g) may be obtained in the critical discussions of Hotop and Lineberger[2, 4], Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(O^-, g, 298.15 K)$ is obtained from $\Delta_f H°(O, g, 0 K)$ by using EA(O) with JANAF[1] enthalpies, $H°(0 K)$–$H°(298.15 K)$, for O^-(g), O(g), and e^-(ref). $\Delta_r H°(O^- \rightarrow O + e^-, 298.15 K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15 K)$ should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state and the fine–structure separation (177.08 ± 0.05 cm^{-1}) for O^-(g) has been experimentally determined;[3] a thorough discussion of the relevant work is given by Hotop and Lineberger.[2] Massey[6] listed the hyperfine splitting of the ground state as 226 cm^{-1} based on a quadratic isoelectronic extrapolation. Use of this value would decrease the entropy at 298.15 K by 0.16 J·K^{-1}·mol^{-1}.

A comparison of the isoelectronic sequence – O^-(g), F(g), Ne^+(g) – would suggest that stable electronic states may exist below EA(O), i.e. below 12000 cm^{-1}. These levels would greatly affect the entropy. However, lacking any experimental evidence as to the stability of these levels, we assume no stable excited states exist.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S° - [G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−6.571	105.814	
100	22.725	133.326	177.481	−4.415		
200	22.271	149.016	159.790	−2.155		
250	21.936	153.948	158.148	−1.050		
298.15	21.692	157.790	157.790	0.	101.846	91.638	−16.055
300	21.684	157.924	157.790	0.040	101.821	91.575	−15.945
350	21.500	161.252	158.054	1.119	101.123	89.922	−13.420
400	21.364	164.114	158.636	2.191	100.407	88.371	−11.540
450	21.262	166.624	159.387	3.256	99.675	86.910	−10.088
500	21.184	168.860	160.225	4.318	98.926	85.532	−8.935
600	21.075	172.712	161.995	6.430	97.380	82.997	−7.226
700	21.005	175.955	163.764	8.534	95.778	80.726	−6.024
800	20.958	178.757	165.467	10.632	94.129	78.688	−5.138
900	20.924	181.223	167.083	12.726	92.442	76.859	−4.461
1000	20.899	183.426	168.609	14.817	90.723	75.219	−3.929
1100	20.881	185.417	170.048	16.906	88.979	73.753	−3.502
1200	20.866	187.233	171.406	18.993	87.213	72.446	−3.154
1300	20.855	188.903	172.688	21.079	85.429	71.288	−2.864
1400	20.846	190.448	173.902	23.164	83.629	70.268	−2.622
1500	20.838	191.886	175.054	25.248	81.814	69.377	−2.416
1600	20.832	193.231	176.148	27.332	79.985	68.607	−2.240
1700	20.827	194.494	177.191	29.415	78.144	67.952	−2.088
1800	20.823	195.684	178.185	31.497	76.289	67.406	−1.956
1900	20.819	196.810	179.136	33.580	74.423	66.963	−1.841
2000	20.816	197.878	180.047	35.661	72.545	66.619	−1.740
2100	20.813	198.893	180.920	37.743	70.655	66.369	−1.651
2200	20.811	199.861	181.760	39.824	68.754	66.210	−1.572
2300	20.809	200.786	182.567	41.905	66.841	66.137	−1.502
2400	20.807	201.672	183.345	43.986	64.917	66.148	−1.440
2500	20.805	202.521	184.095	46.066	62.981	66.239	−1.384
2600	20.804	203.337	184.819	48.147	61.035	66.407	−1.334
2700	20.803	204.122	185.520	50.227	59.078	66.651	−1.289
2800	20.801	204.879	186.198	52.307	57.111	66.968	−1.249
2900	20.800	205.609	186.855	54.387	55.133	67.354	−1.213
3000	20.800	206.314	187.492	56.467	53.146	67.810	−1.181
3100	20.799	206.996	188.110	58.547	51.150	68.332	−1.151
3200	20.798	207.656	188.710	60.627	49.144	68.918	−1.125
3300	20.797	208.296	189.294	62.707	47.130	69.567	−1.101
3400	20.797	208.917	189.862	64.787	45.107	70.277	−1.080
3500	20.796	209.520	190.415	66.866	43.076	71.047	−1.060
3600	20.795	210.106	190.954	68.946	41.037	71.875	−1.043
3700	20.795	210.676	191.480	71.025	38.991	72.759	−1.027
3800	20.794	211.230	191.992	73.105	36.938	73.700	−1.013
3900	20.794	211.770	192.492	75.184	34.878	74.694	−1.000
4000	20.794	212.297	192.981	77.264	32.811	75.741	−0.989
4100	20.793	212.810	193.458	79.343	30.737	76.840	−0.979
4200	20.793	213.311	193.925	81.422	28.657	77.990	−0.970
4300	20.793	213.800	194.382	83.502	26.571	79.189	−0.962
4400	20.792	214.278	194.828	85.581	24.479	80.437	−0.955
4500	20.792	214.746	195.266	87.660	22.380	81.732	−0.949
4600	20.792	215.203	195.694	89.739	20.276	83.074	−0.943
4700	20.792	215.650	196.114	91.818	18.165	84.462	−0.939
4800	20.791	216.088	196.526	93.897	16.048	85.895	−0.935
4900	20.791	216.516	196.929	95.977	13.925	87.372	−0.931
5000	20.791	216.936	197.325	98.056	11.795	88.893	−0.929
5100	20.791	217.348	197.714	100.135	9.658	90.456	−0.926
5200	20.791	217.752	198.095	102.214	7.514	92.061	−0.925
5300	20.790	218.148	198.470	104.293	5.363	93.708	−0.924
5400	20.790	218.536	198.838	106.372	3.205	95.395	−0.923
5500	20.790	218.918	199.200	108.451	1.038	97.122	−0.922
5600	20.790	219.292	199.555	110.530	−1.137	98.889	−0.922
5700	20.790	219.660	199.905	112.609	−3.321	100.694	−0.923
5800	20.790	220.022	200.248	114.688	−5.515	102.538	−0.923
5900	20.790	220.377	200.586	116.767	−7.718	104.419	−0.924
6000	20.789	220.727	200.919	118.846	−9.932	106.339	−0.926

PREVIOUS: March 1977 (1 atm) CURRENT: September 1982 (1 bar)

$S°(298.15\ K) = 222.776 \pm 0.021\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -23.24 \pm 14.6\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -23.26 \pm 4.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^2\Pi_{1/2}$	0	2
$X^2\Pi_{3/2}$	224	2
$B^2\Sigma^+$	30696	2
$B'^2\Pi_i$	32884	4
$D'^2\Pi_r$	38055	4
$A^2\Sigma^+$	40485	2
$C'^2\Sigma^-$	43629	2
$C^2\Sigma^-$	47251	2
$D^2\Pi_r$	48580	4

$\omega_e = 1233.3\ cm^{-1}$ $\omega_e x_e = 6.56\ cm^{-1}$ $\sigma = 1$

$B_e = 0.7337\ cm^{-1}$ $\alpha_e = 0.0056\ cm^{-1}$ $r_e = 1.4757$ Å

Enthalpy of Formation

The dissociation energy of PO has been reported by various investigators to be from 5.15 eV to 7.4 eV. All of these values have been based on the spectroscopic properties of PO. Recently Drowart *et al.*[1] have measured the dissociation energy by a complex series of exchange reactions in a mass–spectrometer from which they calculate a dissociation energy of 142.2 ± 2.5 kcal·mol^{-1} (6.17 cal·K^{-1}·mol^{-1}). Drowart *et al.*[1] also point out the agreement with the observed predissociation in the D' state. Couet *et al.*[2] and Verma and Dixit[3] have observed this predissociation. It was thought to occur between the 0 and 1 levels but recently Verma[4] has shown that the vibrational numbering is in error. This does not affect the predissociation, however, which we take as 49210 ± 350 cm^{-1}. If this is to ground state products, the dissociation energy is 140.7 ± 1.0 kcal·mol^{-1}. The linear Birge–Sponer extrapolation (LBX) of the ground state vibrational energy levels yields $D_0°$ = 164 kcal·mol^{-1}, when corrected by the method of Hildenbrand[5] $D_0°$ = 138.1 kcal·mol^{-1}, in excellent agreement with the predissociation limit.

The much shorter extrapolation of the $B^2\Sigma^+$ levels yields $D_0°$ = 157.5,[3] 155.0[6] and 152.7[7] kcal·mol^{-1} using the LBX method, a non–linear extrapolation[8] yields 151.0 kcal·mol^{-1}. All these values assume ground state atoms as the products, which must be the case since a $^2\Sigma^+$ state exists which correlates with those products and the $B^2\Sigma^+$ state must be this state or be formed by an avoided crossing. It is possible then that these values are high due to a potential maximum in the $B^2\Sigma^+$ state.

The adopted value is $D_0°$ = 140.7 ± 1 kcal·mol^{-1} and this yields $\Delta_f H°$(PO, g, 298.15 K) = −23.548 kJ·mol^{-1}.

Heat Capacity and Entropy

The ground–state constants are from Verma[9] and Verma and Dixit.[3] The ground–state splitting is from Rao[10] who also reported the excitation energy of the A state. The energy of the B state is due to Singh,[11] while that of the B' state is from Verma.[9] The C state energy is due to Dressler[6] while Narisimham[12] reported the C' state energy. Verma and Dixit[3] reported the D state energy and Verma[4] the D' state energy, which is considerably different from earlier reports. The E' state reported by Santaram and Rao[13] has been shown to coincide with the D' state by Verma and Dixit.[3] States above 50000 cm^{-1} were not included. Other states in the 40,000 cm^{-1} region have been proposed[14] from perturbation analyses.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.395	−23.241	−23.241	INFINITE
100	32.287	187.462	251.313	−6.385	−22.571	−30.883	16.131
200	32.204	210.041	225.686	−3.129	−23.033	−39.268	10.256
250	31.821	217.180	223.299	−1.530	−23.255	−43.303	9.048
298.15	31.762	222.776	222.776	0.	−23.548	−47.139	8.258
300	31.765	222.972	222.776	0.059	−23.560	−47.285	8.233
350	31.970	227.882	223.164	1.651	−24.642	−51.140	7.632
400	32.329	232.173	224.027	3.258	−25.098	−54.894	7.168
450	32.754	236.005	225.149	4.885	−25.546	−58.592	6.801
500	33.193	239.479	226.411	6.534	−25.985	−62.240	6.502
600	34.005	245.604	229.113	9.895	−26.836	−69.410	6.043
700	34.678	250.898	231.855	13.330	−27.660	−76.441	5.704
800	35.213	255.565	234.533	16.826	−28.466	−83.354	5.442
900	35.636	259.738	237.106	20.369	−29.258	−90.168	5.233
1000	35.973	263.511	239.561	23.950	−30.040	−96.893	5.061
1100	36.244	266.953	241.897	27.562	−30.816	−103.541	4.917
1200	36.465	270.116	244.118	31.197	−95.159	−109.040	4.746
1300	36.649	273.042	246.232	34.853	−95.153	−110.197	4.428
1400	36.803	275.764	248.245	38.526	−95.150	−111.354	4.155
1500	36.934	278.308	250.166	42.213	−95.150	−112.512	3.918
1600	37.047	280.695	252.000	45.912	−95.155	−113.669	3.711
1700	37.146	282.944	253.755	49.622	−95.164	−114.826	3.528
1800	37.233	285.070	255.436	53.341	−95.179	−115.982	3.366
1900	37.311	287.085	257.049	57.068	−95.201	−117.137	3.220
2000	37.381	289.001	258.599	60.803	−95.229	−118.291	3.089
2100	37.445	290.826	260.091	64.544	−95.263	−119.444	2.971
2200	37.504	292.570	261.528	68.292	−95.305	−120.594	2.863
2300	37.558	294.238	262.914	72.045	−95.355	−121.742	2.765
2400	37.608	295.837	264.253	75.803	−95.412	−122.889	2.675
2500	37.655	297.374	265.547	79.566	−95.478	−124.032	2.592
2600	37.699	298.851	266.800	83.334	−95.551	−125.173	2.515
2700	37.741	300.275	268.013	87.106	−95.631	−126.310	2.444
2800	37.781	301.648	269.190	90.882	−95.720	−127.445	2.378
2900	37.819	302.975	270.332	94.662	−95.816	−128.577	2.316
3000	37.856	304.257	271.442	98.446	−95.919	−129.705	2.258
3100	37.892	305.499	272.521	102.234	−96.030	−130.829	2.204
3200	37.926	306.703	273.570	106.024	−96.147	−131.950	2.154
3300	37.960	307.870	274.592	109.819	−96.272	−133.067	2.106
3400	37.993	309.004	275.587	113.616	−96.402	−134.180	2.061
3500	38.025	310.106	276.558	117.417	−96.539	−135.289	2.019
3600	38.057	311.177	277.505	121.221	−96.681	−136.394	1.979
3700	38.089	312.221	278.429	125.029	−96.829	−137.495	1.941
3800	38.121	313.237	279.332	128.839	−96.982	−138.592	1.905
3900	38.153	314.227	280.214	132.653	−97.141	−139.685	1.871
4000	38.186	315.194	281.076	136.470	−97.303	−140.774	1.838
4100	38.219	316.137	281.920	140.290	−97.471	−141.858	1.807
4200	38.252	317.059	282.746	144.114	−97.642	−142.939	1.778
4300	38.286	317.959	283.554	147.941	−97.818	−144.015	1.749
4400	38.322	318.840	284.346	151.771	−97.998	−145.088	1.722
4500	38.358	319.701	285.122	155.605	−98.181	−146.156	1.697
4600	38.396	320.545	285.883	159.443	−98.368	−147.220	1.672
4700	38.435	321.371	286.630	163.284	−98.558	−148.280	1.648
4800	38.476	322.180	287.362	167.130	−98.752	−149.336	1.625
4900	38.519	322.974	288.080	170.980	−98.949	−150.387	1.603
5000	38.563	323.753	288.786	174.834	−99.150	−151.435	1.582
5100	38.610	324.517	289.479	178.692	−99.354	−152.479	1.562
5200	38.659	325.267	290.160	182.556	−99.561	−153.519	1.542
5300	38.710	326.004	290.830	186.424	−99.772	−154.554	1.523
5400	38.763	326.728	291.488	190.298	−99.987	−155.586	1.505
5500	38.820	327.440	292.135	194.177	−100.205	−156.614	1.487
5600	38.879	328.140	292.772	198.062	−100.427	−157.637	1.470
5700	38.941	328.829	293.398	201.953	−100.653	−158.657	1.454
5800	39.005	329.506	294.015	205.850	−100.883	−159.672	1.438
5900	39.073	330.174	294.622	209.754	−101.118	−160.684	1.423
6000	39.144	330.831	295.220	213.665	−101.357	−161.691	1.408

PREVIOUS: June 1971 (1 atm) CURRENT: June 1971 (1 bar)

$S°(298.15\ K) = 66.316 \pm 0.8\ J·K^{-1}·mol^{-1}$
$T_{trs} = 762 \pm 1\ K$

$\Delta_f H°(0\ K) = -217.297 \pm 0.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -219.409 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0.167 \pm 0.29\ kJ·mol^{-1}$

Enthalpy of Formation

The difference in the enthalpies of formation of red and yellow PbO has been determined directly, using a solution calorimeter, by Knacke and Prescher[1] as $394 \pm 70\ cal·K^{-1}·mol^{-1}$ by dissolving both forms in nitric acid. This difference and $\Delta_f H°$(PbO, yellow, 298.15 K) = $-52.12 \pm 0.15\ kcal·mol^{-1}$ yields $\Delta_f H°$(PbO, red, 298.15 K) = $-52.51 \pm 0.2\ kcal·mol^{-1}$. Smith and Woods[2] have measured the emf of reversible cells to obtain the Gibbs energy of the reaction PbO(red, cr) + H_2(g) → Pb(cr) + H_2O(l) at two temperatures. From a 2nd law analysis of these data, we obtain $\Delta_r H°$ = $-15.91\ kcal·mol^{-1}$ which yields $\Delta_f H°$(PbO, red, 298.15 K) = $-52.41 \pm 0.2\ kcal·mol^{-1}$.

If we assume the entropy to be accurately known, then the enthalpy of formation can be calculated directly from the Gibbs energies of reaction. Smith and Woods,[2] for the reaction given above, found $\Delta_r G°(298.15\ K) = -11.513\ kcal·mol^{-1}$, in combination with $\Delta_f G°(H_2O, l, 298.15\ K) = -56.687\ kcal·mol^{-1}$ [3] yields $\Delta_f G°$(PbO, red, 298.15 K) = $-45.182\ kcal·mol^{-1}$. This Gibbs energy with JANAF entropies[4] is equivalent to $\Delta_f H°$(PbO, red, 298.15 K) = $-52.45\ kcal·mol^{-1}$. Spencer and Mote[5] measured the Gibbs energy of the reaction Pb(cr) + HgO(cr) → PbO(red, cr) + Hg(l) by means of a reversible cell and obtained $\Delta_r G°(298.15\ K) = -31.265\ kcal·mol^{-1}$. This value combined with $\Delta_f G°$(HgO, cr, 298.15 K) = $-13.983\ kcal·mol^{-1}$ [4] yields $\Delta_f G°$(PbO, red, 298.15 K) = $-45.248\ kcal·mol^{-1}$, which with JANAF entropies[4] is equivalent to $\Delta_f H°$(PrO, red, 298.15 K) = $52.52\ kcal·mol^{-1}$.

It is apparent that the data for enthalpy, Gibbs energy and entropy are all in excellent agreement, thus we adopt $\Delta_f H°$(PbO, red, 298.15 K) = $-52.44 \pm 0.2\ kcal·mol^{-1}$. The adopted value was selected within all the uncertainties to assure the correct crossover of the red and yellow forms at 762 K.

Heat Capacity and Entropy

The heat capacity has been reported by King[6] from 53 to 296 K and the entropy was obtained by integration of these data based on $S°(51\ K) = 2.73\ cal·K^{-1}·mol^{-1}$. This extrapolated portion was obtained by use of a Debye Einstein fit of the measured data. The value was then corrected by analogy with the $0.25\ cal·K^{-1}·mol^{-1}$ difference between the extrapolation for PbO(cr, yellow) by King[6] and the measured amount. The justification for this procedure is the similarity of the two curves at all other temperatures. The high temperature heat capacities were obtained by fitting an orthogonal polynomial through the low temperature data of King[6] and the enthalpies of Spencer and Spicer.[7]

Transition Data

The temperature of transition has been reported by Cohen and Addink[8] and Petersen.[9] The enthalpy of transition is calculated from the adopted enthalpy at 298.15 K and the enthalpy difference, $H°(762\ K) - H°(298.15\ K)$, between PbO yellow and red.

Vaporization Data

The vapor species over PbO(cr, l) consists of $(PbO)_x$ where x = 1–6;[10, 11] thus a value for the heat of sublimation is not given.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−9.109	−217.297	−217.297	INFINITE
100	26.870	24.765	101.583	−7.682	−219.089	−209.218	109.284
200	40.476	48.028	69.262	−4.247	−219.634	−199.037	51.983
298.15	45.773	66.316	66.316	0.000	−219.409	−189.283	33.162
300	45.866	66.600	66.317	0.085	−219.401	−189.096	32.925
400	50.375	80.434	68.173	4.904	−218.796	−179.077	23.385
500	53.430	92.066	71.821	10.123	−217.921	−169.245	17.681
600	55.396	101.992	76.042	15.570	−216.942	−159.601	13.894
700	56.651	110.626	80.380	21.172	−220.789	−149.325	11.143
762.000	57.430	115.466	83.040	24.709	- - - - - - - I <- - > II - - - - - - -		
800	57.907	118.273	84.647	26.900	−219.747	−139.186	9.088
900	59.162	125.166	88.773	32.754	−218.581	−129.185	7.498
1000	60.417	131.464	92.731	38.733	−217.288	−119.320	6.233
1100	61.672	137.281	96.520	44.837	−215.863	−109.591	5.204
1200	62.927	142.701	100.145	51.067	−214.301	−99.998	4.353
1300	64.183	147.788	103.616	57.423	−212.608	−90.540	3.638
1400	65.438	152.590	106.944	63.904	−210.796	−81.218	3.030

PREVIOUS: March 1962 CURRENT: December 1971

$S°(298.15\ K) = 68.701 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1159 \pm 5\ K$

$\Delta_f H°(0lthsp;lK) = -216.080\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -218.062 \pm 0.63\ kJ·mol^{-1}$
$\Delta_{fus} H° = 25.522 \pm 0.4\ kJ·mol^{-1}$

Enthalpy of Formation

Espada *et al.*[1] have measured calorimetrically the heat of the reaction PbO(yellow, cr) + H_2(g) → Pb(cr) + H_2O(l) as $\Delta_f H°(298.15\ K) = -16.20 \pm 0.07$ kcal·mol^{-1} which yields the adopted enthalpy of formation.

Spencer and Mote[2] have measured the Gibbs energy of the cell reaction Pb(cr) + HgO(cr) → PbO(yellow, cr) + Hg(l) as −31.120 kcal·mol^{-1}. With JANAF auxillary data[3] we obtain $\Delta_f G°$PbO(yellow, 298.15 K) = −45.103 kcal·mol^{-1} which corresponds to $\Delta_f H°$PbO, yellow, 298.15 K) = −52.13 kcal·mol^{-1} in excellent agreement with the adopted value.

Charette and Flengas[13] measured the Gibbs form of energy directly in a high temperature electrolytic cell. Alcock and Bedford[14] measured the Gibbs energy of the reactions (a)PbO(cr) + Ni(cr) → NiO(cr) + Pb(l) and (b)Cu_2O(cr) + Pb(l) = PbO(cr) + 2 Cu(cr) in high temperature electrolytic cells.

Source	T/K	$\Delta_r H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(PbO, 298.15 K), kcal·mol^{-1}
[13]	770–1160	−52.3	−52.93 ± 0.26	−0.6 ± 0.2	−52.93 ± 0.26
[14a]	780–1070	−3.9	2.27 ± 1.8	6.6 ± 0.2	−54.0 ± 0.7
[14b]	710–1050	−12.1	−12.61 ± 0.25	−0.6 ± 0.2	−52.28 ± 0.7

These values indicate that the overall consistency between enthalpies of formation, enthalpies, entropy and Gibbs energies is generally within the experimental error.

Heat Capacity and Entropy

The low temperature heat capacity has been measured from 12.5 K to 302.7 K by Kostryukov and Morozova[4] and from 54.1 K to 296.1 K by King.[5] the two sets of data are in reasonable agreement with differences up to 0.5%. A line fitted through both data sets yields an entropy within the stated uncertainty of the Russian set, whose results we adopted.

The high temperature heat capacity was derived from the enthalpy measurements of Rodigina *et al.*[6] by curve fitting with orthogonal polynomials. The curve was constrained to join smoothly with the low temperature heat capacities. The adopted values are in good agreement with enthalpies reported by Regnault,[7] Magnus[8] and Kopp.[9] The enthalpies reported by Spencer and Spicer[10] lie about 3% higher than the adopted values are, admitted to be not too accurate. The values reported by Knacke and Prescher[11] lie 5 to 6% higher than the adopted values.

Fusion Data

The melting point was selected by Schnedier[12] in his review of metal oxide melting points. The enthalpy of melting was calculated from the enthalpy equation derived from the work of Rodigina *et al.*[6] for crystal and liquid. Knacke and Prescher[11] report a heat of melting of 6.57 kcal·mol^{-1} from their enthalpy measurements.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.000	0.000	INFINITE	−9.238	−216.080	−216.080	INFINITE
100	27.698	28.284	105.269	−7.699	−217.759	−208.239	108.773
200	40.041	51.547	72.990	−4.289	−218.329	−198.435	51.826
298.15	45.773	68.701	68.701	0.000	−218.062	−188.647	33.050
300	45.834	68.985	68.702	0.085	−218.054	−188.464	32.815
400	48.526	82.565	70.536	4.812	−217.541	−178.675	23.333
500	50.463	93.609	74.080	9.765	−216.931	−169.027	17.658
600	52.103	102.958	78.133	14.895	−216.270	−159.508	13.886
700	53.605	111.104	82.274	20.181	−220.433	−149.304	11.141
762.000	54.495	115.690	84.808	23.532	-------- I <--> II --------		
800	55.028	118.355	86.339	25.613	−219.687	−139.192	9.088
900	56.409	124.917	90.266	31.185	−218.803	−129.182	7.498
1000	57.764	130.930	94.036	36.894	−217.779	−119.277	6.230
1100	59.099	136.499	97.646	42.738	−216.615	−109.482	5.199
1159.000	59.884	139.607	99.704	46.248	----- II <--> LIQUID -----		
1200	60.421	141.698	101.103	48.714	−215.307	−99.800	4.344
1300	61.739	146.586	104.415	54.822	−213.861	−90.232	3.626
1400	63.049	151.209	107.594	61.061	−212.291	−80.780	3.014
1500	64.350	155.604	110.650	67.431	−210.606	−71.445	2.488

PREVIOUS: March 1962 CURRENT: December 1971

$S°(298.15\ K)$ = [73.376] $J·K^{-1}·mol^{-1}$
T_{fus} = 1159 ± 5 K

$\Delta_f H°(298.15\ K)$ = [−202.249] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 25.522 ± 0.4 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from that of PbO (yellow, cr) by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1159\ K)–H°(298.15\ K)$, between PbO(yellow, cr) and PbO(l). Direct measurements of the Gibbs energy chang in the reaction PbO(l) + C(cr) → Pb(l) + CO(g) have been reported by Kvyatkovskii *et al.*[1] Charette and Flengas[2] and Delimarskii and Andreeva[3] have also determined the Gibbs energy of formation of the liquid directly in a high temperature cell. 2nd– and 3rd law analysis of these data are summarized below.

Source	T/K	$\Delta_f H°$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(PbO, l,298.15 K) kcal·mol^{-1}
1	1173–1423	34.5 ± 6.5	22.81 ± 2.49	−8.6 ± 4.9	−48.20 ± 2.5
2	1160–1371	−49.9 ± 0.2	−49.24 ± 0.13	0.5 ± 0.1	−49.24 ± 0.13
3	1173–1253	−46.9 ± 5.6	−48.51 ± 0.39	−1.5 ± 4.6	−48.51 ± 0.39

Heat Capacity and Entropy

The heat capacity was obtained from the enthalpy determinations of Rodigina *et al.*[4] and Knacke and Prescher.[5] The absolute enthalpy values differ by 2–3% but the constant heat capacities derived from each set agree very well. The entropy at 298.15 K is calculated from that of the yellow crystal in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the yellow–crystal table for details.

Vaporizaton Data

Refer to the red–crystal table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	64.998	73.376	73.376	0.000	−202.249	−174.228	30.524
300	64.998	73.778	73.378	0.120	−202.205	−174.054	30.306
400	64.999	92.478	75.927	6.620	−199.920	−165.018	21.549
500	65.000	106.982	80.742	13.120	−197.763	−156.545	16.354
600	65.000	118.833	86.133	19.620	−195.732	−148.494	12.928
700	65.000	128.853	91.538	26.120	−198.681	−139.976	10.445
800	65.000	137.532	96.757	32.620	−196.867	−131.714	8.600
900	65.000	145.188	101.721	39.120	−195.055	−123.678	7.178
1000	65.000	152.036	106.416	45.620	−193.240	−115.845	6.051
1100	65.000	158.232	110.850	52.120	−191.419	−108.193	5.138
1159.000	65.000	161.628	113.349	55.955	----- II <--> LIQUID -----		
1200	65.000	163.887	115.037	58.620	−189.588	−100.708	4.384
1300	65.000	169.090	118.998	65.120	−187.750	−93.376	3.752
1400	65.000	173.907	122.750	71.620	−185.919	−86.185	3.216
1500	65.000	178.392	126.312	78.120	−184.104	−79.124	2.755
1600	65.000	182.587	129.699	84.620	−182.310	−72.184	2.357
1700	65.000	186.527	132.927	91.120	−180.542	−65.356	2.008
1800	65.000	190.243	136.009	97.620	−178.801	−58.631	1.701
1900	65.000	193.757	138.957	104.120	−177.091	−52.001	1.430
2000	65.000	197.091	141.781	110.620	−175.412	−45.461	1.187
2100	65.000	200.262	144.491	117.120	−350.987	−31.889	0.793
2200	65.000	203.286	147.095	123.620	−348.984	−16.741	0.397
2300	65.000	206.176	149.602	130.120	−347.080	−1.682	0.038
2400	65.000	208.942	152.017	136.620	−345.278	13.296	−0.289
2500	65.000	211.595	154.347	143.120	−343.578	28.201	−0.589

PREVIOUS: March 1962 CURRENT: December 1971

0 to 762 K crystal, red
762 to 1159 K crystal, yellow
above 1159 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−9.109	−217.297	−217.297	INFINITE
100	26.870	24.765	101.583	−7.682	−219.089	−209.218	109.284
200	40.476	48.028	69.262	−4.247	−219.634	−199.037	51.983
298.15	45.773	66.316	66.316	0.000	−219.409	−189.283	33.162
300	45.866	66.600	66.317	0.085	−219.401	−189.096	32.925
400	50.375	80.434	68.173	4.904	−218.796	−179.077	23.385
500	53.430	92.066	71.821	10.123	−217.921	−169.245	17.681
600	55.396	101.992	76.042	15.570	−216.942	−159.601	13.894
700	56.651	110.626	80.380	21.172	−220.789	−149.325	11.143
762.000	57.430	115.466	83.040	24.709	I <--> II		
762.000	54.495	115.690	83.040	24.880	TRANSITION		
800	55.028	118.355	84.654	26.961	−219.687	−139.192	9.088
900	56.409	124.917	88.769	32.533	−218.803	−129.182	7.498
1000	57.764	130.930	92.689	38.242	−217.779	−119.277	6.230
1100	59.099	136.499	96.421	44.085	−216.615	−109.482	5.199
1159.000	59.884	139.607	98.541	47.595	II <--> LIQUID		
1159.000	65.000	161.628	98.541	73.117	TRANSITION		
1200	65.000	163.887	100.735	75.782	−189.586	−100.706	4.384
1300	65.000	169.090	105.796	82.282	−187.748	−93.374	3.752
1400	65.000	173.907	110.491	88.782	−185.918	−86.183	3.216
1500	65.000	178.392	114.870	95.282	−184.103	−79.123	2.755
1600	65.000	182.587	118.973	101.782	−182.309	−72.183	2.357
1700	65.000	186.527	122.832	108.282	−180.540	−65.354	2.008
1800	65.000	190.243	126.475	114.782	−178.800	−58.629	1.701
1900	65.000	193.757	129.924	121.282	−177.089	−52.000	1.430
2000	65.000	197.091	133.200	127.782	−175.410	−45.459	1.187
2100	65.000	200.262	136.318	134.282	−350.985	−31.887	0.793
2200	65.000	203.286	139.294	140.782	−348.982	−16.739	0.397
2300	65.000	206.176	142.140	147.282	−347.078	−1.681	0.038
2400	65.000	208.942	144.866	153.782	−345.276	13.298	−0.289
2500	65.000	211.595	147.482	160.282	−343.577	28.203	−0.589

PREVIOUS: CURRENT: December 1971

$S°(298.15\ K) = 240.039 \pm 0.021\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 72.55 \pm 7.1\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 70.29 \pm 7.1\ kJ·mol^{-1}$

Electronic States and Molecular Constants (σ = 1)

State	ϵ_i, cm^{-1}	g_i	r_e, Å	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	$\omega_e x_e / B_e$	$\omega_e / \omega_e x_e$
X O^+	0	1	1.922	0.3074	0.00212	721.8	3.70	12.036	195.08
A O^+	20088	1	2.095	0.2587	0.00138	451.7	3.33	12.872	135.65
B 1	22531	2	2.071	0.2646	0.0026	493.5	2.26	8.541	218.36
C O^+	24108	1	2.11	0.254	0.002	[534]	[3.9]	[15.354]	136.92
C'1	25720	2	2.14	0.248	0.0018	[475]	[2.7]	[10.887]	175.92
D 1	30464	2	2.046	0.2711	0.0031	530.5	2.92	10.771	181.68
E O^+	34680	1	[2.183]	[0.2382]	[0.0014]	[440]	[2.6]	169.23	

Enthalpy of Formation

A value for the dissociation energy can be calculated by applying the Hildenbrand formula[1] to the linear Birge Sponer extrapolation of the ground state vibrational levels. This procedure yields a $D° = 91.4\ kcal·mol^{-1}$, corresponding to $\Delta_f H°(0\ K) = 14.5\ kcal·mol^{-1}$.

Recently, Singh and Nair[3] have calculated $D_0° = 99.2\ kcal·mol^{-1}$ from a special potential energy curve which takes into account the electronegativity of the atoms.

The enthalpy of sublimation of PbO(yellow, cr) to monomeric PbO has been measured mass spectrometrically by Drowart *et al.*[2] Our analysis of their vapor pressure data yields $\Delta_{sub}H°(298.15\ K) = 68.9 \pm 1.5\ kcal·mol^{-1}$, which yields $\Delta_f H°(PbO, g, 298.15\ K) = 16.8 \pm 1.7\ kcal·mol^{-1}$. This value is adopted and corresponds to a dissociation energy at 0 K of 88.6 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The tabulated molecular and electronic constants are taken from Barrow *et al.*[4] The state designations are those used by Barrow *et al.* who interpret the spectra in terms of type c coupling, when the state designations Σ, Π, etc. no longer have meaning. The estimated values for $\omega_e x_e$ for the C' and E states were obtained from the B_e values by averaging the $\omega_e x_e / B_e$ ratio for the known states. The functions were calculated from the partition function $Q = Q_{ti}\Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$, the values for Q_r^i and Q_v^i were calculated with first order anharmonic corrections.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−8.961	72.550	72.550	INFINITE
100	29.136	207.019	267.535	−6.052	72.241	63.887	−33.371
200	30.424	227.495	242.946	−3.090	71.222	55.926	−14.606
250	31.516	234.401	240.568	−1.542	70.736	52.159	−10.898
298.15	32.508	240.039	240.039	0.	70.291	48.622	−8.518
300	32.544	240.240	240.039	0.060	70.275	48.487	−8.442
350	33.415	245.324	240.439	1.710	69.832	44.891	−6.700
400	34.123	249.834	241.337	3.399	69.399	41.358	−5.401
450	34.692	253.887	242.510	5.120	68.965	37.879	−4.397
500	35.149	257.567	243.834	6.866	68.523	34.448	−3.599
600	35.822	264.039	246.677	10.417	67.605	27.719	−2.413
700	36.281	269.597	249.564	14.024	61.762	21.946	−1.638
800	36.608	274.464	252.378	17.669	60.722	16.329	−1.066
900	36.852	278.791	255.077	21.342	59.707	10.841	−0.629
1000	37.040	282.684	257.646	25.038	58.717	5.465	−0.285
1100	37.191	286.222	260.086	28.749	57.749	0.187	−0.009
1200	37.315	289.463	262.401	32.475	56.807	−5.004	0.218
1300	37.420	292.454	264.599	36.212	55.881	−10.118	0.407
1400	37.510	295.231	266.689	39.958	54.958	−15.160	0.566
1500	37.590	297.821	268.679	43.713	54.029	−20.136	0.701
1600	37.662	300.250	270.577	47.476	53.085	−25.050	0.818
1700	37.727	302.535	272.390	51.245	52.123	−29.904	0.919
1800	37.788	304.693	274.126	55.021	51.139	−34.701	1.007
1900	37.844	306.738	275.789	58.803	50.131	−39.442	1.084
2000	37.898	308.680	277.385	62.590	49.097	−44.130	1.153
2100	37.951	310.530	278.920	66.382	−129.185	−41.650	1.036
2200	38.003	312.297	280.397	70.180	−129.884	−37.465	0.890
2300	38.054	313.988	281.821	73.983	−130.678	−33.247	0.755
2400	38.108	315.608	283.195	77.791	−131.568	−28.993	0.631
2500	38.164	317.165	284.523	81.605	−132.554	−24.699	0.516
2600	38.224	318.663	285.808	85.424	−133.636	−20.363	0.409
2700	38.290	320.107	287.051	89.250	−134.811	−15.985	0.309
2800	38.362	321.501	288.257	93.082	−136.073	−11.561	0.216
2900	38.444	322.848	289.427	96.922	−137.418	−7.091	0.128
3000	38.536	324.153	290.563	100.771	−138.838	−2.573	0.045
3100	38.641	325.418	291.667	104.630	−140.326	1.994	−0.034
3200	38.760	326.647	292.741	108.500	−141.875	6.609	−0.108
3300	38.895	327.842	293.786	112.383	−143.474	11.274	−0.178
3400	39.048	329.005	294.805	116.280	−145.115	15.988	−0.246
3500	39.220	330.139	295.799	120.193	−146.789	20.751	−0.310
3600	39.413	331.247	296.768	124.124	−148.487	25.562	−0.371
3700	39.629	332.330	297.714	128.076	−150.200	30.420	−0.429
3800	39.869	333.390	298.639	132.051	−151.919	35.325	−0.486
3900	40.134	334.429	299.544	136.051	−153.635	40.275	−0.539
4000	40.425	335.448	300.429	140.079	−155.342	45.268	−0.591
4100	40.743	336.450	301.295	144.137	−157.030	50.304	−0.641
4200	41.088	337.436	302.144	148.228	−158.693	55.381	−0.689
4300	41.461	338.407	302.976	152.355	−160.324	60.498	−0.735
4400	41.862	339.365	303.792	156.521	−161.917	65.652	−0.779
4500	42.290	340.311	304.593	160.729	−163.466	70.841	−0.822
4600	42.746	341.245	305.380	164.980	−164.965	76.064	−0.864
4700	43.229	342.169	306.153	169.279	−166.410	81.320	−0.904
4800	43.738	343.085	306.913	173.627	−167.797	86.606	−0.942
4900	44.272	343.992	307.660	178.027	−169.121	91.920	−0.980
5000	44.830	344.892	308.396	182.482	−170.380	97.260	−1.016
5100	45.410	345.786	309.120	186.994	−171.571	102.625	−1.051
5200	46.012	346.673	309.834	191.565	−172.690	108.012	−1.085
5300	46.634	347.555	310.537	196.197	−173.736	113.420	−1.118
5400	47.273	348.433	311.231	200.892	−174.708	118.847	−1.150
5500	47.928	349.306	311.915	205.652	−175.605	124.292	−1.180
5600	48.596	350.176	312.591	210.478	−176.425	129.752	−1.210
5700	49.277	351.042	313.258	215.372	−177.168	135.226	−1.239
5800	49.966	351.905	313.917	220.334	−177.834	140.713	−1.267
5900	50.663	352.765	314.568	225.365	−178.423	146.210	−1.294
6000	51.364	353.623	315.212	230.466	−178.938	151.717	−1.321

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 221.944 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 5.03 \pm 1.3\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 5.01 \pm 1.3\ kJ \cdot mol^{-1}$

Electronic States and Molecular Constants (σ = 1)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^3\Sigma^-$	0	3	1148.19	6.12	0.72082	0.00574	1.4811
$a^1\Delta$	6350	2	[1148.19]	[6.12]	0.7119	[0.00574]	1.494
$b^1\Sigma^+$	10510	1	1067.66	7.8	0.70261	0.00635	1.5005
$A^3\Pi_0$	38292	2	415.2	1.6	0.6067	0.0194	
$A^3\Pi_1$	38455	2	413.3	1.6	0.6107	0.0194	1.6094
$A^3\Pi_2$	38616	2	412.7	1.7	0.6164	0.0204	
$B^3\Sigma^-$	41629	3	630.4	4.8	0.502	0.0062	1.775
$C^3\Pi$	42200	6	170	[0]	[0.5]	[0]	2.2

Enthalpy of Formation

The selection for $\Delta_f H°(0\ K)$ of SO(g), 1.2 ± 3 $kcal \cdot mol^{-1}$, was derived from one of the two independent means, pointed out by Okabe[1] that employs principally spectroscopic data: $\Delta_f H°(SO, g, 0\ K) = 1/2\ D_0°(S_2) + 1/2\ D_0°(O_2) - D_0°(SO) + 1/2\ \Delta_f H°(S_2, g, 0\ K)$. The data employed are as follows. Ricks and Barrow[2] give $D_0°(S_2) = 100.69 \pm 0.01$ $kcal \cdot mol^{-1}$. Brix and Herzberg[3] give $D_0°(O_2) = 117.97 \pm 0.046$ $kcal \cdot mol^{-1}$. On the basis of analysis of spectroscopic data to 1964, JANAF[4] gives $D_0°(SO) = 123.5 \pm 0.3$ $kcal \cdot mol^{-1}$. NBS[5] gives $\Delta_f H°(S_2, g, 0\ K) = 30.65 \pm 0.2$ $kcal \cdot mol^{-1}$. Assuming the dissociation products of SO are $S(^1D_2)$ and $O(^3P)$, Colin[6] concludes $D_0°(SO) = 123.56 \pm 0.23$ $kcal \cdot mol^{-1}$. A systematic error of 0.65 $kcal \cdot mol^{-1}$ is incurred if the assumption is wrong. Support for this assumption is as follows: 1) Okabe[7] concludes that $D_0°(OS–O) = 130.06 \pm 0.5$ $kcal \cdot mol^{-1}$assuming the predissociation of SO_2 is to ground state products. Using $\Delta_f H°(SO_2, g, 0\ K) = -70.336$ $kcal \cdot mol^{-1}$ from[5] and the relation: $\Delta_f H°(SO, g, 0\ K) = D_0°(OS–O) - 1/2\ D_0°(O_2) + \Delta_f H°(SO_2, g, 0\ K)$, one obtains $\Delta_f H°(SO, g, 0\ K) = 0.7 \pm 0.7$ $kcal \cdot mol^{-1}$; 2) Assuming the threshold energy for fluorescence of SO, 217.00 ± 0.7 $kcal \cdot mol^{-1}$ (see Okabe),[8] corresponds to the minimum energy for the reaction $OSCl_2 = SO(A^3\Pi_0) + 2\ Cl(^2P_{3/2})$ and using 108.43 $kcal \cdot mol^{-1}$ for the difference in energy between the lowest vibrational levels of $SO(A^3\Pi_0)$ and $SO(X^3\Sigma^-)$ (Colin)[6] one obtains $\Delta_f H°(SO, g, 0\ K) = 1.3 \pm 0.7$ $kcal \cdot mol^{-1}$. This is based on $\Delta_f H°(OSCl_2, g, 0\ K) = -50.07$ $kcal \cdot mol^{-1}$[5] and $D_0°(Cl_2, 0\ K) = 57.177 \pm 0.005$ $kcal \cdot mol^{-1}$ given by Douglas *et al.*);[9] 3) Re–examination of the photoionization–yield curves of SO_2^+ and SO^+obtained by Dibeler and Liston[10] suggests that their reported threshold for $SO \rightarrow SO^+ + O + e-$ should be increased from 15.81 ± 0.02 $cal \cdot K^{-1} \cdot mol^{-1}$ to 16.00 eV. Using the latter and the ionization energy of SO given by Jonathon *et al.*[11] of 10.34 ± 0.02 eV and the relation $\Delta_f H°(SO, g, 0\ K) = D_0°(S–O) - 1/2\ D_0°(O_2) + \Delta_f H°(SO_2, g, 0\ K)$, one obtains $\Delta_f H°(SO, g, 0\ K) = 1.20 \pm 0.5$ $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The vibrational and rotational constants of the respective electronic levels were taken from Rosen.[12] The thermodynamic functions are calculated using first–order anharmonic corrections to Q_v^1 and Q_r^1 in the partition function $Q = Q_{tr}\Sigma Q_v^1 Q_r^1 g_i \exp(-c_2\epsilon_i/T)$. The National Bureau of Standards prepared this table[13] by critical analysis of data existing in 1972. Using molecular constants and $\Delta_f H°$ selected by NBS,[13] we recalculate the table in terms of 1973 fundamental constants,[14] 1975 atomic weights,[15] and current JANAF reference states for the elements.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.733	5.028	5.028	INFINITE
100	29.106	189.916	248.172	−5.826	5.793	−3.281	1.714
200	29.269	210.114	224.668	−2.911	5.610	−12.337	3.222
250	29.634	216.680	222.437	−1.439	5.333	−16.793	3.509
298.15	30.173	221.944	221.944	0.	5.007	−21.026	3.684
300	30.197	222.130	221.944	0.056	4.994	−21.187	3.689
350	30.867	226.835	222.314	1.582	4.616	−25.521	3.809
400	31.560	231.002	223.144	3.143	1.998	−29.711	3.880
450	32.221	234.758	224.230	4.738	0.909	−33.619	3.902
500	32.826	238.184	225.456	6.364	−0.238	−37.391	3.906
600	33.838	244.263	228.097	9.699	−2.067	−44.643	3.887
700	34.612	249.540	230.791	13.124	−3.617	−51.614	3.851
800	35.206	254.202	233.432	16.616	−5.005	−58.374	3.811
900	35.672	258.377	235.976	20.161	−59.419	−63.886	3.708
1000	36.053	262.155	238.408	23.748	−59.420	−64.382	3.363
1100	36.379	265.607	240.726	27.369	−59.424	−64.878	3.081
1200	36.672	268.785	242.933	31.022	−59.432	−65.374	2.846
1300	36.946	271.731	245.037	34.703	−59.446	−65.869	2.647
1400	37.210	274.479	247.043	38.411	−59.462	−66.362	2.476
1500	37.469	277.055	248.959	42.145	−59.482	−66.854	2.328
1600	37.725	279.482	250.791	45.905	−59.505	−67.345	2.199
1700	37.980	281.776	252.547	49.690	−59.528	−67.834	2.084
1800	38.232	283.954	254.232	53.501	−59.552	−68.323	1.983
1900	38.482	286.028	255.851	57.336	−59.575	−68.809	1.892
2000	38.727	288.008	257.410	61.197	−59.597	−69.294	1.810
2100	38.967	289.904	258.912	65.082	−59.618	−69.779	1.736
2200	39.200	291.722	260.363	68.990	−59.636	−70.262	1.668
2300	39.425	293.469	261.764	72.921	−59.652	−70.745	1.607
2400	39.641	295.152	263.121	76.875	−59.666	−71.227	1.550
2500	39.847	296.774	264.434	80.849	−59.678	−71.708	1.498
2600	40.043	298.341	265.709	84.844	−59.687	−72.189	1.450
2700	40.229	299.856	266.945	88.857	−59.694	−72.670	1.406
2800	40.404	301.322	268.147	92.889	−59.699	−73.150	1.365
2900	40.568	302.742	269.316	96.938	−59.702	−73.631	1.326
3000	40.721	304.120	270.453	101.002	−59.705	−74.111	1.290
3100	40.864	305.458	271.561	105.082	−59.707	−74.591	1.257
3200	40.996	306.757	272.640	109.175	−59.708	−75.072	1.225
3300	41.119	308.021	273.693	113.281	−59.710	−75.552	1.196
3400	41.232	309.250	274.721	117.398	−59.712	−76.032	1.168
3500	41.336	310.447	275.725	121.527	−59.716	−76.512	1.142
3600	41.432	311.613	276.706	125.665	−59.722	−76.991	1.117
3700	41.520	312.749	277.665	129.813	−59.730	−77.471	1.094
3800	41.601	313.857	278.603	133.969	−59.741	−77.950	1.071
3900	41.676	314.939	279.520	138.133	−59.755	−78.429	1.050
4000	41.745	315.995	280.419	142.304	−59.774	−78.908	1.030
4100	41.810	317.027	281.299	146.482	−59.796	−79.386	1.011
4200	41.871	318.035	282.162	150.666	−59.824	−79.863	0.993
4300	41.929	319.021	283.008	154.856	−59.857	−80.340	0.976
4400	41.986	319.985	283.837	159.051	−59.896	−80.816	0.959
4500	42.042	320.930	284.651	163.253	−59.941	−81.291	0.944
4600	42.098	321.854	285.450	167.460	−59.992	−81.765	0.928
4700	42.156	322.760	286.234	171.673	−60.049	−82.238	0.914
4800	42.217	323.648	287.004	175.891	−60.113	−82.709	0.900
4900	42.282	324.520	287.761	180.116	−60.183	−83.179	0.887
5000	42.352	325.374	288.505	184.348	−60.259	−83.648	0.874
5100	42.429	326.214	289.236	188.587	−60.342	−84.114	0.862
5200	42.514	327.039	289.955	192.834	−60.430	−84.580	0.850
5300	42.608	327.849	290.663	197.090	−60.524	−85.043	0.838
5400	42.712	328.647	291.359	201.356	−60.623	−85.505	0.827
5500	42.829	329.431	292.044	205.633	−60.726	−85.965	0.816
5600	42.959	330.204	292.718	209.922	−60.832	−86.423	0.806
5700	43.104	330.966	293.383	214.225	−60.941	−86.879	0.796
5800	43.265	331.717	294.037	218.543	−61.051	−87.333	0.787
5900	43.444	332.458	294.682	222.879	−61.162	−87.786	0.777
6000	43.642	333.190	295.318	227.233	−61.271	−88.235	0.768

PREVIOUS: June 1977 (1 atm) CURRENT: June 1977 (1 bar)

$S°(298.15\ K) = 267.020\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = [-58.86 \pm 33.5]\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [-56.48 \pm 33.5]\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
679(1)
388(1)
1165(1)

Ground State Quantum Weight: 1 $\sigma = 1$
Point Group: C_s
Bond Distances: S–S = 1.884 Å S–O = 1.465 Å
Bond Angle: S–S–O = 118°
Product of the Moments of Inertia: $I_A I_B I_C = 6.270091 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

There is no direct measurement of the standard enthalpy of formation for S_2O(g). Blukis and Myers[1] have discussed the discrepancy of the values of $\Delta_f H°$(0 K) which vary from −1 to −35 kcal·mol^{-1}. Hagman[2] reported $\Delta_f H° = -17$ kcal·mol^{-1} from his ionization and appearance potential measurements by mass spectrometry. Steudel and Schenk[3] estimated the enthalpy of formation as −22.7 kcal·mol^{-1}. If the bond dissociation energies $D_0°$(S–O) = 123.5 kcal·mol^{-1} and $D_0°$(S–S) = 101 kcal·mol^{-1} were used to estimate the dissociation energy of S_2O (i.e., $D_0°(S_2O)$ = 224.5 kcal·mol^{-1}), one will obtain $\Delta_f H = -35.3$ kcal mμccirclol^{-1}. Jones[4] reported the predissociation energy, 91 kcal·mol^{-1} for sulfur monoxide from the infrared and ultraviolet spectra. [Meschi and Myers[5] have concluded from their experiment that the so–called sulfur monoxide is S_2O.] Therefore, if SO(g) + S(g) were the dissociation products, the $\Delta_f H°$ would be −25.4 kcal·mol^{-1} and if S_2(g) + O(g) were the products, the $\Delta_f H°$ would be −1.2 kcal·mol^{-1}. (All JANAF auxiliary data used in calculation.)

Dewing and Richardson[6] have investigated the gas phase equilibria in the sulfur–oxygen vapor at 1250° and 1500°C, respectively. Blukis and Myers[1] recalculated their data based on the assumption that the S_2O (instead of SO) was the major product in the equilibrium, and obtained $\Delta_f H° = -13$ kcal·mol^{-1} for S_2O(g) which is adopted in this table.

Heat Capacity and Entropy

The bond distance, angle, and vibrational frequencies were obtained from the microwave and infrared spectra measurements by Meschi and Myers[5] and Blukis and Myers.[1] The principal moments of inertia are: $I_A = 2.0209 \times 10^{-39}$, $I_B = 16.6326 \times 10^{-39}$and $I_C = 18.6536 \times 10^{-39}$ g·cm^2.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.128	−58.859	−58.859	INFINITE
100	34.286	225.094	302.941	−7.785	−57.657	−70.249	36.694
200	39.425	250.369	270.911	−4.108	−57.078	−83.076	21.697
250	41.949	259.442	267.734	−2.073	−56.791	−89.608	18.723
298.15	44.114	267.020	267.020	0.	−56.484	−95.956	16.811
300	44.191	267.293	267.020	0.082	−56.472	−96.201	16.750
350	46.136	274.255	267.566	2.341	−56.117	−102.850	15.350
400	47.797	280.527	268.800	4.691	−57.945	−109.465	14.295
450	49.199	286.240	270.425	7.116	−58.203	−115.898	13.453
500	50.379	291.486	272.273	9.607	−58.487	−122.290	12.776
600	52.201	300.842	276.274	14.741	−58.517	−135.040	11.756
700	53.497	308.992	280.378	20.029	−58.203	−147.815	11.030
800	54.436	316.200	284.414	25.429	−57.683	−160.651	10.489
900	55.131	322.653	288.311	30.909	−110.163	−172.478	10.010
1000	55.656	328.491	292.041	36.449	−108.209	−179.507	9.376
1100	56.061	333.815	295.600	42.036	−106.248	−186.732	8.867
1200	56.379	338.707	298.992	47.658	−104.287	−194.135	8.450
1300	56.632	343.230	302.223	53.309	−102.330	−201.702	8.104
1400	56.836	347.435	305.304	58.983	−100.381	−209.419	7.814
1500	57.004	351.362	308.245	64.676	−98.443	−217.275	7.566
1600	57.143	355.045	311.056	70.383	−96.517	−225.260	7.354
1700	57.259	358.513	313.747	76.103	−94.606	−233.365	7.170
1800	57.358	361.789	316.325	81.834	−92.709	−241.582	7.011
1900	57.442	364.893	318.801	87.574	−90.828	−249.904	6.870
2000	57.514	367.841	321.180	93.322	−88.963	−258.325	6.747
2100	57.576	370.648	323.469	99.077	−87.113	−266.839	6.637
2200	57.630	373.328	325.675	104.837	−85.280	−275.440	6.540
2300	57.678	375.891	327.803	110.603	−83.462	−284.124	6.453
2400	57.720	378.347	329.858	116.373	−81.659	−292.888	6.375
2500	57.757	380.704	331.845	122.146	−79.871	−301.726	6.304
2600	57.790	382.970	333.768	127.924	−78.098	−310.635	6.241
2700	57.819	385.151	335.631	133.704	−76.338	−319.612	6.183
2800	57.846	387.254	337.437	139.488	−74.591	−328.654	6.131
2900	57.869	389.285	339.190	145.273	−72.858	−337.759	6.084
3000	57.891	391.247	340.893	151.061	−71.137	−346.922	6.040
3100	57.910	393.145	342.548	156.851	−69.428	−356.143	6.001
3200	57.928	394.984	344.158	162.643	−67.731	−365.420	5.965
3300	57.944	396.767	345.726	168.437	−66.045	−374.749	5.932
3400	57.959	398.497	347.252	174.232	−64.369	−384.128	5.901
3500	57.972	400.177	348.741	180.029	−62.705	−393.557	5.874
3600	57.985	401.811	350.192	185.827	−61.051	−403.034	5.848
3700	57.996	403.400	351.609	191.626	−59.408	−412.556	5.824
3800	58.007	404.946	352.992	197.426	−57.775	−422.122	5.802
3900	58.017	406.453	354.344	203.227	−56.152	−431.731	5.782
4000	58.026	407.922	355.665	209.029	−54.539	−441.382	5.764
4100	58.034	409.355	356.957	214.832	−52.937	−451.073	5.747
4200	58.042	410.754	358.221	220.636	−51.345	−460.803	5.731
4300	58.049	412.120	359.459	226.440	−49.763	−470.570	5.716
4400	58.056	413.454	360.671	232.246	−48.193	−480.375	5.703
4500	58.062	414.759	361.859	238.052	−46.633	−490.215	5.690
4600	58.068	416.035	363.022	243.858	−45.084	−500.090	5.679
4700	58.074	417.284	364.164	249.665	−43.547	−509.998	5.668
4800	58.079	418.507	365.283	255.473	−42.022	−519.938	5.658
4900	58.084	419.704	366.382	261.281	−40.509	−529.910	5.649
5000	58.088	420.878	367.460	267.090	−39.008	−539.913	5.640
5100	58.093	422.028	368.519	272.899	−37.521	−549.946	5.633
5200	58.097	423.156	369.559	278.708	−36.047	−560.008	5.625
5300	58.101	424.263	370.580	284.518	−34.587	−570.098	5.619
5400	58.104	425.349	371.584	290.328	−33.141	−580.216	5.612
5500	58.108	426.415	372.572	296.139	−31.711	−590.360	5.607
5600	58.111	427.462	373.543	301.950	−30.295	−600.530	5.602
5700	58.114	428.491	374.498	307.761	−28.896	−610.725	5.597
5800	58.117	429.502	375.437	313.573	−27.513	−620.945	5.592
5900	58.120	430.495	376.362	319.385	−26.147	−631.189	5.588
6000	58.123	431.472	377.272	325.197	−24.798	−641.455	5.584

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 211.579\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -101.57 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -100.42 \pm 8.4\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma^+$	0	1
	[30000]	6
	42640	2

$\omega_e = 1241.44\ cm^{-1}$ $\omega_e x_e = 5.92\ cm^{-1}$ $\sigma = 1$
$B_e = 0.7273\ cm^{-1}$ $\alpha_e = 0.00508\ cm^{-1}$ $r_e = 1.509$ Å

Enthalpy of Formation

The adopted value is based on equilibrium data summarized below. The more reliable results from three different reactions lie in the range from about −23 to −28 kcal·mol^{-1}. Extreme values, including −20 and −32 kcal·mol^{-1}, can be discounted on experimental grounds. Margrave[1] recently reported $\Delta_f H°(298.15\ K) = 82.8 \pm 1.5$ kcal·mol^{-1} for 0.5 SiO_2(s) + 0.5 Si(s) = SiO(g), but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta_f H(298.15\ K) = -25.4$ kcal·mol^{-1}. Reaction A involves the nominal composition SiO(s) which is treated as an intimate mixture of 0.5 Si(cr) + 0.5 SiO_2(high cristobalite). X-ray studies[13,14] suggest that the condensed "SiO" used in[4,8] is probably a mixture of Si and amorphous or vitreous SiO_2. The adopted $\Delta_f H°$ corresponds to $D_0° = 190 \pm 3$ kcal·mol^{-1}. This may be compared with $D_0° = 179$ kcal·mol^{-1}obtained by linear Birge–Sponer extrapolation of the ground state vibrational constants and with $D_0° = 185 \pm 7$ kcal·mol^{-1} obtained by Barrow[15] from $D_0°$(LBX) = 77.5 kcal·mol^{-1} for the excited state at 52580 cm^{-1}. Barrow assumed $D_0°/D_0°$(LBX) = 0.456 based on related molecules.

Source	Reaction	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1}		Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
Ramstad[2]	A	Carrier gas	1510–1758	6	80.2 ± 2.3	85.08	3.0 ± 1.4	−23.1
Bergman[3]	A	$\Delta_{sub}H°$ by explosion	–	–	–	87 ± 2	–	−22
Gunther[4]	A*	Knudsen wt. gain	1202–1520	18	97.0 ± 0.7	86.76	−7.6 ± 0.5	−21.5
Porter[5]	A**	Knudsen mass spec.	1345–1463	2	105.1	87.35	−13	−20.9
Tombs [6]	A	Carrier gas	1573–1920	7	66.4 ± 1.1	84.75	11 ± 1	−23.5
Schafer[7]	A	Knudsen wt. loss	1336–1460	21	78.7 ± 1.5	82.74	2.9 ± 1.0	−25.5
Gel'd [8]	A*	Knudsen wt. loss	1173–1428	11	77.2 ± 1.8	85.87	6.8 ± 1.4	−22.3
Ramstad[2]	B***	Carrier gas	1698–1873	4	142.6 ± 0.7	133.79	−4.9 ± 0.4	−24.8
Bowles[2]	B***	Carrier gas	1703–1898	–	135	132.3	−2	−26.3
Tombs [6]	B***	Carrier gas	1501–1926	23	88 ± 3	127.3	22 ± 2	−31.3
Grube [9]	B***	Carrier gas	1473–1773	4	112 ± 3	134.4	13 ± 2	−24.2
Nesmeyanov[10]	C**	Knudsen collection	1653–1739	24	–	–	–	−20.5
Yang [11]	C	Knudsen wt. loss	1818–1960	15	199.3 ± 3.4	194.5	−2 ± 1.8	−21.9
Porter[5]	C	Knudsen mass spec.	1800–1900	2	130	184.4	29	−32.0
Cochran[12]	D	Knudsen effusion	?	–	–	11.5	–	−25.3

A) 0.5 SiO_2(high cristo.) + 0.5 Si(cr, l) = SiO(g) C) SiO_2(high cristo.) = 0.5 O_2(g) + SiO(g)
B) SiO_2(high cristo.) + H_2(g) = H_2O(g) + SiO(g) D) SiO_2(l) + Mg(g) = MgO(cr) + SiO(g)
*Starting material was "SiO" **Starting material was tridymite ***Starting material was quartz

Heat Capacity and Entropy

All constants for the ground state and the $A^1\Pi$ State at 42640 cm^{-1} are taken from the analysis of the A→X system reported by Lagerqvist.[16] An intercombination transition has been observed and assigned as $^1\Sigma^-$ a $^3\Pi_r$ by Verma.[17] The value of the a–X excitation energy is unknown but is estimated here as 30000 ± 5000 cm^{-1} by comparison with the a and A states of CO and Al Cl. Several additional states are known[15,16] to lie near or above the A state, but they are omitted because their contribution to the thermal functions is negligible.

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Continued on page 1813

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−8.715	−101.571	−101.571	INFINITE
100	29.105	179.626	237.700	−5.807	−100.382	−109.296	57.090
200	29.204	199.813	214.286	−2.894	−100.103	−118.385	30.919
250	29.466	206.354	212.069	−1.429	−100.217	−122.945	25.688
298.15	29.899	211.579	211.579	0.	−100.416	−127.305	22.303
300	29.918	211.764	211.580	0.055	−100.425	−127.472	22.195
350	30.500	216.419	211.946	1.565	−100.688	−131.959	19.694
400	31.135	220.533	212.767	3.106	−100.981	−136.407	17.813
450	31.768	224.236	213.839	4.679	−101.291	−140.817	16.346
500	32.365	227.615	215.050	6.282	−101.612	−145.191	15.168
600	33.399	233.611	217.656	9.572	−102.278	−153.845	13.393
700	34.213	238.823	220.316	12.955	−102.971	−162.385	12.117
800	34.845	243.434	222.923	16.409	−103.694	−170.824	11.154
900	35.336	247.568	225.436	19.919	−104.449	−179.170	10.399
1000	35.722	251.312	227.839	23.473	−105.237	−187.431	9.790
1100	36.030	254.731	230.131	27.061	−106.059	−195.610	9.289
1200	36.279	257.877	232.314	30.677	−106.917	−203.714	8.867
1300	36.484	260.790	234.393	34.315	−107.810	−211.744	8.508
1400	36.655	263.500	236.377	37.972	−108.742	−219.705	8.197
1500	36.800	266.034	238.270	41.645	−109.714	−227.597	7.926
1600	36.923	268.413	240.081	45.332	−110.727	−235.423	7.686
1700	37.031	270.655	241.814	49.029	−161.960	−242.737	7.458
1800	37.125	272.774	243.476	52.737	−162.830	−247.464	7.181
1900	37.209	274.784	245.071	56.454	−163.703	−252.142	6.932
2000	37.283	276.694	246.605	60.179	−164.579	−256.774	6.706
2100	37.351	278.515	248.081	63.910	−165.459	−261.362	6.501
2200	37.412	280.254	249.504	67.649	−166.345	−265.908	6.313
2300	37.469	281.918	250.878	71.393	−167.236	−270.414	6.141
2400	37.521	283.514	252.205	75.142	−168.132	−274.881	5.983
2500	37.569	285.046	253.488	78.897	−169.035	−279.310	5.836
2600	37.615	286.521	254.730	82.656	−169.943	−283.703	5.700
2700	37.658	287.941	255.934	86.420	−170.858	−288.061	5.573
2800	37.700	289.312	257.102	90.188	−171.778	−292.385	5.455
2900	37.739	290.635	258.235	93.960	−172.705	−296.677	5.344
3000	37.778	291.915	259.337	97.735	−173.637	−300.935	5.240
3100	37.816	293.155	260.408	101.515	−174.575	−305.163	5.142
3200	37.853	294.356	261.450	105.299	−175.518	−309.361	5.050
3300	37.891	295.521	262.465	109.086	−176.466	−313.529	4.963
3400	37.929	296.653	263.454	112.877	−177.418	−317.668	4.880
3500	37.968	297.753	264.418	116.672	−178.375	−321.779	4.802
3600	38.009	298.823	265.359	120.470	−563.487	−315.402	4.576
3700	38.052	299.865	266.278	124.273	−564.037	−308.503	4.355
3800	38.097	300.880	267.175	128.081	−564.591	−301.589	4.146
3900	38.145	301.871	268.052	131.893	−565.149	−294.661	3.947
4000	38.196	302.837	268.910	135.710	−565.709	−287.718	3.757
4100	38.251	303.781	269.749	139.532	−566.272	−280.761	3.577
4200	38.311	304.703	270.570	143.360	−566.835	−273.791	3.405
4300	38.375	305.606	271.374	147.195	−567.399	−266.807	3.241
4400	38.445	306.489	272.162	151.036	−567.962	−259.810	3.084
4500	38.521	307.353	272.935	154.884	−568.524	−252.800	2.934
4600	38.602	308.201	273.692	158.740	−569.084	−245.778	2.791
4700	38.690	309.032	274.435	162.604	−569.642	−238.744	2.653
4800	38.785	309.848	275.165	166.478	−570.196	−231.698	2.521
4900	38.887	310.648	275.881	170.362	−570.746	−224.639	2.395
5000	38.997	311.435	276.584	174.256	−571.291	−217.571	2.273
5100	39.114	312.208	277.275	178.161	−571.832	−210.491	2.156
5200	39.239	312.969	277.954	182.079	−572.367	−203.401	2.043
5300	39.372	313.718	278.622	186.009	−572.897	−196.300	1.935
5400	39.513	314.455	279.279	189.953	−573.421	−189.190	1.830
5500	39.662	315.181	279.925	193.912	−573.937	−182.070	1.729
5600	39.820	315.897	280.561	197.886	−574.448	−174.940	1.632
5700	39.986	316.604	281.187	201.876	−574.951	−167.801	1.538
5800	40.161	317.301	281.803	205.884	−575.448	−160.654	1.447
5900	40.343	317.989	282.411	209.909	−575.938	−153.499	1.359
6000	40.534	318.668	283.010	213.953	−576.420	−146.334	1.274

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

$S°(298.15\ K) = 55.52 \pm 0.4\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2938 \pm 20\ K$

$\Delta_f H°(0\ K) = -589.80 \pm 3.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -592.04 \pm 3.3\ kJ·mol^{-1}$
$\Delta_{fus} H° = [75.312]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is from U.S. Natl. Bur. Stand. Tech.[1] The adopted value was derived[2] from $\Delta_f H° = -198.1\ kcal·mol^{-1}$ for $SrCl_2$(cr), $\Delta_{sol} H°$ of $SrCl_2$ in HCl(aq), and calorimetric data for $\Delta_r H°$ of SrO(cr) + (x+2)HCl(n H_2O) → [$SrCl_2$(aq) + H_2O(aq) + x HCl(n' H_2O)]. Data of Adami and Conway[3] yield $\Delta_f H°$(SrO, cr) = $-141.3\ kcal·mol^{-1}$, while those of Monaenkova and Vorob'ev[4] yield = $141.7\ kcal·mol^{-1}$. Flidlider *et al.*[5] derived $-140.5\ kcal·mol^{-1}$ from their (unpublished) data for SrO(cr) and similar measurements for Sr(cr) by Guntz and Benoit.[6] Brisi and Abbattistra[7] omit the mole ratios necessary for treatment of their data, but an approximate calculation suggests consistency with the adopted value. We omit from this discussion the early data which Parker[1, 2] reviewed in selecting the adopted value.

Direct measurements of $\Delta_c H°$ of Sr(cr) by Mah[8] gave $-144.44 \pm 0.4\ kcal·mol^{-1}$. The negative bias of about 3 $kcal·mol^{-1}$ presumably resulted from inadequate allowance for side reactions, e.g., with combustion products of Mylar used to contain the Sr. Parker[2] noted that the combustion value is incompatible with data for $SrCl_2$(cr) and related compounds. We find that the combustion value is also less consistent with equilibrium data for $SrCl_2$(l and g). There is a similar, but much larger, discrepancy for Ba compunds (cf, BaO, crystal). Although impurity effects are of concern in all studies, the evidence predominantly favors the solution calorimetry.

Heat Capacity and Entropy

$C_p°$ is based on data (1.4–310 K) of Gmelin[9] who reported smoothed values only in the range 4 to 300 K. Based on Gmelin's graphs, we have corrected several typographical errors and resmoothed $C_p°$ above 250 K where the scatter increases significantly. The entropy is obtained by integration of our adopted $C_p°$ using $S° = 0.0003\ cal·K^{-1}·mol^{-1}$ at 4 K. Gmelin reported $S°(273.15\ K) = 12.40 \pm 0.02\ cal·K^{-1}·mol^{-1}$ compared with 12.33 from our integration. $C_p°$ data (58–298 K) of Anderson[10] are lower at all temperatures with deviations ranging from −4.7% (61 K) to −0.3% (223 K) and −0.7% (298 K).

$C_p°$ above 300 K is from constrained fitting of enthalpy data (363–1266 K) of Lander.[11] The calorimeter[11] was calibrated with Pt, but details are lacking to assess the bias due to minor changes in the enthalpy of Pt.[12] Deviations of Lander's data from the adopted curve range from −0.7 to +1.1%.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.675	−589.801	−589.801	INFINITE
100	24.949	15.242	91.864	−7.662	−591.740	−581.794	303.898
200	40.409	38.334	59.542	−4.242	−592.263	−571.540	149.271
298.15	45.409	55.522	55.522	0.000	−592.036	−561.402	98.355
500	50.534	80.376	60.880	9.748	−590.937	−540.947	56.512
600	52.049	89.728	64.929	14.880	−590.315	−531.007	46.228
700	53.262	97.845	69.064	20.147	−589.709	−521.171	38.890
800	54.300	105.026	73.119	25.526	−589.138	−511.419	33.392
900	55.220	111.476	77.029	31.002	−589.238	−501.664	29.116
1000	56.074	117.338	80.771	36.568	−588.437	−491.977	25.698
1100	56.873	122.720	84.343	42.215	−595.481	−482.006	22.889
1200	57.639	127.702	87.751	47.941	−595.475	−471.690	20.532
1300	58.379	132.345	91.005	53.742	−595.412	−461.376	18.538
1400	59.103	136.698	94.115	59.616	−595.291	−451.070	16.830
1500	59.810	140.800	97.092	65.562	−595.112	−440.775	15.349
1600	60.509	144.682	99.946	71.578	−594.876	−430.493	14.054
1700	61.199	148.371	102.687	77.664	−731.497	−419.048	12.876
1800	61.881	151.889	105.323	83.818	−729.287	−400.732	11.629
1900	62.559	155.253	107.863	90.040	−727.026	−382.541	10.517
2000	63.229	158.479	110.314	96.329	−724.717	−364.469	9.519
2100	63.898	161.580	112.682	102.685	−722.365	−346.515	8.619
2200	64.563	164.568	114.973	109.109	−719.974	−328.672	7.804
2300	65.229	167.452	117.192	115.598	−717.551	−310.940	7.062
2400	65.890	170.242	119.345	122.154	−715.100	−293.314	6.384
2500	66.551	172.945	121.435	128.776	−712.631	−275.791	5.762
2600	67.208	175.568	123.467	135.464	−710.151	−258.366	5.191
2700	67.864	178.117	125.444	142.218	−707.669	−241.036	4.663
2800	68.517	180.597	127.370	149.037	−705.195	−223.799	4.175
2900	69.174	183.013	129.247	155.921	−702.739	−206.650	3.722
2938.000	69.425	183.915	129.948	158.555	--- CRYSTAL <--> LIQUID ---		
3000	69.827	185.369	131.079	162.871	−700.309	−189.585	3.301
3100	70.479	187.669	132.867	169.887	−697.917	−172.600	2.908
3200	71.132	189.917	134.615	176.967	−695.572	−155.692	2.541
3300	71.785	192.116	136.324	184.113	−693.282	−138.857	2.198
3400	72.438	194.269	137.997	191.324	−691.058	−122.089	1.876
3500	73.086	196.378	139.635	198.600	−688.907	−105.387	1.573
3600	73.739	198.446	141.240	205.942	−686.837	−88.744	1.288

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = [80.846]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [-517.292]\ kJ·mol^{-1}$

$T_{fus} = 2938 \pm 20\ K$ $\Delta_{fus}H° = [75.312]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(SrO, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(2938 K)–$H°$(298.15 K), between the crystal and the liquid.

Heat Capacity and Entropy

$C_p°$ of the liquid is estimated as β cal·K^{-1} g atom^{-1} by comparison with other oxides. $C_p°$ is taken from the crystal in the range from 298 K up to the glass transition assumed at 2000 K. $S°$(298.15 K) is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Foex[1,2] obtained T_{fus} = 2660°C from a solar furnace study using SrO as its own container. We adopt this result but increase it by 5 for conversion to IPTS 68. The much lower value (2420°C) of Schumacher[3,4] probably resulted from contamination by WO_3 from tungsten supports of the sample. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ is 6 cal·K^{-1} g atom^{-1}. Phase data for the binary system SrO $SrZrO_3$[2] yield $\Delta_{fus}H° = 10 \pm 2$ kcal·mol^{-1} assuming ideal behavior in the liquid. Comparison with the very non ideal behavior of other mixed oxides suggests that the SrO data[2] are not inconsistent with $\Delta_{fus}H° = 18$ kcal·mol^{-1}.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	45.409	80.846	80.846	0.000	−517.292	−494.209	86.583
300	45.480	81.128	80.847	0.084	−517.285	−494.066	86.025
400	48.480	94.650	82.671	4.792	−516.792	−486.396	63.517
500	50.534	105.701	86.205	9.748	−516.193	−478.865	50.027
600	52.049	115.053	90.254	14.880	−515.571	−471.458	41.044
700	53.262	123.170	94.389	20.147	−514.965	−464.154	34.636
800	54.300	130.351	98.444	25.526	−514.394	−456.935	29.835
900	55.220	136.800	102.353	31.002	−514.494	−449.713	26.101
1000	56.074	142.663	106.096	36.568	−513.693	−442.557	23.117
1100	56.873	148.045	109.668	42.215	−520.737	−435.119	20.662
1200	57.639	153.027	113.076	47.941	−520.731	−427.335	18.601
1300	58.379	157.670	116.330	53.742	−520.668	−419.555	16.858
1400	59.103	162.023	119.440	59.616	−520.547	−411.781	15.364
1500	59.810	166.125	122.417	65.562	−520.368	−404.018	14.069
1600	60.509	170.007	125.271	71.578	−520.132	−396.269	12.937
1700	61.199	173.696	128.012	77.664	−656.753	−387.356	11.902
1800	61.881	177.213	130.648	83.818	−654.543	−371.573	10.783
1900	62.559	180.577	133.188	90.040	−652.282	−355.914	9.785
2000	63.229	183.803	135.639	96.329	−649.973	−340.375	8.890
2000.010	63.229	183.804	135.639	96.330	GLASS <-> LIQUID		
2000.010	66.944	183.804	135.639	96.330	TRANSITION		
2100	66.944	187.070	138.011	103.024	−647.283	−324.961	8.083
2200	66.944	190.184	140.312	109.718	−644.621	−309.675	7.353
2300	66.944	193.160	142.545	116.412	−641.992	−294.509	6.689
2400	66.944	196.009	144.714	123.107	−639.404	−279.457	6.082
2500	66.944	198.741	146.821	129.801	−636.862	−264.511	5.527
2600	66.944	201.367	148.869	136.496	−634.376	−249.667	5.016
2700	66.944	203.894	150.860	143.190	−631.953	−234.916	4.545
2800	66.944	206.328	152.798	149.884	−629.604	−220.254	4.109
2900	66.944	208.677	154.685	156.579	−627.337	−205.675	3.705
2938.000	66.944	209.549	155.389	159.123	CRYSTAL <-> LIQUID		
3000	66.944	210.947	156.522	163.273	−625.163	−191.172	3.329
3100	66.944	213.142	158.314	169.968	−623.092	−176.740	2.978
3200	66.944	215.267	160.060	176.662	−621.133	−162.374	2.650
3300	66.944	217.327	161.765	183.356	−619.295	−148.066	2.344
3400	66.944	219.326	163.428	190.051	−617.588	−133.813	2.056
3500	66.944	221.266	165.053	196.745	−616.019	−119.607	1.785
3600	66.944	223.152	166.641	203.440	−614.595	−105.444	1.530
3700	66.944	224.986	168.193	210.134	−613.323	−91.319	1.289
3800	66.944	226.772	169.711	216.828	−612.208	−77.226	1.062
3900	66.944	228.510	171.197	223.523	−611.253	−63.160	0.846
4000	66.944	230.205	172.651	230.217	−610.461	−49.117	0.641
4100	66.944	231.858	174.075	236.912	−609.835	−35.092	0.447
4200	66.944	233.472	175.470	243.606	−609.370	−21.080	0.262
4300	66.944	235.047	176.837	250.300	−609.071	−7.077	0.086
4400	66.944	236.586	178.178	256.995	−608.935	6.921	−0.082
4500	66.944	238.090	179.493	263.689	−608.957	20.918	−0.243
4600	66.944	239.562	180.783	270.384	−609.068	34.911	−0.396
4700	66.944	241.001	182.049	277.078	−609.376	48.914	−0.544
4800	66.944	242.411	183.291	283.772	−609.822	62.924	−0.685
4900	66.944	243.791	184.512	290.467	−610.402	76.946	−0.820
5000	66.944	245.143	185.711	297.161	−611.102	90.980	−0.950

PREVIOUS: CURRENT: December 1972

0 to 2938 K crystal
above 2938 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.675	−589.801	−589.801	INFINITE
100	24.949	15.242	91.864	−7.662	−591.740	−581.794	303.898
200	40.409	38.334	59.542	−4.242	−592.263	−571.540	149.271
298.15	45.409	55.522	55.522	0.000	−592.036	−561.402	98.355
300	45.480	55.803	55.523	0.084	−592.029	−561.212	97.716
400	48.480	69.325	57.346	4.792	−591.536	−551.010	71.955
500	50.534	80.376	60.880	9.748	−590.937	−540.947	56.512
600	52.049	89.728	64.929	14.880	−590.315	−531.007	46.228
700	53.262	97.845	69.064	20.147	−589.709	−521.171	38.890
800	54.300	105.026	73.119	25.526	−589.138	−511.419	33.392
900	55.220	111.476	77.029	31.002	−589.238	−501.664	29.116
1000	56.074	117.338	80.771	36.568	−588.437	−491.977	25.698
1100	56.873	122.720	84.343	42.215	−595.481	−482.006	22.889
1200	57.639	127.702	87.751	47.941	−595.475	−471.690	20.532
1300	58.379	132.345	91.005	53.742	−595.412	−461.376	18.538
1400	59.103	136.698	94.115	59.616	−595.291	−451.070	16.830
1500	59.810	140.800	97.092	65.562	−595.112	−440.775	15.349
1600	60.509	144.682	99.946	71.578	−594.876	−430.493	14.054
1700	61.199	148.371	102.687	77.664	−731.497	−419.048	12.876
1800	61.881	151.889	105.323	83.818	−729.287	−400.732	11.629
1900	62.559	155.253	107.863	90.040	−727.026	−382.541	10.517
2000	63.229	158.479	110.314	96.329	−724.717	−364.469	9.519
2100	63.898	161.580	112.682	102.685	−722.365	−346.515	8.619
2200	64.563	164.568	114.973	109.109	−719.974	−328.672	7.804
2300	65.229	167.452	117.192	115.598	−717.551	−310.940	7.062
2400	65.890	170.242	119.345	122.154	−715.100	−293.314	6.384
2500	66.551	172.945	121.435	128.776	−712.631	−275.791	5.762
2600	67.208	175.568	123.467	135.464	−710.151	−258.366	5.191
2700	67.864	178.117	125.444	142.218	−707.669	−241.036	4.663
2800	68.517	180.597	127.370	149.037	−705.195	−223.799	4.175
2900	69.174	183.013	129.247	155.921	−702.739	−206.650	3.722
2938.000	69.425	183.915	129.948	158.555	CRYSTAL <--> LIQUID TRANSITION		
2938.000	66.944	209.549	129.948	233.867			
3000	66.944	210.947	131.608	238.017	−625.163	−191.172	3.329
3100	66.944	213.142	134.203	244.712	−623.092	−176.740	2.978
3200	66.944	215.267	136.703	251.406	−621.133	−162.374	2.650
3300	66.944	217.327	139.115	258.100	−619.295	−148.066	2.344
3400	66.944	219.326	141.445	264.795	−617.588	−133.812	2.056
3500	66.944	221.266	143.698	271.489	−616.019	−119.607	1.785
3600	66.944	223.152	145.879	278.184	−614.595	−105.444	1.530
3700	66.944	224.986	147.992	284.878	−613.323	−91.319	1.289
3800	66.944	226.772	150.042	291.572	−612.208	−77.226	1.062
3900	66.944	228.510	152.032	298.267	−611.253	−63.160	0.846
4000	66.944	230.205	153.965	304.961	−610.461	−49.117	0.641
4100	66.944	231.858	155.845	311.656	−609.835	−35.092	0.447
4200	66.944	233.472	157.674	318.350	−609.370	−21.080	0.262
4300	66.944	235.047	159.455	325.044	−609.071	−7.077	0.086
4400	66.944	236.586	161.191	331.739	−608.935	6.921	−0.082
4500	66.944	238.090	162.883	338.433	−608.957	20.918	−0.243
4600	66.944	239.562	164.534	345.128	−609.068	34.911	−0.396
4700	66.944	241.001	166.146	351.822	−609.376	48.914	−0.544
4800	66.944	242.411	167.720	358.516	−609.822	62.924	−0.685
4900	66.944	243.791	169.258	365.211	−610.402	76.946	−0.820
5000	66.944	245.143	170.762	371.905	−611.102	90.980	−0.950

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = 230.058 \pm 0.4\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -11.52 \pm 16.7\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -13.39 \pm 16.7\ kJ·mol^{-1}$

Electronic States and Molecular Constants (σ–1)

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	$B_e°$, cm^{-1}	α_e, cm^{-1}	r_e, A	Source
$X^1\Sigma^+$	0.0	1	653.2	3.92	0.33798	0.00219	1.9199	1-4
$a^3\Pi$	9055	6	463.5	1.61	0.2584	0.0020	2.195	1
$A''^1\Pi$	9794	2	460.3	1.61	0.2610	0.0023	2.184	1
$^3\Sigma^+$	[8000]	3	[619.6]	[0.9]	[0.3047]	[0.0011]	[2.021]	5
$A^1\Sigma^+$	10870	1	619.6	0.9	0.30471	0.00112	2.021	1,4
$^3\Sigma^+$	[22000]	3	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^3\Delta$	[22000]	6	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^1\Delta$	[24000]	2	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^3\Sigma^-$	[24000]	3	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$^1\Sigma^-$	[24000]	1	[480]	[2.6]	[0.272]	[0.002]	[2.14]	5
$C^1\Sigma^+$	28546	1	480.2	2.6	0.2742	0.0021	2.132	4
$^3\Pi$	[23000]	6	[520]	[3.2]	[0.2936]	[0.0015]	[2.06]	5
$B^1\Pi$	24636	2	519.9	3.24	0.2936	0.0015	2.060	4

Enthalpy of Formation

We adopt $D° = 101.0 \pm 4$ and $\Delta_f H°(298.15\ K) = -3.2 \pm 4\ kcal·mol^{-1}$ based on the equilibria analyzed below. Greatest weight is given to the conventional mass–spectrometric studies.[7,8] We give "<" or ">" for the resulting $D°$ values which we feel may be biased. The JANAF differences in $\Delta_f H°(298.15\ K)$ for MoO_3–MoO_2 and WO_3–WO_2 may be biased by ~4 and ~–3 kcal·mol^{-1}, respectively; this would cause bias of the opposite sign in $D°$ values derived from reactions C and D. With these adjustments, our analyses would be comparable with those of Brewer and Rosenblatt[10] based on a $^1\Sigma$ ground state.

Less reliable data were reviewed by Drowart *et al.*[8] and Schofield.[11] Subsequent studies include two new techniques: nonisothermal Langmuir mass–spectrometry[9] and crossed–beam reaction threshold.[12] The former yields $D° = 98.3$ and >96 kcal·mol^{-1} (see reactions E and F below). JANAF data for the reaction SrO(cr) = Sr(g) + O(g) suggest that the P_0 assumed[9] for reaction F is too large. JANAF pressures for Sr(g) and O(g) may be combined with the estimated composition[3] of 5% SrO(g) to calculate $K_p°$ for reaction F and $D° = 93.5 \pm 8$ kcal·mol^{-1}. $D°$ would increase to 97 kcal·mol^{-1} if the beam in the magnetic– deflection experiment[3] contained 10% SrO(g) rather than 5%. The crossed–beam reaction[12] was interpreted to give $D° = 112.5(+3.5\ to\ -0.71$ kcal·mol^{-1}. We assume this value has a positive bias. Finally, Kalff[13] used spectrometry of CO–N_2O flames to derive $D° = 93.6 \pm 2.3$ kcal·mol^{-1}. This value becomes ~99 kcal·mol^{-1} when adjusted to be consistent with the JANAF free energy functions.

Source	Method	Reaction[a]	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15K) kcal·mol^{-1}	$D°$
7	Knudsen mass spec.	A	1931–2170	5	9.5 ± 7.1	42 ± 15	22.6 ± 2.8	−3.3 ± 3	101.2
8	Knudsen mass spec.	B	2156–2321	4	−40.0 ± 10	−73 ± 22	16.3 ± 5.8	−4.1 ± 6	101.9
	Knudsen mass spec.	C	1987–2233	8	−2.5 ± 6.1	40 ± 13	45.4 ± 2.6	1.5 ± 6	>96.4
	Knudsen mass spec.	D	2326	1	–	–	44.9	−4.2 ± 5	<102.0
9	Langmuir mass spec.[b]	E	1747–1850	Eqn.	−3.8	134.2	141.0 ± 0.7	−0.5 ± 3	98.3
	Langmuir mass spec.	F[c]	1747–1850	Eqn.	3.3	102.9	97.0	1.8 ± 3	>96.0
3	Magnetic deflection	F	~2500	1	–	–	94.5	4.3 ± 8	93.5

[a]Reactions: A) Sr(g) + SO(g) = SrO(g) + S(g) B) Sr(g) + O_2(g) = SrO(g) + O(g) C) Sr(g) + MoO_3(g) = SrO(g) + MoO_2(g)
D) Sr(g) + WO_3(g) = SrO(g) + WO_2(g) E) SrO(cr) = SrO(g) F) SrO(g) = Sr(g) + O(g)

[b]Nonisothermal. [c]$P_0 = 0.4273 P_{Sr}$ assumed.

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational–rotational constants of the observed states are from Field[1] and Rosen.[4] The long–sought $a^3\Pi$ and $A^1\Pi$ states of CaO, SrO and BaO were characterized by Field[1] using a new method for assignment of perturbations. This study resolved the long–standing controversy over low–lying electronic levels and confirmed[1] that $X^1\Sigma^+$ is the ground state.[3] We estimate the other potentially low–lying state ($^3\Sigma^+$) at 8000 cm^{-1} by assuming that it lies 3000 ± 2500 cm^{-1}[1,5] below the isoconfigurational A state. Other predicted states and thier vibrational–rotational constants are estimated in isoconfigurational groups by comparison with BeO, MgO, CaO and BaO.[5] Comparisons are facilitated by listing the states in the isoconfigurational order of MgO.[5,6] Our thermodynamic functions correspond to an "effective" ground state with $1<g<2$ instead of $g = 2$.[11] Our functions are calculated using first–order anharmonic corrections to Q_r^1 and Q_v^1 in the partition function $Q = Q_t \Sigma Q_r^1 Q_v^1 g_i \exp(-c_2\epsilon_i/T)$.

Continued on page 1813

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−9.041	−11.519	−11.519	INFINITE
100	29.175	196.665	257.973	−6.131	−11.561	−19.758	9.320
200	30.890	217.295	233.018	−3.145	−12.519	−27.588	7.205
250	32.086	224.318	230.597	−1.570	−12.976	−31.307	6.541
298.15	33.092	230.058	230.058	0.	−13.389	−34.793	6.096
300	33.127	230.263	230.059	0.061	−13.404	−34.926	6.081
350	33.967	235.435	230.465	1.739	−13.817	−38.480	5.743
400	34.627	240.015	231.378	3.455	−14.225	−41.976	5.481
450	35.146	244.125	232.570	5.200	−14.640	−45.420	5.272
500	35.557	247.850	233.915	6.968	−15.070	−48.817	5.100
600	36.154	254.389	236.797	10.555	−15.992	−55.481	4.830
700	36.559	259.995	239.720	14.192	−17.016	−61.983	4.625
800	36.854	264.897	242.567	17.863	−18.153	−68.331	4.462
900	37.089	269.251	245.295	21.561	−20.032	−74.457	4.321
1000	37.309	273.170	247.890	25.281	−21.077	−80.448	4.202
1100	37.561	276.738	250.353	29.024	−30.025	−85.969	4.082
1200	37.894	280.020	252.690	32.796	−31.974	−90.969	3.960
1300	38.360	283.070	254.911	36.607	−33.900	−95.807	3.850
1400	39.004	285.935	257.025	40.474	−35.787	−100.498	3.750
1500	39.862	288.654	259.044	44.415	−37.612	−105.056	3.658
1600	40.957	291.260	260.977	48.454	−39.353	−109.495	3.575
1700	42.293	293.782	262.833	52.614	−177.899	−112.649	3.461
1800	43.859	296.243	264.621	56.920	−177.537	−108.820	3.158
1900	45.625	298.661	266.349	61.393	−177.025	−105.016	2.887
2000	47.549	301.049	268.024	66.051	−176.349	−101.243	2.644
2100	49.576	303.418	269.653	70.906	−175.497	−97.507	2.425
2200	51.648	305.772	271.242	75.967	−174.468	−93.817	2.227
2300	53.703	308.114	272.794	81.235	−173.266	−90.177	2.048
2400	55.681	310.441	274.314	86.705	−171.902	−86.594	1.885
2500	57.532	312.752	275.805	92.367	−170.393	−83.070	1.736
2600	59.211	315.042	277.271	98.206	−168.762	−79.608	1.599
2700	60.688	317.305	278.712	104.203	−167.037	−76.212	1.474
2800	61.941	319.536	280.130	110.336	−165.249	−72.880	1.360
2900	62.963	321.728	281.527	116.583	−163.429	−69.614	1.254
3000	63.752	323.876	282.903	122.921	−161.612	−66.410	1.156
3100	64.320	325.976	284.258	129.326	−159.830	−63.266	1.066
3200	64.681	328.025	285.594	135.778	−158.114	−60.179	0.982
3300	64.855	330.018	286.910	142.256	−156.492	−57.144	0.905
3400	64.865	331.955	288.207	148.743	−154.992	−54.156	0.832
3500	64.736	333.834	289.484	155.225	−153.636	−51.210	0.764
3600	64.489	335.654	290.741	161.687	−152.445	−48.301	0.701
3700	64.148	337.416	291.979	168.119	−151.434	−45.423	0.641
3800	63.734	339.122	293.197	174.514	−150.619	−42.568	0.585
3900	63.265	340.771	294.396	180.864	−150.008	−39.733	0.532
4000	62.758	342.367	295.575	187.166	−149.609	−36.911	0.482
4100	62.225	343.910	296.736	193.415	−149.428	−34.097	0.434
4200	61.680	345.403	297.877	199.610	−149.462	−31.284	0.389
4300	61.131	346.848	298.999	205.751	−149.717	−28.467	0.346
4400	60.586	348.247	300.102	211.837	−150.190	−25.643	0.304
4500	60.051	349.602	301.187	217.868	−150.874	−22.805	0.265
4600	59.531	350.917	302.254	223.847	−151.701	−19.955	0.227
4700	59.029	352.191	303.303	229.775	−152.775	−17.080	0.190
4800	58.547	353.429	304.335	235.654	−154.037	−14.179	0.154
4900	58.088	354.632	305.349	241.485	−155.480	−11.251	0.120
5000	57.651	355.801	306.346	247.272	−157.088	−8.292	0.087
5100	57.237	356.938	307.327	253.016	−158.837	−5.300	0.054
5200	56.846	358.046	308.292	258.720	−160.754	−2.272	0.023
5300	56.477	359.125	309.241	264.386	−162.809	0.796	−0.008
5400	56.130	360.177	310.174	270.016	−164.993	3.902	−0.038
5500	55.804	361.204	311.093	275.613	−167.295	7.051	−0.067
5600	55.498	362.207	311.997	281.178	−169.704	10.243	−0.096
5700	55.210	363.187	312.886	286.713	−172.211	13.478	−0.124
5800	54.940	364.145	313.762	292.220	−174.807	16.759	−0.151
5900	54.686	365.082	314.624	297.702	−177.271	20.060	−0.178
6000	54.448	365.999	315.472	303.158	−179.985	23.427	−0.204

PREVIOUS: June 1974 (1 atm) CURRENT: June 1974 (1 bar)

$S°(298.15\ K) = 241.116 \pm 2.1\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 193.72 \pm 62.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 192.46 \pm 62.8\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$X^2\Delta_{3/2}$	0	2	$^2\phi_{7/2}$	22918.75	4	$^2\Delta_{5/2}$	27290.63	2
$^2\Delta_{5/2}$	3505.43	2	$^2\Pi_{1/2}$	23341.74	2	$^2\Delta_{3/2}$	32373.60	2
$^2\Delta_{3/2}$	10860.95	4	$^2\phi_{5/2}$	24058.42	2	$^2\Delta_{5/2}$	35785.83	4
$^2\Pi_{1/2}$	11062.00	4	$^2\Pi_{3/2}$	25593.13	2	$^2\Delta_{5/2}$	35886.20	2
$^2\phi_{5/2}$	12852.02	4	$^2\phi_{7/2}$	26121.50	2	$^2\Delta_{5/2}$	36615.00	4
$^2\Delta_{3/2}$	13569.27	4	$^2\Delta_{3/2}$	26673.04	2	$^2\Delta_{5/2}$	36785.00	4
$^2\phi_{5/2}$	15880.62	4						

$\omega_e = 1028.69\ cm^{-1}$ $\omega_e x_e = 3.51\ cm^{-1}$ $\sigma = 1$
$B_e = 0.402840\ cm^{-1}$ $\alpha_e = 0.00182\ cm^{-1}$ $r_e = 1.6872$ Å

Enthalpy of Formation

Based on the adopted ground state vibrational constants, a linear Birge–Sponer extrapolation yields $D_0° = 9.28$ eV (214.02 kcal·mol^{-1}). Applying a correction for the ionicity in the Ta–O bond,[1] we recalculate $D_0° = 8.57$ eV (199.94 kcal·mol^{-1}). This in turn leads to $\Delta_f H°$(TaO, g, 298.15 K) = 45.52 kcal·mol^{-1}, using auxiliary data.[2]

Inghram *et al.*[3] and Krikorian and Carpenter[4] have presented mass spectrometric evidence indicating that the predominant vapors in the vaporization of Ta–Ta_2O_5 mixtures in Ta Knudsen cells are TaO and TaO_2.

Source	Reaction	Data Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law
[3]	A*	1	2022	—	147.31	–	–	+49.51
[4]	A	2	1927–2034	162.80	175.47	6.4	+65.00	+77.67
[3]	B*	5	2151–2278	193.95	144.81	−22.3 ± 14.1	+100.30	+51.26
[4]	B	3	2180–2271	166.53	172.90	2.8 ± 7.9	+72.98	+79.35
[16]	C	graph	1900–2900	54.15	93.33	17.5	54.15	93.33

*Recalculated pressures using Otvis and Stevenson method for estimating ionization cross sections.[4,5]
A: 0.6 Ta(cr) + 0.2 Ta_2O_5(cr) = TaO(g) B: 0.6 Ta(cr) + 0.2 Ta_2O_5(l) = TaO(g) C: Ta(cr) + 1/2 O_2(g) = TaO(g)

The discrepancies here are rather severe and indicate considerable uncertainty in the system studied. In addition to the standard difficulties in a Knudsen cell system and the subsequent assumptions used for a 2nd and 3rd law analysis, there is an additional problem of oxygen diffusing through the walls of the Ta Knudsen cell, followed by volatilization of TaO(g) from the outer surfaces.[4,6] Based on JANAF values for Ta_2O_5(cr) and Ta_2O_5(l), $\Delta_r H°$(298.15 K) for reaction (A) should be 4.25 kcal·mol^{-1} more positive than reaction (B). The 3rd law results of Krikorian and Carpetner[4] for reactions (A) and (B) differ by 2.57 kcal·mol^{-1} but the 2nd law results differ by 3.73 kcal·mol^{-1} in the wrong direction. The 3rd law results of Inghram *et al.*[3] differ by 2.50. It is interesting to note that if the pressures reported by Krikorian and Carpetner[4] are multiplied by a factor of 1000, a 3rd law analysis yields results in excellent agreement with the 3rd law results of Inghram *et al.*[3] 2nd law values would still be in disagreement, however, and serious 3rd law drifts would still be present. Drowart *et al.*[16] observed the vapors over a Ta wire at various oxygen pressures in the range 1900–2900 K. Our analysis of their graphically displayed results does not clarify the situation as there is again a large 3rd law drift. Inghram *et al.*[3] also measured the ion currents corresponding to ZrO(g) and TaO(g) over mixtures of ZrO_2(cr) and Ta(cr) in a Ta Knudsen cell. The reaction was stated as ZrO_2(cr) + Ta(cr) = ZrO(g) + TaO(g). A 2nd law analysis of seven data points yielded $\Delta_r H°$(2200 K) = 317 ± 7 kcal·mol^{-1} as reported by Inghram *et al.*[3] Using auxiliary data,[2] this leads to $\Delta_f H°$(TaO, g, 298.15 K) = 51 ± 12 kcal·mol^{-1}, where + 12 kcal·mol^{-1}reflects the additional uncertainty in $\Delta H°$(298.15 K) for ZrO(g). Goldstein *et al.*,[7] in studying the vaporization of $Nd_2O_3$from Ta Knudsen cells in the range 2040–2450 K, determined the enthalpy of reaction for Nd_2O_3(cr) + Ta(cr) = 2 NdO(g) + TaO(g). They reported $D_0° = 9.36 \pm 0.2$ eV for TaO(g). This leads to $\Delta_f H°$(TaO, g, 298.15 K) = 29.6 ± 5.0 kcal·mol^{-1}.

Brewer and Rosenblatt[17] have suggested Gibbs energy functions which are 1.38 to 2.14 cal·K^{-1}·mol^{-1} more positive than those adopted here. The reason for the difference is that Brewer and Rosenblatt[17] based their functions on low lying electronic states as observed in Ta^{++}(g). The $\Delta_f H°$(298.15 K) values derived from the 3rd law would increase by roughly 3.5–4.2 kcal·mol^{-1} with the drift becoming more positive by 2–3 cal·K^{-1}·mol^{-1} if we were to use Brewer and Rosenblatt's valves.

Continued on page 1813

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−8.766	193.721	193.721	INFINITE
100	29.105	208.958	267.528	−5.857	194.182	183.566	−95.885
200	29.398	229.177	243.870	−2.939	193.393	173.223	−45.241
250	29.921	235.789	241.615	−1.457	192.921	168.235	−35.151
298.15	30.600	241.116	241.116	0.	192.464	163.522	−28.648
300	30.628	241.305	241.116	0.057	192.447	163.343	−28.441
350	31.394	246.084	241.492	1.607	191.986	158.529	−23.659
400	32.136	250.325	242.336	3.196	191.541	153.780	−20.082
450	32.815	254.150	243.439	4.820	191.108	149.086	−17.305
500	33.424	257.639	244.687	6.476	190.683	144.439	−15.089
600	34.463	263.828	247.375	9.872	189.839	135.270	−11.776
700	35.344	269.208	250.118	13.363	188.999	126.242	−9.420
800	36.137	273.980	252.808	16.938	188.171	117.333	−7.661
900	36.875	278.280	255.403	20.589	187.363	108.527	−6.299
1000	37.564	282.201	257.890	24.311	186.575	99.810	−5.214
1100	38.201	285.812	260.266	28.100	185.799	91.171	−4.329
1200	38.779	289.161	262.536	31.950	185.027	82.603	−3.596
1300	39.297	292.286	264.706	35.854	184.256	74.099	−2.977
1400	39.759	295.215	266.781	39.807	183.492	65.654	−2.450
1500	40.173	297.973	268.770	43.804	182.742	57.263	−1.994
1600	40.549	300.577	270.677	47.840	182.007	48.922	−1.597
1700	40.900	303.046	272.509	51.913	181.279	40.626	−1.248
1800	41.237	305.394	274.272	56.020	180.539	32.373	−0.939
1900	41.572	307.632	275.969	60.160	179.770	24.163	−0.664
2000	41.915	309.773	277.606	64.335	178.971	15.994	−0.418
2100	42.272	311.827	279.187	68.544	178.142	7.865	−0.196
2200	42.650	313.802	280.716	72.790	177.286	−0.223	0.005
2300	43.050	315.707	282.196	77.075	176.402	−8.272	0.188
2400	43.475	317.548	283.631	81.401	175.487	−16.282	0.354
2500	43.923	319.332	285.023	85.771	174.539	−24.253	0.507
2600	44.393	321.063	286.376	90.186	173.551	−32.186	0.647
2700	44.882	322.748	287.692	94.650	172.514	−40.079	0.775
2800	45.385	324.389	288.974	99.163	171.417	−47.933	0.894
2900	45.898	325.991	290.223	103.727	170.249	−55.746	1.004
3000	46.417	327.555	291.441	108.343	168.993	−63.518	1.106
3100	46.937	329.086	292.631	113.011	167.630	−71.246	1.200
3200	47.454	330.584	293.794	117.730	166.142	−78.929	1.288
3300	47.962	332.052	294.931	122.501	128.049	−86.092	1.363
3400	48.459	333.492	296.044	127.322	126.662	−92.560	1.422
3500	48.940	334.903	297.134	132.192	125.316	−98.988	1.477
3600	49.402	336.288	298.202	137.110	124.010	−105.378	1.529
3700	49.843	337.648	299.250	142.072	122.741	−111.732	1.577
3800	50.260	338.983	300.278	147.077	121.509	−118.053	1.623
3900	50.652	340.294	301.288	152.123	120.309	−124.341	1.665
4000	51.018	341.581	302.279	157.207	119.141	−130.599	1.705
4100	51.356	342.845	303.253	162.326	118.002	−136.829	1.743
4200	51.667	344.086	304.210	167.477	116.889	−143.031	1.779
4300	51.950	345.305	305.152	172.658	115.799	−149.206	1.812
4400	52.205	346.502	306.078	177.866	114.730	−155.357	1.844
4500	52.433	347.678	306.990	183.098	113.679	−161.483	1.874
4600	52.635	348.833	307.887	188.352	112.644	−167.587	1.903
4700	52.811	349.967	308.770	193.624	111.621	−173.668	1.930
4800	52.963	351.080	309.640	198.913	110.608	−179.727	1.956
4900	53.091	352.174	310.497	204.216	109.603	−185.765	1.980
5000	53.197	353.247	311.341	209.531	108.603	−191.783	2.004
5100	53.282	354.302	312.173	214.855	107.606	−197.780	2.026
5200	53.348	355.337	312.993	220.187	106.610	−203.759	2.047
5300	53.395	356.354	313.802	225.524	105.612	−209.718	2.067
5400	53.425	357.352	314.599	230.865	104.610	−215.658	2.086
5500	53.440	358.332	315.385	236.208	103.602	−221.580	2.104
5600	53.440	359.295	316.161	241.553	102.586	−227.483	2.122
5700	53.427	360.241	316.926	246.896	101.561	−233.368	2.139
5800	53.401	361.170	317.681	252.238	−638.230	−236.433	2.129
5900	53.365	362.083	318.426	257.576	−639.492	−229.496	2.032
6000	53.318	362.979	319.161	262.910	−640.813	−222.535	1.937

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 34.769 \pm 2.1\ J·K^{-1}·mol^{-1}$
$T_{trs} = [1265]\ K$

$\Delta_f H°(0\ K) = -539.668 \pm 12.6\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -542.665 \pm 12.6\ kJ·mol^{-1}$
$\Delta_{trs} H° = [4.2]\ kJ·mol^{-1}$

Enthalpy of Formation

Recent data tend to support our speculation[1] that previous calorimetric data refer to ill defined states of TiO(α, β). New combustion calorimetry[2] at 1100 K gave $\Delta_f H°(298.15\ K) = -129.9 \pm 1.1\ kcal·mol^{-1}$ which is ~5 kcal·mol^{-1} more negative than two earlier combustion studies[3,4] near room temperature. The difference was attributed[2] to use of samples consisting of α–phase[2] or mainly β–phase.[3,4] This interpretation is reasonable but unproved; it is neither confirmed nor refuted by incomplete published descriptions of the samples. Previously, the samples[3,4] were assumed to be α phase since similar material gave a discontinuity in enthalpy data above 1200 K.

Lyon[5] proposed that $\Delta_f H°$ may be affected by vacancy concentration, which varies from ~14 to 15%[5] in samples of stoichiometric β–TiO obtained at normal pressure. Samples with vacancy concentrations dow to 0% have been prepared[6] at high pressure. PVT data[6] allowed calculation[5] of values of $\Delta_f H°$ for TiO(β, 0% vacancies) → TiO(β, 14% vacancies). These values, if valid, suggest that $\Delta_f H°$ should be quite different for vacancy free β–TiO and significantly different even for the normal range of vacancy concentrations. Ideal ordered α–TiO, containing 1/6 or 16.7% vacancies, should involve additional changes in volume[5] and $\Delta_f H°$. In summary, the discrepancy in $\Delta_f H°$ may arise from sample differences – phase, composition and vacancy concentration – or from bias in the reaction calorimetry.

Our choice of $\Delta_f H°$ is influenced by $\Delta_f G°$ values derived from oxygen potentials[7,8] over $TiO_x (0 < \times < 1.5)$. We use solid state emf data[7] for many compositions in the range $0.6 < \times < 1.6$; these are converted to $\Delta_f G(O_2)$ with the authors' results[7] for the reference couples Ta/Ta_2O_5 and "$TiO_{1.3}$", the integrated over appropriate ranges of x in order to obtain $\Delta_f G°$. For reaction C relating TiO(β) to Ti_2O_3 we obtain $\Delta_f G° = -38.20(1300\ K), -37.49(1400\ K), -36.82(1500\ K), -36.180(1600\ K)$ and $-35.52(1700\ K)\ kcal·mol^{-1}$ with an estimated uncertainty of $\pm 1\ kcal·mol^{-1}$ (~3%). Combination with $\Delta_f G°$[09] of Ti_2O_3 yields $\Delta_f G°(TiO, \beta) = -131.5 + 23.5\ (T/1000)$; hopefully, the uncertainty does not exceed 1.5 kcal·mol^{-1}, based on a revised uncertainty of 1 kcal·mol^{-1} for Ti_2O_3.

Approximate values of $\Delta_f G°(TiO)$ may be derived from $TiO_{0.334}$(cr) and Ti(cr). Calorimetric data[10] yield $\Delta_f G°(TiO_{0.334}) = -46.1 + 8.40\ (T/1000)$ for $1200 < T < 1700$; this equation excludes the added disordering entropy[10] which now is known to be included, at least partially, in order disorder transitions of the alloy near 800 K.[11] $\Delta_f G(O_2)$ in the range $0.334 < \times < 0.5$ is approximated by limiting values, i.e., the mean from $\times < 0.334$ and the univariant value[7] at $x = 0.6$, in order to get negative and positive limits for $\Delta_f G°(TiO)$. These limits differ by 1 to 2.5 kcal·mol^{-1} at 1300 to 1700 K; mean $\Delta_f G°$ values are -102.0 (1300 K), -96.8(1400 K), -92.6(1500 K), -89.3(1600 K) and -86.0 kcal·mol^{-1}(1700 K). Equilibration with Ca/CaO and Mg/MgO[8] near 1200 K gave $\Delta_f G(O_2)$ for $\times < 0.3$; we combine these by interpolation with values[7] at $\times > 0.6$ to give $\Delta_f G°(TiO) = -107.3(1173\ K), -106.6(1200\ K)$ and -103.8 kcal·mol^{-1}(1273 K). $\Delta_f G°$ values derived from Ti(cr) and $TiO_{0.334}$(cr) are relatively uncertain, perhaps by 5 kcal·mol^{-1}, due to gaps in $\Delta_f G(O_2)$ and to greater uncertainty in emf and x.

$\Delta_f H°$ values from $\Delta_c H°$ and from 3rd law analyses of $\Delta_f G°$ are compared below. $\Delta_f H°$ from Ti_2O_3[7,9] is consistent with the new $\Delta_c H°$[02] but ~5 kcal·mol^{-1} more negative than the earlier value[3] which we assume to refer to β–TiO. $\Delta_f H°$ from Ti_2O_3[7,9] and from $\Delta_c H°$[3] could be made consistent if, as proposed by Charlu *et al.*,[2] $\Delta_t S°$ and $S°(\beta)$ were increased by 3 cal·K^{-1}·mol^{-1}[see β TiO [9]]. If G. L. Humphrey[3] instead of T. V. Chartu *et al.*[2] were correct for α–TiO, $\Delta_f G(O_2)$ would have to be 14% larger than observed. The more uncertain $\Delta_f H°$ from $TiO_{0.334}$[7,9] is very temperature dependent (large δS); it agrees with T.V. Charlu *et al.*[2] at 1350 K and with[3] at 1700 K. $\Delta_f H°$ from Ti[7–9] is even more negative than.[2] We adopt $\Delta_f H° = -129.7\ kcal·mol^{-1}$ but increase the uncertainty to + 3 kcal·mol^{-1} to allow for possible uncertainties in the samples.

Source	Method	Reaction[a]	T/K	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K),[b] kcal·mol^{-1} Authors	TiO(α)	TiO(β)
[2]	$\Delta_c H°$	A	1100–298	–	−96.05 ± 1.1	−129.86	−129.7	[−128.7]
[3]	$\Delta_c H°$	B	303–298	–	−101.61 ± 0.12	−123.9 ± 0.3	[−125.2]	−124.2
[4]	$\Delta_c H°$	B	293	–	−99.5	−124.5 ± 0.4	[−127.3]	−126.3
[7,9] From Ti_2O_3	emf,$\Delta_f G°$	C	1300–1700	2.9	−52.77	–	[−130.0]	−129.0
[7,9] From $TiO_{0.334}$	emf, $\Delta_f G°(O_2)$	D	1300–1700	−19.0	−127.5	–	[−128.5]	−127.5
[7,9] From Ti(cr)	emf, $\Delta_f G(O_2)$	D	1273	–	−133.2	–	[−134.2]	−133.2
		E	1173–1200	−2.5	−135.4	–	−135.4	[−134.4]

[a] A) $TiO(\alpha?) + 1/2\ O_2(g) = TiO_2$(rutile) B) $TiO(\beta?) + 1/2\ O_2 = TiO_2$(rutile) C) $TiO(\beta) + 1/4\ O_2(g) = 1/2\ Ti_2O_3$(cr)
D) $Ti(\beta) + 1/2\ O_2(g) = TiO(\beta)$ E) $Ti(\beta) + 1/2\ O_2(g) = TiO(\alpha?)$.
[b] $\Delta_f H°$ in brackets calculated from $\Delta_{trs} H° = [1.0]\ kcal·mol^{-1}$

Heat Capacity and Entropy

$C_p°$ is from data (52.6–296 K) of Shomate[12] and enthalpy data (357–1771 K) of Naylor.[13] $S°(298.15\ K) = 8.31\ cal·K^{-1}mol^{-1}$ is calculated from $C_p°$ based on $S°(50\ K) = 0.23\ cal·K^{-1}·mol^{-1}$. Ideal, ordered α–TiO should have no configurational entropy at $T/K = 0$.[14] We assume that $C_p°(\alpha) = C_p°(\beta)$ and fit the enthalpy data (357–1200 K and 1273–1771 K) by a single curve after subtracting the apparent $\Delta_{trs} H° = 0.83$ kcal·mol^{-1} from points above T_{trs}. The single curve gives larger deviations than separate fits of the two regions, but the increases are of marginal significance.

Continued on page 1813

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−6.174	−539.668	−539.668	INFINITE
100	12.765	5.732	63.375	−5.764	−541.270	−532.352	278.072
200	30.681	20.585	38.164	−3.516	−542.394	−522.918	136.572
298.15	39.957	34.769	34.769	0.000	−542.665	−513.278	89.924
300	40.062	35.017	34.770	0.074	−542.665	−513.096	89.338
400	44.978	47.274	36.408	4.346	−542.491	−503.257	65.719
500	48.242	57.679	39.648	9.015	−542.092	−493.491	51.555
600	50.836	66.709	43.422	13.972	−541.541	−483.821	42.120
700	53.095	74.719	47.331	19.171	−540.857	−474.253	35.389
800	55.187	81.947	51.214	24.586	−540.035	−464.793	30.348
900	57.153	88.561	55.001	30.204	−539.111	−455.442	26.433
1000	59.078	94.682	58.667	36.016	−538.152	−446.197	23.307
1100	60.961	100.402	62.203	42.018	−537.219	−437.047	20.754
1200	62.802	105.785	65.613	48.206	−540.300	−427.861	18.624
1265.000	63.998	109.129	67.764	52.327	---- ALPHA <--> BETA ----		
1300	64.643	110.884	68.901	54.578	−538.700	−418.555	16.818
1400	66.442	115.741	72.075	61.133	−537.011	−409.376	15.274
1500	68.241	120.386	75.142	67.867	−535.248	−400.320	13.940
1600	70.040	124.848	78.110	74.781	−533.422	−391.384	12.777
1700	71.839	129.148	80.986	81.875	−531.546	−382.564	11.755
1800	73.597	133.304	83.778	89.147	−529.636	−373.856	10.849
1900	75.396	137.331	86.491	96.597	−527.704	−365.254	10.042
2000	77.153	141.243	89.131	104.224	−540.450	−356.300	9.306
2100	78.910	145.050	91.704	112.027	−539.263	−347.121	8.634
2200	80.668	148.762	94.214	120.006	−537.912	−338.002	8.025
2300	82.467	152.387	96.664	128.163	−536.394	−328.949	7.471
2400	84.224	155.934	99.060	136.497	−534.710	−319.965	6.964
2500	85.981	159.408	101.405	145.007	−532.861	−311.055	6.499

PREVIOUS: March 1967 CURRENT: December 1973

$S°(298.15\ K) = [38.077]\ J·K^{-1}·mol^{-1}$
$T_{trs} = [1265]\ K$
$T_{fus} = 2023 \pm 30\ K$

$\Delta_f H°(298.15\ K) = [-538.481]\ kJ·mol^{-1}$
$\Delta_{trs}H° = [4.2]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [41.8]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of α–TiO by adding $\Delta_{trs}H°$ to the difference in $H°(1265\ K)–H°(298.15\ K)$ between α– and β–TiO. $\Delta_f G°$ data for β–TiO are reviewed on the table for α–TiO.[9] Values of $\Delta_f H°$ derived from $\Delta_f G°$ depend on the value of $S°$ (see Entropy). There are additional references on the $\Delta_f G°$ which deserve comment. Solid state emf data of Hoch *et al.*[18] are insufficient to yield $\Delta_f G°(\beta)$, especially in the direct way used by Drowart *et al.*[19] Their interpretation is inconsistent with phase diagrams[20,17] and extensive emf data[7] which show bivariant behavior in which $\Delta_f G(O_2)$ is a strong function of (O/Ti). It is not useful to reinterpret the emf data;[18] they show a temperature dependence of the wrong sign and we do not know the necessary electrode compositions. The often quoted $\Delta_f G°$ of Kubaschewski and Dench[21] is not an independent value since it assumes the correctness of the calorimetric data of the Bureau of Mines.[3,12,13] Kubaschewski's reassessment[22,8] of $\Delta_f G°(O_2)$ is superseded[9] due to new data.[7]

Heat Capacity and Entropy

We assume $C_p°(\beta) = C_p°(\alpha)$ as discussed on the table for α–TiO. $S°$ is calculated in a manner analogous to that of $\Delta_f H°$. $S°$ might be too low by as much as 3 or 4 $cal·K^{-1}·mol^{-1}$ [2] due to a possible uncertainty in $\Delta_{trs}H°$ (refer to Transition Data). The possibility exists because experimental samples[2–4,12,13] were not adequately characterized as to phase and vacancy concentration.

Phase Data

Stoichiometric TiO has been identified in two crystalline forms. High temperature β–TiO has a cubic NaCl–type structure,[23] while low temperature α–TiO has a closely related monoclinic structure.[24,25] Ideal α–TiO is an ordered array in which 1/6 of the lattice sites are vacant; half of the Ti and O atoms are missing alternately in every third (110) plane.[24] β–TiO obtained at normal pressures appears to have a lower and somewhat variable (~14–15%) vacancy concentration,[5] depending on conditions of preparation. Vacancy concentration can be reduced to arbitrary values (including zero) at high pressure by quenching from high temperature.[6] The process is reversed on reheating at normal pressure. Vacancy concentration[6,26] and vacancy disorder[20,25–27] in β–TiO appear to increase with increasing temperature, but definite conclusions are hampered since most data are for samples quenched to room temperature. Hilti[25] claimed two transitions: α→cubic (vacancy superlattice)→cubic (random vacancies). Jostsons and McDougall[20] designated the β– and α phases as γ and γ' in order to avoid confusion with other Ti–O alloys. The relatively wide homogeneity ranges of α– and β–TiO are summarized in recent phase diagrams[20, 17] and emf studies.[7] Limits of stability of α–TiO and the identity of its adjacent phases are less well established[20, 17] than for β phase. TiO is metallic, exhibiting weak paramagnetism[27] and superconductivity with T_c below 1 K.[26] Ordering of the vacancies by annealing had little effect on T_c.[26]

Transition Data

The nature and kinetics of α=β are crucial since we lack definite knowledge of the phases used in thermochemical studies. The transition α→β is more rapid than the reverse one. β–TiO is readily retained by quenching, but α can be obtained only by annealing[23 30] for several hours below T_{trs}. Moreover, there is disagreement as to whether the transition α→β proceeds directly[20] or via an intermediate peritectic decomposition, e.g. $Ti_2O + \beta\text{–}TiO_{1+x}$.[17] Emf data[7] seem more consistent with the latter, but none of the evidence is definitive.[17,20,24,27–30] Lyon[5] suggested that peritectic decomposition is an alternative to direct reduction of vacancy concentration on going from α to β (refer to Phase Data). The difference in vacancy concentration, if real, may preclude direct equilibrium between ideal α and normal β. This could invalidate calculation of $\Delta_{trs}S$ from $\Delta_{trs}H°$.[5]

Approximate ranges for T_{trs} include 1235–1270 K from enthalpy data;[13] 1235–1273 K from thermal analysis;[29] between 1223 and 1263 K,[20,24] between 1223 and 1288 K,[29] and between 1173 and 1223 K,[28,30] each based on the presence of α in samples quenched from various annealing temperatures. Later resistivity data[27] on Pearson's samples[28] suggest that T_{trs} is between 1233 and 1303 K. Hilti[25] reported 1253 K for the first transition and 1523 K for the second. The latter transition is not apparent in the enthalpy data.[13]

We adopt $T_{trs} = 1265$ K and arbitrarily take $\Delta_{trs}H° = 1.0\ kcal·mol^{-1}$. The apparent enthalpy difference ($\Delta_f H° = 0.83\ kcal·mol^{-1}$) at T_{trs} is equal to $\Delta_{trs}H°$ only if Naylor's sample[13] was originally α–TiO and returned to α form during drop calorimetry from above T_{trs}. Charlu *et al.*[2] proposed instead, based on the difference in $\Delta_c H°$ values, that $\Delta_{trs}H° = \sim 5\ kcal·mol^{-1}$ and $\Delta_{trs}S° = \Delta_{trs}H°/T_{trs} = \sim 4\ cal·K^{-1}·mol^{-1}$. The resulting increase in $S°(\beta)$ would change our third law analysis of $\Delta_f G°$ for reactions C and D (see α–TiO). It would minimize the discrepancy between $\Delta_c H°$[3,4] and the third law $\Delta_f H°$ but would more than double the discrepancy (δS) in the temperature dependence of $\Delta_f G°(\beta)$ derived from Ti_2O_3.[7,9] We prefer to minimize δS even though the larger value is compatible with the estimated uncertainty in $\Delta_f G°(\beta)$.

Entropy calculations are available for processes somewhat related to α=β. The configurational entropy of TiO(β) with random vacancies was shown to be 2.0 $cal·K^{-1}·mol^{-1}$.[14] $\Delta_{fus}S°$ of 1.5 to 2.3 $cal·K^{-1}·mol^{-1}$ for TiO(β, 0% vacancies) → TiO(β, 14.4% vacancies) was calculated by Lyon[5] from compressibility, thermal expansion and a PV isotherm. Taylor and Doyle[6] reported observing β TiO, presumably with much reduced vacancy concentration, at 56.4 kbar and 1153 K. This yields $\Delta_T \leq -80°$ assuming the $T_{trs} > 1233$ K at 1 atm. We estimate $\Delta V = -0.16\ cm^3·mol^{-1}$ from the densities[6,23] observed at 25°C and combine it with ΔP to calculate $\Delta_{trs}S° = \sim 2.6\ cal·K^{-1}·mol^{-1}$ for α→β. This calculation is highly uncertain; it is invalid if the transition is not an equilibrium one.

Fusion Data – Refer to the liquid table for details.

References - Refer to the liquid table

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	39.957	38.077	38.077	0.000	−538.481	−510.080	89.364
300	40.062	38.324	38.078	0.074	−538.480	−509.904	88.782
400	44.978	50.582	39.715	4.346	−538.307	−500.396	65.345
500	48.242	60.987	42.956	9.015	−537.908	−490.961	51.290
600	50.836	70.016	46.730	13.972	−537.356	−481.621	41.929
700	53.095	78.026	50.639	19.171	−536.673	−472.384	35.250
800	55.187	85.254	54.521	24.586	−535.851	−463.255	30.247
900	57.153	91.868	58.309	30.204	−534.927	−454.235	26.363
1000	59.078	97.990	61.974	36.016	−533.967	−445.321	23.261
1100	60.961	103.709	65.511	42.018	−533.035	−436.501	20.728
1200	62.802	109.093	68.921	48.206	−536.116	−427.646	18.615
1265.000	64.013	112.436	71.071	52.327	---- ALPHA <--> BETA ----		
1300	64.643	114.192	72.209	54.578	−534.515	−418.671	16.822
1400	66.442	119.048	75.382	61.133	−532.827	−409.822	15.291
1500	68.241	123.694	78.449	67.867	−531.063	−401.098	13.967
1600	70.040	128.155	81.417	74.781	−529.238	−392.492	12.814
1700	71.839	132.456	84.294	81.875	−527.362	−384.003	11.799
1800	73.597	136.612	87.086	89.147	−525.452	−375.625	10.900
1900	75.396	140.639	89.799	96.597	−523.520	−367.354	10.099
2000	77.153	144.551	92.439	104.224	−536.265	−358.732	9.369
2023.000	77.551	145.436	93.037	106.003	---- BETA <--> LIQUID ----		
2100	78.910	148.358	95.012	112.027	−535.079	−349.883	8.703
2200	80.668	152.069	97.521	120.006	−533.728	−341.095	8.099
2300	82.467	155.695	99.972	128.163	−532.210	−332.373	7.548
2400	84.224	159.242	102.368	136.497	−530.526	−323.720	7.046
2500	85.981	162.716	104.713	145.008	−528.677	−315.140	6.584

PREVIOUS: March 1967 CURRENT: December 1973

Titanium Oxide (TiO) LIQUID M_r = 63.8794

$S°(298.15\ K) = [60.140]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2023 \pm 30\ K$

$\Delta_f H°(298.15\ K) = [-493.939]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [41.8]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(TiO, l, 298.15 K) is calculated from that of β–TiO by addition of $\Delta_{fus} H°$ and the enthalpy difference in enthalpy, $H°$(2023 K)–$H°$(298.15 K), between β and liquid.

Heat Capacity and Entropy

$S°$(298.15 K) is calculated in a manner analogous to that used for $\Delta_f H°$. $C_p°$ is estimated as 8 $cal·K^{-1}\ g·atom^{-1}$. Below the assumed glass transition at 1200 K, $C_p°$ is taken to be the same as that of the crystal.

Fusion Data

T_{fus} was observed to be 1750°C,[31] 1760 ± 25°C[32] and >1750°C.[33] Incipient melting, partial melting and complete melting were observed[29] at approximately 1710°, 1730° and 1760°C, respectively. We adopt 1750 ± 30°C and estimate $\Delta_{fus} H°$ such that $\Delta_{fus} S°$ is 2.5 $cal·K^{-1}$ $cal·K^{-1}g·atom$.[1] TiO does not melt congruently;[17,20,29,32,33] there are various interpretations of the liquidus curve.

Vaporization Data

The vapor over TiO(cr, l) is mainly TiO and Ti, so the residue increases in (O/Ti) ratio.[34]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	39.957	60.140	60.140	0.000	−493.939	−472.116	82.713
300	40.062	60.387	60.140	0.074	−493.938	−471.981	82.179
400	44.978	72.644	61.778	4.346	−493.765	−464.679	60.681
500	48.242	83.049	65.018	9.015	−493.366	−457.450	47.790
600	50.836	92.079	68.792	13.972	−492.814	−450.317	39.204
700	53.095	100.089	72.702	19.171	−492.131	−443.286	33.078
800	55.187	107.317	76.584	24.586	−491.309	−436.363	28.492
900	57.153	113.931	80.371	30.204	−490.385	−429.549	24.930
1000	59.078	120.053	84.037	36.016	−489.425	−422.841	22.087
1100	60.961	125.772	87.574	42.018	−488.493	−416.229	19.765
1200	62.802	131.156	90.984	48.206	−491.573	−409.579	17.829
1200.000	62.802	131.156	90.984	48.206	GLASS <--> LIQUID		
1200.000	66.944	131.156	90.984	48.206	TRANSITION		
1300	66.944	136.514	94.283	54.901	−489.651	−402.825	16.186
1400	66.944	141.475	97.479	61.595	−487.822	−396.215	14.783
1500	66.944	146.094	100.567	68.290	−486.098	−389.733	13.572
1600	66.944	150.414	103.549	74.984	−484.492	−383.361	12.515
1700	66.944	154.473	106.427	81.678	−483.016	−377.086	11.586
1800	66.944	158.299	109.203	88.373	−481.684	−370.895	10.763
1900	66.944	161.919	111.883	95.067	−480.507	−364.772	10.028
2000	66.944	165.352	114.472	101.762	−494.186	−358.254	9.357
2023.000	66.944	166.118	115.054	103.301	---- BETA <--> LIQUID		----
2100	66.944	168.619	116.973	108.456	−494.108	−351.460	8.742
2200	66.944	171.733	119.392	115.150	−494.041	−344.668	8.183
2300	66.944	174.709	121.733	121.845	−493.986	−337.880	7.673
2400	66.944	177.558	124.000	128.539	−493.942	−331.094	7.206
2500	66.944	180.291	126.197	135.234	−493.909	−324.309	6.776
2600	66.944	182.916	128.328	141.928	−493.886	−317.526	6.379
2700	66.944	185.443	130.397	148.622	−493.874	−310.743	6.012
2800	66.944	187.877	132.407	155.317	−493.872	−303.960	5.670
2900	66.944	190.226	134.360	162.011	−493.880	−297.178	5.353
3000	66.944	192.496	136.261	168.706	−493.898	−290.395	5.056
3100	66.944	194.691	138.110	175.400	−493.925	−283.611	4.779
3200	66.944	196.816	139.912	182.094	−493.962	−276.826	4.519
3300	66.944	198.876	141.668	188.789	−494.006	−270.040	4.274
3400	66.944	200.875	143.380	195.483	−494.060	−263.252	4.044
3500	66.944	202.815	145.050	202.178	−494.121	−256.463	3.828
3600	66.944	204.701	146.681	208.872	−494.190	−249.672	3.623
3700	66.944	206.535	148.274	215.566	−903.365	−235.090	3.319
3800	66.944	208.321	149.831	222.261	−902.214	−217.044	2.983
3900	66.944	210.060	151.353	228.955	−901.125	−199.027	2.666
4000	66.944	211.754	152.842	235.650	−900.098	−181.038	2.364
4100	66.944	213.407	154.299	242.344	−899.129	−163.074	2.078
4200	66.944	215.021	155.726	249.038	−898.218	−145.133	1.805
4300	66.944	216.596	157.123	255.733	−897.362	−127.212	1.545
4400	66.944	218.135	158.492	262.427	−896.559	−109.311	1.298
4500	66.944	219.639	159.835	269.122	−895.809	−91.428	1.061

PREVIOUS: March 1967 CURRENT: December 1973

0	to	1265	K crystal, alpha
126	to	2023	K crystal, beta
above		2023	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−6.174	−539.668	−539.668	INFINITE
100	12.765	5.732	63.375	−5.764	−541.270	−532.352	278.072
200	30.681	20.585	38.164	−3.516	−542.394	−522.918	136.572
298.15	39.957	34.769	34.769	0.000	−542.665	−513.278	89.924
300	40.062	35.017	34.770	0.074	−542.665	−513.096	89.338
400	44.978	47.274	36.408	4.346	−542.491	−503.257	65.719
500	48.242	57.679	39.648	9.015	−542.092	−493.491	51.555
600	50.836	66.709	43.422	13.972	−541.541	−483.821	42.120
700	53.095	74.719	47.331	19.171	−540.857	−474.253	35.389
800	55.187	81.947	51.214	24.586	−540.035	−464.793	30.348
900	57.153	88.561	55.001	30.204	−539.111	−455.442	26.433
1000	59.078	94.682	58.667	36.016	−538.152	−446.197	23.307
1100	60.961	100.402	62.203	42.018	−537.219	−437.047	20.754
1200	62.802	105.785	65.613	48.206	−540.300	−427.861	18.624
1265.000	63.998	109.129	67.764	52.327	ALPHA <--> BETA TRANSITION		
1265.000	64.013	112.436	67.764	56.511			
1300	64.643	114.192	68.990	58.763	−534.515	−418.671	16.822
1400	66.442	119.048	72.394	65.317	−532.827	−409.822	15.291
1500	68.241	123.694	75.660	72.051	−531.063	−401.098	13.967
1600	70.040	128.155	78.802	78.965	−529.238	−392.492	12.814
1700	71.839	132.456	81.833	86.059	−527.362	−384.003	11.799
1800	73.597	136.612	84.761	93.331	−525.452	−375.625	10.900
1900	75.396	140.639	87.597	100.781	−523.520	−367.354	10.099
2000	77.153	144.551	90.347	108.409	−536.265	−358.731	9.369
2023.000	77.551	145.436	90.968	110.188	BETA <--> LIQUID TRANSITION		
2023.000	66.944	166.118	90.968	152.028			
2100	66.944	168.619	93.770	157.182	−494.108	−351.460	8.742
2200	66.944	171.733	97.243	163.877	−494.041	−344.668	8.183
2300	66.944	174.709	100.547	170.571	−493.986	−337.880	7.673
2400	66.944	177.558	103.697	177.266	−493.942	−331.094	7.206
2500	66.944	180.291	106.707	183.960	−493.909	−324.309	6.776
2600	66.944	182.916	109.588	190.654	−493.886	−317.526	6.379
2700	66.944	185.443	112.351	197.349	−493.874	−310.743	6.012
2800	66.944	187.877	115.005	204.043	−493.872	−303.960	5.670
2900	66.944	190.226	117.558	210.738	−493.880	−297.178	5.353
3000	66.944	192.496	120.019	217.432	−493.898	−290.395	5.056
3100	66.944	194.691	122.392	224.126	−493.925	−283.611	4.779
3200	66.944	196.816	124.685	230.821	−493.962	−276.826	4.519
3300	66.944	198.876	126.902	237.515	−494.006	−270.040	4.274
3400	66.944	200.875	129.048	244.210	−494.060	−263.252	4.044
3500	66.944	202.815	131.129	250.904	−494.121	−256.463	3.828
3600	66.944	204.701	133.146	257.598	−494.190	−249.672	3.623
3700	66.944	206.535	135.105	264.293	−903.365	−235.090	3.319
3800	66.944	208.321	137.008	270.987	−902.214	−217.044	2.983
3900	66.944	210.060	138.859	277.682	−901.125	−199.027	2.666
4000	66.944	211.754	140.661	284.376	−900.098	−181.038	2.364
4100	66.944	213.408	142.415	291.070	−899.129	−163.074	2.078
4200	66.944	215.021	144.124	297.765	−898.218	−145.133	1.805
4300	66.944	216.596	145.791	304.459	−897.362	−127.212	1.545
4400	66.944	218.135	147.418	311.154	−896.559	−109.311	1.298
4500	66.944	219.639	149.006	317.848	−895.809	−91.428	1.061

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 233.474 \pm 0.25\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 53.93 \pm 8.4\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 54.39 \pm 8.4\ kJ·mol^{-1}$

Electronic States and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	α_e, cm^{-1}	B_e, cm^{-1}	r_e, Å	Source
$X^3\Delta$	0	2	1008.26	4.13	0.00303	0.5354	1.620	1,2
	96.4	2						
	197.5	2						
$E^3\Pi$	11800.0	6	919.	[3.8]	[0.0029]	[0.5134]	[1.654]	3,4
$A^3\phi$	14019.4	2	867.71	3.94	0.00318	0.50734	1.664	1,2
	14192.3	2						
	14360.7	2						
$B^3\Pi$	16226.4	2	873.	4.	[0.0032]	0.5079	1.663	2,4
	16248.0	2						
	16264.2	2						
$C^3\Delta$	19341.7	2	837.86	4.546	0.0029	0.4889	1.695	1,2
	19437.4	2						
	19531.6	2						
$a^1\Delta$	[1000.]	2	1016.3	3.93	[0.003]	0.5377	1.616	1,3–7
$d^1\Sigma^+$	[3219.]	1	1023.8	4.64	0.00337	0.5490	1.600	1,4
$b^1\Pi$	[12273.]	2	918.7	3.75	0.00286	0.5134	1.654	1,4
$c^1\phi$	[18841.]	2	916.7	4.33	[0.0032]	0.5228	1.639	1,4
$f^1\Delta$	[20069.]	2	[933.]	[4.2]	[0.003]	0.5037	1.670	8,5,4
$e^1\Sigma$	[27517.]	1	853.9	4.7	0.0025	0.4892	1.694	9,5,4

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = 13.0 \pm 2$ kcal·mol^{-1} and $D_0° = 158.5 \pm 2$ kcal·mol^{-1} are selected from reactions A, B, C and E[16] which are summarized below. The first three are isomolecular exchange reactions studied by mass spectrometry.[13,14] Reaction E is obtained from univariant Ti_2O_3–Ti_3O_5 by combining Knudsen effusion with the pressure ratio (TiO_2/TiO) = 0.246 obtained from mass spectrometry.[16] We use the same analysis[16] for (E),[17] although the condensed phase may not be univariant. We presume that the smaller $D_0° = 145.4$ kcal·mol^{-1}from reaction D is due to bias in the mass-spectrometric values[15] for the partial pressure of O(g). Larger values of $D°$ from sublimation[17,19] and vaporization[18] of TiO are subject to bias due to presence of species other than TiO in the vapor and to unknown liquid activities. Activities of TiO in TiO_x(cr) are very close to unity at $x = 1.0$–1.1 and 1900 K according to emf data.[20]

The analysis of Drowart *et al.*[14] was the key to resolution of the discrepancy in $D_0°$,[21] later studies[13,16] confirmed their analysis. Our analysis uses $D_0°$(GeO, g) = 156.4 ± 1.5, $D_0°$(ScO, g) = 160.4 ± 2.0, and $D_0°$(YO, g) = 170.4 ± 2.5 kcal·mol^{-1} with other auxiliary data and newly calculated Gibbs–energy functions, all of which are essentially consistent with Drowart *et al.*[14,22] Our selected $D_0°$(TiO) = 158.5 ± 2 kcal·mol^{-1} may be compared with 174.5 and 156.3 kcal·mol^{-1} calculated by linear Birge–Sponer extrapolation of present[1] and older[23] vibrational constants of $X^3\Delta$. Kushawaha[24] used the older constants in construction of RKRV potential energy curves and thereby estimated $D_0° = 165.4$ kcal·mol^{-1}. He also derived $D_0° = 167.8 \pm 20$ kcal·mol^{-1} from a chemiluminescent reaction,[10] but we dismiss this since auxiliary data for KO and TiCl were estimates.

Source	Method	Reaction[a]	T/K	Data Points	$\delta S°$ cal·K^{-1}·mol^{-1}	$\Delta_r H°$(298.15 K), kcal mol 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$D_0°$
13	Mass spec.	A	2145–2418	9	−6.4 ± 5.0	−11.5 ± 11.3	3.2 ± 2.8	11.7 ± 3.4	159.8
	Mass spec.	B	~2023–2417	24[b]	0.2 ± 1.5	−2.6 ± 3.3	−3.0 ± 1.5	14.0 ± 2.7	157.4
14	Mass spec.	B	1951–2463	Eqn.	0.0 ± 0.1	−3.0	−3.0	14.0 ± 2.4	157.4
	Mass spec.	C	2313	1	–	–	−12.0	13.0 ± 3.0	158.5
15	Mass spec.	D	2015–2240	12, 6	−0.2 ± 2.6	145.2 ± 5.4	146.5 ± 1.6	26.1 ± 2	145.4
16	Knudsen eff.	E	1937–2044	12	−2.0 ± 3.6	150.6 ± 7.1	154.7 ± 0.8	12.3 ± 3.5	159.1
17	Knudsen eff.	E	1971–2085	15	0.0 ± 12	152.0 ± 2.5	152.0 ± 2.8	9.7 ± 3.6	161.8
	Knudsen eff.	F	1847–1968	8	11 ± 3	157.1 ± 5	135.1 ± 3	6.4 ± 4	165.0
18	Mass spec.	G	2027–2072	2	48	225.	125.5 ± 4	7.5 ± 7	164.0

[a] A) TiO(g) + Ge(g) = Ti(g) + GeO(g); B) TiO(g) + Sc(g) = Ti(g) + ScO(g);
C) TiO(g) + Y(g) = Ti(g) + YO(g); D) TiO(g) = Ti(g) + O(g) from difference of two observed reactions $TiO_2(g) = O + TiO$ and $TiO_2 + Ti = 2\ TiO$;
E) $2\ Ti_2O_3(cr) = Ti_3O_5(\beta) + TiO(g)$; F) TiO(high) = TiO(g)
G) TiO(l) → TiO(g)
[b] Extreme points selected from large data set.

Continued on page 1813

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.630	53.934	53.934	INFINITE
100	33.880	198.046	262.006	−6.396	55.155	44.842	−23.423
200	31.771	220.717	236.408	−3.138	55.040	34.491	−9.008
250	31.908	227.809	234.005	−1.549	54.737	29.387	−6.140
298.15	32.476	233.474	233.474	0.	54.392	24.535	−4.298
300	32.502	233.675	233.474	0.060	54.378	24.350	−4.240
350	33.263	238.741	233.873	1.704	53.997	19.375	−2.892
400	34.021	243.233	234.767	3.386	53.605	14.456	−1.888
450	34.702	247.280	235.937	5.105	53.208	9.586	−1.113
500	35.285	250.968	237.258	6.855	52.804	4.760	−0.497
600	36.176	257.485	240.100	10.431	51.975	−4.771	0.415
700	36.786	263.110	242.995	14.081	51.109	−14.161	1.057
800	37.212	268.051	245.824	17.782	50.217	−23.425	1.529
900	37.518	272.453	248.543	21.519	49.261	−32.573	1.891
1000	37.745	276.418	251.136	25.283	48.172	−41.609	2.173
1100	37.918	280.024	253.600	29.066	46.886	−50.527	2.399
1200	38.052	283.330	255.942	32.865	41.416	−59.198	2.577
1300	38.158	286.380	258.168	36.676	40.455	−67.545	2.714
1400	38.245	289.211	260.285	40.496	39.409	−75.814	2.829
1500	38.319	291.852	262.302	44.324	38.267	−84.005	2.925
1600	38.386	294.327	264.227	48.160	37.014	−92.116	3.007
1700	38.450	296.656	266.067	52.001	35.637	−100.145	3.077
1800	38.516	298.856	267.828	55.850	34.124	−108.089	3.137
1900	38.588	300.940	269.517	59.705	32.461	−115.945	3.188
2000	38.669	302.922	271.138	63.568	15.951	−123.256	3.219
2100	38.762	304.810	272.697	67.439	13.206	−130.149	3.237
2200	38.869	306.616	274.198	71.321	10.459	−136.911	3.251
2300	38.992	308.346	275.645	75.213	7.713	−143.548	3.260
2400	39.132	310.009	277.042	79.120	4.969	−150.066	3.266
2500	39.290	311.609	278.393	83.040	2.229	−156.469	3.269
2600	39.466	313.154	279.701	86.978	−0.505	−162.763	3.270
2700	39.661	314.647	280.967	90.934	−3.232	−168.952	3.269
2800	39.874	316.093	282.196	94.911	−5.948	−175.040	3.265
2900	40.105	317.496	283.389	98.910	−8.651	−181.032	3.261
3000	40.352	318.860	284.549	102.932	−11.341	−186.930	3.255
3100	40.614	320.187	285.677	106.981	−14.014	−192.738	3.248
3200	40.890	321.481	286.776	111.056	−16.670	−198.462	3.240
3300	41.179	322.744	287.847	115.159	−19.306	−204.102	3.231
3400	41.478	323.978	288.892	119.292	−21.921	−209.662	3.221
3500	41.787	325.184	289.911	123.455	−24.513	−215.146	3.211
3600	42.103	326.366	290.908	127.649	−27.082	−220.557	3.200
3700	42.425	327.524	291.882	131.876	−438.725	−218.108	3.079
3800	42.751	328.660	292.835	136.135	−440.010	−212.127	2.916
3900	43.080	329.774	293.768	140.426	−441.324	−206.113	2.761
4000	43.409	330.869	294.681	144.751	−442.666	−200.065	2.613
4100	43.738	331.945	295.577	149.108	−444.034	−193.983	2.471
4200	44.064	333.003	296.456	153.498	−445.427	−187.868	2.336
4300	44.386	334.044	297.318	157.921	−446.843	−181.719	2.207
4400	44.703	335.068	298.164	162.375	−448.281	−175.537	2.084
4500	45.015	336.076	298.996	166.861	−449.739	−169.322	1.965
4600	45.319	337.068	299.812	171.378	−451.216	−163.074	1.852
4700	45.614	338.046	300.616	175.925	−452.711	−156.794	1.743
4800	45.901	339.010	301.405	180.500	−454.222	−150.482	1.638
4900	46.178	339.959	302.183	185.104	−455.750	−144.138	1.537
5000	46.444	340.895	302.947	189.736	−457.293	−137.763	1.439
5100	46.699	341.817	303.701	194.393	−458.850	−131.357	1.345
5200	46.943	342.726	304.442	199.075	−460.421	−124.920	1.255
5300	47.174	343.622	305.173	203.781	−462.005	−118.453	1.167
5400	47.394	344.506	305.893	208.509	−463.602	−111.956	1.083
5500	47.602	345.378	306.603	213.259	−465.211	−105.430	1.001
5600	47.797	346.237	307.303	218.029	−466.833	−98.873	0.922
5700	47.980	347.085	307.994	222.818	−468.467	−92.288	0.846
5800	48.150	347.921	308.675	227.625	−470.113	−85.674	0.772
5900	48.309	348.745	309.347	232.448	−471.772	−79.032	0.700
6000	48.455	349.558	310.011	237.286	−473.442	−72.361	0.630

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 39.011 \pm 0.8\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2063 \pm 10\ K$

$\delta_f H°(0\ K) = -429.715 \pm 6.3\ kJ·mol^{-1}$
$\delta_f H°(298.15\ K) = -431.789 \pm 6.3\ kJ·mol^{-1}$
$\delta_{fus} H° = [54.4]\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpies of formation for the vanadium oxides are based on the combustion studies by Mah and Kelley.[1] The adopted value is $\delta_f H°$(VO, cr, 298.15 K) = −103.2 kcal·mol^{-1}, as reported by Mah and Kelley.[1] For more details, refer to the V_2O_5(cr) table.[2] We increase their stated uncertainty limits of +0.3 kcal·mol^{-1} to ±1.5 kcal·mol^{-1} so as to more adequately include all uncertainties in the experimental procedure, rather than just the scatter in the final results.

Other enthalpy of formation results for VO(cr) derived from combustion studies are reported as −102 kcal·mol^{-1} by Samsonov[3] and −102 ± 1 kcal·mol^{-1} by Vol'f and Ariya.[4] However, the latter study[4] also reported a corresponding result for V_2O_5(cr) which is 5.4 kcal·mol^{-1} more negative than the adopted JANAF value.[2] Older work by Kobayashi[5] involving water vapor equilibrium on vanadium and its oxides and by Mixter[6] involving sodium peroxide fusions are not considered.

Heat Capacity and Entropy

Todd and Bonnickson[7] measured the heat capacity of VO(cr) in the region 55–296 K. The sample, estimated to be 98.2% pure, was prepared by heating a mixture of V(cr) and V_2O_3(cr) in a hydrogen atmosphere. The heat capacity results showed an anomaly similar to that found by Anderson[8] for V_2O_3(cr). Todd and Bonnickson[7] concluded that the 20 cal·K^{-1}·mol^{-1} in excess to that expected for a smooth $C_p°$ curve in the region 168–191 K was evidence of either an incomplete reaction in preparing VO(cr) or subsequent disproportionation. Experimental data in this region were not reported. Using the Debye function D(398/T) as suggested by Todd and Bonnickson,[7] we calculate $S°(50\ K) = 0.297$ cal·K^{-1}·mol^{-1} and $H°(50\ K) - H°(0\ K) = 11.051$ cal·mol^{-1}. The data are graphically curve fitted assuming a smooth sequence of "data points" in the region 168–191 K. Near 298.15 K the heat capacity data of Todd and Bonnickson[7] and the derivative of the smoothed enthalpy data of Orr[9] were constrained to join smoothly. Orr[9] used the same sample as did Todd and Bonnickson[7] and measured the enthalpy (fourteen data points) in the region 394–1698 K. The heat capacities derived from the Orr[9] data were extrapolated to T_{fus} and above.

The heat capacity, entropy and enthalpy values at 298.15 K reported by Chernyaev *et al.*[10] for VO_x, where $x = 0.86, 0.99, 1.24$ and 1.30, led to values for VO(cr) which are considerably lower than our adopted values. For example, the $S°(298.15\ K)$ value derived from the data of Chernyaev *et al.*[10,22] is roughly 1.3 cal·K^{-1}·mol^{-1} lower than our adopted value.

Phase Data

Vanadium monoxide crystallizes in the cubic NaCl type structure and is stable over a wide range of composition, roughly between the limit $VO_{0.80}$ and $VO_{1.30}$. Details and many references may be found in Stringer[20] and Alexander and Carlson.[21]

Transition Data

There exists a large volume of literature dealing with transitions in the vanadium oxide condensed phases. These various oxides show widely varying electric and magnetic properties, as is discussed by Adler.[11] In the case of VO(cr), which has a wide homogeneity range, the reported data in the region of 120 K is conflicting. Sample purity, stoichiometry, and preparation undoubtedly play a major role in the appearance or lack of appearance of a possible transition. Much of the literature does not provide adquate sample characterization for an unequivical analysis of the data.

Conductivity measurements by Morin[12] on single crystals of VO(cr) and numerous measurements, including NMR, by Warren *et al.*[13] indicated a transition in the region 114–126 K and 88–125 K, respectively. The transition was described by Morin[12] as a semiconductor metal type. This is further discussed by Zhuze *et al.*[14] and Hyland.[15] However, Kawano *et al.*[16] and Takei and Koide[17] presented evidence on electric and magnetic properties and thermoelectric power for various vanadium monoxides within its homogeneity range which did not indicate any transition. Recent studies by Warren *et al.*[18] also indicated no evidence of a transition and, in addition, stated that the sample used in a previous study[13] was mainly V_2O_3(cr) as determined by x-ray analysis. Many more references on this subject may be found in the compilation by Neuberger[19] and in a review of the V–O system by Stringer.[20]

We conclude that there is no transition below T_{fus} for VO(cr) based primarily on the work cited above.[16–18]

Fusion Data – Refer to the liquid table for details.

Sublimation Data

At temperatures approaching T_{fus}, VO(cr) is reported to yield a vapor containing V(g), VO(g), and VO_2(g).[2]

References

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[2]JANAF Thermochemical Tables: V_2O_5(cr), 6–30–73; VO(g), 12–31–73.
[3]G. V. Samsonov, Ukrain. Khim. Zhur. **23**, 287 (1957); Chem. Abstr. **52**, 1826g (1958).
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[5]M. Kobayashi, Bull. Chem. Soc. Japan **8**, 231 (1933); Science Repts. Tohoku Imp. Univ., 1st Ser. **22**, 1240 (1933).

Continued on page 1814

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−6.908	−429.715	−429.715	INFINITE
100	13.895	6.730	71.088	−6.436	−431.184	−422.473	220.677
200	34.100	23.035	42.859	−3.965	−432.005	−413.352	107.956
298.15	45.501	39.011	39.011	0.000	−431.789	−404.210	70.816
300	45.647	39.293	39.012	0.084	−431.778	−404.039	70.350
400	49.580	53.063	40.863	4.880	−431.032	−394.899	51.569
500	51.651	64.356	44.466	9.945	−430.157	−385.966	40.322
600	53.530	73.940	48.599	15.204	−429.199	−377.216	32.840
700	55.343	82.329	52.831	20.648	−428.158	−368.633	27.508
800	57.099	89.834	56.995	26.271	−427.037	−360.206	23.519
900	58.803	96.658	61.029	32.067	−425.846	−351.922	20.425
1000	60.463	102.940	64.910	38.030	−424.586	−343.776	17.957
1100	62.086	108.779	68.635	44.158	−423.259	−335.758	15.944
1200	63.677	114.250	72.211	50.446	−421.879	−327.864	14.272
1300	65.243	119.408	75.645	56.892	−420.450	−320.087	12.861
1400	66.791	124.300	78.947	63.494	−418.983	−312.422	11.657
1500	68.325	128.961	82.127	70.250	−417.478	−304.863	10.616
1600	69.842	133.419	85.195	77.159	−415.936	−297.405	9.709
1700	71.351	137.698	88.158	84.218	−414.366	−290.045	8.912
1800	72.851	141.819	91.025	91.429	−412.774	−282.778	8.206
1900	74.339	145.798	93.804	98.788	−411.171	−275.599	7.577
2000	75.847	149.649	96.500	106.297	−409.565	−268.506	7.013
2063.000	76.747	152.015	98.160	111.104	--- CRYSTAL <---> LIQUID ---		
2100	77.298	153.385	99.121	113.954	−407.967	−261.492	6.504
2200	78.781	157.015	101.670	121.758	−429.269	−254.449	6.041
2300	80.250	160.549	104.154	129.710	−427.853	−246.534	5.599
2400	81.718	163.996	106.576	137.808	−426.302	−238.684	5.195
2500	83.183	167.361	108.940	146.053	−424.615	−230.900	4.824
2600	84.646	170.652	111.250	154.445	−422.792	−223.187	4.484

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [69.137]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2063 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-370.901]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [54.4]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(VO, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the differences in enthalpy, $H°$(2063 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 7.5 $cal·K^{-1}$ g atom.[1] Below the assumed transition temperature at 1200 K, $C_p°$ is assumed to be the same as in the crystal. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Alexander and Carlson[1] proposed a phase diagram for the V–VO system based on melting point determinations, differential thermal analysis, metallographic observations, and x-ray parametric measurements. These authors[1] reported that VO(cr) melts congruently at 2063 ± 10 K. We adopt this value for T_{fus}. In a phase diagram proposed by Stringer[2] a melting temperature of 1998 K was suggested but the melting was not congruent.

VO(cr) has a sodium chloride structure and is stable over a wide range of composition, as is discussed, for example by Stringer.[2] $\Delta_{fus} H°$ is estimated based on $\Delta_{fus} S° = 6.3\ cal·K^{-1}·mol^{-1}$ as in NaCl.[3] Since VO(cr) has a defect structure, a comparison with the $\Delta_{fus} S°$ value of NaCl is not entirely satisfactory. We make this comparison, however, pending further data.

Vaporization Data

There are no data available in the literature dealing with the vaporization of VO(l). We anticipate substantial decomposition to occur during heat treatment of VO(l). See VO(g) table for further information.[3]

References

[1]D. G. Alexander and O. N. Carlson, Met. Trans. **2**, 2805 (1971).
[2]J. Stringer, J. Less Common Metals **8**, 1 (1965).
[3]JANAF Thermochemical Tables: NaCl(cr), 9–30–64; VO(g), 12–31–73.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	45.501	69.137	69.137	0.000	−370.901	−352.304	61.722
300	45.647	69.419	69.138	0.084	−370.890	−352.189	61.322
400	49.580	83.188	70.988	4.880	−370.144	−346.062	45.191
500	51.651	94.481	74.592	9.945	−369.269	−340.141	35.534
600	53.530	104.066	78.725	15.204	−368.311	−334.403	29.112
700	55.343	112.454	82.956	20.648	−367.270	−328.833	24.538
800	57.099	119.959	87.121	26.271	−366.149	−323.418	21.117
900	58.803	126.783	91.154	32.067	−364.958	−318.147	18.465
1000	60.463	133.065	95.035	38.030	−363.698	−313.013	16.350
1100	62.086	138.904	98.761	44.158	−362.371	−308.008	14.626
1200	63.676	144.375	102.336	50.446	−360.991	−303.127	13.195
1200.000	63.676	144.375	102.336	50.446	GLASS <--> LIQUID TRANSITION		
1200.000	62.760	144.375	102.336	50.446			
1300	62.760	149.399	105.766	56.722	−359.733	−298.357	11.988
1400	62.760	154.050	109.051	62.998	−358.591	−293.679	10.957
1500	62.760	158.380	112.197	69.274	−357.566	−289.079	10.067
1600	62.760	162.430	115.211	75.550	−356.656	−284.543	9.289
1700	62.760	166.235	118.102	81.826	−355.870	−280.061	8.605
1800	62.760	169.822	120.876	88.102	−355.212	−275.621	7.998
1900	62.760	173.215	123.542	94.378	−354.693	−271.214	7.456
2000	62.760	176.434	126.107	100.654	−354.319	−266.831	6.969
2063.000	62.760	178.381	127.674	104.608	--- CRYSTAL <--> LIQUID ---		
2100	62.760	179.497	128.577	106.930	−354.103	−262.463	6.528
2200	62.760	182.416	130.959	113.206	−376.933	−257.996	6.126
2300	62.760	185.206	133.257	119.482	−377.193	−252.584	5.736
2400	62.760	187.877	135.478	125.758	−377.464	−247.161	5.379
2500	62.760	190.439	137.625	132.034	−377.745	−241.726	5.051
2600	62.760	192.900	139.704	138.310	−378.038	−236.279	4.747
2700	62.760	195.269	141.719	144.586	−378.341	−230.821	4.466
2800	62.760	197.551	143.672	150.862	−378.654	−225.352	4.204
2900	62.760	199.754	145.568	157.138	−378.977	−219.871	3.960
3000	62.760	201.881	147.410	163.414	−379.310	−214.379	3.733
3100	62.760	203.939	149.201	169.690	−379.652	−208.875	3.520
3200	62.760	205.932	150.942	175.966	−380.004	−203.361	3.320
3300	62.760	207.863	152.638	182.242	−380.364	−197.836	3.131
3400	62.760	209.737	154.290	188.518	−380.732	−192.299	2.954
3500	62.760	211.556	155.900	194.794	−381.108	−186.751	2.787

PREVIOUS: CURRENT: December 1973

0	to	2063	K crystal
above		2063	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−6.908	−429.715	−429.715	INFINITE
100	13.895	6.730	71.088	−6.436	−431.184	−422.473	220.677
200	34.100	23.035	42.859	−3.965	−432.005	−413.352	107.956
298.15	45.501	39.011	39.011	0.000	−431.789	−404.210	70.816
300	45.647	39.293	39.012	0.084	−431.778	−404.039	70.350
400	49.580	53.063	40.863	4.880	−431.032	−394.899	51.569
500	51.651	64.356	44.466	9.945	−430.157	−385.966	40.322
600	53.530	73.940	48.599	15.204	−429.199	−377.216	32.840
700	55.343	82.329	52.831	20.648	−428.158	−368.633	27.508
800	57.099	89.834	56.995	26.271	−427.037	−360.206	23.519
900	58.803	96.658	61.029	32.067	−425.846	−351.922	20.425
1000	60.463	102.940	64.910	38.030	−424.586	−343.776	17.957
1100	62.086	108.779	68.635	44.158	−423.259	−335.758	15.944
1200	63.677	114.250	72.211	50.446	−421.879	−327.864	14.272
1300	65.243	119.408	75.645	56.892	−420.450	−320.087	12.861
1400	66.791	124.300	78.947	63.494	−418.983	−312.422	11.657
1500	68.325	128.961	82.127	70.250	−417.478	−304.863	10.616
1600	69.842	133.419	85.195	77.159	−415.936	−297.405	9.709
1700	71.351	137.698	88.158	84.218	−414.366	−290.045	8.912
1800	72.851	141.819	91.025	91.429	−412.774	−282.778	8.206
1900	74.339	145.798	93.804	98.788	−411.171	−275.599	7.577
2000	75.847	149.649	96.500	106.297	−409.565	−268.506	7.013
2063.000	76.747	152.015	98.160	111.104	CRYSTAL <-- -> LIQUID TRANSITION		
2063.000	62.760	178.381	98.160	165.496			
2100	62.760	179.497	99.583	167.818	−354.103	−262.463	6.528
2200	62.760	182.416	103.282	174.094	−376.933	−257.996	6.126
2300	62.760	185.206	106.784	180.370	−377.193	−252.584	5.736
2400	62.760	187.877	110.108	186.646	−377.464	−247.161	5.379
2500	62.760	190.439	113.270	192.922	−377.745	−241.726	5.051
2600	62.760	192.900	116.286	199.198	−378.038	−236.279	4.747
2700	62.760	195.269	119.167	205.474	−378.341	−230.821	4.466
2800	62.760	197.551	121.926	211.750	−378.654	−225.352	4.204
2900	62.760	199.754	124.572	218.026	−378.977	−219.871	3.960
3000	62.760	201.881	127.114	224.302	−379.310	−214.379	3.733
3100	62.760	203.939	129.559	230.578	−379.652	−208.875	3.520
3200	62.760	205.932	131.915	236.854	−380.004	−203.361	3.320
3300	62.760	207.863	134.187	243.130	−380.364	−197.836	3.131
3400	62.760	209.737	136.382	249.406	−380.732	−192.299	2.954
3500	62.760	211.556	138.504	255.682	−381.108	−186.751	2.787

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 230.901 \pm 2.1\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 127.82 \pm 20.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 127.61 \pm 20.9\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^4\Sigma^-$	0	4
$B^4\Pi$	12706.8	8
$C^4\Sigma^-$	17420.3	4
	23890	[4]

$\omega_e = 1012.36\ cm^{-1}$ $\omega_e x_e = 5.26\ cm^{-1}$ $\sigma = 1$
$B_e = 0.54825\ cm^{-1}$ $\alpha_e = 0.00352\ cm^{-1}$ $r_e = 1.589$ Å

Enthalpy of Formation

Based on the adopted ground state vibrational constants, a linear Birge–Sponer extrapolation yields a dissociation energy of $D_0° = 6.039$ eV (139.3 kcal·mol^{-1}) for VO(g). Applying a correction for the ionicity in the V–O bond[1], we recalculate $D_0° = 6.495$ eV (149.8 kcal·mol^{-1}). This latter value leads to a $\Delta_f H°(298.15\ K)$ value of 31.6 kcal·mol^{-1} using auxiliary data.[2]

Berkowitz *et al.*[3] determined the composition and partial pressures of the vapor over VO(cr) by employing a mass spectrometer to analyze the vapors effusing from a tungsten Knudsen cell containing VO(cr). The vapors detected mass spectrometrically at 1945 K were reported to be V(g), VO(g), and VO_2(g). The VO^+ intensity was determined in two sets of experiments using the temperature variation method. Berkowitz *et al.*[3] analyzed these results using 2nd law methods and reported $\Delta_f H°(T) = 125.2$ kcal·mol^{-1} (1690–1945 K) and 124.6 kcal·mol^{-1} (1680–1950 K) for the reaction VO(cr) = VO(g). Assigning these enthalpies of reaction to an intermediate temperature of 1800 K, we calculate $\Delta_f H°$(VO, g, 298.15 K) = 30.1 and 30.4 kcal·mol^{-1}, respectively, using auxiliary data.[2] Berkowitz *et al.*[3] also used the absolute pressure method and determined the partial pressure of VO(g) at two temperatures, 1875 K and 1876 K. The two absolute pressure data points differ in value by ~25%. A 3rd law analysis of these two data points leads to $\Delta_f H°$(VO, g, 298.15 K) of 23.6 and 24.7 kcal·mol^{-1}. We prefer the 2nd law results of Berkowtiz *et al.*[3] since each result is based on multiple data points (–6) which cover a 260 K range.

Coppens *et al.*[4] used a combination of mass spectrometric and Knudsen cell techniques to determine the partial pressures necessary to define the equilibrium in the system VO(g) + Ge(g) = GeO(g) + V(g). The authors analyzed eight data points (1927– 2145 K) by the 3rd law method and reported $\Delta_f H°(0\ K) = 7.60 \pm 0.38$ kcal·mol^{-1} which actually applies to the reverse reaction.[14] The Gibbs energy functions used by Coppens *et al.*[4] for VO are very similar to those adopted here. Using auxiliary data,[2,5] we calculate $\Delta_f H°(298.15\ K) = 29.1$ kcal·mol^{-1} for VO(g).

An effusion–mass spectrometric investigation of the vapors in equilibrium with V_2O_3(cr) was conducted by Farber *et al.*[6] Their study, using an aluminum cell, showed that the vapors at 2270 K contained V(g), VO(g), and VO_2(g) as well as Al(g), AlO(g), and Al_2O(g). A 3rd law analysis of the data at 2270 K yields $\Delta_f H°(298.15\ K) = -26.5$ kcal·mol^{-1} for the reaction AlO(g) + V(g) = VO(g) + Al(g). Using auxiliary data[2] we calculate $\Delta_f H°(298.15\ K) = 38.7$ kcal·mol^{-1} for VO(g). Farber *et al.*,[6] however, reported the use of a more recent determination of $\Delta_f H°(298.15\ K)$ for AlO(g).[7] If this latter value (+16.57 kcal·mol^{-1}) is used, then the $\Delta_f H°(298.15\ K)$ value for VO(g) is 35.3 kcal·mol^{-1}.

Frantseva and Semenov[8] studied the evaporation of V_2O_3(cr) by a mass spectrometer used in conjunction with a double effusion chamber. They reported a $D_0°$ value for VO(g) which is dependent, however, on their $D_0°$ value for VO_2(g).[2] The mass spectrometric study by Shchukarev *et al.*[9] detected VO(g) above V_2O_4(cr) and V_2O_3(cr) but there was insufficient data reported to permit the calculation of a $\Delta_f H°(298.15\ K)$ value for VO(g).

We adopt $\Delta_f H°(298.15\ K) = 30.5$ kcal·mol^{-1} for VO(g). This value is a rounded average of the two 2nd law treatments from Berkowitz *et al.*[3] and the results from Coppens *et al.*[4] Each of these three sets of experiments involve multiple data points. Most of the remaining studies each involved only one data point. However, it should be noted that the $\Delta_f H°(298.15\ K)$ derived from the Hildenbrand correction to the linear Birge–Sponer extrapolation is within 1.1 kcal·mol^{-1} of the adopted value. The adopted enthalpy of formation leads to a dissociation energy of $D_0° = 150.9$ kcal·mol^{-1} or 6.542 eV.

Heat Capacity and Entropy

Much of the spectroscopic work involving VO(g) has been reviewed and referenced by Rosen[10] and Weltner.[11] The adopted vibrational and rotational constants as well as the electronic levels are those tabulated by Rosen.[10] The EPR work of Kasai[12] and the optical absorption study by Richards and Barrow[13] established that the ground state was $^4\Sigma^-$. As reported in Rosen[10] there is evidence from matrix studies indicating a transition at 23890 cm^{-1}. We assume this level has a quantum weight of 4. the full weight of 8 is assigned to be B $^4\Pi$ state, rather than estimating the splitting. The Gibbs energy functions used here are approximately 3 cal·K^{-1}·mol^{-1} less than those proposed by Brewer and Rosenblatt.[14] The difference arises from the fact that Brewer and Rosenblatt approximated the VO electronic levels by using V^{++} electronic levels (which include many low lying levels) whereas we have used the observed VO electronic levels.

Continued on page 1814

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.773	127.820	127.820	INFINITE
100	29.106	198.710	257.359	−5.865	128.787	118.300	−61.794
200	29.433	218.937	233.663	−2.945	128.415	107.888	−28.178
250	29.991	225.560	231.402	−1.461	128.027	102.800	−21.479
298.15	30.697	230.901	230.901	0.	127.612	97.978	−17.165
300	30.726	231.091	230.902	0.057	127.596	97.795	−17.028
350	31.510	235.886	231.278	1.613	127.147	92.863	−13.859
400	32.258	240.143	232.125	3.207	126.696	87.996	−11.491
450	32.931	243.982	233.233	4.837	126.246	83.186	−9.656
500	33.520	247.483	234.486	6.499	125.798	78.425	−8.193
600	34.459	253.682	237.182	9.900	124.898	69.035	−6.010
700	35.147	259.048	239.931	13.382	123.977	59.797	−4.462
800	35.656	263.777	242.622	16.924	123.016	50.694	−3.310
900	36.040	267.999	245.211	20.509	121.997	41.714	−2.421
1000	36.337	271.813	247.684	24.129	120.914	32.851	−1.716
1100	36.571	275.287	250.038	27.775	119.758	24.100	−1.144
1200	36.761	278.478	252.276	31.442	118.517	15.458	−0.673
1300	36.919	281.427	254.407	35.126	117.184	6.923	−0.278
1400	37.053	284.168	256.436	38.825	115.748	−1.505	0.056
1500	37.171	286.728	258.371	42.536	114.208	−9.827	0.342
1600	37.279	289.131	260.219	46.258	112.565	−18.043	0.589
1700	37.382	291.394	261.987	49.992	110.808	−26.153	0.804
1800	37.484	293.533	263.681	53.735	108.933	−34.156	0.991
1900	37.588	295.563	265.306	57.488	106.930	−42.052	1.156
2000	37.699	297.494	266.867	61.253	104.792	−49.838	1.302
2100	37.819	299.336	268.370	65.029	102.508	−57.514	1.431
2200	37.950	301.098	269.818	68.817	77.190	−64.973	1.543
2300	38.093	302.788	271.215	72.619	74.457	−71.374	1.621
2400	38.251	304.413	272.564	76.436	71.727	−77.656	1.690
2500	38.424	305.978	273.870	80.270	69.003	−83.824	1.751
2600	38.612	307.488	275.134	84.121	66.286	−89.884	1.806
2700	38.815	308.949	276.359	87.992	63.578	−95.839	1.854
2800	39.033	310.365	277.549	91.885	60.881	−101.693	1.897
2900	39.266	311.738	278.704	95.800	58.197	−107.453	1.935
3000	39.512	313.074	279.828	99.738	55.527	−113.119	1.970
3100	39.771	314.374	280.921	103.702	52.872	−118.696	2.000
3200	40.041	315.640	281.986	107.693	50.236	−124.189	2.027
3300	40.321	316.877	283.025	111.711	47.618	−129.599	2.051
3400	40.609	318.085	284.038	115.757	45.020	−134.930	2.073
3500	40.905	319.266	285.028	119.833	42.443	−140.186	2.092
3600	41.206	320.423	285.995	123.939	39.889	−145.367	2.109
3700	41.512	321.556	286.941	128.075	−409.450	−149.278	2.107
3800	41.820	322.667	287.867	132.241	−410.271	−142.235	1.955
3900	42.130	323.757	288.773	136.439	−411.119	−135.170	1.810
4000	42.440	324.828	289.661	140.667	−411.995	−128.084	1.673
4100	42.749	325.880	290.532	144.927	−412.900	−120.975	1.541
4200	43.055	326.913	291.386	149.217	−413.834	−113.843	1.416
4300	43.358	327.930	292.224	153.537	−414.799	−106.689	1.296
4400	43.656	328.930	293.047	157.888	−415.795	−99.513	1.181
4500	43.948	329.915	293.855	162.268	−416.823	−92.313	1.072
4600	44.234	330.884	294.650	166.678	−417.886	−85.090	0.966
4700	44.514	331.838	295.431	171.115	−418.982	−77.844	0.865
4800	44.785	332.778	296.199	175.580	−420.115	−70.573	0.768
4900	45.048	333.704	296.955	180.072	−421.286	−63.279	0.675
5000	45.301	334.617	297.699	184.589	−422.495	−55.960	0.585
5100	45.546	335.516	298.432	189.132	−423.745	−48.617	0.498
5200	45.781	336.403	299.153	193.698	−425.036	−41.250	0.414
5300	46.006	337.277	299.865	198.288	−426.371	−33.856	0.334
5400	46.220	338.139	300.565	202.899	−427.752	−26.438	0.256
5500	46.424	338.989	301.256	207.531	−429.180	−18.993	0.180
5600	46.618	339.828	301.938	212.183	−430.658	−11.521	0.107
5700	46.802	340.654	302.610	216.855	−432.187	−4.024	0.037
5800	46.975	341.470	303.273	221.543	−433.769	3.502	−0.032
5900	47.137	342.274	303.927	226.249	−435.406	11.054	−0.098
6000	47.290	343.068	304.573	230.971	−437.102	18.636	−0.162

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K)$ = [248.198] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 425.65 ± 41.8 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 425.09 ± 41.8 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
[$^3\Sigma^-$]	[0]	[3]
	[14160]	[1]
	[17211]	[2]
	[19189]	[6]

ω_e = 1065 cm^{-1} $\omega_e x_e$ = [3.85] cm^{-1} σ = 1
B_e = [0.3498] cm^{-1} α_e = [0.0016] cm^{-1} r_e = [1.81] Å

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(WO, g, 298.15 K) = 101.6 kcal·mol^{-1}, is derived from the enthalpy of reaction, $\Delta_r H°(298.15\ K) = -42.0$ kcal·mol^{-1} for WO(g) → W(cr) + O(g) with all JANAF auxiliary data. The value of $\Delta_r H°(298.15\ K)$ was calculated by the 3rd law method from the partial pressure data which were determined mass-spectrometrically in the temperature range from 2188 to 2475 K by DeMaria *et al.*[1] The drift in the 3rd law analysis was −20 ± 7 cal·K^{-1}·mol^{-1}.

Heat Capacity and Entropy

The fundamental vibrational frequency, the ground state configuration, and the probable electronic levels for tungsten monoxide (g) were obtained from the infrared and ultraviolet spectroscopic investigations by matrix isolation by Weltner and McLeod.[2] The rotational constant B_e was calculated from the estimated bond distance of WO(g). The value x_e was calculated from the relation $x_e u^{1/2} = 0.014$ which was given by Barrow and Caunt.[3] The constant (0.014) was estimated based on ZrO(g) and VO(g). The value of α_e was calculated from the Morse potential function.

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[3]R. F. Barrow and A. D. Caunt, Proc. Roy. Soc. (London) **219A**, 120 (1953).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.757	425.652	425.652	INFINITE
100	29.104	216.077	274.560	−5.848	426.456	414.475	−216.500
200	29.360	236.289	250.944	−2.931	425.910	402.656	−105.163
250	29.843	242.888	248.696	−1.452	425.504	396.888	−82.925
298.15	30.490	248.198	248.198	0.	425.094	391.414	−68.574
300	30.517	248.386	248.198	0.056	425.079	391.205	−68.115
350	31.261	253.146	248.573	1.601	424.661	385.593	−57.547
400	31.990	257.369	249.413	3.182	424.255	380.039	−49.628
450	32.659	261.176	250.512	4.799	423.861	374.536	−43.475
500	33.251	264.648	251.754	6.447	423.476	369.076	−38.557
600	34.210	270.800	254.429	9.822	422.714	358.268	−31.190
700	34.919	276.129	257.157	13.280	421.944	347.587	−25.937
800	35.446	280.828	259.828	16.800	421.150	337.019	−22.005
900	35.844	285.027	262.399	20.365	420.324	326.552	−18.953
1000	36.150	288.820	264.854	23.966	419.460	316.178	−16.515
1100	36.391	292.277	267.192	27.593	418.554	305.894	−14.526
1200	36.585	295.452	269.417	31.242	417.604	295.694	−12.871
1300	36.744	298.387	271.534	34.909	416.609	285.574	−11.475
1400	36.878	301.115	273.551	38.590	415.567	275.534	−10.280
1500	36.995	303.663	275.474	42.284	414.478	265.569	−9.248
1600	37.100	306.054	277.311	45.989	413.339	255.678	−8.347
1700	37.199	308.307	279.069	49.704	412.151	245.861	−7.554
1800	37.296	310.436	280.753	53.429	410.914	236.114	−6.852
1900	37.396	312.455	282.369	57.163	409.626	226.438	−6.225
2000	37.502	314.376	283.922	60.908	408.289	216.831	−5.663
2100	37.616	316.208	285.416	64.664	406.902	207.292	−5.156
2200	37.740	317.961	286.856	68.432	405.467	197.821	−4.697
2300	37.878	319.641	288.245	72.212	403.983	188.415	−4.279
2400	38.029	321.257	289.587	76.008	402.454	179.075	−3.897
2500	38.195	322.812	290.885	79.819	400.879	169.800	−3.548
2600	38.376	324.314	292.142	83.647	399.264	160.588	−3.226
2700	38.572	325.766	293.360	87.494	397.583	151.440	−2.930
2800	38.783	327.172	294.543	91.362	395.804	142.356	−2.656
2900	39.009	328.537	295.692	95.252	393.888	133.337	−2.402
3000	39.248	329.864	296.809	99.164	391.810	124.388	−2.166
3100	39.499	331.155	297.896	103.101	389.529	115.511	−1.946
3200	39.761	332.413	298.955	107.064	387.015	106.711	−1.742
3300	40.033	333.640	299.988	111.054	384.244	97.994	−1.551
3400	40.314	334.840	300.995	115.071	381.182	89.365	−1.373
3500	40.602	336.012	301.979	119.117	377.765	80.830	−1.206
3600	40.896	337.160	302.940	123.192	373.899	72.400	−1.050
3700	41.193	338.285	303.880	127.296	334.719	64.275	−0.907
3800	41.494	339.387	304.800	131.431	333.242	56.986	−0.783
3900	41.796	340.469	305.701	135.595	331.789	49.735	−0.666
4000	42.098	341.531	306.584	139.790	330.360	42.521	−0.555
4100	42.398	342.574	307.449	144.015	328.954	35.343	−0.450
4200	42.696	343.600	308.297	148.269	327.572	28.198	−0.351
4300	42.991	344.608	309.130	152.554	326.213	21.086	−0.256
4400	43.281	345.599	309.948	156.868	324.877	14.006	−0.166
4500	43.566	346.575	310.751	161.210	323.564	6.955	−0.081
4600	43.844	347.536	311.540	165.580	322.273	−0.067	0.001
4700	44.115	348.482	312.316	169.978	321.004	−7.060	0.078
4800	44.378	349.413	313.079	174.403	319.754	−14.027	0.153
4900	44.633	350.331	313.830	178.854	318.525	−20.968	0.224
5000	44.878	351.235	314.569	183.329	317.313	−27.884	0.291
5100	45.115	352.126	315.297	187.829	316.120	−34.776	0.356
5200	45.341	353.004	316.014	192.352	314.942	−41.645	0.418
5300	45.558	353.870	316.720	196.897	313.779	−48.491	0.478
5400	45.764	354.724	317.416	201.463	312.630	−55.316	0.535
5500	45.960	355.565	318.102	206.050	311.492	−62.119	0.590
5600	46.146	356.395	318.778	210.655	310.366	−68.901	0.643
5700	46.321	357.213	319.445	215.278	309.248	−75.664	0.693
5800	46.486	358.020	320.103	219.919	308.139	−82.407	0.742
5900	46.640	358.816	320.753	224.575	307.035	−89.132	0.789
6000	46.784	359.601	321.394	229.246	305.936	−95.837	0.834

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

Zirconium Oxide (ZrO) IDEAL GAS $M_r = 107.2194$

$S°(298.15\ K) = 227.627 \pm 8.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 59.63 \pm 50.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 58.58 \pm 50.2\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	[18000]	2
[4000]	6	[22000]	6
[6000]	2	[25500]	2
15500	2	27300	1
[15700]	6	[28500]	6
[17500]	6		

$\omega_e = 978\ cm^{-1}$ $\omega_e x_e = 4\ cm^{-1}$ $\sigma = 1$

$B_e = 0.4142\ cm^{-1}$ $\alpha_e = 0.0023\ cm^{-1}$ $r_e = 1.711$ Å

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = 14.0 \pm 12$ kcal·mol^{-1} is calculated from $\Delta_r H°(298.15\ K) = 290.342 \pm 12.8$ kcal·mol^{-1} for the reaction $Zr(cr) + ZrO_2(cr) = 2\ ZrO(g)$. The value of $\Delta_r H°(298.15\ K)$ is obtained by the 3rd law analysis from the mass spectrometric studies of Chupka *et al.*[1] They observed the variation of the ZrO+ ion intensity over the system $Zr + ZrO_2$ and reported equilibrium constants for the reaction $Zr + ZrO_2 \rightarrow 2\ ZrO$ in the range 2124–2322 K. The 3rd law drift is $-58 \pm 28\ cal \cdot K^{-1} \cdot mol^{-1}$.

Heat Capacity and Entropy

The ground state of ZrO(g) was assumed to be $^1\Sigma^+$ as determined from the matrix isolation spectra of Weltner *et al.*[2] Previously this had been described as the lower state in the A band system reported by Uhler and Akerlind.[3]

All molecular constants were obtained from Uhler and Akerlind[3] except $\omega_e = 978\ cm^{-1}$ and $\omega_e x_e = 4\ cm^{-1}$ which were calculated from ω and $\alpha_e = 0.0023\ cm^{-1}$ using the equations

$$\alpha_e = \frac{6\,(\omega_e \cdot B_e^3)^{1/2}}{\omega_e} - \frac{6\,B_e^2}{\omega_e} \text{ and } \omega = \omega_e - 2\,\omega_e x_e = 969.76\ cm^{-1}$$

The higher electronic levels were obtained or estimated from the correlation diagram given by Weltner and McLeon.[2]

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Zirconium Oxide (ZrO) $O_1Zr_1(g)$

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.786	59.629	59.629	INFINITE
100	29.106	195.385	254.156	−5.877	60.199	50.732	−26.500
200	29.489	215.622	230.400	−2.956	59.472	41.506	−10.840
250	30.099	222.263	228.131	−1.467	59.016	37.067	−7.745
298.15	30.845	227.627	227.627	0.	58.576	32.880	−5.760
300	30.875	227.818	227.628	0.057	58.559	32.721	−5.697
350	31.680	232.639	228.007	1.621	58.114	28.450	−4.246
400	32.439	236.919	228.858	3.224	57.681	24.241	−3.166
450	33.124	240.780	229.972	4.864	57.258	20.087	−2.332
500	33.745	244.303	231.231	6.536	56.838	15.979	−1.669
600	34.906	250.558	233.944	9.968	56.000	7.886	−0.687
700	36.165	256.031	236.716	13.520	55.158	−0.066	0.005
800	37.695	260.956	239.443	17.211	54.330	−7.899	0.516
900	39.539	265.500	242.089	21.070	53.539	−15.629	0.907
1000	41.624	269.772	244.645	25.126	52.809	−23.275	1.216
1100	43.811	273.841	247.116	29.398	52.155	−30.851	1.465
1200	45.942	277.746	249.507	33.887	47.867	−38.149	1.661
1300	47.875	281.501	251.824	38.580	47.900	−45.317	1.821
1400	49.510	285.111	254.074	43.452	48.055	−52.493	1.959
1500	50.791	288.573	256.259	48.470	48.289	−59.683	2.078
1600	51.705	291.882	258.383	53.598	48.556	−66.890	2.184
1700	52.273	295.035	260.447	58.799	48.811	−74.113	2.277
1800	52.538	298.032	262.453	64.042	49.011	−81.350	2.361
1900	52.552	300.874	264.401	69.299	49.116	−88.596	2.436
2000	52.372	303.565	266.292	74.546	49.096	−95.844	2.503
2100	52.049	306.113	268.128	79.768	48.922	−103.087	2.564
2200	51.629	308.525	269.910	84.953	27.249	−109.573	2.602
2300	51.152	310.810	271.639	90.092	26.289	−115.771	2.629
2400	50.648	312.976	273.317	95.182	25.269	−121.926	2.654
2500	50.140	315.034	274.945	100.222	24.187	−128.037	2.675
2600	49.646	316.990	276.525	105.211	23.044	−134.103	2.694
2700	49.179	318.855	278.058	110.152	21.842	−140.125	2.711
2800	48.747	320.636	279.547	115.048	20.585	−146.101	2.726
2900	48.354	322.339	280.994	119.902	19.277	−152.031	2.738
3000	48.004	323.973	282.399	124.720	17.922	−157.915	2.750
3100	47.697	325.542	283.766	129.505	16.525	−163.753	2.759
3200	47.433	327.052	285.095	134.261	15.090	−169.546	2.768
3300	47.209	328.508	286.389	138.993	13.622	−175.294	2.775
3400	47.025	329.914	287.648	143.704	12.126	−180.996	2.781
3500	46.876	331.275	288.875	148.399	10.605	−186.654	2.786
3600	46.762	332.594	290.072	153.080	9.063	−192.268	2.790
3700	46.677	333.874	291.238	157.752	7.504	−197.839	2.793
3800	46.621	335.118	292.377	162.417	5.930	−203.367	2.795
3900	46.589	336.328	293.488	167.077	4.345	−208.855	2.797
4000	46.579	337.508	294.574	171.735	2.752	−214.301	2.798
4100	46.588	338.658	295.635	176.394	1.152	−219.708	2.799
4200	46.614	339.781	296.673	181.054	−0.453	−225.075	2.799
4300	46.654	340.878	297.688	185.717	−2.061	−230.404	2.799
4400	46.707	341.951	298.682	190.385	−3.670	−235.696	2.798
4500	46.770	343.002	299.655	195.059	−5.279	−240.951	2.797
4600	46.841	344.030	300.609	199.739	−6.887	−246.171	2.795
4700	46.918	345.039	301.544	204.427	−8.495	−251.355	2.794
4800	47.001	346.027	302.460	209.123	−571.037	−244.888	2.665
4900	47.088	346.997	303.359	213.827	−572.292	−238.080	2.538
5000	47.176	347.950	304.241	218.540	−573.562	−231.247	2.416
5100	47.267	348.885	305.108	223.263	−574.846	−224.388	2.298
5200	47.357	349.803	305.958	227.994	−576.141	−217.504	2.185
5300	47.447	350.706	306.794	232.734	−577.448	−210.594	2.076
5400	47.536	351.594	307.616	237.483	−578.765	−203.660	1.970
5500	47.622	352.467	308.423	242.241	−580.092	−196.702	1.868
5600	47.707	353.326	309.217	247.008	−581.428	−189.719	1.770
5700	47.788	354.171	309.999	251.782	−582.772	−182.712	1.674
5800	47.865	355.003	310.767	256.565	−584.124	−175.681	1.582
5900	47.939	355.822	311.524	261.355	−585.483	−168.628	1.493
6000	48.008	356.628	312.269	266.153	−586.851	−161.551	1.406

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

0 to 6000 K Ideal Diatomic Gas

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 205.147 \pm 0.035$ $\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$

State	g_i	T, cm^{-1}	ω_e, cm^{-1}	Electronic and Molecular constants ($\sigma = 2$) Vibrational Anharmonicity, cm^{-1}	B_e, cm^{-1}	α_i, cm^{-1}	D_e, cm^{-1}	β_i, cm^{-1}
$X\ ^3\Sigma_g^-$	3	0	1580.1932	$\omega_e x_e$ 11.980804	1.445622	0.01593268^{-5}		
				$\omega_e y_e$ 0.047474736	6.406456×10^{-5}			
				$\omega_e z_e$ -1.272748×10^{-3}	-2.846158×10^{-6}			
$a\ ^1\Delta_g$	2	7882.39	[1509.3]	$\omega_e x_e$ [12.9]	1.4263	0.0171	$[4.97 \times 10^{-6}]$	
$b\ ^1\Delta_g^+$	1	13120.9085	1432.6661	$\omega_e x_e$ 13.9336	1.4004796	0.018169303	5.356×10^{-6}	0.077×10^{-6}
				$\omega_e y_e$ −0.0143	-4.294192×10^{-5}			
$c^1\Sigma_u^-$	1	32664.1	794.29	$\omega_e x_e$ 12.736	0.9155	0.01391	$[10.5 \times 10^{-6}]$	
				$\omega_e y_e$ −0.2444		−0.000740		
				$\omega_e z_e$ 0.00055				
$c^3\Delta_{ui}$	6	34319	[750]	$\omega_e x_e$ [14]	[0.91]	[0.014]		
$A^3\Sigma_u^+$	3	35007.15	799.08	$\omega_e x_e$ 12.16	0.91053	0.01416	4.79×10^{-6}	-0.30×10^{-6}
				$\omega_e y_e$ −0.550		−0.00097		0.10×10^{-6}
$B^3\Sigma_u^-$	3	49358.15	709.05770	$\omega_e x_e$ 10.614080	0.818975	0.0119225		
				$\omega_e y_e$ −0.059212435		-6.30472×10^{-4}		
				$\omega_e z_e$ −0.023974994				

Enthalpy of Formation

Zero by Definition.

Heat Capacity and Entropy

The thermal functions are calculated using the program of McBride and Gordon>[1] The contributions of vibrational anharmonicity, rotation–vibration interaction, and centrifugal stretching are calculated via the procedures given by Pennington and Kobe.[3] In this procedure the energy levels are calculated as follows: $\epsilon = T + G(v) - G(o) + B_v J(J+1) - D_v J^2(J+1)^2$where $G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e (v+1/2)^3 + \omega_e y_e (v+1/2)^4$ and $B_v = B_e - \alpha_1(v+1/2) + \alpha_2(v+1/2)^2 + \alpha_3(v+1/2)^3$ and $D_v = D_e + \beta_i(v+1/2)$. Where a value of D_e is not available it is calculated to be $D_e = 4B_e^3/\omega_e^2$.

Molecular constant data in the table above is from Krupenie[2] with the exception of B_e and α_i for the C $^3\Delta_{ui}$ state which we have estimated by analogy with neighboring states of the same electron configuration. Electronic levels above 50,000 cm^{-1}given by Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K.

The value of $S°(298.15\ K)$ agrees exactly with the CODATA recommended value.[4] It also agrees with the values of McBride *et al.*[5] and Gurvich *et al.*[6] within the stated uncertainty. The uncertainty in $S°(298.15\ K)$ is due to uncertainties in fundamental constants (particularly the gas constant), the atomic weight, and the ground state molecular constants. At high temperatures, further uncertainties arise from excited state molecular constants and approximate procedures used to account for higher vibrational–rotational levels of all states. Despite these increased uncertainties, our values of $S°$ are within 0.016 (6000 K) and 0.035 (5000 K) $cal \cdot K^{-1} \cdot mol^{-1}$ of those calculated by superior methods[5,6] using older molecular constants.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−8.683	0.	0.	0.
100	29.106	173.307	231.094	−5.779	0.	0.	0.
200	29.126	193.485	207.823	−2.868	0.	0.	0.
250	29.201	199.990	205.630	−1.410	0.	0.	0.
298.15	29.376	205.147	205.147	0.	0.	0.	0.
300	29.385	205.329	205.148	0.054	0.	0.	0.
350	29.694	209.880	205.506	1.531	0.	0.	0.
400	30.106	213.871	206.308	3.025	0.	0.	0.
450	30.584	217.445	207.350	4.543	0.	0.	0.
500	31.091	220.693	208.524	6.084	0.	0.	0.
600	32.090	226.451	211.044	9.244	0.	0.	0.
700	32.981	231.466	213.611	12.499	0.	0.	0.
800	33.733	235.921	216.126	15.835	0.	0.	0.
900	34.355	239.931	218.552	19.241	0.	0.	0.
1000	34.870	243.578	220.875	22.703	0.	0.	0.
1100	35.300	246.922	223.093	26.212	0.	0.	0.
1200	35.667	250.010	225.209	29.761	0.	0.	0.
1300	35.988	252.878	227.229	33.344	0.	0.	0.
1400	36.277	255.556	229.158	36.957	0.	0.	0.
1500	36.544	258.068	231.002	40.599	0.	0.	0.
1600	36.796	260.434	232.768	44.266	0.	0.	0.
1700	37.040	262.672	234.462	47.958	0.	0.	0.
1800	37.277	264.796	236.089	51.673	0.	0.	0.
1900	37.510	266.818	237.653	55.413	0.	0.	0.
2000	37.741	268.748	239.160	59.175	0.	0.	0.
2100	37.969	270.595	240.613	62.961	0.	0.	0.
2200	38.195	272.366	242.017	66.769	0.	0.	0.
2300	38.419	274.069	243.374	70.600	0.	0.	0.
2400	38.639	275.709	244.687	74.453	0.	0.	0.
2500	38.856	277.290	245.959	78.328	0.	0.	0.
2600	39.068	278.819	247.194	82.224	0.	0.	0.
2700	39.276	280.297	248.393	86.141	0.	0.	0.
2800	39.478	281.729	249.558	90.079	0.	0.	0.
2900	39.674	283.118	250.691	94.036	0.	0.	0.
3000	39.864	284.466	251.795	98.013	0.	0.	0.
3100	40.048	285.776	252.870	102.009	0.	0.	0.
3200	40.225	287.050	253.918	106.023	0.	0.	0.
3300	40.395	288.291	254.941	110.054	0.	0.	0.
3400	40.559	289.499	255.940	114.102	0.	0.	0.
3500	40.716	290.677	256.916	118.165	0.	0.	0.
3600	40.868	291.826	257.870	122.245	0.	0.	0.
3700	41.013	292.948	258.802	126.339	0.	0.	0.
3800	41.154	294.044	259.716	130.447	0.	0.	0.
3900	41.289	295.115	260.610	134.569	0.	0.	0.
4000	41.421	296.162	261.485	138.705	0.	0.	0.
4100	41.549	297.186	262.344	142.854	0.	0.	0.
4200	41.674	298.189	263.185	147.015	0.	0.	0.
4300	41.798	299.171	264.011	151.188	0.	0.	0.
4400	41.920	300.133	264.821	155.374	0.	0.	0.
4500	42.042	301.076	265.616	159.572	0.	0.	0.
4600	42.164	302.002	266.397	163.783	0.	0.	0.
4700	42.287	302.910	267.164	168.005	0.	0.	0.
4800	42.413	303.801	267.918	172.240	0.	0.	0.
4900	42.542	304.677	268.660	176.488	0.	0.	0.
5000	42.675	305.538	269.389	180.749	0.	0.	0.
5100	42.813	306.385	270.106	185.023	0.	0.	0.
5200	42.956	307.217	270.811	189.311	0.	0.	0.
5300	43.105	308.037	271.506	193.614	0.	0.	0.
5400	43.262	308.844	272.190	197.933	0.	0.	0.
5500	43.426	309.639	272.864	202.267	0.	0.	0.
5600	43.599	310.424	273.527	206.618	0.	0.	0.
5700	43.781	311.197	274.181	210.987	0.	0.	0.
5800	43.973	311.960	274.826	215.375	0.	0.	0.
5900	44.175	312.713	275.462	219.782	0.	0.	0.
6000	44.387	313.457	276.089	224.210	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1977 (1 bar)

$S°(298.15\ K) = 206.2 \pm 0.8\ J\cdot K\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 1164.7 \pm 0.8\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [1170.888]\ kJ\cdot mol^{-1}$

Electronic and Molecular Constants (σ = 2)							
State	g_i	T_o, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
$X^2\Pi_g$	4	0	1905.13	16.2818	1.68912	0.0195769	1.116384
$a^4\Pi_{ui}$	8	32524	1035.534	10.32194	1.104320	0.01545646	1.31816042
$A^2\Pi_u$	4	40070	898.17	13.568	1.06297	0.02058	1.408220
$b^4\Sigma_g^-$	4	49191	119.913	17.13456	1.287297	0.02206747	1.2796516

Enthalpy of Formation

The adopted value for the enthalpy of formation of O_2^+(g), $\Delta_f H°(0\ K) = 278.37 \pm 0.2\ kcal\cdot mol^{-1}$ is that recommended in a critical review on the energetics of gaseous ions by Rosenstock *et al.*[1] This value is derived from ionization potentials determined in the photoelectron spectrum of O_2 by Edqvist *et al.*,[2] the IP values are 12.071 ± 0.005 ev for the $X^2\Pi_{3/2g}$ state and 12.095 ± 0.005 ev for the $X^2\Pi_{1/2g}$ state.

$\Delta_f H°(O_2^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(O_2, g, 0\ K)$ by using IP(O_2) with JANAF enthalpies, $H°(0\ K)-H°(298.15\ K)$, for O_2(g) O_2^+(g), and e^-(ref). $\Delta_f H°(O_2 \rightarrow O_2^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[1] $\Delta_f H°(298.15\ K)$ should be changed by $-6.197\ kJ\cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic and molecular constants are from the critical review of Krupenie.[3] Electronic levels above 50000 cm^{-1} given by Krupenie are not included since they make negligible contributions to the thermodynamic properties at 6000 K. The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_{ti}\Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$. Use of the program of McBride and Gordon[4] yields the same results.

The ground state is taken to be $^2\Pi_{3/2g}$ with a separation of the ground state doublet levels of ~200 cm^{-1}. The hypothetical $^2\Pi$ state without spin–orbit splitting would be 100 cm^{-1} higher.[3] Such a shift of the electronic energy levels does not significantly alter the thermal functions. The main source of error in the $S°(298.15\ K)$ value lies in the neglect of a more exact treatment of the splitting of the $X^2\Pi$ ground state.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.674	1164.700		
100	29.105	174.406	232.113	−5.771			
200	29.111	194.582	208.881	−2.860			
250	29.132	201.079	206.695	−1.404			
298.15	29.195	206.215	206.215	0.	1170.888	1164.315	−203.983
300	29.199	206.396	206.216	0.054	1170.926	1164.274	−202.718
350	29.342	210.906	206.572	1.517	1171.952	1163.084	−173.581
400	29.573	214.839	207.364	2.990	1172.970	1161.748	−151.709
450	29.882	218.339	208.393	4.476	1173.978	1160.285	−134.682
500	30.250	221.506	209.548	5.979	1174.978	1158.710	−121.050
600	31.078	227.093	212.019	9.045	1176.963	1155.269	−100.575
700	31.916	231.947	214.526	12.195	1178.937	1151.497	−85.926
800	32.687	236.260	216.978	15.426	1180.910	1147.442	−74.920
900	33.364	240.150	219.340	18.729	1182.886	1143.140	−66.346
1000	33.945	243.697	221.601	22.095	1184.869	1138.618	−59.475
1100	34.440	246.956	223.760	25.515	1186.859	1133.897	−53.844
1200	34.859	249.971	225.820	28.981	1188.854	1128.994	−49.144
1300	35.216	252.776	227.787	32.485	1190.854	1123.924	−45.160
1400	35.521	255.397	229.667	36.022	1192.856	1118.701	−41.739
1500	35.784	257.857	231.465	39.588	1194.859	1113.334	−38.770
1600	36.011	260.174	233.187	43.178	1196.861	1107.834	−36.167
1700	36.210	262.363	234.840	46.789	1198.859	1102.208	−33.867
1800	36.384	264.438	236.427	50.419	1200.851	1096.465	−31.819
1900	36.538	266.409	237.954	54.065	1202.837	1090.612	−29.983
2000	36.675	268.287	239.424	57.726	1204.813	1084.654	−28.328
2100	36.798	270.079	240.841	61.399	1206.780	1078.598	−26.829
2200	36.908	271.793	242.209	65.085	1208.736	1072.449	−25.463
2300	37.009	273.436	243.532	68.781	1210.680	1066.210	−24.214
2400	37.101	275.013	244.811	72.486	1212.611	1059.887	−23.068
2500	37.185	276.530	246.049	76.201	1214.529	1053.484	−22.011
2600	37.263	277.990	247.250	79.923	1216.434	1047.004	−21.035
2700	37.336	279.397	248.415	83.653	1218.325	1040.452	−20.129
2800	37.403	280.756	249.546	87.390	1220.203	1033.830	−19.286
2900	37.466	282.070	250.645	91.134	1222.068	1027.140	−18.501
3000	37.526	283.341	251.713	94.883	1223.919	1020.387	−17.767
3100	37.583	284.573	252.754	98.639	1225.757	1013.573	−17.079
3200	37.637	285.767	253.767	102.400	1227.583	1006.699	−16.433
3300	37.689	286.926	254.754	106.166	1229.397	999.768	−15.825
3400	37.740	288.051	255.717	109.938	1231.200	992.783	−15.252
3500	37.790	289.146	256.656	113.714	1232.991	985.744	−14.711
3600	37.838	290.211	257.574	117.496	1234.772	978.655	−14.200
3700	37.887	291.249	258.470	121.282	1236.542	971.515	−13.715
3800	37.936	292.260	259.346	125.073	1238.304	964.330	−13.256
3900	37.985	293.246	260.203	128.869	1240.056	957.097	−12.819
4000	38.035	294.208	261.041	132.670	1241.800	949.819	−12.403
4100	38.088	295.148	261.861	136.476	1243.536	942.498	−12.008
4200	38.142	296.067	262.665	140.288	1245.265	935.135	−11.630
4300	38.199	296.965	263.452	144.105	1246.987	927.731	−11.270
4400	38.258	297.844	264.224	147.927	1248.702	920.286	−10.925
4500	38.322	298.704	264.980	151.756	1250.412	912.802	−10.596
4600	38.389	299.547	265.723	155.592	1252.116	905.281	−10.280
4700	38.462	300.373	266.451	159.434	1253.815	897.723	−9.977
4800	38.539	301.184	267.166	163.284	1255.508	890.129	−9.687
4900	38.622	301.979	267.869	167.142	1257.197	882.500	−9.408
5000	38.711	302.761	268.559	171.009	1258.881	874.836	−9.139
5100	38.807	303.528	269.237	174.885	1260.561	867.139	−8.881
5200	38.910	304.283	269.904	178.771	1262.237	859.407	−8.633
5300	39.020	305.025	270.559	182.667	1263.910	851.645	−8.393
5400	39.138	305.755	271.204	186.575	1265.578	843.850	−8.163
5500	39.265	306.475	271.839	190.495	1267.242	836.025	−7.940
5600	39.400	307.183	272.464	194.428	1268.903	828.170	−7.725
5700	39.545	307.882	273.079	198.375	1270.559	820.285	−7.517
5800	39.699	308.571	273.685	202.338	1272.213	812.372	−7.316
5900	39.863	309.251	274.282	206.316	1273.862	804.428	−7.122
6000	40.036	309.922	274.871	210.310	1275.507	796.458	−6.934

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 209.591 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -42.46 \pm 0.75\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-48.593]\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	$\epsilon_i cm^{-1}$	g_i
$^2\Pi_g$	0	4

$\omega_e = 1089 \pm 40\ cm^{-1}$ $\omega_e x_e = 12.1 \pm 1.6\ cm^{-1}$ $\sigma = 2$

$B_e = 1.17 \pm 0.02\ cm^{-1}$ $\alpha_e = [0.017]\ cm^{-1}$ $r_e = 1.341 \pm 0.010$ Å

Enthalpy of Formation

The enthalpy of formation at 0 K for O_2^-(g) is based n the electron affinity value derived from a thorough analysis of the laser photodetachment measurements of Celotta *et al.*[1] This study let to $EA(O_2) = 0.440 \pm 0.008$ eV. Using auxiliary data,[2] we calculate $\Delta_f H°(O_2^-, g, 0\ K) = 10.15 \pm 0.18\ kcal \cdot mol^{-1}$ and $D_0°(O_2^-) = 94.4 \pm 0.3\ kcal \cdot mol^{-1}$; the latter value assumes dissociation into ground state O(g) and O^-(g). The adopted $EA(O_2)$ value is also recommended by Rosenstock *et al.*[3] and Massey.[4] Both of these latter studies have reviewed and summarized earlier work from which EA values could be derived.

$\Delta_f H°(O_2^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(O_2, g, 0\ K)$ by using $EA(O_2)$ with JANAF[2] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for O_2^-(g), O_2(g), and e^-(g). $\Delta_r H°(O_2^- \rightarrow O_2 + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°(298.15\ K)$ should be changed by $+6.197\ kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The laser photodetachment study of Celotta *et al.*[1] which yielded a precise value for $EA(O_2)$ also yielded precise values for r_e and B_e as well as values for ω_e and $\omega_e x_e$. We adopt these values and calculate α_e assuming a Morse function for the ground state. Support for these values comes from recent studies based on total scattering cross section[5] and differential eleastic cross section.[6,7] Other (earlier) studies yielding vibrational information are discussed by Krupenie.[8] The recent ab initio study by Das *et al.*[11] suggests slightly different vibrational–rotational constants ($\omega_e = 1098$, $\omega_e x_e = 9.04$, $B_e = 1.135$, and $\alpha_e = 0.0151\ cm^{-1}$).

The ground and excited electronic states are discussed by Krupenie,[8] Massey,[4] and Das *et al.*[11] The approximate theoretical potential energy diagram given by Krupenie[8] suggests a $^2\Pi_g$ ground state with three rather low lying excited states: $^4\Sigma_u^-$ at ~21000 cm^{-1}, $^2\Pi_u$ at ~28500 cm^{-1}, and $^2\Sigma_u^-$ at ~32300 cm^{-1}. The ab initio study by Das *et al.*[11] suggests the same ordering of the levels at 19833 cm^{-1}, 27213 cm^{-1}, and 30076 cm^{-1}. The fluorescence observed by Rolfe[9] was assigned as $^2\Pi_{ui} \rightarrow X^2\Pi_{gi}$, but an upper state assignment of $^2\Sigma_u^-$ cannot be ruled out.[8] This study indicated that the presumed $^2\Pi_{ui}$ state lies at 29400 cm^{-1} (which we adopt), in good agreement with the calculated potential energy diagram. Hurst and Bortner[10] obtained evidence of excitation to an electronic state of O_2^- (presumable $^4\Sigma_u^-$) which lies approximately 1 eV above the ground state. The potential energy diagrams given by Krupenie[8] and Das *et al.*[11] suggest this level is significantly higher. The position of this level will not significantly affect the entropy values.

The three excited states are predicted to be quite shallow (binding energies ~1 eV) as compared to the ground state. The inclusion in our calcualtion of such states, with the use of appropriate vibrational–rotational constants as given by Das *et al.*[11] would lead to erroneous heat capacity values above 3000 K. The proper inclusion of these three excited states would require a direct summation technique with rotational cutoff.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.752	−42.464		
100	29.110	177.477	235.940	−5.846			
200	29.353	197.692	212.335	−2.929			
250	29.818	204.287	210.089	−1.451			
298.15	30.453	209.591	209.591	0.	−48.593	−43.663	7.650
300	30.480	209.780	209.592	0.056	−48.629	−43.633	7.597
350	31.224	214.534	209.966	1.599	−49.603	−42.723	6.376
400	31.962	218.752	210.805	3.179	−50.557	−41.674	5.442
450	32.648	222.557	211.903	4.794	−51.498	−40.507	4.702
500	33.262	226.029	213.144	6.442	−52.431	−39.236	4.099
600	34.271	232.187	215.818	9.821	−54.290	−36.422	3.171
700	35.032	237.530	218.546	13.288	−56.156	−33.297	2.485
800	35.609	242.247	221.220	16.821	−58.038	−29.904	1.953
900	36.055	246.468	223.795	20.406	−59.938	−26.273	1.525
1000	36.407	250.285	226.256	24.029	−61.855	−22.430	1.172
1100	36.691	253.769	228.601	27.685	−63.787	−18.393	0.873
1200	36.926	256.972	230.834	31.366	−65.734	−14.181	0.617
1300	37.123	259.936	232.960	35.069	−67.693	−9.805	0.394
1400	37.293	262.693	234.986	38.790	−69.664	−5.279	0.197
1500	37.441	265.271	236.920	42.527	−71.647	−0.611	0.021
1600	37.572	267.692	238.769	46.277	−73.642	4.190	−0.137
1700	37.690	269.973	240.538	50.041	−75.649	9.116	−0.280
1800	37.798	272.131	242.234	53.815	−77.669	14.160	−0.411
1900	37.897	274.177	243.861	57.600	−79.702	19.317	−0.531
2000	37.989	276.123	245.426	61.394	−81.749	24.582	−0.642
2100	38.075	277.979	246.933	65.197	−83.810	29.949	−0.745
2200	38.157	279.752	248.384	69.009	−85.885	35.415	−0.841
2300	38.234	281.450	249.785	72.829	−87.975	40.975	−0.931
2400	38.308	283.079	251.139	76.656	−90.079	46.626	−1.015
2500	38.380	284.644	252.448	80.490	−92.198	52.366	−1.094
2600	38.448	286.151	253.715	84.332	−94.332	58.190	−1.169
2700	38.515	287.603	254.944	88.180	−96.479	64.098	−1.240
2800	38.580	289.005	256.135	92.035	−98.641	70.085	−1.307
2900	38.644	290.360	257.292	95.896	−100.816	76.148	−1.372
3000	38.706	291.671	258.416	99.763	−103.004	82.288	−1.433
3100	38.767	292.941	259.510	103.637	−105.204	88.501	−1.491
3200	38.826	294.173	260.574	107.517	−107.417	94.784	−1.547
3300	38.885	295.368	261.610	111.402	−109.641	101.137	−1.601
3400	38.943	296.530	262.620	115.294	−111.876	107.558	−1.652
3500	39.001	297.660	263.605	119.191	−114.121	114.045	−1.702
3600	39.057	298.759	264.567	123.094	−116.376	120.596	−1.750
3700	39.113	299.830	265.505	127.002	−118.641	127.209	−1.796
3800	39.169	300.874	266.422	130.916	−120.914	133.885	−1.840
3900	39.224	301.892	267.319	134.836	−123.195	140.620	−1.883
4000	39.279	302.886	268.196	138.761	−125.484	147.413	−1.925
4100	39.333	303.857	269.054	142.692	−127.780	154.264	−1.965
4200	39.387	304.805	269.894	146.628	−130.084	161.171	−2.004
4300	39.440	305.732	270.716	150.569	−132.395	168.133	−2.042
4400	39.494	306.640	271.523	154.516	−134.713	175.149	−2.079
4500	39.547	307.528	272.313	158.468	−137.037	182.217	−2.115
4600	39.599	308.398	273.088	162.425	−139.369	189.337	−2.150
4700	39.652	309.250	273.848	166.387	−141.708	196.508	−2.184
4800	39.704	310.085	274.594	170.355	−144.053	203.729	−2.217
4900	39.756	310.904	275.327	174.328	−146.407	210.999	−2.249
5000	39.808	311.708	276.047	178.307	−148.768	218.317	−2.281
5100	39.860	312.497	276.754	182.290	−151.138	225.683	−2.311
5200	39.912	313.271	277.449	186.279	−153.516	233.094	−2.341
5300	39.963	314.032	278.132	190.272	−155.904	240.552	−2.371
5400	40.015	314.780	278.803	194.271	−158.302	248.054	−2.399
5500	40.066	315.514	279.464	198.275	−160.711	255.601	−2.427
5600	40.117	316.237	280.114	202.285	−163.131	263.193	−2.455
5700	40.168	316.947	280.754	206.299	−165.565	270.827	−2.482
5800	40.219	317.646	281.385	210.318	−168.011	278.505	−2.508
5900	40.270	318.334	282.005	214.343	−170.473	286.223	−2.534
6000	40.321	319.011	282.616	218.372	−172.950	293.986	−2.559

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K)$ = [253.685] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = [−311.142] $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [−314.524] $kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[980](1)
[515](1)
[1044](1)

Ground State Quantum Weight: 2 σ = 2
Point Group: C_{2v}
Bond Distance: P–O = [1.485] Å
Bond Angle: O–P–O = [134°4']
Product of the Moments of Inertia: $I_A I_B I_C$ = [94.2392 × 10^{-117}] $g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is calculated from an estimated enthalpy of dissociation (270 ± 25 $kcal·mol^{-1}$) reported by Brewer and Rosenblatt.[1]

Heat Capacity and Entropy

The molecular constants selected for this table were estimated by Gordon.[2] The molecular constants for PO_2(g) have been estimated by Gordon[2], Potter *et al.*[3] and Henderson and Scheffee.[4] The entropies at 3000 K calculated from these three estimates differ by less than 0.8 $cal·K^{-1}·mol^{-1}$. The principal moments of inertia are: I_A = [0.8775 × 10^{-39}], I_B = [9.9337 × 10^{-39}], and I_C = [10.8112 × 10^{-39}] $g^3·cm^6$

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.662	−311.142	−311.142	INFINITE
100	33.536	214.043	287.365	−7.332	−311.604	−313.909	163.969
200	36.825	238.134	257.323	−3.838	−313.285	−315.789	82.476
250	39.137	246.597	254.354	−1.939	−313.936	−316.339	66.095
298.15	41.407	253.685	253.685	0.	−314.524	−316.748	55.493
300	41.493	253.942	253.686	0.077	−314.546	−316.762	55.153
350	43.699	260.506	254.199	2.207	−315.827	−317.015	47.312
400	45.659	266.472	255.366	4.442	−316.403	−317.145	41.415
450	47.347	271.950	256.909	6.769	−316.910	−317.206	36.820
500	48.779	277.015	258.669	9.173	−317.364	−317.214	33.139
600	50.998	286.116	262.503	14.168	−318.161	−317.107	27.607
700	52.574	294.103	266.458	19.351	−318.865	−316.875	23.646
800	53.710	301.201	270.366	24.668	−319.517	−316.546	20.668
900	54.548	307.578	274.152	30.083	−320.140	−316.137	18.348
1000	55.178	313.359	277.788	35.571	−320.747	−315.660	16.488
1100	55.663	318.642	281.266	41.114	−321.346	−315.122	14.964
1200	56.042	323.502	284.586	46.700	−385.513	−313.451	13.644
1300	56.344	328.001	287.754	52.320	−385.334	−307.453	12.354
1400	56.587	332.185	290.780	57.967	−385.164	−301.469	11.248
1500	56.786	336.096	293.672	63.636	−385.003	−295.497	10.290
1600	56.951	339.767	296.440	69.323	−384.853	−289.535	9.452
1700	57.089	343.224	299.091	75.025	−384.716	−283.581	8.713
1800	57.206	346.490	301.635	80.740	−384.593	−277.636	8.057
1900	57.305	349.586	304.078	86.466	−384.486	−271.697	7.469
2000	57.390	352.527	306.427	92.201	−384.395	−265.763	6.941
2100	57.464	355.329	308.690	97.944	−384.321	−259.833	6.463
2200	57.528	358.004	310.871	103.693	−384.265	−253.906	6.028
2300	57.584	360.563	312.976	109.449	−384.227	−247.982	5.632
2400	57.634	363.014	315.010	115.210	−384.208	−242.059	5.268
2500	57.678	365.368	316.978	120.976	−384.209	−236.136	4.934
2600	57.717	367.631	318.883	126.745	−384.228	−230.213	4.625
2700	57.751	369.810	320.729	132.519	−384.266	−224.289	4.339
2800	57.782	371.911	322.520	138.295	−384.322	−218.362	4.074
2900	57.810	373.939	324.258	144.075	−384.398	−212.435	3.826
3000	57.836	375.899	325.947	149.857	−384.491	−206.503	3.596
3100	57.859	377.796	327.589	155.642	−384.602	−200.568	3.380
3200	57.880	379.633	329.187	161.429	−384.730	−194.630	3.177
3300	57.899	381.415	330.743	167.218	−384.875	−188.687	2.987
3400	57.916	383.143	332.258	173.009	−385.037	−182.739	2.807
3500	57.932	384.822	333.736	178.801	−385.214	−176.787	2.638
3600	57.947	386.455	335.178	184.595	−385.406	−170.829	2.479
3700	57.960	388.043	336.586	190.390	−385.613	−164.866	2.327
3800	57.972	389.588	337.960	196.187	−385.834	−158.896	2.184
3900	57.984	391.094	339.303	201.985	−386.070	−152.921	2.048
4000	57.995	392.563	340.617	207.784	−386.318	−146.940	1.919
4100	58.004	393.995	341.901	213.584	−386.580	−140.953	1.796
4200	58.014	395.393	343.158	219.385	−386.855	−134.958	1.678
4300	58.022	396.758	344.389	225.187	−387.143	−128.957	1.567
4400	58.030	398.092	345.594	230.989	−387.443	−122.950	1.460
4500	58.038	399.396	346.775	236.793	−387.756	−116.936	1.357
4600	58.045	400.672	347.933	242.597	−388.082	−110.914	1.259
4700	58.051	401.920	349.069	248.401	−388.420	−104.885	1.166
4800	58.057	403.142	350.183	254.207	−388.771	−98.848	1.076
4900	58.063	404.339	351.276	260.013	−389.136	−92.804	0.989
5000	58.069	405.513	352.349	265.819	−389.515	−86.752	0.906
5100	58.074	406.662	353.402	271.627	−389.908	−80.693	0.826
5200	58.078	407.790	354.437	277.434	−390.315	−74.627	0.750
5300	58.083	408.897	355.455	283.242	−390.737	−68.551	0.676
5400	58.087	409.982	356.454	289.051	−391.176	−62.469	0.604
5500	58.091	411.048	357.437	294.860	−391.632	−56.378	0.535
5600	58.095	412.095	358.404	300.669	−392.105	−50.277	0.469
5700	58.099	413.123	359.355	306.479	−392.597	−44.169	0.405
5800	58.102	414.134	360.291	312.289	−393.108	−38.051	0.343
5900	58.106	415.127	361.212	318.099	−393.640	−31.927	0.283
6000	58.109	416.104	362.119	323.910	−394.193	−25.790	0.225

PREVIOUS: September 1962 (1 atm) CURRENT: September 1962 (1 bar)

$S°(298.15\ K) = 71.797 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -269.874 \pm 2.9\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -274.470 \pm 2.9\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Espada *et al.*[1] have calorimetrically determined the heat of the reaction $PbO_2(cr) + 2\ H_2(g) \rightarrow Pb(cr) + 2\ H_2O(l)$ as -71.02 ± 0.16 kcal·mol^{-1} from which they derive $\Delta_f H°(PbO_2, cr, 298.15\ K) = -65.61 \pm 0.32$ kcal·mol^{-1}. This value assumes that the PbO_2 was 100% pure, in fact it is virtually impossible[2] to prepare a sample free of water and fully oxidized. Thus, Espada *et al.*[1] have increased their uncertainty to ± 0.7 kcal·mol^{-1} to cover the likely spread of values assuming typical compositions.

Millar[3] has recalculated the data of Glasstone for the Gibbs energy of the cell reaction $PbO_2(cr) + H_2(g) \rightarrow PbO(red) + H_2O(l)$ as $\Delta_f G°(298.15\ K) = -49.600$ kcal·mol^{-1}. With auxiliary Gibbs energy data[4,5] we calculate $\Delta_f G°(PbO_2, cr, 298.15\ K) = -52.33$ kcal·mol^{-1} which corresponds to $\Delta_f H°(PbO_2, cr, 298.15\ K) = -66.45$ kcal·mol^{-1} in reasonable agreement with the value reported by Espada *et al.*[1]

We adopt the value $\Delta_f H°(PbO_2, cr, 298.15\ K) = -65.6 \pm 0.7$ kcal·mol^{-1}.

Heat Capacity and Entropy

Duisman and Giauque[2] have reported the heat capacity of PbO_2 from 15 to 318 K and have calculated the entropy at 298.15 K based on $S°(15\ K) = 0.079$ cal·K^{-1}·mol^{-1}. They had considerable difficulty in preparing a suitable sample of PbO and finally used a sample containing PbO and H_2O, as impurities, for which significant corrections were made to the measured data. Millar[3] also has measured the heat capacity from 70 to 298 K but is 7% higher than the adopted values.

High temperature enthalpy data have been reported by Palmaer[6] and Bousquet *et al.*[7] but these data suffer from unknown amounts of impurity, for which the correction is probably substantial, and decomposition to intermediate oxides. Thus, the heat capacity above room temperature was estimated by a graphical extrapolation of the low temperature heat capacity.

Decomposition Data

Numerous investigators have reported the decomposition of PbO_2 at elevated temperatures, however, the exact processes are still not well defined. Otto[8] indicates a three step process to Pb_3O_4, but the intermediate compositions are not established. The temperature at which the decomposition pressure of oxygen reaches 0.2 atm was reported as 260°C by Otto while White and Roy[9] indicate 293°C. The enthalpies and entropies reported are in serious disagreement with adopted values and indicate failure to attain equilibrium.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−10.965	−269.874	−269.874	INFINITE
100	29.878	21.983	117.951	−9.597	−273.176	−254.361	132.865
200	49.957	49.530	77.063	−5.507	−274.522	−234.876	61.343
298.15	61.170	71.797	71.797	0.000	−274.470	−215.397	37.737
300	61.318	72.176	71.799	0.113	−274.461	−215.030	37.440
400	67.613	90.754	74.289	6.586	−273.688	−195.323	25.507
500	71.698	106.314	79.180	13.567	−272.580	−175.855	18.371
600	74.517	119.649	84.841	20.885	−271.311	−156.628	13.636
700	76.210	131.267	90.661	28.424	−274.848	−136.820	10.210
800	77.571	141.536	96.391	36.116	−273.510	−117.192	7.652
900	78.602	150.736	101.927	43.927	−272.090	−97.737	5.673
1000	79.301	159.056	107.231	51.825	−270.609	−78.443	4.097
1100	79.669	166.634	112.292	59.777	−269.091	−59.300	2.816
1200	79.705	173.570	117.114	67.748	−267.562	−40.296	1.754

PREVIOUS: March 1962 CURRENT: December 1971

$S°(298.15\ K) = 248.212 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -294.299 \pm 0.21\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -296.842 \pm 0.21\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
1151.38(1)
517.69(1)
1361.76(1)

Ground State Quantum Weight: 1

Point Group: C_{2v} $\sigma = 2$

Bond Distance: S–O = 1.432 ± 0.003 Å

Bond Angle: O–S–O = 119.53° ± 0.40°

Product of the Moments of Inertia: $I_A I_B I_C = 1.070 \times 10^{-115}\ g^3 \cdot cm^6$

Enthalpy of Formation

Eckman and Rossini[1] measured the enthalpy of combustion of rhombic sulfur to SO_2. Changes due to different atomic weights and electrical constants, though negligible, have been made.

Heat Capacity and Entropy

The functions were calculated by Gordon[2] using the method of Pennington and Kobe.[3] Structural parameters are given by Sirvetz,[4] obtained from microwave measurements. Frequencies were measured by Shelton *et al.*[5] A 3rd law value of $S°(298.15\ K) = 59.24\ cal \cdot K^{-1} \cdot mol^{-1}$ was obtained by Giauque and Stevenson.[6] The principal moments of inertia are (all in $g \cdot cm^2$): $I_A = 1.380 \times 10^{-39}$, $I_B = 8.131 \times 10^{-39}$, and $I_C = 9.534 \times 10^{-39}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.000	0.000	INFINITE	−10.552	−294.299	−294.299	INFINITE
100	33.526	209.025	281.199	−7.217	−294.559	−296.878	155.073
200	36.372	233.033	251.714	−3.736	−295.631	−298.813	78.042
298.15	39.878	248.212	248.212	0.000	−296.842	−300.125	52.581
300	39.945	248.459	248.213	0.074	−296.865	−300.145	52.260
400	43.493	260.448	249.824	4.250	−300.257	−300.971	39.303
500	46.576	270.495	252.979	8.758	−302.736	−300.871	31.432
600	49.049	279.214	256.641	13.544	−304.694	−300.305	26.144
700	50.961	286.924	260.427	18.548	−306.291	−299.444	22.345
800	52.434	293.829	264.178	23.721	−307.667	−298.370	19.482
900	53.580	300.073	267.825	29.023	−362.026	−296.051	17.182
1000	54.484	305.767	271.339	34.428	−361.940	−288.725	15.081
1100	55.204	310.995	274.710	39.914	−361.835	−281.409	13.363
1200	55.794	315.824	277.937	45.464	−361.720	−274.102	11.931
1300	56.279	320.310	281.026	51.069	−361.601	−266.806	10.720
1400	56.689	324.496	283.983	56.718	−361.484	−259.518	9.683
1500	57.036	328.419	286.816	62.404	−361.372	−252.239	8.784
1600	57.338	332.110	289.533	68.123	−361.268	−244.967	7.997
1700	57.601	335.594	292.141	73.870	−361.176	−237.701	7.304
1800	57.831	338.893	294.647	79.642	−361.096	−230.440	6.687
1900	58.040	342.026	297.059	85.436	−361.031	−223.183	6.136
2000	58.229	345.007	299.383	91.250	−360.981	−215.929	5.639
2100	58.400	347.853	301.624	97.081	−360.948	−208.678	5.191
2200	58.555	350.573	303.787	102.929	−360.931	−201.427	4.782
2300	58.702	353.179	305.878	108.792	−360.930	−194.177	4.410
2400	58.840	355.680	307.902	114.669	−360.947	−186.927	4.068
2500	58.965	358.085	309.861	120.559	−360.980	−179.675	3.754
2600	59.086	360.400	311.761	126.462	−361.030	−172.422	3.464
2700	59.199	362.632	313.604	132.376	−361.095	−165.166	3.195
2800	59.308	364.787	315.394	138.302	−361.175	−157.908	2.946
2900	59.413	366.870	317.133	144.238	−361.270	−150.648	2.713
3000	59.513	368.886	318.825	150.184	−361.379	−143.383	2.497
3100	59.609	370.839	320.471	156.140	−361.502	−136.114	2.294
3200	59.706	372.733	322.075	162.106	−361.638	−128.842	2.103
3300	59.794	374.572	323.638	168.081	−361.786	−121.565	1.924
3400	59.881	376.358	325.162	174.065	−361.946	−114.283	1.756
3500	59.969	378.095	326.650	180.057	−362.118	−106.996	1.597
3600	60.053	379.786	328.103	186.058	−362.300	−99.704	1.447
3700	60.137	381.432	329.522	192.068	−362.493	−92.408	1.305
3800	60.216	383.037	330.909	198.086	−362.697	−85.105	1.170
3900	60.296	384.602	332.266	204.111	−362.911	−77.796	1.042
4000	60.375	386.130	333.593	210.145	−363.134	−70.484	0.920
4100	60.450	387.621	334.893	216.186	−363.368	−63.164	0.805
4200	60.530	389.079	336.166	222.235	−363.611	−55.840	0.694
4300	60.605	390.504	337.413	228.292	−363.864	−48.508	0.589
4400	60.676	391.898	338.636	234.356	−364.128	−41.172	0.489
4500	60.752	393.263	339.834	240.427	−364.401	−33.829	0.393
4600	60.823	394.599	341.010	246.506	−364.686	−26.480	0.301
4700	60.894	395.908	342.165	252.592	−364.981	−19.125	0.213
4800	60.969	397.190	343.298	258.685	−365.288	−11.763	0.128
4900	61.036	398.448	344.410	264.785	−365.607	−4.394	0.047
5000	61.107	399.682	345.504	270.893	−365.938	2.981	−0.031
5100	61.178	400.893	346.578	277.007	−366.283	10.364	−0.106
5200	61.250	402.082	347.634	283.128	−366.641	17.751	−0.178
5300	61.317	403.249	348.672	289.257	−367.014	25.148	−0.248
5400	61.388	404.396	349.693	295.392	−367.403	32.550	−0.315
5500	61.455	405.523	350.698	301.534	−367.807	39.960	−0.380
5600	61.522	406.631	351.687	307.683	−368.230	47.379	−0.442
5700	61.588	407.720	352.661	313.838	−368.671	54.804	−0.502
5800	61.655	408.792	353.619	320.000	−369.131	62.238	−0.561
5900	61.727	409.846	354.563	326.169	−369.611	69.677	−0.617
6000	61.793	410.884	355.493	332.346	−370.113	77.128	−0.671

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 50.053\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 543 \pm 3$ K(low cristobalite → high cristobalite)
$T_{trs2} = 1079 \pm 250$ K(high quartz → high cristobalite)
$T_{fus} = 1996 \pm 5$ K(high cristobalite → liquid)

$\Delta_f H°(298.15\ K) = -905.489\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 1.343 \pm 0.25\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 2.008 \pm 0.63\ kJ·mol^{-1}$
$\Delta_{fus} H° = 9.581 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of low cristobalite by addition of $\Delta_{trs}H° = 0.321$ kcal·mol^{-1} and the difference between $H°$(543 K)–$H°$(298.15 K) for low and high forms.

Heat Capacity and Entropy

$C_p°$ is derived from enthalpies of Mosesman[1] and White[2] whose data deviate from the adopted functions by −0.6 to +0.5% and +0.9 to 0.0%, respectively. White's deviations for cristobalite have a magnitude and trend similar to his deviations for quartz and vitreous siica. Data of Wietzel[3] for his sample prepared at 1600°C deviate by + 3% at 673 K and + 1.6% at 1973 K. $C_p°$ below 543 K is smoothly extrapolated to give the proper trend in the Gibbs energy, but the heat capacity at 298 K is not realistic. The entropy is calculated in a manner analogous to that of the enthalpy of formation.

Transition Data

Literature on the polymorphism of SiO_2 is voluminous but is summarized in detail in recent books by Sosman[4] and Eitel.[5] The known phases of SiO_2 include quartz, tridymite(?), cristobalite, vitreous silica and the more recently discovered high pressures phases. Muan[6] concisely reviewed the still controversial question of whether tridymite is stabilized only by the presence of foreign ions or whether it is a stable phase of SiO_2 intermediate between quartz and cristobalite. Transitions among the different phases are generally sluggish because of large energy barriers to the structural change and small differences in Gibbs free energies. As a result, the phases often persist far into metastable regions. In contrast, transitions within a particular phase are rapid and reversible (i.e., the low → high inversions of quartz or cristobalite).

High cristobalite is the stable phase near T_{fus}. It becomes metastable with respect to quartz at lower temperatures but persists down to the high → low inversion at 543 K (see table for low cristobalite). The high form is cubic and the low form tetragonal.[12, 13]

The adopted tables give 1079 ± 250 K as the temperature at which $\Delta_r G° \approx 0$ for high quartz → high cristobalite; $\Delta_{trs}H° = 0.48 \pm 0.15$ kcal·mol^{-1} is the corresponding enthalpy difference. The uncertainty in T_{trs} is derived from that in $\Delta_{trs}H°$ which, in turn, is taken from $\Delta_r H°(970\ K) = 0.45 \pm 0.15$ kcal·mol^{-1} obtained by Holm[7] from $\Delta_{sol}H°$ measurements in an oxide melt. It is apparent that T_{trs} is extremely sensitive to small changes in G or H. Holmquist[8] tentatively placed this inversion at 1298 ± 25 K but did observe cristobalite formation at temperatures as low as 1171 K.

Fusion Data

Melting point data were reviewed by Schneider[9] and adjusted to the 1948 International Temperature Scale. The adopted melting point for cristobalite is based on Greig.[10] $\Delta_{fus}H°$ is calculated as the difference in $\Delta_f H°$ for liquid and crystal at T_{fus}. Mackenzie *et al.*[11] showed that cristobalite may be superheated by as much as 40° above T_{fus} due to its slow rate of fusion.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	26.581	50.053	50.053	0.000	−905.489	−853.636	149.554
300	27.154	50.219	50.054	0.050	−905.530	−853.315	148.575
400	47.413	61.218	51.416	3.921	−906.752	−835.678	109.128
500	56.856	72.923	54.555	9.184	−906.826	−817.885	85.444
600	62.049	83.788	58.536	15.151	−906.394	−800.132	69.658
700	65.229	93.609	62.857	21.526	−905.721	−782.473	58.389
800	67.337	102.466	67.264	28.161	−904.932	−764.919	49.944
900	68.823	110.487	71.628	34.973	−904.088	−747.468	43.382
1000	69.923	117.798	75.885	41.913	−903.221	−730.112	38.137
1100	70.772	124.504	80.004	48.949	−902.350	−712.843	33.850
1200	71.446	130.691	83.974	56.061	−901.485	−695.653	30.281
1300	71.998	136.432	87.791	63.234	−900.636	−678.535	27.264
1400	72.467	141.786	91.459	70.458	−899.808	−661.482	24.680
1500	72.869	146.799	94.983	77.725	−899.006	−644.487	22.443
1600	73.220	151.514	98.370	85.030	−898.235	−627.544	20.487
1700	73.534	155.962	101.628	92.368	−947.674	−610.202	18.749
1800	73.814	160.173	104.765	99.735	−946.742	−590.378	17.132
1900	74.074	164.171	107.787	107.130	−945.806	−570.605	15.687
2000	74.316	167.977	110.702	114.549	−944.869	−550.882	14.388
2100	74.542	171.608	113.517	121.992	−943.931	−531.206	13.213
2200	74.751	175.081	116.237	129.457	−942.994	−511.573	12.146
2300	74.952	178.408	118.868	136.942	−942.059	−491.985	11.173
2400	75.145	181.602	121.416	144.447	−941.126	−472.437	10.282
2500	75.333	184.674	123.885	151.971	−940.197	−452.927	9.463
2600	75.509	187.632	126.280	159.513	−939.271	−433.454	8.708
2700	75.684	190.485	128.606	167.073	−938.348	−414.017	8.010
2800	75.852	193.240	130.865	174.650	−937.428	−394.614	7.362
2900	76.015	195.905	133.062	182.243	−936.512	−375.245	6.759
3000	76.178	198.485	135.200	189.853	−935.599	−355.906	6.197

PREVIOUS: CURRENT: June 1967

Cristobalite, Low (SiO_2) CRYSTAL M_r = 60.0843

$S°(298.15\ K) = 43.396 \pm 0.13\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 543 \pm 3$ K (low cristobalite → high cristobalite)

$\Delta_f H°(0\ K) = -903.482 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -908.346 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.343 \pm 0.25\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of quartz using $\Delta_f H°(970\ K) = 0.45 \pm 0.15\ kcal \cdot mol^{-1}$ for high quartz → high cristobalite, as determined by Holm[1] from $\Delta_{sol} H°$ is an oxide melt. This value reduces to $\Delta_f H°(298.15\ K) = 0.60\ kcal \cdot mol^{-1}$ for low quartz → low cristobalite. Kracek[2] obtained essentially the same value, $\Delta_f H°(298.15\ K) = 0.63\ kcal \cdot mol^{-1}$, from $\Delta_{sol} H°$ in HF(aq, 74.7 °C), while Hummel[3] found $\Delta_f H°(298.15\ K) = 1.80\ kcal \cdot mol^{-1}$ from $\Delta_{sol} H°$ in HF(aq, 26.5 °C). The larger $\Delta_f H°$ corresponds to a less negative $\Delta_f H°$ (i.e., less stable) and suggests that the sample of Hummel has disorder approaching that of vitreous silica. Presumably, this disagreement arises from different methods of preparation of cristobalite from quartz. Holm heated for 24 hours at 1743 K, while Hummel heated for 4 hours at 1973 K. Hummel's sample was then ground and treated with dilute HF to remove amorphous surface layers created by grinding; particles smaller than 2.5 microns were used in order to obtain adequate rates of dissolution. Neither author gave X-ray or DTA evidence to confirm that the samples were the more stable, ordered form of cristobalite.[15]

The calorimetric data are summarized below along with equilibrium data which confirm the adopted values of $\Delta_f H°$ for cristobalite and quartz. Data from Matoba[5] and Rein[6] were reduced to the standard state of Si(l) using activity coefficients from the curves of.[10]

Source	Method	Reaction	T/K	Data Points	$\Delta_r H(T)$ kcal·mol^{-1}	$\Delta_r H°(298.15\ K)$ kcal·mol^{-1}	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	$\Delta_{sol} H°$ in oxide melt	A	970	3	0.45 ± 0.15	0.6	–	−217.10
2	$\Delta_{sol} H°$ in HF(aq, 26.5°C)	A	299.65	8	1.80 ± 0.2	1.80	–	−215.90 [3]
	$\Delta_{sol} H°$ in HF(aq, 74.7°C)	A	298 348	–	–	0.63 ± 0.05	–	−217.07
4	$\Delta_{sol} H°$ in HF(aq, 73.7°C)	A	298 347	6	–	0.93 ± 0.1	–	−216.77
5	Keq + γ(Si)	B	1843–1953	3	104.5 ± 0.6*	−112.48*	0.8	−217.17
6	Keq + γ(Si)	C	1773–1798	5	–	175.42*	31 ± 37	−217.38
	Keq + γ(Si)	D	1823–1873	6	–	228.5*	10 ± 6	−212.3
7	$K°_p$	E	1703–1829	14	145.9 ± 1.3*	146.92*	−2.3 ± 0.7	−217.94
8	$K°_p$	E	1673–1853	5	145.5 ± 3.5*	147.43*	−1.9 ± 1.9	−218.45

*Values at T are from 2nd law analysis while those at 298.15 K are from 3rd law.

Reactions:
A) SiO_2(quartz, low or high) = SiO_2(cristobalite, low or high)
B) SiO_2(high cristobalite) + 2 H_2(g) = Si(l) + 2 H_2O(g)
C) SiO_2(high cristobalite) + 2 C(graph) = Si(l) + 2 CO(g)
D) SiO_2(high cristobalite) + 2 SiC(β) = 3 Si(l) + 2 CO(g)
E) SiO_2(high cristobalite) + 3 C(graph) = SiC(β) + 2 CO(g)

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Westrum.[11] Earlier data of Anderson[12] are in satisfactory agreement. The entropy is obtained from $C_p°$ using $S°(5\ K) = 0.0007\ cal \cdot K^{-1} \cdot mol^{-1}$. $C_p°$ above 300 K is derived from enthalpy data of Mosesman[13] and White.[14] The former deviate from the adopted functions by −0.7 to 0.5% and the latter by + 0.4%. Although the functions above 300 K appear to be reliable, it would be desirable to have new data for a well characterized sample (see Transition Data).

Transition Data

Low cristobalite is metastable with respect to quartz but persists up to T_{trs}. T_{trs} is taken as the temperature at the peak in the heating curve for well ordered cristobalite; however, see[15, 16] for detaled discussions of temperatures about 25 lower which were found from cooling curves. $\Delta_{trs} H°$ is derived from enthalpy data[13, 14] for high cristobalite using the adopted enthalpy for the low form. The enthalpy data of Mosesman[13] gave a lower T_{trs} which suggests that the sample was less well-ordered than desirable. $\Delta_{trs} H°$ is confirmed, however, by other data which are summarized below. Additional polymorphism is discussed on the table for high cristobalite.

Source	Method	$\Delta_{trs} H°$, kcal·mol^{-1}
13	Enthalpy data	0.321
17	Microcalorimetric thermal analysis	0.318 ± 0.018
18	ΔV and dT/DP	0.27
19	Differential thermal analysis	0.26 ± 0.01

References

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Continued on page 1814

Silicon Oxide, Cristobalite, Low (SiO_2) O_2Si_1(cr)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.000	0.000	INFINITE	−7.037	−903.482	−903.482	INFINITE
100	16.000	11.247	74.760	−6.351	−905.967	−889.378	464.563
200	32.995	27.878	47.145	−3.853	−907.559	−872.105	227.770
298.15	44.953	43.396	43.396	0.000	−908.346	−854.509	149.706
300	45.145	43.675	43.397	0.083	−908.355	−854.175	148.725
400	53.145	57.848	45.275	5.029	−908.501	−836.079	109.181
500	58.672	70.326	49.064	10.631	−908.236	−817.997	85.456
600	62.969	81.426	53.549	16.726	−907.677	−799.998	69.646
700	65.689	91.348	58.254	23.166	−906.940	−782.108	58.362
800	67.572	100.247	62.956	29.832	−906.119	−764.330	49.906
900	69.036	108.292	67.554	36.664	−905.254	−746.658	43.335
1000	70.291	115.633	72.000	43.632	−904.359	−729.084	38.083

PREVIOUS: CURRENT: June 1967

$S°(298.15\ K) = 41.463 \pm 0.13\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 847 \pm 1.5$ K (low quartz → high quartz)
$T_{trs2} = 1079 \pm 250$ K (high quartz → high cristobalite)
$T_{fus} = 1696 \pm 50$ K (high quartz → liquid)

$\Delta_f H°(0\ K) = -905.872 \pm 1.7\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -910.857 \pm 1.7\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 0.728 \pm 0.17\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 2.008 \pm 0.63\ kJ·mol^{-1}$
$\Delta_{fus} H° = 7.699 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is based on data of Wise[1] for combustion of SiO_2(low quartz) and Si(cr) in F_2 to form SiF_4(g). Good[2] burned a mixture of Si(cr) and vinylidene fluoride polymer in oxygen in the presence of HF(aq) to form H_2SiF_6(aq, HF). Combining this result with a previous heat of solution of quartz,[3] the authors derived $\Delta_f H°(298.15\ K) = -217.5 \pm 0.5$ kcal·mol^{-1}. Agreement with the adopted value is excellent, considering the complexity of the latter scheme. Both schemes are independent of $\Delta_f H°$(HF), although the polymer Si scheme depends on the heat of dilution of HF(aq). Wise[1] has reviewed other data which confirm the adopted value rather than the oxygen combustion value[4] of 209.9 kcal·mol^{-1}. Pertinent equilibrium data are analyzed on the table of SiO_2(low cristobalite), while the calorimetric results are summarized below.

Source	Reaction	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}
1	SiO_2(low quartz) + 2 F_2(g) → SiF_4(g) + O_2(g)	−168.26 ± 0.28	−217.72 ± 0.34
2	See text.	—	−217.5 ± 0.5
3	Si(cr) + 2 O_2(g) → SiO_2(low quartz)	209.9	−209.9

Heat Capacity and Entropy

Heat capacities below 300 K are based on data of Jones[5] and Westrum.[6] Earlier data of Anderson[7] are in good agreement. The entropy is obtained from $C_p°$ using $S°(2\ K) = 0.00001$ cal·K^{-1}·mol^{-1} from 300 to 847 K is derived from adiabatic calorimetric data of Moser[8] and Sinel'nikov.[9] The adopted $C_p°$ is discontinuous at 847 K and $\Delta C_p° = -2.17$ cal·K^{-1}·mol^{-1}. Values above the transition temperature are based on data of Moser and on data up to 1473 K obtained with a thermal analysis method by Leonidov.[10] $C_p°$ is extrapolated linearly to higher temperatures.

From a review of data available before 1953, Kelley[11] selected almost identical enthalpies below 847 K but a value higher by 96 cal·K^{-1}·mol^{-1} at 900 K. The higher value, due to use of a larger $\Delta_{trs1} H°$, was presumably based on Roth,[12] Wietze[13] and White[14] whose enthalpy data were given the most weight by Kelley. Near 900 K these three sets of data deviate from the adopted function by −150 ± 30, +130 ± 40 and +15 ± 35 kcal·mol^{-1}, respectively; however, a recent enthalpy datum[15] obtained by transposed temperature drop calorimetry deviates + 75 cal·K^{-1}·mol^{-1} at 968 K.

Transition Data

$T_{trs1} = 847 \pm 1.5$ K is based on thermal analysis of many specimens by Keith and Tuttle.[16] Wide variations in T_{trs1} for some specimens were attributed by the authors to small amounts of impurities. The discontinuity in the volume curve[17] during inversion from trigonal low quartz to hexagonal high quartz suggests that the transition should be treated as first order. Thus, the enthalpy of transition is derived as (1011–854+17) = 174 cal·K^{-1}·mol^{-1}, where 1011 ± 6 is $H°$(873.15 K)–$H°$(823.15 K) measured by Moser,[8] 854 is the corresponding increment calculated from the JANAF $C_p°$ and 17 is an endpoint correction for the difference between the observed and adopted curves below 823.15 K. Some recent data which confirm the adopted $\Delta_{trs1} H°$ are summarized below.

Source	Method	$\Delta_{trs1} H°$, kcal·mol^{-1}
8	H and $C_p°$ from adiabatic calorimetry	0.174
9	Integration of $C_p°$ from adiabatic calorimetry	0.143
10	Thermal analysis	0.198
17	ΔV with $dT/dP = 0.026$ K/atm	0.12
18	Microcalorimetric thermal analysis, Single crystal	0.156, 0.165, 0.178 ± − .010
	Various crushed samples	0.124 to 0.193

Additional polymorphism of SiO_2 is discussed on the table for high cristobalite. Quartz has been superheated through the cristobalite region to some 300 above its metastable melting point. This melting point is calculated from the adopted tables as 1696 ± 50 K, which agrees well with the range 1673–1723 K indicated by the data of Mackenzie.[19] The adopted tables predict the inversion of high quartz to high cristobalite at 1079 ± 250 K. Holmquist[20] tentatively placed this inversion at 1298 ± 25 K. $\Delta_{trs2} H°$ and $\Delta_{fus} H°$ are calculated from the differences in the $\Delta_f H°$ values of the appropriate phases at T_{trs2} and T_{fus}.

Continued on page 1814

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−6.916	−905.872	−905.872	INFINITE
100	15.686	9.694	72.496	−6.280	−908.406	−891.662	465.756
200	32.639	26.087	45.187	−3.820	−910.036	−874.223	228.324
298.15	44.589	41.463	41.463	0.000	−910.857	−856.443	150.045
300	44.769	41.740	41.464	0.083	−910.866	−856.106	149.061
400	53.430	55.874	43.333	5.017	−911.024	−837.812	109.407
500	59.643	68.499	47.127	10.686	−910.692	−819.539	85.617
600	64.417	79.808	51.648	16.896	−910.017	−801.368	69.765
700	68.768	90.063	56.414	23.554	−909.062	−783.331	58.453
800	73.701	99.555	61.220	30.668	−907.794	−765.452	49.979
847.000	76.509	103.840	63.467	34.196	I <--> II		
847.000	67.417	104.700	63.467	34.924	TRANSITION		
900	67.948	108.807	66.017	38.512	−905.918	−747.785	43.400
1000	68.952	116.018	70.662	45.357	−905.145	−730.256	38.145
1100	69.956	122.637	75.090	52.302	−904.365	−712.805	33.848
1200	70.961	128.767	79.311	59.348	−903.567	−695.426	30.271
1300	71.965	134.487	83.338	66.494	−902.744	−678.114	27.247
1400	72.969	139.857	87.185	73.741	−901.893	−660.866	24.657
1500	73.973	144.925	90.867	81.088	−901.011	−643.681	22.415
1600	74.977	149.731	94.397	88.535	−900.097	−626.555	20.455
1696.000	75.940	154.128	97.654	95.779	------ II <--> LIQUID -----		
1700	75.981	154.307	97.787	96.083	−949.326	−609.041	18.714
1800	76.986	158.678	101.050	103.732	−948.113	−589.059	17.094
1900	77.990	162.868	104.194	111.480	−946.823	−569.146	15.647
2000	78.994	166.894	107.229	119.330	−945.456	−549.303	14.346

PREVIOUS: December 1962 CURRENT: June 1967

Silicon Oxide (SiO_2) LIQUID M_r = 64.0843

$S°(298.15\ K) = 47.928 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{fus} = 1996 \pm 5$ K(high cristobalite → liquid)

$\Delta_f H°(0\ K) = 897.756\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -902.661\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = 9.581 \pm 2.1\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(l, supercooled, 298.15 K) is calculated from that of quartz using $\Delta_r H°(970\ K) = 1.45 \pm 0.15\ kcal \cdot mol^{-1}$ for high quartz Å SiO_2(l), as determined by Holm[1] from $\Delta_{sol} H°$ in an oxide melt. This value reduces to $\Delta_r H°(298.15\ K) = 1.96\ kcal \cdot mol^{-1}$ for low quartz → SiO_2(l) and is consistent within $\pm 0.3\ kcal \cdot mol^{-1}$ with other calorimetric data summarized below. Earlier results were reviewed by Hummel.[4]

Source	Method	Reaction	T/K	$\Delta_r H°$(T) kcal·mol^{-1}	$\Delta_r H°$(298.15 K) kcal·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[1]	$\Delta_{sol} H°$ in oxide melt	A	970	1.45 ± 0.15	1.96	−215.74
[2]	$\Delta_r H°$ in flourine	B	298	1.78 ± 0.46	1.78	−215.92
[3]	$\Delta_{sol} H°$ in HF(aq, 74.7 C)	A	298–348	–	2.18 ± 0.05	−215.52
[4]	$\Delta_{sol} H°$ in HF(aq, 26.5 C)	A	300	2.27 ± 0.2	2.27	−215.43

A. SiO_2(quartz, low or high) → SiO_2(l)

B. $SiO_2(l) + 2\ F_2(g) \rightarrow SiF_4(g) + O_2(g)$

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Flubacher[5] and Westrum[6] for samples annealed at 1100 and 1070°C, respectively. Data of Turdakin[7] are higher by about 1% in the range 60–160 K and at 300 K but are in agreement elsewhere. The entropy is calculated from $C_p°$ using $S°(2.34\ K) - S°(0\ K) = 0.0001\ cal \cdot K^{-1} mol^{-1}$ and $S°(0\ K) = 1.098\ cal \cdot K^{-1} \cdot mol^{-1}$. $C_p°$ data[6] for a different sample annealed at 1300°C yield an entropy larger by <0.04 $cal \cdot K^{-1} \cdot mol^{-1}$. Earlier data were reviewed by Kelley.[8] The residual entropy is calculated from $S°(0\ K) = S°(1996\ K) - S°(1996;0\ K) = 41.258 - 40.160 = 1.098\ cal \cdot K^{-1} \cdot mol^{-1}$, where 40.160 is obtained from the adopted functions, while 41.258 is the sum of $\Delta_{fus} S° = 1.14\ cal \cdot K^{-1} \cdot mol^{-1}$ and $S°(1996\ K) = 40.111\ cal \cdot K^{-1} \cdot mol^{-1}$ for high cristobalite. We estimate the uncertainty as ±0.3 $cal \cdot K^{-1} \cdot mol^{-1}$, primarily from the uncertainty in $\Delta_{fus} H°$.

$C_p°$ above 300 K is based on adiabatic calorimetric data of Moser[9] up to 900 K. Enthalpy data of White[10] and Fischer[11] are in excellent agreement. $C_p°$ from 900 to 1500 K is derived from enthalpy data of Southard[12] and White.[10] Maximum deviation of the data from the adopted values in this range is 0.5%. Enthalpy data of Egan[13] and Kelley[14] deviate from the adopted values by less than 1% in the range 1000–1500 K, although large positive deviations appear at lower temperatures.

In the region 1500–1700 K, the adopted $C_p°$ shows a rapid, sigmoidal rise which is suggested by the enthalpy data of Wietzel.[15] This is presumed to be the glass transition region in which $C_p°$ rises to that of the stable liquid. $C_p°$ above 1700 K is estimated as 20.5 $cal \cdot K^{-1} \cdot mol^{-1}$ or 6.83 $cal \cdot K^{-1}$ g atom^{-1}. This value is consistent with the enthalpy data[15] and with liquid heat capacities of Al_2O_3, $Na_2Si_2O_5$, and Na_2SiO_3.

Fusion Data

The melting point of high cristobalite is 1996 ± 5 K, while the metastable melting point of high quartz is 1696 ± 50 K. $\Delta_{fus} H°$ is the difference between $\Delta_f H°$ for liquid and high cristobalite at T_{fus}. Values ranging from 1.8 to 3.6 $kcal \cdot mol^{-1}$ have been derived from various interpretations of phase diagrams.[1]

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Silicon Oxide (SiO_2) O_2Si_1(l)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.000	4.594	INFINITE	−6.996	−897.756	−897.756	INFINITE
100	16.154	15.983	78.952	−6.297	−900.228	−884.112	461.813
200	32.736	32.602	51.618	−3.803	−901.824	−867.314	226.519
298.15	44.183	47.928	47.928	0.000	−902.661	−850.175	148.947
300	44.367	48.202	47.929	0.082	−902.671	−849.850	147.972
400	52.518	62.156	49.776	4.952	−902.893	−832.194	108.673
500	58.082	74.510	53.513	10.499	−902.684	−814.537	85.094
600	62.045	85.468	57.943	16.515	−902.203	−796.949	69.381
700	64.973	95.263	62.587	22.873	−901.548	−779.457	58.164
800	67.208	104.091	67.233	29.486	−900.780	−762.067	49.758
900	68.956	112.112	71.780	36.298	−899.936	−744.777	43.226
1000	70.350	119.452	76.186	43.266	−899.041	−727.585	38.005
1100	71.475	126.211	80.430	50.359	−898.113	−710.484	33.738
1200	72.396	132.471	84.509	57.554	−897.165	−693.469	30.186
1300	73.157	138.296	88.425	64.832	−896.211	−676.533	27.183
1400	73.848	143.743	92.184	72.183	−895.256	−659.670	24.613
1500	74.475	148.852	95.794	79.587	−894.317	−642.876	22.387
1600	80.040	153.767	99.263	87.206	−893.232	−626.146	20.442
1696.000	85.772	158.655	102.487	95.261	----- II <--> LIQUID -----		
1700	85.772	158.857	102.619	95.604	−941.610	−609.059	18.714
1800	85.772	163.759	105.881	104.181	−939.468	−589.559	17.109
1900	85.772	168.397	109.050	112.759	−937.350	−570.178	15.675
2000	85.772	172.796	112.128	121.336	−935.255	−550.907	14.388
2100	85.772	176.981	115.118	129.913	−933.183	−531.741	13.226
2200	85.772	180.971	118.021	138.490	−931.133	−512.672	12.172
2300	85.772	184.784	120.842	147.067	−929.106	−493.697	11.212
2400	85.772	188.434	123.582	155.645	−927.102	−474.809	10.334
2500	85.772	191.936	126.247	164.222	−925.119	−456.004	9.528
2600	85.772	195.300	128.839	172.799	−923.158	−437.279	8.785
2700	85.772	198.537	131.360	181.376	−921.217	−418.628	8.099
2800	85.772	201.656	133.816	189.953	−919.297	−400.048	7.463
2900	85.772	204.666	136.207	198.531	−917.397	−381.538	6.872
3000	85.772	207.574	138.538	207.108	−915.517	−363.092	6.322
3100	85.772	210.386	140.810	215.685	−913.655	−344.708	5.808
3200	85.772	213.109	143.027	224.262	−911.811	−326.385	5.328
3300	85.772	215.749	145.191	232.839	−909.985	−308.119	4.877
3400	85.772	218.309	147.304	241.417	−908.175	−289.907	4.454
3500	85.772	220.796	149.369	249.994	−906.381	−271.749	4.056
3600	85.772	223.212	151.387	258.571	−1288.754	−243.181	3.528
3700	85.772	225.562	153.360	267.148	−1286.577	−214.168	3.024
3800	85.772	227.849	155.290	275.725	−1284.416	−185.212	2.546
3900	85.772	230.077	157.179	284.303	−1282.269	−156.313	2.094
4000	85.772	232.249	159.029	292.880	−1280.137	−127.470	1.665
4100	85.772	234.367	160.841	301.457	−1278.019	−98.680	1.257
4200	85.772	236.434	162.616	310.034	−1275.914	−69.941	0.870
4300	85.772	238.452	164.356	318.611	−1273.822	−41.252	0.501
4400	85.772	240.424	166.063	327.189	−1271.742	−12.612	0.150
4500	85.772	242.351	167.737	335.766	−1269.674	15.981	−0.186

PREVIOUS: December 1962 CURRENT: June 1967

0	to	847	K crystal, low quartz (trigonal)
847	to	1079	K crystal, high quartz (hexagonal)
1079	to	1996	K crystal, high cristobalite
above		1996	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−6.916	−905.872	−905.872	INFINITE
100	15.686	9.694	72.496	−6.280	−908.406	−891.662	465.756
200	32.639	26.087	45.187	−3.820	−910.036	−874.223	228.324
298.15	44.589	41.463	41.463	0.000	−910.857	−856.443	150.045
300	44.769	41.740	41.464	0.083	−910.866	−856.106	149.061
400	53.430	55.874	43.333	5.017	−911.024	−837.812	109.407
500	59.643	68.499	47.127	10.686	−910.692	−819.539	85.617
600	64.417	79.808	51.648	16.896	−910.017	−801.368	69.765
700	68.768	90.063	56.414	23.554	−909.062	−783.331	58.453
800	73.701	99.555	61.220	30.668	−907.794	−765.452	49.979
847.000	76.509	103.840	63.467	34.196	I <--> II		
847.000	67.417	104.700	63.467	34.924	TRANSITION		
900	67.948	108.807	66.017	38.512	−905.918	−747.785	43.400
1000	68.952	116.018	70.662	45.357	−905.145	−730.256	38.145
1100	69.956	122.637	75.090	52.302	−904.365	−712.805	33.848
1200	70.961	128.767	79.311	59.348	−903.567	−695.426	30.271
1300	71.965	134.487	83.338	66.494	−902.744	−678.114	27.247
1400	72.969	139.857	87.185	73.741	−901.893	−660.866	24.657
1500	73.973	144.925	90.867	81.088	−901.011	−643.681	22.415
1600	74.977	149.731	94.397	88.535	−900.097	−626.555	20.455
1696.000	75.940	154.128	97.654	95.779	II <--> LIQUID		
1696.000	85.772	158.655	97.654	103.456	TRANSITION		
1700	85.772	158.857	97.798	103.799	−941.610	−609.059	18.714
1800	85.772	163.759	101.328	112.377	−939.468	−589.559	17.109
1900	85.772	168.397	104.737	120.954	−937.350	−570.178	15.675
2000	85.772	172.796	108.031	129.531	−935.255	−550.907	14.388
2100	85.772	176.981	111.215	138.108	−933.183	−531.741	13.226
2200	85.772	180.971	114.296	146.685	−931.133	−512.672	12.172
2300	85.772	184.784	117.278	155.263	−929.106	−493.697	11.212
2400	85.772	188.434	120.168	163.840	−927.102	−474.809	10.334
2500	85.772	191.936	122.969	172.417	−925.119	−456.004	9.528
2600	85.772	195.300	125.687	180.994	−923.158	−437.279	8.785
2700	85.772	198.537	128.325	189.571	−921.217	−418.628	8.099
2800	85.772	201.656	130.889	198.149	−919.297	−400.048	7.463
2900	85.772	204.666	133.381	206.726	−917.397	−381.538	6.872
3000	85.772	207.574	135.806	215.303	−915.517	−363.092	6.322
3100	85.772	210.386	138.167	223.880	−913.655	−344.708	5.808
3200	85.772	213.109	140.466	232.457	−911.811	−326.385	5.328
3300	85.772	215.749	142.708	241.035	−909.985	−308.119	4.877
3400	85.772	218.309	144.894	249.612	−908.175	−289.907	4.454
3500	85.772	220.796	147.027	258.189	−906.381	−271.749	4.056
3600	85.772	223.212	149.110	266.766	−1288.754	−243.181	3.528
3700	85.772	225.562	151.145	275.343	−1286.577	−214.168	3.024
3800	85.772	227.849	153.133	283.921	−1284.416	−185.212	2.546
3900	85.772	230.077	155.078	292.498	−1282.269	−156.313	2.094
4000	85.772	232.249	156.980	301.075	−1280.137	−127.470	1.665
4100	85.772	234.367	158.842	309.652	−1278.019	−98.680	1.257
4200	85.772	236.434	160.665	318.229	−1275.914	−69.941	0.870
4300	85.772	238.452	162.450	326.807	−1273.822	−41.252	0.501
4400	85.772	240.424	164.200	335.384	−1271.742	−12.612	0.150
4500	85.772	242.351	165.916	343.961	−1269.674	15.981	−0.186

PREVIOUS: CURRENT: June 1967

Silicon Oxide (SiO_2) IDEAL GAS $M_r = 60.0843$

$S°(298.15\ K) = [228.976]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -304.11 \pm 33.5\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -305.43 \pm 33.5\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[980] (1)
[370] (2)
[1430] (1)

Ground State Quantum Weight: [1] $\sigma = [2]$
Point Group: [$D_{\infty h}$]
Bond Angle: O–Si–O = [180]°
Bond Distance: Si–O = [1.55] Å
Rotational Constant: $B_O = [0.219280]\ cm^{-1}$

Enthalpy of Formation

The adopted value is based on the data summarized below. Margrave[1] has reported a value of $\Delta_{sub}H°(298.15\ K) = 140.9 \pm 1\ kcal·mol^{-1}$ but details are not yet available. Assuming that this corresponds to reaction A below, we calculate $\Delta_f H°(298.15\ K) = -75.5\ kcal·mol^{-1}$. Firsova[2] reported two values of the sublimation pressure which were derived from Knudsen effusion data using auxiliary data for SiO(g). Porter[4] derived two pressures from a mass spectrometric study and also obtained a 2nd law value for $\Delta_{sub}H°$ from ion intensities. The resulting range for $\Delta_{sub}H°(298.15\ K)$, 136 to 141 $kcal·mol^{-1}$, is consistent with the lower limit of 130 $kcal·mol^{-1}$, obtained by Bergman[3] from a method involving explosion in a spherical bomb. An alternative analysis of the mass spectrometric data[4] using the gas phase reaction B suggests an even higher $\Delta_{sub}H°$ of 148 $kcal·mol^{-1}$. The adopted $\Delta_f H°$ corresponds to $\Delta_{sub}H°(298.15\ K) = 143.4 \pm 8\ kcal·mol^{-1}$ and to $\Delta_{at}H(0\ K) = 297.3 \pm 8\ kJ·mol^{-1}$.

Source	Reaction	Method	T/K	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta H°(298.15\ K)$, kcal·mol^{-1}
Margrave (1967)	A	–	–	–	140.9 ± 1	–	−75.5
Firsova (1960)	A	Knudsen, calculation	1600–1800	–	137.0 ± 2	–	−79.4
Bergman (1959)	A	Explosion	–	–	>130	–	>−86
Porter (1955)	A	Knudsen mass spec.	1800–1900	128	139.6 ± 0.3	6	−76.8
	A	Ion intensities	1750–1980	136 ± 8	–	–	−80
	B	Knudsen mass spec.	1800–1900	−2	−44.8 ± 1.2	−23	−68.8

A. SiO_2(high cristobalite) = SiO_2(g) B. SiO(g)+1/2O_2(g) = SiO_2(g)

Heat Capacity and Entropy

Point group, ground state quantum weight and the linear symmetrical configuration are estimated by analogy with the properties of CO_2. From the bond lengths in SiO, CO_2 and CO, the length in SiO_2 is estimated as 1.509 × 1.160/1.128. Bond lengths and atomization energies for these molecules are reasonably consistent with the existence of six–electron bonds in the monoxides and four–electron bonds in the dioxides.[5] Vibrational frequencies are estimated from a valence bond calculation using force constants, $k = 9 \times 10^5$ and $k\delta/l^2 = 0.3 \times 10^5$ dyne/cm, which are obtained from those of SiO, CO_2 and CO.

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Silicon Oxide (SiO_2) O_2Si_1(g)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.581	−304.112	−304.112	INFINITE
100	31.422	188.175	264.459	−7.628	−304.330	−305.433	159.542
200	38.997	212.419	232.851	−4.086	−304.878	−306.331	80.006
250	41.746	221.426	229.688	−2.066	−305.165	−306.662	64.074
298.15	44.007	228.976	228.976	0.	−305.432	−306.926	53.772
300	44.089	229.249	228.977	0.081	−305.442	−306.935	53.442
350	46.161	236.204	229.522	2.339	−305.696	−307.163	45.842
400	48.007	242.491	230.756	4.694	−305.922	−307.357	40.137
450	49.641	248.241	232.384	7.136	−306.121	−307.524	35.696
500	51.076	253.547	234.238	9.655	−306.298	−307.670	32.142
600	53.416	263.076	238.269	14.885	−306.604	−307.915	26.806
700	55.180	271.449	242.423	20.319	−306.872	−308.112	22.992
800	56.513	278.909	246.526	25.906	−307.130	−308.272	20.128
900	57.531	285.627	250.503	31.611	−307.394	−308.399	17.899
1000	58.317	291.730	254.326	37.405	−307.672	−308.496	16.114
1100	58.934	297.319	257.984	43.269	−307.974	−308.563	14.652
1200	59.425	302.468	261.479	49.187	−308.302	−308.603	13.433
1300	59.820	307.241	264.818	55.150	−308.663	−308.613	12.400
1400	60.143	311.687	268.009	61.149	−309.060	−308.595	11.514
1500	60.409	315.845	271.061	67.177	−309.497	−308.547	10.745
1600	60.631	319.751	273.983	73.229	−309.978	−308.468	10.070
1700	60.817	323.433	276.785	79.302	−360.682	−307.911	9.461
1800	60.976	326.914	279.474	85.392	−361.028	−304.797	8.845
1900	61.111	330.214	282.058	91.497	−361.383	−301.663	8.293
2000	61.228	333.352	284.545	97.614	−361.747	−298.511	7.796
2100	61.330	336.342	286.941	103.742	−362.125	−295.340	7.346
2200	61.418	339.197	289.252	109.879	−362.515	−292.150	6.937
2300	61.496	341.929	291.483	116.025	−362.919	−288.943	6.562
2400	61.564	344.547	293.640	122.178	−363.339	−285.718	6.218
2500	61.625	347.062	295.727	128.337	−363.774	−282.475	5.902
2600	61.679	349.480	297.748	134.503	−364.225	−279.214	5.609
2700	61.727	351.809	299.707	140.673	−364.691	−275.935	5.338
2800	61.770	354.054	301.609	146.848	−365.173	−272.639	5.086
2900	61.809	356.223	303.455	153.027	−365.672	−269.326	4.851
3000	61.845	358.319	305.249	159.210	−366.186	−265.995	4.631
3100	61.877	360.347	306.993	165.396	−366.715	−262.646	4.426
3200	61.906	362.312	308.692	171.585	−367.259	−259.281	4.232
3300	61.933	364.217	310.346	177.777	−367.818	−255.898	4.051
3400	61.957	366.067	311.957	183.971	−368.390	−252.497	3.879
3500	61.979	367.863	313.529	190.168	−368.977	−249.081	3.717
3600	62.000	369.609	315.063	196.367	−753.729	−235.186	3.412
3700	62.019	371.308	316.560	202.568	−753.928	−220.779	3.117
3800	62.036	372.962	318.023	208.771	−754.141	−206.366	2.837
3900	62.052	374.574	319.452	214.975	−754.367	−191.948	2.571
4000	62.067	376.145	320.850	221.181	−754.606	−177.524	2.318
4100	62.081	377.678	322.217	227.389	−754.858	−163.094	2.078
4200	62.094	379.174	323.556	233.597	−755.122	−148.658	1.849
4300	62.106	380.635	324.866	239.807	−755.396	−134.215	1.630
4400	62.117	382.063	326.150	246.018	−755.683	−119.766	1.422
4500	62.128	383.459	327.408	252.231	−755.979	−105.310	1.222
4600	62.137	384.825	328.641	258.444	−756.287	−90.848	1.032
4700	62.147	386.161	329.851	264.658	−756.606	−76.378	0.849
4800	62.155	387.470	331.038	270.873	−756.936	−61.902	0.674
4900	62.163	388.752	332.203	277.089	−757.278	−47.418	0.505
5000	62.171	390.007	333.346	283.306	−757.632	−32.927	0.344
5100	62.178	391.239	334.469	289.523	−757.997	−18.429	0.189
5200	62.185	392.446	335.573	295.742	−758.376	−3.925	0.039
5300	62.192	393.631	336.657	301.960	−758.769	10.588	−0.104
5400	62.198	394.793	337.723	308.180	−759.177	25.108	−0.243
5500	62.203	395.935	338.771	314.400	−759.599	39.635	−0.376
5600	62.209	397.055	339.802	320.621	−760.038	54.171	−0.505
5700	62.214	398.157	340.816	326.842	−760.495	68.714	−0.630
5800	62.219	399.239	341.814	333.063	−760.972	83.267	−0.750
5900	62.224	400.302	342.796	339.286	−761.468	97.825	−0.866
6000	62.228	401.348	343.763	345.508	−761.985	112.395	−0.978

PREVIOUS: September 1967 (1 atm) CURRENT: September 1967 (1 bar)

Silicon Oxide (SiO_2) O_2Si_1(g)

$S°(298.15\ K)$ = [280.306 ± 11.72] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -197.73 \pm 62.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -200.83 \pm 62.8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
X^2B_1	0	2
$^2A_1$	11618	2
$^2A_2$	16236	2

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
971 (1)
[300] (1)
912 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: Ta–O = [1.69] Å
Bond Angle: O–Ta–O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [6.232542 × 10^{-115}] $g^3·cm^6$

Enthalpy of Formation

Inghram, *et al.*[1] and Krikorian and Carpenter[2] have presented mass spectrometric evidence indicating that the predominant vapors in the vaporization of Ta–Ta_2O_5 mixtures in Ta Knudsen cells are TaO and TaO_2. As in the case with TaO(g),[5] the absolute pressures of TaO_2(g) calculated from both studies differ by a factor of roughly 1000 in the range 2022–2278 K (IPTS–68). Results of our 2nd and 3rd law analysis of these and other data are presented below.

Source	Reaction	Data Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law
1	A*	2	2022–2023	–	156.13	–	–	−39.47
1	B*	4	2151–2209	51.67	150.86	45 ± 41	–	−36.25
2	B	1	2271	–	184.67	–	–	−2.44
1	C*	4	2022–2179	70.72	70.05	−0.3 ± 4.5	−49.44	−48.10
2	C	1	2271	–	81.03	–	–	−70.06
3	D	graph	1900–2860	−19.83	26.38	20.6 ± 2.8	−19.83	26.38

*Recalculated pressures using Otvis and Stevenson method for estimating ionization cross sections;[2,4]procedure increases $\Delta_f H°$ by ~3 kcal·mol^{-1}.

A: 0.2 Ta(cr) + 0.4 Ta_2O_5(cr) = TaO_2(g) C: 0.5 Ta(cr) + 0.5 TaO_2(g) = TaO(g)
B: 0.2 Ta(cr) + 0.4 Ta_2O_5(l) = TaO_2(g) D: Ta(cr) + O_2(g) = TaO_2(g)

As was observed in the TaO(g) table,[5] the results of the 2nd and 3rd law analysis show considerable scatter. We adopt $\Delta_f H°(TaO_2, g, 298.15\ K) = -48.0$ kcal·mol^{-1} based primarily on our analysis of the data from Inghram *et al.*[1] for the reaction 0.5 Ta(cr) + 0.5 TaO_2(g) = TaO(g). For this reaction we adopt a rounded result of $\Delta_r H°(298.15\ K) = 70.0$ kcal·mol^{-1}. The adopted $\Delta_f H°(298.15\ K)$ value leads to a dissocation energy $D_0° = 15.3$ eV (3520 kcal·mol^{-1}) for the process $TaO_2(g) = Ta(g) + 2\ O(g)$. This value is 1.8 times the dissociation energy of TaO(g).[5]

Heat Capacity and Entropy

The electronic levels and vibrational frequencies are those reported by Weltner and McLeod.[7] The results were based on a matrix isolation study of TaO_2 trapped in argon and neon matrices at 20 K and 4 K, respectively. The infrared spectrum was interpreted to favor a bent molecule in the ground state. Kaufman *et al.*[8] reported that TaO_2(g) is bent based on the deflection of molecular beams of TaO_2 by an electronic quadrupole. This latter result is dependent, however, on there being no low lying electronic states. The bending frequency for the ground state has not been observed but is estiamted to be 300 cm^{-1} based on the observed $\nu_2 = 285\ cm^{-1}$ value for the $^2A_1$ state.[7] The Ta–O bond distance is estimated to be the same as in TaO(g)[5] whereas the bond angle is estimated to be 110°.

It should be noted that the Gibbs energy functions used here are roughly 2–4 cal·K^{-1} g·atom^{-1} more positive those of Brewer and Rosenblatt[6] for linear TaO_2; the 3rd law $\Delta_f H°(298.15\ K)$ values in the above table would change by ~4.5 kcal·mol^{-1}.

Continued on page 1814

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−11.262	−197.730	−197.730	INFINITE
100	35.386	237.647	316.528	−7.888	−198.255	−203.075	106.076
200	39.861	263.617	284.196	−4.116	−199.646	−207.356	54.156
250	41.977	272.738	281.019	−2.070	−200.283	−209.208	43.712
298.15	44.000	280.306	280.306	0.	−200.832	−210.876	36.945
300	44.076	280.578	280.306	0.081	−200.852	−210.938	36.728
350	46.019	287.521	280.850	2.335	−201.348	−212.579	31.726
400	47.726	293.780	282.082	4.679	−201.784	−214.153	27.966
450	49.181	299.488	283.703	7.103	−202.176	−215.675	25.035
500	50.404	304.735	285.548	9.594	−202.538	−217.155	22.686
600	52.279	314.100	289.545	14.733	−203.218	−220.015	19.154
700	53.596	322.264	293.648	20.031	−203.879	−222.762	16.623
800	54.538	329.486	297.685	25.440	−204.540	−225.414	14.718
900	55.229	335.951	301.584	30.930	−205.212	−227.983	13.232
1000	55.746	341.798	305.318	36.480	−205.903	−230.477	12.039
1100	56.143	347.131	308.880	42.076	−206.627	−232.899	11.059
1200	56.453	352.030	312.275	47.706	−207.393	−235.254	10.240
1300	56.701	356.559	315.509	53.364	−208.202	−237.543	9.545
1400	56.903	360.768	318.593	59.045	−209.045	−239.769	8.946
1500	57.073	364.700	321.538	64.744	−209.914	−241.933	8.425
1600	57.218	368.388	324.352	70.458	−210.804	−244.039	7.967
1700	57.348	371.861	327.045	76.187	−211.722	−246.088	7.561
1800	57.467	375.142	329.627	81.928	−212.686	−248.083	7.199
1900	57.581	378.253	332.105	87.680	−213.712	−250.021	6.874
2000	57.692	381.209	334.487	93.444	−214.804	−251.904	6.579
2100	57.805	384.026	336.779	99.219	−215.960	−253.731	6.311
2200	57.922	386.718	338.989	105.005	−217.180	−255.501	6.066
2300	58.043	389.296	341.120	110.803	−218.466	−257.215	5.842
2400	58.170	391.768	343.179	116.614	−219.822	−258.871	5.634
2500	58.305	394.146	345.171	122.437	−221.254	−260.469	5.442
2600	58.447	396.435	347.099	128.275	−222.768	−262.008	5.264
2700	58.596	398.644	348.967	134.127	−224.376	−263.486	5.097
2800	58.753	400.778	350.780	139.994	−226.087	−264.904	4.942
2900	58.917	402.842	352.540	145.878	−227.914	−266.259	4.796
3000	59.088	404.843	354.250	151.778	−229.875	−267.548	4.658
3100	59.264	406.783	355.913	157.696	−231.985	−268.769	4.529
3200	59.445	408.667	357.533	163.631	−234.265	−269.920	4.406
3300	59.631	410.499	359.110	169.585	−273.190	−270.526	4.282
3400	59.820	412.282	360.648	175.557	−275.449	−270.411	4.154
3500	60.011	414.019	362.148	181.549	−277.706	−270.230	4.033
3600	60.205	415.712	363.612	187.560	−279.958	−269.985	3.917
3700	60.398	417.365	365.043	193.590	−282.206	−269.677	3.807
3800	60.592	418.978	366.441	199.639	−284.449	−269.308	3.702
3900	60.785	420.554	367.809	205.708	−286.686	−268.880	3.601
4000	60.976	422.096	369.147	211.796	−288.918	−268.395	3.505
4100	61.165	423.604	370.456	217.903	−291.143	−267.854	3.413
4200	61.350	425.080	371.739	224.029	−293.363	−267.260	3.324
4300	61.532	426.525	372.997	230.173	−295.576	−266.612	3.239
4400	61.710	427.942	374.230	236.335	−297.784	−265.913	3.157
4500	61.882	429.331	375.439	242.515	−299.986	−265.164	3.078
4600	62.050	430.693	376.625	248.712	−302.184	−264.367	3.002
4700	62.212	432.029	377.790	254.925	−304.377	−263.520	2.929
4800	62.368	433.340	378.933	261.154	−306.567	−262.628	2.858
4900	62.518	434.628	380.057	267.398	−308.755	−261.689	2.790
5000	62.662	435.892	381.161	273.657	−310.940	−260.706	2.724
5100	62.799	437.135	382.246	279.931	−313.126	−259.680	2.660
5200	62.930	438.355	383.314	286.217	−315.312	−258.612	2.598
5300	63.053	439.555	384.364	292.516	−317.499	−257.499	2.538
5400	63.170	440.735	385.397	298.827	−319.691	−256.347	2.480
5500	63.280	441.895	386.413	305.150	−321.886	−255.155	2.423
5600	63.384	443.036	387.414	311.483	−324.088	−253.920	2.368
5700	63.480	444.159	388.400	317.826	−326.298	−252.648	2.315
5800	63.570	445.264	389.371	324.179	−1067.272	−248.535	2.238
5900	63.653	446.351	390.327	330.540	−1069.715	−234.400	2.075
6000	63.730	447.422	391.270	336.910	−1072.215	−220.220	1.917

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 49.907 \pm 0.33\ J \cdot K^{-1} \cdot mol^{-1}$

T_{fus}(anatase → liquid) = [1949 ± 60 K]

$\Delta_f H°(0\ K) = -933.837 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -938.722 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_{fus} H° = [57.990]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of TiO_2(rutile) using $\Delta_r H°(968\ K) = -1.57 \pm 0.19\ kcal \cdot mol^{-1}$ for anatase → rutile. Navrotsky and Kleppa,[1] using oxide melt calorimetry, derived $\Delta_r H°$ from the difference in $\Delta_{sol} H°$ between anatase and rutile. Reduction of their value using JANAF enthalpies yields $\Delta_r H°(298.15\ K) = -1.44 \pm 0.3$ and $\Delta_f H°$(anatase, 298.15 K) = $-224.36 \pm 0.5\ kcal \cdot mol^{-1}$.Uncertainties in the enthalpies and in $\Delta_f H°$(rutile) contribute significantly to the overall uncertainty. Kybett and Margrave[2] derived $\Delta_f H°(298.15\ K) = -223 \pm 1\ kcal \cdot mol^{-1}$ from fluorine calorimetry. Their reaction was TiO_2(anatase) + 2 F_2(g) → TiF_4(cr) + O_2(g), but they gave no experimental data. Kybett's results for anatase and rutile may be combined to yield $\Delta_r H°(298.15\ K) = -2 \pm 1.4\ kcal \cdot mol^{-1}$ for anatase → rutile; this is consistent with the adopted value. Values for $\Delta_r G° = \Delta_r H°$ of -0.2 to $-0.3\ kcal \cdot mol^{-1}$ for anatase → rutile were derived by Schuiling and Vink[12] from relative solubilities in aqueous NaCl at 200° and 300°C. We suspect that this less negative result arises from saturating solid phases which differ in physical form and chemical composition from standard state macrocrystalline anatase (refer to Phase Data).

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Shomate,[3] (52–296 K) and his Debye Einstein extrapolation to absolute zero. The entropy is calculated by polynomial integration of $C_p°$ based on $S°(50\ K) = 0.45\ cal \cdot K^{-1} \cdot mol^{-1}$.

$C_p°$ above 300 K is from constrained fitting of enthalpy data (739–1305 K) of Naylor.[4] Naylor's points at 416 and 546 K are omitted due to positive bias in this temperature range. Enthalpy data (580–1001 K) of Lietz[5] deviate by $-3.7 \pm 1.2\%$ at all temperatures. Similar discrepancies exist in Lietz' data for TiO_2(rutile). These discrepancies and the bias in Naylor's data near room temperature are discussed on the table for rutile.[6] The choice between Naylor[4] and Lietz[5] is not clearcut, but we feel that Naylor's data lead to more reasonable values of $C_p°$. New data on a well characterized sample are needed.

The two discrepant studies[4,5] do agree that the enthalpy of anatase is slightly larger than that of rutile at all temperatures in the observed region. Our adopted $C_p°$ reproduces the approximate enthalpy difference between anatase and rutile as observed by each author.[4,5]

Phase Data

Both anatase and rutile have tetragonal crystal structures, but in anatase the elongated unit cell contains four molecules compared with two in the unit cell of rutile. Anatase transforms exothermally and irreversibly to rutile at temperatures above κ1200 K.[7-9] The rate of transformation is relatively slow and is governed by the nature and amount of impurities.[7] Certain impurities markedly decrease the transformation temperature which can be as low as 700 K in the presence of an alkali flux.[10] These observations led to the conclusion that anatase is a metastable phase which persists up to a temperature sufficient to activate the crystal rearrangement. This was confirmed by the calorimetric data of Navrotsky and Kleppa,[1] who concluded that anatase is metastable with respect to rutile at all temperatures.

Lietz[5] reported a transition in anatase at κ918 K based on his enthalpy data and on changes in prism angles measured by Schroder.[11] We reject Lietz' T_{trs}, since his $\Delta_{trs} H°$ is not distinguishable from his experimental scatter. Lietz' data for rutile and anatase exhibit remarkably similar deviations in this temperature region. Schroder's data have the same deficiency. Lattice parameter data[13] show scatter but no obvious change in this temperature range.

Characterization of anatase samples is particularly important for interpreting physical and chemical properties. Anatase precipitated from acidic sulfate solutions consists of agglomerates of very small crystals with large amounts of water and SO_3.[14] X-ray and electron diffraction show the major lines of anatase but fail to show the impurities, suggesting that the latter are present in noncrystalline form. These precipitates[14] lose water near 150°C and SO_3 near 650°C; crystal growth starts near 600°C. Precipitates from other media give anatase at lower temperatures,[15] but calcination temperatures of at least 650°C are needed fror complete conversion of these precipitates into pure, macrocrystalline anatase. This suggests an alternative explanation for reports[5, 11] of T_{trs} ~645°C.

Fusion Data

T_{fus} is hypothetical in the sense that metastable anatase probably will convert to rutile (see Phase Data) before it can be superheated to the melting point. T_{fus} is calculated as the temperature at which $\Delta_r G° = 0$ for TiO_2(anatase) → TiO_2(l). $\Delta_{fus} H°$ is the calculated difference in $\Delta_f H°$ at T_{fus}.

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Continued on page 1814

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.627	−933.837	−933.837	INFINITE
100	19.159	9.623	89.203	−7.958	−936.632	−919.438	480.265
200	41.865	30.501	54.580	−4.816	−938.318	−901.476	235.441
298.15	55.271	49.907	49.907	0.000	−938.722	−883.266	154.745
300	55.471	50.249	49.908	0.102	−938.721	−882.922	153.730
400	63.593	67.433	52.195	6.095	−938.313	−864.368	112.875
500	68.145	82.156	56.753	12.702	−937.506	−845.970	88.378
600	70.890	94.842	62.069	19.664	−936.529	−827.753	72.062
700	72.655	105.911	67.559	26.846	−935.488	−809.706	60.421
800	73.860	115.696	72.976	34.176	−934.421	−791.810	51.700
900	74.726	124.448	78.218	41.607	−933.386	−774.046	44.924
1000	75.354	132.355	83.242	49.112	−932.464	−756.393	39.510
1100	75.814	139.559	88.039	56.672	−931.729	−738.823	35.084
1200	76.191	146.172	92.612	64.272	−935.171	−721.191	31.393
1300	76.484	152.283	96.970	71.907	−934.101	−703.403	28.263
1400	76.735	157.960	101.126	79.568	−933.112	−685.695	25.584
1500	76.944	163.262	105.094	87.252	−932.219	−668.054	23.264
1600	77.111	168.233	108.886	94.955	−931.438	−650.470	21.236
1700	77.237	172.912	112.516	102.673	−930.785	−632.930	19.448
1800	77.362	177.330	115.995	110.403	−930.274	−615.425	17.859
1900	77.446	181.515	119.335	118.143	−929.921	−597.943	16.439
2000	77.530	185.490	122.544	125.892	−944.427	−580.022	15.149

PREVIOUS: September 1966 CURRENT: December 1973

$S°(298.15\ K) = 50.292 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2130 \pm 20\ K$ (rutile → liquid)

$\Delta_f H°(0\ K) = -939.870 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -944.747 \pm 1.3\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [66.944 \pm 16.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is the value obtained by Mah *et al.*[1] a study by oxygen calorimetry. Eighteen combustions[1] of three well-characterized samples of titanium metal led to a selected value of -225.8 ± 0.1 kcal·mol^{-1}. This is comparable with other oxygen-combustion values of -225.5 ± 0.2,[2] -224.9 ± 0.4[3] and -225.3 ± 0.3[4] and a fluorine combustion value of -225 ± 1[5] derived from the reaction TiO_2(rutile) + 2 F_2(g) → TiF_4(cr) + O_2(g). No experimental data were given in the latter study.[5]

The 1967 JANAF Table[6] assigned an uncertainty of ± 1 kcal·mol^{-1} to $\Delta_f H°$ due to possible uncertainty in corrections for oxygen deficiency in the rutile produced by combusion.[1, 3] The atomic ratio O/Ti in the combustion product was determined by ignition to constant weight in air[1,2] or in wet oxygen[3] at 1000°C. Ratios obtained were 1.985 to 1.994,[1] 2.00[2] and about 1.95.[3] Mah's corrections to the stoichiometric composition correspond to about −0.8 to −1.7 kcal·mol^{-1} in $\Delta_f H°$. Our opinion of the reliability of these corrections has changed due to new information on the crystal structure, $\Delta_f G°$ and $\Delta_f S°$ of oxygen deficient compositions.[7, 8] Mah's O/Ti ratios are at compositions where there appears to be hysteresis in measurements of the oxygen potential near 1300 K.[7] The full range of the hysteresis corresponds to less than 20% of the oxygen potential. We assume that this percentage is an upper limit for error which might be introduced in the corrections of $\Delta_f G°$ and $\Delta_f H°$ from the observed O/Ti ratios to the stoichiometric composition. Thus, we assign an uncertainty of ± 0.3 kcal·mol^{-1} to $\Delta_f H° = -225.8$, but note that the less negative value of -224.9 ± 0.4 kcal·mol^{-1} [3] is one of several alternatives for minimizing the deviation from integral values of $\Delta_r G°$[7] relating rutile to Ti_3O_5 at 1304 K.

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Sandin and Keesom,[9] (0.3–20 K), Dugdale *et al.*,[10] (12–270 K) and Shomate,[11] (52–298 K). Smoothed values rather than data points were reported in the first two studies[9, 10] and only in the range 20–50 K by Dugdale.[10] Dugdale's deviation plot indicates that the smooth curves[10, 11] agree within about ±0.3% above 77 K, but at lower temperatures the data of Shomate show a positive bias increasing to over 2% at 52 K. We adopt Dugdale's curve below 80 K and calculate $S°$ by polynomial integrations of $C_p°$. The extrapolation below 0.3 K is insignificant. $C_p°$ data (69–295 K) of McDonald and Seltz[12] are omitted since they are roughly 3% higher than the adopted curve.

$C_p°$ above 300 K is from constrained fitting of enthalpy data (763–1746 K) of Naylor.[13] The point at 394 K is omitted due to positive bias (~6%) in the drop calorimeter at the lowest temperature; a similar bias is observed in Naylor's data for the four other titanium oxides and in materials such as MgF_2 studied at nearly the same time. This bias and the low purity (97.9%) of Naylor's sample are unfortunate; they favor the selection of two more recent enthalpy studies[14, 15] which conflict with that of Naylor. The adopted curve is favored, however, by four enthalpy points observed at 965 K by Navrotsky *et al.*[16] and by comparisons with $C_p°$ for GeO_2, MnO_2, and V_2O_4, which have the same tetragonal-SnO_2 crystal structure as rutile.

Enthalpy data of Lietz,[15] (578–1283 K) deviate from the adopted curve by ~−3% at all temperatures; similar deviations occur in his data for TiO_2(anatase). Data of Slyusar *et al.*,[14] (645–1990 K) deviate by ~−4% below 1136 K and by −1.7 to +3.4% at higher temperatures. The discontinuity of almost 3% in the data near 1100 K seems to correspond to the temperature at which the authors switched container materials and temperature sensors.[14] Data for Ti_2O_3, Ti_3O_5 and Ti_4O_7[14] also have discontinuities in this region; the data below the discontinuity for Ti_2O_3 show a negative bias like rutile. Moreoever, the authors[14] report T_{fus} = 2014 K, which is ~100 too low for rutile. Other data are too scattered[17] and too uncertain[18, 19] to help resolve the difference with Naylor.[13]

These discrepancies cause us to reject the data of Slyusar *et al.*[14] and to consider as coincidence the agreement with Lietz.[15] These two data sets yield $C_p°$ values deviating from the adopted curve by −0.8 cal·K^{-1}·mol^{-1} at 700 K, 0.0 at 1100 K, and +3 at 2000 K. New data on a pure sample of rutile are needed to resolve the disagreement. We note that use of the rejected $C_p°$ curve is one of several alternatives for minimizing the deviation from equilibria[7] relating rutile to Ti_3O_5 at 1304 K.

Fusion Data – Refer to the liquid table for details.

Sublimation Data

$\Delta_{sub} H°(298.15\ K) = 152.8 \pm 3$ kcal·mol^{-1} is calculated from $\Delta_f H°(TiO_2, g)$. Sublimation makes TiO_2(cr) deficient in oxygen.

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Continued on page 1815

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−8.636	−939.870	−939.870	INFINITE
100	18.502	10.142	89.638	−7.950	−942.649	−925.506	483.435
200	42.012	30.807	54.969	−4.833	−944.360	−907.579	237.035
298.15	55.103	50.292	50.292	0.000	−944.747	−889.406	155.820
300	55.287	50.633	50.293	0.102	−944.746	−889.063	154.800
400	62.835	67.671	52.564	6.043	−944.390	−870.541	113.681
500	67.203	82.201	57.077	12.562	−943.670	−852.157	89.024
600	69.931	94.712	62.331	19.429	−942.789	−833.936	72.601
700	71.764	105.638	67.754	26.519	−941.841	−815.868	60.881
800	73.078	115.311	73.106	33.764	−940.857	−797.939	52.100
900	74.057	123.977	78.285	41.122	−939.896	−780.132	45.278
1000	74.852	131.822	83.253	48.569	−939.032	−762.428	39.825
1100	75.479	138.986	87.999	56.086	−938.339	−744.803	35.368
1200	76.023	145.577	92.526	63.662	−941.807	−727.113	31.650
1300	76.525	151.683	96.844	71.290	−940.742	−709.265	28.499
1400	76.944	157.370	100.967	78.964	−939.741	−691.497	25.800
1500	77.320	162.691	104.906	86.677	−938.819	−673.798	23.464
1600	77.655	167.692	108.676	94.426	−937.992	−656.158	21.421
1700	77.990	172.410	112.287	102.209	−937.274	−638.566	19.621
1800	78.283	176.876	115.753	110.022	−936.679	−621.013	18.021
1900	78.576	181.117	119.082	117.865	−936.224	−603.489	16.591
2000	78.868	185.155	122.286	125.738	−950.606	−585.531	15.293
2100	79.161	189.010	125.372	133.640	−951.213	−567.263	14.110
2130.000	79.228	190.133	126.276	136.016	--- CRYSTAL <--> LIQUID ---		
2200	79.412	192.698	128.349	141.568	−951.817	−548.964	13.034
2300	79.663	196.234	131.224	149.522	−952.417	−530.640	12.051
2400	79.914	199.630	134.004	157.501	−953.015	−512.289	11.150
2500	80.165	202.897	136.695	165.505	−953.610	−493.913	10.320

PREVIOUS: September 1966 CURRENT: December 1973

$S°(298.15\ K)$ = [72.345] $J·K^{-1}·mol^{-1}$
T_{fus} = 2130 ± 20 K (rutile → liquid)

$\Delta_f H°(298.15\ K)$ = [−894.055] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [66.944 ± 16.7] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(TiO_2, l, 298.15\ K)$ is calculated from that of TiO_2(rutile) by adding $\Delta_{fus}H°$ to the difference in enthalpy, $H°(2130\ K)-H°(298.15\ K)$, between rutile and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 8 cal $K^{-1}·g\text{–}atom^{-1}$ by comparison with MgF_2, $CaCl_2$, V_2O_4 and WO_3. Below the assumed glass transition at 1400 K, $C_p°$ is taken to be the same as that of TiO_2(rutile). $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Schneider[1] reviewed eleven melting point studies and converted the values to IPTS–48. Eight of the results fall in the range 2113 ± 10 K for measurements in air. Brauer and Littke,[2] using an atmosphere of oxygen–argon mixtures, found 2103 ± 15 K in air, 2113 ± 15 K with oxygen at 300 torr, 2133 ± 15 K at 500 torr and 2143 ± 15 K at higher oxygen pressures. The authors[2] interpreted the sharp increase in T_{fus} with increased oxygen pressure as being due to suppression of the oxygen deficiency in TiO_2. The residue of the sample melted in air gave an oxygen stoichiometry of 1.996 compared with 2.000 at higher oxygen pressures; the color showed a corresponding change from dark blue to bright yellow. The oxygen deficiency may have been even greater if there was significant reoxidation during cooling to room temperature. Schneider[1] questioned the attainment of black–body conditions in the temperature measurements; in fact, Brauer and Littke[2] tried to compensate for the change in sample color by use of similarly colored compounds in calibrations of the pyrometer. We wonder if this eliminated all relative bias in the melting temperatures.

T_{fus} = 2130 ± 20 K is adopted. This is intermediate between the data in air and those at highest oxygen pressures. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ = 7.5 cal $K^{-1}·mol^{-1}$, or 2.5 cal $K^{-1}·g·atom^{-1}$, based on observed data for isostructural V_2O_4. The resulting $\Delta_{fus}H°$ of 16 ± 4 $kcal·mol^{-1}$ may be compared with approximate values of $\Delta_{fus}H°$ derived from binary phase data. We obtain 12 $kcal·mol^{-1}$ from the binary with Al_2O_3,[3] 14 $kcal·mol^{-1}$ from BaO[4] and ZrO_2,[5] 16 $kcal·mol^{-1}$ from Ta_2O_5[6] and 21 $kcal·mol^{-1}$ from WO3.[7] These values are derived by calculating apparent $\Delta_{fus}H°$ values assuming activity coefficients of unity and then extrapolating the apparent values to $(T_{fus}–T) = 0$ in order to minimize activity effects. We omit other binary systems which deviate grossly from ideality. Uncertainties in the binary results are estimated to be about ±5 $kcal·mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	55.103	72.345	72.345	0.000	−894.055	−845.289	148.091
300	55.287	72.686	72.346	0.102	−894.054	−844.987	147.125
400	62.835	89.724	74.617	6.043	−893.698	−828.670	108.213
500	67.203	104.254	79.130	12.562	−892.978	−812.492	84.880
600	69.931	116.765	84.384	19.429	−892.097	−796.475	69.339
700	71.764	127.691	89.807	26.519	−891.149	−780.613	58.250
800	73.078	137.364	95.159	33.764	−890.166	−764.889	49.942
900	74.057	146.030	100.338	41.122	−889.204	−749.288	43.488
1000	74.852	153.875	105.306	48.569	−888.340	−733.789	38.329
1100	75.479	161.039	110.052	56.086	−887.647	−718.369	34.113
1200	76.023	167.630	114.579	63.662	−891.115	−702.884	30.596
1300	76.525	173.736	118.897	71.290	−890.050	−687.242	27.614
1400	76.944	179.423	123.020	78.964	−889.049	−671.679	25.061
1400.000	76.944	179.423	123.020	78.964	GLASS <--> LIQUID TRANSITION		
1400.000	100.416	179.423	123.020	78.964			
1500	100.416	186.351	127.014	89.006	−885.798	−656.268	22.853
1600	100.416	192.832	130.927	99.047	−882.679	−641.068	20.929
1700	100.416	198.919	134.749	109.089	−879.701	−626.059	19.236
1800	100.416	204.659	138.475	119.131	−876.879	−611.221	17.737
1900	100.416	210.088	142.103	129.172	−874.225	−596.536	16.400
2000	100.416	215.239	145.632	139.214	−886.438	−581.532	15.188
2100	100.416	220.138	149.064	149.255	−884.906	−566.324	14.087
2130.000	100.416	221.563	150.075	152.268	--- CRYSTAL <--> LIQUID ---		
2200	100.416	224.809	152.402	159.297	−883.396	−551.189	13.087
2300	100.416	229.273	155.648	169.339	−881.909	−536.122	12.176
2400	100.416	233.547	158.805	179.380	−880.444	−521.120	11.342
2500	100.416	237.646	161.877	189.422	−879.001	−506.177	10.576
2600	100.416	241.584	164.868	199.463	−877.579	−491.293	9.870
2700	100.416	245.374	167.780	209.505	−876.179	−476.462	9.218
2800	100.416	249.026	170.617	219.547	−874.799	−461.682	8.613
2900	100.416	252.550	173.381	229.588	−873.438	−446.953	8.050
3000	100.416	255.954	176.077	239.630	−872.098	−432.269	7.526
3100	100.416	259.247	178.707	249.671	−870.775	−417.630	7.037
3200	100.416	262.435	181.274	259.713	−869.471	−403.034	6.579
3300	100.416	265.525	183.781	269.755	−868.184	−388.478	6.149
3400	100.416	268.522	186.229	279.796	−866.914	−373.960	5.745
3500	100.416	271.433	188.622	289.838	−865.660	−359.480	5.365
3600	100.416	274.262	190.962	299.879	−864.422	−345.035	5.006
3700	100.416	277.013	193.251	309.921	−1272.296	−322.836	4.558
3800	100.416	279.691	195.491	319.963	−1269.853	−297.207	4.085
3900	100.416	282.300	197.683	330.004	−1267.478	−271.642	3.638
4000	100.416	284.842	199.830	340.046	−1265.171	−246.138	3.214

PREVIOUS: September 1966 CURRENT: December 1973

0 to 2130 K crystal, rutile
above 2130 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.636	−939.870	−939.870	INFINITE
100	18.502	10.142	89.638	−7.950	−942.649	−925.506	483.435
200	42.012	30.807	54.969	−4.833	−944.360	−907.579	237.035
298.15	55.103	50.292	50.292	0.000	−944.747	−889.406	155.820
500	67.203	82.201	57.077	12.562	−943.670	−852.157	89.024
600	69.931	94.712	62.331	19.429	−942.789	−833.936	72.601
700	71.764	105.638	67.754	26.519	−941.841	−815.868	60.881
800	73.078	115.311	73.106	33.764	−940.857	−797.939	52.100
900	74.057	123.977	78.285	41.122	−939.896	−780.132	45.278
1000	74.852	131.822	83.253	48.569	−939.032	−762.428	39.825
1100	75.479	138.986	87.999	56.086	−938.339	−744.803	35.368
1200	76.023	145.577	92.526	63.662	−941.807	−727.113	31.650
1300	76.525	151.683	96.844	71.290	−940.742	−709.265	28.499
1400	76.944	157.370	100.967	78.964	−939.741	−691.497	25.800
1500	77.320	162.691	104.906	86.677	−938.819	−673.798	23.464
1600	77.655	167.692	108.676	94.426	−937.992	−656.158	21.421
1700	77.990	172.410	112.287	102.209	−937.274	−638.566	19.621
1800	78.283	176.876	115.753	110.022	−936.679	−621.013	18.021
1900	78.576	181.117	119.082	117.865	−936.224	−603.489	16.591
2000	78.868	185.155	122.286	125.738	−950.606	−585.531	15.293
2100	79.161	189.010	125.372	133.640	−951.213	−567.263	14.110
2130.000	79.228	190.133	126.276	136.016	CRYSTAL <--> LIQUID TRANSITION		
2130.000	100.416	221.563	126.276	202.960			
2200	100.416	224.809	129.360	209.989	−883.396	−551.188	13.087
2300	100.416	229.273	133.608	220.030	−881.909	−536.122	12.176
2400	100.416	233.547	137.683	230.072	−880.444	−521.120	11.342
2500	100.416	237.646	141.601	240.114	−879.001	−506.177	10.576
2600	100.416	241.584	145.371	250.155	−877.579	−491.293	9.870
2700	100.416	245.374	149.005	260.197	−876.179	−476.462	9.218
2800	100.416	249.026	152.512	270.238	−874.799	−461.682	8.613
2900	100.416	252.550	155.901	280.280	−873.438	−446.953	8.050
3000	100.416	255.954	159.180	290.322	−872.098	−432.269	7.526
3100	100.416	259.247	162.355	300.363	−870.775	−417.630	7.037
3200	100.416	262.435	165.433	310.405	−869.471	−403.034	6.579
3300	100.416	265.525	168.420	320.446	−868.184	−388.478	6.149
3400	100.416	268.522	171.320	330.488	−866.914	−373.960	5.745
3500	100.416	271.433	174.139	340.530	−865.660	−359.480	5.365
3600	100.416	274.262	176.881	350.571	−864.422	−345.035	5.006
3700	100.416	277.013	179.550	360.613	−1272.296	−322.836	4.558
3800	100.416	279.691	182.151	370.654	−1269.853	−297.207	4.085
3900	100.416	282.300	184.685	380.696	−1267.478	−271.642	3.638
4000	100.416	284.842	187.157	390.738	−1265.171	−246.138	3.214

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 260.148 \pm 4.2\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = -303.28 \pm 12.6\ kJ\cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -305.43 \pm 12.6\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights			
ϵ_i, cm^{-1}	g_i	ϵ_i, cm^{-1}	g_i
0	1	18880	[3]

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
962 (1)	[270] (1)	935 (1)

Point Group: C_{2v} $\sigma = 2$
Bond Distance: TiO = [1.62 ± 0.08] Å
Bond Angle: O–Ti–O = 110° ± 15°
Product of the Moments of Inertia: $I_A I_B I_C = [3.115429 \times 10^{-115}]\ g^3\cdot cm^6$

Enthalpy of Formation

$\Delta_f H° = -73.0 \pm 3\ kcal\cdot mol^{-1}$ is selected from the ten data sets analyzed below. These include four different reactions studied by Knudsen effusion or mass spectrometry. Our adopted value is consistent with all but two of the data sets, namely reactions C[2] and D[5]. We presume that the less negative $\Delta_f H° = -59.1$ from reaction C is due to bias in the mass–spectrometric values[2] for the partial pressure of O(g). The more negative $\Delta_f H° = -86.0$ from the sublimation reaction D corresponds to effusion pressures too large by a factor of ~25; allowance for the activity of TiO_2 in the oxygen–deficient condensed phase[5] increases the discrepancy. Gross mass transport from the cell by species other than TiO_2 may have occurred,[3] since mass–spectrometric pressures[3, 6] are fairly consistent with our $\Delta_f H°$. We give little weight to reactions D and E due to problems in interpretation of the vapor composition[5, 6] and the activity of oxygen–deficient TiO_2(cr, l).

Activity effects appear to be minor for TiO_2 in TiO_x(cr) in the range $1.833 < \times < 1.889$. Univariant, two–phase systems involving the crystals Ti_6O_{11}, Ti_7O_{13}, Ti_8O_{15} and Ti_9O_{17} occur in this region. Our calculations based on emf data[9] yield $a(TiO_2) \geq \sim 0.7$ at 1900 K; these values change only slowly with × and T. Sublimation experiments in this region may involve hysteresis, but the degree should be less than that found in equilibrium data[10] near 1300 K.

Drowart *et al.*[11] provided the key improvement in $\Delta_f H°$ by reinterpretation of the congruent vaporization[4] of Ti_3O_5(cr). Gilles and co–workers[1,12] confirmed the congruency of vaporization and gave supportive mass–spectrometric data. We use JANAF auxiliary data[7] with $D°(TiO) = 158.5 \pm 2\ kcal\cdot mol^{-1}$ to recalculate the vaporization[4] as described in.[1, 11] Resulting partial pressures of TiO_2, TiO and O(g) are analyzed in terms of reaction C. Third–law analysis yields our selected value of $\Delta_f H°$ and $D°(TiO_2) = 302.8 \pm 3\ kcal\cdot mol^{-1}$. $D°$ would decrease by ~1 $kcal\cdot mol^{-1}$ if $D°(TiO)$ were increased by 2 $kcal\cdot mol^{-1}$ in the recalculation. The conclusion[1] that the ionization cross–section ratio $(TiO/TiO_2) = 2.2$ is unchanged in our recalculation; even larger ratios may be expected at low ionizing potentials.[13]

Source	Method	Reaction[a]	T/K	Data Points	$\delta S°$ $cal\cdot K^{-1}\cdot mol^{-1}$	$\Delta_f H°$(298.15 K), $kcal\cdot mol^{-1}$ 2nd law	3rd law	$\Delta_f H°$(298.15) kcal mol^{-1}	$D_0°$
[1] Hampson	Mass spec.	A	2145–2318	5	−3.2 ± 4.0	−19.7 ± 8.9	−12.6 ± 1.0	−74.4 ± 3	304.2
[2] Balducci	Mass spec.	A	2165–2500	6	4.6 ± 0.4	−4.2 ± 0.9	−14.8 ± 1.2	−72.2 ± 3	302.0
[3] Berkowitz	Mass spec.	A	2194	1	–	–	−10.8	−76.2 ± 4	306.0
[1] Hampson	Mass spec.	B	1893	7	–	–	2.5 ± 0.5	−72.8 ± 7	302.6
[2] Balducci	Mass spec.	C	2015–2240	12	4.4 ± 2.5	141.0 ± 5.3	131.6 ± 1.0	−59.1 ± 3	288.9
[4] Wahlbeck	Effusion	C	1837–2014	Eqn.	3.5	152.3	145.6 ± 0.7	−73.0 ± 3	302.8
[5] Groves	Effusion	D	1849–2010	14	−5.5 ± 4.0	129.2 ± 7.7	139.8 ± 1.3	−86.0	315.8
[3] Berkowitz	Mass spec.	D	1881	3	–	–	152.3 ± 3.2	−73.5	303.3
[6] Semenov	Mass spec.	D	1850–2050	Eqn.	−3.6	142.7	149.8 ± 1.0	−76.0	305.8
[6] Semenov	Mass spec.	E	2263–2538	6	−7.2 ± 2.9	122.8 ± 6.9	139.9 ± 1.8	−73.8	303.6

[a]Reactions are A) $TiO_2(g) + Ti(g) = 2\ TiO(g)$ B) $TiO(g) + WO_3(g) = TiO_2(g) + WO_2(g)$ C) $TiO_2(g) = TiO(g) + O(g)$ D) $TiO_2(rutile) = TiO_2(g)$ E) $TiO_2(l) = TiO_2(g)$

Heat Capacity and Entropy

The electronic levels, bond angle and stretching frequencies are from infrared and emission spectra of TiO_2 isolated in rare– gas matrices.[14] We assume the emission at 5295 Å to be a forbidden triplet–singlet transition due to its similarity with CeO_2.[15] Frequency ν_1 was observed both in infrared and emission spectra. The bond angle was derived[14] from $u_3$sing splittings observed for the five Ti isotopes. Earlier electric–deflection experiments[16] at 2500 K had shown that the populated electronic states were polar (i.e., nonlinear). We estimate the bond length to be the same as that of ground–state TiO.[7] Principal moments of inertia are: $I_A = 2.7500 \times 10^{-39}$ $I_B = 9.3573 \times 10^{-39}$, and $I_C = 12.1072 \times 10^{-39}\ g\cdot cm^2$.

Continued on page 1815

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J\cdot K^{-1}mol^{-1}$			$kJ\cdot mol^{-1}$			
0	0.	0.	INFINITE	−11.357	−303.276	−303.276	INFINITE
100	35.950	217.025	296.659	−7.963	−303.347	−306.893	160.304
200	40.232	243.358	264.059	−4.140	−304.352	−310.081	80.985
250	42.214	252.547	260.864	−2.079	−304.913	−311.449	65.074
298.15	44.149	260.148	260.148	0.	−305.432	−312.660	54.777
300	44.222	260.422	260.149	0.082	−305.451	−312.705	54.447
350	46.106	267.382	260.695	2.341	−305.956	−313.873	46.843
400	47.777	273.651	261.929	4.689	−306.429	−314.971	41.131
450	49.210	279.363	263.553	7.114	−306.878	−316.012	36.682
500	50.419	284.612	265.400	9.606	−307.311	−317.004	33.117
600	52.280	293.979	269.402	14.746	−308.156	−318.863	27.759
700	53.591	302.143	273.509	20.044	−309.001	−320.581	23.922
800	54.532	309.363	277.548	25.452	−309.854	−322.177	21.036
900	55.222	315.828	281.448	30.942	−310.761	−323.664	18.785
1000	55.740	321.674	285.183	36.491	−311.795	−325.043	16.979
1100	56.136	327.006	288.747	42.086	−313.024	−326.310	15.495
1200	56.446	331.905	292.142	47.716	−318.438	−327.337	14.249
1300	56.693	336.433	295.377	53.373	−319.344	−328.042	13.181
1400	56.891	340.642	298.462	59.052	−320.337	−328.674	12.263
1500	57.053	344.573	301.406	64.750	−321.431	−329.233	11.465
1600	57.188	348.259	304.220	70.462	−322.641	−329.714	10.764
1700	57.300	351.730	306.914	76.187	−323.980	−330.116	10.143
1800	57.396	355.008	309.496	81.922	−325.465	−330.435	9.589
1900	57.478	358.113	311.973	87.666	−327.108	−330.667	9.091
2000	57.550	361.063	314.355	93.417	−343.612	−330.354	8.628
2100	57.614	363.873	316.646	99.175	−346.363	−329.624	8.199
2200	57.673	366.554	318.854	104.940	−349.130	−328.761	7.806
2300	57.727	369.119	320.985	110.710	−351.915	−327.773	7.444
2400	57.781	371.577	323.042	116.485	−354.716	−326.664	7.110
2500	57.833	373.937	325.031	122.266	−357.534	−325.437	6.800
2600	57.888	376.206	326.956	128.052	−360.368	−324.098	6.511
2700	57.945	378.392	328.820	133.843	−363.217	−322.648	6.242
2800	58.006	380.500	330.629	139.641	−366.081	−321.093	5.990
2900	58.072	382.537	332.384	145.445	−368.959	−319.436	5.754
3000	58.144	384.507	334.088	151.256	−371.849	−317.679	5.531
3100	58.223	386.415	335.746	157.074	−374.750	−315.825	5.322
3200	58.310	388.265	337.358	162.900	−377.661	−313.879	5.124
3300	58.405	390.060	338.928	168.736	−380.580	−311.841	4.936
3400	58.509	391.806	340.458	174.582	−383.505	−309.713	4.758
3500	58.622	393.503	341.949	180.438	−386.437	−307.501	4.589
3600	58.743	395.156	343.404	186.306	−389.371	−305.204	4.428
3700	58.874	396.768	344.825	192.187	−801.407	−295.037	4.165
3800	59.013	398.339	346.213	198.081	−803.110	−281.328	3.867
3900	59.161	399.874	347.569	203.990	−804.869	−267.574	3.584
4000	59.318	401.374	348.895	209.914	−806.679	−253.775	3.314
4100	59.483	402.841	350.193	215.854	−808.539	−239.929	3.057
4200	59.655	404.276	351.464	221.811	−810.446	−226.038	2.811
4300	59.834	405.682	352.709	227.785	−812.397	−212.100	2.577
4400	60.019	407.060	353.928	233.778	−814.390	−198.117	2.352
4500	60.210	408.411	355.124	239.789	−816.421	−184.088	2.137
4600	60.406	409.736	356.297	245.820	−818.489	−170.014	1.931
4700	60.607	411.037	357.448	251.871	−820.591	−155.894	1.733
4800	60.812	412.315	358.578	257.941	−822.725	−141.729	1.542
4900	61.019	413.571	359.687	264.033	−824.889	−127.518	1.359
5000	61.229	414.806	360.777	270.145	−827.081	−113.264	1.183
5100	61.440	416.021	361.849	276.279	−829.299	−98.966	1.014
5200	61.653	417.216	362.902	282.433	−831.542	−84.625	0.850
5300	61.865	418.392	363.938	288.609	−833.807	−70.238	0.692
5400	62.077	419.551	364.957	294.806	−836.095	−55.810	0.540
5500	62.289	420.692	365.960	301.025	−838.403	−41.340	0.393
5600	62.498	421.816	366.947	307.264	−840.731	−26.826	0.250
5700	62.706	422.924	367.920	313.524	−843.079	−12.272	0.112
5800	62.911	424.016	368.877	319.805	−845.444	2.325	−0.021
5900	63.113	425.093	369.821	326.106	−847.828	16.961	−0.150
6000	63.311	426.156	370.751	332.428	−850.230	31.640	−0.275

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = [265.269 \pm 5.9]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -230.56 \pm 41.8\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -232.63 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[970](1)
[300](1)
[930](1)

Ground State Quantum Weight: [2] σ = [2]
Point Group: [C_{2v}]
Bond Distance: V–O = [1.589] Å
Bond Angle: O–V–O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C = [2.858786 \times 10^{-115}]\ g^3·cm^6$

Enthalpy of Formation

Four independent mass spectrometric studies lead to values for $\Delta_f H°(VO_2, g, 298.15\ K)$.[1-4] Shchukarev *et al.*[2] studied the composition of the vapor above V_2O_4 during evaporation from the surface of a platinum strip. A 2nd law sublimation heat, $\Delta_{sub}H° = 104 \pm 2\ kcal·mol^{-1}$, was reported for the range 1500–1800 K. Assuming the reported value corresponds to 1700 K and using auxiliary data,[5] we calculate $\Delta_f H°(VO_2, g, 298.15\ K) = -62.3 \pm 2.0\ kcal·mol^{-1}$. The sublimation was described by 0.5 $V_2O_4(cr) = VO_2(g)$. More recent related work[3] yields a $\Delta_f H°(298.15\ K)$ value approximately 6 $kcal·mol^{-1}$ more positive. This latter work and other investigations are summarized in the following table.

Reference	Reaction	Data Points	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law
3	A	Equation	1673–1818	114.29	114.32	0.02	−56.26	−56.23
3	B	Equation	1818–2273	104.90	103.77	−0.58	−54.30	−55.43
1	C	2	1948	–	−16.23	–	–	−45.97
4	C	1	2270	–	−12.86	–	–	−49.34
4	D	1	2270	–	−40.14	–	–	−32.94 (−39.79)**

**Value is based on recent determination by Farber *et al.*[8] for $\Delta_f H°$(AlO, g, 298.15 K).
Reactions: (A) 0.5 $V_2O_4(cr) = VO_2(g)$ (C) $V(g) + VO_2(g) = 2\ VO(g)$
(B) 0.5 $V_2O_4(l) = VO_2(g)$ (D) $2\ AlO(g) + V(g) = 2\ Al(g) + VO_2(g)$

We adopt $\Delta_f H°(298.15\ K) = -55.6\ kcal·mol^{-1}$ for $VO_2(g)$. This value is an average of the 2nd and 3rd law results of Frantseva and Semenov.[3] These results are independent of the VO(g) data and show small third law drifts. The results of our analysis for reaction (C) for the data of Berkowitz *et al.*[1] and Farber *et al.*[4] show good agreement in $\Delta_r H°(298.15\ K)$ but lead to values for $\Delta_f H°(298.15\ K)$ which are 6–10 $kcal·mol^{-1}$ less negative than our adopted value. Killingbeck[6] studied the evaporation of V_2O_3 from a molybdenum effusion chamber and reported $\Delta_r H°(298.15\ K) = 279.5 \pm 5\ kcal·mol^{-1}$ for $V_2O_3(cr) = VO(g) + VO_2(g)$. Using auxiliary data[5] we calculate $\Delta_f H°(298.15\ K) = -42.3 \pm 5.0\ kcal·mol^{-1}$ for $VO_2(g)$.

The adopted $\Delta_f H°(298.15\ K)$ value corresponds to a dissociation energy $D° = 295.5\ kcal·mol^{-1}$ (12.8 eV) for the process $VO_2(g) = V(g) + 2\ O(g)$. This $D°$ value is 1.96 times the dissociation energy of VO(g).[5]

Heat Capacity and Entropy

The vibrational frequencies and geometry of $VO_2(g)$ are estimated based on existing and estimated data for related metal dioxides such as $TiO_2(g)$, $TaO_2(g)$ and $WO_2(g)$.[5] The V–O bond distance is assumed to be the same as in VO(g).[5]

The ground state quantum weight of 2 is adopted so as to be consistent with $TaO_2(g)$.[5] This introduces an uncertainty of ±1.38 $cal·K^{-1}·mol^{-1}$ in $S°(298.15\ K)$. The estimation of ν_2 at 300 cm^{-1} results in an uncertainty of 0.72 cal K^{-1} mol^{-1} in $S°(298.15\ K)$ for ±100 cm^{-1}. The estimates for $VO_2(g)$ are such that the 3rd law drifts as indicated in the above table are small. Nevertheless, until more data are available for $VO_2(g)$, the uncertainty in the entropy must be considered as ±1.4 $cal·K^{-1}·mol^{-1}$ for a bent molecule. The free energy functions suggested by Brewer and Rosenblatt[7] are roughly 3–4 $cal·K^{-1}·mol^{-1}$ lower than those adopted here. The main reason for the difference is that Brewer and Rosenblatt[7] treated $VO_2(g)$ as a linear molecule.

The electronic levels of the V^{+4} ion as reported by Moore[9] consist of a ground state with quantum weight four and an excited state at 620 cm^{-1} with a quantum weight six. The next excited state is listed at ~148000 cm^{-1}. Inclusion of an estimated state for $VO_2(g)$ at 620 cm^{-1} with a quantum weight of six would raise $S°(298.15\ K)$ by 1.06 $cal·K^{-1}·mol^{-1}$. This is within the estimated uncertainty of $S°(298.15\ K)$.

Continued on page 1815

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−11.254	−230.561	−230.561	INFINITE
100	35.385	222.647	301.443	−7.880	−230.580	−234.796	122.645
200	39.819	248.608	269.153	−4.109	−231.557	−238.670	62.334
250	41.903	257.716	265.981	−2.066	−232.116	−240.383	50.225
298.15	43.907	265.269	265.269	0.	−232.630	−241.928	42.385
300	43.982	265.541	265.270	0.081	−232.650	−241.986	42.134
350	45.916	272.468	265.812	2.330	−233.144	−243.503	36.341
400	47.622	278.714	267.041	4.669	−233.597	−244.951	31.987
450	49.082	284.409	268.659	7.088	−234.017	−246.345	28.595
500	50.311	289.646	270.499	9.573	−234.412	−247.693	25.876
600	52.201	298.996	274.489	14.705	−235.162	−250.278	21.789
700	53.531	307.149	278.585	19.995	−235.902	−252.739	18.860
800	54.485	314.363	282.615	25.398	−236.669	−255.092	16.656
900	55.184	320.822	286.507	30.884	−237.491	−257.347	14.936
1000	55.708	326.665	290.236	36.429	−238.380	−259.506	13.555
1100	56.110	331.994	293.793	42.021	−239.344	−261.572	12.421
1200	56.424	336.891	297.183	47.649	−240.399	−263.547	11.472
1300	56.674	341.417	300.414	53.304	−241.552	−265.430	10.665
1400	56.875	345.625	303.495	58.982	−242.816	−267.220	9.970
1500	57.039	349.554	306.436	64.678	−244.192	−268.916	9.364
1600	57.175	353.240	309.247	70.388	−245.681	−270.516	8.831
1700	57.288	356.710	311.938	76.112	−247.293	−272.020	8.358
1800	57.384	359.987	314.517	81.846	−249.035	−273.425	7.935
1900	57.466	363.092	316.993	87.588	−250.919	−274.729	7.553
2000	57.536	366.041	319.372	93.338	−252.953	−275.931	7.207
2100	57.597	368.850	321.662	99.095	−255.148	−277.026	6.891
2200	57.649	371.531	323.868	104.857	−280.396	−277.908	6.598
2300	57.695	374.094	325.997	110.625	−283.080	−277.735	6.308
2400	57.736	376.551	328.052	116.396	−285.781	−277.445	6.038
2500	57.772	378.908	330.040	122.172	−288.501	−277.042	5.788
2600	57.804	381.175	331.963	127.951	−291.239	−276.530	5.556
2700	57.832	383.357	333.826	133.732	−293.995	−275.912	5.338
2800	57.858	385.461	335.633	139.517	−296.768	−275.191	5.134
2900	57.881	387.491	337.387	145.304	−299.559	−274.372	4.942
3000	57.902	389.454	339.090	151.093	−302.368	−273.455	4.761
3100	57.921	391.353	340.745	156.884	−305.193	−272.444	4.591
3200	57.938	393.192	342.356	162.677	−308.034	−271.343	4.429
3300	57.953	394.975	343.923	168.472	−310.891	−270.153	4.276
3400	57.967	396.705	345.450	174.268	−313.763	−268.875	4.131
3500	57.981	398.386	346.939	180.065	−316.650	−267.513	3.992
3600	57.992	400.020	348.391	185.864	−319.551	−266.068	3.861
3700	58.004	401.609	349.808	191.664	−769.272	−263.342	3.718
3800	58.014	403.156	351.191	197.465	−770.514	−249.651	3.432
3900	58.023	404.663	352.543	203.266	−771.819	−235.927	3.160
4000	58.032	406.132	353.865	209.069	−773.188	−222.169	2.901
4100	58.040	407.565	355.157	214.873	−774.623	−208.376	2.655
4200	58.047	408.964	356.421	220.677	−776.124	−194.547	2.420
4300	58.055	410.330	357.659	226.482	−777.691	−180.681	2.195
4400	58.061	411.664	358.872	232.288	−779.325	−166.779	1.980
4500	58.067	412.969	360.059	238.094	−781.026	−152.839	1.774
4600	58.073	414.245	361.223	243.901	−782.795	−138.860	1.577
4700	58.078	415.494	362.365	249.709	−784.634	−124.841	1.387
4800	58.083	416.717	363.485	255.517	−786.541	−110.783	1.206
4900	58.088	417.915	364.583	261.326	−788.518	−96.684	1.031
5000	58.092	419.089	365.662	267.135	−790.566	−82.544	0.862
5100	58.097	420.239	366.720	272.944	−792.686	−68.362	0.700
5200	58.101	421.367	367.761	278.754	−794.878	−54.140	0.544
5300	58.104	422.474	368.782	284.564	−797.144	−39.872	0.393
5400	58.108	423.560	369.787	290.375	−799.485	−25.563	0.247
5500	58.111	424.626	370.774	296.186	−801.902	−11.210	0.106
5600	58.114	425.673	371.745	301.997	−804.396	3.190	−0.030
5700	58.117	426.702	372.700	307.809	−806.969	17.633	−0.162
5800	58.120	427.713	373.640	313.621	−809.622	32.124	−0.289
5900	58.123	428.706	374.565	319.433	−812.356	46.658	−0.413
6000	58.126	429.683	375.476	325.245	−815.175	61.243	−0.533

PREVIOUS: December 1973 (1 atm) CURRENT: December 1973 (1 bar)

$S°(298.15\ K) = 50.528 \pm 0.29\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -584.745 \pm 0.88\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -589.693 \pm 0.88\ kJ \cdot mol^{-1}$
$\Delta_{sub} H°(298.15\ K) = 666.260\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, $-140.94 \pm 0.21\ kcal \cdot mol^{-1}$, was determined by combustion calorimetry by Mah.[1] Griffis[2] has measured the enthalpy of combustion to WO_3(cr) which yields $\Delta_f H°(WO_2, cr, 298.15\ K) = -139.8 \pm 1.5\ kcal \cdot mol^{-1}$. When recalculated with $\Delta_f H°(WO_3, cr, 298.15\ K) = -201.46\ kcal \cdot mol^{-1}$. This result is less certain because of the incomplete characterization of the final products.

Recent equilibrium data yield essentially the same average of the enthalpy of formation by the 3rd law method. The results are presented as follows.

Source	Reaction	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 3rd law	2nd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[3]	A	1275–1497	10	2.672	0.036	1.9 ± 0.6	−140.62
[3]	B	973–1467	6	11.994	12.076	0.2 ± 0.76	−139.58
[4]	C	923–1223	7	−70.281	−67.943	−2.2 ± 0.2	−140.56
[5]	B	1075–1210	5	12.949	13.051	−0.1 ± 0.4	−141.49
[6]	B	873–1273	30	12.550	10.295	2.1 ± 0.1	−140.70

Reactions: A) 1/2 WO_2(cr) + CO(g) = 1/2 W(cr) + CO_2(g)
B) 1/2 WO_2(cr) + H_2(g) = 1/2 W(cr) + H_2O(g)
C) 1/2 W(cr) + 1/2 O_2(g) = 1/2 WO_2(cr)

Heat Capacity and Entropy

King *et al.*[7] have measured the low temperature heat capacities (53–297 K) and high temperature enthalpy changes (396–1800 K) by drop calorimetry. The low temperature and high temperature heat capacities were joined smoothly at 298.15 K. The entropy was obtained from the heat capacities based on $S°(51\ K) = 0.52\ cal \cdot K^{-1} \cdot mol^{-1}$. It is possible that at temperatures below 50 K the entropy due to the uncoupling of the d^2 electrons will appear contributing an additional $1.3\ cal \cdot K^{-1} \cdot mol^{-1}$.

Decomposition Data

Tungsten dioxide (cr) has no melting point since disproportionation occurs to yield W(cr) and WO_3(l) before melting starts. T_{dcm} = 1997 K is calculated as the temperature at which $\Delta_f G° = 0$ for 3 WO_2(cr) = 2 WO_3(l) + W(cr).

Sublimation Data

The enthalpy of sublimation is calculated from the difference between the enthalpies of formation of WO_2(g) and WO_2(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.000	0.000	INFINITE	−8.708	−584.745	−584.745	INFINITE
100	19.106	9.991	90.199	−8.021	−587.614	−570.321	297.905
200	42.211	30.893	55.247	−4.871	−589.383	−552.210	144.222
298.15	55.739	50.528	50.528	0.000	−589.693	−533.856	93.529
300	55.898	50.873	50.529	0.103	−589.689	−533.509	92.892
400	63.429	68.063	52.822	6.096	−589.131	−514.850	67.233
500	68.157	82.763	57.377	12.693	−588.107	−496.391	51.858
600	71.302	95.484	62.692	19.675	−586.843	−478.164	41.628
700	73.623	106.657	68.191	26.926	−585.447	−460.160	34.338
800	75.474	116.613	73.633	34.384	−583.971	−442.362	28.883
900	76.978	125.592	78.915	42.009	−582.440	−424.752	24.652
1000	78.174	133.767	83.998	49.769	−580.876	−407.315	21.276
1100	79.122	141.264	88.868	57.635	−579.298	−390.035	18.521
1200	79.968	148.184	93.526	65.590	−577.716	−372.899	16.232
1300	80.983	154.622	97.981	73.634	−576.126	−355.895	14.300
1400	82.969	160.690	102.245	81.823	−574.466	−339.016	12.649
1500	85.103	166.491	106.336	90.232	−572.661	−322.261	11.222
1600	88.031	172.080	110.272	98.893	−570.676	−305.631	9.978
1700	91.044	177.508	114.068	107.848	−568.471	−289.132	8.884
1800	93.847	182.791	117.740	117.092	−566.047	−272.769	7.916
1900	96.169	187.929	121.299	126.597	−563.434	−256.546	7.053
2000	98.198	192.914	124.756	136.316	−560.678	−240.465	6.280
2100	99.998	197.750	128.117	146.227	−557.802	−224.525	5.585
2200	101.755	202.442	131.390	156.315	−554.822	−208.723	4.956
2300	103.512	207.004	134.579	166.579	−551.738	−193.061	4.385
2400	105.228	211.445	137.689	177.014	−548.553	−177.534	3.864
2500	106.943	215.776	140.726	187.623	−545.268	−162.142	3.388
2600	108.617	220.003	143.695	198.401	−541.881	−146.884	2.951
2700	110.290	224.133	146.598	209.346	−538.423	−131.757	2.549
2800	111.964	228.175	149.439	220.459	−534.926	−116.759	2.178
2900	113.470	232.130	152.223	231.733	−531.436	−101.886	1.835
3000	115.102	236.004	154.951	243.160	−527.988	−87.133	1.517

PREVIOUS: June 1962 CURRENT: September 1966

$S°(298.15\ K)$ = [285.499] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 78.98 ± 29.3 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 76.57 ± 29.3 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights	
ϵ_i, cm^{-1}	g_i
0	[3]
[25,000]	[10]

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
992 (1)
[300] (1)
928 (1)

Ground State Quantum Weight: [3] σ = [2]
Point Group: [C_{2v}]
Bond[uccircl Distance: W–O = [1.81] Å
Bond Angle: O–W–O = [110]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [9.435202 × 10^{-115}] $g^3·cm^6$

Enthalpy of Formation

DeMaria *et al.*[1] have reported the partial pressures of WO(g), WO_2(g), WO_3(g), and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188 to 2475 K. The adopted value, $\Delta_f H°(WO_2, g, 298.15\ K)$ = 18.3 ± 7 $kcal·mol^{-1}$, was calculated from $\Delta_r H°(298.15\ K)$ = −100.9 $kcal·mol^{-1}$ for W(cr) + 2 O(g) → WO_2(g), which was obtained from 3rd law treatment of their partial pressure data, using all JANAF functions. The 3rd law drift is 15.0 ± 5.2 $cal·K^{-1}·mol^{-1}$. Partial pressures of WO_2(g), WO_3(g) and O(g) at 2242 K have also been reported by Chupka *et al.*[2] in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives $\Delta_r H°(298.15\ K)$ = −105.9 $kcal·mol^{-1}$ which yields $\Delta_f H°(WO_2, g, 298.15\ K)$ = 13.2 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The WO_2(g) was assumed to have a C_{2v} symmetry with a bond angle O–W–O = 110°. The bond distance W–O was estimated to be the same as that in WO(g). The symmetric and asymmetric stretching frequencies were obtained from the infrared spectrum of WO_2 in a neon matrix by Weltner and McLeod.[3] The bending vibrational frequency (300 cm^{-1}) was estimated by comparison with other dioxides. The electronic levels and quantum weights were estimated from W^{+4} ion by analogy with Mo^{+4} ion. The principal moments of inertia are: I_A = 4.8780 × 10^{-39}, I_B = 11.6809 × 10^{-39} and I_C = 16.5589 × 10^{-39} $g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.246	78.977	78.977	INFINITE
100	35.385	242.910	321.628	−7.872	78.795	72.796	−38.025
200	39.783	268.864	289.376	−4.102	77.646	67.224	−17.557
250	41.834	277.961	286.210	−2.062	77.071	64.686	−13.515
298.15	43.812	285.499	285.499	0.	76.567	62.348	−10.923
300	43.887	285.771	285.500	0.081	76.549	62.259	−10.840
350	45.806	292.682	286.042	2.324	76.091	59.915	−8.942
400	47.508	298.913	287.267	4.658	75.691	57.632	−7.526
450	48.970	304.595	288.882	7.071	75.335	55.396	−6.430
500	50.204	309.820	290.718	9.551	75.011	53.199	−5.558
600	52.109	319.152	294.698	14.673	74.415	48.893	−4.256
700	53.454	327.292	298.785	19.954	73.842	44.684	−3.334
800	54.420	334.496	302.807	25.351	73.256	40.559	−2.648
900	55.129	340.949	306.693	30.830	72.641	36.508	−2.119
1000	55.662	346.786	310.415	36.371	71.986	32.528	−1.699
1100	56.071	352.111	313.967	41.958	71.285	28.616	−1.359
1200	56.390	357.004	317.353	47.582	70.536	24.769	−1.078
1300	56.644	361.528	320.579	53.234	69.735	20.988	−0.843
1400	56.849	365.734	323.656	58.909	68.880	17.270	−0.644
1500	57.016	369.662	326.593	64.602	67.970	13.614	−0.474
1600	57.154	373.346	329.401	70.311	67.001	10.022	−0.327
1700	57.270	376.814	332.089	76.033	65.974	6.492	−0.199
1800	57.368	380.091	334.666	81.765	64.886	3.024	−0.088
1900	57.451	383.195	337.139	87.506	63.735	−0.382	0.010
2000	57.523	386.143	339.516	93.254	62.520	−3.725	0.097
2100	57.585	388.952	341.804	99.010	61.240	−7.006	0.174
2200	57.639	391.632	344.008	104.771	59.894	−10.224	0.243
2300	57.686	394.195	346.135	110.537	58.481	−13.381	0.304
2400	57.728	396.651	348.189	116.308	57.001	−16.474	0.359
2500	57.766	399.008	350.175	122.083	55.452	−19.504	0.408
2600	57.801	401.275	352.097	127.861	53.839	−22.470	0.451
2700	57.833	403.457	353.959	133.643	52.134	−25.373	0.491
2800	57.863	405.560	355.765	139.428	50.303	−28.210	0.526
2900	57.892	407.591	357.517	145.216	48.306	−30.980	0.558
3000	57.920	409.555	359.219	151.006	46.118	−33.677	0.586
3100	57.949	411.454	360.874	156.800	43.696	−36.297	0.612
3200	57.978	413.294	362.483	162.596	41.008	−38.836	0.634
3300	58.009	415.079	364.050	168.395	38.031	−41.287	0.654
3400	58.042	416.811	365.577	174.198	34.731	−43.641	0.670
3500	58.077	418.494	367.065	180.004	31.042	−45.894	0.685
3600	58.115	420.131	368.516	185.813	26.871	−48.034	0.697
3700	58.156	421.724	369.933	191.627	−12.647	−49.861	0.704
3800	58.202	423.275	371.316	197.445	−14.494	−50.841	0.699
3900	58.252	424.788	372.668	203.267	−16.350	−51.773	0.693
4000	58.307	426.263	373.989	209.095	−18.214	−52.658	0.688
4100	58.367	427.704	375.282	214.929	−20.086	−53.496	0.682
4200	58.432	429.111	376.547	220.769	−21.963	−54.288	0.675
4300	58.502	430.487	377.785	226.615	−23.847	−55.035	0.669
4400	58.579	431.832	378.998	232.470	−25.735	−55.739	0.662
4500	58.661	433.150	380.187	238.331	−27.628	−56.400	0.655
4600	58.749	434.440	381.353	244.202	−29.524	−57.019	0.647
4700	58.844	435.704	382.496	250.082	−31.423	−57.596	0.640
4800	58.944	436.944	383.617	255.971	−33.325	−58.132	0.633
4900	59.050	438.161	384.718	261.871	−35.230	−58.629	0.625
5000	59.162	439.355	385.799	267.781	−37.136	−59.087	0.617
5100	59.280	440.528	386.860	273.703	−39.045	−59.507	0.609
5200	59.404	441.680	387.904	279.637	−40.956	−59.890	0.602
5300	59.532	442.813	388.929	285.584	−42.868	−60.235	0.594
5400	59.666	443.927	389.937	291.544	−44.783	−60.546	0.586
5500	59.805	445.023	390.929	297.517	−46.700	−60.820	0.578
5600	59.949	446.102	391.904	303.505	−48.620	−61.059	0.570
5700	60.097	447.164	392.865	309.507	−50.543	−61.264	0.561
5800	60.249	448.211	393.810	315.525	−52.470	−61.435	0.553
5900	60.405	449.242	394.741	321.557	−54.401	−61.575	0.545
6000	60.565	450.258	395.657	327.606	−56.337	−61.679	0.537

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

Tungsten Oxide ($WO_{2.72}$) CRYSTAL M_r = 227.3684

$S°(298.15\ K) = [68.425]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -781.153 \pm 2.1\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, -186.7 ± 0.5 kcal·mol^{-1}, is derived from recent equilibrium data which are in excellent agreement, the results are summarized below. In addition, Griffis[1] measured the enthalpy of combustion to WO_3(cr) which yields $\Delta_f H°(WO_{2.72}$, cr, 298.15 K) = -185.4 ± 1 kcal·mol^{-1} when recalculated with $\Delta_f H°(WO_3$, cr, 298.15 K) = -201.46 kcal·mol^{-1}. This result is less certain because of the incomplete characterization of the final products. The emf data reported by Gerasuccirclimov *et al.*[2] give the value of -186.89 kcal·mol^{-1} for the enthalpy of formation at 298.15 K. Ackermann and Rauh[3] have investigated the tungsten oxygen system by mass effusion, mass spectroscopy and X-ray diffraction. In the temperature range from 1300 to 1600 K, they have derived indirectly from their measurements the enthalpy of formation -182.2 kcal·mol^{-1} (corresponding to -187.2 kcal·mol^{-1} at 298.15 K, using the JANAF functions).

Source	Reaction*	T/K	Data Points	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K kcal·mol^{-1}
[4]	A	830–1048	5	2.951	4.095	1.2 ± 0.2	−186.65
[5]	B	1173–1423	–	−45.739	–	–	−186.68
[6]	A	904–1066	4	2.676	4.279	1.6 ± 0.3	−186.83
[7]	A	873–1173	24	4.314	4.314	-0.01 ± 0.06	−186.87

A) 100/72 $WO_{2.72}$(cr) + H_2(g) = 100/72 WO_2(cr) + H_2O(g)

B) WO_2(cr) + 0.72 O_2(g) = $WO_{2.72}$(cr)

Heat Capacity and Entropy

The monoclinic unit cell of $WO_{2.72}$ corresponds to $W_{18}O_{49}$ as shown by the X-ray diffraction studies of Magneli *et al.*[8] The tabulated heat capacities of $WO_{2.72}$(cr) were estimated from those of WO_2(cr) and WO_3(cr) because all three have similar monoclinic structures as identified by Magneli *et al.*

The entropy, $S°(298.15\ K) = 16.35$ cal·K^{-1}·mol^{-1}, was calculated from $\Delta_r S°(298.15\ K) = 7.96 \pm 0.09$ cal·K^{-1}·mol^{-1} for reaction A, using all JANAF values. The value of $\Delta_r S°(298.15\ K)$ was derived from the 2nd law analysis of Griffis' data.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	68.283	68.425	68.425	0.000	−781.153	−708.632	124.149
300	68.408	68.848	68.426	0.126	−781.145	−708.183	123.306
400	76.902	89.731	71.216	7.406	−780.370	−683.959	89.316
500	82.927	107.581	76.748	15.417	−779.034	−660.002	68.950
600	86.985	123.079	83.207	23.923	−777.382	−636.347	55.399
700	89.810	136.719	89.897	32.775	−775.557	−612.984	45.741
800	91.839	148.850	96.522	41.862	−773.653	−589.889	38.516
900	93.471	159.765	102.953	51.131	−771.705	−567.035	32.910
1000	95.019	169.696	109.138	60.558	−769.720	−544.400	28.437
1100	96.441	178.819	115.064	70.131	−767.698	−521.965	24.786
1200	97.822	187.269	120.733	79.843	−765.637	−499.717	21.752
1300	99.286	195.155	126.158	89.697	−763.526	−477.642	19.192
1400	100.751	202.568	131.353	99.701	−761.353	−455.732	17.004
1500	102.006	209.562	136.336	109.838	−759.130	−433.979	15.113
1600	103.261	216.185	141.122	120.102	−756.864	−412.376	13.463
1700	104.516	222.483	145.724	130.491	−754.552	−390.916	12.011
1800	105.772	228.493	150.157	141.005	−752.196	−369.594	10.725
1900	107.027	234.245	154.432	151.645	−749.794	−348.404	9.578
2000	108.282	239.767	158.562	162.410	−747.347	−327.341	8.549
2100	109.537	245.080	162.556	173.301	−744.854	−306.402	7.621
2200	110.792	250.205	166.424	184.318	−742.316	−285.581	6.781
2300	112.048	255.158	170.175	195.460	−739.732	−264.879	6.016
2400	113.303	259.953	173.816	206.727	−737.103	−244.290	5.317
2500	114.558	264.603	177.355	218.120	−734.428	−223.811	4.676
2600	115.813	269.121	180.798	229.639	−731.704	−203.440	4.087
2700	117.068	273.515	184.151	241.283	−728.957	−183.173	3.544
2800	118.324	277.795	187.420	253.053	−726.221	−163.009	3.041
2900	119.579	281.970	190.608	264.948	−723.535	−142.943	2.575
3000	120.834	286.045	193.722	276.968	−720.925	−122.967	2.141

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K)$ = [73.371] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K) = -820.064 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted enthalpy of formation, -196.0 ± 3 kcal·mol^{-1}, is a weighted average of those derived from equilibrium data, in addition the following results have been reported.

Griffis[1] has measured the enthalpy of combustion to WO_3(cr) which yields -195.6 kcal·mol^{-1} when recalculated with $\Delta_f H°(WO_3, cr, 298.15\ K) = -201.46$ kcal·mol^{-1}. This result is less certain because of the incomplete characterization of the final products. Ackermann and Rauh[2] have investigated the tungsten oxygen system by mass effusion, mass spectroscopy, and x-ray diffraction. In the temperature range from 1300 to 1600 K, they have derived indirectly two values of $\Delta_f H°(WO_{2.90}, cr) = -190.9$ and -188.0 kcal·mol^{-1} (corresponding to -196.1 and -193.3 kcal·mol^{-1}, respectively, at 298.15 K, using all JANAF functions).

Source	Reaction	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal k^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
[3]	A	773–898	5	2.168	0.270	-2.3 ± 0.07	-195.4
[4]	A	897–993	4	2.178	0.240	-2.1 ± 0.01	-195.4
[5]	A	873–1073	18	1.504	0.284	-1.3 ± 0.02	-195.4
[3]	B	844–934	5	2.657	0.754	-2.1 ± 0.09	-197.9
[4]	B	915–1021	5	1.585	0.834	-0.76 ± 0.1	-197.9
[5]	B	873–1073	18	3.388	0.589	-2.88 ± 0.02	-197.7
[3]	C	737–798	5	6.762	5.013	-2.3 ± 0.9	-198.0
[6]	D	1023–1273	–	−7.97	–	–	-193.5
[6]	E	1173–1322	–	−13.67	–	–	-200.4

Reactions:
A) $WO_3(cr) + 0.1\ H_2(g) = WO_{2.90}(cr) + 0.1\ H_2O(g)$
B) $WO_{2.90}(cr) + 0.18\ H_2(g) = WO_{2.72}(cr) + 0.18\ H_2O(g)$
C) $WO_{2.90}(cr) + 0.9\ H_2(g) = WO_2(cr) + 0.9\ H_2O(g)$
D) $WO_{2.90}(cr) + 0.05\ O_2(g) = WO_3(cr)$
E) $WO_{2.72}(cr) + 0.09\ O_2(g) = WO_{2.90}(cr)$

Heat Capacity and Entropy

The monoclinic unit cell of $WO_{2.90}$ corresponds to $W_{20}O_{58}$ as shown by the X-ray diffraction studies of Magneli *et al.*[7] The tabulated heat capacities and the entropy, $S°(298.15\ K) = 17.536$ cal·K^{-1}·mol^{-1}, were estimated from those of WO_2(cr) and WO_3(cr) because all three have the similar monoclinic structure as identified by Magneli *et al.*[7]

References

[1] R. C. Griffis, J. Electrochem. Soc. **105**, 398 (1958).
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[4] I. A. Vasil'eva, Ya. I. Perasimov and Yu. P. Simanov, Zh. Fiz. Khim. **34**, 1811 (1960).
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[7] A. Magneli, G. Anderson, B. Blomberg and L. Kihlborg, Anal. Chem. **24**, 1998 (1952).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0							
100							
200							
298.15	71.379	73.371	73.371	0.000	−820.064	−743.513	130.260
300	71.546	73.813	73.372	0.132	−820.056	−743.038	129.374
400	80.333	95.634	76.287	7.739	−819.221	−717.472	93.692
500	86.609	114.277	82.067	16.105	−817.804	−692.189	72.313
600	90.918	130.473	88.815	24.995	−816.053	−667.227	58.087
700	93.931	144.726	95.805	34.245	−814.124	−642.573	47.949
800	95.981	157.409	102.727	43.746	−812.106	−618.203	40.365
900	97.655	168.813	109.447	53.430	−810.049	−594.088	34.480
1000	99.244	179.189	115.910	63.279	−807.953	−570.205	29.784
1100	100.562	188.692	122.101	73.251	−805.849	−546.531	25.953
1200	101.880	197.496	128.021	83.370	−803.700	−523.051	22.768
1300	103.303	205.707	133.685	93.629	−801.506	−499.753	20.080
1400	104.558	213.411	139.107	104.025	−799.266	−476.625	17.783
1500	105.688	220.663	144.305	114.537	−796.996	−453.658	15.798
1600	106.818	227.520	149.293	125.162	−794.699	−430.844	14.066
1700	108.073	234.033	154.088	135.906	−792.364	−408.174	12.542
1800	109.328	240.246	158.703	146.777	−789.987	−385.643	11.191
1900	110.583	246.191	163.153	157.772	−787.566	−363.245	9.986
2000	111.838	251.895	167.448	168.893	−785.101	−340.976	8.905
2100	113.094	257.382	171.601	180.140	−782.593	−318.832	7.931
2200	114.349	262.672	175.621	191.512	−780.042	−296.806	7.047
2300	115.604	267.782	179.517	203.009	−777.448	−274.900	6.243
2400	116.859	272.729	183.299	214.633	−774.810	−253.107	5.509
2500	118.114	277.525	186.972	226.381	−772.128	−231.424	4.835
2600	119.370	282.182	190.545	238.255	−769.399	−209.849	4.216
2700	120.625	286.710	194.023	250.255	−766.648	−188.380	3.644
2800	121.880	291.120	197.413	262.380	−763.911	−167.013	3.116
2900	123.135	295.419	200.718	274.631	−761.226	−145.743	2.625
3000	124.390	299.614	203.945	287.007	−758.618	−124.564	2.169

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K)$ = [74.894] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = Unknown

$\Delta_f H°(298.15\ K)$ = −834.959 ± 12.6 $kJ·mol^{-1}$

Enthalpy of Formation

The adopted value, $\Delta_f H°(WO_{2.96}, cr, 298.15\ K) = -199.56\ kcal·mol^{-1}$, was obtained by 3rd law treatment of $\Delta_f G° = 191{,}600 + 54.0\ T$ ($cal·K^{-1}·mol^{-1}$) in the temperature range from 1300–1550 K, using all JANAF functions. The equation for $\Delta_f G°$ was reported by Ackermann and Rauh[1], based on studies by mass spectroscopy and X-ray diffraction. In this study, $\Delta_f G°$ was obtained by comparison of the Gibbs free energies of sublimation (to gaseous W_2O_6, W_3O_8, W_3O_9 and W_4O_{12}) over the two systems W–WO_2(cr) and $WO_{2.96}$(cr) and $WO_{2.96}$(cr); thus $WO_{2.96}$(cr) was related to WO_2(cr) through the gaseous species.

Battles[2] has reported partial pressures of W_3O_9(g) and W_4O_{12}(g) in equilibrium with WO_3–$WO_{2.90}$(cr). In light of Ackermann and Rauh's observation, the condensed phase was presumed to have the composition of $WO_{2.96}$(cr). The pressure data are in reasonable agreement with the studies of Ackermann and Rauh as summarized below. Values of $\Delta_f H°(WO_{2.96}, cr, 298.15\ K)$ derived from the data of Battles are based on the same author's data for W_3O_9(g), and W_4O_{12}(g) in order to relate $WO_{2.96}$ to WO_2 directly.

Source	Reaction	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	A	1300–1550	56.32	60.82	3.2 ± 0.6	−199.57
1	B	1300–1550	38.35	41.37	2.09 ± 0.09	−199.58
2	B	1274–1418	43.28	40.82	1.85 ± 0.05	−199.72
1	C	1300–1550	33.58	35.81	1.55 ± 0.09	−199.60
2	C	1333–1418	38.74	35.37	−2.46 ± 0.1	−199.95

Reactions:
A) $WO_{2.96}(cr) = 0.44\ W_2O_6(g) + 0.04\ W_3O_8(g)$
B) $WO_{2.96}(cr) = 0.29333\ W_3O_9(g) + 0.04\ W_3O_8(g)$
C) $WO_{2.96}(cr) = 0.22\ W_4O_{12}(g) + 0.04\ W_3O_8(g)$

Heat Capacity and Entropy

The tabulated heat capacities and the entropy at 298.15 K were estiamted from those of WO_2(cr) and WO_3(cr).

Ackermann and Rauh[1] have found that the composition $WO_{2.96}$ probably represents the azeotropic composition of the WO_{3-x} solid solution and is the only single phase which evaporates congruently below 1550 K.

References

[1]R. J. Ackermann and E. G. Rauh, J. Phys. Chem. **67**, 2596 (1963).
[2]J. E. Battles, Ph.D. Thesis, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," Ohio State University (1964).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
298.15	72.383	74.894	74.894	0.000	−834.959	−757.027	132.628
300	72.634	75.342	74.895	0.134	−834.950	−756.544	131.726
400	81.504	97.478	77.852	7.850	−834.095	−730.517	95.396
500	87.864	116.394	83.716	16.339	−832.648	−704.781	73.628
600	92.257	132.825	90.562	25.358	−830.863	−679.371	59.145
700	95.312	147.287	97.653	34.744	−828.895	−654.276	48.823
800	97.404	160.156	104.677	44.384	−826.838	−629.471	41.100
900	99.370	171.735	111.495	54.216	−824.734	−604.925	35.109
1000	100.709	182.264	118.053	64.211	−822.598	−580.616	30.328
1100	102.215	191.936	124.336	74.359	−820.421	−556.523	26.427
1200	103.512	200.886	130.347	84.647	−818.211	−532.630	23.185
1300	104.851	209.224	136.097	95.065	−815.965	−508.922	20.449
1400	106.106	217.041	141.603	105.613	−813.681	−485.389	18.110
1500	107.194	224.399	146.880	116.278	−811.368	−462.020	16.089
1600	108.282	231.351	151.944	127.052	−809.032	−438.806	14.326
1700	109.537	237.954	156.811	137.943	−806.662	−415.740	12.774
1800	110.792	244.250	161.495	148.959	−804.249	−392.814	11.399
1900	112.048	250.274	166.010	160.101	−801.794	−370.023	10.173
2000	113.303	256.053	170.369	171.369	−799.296	−347.363	9.072
2100	114.558	261.612	174.582	182.762	−796.755	−324.828	8.080
2200	115.813	266.970	178.660	194.280	−794.172	−302.415	7.180
2300	117.068	272.145	182.613	205.924	−791.546	−280.122	6.362
2400	118.324	277.154	186.449	217.694	−788.877	−257.944	5.614
2500	119.579	282.010	190.174	229.589	−786.165	−235.877	4.928
2600	120.834	286.724	193.798	241.610	−783.406	−213.920	4.298
2700	122.089	291.308	197.325	253.756	−780.627	−192.069	3.716
2800	123.344	295.771	200.761	266.028	−777.862	−170.321	3.177
2900	124.600	300.121	204.113	278.425	−775.148	−148.672	2.678
3000	125.855	304.367	207.384	290.948	−772.513	−127.114	2.213

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K) = [50.359 \pm 0.33]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1478 \pm 5\ K$
$T_{fus} = 2950\ K$

$\Delta_f H°(0\ K) = -1092.032 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1097.463 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 5.941 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [87.027]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrO_2, cr, 298.15\ K) = -262.3 \pm 0.4\ kcal \cdot mol^{-1}$ is an average of the values $261.5 \pm 0.2\ kcal \cdot mol^{-1}$ and $-263.1 \pm 0.5\ kcal \cdot mol^{-1}$ measured (by combustion calorimetry) by Humphrey[1] and Huber *et al.*,[2] respectively. measured calorimetrically by Neumann *et al.*,[3] Roth *et al.*[4] and by Sieverts *et al.*[5] and was found to be −258.2, −258.8 and −256.1 $kcal \cdot mol^{-1}$, respectively. However, more weight was given to the Humphrey and Huber values.

Heat Capacity and Entropy

The low temperature heat capacities, 54.3–295 K, were measured by Kelley.[6] The heat capacities in the temperature range 298–1478 K were calculated by using the Coughlin and King[7] equation, $C_p° = 16.64 + 1.80 \times 10^{-3} T - 3.36 \times 10^5 T^2$, obtained from their measured enthalpy data (296.8–1841 K). The values from the two sources join smoothly at 298.15 K. Above the transition 1478 K, the heat capacity was taken as constant at 17.80 $cal \cdot K^{-1} \cdot mol^{-1}$. The entropy was calculated at 54.30 K using the Debye and Einstein function D(345/*T*) + E(513/*T*) + E(861/*T*) given by Kelley.[6] The value, $S°(54.3\ K) = 0.5507\ cal \cdot K^{-1} \cdot mol^{-1}$, is thus calculated.

Transition Data

T_{trs} and $\Delta_{trs}H°$ were taken from Coughlin and King.[7]

Fusion Data

T_{fus} and $\Delta_{fus}H°$ were taken from U. S. Nat. Bur. Stand.[8]

References

[1]G. L. Humphrey, J. Amer. Chem. Soc. **76**, 978 (1954).
[2]E. J. Huber, Jr., E. L. Head and C. E. Holley, Jr., J. Phys. Chem. **68**, 3040 (1964).
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[5]A. Sieverts, A. Gotta and S. Halberstadt, Z. Anorg. Chem. **187**, 155 (1930).
[6]K. K. Kelley, Ind. Eng. Chem. **36**, 377 (1944).
[7]J. P. Coughlin and E. G. King, J. Amer. Chem. Soc. **72**, 2262 (1950).
[8]U. S. Nat. Bur. Stand. Circ. 500, 1268 pp. (1952).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.749	−1092.032	−1092.032	INFINITE
100	18.927	9.488	90.390	−8.090	−1095.164	−1077.376	562.764
200	42.778	30.546	55.114	−4.914	−1097.091	−1058.694	276.502
298.15	56.191	50.359	50.359	0.000	−1097.463	−1039.724	182.155
300	56.262	50.707	50.360	0.104	−1097.460	−1039.366	180.970
400	63.848	68.064	52.675	6.155	−1096.940	−1020.063	133.207
500	67.764	82.769	57.264	12.753	−1096.026	−1000.945	104.568
600	70.237	95.356	62.589	19.660	−1094.969	−982.027	85.493
700	72.023	106.323	68.070	26.777	−1093.873	−963.289	71.882
800	73.450	116.036	73.471	34.053	−1092.785	−944.709	61.683
900	74.663	124.759	78.693	41.459	−1091.731	−926.264	53.759
1000	75.747	132.682	83.702	48.981	−1090.727	−907.933	47.426
1100	76.743	139.949	88.489	56.606	−1089.783	−889.699	42.248
1200	77.684	146.667	93.061	64.327	−1092.612	−871.328	37.928
1300	78.580	152.921	97.428	72.141	−1091.250	−852.942	34.272
1400	79.450	158.776	101.603	80.042	−1089.872	−834.662	31.142
1478.000	80.108	163.101	104.735	86.265	I <--> II		
1478.000	74.475	167.121	104.735	92.207	TRANSITION		
1500	74.475	168.222	105.658	93.845	−1082.674	−816.569	28.435
1600	74.475	173.028	109.720	101.293	−1081.921	−798.854	26.080
1700	74.475	177.543	113.578	108.740	−1081.266	−781.183	24.003
1800	74.475	181.800	117.251	116.188	−1080.720	−763.547	22.158
1900	74.475	185.827	120.756	123.635	−1080.293	−745.939	20.507
2000	74.475	189.647	124.105	131.083	−1079.995	−728.349	19.023
2100	74.475	193.280	127.314	138.530	−1079.836	−710.772	17.679
2200	74.475	196.745	130.392	145.978	−1101.150	−692.452	16.441
2300	74.475	200.056	133.349	153.425	−1101.717	−673.863	15.304
2400	74.475	203.225	136.195	160.873	−1102.306	−655.248	14.261
2500	74.475	206.265	138.937	168.320	−1102.918	−636.608	13.301
2600	74.475	209.186	141.583	175.768	−1103.550	−617.943	12.415
2700	74.475	211.997	144.140	183.215	−1104.204	−599.253	11.593
2800	74.475	214.706	146.612	190.663	−1104.878	−580.539	10.830
2900	74.475	217.319	149.005	198.110	−1105.572	−561.801	10.119
2950.000	74.475	218.592	150.174	201.834	----- II <--> LIQUID -----		
3000	74.475	219.844	151.325	205.558	−1106.286	−543.038	9.455
3100	74.475	222.286	153.575	213.005	−1107.018	−524.250	8.834
3200	74.475	224.650	155.759	220.453	−1107.768	−505.440	8.250
3300	74.475	226.942	157.881	227.900	−1108.536	−486.606	7.702
3400	74.475	229.165	159.945	235.348	−1109.320	−467.747	7.186
3500	74.475	231.324	161.954	242.795	−1110.120	−448.866	6.699

PREVIOUS: June 1961 CURRENT: December 1965

$S°(298.15\ K) = [74.657]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2950\ K$

$\Delta_f H°(298.15\ K) = [-1023.155]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [87.027]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrO_2, l, 298.15\ K)$ is calculated from $\Delta_f H°(ZrO_2, cr, 298.15\ K)$ by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(2950\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

A glass transition is assumed at 2000 K. The heat capacity below 2000 K was obtained from the heat capacity of the crystal. Above 2000 K the heat capacity was assumed constant and estimated to be 21.0 $cal·K^{-1}·mol^{-1}$ or 7 $cal·K^{-1}·mol^{-1}$ per g-atom as suggested by Kubaschewski and Evans.[1] The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap}(1 atm) = 4548 K is calculated as the temperature at which the fugacity is 1 atm for the reaction $ZrO_2(l) \rightarrow ZrO_2(g)$. The difference between $\Delta_f H°(4548\ K)$ for $ZrO_2(g)$ and $ZrO_2(l)$ gives $\Delta_{vap} H°(4548\ K) = 149.2\ kcal·mol^{-1}$.

Reference

[1] O. Kubaschewski and E. LL. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York (1958).

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	56.191	74.657	74.657	0.000	−1023.155	−972.661	170.406
300	56.262	75.004	74.658	0.104	−1023.152	−972.347	169.301
400	63.848	92.361	76.972	6.155	−1022.632	−955.474	124.772
500	67.764	107.066	81.561	12.753	−1021.718	−938.785	98.074
600	70.237	119.653	86.886	19.660	−1020.661	−922.297	80.293
700	72.023	130.621	92.367	26.777	−1019.565	−905.989	67.606
800	73.450	140.333	97.768	34.053	−1018.477	−889.839	58.101
900	74.663	149.056	102.990	41.459	−1017.423	−873.823	50.715
1000	75.747	156.979	107.999	48.981	−1016.420	−857.922	44.813
1100	76.743	164.246	112.786	56.606	−1015.475	−842.118	39.989
1200	77.684	170.964	117.358	64.327	−1018.304	−826.176	35.963
1300	78.580	177.218	121.725	72.141	−1016.942	−810.221	32.555
1400	79.450	183.073	125.900	80.042	−1015.565	−794.371	29.638
1478.000	80.107	187.398	129.032	86.265	I <--> II		
1478.000	74.475	191.418	129.032	92.207	TRANSITION		
1500	74.475	192.519	129.955	93.845	−1008.367	−778.707	27.117
1600	74.475	197.325	134.017	101.293	−1007.613	−763.421	24.923
1700	74.475	201.840	137.875	108.740	−1006.958	−748.180	22.989
1800	74.475	206.097	141.548	116.188	−1006.412	−732.974	21.270
1900	74.475	210.124	145.053	123.635	−1005.985	−717.795	19.734
2000	74.475	213.944	148.403	131.083	−1005.687	−702.636	18.351
2000.000	74.475	213.944	148.403	131.083	GLASS <--> LIQUID		
2000.000	87.864	213.944	148.403	131.083	TRANSITION		
2100	87.864	218.231	151.626	139.869	−1004.189	−687.521	17.101
2200	87.864	222.318	154.748	148.655	−1024.164	−671.727	15.949
2300	87.864	226.224	157.771	157.442	−1023.393	−655.725	14.892
2400	87.864	229.963	160.702	166.228	−1022.643	−639.756	13.924
2500	87.864	233.550	163.544	175.015	−1021.916	−623.817	13.034
2600	87.864	236.996	166.304	183.801	−1021.209	−607.908	12.213
2700	87.864	240.312	168.984	192.587	−1020.524	−592.024	11.453
2800	87.864	243.508	171.588	201.374	−1019.860	−576.166	10.749
2900	87.864	246.591	174.122	210.160	−1019.215	−560.332	10.093
2950.000	87.864	248.093	175.363	214.553	II <--> LIQUID		
3000	87.864	249.570	176.587	218.947	−1018.589	−544.518	9.481
3100	87.864	252.451	178.988	227.733	−1017.983	−528.726	8.909
3200	87.864	255.240	181.328	236.519	−1017.394	−512.953	8.373
3300	87.864	257.944	183.609	245.306	−1016.823	−497.199	7.870
3400	87.864	260.567	185.834	254.092	−1016.268	−481.460	7.397
3500	87.864	263.114	188.006	262.879	−1015.729	−465.739	6.951
3600	87.864	265.589	190.127	271.665	−1015.206	−450.032	6.530
3700	87.864	267.997	192.199	280.451	−1014.698	−434.340	6.132
3800	87.864	270.340	194.224	289.238	−1014.204	−418.661	5.755
3900	87.864	272.622	196.206	298.024	−1013.724	−402.995	5.398
4000	87.864	274.847	198.144	306.811	−1013.257	−387.341	5.058
4100	87.864	277.016	200.041	315.597	−1012.803	−371.699	4.736
4200	87.864	279.133	201.899	324.383	−1012.362	−356.068	4.428
4300	87.864	281.201	203.720	333.170	−1011.933	−340.446	4.136
4400	87.864	283.221	205.504	341.956	−1011.517	−324.836	3.856
4500	87.864	285.195	207.253	350.743	−1011.112	−309.235	3.590
4600	87.864	287.127	208.968	359.529	−1010.720	−293.642	3.334
4700	87.864	289.016	210.651	368.315	−1010.340	−278.057	3.090
4800	87.864	290.866	212.303	377.102	−1570.909	−250.863	2.730
4900	87.864	292.678	213.925	385.888	−1570.207	−223.369	2.381
5000	87.864	294.453	215.518	394.675	−1569.534	−195.889	2.046

PREVIOUS: June 1961 CURRENT: December 1965

0 to 1478 K crystal, I
1478 to 2950 K crystal, II
above 2950 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−8.749	−1092.032	−1092.032	INFINITE
100	18.927	9.488	90.390	−8.090	−1095.164	−1077.376	562.764
200	42.778	30.546	55.114	−4.914	−1097.091	−1058.694	276.502
298.15	56.191	50.359	50.359	0.000	−1097.463	−1039.724	182.155
300	56.262	50.707	50.360	0.104	−1097.460	−1039.366	180.970
400	63.848	68.064	52.675	6.155	−1096.940	−1020.063	133.207
500	67.764	82.769	57.264	12.753	−1096.026	−1000.945	104.568
600	70.237	95.356	62.589	19.660	−1094.969	−982.027	85.493
700	72.023	106.323	68.070	26.777	−1093.873	−963.289	71.882
800	73.450	116.036	73.471	34.053	−1092.785	−944.709	61.683
900	74.663	124.759	78.693	41.459	−1091.731	−926.264	53.759
1000	75.747	132.682	83.702	48.981	−1090.727	−907.933	47.426
1100	76.743	139.949	88.489	56.606	−1089.783	−889.699	42.248
1200	77.684	146.667	93.061	64.327	−1092.612	−871.328	37.928
1300	78.580	152.921	97.428	72.141	−1091.250	−852.942	34.272
1400	79.450	158.776	101.603	80.042	−1089.872	−834.662	31.142
1478.000	80.107	163.101	104.735	86.265	I <−−> II TRANSITION		
1478.000	74.475	167.121	104.735	92.207			
1500	74.475	168.222	105.658	93.845	−1082.675	−816.569	28.435
1600	74.475	173.028	109.720	101.293	−1081.921	−798.854	26.080
1700	74.475	177.543	113.578	108.740	−1081.266	−781.183	24.003
1800	74.475	181.800	117.251	116.188	−1080.720	−763.547	22.158
1900	74.475	185.827	120.756	123.635	−1080.293	−745.939	20.507
2000	74.475	189.647	124.105	131.083	−1079.995	−728.349	19.023
2100	74.475	193.280	127.314	138.530	−1079.836	−710.772	17.679
2200	74.475	196.745	130.392	145.978	−1101.150	−692.452	16.441
2300	74.475	200.056	133.349	153.425	−1101.717	−673.862	15.304
2400	74.475	203.225	136.195	160.873	−1102.306	−655.248	14.261
2500	74.475	206.265	138.937	168.320	−1102.918	−636.608	13.301
2600	74.475	209.186	141.583	175.768	−1103.550	−617.943	12.415
2700	74.475	211.997	144.140	183.215	−1104.204	−599.253	11.593
2800	74.475	214.706	146.612	190.663	−1104.878	−580.539	10.830
2900	74.475	217.319	149.005	198.110	−1105.572	−561.801	10.119
2950.000	74.475	218.592	150.174	201.834	II <−−> LIQUID TRANSITION		
2950.000	87.864	248.093	150.174	288.861			
3000	87.864	249.570	151.818	293.254	−1018.589	−544.518	9.481
3100	87.864	252.451	155.018	302.041	−1017.983	−528.726	8.909
3200	87.864	255.240	158.107	310.827	−1017.394	−512.953	8.373
3300	87.864	257.944	161.091	319.614	−1016.823	−497.199	7.870
3400	87.864	260.567	163.979	328.400	−1016.268	−481.460	7.397
3500	87.864	263.114	166.775	337.186	−1015.729	−465.739	6.951
3600	87.864	265.589	169.486	345.973	−1015.206	−450.032	6.530
3700	87.864	267.997	172.116	354.759	−1014.698	−434.340	6.132
3800	87.864	270.340	174.670	363.546	−1014.204	−418.661	5.755
3900	87.864	272.622	177.152	372.332	−1013.724	−402.995	5.398
4000	87.864	274.847	179.567	381.118	−1013.257	−387.341	5.058
4100	87.864	277.016	181.917	389.905	−1012.803	−371.699	4.736
4200	87.864	279.133	184.207	398.691	−1012.362	−356.068	4.428
4300	87.864	281.201	186.439	407.478	−1011.933	−340.446	4.136
4400	87.864	283.221	188.615	416.264	−1011.517	−324.836	3.856
4500	87.864	285.195	190.740	425.050	−1011.112	−309.234	3.590
4600	87.864	287.127	192.814	433.837	−1010.720	−293.642	3.334
4700	87.864	289.016	194.841	442.623	−1010.340	−278.057	3.090
4800	87.864	290.866	196.822	451.410	−1570.909	−250.863	2.730
4900	87.864	292.678	198.760	460.196	−1570.207	−223.369	2.381
5000	87.864	294.453	200.656	468.982	−1569.534	−195.889	2.046

PREVIOUS: CURRENT: December 1965

Zirconium Oxide (ZrO_2) IDEAL GAS $M_r = 123.2188$ Zirconium Oxide (ZrO_2) $O_2Zr_1(g)$

$S°(298.15\ K) = 273.746\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -284.01 \pm 46.0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -286.19 \pm 46.0\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
884 (1)
[137] (1)
818 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Bond Distance: O–Zr = 1.711 Å
Bond Angle: O–Zr–O = 109°
Product of the Moments of Inertia: $I_A I_B I_C = 5.682779 \times 10^{-115}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(ZrO_2, g, 298.15\ K) = -68.4 \pm 11\ kcal·mol^{-1}$ was calculated from the $\Delta_r H°(298.15\ K) = 193.867 \pm 11.25\ kcal·mol^{-1}$ for the reaction $ZrO_2(cr) \rightarrow ZrO_2(g)$. The value of $\Delta_r H°(298.15\ K)$ was obtained by the 3rd law method using the determined vapor pressures (at the range 2331–2480 K) by Chupka *et al.*[1] They observed the variation of the ZrO_2^+ ion intensity over ZrO_2 reported equilibrium constants for the reaction $ZrO_2(cr) \rightarrow ZrO_2(g)$ in the range 2331–2480 K. The 3rd law drift is $80 \pm 23\ cal·K^{-1}·mol^{-1}$.

Heat Capacity and Entropy

The vibrational frequencies $\nu_1 = 884$, $\nu_2 = [137]$, $\nu_3 = 818$ and angle O–Zr–O = 109° were obtained from Linevsky.[2] The bond distance r_e(O–Zr) = 1.711 Å was obtained from Uhler and Akerline.[3] The principal moments of inertia are: $I_A = 3.8834 \times 10^{-39}$, $I_B = 10.3101 \times 10^{-39}$, $I_C = 14.1935 \times 10^{-39}\ g·cm^2$.

References

[1]W. A. Chupka, J. Berkowitz and M. G. Inghram, J. Chem. Phys. **26**, 1207 (1957).
[2]M. J. Linevsky, Spectroscopic Studies of the Vaporization of Refractory Materials, AFML TR–64–420, Air Force Materials Lab. Research and Technology Division, Wright Patterson Air Force Base, Ohio (1965).
[3]U. Uhler and L. Akerlind, Arkiv Fysik **10**, 431 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−12.008	−284.013	−284.013	INFINITE
100	39.345	227.980	312.150	−8.417	−284.213	−288.275	150.579
200	42.320	256.161	277.836	−4.335	−285.235	−291.960	76.252
250	44.193	265.801	274.494	−2.173	−285.747	−293.581	61.340
298.15	46.061	273.746	273.746	0.	−286.186	−295.049	51.691
300	46.131	274.031	273.747	0.085	−286.201	−295.105	51.382
350	47.910	281.279	274.315	2.437	−286.597	−296.556	44.259
400	49.444	287.779	275.599	4.872	−286.945	−297.955	38.909
450	50.727	293.679	277.285	7.377	−287.262	−299.312	34.743
500	51.787	299.081	279.198	9.941	−287.560	−300.635	31.407
600	53.383	308.673	283.332	15.205	−288.147	−303.195	26.395
700	54.482	316.990	287.559	20.601	−288.772	−305.654	22.808
800	55.258	324.318	291.705	26.090	−289.469	−308.019	20.112
900	55.822	330.861	295.699	31.646	−290.267	−310.291	18.009
1000	56.242	336.765	299.515	37.250	−291.180	−312.468	16.322
1100	56.561	342.141	303.149	42.891	−292.220	−314.548	14.937
1200	56.810	347.074	306.607	48.560	−297.101	−316.305	13.768
1300	57.007	351.629	309.897	54.251	−297.862	−317.875	12.772
1400	57.165	355.860	313.031	59.960	−298.677	−319.384	11.916
1500	57.294	359.808	316.019	65.683	−299.559	−320.833	11.172
1600	57.401	363.509	318.873	71.418	−300.518	−322.221	10.519
1700	57.490	366.992	321.602	77.163	−301.566	−323.545	9.941
1800	57.565	370.280	324.216	82.916	−302.714	−324.806	9.426
1900	57.629	373.394	326.723	88.676	−303.975	−325.999	8.962
2000	57.684	376.352	329.131	94.441	−305.358	−327.123	8.544
2100	57.731	379.167	331.447	100.212	−306.876	−328.175	8.163
2200	57.772	381.854	333.678	105.987	−329.863	−328.404	7.797
2300	57.808	384.423	335.829	111.766	−332.098	−328.289	7.456
2400	57.840	386.884	337.905	117.549	−334.353	−328.075	7.140
2500	57.868	389.246	339.912	123.334	−336.626	−327.767	6.848
2600	57.893	391.516	341.853	129.122	−338.918	−327.367	6.577
2700	57.915	393.701	343.733	134.912	−341.229	−326.879	6.324
2800	57.935	395.808	345.556	140.705	−343.559	−326.305	6.087
2900	57.952	397.841	347.324	146.499	−345.906	−325.648	5.866
3000	57.969	399.806	349.041	152.295	−348.271	−324.908	5.657
3100	57.983	401.707	350.709	158.093	−350.653	−324.090	5.461
3200	57.997	403.548	352.332	163.892	−353.052	−323.196	5.276
3300	58.009	405.333	353.911	169.692	−355.466	−322.226	5.100
3400	58.020	407.065	355.449	175.494	−357.897	−321.181	4.934
3500	58.030	408.747	356.948	181.296	−360.342	−320.066	4.777
3600	58.039	410.382	358.409	187.100	−362.802	−318.881	4.627
3700	58.048	411.972	359.836	192.904	−365.276	−317.627	4.484
3800	58.056	413.520	361.228	198.709	−367.763	−316.305	4.348
3900	58.063	415.028	362.588	204.515	−370.263	−314.918	4.218
4000	58.070	416.498	363.918	210.322	−372.776	−313.468	4.093
4100	58.076	417.932	365.218	216.129	−375.301	−311.954	3.974
4200	58.082	419.332	366.490	221.937	−377.839	−310.378	3.860
4300	58.087	420.699	367.735	227.745	−380.388	−308.741	3.750
4400	58.092	422.034	368.954	233.554	−382.949	−307.046	3.645
4500	58.097	423.340	370.148	239.364	−385.521	−305.292	3.544
4600	58.102	424.617	371.318	245.174	−388.106	−303.481	3.446
4700	58.106	425.866	372.465	250.984	−390.702	−301.613	3.352
4800	58.110	427.090	373.591	256.795	−954.246	−288.073	3.135
4900	58.113	428.288	374.695	262.606	−956.519	−274.170	2.923
5000	58.117	429.462	375.778	268.418	−958.821	−260.221	2.719
5100	58.120	430.613	376.842	274.230	−961.152	−246.226	2.522
5200	58.123	431.741	377.887	280.042	−963.511	−232.186	2.332
5300	58.126	432.849	378.914	285.854	−965.897	−218.098	2.149
5400	58.129	433.935	379.923	291.667	−968.310	−203.967	1.973
5500	58.131	435.002	380.914	297.480	−970.749	−189.790	1.802
5600	58.134	436.049	381.890	303.293	−973.213	−175.568	1.638
5700	58.136	437.078	382.849	309.107	−975.703	−161.303	1.478
5800	58.138	438.089	383.793	314.920	−978.218	−146.992	1.324
5900	58.140	439.083	384.721	320.734	−980.757	−132.641	1.174
6000	58.142	440.060	385.636	326.548	−983.321	−118.243	1.029

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = 238.932\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 145.348 \pm 1.7\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 142.674 \pm 1.7\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
1110 (1)
705 (1)
1043 (1)

Ground State Quantum Weight: 1 $\sigma = 2$
Point Group: C_{2v}
Rotational Constants: $A_{000} = 3.55381\ cm^{-1}$ $B_{000} = 0.44530\ cm^{-1}$ $C_{000} = 0.39477\ cm^{-1}$
Anharmonicity Constants: $X_{11} = -3.8\ cm^{-1}$ $X_{33} = -4.0\ cm^{-1}$ $X_{23} = -3.5\ cm^{-1}$
$X_{22} = -3.5\ cm^{-1}$ $X_{12} = -2.0\ cm^{-1}$ $X_{31} = -9.0\ cm^{-1}$

Enthalpy of Formation

Gunther *et al.*[1] measured ΔE for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in a calorimeter calibrated by means of the reaction $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$ and found the ratio of the ΔE values for these reactions to be 0.5077 ± 0.0024. The temperature of the experiments is not reported and is assumed to have been 18 °C. From the above ratio, $\Delta_f H°(298.15\ K)$ is calculated to be 33.89 ± 0.36 $cal \cdot mol^{-1}$. Kailan and Jahn[2] measured $\Delta_r H°$ at an unspecified temperature for the reaction $O_3(g) \rightarrow 3/2\ O_2(g)$ in an electrically calibrated calorimeter. If the temperature of the experiments is assumed to have been 18 °C and the current joule–calorie conversion factor is used, $\Delta_f H°(298.15\ K)$ is found to be 34.3 ± 0.6 $kcal \cdot mol^{-1}$. Variability in the O_3 content of the feed gas is allowed for in the uncertainty. The value adopted here is 34.1 ± 0.4 $kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Gordon[3] has calculated the thermodynamic functions from 298.15 to 6000 K by the method of Pennington and Kobe[4] which takes vibration–rotation interaction and anharmonicity into account. Gordon's data are from Pierce.[5] The functions below 298.15 K have been calculated for a rigidly rotating harmonic oscillator.

References

[1]P. Gunther, E. Wassmuth and L. A. Schryver, Z. Phys. Chem. **158**, 297 (1932).
[2]A. Kailan and S. Jahn, Z. Anorg. Chem. **68**, 243 (1910).
[3]J. S. Gordon, Thiokol Chemical Corp., personal communication, (April 1961).
[4]R. E. Pennington and K. A. Kobe, J. Chem. Phys. **22**, 1442 (1954).
[5]L. Pierce, J. Chem. Phys. **24**, 139 (1956).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−10.351	145.348	145.348	INFINITE
100	33.292	200.791	271.040	−7.025	144.318	150.235	−78.474
200	35.058	224.221	242.401	−3.636	143.340	156.541	−40.884
298.15	39.238	238.932	238.932	0.000	142.674	163.184	−28.589
300	39.330	239.175	238.933	0.073	142.665	163.311	−28.435
400	43.744	251.116	240.531	4.234	142.370	170.247	−22.232
500	47.262	261.272	243.688	8.792	142.340	177.224	−18.514
600	49.857	270.129	247.373	13.654	142.462	184.191	−16.035
700	51.752	277.963	251.194	18.738	142.665	191.130	−14.262
800	53.154	284.969	254.986	23.986	142.907	198.037	−12.931
900	54.208	291.292	258.674	29.356	143.169	204.913	−11.893
1000	55.024	297.048	262.228	34.819	143.439	211.759	−11.061
1100	55.660	302.323	265.637	40.355	143.711	218.578	−10.379
1200	56.174	307.189	268.899	45.947	143.980	225.372	−9.810
1300	56.593	311.702	272.020	51.586	144.245	232.144	−9.328
1400	56.948	315.909	275.007	57.264	144.502	238.896	−8.913
1500	57.245	319.849	277.866	62.974	144.750	245.629	−8.554
1600	57.501	323.551	280.607	68.711	144.987	252.347	−8.238
1700	57.722	327.044	283.237	74.473	145.211	259.050	−7.960
1800	57.919	330.349	285.763	80.255	145.419	265.740	−7.712
1900	58.095	333.485	288.193	86.056	145.611	272.419	−7.489
2000	58.250	336.469	290.533	91.873	145.784	279.089	−7.289
2100	58.396	339.315	292.789	97.705	145.938	285.750	−7.108
2200	58.526	342.035	294.966	103.552	146.072	292.406	−6.943
2300	58.647	344.639	297.069	109.410	146.185	299.054	−6.792
2400	58.764	347.137	299.104	115.281	146.276	305.698	−6.653
2500	58.869	349.538	301.073	121.163	146.346	312.339	−6.526
2600	58.969	351.849	302.982	127.055	146.393	318.978	−6.408
2700	59.066	354.077	304.833	132.956	146.419	325.616	−6.299
2800	59.158	356.226	306.631	138.868	146.424	332.253	−6.198
2900	59.245	358.304	308.377	144.788	146.408	338.889	−6.104
3000	59.329	360.314	310.075	150.716	146.371	345.527	−6.016
3100	59.409	362.260	311.727	156.653	146.314	352.167	−5.934
3200	59.488	364.148	313.336	162.598	146.238	358.808	−5.857
3300	59.563	365.980	314.904	168.551	146.144	365.451	−5.785
3400	59.639	367.759	316.432	174.511	146.033	372.100	−5.717
3500	59.714	369.489	317.923	180.479	145.905	378.750	−5.653
3600	59.781	371.172	319.379	186.453	145.761	385.405	−5.592
3700	59.852	372.811	320.801	192.435	145.601	392.063	−5.535
3800	59.919	374.408	322.191	198.424	145.427	398.728	−5.481
3900	59.986	375.965	323.550	204.419	145.239	405.396	−5.430
4000	60.053	377.485	324.879	210.421	145.038	412.069	−5.381
4100	60.120	378.968	326.181	216.429	144.823	418.747	−5.335
4200	60.183	380.418	327.455	222.445	144.597	425.431	−5.291
4300	60.245	381.835	328.703	228.466	144.358	432.121	−5.249
4400	60.308	383.220	329.926	234.494	144.106	438.815	−5.209
4500	60.371	384.576	331.126	240.528	143.844	445.516	−5.171
4600	60.434	385.904	332.302	246.568	143.568	452.222	−5.135
4700	60.492	387.204	333.457	252.614	143.281	458.935	−5.100
4800	60.555	388.479	334.590	258.667	142.981	465.655	−5.067
4900	60.614	389.728	335.702	264.725	142.667	472.381	−5.036
5000	60.672	390.953	336.795	270.789	142.340	479.113	−5.005
5100	60.731	392.155	337.869	276.859	141.999	485.853	−4.976
5200	60.789	393.335	338.924	282.935	141.643	492.597	−4.948
5300	60.848	394.493	339.962	289.017	141.270	499.351	−4.921
5400	60.906	395.631	340.982	295.105	140.880	506.110	−4.896
5500	60.965	396.749	341.986	301.199	140.472	512.876	−4.871
5600	61.024	397.848	342.974	307.298	140.045	519.653	−4.847
5700	61.078	398.929	343.946	313.403	139.596	526.434	−4.824
5800	61.137	399.992	344.903	319.514	139.126	533.226	−4.802
5900	61.191	401.037	345.846	325.630	138.631	540.023	−4.781
6000	61.250	402.066	346.774	331.752	138.111	546.832	−4.761

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$\Delta_f H°(0\ K) = -1138.091 \pm 4.2\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 109.927 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1144.993 \pm 4.2\ kJ \cdot mol^{-1}$

$T_{fus} = 1037\ K$

Enthalpy of Formation

The enthalpy of the reaction PbO(red) + SiO_2(cr) → $PbSiO_3$(cr) was reported by Kelley.[1] This value for the enthalpy of reaction of the oxides has been converted to the enthalpy of formation using JANAF auxiliary data.[4] The above $\Delta_f H°(298.15\ K) = 3.75 \pm 0.12\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

In the low temperature region (53,25–298.15 K) the $C_p°$ values are those determined by King.[2] Above 298.15 $C_p°$ values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.25 K using the Debye and Einstein functions D(140/T) + E(213/T) + 2E(596/T) + E(1440/T) given by King.[2] $S°(53.25\ K) = 3.662\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was taken from Geller *et al.*[3]

References

[1]K. K. Kelley, U. S. Bur. Mines RI 5901, (1962).
[2]E. G. King, J. Amer. Chem. Soc. **81**, 799–800 (1959).
[3]Geller, Creamer and Bunting, J. Res. Nat. Bur. Stand. **13**, 237 (1934).
[4]JANAF Thermochemical Tables: PbO(cr, red), 3–31–62; SiO_2(cr), 12–31–62.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.000	0.000	INFINITE	−16.219	−1138.091	−1138.091	INFINITE
100	44.683	37.168	177.245	−14.008	−1142.269	−1115.924	582.899
200	72.562	77.500	117.638	−8.028	−1144.359	−1088.626	284.320
298.15	90.040	109.927	109.927	0.000	−1144.993	−1061.094	185.899
300	90.333	110.485	109.929	0.167	−1144.995	−1060.574	184.662
400	102.843	138.266	113.631	9.854	−1144.615	−1032.467	134.826
500	111.964	162.238	121.011	20.614	−1143.535	−1004.544	104.944
600	118.742	183.282	129.672	32.166	−1141.987	−976.885	85.045
700	123.428	201.958	138.690	44.288	−1145.017	−948.711	70.794
800	126.566	218.655	147.661	56.795	−1143.041	−920.801	60.122
900	128.784	233.697	156.399	69.568	−1140.924	−893.146	51.837
1000	130.332	247.349	164.822	82.527	−1138.724	−865.733	45.221
1100	131.545	259.829	172.900	95.622	−1136.473	−838.542	39.819
1200	132.591	271.321	180.629	108.831	−1134.180	−811.559	35.326
1300	133.428	281.967	188.020	122.132	−1131.864	−784.767	31.532
1400	134.223	291.884	195.089	135.514	−1129.547	−758.154	28.287
1500	135.018	301.173	201.854	148.978	−1127.234	−731.708	25.480
1600	135.645	309.907	208.338	162.512	−1124.940	−705.414	23.029
1700	136.189	318.147	214.557	176.103	−1172.856	−678.816	20.857
1800	136.775	325.949	220.530	189.753	−1170.401	−649.826	18.857
1900	137.152	333.354	226.275	203.450	−1167.953	−620.972	17.072
2000	137.444	340.397	231.807	217.180	−1165.526	−592.246	15.468

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 256.769\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -390.025 \pm 0.71\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -395.765 \pm 0.71\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
1068 (1)
495 (1)
1391 (2)
529 (2)

Ground State Quantum Weight: 1 $\sigma = 6$
Point Group: D_{3h}
Bond Distance: S–O = 1.43 Å
Bond Angle: O–S–O = 120°
Product of the Moments of Inertia: $I_A I_B I_C = 1.0824273 \times 10^{-114}\ g^3·cm^6$

Enthalpy of Formation

The enthalpy of formation is calculated from the reaction $SO_2 + 1/2\ O_2 \rightarrow SO_3$ for which three sets of equilibrium constants are available. A summary of the 2nd and 3rd law treatment of the data is given below.

Source	T/K	Data Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
[1]	933– 945 K	5	−27.67 ± 2.7	−23.608	3.7 ± 2.9
[2]	801–1170 K	8	−23.45 ± 0.1	−23.661	−0.8 ± 0.1
[3]	850–1001 K	11	−22.74 ± 0.6	−23.614	−1.5 ± 0.6
*	801–1170 K	23*	−23.40 ± 0.2	−23.638	−0.9 ± 0.2

*Combination of above references with one point omitted due to failure of a statistical test.

The combined set was adopted though it appears that the three sets are not in excellent agreement, and the combination heavily favors reference 2. Although there is a definite trend in all the data, it cannot be considered definitive enough for use in the modification of the SO_3 functions.

Heat Capacity and Entropy

The bond length and angles are taken from the electron diffraction data of Palmer.[4] The vibrational frequencies are taken from the infrared studies of Lovejoy *et al.*[5] which are in excellent accord with those of Bent and Ladner[6] using different techniques. These values differ from the assignment used by Stockmayer *et al.*[7] in their analysis of the thermodynamic properties of SO_3.

The principal moments of inertia are: $I_A = I_B = 8.1493 \times 10^{-39}$ and $I_C = 16.2987 \times 10^{-39}\ g·cm^2$.

References

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[3] A. F. Kapustinsky and L. M. Shamovsky, Acta Physicochem. USSR **4**, 791 (1936).
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[5] R. W. Lovejoy, J. H. Colwell, D. F. Eggers and G. D. Halsey, J. Chem. Phys. **36**, 612 (1962).
[6] R. Bent and W. R. Ladner, Spectrochim. Acta **19**, 931 (1963).
[7] W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, J. Chem. Phys. **12**, 408 (1944).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−11.697	−390.025	−390.025	INFINITE
100	34.076	212.371	295.976	−8.361	−391.735	−385.724	201.481
200	42.336	238.259	261.145	−4.577	−393.960	−378.839	98.943
250	46.784	248.192	257.582	−2.348	−394.937	−374.943	78.340
298.15	50.661	256.769	256.769	0.	−395.765	−371.016	65.000
300	50.802	257.083	256.770	0.094	−395.794	−370.862	64.573
350	54.423	265.191	257.402	2.726	−396.543	−366.646	54.719
400	57.672	272.674	258.849	5.530	−399.412	−362.242	47.304
450	60.559	279.637	260.777	8.487	−400.656	−357.529	41.501
500	63.100	286.152	262.992	11.580	−401.878	−352.668	36.843
600	67.255	298.041	267.862	18.107	−403.675	−342.647	29.830
700	70.390	308.655	272.945	24.997	−405.014	−332.365	24.801
800	72.761	318.217	278.017	32.160	−406.068	−321.912	21.019
900	74.570	326.896	282.973	39.531	−460.062	−310.258	18.007
1000	75.968	334.828	287.768	47.060	−459.581	−293.639	15.338
1100	77.065	342.122	292.382	54.714	−459.063	−277.069	13.157
1200	77.937	348.866	296.811	62.466	−458.521	−260.548	11.341
1300	78.639	355.133	301.060	70.296	−457.968	−244.073	9.807
1400	79.212	360.983	305.133	78.189	−457.413	−227.640	8.493
1500	79.685	366.465	309.041	86.135	−456.863	−211.247	7.356
1600	80.079	371.620	312.793	94.124	−456.323	−194.890	6.363
1700	80.410	376.485	316.398	102.149	−455.798	−178.567	5.487
1800	80.692	381.090	319.865	110.204	−455.293	−162.274	4.709
1900	80.932	385.459	323.203	118.286	−454.810	−146.009	4.014
2000	81.140	389.616	326.421	126.390	−454.351	−129.768	3.389
2100	81.319	393.579	329.525	134.513	−453.919	−113.549	2.824
2200	81.476	397.366	332.523	142.653	−453.514	−97.350	2.311
2300	81.614	400.990	335.422	150.807	−453.137	−81.170	1.843
2400	81.735	404.466	338.227	158.975	−452.790	−65.006	1.415
2500	81.843	407.805	340.944	167.154	−452.472	−48.855	1.021
2600	81.939	411.017	343.578	175.343	−452.183	−32.716	0.657
2700	82.025	414.111	346.133	183.541	−451.922	−16.587	0.321
2800	82.102	417.096	348.614	191.748	−451.690	−0.467	0.009
2900	82.171	419.978	351.026	199.961	−451.487	15.643	−0.282
3000	82.234	422.765	353.371	208.182	−451.311	31.748	−0.553
3100	82.290	425.462	355.653	216.408	−451.161	47.849	−0.806
3200	82.342	428.076	357.876	224.640	−451.038	63.943	−1.044
3300	82.389	430.610	360.042	232.876	−450.940	80.034	−1.267
3400	82.432	433.070	362.153	241.117	−450.866	96.124	−1.477
3500	82.472	435.460	364.214	249.363	−450.817	112.210	−1.675
3600	82.508	437.784	366.225	257.612	−450.792	128.297	−1.862
3700	82.542	440.045	368.190	265.864	−450.789	144.382	−2.038
3800	82.573	442.247	370.110	274.120	−450.809	160.469	−2.206
3900	82.601	444.392	371.987	282.379	−450.850	176.556	−2.365
4000	82.628	446.484	373.824	290.640	−450.914	192.643	−2.516
4100	82.653	448.524	375.621	298.904	−450.999	208.733	−2.659
4200	82.676	450.516	377.381	307.171	−451.105	224.825	−2.796
4300	82.697	452.462	379.104	315.439	−451.234	240.921	−2.927
4400	82.717	454.364	380.793	323.710	−451.383	257.019	−3.051
4500	82.735	456.223	382.449	331.983	−451.555	273.120	−3.170
4600	82.753	458.041	384.072	340.257	−451.749	289.225	−3.284
4700	82.769	459.821	385.665	348.533	−451.965	305.336	−3.393
4800	82.785	461.564	387.228	356.811	−452.205	321.452	−3.498
4900	82.799	463.271	388.763	365.090	−452.469	337.573	−3.599
5000	82.813	464.944	390.270	373.371	−452.757	353.700	−3.695
5100	82.825	466.584	391.750	381.653	−453.071	369.832	−3.788
5200	82.837	468.192	393.205	389.936	−453.412	385.969	−3.877
5300	82.849	469.770	394.634	398.220	−453.780	402.116	−3.963
5400	82.860	471.319	396.040	406.505	−454.178	418.268	−4.046
5500	82.870	472.840	397.423	414.792	−454.605	434.427	−4.126
5600	82.879	474.333	398.783	423.079	−455.065	450.597	−4.203
5700	82.889	475.800	400.121	431.368	−455.557	466.773	−4.277
5800	82.897	477.242	401.439	439.657	−456.084	482.960	−4.350
5900	82.906	478.659	402.735	447.947	−456.647	499.153	−4.419
6000	82.913	480.052	404.012	456.238	−457.248	515.359	−4.487

PREVIOUS: September 1965 (1 atm) CURRENT: September 1965 (1 bar)

$S°(298.15\ K) = 77.253 \pm 0.21\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 470 \pm 20\ K$
$T_{fus} = 2115 \pm 10\ K$

$\Delta_f H°(0\ K) = -1512.287 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1520.884 \pm 8.4\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.138\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [105]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Humphrey[1] measured $\Delta_f H°(298.15\ K) = -88.11 \pm 0.1\ kcal \cdot mol^{-1}$ for the reaction $Ti_2O_3(cr) + 0.5\ O_2(g) = 2\ TiO_2$(rutile) using bomb calorimetry. When combined with $\Delta_f H°(298.15\ K) = -225.8\ kcal \cdot mol^{-1}$ for rutile, this yields $-363.5 \pm 2\ kcal \cdot mol^{-1}$ as the adopted $\Delta_f H°(298.15\ K)$ for Ti_2O_3. The less negative value of $-362.8 \pm 0.8\ kcal \cdot mol^{-1}$ was obtained by Ariya *et al.*[2] from their heats of combustion of various compositions in the Ti–O system. Ariya *et al.*[2] used an estimated correction for the formation of TiO_{2-x}, while Humphrey[1] obtained values of 0.1 to 1.3 $kcal \cdot mol^{-1}$ by grinding the product and reburning it with while oil. Most of the assigned uncertainty arises from this problem [see TiO_2(rutile) for further details].

Heat Capacity and Entropy

$C_p°$ is based on data of Sjostrand and Keesom, (0.4–20 K)[3] and Paukov and Berezovskii, (12–305 K).[4] The two sets of data disagree in the region of overlap. Paukov[4] appears to have a positive bias at the lowest temperatures (12–18 K), so we adopt a curve which shifts gradually from Sjostrand at 10 K to Paukov at 30 K. Deviations of Paukov[4] from the adopted $C_p°$ are +36% (12 K) and +3% (20 K). Earlier data of Shomate, (53–296 K)[5] deviate by +0.6% to +4.1% with extreme deviations of 3.0% at 53 K and 2.9 to 4.1% in a "hump" observed by Shomate near 240 K. No hump was found by Paukov. $S°$ is derived from $C_p°$ based on an extrapolation which is negligible.

$C_p°$ between 298 K and 470 K is a smooth extrapolation of the low temperature curve using the approximate shape found by Barros *et al.*,[6] (150–700 K) via differential scanning calorimetry (Perkin–Elmer DSC–1B). The DSC data[6] have a positive bias of ~10%, over twice as large as we might expect for this apparatus so the results do not help establish $C_p°$ between 298 K and T_{trs}. Data measured by a conduction type calorimeter, (323–523 K)[7] have a large negative bias near 400 K. Drop–calorimetric data, (375–472 K)[8] deviate from the adopted enthalpies by +5 to +2%.

$C_p°$ above the λ–transition is derived from enthalpy data, (487–1750 K)[8] by fitting only the region above 549 K. Maximum deviations from the adopted cruve are ±0.4% in the fitted region and +0.9% at 526 K. Enthalpy data (493–1082 K) reported graphically by Erofeeva *et al.*[9] deviate by about −6 to −2%.

Slyusar *et al.*[15] recently reported new enthalpy data for Ti_2O_3, Ti_3O_5, Ti_4O_7 and TiO_2. The new data for Ti_3O_5 and $TiO_2$are in reasonable agreement with existing JANAF Tables,[16] but those for Ti_2O_3 cross the adopted values near 1100 K and deviate by $-4.5 \pm 1\%$ (672–878 K) and $+3.4 \pm 1.1\%$ (1158–2027 K). The transition vanishes for Ti_2O_3 samples doped with 4% V_2O_3[6] and may be affected by other impurities or non stoichiometry. We feel that Slyusar *et al.*[15] have not characterized their sample adequately. We tentatively reject their data pending new measurements on a well characterized sample.

Transition Data

We arbitrarily choose $T_{trs} = 470 \pm 20$ K and derive $\Delta_{trs} H°$ as the difference between the adopted enthalpy curves at that temperature. Reported values of $\Delta_{trs} H°$ include 0.380 ± 0.025[6], 0.036[7] and 0.215 $kcal \cdot mol^{-1}$;[8] each derives from different data and difference base lines.

Convenience dictates that we treat the electrical transition as first order although recent $C_p°$ data[6] suggest a gradual λ–type anomaly peaking near 470 K and extending from about 380 to 560 K. There is no change in the corundum type symmetry, but the lattice parameters shift rapidly in this temperature range.[10, 11] Honig[11] summarized evidence on the nature of the change from semiconductor to semimetal and noted that the transition can be explained without invoking antiferromagnetic ordering. Recent studies[6, 12, 14] are consistent with this interpretation.

Fusion Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−14.088	−1512.287	−1512.287	INFINITE
100	26.175	11.058	143.900	−13.284	−1516.961	−1490.419	778.515
200	70.793	43.832	85.316	−8.297	−1520.175	−1462.405	381.941
298.15	95.814	77.253	77.253	0.000	−1520.884	−1433.829	251.201
300	96.190	77.847	77.255	0.178	−1520.881	−1433.288	249.558
400	117.529	108.277	81.264	10.805	−1519.938	−1404.187	183.368
470.010	141.716	128.963	86.822	19.807	ALPHA <--> BETA		
470.010	127.653	131.384	86.822	20.945	TRANSITION		
500	130.248	139.362	89.735	24.813	−1515.999	−1375.626	143.711
600	136.440	163.704	100.081	38.174	−1513.028	−1347.825	117.339
700	140.331	185.051	110.727	52.027	−1509.833	−1320.542	98.540
800	142.967	203.971	121.223	66.199	−1506.516	−1293.726	84.472
900	144.892	220.928	131.375	80.597	−1503.208	−1267.327	73.554
1000	146.356	236.272	141.110	95.162	−1500.078	−1241.288	64.838
1100	147.528	250.277	150.407	109.858	−1497.276	−1215.547	57.722
1200	148.532	263.158	159.273	124.662	−1502.785	−1189.806	51.791
1300	149.369	275.081	167.729	139.558	−1499.224	−1163.870	46.765
1400	150.080	286.177	175.798	154.531	−1495.789	−1138.203	42.467
1500	150.750	296.554	183.506	169.573	−1492.509	−1112.777	38.750
1600	151.377	306.304	190.879	184.680	−1489.413	−1087.564	35.505
1700	151.921	315.497	197.942	199.845	−1486.531	−1062.538	32.648
1800	152.465	324.197	204.716	215.065	−1483.892	−1037.675	30.113
1900	152.925	332.452	211.224	230.334	−1481.528	−1012.950	27.848
2000	153.427	340.309	217.483	245.652	−1508.838	−987.436	25.789
2100	153.888	347.806	223.512	261.018	−1508.597	−961.372	23.913
2115.000	153.953	348.902	224.398	263.327	---- BETA <--> LIQUID		----
2200	154.306	354.975	229.326	276.427	−1508.348	−935.318	22.207
2300	154.766	361.844	234.939	291.881	−1508.087	−909.278	20.650
2400	155.185	368.440	240.365	307.379	−1507.817	−883.249	19.223
2500	155.603	374.783	245.616	322.919	−1507.537	−857.231	17.911
2600	155.980	380.894	250.702	338.497	−1507.250	−831.224	16.700
2700	156.398	386.788	255.634	354.117	−1506.954	−805.229	15.578
2800	156.774	392.483	260.420	369.775	−1506.649	−779.244	14.537
2900	157.151	397.991	265.070	385.471	−1506.337	−753.272	13.568
3000	157.569	403.325	269.590	401.207	−1506.015	−727.309	12.664

PREVIOUS: June 1967 CURRENT: June 1973

$S°(298.15\ K) = [127.126]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 2115 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [-1418.459]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [105]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ti_2O_3, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2115\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 7.5 $cal·K^{-1}$ g atom.[1] Below the assumed glass transition at 1400 K, $C_p°$ is taken from the crystal; the high temperature curve is extrapolated down to 298.15 K. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°(298.15\ K)$.

Fusion Data

T_{fus} is the value quoted by Wahlbeck and Gilles[1] based on work of K. D. Carlson. The adopted value is converted to IPTS–68. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ is 12 $cal·K^{-1}·mol^{-1}$ as observed[2] for Al_2O_3(α, corundum). Other reported melting points were summarized earlier.[3] Slyusar *et al.*[4] recently obtained T_{fus} = 2043 K in an enthalpy study, but we tentatively reject this work (see Ti_2O_3, crystal).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	94.851	127.126	127.126	0.000	−1418.459	−1346.273	235.861
300	95.521	127.714	127.127	0.176	−1418.458	−1345.825	234.329
400	119.118	158.902	131.219	11.073	−1417.245	−1321.744	172.602
500	130.248	186.808	139.609	23.600	−1414.787	−1298.137	135.615
600	136.440	211.151	149.550	36.961	−1411.816	−1275.081	111.006
700	140.331	232.498	159.907	50.814	−1408.621	−1252.543	93.466
800	142.967	251.418	170.186	64.986	−1405.305	−1230.471	80.342
900	144.892	268.374	180.170	79.384	−1401.996	−1208.817	70.158
1000	146.356	283.719	189.770	93.949	−1398.867	−1187.523	62.030
1100	147.528	297.724	198.956	108.644	−1396.065	−1166.527	55.394
1200	148.532	310.605	207.731	123.449	−1401.573	−1145.531	49.864
1300	149.369	322.528	216.109	138.345	−1398.013	−1124.339	45.177
1400	150.080	333.624	224.111	153.318	−1394.577	−1103.417	41.169
1400.000	150.080	333.624	224.111	153.318	GLASS <--> LIQUID		
1400.000	156.900	333.624	224.111	153.318	TRANSITION		
1500	156.900	344.449	231.777	169.008	−1390.649	−1082.759	37.705
1600	156.900	354.575	239.139	184.698	−1386.969	−1062.354	34.682
1700	156.900	364.087	246.212	200.388	−1383.562	−1042.171	32.022
1800	156.900	373.055	253.012	216.078	−1380.453	−1022.181	29.663
1900	156.900	381.538	259.555	231.768	−1377.668	−1002.355	27.557
2000	156.900	389.586	265.857	247.458	−1404.606	−981.758	25.641
2100	156.900	397.241	271.933	263.148	−1404.042	−960.630	23.894
2115.000	156.900	398.358	272.825	265.502	BETA <--> LIQUID		
2200	156.900	404.540	277.796	278.838	−1403.512	−939.527	22.307
2300	156.900	411.515	283.459	294.528	−1403.015	−918.449	20.859
2400	156.900	418.192	288.935	310.218	−1402.552	−897.391	19.531
2500	156.900	424.597	294.234	325.908	−1402.122	−876.351	18.310
2600	156.900	430.751	299.367	341.598	−1401.724	−855.329	17.184
2700	156.900	436.673	304.344	357.288	−1401.357	−834.320	16.141
2800	156.900	442.379	309.172	372.978	−1401.021	−813.324	15.173
2900	156.900	447.885	313.861	388.668	−1400.715	−792.342	14.272
3000	156.900	453.204	318.418	404.358	−1400.438	−771.368	13.431
3100	156.900	458.348	322.849	420.048	−1400.189	−750.402	12.644
3200	156.900	463.330	327.162	435.738	−1399.967	−729.446	11.907
3300	156.900	468.158	331.361	451.428	−1399.771	−708.496	11.215
3400	156.900	472.842	335.454	467.118	−1399.600	−687.550	10.563
3500	156.900	477.390	339.445	482.808	−1399.454	−666.610	9.949

PREVIOUS: June 1967 CURRENT: June 1973

0	to	470	K crystal, α
470	to	2115	K crystal, β
above		2115	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−14.088	−1512.287	−1512.287	INFINITE
100	26.175	11.058	143.900	−13.284	−1516.961	−1490.419	778.515
200	70.793	43.832	85.316	−8.297	−1520.175	−1462.405	381.941
298.15	95.814	77.253	77.253	0.000	−1520.884	−1433.829	251.201
300	96.190	77.847	77.255	0.178	−1520.881	−1433.288	249.558
400	117.529	108.277	81.264	10.805	−1519.938	−1404.187	183.368
470.010	141.716	128.963	86.822	19.807	ALPHA <--> BETA		
470.010	127.653	131.384	86.822	20.945	TRANSITION		
500	130.248	139.362	89.735	24.813	−1515.999	−1375.626	143.711
600	136.440	163.704	100.081	38.174	−1513.028	−1347.825	117.339
700	140.331	185.051	110.727	52.027	−1509.833	−1320.542	98.540
800	142.967	203.971	121.223	66.199	−1506.516	−1293.726	84.472
900	144.892	220.928	131.375	80.597	−1503.208	−1267.327	73.554
1000	146.356	236.272	141.110	95.162	−1500.078	−1241.288	64.838
1100	147.528	250.277	150.407	109.858	−1497.276	−1215.547	57.722
1200	148.532	263.158	159.273	124.662	−1502.785	−1189.806	51.791
1300	149.369	275.081	167.729	139.558	−1499.224	−1163.870	46.765
1400	150.080	286.177	175.798	154.531	−1495.789	−1138.203	42.467
1500	150.750	296.554	183.506	169.573	−1492.509	−1112.777	38.750
1600	151.377	306.304	190.879	184.680	−1489.413	−1087.564	35.505
1700	151.921	315.497	197.942	199.845	−1486.531	−1062.538	32.648
1800	152.465	324.197	204.716	215.065	−1483.892	−1037.675	30.113
1900	152.925	332.452	211.224	230.334	−1481.528	−1012.950	27.848
2000	153.427	340.309	217.483	245.652	−1508.838	−987.436	25.789
2100	153.888	347.806	223.512	261.018	−1508.597	−961.372	23.913
2115.000	153.953	348.902	224.398	263.327	BETA <--> LIQUID		
2115.000	156.900	398.358	224.398	367.927	TRANSITION		
2200	156.900	404.540	231.239	381.263	−1403.512	−939.527	22.307
2300	156.900	411.515	238.927	396.953	−1403.015	−918.449	20.859
2400	156.900	418.192	246.258	412.643	−1402.552	−897.391	19.531
2500	156.900	424.597	253.264	428.333	−1402.122	−876.351	18.310
2600	156.900	430.751	259.973	444.023	−1401.724	−855.329	17.184
2700	156.900	436.673	266.408	459.713	−1401.357	−834.320	16.141
2800	156.900	442.379	272.592	475.403	−1401.021	−813.324	15.173
2900	156.900	447.885	278.542	491.093	−1400.715	−792.342	14.272
3000	156.900	453.204	284.276	506.783	−1400.438	−771.368	13.431
3100	156.900	458.348	289.809	522.473	−1400.189	−750.402	12.644
3200	156.900	463.330	295.154	538.163	−1399.967	−729.446	11.907
3300	156.900	468.158	300.324	553.853	−1399.771	−708.496	11.215
3400	156.900	472.842	305.329	569.543	−1399.600	−687.550	10.563
3500	156.900	477.390	310.180	585.233	−1399.454	−666.610	9.949

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = 98.067 \pm 1.3\ J\cdot K^{-1}\cdot mol^{-1}$
$T_{trs} = 168.8 \pm 0.2\ K$
$T_{fus} = 2340 \pm 20\ K$

$\Delta_f H°(0\ K) = -1213.971 \pm 6.3\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -1218.799 \pm 6.3\ kJ\cdot mol^{-1}$
$\Delta_{trs} H° = 1.623\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = [117.152]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

The adopted enthalpies of formation for the vanadium oxides, and in particular V_2O_3(cr), are based on the combustion studies by Mah and Kelley.[1] The adopted value is $\Delta_f H°(V_2O_3, cr, 298.15\ K) = -291.3\ kcal\cdot mol^{-1}$ as reported by Mah and Kelley.[1] For more details refer to the V_2O_5(cr) table.[2] We assign an uncertainty limit of ± 1.5 $kcal\cdot mol^{-1}$.

Charlu and Kleppa[3] reported a enthalpy of formation value of − 291.0 ± 0.9 $kcal\cdot mol^{-1}$ for V_2O_3 based on oxidation studies to V_2O_5(cr) in a high temperature microcalorimeter. An advantage of this technique is that complete oxidation to V_2O_5(cr) was achieved whereas in the study by Mah and Kelley[1] a mixture of the two oxides V_2O_4 and V_2O_5 was obtained. Other combustion studies have been reported by Siemonsen and Ulich[4] and Vol'f and Ariya.[5] Additional enthalpy of formation values may be obtained from the sodium peroxide fusion studies by Mixter[6] and Ruff and Friedrich[7] and the following equilibrium studies involving vanadium and its oxides: H_2O/H_2 by Kobayashi,[8] Muller,[9] and Karasev, Polyakov and Samarin;[10] and CO/CO_2 by Spencer and Justice.[11] As an example, the study by Spencer and Justice[11] leads to $\Delta_f H°(298.15\ K) = -287.9\ kcal\cdot mol^{-1}$ for V_2O_3(cr). The analysis, based on data in the range 1024–1169 K, indicates a third law drift of $-0.96 \pm 0.43\ cal\cdot K^{-1}\cdot mol^{-1}$.

Heat Capacity and Entropy

Anderson[12] measured the heat capacity of V_2O_3(cr) in the range 57–287 K. The data indicated an anomaly in the region 165–182 K. These heat capacity data are joined smoothly at 298 K with the high temperature heat capacity values as derived from the enthalpy measurements of Cook.[13] The adopted $C_p°$ values are based on these two studies.[12,13] Using the combination of Debye and Einstein functions as suggested by Anderson,[12] we calculate $S°(50\ K) = 0.783\ cal\cdot K^{-1}\cdot mol^{-1}$ and $H°(50;0) = 0.0284\ kcal\cdot mol^{-1}$. There is considerable scatter in the data of Cook;[13] the deviations from the adopted values range from −0.8 to 0.6% except for the data point at 369.1 K which is −1.4% low (~25 $cal\cdot K^{-1}\cdot mol^{-1}$).

Khlyustov *et al.*[14] measured the heat capacity of V_2O_3 in the region 120–190 K. For $T < T_{trs}$, this latter study lies above the Anderson data by ~7% while for $T > T_{trs}$, it is 10% higher. Three other studies examined the heat capacity in the range 343–573 K.[15,16,17] These latter three studies indicated irregularities in the $C_p°$ values in the region of investigation. We do not adopt these works, pending further independent verification.

Phase Data

A review of the literature of the V–O system by Stringer[18] stated that V_2O_3 has a homogeneity range of roughly $VO_{1.44}$ to $VO_{1.65}$. On cooling V_2O_3(cr) through T_{trs}, the crystal undergoes a structural distortion from hexagonal corundum to monoclinic. Numerous references as to the homogeneity range and crystal structure are contained, for example, in the reviews by Stringer[18] and Adler[19] as well as in the x–ray study by Minomura and Nagasaki.[20]

Transition Data

The heat capacity data of Anderson[12] indicated an anomaly at 168.8 K. The anomaly appeared similar to a λ–type transition and a smooth curve is easily drawn joining the heat capacity data on either side of the transition. Anderson[12] made five measurements to determine the energy necessary to heat V_2O_3(cr) through the transition. The mean enthalpy of the five measurements from 161.3 to 180.0 K was reported as 692.2 ± 2.4 $cal\cdot K^{-1}\cdot mol^{-1}$. Subtracting the calculated base heat in this same region, we calculate $\Delta_{trs} H° = 0.388\ kcal\cdot mol^{-1}$. We adopt $T_{trs} = 168.8$ K and $\Delta_{trs} H° = 0.388\ kcal\cdot mol^{-1}$, and consider it to be first order.

Khlyustov *et al.*[14] reported heat capacity data in the region 123–184 K and reported a transition which resembled a type with a maximum at 165.66 K with $\Delta_{trs} H° = 0.356\ kcal\cdot mol^{-1}$. Although both heat capacity studies[12,14] appeared to indicate a second order transition, Minomura and Nagasaki[20] determined through x–ray measurements that V_2O_3(cr) undergoes a discontinuous volume contraction (~3%) at T_{trs}, indicative of a first order transition. Austin[21] and Feinlieb and Paul[22] studied the pressure dependence of T_{trs} and reported $(dT_{trs}/dP)_{trs}$ values. Using the Clausius Clapeyron equation for a first order transition with Δ_{vap} from Minomura and Nagasaki,[20] we calculate $\Delta_{trs} H° = 0.863$ and 1.020 $kcal\cdot mol^{-1}$, respectively. The calorimetric value for $\Delta_{trs} H°$ is more reliable than these latter two determinations. For further information on this transition, the review by Adler[19] is suggested. There are indications of possible transitional behavior above room temperature.[15,16,17,19] We adopt only regular behavior above 298.15 K.

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The experimental evidence indicated that, although V_2O_3(cr) sublimes congruently, the vapors do not contain V_2O_3(g).[23]

Continued on page 1815

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−17.476	−1213.971	−1213.971	INFINITE
100	28.627	14.163	179.288	−16.512	−1218.342	−1192.325	622.807
168.800	63.053	38.652	116.725	−13.179	I <--> II TRANSITION		
168.800	63.136	48.269	116.725	−11.555			
200	80.107	60.767	107.019	−9.250	−1219.118	−1165.403	304.372
298.15	104.963	98.067	98.067	0.000	−1218.799	−1139.036	199.554
300	105.260	98.717	98.069	0.194	−1218.779	−1138.542	198.238
400	117.540	130.898	102.373	11.410	−1217.149	−1112.018	145.215
500	123.750	157.887	110.854	23.516	−1214.951	−1085.983	113.452
600	127.326	180.791	120.651	36.084	−1212.566	−1060.412	92.317
700	130.071	200.631	130.691	48.958	−1210.125	−1035.245	77.251
800	132.639	218.168	140.550	62.094	−1207.662	−1010.430	65.974
900	135.246	233.940	150.065	75.488	−1205.180	−985.925	57.222
1000	137.957	248.329	159.182	89.147	−1202.658	−961.698	50.234
1100	140.786	261.609	167.897	103.083	−1200.079	−937.726	44.529
1200	143.718	273.984	176.228	117.307	−1197.445	−913.992	39.785
1300	146.741	285.607	184.199	131.830	−1194.750	−890.480	35.780
1400	149.841	296.594	191.839	146.658	−1191.997	−867.177	32.355
1500	153.005	307.040	199.173	161.800	−1189.178	−844.074	29.393
1600	156.221	317.017	206.229	177.261	−1186.283	−821.161	26.808
1700	159.481	326.585	213.029	193.045	−1183.324	−798.431	24.533
1800	162.782	335.794	219.595	209.158	−1180.305	−775.877	22.515
1900	166.112	344.684	225.946	225.603	−1177.243	−753.492	20.715
2000	169.468	353.290	232.099	242.382	−1174.151	−731.269	19.099
2100	172.847	361.640	238.070	259.497	−1171.047	−709.202	17.640
2200	176.246	369.759	243.872	276.952	−1213.709	−687.072	16.313
2300	179.655	377.669	249.518	294.747	−1210.901	−663.196	15.062
2340.000	181.021	380.778	251.736	301.960	----- II <--> LIQUID -----		
2400	183.086	385.388	255.019	312.884	−1207.784	−639.449	13.917
2500	186.526	392.931	260.386	331.364	−1204.357	−615.837	12.867
2600	189.978	400.314	265.626	350.189	−1200.617	−592.369	11.901
2700	193.437	407.549	270.749	369.360	−1196.563	−569.051	11.009
2800	196.907	414.646	275.762	388.877	−1192.193	−545.888	10.184

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [152.250]\ J·K^{-1}·mol^{-1}$ $\delta_f H°(298.15\ K) = [-1093.054]\ kJ·mol^{-1}$

$T_{fus} = 2340 \pm 20\ K$ $\Delta_{fus}H° = [117.152]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(V_2O_3, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2340\ K)–H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

$C_p°$ for the liquid phase is estimated to be a constant 7.5 $cal·K^{-1}$ g atom.[1] Below the assumed glass transition temperature at 1600 K, $C_p°$ is taken from the crystal. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

$T_{fus} = 2340 \pm 20$ K is the value extracted from the V–O phase diagram proposed by Stringer.[1] This value is adopted and corrected to IPTS–68. $\Delta_{fus}H°$ is estimated such that $\Delta_{fus}S°$ is 12 $cal·K^{-1}·mol^{-1}$ as observed[2] for Al_2O_3(α, corundum).

Vaporization Data

There is no evidence as to the existence of V_2O_3(g) and thus we do not report any heat of vaporization. See VO(g) and VO_2(g) tables for more information.[2]

References

[1]J. Stringer, J. Less Common Metals **8**, 1 (1965).
[2]JANAF Thermochemical Tables: Al_2O_3(cr, α), 6–30–72; VO(g) and VO_2(g), 12–31–73.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	104.964	152.250	152.250	0.000	−1093.054	−1029.446	180.355
300	105.260	152.900	152.252	0.194	−1093.033	−1029.051	179.174
400	117.540	185.081	156.556	11.410	−1091.403	−1007.946	131.624
500	123.750	212.069	165.037	23.516	−1089.206	−987.329	103.146
600	127.326	234.974	174.833	36.084	−1086.821	−967.176	84.200
700	130.071	254.813	184.873	48.958	−1084.380	−947.427	70.698
800	132.639	272.350	194.733	62.094	−1081.917	−928.031	60.594
900	135.246	288.123	204.247	75.488	−1079.435	−908.944	52.754
1000	137.957	302.511	213.365	89.147	−1076.912	−890.135	46.496
1100	140.786	315.792	222.080	103.083	−1074.334	−871.582	41.388
1200	143.718	328.167	230.411	117.307	−1071.700	−853.265	37.142
1300	146.741	339.789	238.382	131.830	−1069.004	−835.172	33.558
1400	149.841	350.777	246.021	146.658	−1066.252	−817.287	30.493
1500	152.464	361.210	253.356	161.782	−1063.451	−799.602	27.845
1600	157.846	371.198	260.410	177.261	−1060.537	−782.105	25.533
1600.000	157.846	371.198	260.410	177.261	GLASS <--> LIQUID		
1600.000	156.900	371.198	260.410	177.261	TRANSITION		
1700	156.900	380.710	267.210	192.951	−1057.674	−764.793	23.499
1800	156.900	389.678	273.767	208.641	−1055.077	−747.641	21.696
1900	156.900	398.162	280.093	224.331	−1052.770	−730.625	20.086
2000	156.900	406.209	286.199	240.021	−1050.767	−713.723	18.641
2100	156.900	413.865	292.098	255.711	−1049.088	−696.914	17.335
2200	156.900	421.164	297.800	271.401	−1093.514	−679.966	16.144
2300	156.900	428.138	303.316	287.091	−1092.811	−661.185	15.016
2340.000	156.900	430.843	305.473	293.367	II <--> LIQUID		
2400	156.900	434.816	308.657	302.781	−1092.141	−642.434	13.982
2500	156.900	441.221	313.832	318.471	−1091.505	−623.709	13.032
2600	156.900	447.374	318.851	334.161	−1090.900	−605.009	12.155
2700	156.900	453.296	323.722	349.851	−1090.326	−586.332	11.343
2800	156.900	459.002	328.452	365.541	−1089.784	−567.675	10.590
2900	156.900	464.508	333.049	381.231	−1089.271	−549.038	9.889
3000	156.900	469.827	337.520	396.921	−1088.787	−530.417	9.235
3100	156.900	474.972	341.871	412.611	−1088.332	−511.812	8.624
3200	156.900	479.953	346.109	428.301	−1087.903	−493.223	8.051
3300	156.900	484.781	350.238	443.991	−1087.500	−474.646	7.513
3400	156.900	489.465	354.265	459.681	−1087.123	−456.079	7.007
3500	156.900	494.013	358.193	475.371	−1086.769	−437.525	6.530
3600	156.900	498.433	362.027	491.061	−1086.439	−418.979	6.079
3700	156.900	502.732	365.772	506.751	−1979.745	−398.042	5.619
3800	156.900	506.916	369.432	522.441	−1976.085	−355.342	4.885
3900	156.900	510.992	373.010	538.131	−1972.548	−312.736	4.189
4000	156.900	514.964	376.509	553.821	−1969.135	−270.222	3.529

PREVIOUS: CURRENT: December 1973

0	to	168.8	K crystal, I
168.8	to	2340	K crystal, II
above		2340	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.000	0.000	INFINITE	−17.476	−1213.971	−1213.971	INFINITE
100	28.627	14.163	179.288	−16.512	−1218.342	−1192.325	622.807
168.800	63.053	38.652	116.725	−13.179	I <--> II		
168.800	63.136	48.269	116.725	−11.555	TRANSITION		
200	80.107	60.767	107.019	−9.250	−1219.118	−1165.403	304.372
298.15	104.963	98.067	98.067	0.000	−1218.799	−1139.036	199.554
300	105.260	98.717	98.069	0.194	−1218.779	−1138.542	198.238
400	117.540	130.898	102.373	11.410	−1217.149	−1112.018	145.215
500	123.750	157.887	110.854	23.516	−1214.951	−1085.983	113.452
600	127.326	180.791	120.651	36.084	−1212.566	−1060.412	92.317
700	130.071	200.631	130.691	48.958	−1210.125	−1035.245	77.251
800	132.639	218.168	140.550	62.094	−1207.662	−1010.430	65.974
900	135.246	233.940	150.065	75.488	−1205.180	−985.925	57.222
1000	137.957	248.329	159.182	89.147	−1202.658	−961.698	50.234
1100	140.786	261.609	167.897	103.083	−1200.079	−937.726	44.529
1200	143.718	273.984	176.228	117.307	−1197.445	−913.992	39.785
1300	146.741	285.607	184.199	131.830	−1194.750	−890.480	35.780
1400	149.841	296.594	191.839	146.658	−1191.997	−867.177	32.355
1500	153.005	307.040	199.173	161.800	−1189.178	−844.074	29.393
1600	156.221	317.017	206.229	177.261	−1186.283	−821.161	26.808
1700	159.481	326.585	213.029	193.045	−1183.324	−798.431	24.533
1800	162.782	335.794	219.595	209.158	−1180.305	−775.877	22.515
1900	166.112	344.684	225.946	225.603	−1177.243	−753.492	20.715
2000	169.468	353.290	232.099	242.382	−1174.151	−731.269	19.099
2100	172.847	361.640	238.070	259.497	−1171.047	−709.202	17.640
2200	176.246	369.759	243.872	276.952	−1213.709	−687.072	16.313
2300	179.655	377.669	249.518	294.747	−1210.901	−663.196	15.062
2340.000	181.021	380.778	251.736	301.960	II <--> LIQUID		
2340.000	156.900	430.843	251.736	419.112	TRANSITION		
2400	156.900	434.816	256.263	428.526	−1092.141	−642.434	13.982
2500	156.900	441.221	263.534	444.216	−1091.505	−623.709	13.032
2600	156.900	447.374	270.487	459.906	−1090.900	−605.009	12.155
2700	156.900	453.296	277.149	475.596	−1090.326	−586.332	11.343
2800	156.900	459.002	283.543	491.286	−1089.784	−567.675	10.590
2900	156.900	464.508	289.688	506.976	−1089.271	−549.038	9.889
3000	156.900	469.827	295.605	522.666	−1088.787	−530.418	9.235
3100	156.900	474.972	301.308	538.356	−1088.332	−511.812	8.624
3200	156.900	479.953	306.814	554.046	−1087.903	−493.223	8.051
3300	156.900	484.781	312.134	569.736	−1087.500	−474.646	7.513
3400	156.900	489.465	317.281	585.426	−1087.123	−456.079	7.007
3500	156.900	494.013	322.266	601.116	−1086.769	−437.525	6.530
3600	156.900	498.433	327.098	616.806	−1086.439	−418.979	6.079
3700	156.900	502.732	331.787	632.496	−1979.745	−398.042	5.619
3800	156.900	506.916	336.341	648.186	−1976.085	−355.342	4.885
3900	156.900	510.992	340.767	663.876	−1972.548	−312.736	4.189
4000	156.900	514.964	345.073	679.566	−1969.135	−270.222	3.529

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 75.912 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1050\ K$
$T_{fus} = 1745\ K$

$\Delta_f H°(298.15\ K) = -842.909 \pm 0.8\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 1.485\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 73.429\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The selected enthalpy of formation, $\Delta_f H°(WO_3, cr, 298.15\ K) = -201.46 \pm 0.2\ kcal \cdot mol^{-1}$, was determined by Mah[1] using bomb calorimetry. Huff *et al.*[2] have reviewed the literature enthalpy of formation data and also measured calorimetrically the enthalpy of formation, $-201.84 \pm 0.1\ kcal \cdot mol^{-1}$, which is in good agreement with the value selected. Other combustion values were reported as $\Delta_f H°(298.15\ K) = -199 \pm 1\ kcal \cdot mol^{-1}$ by Griffis;[3] and $\Delta_f H°(298.15\ K) = -205.3\ kcal \cdot mol^{-1}$ by Vasil'eva *et al.*[4] Griffis[5] also derived the enthalpy of formation, $-202.8 \pm 1\ kcal \cdot mol^{-1}$, from equilibrium data.

Heat Capacity and Entropy

The low temperature (55–296.7 K) heat capacities and high temperature (399.6–1835.8 K) enthalpy data have been measured by King *et al.*,[6] and these data have been used to derive the tabulated heat capacities. Low temperature and high temperature values were joined smoothly at 298.15 K. The entropy was calculated from the heat capacities based on $S°(51\ K) = 1.31\ cal \cdot K^{-1} \cdot mol^{-1}$.

King *et al.*[6] were apparently unaware of the transition near 593 K which was reported by Perri *et al.*,[7] and they did not take sufficient points in that region for the precise enthalpy curve. We have adopted only one curve through the region because of the insufficiency of the data and also because the heat effects appear to be small or gradual.

Transition and Fusion Data

The enthalpy of transition, the transition point, the enthalpy of melting and the melting point were derived from the high temperature enthalpy data of King *et al.*[6]

The melting point, 1746 ± 1 K, has also been quoted by Schneider.[8]

In the high temperature x-ray diffractometric studies, Perri *et al.*[7] indicate that WO_3 undergoes a phase transition from monoclinic to orthorhombic at approximately 593 K and from orthorhombic to tetragonal at 993 K.

Sublimation Data

The values of $\Delta_{sub} H°(298.15\ K)$ are calculated as the enthalpy of sublimation of one mole of crystal to one mole of monomer, 1/2 mole of dimer, 1/3 mole of trimer and 1/4 mole of tetramer, respectively.

References

[1] A. D. Mah, J. Amer. Chem. Soc. **81**, 1582 (1959).
[2] G. Huff, E. Squitieri and P. E. Snyder, J. Amer. Chem. Soc. **70**, 3380 (1948).
[3] R. C. Griffis, J. Electrochem. Soc. **105**, 398 (1958).
[4] I. A. Vasil'eva, V. I. Gerassimov, and Y. P. Simanov, Zh. Fiz. Khim. **31**, 682 (1957).
[5] R. C. Griffis, J. Electrochem. Soc. **106**, 418 (1959).
[6] E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664, (1960).
[7] J. A. Perri, E. Banks, and B. Post, J. Appl. Phys. **28**, 1272 (1957).
[8] S. J. Schneider, U.S. Nat. Bur. Stand. Monograph 68, (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−12.349	−837.259	−837.259	INFINITE
100	30.449	18.862	130.106	−11.124	−841.044	−815.973	426.221
200	58.196	49.480	82.212	−6.546	−842.841	−790.036	206.336
298.15	73.139	75.912	75.912	0.000	−842.909	−764.057	133.860
300	73.304	76.365	75.914	0.135	−842.900	−763.568	132.949
400	82.209	98.738	78.904	7.934	−842.022	−737.237	96.273
500	88.641	117.815	84.825	16.495	−840.563	−711.200	74.299
600	93.113	134.397	91.736	25.597	−838.758	−685.493	59.677
700	96.141	148.993	98.894	35.069	−836.769	−660.104	49.258
800	98.239	161.975	105.983	44.794	−834.694	−635.007	41.462
900	99.923	173.645	112.864	54.703	−832.582	−610.173	35.414
1000	101.671	184.261	119.480	64.781	−830.431	−585.575	30.587
1050.000	102.508	189.242	122.684	69.886	I <--> II		
1050.000	98.144	190.655	122.684	71.369	TRANSITION		
1100	98.963	195.239	125.879	76.296	−826.958	−561.262	26.652
1200	100.601	203.920	132.025	86.275	−825.128	−537.188	23.383
1300	102.238	212.037	137.871	96.417	−823.230	−513.269	20.623
1400	103.875	219.674	143.444	106.722	−821.261	−489.499	18.263
1500	105.512	226.896	148.769	117.192	−819.216	−465.873	16.223
1600	107.149	233.758	153.868	127.825	−817.094	−442.386	14.442
1700	108.787	240.303	158.761	138.621	−814.892	−419.034	12.875
1745.000	109.537	243.155	160.901	143.534	----- II <--> LIQUID		-----
1800	110.458	246.569	163.467	149.583	−812.608	−395.814	11.486
1900	112.131	252.586	168.000	160.713	−810.240	−372.723	10.247
2000	113.805	258.380	172.375	172.010	−807.788	−349.758	9.135
2100	115.478	263.973	176.604	183.474	−805.252	−326.919	8.132
2200	117.152	269.383	180.699	195.105	−802.632	−304.201	7.223
2300	118.826	274.628	184.670	206.904	−799.928	−281.606	6.395
2400	120.499	279.720	188.524	218.870	−797.139	−259.130	5.640
2500	122.173	284.673	192.272	231.004	−794.266	−236.772	4.947
2600	123.846	289.498	195.919	243.305	−791.305	−214.530	4.310
2700	125.520	294.203	199.472	255.773	−788.282	−192.404	3.722
2800	127.194	298.798	202.938	268.409	−785.231	−170.389	3.179
2900	128.867	303.291	206.321	281.212	−782.191	−148.486	2.675
3000	130.541	307.688	209.627	294.182	−779.188	−126.684	2.206

PREVIOUS: March 1963 CURRENT: September 1966

$S°$(298.15 K) = [103.508] J·K^{-1}·mol^{-1}
T_{fus} = 1745 K

$\Delta_f H°$(298.15 K) = [−788.915] kJ·mol^{-1}
$\Delta_{fus} H°$ = 73.429 kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°$(l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°$(1745 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity between the melting point and 1836 K was determined from the enthalpy measurement by King *et al.*[1] The heat capacity was assumed constant above and below the measured range. At 1000 K, a glass transition was assumed below which the heat capacity was assumed to be that of the crystal. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion and Vaporization Data

The heat and temperature of melting were obtained from King *et al.*[1]

T_{vap}(to equilibrium vapor) = 2110 K is the temperature at which the total pressure reaches one atm based on the calculated partial pressures of WO_3(g), W_2O_6(g), W_3O_8(g), W_3O_9(g), and W_4O_{12}(g). $\Delta_{vap} H°$(to equilbrium vapor) = 18.3 kcal·mol^{-1} at the boiling point is calculated as the enthalpy of vaporization of one mole of the liquid to vapor containing 23.7 mole percent of W_2O_6(g), 0.57 mole percent of W_3O_8(g), 58.2 mole percent of W_3O_9(g) and 17.53 mole percent of W_4O_{12}(g).

Reference

[1]E. G. King, W. W. Weller and A. U. Christensen, U. S. Bur. Mines RI 5664, (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	73.140	103.508	103.508	0.000	−788.915	−718.291	125.842
300	73.304	103.961	103.509	0.135	−788.906	−717.853	124.989
400	82.209	126.334	106.499	7.934	−788.028	−694.281	90.664
500	88.641	145.410	112.421	16.495	−786.570	−671.004	70.099
600	93.113	161.993	119.332	25.597	−784.764	−648.056	56.418
700	96.141	176.589	126.490	35.069	−782.775	−625.427	46.670
800	98.239	189.571	133.579	44.794	−780.701	−603.090	39.378
900	99.923	201.241	140.459	54.703	−778.588	−581.015	33.721
1000	101.671	211.857	147.076	64.781	−776.437	−559.177	29.208
1000.000	101.671	211.857	147.076	64.781	GLASS <--> LIQUID TRANSITION		
1000.000	131.796	211.857	147.076	64.781			
1100	131.796	224.418	153.545	77.961	−771.300	−537.701	25.533
1200	131.796	235.886	159.936	91.140	−766.268	−516.687	22.491
1300	131.796	246.435	166.190	104.320	−761.333	−496.090	19.933
1400	131.796	256.203	172.275	117.499	−756.490	−475.869	17.755
1500	131.796	265.296	178.176	130.679	−751.735	−455.991	15.879
1600	131.796	273.802	183.890	143.859	−747.066	−436.427	14.248
1700	131.796	281.792	189.416	157.038	−742.481	−417.153	12.818
1745.000	131.796	285.235	191.843	162.969	II <--> LIQUID		
1800	131.796	289.325	194.759	170.218	−737.980	−398.147	11.554
1900	131.796	296.451	199.926	183.397	−733.562	−379.388	10.430
2000	131.796	303.211	204.922	196.577	−729.227	−360.860	9.425
2100	131.796	309.641	209.757	209.757	−724.975	−342.546	8.520
2200	131.796	315.772	214.438	222.936	−720.807	−324.433	7.703
2300	131.796	321.631	218.972	236.116	−716.722	−306.508	6.961
2400	131.796	327.240	223.367	249.295	−712.720	−288.759	6.285
2500	131.796	332.620	227.630	262.475	−708.802	−271.175	5.666
2600	131.796	337.790	231.769	275.655	−704.962	−253.746	5.098
2700	131.796	342.764	235.788	288.834	−701.227	−236.462	4.575
2800	131.796	347.557	239.695	302.014	−697.633	−219.314	4.091
2900	131.796	352.182	243.494	315.193	−694.216	−202.294	3.644
3000	131.796	356.650	247.192	328.373	−691.004	−185.386	3.228

PREVIOUS: March 1963 CURRENT: September 1966

0 to 1050 K crystal, I
1050 to 1745 K crystal, II
above 1745 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−12.349	−837.259	−837.259	INFINITE
100	30.449	18.862	130.106	−11.124	−841.044	−815.973	426.221
200	58.196	49.480	82.212	−6.546	−842.841	−790.036	206.336
298.15	73.139	75.912	75.912	0.000	−842.909	−764.057	133.860
300	73.304	76.365	75.914	0.135	−842.900	−763.568	132.949
400	82.209	98.738	78.904	7.934	−842.022	−737.237	96.273
500	88.641	117.815	84.825	16.495	−840.563	−711.200	74.299
600	93.113	134.397	91.736	25.597	−838.758	−685.493	59.677
700	96.141	148.993	98.894	35.069	−836.769	−660.104	49.258
800	98.239	161.975	105.983	44.794	−834.694	−635.007	41.462
900	99.923	173.645	112.864	54.703	−832.582	−610.173	35.414
1000	101.671	184.261	119.480	64.781	−830.431	−585.575	30.587
1050.000	102.508	189.242	122.684	69.886	I <--> II		
1050.000	98.144	190.655	122.684	71.369	TRANSITION		
1100	98.963	195.239	125.879	76.296	−826.958	−561.262	26.652
1200	100.601	203.920	132.025	86.275	−825.128	−537.188	23.383
1300	102.238	212.037	137.871	96.417	−823.230	−513.269	20.623
1400	103.875	219.674	143.444	106.722	−821.261	−489.499	18.263
1500	105.512	226.896	148.769	117.192	−819.216	−465.873	16.223
1600	107.149	233.758	153.868	127.825	−817.094	−442.386	14.442
1700	108.787	240.303	158.761	138.621	−814.892	−419.034	12.875
1745.000	109.537	243.155	160.901	143.534	II <--> LIQUID		
1745.000	131.796	285.235	160.901	216.963	TRANSITION		
1800	131.796	289.325	164.763	224.212	−737.980	−398.147	11.554
1900	131.796	296.451	171.508	237.391	−733.562	−379.388	10.430
2000	131.796	303.211	177.926	250.571	−729.227	−360.860	9.425
2100	131.796	309.641	184.046	263.750	−724.975	−342.546	8.520
2200	131.796	315.772	189.895	276.930	−720.807	−324.433	7.703
2300	131.796	321.631	195.496	290.110	−716.722	−306.508	6.961
2400	131.796	327.240	200.870	303.289	−712.720	−288.759	6.285
2500	131.796	332.620	206.033	316.469	−708.802	−271.175	5.666
2600	131.796	337.790	211.002	329.648	−704.962	−253.746	5.098
2700	131.796	342.764	215.790	342.828	−701.227	−236.462	4.575
2800	131.796	347.557	220.411	356.008	−697.633	−219.314	4.091
2900	131.796	352.182	224.876	369.187	−694.216	−202.294	3.644
3000	131.796	356.650	229.194	382.367	−691.004	−185.386	3.228

PREVIOUS: CURRENT: September 1966

$S°(298.15\ K)$ = [286.440] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -288.47 \pm 29.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -292.88 \pm 29.3\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[564](1)	1040 (2)
[347](1)	[320](2)

Ground State Quantum Weight: 1 σ = [6]
Point Group: [D_{3h}]
Bond[uccirc]l Distance: W–O = [1.81] Å
Bond Angle: O–W–O = [120]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [4.4509666 × 10^{-114}] $g^3·cm^6$

Enthalpy of Formation

The Gibbs energy of formation of gaseous tungsten trioxide, $\Delta_f G°(WO_3, g) = -75{,}700 + 15.54\,T\ cal·K^{-1}·mol^{-1}$, over the temperature range 1920–2020 K has been reported by Ackermann and Thorn,[1] using the reaction 3 MgO(cr) + W(cr) → 3 Mg(g) + WO_3(g). 3rd law calculation gives $\Delta_f H°(WO_3, g, 298.15\ K) = -71.3\ kcal·mol^{-1}$ using JANAF functions. The 2nd law value of $\Delta_f H°(298.15\ K)$ is $-74.8\ kcal·mol^{-1}$.

DeMaria *et al.*[2] have reported the partial pressures of WO(g), WO_2(g), WO_3(g) and O(g) in a mass spectrometric study of aluminum oxide vaporized from a tungsten cell from 2188 to 2475 K. 3rd law treatment of their partial pressure data gives $\Delta_f H°(298.15\ K) = -245.2\ kcal·mol^{-1}$ for W(cr) + 3 O(g) → WO(g) which yields $\Delta_f H°(WO_3, g, 298.15\ K) = -66.5\ kcal·mol^{-1}$. The 3rd law drift is 21 ± 7 $cal·K^{-1}·mol^{-1}$. Partial pressures of WO_2(g), WO_3(g), and O(g) at 2242 K have also been reported by Chupka *et al.*[3] in a mass spectrometric study of beryllium oxide in a tungsten cell. Similar calculation gives $\Delta_f H°(WO_3, g, 298.15\ K) = -73.0\ kcal·mol^{-1}$.

The value, $-70 \pm 7\ kcal·mol^{-1}$, is selected for the enthalpy of formation at 298.15 K.

Heat Capacity and Entropy

The WO_3(g) was assumed to be a planar D_{3h} molecule with a bond angle O–W–O = 120°. The bond distance W–O was estimated to be the same as that in WO(g). Weltner and McLeod[4] have observed the vibrational frequency of 1040 cm^{-1} in the infrared spectrum by matrix isolation, and also estimated the frequencies 347 and 564 cm^{-1} based on the stretching force constant of WO(g). The estimation of 320 cm^{-1} was obtained from DeMaria *et al.*[2] These frequencies have been adopted in the tabulation. The principal moments of inertia are $I_A = I_B = 13.0559 \times 10^{-39}$, and $I_C = 26.1119 \times 10^{-39}\ g·cm^2$.

References

[1]R. J. Ackermann and R. J. Thorn, J. Phys. Chem. **64**, 350 (1960).
[2]G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram, J. Chem. Phys. **32**, 1373 (1960).
[3]W. A. Chupka, J. Berkowitz and C. F. Giese, J. Chem. Phys. **30**, 827 (1959).
[4]W. Weltner, Jr. and D. McLeod, Jr., J. Mol. Spectrosc. **17**, 276 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−13.592	−288.474	−288.474	INFINITE
100	38.449	232.689	334.270	−10.158	−290.049	−286.361	149.580
200	52.190	263.843	291.760	−5.583	−291.849	−281.917	73.629
250	57.112	276.037	287.423	−2.847	−292.456	−279.361	58.369
298.15	61.005	286.440	286.440	0.	−292.880	−276.798	48.494
300	61.141	286.817	286.441	0.113	−292.894	−276.698	48.177
350	64.479	296.501	287.198	3.256	−293.189	−273.973	40.888
400	67.241	305.297	288.919	6.551	−293.376	−271.214	35.417
450	69.521	313.353	291.193	9.972	−293.482	−268.437	31.159
500	71.402	320.778	293.785	13.497	−293.533	−265.651	27.752
600	74.248	334.064	299.417	20.788	−293.538	−260.073	22.641
700	76.231	345.667	305.213	28.318	−293.491	−254.499	18.991
800	77.646	355.944	310.925	36.015	−293.444	−248.932	16.254
900	78.681	365.152	316.447	43.834	−293.422	−243.370	14.125
1000	79.457	373.484	321.741	51.743	−293.440	−237.808	12.422
1100	80.052	381.086	326.796	59.720	−293.506	−232.241	11.028
1200	80.516	388.072	331.615	67.749	−293.625	−226.667	9.867
1300	80.885	394.532	336.209	75.820	−293.799	−221.081	8.883
1400	81.182	400.538	340.592	83.924	−294.031	−215.478	8.040
1500	81.425	406.147	344.778	92.054	−294.325	−209.858	7.308
1600	81.626	411.409	348.779	100.207	−294.683	−204.216	6.667
1700	81.794	416.363	352.611	108.379	−295.106	−198.549	6.101
1800	81.936	421.042	356.284	116.565	−295.598	−192.855	5.597
1900	82.057	425.475	359.810	124.765	−296.159	−187.132	5.145
2000	82.160	429.687	363.199	132.976	−296.793	−181.378	4.737
2100	82.250	433.698	366.461	141.197	−297.501	−175.590	4.368
2200	82.328	437.526	369.605	149.426	−298.283	−169.766	4.031
2300	82.396	441.187	372.638	157.662	−299.141	−163.906	3.722
2400	82.456	444.695	375.568	165.904	−300.077	−158.007	3.439
2500	82.509	448.062	378.401	174.153	−301.089	−152.067	3.177
2600	82.557	451.299	381.143	182.406	−302.175	−146.085	2.935
2700	82.599	454.416	383.799	190.664	−303.363	−140.058	2.710
2800	82.637	457.420	386.375	198.926	−304.686	−133.986	2.500
2900	82.671	460.321	388.876	207.191	−306.184	−127.865	2.303
3000	82.701	463.124	391.304	215.460	−307.882	−121.687	2.119
3100	82.729	465.836	393.665	223.731	−309.824	−115.449	1.945
3200	82.754	468.463	395.961	232.005	−312.041	−109.145	1.782
3300	82.778	471.010	398.197	240.282	−314.556	−102.767	1.627
3400	82.799	473.481	400.375	248.561	−317.404	−96.306	1.480
3500	82.818	475.882	402.499	256.842	−320.650	−89.758	1.340
3600	82.836	478.215	404.570	265.124	−324.387	−83.109	1.206
3700	82.852	480.485	406.591	273.409	−363.482	−76.159	1.075
3800	82.867	482.695	408.565	281.695	−364.915	−68.373	0.940
3900	82.881	484.847	410.493	289.982	−366.367	−60.549	0.811
4000	82.894	486.946	412.378	298.271	−367.838	−52.690	0.688
4100	82.906	488.993	414.222	306.561	−369.328	−44.793	0.571
4200	82.917	490.991	416.026	314.852	−370.835	−36.859	0.458
4300	82.927	492.942	417.792	323.144	−372.359	−28.889	0.351
4400	82.937	494.849	419.522	331.438	−373.901	−20.884	0.248
4500	82.946	496.713	421.217	339.732	−375.461	−12.844	0.149
4600	82.955	498.536	422.878	348.027	−377.037	−4.769	0.054
4700	82.963	500.320	424.507	356.323	−378.632	3.341	−0.037
4800	82.970	502.067	426.104	364.619	−380.244	11.485	−0.125
4900	82.977	503.778	427.672	372.917	−381.875	19.664	−0.210
5000	82.984	505.454	429.211	381.215	−383.524	27.876	−0.291
5100	82.990	507.097	430.722	389.513	−385.194	36.121	−0.370
5200	82.996	508.709	432.206	397.813	−386.883	44.396	−0.446
5300	83.001	510.290	433.665	406.113	−388.594	52.708	−0.519
5400	83.006	511.841	435.098	414.413	−390.328	61.050	−0.591
5500	83.011	513.365	436.507	422.714	−392.085	69.424	−0.659
5600	83.016	514.860	437.893	431.015	−393.867	77.833	−0.726
5700	83.021	516.330	439.257	439.317	−395.675	86.271	−0.791
5800	83.025	517.774	440.598	447.619	−397.510	94.743	−0.853
5900	83.029	519.193	441.918	455.922	−399.375	103.244	−0.914
6000	83.033	520.588	443.218	464.225	−401.270	111.780	−0.973

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$\Delta_f H°(0\ K) = -1369.466 \pm 14.6\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 186.832 \pm 2.1\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -1377.875 \pm 14.6\ kJ \cdot mol^{-1}$

$T_{fus} = 1016\ K$

Enthalpy of Formation

The enthalpy of the reaction 2 PbO(cr) + SiO_2(cr) → Pb_2SiO_4(cr) was reported by Kubaschewski and Evans.[1] This value for the enthalpy of reaction of the oxides has been converted to the enthalpy of formation using JANAF auxiliary data.[4] The above $\Delta_f H°(298.15\ K) = -7.00 \pm 3.5\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

In the low temperature region (53.07–298.15 K) the $C_p°$ values are those determined by King.[2] Above 298.15, $C_p°$ values were estimated by summing the values for the constituent oxides and graphically smoothing these into the low temperature measurements. The entropy was calculated at 53.07 K using the Debye and Einstein functions D(78.5/T) + 2E(164/T) + 3E(547/T) + E(1379/T) given by King.[2] $S°(53.07\ K) = 8.248\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

T_{fus} was taken from Geller *et al.*[3]

References

[1]O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," Pergamon Press, New York (1958).
[2]E. G. King, J. Amer. Chem. Soc. **81**, 799–800 (1959).
[3]Geller, Creamer and Bunting, J. Res. Nat. Bur. Stand. **13**, 237 (1934).
[4]JANAF Thermochemical Tables: PbO(cr), 3–31–62; SiO_2(cr), 12–31–62.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−25.932	−1369.466	−1369.466	INFINITE
100	73.789	72.007	291.667	−21.966	−1375.108	−1339.898	699.891
200	113.968	136.700	198.686	−12.397	−1377.589	−1303.493	340.437
298.15	136.984	186.832	186.832	0.000	−1377.875	−1267.007	221.974
300	137.235	187.680	186.835	0.254	−1377.866	−1266.320	220.486
400	152.005	229.255	192.403	14.741	−1376.901	−1229.256	160.524
500	163.762	264.478	203.383	30.547	−1375.118	−1192.537	124.583
600	173.343	295.224	216.181	47.426	−1372.712	−1156.238	100.659
700	180.121	322.489	229.458	65.122	−1379.617	−1118.781	83.484
800	184.180	346.822	242.636	83.349	−1376.607	−1081.721	70.629
900	186.774	368.668	255.447	101.899	−1373.401	−1045.052	60.653
1000	189.117	388.473	267.775	120.699	−1370.045	−1008.747	52.692
1100	190.790	406.580	279.582	139.698	−1366.569	−972.784	46.194
1200	192.046	423.232	290.868	158.836	−1363.015	−937.142	40.793
1300	193.719	438.670	301.651	178.125	−1359.374	−901.800	36.235
1400	195.309	453.086	311.959	197.578	−1355.656	−866.741	32.338
1500	196.648	466.607	321.823	217.177	−1351.892	−831.950	28.971
1600	197.903	479.339	331.273	236.906	−1348.109	−797.410	26.033
1700	199.033	491.371	340.340	256.753	−1394.502	−762.660	23.434
1800	200.121	502.778	349.050	276.710	−1390.499	−725.609	21.057
1900	201.292	513.629	357.429	296.780	−1386.467	−688.780	18.936
2000	202.506	523.985	365.500	316.970	−1382.402	−652.165	17.033

PREVIOUS: CURRENT: June 1965

$S°(298.15\ K) = 211.961 \pm 6.7\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -710.871 \pm 6.2\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -718.686 \pm 6.2\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Espada *et al.*[1] have measured the enthalpy of the reduction reaction $PbO_{1.3}$(cr) + 1.3 H_2(g) → Pb(cr) + 1.3 H_2O(l) as $-32.07\ kcal \cdot mol^{-1}$ as $-32.07\ kcal \cdot mol^{-1}$. They assumed that the sample consisted of 90.1% mol percent $PbO_{1.333}$ and 9.9 mol PbO and corrected the observed enthalpy of reaction to $-33.82 \pm 0.25\ kcal \cdot mol^{-1}$ for the reaction $PbO_{1.333}$(cr) + 1.333 H_2(g) → Pb(cr) + 1.333 H_2O(l). This leads to $\Delta_f H°(Pb_3O_4, cr) = -171.77 \pm 1.5\ kcal \cdot mol^{-1}$ which is adopted.

Andrews and Brown[2] used reversible cells to obtain $\Delta_r G°(298.15\ K) = -6940\ cal \cdot K^{-1} \cdot mol^{-1}$ for the reaction Hg(l) + Pb_3O_4(cr) → HgO(cr) + 3 PbO(red, cr), with JANAF auxiliary data[3] this yields $\Delta_f G(Pb_3O_4, cr, 298.15\ K) = -142.76 \pm 0.6\ kcal \cdot mol^{-1}$ which is equivalent to $\Delta_f H°(Pb_3O_4, cr, 298.15\ K) = -170.73 \pm 1.1\ kcal \cdot mol^{-1}$. This value is in agreement with the adopted value within the combined uncertainties.

Reinders and Hamburger[4] and Otto[5] studied the decomposition pressure of the reaction Pb_3O_4(cr) → 3 PbO(cr) + 0.5 O_2(g) a 2nd and 3rd law analysis of their data is given below.

Source	Data Points	T/K	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
[4]	16	718–880	20.19 ± 0.14	19.08 ± 0.17	−1.4 ± 0.2	−175.44
[5]	19	757–911	20.84 ± 0.10	18.98 ± 0.22	−2.2 ± 0.1	−175.34

Although these two sets of data are in good agreement, they are outside the adopted enthalpy of formation uncertainty limits, and realistic adjustments of the entropy or heat capacity fail to eliminate this discrepancy.

In addition there have been cell measurements linking PbO_2 and Pb_3O_4, which serve to indicate the overall consistency of the lead oxygen system. The absolute uncertainty in the enthalpy of formation and the difficulty of preparing pure PbO_2 make it a poor choice on which to base the heat of formation of Pb_3O_4. Andrews and Brown[2] obtained $\Delta_r G°(298.15\ K) = -18.12\ kcal \cdot mol^{-1}$ for the reaction 2 Hg(l) + 3 PbO_2(cr) → Pb_3O_4(cr) + 2 HgO(cr). This yields $\Delta_f G°(Pb_3O_4, cr, 298.15\ K) = -144.62 \pm 2.1\ kcal \cdot mol^{-1}$ with JANAF auxiliary data,[3] which corresponds to $\Delta_f H°(Pb_3O_4, cr, 298.15\ K) = -172.59 \pm 2.6\ kcal \cdot mol^{-1}$. Millar[6] has recalculated the data of Glasstone for the reaction 3 PbO_2(cr) + 2 H_2(g) → Pb_3O_4 + 2 H_2O(l) as $\Delta_r G°(298.15\ K) = -104.36\ kcal \cdot mol^{-1}$ which with auxiliary data[3,7] yields $\Delta_f G°(Pb_3O_4, cr, 298.15\ K) = -145.45 \pm 2.1\ kcal \cdot mol^{-1}$ which corresponds to $\Delta_f H°(Pb_3O_4, cr, 298.15\ K) = -173.42 \pm 2.6\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

The low temperature enthalpy capacity from 71.5 K to 292.6 K has been reported by Millar.[6] These values were used to calculate $S°(298.15\ K)$ based on $S°(70.8\ K) = 12.67\ cal \cdot K^{-1} \cdot mol^{-1}$.[7] Enthalpies in the range 365 to 781 K have been reported by Bousquet *et al.*[8] These data encompass the range where the dissociation pressure is significant (76 mm) and we have not used the data above 600 K. The mean heat capacities were plotted at the mean temperatures for the five points used and a smooth curve was drawn graphically through them and the low temperature data set. The four highest points of Millar[6] were not used since at least two were reported as bad points and they did not fit onto the smooth curve.

Decomposition Data

The decomposition pressure reaches 1 atm at 869.7 according to Reinders and Hamburger[4] and at 867.2 K according to Otto.[5] This table indicates a temperature of 690 K for the decomposition pressure to reach 1 atm. The significant difference is due to the fact that heat and entropy derived from the dissociation cannot be simultaneously satisfied by any realistic variation of the entropy and heat capacity of Pb_3O_4.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−30.188	−710.871	−710.871	INFINITE
100	87.195	79.860	331.486	−25.163	−716.955	−679.231	354.794
200	130.122	155.101	225.392	−14.058	−719.246	−640.309	167.232
298.15	154.934	211.961	211.961	0.000	−718.686	−601.606	105.399
300	155.344	212.921	211.964	0.287	−718.656	−600.879	104.622
400	173.050	260.195	218.289	16.762	−716.310	−561.936	73.381
500	184.096	300.077	230.766	34.656	−712.976	−523.715	54.712
600	190.790	334.272	245.237	53.421	−709.197	−486.213	42.329
700	194.974	363.996	260.126	72.709	−719.884	−446.962	33.353
800	199.158	390.305	274.785	92.416	−715.902	−408.241	26.655
900	203.342	414.004	288.958	112.541	−711.544	−370.041	21.477
1000	207.526	435.645	302.560	133.084	−706.789	−332.348	17.360
1100	211.710	455.620	315.578	154.046	−701.619	−295.150	14.016
1200	215.894	474.221	328.032	175.426	−696.018	−258.442	11.250
1300	220.078	491.667	339.955	197.225	−689.997	−222.219	8.929
1400	224.262	508.130	351.385	219.442	−683.595	−186.474	6.957
1500	228.446	523.745	362.360	242.078	−676.835	−151.199	5.265

PREVIOUS: March 1962 CURRENT: December 1971

$S°(298.15\ K) = 110.541 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs1}(\alpha \rightarrow \alpha', proposed) = [540]\ K$
$T_{trs2}(\alpha' \rightarrow \beta) = 1013 \pm 5\ K$

$\Delta_f H°(0\ K) = -969.934 \pm 0.10\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -980.144 \pm 0.10\ kJ \cdot mol^{-1}$
$\Delta_{trs1} H°(\alpha \rightarrow \alpha') = [5.021]\ kJ \cdot mol^{-1}$
$\Delta_{trs2} H°(\alpha' \rightarrow \beta) = 20.334 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Adami and King[1] determined calorimetrically the enthalpies of solution of crystalline ZnO and $ZnSO_4$ in hydrochloric acid solution. From these measurements they derived the enthalpy for the reaction $ZnC(cr) + H_2SO_4 \cdot 7.068\ H_2O(l) \rightarrow ZnSO_4(cr) + 8.068\ H_2O(l)$ as $\Delta_f H°(298.15\ K) = -9.250 \pm 0.080\ kcal \cdot mol^{-1}$. Combining this result with the enthalpies of formation of ZnO[2], $H_2SO_4 \cdot 7.068\ H_2O$,[3,4] and H_2O,[4] we derive $\Delta_f H°(ZnSO_4, cr, 298.15\ K) -234.26 \pm 0.25\ kcal \cdot mol^{-1}$ which is the value adopted for this tabulation.

The enthalpy of solution at infinite dilution, $\Delta_{sol} H°(ZnSO_4, cr, 298.15\ K) = -19.9 \pm 0.2\ kcal \cdot mol^{-1}$ was taken from the work of Larson *et al.*[5] When this result is combined with enthalpies of formation of the infinitely dilute ions from,[4] we obtain $\Delta_f H°(ZnSO_4, aq, 1infinitel, 298.15\ K) = -254.06 \pm 0.14\ kcal \cdot mol^{-1}$ and $\Delta_f H°(ZnSO_4, cr, 298.15\ K) = -234.16 \pm 0.34\ kcal \cdot mol^{-1}$.

Ishikawa and Murooka[6] determined $\Delta_f H°(298.15\ K) = -56.330\ kcal \cdot mol^{-1}$ from cell measurements for the reaction $Zn(cr) + Hg_2SO_4(cr) = ZnSO_4(cr) + 2\ Hg(l)$ as reported by Kelley.[7] When this result is combined with JANAF auxiliary data for Zn(cr)[8] and with data from CODATA[9] for Hg(l) and Hg_2SO_4(cr), we obtain $\Delta_f H°(ZnSO_4, cr, 298.15\ K) = -234.01 \pm 1.0\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Low temperature heat capacities of $ZnSO_4$(cr, α) have been measured by Weller[10] from 51.7–296.5 K. A small heat capacity maximum was observed at 124.37 K. Our adopted value of $S°(298.15\ K) = 26.42 \pm 0.3\ cal \cdot K^{-1} \cdot mol^{-1}$ obtained from $C_p°$ is based on $S°(51\ K) = 2.27\ cal \cdot K^{-1} \cdot mol^{-1}$ obtained by Weller[10] by extrapolation of the measured heat capacity with a combination of Debye and Einstein functions. We have smoothed the data of Weller[10] by fitting the data with orthogonal polynomials over selected overlapping temperature intervals.

High temperature enthalpy data have been measured by Hosmer and Krikorian,[11] 510–1168 K as well as by Voskresenskaya and Patsukova,[12] 523 806 K, Krestovnikov and Feigina,[13] 573–1073 K, and by Chizhikov and Khirik,[14] 373–973 K. The enthalpy data of Hosmer and Krikorian[11] is higher than the data of Voskresenskaya and Patsukova[12] or Krestovnikov and Feigina.[13] Wet chemical and x-ray analysis of their sample[11] indicate that the sample was pure zinc sulfate. The lower results of[12] and[13] may be due to decomposition to the oxy sulfate which can occur in vacuum dehydration.[11] We adopt the enthalpy results from Hosmer and Krikorian.[11] Problems remain in matching the low temperature heat capacity data to the high temperature enthalpy data (300–600 K region). There are at least three possibilities for the mismatch: 1) an unobserved transition occurs between 300–600 K, 2) the data of W.W. Weller[10] and P.K. Hosmer and O.H. Krikorian[11] are essentially correct but were measured on different materials, or 3) a bias exists in the data from one of the calorimeters. In the absence of other information, we arbitrarily adopt a transition at 540 K with $\Delta_{trs} H° = 1.20\ kcal \cdot mol^{-1}$. Below 540 K, we adopt heat capacities based on an extrapolation of the work of Weller.[10] Above 540 K, we adopt heat capacities based on the enthalpy data of Hosmer and Krikorian.[11]

Transition Data

$ZnSO_4$(cr, α) is the low-temperature form of zinc sulfate, also known as the mineral zinkosite and $ZnSO_4$(cr, II). The crystals are orthorhombic, space group D_{2h}^{16}–Pnma.[15] The transition to the high-temperature (β-phase) cubic form (space group F43m),[16] occurs at 1013 ± 5 K.[15] The heat of transition is based on the drop calorimetry measurement of Hosmer and Krikorian[11] which is in good agreement with the DTA measurement of Ingraham and Marier,[17] 4.74 $kcal \cdot mol^{-1}$. Decomposition occurs through an oxy-sulfate intermediate which has the probable composition $ZnO \cdot 2\ ZnSO_4$.[11]

Hosmer and Krikorian[11] have also measured enthalpies of the high temperature $ZnSO_4$(cr, β) phase of zinc sulfate. We adopt their results (1038–1168 K), which imply a constant heat capacity, and extrapolate this value to 2000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−17.238	−969.934	−969.934	INFINITE
100	47.585	31.581	183.544	−15.196	−975.390	−940.983	491.519
200	78.053	75.224	118.947	−8.745	−978.636	−905.195	236.413
298.15	99.035	110.541	110.541	0.000	−980.144	−868.777	152.206
300	99.370	111.155	110.543	0.184	−980.158	−868.086	151.147
400	116.022	142.074	114.647	10.971	−982.499	−830.588	108.464
500	131.210	169.620	122.933	23.344	−982.857	−792.557	82.798
540.000	136.817	179.933	126.775	28.705	I <--> II		
540.000	136.817	189.231	126.775	33.726	TRANSITION		
600	137.444	203.678	133.755	41.954	−976.948	−755.128	65.740
700	138.574	224.950	145.301	55.755	−983.260	−718.162	53.590
800	139.704	243.528	156.442	69.668	−982.369	−680.351	44.422
900	140.875	260.050	167.053	83.698	−1034.546	−641.575	37.236
1000	142.005	274.954	177.110	97.844	−1032.317	−598.031	31.238
1013.000	142.130	276.789	178.377	99.691	ALPHA <--> BETA		
1013.000	145.185	296.862	178.377	120.025	TRANSITION		
1100	145.185	308.825	188.228	132.656	−1009.533	−556.465	26.424
1200	145.185	321.457	198.812	147.175	−1122.238	−513.448	22.350
1300	145.185	333.078	208.699	161.693	−1118.867	−462.853	18.598
1400	145.185	343.838	217.972	176.212	−1115.572	−412.515	15.391
1500	145.185	353.854	226.701	190.730	−1112.348	−362.410	12.620
1600	145.185	363.224	234.944	205.249	−1109.190	−312.517	10.203
1700	145.185	372.026	242.751	219.767	−1106.097	−262.820	8.075
1800	145.185	380.325	250.166	234.286	−1103.065	−213.304	6.190
1900	145.185	388.174	257.225	248.804	−1100.093	−163.954	4.507
2000	145.185	395.622	263.960	263.323	−1097.180	−114.759	2.997

PREVIOUS: CURRENT: March 1979

$S°(298.15\ K) = 84.026 \pm 1.3\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2012.774 \pm 2.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -2023.951 \pm 2.9\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(ZrSiO_4, cr, 298.15\ K)$ was calculated from the $\Delta_r H°(298.15\ K)$ of its constituent oxides $ZrO_2(cr) + SiO(cr) = ZrSiO_4(cr)$ and the $\Delta_f H°(298.15\ K)$ values for $ZrO_2(cr)$ and $SiO_2(cr)$ in JANAF tables.[4] The $\Delta_r H°(298.15\ K) = -4.736\ kcal·mol^{-1}$ was based on the Gibbs energy of formation of its constituent oxides at the decomposition temperature 1811 K.

Heat Capacity and Entropy

At low temperatures, $C_p°$ were used from Kelley.[1] From 298–940 K, $C_p°$ was calculated by using the Coughlin and King[2] equation $C_p° = 31.48 + 3.92 \times 10^{-3}T - 8.08 \times 10^5 T^{-2}$ which joined smoothly with the low temperature data. Above 940 K the data were estimated by extending the curve smoothly. The entropy was calculated at 52.7 K using the Debye and Einstein[3] functions D(321/T) + 2E(407/T) + 2E(796/T) + E(1624/T) given by Kelley.[2] $S°(52.7\ K) = 0.65404\ cal·K^{-1}·mol^{-1}$.

Decomposition Data

T_{dcm} is the temperature at which $\Delta_r G° = 0$ for the reaction $ZrSiO_4(cr) \rightarrow ZrO_2(cr) + SiO_2(cr)$. $T_{dcm} = 1811$ K was taken from Curtis and Sowman.[3]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−14.905	−2012.774	−2012.774	INFINITE
100	31.034	14.070	153.089	−13.902	−2018.733	−1983.690	1036.173
200	73.298	49.742	92.291	−8.510	−2022.535	−1946.946	508.490
298.15	98.659	84.026	84.026	0.000	−2023.951	−1909.475	334.532
300	99.119	84.638	84.028	0.183	−2023.961	−1908.764	332.345
400	114.642	115.379	88.114	10.906	−2023.861	−1870.349	244.243
500	125.938	142.241	96.311	22.965	−2022.823	−1832.076	191.396
600	133.679	165.925	105.980	35.967	−2021.207	−1794.071	156.188
700	138.825	186.935	116.073	49.603	−2019.294	−1756.364	131.061
800	142.674	205.738	126.127	63.689	−2017.241	−1718.942	112.235
900	145.268	222.698	135.931	78.091	−2015.160	−1681.779	97.608
1000	147.277	238.112	145.390	92.723	−2013.119	−1644.847	85.918
1100	148.741	252.222	154.470	107.528	−2011.159	−1608.115	76.363
1200	149.704	265.209	163.164	122.454	−2013.031	−1571.335	68.398
1300	150.164	277.211	171.481	137.449	−2010.811	−1534.618	61.662
1400	150.415	288.349	179.436	152.478	−2008.702	−1498.068	55.894
1500	150.624	298.735	187.047	167.532	−2006.718	−1461.664	50.900
1600	150.624	308.456	194.335	182.595	−2004.883	−1425.388	46.534
1700	150.624	317.588	201.319	197.657	−2053.390	−1388.775	42.672
1800	150.624	326.197	208.020	212.719	−2051.665	−1349.731	39.168
1900	150.624	334.341	214.456	227.782	−2050.081	−1310.778	36.036
2000	150.624	342.067	220.645	242.844	−2048.650	−1271.905	33.219
2100	150.624	349.416	226.603	257.907	−2047.382	−1233.100	30.672
2200	150.624	356.423	232.346	272.969	−2067.609	−1193.604	28.340
2300	150.624	363.118	237.887	288.031	−2067.111	−1153.889	26.206
2400	150.624	369.529	243.240	303.094	−2066.658	−1114.194	24.250
2500	150.624	375.678	248.415	318.156	−2066.249	−1074.516	22.451
2600	150.624	381.585	253.424	333.219	−2065.883	−1034.854	20.790
2700	150.624	387.270	258.277	348.281	−2065.559	−995.205	19.253
2800	150.624	392.748	262.982	363.343	−2065.275	−955.567	17.826
2900	150.624	398.033	267.549	378.406	−2065.032	−915.940	16.498
3000	150.624	403.140	271.984	393.468	−2064.827	−876.320	15.258

PREVIOUS: September 1961 CURRENT: June 1965

$S°(298.15\ K) = 103.525 \pm 2.1\ J·K^{-1}·mol^{-1}$
$T_{trs} = 340 \pm 5\ K$
$T_{fus} = 1818 \pm 15\ K$

$\Delta_f H°(0\ K) = -1418.617 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1427.162 \pm 6.3\ kJ·mol^{-1}$
$\Delta_{trs} H° = 8.996 \pm 0.8\ kJ·mol^{-1}$
$\Delta_{fus} H° = 112.068 \pm 2.5\ kJ·mol^{-1}$

Enthalpy of Formation

The adopted $\Delta_f H°$ values for the vanadium oxides, and in particular V_2O_4(cr) are based on the combustion studies by Mah and Kelley.[1] The adopted value is −341.1 kcal·mol^{-1} which was obtained by rounding the reported value of Mah and Kelley.[1] For more details refer to the V_2O_5(cr) table.[2] Charlu and Kleppa[3] reported a enthalpy of formation value at $\Delta_f H°(298.15\ K) = -342.4 \pm 0.78$ kcal·mol^{-1} based on oxidation studies to V_2O_5(cr) in a high temperature microcalorimeter. The combustion by this technique yielded complete oxidation to V_2O_5(cr) as opposed to the method of Mah and Kelley,[1] whereby $\Delta_f H°$ for V_2O_4(cr) was determined simultaneously with that for V_2O_5(cr) due to incomplete combustion of V(cr). A combustion study by Siemonsen and Ulich[4] led to the reported value of -342 ± 2 kcal·mol^{-1} for $\Delta_f H°(V_2O_4, cr, 293\ K)$. Additional thermodynamic data which relate V_2O_3(cr) with V_2O_4(cr) or V_2O_5(cr) is contained in the sodium oxide fusion studies by Mixter,[5] the H_2O–H_2 equilibrium study by Muller,[6] the CO–CO_2 equilibrium study by Spencer and Justice,[7] and the reduction of V_2O_5(cr) with SO_2 by Flood and Kleppa.[8] See V_2O_3(cr) table for some additional information.[2]

Heat Capacity and Entropy

Anderson[9] measured the heat capacity of V_2O_4 (reported purity of 99.5% or better) in the range 61.4–279.4 K. Using the combination of Debye and Einstein functions suggested by Anderson,[9] we calculate $S°(60\ K) = 1.48$ cal·K^{-1}·mol^{-1} and $H°(60;0) = 63.66$ cal·K^{-1}·mol^{-1}. The data of Anderson[9] show considerable scatter from our adopted values, with a ± 2.0% deviation being typical for this data. Cook[10] measured the enthalpy of V_2O_4 in the range 315–1856 K. The enthalpy data for $T < T_{trs}$ appears too high to be fully consistent with $C_p°$ data of Anderson.[9] The adopted $C_p°$ values in the region 280–340 K join smoothly with a positive power polynomial fit of the data of Anderson[4] and lead to enthalpy values at 315.5, 322.8, and 323.0 K which are roughly 48, 34, and 39 kcal·mol^{-1}, respectively, less than the data of Cook.[10] This is a difference of 5–10%. The enthalpy data in the region T_{trs}–T_{fus} are fit to a Kelley type equation and then differentiated to yield our adopted $C_p°$ values. The data of Cook[10] also shows considerable scatter, with deviations ranging from −0.69% to +1.12%.

Three $C_p°$ studies concentrated on the region near T_{trs} but presented only graphical data.[11–13] Kawakubo and Nakagawa[11] reported $C_p°$ values between 30 °C and 90 °C which are roughly 18% higher than our adopted values below the transition and 25% higher above the transition. Ryder *et al.*[12] and Chandrashekhar *et al.*[13] measured $C_p°$ values in the range 40–375 K and 150–730 K. These latter two works agree well graphically in their region of overlap. The $C_p°$ values above T_{trs} are very similar to our adopted values; at 500 K the adopted values are less than 0.1 cal·K^{-1}·mol^{-1} higher while at 700 K, roughly 0.75 cal·K^{-1}·mol^{-1} lower. Below T_{trs}, the differences are more substantial; the adopted values lying approximately 1.5 cal·K^{-1}·mol^{-1} higher.

Phase Data

Minomura and Nagasaki[14] referenced earlier x-ray data and provided additional data to show that V_2O_4 undergoes a structural distortion to lower symmetry on cooling through a transition temperature of 340 K; tetragonal rutile to a monoclinic structure with the unit cell doubling in size. Recent crystallographic investigations by Kawada *et al.*[15] verified the doubling of the size of the unit cell and also detected considerable distortion of the shape of the unit cell. The literature review on the V O system by Stringer[16] indicated that there are a series of oxides between V_3O_5 and V_2O_4. These oxides may be considered as members of a homologous series with $V_2O_4(VO_2)$ being the series limit.[16] Numerous references on phase data are contained in the reviews by Stringer,[16] Adler[17] and Neuberger.[18]

Transition Data

Minomura and Nagasaki[14] repored that the structural distortion occurs at 340 K. This value is consistent with the enthalpy data of Cook.[10] Kawakubo and Nakagawa[11] measured the temperature dependence of five physical properties through the transition point and concluded that the transition occurs at 338 K. We adopt $T_{trs} = 340 + 5$ K.

Using our adopted enthalpy values for $T < T_{trs}$ and $T > T_{trs}$, we calculate and adopt $\Delta_{fus} H° = 2.15 \pm 0.20$ kcal·mol^{-1}. Ryder *et al.*[12] reported a value of 2.040 ± 0.010 kcal·mol^{-1} and Chandrashekhar *et al.*,[13] a value of 2.24 kcal·mol^{-1}. The values of $\Delta_{fus} H° = 1.60$ and 1.50 kcal·mol^{-1} reported by Klemm and Grimm[19] and Kawakubo and Nakagawa,[11] respectively, are considered too low. In our tabulation, the transition is treated as being first order. Controversy exists concerning the order of the transition, as discussed by Adler.[17] Additional references may be found in Stringer,[16] Adler[17] and Neuberger.[18]

Fusion Data

Refer to the liquid table for details.

References

[1] A. D. Mah and K. K. Kelley, U. S. Bur. Mines RI 5858, (1961).
[2] JANAF Thermochemical Tables: V_2O_5(cr), 6-30-73; V_2O_3(cr), 12-31-73.
[3] F. V. Charlu and O. J. Kleppa, High Temp. Soc. **5**, 260 (1973).
[4] H. Siemonsen and H. Ulich, Z. Electrochem. **46**, 141 (1940).
[5] W. G. Mixter, Amer. J. Sci. **34**, 141 (1912).

Continued on page 1815

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−18.100	−1418.617	−1418.617	INFINITE
100	36.907	18.652	186.891	−16.824	−1424.127	−1389.894	726.006
200	90.274	62.333	113.357	−10.205	−1427.002	−1354.252	353.694
298.15	115.399	103.525	103.525	0.000	−1427.162	−1318.445	230.986
300	115.787	104.240	103.527	0.214	−1427.150	−1317.770	229.444
340.000	123.336	119.218	104.501	5.004	I <--> II		
340.000	127.621	145.675	104.501	13.999	TRANSITION		
400	135.281	167.065	112.309	21.902	−1416.532	−1283.094	167.555
500	143.269	198.162	126.456	35.853	−1414.020	−1250.016	130.588
600	148.448	224.758	140.677	50.448	−1411.187	−1217.477	105.991
700	152.175	247.927	154.379	65.483	−1408.212	−1185.426	88.458
800	155.457	268.466	167.380	80.868	−1405.169	−1153.807	75.336
900	158.157	286.934	179.655	96.551	−1402.101	−1122.571	65.152
1000	160.682	303.729	191.236	112.494	−1399.025	−1091.677	57.023
1100	162.987	319.153	202.173	128.678	−1395.953	−1061.091	50.387
1200	165.209	333.430	212.523	145.089	−1392.908	−1030.784	44.869
1300	167.330	346.738	222.341	161.716	−1389.898	−1000.729	40.210
1400	169.406	359.215	231.677	178.553	−1386.944	−970.904	36.225
1500	171.429	370.972	240.575	195.595	−1384.045	−941.289	32.779
1600	173.427	382.100	249.076	212.838	−1381.201	−911.865	29.769
1700	175.302	392.669	257.214	230.273	−1378.439	−882.616	27.119
1800	177.343	402.746	265.022	247.904	−1375.760	−853.528	24.769
1818.000	177.728	404.513	266.394	251.100	----- II <--> LIQUID -----		
1900	179.276	412.387	272.526	265.737	−1373.179	−824.586	22.669
2000	181.192	421.632	279.752	283.760	−1370.723	−795.777	20.784
2100	183.092	430.518	286.721	301.975	−1368.413	−767.087	19.080
2200	184.975	439.079	293.453	320.378	−1412.030	−738.293	17.529

PREVIOUS: September 1973 CURRENT: December 1973

$S°(298.15\ K) = [173.473]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1818 \pm 15\ K$

$\Delta_f H°(298.15\ K) = [-1332.151]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 112.068 \pm 2.5\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(V_2O_4, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1818\ K)-H°(298.15\ K)$, between V_2O_4(cr) and V_2O_4(l).

Heat Capacity and Entropy

Cook[1] measured the enthalpy of V_2O_4(l) in the region 1829.7–1856.8 K and represented the data by the equation $H°(T)-H°(298.15\ K) = 51.00\ T-5910\ cal·K^{-1}·mol^{-1}$. Thus $C_p°$ for the liquid is adopted as 51.00 $cal·K^{-1}·mol^{-1}$. Since the enthalpy measurements only cover a range of 39 K in the liquid region, the value of $C_p°$ should not be viewed as a precise value. A glass transition is assumed at 1200 K. Below 1200 K, the $C_p°$ values are those of the crystal with the exception that the values of $C_p°$ between 298 and 340 K are a smooth extrapolation of the crystal values above T_{trs}. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

The melting point of V_2O_4(cr) is adopted as 1818 K, based on the enthalpy data of Cook.[1] The enthalpy of melting is calculated from the difference in $H°-(1818\ K)\ H°(298.15\ K)$ for V_2O_4(l) and V_2O_4(cr).

References – V_2O_4(l)

[1]O. A. Cook, J. Amer. Chem. Soc. **69**, 331 (1947).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	120.081	173.473	173.473	0.000	−1332.151	−1244.289	217.994
300	120.499	174.217	173.475	0.223	−1332.130	−1243.744	216.555
400	135.281	211.142	178.409	13.093	−1330.330	−1214.523	158.600
500	143.269	242.239	188.151	27.044	−1327.818	−1185.852	123.885
600	148.448	268.835	199.436	41.639	−1324.985	−1157.722	100.789
700	152.175	292.004	211.041	56.674	−1322.010	−1130.079	84.327
800	155.457	312.543	222.469	72.060	−1318.967	−1102.867	72.010
900	158.157	331.011	233.520	87.742	−1315.899	−1076.039	62.452
1000	160.682	347.807	244.122	103.685	−1312.823	−1049.552	54.823
1100	163.033	363.233	254.258	119.872	−1309.748	−1023.374	48.596
1200	165.209	377.513	263.942	136.286	−1306.700	−997.475	43.419
1200.000	165.209	377.513	263.942	136.286	GLASS <– –> LIQUID TRANSITION		
1200.000	213.384	377.513	263.942	136.286			
1300	213.384	394.593	273.344	157.624	−1298.979	−972.021	39.056
1400	213.384	410.407	282.576	178.963	−1291.523	−947.152	35.339
1500	213.384	425.129	291.595	200.301	−1284.329	−922.807	32.135
1600	213.384	438.900	300.375	221.639	−1277.389	−898.933	29.347
1700	213.384	451.836	308.908	242.978	−1270.723	−875.485	26.900
1800	213.384	464.033	317.191	264.316	−1264.336	−852.422	24.737
1818.000	213.384	466.156	318.655	268.157	----- II <–> LIQUID -----		
1900	213.384	475.570	325.226	285.655	−1258.250	−829.705	22.810
2000	213.384	486.515	333.019	306.993	−1252.480	−807.301	21.085
2100	213.384	496.926	340.578	328.331	−1247.045	−785.177	19.530
2200	213.384	506.853	347.912	349.670	−1287.728	−763.093	18.118
2300	213.384	516.338	355.030	371.008	−1283.291	−739.346	16.791
2400	213.384	525.420	361.942	392.347	−1278.900	−715.792	15.579
2500	213.384	534.131	368.657	413.685	−1274.552	−692.418	14.467
2600	213.384	542.500	375.183	435.023	−1270.247	−669.218	13.445
2700	213.384	550.553	381.530	456.362	−1265.984	−646.182	12.501
2800	213.384	558.313	387.706	477.700	−1261.761	−623.303	11.628
2900	213.384	565.801	393.719	499.039	−1257.579	−600.576	10.818
3000	213.384	573.035	399.576	520.377	−1253.435	−577.991	10.064

PREVIOUS: CURRENT: June 1973

0	to	340	K crystal, I
340	to	1818	K crystal, II
above		1818	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	−18.100	−1418.617	−1418.617	INFINITE
100	36.907	18.652	186.891	−16.824	−1424.127	−1389.894	726.006
200	90.274	62.333	113.357	−10.205	−1427.002	−1354.252	353.694
298.15	115.399	103.525	103.525	0.000	−1427.162	−1318.445	230.986
300	115.787	104.240	103.527	0.214	−1427.150	−1317.770	229.444
340.000	123.336	119.218	104.501	5.004		I <--> II	
340.000	127.621	145.675	104.501	13.999		TRANSITION	
400	135.281	167.065	112.309	21.902	−1416.532	−1283.094	167.555
500	143.269	198.162	126.456	35.853	−1414.020	−1250.016	130.588
600	148.448	224.758	140.677	50.448	−1411.187	−1217.477	105.991
700	152.175	247.927	154.379	65.483	−1408.212	−1185.426	88.458
800	155.457	268.466	167.380	80.868	−1405.169	−1153.807	75.336
900	158.157	286.934	179.655	96.551	−1402.101	−1122.571	65.152
1000	160.682	303.729	191.236	112.494	−1399.025	−1091.677	57.023
1100	162.987	319.153	202.173	128.678	−1395.953	−1061.091	50.387
1200	165.209	333.430	212.523	145.089	−1392.908	−1030.784	44.869
1300	167.330	346.738	222.341	161.716	−1389.898	−1000.729	40.210
1400	169.406	359.215	231.677	178.553	−1386.944	−970.904	36.225
1500	171.429	370.972	240.575	195.595	−1384.045	−941.289	32.779
1600	173.427	382.100	249.076	212.838	−1381.201	−911.865	29.769
1700	175.302	392.669	257.214	230.273	−1378.439	−882.616	27.119
1800	177.343	402.746	265.022	247.904	−1375.760	−853.528	24.769
1818.000	177.728	404.513	266.394	251.100		II <--> LIQUID	
1818.000	213.384	466.156	266.394	363.168		TRANSITION	
1900	213.384	475.570	275.220	380.666	−1258.250	−829.705	22.810
2000	213.384	486.515	285.513	402.004	−1252.480	−807.301	21.085
2100	213.384	496.926	295.335	423.342	−1247.045	−785.177	19.530
2200	213.384	506.853	304.725	444.681	−1287.728	−763.093	18.118
2300	213.384	516.338	313.721	466.019	−1283.291	−739.346	16.791
2400	213.384	525.420	322.354	487.358	−1278.900	−715.792	15.579
2500	213.384	534.131	330.652	508.696	−1274.552	−692.418	14.467
2600	213.384	542.500	338.640	530.034	−1270.247	−669.218	13.445
2700	213.384	550.553	346.341	551.373	−1265.984	−646.182	12.501
2800	213.384	558.313	353.773	572.711	−1261.761	−623.303	11.628
2900	213.384	565.801	360.956	594.050	−1257.579	−600.576	10.818
3000	213.384	573.035	367.906	615.388	−1253.435	−577.991	10.064

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 143.114 \pm 1.3\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2058 \pm 30\ K$

$\Delta_f H°(0\ K) = -2035.947 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -2045.976 \pm 4.2\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [120.081 \pm 16.7]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ta_2O_5, cr, 298.15\ K)$ values show scatter due to uncertainties concerning the polymorphic state of the sample and/or the incomplete specification of sample purity.[1] The reported values for $\Delta_f H°(Ta_2O_5, cr, 298.15\ K)$ based on bomb calorimetry studies are as follows:

Source	Ta(cr) purity,%	% run*	$\Delta_f H°$(Ta2O5,cr,2 918.15K) kcal·mol^{-1}
[2]			309.5
[3]	99.96	>99.0	−498.3
[4]			−480.5
[5]	99.9	72.92–93.83	−486.0 ± 0.5
[6]			−499.9 ± 1.0
[7]	99.89	97.23–99.99	−489.0 ± 0.5**
[8]	99.80		−487.7 ± 0.9
[9]	99.16, 99.7	99.5–99.9	−489.3 ± 0.4
[10]			−480.0 ± 0.8

*Refers to extent of reaction 2 Ta(cr) + 5/2 O_2(g) = Ta_2O_5(cr)
**The reported value of −488.8 ± 0.5 was corrected by Huber *et al.*[8] in order to have the value based on the current atomic weight of Ta.

The value chosen for $\Delta_f H°(Ta_2O_5, cr, 298.15\ K)$ is −489.0 ± 0.5 based primarily on the work by Humphrey[7] and Kornilov *et al.*[9] Worrell,[17] using a high temperature galvanic cell, obtained $\Delta_f G\beta$ values of Ta_2O_5 in the range 1050–1300 K which are approximately 0.6–1.1 kcal·mol^{-1} more negative than the values tabulated here. Ignatowicz and Davies[12] using a galvanic cell approach reported $\Delta_f G°$ values for Ta_2O_5 in the range 1073–1373 K. Barbi[11,13] determined $\Delta_f G°$ based on emf measurements in the range 1079–1776 K while Rezukhina and Kravchenko[16] worked in the range 1200–1350 K. A third law analysis of the reported smoothed results yields the following.

Source	$\Delta_f H°(298.15\ K)$, kcal·mol^{-1}	cal·K^{-1}·mol^{-1}
[11]	−484.8	0.85
[12]	−487.9	−0.65
[13]*	−484.7	+0.95
[16]	−487.9	+0.83

*Actual experimental data was analyzed.

These latter three works[12,13,16] did not specify purity of sample or the state of polymorphism.

Based on the recent critical review by Reisman and Holtzberg,[1] this discussion has been concerned with the low temperature β–phase of Ta_2O_5. Even though two $\Delta_f H°(298.15\ K)$ studies[9,10] apparently deal with the high temperature α phase, there does not appear to be any difference in the $\Delta_f H°(298.15\ K)$ values for the α phase or β–phase, within experimental error.[1]

Heat Capacity and Entropy

Kelley[14] measured the heat capacity of Ta_2O_5(cr) from 53.4 K to 294.2 K and fitted the data (29 data points) with a combination of Debye and Einstein functions. These functions were used to calculate $S°(50\ K) = 2.47\ cal \cdot K^{-1} \cdot mol^{-1}$. Orr[15] measured the enthalpy of Ta_2O_5(cr) from 395.6 K to 1802.6 K (15 data points). Nine data points at the high temperature end of the Kelley data were fitted by a four term polynomial, and integrated to yield enthalpy values in the vicinity of 298.15 K. These enthalpy values were combined with the Orr data, fitted to a six term polynomial, and extrapolated to 2800 K. The complete Kelley data was also fitted by a six term polynomial. The Nb_2O_5 heat capacity and enthalpy data presented in these tables are treated in the same manner so as to maintain consistency between the results for Nb_2O_5 and Ta_2O_5.

The Ta_2O_5(cr) sample used by Kelley[14] and Orr[15] was the same. Presumably both were using the low temperature β phase of Ta_2O_5, as discussed by Reisman and Holtzberg[1] and Orr.[15] The enthalpy data of Orr[15] did not conclusively indicate any phase transitions, i.e., the $\beta \rightarrow \alpha$ transition, in the vicinity of 1633 K, as reported by Reisman and Holtzberg.[1]

Fusion Data

Refer to the liquid table for details.

Continued on page 1815

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.000	0.000	INFINITE	−23.041	−2035.947	−2035.947	INFINITE
100	58.082	37.108	243.530	−20.642	−2042.799	−1999.955	1044.669
200	108.311	94.161	154.766	−12.121	−2046.060	−1955.515	510.728
298.15	135.034	143.114	143.114	0.000	−2045.976	−1911.004	334.800
300	135.342	143.950	143.116	0.250	−2045.956	−1910.167	332.590
400	147.515	184.681	148.588	14.437	−2044.314	−1865.126	243.561
500	156.862	218.636	159.293	29.671	−2041.946	−1820.591	190.196
600	164.431	247.930	171.680	45.750	−2039.087	−1776.582	154.665
700	170.431	273.746	184.453	62.505	−2035.876	−1733.081	129.324
800	175.197	296.825	197.083	79.794	−2032.397	−1690.059	110.350
900	179.038	317.683	209.342	97.507	−2028.710	−1647.487	95.618
1000	182.753	336.753	221.144	115.610	−2024.820	−1605.335	83.854
1100	184.824	354.267	232.461	133.987	−2020.837	−1563.579	74.248
1200	187.071	370.448	243.294	152.584	−2016.807	−1522.187	66.259
1300	189.021	385.500	253.661	171.391	−2012.725	−1481.134	59.513
1400	190.740	399.572	263.586	190.380	−2008.590	−1440.398	53.742
1500	192.280	412.785	273.096	209.533	−2004.394	−1399.959	48.751
1600	193.673	425.239	282.220	228.831	−2000.138	−1359.802	44.393
1700	194.953	437.020	290.982	248.263	−1995.845	−1319.912	40.556
1800	196.138	448.197	299.409	267.819	−1991.558	−1280.276	37.153
1900	197.246	458.831	307.522	287.488	−1987.315	−1240.876	34.114
2000	198.288	468.975	315.343	307.265	−1983.130	−1201.698	31.385
2058.000	198.870	474.652	319.753	318.783	--- CRYSTAL <--> LIQUID ---		
2100	199.278	478.674	322.891	327.144	−1979.005	−1162.728	28.921
2200	200.225	487.967	330.185	347.120	−1974.946	−1123.952	26.686
2300	201.133	496.887	337.240	367.188	−1970.962	−1085.361	24.649
2400	202.012	505.466	344.072	387.345	−1967.065	−1046.941	22.786
2500	202.859	513.730	350.694	407.589	−1963.269	−1008.681	21.075
2600	203.685	521.702	357.119	427.916	−1959.594	−970.570	19.499
2700	204.491	529.404	363.358	448.325	−1956.062	−932.597	18.042
2800	205.275	536.855	369.422	468.814	−1952.699	−894.753	16.692

PREVIOUS: CURRENT: December 1972

Tantalum Oxide (Ta_2O_5) LIQUID M_r = 441.89128

$S°(298.15\ K)$ = [183.050] $J·K^{-1}·mol^{-1}$
T_{fus} = 2058 ± 30 K

$\Delta_f H°(298.15\ K)$ = [−1957.171] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [120.081 ± 16.7] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ta_2O_5, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2058\ K)-H°(298.15\ K)$, between Ta_2O_5(cr) and Ta_2O_5(l).

Heat Capacity and Entropy

The heat capacity for Ta_2O_5(l) is estimated to be 58.00 $cal·K^{-1}·mol^{-1}$ by analogy with Nb_2O_5(l). A glass transition temperature is assumed at 1400 K. The heat capacity values used below 1400 K are those of Ta_2O_5(cr). The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation.

Fusion Data

The melting point of β Ta_2O_5 is chosen as 2058 ± 30 K based on work by Reisman *et al.*[1] The melting point data and the Ta_2O_5 polymorphism are discussed by Reisman and Holtzberg[2] The heat of fusion, $\Delta_{fus}H°$, is estimated from the entropy of fusion for Nb_2O_5 as reported in these tables. Using the Nb_2O_5 entropy of fusion value of 24.92 $cal·K^{-1}·mol^{-1}$ and a melting temperature of 2058 K, the enthalpy of fusion for Ta_2O_5 is calculated to be 28.7 ± 4 $kcal·mol^{-1}$.

References

[1]A. Reisman, F. Holtzberg, M. Berkenblit, and M. Berry, J. Amer. Chem. Soc. **8**, 4514 (1956).
[2]A. Reisman and F. Holtzberg, High Temperature Oxides **2**, 217 (1970).

Tantalum Oxide (Ta_2O_5) O_5Ta_2(l)

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	135.034	183.050	183.050	0.000	−1957.171	−1834.107	321.328
300	135.342	183.886	183.052	0.250	−1957.151	−1833.343	319.213
400	147.515	224.617	188.524	14.437	−1955.509	−1792.296	234.050
500	156.862	258.572	199.230	29.671	−1953.141	−1751.754	183.005
600	164.431	287.866	211.616	45.750	−1950.282	−1711.739	149.020
700	170.431	313.682	224.389	62.505	−1947.071	−1672.231	124.783
800	175.197	336.761	237.019	79.794	−1943.592	−1633.204	106.637
900	179.038	357.619	249.279	97.507	−1939.905	−1594.624	92.550
1000	182.753	376.690	261.080	115.610	−1936.016	−1556.467	81.301
1100	184.824	394.203	272.397	133.987	−1932.032	−1518.704	72.117
1200	187.071	410.384	283.230	152.584	−1928.002	−1481.306	64.480
1300	189.021	425.436	293.597	171.391	−1923.920	−1444.247	58.031
1400	190.740	439.508	303.522	190.381	−1919.785	−1407.503	52.515
1400.000	190.740	439.508	303.522	190.381	GLASS <--> LIQUID TRANSITION		
1400.000	242.672	439.508	303.522	190.381			
1500	242.672	456.251	313.152	214.648	−1910.474	−1371.238	47.751
1600	242.672	471.913	322.591	238.915	−1901.249	−1335.590	43.603
1700	242.672	486.624	331.811	263.182	−1892.121	−1300.516	39.960
1800	242.672	500.495	340.801	287.450	−1883.122	−1265.977	36.738
1900	242.672	513.616	349.554	311.717	−1874.282	−1231.933	33.868
2000	242.672	526.063	358.071	335.984	−1865.606	−1198.350	31.298
2058.000	242.672	533.001	362.904	350.059	--- CRYSTAL <--> LIQUID ---		
2100	242.672	537.903	366.355	360.251	−1857.093	−1165.197	28.983
2200	242.672	549.192	374.411	384.518	−1848.743	−1132.445	26.888
2300	242.672	559.980	382.247	408.786	−1840.560	−1100.071	24.983
2400	242.672	570.308	389.869	433.053	−1832.552	−1068.049	23.245
2500	242.672	580.214	397.286	457.320	−1824.733	−1036.356	21.653
2600	242.672	589.732	404.506	481.587	−1817.118	−1004.971	20.190
2700	242.672	598.890	411.537	505.854	−1809.728	−973.875	18.841
2800	242.672	607.716	418.386	530.122	−1802.587	−943.049	17.593
2900	242.672	616.231	425.063	554.389	−1795.721	−912.475	16.435
3000	242.672	624.458	431.573	578.656	−1789.164	−882.130	15.359
3100	242.672	632.415	437.924	602.923	−1782.950	−851.997	14.356
3200	242.672	640.120	444.123	627.190	−1777.119	−822.063	13.419
3300	242.672	647.587	450.176	651.458	−1844.626	−791.361	12.526
3400	242.672	654.832	456.089	675.725	−1838.846	−759.529	11.669
3500	242.672	661.866	461.869	699.992	−1833.107	−727.869	10.863
3600	242.672	668.703	467.519	724.259	−1827.406	−696.371	10.104
3700	242.672	675.352	473.047	748.526	−1821.742	−665.033	9.389
3800	242.672	681.823	478.456	772.794	−1816.114	−633.844	8.713
3900	242.672	688.127	483.752	797.061	−1810.520	−602.804	8.074
4000	242.672	694.271	488.939	821.328	−1804.960	−571.909	7.468
4100	242.672	700.263	494.020	845.595	−1799.432	−541.151	6.894
4200	242.672	706.111	499.001	869.862	−1793.936	−510.528	6.349
4300	242.672	711.821	503.884	894.130	−1788.471	−480.034	5.831
4400	242.672	717.400	508.673	918.397	−1783.036	−449.670	5.338
4500	242.672	722.853	513.372	942.664	−1777.632	−419.428	4.869
4600	242.672	728.187	517.984	966.931	−1772.258	−389.306	4.421
4700	242.672	733.406	522.513	991.198	−1766.916	−359.298	3.993
4800	242.672	738.515	526.960	1015.466	−1761.604	−329.405	3.585
4900	242.672	743.519	531.328	1039.733	−1756.324	−299.621	3.194
5000	242.672	748.421	535.621	1064.000	−1751.077	−269.945	2.820

PREVIOUS: CURRENT: December 1972

Tantalum Oxide (Ta_2O_5) O_5Ta_2(l)

0	to	2058	K crystal
above		2058	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−23.041	−2035.947	−2035.947	INFINITE
100	58.082	37.108	243.530	−20.642	−2042.799	−1999.955	1044.669
200	108.311	94.161	154.766	−12.121	−2046.060	−1955.515	510.728
298.15	135.034	143.114	143.114	0.000	−2045.976	−1911.004	334.800
300	135.342	143.950	143.116	0.250	−2045.956	−1910.167	332.590
400	147.515	184.681	148.588	14.437	−2044.314	−1865.126	243.561
500	156.862	218.636	159.293	29.671	−2041.946	−1820.591	190.196
600	164.431	247.930	171.680	45.750	−2039.087	−1776.582	154.665
700	170.431	273.746	184.453	62.505	−2035.876	−1733.081	129.324
800	175.197	296.825	197.083	79.794	−2032.397	−1690.059	110.350
900	179.038	317.683	209.342	97.507	−2028.710	−1647.487	95.618
1000	182.753	336.753	221.144	115.610	−2024.820	−1605.335	83.854
1100	184.824	354.267	232.461	133.987	−2020.837	−1563.579	74.248
1200	187.071	370.448	243.294	152.584	−2016.807	−1522.187	66.259
1300	189.021	385.500	253.661	171.391	−2012.725	−1481.134	59.513
1400	190.740	399.572	263.586	190.380	−2008.590	−1440.398	53.742
1500	192.280	412.785	273.096	209.533	−2004.394	−1399.959	48.751
1600	193.673	425.239	282.220	228.831	−2000.138	−1359.802	44.393
1700	194.953	437.020	290.982	248.263	−1995.845	−1319.912	40.556
1800	196.138	448.197	299.409	267.819	−1991.558	−1280.276	37.153
1900	197.246	458.831	307.522	287.488	−1987.315	−1240.876	34.114
2000	198.288	468.975	315.343	307.265	−1983.130	−1201.698	31.385
2058.000	198.870	474.652	319.753	318.783	CRYSTAL <-- --> LIQUID TRANSITION		
2058.000	242.672	533.001	319.753	438.864			
2100	242.672	537.903	324.067	449.056	−1857.093	−1165.197	28.983
2200	242.672	549.192	334.045	473.323	−1848.743	−1132.445	26.888
2300	242.672	559.980	343.636	497.591	−1840.560	−1100.071	24.983
2400	242.672	570.308	352.867	521.858	−1832.552	−1068.049	23.245
2500	242.672	580.214	361.764	546.125	−1824.733	−1036.355	21.653
2600	242.672	589.732	370.350	570.392	−1817.118	−1004.971	20.190
2700	242.672	598.890	378.646	594.659	−1809.728	−973.875	18.841
2800	242.672	607.716	386.670	618.927	−1802.587	−943.049	17.593
2900	242.672	616.231	394.440	643.194	−1795.721	−912.475	16.435
3000	242.672	624.458	401.971	667.461	−1789.164	−882.130	15.359
3100	242.672	632.415	409.277	691.728	−1782.950	−851.997	14.356
3200	242.672	640.120	416.371	715.995	−1777.119	−822.063	13.419
3300	242.672	647.587	423.265	740.263	−1844.626	−791.361	12.526
3400	242.672	654.832	429.970	764.530	−1838.846	−759.529	11.669
3500	242.672	661.866	436.496	788.797	−1833.107	−727.869	10.863
3600	242.672	668.703	442.851	813.064	−1827.406	−696.371	10.104
3700	242.672	675.352	449.046	837.331	−1821.742	−665.033	9.389
3800	242.672	681.823	455.087	861.599	−1816.114	−633.844	8.713
3900	242.672	688.127	460.982	885.866	−1810.520	−602.804	8.074
4000	242.672	694.271	466.737	910.133	−1804.960	−571.909	7.468
4100	242.672	700.263	472.360	934.400	−1799.432	−541.151	6.894
4200	242.672	706.111	477.857	958.667	−1793.936	−510.528	6.349
4300	242.672	711.821	483.231	982.935	−1788.471	−480.034	5.831
4400	242.672	717.400	488.490	1007.202	−1783.036	−449.670	5.338
4500	242.672	722.853	493.638	1031.469	−1777.632	−419.428	4.869
4600	242.672	728.187	498.679	1055.736	−1772.258	−389.306	4.421
4700	242.672	733.406	503.618	1080.003	−1766.916	−359.298	3.993
4800	242.672	738.515	508.459	1104.271	−1761.604	−329.405	3.585
4900	242.672	743.519	513.205	1128.538	−1756.324	−299.621	3.194
5000	242.672	748.421	517.860	1152.805	−1751.077	−269.945	2.820

PREVIOUS: CURRENT: December 1972

Titanium Oxide, Alpha (α–Ti_3O_5) CRYSTAL M_r = 223.6370

$S°(298.15\ K) = 129.369 \pm 1.7\ J \cdot K^{-1} \cdot mol^{-1}$

$T_{trs}(\alpha \rightarrow \beta) = 450 \pm 20\ K$

$\Delta_f H°(0\ K) = -2446.057\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -2459.146 \pm 4.2\ kJ \cdot mol^{-1}$

$\Delta_{trs} H° = [13.263 \pm 5.0]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K) = -587.75\ kcal \cdot mol^{-1}$ is calculated from that of TiO_2(rutile) using $\Delta_c H° = -89.65 \pm 0.05\ kcal \cdot mol^{-1}$ determined by Humphrey[1] from combustion calorimetry. Ariya *et al.*[2] reported $\Delta_f H° = -587.0 \pm 1.0\ kcal \cdot mol^{-1}$ derived from their own values of $\Delta_c H°$ for $Ti_3O_{5.03}$ and Ti(cr). Tests for incomplete combustion were made by grinding the product and igniting it to constant weight in air[1] or in moist oxygen.[2] Humphrey[1] reported that his rutile was bright yellow in color and did not gain weight. This implies an atomic ratio (O/Ti) ≥2.00, compared with the value of ~1.95 reported by Ariya *et al.*[2] New high–temperature calorimetry by Charlu *et al.*[9] gave $\Delta_c H°(1100) = -93.57 \pm 1.3\ kcal \cdot mol^{-1}$ after linear correction to (O/Ti) = 2.00 from 1.97 produced by combustion. Our reduction to 298 K and $Ti_3O_5(\alpha)$ yields $\Delta_c H° = -90.36 \pm 2.5\ kcal \cdot mol^{-1}$, including an assumed uncertainty allowance of 1% for the weight gains.

The calorimetric data are compared below with new high–temperature data for $\Delta_r G°$.[3,4] Emf data[4] for reaction B are consistent with the adopted $\Delta_f H°$, but integrated values of $\Delta_r G°$ for reaction A yield $\Delta_f H°$ more negative by $1.8\ kcal \cdot mol^{-1}$. Perhaps coincidentally, the $\Delta_c H°$ of Ariya *et al.*[2] yields $\Delta_f H°$ more negative by $1.9\ kcal \cdot mol^{-1}$ when combined with the JANAF $\Delta_f H°$[05] for TiO_2(rutile). Merritt *et al.*[3] obtained $\Delta_r G°$ for the combustion reaction A by integrating extensive data for equilibrium oxygen potentials of the many stable phases and solid solutions between TiO_2 and Ti_3O_5. They determined the oxide composition by mass during equilibration with ($H_2 + H_2O$) gas mixtures of known oxygen potential. Gross hysteresis was observed in three regions of composition. Oxygen potentials in these regions were deduced with a reasonable assumption, combined with Zador's emf data for oxygen–deficient rutile, and integrated to yield $\Delta_r G°(1304\ K) = -56.14 \pm 0.43\ kcal \cdot mol^{-1}$ for reaction A. We obtain $\Delta_r G° = -57.30\ kcal \cdot mol^{-1}$ at 1273 K and −51.15 at 1473 K by similar integrations of oxygen potentials derived from emf data relative to Fe/FeO and Cr/Cr_2O_3 reported by Suzuki and Sambongi.[4]

Suzuki and Sambongi[4] also reported solid–state emf data which relate Ti_3O_5 to Ti_2O_3. We convert their (graphical) emf data[4] to oxygen potentials using the authors' self–consistent data for the reference couples. The results for reaction B yield $\Delta_r H°$ and $\Delta_r S°$ values consistent with our adopted tables. 3rd law values of $\Delta_r H°(298.15\ K)$ of −42.29, −42.15 and −42.13 $kcal \cdot mol^{-1}$agree with −42.52[1], −42.8 ± 1.3[2] and −42.0[9] which can be calculated from combustion calorimetry.

The discrepancy in reaction A may be due to undetected bias (2% too small in magnitude) in $\Delta_r G°$, but alternative possibilities include bias in $S°$ (see Ti_3O_5, β), $\Delta_c H°$ or enthalpy (see TiO_2, rutile).

Source	Method	Reaction[a]	T/K	δS $cal \cdot K^{-1} \cdot mol^{-1}$	$\Delta_r H°(298.15\ K)$ $kcal \cdot mol^{-1}$	$\Delta_f H°(298.15\ K)$, $kcal \cdot mol^{-1}$ Authors	JANAF
1	$\Delta_c H°$	A	303→298	–	−89.65 ± 0.05	−586.9 ± 0.7	−587.75 ± 09
2	$\Delta_c H°$	A	293	–	−87.7	−587.0 ± 1.0	−589.7
9	$\Delta_c H°$	A	1100→298	–	−90.36 ± 2.5	−586.3	−587.0 ± 2.7
3	$\Delta_r G(O_2)$	A	1304	–	−87.81 ± 0.6	–	−589.6 ± 1.1
4	$\Delta_r G(O_2)$, emf	A	1273–1473	−3.5	−87.81 ± 1	–	−589.6 ± 1.4
4	emf, Cr/Cr_2O_3	B[b]	~940–1740	0.6	−42.29	–	−587.5[d]
	emf, Ta/Ta_2O_5	B[b]	~1100–1750	0.0	−42.15	–	−587.4[d]
	emf, "$TiO_{1.3}$"	B[b]	~1300–1700	0.0	−42.13	–	−587.4[d]

[a]Reactions: A) $Ti_3O_5(\alpha, \beta) + 1/2\ O_2 \rightarrow 3\ TiO_2$(rutile); B)$3/2\ Ti_2O_3(\alpha, \beta) + 1/4\ O_2 \rightarrow Ti_3O_5(\alpha, \beta)$.

[b]$\Delta_r G°$ from integration of $\Delta_r G$(O)assuming negligible homogeneity range for TiO. Alternative $\Delta G°$, assuming a linear variation of $\Delta_f G°(O_2)$ for $1.42 < X < 1.56$, changes δS by ~0.2 and $\Delta_r H°$ and $\Delta_f H°$ by ~−0.3.

Heat Capacity and Entropy

$C_p°$ below 300 K is based on data of Shomate, (53–297 K)[6] and his Debye–Einstein extrapolation to absolute zero. The entropy is calculated by polynomial integration of $C_p°$ based on $S°(50\ K) = 0.87\ cal \cdot K^{-1} \cdot mol^{-1}$. Our assigned entropy uncertainty of $\pm 0.4\ cal \cdot K^{-1} \cdot mol^{-1}$ includes an additional contribution because the sample gave weak, fuzzy x–ray lines and was only 99.1% pure. Apparently there are new $C_p°$ data (12–300 K) which are unpublished and not yet available.[10] $C_p°$ is extrapolated smoothly from 300 K to 450 K and to higher temperatures where $Ti_3O_5(\beta)$ is the stable form. Our extrapolation probably represents the lower limit for the true $C_p°$ below T_{trs}, while the curve of Furukawa and Reilly[7] is an upper limit. The equations reported by Naylor[8] yield even higher enthalpies and fail to join properly with the low temperature data at 298 K. This is due to complications in the enthalpy data (see below) and to positive bias in the drop calorimeter in this temperature range.[5]

Naylor[8] measured enthalpy data (326–1340 K) which revealed a transition at ~450 K. When the samples were heated above this temperature, they did not return to the original state on cooling. Enthalpies were then systematically higher by up to 10%. The change in the enthalpy curve seemed to depend on both the temperature and time of heating above T_{trs}. Regrinding was the only method found for returning the sample to its original state. X–ray diffraction at room temperature revealed no difference between these two states, but failure to detect a difference may be due to the weak, fuzzy x–ray lines.[6,8] Possible explanations for the anomalous enthalpy data are noted in Transition Data.

Transition Data

Refer to the β–crystal table for details

Continued on page 1816

Titanium Oxide, Alpha (Ti_3O_5) O_5Ti_3(cr)

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.000	0.000	INFINITE	−23.108	−2446.057	−2446.057	INFINITE
100	46.116	21.062	237.166	−21.610	−2453.501	−2409.803	1258.752
200	114.445	75.659	142.352	−13.339	−2458.258	−2363.911	617.390
298.15	154.808	129.369	129.369	0.000	−2459.146	−2317.293	405.980
300	155.477	130.329	129.372	0.287	−2459.135	−2316.413	403.323
400	182.841	179.228	135.852	17.350	−2457.340	−2269.052	296.308
450	189.954	201.217	141.909	26.688	−2455.868	−2245.602	260.663
500	194.138	221.452	148.866	36.293	−2454.266	−2222.324	232.165
600	200.832	257.461	164.038	56.054	−2450.880	−2176.251	189.459
700	206.062	288.828	179.673	76.409	−2447.326	−2130.758	158.999
800	210.037	316.611	195.087	97.219	−2443.632	−2085.786	136.188
900	213.384	341.551	209.999	118.397	−2439.941	−2041.278	118.473
1000	215.894	364.163	224.302	139.861	−2436.495	−1997.170	104.321
1100	218.405	384.861	237.971	161.579	−2433.495	−1953.386	92.759
1200	220.497	403.954	251.017	183.524	−2442.906	−1909.496	83.118
1300	222.589	421.689	263.472	205.682	−2438.647	−1865.218	74.945
1400	224.262	438.246	275.371	228.025	−2434.515	−1821.264	67.952
1500	225.936	453.775	286.752	250.535	−2430.558	−1777.600	61.902

PREVIOUS: March 1967 CURRENT: December 1973

$S°(298.15\ K) = [157.617]\ J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 450 \pm 20\ K$
$T_{fus} = 2050 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-2446.189]\ kJ·mol^{-1}$
$\Delta_{trs}H°[13.263 \pm 5.0]\ kJ·mol^{-1}$
$\Delta_{fus}H° = [171.544]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of $Ti_3O_5(\alpha)$ by adding $\Delta_{trs}H°$ to the difference in $H°(450\ K)–H°(298.15\ K)$ between the α– and β– phases. Experimental data for $\Delta_f G°$ of the β–phase are analyzed on the table for the α–phase.

Heat Capacity and Entropy

$C_p°$ of the β–phase is derived from fitting of enthalpy data of Naylor, (504–1340 K)[1] and Slyusar *et al.*, (580–1994 K).[2] Naylor's data below 482 K are omitted due to thermal hysteresis in the transition; even the points near 500 K show unusual scatter. The new data of Slyusar *et al.*[2] are suspect due to a discontinuity of almost 4% at ~1250 K where the authors switched container materials and temperature sensors. Their data[2] for Ti_2O_3 and TiO_2(rutile) show similar discontinuities and appear to have a bias of about −4% below 1100 K. Their data for Ti_3O_5 do not differ significantly from those of Naylor,[1] so we combine the two sets.

$S°$ is calculated in a manner analogous to that of $\Delta_f H°$. The uncertainty in $S°$ may be as large as $\pm 2.6\ cal·K^{-1}·mol^{-1}$ due to uncertainty in $\Delta_{trs}H°$, if significant fractions of the β–phase failed to revert to the α–phase during drop calorimetry.[1,2] Naylor's data[1] suggest that this may be the case, but Slyusar *et al.*[2] make no mention of the problem (see Transition Data). Excluding this possible uncertainty, we estimate that $S°$ of $Ti_3O_5(\beta)$ is uncertain by $\pm 0.6\ cal·K^{-1}·mol^{-1}$.

Transition Data and Phase Data

Ti_3O_5 has been identified in three crystalline structures. Low–temperature α–Ti_3O_5 is monoclinic,[3] high–temperature β–Ti_3O_5 is a pseudobrookite type with slight monoclinic distortion[3] and metastable γ–Ti_3O_5[4] is analogous to V_3O_5.[3,4] Based on its similarity to V_3O_5, γ is the lowest member of the homologous series of phases Ti_nO_{2n-1} with structures related to rutile.[9,10] The magnetic anomaly, observed near 250 K in γ–Ti_3O_5,[4] corresponds to those observed at lower temperatures in Ti_4O_7 and higher homologues. We give the subsequent phase observations because they may have bearing on the anomalous enthalpy data and the discrepancy in $\Delta_f G°$ at high temperatures.

Our designations for the stable phases α and β are reversed from those of Asbrink *et al.*[4] These phases were called M– type (our α), D–type and D'–type (our β) by Iwasaki *et al.*[11] D– and D'–types differed only in their low–temperature oxidation products; D–type gave rutile, while D'–type gave mixtures of anatase and rutile.[11] D–type was obtained by H_2–reduction of anatase and D'–type by action of H_2 on rutile and Ti or CO on either anatase or rutile. D–type presumably is metastable; Iwasaki *et al.*[11] postulated free energy diagrams to explain conversion of D–type to other forms. The observations also can be explained be assuming that conversion of D–type is hindered kinetically, like TiO_2(anatase) → TiO_2(rutile), until gradually activated at elevated temperature. X–ray patterns of D–type, though not well defined, were similar to those of D'–type.[11] Thus, D–type is not the Ti_nO_{2n-1} homologue (γ–Ti_3O_5), as postulated[11] on the basis of oxidation behavior. D– and D'–types may have the same crystal structure but differ in degree of ordering or content of impurities.

Enthalpy data of Naylor[1] gave T_{trs} ~450 K for α → β. X–ray diffraction,[4–6] DTA,[5] magnetic susceptibility,[4,6] and electrical conductivity[5] confirm the transition temperature. The transition is reversible[3,5–7] but exhibits thermal hysteresis of about ±20°.[5,6] More important to interpretation of enthalpy measurements is the observation that the β–phase is stabilized[5,3] at room temperature by small amounts of impurities such as Fe, W and Mg. Samples doped with 5% Fe did not transform; those with 2% Fe gave a much–reduced endotherm (DTA) at ~75° below the normal T_{trs}.[5] Accidental contamination by W stabilized the β–form.[5]

$\Delta_{trs}H° = 3.17\ kcal·mol^{-1}$ is calculated at T_{trs} from the difference in enthalpy between our β–phase curve fit and our adopted α–phase. Alternative enthalpy curves[8] gave $\Delta_{trs}H° = 2.48\ kcal·mol^{-1}$. These calculations assume that the β–phase reverted completely to α–phase at room temperature during drop calorimetry.[1,2] Naylor's anomalous enthalpies[1] for the α–phase suggest that part of his sample may have been stabilized in the β–form due to impurities. Other metastable phases may have been present. If the drop–calorimetric samples did not revert completely to α–phase, the true value of $\Delta_{trs}H°$ should be larger than the value calculated on the assumption of complete reversion. $\Delta_f G°$ data (see Ti_3O_5, α) tend to favor an entropy greater than or equal to the adopted value, but DTA data[5] gave $\Delta_{trs}H° = 1.6 \pm 0.4\ kcal·mol^{-1}$, opposite to the expected direction. We emphasize this unsatisfactory situation by placing $\Delta_{trs}H°$ in brackets and assigning an uncertainty of $\pm 1.2\ kcal·mol^{-1}$. The seeming contradictions should be resolved easily by study of a well–characterized sample in an adiabatic calorimeter or an accurate differential–scanning calorimeter.

Fusion Data and Sublimation Data

Refer to the liquid table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	173.962	157.617	157.617	0.000	−2446.189	−2312.759	405.186
300	174.054	158.694	157.621	0.322	−2446.143	−2311.931	402.543
400	179.075	209.454	164.508	17.978	−2443.756	−2267.558	296.113
450	181.586	230.691	170.702	26.995	−2442.604	−2245.602	260.663
500	184.096	249.952	177.679	36.137	−2441.465	−2223.774	232.316
600	189.117	283.961	192.632	54.798	−2439.180	−2180.450	189.825
700	194.138	313.490	207.833	73.960	−2436.818	−2137.514	159.503
800	199.158	339.742	222.710	93.625	−2434.270	−2094.928	136.785
900	204.179	363.489	237.053	113.792	−2431.589	−2052.670	119.134
1000	209.200	385.261	250.800	134.461	−2428.938	−2010.711	105.029
1100	214.221	405.436	263.952	155.632	−2426.485	−1969.009	93.500
1200	219.242	424.291	276.536	177.305	−2436.168	−1927.162	83.887
1300	224.262	442.038	288.591	199.480	−2431.892	−1884.917	75.737
1400	229.283	458.841	300.157	222.158	−2427.425	−1843.008	68.763
1500	234.304	474.831	311.273	245.337	−2422.799	−1801.425	62.731
1600	239.325	490.113	321.976	269.018	−2418.050	−1760.154	57.463
1700	244.346	504.773	332.301	293.202	−2413.214	−1719.183	52.824
1800	249.366	518.881	342.277	317.888	−2408.329	−1678.499	48.709
1900	254.387	532.498	351.932	343.075	−2403.433	−1638.087	45.034
2000	259.408	545.674	361.292	368.765	−2442.627	−1596.570	41.698
2100	264.429	558.452	370.378	394.957	−2440.070	−1554.329	38.662
2200	269.450	570.869	379.210	421.651	−2437.067	−1512.218	35.905
2300	274.470	582.958	387.807	448.847	−2433.619	−1470.256	33.391
2400	279.491	594.745	396.185	476.545	−2429.725	−1428.453	31.089
2500	284.512	606.256	404.358	504.745	−2425.383	−1386.821	28.976

PREVIOUS: March 1967 CURRENT: December 1973

$S°(298.15\ K)$ = [232.446] $J·K^{-1}·mol^{-1}$
T_{fus} = 2050 ± 20 K

$\Delta_f H°(298.15\ K)$ = [−2289.059] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = [171.544] $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ti_3O_5, l, 298.15\ K)$ is calculated from that of $Ti_3O_5(\beta l)$ by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2050\ K)–H°(298.15\ K)$, between the β–phase and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 8 $cal·K^{-1}$ g $atom^{-1}$. Below the assumed glass transition at 1400 K, $C_p°$ is taken to be the same as that of $Ti_3O_5(\beta)$. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

$Ti_3O_5(\beta)$ melts incongruently at 2047 ± 10 K according to Wahlbeck and Gilles.[1] Their phase diagram[1] suggests that melting starts at 2047 K and completes near 2077 K. The latter value is close to the melting point of 2083 K reported by Slyusar *et al.*,[2] but is almost 90° above the value of ~1990 which may be interpolated from the liquidus curve of Brauer and Littke[3] for the Ti–O system. Conversion of the value of Wahlbeck and Gilles[1] to IPTS 68 yields 2050 K, which is adopted.

Sublimation and Vaporization Data

$Ti_3O_5(\beta)$ is the congruently vaporizing crystalline phase in the Ti–O system according to the studies of Gilles and coworkers.[4-6] Studies of liquid samples[7] showed that the congruently vaporizing composition is between Ti_3O_5 and Ti_4O_7. The principal reaction[4] in congruent vaporization is $Ti_3O_5 \rightarrow TiO(g) + 2\ TiO_2(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	173.962	232.446	232.446	0.000	−2289.059	−2177.939	381.566
300	174.054	233.522	232.449	0.322	−2289.013	−2177.250	379.093
400	179.075	284.282	239.336	17.978	−2286.625	−2140.359	279.502
500	184.096	324.781	252.507	36.137	−2284.335	−2104.058	219.809
600	189.117	358.789	267.460	54.798	−2282.050	−2068.217	180.054
700	194.138	388.319	282.661	73.960	−2279.687	−2032.764	151.687
800	199.158	414.570	297.539	93.625	−2277.139	−1997.660	130.434
900	204.179	438.318	311.882	113.792	−2274.459	−1962.886	113.923
1000	209.200	460.090	325.629	134.461	−2271.808	−1928.410	100.730
1100	214.221	480.264	338.781	155.632	−2269.355	−1894.191	89.948
1200	219.242	499.119	351.365	177.305	−2279.038	−1859.826	80.956
1300	224.262	516.866	363.420	199.480	−2274.762	−1825.064	73.332
1400	229.283	533.669	374.985	222.158	−2270.295	−1790.638	66.810
1400.000	229.283	533.669	374.985	222.158	GLASS <--> LIQUID		
1400.000	267.776	533.669	374.985	222.158	TRANSITION		
1500	267.776	552.144	386.187	248.935	−2262.071	−1756.666	61.173
1600	267.776	569.426	397.105	275.713	−2254.226	−1723.230	56.258
1700	267.776	585.660	407.724	302.490	−2246.795	−1690.273	51.936
1800	267.776	600.965	418.039	329.268	−2239.818	−1657.741	48.106
1900	267.776	615.443	428.051	356.046	−2233.333	−1625.582	44.690
2000	267.776	629.178	437.767	382.823	−2271.438	−1592.390	41.589
2050.000	267.776	635.790	442.516	396.212	---- BETA <--> LIQUID ----		
2100	267.776	642.243	447.195	409.601	−2268.296	−1558.516	38.766
2200	267.776	654.700	456.346	436.378	−2265.210	−1524.788	36.203
2300	267.776	666.603	465.231	463.156	−2262.180	−1491.201	33.866
2400	267.776	678.000	473.861	489.934	−2259.206	−1457.745	31.727
2500	267.776	688.931	482.246	516.711	−2256.287	−1424.411	29.761
2600	267.776	699.433	490.399	543.489	−2253.421	−1391.193	27.949
2700	267.776	709.539	498.329	570.266	−2250.608	−1358.083	26.274
2800	267.776	719.278	506.048	597.044	−2247.846	−1325.077	24.720
2900	267.776	728.674	513.563	623.822	−2245.133	−1292.170	23.275
3000	267.776	737.752	520.886	650.599	−2242.470	−1259.354	21.927
3100	267.776	746.533	528.024	677.377	−2239.852	−1226.626	20.669
3200	267.776	755.034	534.986	704.154	−2237.280	−1193.984	19.490
3300	267.776	763.274	541.779	730.932	−2234.751	−1161.421	18.384
3400	267.776	771.268	548.412	757.710	−2232.264	−1128.932	17.344
3500	267.776	779.030	554.891	784.487	−2229.818	−1096.518	16.365
3600	267.776	786.574	561.222	811.265	−2227.409	−1064.171	15.441
3700	267.776	793.910	567.412	838.042	−3452.333	−1008.528	14.238
3800	267.776	801.051	573.467	864.820	−3446.295	−942.558	12.956
3900	267.776	808.007	579.392	891.598	−3440.457	−876.746	11.743
4000	267.776	814.787	585.193	918.375	−3434.815	−811.083	10.592

PREVIOUS: March 1967 CURRENT: December 1973

0	to	450	K crystal, alpha
450	to	2050	K crystal, beta
above		2050	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−23.108	−2446.057	−2446.057	INFINITE
100	46.116	21.062	237.166	−21.610	−2453.501	−2409.803	1258.752
200	114.445	75.659	142.352	−13.339	−2458.258	−2363.911	617.390
298.15	154.808	129.369	129.369	0.000	−2459.146	−2317.293	405.980
300	155.477	130.329	129.372	0.287	−2459.135	−2316.413	403.323
400	182.841	179.228	135.852	17.350	−2457.340	−2269.052	296.308
450	189.954	201.217	141.909	26.688	−2455.868	−2245.602	260.663
450.000	181.586	230.691	141.909	39.952	---- ALPHA <--> BETA ----		
500	184.096	249.952	151.765	49.094	−2441.465	−2223.774	232.316
600	189.117	283.961	171.037	67.754	−2439.180	−2180.450	189.825
700	194.138	313.490	189.323	86.917	−2436.818	−2137.514	159.503
800	199.158	339.742	206.514	106.582	−2434.270	−2094.928	136.785
900	204.179	363.489	222.657	126.749	−2431.589	−2052.670	119.134
1000	209.200	385.261	237.844	147.418	−2428.938	−2010.711	105.029
1100	214.221	405.436	252.173	168.589	−2426.485	−1969.009	93.500
1200	219.242	424.291	265.739	190.262	−2436.168	−1927.162	83.887
1300	224.262	442.038	278.624	212.437	−2431.892	−1884.917	75.737
1400	229.283	458.841	290.902	235.114	−2427.425	−1843.008	68.763
1500	234.304	474.831	302.635	258.294	−2422.799	−1801.425	62.731
1600	239.325	490.113	313.878	281.975	−2418.050	−1760.154	57.463
1700	244.346	504.773	324.679	306.159	−2413.214	−1719.183	52.824
1800	249.366	518.881	335.079	330.844	−2408.329	−1678.499	48.709
1900	254.387	532.498	345.113	356.032	−2403.433	−1638.087	45.034
2000	259.408	545.674	354.813	381.722	−2442.627	−1596.570	41.698
2050.000	261.918	552.111	359.547	394.755	BETA <--> LIQUID TRANSITION		
2050.000	267.776	635.791	359.547	566.299			
2100	267.776	642.243	366.201	579.688	−2268.296	−1558.516	38.766
2200	267.776	654.700	379.034	606.465	−2265.210	−1524.788	36.203
2300	267.776	666.603	391.280	633.243	−2262.180	−1491.201	33.866
2400	267.776	678.000	402.991	660.020	−2259.206	−1457.745	31.727
2500	267.776	688.931	414.212	686.798	−2256.287	−1424.411	29.761
2600	267.776	699.433	424.981	713.576	−2253.421	−1391.193	27.949
2700	267.776	709.539	435.334	740.353	−2250.608	−1358.083	26.274
2800	267.776	719.278	445.302	767.131	−2247.846	−1325.077	24.720
2900	267.776	728.674	454.913	793.908	−2245.133	−1292.170	23.275
3000	267.776	737.752	464.190	820.686	−2242.470	−1259.354	21.927
3100	267.776	746.533	473.157	847.464	−2239.852	−1226.626	20.669
3200	267.776	755.034	481.834	874.241	−2237.280	−1193.984	19.490
3300	267.776	763.274	490.238	901.019	−2234.751	−1161.421	18.384
3400	267.776	771.268	498.387	927.796	−2232.264	−1128.932	17.344
3500	267.776	779.030	506.295	954.574	−2229.818	−1096.518	16.365
3600	267.776	786.574	513.976	981.352	−2227.409	−1064.171	15.441
3700	267.776	793.910	521.443	1008.129	−3452.333	−1008.528	14.238
3800	267.776	801.051	528.708	1034.907	−3446.295	−942.558	12.956
3900	267.776	808.007	535.780	1061.684	−3440.457	−876.746	11.743
4000	267.776	814.787	542.671	1088.462	−3434.815	−811.083	10.592

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = 130.549 \pm 2.1\ J·K^{-1}·mol^{-1}$
$T_{fus} = 943 \pm 10\ K$

$\Delta_f H°(0\ K) = -1541.109 \pm 6.3\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -1550.590 \pm 6.3\ kJ·mol^{-1}$
$\Delta_{fus} H° = 64.517 \pm 3.14\ kJ·mol^{-1}$

Enthalpy of Formation

A review[1] of early experimental studies led to a value of 373 $kcal·mol^{-1}$ for $\Delta_f H°(V_2O_5, cr, 298.15\ K)$. More recent combustion studies on V(cr) have led to the following $\Delta_f H°(298.15\ K)$ values for V_2O_5(cr).

Source	Year	$\Delta_f H°(V_2O_5, cr, 298.15\ K)$, $kcal·mol^{-1}$
[2]	1969	-376 ± 2
[3]	1960	-370 ± 1
[4]	1961	-370.6 ± 0.5
[5]	1963	-371.9 ± 1.0

We adopt $370.6 \pm 1\ kcal·mol^{-1}$ as the enthalpy of formation of V_2O_5(cr) at 298.15 K. This value is the Mah and Kelley result[4] but it is also in good agreement with the results of Golutvin and Kozlovskaya[3] and Volkova and Gel'd.[5] The same value was recently adopted by NBS.[6]

The combustion of vanadium and its oxides, as reported by Mah and Kelley,[4] led to two problems: (1) the oxide products liquefy before the pentoxide composition is obtained and (2) the oxide products are corrosive and cause a container problem. The combustion of vanadium led to varying mixtures of V_2O_4(rutile) and V_2O_5. This was verified by x-ray diffraction. The enthalpy of formation values for V_2O_4 and V_2O_5 were derived from the same set of experiments.[4]

Heat Capacity and Entropy

Using a V_2O_5 sample with a reported purity of 99.5% or better, Anderson[7] measured the heat capacity in the range 56.8–289.5 K. Using the combination of Debye and Einstein functions suggested by Anderson,[7] we calculate $S°(60\ K) = 2.81\ cal·K^{-1}·mol^{-1}$ and $H°(60\ K) - H°(0\ K) = 130.59\ cal·mol^{-1}$. Cook[8] measured the enthalpy of V_2O_5 in the range 372–1513 K. The enthalpy data are fit to a Kelley type equation with the constraint that the data join smoothly with a portion of the integrated data of Anderson.[7] The enthalpy data appear to lie too high in comparison with the integrated data of Anderson.[7] A better fit is obtained by neglecting the 289.5 data point of Anderson. The Anderson data show considerable scatter and deviate from our adopted $C_p°$ values by ±4% below 65 K and ±1.8% between 65 and 280 K. The 289.5 K data point is 2.7% lower than the adopted value. The Cook data deviates from the adopted enthalpy values by roughly 8% (200 $cal·mol^{-1}$) at 371.6 K with the difference decreasing to 2 $cal·K^{-1}·mol^{-1}$ at 754.4 K. In the range 771.1–921.1 K the enthalpy difference ranges from −121 to +139 $cal·K^{-1}·mol^{-1}$.

Fusion Data

The melting point of V_2O_5 is adopted as $T_{fus} = 943 \pm 10$ K as derived from the enthalpy studies of Cook.[8] The heat of melting is calculated to be $\Delta_{fus} H° = 15.42 \pm 0.75\ kcal·mol^{-1}$ based on our analyses of Cook's enthalpy data. Refer to the heat capacity discussion for V_2O_5(cr) and V_2O_5(l) for details. By way of comparison, Kohlmuller and Leitner[9] reported $T_{fus} = 937.9$ K and $\Delta_{fus} H° = 14.5\ kcal·mol^{-1}$ while Pantony and Vasu[10] reported $T_{fus} = 951.12$ K and $\Delta_{fus} H° = 13.8\ kcal·mol^{-1}$. The latter two studies[9,10] involved cryoscopic techniques. Murphy and West[11] reported $T_{fus} = 943$ K based on DTA measurements and Holtzberg *et al.*[12] determined $T_{fus} = 947 \pm 5$ K in their study of the phases in the K_2O V_2O_5 system.

The variance in the reported T_{fus} values is probably attributable to the presence of V_2O_4(cr). Refer to the discussion in the section on Sublimation Data in the V_2O_5(cr) table and Decomposition Data in the V_2O_5(l) table.

Sublimation Data

Using the combination of Knudsen effusion and mass spectrometric techniques, Berkowitz *et al.*[13] concluded that V_2O_5(cr) did not "vaporize" invariantly. The temperature range investigated was not reported. Their conclusion was based on two observations: (1) some reduced vanadium oxide species were present in the gas phase, and (2) oxygen was also found to be effusing from the Knudsen cell. Chizhikov *et al.*[14] studied the dissociation of V_2O_5 at temperatures below T_{fus} using mass spectrometry. They assumed reduced vanadium oxides, in addition to V_4O_{10}, were present in the vapor upon dissociation of V_2O_5(cr) in vacuum. We conclude that there is no invariant sublimation process for V_2O_5(cr) and thus we do not calculate a $\Delta_{sub} H°(298.15\ K)$ value. For related discussion refer to V_2O_5(l) table.

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Continued on page 1816

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−21.506	−1541.109	−1541.109	INFINITE
100	52.647	31.564	238.170	−20.661	−1548.502	−1506.895	787.121
200	101.123	84.203	141.649	−11.489	−1550.281	−1462.556	381.980
298.15	130.599	130.549	130.549	0.000	−1550.590	−1419.348	248.664
300	131.027	131.358	130.552	0.242	−1550.577	−1418.533	246.989
400	150.950	171.988	135.954	14.414	−1548.962	−1374.719	179.520
500	161.753	206.948	146.747	30.100	−1546.243	−1331.458	139.096
600	168.314	237.044	159.348	46.617	−1543.068	−1288.795	112.200
700	173.234	263.370	172.367	63.702	−1539.671	−1246.682	93.029
800	177.251	286.771	185.232	81.231	−1536.152	−1205.066	78.683
900	180.749	307.858	197.705	99.138	−1532.562	−1163.895	67.551
943.000	182.004	316.323	202.922	106.937	--- CRYSTAL <---> LIQUID ---		
1000	183.678	327.054	209.694	117.359	−1528.939	−1123.126	58.666
1100	186.606	344.697	221.176	135.874	−1525.292	−1082.721	51.414
1200	189.535	361.060	232.159	154.681	−1521.624	−1042.649	45.385
1300	192.464	376.346	242.669	173.781	−1517.934	−1002.884	40.296
1400	195.393	390.717	252.736	193.173	−1514.230	−963.403	35.945
1500	198.322	404.297	262.391	212.859	−1510.509	−924.189	32.183

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = [191.956]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 943 \pm 10\ K$
$T_{dcm} = 1963\ K$

$\Delta_f H°(298.15\ K) = [-1491.209]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 64.517 \pm 3.14\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(V_2O_5, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(943\ K)-H°(298.15\ K)$, between V_2O_5(cr) and V_2O_5(l).

Heat Capacity and Entropy

Cook[1] measured the enthalpy of V_2O_5 in the range 372–1513 K. In the liquid region ($T > 943$ K), Cook[1] represented his data by a straight line with a slope of $C_p° = 45.60\ cal·K^{-1}·mol^{-1}$. We adopt this value of V_2O_5(l). A glass transition is assumed at 600 K. The heat capacity values used below 600 K are those of V_2O_5(cr). The entropy at 298.15 K is calculated in a manner analogous to that used in calculating the enthalpy of formation.

Decomposition Data

Polyakov[2] measured the weight loss of molten V_2O_5 in the range 700–1200°C for various oxygen flows. The oxygen pressure was greater than the dissociation pressure of V_2O_5. The vapor pressure was calculated by extrapolating to zero oxygen flow and assuming the vapor was monomeric V_2O_5(g). Polyakov[2] assumed no loss of oxygen. Pak[3] proposed a method of calculating vapor pressures from experimental results obtained by the entrainment method with allowance for diffusion. Using Polystov's data and assuming that the vapor phase is the dimeric molecule V_4O_{10}(g), Pak[3] calculated a heat of vaporization $\Delta_{vap}H°(298.15\ K)$ which is 1.4 $kcal·mol^{-1}$ more positive than Polyakov's reported value of 32.3 $kcal·mol^{-1}$ V_2O_5. Semenov *et al.*[4] determined the vapor pressure of V_4O_{10}(g) over V_2O_5(l) at 1215–1530 K by an improved transfer technique in an oxygen carrier stream. The reported heat of vaporization was calculated to be 3.5 $kcal·mol^{-1}$ more positive than Polyakov's value.

Pantony and Vasu[5] stated that molten V_2O_5 attains a constant weight under fixed oxygen pressure and temperature in a reasonably short length of time while in pure nitrogen it is converted into V_2O_4(cr). Pantony and Vasu[5] studied gravimetrically the dissociation equilibrium of V_2O_5(l) and confirmed its existence by cryoscopic methods. They concluded that the vapor pressure ascribed to V_2O_5(g) or V_4O_{10}(g) and measured by a transpiration weight loss method is due to the loss of oxygen arising from the following dissociation $V_2O_5(soln) = V_2O_4(soln) + 1/2\ O_2(g)$.

An effusion mass spectrometric investigation of the vapor in equilibrium with V_2O_5 in the range 1000–1200 K led Farber *et al.*[6] to the conclusion that the vapor contained not only V_4O_{10}(g), significant amounts of V_4O_8(g), but also other vanadium oxides. We conclude that there is decomposition upon heating V_2O_5(l) in an inert atmosphere or in vacuo. The use of an oxygen atmosphere suppresses decomposition but in the transpiration weight loss experiment it has not been verified that the weight loss is indeed V_4O_{10}(g). We calculate a decomposition temperature, T_{dcm}, as that temperature at which the free energy approaches zero for the reaction $V_2O_5(l) = V_2O_4(l) + 1/2\ O_2(g)$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
298.15	130.599	191.956	191.956	0.000	−1491.209	−1378.274	241.468
300	131.027	192.765	191.959	0.242	−1491.195	−1377.574	239.857
400	150.950	233.396	197.362	14.414	−1489.580	−1339.900	174.973
500	161.753	268.355	208.154	30.100	−1486.861	−1302.780	136.100
600	168.314	298.477	220.757	46.632	−1483.672	−1266.258	110.238
600.000	168.314	298.477	220.757	46.632	GLASS <--> LIQUID		
600.000	190.790	298.477	220.757	46.632	TRANSITION		
700	190.790	327.887	234.015	65.711	−1478.280	−1230.454	91.818
800	190.790	353.364	247.377	84.790	−1473.211	−1195.400	78.052
900	190.790	375.836	260.426	103.869	−1468.449	−1160.962	67.381
943.000	190.790	384.740	265.893	112.073	--- CRYSTAL <--> LIQUID ---		
1000	190.790	395.938	272.990	122.948	−1463.969	−1127.040	58.871
1100	190.790	414.122	285.006	142.027	−1459.757	−1093.553	51.928
1200	190.790	430.723	296.468	161.106	−1455.817	−1060.437	46.160
1300	190.790	445.994	307.390	180.185	−1452.148	−1027.640	41.291
1400	190.790	460.133	317.802	199.264	−1448.758	−995.114	37.128
1500	190.790	473.296	327.734	218.343	−1445.643	−962.822	33.528
1600	190.790	485.610	337.221	237.422	−1442.797	−930.728	30.385
1700	190.790	497.176	346.293	256.501	−1440.236	−898.804	27.617
1800	190.790	508.082	354.981	275.580	−1437.966	−867.023	25.160
1900	190.790	518.397	363.313	294.659	−1436.009	−835.358	22.966
2000	190.790	528.183	371.314	313.738	−1434.379	−803.788	20.993
2100	190.790	537.492	379.008	332.817	−1433.097	−772.292	19.210
2200	190.790	546.368	386.415	351.896	−1477.943	−740.637	17.585
2300	190.790	554.849	393.555	370.975	−1477.681	−707.130	16.059
2400	190.790	562.969	400.446	390.054	−1477.475	−673.634	14.661
2500	190.790	570.757	407.104	409.133	−1477.324	−640.143	13.375
2600	190.790	578.240	413.543	428.212	−1477.227	−606.658	12.188
2700	190.790	585.440	419.777	447.292	−1477.182	−573.175	11.089
2800	190.790	592.379	425.818	466.371	−1477.188	−539.693	10.068
2900	190.790	599.074	431.678	485.450	−1477.243	−506.212	9.118
3000	190.790	605.542	437.366	504.529	−1477.348	−472.725	8.231

PREVIOUS: CURRENT: June 1973

0 to 943 K crystal
above 943 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.000	0.000	INFINITE	−21.506	−1541.109	−1541.109	INFINITE
100	52.647	31.564	238.170	−20.661	−1548.502	−1506.895	787.121
200	101.123	84.203	141.649	−11.489	−1550.281	−1462.556	381.980
298.15	130.599	130.549	130.549	0.000	−1550.590	−1419.348	248.664
300	131.027	131.358	130.552	0.242	−1550.577	−1418.533	246.989
400	150.950	171.988	135.954	14.414	−1548.962	−1374.719	179.520
500	161.753	206.948	146.747	30.100	−1546.243	−1331.458	139.096
600	168.314	237.044	159.348	46.617	−1543.068	−1288.795	112.200
700	173.234	263.370	172.367	63.702	−1539.671	−1246.682	93.029
800	177.251	286.771	185.232	81.231	−1536.152	−1205.066	78.683
900	180.749	307.858	197.705	99.138	−1532.562	−1163.895	67.551
943.000	182.004	316.323	202.922	106.937	CRYSTAL <--> LIQUID		
943.000	190.790	384.740	202.922	171.455	TRANSITION		
1000	190.790	395.938	213.608	182.330	−1463.969	−1127.040	58.871
1100	190.790	414.122	231.023	201.409	−1459.757	−1093.553	51.928
1200	190.790	430.723	246.983	220.488	−1455.817	−1060.437	46.160
1300	190.790	445.994	261.712	239.567	−1452.148	−1027.640	41.291
1400	190.790	460.133	275.386	258.646	−1448.758	−995.114	37.128
1500	190.790	473.296	288.146	277.725	−1445.643	−962.822	33.528
1600	190.790	485.610	300.107	296.804	−1442.797	−930.728	30.385
1700	190.790	497.176	311.363	315.883	−1440.236	−898.804	27.617
1800	190.790	508.082	321.992	334.962	−1437.966	−867.023	25.160
1900	190.790	518.397	332.060	354.041	−1436.009	−835.358	22.966
2000	190.790	528.183	341.623	373.120	−1434.379	−803.788	20.993
2100	190.790	537.492	350.731	392.199	−1433.097	−772.292	19.210
2200	190.790	546.368	359.423	411.278	−1477.943	−740.637	17.585
2300	190.790	554.849	367.737	430.357	−1477.681	−707.130	16.059
2400	190.790	562.969	375.703	449.436	−1477.475	−673.634	14.661
2500	190.790	570.757	383.351	468.515	−1477.324	−640.143	13.375
2600	190.790	578.240	390.704	487.594	−1477.227	−606.658	12.188
2700	190.790	585.440	397.784	506.673	−1477.182	−573.175	11.089
2800	190.790	592.379	404.610	525.752	−1477.188	−539.693	10.068
2900	190.790	599.074	411.201	544.831	−1477.243	−506.212	9.118
3000	190.790	605.542	417.572	563.910	−1477.348	−472.725	8.231

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = 345.641 \pm 33.5\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -2189.97 \pm 3.35\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -2214.31 \pm 33.5\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
613 (1)	465 (2)
613 (1)	643 (3)
302 (3)	919 (3)
370 (3)	1029 (2)
407 (3)	636 (3)

Ground State Quantum Weight: 1 $\sigma = 12$
Point Group: T_d
Bond Distances: P–O = 1.65 ± 0.02 Å
Bond Angles: P–O–P = 127.5 ± 1.0° O–P–O = 99° ± 1°
Product of the Moments of Inertia: $I_A I_B I_C = 4.838017 \times 10^{-112}\ g^3 \cdot cm^6$

Enthalpy of Formation

$\Delta_f H°(P_4O_6, l, 298.15\ K)$ was measured by Koerner and Daniels.[1] The measurement was made by burning samples of red phosphorus in nitric oxide in a flow calorimeter. Calculation of the enthalpy of formation of the gas was made using $\Delta_{vap} H°(298.15\ K) = 11.46\ kcal \cdot mol^{-1}$ as reported by Farr.[2]

Heat Capacity and Entropy

The vibrational levels are from the Raman data of Gerding *et al.*[3] and infrared spectra data of Sidorov and Sobolev.[4] Bond distances and angles are from electron diffraction data by Hampson and Stosick.[5]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−23.153	−2189.970	−2189.970	INFINITE
100	47.025	247.701	443.275	−19.557	−2198.637	−2164.340	1130.535
200	101.296	296.685	357.555	−12.174	−2209.040	−2126.586	555.407
250	125.151	321.933	347.911	−6.494	−2212.101	−2105.599	439.941
298.15	143.937	345.641	345.641	0.	−2214.307	−2084.877	365.262
300	144.581	346.534	345.644	0.267	−2214.379	−2084.074	362.870
350	160.035	370.028	347.464	7.897	−2218.922	−2061.933	307.727
400	172.246	392.227	351.686	16.216	−2220.352	−2039.401	266.319
450	181.911	413.094	357.362	25.080	−2221.305	−2016.721	234.095
500	189.609	432.674	363.925	34.375	−2221.900	−1993.955	208.307
600	200.809	468.305	378.414	53.935	−2222.349	−1948.310	169.615
700	208.312	499.860	393.554	74.414	−2222.164	−1902.645	141.977
800	213.527	528.037	408.635	95.521	−2221.598	−1857.035	121.252
900	217.274	553.414	423.335	117.071	−2220.794	−1811.511	105.137
1000	220.045	576.457	437.513	138.944	−2219.838	−1766.085	92.251
1100	222.147	597.533	451.116	161.058	−2218.781	−1720.759	81.712
1200	223.776	616.935	464.137	183.358	−2471.947	−1671.220	72.746
1300	225.062	634.899	476.590	205.802	−2467.683	−1604.666	64.476
1400	226.095	651.617	488.502	228.362	−2463.415	−1538.440	57.400
1500	226.935	667.246	499.903	251.014	−2459.153	−1472.520	51.278
1600	227.628	681.914	510.825	273.744	−2454.906	−1406.883	45.930
1700	228.206	695.732	521.299	296.536	−2450.683	−1341.511	41.220
1800	228.693	708.790	531.356	319.382	−2446.490	−1276.387	37.040
1900	229.107	721.166	541.023	342.272	−2442.334	−1211.495	33.306
2000	229.462	732.927	550.327	365.201	−2438.217	−1146.820	29.952
2100	229.768	744.130	559.291	388.163	−2434.145	−1082.351	26.922
2200	230.034	754.825	567.937	411.154	−2430.121	−1018.072	24.172
2300	230.267	765.056	576.287	434.169	−2426.148	−953.979	21.666
2400	230.471	774.861	584.358	457.206	−2422.226	−890.057	19.372
2500	230.652	784.273	592.168	480.262	−2418.358	−826.296	17.265
2600	230.813	793.322	599.732	503.336	−2414.543	−762.689	15.323
2700	230.957	802.036	607.064	526.424	−2410.783	−699.227	13.527
2800	231.085	810.438	614.178	549.527	−2407.077	−635.903	11.863
2900	231.201	818.549	621.086	572.641	−2403.425	−572.714	10.316
3000	231.305	826.389	627.800	595.766	−2399.825	−509.646	8.874
3100	231.399	833.975	634.329	618.902	−2396.278	−446.697	7.527
3200	231.485	841.323	640.683	642.046	−2392.781	−383.865	6.266
3300	231.564	848.447	646.872	665.199	−2389.333	−321.141	5.083
3400	231.635	855.361	652.903	688.358	−2385.933	−258.518	3.972
3500	231.700	862.076	658.784	711.525	−2382.581	−195.997	2.925
3600	231.761	868.605	664.522	734.698	−2379.273	−133.570	1.938
3700	231.816	874.955	670.124	757.877	−2376.009	−71.235	1.006
3800	231.867	881.138	675.596	781.061	−2372.789	−8.985	0.124
3900	231.914	887.162	680.943	804.251	−2369.609	53.180	−0.712
4000	231.958	893.034	686.173	827.444	−2366.471	115.261	−1.505
4100	231.999	898.762	691.288	850.642	−2363.372	177.266	−2.258
4200	232.036	904.353	696.295	873.844	−2360.312	239.195	−2.975
4300	232.071	909.813	701.197	897.049	−2357.291	301.054	−3.657
4400	232.104	915.149	705.999	920.258	−2354.308	362.840	−4.307
4500	232.135	920.365	710.705	943.470	−2351.363	424.559	−4.928
4600	232.163	925.468	715.319	966.685	−2348.457	486.213	−5.521
4700	232.190	930.461	719.843	989.903	−2345.590	547.806	−6.088
4800	232.216	935.350	724.282	1013.123	−2342.762	609.338	−6.631
4900	232.239	940.138	728.639	1036.346	−2339.975	670.813	−7.151
5000	232.262	944.830	732.916	1059.571	−2337.229	732.230	−7.650
5100	232.283	949.430	737.116	1082.798	−2334.527	793.593	−8.128
5200	232.302	953.940	741.243	1106.027	−2331.869	854.900	−8.588
5300	232.321	958.365	745.298	1129.258	−2329.258	916.161	−9.029
5400	232.339	962.708	749.284	1152.491	−2326.696	977.370	−9.454
5500	232.355	966.971	753.203	1175.726	−2324.185	1038.532	−9.863
5600	232.371	971.158	757.058	1198.962	−2321.727	1099.653	−10.257
5700	232.386	975.271	760.850	1222.200	−2319.326	1160.726	−10.637
5800	232.400	979.313	764.582	1245.440	−2316.984	1221.761	−11.003
5900	232.414	983.286	768.255	1268.680	−2314.704	1282.749	−11.357
6000	232.427	987.192	771.872	1291.922	−2312.491	1343.707	−11.698

PREVIOUS: December 1962 CURRENT: December 1962 (1 bar)

$S°(298.15\ K) = [415.601]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1157.96\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1163.99 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies ν, cm^{-1}
[600] (4)
[300] (8)
[172] (6)

Ground State Quantum Weight: [1] σ = [4]
Point Group: [D_{2h}]
Bond Distance: W–O = [1.81] Å
Bond Angles: O–W–O = [109.47]° W–O_{bridge}–W = [70.53]°
Product of the Moments of Inertia: $I_A I_B I_C = [5.918184 \times 10^{-112}]\ g^3·cm^6$

Enthalpy of Formation

The adopted value, $\Delta_f H°(W_2O_6, g, 298.15\ K) = -278.2\ kcal·mol^{-1}$, was reduced from $\Delta_f H°(1450\ K) = -272.5\ kcal·mol^{-1}$, reported by Ackermann and Rauh.[1] They have studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 1600 K by mass spectrometry, mass effusion, and X-ray diffraction, and also have determined $\Delta_f G°(W_2O_6, g) = 272{,}500 + 54.98T\ cal·K^{-1}·mol^{-1}$ from partial pressure measurements over the W–WO_2(cr) system.

Battles[2] has also studied the same system in the temperature range from 1418 to 1527 K. Third law calculation of the partial pressure data gives $\Delta_r H°(298.15\ K) = 144.0\ kcal·mol^{-1}$ for 3 WO_2(cr) = W_2O_6(g) + W(cr) which yields $\Delta_f H°(W_2O_6, g, 298.15\ K) = -278.8\ kcal·mol^{-1}$ using all JANAF functions. This value is in good agreement with the value adopted.

Norman and Staley[3] have obtained $\Delta_r H°(1800\ K) = -127\ kcal·mol^{-1}$ for 2 WO_3(g) = W_2O_6(g) by mass spectrometric study of the vapor over WO_3 dissolved in $CaO–Al_2O_3–SiO_2$. The value of $\Delta_r H°$ was determined by the 2nd law method from ion intensities and leads to $\Delta_f H°(W_2O_6, g, 298.15\ K) = -275\ kcal·mol^{-1}$, using all JANAF functions (dated Sept. 30, 1966). The absolute pressure values reported by Norman and Staley appear to be quite inconsistent with the JANAF functions since they lead to $\Delta_f H°(W_2O_6, g, 298.15\ K) = -246\ kcal·mol^{-1}$ by the 3rd law method.

Source	Reaction	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15K)$ $kcal·mol^{-1}$
1	3 WO_2(cr) = W_2O_6(g) + W(cr)	1300–1600	144.54	144.63	0.01	−278.2*
2	3 WO_2(cr) = W_2O_6(g) + W(cr)	1418–1527	142.66	143.97	0.85 ± 0.40	−278.8*
3	2 WO_3(g) = W_2O_6(g)	1700–1900	−135	−106		−275**

*3rd law value adopted in calculation **2nd law value adopted in calculation

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 600 cm^{-1} (4), 300 cm^{-1} (8), and 172 cm^{-1} (6) in order to give the entropy at 1450 K, $S°(1450\ K) = 164.66\ cal·K^{-1}·mol^{-1}$, corresponding to $\Delta_f S°(1450\ K) = 54.98\ cal·K^{-1}·mol^{-1}$ which was reported by Ackermann and Rauh.[1] The adopted value, $S°(W_2O_6, g, 298.15\ K) = 99.3\ cal·K^{-1}·mol^{-1}$, was reduced from the entropy at 1450 K, using JANAF functions. Second law calculation of the partial pressure data of Battles gives $\Delta_r S°(1470\ K) = 63.5\ cal·K^{-1}·mol^{-1}$ for 3 WO_2(cr) = W_2O_6(g) + W(cr). This yields $S°(W_2O_6, g, 298.15\ K) = 97.9\ cal·K^{-1}·mol^{-1}$.

The molecular configuration for W_2O_6(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and two of these tetrahedra share a common oxygen edge to form a planar four-member ring. The bond distance W–O was estimated as 1.81 Å and the bond angle O–W–O = 109.47° and W–O_{bridge}–W = 70.53°. The principal moments of inertia are: $I_A = 34.8158 \times 10^{-39}$, $I_B = 124.7049 \times 10^{-39}$, and $I_C = 136.3101 \times 10^{-39}\ g·cm^2$.

References

[1] R. J. Ackermann and E. G. Rauh, J. Phys. Chem. 67, 2596 (1963).
[2] J. E. Battles, Ph.D. dissertation, "A Mass Spectrometric Investigation of Tungsten Dioxide and Tungsten Trioxide," the Ohio State University, (1964).
[3] J. H. Norman and H. G. Staley, J. Chem. Phys. **43**, 3804 (1965).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−29.966	−1157.958	−1157.958	INFINITE
100	81.358	284.301	535.415	−25.111	−1163.122	−1137.638	594.241
200	131.491	358.417	429.062	−14.129	−1164.889	−1111.172	290.208
250	144.838	389.289	418.085	−7.199	−1164.646	−1097.760	229.364
298.15	153.665	415.601	415.601	0.	−1163.989	−1084.931	190.075
300	153.946	416.552	415.604	0.285	−1163.957	−1084.441	188.818
350	160.314	440.789	417.503	8.150	−1162.969	−1071.263	159.877
400	164.881	462.511	421.795	16.286	−1161.796	−1058.240	138.192
450	168.240	482.134	427.427	24.618	−1160.519	−1045.372	121.344
500	170.768	499.997	433.805	33.096	−1159.192	−1032.649	107.880
600	174.231	531.464	447.530	50.360	−1156.521	−1007.592	87.719
700	176.420	558.498	461.497	67.901	−1153.947	−982.975	73.351
800	177.883	582.157	475.132	85.620	−1151.527	−958.718	62.598
900	178.907	603.171	488.213	103.463	−1149.279	−934.754	54.252
1000	179.649	622.061	500.669	121.392	−1147.203	−911.031	47.587
1100	180.205	639.211	512.496	139.386	−1145.294	−887.507	42.144
1200	180.630	654.910	523.719	157.429	−1143.547	−864.150	37.615
1300	180.963	669.382	534.374	175.509	−1141.956	−840.932	33.789
1400	181.229	682.802	544.503	193.619	−1140.519	−817.832	30.514
1500	181.444	695.314	554.145	211.753	−1139.234	−794.829	27.678
1600	181.621	707.029	563.338	229.907	−1138.101	−771.906	25.200
1700	181.767	718.045	572.117	248.077	−1137.121	−749.050	23.015
1800	181.890	728.438	580.516	266.260	−1136.295	−726.248	21.075
1900	181.995	738.275	588.562	284.454	−1135.623	−703.486	19.340
2000	182.084	747.612	596.283	302.658	−1135.109	−680.756	17.780
2100	182.161	756.498	603.703	320.870	−1134.753	−658.047	16.368
2200	182.228	764.974	610.842	339.090	−1134.556	−635.351	15.085
2300	182.286	773.076	617.721	357.316	−1134.519	−612.662	13.914
2400	182.338	780.835	624.357	375.547	−1134.644	−589.972	12.840
2500	182.383	788.279	630.766	393.783	−1134.929	−567.271	11.852
2600	182.423	795.433	636.963	412.023	−1135.368	−544.557	10.940
2700	182.459	802.319	642.960	430.268	−1136.015	−521.821	10.095
2800	182.491	808.955	648.771	448.515	−1136.937	−499.056	9.310
2900	182.520	815.359	654.405	466.766	−1138.213	−476.256	8.578
3000	182.546	821.547	659.874	485.019	−1139.894	−453.401	7.894
3100	182.569	827.533	665.187	503.275	−1142.066	−430.482	7.254
3200	182.590	833.330	670.351	521.533	−1144.789	−407.488	6.652
3300	182.610	838.949	675.375	539.793	−1148.112	−384.399	6.085
3400	182.628	844.401	680.267	558.055	−1152.105	−361.196	5.549
3500	182.644	849.695	685.032	576.318	−1156.894	−337.868	5.042
3600	182.659	854.840	689.678	594.583	−1162.669	−314.387	4.562
3700	182.673	859.845	694.210	612.850	−1239.161	−290.351	4.099
3800	182.685	864.717	698.633	631.118	−1240.331	−264.689	3.638
3900	182.697	869.462	702.953	649.387	−1241.541	−238.998	3.201
4000	182.708	874.088	707.174	667.657	−1242.790	−213.277	2.785
4100	182.718	878.599	711.300	685.928	−1244.078	−187.524	2.389
4200	182.727	883.003	715.336	704.201	−1245.402	−161.738	2.012
4300	182.736	887.302	719.285	722.474	−1246.762	−135.919	1.651
4400	182.744	891.504	723.152	740.748	−1248.159	−110.072	1.307
4500	182.752	895.610	726.939	759.023	−1249.591	−84.191	0.977
4600	182.759	899.627	730.649	777.298	−1251.059	−58.278	0.662
4700	182.765	903.558	734.287	795.574	−1252.563	−32.331	0.359
4800	182.772	907.406	737.853	813.851	−1254.104	−6.352	0.069
4900	182.778	911.174	741.352	832.129	−1255.683	19.661	−0.210
5000	182.783	914.867	744.786	850.407	−1257.300	45.705	−0.477
5100	182.788	918.487	748.156	868.685	−1258.958	71.782	−0.735
5200	182.793	922.036	751.466	886.964	−1260.656	97.888	−0.983
5300	182.798	925.518	754.717	905.244	−1262.398	124.034	−1.222
5400	182.802	928.935	757.912	923.524	−1264.187	150.208	−1.453
5500	182.806	932.289	761.052	941.804	−1266.022	176.416	−1.675
5600	182.810	935.583	764.139	960.085	−1267.907	202.662	−1.890
5700	182.814	938.819	767.176	978.366	−1269.846	228.937	−2.098
5800	182.817	941.998	770.162	996.648	−1271.840	255.252	−2.299
5900	182.821	945.123	773.101	1014.930	−1273.892	281.593	−2.493
6000	182.824	948.196	775.994	1033.212	−1276.007	307.978	−2.681

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K) = 198.740 \pm 12.6\ J·K^{-1}·mol^{-1}$
$T_{trs1} = 130 \pm 8\ K$
$T_{trs2} = 150 \pm 3\ K$
$T_{fus} = 1950 \pm 20\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -3404.521 \pm 6.3\ kJ·mol^{-1}$
$\Delta_{trs1} H° = 95 \pm 5\ kJ·mol^{-1}$
$\Delta_{trs2} H° = 468 \pm 5\ kJ·mol^{-1}$
$\Delta_{fus} H° = [225.936]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$ is calculated from that of $Ti_3O_5(\beta)$ using $\Delta_f H°(298.15\ K) = -34.16\ kcal·mol^{-1}$ for 4/3 $Ti_3O_5(\beta)$ + 1/6 $O_2(g)$ + Ti_4O_7(cr). $\Delta_r H°$ is derived by the 3rd law method from two concordant studies[1,2] of high temperature equilibria. Merritt *et al.*[1] obtained isothermal gravimetric equilibrium over the two phase system Ti_3O_5–Ti_4O_7 using ($H_2 + H_2O$) gas mixtures of known oxygen potential. Integration yields $\Delta_r G°(1304\ K) = -20.29 \pm 0.16\ kcal·mol^{-1}$. Suzuki and Sambongi[2] reported solid state emf data relative to the couple Cr/Cr_2O_3 over a range of ~500°. We convert their (graphical) emf data[2] to oxygen potentials, using the authors' self consistent data for Cr/Cr_2O_3, and integrate to get $\Delta_r G°$. Vasil'eva and Shaulova[3] reported an equation for the oxygen potential based on their emf data relative to Fe/$Fe_{0.95}O$ over a range of ~90°. Equilibration data of Porter[4] are not considered because of the likelihood of oxidation during quenching of the composition.[1]

3rd law analyses of the equilibria for 4/3 $Ti_3O_5(\beta)$ + 1/6 $O_2(g) \rightarrow Ti_4O_7$(cr) are summarized below. Merritt *et al.*[1] agree closely with Suzuki and Sambongi[2] but the earlier emf study[3] yields a $\Delta_f H°$ which is 1.9 $kcal·mol^{-1}$ less negative. All three studies agree with the earlier conclusion of Wahlbeck and Gilles[5] that Ti_4O_7 is stable with respect to disproportionation into $Ti_3O_5(\beta)$ and TiO_2(rutile). We dismiss the $\Delta_f H°$ derived from Vasil'eva[3] since it implies the contrary when combined with our adopted $S°$ and $C_p°$. We adopt $\Delta_f H° = -813.7 \pm 1.5\ kcal·mol^{-1}$, where the uncertainty includes the possibility that $\Delta_{trs} H°$ and $S°$ of $Ti_3O_5(\beta)$ are biased.[6]

Source	Method	T/K	δS cal·K⁻¹·mol⁻¹	$\Delta_f H°$(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol⁻¹
1	Gravimetric	1304	–	–	−34.10	−813.63
2	emf	~1273–1773	0.1	−34.0	−34.20	−813.74
3	emf	1168–1257	2.0	−29.8	−32.31	−811.84

Heat Capacity and Entropy

$C_p°$ is based on constrained fitting of enthalpy data (679–1937 K) of Slyusar et al.[6] The constraints required that the enthalpy be zero at the reference temperature (298.15 K) and that $C_p° = 50\ cal·K^{-1}·mol^{-1}$ and $dC_p°/dT$ ~0.09 $cal·K^{-1}·mol^{-1}$ at 300 K. The latter values are estimated by comparison with TiO_2, Ti_3O_5, Ti_2O_3 and TiO[6]. Deviations of the data from the resulting fit have a pattern[6] similar to that found with the authors' data[7] for $Ti_3O_5(\beta)$. The enthalpies of Slyusar *et al.*[7] for TiO_2, Ti_2O_3, Ti_3O_5 and Ti_4O_7 are less than satisfactory due to inconsistencies in H near 1200 K and in the reported values of T_{fus}.[6] Our constraints for Ti_4O_7 are an attempt to minimize the effects of the inconsistencies. They lead to a reasonable variation of $C_p°$ with temperature. We assume that there are no phase transitions above 298 K.

$S°(298.15\ K) = 47.5 \pm 3\ cal·K^{-1}·mol^{-1}$ is derived from the emf data of Suzuki and Sambongi.[2] The uncertainty includes the possibility that $\Delta_{trs} H°$ and $S°$ of $Ti_3O_5(\beta)$ are biased;[6] excluding this possibility, we estimate an uncertainty of $\pm 1.5\ cal·K^{-1}·mol^{-1}$. $S°(298.15\ K) = 49.5\ cal·K^{-1}·mol^{-1}$ can be derived from the less reliable data of Vasil'eva and Shaulova.[3] These authors[3] derived $S°(298.15\ K) = 42\ cal·K^{-1}·mol^{-1}$ which is clearly too low. Unfortunately, the entropy derived form $C_p°$ data (12–300 K) of Berezovskii *et al.*[11] is unpublished and not yet available. These workers also measured $C_p°$ of the higher monologues Ti_5O_9, Ti_6O_{11} and Ti_9O_{17}.

Transition Data and Phase Data

Transition temperatures near 130 K and 150 K were found by use of DTA,[8] elecrical conductivity,[8] magnetic susceptibility[9] and x-ray diffraction.[8, 10] The three crystalline phases are triclinic; the two transitions involve no change in symmetry but only rearrangements of atoms within the unit cell.[10] There is obvious thermal hysteresis in the transition near 130 K. DTA endotherms[8] suggest that $\Delta_{trs} H°$ (150 K) is considerably larger than $\Delta_{trs} H°$(130 K). $\Delta_{trs} H°$ values presumably were obtained with the $C_p°$ data,[11] but these are not yet available.

Ti_4O_7 is the lowest stable phase in the homologous series of structures Ti_nO_{2n-1} related to rutile. Phases exist with n = 4,5,6,7,8,9 and certain higher integer values. These were reviewed in detail by Bursill and Hyde[12] in terms of the persistent structural phenomenon crystallographic shear. Equilibrium data[1, 2] emphasize that $\Delta_r G°$ is negative, but were small in magnitude, for formation of Ti_nO_{2n-1} from its two nearest neighbors. Kinetic limitations can cause hysteresis in measured properties.[1]

FusionData

Refer to the liquid table for details.

Sublimation Data

Ti_4O_7(cr) vaporizes incongruently such that the residue approaches the congruently vaporizing composition of $Ti_3O_5(\beta)$.

References

[1]R. R. Merritt, B. G. Hyde, L. A. Bursill and D. K. Philp, Phil. Trans. Roy. Soc. London, Ser. A **274**, (1245), 627 (1973)
[2]K. Suzuki and K, Sambongi, Tetsu To Hagane **58**, 1579 (1972).

Continued on page 1816

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
298.15	208.489	198.740	198.740	0.000	−3404.521	−3213.016	562.907
300	209.200	200.032	198.744	0.386	−3404.512	−3211.828	559.229
400	239.911	264.765	207.361	22.961	−3402.790	−3147.798	411.060
500	258.864	320.495	224.551	47.972	−3399.447	−3084.414	322.226
600	271.165	368.848	244.663	74.511	−3395.268	−3021.790	263.070
700	279.659	411.321	265.500	102.075	−3390.647	−2959.904	220.871
800	285.976	449.097	286.132	130.372	−3385.729	−2898.703	189.266
900	290.830	483.070	306.158	159.221	−3380.763	−2838.124	164.720
1000	294.805	513.923	325.416	188.508	−3376.077	−2778.086	145.112
1100	298.152	542.182	343.855	218.159	−3371.968	−2718.492	129.090
1200	301.081	568.252	361.483	248.123	−3384.403	−2658.763	115.733
1300	303.675	592.456	378.330	278.363	−3378.626	−2598.529	104.410
1400	306.018	615.047	394.441	308.849	−3373.023	−2538.733	94.721
1500	308.235	636.236	409.861	339.563	−3367.654	−2479.330	86.338
1600	310.285	656.196	424.639	370.490	−3362.581	−2420.276	79.014
1700	312.210	675.065	438.820	401.615	−3357.867	−2361.528	72.561
1800	314.051	692.962	452.446	432.929	−3353.574	−2303.047	66.833
1900	315.850	709.991	465.557	464.424	−3349.758	−2244.790	61.714
1950.000	316.729	718.207	471.930	480.239	--- CRYSTAL <--> LIQUID ---		
2000	317.607	726.237	478.188	496.097	−3405.222	−2184.907	57.064
2100	319.281	741.773	490.372	527.942	−3405.522	−2123.883	52.829
2200	320.913	756.664	502.140	559.952	−3405.736	−2062.845	48.978
2300	322.545	770.965	513.520	592.125	−3405.865	−2001.803	45.462
2400	324.134	784.726	524.535	624.459	−3405.911	−1940.757	42.239

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [291.066]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1950 \pm 20\ K$

$\Delta_f H°(298.15\ K) = [-3216.035]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [225.936]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(Ti_4O_7, l, 298.15\ K)$ is calculated from that of Ti_4O_7(cr) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1950\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

$C_p°$ is estimated as 8 $cal·K^{-1}$ $g\text{–}atoms^{-1}$. Below the assumed glass transition at 1300 K, $C_p°$ is taken to be the same as that of the crystal. $S°(298.15\ K)$ is calculated in a manner analogous to that used for $\Delta_f H°$.

Fusion Data

Hampson and Gilles[1] reported that $T_{fus} < 1943$ K, which is in reasonable agreement with $T_{fus} \sim 1955$ K obtained from the liquidus curve of Brauer and Littke.[2] The value of 1993 K reported by Slyusar *et al.*[3] is over 40° higher than our adopted value of 1950 ± 20 K. Ti_4O_7 probably melts incongruently, but the data[2] are not completely conclusive on this point.

Vaporization Data

Studies of liquid samples[4] showed that the congruently vaporizing composition is between Ti_3O_5 and Ti_4O_7. The principal products[1] of vaporization are TiO_2(g) and TiO(g).

References

[1]P. J. Hampson and P. W. Gilles, J. Chem. Phys. **55**, 3712 (1971).
[2]G. Brauer and W. Littke, J. Inorg. Nucl. Chem. **16**, 67 (1960).
[3]N. P. Slyusar, A. D. Krivorotenko, E. N. Fomichev, A. A. Kalashnik and V. P. Bondarenko, Teplofiz. Vys. Temp. **11**, 213 (1973).
[4]P. W. Gilles, H. F. Franzen, G. D. Stone and P. G. Wahlbeck, J. Chem. Phys. **48**, 1938 (1968).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	208.489	291.066	291.066	0.000	−3216.035	−3052.056	534.708
300	209.200	292.358	291.070	0.386	−3216.026	−3051.039	531.233
400	239.911	357.091	299.687	22.961	−3214.304	−2996.243	391.269
500	258.864	412.821	316.877	47.972	−3210.960	−2942.090	307.358
600	271.165	461.174	336.989	74.511	−3206.781	−2888.699	251.484
700	279.659	503.647	357.826	102.075	−3202.160	−2836.046	211.628
800	285.976	541.423	378.458	130.372	−3197.242	−2784.078	181.782
900	290.830	575.396	398.484	159.221	−3192.277	−2732.732	158.604
1000	294.805	606.249	417.742	188.508	−3187.591	−2681.926	140.089
1100	298.152	634.508	436.181	218.159	−3183.482	−2631.564	124.963
1200	301.081	660.578	453.809	248.123	−3195.917	−2581.068	112.351
1300	303.675	684.782	470.656	278.364	−3190.139	−2530.066	101.659
1300.000	303.675	684.782	470.656	278.364	GLASS <- -> LIQUID		
1300.000	368.192	684.782	470.656	278.364	TRANSITION		
1400	368.192	712.068	486.937	315.183	−3178.202	−2479.742	92.520
1500	368.192	737.471	502.803	352.002	−3166.728	−2430.256	84.629
1600	368.192	761.233	518.220	388.821	−3155.763	−2381.518	77.749
1700	368.192	783.555	533.178	425.641	−3145.356	−2333.450	71.698
1800	368.192	804.600	547.678	462.460	−3135.557	−2285.977	66.337
1900	368.192	824.507	561.729	499.279	−3126.417	−2239.030	61.555
1950.000	368.192	834.071	568.590	517.689	--- CRYSTAL <- -> LIQUID ---		
2000	368.192	843.393	575.344	536.098	−3176.735	−2190.733	57.216
2100	368.192	861.357	588.539	572.917	−3172.060	−2141.548	53.268
2200	368.192	878.485	601.332	609.737	−3167.465	−2092.582	49.684
2300	368.192	894.852	613.741	646.556	−3162.948	−2043.826	46.417
2400	368.192	910.522	625.783	683.375	−3158.509	−1995.265	43.426
2500	368.192	925.553	637.475	720.194	−3154.147	−1946.887	40.678
2600	368.192	939.993	648.834	757.013	−3149.859	−1898.681	38.145
2700	368.192	953.889	659.877	793.833	−3145.645	−1850.638	35.803
2800	368.192	967.279	670.618	830.652	−3141.503	−1802.750	33.631
2900	368.192	980.200	681.072	867.471	−3137.430	−1755.012	31.611
3000	368.192	992.682	691.252	904.290	−3133.426	−1707.410	29.729
3100	368.192	1004.755	701.171	941.109	−3129.486	−1659.939	27.970
3200	368.192	1016.445	710.842	977.929	−3125.610	−1612.599	26.323
3300	368.192	1027.774	720.275	1014.748	−3121.795	−1565.377	24.778
3400	368.192	1038.766	729.482	1051.567	−3118.037	−1518.268	23.325
3500	368.192	1049.439	738.472	1088.386	−3114.337	−1471.271	21.958
3600	368.192	1059.811	747.254	1125.205	−3110.690	−1424.377	20.667
3700	368.192	1069.899	755.839	1162.025	−4743.489	−1346.433	19.008
3800	368.192	1079.718	764.233	1198.844	−4735.007	−1254.732	17.247
3900	368.192	1089.282	772.446	1235.663	−4726.794	−1163.252	15.580
4000	368.192	1098.604	780.484	1272.482	−4718.845	−1071.983	13.999

PREVIOUS: CURRENT: December 1973

0	to	130	K crystal, I
130	to	150	K crystal, II
150	to	1950	K crystal, III
above		1950	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	208.489	198.740	198.740	0.000	−3404.521	−3213.016	562.907
300	209.200	200.032	198.744	0.386	−3404.512	−3211.828	559.229
400	239.911	264.765	207.361	22.961	−3402.790	−3147.798	411.060
500	258.864	320.495	224.551	47.972	−3399.447	−3084.414	322.226
600	271.165	368.848	244.663	74.511	−3395.268	−3021.790	263.070
700	279.659	411.321	265.500	102.075	−3390.647	−2959.904	220.871
800	285.976	449.097	286.132	130.372	−3385.729	−2898.703	189.266
900	290.830	483.070	306.158	159.221	−3380.763	−2838.124	164.720
1000	294.805	513.923	325.416	188.508	−3376.077	−2778.086	145.112
1100	298.152	542.182	343.855	218.159	−3371.968	−2718.492	129.090
1200	301.081	568.252	361.483	248.123	−3384.403	−2658.763	115.733
1300	303.675	592.456	378.330	278.363	−3378.626	−2598.529	104.410
1400	306.018	615.047	394.441	308.849	−3373.023	−2538.733	94.721
1500	308.235	636.236	409.861	339.563	−3367.654	−2479.330	86.338
1600	310.285	656.196	424.639	370.490	−3362.581	−2420.276	79.014
1700	312.210	675.065	438.820	401.615	−3357.867	−2361.528	72.561
1800	314.051	692.962	452.446	432.929	−3353.574	−2303.047	66.833
1900	315.850	709.991	465.557	464.424	−3349.758	−2244.790	61.714
1950.000	316.729	718.207	471.930	480.239	CRYSTAL <--> LIQUID		
1950.000	368 .192	834.071	471.930	706.175	TRANSITION		
2000	368.192	843.393	481.101	724.584	−3176.735	−2190.732	57.216
2100	368.192	861.357	498.784	761.404	−3172.060	−2141.548	53.268
2200	368.192	878.485	515.657	798.223	−3167.465	−2092.582	49.684
2300	368.192	894.852	531.790	835.042	−3162.948	−2043.826	46.417
2400	368.192	910.522	547.247	871.861	−3158.509	−1995.265	43.426
2500	368.192	925.553	562.080	908.680	−3154.147	−1946.887	40.678
2600	368.192	939.993	576.340	945.500	−3149.859	−1898.681	38.145
2700	368.192	953.889	590.067	982.319	−3145.645	−1850.638	35.803
2800	368.192	967.279	603.301	1019.138	−3141.503	−1802.750	33.631
2900	368.192	980.200	616.076	1055.957	−3137.430	−1755.012	31.611
3000	368.192	992.682	628.423	1092.776	−3133.426	−1707.410	29.729
3100	368.192	1004.755	640.369	1129.596	−3129.486	−1659.939	27.970
3200	368.192	1016.445	651.940	1166.415	−3125.610	−1612.599	26.323
3300	368.192	1027.774	663.158	1203.234	−3121.795	−1565.377	24.778
3400	368.192	1038.766	674.044	1240.053	−3118.037	−1518.268	23.325
3500	368.192	1049.439	684.618	1276.872	−3114.337	−1471.271	21.958
3600	368.192	1059.811	694.897	1313.692	−3110.690	−1424.377	20.667
3700	368.192	1069.899	704.896	1350.511	−4743.489	−1346.433	19.008
3800	368.192	1079.718	714.632	1387.330	−4735.007	−1254.732	17.247
3900	368.192	1089.282	724.116	1424.149	−4726.794	−1163.252	15.580
4000	368.192	1098.604	733.362	1460.968	−4718.845	−1071.983	13.999

PREVIOUS: CURRENT: December 1973

$S°(298.15\ K) = [494.013]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -1700.31\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -1710.00 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[800] (6)	[199] (3)
[350] (4)	[150] (6)
[242] (8)	

Ground State Quantum Weight: [1] σ = [4]
Point Group: [D_{2d}]
Bond Distance: W–O = [1.81] Å
Bond Angle: O–W–O = [109.47]°
Product of the Moments of Inertia: $I_A I_B I_C = [7.651013 \times 10^{-111}]\ g^3·cm^6$

Enthalpy of Formation

Ackermann and Rauh[1] have studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 1600 K by mass spectrometry, mass effusion and x-ray diffracton, and also have determined the $\Delta_f G°(W_3O_8, g) = -400{,}900 + 9054\ T$ $cal·K^{-1}·mol^{-1}$ from partial pressure measurements over W–WO_2(cr). The adopted value, $\Delta_f H°(W_3O_8, g, 298.15\ K) = -408.7\ kcal·mol^{-1}$ was reduced from $\Delta_f H°(W_3O_8, g, 1450\ K) = -400.9\ kcal·mol^{-1}$, using JANAF functions.

Source	Reaction	T/K	$\Delta_r H°$(298.15 K), $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal^{-1}·mol^{-1}$	$\Delta_f H°$(298.15K) $kcal·mol^{-1}$
1	$4\ WO_2(cr) = W_3O_8(g) + W(cr)$	1300–1600	155.05	155.09	−0.04	−408.7

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1}(6), 350 cm^{-1}(4), 242 cm^{-1}(8), 199 cm^{-1}(3) and 150 cm^{-1}(6) in order to give the entropy at 1450 K, $S°(1450\ K) = 208.18\ cal·K^{-1}·mol^{-1}$, corresponding to $\Delta_f S°(1450\ K) = -90.54\ cal·K^{-1}·mol^{-1}$, which was reported by Ackermann and Rauh.[1]

The molecular configuration for W_3O_8(g) was estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, the three tetrahedra are connected by two common edges, and also the three tungsten atoms are in the same axis. The bond distance W–O was estimated as 1.81 Å and the bond angle < OWO = 109.47°. The principal moments of inertia are: $I_A = 46.4211 \times 10^{-39}$ and $I_B = I_C = 405.9772 \times 10^{-39}\ g·cm^2$.

Reference

[1]R. J. Ackermann and E. G. Rauh, J. Phys. Chem. **67**, 2596 (1963).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−39.964	−1700.312	−1700.312	INFINITE
100	112.720	315.859	655.406	−33.955	−1707.878	−1667.258	870.886
200	177.022	417.309	512.062	−18.951	−1710.541	−1625.251	424.472
250	194.050	458.740	497.345	−9.651	−1710.544	−1603.915	335.120
298.15	206.277	494.013	494.013	0.	−1710.001	−1583.420	277.409
300	206.684	495.291	494.017	0.382	−1709.971	−1582.635	275.561
350	216.267	527.904	496.571	10.967	−1708.965	−1561.487	233.039
400	223.618	557.284	502.354	21.972	−1707.657	−1540.504	201.169
450	229.316	583.965	509.963	33.301	−1706.151	−1519.699	176.402
500	233.784	608.366	518.601	44.883	−1704.524	−1499.068	156.607
600	240.175	651.597	537.257	68.604	−1701.114	−1458.296	126.956
700	244.386	688.958	556.321	92.846	−1697.693	−1418.098	105.820
800	247.281	721.792	574.995	117.438	−1694.384	−1378.384	89.999
900	249.344	751.043	592.960	142.275	−1691.235	−1339.074	77.718
1000	250.861	777.396	610.108	167.288	−1688.271	−1300.106	67.911
1100	252.006	801.362	626.422	192.434	−1685.499	−1261.424	59.900
1200	252.891	823.329	641.928	217.681	−1682.920	−1222.988	53.235
1300	253.588	843.600	656.672	243.006	−1680.538	−1184.758	47.604
1400	254.146	862.414	670.704	268.394	−1678.352	−1146.704	42.784
1500	254.599	879.964	684.076	293.832	−1676.367	−1108.801	38.612
1600	254.973	896.408	696.838	319.311	−1674.586	−1071.022	34.965
1700	255.284	911.875	709.037	344.824	−1673.011	−1033.348	31.751
1800	255.546	926.474	720.715	370.366	−1671.646	−995.763	28.896
1900	255.768	940.297	731.911	395.932	−1670.495	−958.246	26.344
2000	255.958	953.421	742.662	421.519	−1669.561	−920.784	24.048
2100	256.123	965.913	752.998	447.123	−1668.849	−883.363	21.972
2200	256.265	977.831	762.948	472.743	−1668.359	−845.969	20.086
2300	256.390	989.226	772.541	498.376	−1668.095	−808.596	18.364
2400	256.500	1000.140	781.798	524.020	−1668.057	−771.230	16.785
2500	256.597	1010.613	790.743	549.675	−1668.247	−733.859	15.333
2600	256.683	1020.678	799.394	575.339	−1668.654	−696.476	13.992
2700	256.760	1030.367	807.770	601.011	−1669.359	−659.071	12.750
2800	256.829	1039.706	815.888	626.691	−1670.466	−621.633	11.597
2900	256.890	1048.720	823.762	652.377	−1672.090	−584.151	10.522
3000	256.946	1057.430	831.407	678.069	−1674.311	−546.598	9.517
3100	256.997	1065.856	838.834	703.766	−1677.257	−508.959	8.576
3200	257.043	1074.016	846.057	729.468	−1681.020	−471.217	7.692
3300	257.084	1081.926	853.085	755.174	−1685.674	−433.343	6.859
3400	257.123	1089.601	859.929	780.885	−1691.321	−395.309	6.073
3500	257.158	1097.055	866.598	806.599	−1698.154	−357.096	5.329
3600	257.190	1104.300	873.101	832.316	−1706.457	−318.666	4.624
3700	257.219	1111.347	879.445	858.037	−1820.827	−279.412	3.945
3800	257.247	1118.207	885.639	883.760	−1822.207	−237.730	3.268
3900	257.272	1124.890	891.688	909.486	−1823.639	−196.013	2.625
4000	257.295	1131.403	897.600	935.214	−1825.122	−154.263	2.014
4100	257.317	1137.757	903.380	960.945	−1826.655	−112.472	1.433
4200	257.337	1143.958	909.035	986.678	−1828.236	−70.644	0.879
4300	257.356	1150.013	914.569	1012.412	−1829.865	−28.776	0.350
4400	257.373	1155.930	919.987	1038.149	−1831.542	13.127	−0.156
4500	257.390	1161.714	925.295	1063.887	−1833.265	55.069	−0.639
4600	257.405	1167.372	930.496	1089.627	−1835.035	97.050	−1.102
4700	257.419	1172.908	935.595	1115.368	−1836.854	139.073	−1.546
4800	257.433	1178.327	940.596	1141.111	−1838.720	181.134	−1.971
4900	257.446	1183.635	945.502	1166.854	−1840.637	223.236	−2.380
5000	257.457	1188.837	950.317	1192.600	−1842.604	265.376	−2.772
5100	257.469	1193.935	955.044	1218.346	−1844.625	307.557	−3.150
5200	257.479	1198.935	959.686	1244.093	−1846.700	349.773	−3.514
5300	257.489	1203.839	964.247	1269.842	−1848.832	392.037	−3.864
5400	257.499	1208.652	968.728	1295.591	−1851.026	434.335	−4.201
5500	257.508	1213.377	973.134	1321.341	−1853.281	476.676	−4.527
5600	257.516	1218.017	977.465	1347.093	−1855.605	519.063	−4.842
5700	257.524	1222.575	981.725	1372.845	−1857.998	561.487	−5.145
5800	257.532	1227.054	985.917	1398.597	−1860.464	603.959	−5.439
5900	257.539	1231.457	990.041	1424.351	−1863.009	646.464	−5.723
6000	257.546	1235.785	994.101	1450.105	−1865.636	689.023	−5.998

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$S°(298.15\ K)$ = [504.674] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2011.05\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = -2023.38 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[800](6)	[200](6)
[396](3)	[150](6)
[330](9)	

Ground State Quantum Weight: [1] σ = [6]
Point Group: [D_{3h}]
Bond Distance: W–O = [1.81] Å
Bond Angles: O–W–O = [109.47]° W–O_{bridge} – W = [130.53]°
Product of the Moments of Inertia: $I_A I_B I_C$ = [$3.865176 \times 10^{-110}$] $g^3·cm^6$

Enthalpy of Formation

The adopted value, $\Delta_f H°(W_3O_9, g, 298.15\ K) = -483.6\ kcal·mol^{-1}$, was reduced from $\Delta_f H°(W_3O_9, g, 1450\ K) = -474.1\ kcal·mol^{-1}$ of Ackermann and Rauh,[1] who studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 16000 K by mass spectrometry, mass effusion and x-ray diffraction, and determined $\Delta_f G°(W_3O_9, g) = -474{,}100 + 110.26T\ cal·K^{-1}·mol^{-1}$ from partial pressure measurements over W–WO_2(cr). They reviewed the previous determinations[1–4] of the thermodynamic properties of sublimation of WO_3 and also pointed out that it was not possible to make quantitative observations on stoichiometric WO_3 in vacuo since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches $WO_{2.96}$. This is probably the cause of previous discrepancies in sublimation studies.

Battles[2] has also studied that the partial pressure of W_3O_9(g) over W–WO_2(cr) in the temperature range from 1389 to 1527 K. 3rd law calculation of the partial pressure data gives $\Delta_r H°(298.15\ K) = 148.2\ kcal·mol^{-1}$ for 4.5 WO_2(cr) = W_3O_9(g) + 1.5 W(cr) which yields $\Delta_f H°(W_3O_9, g, 298.15\ K) = -486.0\ kcal·mol^{-1}$, using all JANAF functions.

Normand and Staley[3] have obtained $\Delta_r H°(1800\ K) = -240\ kcal·mol^{-1}$ for 3 WO_3(g) = W_3O_9(g) by mass spectrometric study of the vapor over WO_3 dissolved in CaO–Al_2O_3–SiO_2. The value of $\Delta_r H°$ was determined by the 2nd law method from ion intensities and leads to $\Delta_f H°(W_3O_9, g) = -463.4\ kcal·mol^{-1}$. Using all JANAF functions (dated September 30, 1966). The absolute pressure values reported by Norman and Staley also appear to be quite inconsistent with the JANAF functions since they lead to −443 $kcal·mol^{-1}$ by the 3rd law method.

Source	Reaction	T/K	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
1	4.5 WO_2(cr) = W_3O_9(g) + 1.5 W(cr)	1300–1600	150.61	150.64	−0.05	−483.6*
2	4.5 WO_2(cr) = W_3O_9(g) + 1.5 W(cr)	1389–1527	148.20	148.20	−1.91 ± 0.24	−486.0*
3	3 WO_3(g) = W_3O_9(g)	1700–1900	−253.4	−233		−463.4**

*3rd law value adopted in calculation** 2nd law value adopted in calculation

Heat Capacity and Entropy

The heat capacity was approximated by making a tenative choice of the vibrational frequencies of 800 cm^{-1}(6), 396 cm^{-1}(3), 330 cm^{-1}(9), 200 cm^{-1}(6), and 150 cm^{-1}(6) in order to give the entropy at 1450 K. $S°(1450 = 219.14\ cal·K^{-1}·mol^{-1}$, corresponding to $\Delta_f S°(1450\ K) = 110.26\ cal·K^{-1}·mol^{-1}$, reported by Ackermann and Rauh.[1] The adopted value, $S°(W_3O_9, g, 298.15\ K) = 120.6\ cal·K^{-1}·mol^{-1}$, was reduced from the entropy at 1450 K, using JANAF functions. 2nd law calculation of the partial pressure data of Battles[2] gives $\Delta_r S°(1455\ K) = 71.7\ cal·K^{-1}·mol^{-1}$ for 4.5 WO_2(cr) = W_3O_9(g) + 1.5 W(cr). This yields $S°(W_3O_9, g, 298.15\ K) = 122.4\ cal·K^{-1}·mol^{-1}$.

The molecular configuration for W_3O_9(g) is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedra shares two oxygen atoms to form a planar six–member ring. The bond distance W–O is estimated as 1.81 Å and the bond angles O–W–O = 109.47° and W–O_{bridge}–W = 130.53°. The principal moments of inertia are: $I_A = I_B = 280.4787 \times 10^{-39}$ and $I_C = 491.3257 \times 10^{-39}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−41.659	−2011.047	−2011.047	INFINITE
100	111.355	318.753	675.866	−35.711	−2020.127	−1971.131	1029.613
200	186.893	422.590	524.066	−20.295	−2023.834	−1920.252	501.518
250	208.026	466.694	508.266	−10.393	−2023.962	−1894.323	395.797
298.15	222.942	504.674	504.674	0.	−2023.382	−1869.398	327.511
300	223.433	506.055	504.678	0.413	−2023.349	−1868.443	325.325
350	234.911	541.401	507.443	11.885	−2022.194	−1842.710	275.009
400	243.591	573.362	513.718	23.858	−2020.665	−1817.170	237.298
450	250.250	602.454	521.986	36.211	−2018.894	−1791.837	207.991
500	255.430	629.100	531.384	48.858	−2016.973	−1766.710	184.567
600	262.784	676.370	551.710	74.796	−2012.925	−1717.036	149.481
700	267.594	717.264	572.506	101.331	−2008.839	−1668.045	124.471
800	270.884	753.225	592.894	128.265	−2004.856	−1619.634	105.751
900	273.223	785.273	612.521	155.476	−2001.036	−1571.712	91.220
1000	274.939	814.153	631.264	182.889	−1997.404	−1524.206	79.616
1100	276.232	840.421	649.102	210.450	−1993.970	−1477.053	70.139
1200	277.230	864.501	666.063	238.125	−1990.738	−1430.205	62.255
1300	278.015	886.723	682.193	265.889	−1987.708	−1383.619	55.594
1400	278.644	907.350	697.548	293.723	−1984.883	−1337.257	49.894
1500	279.154	926.592	712.183	321.614	−1982.266	−1291.092	44.960
1600	279.575	944.622	726.153	349.551	−1979.861	−1245.093	40.648
1700	279.924	961.582	739.508	377.526	−1977.669	−1199.238	36.848
1800	280.219	977.591	752.294	405.534	−1975.697	−1153.508	33.474
1900	280.469	992.749	764.554	433.569	−1973.946	−1107.879	30.458
2000	280.683	1007.140	776.327	461.627	−1972.423	−1062.336	27.745
2100	280.867	1020.839	787.647	489.704	−1971.130	−1016.865	25.293
2200	281.028	1033.909	798.546	517.799	−1970.069	−971.447	23.065
2300	281.168	1046.404	809.053	545.909	−1969.243	−926.076	21.032
2400	281.291	1058.374	819.193	574.032	−1968.653	−880.736	19.169
2500	281.400	1069.859	828.992	602.167	−1968.301	−835.414	17.455
2600	281.496	1080.897	838.470	630.312	−1968.175	−790.102	15.873
2700	281.583	1091.523	847.646	658.466	−1968.357	−744.787	14.409
2800	281.660	1101.765	856.540	686.628	−1968.949	−699.459	13.049
2900	281.729	1111.650	865.168	714.798	−1970.069	−654.106	11.782
3000	281.792	1121.202	873.544	742.974	−1971.795	−608.699	10.598
3100	281.849	1130.443	881.683	771.156	−1974.254	−563.221	9.490
3200	281.900	1139.392	889.597	799.343	−1977.538	−517.657	8.450
3300	281.947	1148.067	897.299	827.536	−1981.721	−471.975	7.471
3400	281.990	1156.485	904.799	855.732	−1986.906	−426.148	6.547
3500	282.029	1164.659	912.107	883.933	−1993.284	−380.155	5.674
3600	282.065	1172.605	919.233	912.138	−2001.139	−333.958	4.846
3700	282.098	1180.334	926.186	940.346	−2115.069	−286.949	4.051
3800	282.129	1187.857	932.974	968.558	−2116.015	−237.524	3.265
3900	282.157	1195.186	939.603	996.772	−2117.019	−188.075	2.519
4000	282.184	1202.330	946.083	1024.989	−2118.081	−138.604	1.810
4100	282.208	1209.298	952.418	1053.209	−2119.200	−89.104	1.135
4200	282.231	1216.099	958.615	1081.431	−2120.372	−39.575	0.492
4300	282.252	1222.740	964.681	1109.655	−2121.599	9.984	−0.121
4400	282.271	1229.229	970.620	1137.881	−2122.879	59.568	−0.707
4500	282.290	1235.573	976.437	1166.109	−2124.210	109.182	−1.267
4600	282.307	1241.777	982.139	1194.339	−2125.596	158.827	−1.804
4700	282.323	1247.849	987.728	1222.570	−2127.035	208.505	−2.317
4800	282.338	1253.793	993.209	1250.803	−2128.529	258.213	−2.810
4900	282.352	1259.615	998.587	1279.038	−2130.079	307.956	−3.283
5000	282.366	1265.319	1003.864	1307.274	−2131.686	357.728	−3.737
5100	282.378	1270.911	1009.046	1335.511	−2133.353	407.534	−4.174
5200	282.390	1276.394	1014.135	1363.749	−2135.081	457.367	−4.594
5300	282.401	1281.773	1019.134	1391.989	−2136.873	507.244	−4.999
5400	282.412	1287.052	1024.047	1420.230	−2138.735	557.147	−5.389
5500	282.422	1292.234	1028.876	1448.471	−2140.667	607.087	−5.766
5600	282.431	1297.323	1033.624	1476.714	−2142.674	657.068	−6.129
5700	282.440	1302.322	1038.294	1504.958	−2144.760	707.079	−6.480
5800	282.449	1307.234	1042.889	1533.202	−2146.929	757.134	−6.819
5900	282.457	1312.063	1047.411	1561.447	−2149.185	807.216	−7.147
6000	282.465	1316.810	1051.861	1589.693	−2151.535	857.349	−7.464

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

$\Delta_f H°(0\ K) = -2979.041 \pm 8.9\ kJ \cdot mol^{-1}$

$S°(298.15\ K) = 228.781 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = -3009.936 \pm 8.9\ kJ \cdot mol^{-1}$

$T_{sub} = 631\ K$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°(298.15\ K)$ of P_4O_{10}(cr) has been reported by many investigators. The most recent value, $\Delta_r H°(298.15\ K) = -719.4 \pm 2.0\ kcal \cdot mol^{-1}$ for the reaction P_4(α, white, cr) + 5 O_2(g) = P_4O_{10}(hex, cr) was determined by Egan and Luff.[1] This $\Delta_r H°(298.15\ K)$ value was derived from energy of combustion, $\Delta_c E = -716.397\ kcal \cdot mol^{-1}$, which is an average value of many measurements using three different sample forms, i.e., uncoated phosphorus, lucite coated phosphorus and cellulose acetate coated phosphorus. The adopted $\Delta_f H°(P_4O_{10}, cr, 298.15\ K)$ value was recalculated based on the P(red, V, cr) as reference state.

The enthalpy of combustion of white phosphorus was determined as $713.2 \pm 1.0\ kcal \cdot mol^{-1}$ by Holmes[2] yielding $\Delta_f H°(P_4O_{10}, cr, 298.15\ K) = -696.5 \pm 1.3\ kcal \cdot mol^{-1}$, based on P(red, V, cr) as reference state. The enthalpy of formation of P_2O_5 from red phosphorus was reported to be $355 \pm 2\ kcal \cdot mol^{-1}$ by Koerner and Daniels.[3] The product, P_2O_5, was considered to be a mixture of two forms, i.e., crystalline and amorphous. The other $\Delta_f H°(P_4O_{10}, cr, 298.15\ K)$ values reported by early investigators were reviewed by Egan and Luff.[1]

Heat Capacity and Entropy

The heat capacities (12–324 K) and $S°(298.15\ K)$ adopted were taken from Andon *et al.*[4] The $C_p°$ values above 324 K were obtained by graphical extrapolation. The $S°(298.15\ K)$ value was calculated based on $S°(10\ K) = 0.36\ cal \cdot K^{-1} \cdot mol^{-1}$.

Low temperature (15–310 K) and high temperature (298.15–623.15 K) heat capacities were also measured by Thermal Laboratory[5] and Frandsen,[6] respectively. The low temperature data were not adopted because they are less satisfactory than the data of Andon *et al.*[4] The high temperature data were not used because the sample employed for enthalpy measurements was not explicitly reported as pure hexagonal form.

Sublimation Data

The value of $\Delta_{sub} H°(298.15\ K)$ was derived from the vapor pressure data by both the 2nd and 3rd law analyses. See the P_4O_{10}(g) table for details. T_{sub} is the temperature at which the Gibbs energy change of the reaction P_4O_{10}(hex, cr) = P_4O_{10}(g) approaches zero. Sublimation temperature for P_4O_{10}(cr) was derived to be 632 K, 636 K (average of three determinations) and 623.7 K (average of two determinations) by Frandsen[6] from the vapor pressure data reported by Hoeflake and Scheffer,[7] Smits[8] and Smits and Rutgers,[9] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.000	0.000	INFINITE	−33.962	−2979.041	−2979.041	INFINITE
100	77.613	77.530	376.309	−29.878	−2993.030	−2907.054	1518.489
200	154.557	155.896	246.521	−18.125	−3004.886	−2816.879	735.693
298.15	211.710	228.781	228.781	0.000	−3009.936	−2723.335	477.117
300	212.673	230.094	228.785	0.393	−3009.992	−2721.557	473.865
400	260.245	297.978	237.719	24.104	−3014.145	−2624.398	342.711
500	299.993	360.390	256.096	52.147	−3011.926	−2527.145	264.009
600	335.975	418.323	278.362	83.977	−3006.425	−2430.655	211.607
700	368.192	472.581	302.272	119.216	−2997.988	−2335.322	174.264
800	396.643	523.641	326.783	157.486	−2986.933	−2241.381	146.347
900	421.747	571.849	351.360	198.440	−2973.536	−2148.968	124.723
1000	442.667	617.389	375.707	241.682	−2958.135	−2058.158	107.507
1100	461.077	660.477	399.655	286.904	−2940.989	−1968.976	93.499
1200	475.302	701.230	423.104	333.751	−3176.705	−1877.108	81.708
1300	486.181	739.718	445.993	381.843	−3153.960	−1769.725	71.108
1400	494.967	776.080	468.284	430.914	−3130.407	−1664.124	62.089
1500	502.080	810.481	489.961	480.780	−3106.213	−1560.231	54.332

PREVIOUS: December 1962 CURRENT: December 1965

$S°(298.15\ K)$ = [403.964] $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2870.18 \pm 8.9\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -2904.08 \pm 8.9\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies			
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
424(1)	650 (2)	750(3)	764(3)
721(1)	952 (2)	257(3)	1015(3)
1417(1)	[170](3)	329(3)	1390(3)
278(2)	[470](3)	573(3)	

Ground State Quantum Weight: [1] $7\sigma = 12$
Point Group: T_d
Bond Distances: $P–O_{apical} = 1.40 \pm 0.03$ Å P–O = 1.60 ± 0.01 Å P–P = 2.83 ± 0.03 Å
Bond Angles: $O_{apical}–P–O = 117 \pm 1°$ O–P–O = 101 ± 1° P–O–P = 124°30' ± 1°
Product of the Moments of Inertia: $I_A I_B I_C = 2.939188 \times 10^{-111}\ g^3·cm^6$

Enthalpy of Formation

$\Delta_f H°(P_4O_{10}, g, 298.15\ K)$ was calculated from the enthalpies of formation and sublimation for P_4O_{10}(hex, cr). The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, was derived from vapor pressure data by the second and third law methods. The results obtained are presented as follows.

Source	T/K	$\Delta_{sub}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
[1]	260.0–401.0	25.42 ± 0.07	25.33	−0.39 ± 0.13
[2]	216.2–300.4	25.59 ± 0.06	25.35	−0.18 ± 0.14
	283.6–389.3	25.45 ± 0.07	25.35	−0.10 ± 0.07

The value of $\Delta_{sub}H°(298.15\ K)$ adopted was 25.34 + 0.08 $kcal·mol^{-1}$. There are many vapor pressure measurements reported but only the above two over P_4O_{10}(hex, cr).

It has been shown that P_4O_{10} has three solid phases and two liquid phases. The three solid phases are hexagonal, orthorhombic and tetragonal. As temperature increases, the thermal stability of P_4O_{10} follows the same order. The metastable liquid, according to data of Hoeflake and Scheffer[1] is from hexagonal form. The stable liquid is from tetragonal form. Hill *et al.*[3] reported that molecules of P_4O_{10} having the same structure as in the vapor are present in the hexagonal form of the solid. The vapor pressures of P_4O_{10} over different condensed phases have been measured by many investigators and reviewed by Farr.[4] The complexity of the solid state of P_4O_{10} has also been discussed by Smits and Rutgers,[5] Smits,[6] Smits *et al.*[7] and Smits.[8]

Heat Capacity and Entropy

The molecular structure and constants were obtained from Akishin *et al.*[9] The molecular structure of P_4O_{10}(g) has also been studied by the electron diffraction method by Maxwell *et al.*[10] and Hampson and Stosick.[11] The model of the P_4O_{10} molecule was later confirmed by the x-ray method reported by Decker and MacGillavry[12] and spectroscopic studies reported by Gerding and DeDecker[13] and Sidorov and Sobolev.[14] All vibrational frequencies were obtained from Egan[15] except nine frequencies, i.e. 170(3), 470(3), and 750(3) cm^{-1} which were estimated in order to make the second and third law values of $\Delta_{sub}H°(298.15\ K)$ agree. The principal moments of inertia are: $I_A = I_B = I_C = 143.2430 \times 10^{-39}\ g·cm^2$. The heat capacities (549–1098°C or 822–1371 K) of P_4O_{10}(g) have been determined by Frandsen.[16] His results are in fair agreement with the calculated ones.

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Continued on page 1816

Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−30.951	−2870.176	−2870.176	INFINITE
100	70.439	269.420	534.866	−26.545	−2883.841	−2817.054	1471.478
200	136.770	339.152	419.662	−16.102	−2897.007	−2745.652	717.091
250	165.183	372.796	406.944	−8.537	−2901.099	−2707.317	565.663
298.15	188.804	403.964	403.964	0.	−2904.081	−2669.711	467.722
300	189.639	405.134	403.967	0.350	−2904.179	−2668.257	464.585
350	210.273	435.963	406.355	10.363	−2909.292	−2628.464	392.277
400	227.511	465.202	411.900	21.321	−2911.072	−2588.215	337.986
450	241.860	492.853	419.373	33.066	−2912.178	−2547.785	295.739
500	253.807	518.973	428.039	45.467	−2912.751	−2507.262	261.932
600	272.134	566.965	447.269	71.818	−2912.729	−2426.144	211.215
700	285.128	609.946	467.494	99.717	−2911.633	−2345.122	174.995
800	294.543	648.667	487.761	128.724	−2909.840	−2264.308	147.844
900	301.519	683.781	507.621	158.544	−2907.577	−2183.748	126.741
1000	306.801	715.835	526.863	188.972	−2904.990	−2103.459	109.873
1100	310.877	745.276	545.399	219.864	−2902.173	−2023.439	96.085
1200	314.081	772.469	563.203	251.119	−3153.482	−1939.372	84.419
1300	316.638	797.713	580.283	282.659	−3147.288	−1838.447	73.870
1400	318.708	821.257	596.664	314.430	−3141.035	−1738.001	64.846
1500	320.406	843.305	612.380	346.388	−3134.750	−1638.004	57.040
1600	321.814	864.030	627.467	378.501	−3128.454	−1538.426	50.224
1700	322.995	883.576	641.962	410.744	−3122.165	−1439.242	44.223
1800	323.993	902.067	655.904	443.094	−3115.899	−1340.429	38.898
1900	324.845	919.608	669.325	475.537	−3109.669	−1241.961	34.144
2000	325.577	936.290	682.260	508.059	−3103.484	−1143.821	29.874
2100	326.211	952.190	694.738	540.650	−3097.355	−1045.988	26.018
2200	326.763	967.379	706.788	573.299	−3091.289	−948.444	22.519
2300	327.246	981.915	718.436	606.000	−3085.291	−851.178	19.331
2400	327.672	995.851	729.707	638.746	−3079.366	−754.172	16.414
2500	328.050	1009.235	740.622	671.533	−3073.517	−657.409	13.736
2600	328.385	1022.108	751.203	704.355	−3067.746	−560.879	11.268
2700	328.685	1034.507	761.467	737.208	−3062.056	−464.568	8.988
2800	328.954	1046.466	771.434	770.091	−3056.445	−368.466	6.874
2900	329.196	1058.014	781.118	802.998	−3050.914	−272.569	4.909
3000	329.415	1069.178	790.535	835.929	−3045.464	−176.855	3.079
3100	329.613	1079.982	799.698	868.881	−3040.091	−81.321	1.370
3200	329.793	1090.450	808.622	901.851	−3034.796	14.035	−0.229
3300	329.957	1100.601	817.316	934.839	−3029.575	109.229	−1.729
3400	330.108	1110.453	825.794	967.842	−3024.427	204.269	−3.138
3500	330.245	1120.024	834.064	1000.860	−3019.352	299.155	−4.465
3600	330.372	1129.329	842.138	1033.891	−3014.344	393.899	−5.715
3700	330.488	1138.383	850.022	1066.934	−3009.405	488.502	−6.896
3800	330.596	1147.198	857.727	1099.988	−3004.531	582.980	−8.014
3900	330.695	1155.787	865.260	1133.053	−2999.720	677.326	−9.072
4000	330.788	1164.160	872.629	1166.127	−2994.972	771.546	−10.075
4100	330.873	1172.329	879.839	1199.210	−2990.286	865.651	−11.029
4200	330.953	1180.304	886.898	1232.301	−2985.658	959.642	−11.935
4300	331.027	1188.092	893.813	1265.400	−2981.091	1053.526	−12.798
4400	331.096	1195.703	900.588	1298.507	−2976.583	1147.299	−13.620
4500	331.161	1203.144	907.229	1331.620	−2972.132	1240.972	−14.405
4600	331.221	1210.423	913.741	1364.739	−2967.742	1334.546	−15.154
4700	331.278	1217.547	920.130	1397.864	−2963.413	1428.029	−15.871
4800	331.331	1224.523	926.399	1430.994	−2959.145	1521.419	−16.556
4900	331.381	1231.355	932.553	1464.130	−2954.941	1614.724	−17.213
5000	331.429	1238.050	938.596	1497.270	−2950.801	1707.940	−17.843
5100	331.473	1244.614	944.532	1530.416	−2946.730	1801.076	−18.447
5200	331.515	1251.051	950.365	1563.565	−2942.728	1894.126	−19.027
5300	331.554	1257.366	956.098	1596.718	−2938.801	1987.109	−19.584
5400	331.592	1263.564	961.735	1629.876	−2934.952	2080.012	−20.120
5500	331.627	1269.648	967.278	1663.037	−2931.182	2172.844	−20.636
5600	331.660	1275.624	972.731	1696.201	−2927.500	2265.616	−21.133
5700	331.692	1281.495	978.097	1729.369	−2923.907	2358.316	−21.612
5800	331.722	1287.264	983.378	1762.539	−2920.408	2450.960	−22.073
5900	331.751	1292.934	988.576	1795.713	−2917.010	2543.532	−22.519
6000	331.778	1298.510	993.696	1828.890	−2913.718	2636.061	−22.949

PREVIOUS: December 1965 (1 atm) CURRENT: December 1965 (1 bar)

$S°(298.15\ K) = [605.272]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = -2789.53 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = -2804.12 \pm 41.8\ kJ·mol^{-1}$

Vibrational Frequencies and Degeneracies	
ν, cm^{-1}	ν, cm^{-1}
[800](8)	[240](8)
[300](8)	[200](18)

Ground State Quantum Weight: [1] σ = [8]
Point Group: [D_{4h}]
Bond Distance: W–O = [1.81] Å
Bond Angles: O–W–O = [109.47]° W–O_{bridge}–W = [160.53]°
Product of the Moments of Inertia: $I_A I_B I_C = [3.854 \times 10^{-109}]\ g^3·cm^6$

Enthalpy of Formation

The adopted value, $\Delta_f H°(W_4O_{12}, g, 298.15\ K) = -670.2\ kcal·mol^{-1}$, was reduced from $\Delta_f H°(W_4O_{12}, g, 1450\ K) = -655.6\ kcal·mol^{-1}$ of Ackermann and Rauh[1] who studied the sublimation behavior of the tungsten–oxygen system over the temperature range from 1300 to 1600 K by mass spectrometry, mass effusion and x-ray diffraction, and determined $\Delta_f G°(W_4O_{12}, g) = -655{,}600 + 160.29\ T\ cal·K^{-1}mol^{-1}$ from partial pressure measurements over the W–WO_2(cr). They reviewed the previous determinations[1–4] of the thermodynamic properties of sublimation of WO_3 and also pointed out that it was not possible to make quantitative observations of stoichiometric WO_3 in vacuo since it is a "bivariant" system and the ion current is not constant until the composition of the sample reaches $WO_{2.96}$. This is probably the cause of previous discrepancies in sublimation studies.

Battles[2] has also studied the partial pressure of W_4O_{12}(g) over W–WO_2(cr) in the temperature range from 1449 to 1527 K. 3rd law calculation of the partial pressure data gives $\Delta_f H°(298.15\ K) = 172.0\ kcal·mol^{-1}$ for 6 WO_2(cr) = W_4O_{12}(g) + 2 W(cr) which yields $\Delta_f H°(W_4O_{12}, g, 298.15\ K) = -673.6\ kcal·mol^{-1}$, using all JANAF functions.

Source	Reaction	T/K	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$,(298.15 K) kcal·mol^{-1}
1	6 WO_2(cr) = W_4O_{12}(g) + 2 W(cr)	1300–1600	175.41	175.55	0.01	−670.2
2	6 WO_2(cr) = W_4O_{12}(g) + 2 W(cr)	1449–1257	176.16	172.01	−2.90 ± 0.39	−673.6

Heat Capacity and Entropy

The heat capacity was approximated by making a tentative choice of the vibrational frequencies of 800 cm^{-1}(8), 300 cm^{-1}(8), 240 cm^{-1}(8), and 200 cm^{-1}(18) in order to give the entropy at 1450 K, $S°(1450\ K) = 278.9\ cal·K^{-1}·mol^{-1}$, corresponding to $\Delta_f S°(1450\ K) = -160.29\ cal·K^{-1}·mol^{-1}$, reported by Ackermann and Rauh.[1] The adopted value, $S°(W_4O_{12}, g, 298.15\ K) = 144.6\ cal·K^{-1}·mol^{-1}$, was reduced from the entropy at 1450 K, using JANAF functions. 2nd law calculation of the partial pressure data of Battles gives $\Delta_f S°(1487\ K) = 82.3\ cal·K^{-1}·mol^{-1}$ for 6 WO_2(cr) = W_4O_{12}(g) + 2 W(cr). This yields $S°(W_4O_{12}, g, 298.15\ K) = 147.4\ cal·K^{-1}·mol^{-1}$.

The molecular configuration for W_4O_{12}(g) is estimated by assuming that the oxygens are tetrahedrally located around the tungsten atoms, and that each tetrahedra shares two oxygen atoms to form a planar eight-member ring. The bond distance W–O is estimated as 1.81 Å and the bond angles O–W–O = 109.47° and W–O_{bridge}–W = 160.53°. The principal moments of inertia are: $I_A = I_B = 5.935 \times 10^{-37}$ and $I_C = 1.094 \times 10^{-36}\ g·cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−57.403	−2789.527	−2789.527	INFINITE
100	155.404	342.363	846.055	−50.369	−2802.530	−2728.938	1425.451
200	264.535	490.351	632.324	−28.395	−2806.053	−2653.323	692.977
250	290.904	552.391	610.266	−14.469	−2805.502	−2615.182	546.412
298.15	309.177	605.272	605.272	0.	−2804.117	−2578.641	451.767
300	309.778	607.186	605.277	0.573	−2804.051	−2577.242	448.738
350	323.782	656.042	609.104	16.428	−2801.950	−2539.600	379.015
400	334.379	700.000	617.765	32.894	−2799.410	−2502.290	326.766
450	342.521	739.875	629.152	49.825	−2796.588	−2465.317	286.167
500	348.867	776.305	642.072	67.117	−2793.598	−2428.668	253.721
600	357.895	840.770	669.957	102.488	−2787.414	−2356.261	205.131
700	363.813	896.414	698.424	138.593	−2781.241	−2284.891	170.501
800	367.868	945.276	726.289	175.189	−2775.246	−2214.397	144.585
900	370.754	988.780	753.082	212.128	−2769.495	−2144.639	124.472
1000	372.873	1027.958	778.644	249.314	−2764.016	−2075.507	108.413
1100	374.471	1063.575	802.952	286.685	−2758.816	−2006.909	95.300
1200	375.705	1096.213	826.049	324.197	−2753.895	−1938.773	84.393
1300	376.676	1126.326	848.004	361.817	−2749.253	−1871.037	75.179
1400	377.453	1154.270	868.895	399.525	−2744.890	−1803.647	67.295
1500	378.085	1180.334	888.798	437.303	−2740.810	−1736.560	60.472
1600	378.605	1204.752	907.790	475.138	−2737.017	−1669.735	54.511
1700	379.038	1227.718	925.941	513.021	−2733.513	−1603.139	49.258
1800	379.402	1249.394	943.314	550.944	−2730.304	−1536.742	44.595
1900	379.712	1269.915	959.968	588.900	−2727.394	−1470.513	40.427
2000	379.976	1289.399	975.957	626.885	−2724.788	−1404.430	36.680
2100	380.205	1307.944	991.328	664.894	−2722.491	−1338.470	33.293
2200	380.404	1325.636	1006.124	702.925	−2720.506	−1272.608	30.216
2300	380.577	1342.549	1020.387	740.974	−2718.836	−1206.836	27.408
2400	380.730	1358.750	1034.150	779.039	−2717.481	−1141.129	24.836
2500	380.864	1374.294	1047.447	817.119	−2716.444	−1075.470	22.471
2600	380.984	1389.235	1060.307	855.212	−2715.711	−1009.846	20.288
2700	381.091	1403.615	1072.758	893.316	−2715.388	−944.241	18.267
2800	381.187	1417.476	1084.823	931.430	−2715.614	−878.640	16.391
2900	381.273	1430.854	1096.526	969.553	−2716.543	−813.024	14.644
3000	381.350	1443.781	1107.887	1007.684	−2718.281	−747.356	13.013
3100	381.420	1456.287	1118.925	1045.822	−2720.997	−681.614	11.485
3200	381.484	1468.397	1129.658	1083.968	−2724.814	−615.773	10.051
3300	381.542	1480.137	1140.101	1122.119	−2729.830	−549.794	8.703
3400	381.596	1491.528	1150.271	1160.276	−2736.182	−483.637	7.430
3500	381.644	1502.590	1160.180	1198.438	−2744.126	−417.277	6.228
3600	381.689	1513.342	1169.841	1236.605	−2754.039	−350.659	5.088
3700	381.730	1523.801	1179.267	1274.776	−2905.385	−282.975	3.995
3800	381.768	1533.981	1188.468	1312.951	−2906.086	−212.085	2.915
3900	381.803	1543.898	1197.455	1351.129	−2906.866	−141.178	1.891
4000	381.835	1553.565	1206.237	1389.311	−2907.723	−70.256	0.917
4100	381.866	1562.994	1214.824	1427.496	−2908.655	0.693	−0.009
4200	381.894	1572.196	1223.224	1465.684	−2909.660	71.664	−0.891
4300	381.920	1581.183	1231.445	1503.875	−2910.737	142.663	−1.733
4400	381.944	1589.963	1239.493	1542.068	−2911.885	213.682	−2.537
4500	381.967	1598.547	1247.377	1580.264	−2913.103	284.729	−3.305
4600	381.988	1606.942	1255.103	1618.461	−2914.392	355.804	−4.040
4700	382.008	1615.158	1262.677	1656.661	−2915.754	426.912	−4.745
4800	382.027	1623.201	1270.104	1694.863	−2917.187	498.048	−5.420
4900	382.044	1631.078	1277.391	1733.066	−2918.696	569.218	−6.068
5000	382.061	1638.796	1284.542	1771.272	−2920.281	640.416	−6.690
5100	382.076	1646.362	1291.563	1809.479	−2921.947	711.648	−7.289
5200	382.091	1653.782	1298.457	1847.687	−2923.694	782.906	−7.864
5300	382.105	1661.060	1305.230	1885.897	−2925.527	854.210	−8.419
5400	382.118	1668.202	1311.886	1924.108	−2927.452	925.540	−8.953
5500	382.131	1675.214	1318.429	1962.320	−2929.471	996.907	−9.468
5600	382.142	1682.100	1324.861	2000.534	−2931.590	1068.320	−9.965
5700	382.153	1688.863	1331.188	2038.749	−2933.815	1139.764	−10.445
5800	382.164	1695.510	1337.413	2076.965	−2936.150	1211.255	−10.909
5900	382.174	1702.043	1343.537	2115.182	−2938.602	1282.773	−11.357
6000	382.184	1708.466	1349.566	2153.399	−2941.178	1354.349	−11.791

PREVIOUS: September 1966 (1 atm) CURRENT: September 1966 (1 bar)

Continued from page 1728

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Continued from page 1733

Due to the large scatter in the mass spectrometric results, we prefer not to average the resulting $\Delta_f H°$ values but to rely on correlations with VO(g) and NbO(g). There has been good agreement for VO(g) and NbO(g) between the adopted JANAF $\Delta_f H°$(298.15 K) value and the value derived from the Birge–Sponer result corrected for ionicity.[2] Thus we adopt $\Delta_f H°$(TaO, g, 298.15 K) = 46.0 ± 15.0 kcal·mol^{-1}, which is a rounded value based on the adjusted Birge–Sponer result. This corresponds to D_0° = 8.65 ± 0.65 eV.

Heat Capacity and Entropy

The band spectrum attributable to TaO(g) has been observed by many investigators.[8–13] Weltner and McLeod[14] studied TaO spectroscopically in the infrared, visible, and near–ultraviolet regions by means of matrix isolation techniques. Sixteen electronic transitions were observed from the $X^2\Delta_{3/2}$ state, determined to be the ground state. Cheetham and Barrow[15] characterized nineteen electronic states from a rotational analysis of the emission spectrum of TaO in the region 2740–9500 Å. The combination of the results of these latter two studies as given by Cheetham and Barrow[15] provides the adopted vibrational and rotational constants as well as the electronic levels. Cheetham and Barrow[15] indicated the possibility of other low lying states based on the early work by Kiess and Stowell.[8]

The electronic states listed by Cheetham and Barrow[15] are actually sublevels as indicated by the value. The quantum weight of 2 is assigned if the two sublevels which are part of the same state are present (i.e. similar ω_e and $\omega_e x_e$ values of rthe same Δ state but different value). If the two sublevels of a particular Δ state are not accounted for, then a quantum weight of 4 is assigned to that sublevel which is tabulated.

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Continued from page 1734

Recent C_p° data (60–298 K) for $TiO_{1.01}$[15] are larger at all temperatures with deviations of 2–3% at 110–250 K increasing to 5% at 298 K and 7% at 60 K. The new data yield $S°$(298.15 K) = 8.55 cal·K^{-1}·mol^{-1} of TiO. We know nothing about the TiO sample,[15] but it also may have been used to obtain enthalpies (700–2300 K) which are not yet published.[16] Shomate,[12] Naylor[13] and later Humphrey,[3] (see $\Delta_f H°$) all used the same sample, 99.2% pure with Si and C as impurities. The (O/Ti) ratio was 0.994.[17] Vacancy concentration is unknown and the phase is uncertain.

Transition Data and Phase Data – Refer to the β-crystal table for details.

Sublimation Data – This is the difference in $\Delta_f H°$ for TiO(g) and TiO(α).

References – References are listed on liquid table.

Continued from page 1738

Heat Capacity and Entropy

Electronic levels (T_0) and vibrational–rotational constants are from Rosen[1] as supplemented[4] by extensive new data.[2,3,5,8,9] Additional states near 32000 cm^{-1} [10, 3] are omitted since their effect is negligible. We estimate unknown spectroscopic constants from known values for states arising from like molecular–orbital configurations.[11] Although $^3\Delta$ is the ground state,[6] several authors[1–3, 12] noted that energy levels of all singlet states are approximate due to uncertainty in the low–lying $a^1\Delta$. We revise $a^1\Delta$ from 581 cm^{-1} [16] to 1000 ± 400 cm^{-1} based on the temperature dependence of band intensities,[6,7] the requirement that $b^1\Pi$ lie above $E^3\Pi$ observed at 11894 cm^{-1} in a Ne–matrix,[3] and the assumption that $f^1\Delta$[8,4] is the perturber of $C^3\Delta^5$. The new E and f states confirm empirical predictions[11] which suggest additional unobserved levels at ~13000 ($^3\Sigma$) and 15000 cm$^{-1}\Sigma$). We omit these states since their predicted energies are less well established and their contributions to C_p° and $S°$ would be quite small. The functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_e\Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

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The bending frequency is estimated as 270 ± 80 cm^{-1} from the following information. A value of 272 cm^{-1} derived from the three-constant valence-force field[17] using ν_1, ν_3 and $(k\delta/l^2)/k_1 = 0.040$ transferred from isoelectronic CaF_2.[18] The resulting value of k_{12}/k_1 is similar to that of CaF_2. The inferior two-constant central-force field gives $\nu_2 = 325$ cm^{-1}. Bending modes have been observed[19] for electronic states of TaO_2 (285 and 281 cm^{-1}) and WO_2 (300 cm^{-1}). These molecules have stretching frequencies similar to TiO_2, but the excited states may be linear rather than bent as are the ground states. We estimate that $S°(298.15\ K)$ is uncertain by about 0.7 and 0.3 $cal \cdot K^{-1} \cdot mol^{-1}$ due to uncertainties in ν_2 and the geometry, respectively.

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REFERENCE STATE

0	to	195.4	K crystal, white, beta
195.4	to	317.3	K crystal, white, alpha
317.3	to	1180.008	K liquid
above		1180.008	K ideal diatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−5.360	0.	0.	0.
100	13.728	17.688	62.415	−4.473	0.	0.	0.
195.400	21.117	28.969	43.439	−2.827	ALPHA <--> BETA TRANSITION		
195.400	20.941	31.637	43.439	−2.306			
200	21.092	32.126	43.173	−2.209	0.	0.	0.
298.15	23.825	41.077	41.077	0.	0.	0.	0.
300	23.870	41.225	41.078	0.044	0.	0.	0.
317.300	24.351	42.574	41.123	0.460	BETA <--> LIQUID TRANSITION		
317.300	26.326	44.649	41.123	1.119			
400	26.326	50.747	42.507	3.296	0.	0.	0.
500	26.326	56.621	44.764	5.929	0.	0.	0.
600	26.326	61.421	47.152	8.561	0.	0.	0.
700	26.326	65.479	49.488	11.194	0.	0.	0.
800	26.326	68.995	51.711	13.826	0.	0.	0.
900	26.326	72.095	53.807	16.459	0.	0.	0.
1000	26.326	74.869	55.777	19.092	0.	0.	0.
1100	26.326	77.378	57.629	21.724	0.	0.	0.
1180.008	26.326	79.226	59.031	23.830	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1180.008	18.540	133.233	59.031	87.558			
1200	18.551	133.544	60.270	87.929	0.	0.	0.
1300	18.604	135.031	65.964	89.787	0.	0.	0.
1400	18.648	136.412	70.948	91.649	0.	0.	0.
1500	18.686	137.699	75.355	93.516	0.	0.	0.
1600	18.720	138.907	79.290	95.386	0.	0.	0.
1700	18.750	140.042	82.831	97.260	0.	0.	0.
1800	18.776	141.115	86.039	99.136	0.	0.	0.
1900	18.801	142.131	88.965	101.015	0.	0.	0.
2000	18.823	143.096	91.647	102.896	0.	0.	0.
2100	18.844	144.015	94.119	104.780	0.	0.	0.
2200	18.864	144.892	96.407	106.665	0.	0.	0.
2300	18.883	145.731	98.534	108.553	0.	0.	0.
2400	18.901	146.535	100.517	110.442	0.	0.	0.
2500	18.918	147.306	102.373	112.333	0.	0.	0.
2600	18.934	148.049	104.116	114.225	0.	0.	0.
2700	18.950	148.764	105.756	116.119	0.	0.	0.
2800	18.965	149.453	107.305	118.015	0.	0.	0.
2900	18.980	150.119	108.770	119.912	0.	0.	0.
3000	18.994	150.763	110.159	121.811	0.	0.	0.
3100	19.009	151.386	111.479	123.711	0.	0.	0.
3200	19.022	151.989	112.735	125.613	0.	0.	0.
3300	19.036	152.575	113.934	127.516	0.	0.	0.
3400	19.050	153.143	115.079	129.420	0.	0.	0.
3500	19.063	153.696	116.174	131.326	0.	0.	0.
3600	19.076	154.233	117.224	133.233	0.	0.	0.
3700	19.089	154.756	118.231	135.141	0.	0.	0.
3800	19.102	155.265	119.199	137.050	0.	0.	0.
3900	19.114	155.761	120.130	138.961	0.	0.	0.
4000	19.127	156.245	121.027	140.873	0.	0.	0.
4100	19.140	156.718	121.892	142.787	0.	0.	0.
4200	19.152	157.179	122.727	144.701	0.	0.	0.
4300	19.164	157.630	123.533	146.617	0.	0.	0.
4400	19.176	158.071	124.313	148.534	0.	0.	0.
4500	19.189	158.502	125.068	150.452	0.	0.	0.
4600	19.201	158.924	125.799	152.372	0.	0.	0.
4700	19.213	159.337	126.509	154.292	0.	0.	0.
4800	19.225	159.741	127.197	156.214	0.	0.	0.
4900	19.237	160.138	127.865	158.137	0.	0.	0.
5000	19.248	160.527	128.514	160.062	0.	0.	0.
5200	19.272	161.282	129.760	163.914	0.	0.	0.
5400	19.296	162.010	130.941	167.771	0.	0.	0.
5600	19.319	162.712	132.063	171.632	0.	0.	0.
5800	19.342	163.390	133.132	175.498	0.	0.	0.
6000	19.366	164.047	134.152	179.369	0.	0.	0.

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 22.59 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-11.15]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-12.85]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is derived from $\Delta_r G°(820\ K) = 0$ for the process P(black)→P(red, IV). This calculation is based on the assumption that at 820 K the conversion of black to red phosphorus is known to occur.[1]

Heat Capacity and Entropy

The thermal functions are derived from the heat capacity measurments of Stephenson *et al.*[1] who reported measured values from 17.70 to 295.89 K.

Reference

[1]C. C. Stephenson, R. L. Potter, T. G. Maple and J. C. Morrow, J. Chem. Thermodynamics **1**, 59 (1969).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−3.660	−11.151	−11.151	INFINITE
100	9.063	5.673	38.599	−3.293	−11.671	−10.469	5.469
200	17.343	14.800	24.438	−1.928	−12.569	−9.104	2.378
250	19.778	18.944	22.931	−0.997	−12.730	−8.218	1.717
298.15	21.547	22.586	22.586	0.	−12.851	−7.338	1.286
300	21.602	22.719	22.586	0.040	−12.855	−7.304	1.272
350	22.644	26.129	22.853	1.147	−13.684	−6.298	0.940
400	23.531	29.213	23.458	2.302	−13.845	−5.232	0.683
450	24.183	32.022	24.256	3.495	−13.969	−4.147	0.481
500	24.836	34.604	25.164	4.720	−14.060	−3.051	0.319
600	26.146	39.246	27.132	7.268	−14.144	−0.839	0.073
700	27.547	43.382	29.163	9.953	−14.092	1.376	−0.103
800	28.970	47.153	31.179	12.779	−13.899	3.575	−0.233
900	30.393	50.647	33.151	15.747	−13.563	5.740	−0.333
1000	31.815	53.923	35.066	18.857	−13.085	7.861	−0.411

PREVIOUS: CURRENT: June 1969

$S°(298.15\ K) = 23.197 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = [-10.71]\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = [-12.44]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Stevenson *et al.*[1] have referenced the fluorine bomb calorimetry study of O'Hare and Hubbard[2] which yielded $\Delta_f H° = -1.2 \pm 1.0$ kcal·mol^{-1} for P(red, IV) → P(red, V).

Heat Capacity and Entropy

The thermal functions are derived from the heat capacity measurments of Stephenson *et al.*[1] who reported measured values from 16.15 to 304.93 K.

Reference

[1]C. C. Stephenson, R. L. Potter, T. G. Maple and J. C. Morrow, J. Chem. Thermodynamics **1**, 59 (1969).
[2]P. A. G. O'Hare and W. N. Hubbard, Trans. Faraday Soc. **62**, 2709 (1966).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−3.635	−10.714	−10.714	INFINITE
100	8.807	6.537	39.017	−3.248	−11.214	−10.099	5.275
200	17.175	15.494	25.028	−1.907	−12.136	−8.810	2.301
250	19.581	19.599	23.538	−0.985	−12.306	−7.958	1.663
298.15	21.263	23.197	23.197	0.	−12.439	−7.108	1.245
300	21.313	23.329	23.197	0.039	−12.444	−7.075	1.232
350	22.356	26.694	23.461	1.132	−13.287	−6.099	0.910
400	23.242	29.739	24.058	2.272	−13.463	−5.060	0.661
450	23.894	32.514	24.846	3.451	−13.601	−4.001	0.464
500	24.548	35.066	25.742	4.662	−13.706	−2.928	0.306
600	25.857	39.655	27.687	7.181	−13.819	−0.760	0.066
700	27.259	43.746	29.694	9.837	−13.796	1.417	−0.106
800	28.681	47.479	31.687	12.634	−13.632	3.581	−0.234
900	30.104	50.939	33.636	15.573	−13.325	5.715	−0.332
1000	31.526	54.185	35.530	18.655	−12.876	7.808	−0.408

PREVIOUS: CURRENT: June 1969

$S°(298.15\ K) = 22.85 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 870\ K$

$\Delta_f H°(0\ K) = -15.707\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -17.460\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 18.8 \pm 0.8\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is obtained from the enthalpies of sublimation represented by reaction I and II at 298.15 K.

(I) 4P(cr, white) → P_4(g) 14.08 kcal·mol^{-1}
(II) 4P(cr, red V) → P_4(g) 30.771 kcal·mol^{-1}

Of the calorimetric determinations only those of Giran[12] result in a reliable value for the enthalpy of formation, 4.4 ± 0.4 kcal·mol^{-1}. A comprehensive review is given by Rodewald.[13]

Heat Capacity and Entropy

The only reliable low temperature measurements, 15 to 305 K, are reported by Potter.[1] A value at 10 K was obtained by graphical extrapolation and a T^3 function was assumed from 0 to 10 K. High temperature heat capacities were obtained from a smooth curve joining the measurements of Kubashewski and Schrag[2] in the range 573 to 773 K and that of Regnault[3] at 331 K with those of Potter.[1] Measurements of Wigand[4] are too high. The uncertainty in the high temperature heat capacity is about 2%.

Fusion Data

The values of $\Delta_{fus}H$ and T_{fus} were calculated from the functions of the red (V) crystal and liquid. This may be compared with a reported triple point of 862.7 K by Smits and Bokhorst.[5]

Sublimation Data

Vapor pressure measurements on the triclinic allotrope, T. V. A. designation V, are reported by Farr.[6] These data lead to a sublimation point of 704 K and $\Delta_{sub}H$(298.15 K) of 30.77 ± 0.4 kcal·mol^{-1} of P_4. Smits and Bokhorst[7] measured the vapor pressure of a sample whose preparation indicates that is was probably P(cr, red, V). These results lead to $\Delta_{sub}H$(298.15 K) = 30.6 ± 1 kcal·mol^{-1} of P_4(g). An unpublished value of 30.84 kcal·mol^{-1} of P_4 by Stephenson[8] is quoted by Kane.

Stevenson and Yost[9] show that the vapor density measurements of Stock *et al.*[10] are best explained by a vapor essentially composed of only P_4(g) below 800 K. This conclusion is supported by recent mass spectrometer measurements of Kane and Reynolds.[11]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−3.607	−15.707	−15.707	INFINITE
100	8.724	6.303	38.578	−3.227	−16.215	−15.076	7.875
200	17.046	15.193	24.675	−1.896	−17.147	−13.760	3.594
250	19.464	19.270	23.192	−0.980	−17.323	−12.892	2.694
298.15	21.187	22.853	22.853	0.	−17.460	−12.026	2.107
300	21.251	22.984	22.853	0.039	−17.465	−11.992	2.088
350	22.293	26.340	23.116	1.128	−18.311	−10.999	1.642
400	23.179	29.376	23.711	2.266	−18.490	−9.942	1.298
450	23.832	32.144	24.497	3.441	−18.631	−8.864	1.029
500	24.485	34.689	25.390	4.649	−18.739	−7.773	0.812
600	25.794	39.267	27.330	7.162	−18.859	−5.566	0.485
700	27.196	43.241	29.324	9.742	−18.912	−3.345	0.250
800	36.987	47.698	31.335	13.091	−18.196	−1.158	0.076
900	30.041	51.571	33.380	16.372	−17.547	0.925	−0.054
1000	31.464	54.736	35.359	19.378	−17.174	2.959	−0.155

PREVIOUS: CURRENT: June 1961

$S°(298.15\ K) = 41.077 \pm 0.08\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 195.4 \pm 0.1$ K (white β → white α)
$T_{fus} = 317.30 \pm 0.05$ K

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.521 \pm 0.001\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 0.659 \pm 0.002\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition. The enthalpies of white and red V phosphorus are tied together by the enthalpies of sublimation as determined by Giran.[1] A comprehensive review is given by Rodewald.[2]

Heat Capacity and Entropy

Low temperature measurements, 15–315 K, were made by Maples.[3] A Debye temperature, θ_D 124 K, was used to extrapolate to $T/K = 0$. Young and Hildenbrand[4] obtained heat capacities from enthalpy measurements that are 4% higher than those from the low Maples[3] temperature calorimeter which are preferred because of the proximity to the melting point.

Transition Data

Observed by Maples.[3]

Fusion Data

The selected enthalpy of fusion is that observed by Maples.[3] Young and Hildenbrand[4] obtain 125 $cal \cdot mol^{-1}$ for the same quantity. Maples'[3] value is consistent with vapor pressures and other thermochemical data; see the liquid and P_4(g) tables for details.

Sublimation Data

The vapor pressure measurements of Dainton and Kimberly[5] are the most precise and lead to $\Delta_{sub} H°(298.15\ K) = 14.08 \pm 0.2\ kcal \cdot mol^{-1}$ of P_4(g). Measurements of Jolibois,[6] Smits and Bokhorst,[7] and Centzwer[8] lead to values that agree within the assigned uncertainty.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S° - [G° - H°(T_r)]/T$		$H° - H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.360	0.	0.	0.
100	13.728	17.688	62.415	−4.473	0.	0.	0.
195.400	21.117	28.969	43.439	−2.827	ALPHA <--> BETA		
195.400	20.941	31.637	43.439	−2.306	TRANSITION		
200	21.092	32.126	43.173	−2.209	0.	0.	0.
250	22.564	36.992	41.463	−1.118	0.	0.	0.
298.15	23.825	41.077	41.077	0.	0.	0.	0.
300	23.870	41.225	41.078	0.044	0.	0.	0.
317.300	24.351	42.574	41.123	0.460	---- BETA <--> LIQUID		
350	24.731	44.981	41.372	1.263	−0.717	0.071	−0.011
400	25.313	48.321	42.036	2.514	−0.782	0.188	−0.025
450	25.997	51.344	42.905	3.798	−0.815	0.312	−0.036
500	26.485	54.110	43.889	5.110	−0.818	0.437	−0.046
600	26.485	58.939	46.007	7.759	−0.802	0.687	−0.060
700	26.485	63.021	48.154	10.407	−0.786	0.934	−0.070
800	26.485	66.558	50.238	13.056	−0.771	1.179	−0.077
900	26.485	69.677	52.228	15.704	−0.755	1.422	−0.083
1000	26.485	72.468	54.115	18.353	−0.739	1.662	−0.087

PREVIOUS: CURRENT: June 1961

$S°(298.15\ K) = [43.011]\ J·K^{-1}·mol^{-1}$
$T_{fus}(white \rightarrow l) = 317.30 \pm 0.05\ K$
$T_{fus}(red, V \rightarrow l) = 870\ K$

$\Delta_f H°(298.15\ K) = [0.615]\ kJ·mol^{-1}$
$\Delta_{fus}H(white \rightarrow l) = 0.659\ kJ·mol^{-1}$
$\Delta_{fus}H(red, V \rightarrow l) = 18.8 \pm 0.002\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation for P(l) is calculated from that of P(white) by adding the enthalpy of fusion (white to liquid) and the difference in enthalpy, $H°(317.30\ K)–H°(298.15\ K)$, between the white crystal and liquid.

Heat Capacity and Entropy

Young and Hildenbrand[1] obtained an equation from enthalpy measurements which decreased with temperature. However, a better fit to the thermochemical data results if a constant heat capacity is assumed.

The entropy is derived from low temperature measurements on white phosphorus. See the white phosphorus table for details.

Vaporization Data

MacRae and Van Voorhis,[2] determinations of the vapor pressure, 44 to 150°C, are the most precise and lead to a $\Delta_{vap}H(298.15\ K)$ of $13.504 \pm 0.1\ kcal·mol^{-1}$ of P_4. A vapor pressure equation derived by Farr,[3] to fit the measurements reported in the literature leads to a value of $13.6 \pm 0.1\ kcal·mol^{-1}$ of P_4. The boiling point is calculated from the functions of P(l) and P_4(g), and may be compared with the values of 552.7 and 553.7 resulting from Farr's[3] equation and observations of Smits and Bokhorst,[4] respectively.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	26.326	43.011	43.011	0.	0.615	0.038	−0.007
300	26.326	43.173	43.011	0.049	0.619	0.035	−0.006
317.300	26.326	44.649	43.061	0.504	---- BETA <--> LIQUID ----		
350	26.326	47.232	43.332	1.365	0.	0.	0.
400	26.326	50.747	44.044	2.681	0.	0.	0.
450	26.326	53.848	44.964	3.998	0.	0.	0.
500	26.326	56.621	45.994	5.314	0.	0.	0.
600	26.326	61.421	48.177	7.946	0.	0.	0.
700	26.326	65.479	50.366	10.579	0.	0.	0.
800	26.326	68.995	52.480	13.212	0.	0.	0.
900	26.326	72.095	54.491	15.844	0.	0.	0.
1000	26.326	74.869	56.392	18.477	0.	0.	0.
1100	26.326	77.378	58.188	21.109	0.	0.	0.
1180.008	26.326	79.226	59.552	23.216	----- FUGACITY = 1 bar -----		
1200	26.326	79.669	59.884	23.742	−63.572	1.078	−0.047
1300	26.326	81.776	61.488	26.374	−62.797	6.434	−0.259
1400	26.326	83.727	63.008	29.007	−62.027	11.731	−0.438
1500	26.326	85.543	64.450	31.640	−61.262	16.973	−0.591
1600	26.326	87.242	65.822	34.272	−60.499	22.164	−0.724
1700	26.326	88.838	67.129	36.905	−59.740	27.307	−0.839
1800	26.326	90.343	68.378	39.537	−58.984	32.405	−0.940
1900	26.326	91.766	69.572	42.170	−58.230	37.462	−1.030
2000	26.326	93.117	70.715	44.802	−57.479	42.479	−1.109

PREVIOUS: CURRENT: June 1961

0	to 195.4K	crystal, white, beta
195.4	to 317.3K	crystal, white, alpha
above	317.3K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−5.360	0.	0.	0.
100	13.728	17.688	62.415	−4.473	0.	0.	0.
195.400	21.117	28.969	43.439	−2.827	ALPHA <--> BETA		
195.400	20.941	31.637	43.439	−2.306	TRANSITION		
200	21.092	32.126	43.173	−2.209	0.	0.	0.
250	22.564	36.992	41.463	−1.118	0.	0.	0.
298.15	23.825	41.077	41.077	0.	0.	0.	0.
300	23.870	41.225	41.078	0.044	0.	0.	0.
317.300	24.351	42.574	41.123	0.460	BETA <--> LIQUID		
317.300	26.326	44.649	41.123	1.119	TRANSITION		
350	26.326	47.232	41.575	1.980	0.	0.	0.
400	26.326	50.747	42.507	3.296	0.	0.	0.
450	26.326	53.848	43.598	4.612	0.	0.	0.
500	26.326	56.621	44.764	5.929	0.	0.	0.
600	26.326	61.421	47.152	8.561	0.	0.	0.
700	26.326	65.479	49.488	11.194	0.	0.	0.
800	26.326	68.995	51.711	13.826	0.	0.	0.
900	26.326	72.095	53.807	16.459	0.	0.	0.
1000	26.326	74.869	55.777	19.092	0.	0.	0.
1100	26.326	77.378	57.629	21.724	0.	0.	0.
1180.008	26.326	79.226	59.031	23.830	FUGACITY = 1 bar		
1200	26.326	79.669	59.371	24.357	−63.572	1.078	−0.047
1300	26.326	81.776	61.015	26.989	−62.797	6.434	−0.259
1400	26.326	83.727	62.568	29.622	−62.027	11.731	−0.438
1500	26.326	85.543	64.040	32.254	−61.262	16.973	−0.591
1600	26.326	87.242	65.438	34.887	−60.499	22.164	−0.724
1700	26.326	88.838	66.768	37.520	−59.740	27.307	−0.839
1800	26.326	90.343	68.036	40.152	−58.984	32.405	−0.940
1900	26.326	91.766	69.248	42.785	−58.230	37.462	−1.030
2000	26.326	93.117	70.408	45.417	−57.479	42.479	−1.109

PREVIOUS: CURRENT: June 1961

IP(P, g) = 84580 ± 10 cm^{-1}
$S°$(298.15 K) = 163.198 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 315.55 ± 1.0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 316.39 ± 1.0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4S_{3/2}$	0.0	4
$^2D_{3/2}$	11360.80	4
$^2D_{5/2}$	11376.40	6
$^2P_{1/2}$	18722.65	2
$^2P_{3/2}$	18747.95	4

Enthalpy of Formation

The value adopted for the enthalpy of formation, $\Delta_f H°$(298.15 K) = 316.39 ± 1.0 $kJ·mol^{-1}$, of the monatomic gas is that recommended by CODATA.[1] It is derived from $\Delta_f H°(P_2, g, 298.15\ K)$,[1,2] and the dissociation energy $D_0°(P_2)$ = 40596 ± 20 cm^{-1} obtained by Herzberg.[3]

Heat Capacity and Entropy

The electronic energy levels are given in the compilations by Moore.[4,5] There are 2.45 levels observed below the ionization potential. Only the ground state and the four lowest lying levels are used in the calculation. These are the contributions of the levels arising from three terms $^4S°$, $^2D°$, and $^2P°$– of the $3s^23\ p^3$ configuration. The remaining levels lie above 55000 cm^{-1} and do not contribute significantly even at 6000 K. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations beyond 6000 K may require consideration of higher excited states, estimation of missing levels, and utilization of proper cut off procedures.[6]

CODATA[1] used a slightly different values for the relative atomic mass and the fundamental constants. This causes a difference in the $S°$(298.15 K) value of 0.004 $J·K^{-1}·mol^{-1}$.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	315.553	315.553	INFINITE
100	20.786	140.490	181.678	−4.119	316.744	304.464	−159.036
200	20.786	154.898	165.099	−2.040	316.559	292.005	−76.264
250	20.786	159.536	163.540	−1.001	316.507	285.871	−59.729
298.15	20.786	163.198	163.198	0.	316.390	279.980	−49.051
300	20.786	163.326	163.198	0.038	316.384	279.754	−48.709
350	20.786	166.530	163.451	1.078	315.488	273.733	−40.852
400	20.786	169.306	164.013	2.117	315.211	267.787	−34.969
450	20.786	171.754	164.740	3.156	314.934	261.876	−30.398
500	20.786	173.944	165.553	4.196	314.657	255.996	−26.744
600	20.786	177.734	167.277	6.274	314.103	244.315	−21.270
700	20.786	180.938	169.005	8.353	313.549	232.728	−17.366
800	20.786	183.714	170.674	10.431	312.995	221.220	−14.444
900	20.786	186.162	172.262	12.510	312.441	209.781	−12.175
1000	20.786	188.352	173.763	14.589	311.887	198.404	−10.364
1100	20.788	190.333	175.181	16.667	311.333	187.083	−8.884
1200	20.791	192.142	176.520	18.746	247.207	176.890	−7.700
1300	20.797	193.806	177.787	20.826	247.429	171.021	−6.872
1400	20.810	195.348	178.987	22.906	247.647	165.135	−6.161
1500	20.831	196.785	180.126	24.988	247.862	159.234	−5.545
1600	20.865	198.130	181.210	27.073	248.076	153.319	−5.005
1700	20.914	199.396	182.242	29.161	248.291	147.390	−4.529
1800	20.981	200.593	183.229	31.256	248.510	141.448	−4.105
1900	21.068	201.730	184.173	33.358	248.733	135.494	−3.725
2000	21.178	202.813	185.078	35.470	248.964	129.528	−3.383
2100	21.312	203.850	185.948	37.595	249.205	123.551	−3.073
2200	21.471	204.845	186.784	39.734	249.458	117.561	−2.791
2300	21.653	205.803	187.590	41.890	249.727	111.560	−2.534
2400	21.859	206.729	188.369	44.065	250.013	105.547	−2.297
2500	22.088	207.626	189.121	46.262	250.320	99.521	−2.079
2600	22.337	208.497	189.850	48.483	250.648	93.483	−1.878
2700	22.605	209.345	190.556	50.730	251.001	87.431	−1.691
2800	22.890	210.172	191.242	53.005	251.380	81.366	−1.518
2900	23.189	210.981	191.909	55.309	251.786	75.287	−1.356
3000	23.500	211.772	192.558	57.643	252.222	69.194	−1.205
3100	23.821	212.548	193.190	60.009	252.688	63.085	−1.063
3200	24.148	213.309	193.807	62.407	253.185	56.961	−0.930
3300	24.480	214.057	194.409	64.839	253.713	50.821	−0.804
3400	24.814	214.793	194.998	67.303	254.273	44.664	−0.686
3500	25.148	215.517	195.574	69.802	254.866	38.491	−0.574
3600	25.480	216.230	196.138	72.333	255.490	32.300	−0.469
3700	25.808	216.933	196.690	74.897	256.146	26.091	−0.368
3800	26.129	217.625	197.232	77.494	256.834	19.864	−0.273
3900	26.444	218.308	197.764	80.123	257.552	13.619	−0.182
4000	26.749	218.982	198.286	82.783	258.299	7.355	−0.096
4100	27.045	219.646	198.799	85.473	259.076	1.072	−0.014
4200	27.329	220.301	199.303	88.191	259.880	−5.231	0.065
4300	27.601	220.947	199.799	90.938	260.711	−11.553	0.140
4400	27.860	221.585	200.287	93.711	261.567	−17.894	0.212
4500	28.106	222.214	200.767	96.510	262.447	−24.255	0.282
4600	28.338	222.834	201.240	99.332	263.350	−30.637	0.348
4700	28.555	223.446	201.706	102.177	264.274	−37.037	0.412
4800	28.758	224.049	202.165	105.042	265.218	−43.458	0.473
4900	28.947	224.644	202.618	107.928	266.180	−49.899	0.532
5000	29.121	225.231	203.064	110.831	267.160	−56.360	0.589
5100	29.281	225.809	203.505	113.752	268.154	−62.840	0.644
5200	29.426	226.379	203.939	116.687	269.163	−69.340	0.697
5300	29.557	226.941	204.368	119.636	270.185	−75.859	0.748
5400	29.675	227.494	204.791	122.598	271.218	−82.398	0.797
5500	29.779	228.040	205.209	125.571	272.260	−88.956	0.845
5600	29.871	228.577	205.621	128.553	273.311	−95.533	0.891
5700	29.950	229.107	206.029	131.545	274.370	−102.129	0.936
5800	30.016	229.628	206.431	134.543	275.435	−108.743	0.979
5900	30.072	230.142	206.828	137.547	276.505	−115.376	1.021
6000	30.116	230.647	207.221	140.557	277.578	−122.027	1.062

PREVIOUS: June 1961 (1 atm) CURRENT: December 1982 (1 bar)

$IP(P^+, g) = 159100 \pm 100\ cm^{-1}$
$S°(298.15\ K) = 166.970 \pm 0.02\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1327.35 \pm 0.42\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [1336.333]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0.0	1
$^3P_1$	164.8	3
$^3P_2$	469.0	5
$^1D_2$	8882.6	5
$^1S_0$	21576.2	1

Enthalpy of Formation

$\Delta_f H°(P^+, g, 0\ K)$ is calculated from $\Delta_f H°(P, g, 0\ K)$[1] using the spectroscopic value of IP(P) = 84580 ± 10 cm^{-1} (1011.80 ± 1 0.12 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants,[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(P^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(P, g, 0\ K)$ by using IP(P) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for P(g), $P^+(g)$, and e^-(ref). $\Delta_f H°(P \rightarrow P^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is approximately 52000 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.141	1327.354		
100	30.205	135.606	191.683	−5.608			
200	28.395	156.122	169.413	−2.658			
250	27.038	162.312	167.402	−1.273			
298.15	25.856	166.970	166.970	0.	1336.333	1292.543	−226.448
300	25.815	167.130	166.971	0.048	1336.375	1292.272	−225.004
350	24.826	171.032	167.281	1.313	1336.744	1284.905	−191.762
400	24.058	174.295	167.959	2.534	1337.688	1277.434	−166.816
450	23.466	177.093	168.822	3.722	1338.599	1269.848	−147.400
500	23.010	179.540	169.774	4.883	1339.483	1262.161	−131.857
600	22.372	183.675	171.759	7.150	1341.196	1246.535	−108.520
700	21.966	187.091	173.712	9.365	1342.857	1230.626	−91.830
800	21.694	190.005	175.571	11.547	1344.485	1214.481	−79.297
900	21.505	192.548	177.319	13.707	1346.091	1198.134	−69.538
1000	21.371	194.807	178.957	15.850	1347.680	1181.609	−61.721
1100	21.274	196.839	180.492	17.982	1349.258	1164.926	−55.318
1200	21.206	198.687	181.932	20.106	1287.256	1149.177	−50.022
1300	21.160	200.382	183.287	22.224	1289.595	1137.576	−45.708
1400	21.134	201.949	184.565	24.338	1291.925	1125.795	−42.004
1500	21.126	203.407	185.773	26.451	1294.250	1113.847	−38.788
1600	21.134	204.771	186.918	28.564	1296.571	1101.744	−35.968
1700	21.156	206.053	188.006	30.679	1298.891	1089.497	−33.476
1800	21.192	207.263	189.043	32.796	1301.210	1077.112	−31.257
1900	21.239	208.410	190.032	34.917	1303.531	1064.599	−29.268
2000	21.296	209.501	190.979	37.044	1305.855	1051.964	−27.474
2100	21.362	210.541	191.886	39.177	1308.183	1039.212	−25.849
2200	21.435	211.537	192.756	41.317	1310.516	1026.349	−24.369
2300	21.514	212.491	193.594	43.464	1312.855	1013.380	−23.015
2400	21.596	213.409	194.400	45.619	1315.200	1000.309	−21.771
2500	21.681	214.292	195.179	47.783	1317.551	987.140	−20.625
2600	21.768	215.144	195.930	49.956	1319.910	973.877	−19.565
2700	21.855	215.967	196.657	52.137	1322.275	960.524	−18.582
2800	21.941	216.763	197.361	54.327	1324.648	947.082	−17.668
2900	22.026	217.535	198.043	56.525	1327.028	933.556	−16.815
3000	22.110	218.283	198.706	58.732	1329.414	919.947	−16.018
3100	22.190	219.009	199.349	60.947	1331.808	906.259	−15.270
3200	22.268	219.715	199.974	63.170	1334.208	892.493	−14.568
3300	22.343	220.401	200.583	65.400	1336.614	878.652	−13.908
3400	22.414	221.069	201.176	67.638	1339.026	864.738	−13.285
3500	22.481	221.720	201.754	69.883	1341.444	850.753	−12.697
3600	22.545	222.354	202.317	72.134	1343.867	836.699	−12.140
3700	22.605	222.973	202.867	74.392	1346.295	822.578	−11.613
3800	22.660	223.576	203.404	76.655	1348.727	808.391	−11.112
3900	22.712	224.166	203.929	78.924	1351.164	794.140	−10.636
4000	22.760	224.741	204.442	81.197	1353.604	779.826	−10.183
4100	22.804	225.304	204.944	83.476	1356.048	765.451	−9.752
4200	22.845	225.854	205.435	85.758	1358.494	751.017	−9.340
4300	22.882	226.392	205.916	88.045	1360.943	736.524	−8.947
4400	22.916	226.918	206.388	90.334	1363.395	721.975	−8.571
4500	22.946	227.434	206.850	92.628	1365.848	707.369	−8.211
4600	22.973	227.938	207.303	94.924	1368.303	692.709	−7.866
4700	22.998	228.433	207.747	97.222	1370.760	677.996	−7.535
4800	23.019	228.917	208.183	99.523	1373.217	663.230	−7.217
4900	23.038	229.392	208.611	101.826	1375.676	648.414	−6.912
5000	23.054	229.858	209.031	104.131	1378.135	633.546	−6.619
5100	23.068	230.314	209.444	106.437	1380.594	618.630	−6.336
5200	23.080	230.762	209.850	108.744	1383.054	603.666	−6.064
5300	23.090	231.202	210.249	111.053	1385.513	588.654	−5.802
5400	23.097	231.634	210.641	113.362	1387.972	573.596	−5.548
5500	23.103	232.058	211.026	115.672	1390.430	558.492	−5.304
5600	23.107	232.474	211.406	117.983	1392.888	543.344	−5.068
5700	23.110	232.883	211.779	120.294	1395.345	528.152	−4.840
5800	23.111	233.285	212.146	122.605	1397.801	512.916	−4.619
5900	23.110	233.680	212.508	124.916	1400.256	497.639	−4.406
6000	23.108	234.068	212.864	127.227	1402.710	482.319	−4.199

PREVIOUS: CURRENT: December 1982 (1 bar)

Phosphorus, Ion (P^-) IDEAL GAS $M_r = 30.97431$ Phosphorus, Ion (P^-) $P^-(g)$

EA(P, g) = 0.7465 ± 0.0003 eV
$S°(298.15\ K) = 169.124 \pm 0.001\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 243.527 \pm 1.0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [238.717]\ kJ \cdot mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0	5
$^3P_1$	181	3
$^3P_0$	263	1
$^1D_2$	6675	5
$^1S_0$	16131	1

Enthalpy of Formation

$\Delta_f H°(P^-, g, 0\ K)$ is calculated from $\Delta_f H°(P, g, 0\ K)$[1] using the adopted electron affinity of EA(P) = 0.7465 ± 0.0003 eV (72.026 ± 0.029 $kJ \cdot mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on tunable laser photodetachment threshold studies.[3,4] Additional information on $P^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,5] Rosenstock *et al.*[6] and Massey.[7]

$\Delta_f H°(P^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(P, g, 0\ K)$ by using EA(P) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for $P^-(g)$, P(g), and e^-(ref). $\Delta_r H°(P^- \rightarrow P + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[6] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $P^-(g)$ is given by Hotop and Lineberger,[2,5] Rosenstock,[6] and Massey.[7] The fine sturcture seperation has been measured experimentally via a tunetable laser photodetachment threshold technique[3,4] and is that recommended by Hotop and Lineberger.[2]

References

[1]JANAF Thermochemical Tables: P(g), 12–31–82; e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
[3]D. Feldmann, Z. Physik A **277**, 19 (1976).
[4]J. Slater and W. C. Lineberger, Phys. Rev. A **15**, 2277 (1977).
[5]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[6]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[7]H. S. W. Massey, "Negative Ions", 3rd ed., Cambridge University Press, Cambridge, 741 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.748	243.527		
100	23.554	143.795	189.435	−4.564			
200	23.042	160.101	171.176	−2.215			
250	22.540	165.187	169.490	−1.076			
298.15	22.168	169.124	169.124	0.	238.717	206.795	−36.230
300	22.156	169.261	169.124	0.041	238.676	206.597	−35.972
350	21.873	172.654	169.393	1.141	236.801	201.412	−30.059
400	21.664	175.560	169.986	2.230	235.534	196.443	−25.653
450	21.508	178.102	170.750	3.309	234.257	191.634	−22.244
500	21.388	180.362	171.600	4.381	232.974	186.966	−19.532
600	21.222	184.245	173.394	6.511	230.393	178.007	−15.497
700	21.116	187.508	175.184	8.627	227.798	169.481	−12.647
800	21.047	190.323	176.904	10.735	225.195	161.328	−10.534
900	21.004	192.799	178.535	12.838	222.586	153.501	−8.909
1000	20.983	195.011	180.074	14.937	219.974	145.965	−7.624
1100	20.982	197.011	181.525	17.035	217.361	138.690	−6.586
1200	21.002	198.837	182.892	19.134	151.176	132.732	−5.778
1300	21.042	200.520	184.184	21.236	149.342	131.269	−5.274
1400	21.100	202.081	185.408	23.343	147.508	129.948	−4.848
1500	21.174	203.539	186.568	25.456	145.676	128.758	−4.484
1600	21.261	204.909	187.672	27.578	143.849	127.689	−4.169
1700	21.360	206.200	188.725	29.709	142.028	126.735	−3.894
1800	21.467	207.424	189.730	31.850	140.214	125.888	−3.653
1900	21.579	208.588	190.692	34.003	138.409	125.142	−3.440
2000	21.694	209.698	191.615	36.166	136.612	124.490	−3.251
2100	21.810	210.759	192.501	38.341	134.826	123.928	−3.083
2200	21.924	211.776	193.354	40.528	133.048	123.450	−2.931
2300	22.036	212.753	194.177	42.726	131.280	123.054	−2.795
2400	22.144	213.693	194.970	44.935	129.522	122.734	−2.671
2500	22.246	214.599	195.738	47.155	127.772	122.487	−2.559
2600	22.344	215.474	196.480	49.384	126.030	122.310	−2.457
2700	22.435	216.319	197.199	51.623	124.296	122.200	−2.364
2800	22.520	217.136	197.897	53.871	122.570	122.154	−2.279
2900	22.598	217.928	198.574	56.127	120.850	122.169	−2.201
3000	22.670	218.695	199.232	58.390	119.136	122.244	−2.128
3100	22.735	219.440	199.872	60.661	117.427	122.376	−2.062
3200	22.794	220.162	200.495	62.937	115.724	122.563	−2.001
3300	22.847	220.865	201.101	65.219	114.024	122.803	−1.944
3400	22.894	221.547	201.693	67.506	112.328	123.094	−1.891
3500	22.936	222.212	202.269	69.798	110.636	123.435	−1.842
3600	22.972	222.858	202.832	72.093	108.946	123.825	−1.797
3700	23.004	223.488	203.382	74.392	107.258	124.262	−1.754
3800	23.030	224.102	203.919	76.694	105.571	124.744	−1.715
3900	23.053	224.700	204.445	78.998	103.886	125.270	−1.678
4000	23.072	225.284	204.958	81.304	102.201	125.840	−1.643
4100	23.087	225.854	205.461	83.612	100.517	126.452	−1.611
4200	23.098	226.411	205.953	85.921	98.834	127.105	−1.581
4300	23.106	226.954	206.435	88.232	97.149	127.798	−1.552
4400	23.112	227.486	206.908	90.543	95.465	128.530	−1.526
4500	23.115	228.005	207.371	92.854	93.779	129.301	−1.501
4600	23.115	228.513	207.825	95.165	92.093	130.108	−1.477
4700	23.113	229.010	208.270	97.477	90.405	130.953	−1.455
4800	23.109	229.497	208.708	99.788	88.716	131.834	−1.435
4900	23.104	229.973	209.137	102.099	87.025	132.749	−1.415
5000	23.096	230.440	209.558	104.409	85.332	133.700	−1.397
5100	23.088	230.897	209.972	106.718	83.637	134.684	−1.379
5200	23.077	231.345	210.379	109.026	81.940	135.701	−1.363
5300	23.066	231.785	210.779	111.333	80.241	136.752	−1.348
5400	23.053	232.216	211.172	113.639	78.539	137.834	−1.333
5500	23.040	232.639	211.558	115.944	76.835	138.947	−1.320
5600	23.025	233.054	211.938	118.247	75.128	140.092	−1.307
5700	23.010	233.461	212.312	120.549	73.419	141.267	−1.295
5800	22.994	233.861	212.680	122.849	71.707	142.473	−1.283
5900	22.977	234.254	213.043	125.148	69.992	143.707	−1.272
6000	22.960	234.640	213.399	127.445	68.274	144.971	−1.262

PREVIOUS: CURRENT: December 1982 (1 bar)

$S°(298.15\ K) = 234.241\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 138.8 \pm 41.8\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 138.6 \pm 41.8\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2\Pi$	0	2
$A^2\Sigma$	324	2
$B^2\Pi$	[20000]	2
$C^2\Sigma$	22000	4
	34594	2

$\omega_e = 743.5 \pm 3.8\ cm^{-1}$ $\omega_e x_e = 3.8 \pm 0.9\ cm^{-1}$ $\sigma = 1$
$B_e = [0.29]\ cm^{-1}$ $\alpha_e = [0.0016]\ cm^{-1}$ $r_e = [1.92]$ Å

Enthalpy of Formation

The dissociation energy, $D_0°$, of PS(g) is estimated to be 140 ± 25 kcal·mol^{-1} by comparison with the corresponding quantity for PO(g) and from a linear Birge-Sponer extrapolation of the third excited ($C^2\Sigma$) electronic state potential function. It is assumed that the ($C^2\Sigma$) state dissociates to S(g) in its ground (^{3}P) state and P(g) in its first excited (^{2}D) state. The fundamental vibrational frequency in the $C^2\Sigma$ state (ω_e') is 531.8 ± 2.5 cm^{-1} and the corresponding anharmonic term ($\omega_e x_e$) is 2.6 ± 0.5 cm^{-1}. These constants are calculated from a reanalysis of the spectral data of Dressler.[1] The corresponding enthalpy of formation of PS(g) is 37.3 ± 25 kcal·mol^{-1}. The excited state ($C^2\Sigma$) data are used to calculate $D_0°$ instead of the ground state ($X^2\Pi$) data because the vibrational constants of the upper level are known more accurately and because the extrapolation is 50 kcal·mol^{-1} smaller for this level.

Heat Capacity and Entropy

The spectra of PS(g) have been studied by Dressler[1] in the near UV and visible regions. He reported the above electronic levels which correspond to the doublet pi ground state and two of the excited levels ($B^2\Pi$, $C^2\Sigma$). The level of the first excited electronic state ($A^2\Sigma$) is estimated by analogy with NO(g).

Dressler[1] estimated the value of the rotational constant B_e. The value of α_e is calculated from the Morse potential function. The bond distance is calculated from B_e. The fundamental vibrational frequency ω_e and the anharmonic vibrational term $\omega_e x_e$ are calculated from a reanalysis of the spectral data reported by Dressler.[1]

References

[1]K. Dressler, Helv. Phys. Scta. **28**, 563 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.610	138.765	138.765	INFINITE
100	30.805	197.931	264.579	−6.665	140.134	123.361	−64.437
200	33.947	220.417	237.429	−3.402	139.491	106.560	−27.831
250	34.711	228.080	234.819	−1.685	139.097	98.370	−20.553
298.15	35.243	234.241	234.241	0.	138.603	90.569	−15.867
300	35.260	234.459	234.242	0.065	138.582	90.271	−15.718
350	35.679	239.928	234.673	1.839	137.254	82.337	−12.288
400	36.008	244.714	235.635	3.632	134.300	74.630	−9.746
450	36.268	248.971	236.885	5.439	132.865	67.248	−7.806
500	36.478	252.803	238.288	7.258	131.365	60.040	−6.272
600	36.790	259.484	241.280	10.922	128.812	46.022	−4.007
700	37.008	265.172	244.297	14.613	126.523	32.407	−2.418
800	37.169	270.125	247.223	18.322	124.389	19.108	−1.248
900	37.292	274.510	250.016	22.045	69.223	7.153	−0.415
1000	37.392	278.445	252.665	25.779	68.468	0.296	−0.015
1100	37.474	282.012	255.173	29.523	67.708	−6.484	0.308
1200	37.544	285.276	257.548	33.274	3.367	−12.117	0.527
1300	37.606	288.284	259.798	37.031	3.364	−13.407	0.539
1400	37.662	291.073	261.934	40.795	3.347	−14.697	0.548
1500	37.712	293.673	263.964	44.564	3.316	−15.984	0.557
1600	37.759	296.108	265.898	48.337	3.271	−17.270	0.564
1700	37.803	298.399	267.743	52.115	3.213	−18.552	0.570
1800	37.845	300.561	269.506	55.898	3.142	−19.830	0.575
1900	37.885	302.608	271.195	59.684	3.061	−21.104	0.580
2000	37.924	304.552	272.815	63.475	2.968	−22.373	0.584
2100	37.962	306.403	274.371	67.269	2.867	−23.638	0.588
2200	38.000	308.170	275.867	71.067	2.757	−24.898	0.591
2300	38.037	309.860	277.309	74.869	2.639	−26.152	0.594
2400	38.074	311.480	278.699	78.675	2.515	−27.401	0.596
2500	38.112	313.035	280.041	82.484	2.385	−28.645	0.599
2600	38.150	314.530	281.339	86.297	2.250	−29.884	0.600
2700	38.190	315.971	282.595	90.114	2.110	−31.117	0.602
2800	38.231	317.361	283.812	93.935	1.968	−32.345	0.603
2900	38.274	318.703	284.993	97.760	1.822	−33.568	0.605
3000	38.319	320.001	286.138	101.590	1.675	−34.786	0.606
3100	38.367	321.259	287.251	105.424	1.525	−35.999	0.607
3200	38.418	322.477	288.333	109.263	1.375	−37.207	0.607
3300	38.471	323.660	289.385	113.108	1.225	−38.410	0.608
3400	38.528	324.810	290.410	116.958	1.074	−39.609	0.609
3500	38.588	325.927	291.409	120.814	0.924	−40.803	0.609
3600	38.652	327.015	292.383	124.676	0.775	−41.993	0.609
3700	38.720	328.075	293.334	128.544	0.626	−43.179	0.610
3800	38.792	329.109	294.262	132.420	0.480	−44.361	0.610
3900	38.868	330.117	295.168	136.303	0.335	−45.539	0.610
4000	38.948	331.103	296.054	140.193	0.192	−46.714	0.610
4100	39.032	332.065	296.921	144.092	0.051	−47.885	0.610
4200	39.120	333.007	297.769	148.000	−0.087	−49.052	0.610
4300	39.212	333.928	298.599	151.916	−0.223	−50.216	0.610
4400	39.307	334.831	299.412	155.842	−0.356	−51.377	0.610
4500	39.407	335.715	300.209	159.778	−0.485	−52.536	0.610
4600	39.510	336.583	300.991	163.724	−0.612	−53.691	0.610
4700	39.617	337.434	301.757	167.680	−0.735	−54.843	0.610
4800	39.727	338.269	302.509	171.647	−0.854	−55.993	0.609
4900	39.840	339.089	303.247	175.626	−0.970	−57.141	0.609
5000	39.957	339.895	303.972	179.615	−1.082	−58.286	0.609
5100	40.076	340.688	304.684	183.617	−1.191	−59.429	0.609
5200	40.197	341.467	305.384	187.631	−1.295	−60.570	0.608
5300	40.321	342.234	306.072	191.657	−1.395	−61.709	0.608
5400	40.447	342.989	306.749	195.695	−1.491	−62.846	0.608
5500	40.575	343.732	307.414	199.746	−1.583	−63.981	0.608
5600	40.705	344.464	308.070	203.810	−1.670	−65.115	0.607
5700	40.836	345.186	308.714	207.887	−1.753	−66.247	0.607
5800	40.968	345.897	309.349	211.977	−1.831	−67.378	0.607
5900	41.102	346.599	309.975	216.081	−1.905	−68.508	0.607
6000	41.236	347.291	310.591	220.198	−1.974	−69.636	0.606

PREVIOUS: June 1967 (1 atm) CURRENT: June 1967 (1 bar)

$S°(298.15\ K) = 218.13 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 145.47 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 143.65 \pm 2.1\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1\Sigma$	0	1

$\omega_e = 780.43\ cm^{-1}$ $\omega_e x_e = 2.804\ cm^{-1}$ $\sigma = 2$
$B_e = 0.30327\ cm^{-1}$ $\alpha_e = 0.00142\ cm^{-1}$ $r_e = 1.8943$ Å

Enthalpy of Formation

Stevenson and Yost[1] have shown that the vapor density measurements of Stock *et al.*[2] best fit a vapor composed of P_2(g) and P_4(g). From these data, Farr[3] calculated the equilibrium constants which lead to $\Delta_r H°(298.15\ K) = 54.59 \pm 0.01\ kcal \cdot mol^{-1}$ for the process $P_4(g) \rightarrow P_2(g)$; from which the value for $\Delta_f H°(P_2, g, 298.15\ K)$ is calculated using $\Delta_f H°(P_4, g, 298.15\ K) = 30.77\ kcal \cdot mol^{-1}$.

Heat Capacity and Entropy

Molecular and spectroscopic constants are those listed by Herzberg.[4] More recent measurements of Dressler[5] are in agreement with the values selected by Herzberg.[4]

The dissociation energy, $D_0° = 116 \pm 1\ kcal \cdot mol^{-1}$, is given by Gaydon.[6]

References

[1]D. P. Stevenson and D. M. Yost, J. Chem. Phys. **9**, 403 (1941).
[2]A. Stock, G. E. Gibson, and E. Stamm, Ber. **45**, 3527 (1912).
[3]T. D. Farr, Tennessee Valley Authority, Chemical Engineering Report No. 8,
[4]G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, (1945).
[5]K. Dressler, Helv. Phys. Acta **28**, 563 (1955).
[6]A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd ed., Chapman and Hall, Ltd., London, 261 pp. (1953).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.904	145.469	145.469	INFINITE
100	29.120	185.370	245.321	−5.995	146.604	131.604	−68.743
200	30.103	205.754	220.998	−3.049	145.023	116.723	−30.485
250	31.082	212.574	218.653	−1.520	144.369	109.721	−22.925
298.15	32.034	218.131	218.131	0.	143.653	103.112	−18.065
300	32.069	218.329	218.132	0.059	143.625	102.861	−17.910
350	32.945	223.340	218.525	1.685	141.379	96.272	−14.368
400	33.679	227.789	219.410	3.351	140.413	89.894	−11.739
450	34.280	231.792	220.568	5.051	139.479	83.636	−9.708
500	34.770	235.430	221.875	6.778	138.574	77.480	−8.094
600	35.499	241.838	224.682	10.293	136.824	65.427	−5.696
700	36.000	247.350	227.536	13.870	135.136	53.661	−4.004
800	36.356	252.182	230.321	17.489	133.489	42.135	−2.751
900	36.618	256.480	232.993	21.138	131.873	30.813	−1.788
1000	36.819	260.348	235.538	24.810	130.280	19.670	−1.027
1100	36.976	263.865	237.956	28.500	128.705	8.685	−0.412
1180.008	37.079	266.465	239.802	31.463	----- FUGACITY = 1 bar -----		
1200	37.103	267.088	240.251	32.204	0.	0.	0.
1300	37.208	270.062	242.432	35.920	0.	0.	0.
1400	37.296	272.823	244.505	39.645	0.	0.	0.
1500	37.373	275.399	246.480	43.379	0.	0.	0.
1600	37.440	277.813	248.363	47.120	0.	0.	0.
1700	37.499	280.085	250.163	50.867	0.	0.	0.
1800	37.553	282.230	251.886	54.619	0.	0.	0.
1900	37.602	284.261	253.537	58.377	0.	0.	0.
2000	37.647	286.191	255.121	62.139	0.	0.	0.
2100	37.689	288.029	256.645	65.906	0.	0.	0.
2200	37.728	289.783	258.112	69.677	0.	0.	0.
2300	37.766	291.461	259.526	73.452	0.	0.	0.
2400	37.801	293.069	260.890	77.230	0.	0.	0.
2500	37.835	294.613	262.208	81.012	0.	0.	0.
2600	37.868	296.098	263.483	84.797	0.	0.	0.
2700	37.899	297.527	264.718	88.586	0.	0.	0.
2800	37.930	298.906	265.914	92.377	0.	0.	0.
2900	37.960	300.238	267.075	96.171	0.	0.	0.
3000	37.989	301.525	268.202	99.969	0.	0.	0.
3100	38.017	302.771	269.297	103.769	0.	0.	0.
3200	38.045	303.979	270.362	107.572	0.	0.	0.
3300	38.072	305.150	271.399	111.378	0.	0.	0.
3400	38.099	306.287	272.408	115.187	0.	0.	0.
3500	38.126	307.392	273.392	118.998	0.	0.	0.
3600	38.152	308.466	274.351	122.812	0.	0.	0.
3700	38.178	309.512	275.288	126.628	0.	0.	0.
3800	38.204	310.530	276.202	130.448	0.	0.	0.
3900	38.229	311.523	277.095	134.269	0.	0.	0.
4000	38.254	312.491	277.968	138.093	0.	0.	0.
4100	38.279	313.436	278.821	141.920	0.	0.	0.
4200	38.304	314.359	279.656	145.749	0.	0.	0.
4300	38.328	315.260	280.474	149.581	0.	0.	0.
4400	38.353	316.142	281.275	153.415	0.	0.	0.
4500	38.377	317.004	282.059	157.251	0.	0.	0.
4600	38.401	317.848	282.828	161.090	0.	0.	0.
4700	38.425	318.674	283.582	164.932	0.	0.	0.
4800	38.449	319.483	284.321	168.775	0.	0.	0.
4900	38.473	320.276	285.047	172.621	0.	0.	0.
5000	38.497	321.053	285.759	176.470	0.	0.	0.
5100	38.521	321.816	286.459	180.321	0.	0.	0.
5200	38.544	322.564	287.146	184.174	0.	0.	0.
5300	38.568	323.299	287.821	188.030	0.	0.	0.
5400	38.591	324.020	288.485	191.888	0.	0.	0.
5500	38.615	324.728	289.138	195.748	0.	0.	0.
5600	38.638	325.424	289.779	199.611	0.	0.	0.
5700	38.661	326.108	290.411	203.476	0.	0.	0.
5800	38.685	326.781	291.032	207.343	0.	0.	0.
5900	38.708	327.442	291.644	211.212	0.	0.	0.
6000	38.731	328.093	292.246	215.084	0.	0.	0.

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

$S°(298.15\ K) = 280.0 \pm 0.4\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 66.2 \pm 2.1\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 58.9 \pm 2.1\ kJ \cdot mol^{-1}$

Vibrational Levels and Degeneracies ν, cm^{-1}
606 (1)
363 (2)
464.5(3)

Ground State QuantumWeight: 1 $\sigma = 12$
Point Group: T_d
Bond Length: P–P = 2.21 ± 0.2 Å
Bond Angle: P–P–P = 109.4712°
Product of the Principal Moments of Inertia: $I_A I_B I_C = 15.8528 \times 10^{-114}\ g^3 \cdot cm^6$

Enthalpy of Formation

Taken as the enthalpy of formation of white phosphorus.

Heat Capacity and Entropy

The frequencies and degeneracies are those assigned by Gutowsky and Hoffman.[1] Molecular parameters of the gas were determined from electron diffraction measurements by Maxwell *et al.*[2] Thomas and Gingrich[3] obtained a P–P distance of 2.25 Å from X-ray studies on the liquid. On the basis of the selected values for P(white), a 3rd law entropy of 66.89 $cal \cdot K^{-1} \cdot mol^{-1}$ (for p=1 atm) is derived for P_4(g). The principal moments of inertia are: $I_A = I_B = I_C = 25.1209 \times 10^{-39}$ g cm^2.

References

[1]H. S. Gutowsky and G. S. Hoffman, J. Am. Chem. Soc. **72**, 5751(1950).
[2]L. R. Maxwell, S. B. Hendricks, and V. M. Moseley, J. Chem. Phys. **3**, 699(1935).
[3]C. D. Thomas and N. S. Gingrich, J. Chem. Phys. **6**, 659(1938).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−14.133	66.214	66.214	INFINITE
100	37.232	223.901	331.278	−10.738	66.060	50.745	−26.506
200	55.620	255.381	285.819	−6.087	61.657	36.281	−9.476
250	62.447	268.567	281.073	−3.127	60.250	30.101	−6.289
298.15	67.158	279.992	279.992	0.	58.907	24.416	−4.278
300	67.309	280.408	279.993	0.124	58.854	24.202	−4.214
350	70.765	291.058	280.827	3.581	54.568	18.822	−2.809
400	73.260	300.679	282.717	7.185	52.907	13.830	−1.806
450	75.100	309.419	285.206	10.896	51.353	9.040	−1.049
500	76.486	317.407	288.032	14.687	49.879	4.418	−0.462
600	78.386	331.534	294.136	22.439	47.100	−4.410	0.384
700	79.586	343.714	300.369	30.341	44.472	−12.785	0.954
800	80.388	354.397	306.468	38.343	41.943	−20.791	1.358
900	80.949	363.899	312.331	46.411	39.482	−28.485	1.653
1000	81.356	372.450	317.923	54.527	37.068	−35.907	1.876
1100	81.660	380.219	323.238	62.679	34.689	−43.089	2.046
1200	81.893	387.335	328.287	70.857	−221.952	−45.742	1.991
1300	82.075	393.897	333.085	79.056	−221.184	−31.089	1.249
1400	82.221	399.985	337.649	87.271	−220.420	−16.495	0.615
1500	82.338	405.662	341.996	95.499	−219.659	−1.956	0.068
1600	82.435	410.979	346.143	103.738	−218.902	12.533	−0.409
1700	82.515	415.979	350.106	111.985	−218.148	26.975	−0.829
1800	82.583	420.698	353.898	120.240	−217.398	41.372	−1.201
1900	82.640	425.164	357.532	128.502	−216.653	55.728	−1.532
2000	82.689	429.405	361.020	136.768	−215.911	70.045	−1.829
2100	82.731	433.440	364.374	145.039	−215.174	84.324	−2.097
2200	82.767	437.289	367.601	153.314	−214.440	98.569	−2.340
2300	82.799	440.969	370.712	161.592	−213.711	112.780	−2.561
2400	82.827	444.494	373.713	169.874	−212.987	126.960	−2.763
2500	82.852	447.876	376.612	178.158	−212.266	141.110	−2.948
2600	82.874	451.126	379.416	186.444	−211.550	155.230	−3.119
2700	82.893	454.254	382.130	194.733	−210.839	169.324	−3.276
2800	82.911	457.269	384.760	203.023	−210.131	183.391	−3.421
2900	82.927	460.178	387.311	211.315	−209.429	197.433	−3.556
3000	82.941	462.990	389.787	219.608	−208.730	211.451	−3.682
3100	82.954	465.710	392.193	227.903	−208.036	225.445	−3.799
3200	82.966	468.344	394.531	236.199	−207.346	239.418	−3.908
3300	82.976	470.897	396.807	244.496	−206.661	253.368	−4.010
3400	82.986	473.374	399.023	252.794	−205.980	267.298	−4.107
3500	82.995	475.780	401.182	261.093	−205.303	281.208	−4.197
3600	83.003	478.118	403.286	269.393	−204.631	295.099	−4.282
3700	83.010	480.392	405.340	277.694	−203.964	308.972	−4.362
3800	83.017	482.606	407.344	285.995	−203.300	322.826	−4.438
3900	83.024	484.762	409.302	294.297	−202.641	336.663	−4.509
4000	83.030	486.864	411.215	302.600	−201.987	350.483	−4.577
4100	83.035	488.915	413.085	310.903	−201.337	364.286	−4.641
4200	83.040	490.916	414.914	319.207	−200.692	378.074	−4.702
4300	83.045	492.870	416.704	327.511	−200.051	391.847	−4.760
4400	83.050	494.779	418.457	335.816	−199.414	405.604	−4.815
4500	83.054	496.645	420.174	344.121	−198.782	419.348	−4.868
4600	83.058	498.471	421.856	352.426	−198.154	433.077	−4.918
4700	83.061	500.257	423.506	360.732	−197.531	446.793	−4.966
4800	83.065	502.006	425.123	369.039	−196.912	460.495	−5.011
4900	83.068	503.719	426.709	377.345	−196.298	474.185	−5.055
5000	83.071	505.397	428.266	385.652	−195.688	487.862	−5.097
5100	83.074	507.042	429.795	393.960	−195.082	501.527	−5.137
5200	83.076	508.655	431.296	402.267	−194.481	515.180	−5.175
5300	83.079	510.238	432.771	410.575	−193.885	528.822	−5.212
5400	83.081	511.791	434.220	418.883	−193.293	542.452	−5.247
5500	83.084	513.315	435.644	427.191	−192.705	556.071	−5.281
5600	83.086	514.812	437.044	435.500	−192.122	569.680	−5.314
5700	83.088	516.283	438.422	443.808	−191.543	583.279	−5.345
5800	83.090	517.728	439.777	452.117	−190.969	596.867	−5.375
5900	83.091	519.148	441.110	460.426	−190.399	610.446	−5.404
6000	83.093	520.545	442.422	468.735	−189.834	624.014	−5.433

PREVIOUS: June 1961 (1 atm) CURRENT: June 1961 (1 bar)

Phosphorus Sulfide (P_4S_3) CRYSTAL M_r = 220.07504

$S°(298.15\ K) = [200.832]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 440\ K$

$\Delta_f H°(298.15\ K) = [-224.647]\ kJ·mol^{-1}$
$\Delta_{fus} H° = [9.204]\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°(298.15\ K)$ is estimated from vapor density reported by Yost and Russell.[1] T_{fus} is from Yost and Russell.[1] Other data estimated.

Reference

[1]D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth and Sixth Group Nonmetallic Elements," Prentice Hall, New York (1944).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	146.440	200.832	200.832	0.	−224.647	−206.864	36.242
300	146.440	201.738	200.835	0.271	−224.679	−206.754	35.999
400	146.440	243.866	206.579	14.915	−236.834	−199.434	26.043
440.000	146.440	257.823	210.613	20.773	--- CRYSTAL <--> LIQUID ---		
500	146.440	276.543	217.425	29.559	−244.505	−189.235	19.769
600	146.440	303.242	229.571	44.203	−251.145	−177.539	15.456
700	146.440	325.816	241.749	58.847	−257.072	−164.797	12.297
800	146.440	345.370	253.507	73.491	−262.592	−151.234	9.875
900	146.440	362.619	264.691	88.135	−427.249	−133.753	7.763
1000	146.440	378.048	275.269	102.779	−428.703	−101.065	5.279
1100	146.440	392.005	285.257	117.423	−430.204	−68.228	3.240
1200	146.440	404.747	294.691	132.067	−686.040	−30.940	1.347
1300	146.440	416.468	303.614	146.711	−684.535	23.590	−0.948
1400	146.440	427.321	312.067	161.355	−683.095	78.007	−2.910
1500	146.440	437.424	320.091	175.999	−681.718	132.323	−4.608
1600	146.440	446.875	327.723	190.643	−680.401	186.549	−6.090
1700	146.440	455.753	334.996	205.287	−679.139	240.694	−7.396
1800	146.440	464.123	341.939	219.931	−677.929	294.767	−8.554
1900	146.440	472.041	348.580	234.575	−676.769	348.774	−9.588
2000	146.440	479.552	354.943	249.219	−675.654	402.721	−10.518

PREVIOUS: CURRENT: December 1960

$S°$(298.15 K) = [207.097] J·K^{-1}·mol^{-1}
T_{fus} = 440 K

$\Delta_f H°$(298.15 K) = [−220.784] kJ·mol^{-1}
$\Delta_{fus}H°$ = [9.204] kJ·mol^{-1}

Enthalpy of Formation

$\Delta_f H°(P_4S_3, l, 298.15\ K)$ is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(440\ K)–H°(298.15\ K)$, between the crystal and liquid.

Fusion Data

T_{fus} is from Yost and Russell.[1]

Vaporization Data

T_{vap}(1 atm) = 680 K is given by Yost and Russell.[1]

Reference

[1]D. M. Yost and H. Russell, "Systematic Inorganic Chemistry of the Fifth and Sixth Group Nonmetallic Elements," Prentice Hall, New York (1944).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	184.096	207.097	207.097	0.	−220.784	−204.869	35.892
300	184.096	208.236	207.101	0.341	−220.746	−204.770	35.654
400	184.096	261.197	214.322	18.750	−229.136	−198.668	25.943
440.000	184.096	278.743	219.393	26.114	--- CRYSTAL <--> LIQUID ---		
500	184.096	302.277	227.957	37.160	−233.041	−190.638	19.916
600	184.096	335.842	243.226	55.569	−235.916	−181.869	15.833
700	184.096	364.220	258.536	73.979	−238.077	−172.684	12.886
800	184.096	388.803	273.317	92.389	−239.831	−163.219	10.657
900	184.096	410.486	287.377	110.798	−400.722	−150.307	8.724
1000	184.096	429.882	300.675	129.208	−398.411	−122.607	6.404
1100	184.096	447.429	313.231	147.617	−396.146	−95.137	4.518
1200	184.096	463.447	325.091	166.027	−648.216	−63.557	2.767
1300	184.096	478.183	336.308	184.437	−642.946	−15.050	0.605
1400	184.096	491.826	346.936	202.846	−637.741	33.054	−1.233
1500	184.096	504.527	357.023	221.256	−632.598	80.788	−2.813
1600	184.096	516.408	366.617	239.665	−627.515	128.181	−4.185
1700	184.096	527.569	375.760	258.075	−622.487	175.258	−5.385
1800	184.096	538.092	384.489	276.485	−617.512	222.041	−6.443
1900	184.096	548.045	392.838	294.894	−612.586	268.548	−7.383
2000	184.096	557.488	400.836	313.304	−607.706	314.797	−8.222
2100	184.096	566.470	408.511	331.713	−602.867	360.803	−8.974
2200	184.096	575.034	415.887	350.123	−598.067	406.579	−9.653
2300	184.096	583.218	422.986	368.533	−593.303	452.138	−10.268
2400	184.096	591.053	429.827	386.942	−588.572	497.491	−10.828
2500	184.096	598.568	436.427	405.352	−583.872	542.647	−11.338
2600	184.096	605.788	442.803	423.761	−579.201	587.615	−11.805
2700	184.096	612.736	448.969	442.171	−574.554	632.404	−12.235
2800	184.096	619.431	454.938	460.581	−569.931	677.022	−12.630
2900	184.096	625.891	460.722	478.990	−565.330	721.474	−12.995
3000	184.096	632.133	466.333	497.400	−560.752	765.769	−13.333

PREVIOUS: CURRENT: December 1960

0	to	440	K crystal
above		440	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0							
100							
200							
250							
298.15	146.440	200.832	200.832	0.	−224.647	−206.864	36.242
300	146.440	201.738	200.835	0.271	−224.679	−206.754	35.999
400	146.440	243.866	206.579	14.915	−236.834	−199.434	26.043
440.000	146.440	257.823	210.613	20.773	____ CRYSTAL <--> LIQUID ____		
440.000	184.096	278.743	210.613	29.977	TRANSITION		
500	184.096	302.277	220.231	41.023	−233.041	−190.638	19.916
600	184.096	335.842	236.787	59.433	−235.916	−181.869	15.833
700	184.096	364.220	253.017	77.842	−238.077	−172.684	12.886
800	184.096	388.803	268.488	96.252	−239.831	−163.219	10.657
900	184.096	410.486	283.084	114.661	−400.722	−150.307	8.724
1000	184.096	429.882	296.811	133.071	−398.411	−122.607	6.404
1100	184.096	447.429	309.719	151.481	−396.146	−95.137	4.518
1200	184.096	463.447	321.872	169.890	−648.216	−63.557	2.767
1300	184.096	478.183	333.337	188.300	−642.946	−15.050	0.605
1400	184.096	491.826	344.176	206.709	−637.741	33.054	−1.233
1500	184.096	504.527	354.448	225.119	−632.598	80.788	−2.813
1600	184.096	516.408	364.203	243.529	−627.515	128.181	−4.185
1700	184.096	527.569	373.488	261.938	−622.487	175.258	−5.385
1800	184.096	538.092	382.343	280.348	−617.512	222.040	−6.443
1900	184.096	548.045	390.804	298.757	−612.586	268.548	−7.383
2000	184.096	557.488	398.905	317.167	−607.706	314.797	−8.222
2100	184.096	566.470	406.672	335.577	−602.867	360.803	−8.974
2200	184.096	575.034	414.131	353.986	−598.067	406.579	−9.653
2300	184.096	583.218	421.306	372.396	−593.303	452.138	−10.268
2400	184.096	591.053	428.217	390.805	−588.572	497.491	−10.828
2500	184.096	598.568	434.882	409.215	−583.872	542.647	−11.338
2600	184.096	605.788	441.317	427.625	−579.201	587.615	−11.805
2700	184.096	612.736	447.538	446.034	−574.554	632.404	−12.235
2800	184.096	619.431	453.558	464.444	−569.931	677.022	−12.630
2900	184.096	625.891	459.390	482.853	−565.330	721.474	−12.995
3000	184.096	632.133	465.045	501.263	−560.752	765.769	−13.333

PREVIOUS: CURRENT: December 1960

$S°(298.15\ K)$ = [319.265] $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(298.15\ K)$ = [−151.042] $kJ \cdot mol^{-1}$

Enthalpy of Formation
All data estimated.

Heat Capacity and Entropy
All data estimated.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	154.808	319.265	319.265	0.	−151.042	−168.570	29.533
300	154.808	320.223	319.268	0.286	−151.059	−168.679	29.370
400	154.808	364.758	325.340	15.767	−162.377	−173.334	22.635
500	154.808	399.302	336.806	31.248	−169.211	−175.321	18.316
600	154.808	427.527	349.646	46.729	−175.015	−175.979	15.320
700	154.808	451.391	362.520	62.210	−180.105	−175.731	13.113
800	154.808	472.063	374.950	77.690	−184.788	−174.783	11.412
900	154.808	490.297	386.773	93.171	−348.607	−170.022	9.868
1000	154.808	506.607	397.955	108.652	−349.225	−150.146	7.843
1100	154.808	521.362	408.514	124.133	−349.889	−130.206	6.183
1200	154.808	534.832	418.487	139.614	−604.888	−105.891	4.609
1300	154.808	547.223	427.920	155.094	−602.546	−64.403	2.588
1400	154.808	558.696	436.856	170.575	−600.270	−23.093	0.862
1500	154.808	569.376	445.339	186.056	−598.056	18.056	−0.629
1600	154.808	579.368	453.407	201.537	−595.902	59.060	−1.928
1700	154.808	588.753	461.095	217.018	−593.803	99.930	−3.070
1800	154.808	597.601	468.435	232.498	−591.757	140.679	−4.082
1900	154.808	605.971	475.456	247.979	−589.760	181.315	−4.985
2000	154.808	613.912	482.182	263.460	−587.808	221.847	−5.794
2100	154.808	621.465	488.636	278.941	−585.898	262.283	−6.524
2200	154.808	628.667	494.839	294.422	−584.027	302.628	−7.185
2300	154.808	635.548	500.808	309.902	−582.191	342.889	−7.787
2400	154.808	642.137	506.560	325.383	−580.389	383.072	−8.337
2500	154.808	648.456	512.111	340.864	−578.619	423.179	−8.842
2600	154.808	654.528	517.472	356.345	−576.875	463.217	−9.306
2700	154.808	660.371	522.657	371.826	−575.157	503.188	−9.735
2800	154.808	666.001	527.677	387.306	−573.463	543.095	−10.132
2900	154.808	671.433	532.541	402.787	−571.792	582.943	−10.500
3000	154.808	676.681	537.258	418.268	−570.142	622.733	−10.843
3100	154.808	681.757	541.838	433.749	−568.512	662.469	−11.163
3200	154.808	686.672	546.288	449.230	−566.900	702.152	−11.461
3300	154.808	691.436	550.615	464.710	−565.307	741.785	−11.741
3400	154.808	696.057	554.825	480.191	−563.732	781.370	−12.004
3500	154.808	700.545	558.924	495.672	−562.175	820.909	−12.251
3600	154.808	704.906	562.919	511.153	−560.635	860.404	−12.484
3700	154.808	709.148	566.814	526.634	−559.113	899.857	−12.704
3800	154.808	713.276	570.614	542.114	−557.609	939.268	−12.911
3900	154.808	717.297	574.324	557.595	−556.123	978.640	−13.107
4000	154.808	721.217	577.948	573.076	−554.655	1017.974	−13.293
4100	154.808	725.039	581.489	588.557	−553.207	1057.272	−13.470
4200	154.808	728.770	584.951	604.038	−551.778	1096.535	−13.637
4300	154.808	732.412	588.338	619.518	−550.369	1135.764	−13.797
4400	154.808	735.971	591.653	634.999	−548.981	1174.960	−13.949
4500	154.808	739.450	594.899	650.480	−547.615	1214.125	−14.093
4600	154.808	742.853	598.079	665.961	−546.270	1253.260	−14.231
4700	154.808	746.182	601.195	681.442	−544.948	1292.366	−14.363
4800	154.808	749.441	604.249	696.922	−543.650	1331.444	−14.489
4900	154.808	752.634	607.245	712.403	−542.375	1370.495	−14.610
5000	154.808	755.761	610.184	727.884	−541.124	1409.520	−14.725
5100	154.808	758.827	613.069	743.365	−539.898	1448.521	−14.836
5200	154.808	761.833	615.901	758.846	−538.698	1487.498	−14.942
5300	154.808	764.782	618.682	774.326	−537.523	1526.452	−15.044
5400	154.808	767.675	621.415	789.807	−536.375	1565.384	−15.142
5500	154.808	770.516	624.100	805.288	−535.253	1604.295	−15.236
5600	154.808	773.305	626.739	820.769	−534.157	1643.186	−15.327
5700	154.808	776.045	629.335	836.250	−533.088	1682.058	−15.414
5800	154.808	778.738	631.888	851.730	−532.046	1720.911	−15.498
5900	154.808	781.384	634.399	867.211	−531.031	1759.746	−15.580
6000	154.808	783.986	636.871	882.692	−530.044	1798.564	−15.658

PREVIOUS: CURRENT: December 1960

REFERENCE STATE

0	to	600.6	K	crystal
600.6	to	2019.022	K	liquid
above		2019.022	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
		J·K⁻¹mol⁻¹			kJ·mol⁻¹			
	0	0.	0.	INFINITE	−6.878	0.	0.	0.
	100	24.426	36.829	87.950	−5.112	0.	0.	0.
	200	25.870	54.272	67.210	−2.587	0.	0.	0.
	298.15	26.836	64.785	64.785	0.	0.	0.	0.
@	300	26.853	64.951	64.786	0.050	0.	0.	0.
	400	27.723	72.796	65.849	2.779	0.	0.	0.
	500	28.549	79.071	67.886	5.592	0.	0.	0.
	600	29.404	84.336	70.201	8.481	0.	0.	0.
	600.600	29.414	84.366	70.215	8.499	CRYSTAL <--> LIQUID		
	600.600	30.627	92.314	70.215	13.273	TRANSITION		
	700	30.332	96.984	73.693	16.303	0.	0.	0.
	800	30.016	101.013	76.863	19.321	0.	0.	0.
	900	29.698	104.530	79.746	22.306	0.	0.	0.
	1000	29.397	107.643	82.383	25.261	0.	0.	0.
	1100	29.091	110.431	84.808	28.185	0.	0.	0.
	1200	28.786	112.949	87.050	31.079	0.	0.	0.
	1300	28.652	115.247	89.132	33.950	0.	0.	0.
	1400	28.623	117.368	91.074	36.812	0.	0.	0.
	1500	28.673	119.344	92.893	39.677	0.	0.	0.
	1600	28.786	121.198	94.605	42.549	0.	0.	0.
	1700	28.928	122.948	96.221	45.435	0.	0.	0.
	1800	29.109	124.606	97.753	48.336	0.	0.	0.
	1900	29.296	126.185	99.208	51.256	0.	0.	0.
	2000	29.497	127.693	100.595	54.196	0.	0.	0.
	2019.022	29.541	127.972	100.851	54.758	LIQUID <--> IDEAL GAS		
	2019.022	24.831	215.927	100.851	232.340	FUGACITY = 1 bar		
	2100	25.499	216.916	105.308	234.378	0.	0.	0.
	2200	26.365	218.122	110.408	236.971	0.	0.	0.
	2300	27.261	219.314	115.118	239.652	0.	0.	0.
	2400	28.173	220.493	119.484	242.423	0.	0.	0.
	2500	29.084	221.662	123.547	245.286	0.	0.	0.
	2600	29.979	222.820	127.343	248.240	0.	0.	0.
	2700	30.844	223.968	130.901	251.281	0.	0.	0.
	2800	31.669	225.105	134.245	254.407	0.	0.	0.
	2900	32.444	226.230	137.398	257.613	0.	0.	0.
	3000	33.160	227.342	140.377	260.894	0.	0.	0.
	3100	33.813	228.440	143.200	264.243	0.	0.	0.
	3200	34.398	229.523	145.881	267.654	0.	0.	0.
	3300	34.913	230.589	148.432	271.120	0.	0.	0.
	3400	35.360	231.639	150.864	274.635	0.	0.	0.
	3500	35.737	232.669	153.186	278.190	0.	0.	0.
	3600	36.048	233.680	155.408	281.780	0.	0.	0.
	3700	36.296	234.672	157.537	285.398	0.	0.	0.
	3800	36.485	235.642	159.580	289.037	0.	0.	0.
	3900	36.618	236.592	161.542	292.693	0.	0.	0.
	4000	36.700	237.520	163.430	296.359	0.	0.	0.
	4100	36.737	238.427	165.248	300.031	0.	0.	0.
	4200	36.733	239.312	167.001	303.705	0.	0.	0.
	4300	36.692	240.176	168.693	307.377	0.	0.	0.
	4400	36.619	241.019	170.327	311.042	0.	0.	0.
	4500	36.518	241.841	171.907	314.699	0.	0.	0.
	4600	36.395	242.642	173.436	318.345	0.	0.	0.
	4700	36.252	243.423	174.917	321.978	0.	0.	0.
	4800	36.093	244.185	176.352	325.595	0.	0.	0.
	4900	35.923	244.927	177.744	329.196	0.	0.	0.
	5000	35.743	245.651	179.095	332.779	0.	0.	0.
	5100	35.557	246.357	180.407	336.344	0.	0.	0.
	5200	35.367	247.046	181.682	339.890	0.	0.	0.
	5300	35.175	247.717	182.922	343.417	0.	0.	0.
	5400	34.985	248.373	184.128	346.925	0.	0.	0.
	5500	34.796	249.013	185.302	350.414	0.	0.	0.
	5600	34.612	249.639	186.445	353.885	0.	0.	0.
	5700	34.434	250.250	187.559	357.337	0.	0.	0.
	5800	34.263	250.847	188.645	360.772	0.	0.	0.
	5900	34.097	251.431	189.704	364.189	0.	0.	0.
	6000	33.942	252.003	190.738	367.590	0.	0.	0.

PREVIOUS: March 1962 (1 atm) CURRENT: March 1962 (1 bar)

$S°(298.15\ K) = 64.785 \pm 0.54\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 600.58 \pm 0.00\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 4.77 \pm 0.01\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Heat Capacity measurements have been reported by Horowitz, *et al.*[1] (1–4 K, 14–21 K, 64–77 K), Meads, *et al.*[2] (15–300 K), Douglas and Devir[3] (298.15 K), and many others whose work is listed by Kelley.[4]

Heat capacities from 15 to 300 K and 1 to 4 K (in superconducting state) were taken from Meads *et al.*[2] and Horowitz *et al.*,[1] respectively. The missing data below the melting point were obtained by graphical extrapolation and joined smoothly to the data of Douglas and Dever[3] on approaching the melting point.

Fusion Data

The melting point of pure Pb(cr) was found by McLaren and Mardock[5] to be 327.426 ± 0.002°C. $\Delta_{fus}H°$ was given by Douglas and Dever.[3]

Sublimation Data

The enthalpy of sublimation, $\Delta_{sub}H°(298.15\ K)$, is the enthalpy of formation of the ideal gas, $\Delta_f H°(298.15\ K)$. See the ideal gas table for details.

References

[1]M. Horowitz, A. A. Silvidi, S. F. Malaker and J. G. Daunt, Phys. Rev. **88**, 1182 (1952).
[2]P. V. Meads, W. R. Forsythe and W. F. Giaugue, J. Am. Chem. Soc. **63**, 1902 (1941).
[3]T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. **76**, 4824 (1954).
[4]K. K. Kelley, U. S. Bur. Mines Bull. 584, 232 pp. (1960).
[5]E. H. McLaren and E. G. Mardock, Can. J. Phys. **38**, 577 (1960).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.878	0.	0.	0.
100	24.426	36.829	87.950	−5.112	0.	0.	0.
200	25.870	54.272	67.210	−2.587	0.	0.	0.
250	26.363	60.096	65.225	−1.282	0.	0.	0.
298.15	26.836	64.785	64.785	0.	0.	0.	0.
300	26.853	64.951	64.786	0.050	0.	0.	0.
350	27.288	69.124	65.114	1.403	0.	0.	0.
400	27.723	72.796	65.849	2.779	0.	0.	0.
450	28.139	76.085	66.807	4.175	0.	0.	0.
500	28.549	79.071	67.886	5.592	0.	0.	0.
600	29.404	84.336	70.201	8.481	0.	0.	0.
600.600	29.414	84.366	70.215	8.499	--- CRYSTAL <--> LIQUID ---		
700	30.367	88.941	72.556	11.470	−4.833	0.796	−0.059
800	31.342	93.060	74.866	14.556	−4.765	1.598	−0.104
900	32.313	96.808	77.098	17.738	−4.568	2.382	−0.138
1000	33.288	100.263	79.244	21.018	−4.242	3.138	−0.164
1100	34.263	103.481	81.303	24.396	−3.789	3.856	−0.183
1200	35.238	106.504	83.278	27.871	−3.208	4.526	−0.197
1300	36.208	109.363	85.176	31.443	−2.506	5.143	−0.207
1400	37.183	112.082	87.001	35.113	−1.700	5.701	−0.213
1500	38.158	114.681	88.761	38.880	−0.797	6.199	−0.216

PREVIOUS: CURRENT: March 1962

$S°(298.15\ K) = [71.710]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 600.58 \pm 0.00\ K$

$\Delta_f H°(298.15\ K) = [4.283]\ kJ·mol^{-1}$
$\Delta_{fus} H° = 4.77 \pm 0.01\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of the liquid, $\Delta_f H°(298.15\ K)$, is calculated from that of the crystal by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(600.58\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

Heat capacity values from T_{fus} to 1200 K were taken from Douglas and Dever,[1] Heat capacity values below T_{fus} and above 1200 K were extrapolated, a glass transition being assumed at 400 K.

The entropy is calculated in a manner anologous to that used for the enthalpy of formation.

Vaporization Data

T_{vap} is calculated as the temperature at which $\Delta_r G° = 0$ for the process Pb(l) = Pb(g). $\Delta_{vap} H°$ is calculated as the corresponding enthalpy of formation difference at T_{vap}. At temperatures below T_{vap}, the amount of Pb_2(g) in the vapor is negligible.

References

[1]T. B. Douglas and J. L. Dever, J. Am. Chem. Soc. **76**, 4824 (1954).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_r G°$	log K_f
		J·K^{-1}mol^{-1}		kJ·mol^{-1}			
0							
100							
200							
250							
298.15	26.836	71.710	71.710	0.	4.283	2.218	−0.389
300	26.853	71.876	71.710	0.050	4.283	2.205	−0.384
400	27.723	79.720	72.774	2.779	4.283	1.513	−0.198
400.000	27.723	79.720	72.774	2.779	GLASS <--> LIQUID TRANSITION		
400.000	31.254	79.720	72.774	2.779			
500	30.945	86.661	74.884	5.889	4.579	0.784	−0.082
600	30.635	92.284	77.330	8.972	4.773	0.005	0.
600.600	30.627	92.314	77.345	8.990	--- CRYSTAL <--> LIQUID ---		
700	30.332	96.984	79.811	12.021	0.	0.	0.
800	30.016	101.013	82.216	15.038	0.	0.	0.
900	29.698	104.530	84.504	18.023	0.	0.	0.
1000	29.397	107.643	86.665	20.978	0.	0.	0.
1100	29.091	110.431	88.701	23.902	0.	0.	0.
1200	28.786	112.949	90.619	26.796	0.	0.	0.
1300	28.652	115.247	92.426	29.667	0.	0.	0.
1400	28.623	117.368	94.133	32.530	0.	0.	0.
1500	28.673	119.344	95.748	35.394	0.	0.	0.
1600	28.786	121.198	97.282	38.267	0.	0.	0.
1700	28.928	122.948	98.741	41.152	0.	0.	0.
1800	29.109	124.606	100.132	44.054	0.	0.	0.
1900	29.296	126.185	101.462	46.974	0.	0.	0.
2000	29.497	127.693	102.736	49.914	0.	0.	0.
2019.022	29.541	127.972	102.972	50.475	----- FUGACITY = 1 bar -----		
2100	29.706	129.137	103.959	52.874	−177.221	7.115	−0.177
2200	29.920	130.524	105.135	55.855	−176.833	15.884	−0.377
2300	30.133	131.859	106.268	58.858	−176.511	24.636	−0.560
2400	30.347	133.146	107.361	61.882	−176.259	33.376	−0.726
2500	30.556	134.389	108.418	64.927	−176.077	42.107	−0.880
2600	30.761	135.591	109.440	67.993	−175.964	50.832	−1.021
2700	30.962	136.756	110.430	71.079	−175.920	59.553	−1.152
2800	31.171	137.885	111.391	74.186	−175.939	68.275	−1.274
2900	31.376	138.983	112.323	77.313	−176.018	76.998	−1.387
3000	31.581	140.050	113.230	80.461	−176.151	85.725	−1.493

PREVIOUS: CURRENT: March 1962

CRYSTAL-LIQUID

0	to	600.6	K crystal
above		600.6	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−6.878	0.	0.	0.
100	24.426	36.829	87.950	−5.112	0.	0.	0.
200	25.870	54.272	67.210	−2.587	0.	0.	0.
250	26.363	60.096	65.225	−1.282	0.	0.	0.
298.15	26.836	64.785	64.785	0.	0.	0.	0.
300	26.853	64.951	64.786	0.050	0.	0.	0.
400	27.723	72.796	65.849	2.779	0.	0.	0.
500	28.549	79.071	67.886	5.592	0.	0.	0.
600	29.404	84.336	70.201	8.481	0.	0.	0.
600.600	29.414	84.366	70.215	8.499	____ CRYSTAL <--> LIQUID ____		
600.600	30.627	92.314	70.215	13.273	TRANSITION		
700	30.332	96.984	73.693	16.303	0.	0.	0.
800	30.016	101.013	76.863	19.321	0.	0.	0.
900	29.698	104.530	79.746	22.306	0.	0.	0.
1000	29.397	107.643	82.383	25.261	0.	0.	0.
1100	29.091	110.431	84.808	28.185	0.	0.	0.
1200	28.786	112.949	87.050	31.079	0.	0.	0.
1300	28.652	115.247	89.132	33.950	0.	0.	0.
1400	28.623	117.368	91.074	36.812	0.	0.	0.
1500	28.673	119.344	92.893	39.677	0.	0.	0.
1600	28.786	121.198	94.605	42.549	0.	0.	0.
1700	28.928	122.948	96.221	45.435	0.	0.	0.
1800	29.109	124.606	97.753	48.336	0.	0.	0.
1900	29.296	126.185	99.208	51.256	0.	0.	0.
2000	29.497	127.693	100.595	54.196	0.	0.	0.
2019.022	29.541	127.972	100.851	54.758	- - - - - FUGACITY = 1 bar - - - - -		
2100	29.706	129.137	101.920	57.156	−177.221	7.115	−0.177
2200	29.920	130.524	103.189	60.138	−176.833	15.884	−0.377
2300	30.133	131.859	104.406	63.140	−176.511	24.636	−0.560
2400	30.347	133.146	105.577	66.164	−176.259	33.376	−0.726
2500	30.556	134.389	106.705	69.210	−176.077	42.107	−0.880
2600	30.761	135.591	107.793	72.275	−175.964	50.832	−1.021
2700	30.962	136.756	108.844	75.362	−175.920	59.553	−1.152
2800	31.171	137.885	109.861	78.468	−175.939	68.275	−1.274
2900	31.376	138.983	110.847	81.595	−176.018	76.998	−1.387
3000	31.581	140.050	111.802	84.743	−176.151	85.725	−1.493

PREVIOUS: CURRENT: March 1962

IP(Pb, g) = 59819.4 ± 0.3 cm^{-1}
$S°(298.15\ K)$ = 175.374 ± 0.020 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 195.88 ± 0.80 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 195.20 ± 0.80 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_0$	0.00	1
$^3P_1$	7819.2626	3
$^3P_2$	10650.3271	5
$^1D_2$	21457.90	5
$^1S_0$	29466.81	1

Enthalpy of Formation

The adopted enthalpy of formation value for Pb(g), $\Delta_f H°(298.15\ K)$ = 195.20 ± 0.80 $kJ·mol^{-1}$, is that recommended by CODATA.[1] This value was calculated, according to CODATA, from the vapor pressure measurements cited by Hultgren *et al.*[2] and the more recent measurements by Andon *et al.*,[3] Chang, *et al.*,[4] Kim and Cosgarea,[5] and Shiu and Miner.[6]

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[7,8] is incomplete because many theoretically predicted levels have not been observed. Our calcualtions indicate that any reasonable method of filling in these missing levels (for n<21) and cutting off the summation in the partition function[9] has little effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than those listed above; the next excited state is approximately 34950 cm^{-1} above the ground state. Although we list only a few levels above, all levels listed by Moore[7,8] are considered in the calculation. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calcualtions above 6000 K may require consideration of the excited states (n>21) and use of different fill and cutoff procedures.[9]

The thermal functions at 298.15 K differ from the CODATA recommendations[1] for two reasons. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas CODATA recommendations are based on 1 atm. Second, small changes, 0.005 $J·K^{-1}·mol^{-1}$, arise due to the use of slightly different values for the fundamental constants.

References

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[2] R. Hultgren, P. D. Desai, *et al.*, Selected Values of the Thermodynamic Properties of the Elements, American Society for Metals, Metals Park, Ohio, (1973).
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[8] C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–34, 8 pp. (1970).
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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	195.881	195.881	INFINITE
100	20.786	152.667	193.855	−4.119	196.193	184.610	−96.430
200	20.786	167.075	177.276	−2.040	195.747	173.187	−45.232
250	20.786	171.713	175.716	−1.001	195.481	167.577	−35.013
298.15	20.786	175.374	175.374	0.	195.200	162.228	−28.422
300	20.786	175.503	175.375	0.038	195.189	162.023	−28.211
350	20.786	178.707	175.628	1.078	194.874	156.520	−23.359
400	20.786	181.483	176.190	2.117	194.538	151.064	−19.727
450	20.786	183.931	176.917	3.156	194.181	145.651	−16.907
500	20.786	186.121	177.730	4.196	193.803	140.278	−14.655
600	20.786	189.911	179.453	6.274	192.993	129.648	−11.287
700	20.787	193.115	181.182	8.353	187.250	119.958	−8.951
800	20.790	195.891	182.851	10.432	186.311	110.409	−7.209
900	20.801	198.340	184.439	12.511	185.405	100.976	−5.861
1000	20.829	200.533	185.940	14.592	184.532	91.642	−4.787
1100	20.888	202.520	187.359	16.678	183.693	82.394	−3.913
1200	20.991	204.342	188.699	18.771	182.892	73.221	−3.187
1300	21.155	206.028	189.968	20.878	182.129	64.113	−2.576
1400	21.394	207.604	191.172	23.005	181.393	55.063	−2.054
1500	21.717	209.091	192.317	25.160	180.683	46.064	−1.604
1600	22.132	210.505	193.410	27.352	180.002	37.112	−1.212
1700	22.640	211.862	194.456	29.589	179.355	28.201	−0.867
1800	23.239	213.172	195.460	31.883	178.746	19.327	−0.561
1900	23.922	214.447	196.426	34.240	178.184	10.486	−0.288
2000	24.680	215.693	197.358	36.669	177.673	1.674	−0.044
2019.022	24.831	215.927	197.532	37.140	----- FUGACITY = 1 bar -----		
2100	25.499	216.916	198.260	39.178	0.	0.	0.
2200	26.365	218.122	199.136	41.771	0.	0.	0.
2300	27.261	219.314	199.987	44.452	0.	0.	0.
2400	28.173	220.493	200.817	47.224	0.	0.	0.
2500	29.084	221.662	201.627	50.086	0.	0.	0.
2600	29.979	222.820	202.420	53.040	0.	0.	0.
2700	30.844	223.968	203.197	56.081	0.	0.	0.
2800	31.669	225.105	203.959	59.207	0.	0.	0.
2900	32.444	226.230	204.708	62.413	0.	0.	0.
3000	33.160	227.342	205.444	65.694	0.	0.	0.
3100	33.813	228.440	206.168	69.043	0.	0.	0.
3200	34.398	229.523	206.881	72.454	0.	0.	0.
3300	34.913	230.589	207.583	75.921	0.	0.	0.
3400	35.360	231.639	208.275	79.435	0.	0.	0.
3500	35.737	232.669	208.958	82.990	0.	0.	0.
3600	36.048	233.680	209.630	86.580	0.	0.	0.
3700	36.296	234.672	210.294	90.198	0.	0.	0.
3800	36.485	235.642	210.948	93.837	0.	0.	0.
3900	36.618	236.592	211.594	97.493	0.	0.	0.
4000	36.700	237.520	212.230	101.159	0.	0.	0.
4100	36.737	238.427	212.858	104.831	0.	0.	0.
4200	36.733	239.312	213.477	108.505	0.	0.	0.
4300	36.692	240.176	214.088	112.177	0.	0.	0.
4400	36.619	241.019	214.691	115.842	0.	0.	0.
4500	36.518	241.841	215.285	119.499	0.	0.	0.
4600	36.395	242.642	215.871	123.145	0.	0.	0.
4700	36.252	243.423	216.449	126.778	0.	0.	0.
4800	36.093	244.185	217.019	130.395	0.	0.	0.
4900	35.923	244.927	217.581	133.996	0.	0.	0.
5000	35.743	245.651	218.135	137.579	0.	0.	0.
5100	35.557	246.357	218.682	141.144	0.	0.	0.
5200	35.367	247.046	219.221	144.690	0.	0.	0.
5300	35.175	247.717	219.752	148.217	0.	0.	0.
5400	34.985	248.373	220.276	151.725	0.	0.	0.
5500	34.796	249.013	220.793	155.214	0.	0.	0.
5600	34.612	249.639	221.302	158.685	0.	0.	0.
5700	34.434	250.250	221.805	162.137	0.	0.	0.
5800	34.263	250.847	222.300	165.572	0.	0.	0.
5900	34.097	251.431	222.789	168.989	0.	0.	0.
6000	33.942	252.003	223.271	172.390	0.	0.	0.

PREVIOUS: March 1962 (1 atm) CURRENT: March 1983 (1 bar)

$IP(Pb^+, g) = 121243 \pm 3\ cm^{-1}$
$S°(298.15\ K) = 181.137 \pm 0.02\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 911.480 \pm 0.5\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = [916.996]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{1/2}$	0.000	2
$^3P_{3/2}$	14081.074	4

Enthalpy of Formation

$\Delta_f H°(Pb^+, g, 0\ K)$ is calculated from $\Delta_f H°(Pb, g, 0\ K)$[1] using the spectroscopic value of IP(Pb) = 59819.4 ± 0.3 cm^{-1} (715.599 ± 0.004 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Pb^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Pb, g, 0\ K)$ by using IP(Pb) with JANAF[1] enthalpies, $H°(0\ K)–H°(298.15\ K)$, for Pb(g), $Pb^+(g)$, and e^-(ref). $\Delta_f H°(Pb \rightarrow Pb^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first excited state; the next excited state is 57911 cm^{-1}, above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first excited states. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

Refereces

[1]JANAF Thermochemical Tables: Pb(g), 3–31–62 ; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	911.480		
100	20.786	158.430	199.618	−4.119			
200	20.786	172.838	183.039	−2.040			
250	20.786	177.476	181.480	−1.001			
298.15	20.786	181.137	181.137	0.	916.996	876.051	−153.481
300	20.786	181.266	181.138	0.038	917.024	875.797	−152.490
350	20.786	184.470	181.391	1.078	917.749	868.868	−129.672
400	20.786	187.246	181.953	2.117	918.452	861.837	−112.544
450	20.786	189.694	182.680	3.156	919.134	854.719	−99.213
500	20.786	191.884	183.493	4.196	919.795	847.526	−88.540
600	20.786	195.674	185.217	6.274	921.064	832.952	−72.515
700	20.786	198.878	186.945	8.353	917.399	818.970	−61.112
800	20.786	201.653	188.614	10.431	918.539	804.831	−52.550
900	20.786	204.102	190.202	12.510	919.711	790.547	−45.882
1000	20.786	206.292	191.703	14.589	920.913	776.132	−40.541
1100	20.786	208.273	193.121	16.667	922.146	761.594	−36.165
1200	20.786	210.081	194.460	18.746	923.409	746.943	−32.514
1300	20.787	211.745	195.726	20.825	924.696	732.185	−29.420
1400	20.788	213.286	196.926	22.903	925.991	717.328	−26.764
1500	20.790	214.720	198.065	24.982	927.284	702.379	−24.459
1600	20.794	216.062	199.149	27.061	928.569	687.343	−22.439
1700	20.802	217.323	200.181	29.141	929.842	672.228	−20.655
1800	20.813	218.512	201.167	31.222	931.100	657.037	−19.067
1900	20.830	219.638	202.109	33.304	932.340	641.778	−17.644
2000	20.854	220.707	203.013	35.388	933.563	626.453	−16.361
2100	20.886	221.725	203.880	37.475	757.547	618.183	−15.376
2200	20.927	222.698	204.713	39.566	759.123	611.510	−14.519
2300	20.979	223.629	205.516	41.661	760.616	604.766	−13.735
2400	21.041	224.523	206.289	43.762	762.024	597.960	−13.014
2500	21.116	225.383	207.036	45.870	763.347	591.096	−12.350
2600	21.202	226.213	207.757	47.985	764.588	584.181	−11.736
2700	21.301	227.015	208.456	50.110	765.751	577.220	−11.167
2800	21.411	227.792	209.133	52.246	766.839	570.217	−10.638
2900	21.534	228.545	209.789	54.393	767.858	563.177	−10.144
3000	21.667	229.278	210.427	56.553	768.816	556.103	−9.683
3100	21.811	229.990	211.046	58.727	769.719	548.997	−9.251
3200	21.964	230.685	211.649	60.915	770.576	541.863	−8.845
3300	22.126	231.364	212.236	63.120	771.392	534.703	−8.464
3400	22.296	232.027	212.809	65.341	772.178	527.519	−8.104
3500	22.472	232.675	213.367	67.579	772.939	520.312	−7.765
3600	22.653	233.311	213.912	69.835	773.684	513.084	−7.445
3700	22.839	233.934	214.445	72.110	774.420	505.834	−7.141
3800	23.029	234.546	214.966	74.403	775.152	498.566	−6.853
3900	23.220	235.146	215.476	76.716	775.888	491.277	−6.580
4000	23.413	235.737	215.975	79.048	776.632	483.970	−6.320
4100	23.606	236.317	216.464	81.398	777.389	476.644	−6.073
4200	23.798	236.888	216.944	83.769	778.164	469.300	−5.837
4300	23.989	237.451	217.414	86.158	778.960	461.937	−5.611
4400	24.177	238.004	217.876	88.566	779.782	454.554	−5.396
4500	24.362	238.550	218.329	90.993	780.630	447.153	−5.190
4600	24.543	239.087	218.774	93.439	781.508	439.733	−4.993
4700	24.720	239.617	219.212	95.902	782.418	432.294	−4.804
4800	24.892	240.139	219.643	98.383	783.360	424.834	−4.623
4900	25.059	240.654	220.066	100.880	784.335	417.355	−4.449
5000	25.220	241.162	220.483	103.394	785.344	409.855	−4.282
5100	25.375	241.663	220.894	105.924	786.388	402.335	−4.121
5200	25.523	242.157	221.298	108.469	787.465	394.794	−3.966
5300	25.665	242.645	221.696	111.028	788.576	387.232	−3.816
5400	25.800	243.126	222.088	113.602	789.720	379.649	−3.672
5500	25.928	243.600	222.475	116.188	790.896	372.045	−3.533
5600	26.049	244.069	222.857	118.787	792.103	364.418	−3.399
5700	26.164	244.531	223.233	121.398	793.340	356.770	−3.269
5800	26.271	244.987	223.604	124.020	794.606	349.100	−3.144
5900	26.371	245.437	223.970	126.652	795.900	341.408	−3.023
6000	26.465	245.881	224.332	129.294	797.219	333.693	−2.905

PREVIOUS: CURRENT: March 1983 (1 bar)

EA(Pb, g) = 0.364 ± 0.008 eV
$S°$(298.15 K) = 186.900 ± 0.002 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 160.76 ± 3 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [153.882] kJ·mol^{-1}

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^4S_{3/2}$	0.0	4

Enthalpy of Formation

$\Delta_f H°(Pb^-, g, 0 K)$ is calculated from $\Delta_f H°(Pb, g, 0 K)$[1] using the adopted electron affinity of EA(Pb) = 0.364 ± 0.008 eV (35.120 ± 0.772 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Pb^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Pb^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Pb, g, 0 K)$ by using EA(Pb) with JANAF[1] enthalpies, $H°(0 K) - H°(298.15 K)$, for Pb^-(g), Pb(g), and e^-(ref). $\Delta_r H°(Pb^- \rightarrow Pb + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°$(298.15 K) should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Pb^-(g) is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.197	160.761		
100	20.786	164.193	205.381	−4.119			
200	20.786	178.601	188.802	−2.040			
250	20.786	183.239	187.243	−1.001			
298.15	20.786	186.900	186.900	0.	153.882	123.728	−21.677
300	20.786	187.029	186.901	0.038	153.833	123.541	−21.510
350	20.786	190.233	187.154	1.078	152.479	118.600	−17.700
400	20.786	193.009	187.716	2.117	151.104	113.853	−14.868
450	20.786	195.457	188.443	3.156	149.707	109.281	−12.685
500	20.786	197.647	189.256	4.196	148.290	104.864	−10.955
600	20.786	201.437	190.980	6.274	145.401	96.449	−8.397
700	20.786	204.641	192.708	8.353	137.579	89.322	−6.665
800	20.786	207.417	194.377	10.431	134.562	82.635	−5.396
900	20.786	209.865	195.965	12.510	131.576	76.324	−4.430
1000	20.786	212.055	197.466	14.589	128.622	70.343	−3.674
1100	20.786	214.036	198.884	16.667	125.697	64.657	−3.070
1200	20.786	215.845	200.223	18.746	122.803	59.236	−2.578
1300	20.786	217.508	201.490	20.824	119.933	54.055	−2.172
1400	20.786	219.049	202.689	22.903	117.070	49.095	−1.832
1500	20.786	220.483	203.828	24.982	114.206	44.340	−1.544
1600	20.786	221.824	204.912	27.060	111.333	39.775	−1.299
1700	20.786	223.085	205.944	29.139	108.448	35.391	−1.087
1800	20.786	224.273	206.930	31.217	105.546	31.178	−0.905
1900	20.786	225.396	207.872	33.296	102.626	27.126	−0.746
2000	20.786	226.463	208.775	35.375	99.686	23.228	−0.607
2100	20.786	227.477	209.642	37.453	−80.496	26.593	−0.661
2200	20.786	228.444	210.475	39.532	−83.088	31.753	−0.754
2300	20.786	229.368	211.276	41.610	−85.770	37.032	−0.841
2400	20.786	230.252	212.049	43.689	−88.541	42.431	−0.923
2500	20.786	231.101	212.794	45.768	−91.404	47.946	−1.002
2600	20.786	231.916	213.514	47.846	−94.357	53.578	−1.076
2700	20.786	232.701	214.210	49.925	−97.399	59.326	−1.148
2800	20.786	233.457	214.884	52.004	−100.525	65.187	−1.216
2900	20.786	234.186	215.537	54.082	−103.731	71.162	−1.282
3000	20.786	234.891	216.170	56.161	−107.012	77.248	−1.345
3100	20.786	235.572	216.785	58.239	−110.361	83.445	−1.406
3200	20.786	236.232	217.383	60.318	−113.772	89.751	−1.465
3300	20.786	236.872	217.964	62.397	−117.238	96.165	−1.522
3400	20.786	237.492	218.529	64.475	−120.752	102.684	−1.578
3500	20.786	238.095	219.079	66.554	−124.308	109.308	−1.631
3600	20.786	238.680	219.616	68.632	−127.898	116.033	−1.684
3700	20.786	239.250	220.139	70.711	−131.515	122.859	−1.734
3800	20.786	239.804	220.649	72.790	−135.155	129.782	−1.784
3900	20.786	240.344	221.147	74.868	−138.810	136.802	−1.832
4000	20.786	240.870	221.634	76.947	−142.477	143.916	−1.879
4100	20.786	241.384	222.109	79.025	−146.149	151.121	−1.925
4200	20.786	241.885	222.574	81.104	−149.823	158.416	−1.970
4300	20.786	242.374	223.029	83.183	−153.494	165.798	−2.014
4400	20.786	242.852	223.474	85.261	−157.160	173.266	−2.057
4500	20.786	243.319	223.910	87.340	−160.817	180.817	−2.099
4600	20.786	243.776	224.337	89.418	−164.463	188.449	−2.140
4700	20.786	244.223	224.755	91.497	−168.095	196.160	−2.180
4800	20.786	244.660	225.165	93.576	−171.713	203.949	−2.219
4900	20.786	245.089	225.567	95.654	−175.313	211.812	−2.258
5000	20.786	245.509	225.962	97.733	−178.897	219.749	−2.296
5100	20.786	245.920	226.349	99.811	−182.462	227.757	−2.333
5200	20.786	246.324	226.730	101.890	−186.008	235.836	−2.369
5300	20.786	246.720	227.103	103.969	−189.535	243.982	−2.405
5400	20.786	247.108	227.470	106.047	−193.043	252.194	−2.439
5500	20.786	247.490	227.831	108.126	−196.532	260.471	−2.474
5600	20.786	247.864	228.185	110.204	−200.002	268.812	−2.507
5700	20.786	248.232	228.533	112.283	−203.455	277.214	−2.540
5800	20.786	248.594	228.876	114.362	−206.890	285.677	−2.573
5900	20.786	248.949	229.213	116.440	−210.306	294.199	−2.605
6000	20.786	249.298	229.545	118.519	−213.708	302.778	−2.636

PREVIOUS: CURRENT: March 1983 (1 bar)

Lead Sulfide (PbS) **CRYSTAL** $M_r = 239.26$ **Lead Sulfide (PbS)** **Pb_1S_1(cr)**

$S°(298.15\ K) = 91.34 \pm 1.7\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1386.5 \pm 1.5\ K$

$\Delta_f H°(0\ K) = 98.55 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = -98.32 \pm 2.1\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 18.83 \pm 6.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

2nd and 3rd law analyses are made of the equilibrium data of Jellinek *et al.*,[1] Sudo,[2] and Stubbles and Birchenall,[3] the Gibbs free energies (via emf measurements) of Kapustinskii and Makolkin[4] and of Kiukkola and Wagner[5] and the emf data reported by Thompson and Flengas.[6] The results of our analyses using auxiliary data[7] are summarized in the following table.

Source	Reaction*	T/K	Data Points	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
1	A	788–1273	7	−18.4 ± 0.8	−18.60	−0.16 ± 0.80	−22.5
2	A	855–1048	Equation	−18.0	−20.12	−2.2	−24.0
3	A	859–1193	30	−19.3 ± 0.1	−19.76	−0.42 ± 0.12	−23.6
4	B	288–308	3	−17.7 ± 0.5	−16.63	3.7 ± 1.6	−21.5
5	C	523–573	2	−24.7	−23.84	1.5	−23.5
5	D	600–700	4	−24.5 ± 0.2	−24.79	−0.45 ± 0.32	−23.4
6	E	773–1071	12	−40.7 ± 0.5	−39.63	1.2 ± 0.6	−23.2

*A) $Pb(l) + H_2S(g) = PbS(cr) + H_2(g)$
B) $Pb(cr) + H_2S(g) = PbS(cr) + H_2(g)$
C) $Pb(cr) + S(l) = PbS(cr)$
D) $Pb(l) + S(l) = PbS(cr)$
E) $Pb(l) + 1/2\ S_2(g) = PbS(cr)$

The experiences of Jellinek *et al.*[1] are unsatisfactory[8] and are superseded by two later studies[2,3] of the same equilibrium. The Gibbs energies of Kapustinskii and Makolkin[4] may be dismissed as biased on the basis of inconsistencies in both $\Delta_f H°$ and entropy (drift). The other studies[2,3,5,6] are consistent with the adopted $\Delta_f H°(298.15\ K)$ of 23.5 ± 0.5 kcal·mol^{-1}.

We also calculate $\Delta_f H° = -23.5$ kcal·mol^{-1} from $\Delta_r H°(293\ K) = -13.38 \pm 0.2$ kcal mol^{-1} for the reaction $Pb(NO_3)_2$(aq, 3000 H_2O) + H_2S(aq) → PbS(cr) + 2 HNO_3(aq, 2000 H_2O) studied calorimetrically by Zeumer and Roth.[9] The uncertainty of this calorimetric $\Delta_f H°$ may approach ±1 kcal·mol^{-1} due to the auxiliary data[10] and approximations used in our calculation. Recent DTA data[11] for Pb(cr) + S(l) → PbS(cr) gave $\Delta_r H°(480\ K) = -23.4 \pm 0.3$ kcal·mol^{-1} which we reduce to $\Delta_f H°(298.15\ K) = -22.5 \pm 1$ kcal·mol^{-1}. The uncertainty assigned[11] to $\Delta_f H°$ appears to be too optimistic. Korshunov[12] obtained $\Delta_f H° = -22.38$ kcal·mol^{-1} by combustion of S–Mg–Pb mixtures in a bomb, but the chemical reactions probably were not characterized adequately.

Heat Capacity and Entropy

$C_p°$ is from the work of Parkinson and Quarrington1,[13] $C_p°$ given as smoothed values, 20–260 K and of Anderson,[14] (54–289 K) which were graphically smoothed and extrapolated to 300 K. The data of Parkinson and Quarrington and Anderson are in good agreement; Anderson's values show more scatter. The largest deviation of the Parkinson and Quarrington values from the adopted values is +0.4% at 210 K. Anderson's points are mostly within less than ±1% of the selected values.

Above 300 K, $C_p°$ values are derived from the drop calorimetric enthalpies of Thompson and Flengas,[15] (353–1281 K) with the constraint to join smoothly with the low temperature data. The observed enthalpies differ from the adopted values by +4% at 400 K; above 500 K the deviation is generally within ±0.4%.

Also considered were the low temperature heat capacities measured by Eastman and Rodebush,[16] (64–283 K) and Kelley's equations[17] which are based on the work of Bornemann and Hengstenberg,[18] (273–873 K). The Eastman and Rodebush data appears to be high above 200 K. At 900 K the enthalpy calculated from Kelley's equation is 4% higher than the adopted value.

$S°$(20 K) of 0.83 cal·K^{-1}·mol^{-1} given by Kelley and King[19] is adopted here.

Fusion Data –Refer to the liquid table for details.

Sublimation Data –Refer to the ideal gas table for details.

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Continued on page 1847

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−11.511	−98.545	−98.545	INFINITE
100	39.748	41.296	133.734	−9.244	−98.734	−97.928	51.152
200	47.614	71.920	95.823	−4.781	−98.437	−97.239	25.396
298.15	49.438	91.343	91.343	0.	−98.324	−96.685	16.939
300	49.455	91.649	91.344	0.091	−98.324	−96.675	16.833
400	50.459	106.008	93.295	5.085	−100.657	−96.024	12.539
500	51.463	117.375	97.013	10.181	−102.302	−94.688	9.892
600	52.384	126.839	101.217	15.373	−103.584	−93.039	8.100
700	53.346	134.988	105.473	20.661	−109.465	−90.400	6.746
800	54.308	142.176	109.620	26.045	−110.310	−87.616	5.721
900	55.271	148.627	113.602	31.523	−164.074	−83.658	4.855
1000	56.191	154.498	117.402	37.096	−163.312	−74.763	3.905
1100	57.153	159.900	121.023	42.764	−162.439	−65.949	3.132
1200	58.074	164.912	124.474	48.525	−161.459	−57.220	2.491
1300	59.036	169.599	127.767	54.382	−160.375	−48.577	1.952
1400	59.957	174.008	130.914	60.332	−159.206	−40.020	1.493
1500	60.877	178.176	133.927	66.374	−157.962	−31.550	1.099
1600	61.714	182.132	136.817	72.503	−156.653	−23.164	0.756
1700	62.551	185.898	139.595	78.716	−155.288	−14.863	0.457
1800	63.388	189.497	142.268	85.013	−153.869	−6.643	0.193

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K)$ = [100.795] $J·K^{-1}·mol^{-1}$
T_{fus} = 1386.5 ± 1.5 K

$\Delta_f H°(298.15\ K)$ = [84.064] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 18.83 ± 6.3 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(PbS,l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(1386.5 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity of PbS(l) is estimated to be 16.0 $cal·K^{-1}·mol^{-1}$. This appears reasonable as the $C_p°$ value for PbO(l) is 15.535 $cal·K^{-1}·mol^{-1}$.[12] A glass transition is assumed at 900 K. Below this temperature, the heat capacity values used are those of PbS(cr). $S°$(298.15 K) is calculated in a manner similar to that used for $\Delta_f H°$(298.15 K).

Fusion Data

Employing cryoscopic measurements, Pelton and Flengas[1] and Bell and Flengas[2] determined the melting point of PbS to be 1113.4°C and 1111.9°C, respectively. Pelton and Flengas[1] estimated an accuracy of ±1°C. Miller and Komarek,[3] in studying the retrograde solubility in the Pb–S system, reported T_{fus} = 1113.3 ± 0.5°C. The latter authors have summarized many early determinations of T_{fus} which were in the range 1103–1135°C. We adopt 1386.5 ± 1.5 K for T_{fus} of PbS.

Kelley[4] adopted $\Delta_{fus}H°$ = 4.150 $kcal·mol^{-1}$ based on melting point data obtained by Friedrich[5] for the PbS–Cu_2S system and by Truthe[6] for the PbS–$PbCl_2$ system. Maier[7] recalculated $\Delta_{fus}H°$ from Friedrich's data and obtained 4.155 $kcal·mol^{-1}$. Kelley[4] also calculated $\Delta_{fus}H°$ = 5.03 $kcal·mol^{-1}$ from data on the PbS–Ag_2S system obtained by Friedrich. Other inconclusive works are discussed by Kelley.[4] In the preceding calculations, $\Delta_{fus}H°$ was derived from a graph of log × versus $1/T$ where × is the mole fraction of PbS in the melt and T is the liquidus temperature.

We calculate a $\Delta_{fus}H°$ value for each melting point composition data pair and plot this value against ΔT, the melting point depression of PbS. The resulting plot is extrapolated to $\Delta T = 0$ to obtain $\Delta_{fus}H°$. Friedrich's data then yields $\Delta_{fus}H°$ = 4.33 ± 0.15 $kcal·mol^{-1}$. Truthe's data has considerable scatter but indicates a value of 4 6 $kcal·mol^{-1}$ for $\Delta_{fus}H°$. An analysis of the data reported by Kohlmeyer and Monzer[8] for the PbS–PbO system yields $\Delta_{fus}H°$ = 5 ± 1 $kcal·mol^{-1}$. Unfortunately, these three studies necessitate long extrapolations as the ΔT values are in the range 60 550 K. However, these three binary systems form simple, single eutectic phase diagrams and all are consistent with a $\Delta_{fus}H°$ value of 4.5 $kcal·mol^{-1}$.

Recent work by Pelton and Flengas[1] on PbS alkali halide systems involved ΔT values of 2 17 K so that a much shorter extrapolation is possible. An analysis of their data is tabulated below.

System	Data Points	$\Delta_{fus}H°$, $kcal·mol^{-1}$
PbS–NaCl	3	8.5
PbS–KCl	10	4.5
PbS–RbCl	2	4.3
PbS–CsCl	2	4.6

Even in the PbS KCl system, the scatter is such that it is impossible to precisely define $\Delta_{fus}H°$. We adopt a value of $\Delta_{fus}H°$ = 4.5 ± 1.5 $kcal·mol^{-1}$. This value is consistent with all systems discussed above except for PbS–NaCl.

It should be noted that our analyses treated all systems as though no association, dissociation, or compound formation occurs in the melt. It is possible that the occurrence of any or all of these factors would cause the data to be consistent with a $\Delta_{fus}H°$ which might be larger than the adopted value and even outside our uncertainty limits. For example, Pelton and Flengas[1] discussed their results in the PbS alkali halide systems in terms of an estimated $\Delta_{fus}H°$ = 8.7 $kcal·mol^{-1}$. Their conclusions need modifications with use of our adopted $\Delta_{fus}H°$ = 4.5 $kcal·mol^{-1}$. In addition Blachnik and Kluge[9] have compared SnS and PbS; a difficulty arises in that PbS does not have the same crystal structure as GeS and SnS.[9] Thus, $\Delta_{fus}S°$ is not necessarily expected to the same for all three species.

Decomposition Data

Kohlmeyer[10,11] reported that, although PbS(l) had an apparent boiling point of 1617 K, the vaporization did not yield solely PbS(g). Decomposition occurred to yield sulfide molecules in the melt which were rich in Pb. The temperature at which the fugacity of PbS(g) is 1 atm for PbS(l) = PbS(g) is calculated to be 1593 K. A similar calculation for the reaction PbS(l) = Pb(l) + 1/2 S S_2(g) yields 1999 K.

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Continued on page 1847

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
298.15	49.438	100.795	100.795	0.	−84.064	−85.242	14.934
300	49.455	101.101	100.796	0.091	−84.064	−85.250	14.843
400	50.459	115.459	102.746	5.085	−86.396	−85.544	11.171
500	51.463	126.827	106.464	10.181	−88.042	−85.153	8.896
600	52.384	136.291	110.668	15.373	−89.323	−84.449	7.352
700	53.346	144.440	114.924	20.661	−95.205	−82.755	6.175
800	54.308	151.627	119.071	26.045	−96.049	−80.916	5.283
900	55.271	158.078	123.053	31.522	−149.814	−77.904	4.521
900.000	55.271	158.078	123.053	31.522	GLASS <--> LIQUID		
900.000	66.944	158.078	123.053	31.522	TRANSITION		
1000	66.944	165.131	126.914	38.217	−147.930	−70.014	3.657
1100	66.944	171.512	130.683	44.911	−146.032	−62.315	2.959
1200	66.944	177.336	134.332	51.606	−144.118	−54.788	2.385
1300	66.944	182.695	137.849	58.300	−142.197	−47.422	1.905
1386.500	66.944	187.007	140.782	64.091	--- CRYSTAL <--> LIQUID ---		
1400	66.944	187.656	141.231	64.994	−140.283	−40.204	1.500
1500	66.944	192.275	144.482	71.689	−138.386	−33.122	1.153
1600	66.944	196.595	147.606	78.383	−136.513	−26.165	0.854
1700	66.944	200.654	150.608	85.078	−134.667	−19.325	0.594
1800	66.944	204.480	153.495	91.772	−132.850	−12.593	0.365
1900	66.944	208.099	156.275	98.466	−131.065	−5.961	0.164
2000	66.944	211.533	158.953	105.161	−129.312	0.578	−0.015

PREVIOUS: CURRENT: June 1973

0 to 1386.5 K crystal
above 1386.5 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−11.511	−98.545	−98.545	INFINITE
100	39.748	41.296	133.734	−9.244	−98.734	−97.928	51.152
200	47.614	71.920	95.823	−4.781	−98.437	−97.239	25.396
298.15	49.438	91.343	91.343	0.	−98.324	−96.685	16.939
300	49.455	91.649	91.344	0.091	−98.324	−96.675	16.833
400	50.459	106.008	93.295	5.085	−100.657	−96.024	12.539
500	51.463	117.375	97.013	10.181	−102.302	−94.688	9.892
600	52.384	126.839	101.217	15.373	−103.584	−93.039	8.100
700	53.346	134.988	105.473	20.661	−109.465	−90.400	6.746
800	54.308	142.176	109.620	26.045	−110.310	−87.616	5.721
900	55.271	148.627	113.602	31.523	−164.074	−83.658	4.855
1000	56.191	154.498	117.402	37.096	−163.312	−74.763	3.905
1100	57.153	159.900	121.023	42.764	−162.439	−65.949	3.132
1200	58.074	164.912	124.474	48.525	−161.459	−57.220	2.491
1300	59.036	169.599	127.767	54.382	−160.375	−48.577	1.952
1386.500	59.832	173.428	130.497	59.523	CRYSTAL <--> LIQUID		
1386.500	66.944	187.007	130.497	78.351	TRANSITION		
1400	66.944	187.656	131.045	79.255	−140.283	−40.204	1.500
1500	66.944	192.275	134.975	85.949	−138.386	−33.122	1.153
1600	66.944	196.595	138.693	92.644	−136.513	−26.165	0.854
1700	66.944	200.654	142.219	99.338	−134.667	−19.325	0.594
1800	66.944	204.480	145.573	106.033	−132.850	−12.593	0.365
1900	66.944	208.099	148.769	112.727	−131.065	−5.961	0.164
2000	66.944	211.533	151.823	119.421	−129.312	0.578	−0.015

PREVIOUS: CURRENT: June 1973

$S°(298.15\ K) = 251.41 \pm 0.21\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 133.66 \pm 6.3\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 131.80 \pm 6.3\ kJ·mol^{-1}$

	Electronic State and Molecular Constants (σ=1)						
State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å
X 0$^+$	0	1	429.40	1.30	0.11633	0.000426	2.287
a 1	14821.9	2	285.9	0.88	0.09267	0.000374	2.562
A 0$^+$	18768.9	1	260.83	0.363	0.09634	0.000262	2.513
B 1	21774.5	2	282.17	0.856	0.09992	0.000602	2.467
C 0$^+$	23150.7	1	303.93	1.436	[0.09561]	[0.000347]	[2.522]
C' 1	24952.3	2	283.95	1.171	[0.09358]	[0.000297]	[2.549]
D 1	29587.4	2	297.83	1.365	0.10160	0.00064	2.447
E 0$^+$	34000	1	[262.32]	[1.114]	[0.09095]	[0.000429]	[2.585]

Enthalpy of Formation

Vago and Barrow[1] observed the convergence in the E–X system at 2715 Å. The dissociation energy for PbS(g) is calculated to be 81.85 ± 0.40 kcal·mol^{-1}. Barrow *et al.*[2] analyzed the PbS absorption spectrum in terms of type C coupling and assigned the electronically excited E state to be 0$^+$. If the non–crossing rule is applicable,[2] then the most likely dissociation products are $Pb(^3P_1)$ and $S(^3P_1)$. Using auxiliary data,[3] $\Delta_f H°$(PbS, g, 298.15 K) = 32.00 ± 0.40 kcal·mol^{-1}.

Colin and Drowart[4] have studied the sublimation and dissociation of PbS by means of a Knudsen effusion cell coupled with a mass spectrometer. A 2nd and 3rd law analysis by Colin and Drowart[4] of four sets of experiments (865–1100 K) yielded an average value of 55.7 ± 1.4 kcal·mol^{-1} for the enthalpy of sublimation. It is anticipated that this result is roughly 0.5 kcal·mol^{-1} too large since the Gibbs energy functions for the sublimation used by Colin and Drowart[4] are approximately 0.5 cal·K^{-1}mol^{-1} greater than those presently adopted at 1000 K.[3]

Colin and Drowart[4] presented data for 13 experiments in which either Pb, S_2 or both Pb and S_2 partial pressures were measured in addition the PbS partial pressure. The missing pressure is calculated using the formula $[P(Pb)/P(S_2)][M_r(S_2)/M_r(Pb)]^{1/2} = 2$ as in Colin and Drowart.[4]

Source	Reaction*	T/K	Data Points	Method	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K) kcal·mol^{-1}
4	A	990–1043	5	calc. $P(S_2)$	30.20 ± 14.63	29.04	−1.1 ± 14.3	33.12
	A	979–1118	4	calc. P(Pb)	36.48 ± 10.22	28.31	−7.9 ± 9.9	33.86
	A	1012–1182	4	all P meas.	21.97 ± 4.67	29.32	6.8 ± 4.3	32.85
	B	979–1182	13*	Knudsen–mass spec.	55.25 ± 0.69	55.55	0.3 ± 0.7	32.05
5	B	1123–1268	12*	Entrainment	59.48 ± 0.66	55.00	−3.6 ± 0.5	31.50
6	B	878–1069	6	Knudsen	55.38 ± 0.44	54.88	−0.5 ± 0.4	31.38
7	B	776–927	**	Langmuir	53.16	57.24	4.8	33.74
8	B	825–1025	**		54.56	54.95	0.4	31.45
9	B	1048–1193	10	Knudsen	57.66 ± 1.16	56.12	−1.3 ± 1.0	32.62
10	B	1113–1378	11	Entrainment	57.27 ± 1.35	54.34	−2.3 ± 1.1	30.84
11	B	877–1020	12	torsion–effusion	55.99 ± 0.87	54.55	−1.5 ± 0.9	31.05
			17*	torsion–effusion	57.71 ± 0.53	54.55	−3.2 ± 0.5	31.05
	B	860–975	20	torsion–Langmuir	53.58 ± 1.94	54.68	1.2 ± 2.2	31.18
			7	torsion–Langmuir	53.69 ± 0.70	54.55	0.9 ± 0.7	31.05

* A) PbS(g) = Pb(g) + 1/2 S_2(g) B) PbS(cr) = PbS(g)

* One point rejected due to statistical test. ** Actual data not presented, smoothed data used.

The value adopted for $\Delta_f H°$(PbS, g, 298.15 K) is 31.5 ± 1.5 kcal·mol^{-1}. Most of the uncertainty is attributable to the possible decomposition and/or reaction during sublimation. Colin and Drowart[4] and Isakova *et al.*[10] considered the effect of decomposition whereas many of the other investigators analyzed their data in terms of PbS(g) formation only. In addition, Hansen and Munir[11] attest to the congruency of sublimation using x-ray observations on samluccirclples which had lost at least 30% of their initial weight as a result of heating. The adopted $\Delta_f H°$(298.15 K) is somewhat of a compromise between the spectroscopic work,[1] the mass spectrometric work[4] and the bulk of the sublimation studies. Corruccirclespondingly, $D_0°$(PbS, g) = 82.4 ± 1.5 kcal·mol^{-1}.

$D_0°$(PbS, g) = 86.5 kcal·mol^{-1} is calculated by applying the Hildenbrand formula[12] to the linear Birge–Sponer extrapolation of the ground state vibrational levels. Using auxiliary data,[3] $\Delta_f H°$(298.15 K) = 27.4 kcal·mol^{-1} is obtained.

Continued on page 1847

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}mol^{-1})	$S°$ (J·K^{-1}mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−9.430	133.656	133.656	INFINITE
100	29.787	216.077	281.169	−6.509	134.121	117.448	−61.349
200	33.139	237.771	254.569	−3.360	133.104	101.132	−26.413
250	34.305	245.299	251.986	−1.672	132.467	93.211	−19.475
298.15	35.085	251.412	251.412	0.	131.796	85.711	−15.016
300	35.110	251.629	251.413	0.065	131.769	85.425	−14.874
350	35.671	257.086	251.842	1.835	131.020	77.759	−11.605
400	36.073	261.877	252.803	3.629	128.008	70.292	−9.179
450	36.370	266.144	254.053	5.441	126.497	63.159	−7.331
500	36.596	269.988	255.457	7.265	124.902	56.210	−5.872
600	36.912	276.690	258.454	10.942	122.104	42.739	−3.721
700	37.121	282.397	261.477	14.644	114.638	30.517	−2.277
800	37.272	287.364	264.409	18.364	112.130	18.673	−1.219
900	37.386	291.761	267.208	22.097	56.621	8.216	−0.477
1000	37.477	295.705	269.864	25.841	55.553	2.895	−0.151
1100	37.554	299.280	272.378	29.592	54.509	−2.320	0.110
1200	37.620	302.551	274.758	33.351	53.487	−7.441	0.324
1300	37.679	305.564	277.014	37.116	52.479	−12.477	0.501
1400	37.734	308.359	279.154	40.887	51.469	−17.436	0.651
1500	37.785	310.964	281.189	44.663	50.447	−22.322	0.777
1600	37.836	313.404	283.127	48.444	49.407	−27.140	0.886
1700	37.889	315.699	284.976	52.230	48.345	−31.891	0.980
1800	37.945	317.867	286.744	56.022	47.259	−36.580	1.062
1900	38.008	319.920	288.436	59.819	46.147	−41.207	1.133
2000	38.081	321.871	290.060	63.624	45.010	−45.776	1.196
2100	38.166	323.731	291.619	67.436	−133.372	−43.171	1.074
2200	38.266	325.509	293.119	71.257	−134.166	−38.858	0.923
2300	38.386	327.213	294.565	75.090	−135.047	−34.506	0.784
2400	38.527	328.849	295.960	78.935	−136.013	−30.115	0.655
2500	38.693	330.425	297.307	82.796	−137.064	−25.681	0.537
2600	38.887	331.946	298.610	86.675	−138.195	−21.203	0.426
2700	39.112	333.418	299.872	90.574	−139.398	−16.681	0.323
2800	39.368	334.845	301.096	94.498	−140.669	−12.113	0.226
2900	39.659	336.232	302.284	98.449	−141.997	−7.499	0.135
3000	39.986	337.581	303.438	102.431	−143.375	−2.837	0.049
3100	40.349	338.898	304.560	106.447	−144.791	1.871	−0.032
3200	40.750	340.186	305.654	110.502	−146.235	6.625	−0.108
3300	41.189	341.446	306.719	114.599	−147.696	11.424	−0.181
3400	41.666	342.683	307.759	118.741	−149.164	16.268	−0.250
3500	42.179	343.898	308.774	122.933	−150.628	21.155	−0.316
3600	42.729	345.094	309.766	127.178	−152.077	26.083	−0.378
3700	43.314	346.272	310.737	131.480	−153.502	31.052	−0.438
3800	43.932	347.436	311.688	135.842	−154.892	36.059	−0.496
3900	44.581	348.585	312.619	140.268	−156.239	41.101	−0.550
4000	45.259	349.722	313.532	144.759	−157.536	46.178	−0.603
4100	45.964	350.848	314.429	149.320	−158.773	51.286	−0.653
4200	46.692	351.965	315.309	153.953	−159.946	56.424	−0.702
4300	47.440	353.072	316.175	158.659	−161.047	61.589	−0.748
4400	48.206	354.172	317.026	163.442	−162.072	66.778	−0.793
4500	48.985	355.264	317.863	168.301	−163.017	71.990	−0.836
4600	49.774	356.349	318.688	173.239	−163.877	77.222	−0.877
4700	50.570	357.428	319.501	178.256	−164.651	82.472	−0.917
4800	51.368	358.501	320.302	183.353	−165.337	87.738	−0.955
4900	52.166	359.568	321.093	188.530	−165.932	93.016	−0.992
5000	52.959	360.630	321.873	193.786	−166.437	98.306	−1.027
5100	53.745	361.687	322.643	199.121	−166.851	103.605	−1.061
5200	54.519	362.738	323.404	204.535	−167.175	108.912	−1.094
5300	55.279	363.784	324.156	210.025	−167.410	114.223	−1.126
5400	56.022	364.824	324.900	215.590	−167.559	119.539	−1.156
5500	56.744	365.858	325.635	221.228	−167.622	124.856	−1.186
5600	57.443	366.887	326.363	226.938	−167.603	130.174	−1.214
5700	58.117	367.910	327.082	232.716	−167.504	135.490	−1.242
5800	58.764	368.926	327.795	238.561	−167.329	140.805	−1.268
5900	59.382	369.936	328.501	244.468	−167.081	146.115	−1.294
6000	59.969	370.939	329.200	250.436	−166.764	151.421	−1.318

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K) = [281.334]\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 336.4 \pm 19.2\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 332.6 \pm 19.2\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$[^3\Sigma_g^-]$	0	[3]

$\omega_e = 256.5\ cm^{-1}$ $\omega_e x_e = 2.96\ cm^{-1}$ $\sigma = 2$

$B_e = [0.01727]\ cm^{-1}$ $\alpha = [0.00020]\ cm^{-1}$ $r_e = [3.08]$ Å

Enthalpy of Formation

The enthalpy of formation is calculated from the dissociation energy of $Pb_2(g)$ as reported by Gaydon.[1]

Heat Capacity and Entropy

The values of ω_e and $\omega_e x_e$ are obtained from Herzberg.[2] Those for B_e and α_e are estimated according to the method suggested by Herzberg. The bond distance (r_e) is calculated from the moment of inertia, $I = 1630 \times 10^{-40}$ g cm^2, estimated by Kelley and King.[3] The ground state configuration is assumed to be $^3\Sigma$ by comparison to that for $Si_2(g)$ reported by Douglas.[4]

References

[1]A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, (1953).
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[3]K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592, 149 pp. (1961).
[4]A. E. Douglas, Can. J. Phys. **33**, 801 (1955).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−10.004	336.381	336.381	INFINITE
100	32.267	243.142	313.231	−7.009	335.843	318.895	−166.574
200	35.750	266.807	284.681	−3.575	334.228	302.576	−79.025
250	36.473	274.869	281.939	−1.768	333.425	294.755	−61.586
298.15	36.921	281.334	281.334	0.	332.628	287.380	−50.348
300	36.935	281.562	281.335	0.068	332.597	287.099	−49.988
350	37.258	287.281	281.785	1.924	331.745	279.583	−41.725
400	37.502	292.273	282.791	3.793	330.864	272.191	−35.544
450	37.697	296.702	284.095	5.673	329.951	264.911	−30.750
500	37.861	300.682	285.558	7.562	329.005	257.735	−26.925
600	38.133	307.610	288.673	11.362	327.027	243.665	−21.213
700	38.362	313.506	291.810	15.187	315.209	231.532	−17.277
800	38.568	318.642	294.850	19.034	313.021	219.728	−14.347
900	38.761	323.196	297.751	22.900	310.917	208.194	−12.083
1000	38.945	327.290	300.504	26.786	308.893	196.889	−10.284
1100	39.123	331.010	303.111	30.689	306.947	185.784	−8.822
1200	39.298	334.422	305.580	34.610	305.080	174.852	−7.611
1300	39.470	337.574	307.921	38.549	303.277	164.073	−6.593
1400	39.640	340.505	310.145	42.504	301.508	153.432	−5.725
1500	39.808	343.246	312.261	46.477	299.751	142.916	−4.977
1600	39.976	345.820	314.279	50.466	297.996	132.518	−4.326
1700	40.142	348.249	316.207	54.472	296.231	122.229	−3.756
1800	40.308	350.548	318.051	58.494	294.450	112.045	−3.251
1900	40.473	352.732	319.819	62.533	292.649	101.961	−2.803
2000	40.638	354.812	321.517	66.589	290.825	91.972	−2.402
2100	40.803	356.799	323.151	70.661	−65.467	96.305	−2.395
2200	40.967	358.701	324.724	74.750	−66.564	104.033	−2.470
2300	41.131	360.525	326.241	78.855	−67.821	111.815	−2.539
2400	41.295	362.279	327.706	82.976	−69.243	119.655	−2.604
2500	41.459	363.968	329.123	87.114	−70.831	127.558	−2.665
2600	41.622	365.598	330.495	91.268	−72.584	135.528	−2.723
2700	41.785	367.172	331.824	95.438	−74.496	143.568	−2.777
2800	41.949	368.694	333.114	99.625	−76.562	151.681	−2.830
2900	42.112	370.169	334.366	103.828	−78.771	159.872	−2.880
3000	42.275	371.599	335.584	108.047	−81.113	168.140	−2.928
3100	42.438	372.988	336.768	112.283	−83.576	176.489	−2.974
3200	42.601	374.338	337.921	116.535	−86.146	184.919	−3.018
3300	42.764	375.652	339.045	120.803	−88.810	193.430	−3.062
3400	42.927	376.931	340.140	125.087	−91.554	202.024	−3.104
3500	43.089	378.177	341.209	129.388	−94.364	210.700	−3.145
3600	43.252	379.393	342.253	133.705	−97.227	219.456	−3.184
3700	43.415	380.581	343.273	138.039	−100.129	228.293	−3.223
3800	43.578	381.741	344.270	142.388	−103.058	237.208	−3.261
3900	43.740	382.875	345.245	146.754	−106.003	246.201	−3.297
4000	43.903	383.984	346.200	151.136	−108.954	255.269	−3.333
4100	44.066	385.070	347.135	155.535	−111.900	264.411	−3.369
4200	44.228	386.134	348.051	159.949	−114.833	273.625	−3.403
4300	44.391	387.177	348.949	164.380	−117.745	282.909	−3.437
4400	44.553	388.199	349.829	168.828	−120.629	292.260	−3.470
4500	44.716	389.202	350.693	173.291	−123.480	301.676	−3.502
4600	44.878	390.187	351.541	177.771	−126.292	311.155	−3.533
4700	45.041	391.154	352.373	182.267	−129.060	320.694	−3.564
4800	45.204	392.104	353.191	186.779	−131.783	330.292	−3.594
4900	45.366	393.037	353.995	191.307	−134.456	339.947	−3.624
5000	45.529	393.955	354.785	195.852	−137.078	349.655	−3.653
5100	45.691	394.859	355.562	200.413	−139.647	359.415	−3.681
5200	45.854	395.747	356.326	204.990	−142.162	369.225	−3.709
5300	46.016	396.622	357.078	209.584	−144.623	379.084	−3.736
5400	46.179	397.484	357.819	214.194	−147.029	388.987	−3.763
5500	46.341	398.333	358.548	218.820	−149.381	398.935	−3.789
5600	46.503	399.169	359.266	223.462	−151.680	408.926	−3.814
5700	46.666	399.994	359.973	228.120	−153.926	418.956	−3.839
5800	46.828	400.807	360.670	232.795	−156.121	429.026	−3.864
5900	46.991	401.609	361.357	237.486	−158.263	439.133	−3.888
6000	47.153	402.400	362.034	242.193	−160.359	449.276	−3.911

PREVIOUS: September 1963 (1 atm) CURRENT: September 1963 (1 bar)

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Continued from Page 1845

Heat Capacity and Entropy

The tabulated electronic and molecular constants are taken from Rosen[13] as reviewed and compiled by Barrow. The constants came from the work of Bell and Harvey,[14] Rochester and Howell,[15] Vago and Barrow[1] and Barrow *et al.*[2] The state designations are those which are consistent with type C coupling. In this case, the state designations Σ, Π, etc., no longer have meaning. The estimated values in the tabulation are derived from comparisons of known values in the PbS(g) and PbO(g) systems.[3] The functions are calculated from the partition function $Q = Q_t \Sigma Q_r^i Q_v^i g_i \exp(-C_2\epsilon_i/T)$; the values for Q_r^i and Q_v^i were calculated with first order anharmonic corrections.

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REFERENCE STATE

0	to	312.65 K	crystal
312.5	to	970.385 K	liquid
above		970.385 K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−7.490	0.	0.	0.
100	25.510	47.022	101.811	−5.479	0.	0.	0.
200	27.447	65.316	79.458	−2.828	0.	0.	0.
298.15	31.062	76.778	76.778	0.	0.	0.	0.
300	31.188	76.971	76.779	0.058	0.	0.	0.
312.650	32.401	78.284	76.813	0.460	____ CRYSTAL <--> LIQUID ____		
312.650	32.307	85.300	76.813	2.653	TRANSITION		
400	31.715	93.188	79.566	5.449	0.	0.	0.
500	31.197	100.207	83.020	8.593	0.	0.	0.
600	30.850	105.861	86.371	11.694	0.	0.	0.
700	30.674	110.601	89.503	14.769	0.	0.	0.
800	30.669	114.695	92.402	17.835	0.	0.	0.
900	30.835	118.315	95.084	20.908	0.	0.	0.
970.385	31.053	120.645	96.854	23.086	___ LIQUID <--> IDEAL GAS ___		
970.385	20.786	194.623	96.854	94.873	FUGACITY = 1 bar		
1000	20.786	195.248	99.759	95.489	0.	0.	0.
1100	20.786	197.229	108.531	97.567	0.	0.	0.
1200	20.787	199.037	115.999	99.646	0.	0.	0.
1300	20.790	200.701	122.452	101.725	0.	0.	0.
1400	20.795	202.242	128.097	103.804	0.	0.	0.
1500	20.805	203.677	133.088	105.884	0.	0.	0.
1600	20.821	205.020	137.542	107.965	0.	0.	0.
1700	20.847	206.283	141.549	110.048	0.	0.	0.
1800	20.886	207.476	145.179	112.135	0.	0.	0.
1900	20.941	208.607	148.488	114.226	0.	0.	0.
2000	21.015	209.683	151.521	116.324	0.	0.	0.
2100	21.110	210.710	154.315	118.430	0.	0.	0.
2200	21.231	211.695	156.901	120.547	0.	0.	0.
2300	21.379	212.642	159.304	122.677	0.	0.	0.
2400	21.558	213.555	161.546	124.824	0.	0.	0.
2500	21.769	214.439	163.644	126.989	0.	0.	0.
2600	22.016	215.298	165.614	129.178	0.	0.	0.
2700	22.294	216.134	167.470	131.393	0.	0.	0.
2800	22.616	216.950	169.222	133.638	0.	0.	0.
2900	22.980	217.750	170.882	135.917	0.	0.	0.
3000	23.389	218.536	172.457	138.235	0.	0.	0.
3100	23.846	219.310	173.956	140.596	0.	0.	0.
3200	24.355	220.075	175.385	143.006	0.	0.	0.
3300	24.850	220.827	176.751	145.453	0.	0.	0.
3400	25.442	221.578	178.058	147.966	0.	0.	0.
3500	26.088	222.324	179.312	150.542	0.	0.	0.
3600	26.766	223.067	180.517	153.179	0.	0.	0.
3700	27.516	223.810	181.677	155.893	0.	0.	0.
3800	28.322	224.555	182.796	158.684	0.	0.	0.
3900	29.184	225.302	183.876	161.559	0.	0.	0.
4000	30.060	226.048	184.921	164.507	0.	0.	0.
4100	31.023	226.802	185.933	167.561	0.	0.	0.
4200	32.038	227.561	186.915	170.714	0.	0.	0.
4300	33.104	228.328	187.869	173.970	0.	0.	0.
4400	33.569	229.027	188.791	177.038	0.	0.	0.
4500	34.345	229.761	189.690	180.318	0.	0.	0.
4600	35.326	230.521	190.569	183.780	0.	0.	0.
4700	36.365	231.292	191.427	187.364	0.	0.	0.
4800	37.419	232.069	192.266	191.053	0.	0.	0.
4900	38.481	232.851	193.086	194.848	0.	0.	0.
5000	39.145	233.583	193.883	198.498	0.	0.	0.
5100	40.162	234.368	194.669	202.463	0.	0.	0.
5200	41.169	235.158	195.440	206.530	0.	0.	0.
5300	42.161	235.951	196.197	210.697	0.	0.	0.
5400	43.133	236.749	196.941	214.961	0.	0.	0.
5500	44.078	237.549	197.672	219.322	0.	0.	0.
5600	44.545	238.273	198.381	223.394	0.	0.	0.
5700	45.394	239.069	199.088	227.891	0.	0.	0.
5800	46.204	239.866	199.784	232.472	0.	0.	0.
5900	46.972	240.662	200.470	237.131	0.	0.	0.
6000	47.693	241.458	201.147	241.864	0.	0.	0.

PREVIOUS: CURRENT: December 1983 (1 bar)

$S°(298.15\ K) = 76.78 \pm 0.30\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 312.65 \pm 0.1\ K$

$\Delta_f H°(0\ K) = kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 2.19 \pm 0.09\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The thermal functions for Rb(cr) are derived following CODATA recommendations.[1] That is, these functions are based on the previous evaluation of Hultgren *et al.*,[2] Martin,[3,4] and Shpil'rain *et al.*[5] The prime sources of data are: Lien and Phillips (0.19–4.1 K),[6] Filby and Martin (0.4–1.5 K, 3–320 K),[7] McCallum and Silsbee (1.3–12 K),[8] Dauphinee *et al.* (25–300 K),[9] and Martin (0.4–3 K).[4]

Fusion Data

The adopted fusion temperature, $T_{fus} = 312.65 \pm 0.1$ K, is that recommended by Ohse *et al.*[10] based on their analysis of seven experimental studies: Rengade (312.15 ± 0.05 K),[11] Dauphine *et al.* (311.90 ± 0.5 K),[9] Weatherford *et al.* (312.54 K),[12] Filby and Martin (312.65 ± 0.01 K),[7] Basin *et al.* (312.31 ± 0.05 K),[13] Ott *et al.* (312.45 K),[14] and Martin (312.47 K).[4]

The adopted enthalpy of fusion, $\Delta_{fus} H°$, 2.19 ± 0.09 $kJ \cdot mol^{-1}$, is derived from the studies of Rengade,[11] Filby and Martin,[7] and Martin;[4] all three results being within 1 $kcal \cdot mol^{-1}$.

Sublimation Data

Refer to the ideal gas tables for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−7.490	0.	0.	0.
100	25.510	47.022	101.811	−5.479	0.	0.	0.
200	27.447	65.316	79.458	−2.828	0.	0.	0.
250	28.690	71.560	77.272	−1.428	0.	0.	0.
298.15	31.062	76.778	76.778	0.	0.	0.	0.
300	31.188	76.971	76.779	0.058	0.	0.	0.
312.650	32.401	78.284	76.813	0.460	--- CRYSTAL <--> LIQUID ---		
350	35.848	82.132	77.176	1.735	−2.121	0.259	−0.039
400	40.465	87.220	78.114	3.642	−1.806	0.581	−0.076
450	45.082	92.253	79.406	5.781	−1.246	0.848	−0.098
500	49.699	97.242	80.940	8.151	−0.443	1.040	−0.109
600	58.932	107.119	84.482	13.582	1.888	1.134	−0.099

PREVIOUS: CURRENT: December 1983

$S°(298.15\ K)$ = [83.764] $J·K^{-1}·mol^{-1}$
T_{fus} = 312.65 ± 0.1 K

$\Delta_f H°(298.15\ K)$ = [2.184] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 2.19 ± 0.09 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the crystal by adding the enthalpy of fusion and difference in enthalpy, $H°(298.15\ K)$ lndash $H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacity values for Rb(l) are those recommended by Fink and Leibowitz.[1] These authors reviewed the liquid phase heat capacity and enthalpy studies for all alkali metals and recommended a $C_p°$ equation for Rb(l) based on their evaluation of four enthalpy[2-5] and three heat capacity[6-8] experimental studies. These studies provided information in the liquid region up to 1334 K.

The equation recommened by Fink and Liebowitz[1] is $C_p° = 35.494 - 0.012864\ T + 0.85409 \times 10^{-5}\ T^2$ $(J·K^{-1}·mol^{-1})$.

Vaporization Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	32.418	83.764	83.764	0.	2.184	0.102	−0.018
300	32.403	83.965	83.765	0.060	2.187	0.089	−0.015
312.650	32.307	85.300	83.800	0.469	--- CRYSTAL <--> LIQUID ---		
350	32.038	88.932	84.158	1.671	0.	0.	0.
400	31.715	93.188	85.027	3.264	0.	0.	0.
450	31.435	96.907	86.145	4.843	0.	0.	0.
500	31.197	100.207	87.389	6.409	0.	0.	0.
600	30.850	105.861	90.012	9.510	0.	0.	0.
700	30.674	110.601	92.624	12.584	0.	0.	0.
800	30.669	114.695	95.133	15.650	0.	0.	0.
900	30.835	118.315	97.511	18.724	0.	0.	0.
970.385	31.053	120.645	99.105	20.901	----- FUGACITY = 1 bar -----		
1000	31.171	121.580	99.757	21.823	−71.481	2.186	−0.114
1100	31.678	124.573	101.879	24.964	−70.419	9.502	−0.451
1200	32.356	127.358	103.888	28.164	−69.297	16.718	−0.728
1300	33.205	129.980	105.795	31.441	−68.100	23.838	−0.958
1400	34.225	132.477	107.612	34.811	−66.809	30.863	−1.152
1500	35.415	134.878	109.350	38.291	−65.408	37.791	−1.316
1600	36.776	137.206	111.019	41.899	−63.881	44.622	−1.457

PREVIOUS: CURRENT: December 1983

0	to	312.65	K crystal
above		312.65	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.490	0.	0.	0.
100	25.510	47.022	101.811	−5.479	0.	0.	0.
200	27.447	65.316	79.458	−2.828	0.	0.	0.
250	28.690	71.560	77.272	−1.428	0.	0.	0.
298.15	31.062	76.778	76.778	0.	0.	0.	0.
300	31.188	76.971	76.779	0.058	0.	0.	0.
312.650	32.401	78.284	76.813	0.460	___ CRYSTAL <--> LIQUID ___		
312.650	32.307	85.300	76.813	2.653	TRANSITION		
350	32.038	88.932	77.917	3.855	0.	0.	0.
400	31.715	93.188	79.566	5.449	0.	0.	0.
450	31.435	96.907	81.291	7.028	0.	0.	0.
500	31.197	100.207	83.020	8.593	0.	0.	0.
600	30.850	105.861	86.371	11.694	0.	0.	0.
700	30.674	110.601	89.503	14.769	0.	0.	0.
800	30.669	114.695	92.402	17.835	0.	0.	0.
900	30.835	118.315	95.084	20.908	0.	0.	0.
970.385	31.053	120.645	96.854	23.086	----- FUGACITY = 1 bar -----		
1000	31.171	121.580	97.573	24.007	−71.481	2.186	−0.114
1100	31.678	124.573	99.893	27.148	−70.419	9.502	−0.451
1200	32.356	127.358	102.067	30.349	−69.297	16.719	−0.728
1300	33.205	129.980	104.114	33.625	−68.100	23.839	−0.958
1400	34.225	132.477	106.052	36.995	−66.809	30.863	−1.152
1500	35.415	134.878	107.894	40.476	−65.408	37.791	−1.316
1600	36.776	137.206	109.653	44.084	−63.881	44.622	−1.457

PREVIOUS: CURRENT: December 1983

IP(Rb, g) = 33690.81 ± 0.01 cm^{-1}
$S°(298.15\ K)$ = 170.093 ± 0.025 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(298.15\ K)$ = 82.2 ± 0.4 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 80.9 ± 0.4 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2
$^2P_{1/2}$	12578.96	2
$^2P_{3/2}$	12816.56	4
$^2D_{5/2}$	19355.01	6
$^2D_{3/2}$	19355.45	4
.	.	.
.	.	.
.	.	.
$^2P_{3/2}$	33671.07	4
IP	33690.81	

Enthalpy of Formation

The enthalpy of formation of rubidium gas is chosen to be the value recommended by CODATA[1]. This value was obtained from 2nd and 3rd law analysis of the vapor pressure studies reported by Hultgren *et al.*[2] As stated by CODATA,[1] the correction for the presence of the dimer in the vapor phase was made using a virial treatment, since the dissociation energy of $Rb_2(g)$ was not well established.

The six studies used by Hultgren *et al.*[1] are: Volyak *et al.* (594–970 K),[3] Achener (745–1260 K),[4] Tepper *et al.* (716– 1353 K),[5] Buck and Pauly (307–363 K),[6] Killian (312–377 K),[7] and Scott (365–400 K).[8]

Heat Capacity and Entropy

The thermal functions for the five alkali metal monatomic gases are calculated by the same procedure. Oberved and estimated atomic energy levels are included in the partition function calculation, using an ionization potential lowering (IP–kT) technique as the cutoff procedure in the energy level summation.[11]

The lowest lying levels for these metals [14904 cm^{-1} (Li), 16956 cm^{-1} (Na), 12985 cm^{-1} (K), 12578 cm^{-1} (Rb), and 11178 cm^{-1}(Cs)] do not contribute to the thermal functions below ~1000 K; there is only a translational contribution below this temperature. Above this approximate temperature, the thermal functions become increasingly sensitive to the partition function cutoff procedure used, due to the combined effect of the observation of atomic energy levels of high principal quantum number and a low ionization potential. Energy levels have been observed up to n = 42 (Li), 59(Na), 79(K), 77(Rb), and 73(Cs). However, not all predicted levels have been observed for each of these principal quantum numbers. The ionization potentials vary from 43487.29 cm^{-1} for Li to 31406.1 cm^{-1} for Cs. In calculating the thermal functions with the inclusion of missing levels up to the high principal quantum numbers just mentioned, the Gibbs energy functions show significant differences (depending on the cutoff procedure) above 3000 K.[11]

The atomic energy levels have been taken from the compilation of Moore.[9, 10] Our calculated values for the thermal functions are similar to those recommended by CODATA.[1] They do differ for two reasons, however. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, the entropies at 298.15 K for all alkali metal gases differs by ~0.004 $J·K^{-1}·mol^{-1}$, presumably due to the use of slightly different values for auxiliary data.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	82.192	82.192	INFINITE
100	20.786	147.386	188.573	−4.119	82.260	72.224	−37.726
200	20.786	161.794	171.994	−2.040	81.688	62.393	−16.295
250	20.786	166.432	170.435	−1.001	81.327	57.609	−12.037
298.15	20.786	170.093	170.093	0.	80.900	53.078	−9.299
300	20.786	170.222	170.094	0.038	80.881	52.906	−9.212
350	20.786	173.426	170.347	1.078	78.122	48.550	−7.246
400	20.786	176.202	170.909	2.117	77.568	44.363	−5.793
450	20.786	178.650	171.636	3.156	77.029	40.245	−4.671
500	20.786	180.840	172.448	4.196	76.503	36.186	−3.780
600	20.786	184.630	174.172	6.274	75.480	28.219	−2.457
700	20.786	187.834	175.901	8.353	74.484	20.421	−1.524
800	20.786	190.609	177.570	10.431	73.497	12.766	−0.834
900	20.786	193.058	179.157	12.510	72.502	5.234	−0.304
970.385	20.786	194.623	180.223	13.973	----- FUGACITY = 1 bar -----		
1000	20.786	195.248	180.659	14.589	0.	0.	0.
1100	20.786	197.229	182.077	16.667	0.	0.	0.
1200	20.787	199.037	183.416	18.746	0.	0.	0.
1300	20.790	200.701	184.682	20.825	0.	0.	0.
1400	20.795	202.242	185.882	22.904	0.	0.	0.
1500	20.805	203.677	187.021	24.984	0.	0.	0.
1600	20.821	205.020	188.105	27.065	0.	0.	0.
1700	20.847	206.283	189.137	29.149	0.	0.	0.
1800	20.886	207.476	190.123	31.235	0.	0.	0.
1900	20.941	208.607	191.067	33.326	0.	0.	0.
2000	21.015	209.683	191.971	35.424	0.	0.	0.
2100	21.110	210.710	192.839	37.530	0.	0.	0.
2200	21.231	211.695	193.674	39.647	0.	0.	0.
2300	21.379	212.642	194.478	41.777	0.	0.	0.
2400	21.558	213.555	195.254	43.924	0.	0.	0.
2500	21.769	214.439	196.004	46.090	0.	0.	0.
2600	22.016	215.298	196.729	48.278	0.	0.	0.
2700	22.294	216.134	197.433	50.493	0.	0.	0.
2800	22.616	216.950	198.115	52.738	0.	0.	0.
2900	22.980	217.750	198.778	55.017	0.	0.	0.
3000	23.389	218.536	199.424	57.335	0.	0.	0.
3100	23.846	219.310	200.053	59.696	0.	0.	0.
3200	24.355	220.075	200.667	62.106	0.	0.	0.
3300	24.850	220.827	201.266	64.553	0.	0.	0.
3400	25.442	221.578	201.852	67.066	0.	0.	0.
3500	26.088	222.324	202.427	69.642	0.	0.	0.
3600	26.766	223.067	202.989	72.279	0.	0.	0.
3700	27.516	223.810	203.542	74.993	0.	0.	0.
3800	28.322	224.555	204.085	77.784	0.	0.	0.
3900	29.184	225.302	204.620	80.659	0.	0.	0.
4000	30.060	226.048	205.146	83.607	0.	0.	0.
4100	31.023	226.802	205.665	86.661	0.	0.	0.
4200	32.038	227.561	206.177	89.814	0.	0.	0.
4300	33.104	228.328	206.683	93.070	0.	0.	0.
4400	33.569	229.027	207.177	96.138	0.	0.	0.
4500	34.345	229.761	207.668	99.418	0.	0.	0.
4600	35.326	230.521	208.156	102.880	0.	0.	0.
4700	36.365	231.292	208.640	106.464	0.	0.	0.
4800	37.419	232.069	209.120	110.154	0.	0.	0.
4900	38.481	232.851	209.596	113.948	0.	0.	0.
5000	39.145	233.583	210.063	117.598	0.	0.	0.
5100	40.162	234.368	210.532	121.563	0.	0.	0.
5200	41.169	235.158	210.998	125.630	0.	0.	0.
5300	42.161	235.951	211.461	129.797	0.	0.	0.
5400	43.133	236.749	211.922	134.062	0.	0.	0.
5500	44.078	237.549	212.381	138.422	0.	0.	0.
5600	44.545	238.273	212.828	142.494	0.	0.	0.
5700	45.394	239.069	213.281	146.991	0.	0.	0.
5800	46.204	239.866	213.733	151.572	0.	0.	0.
5900	46.972	240.662	214.182	156.231	0.	0.	0.
6000	47.693	241.458	214.630	160.964	0.	0.	0.

PREVIOUS: CURRENT: December 1983 (1 bar)

IP(Rb^+, g) = 220048 ± 30 cm^{-1}
$S°(298.15\ K) = 164.330 \pm 0.02\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 485.224\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [490.129]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

$\Delta_f H°(Rb^+, g, 0\ K)$ is calculated from $\Delta_f H°(Rb, g, 0\ K)$[1] using the spectroscopic value of IP(Rb) = 33690.81 ± 0.01 cm^{-1}(403.032 ± .0001 $kJ \cdot mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ \cdot mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ \cdot mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Rb^+, g, 298.15\ K)$ is calculated from $\Delta_f H°(Rb, g, 0\ K)$ by using IP(Rb) with JANAF[1]enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Rb(g), $Rb^+(g)$, and e^-(ref). $\Delta_r H°(Rb \rightarrow Rb^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore[6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state; the first excited state is approximately 126454 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.197	485.224		
100	20.786	141.623	182.810	−4.119			
200	20.786	156.031	166.231	−2.040			
250	20.786	160.669	164.672	−1.001			
298.15	20.786	164.330	164.330	0.	490.129	457.771	−80.200
300	20.786	164.459	164.330	0.038	490.148	457.570	−79.670
350	20.786	167.663	164.583	1.078	488.429	452.364	−67.512
400	20.786	170.438	165.146	2.117	488.914	447.179	−58.396
450	20.786	172.887	165.872	3.156	489.414	441.933	−51.298
500	20.786	175.077	166.685	4.196	489.927	436.630	−45.614
600	20.786	178.866	168.409	6.274	490.983	425.871	−37.075
700	20.786	182.071	170.138	8.353	492.066	414.934	−30.963
800	20.786	184.846	171.807	10.431	493.157	403.841	−26.368
900	20.786	187.294	173.394	12.510	494.241	392.611	−22.787
1000	20.786	189.484	174.896	14.589	423.818	383.448	−20.029
1100	20.786	191.465	176.313	16.667	425.896	379.310	−18.012
1200	20.786	193.274	177.653	18.746	427.975	374.984	−16.323
1300	20.786	194.938	178.919	20.824	430.053	370.483	−14.886
1400	20.786	196.478	180.119	22.903	432.131	365.823	−13.649
1500	20.786	197.912	181.258	24.982	434.209	361.014	−12.572
1600	20.786	199.254	182.341	27.060	436.285	356.067	−11.624
1700	20.786	200.514	183.374	29.139	438.358	350.990	−10.785
1800	20.786	201.702	184.359	31.217	440.429	345.791	−10.035
1900	20.786	202.826	185.302	33.296	442.495	340.477	−9.360
2000	20.786	203.892	186.205	35.375	444.555	335.054	−8.751
2100	20.786	204.906	187.071	37.453	446.606	329.528	−8.197
2200	20.786	205.873	187.904	39.532	448.646	323.906	−7.690
2300	20.786	206.797	188.706	41.610	450.673	318.190	−7.226
2400	20.786	207.682	189.478	43.689	452.684	312.387	−6.799
2500	20.786	208.530	190.223	45.768	454.675	306.500	−6.404
2600	20.786	209.346	190.943	47.846	456.643	300.534	−6.038
2700	20.786	210.130	191.639	49.925	458.586	294.493	−5.697
2800	20.786	210.886	192.313	52.004	460.498	288.380	−5.380
2900	20.786	211.615	192.966	54.082	462.376	282.200	−5.083
3000	20.786	212.320	193.600	56.161	464.215	275.955	−4.805
3100	20.786	213.002	194.215	58.239	466.011	269.650	−4.544
3200	20.786	213.662	194.812	60.318	467.759	263.288	−4.298
3300	20.786	214.301	195.393	62.397	469.469	256.871	−4.066
3400	20.786	214.922	195.959	64.475	471.113	250.404	−3.847
3500	20.786	215.524	196.509	66.554	472.694	243.889	−3.640
3600	20.786	216.110	197.045	68.632	474.215	237.330	−3.444
3700	20.786	216.679	197.568	70.711	475.658	230.729	−3.257
3800	20.786	217.234	198.079	72.790	477.024	224.091	−3.080
3900	20.786	217.774	198.577	74.868	478.307	217.418	−2.912
4000	20.786	218.300	199.063	76.947	479.515	210.712	−2.752
4100	20.786	218.813	199.539	79.025	480.619	203.978	−2.599
4200	20.786	219.314	200.004	81.104	481.623	197.218	−2.453
4300	20.786	219.803	200.458	83.183	482.524	190.436	−2.313
4400	20.786	220.281	200.904	85.261	483.613	183.603	−2.180
4500	20.786	220.748	201.339	87.340	484.491	176.763	−2.052
4600	20.786	221.205	201.766	89.418	485.186	169.914	−1.929
4700	20.786	221.652	202.185	91.497	485.759	163.054	−1.812
4800	20.786	222.090	202.595	93.576	486.227	156.183	−1.700
4900	20.786	222.518	202.997	95.654	486.589	149.303	−1.592
5000	20.786	222.938	203.392	97.733	487.097	142.386	−1.487
5100	20.786	223.350	203.779	99.811	487.289	135.490	−1.388
5200	20.786	223.753	204.159	101.890	487.379	128.591	−1.292
5300	20.786	224.149	204.533	103.969	487.370	121.691	−1.199
5400	20.786	224.538	204.900	106.047	487.262	114.792	−1.110
5500	20.786	224.919	205.260	108.126	487.058	107.896	−1.025
5600	20.786	225.294	205.614	110.204	487.144	100.950	−0.942
5700	20.786	225.662	205.963	112.283	486.804	94.057	−0.862
5800	20.786	226.023	206.306	114.362	486.381	87.170	−0.785
5900	20.786	226.379	206.643	116.440	485.879	80.291	−0.711
6000	20.786	226.728	206.975	118.519	485.302	73.422	−0.639

PREVIOUS: CURRENT: December 1983 (1 bar)

EA(Rb, g) = 0.48592 ± 0.00002 eV
$S°(298.15\ K) = 164.330 \pm 0.005\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 35.308 \pm 0.4\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [27.819]\ kJ \cdot mol^{-1}$

Electronic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0.0	1

Enthalpy of Formation

The enthalpy of formation, at 0 K, for Rb^-(g) is calculated from the adopted electron affinity, EA(Rb, g) = 0.48592 ± 0.00002 eV (46.884 ± 0.002 $kJ \cdot mol^{-1}$). This value, recommended by Hotop and Lineberger,[6] was measured by a tunable laser photodetachment threshold technique.[2] Additional discussion on Rb^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[1,6] Rosenstock *et al.*,[3] and Massey.[4]

$\Delta_f H°(Rb^-, g, 298.15\ K)$ is obtained from $\Delta_f H°$(Rb, g, 0 K) by using EA(Rb, g) with JANAF[5] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Rb^-(g), Rb(g), and e^-(ref). $\Delta_r H°(Rb^- \rightarrow Rb + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[3] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention which excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state configuration for Rb^-(g) is given by Hotop and Lineberger[1,6] and Rosenstock *et al.*[3] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	35.308		
100	20.786	141.623	182.810	−4.119			
200	20.786	156.031	166.231	−2.040			
250	20.786	160.669	164.672	−1.001			
298.15	20.786	164.330	164.330	0.	27.819	7.970	−1.396
300	20.786	164.459	164.331	0.038	27.761	7.847	−1.366
350	20.786	167.663	164.584	1.078	23.964	4.917	−0.734
400	20.786	170.438	165.146	2.117	22.370	2.305	−0.301
450	20.786	172.887	165.873	3.156	20.791	−0.109	0.013
500	20.786	175.077	166.685	4.196	19.226	−2.347	0.245
600	20.786	178.866	168.409	6.274	16.125	−6.369	0.555
700	20.786	182.071	170.138	8.353	13.050	−9.875	0.737
800	20.786	184.846	171.807	10.431	9.984	−12.941	0.845
900	20.786	187.295	173.394	12.510	6.910	−15.622	0.907
1000	20.786	189.485	174.896	14.589	−67.670	−15.774	0.824
1100	20.786	191.466	176.314	16.667	−69.748	−10.483	0.498
1200	20.786	193.274	177.653	18.746	−71.827	−5.004	0.218
1300	20.786	194.938	178.919	20.824	−73.906	0.649	−0.026
1400	20.786	196.478	180.119	22.903	−75.985	6.462	−0.241
1500	20.786	197.913	181.258	24.982	−78.065	12.424	−0.433
1600	20.786	199.254	182.341	27.060	−80.146	18.524	−0.605
1700	20.786	200.514	183.374	29.139	−82.230	24.755	−0.761
1800	20.786	201.702	184.359	31.217	−84.316	31.108	−0.903
1900	20.786	202.826	185.302	33.296	−86.407	37.577	−1.033
2000	20.786	203.892	186.205	35.375	−88.505	44.157	−1.153
2100	20.786	204.906	187.072	37.453	−90.611	50.842	−1.265
2200	20.786	205.873	187.904	39.532	−92.728	57.628	−1.368
2300	20.786	206.797	188.706	41.610	−94.858	64.510	−1.465
2400	20.786	207.682	189.478	43.689	−97.005	71.484	−1.556
2500	20.786	208.531	190.223	45.768	−99.171	78.549	−1.641
2600	20.786	209.346	190.943	47.846	−101.360	85.701	−1.722
2700	20.786	210.130	191.640	49.925	−103.574	92.938	−1.798
2800	20.786	210.886	192.314	52.004	−105.819	100.257	−1.870
2900	20.786	211.616	192.967	54.082	−108.098	107.657	−1.939
3000	20.786	212.320	193.600	56.161	−110.416	115.136	−2.005
3100	20.786	213.002	194.215	58.239	−112.777	122.693	−2.067
3200	20.786	213.662	194.812	60.318	−115.187	130.327	−2.127
3300	20.786	214.301	195.393	62.397	−117.634	138.037	−2.185
3400	20.786	214.922	195.959	64.475	−120.147	145.822	−2.240
3500	20.786	215.524	196.509	66.554	−122.724	153.682	−2.294
3600	20.786	216.110	197.046	68.632	−125.360	161.616	−2.345
3700	20.786	216.680	197.569	70.711	−128.074	169.624	−2.395
3800	20.786	217.234	198.079	72.790	−130.865	177.707	−2.443
3900	20.786	217.774	198.577	74.868	−133.740	185.865	−2.489
4000	20.786	218.300	199.063	76.947	−136.688	194.096	−2.535
4100	20.786	218.813	199.539	79.025	−139.742	202.403	−2.579
4200	20.786	219.314	200.004	81.104	−142.895	210.786	−2.622
4300	20.786	219.803	200.459	83.183	−146.151	219.246	−2.663
4400	20.786	220.281	200.904	85.261	−149.219	227.751	−2.704
4500	20.786	220.748	201.339	87.340	−152.499	236.343	−2.743
4600	20.786	221.205	201.766	89.418	−155.961	245.020	−2.782
4700	20.786	221.652	202.185	91.497	−159.545	253.775	−2.820
4800	20.786	222.090	202.595	93.576	−163.235	262.608	−2.858
4900	20.786	222.518	202.997	95.654	−167.029	271.519	−2.894
5000	20.786	222.938	203.392	97.733	−170.679	280.478	−2.930
5100	20.786	223.350	203.779	99.811	−174.644	289.540	−2.965
5200	20.786	223.754	204.159	101.890	−178.711	298.681	−3.000
5300	20.786	224.150	204.533	103.969	−182.878	307.901	−3.035
5400	20.786	224.538	204.900	106.047	−187.143	317.201	−3.068
5500	20.786	224.919	205.260	108.126	−191.503	326.581	−3.102
5600	20.786	225.294	205.615	110.204	−195.575	335.986	−3.134
5700	20.786	225.662	205.963	112.283	−200.072	345.518	−3.166
5800	20.786	226.023	206.306	114.362	−204.653	355.130	−3.198
5900	20.786	226.379	206.643	116.440	−209.312	364.821	−3.230
6000	20.786	226.728	206.975	118.519	−214.045	374.592	−3.261

PREVIOUS: CURRENT: December 1983 (1 bar)

D_0° = 46.91 ± 1.9 kJ·mol^{-1} (natural abundance)
S°(298.15 K) = 271.07 ± 0.08 J·K^{-1}·mol^{-1}

$\Delta_f H^\circ$(0 K) = 117.34 ± 2.5 kJ·mol^{-1}
$\Delta_f H^\circ$(298.15 K) = 113.29 ± 2.5 kJ·mol^{-1}

Spectroscopic Data for $^{85}Rb_2$ (Ground State: $^1\Sigma_g^+$) in cm^{-1}

ω_e = 57.747	$\omega_e x_e$ = 0.1582
B_e = 0.02278	α_e = 4.7 × 10^{-5}
D_e = 1.5 × 10^{-8}	r_e = 4.173 Å

Heat of Formation

Using the adopted value of the dissociation energy for Rb_2(g), D_0° = 46.91 kJ·mol^{-1} (natural abundance Rb_2) as deduced from the ^{85}Rb dissociation energy from reference[4] (D° = 47.277 ± 1.93 kJ·mol^{-1}) and the recommended $\Delta_f H^\circ$(Rb, g, 0 K) = 82.17 kJ·mol^{-1} from NBS,[5] we calculate $\Delta_f H^\circ$(Rb_2, g, 0 K) = 117.34 kJ·mol^{-1}. Using the NBS enthalpy value for Rb(cr) (H°(298.15 K)–H° (0 K) = 7.489 kJ·mol^{-1}) and the current JANAF value for H°(298.15 K)–H°(0 K) of Rb_2(g), we obtain $\Delta_f H^\circ$(Rb_2, g, 298.15 K) = 113.29 kJ·mol^{-1}. Note that in a mass spectrometric study by Piacente *et al.*,[6] the dissociation energy of Rb_2(g) was determined as 41.84 ± 2.1 kJ·mol^{-1}. This value appears to be too low when compared to the alkali metal group trends apparent in plots of D_0° versus r_e or D_0° versus group member.

Heat Capacity and Entropy

The heat capacity and entropy were calculated using a direct summation technique similar to the Li_2(g) species[7] using the data for the $^{85}Rb_2$ species given above.[1,2] Since insufficient spectroscopic data exist for the lower lying excited electronic states, we performed the calculation on the ground state only as discussed in the K_2(g) table.[7] Separate calculations were performed on the isotopic species $^{85}Rb_2$, $^{87}Rb_2$, and $^{85}Rb^{87}Rb$ and the results combined according to the natural atomic isotopic abundances:[3] ^{85}Rb, 72.165%; ^{87}Rb, 27.835%. Spectroscopic input data for the calculation of the isotopic species were calculated from the $^{85}Rb_2$(g) data using reduced mass scaling. The rotational levels were weighted according to the nuclear spins of the atoms (^{85}Rb, I = 5/2; ^{87}Rb, I = 3/2) as follows: $^{85}Rb_2$, even J weight = 0.583, odd J weight = 0.471; $^{87}Rb_2$, even J weight = 0.625, odd J weight = 0.375; $^{85}Rb^{87}Rb$, equal weights of 0.5.

Based on the results for the Cs_2(g) calculation,[7] neglect of the excited states probably results in negligible uncertainties in the thermodynamic functions (except for C_p°) at temperatures below ca. 2000 K. We estimate that the entropy and Gibbs energy function at 3000 K are too low by ca. 0.4 J·K^{-1}·mol^{-1} due to the neglect of the excited states. The adopted value of S°(298.15 K) is 0.07 J·K^{-1}·mol^{-1} larger than that adopted by Gurvich *et al.*[8]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−10.934	117.335	117.335	INFINITE
100	37.185	229.924	304.707	−7.478	116.769	103.181	−53.896
200	37.777	255.918	274.542	−3.725	115.222	90.165	−23.549
298.15	38.116	271.067	271.067	0.	113.290	78.254	−13.710
300	38.123	271.302	271.067	0.071	113.245	78.037	−13.587
400	38.440	282.314	272.567	3.899	106.291	67.916	−8.869
500	38.631	290.917	275.407	7.754	103.858	58.607	−6.123
600	38.475	297.953	278.597	11.614	101.515	49.777	−4.333
700	37.845	303.842	281.795	15.433	99.186	41.338	−3.085
800	36.797	308.831	284.871	19.168	96.789	33.236	−2.170
900	35.490	313.092	287.776	22.784	94.257	25.443	−1.477
1000	34.084	316.758	290.495	26.263	−51.424	22.313	−1.166
1100	32.696	319.941	293.031	29.602	−52.243	29.725	−1.412
1200	31.398	322.730	295.392	32.805	−53.196	37.218	−1.620
1300	30.221	325.196	297.592	35.885	−54.274	44.795	−1.800
1400	29.176	327.396	299.643	38.854	−55.464	52.460	−1.957
1500	28.258	329.377	301.561	41.725	−56.753	60.213	−2.097
1600	27.457	331.175	303.356	44.510	−58.131	68.055	−2.222
1700	26.760	332.818	305.042	47.220	−59.587	75.986	−2.335
1800	26.154	334.330	306.627	49.865	−61.115	84.005	−2.438
1900	25.626	335.729	308.123	52.453	−62.710	92.110	−2.532
2000	25.165	337.032	309.536	54.992	−64.366	100.301	−2.620
2100	24.762	338.250	310.874	57.488	−66.082	108.576	−2.701
2200	24.408	339.393	312.145	59.946	−67.858	116.935	−2.776
2300	24.096	340.471	313.354	62.371	−69.693	125.375	−2.847
2400	23.821	341.491	314.505	64.766	−71.591	133.897	−2.914
2500	23.577	342.458	315.604	67.136	−73.553	142.499	−2.977
2600	23.360	343.379	316.654	69.483	−75.584	151.181	−3.037
2700	23.166	344.257	317.661	71.809	−77.686	159.942	−3.094
2800	22.992	345.096	318.625	74.117	−79.869	168.783	−3.149
2900	22.836	345.900	319.552	76.408	−82.137	177.703	−3.201
3000	22.695	346.672	320.443	78.684	−84.496	186.703	−3.251
3100	22.568	347.414	321.302	80.947	−86.955	195.783	−3.299
3200	22.453	348.128	322.129	83.198	−89.524	204.945	−3.345
3300	22.348	348.818	322.927	85.438	−92.177	214.186	−3.390
3400	22.253	349.483	323.699	87.668	−94.974	223.511	−3.434
3500	22.166	350.127	324.445	89.889	−97.906	232.920	−3.476
3600	22.086	350.750	325.167	92.102	−100.966	242.415	−3.517
3700	22.013	351.354	325.866	94.307	−104.188	251.997	−3.558
3800	21.945	351.941	326.545	96.505	−107.573	261.669	−3.597
3900	21.884	352.510	327.203	98.696	−111.132	271.431	−3.635
4000	21.826	353.063	327.843	100.881	−114.843	281.285	−3.673
4100	21.773	353.601	328.465	103.061	−118.771	291.237	−3.710
4200	21.724	354.126	329.069	105.236	−122.901	301.287	−3.747
4300	21.679	354.636	329.658	107.406	−127.244	311.437	−3.783
4400	21.636	355.134	330.231	109.572	−131.214	321.630	−3.818
4500	21.597	355.620	330.790	111.734	−135.612	331.947	−3.853
4600	21.560	356.094	331.335	113.892	−140.378	342.385	−3.888
4700	21.525	356.558	331.867	116.046	−145.393	352.933	−3.922
4800	21.493	357.010	332.386	118.197	−150.620	363.590	−3.957
4900	21.463	357.453	332.893	120.344	−156.062	374.359	−3.991
5000	21.435	357.887	333.389	122.489	−161.216	385.179	−4.024
5100	21.408	358.311	333.873	124.631	−167.005	396.164	−4.058
5200	21.383	358.726	334.347	126.771	−172.999	407.266	−4.091
5300	21.360	359.133	334.811	128.908	−179.195	418.483	−4.124
5400	21.338	359.532	335.265	131.043	−185.590	429.820	−4.158
5500	21.317	359.924	335.710	133.176	−192.179	441.277	−4.191
5600	21.297	360.308	336.146	135.306	−198.192	452.746	−4.223
5700	21.278	360.684	336.573	137.435	−205.058	464.431	−4.256
5800	21.261	361.054	336.992	139.562	−212.091	476.236	−4.289
5900	21.244	361.418	337.403	141.687	−219.284	488.166	−4.322
6000	21.228	361.775	337.806	143.811	−226.628	500.217	−4.355

PREVIOUS: CURRENT: December 1983 (1 bar)

0 to 6000 K Ideal Monatomic Gas

IP(Rn, g) = 86692.5 ± 0.2 cm^{-1}
$S°$(298.15 K) = 176.235 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 0 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 0 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Heat of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[1,9] Many of the theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[2] has little effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 54620 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.[2]

Thermodynamic functions at 298.15 K are recommended by CODATA[3] for all rare gases except radon. This table agrees with other tabulations except for two minor changes. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the other tabulations are based on 1 atm. Second, entropy differences of the order of 0.001–0.004 $J·K^{-1}·mol^{-1}$ for the rare gases arise due to the use of slightly different values for R and the relative atomic mass; this table uses R = 8.31441 $J·K^{-1}·mol^{-1}$. With some minor changes, our tables agree within the estimated uncertainty with those by Hilsenrath *et al.*,[5] Gurvich *et al.*,[8] and Wagman *et al.*[10] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[6] and the 1973 values,[7] respectively.

Phase Data

Hultgren *et al.*[4] had recommended a melting point of 202 K and a boiling point of 211 K (1 atm). These values are provided for the convenience of the reader and have not been evaluated by the present authors. As a result of the low values, the reference state for radon is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	0.	0.	0.
100	20.786	153.527	194.715	−4.119	0.	0.	0.
200	20.786	167.935	178.136	−2.040	0.	0.	0.
250	20.786	172.574	176.577	−1.001	0.	0.	0.
298.15	20.786	176.235	176.235	0.	0.	0.	0.
300	20.786	176.363	176.235	0.038	0.	0.	0.
350	20.786	179.567	176.488	1.078	0.	0.	0.
400	20.786	182.343	177.050	2.117	0.	0.	0.
450	20.786	184.791	177.777	3.156	0.	0.	0.
500	20.786	186.981	178.590	4.196	0.	0.	0.
600	20.786	190.771	180.314	6.274	0.	0.	0.
700	20.786	193.975	182.043	8.353	0.	0.	0.
800	20.786	196.751	183.711	10.431	0.	0.	0.
900	20.786	199.199	185.299	12.510	0.	0.	0.
1000	20.786	201.389	186.800	14.589	0.	0.	0.
1100	20.786	203.370	188.218	16.667	0.	0.	0.
1200	20.786	205.179	189.557	18.746	0.	0.	0.
1300	20.786	206.843	190.824	20.824	0.	0.	0.
1400	20.786	208.383	192.024	22.903	0.	0.	0.
1500	20.786	209.817	193.163	24.982	0.	0.	0.
1600	20.786	211.159	194.246	27.060	0.	0.	0.
1700	20.786	212.419	195.278	29.139	0.	0.	0.
1800	20.786	213.607	196.264	31.217	0.	0.	0.
1900	20.786	214.731	197.206	33.296	0.	0.	0.
2000	20.786	215.797	198.110	35.375	0.	0.	0.
2100	20.786	216.811	198.976	37.453	0.	0.	0.
2200	20.786	217.778	199.809	39.532	0.	0.	0.
2300	20.786	218.702	200.610	41.610	0.	0.	0.
2400	20.786	219.587	201.383	43.689	0.	0.	0.
2500	20.786	220.435	202.128	45.768	0.	0.	0.
2600	20.786	221.250	202.848	47.846	0.	0.	0.
2700	20.786	222.035	203.544	49.925	0.	0.	0.
2800	20.786	222.791	204.218	52.004	0.	0.	0.
2900	20.786	223.520	204.871	54.082	0.	0.	0.
3000	20.786	224.225	205.505	56.161	0.	0.	0.
3100	20.786	224.906	206.120	58.239	0.	0.	0.
3200	20.786	225.566	206.717	60.318	0.	0.	0.
3300	20.786	226.206	207.298	62.397	0.	0.	0.
3400	20.786	226.826	207.863	64.475	0.	0.	0.
3500	20.786	227.429	208.414	66.554	0.	0.	0.
3600	20.786	228.015	208.950	68.632	0.	0.	0.
3700	20.786	228.584	209.473	70.711	0.	0.	0.
3800	20.786	229.138	209.983	72.790	0.	0.	0.
3900	20.786	229.678	210.481	74.868	0.	0.	0.
4000	20.786	230.205	210.968	76.947	0.	0.	0.
4100	20.786	230.718	211.443	79.025	0.	0.	0.
4200	20.786	231.219	211.908	81.104	0.	0.	0.
4300	20.786	231.708	212.363	83.183	0.	0.	0.
4400	20.786	232.186	212.808	85.261	0.	0.	0.
4500	20.786	232.653	213.244	87.340	0.	0.	0.
4600	20.786	233.110	213.671	89.418	0.	0.	0.
4700	20.786	233.557	214.089	91.497	0.	0.	0.
4800	20.786	233.994	214.499	93.576	0.	0.	0.
4900	20.786	234.423	214.902	95.654	0.	0.	0.
5000	20.786	234.843	215.296	97.733	0.	0.	0.
5100	20.786	235.255	215.684	99.811	0.	0.	0.
5200	20.786	235.658	216.064	101.890	0.	0.	0.
5300	20.786	236.054	216.437	103.969	0.	0.	0.
5400	20.786	236.443	216.804	106.047	0.	0.	0.
5500	20.786	236.824	217.165	108.126	0.	0.	0.
5600	20.786	237.199	217.519	110.204	0.	0.	0.
5700	20.786	237.566	217.868	112.283	0.	0.	0.
5800	20.786	237.928	218.210	114.362	0.	0.	0.
5900	20.786	238.283	218.548	116.440	0.	0.	0.
6000	20.786	238.633	218.879	118.519	0.	0.	0.

PREVIOUS: CURRENT: March 1982 (1 bar)

$S°(298.15\ K) = 187.761 \pm 0.003\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 1037.073 \pm 0.002\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = [1043.270]\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	30895.1	2

Heat of Formation

The ionization limit of neutral radon (86692.5 ± 0.2 cm^{-1}) reported by Moore[1] is adopted as $\Delta_f H°(0\ K)$ for $Rn^+(g)$. The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the latest CODATA fundamental constants.[2] The uncertainty in the ionization limit is estimated to be ±0.2 cm^{-1} which corresponds to an uncertainty of ±0.002 $kJ·mol^{-1}$ in the heat of formation. Gurvich *et al.*[8] adopted the same ionization potential, but the use of slightly different value by Wagman *et al.*[10] results in a heat of formation difference of 0.010 kJ mol^{-1}.

$\Delta_f H°(Rn^+, g, 298.15\ K)$ is obtained from $\Delta_f H°(Rn, g, 0\ K)$ by using IP(Rn) with JANAF[3] enthalpies $H°(0\ K)-H°(298.15\ K)$ for $Rn^+(g)$, Rn(r), and $e^-(r)$. $\Delta_r H°(Rn \rightarrow Rn^+ + e^-, 298.15\ K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°(298.15\ K)$ should be changed by −6.197 $kJ·mol^{-1}$if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights of Moore[4] is incomplete because no levels have been observed. Our calculations indicate that any reasonable method of filling in missing levels and cutting off the summation in the partition function[5] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is estimated to be over 80000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore.[1] The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[5]

The thermodynamic functions reported here agree with those of Green *et al.*,[6] Hilsenrath *et al.*,[7] and Gurvich *et al.*[8] except for two minor changes. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard state pressure of 1 bar, whereas the cited references used a pressure of 1 atm. Second, smaller differences arise from the use of different values for the fundamental constants, the relative ionic mass, and the position of the $^2P_{1/2}$ electronic level.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1037.073		
100	20.786	165.054	206.241	−4.119			
200	20.786	179.461	189.662	−2.040			
250	20.786	184.100	188.103	−1.001			
298.15	20.786	187.761	187.761	0.	1043.270	1033.579	−181.079
300	20.786	187.889	187.761	0.038	1043.309	1033.519	−179.952
350	20.786	191.094	188.014	1.078	1044.348	1031.805	−153.988
400	20.786	193.869	188.577	2.117	1045.387	1029.942	−134.497
450	20.786	196.317	189.303	3.156	1046.427	1027.949	−119.321
500	20.786	198.507	190.116	4.196	1047.466	1025.840	−107.169
600	20.786	202.297	191.840	6.274	1049.545	1021.320	−88.914
700	20.786	205.501	193.569	8.353	1051.623	1016.451	−75.849
800	20.786	208.277	195.238	10.431	1053.702	1011.285	−66.030
900	20.786	210.725	196.825	12.510	1055.780	1005.858	−58.378
1000	20.786	212.915	198.327	14.589	1057.859	1000.200	−52.245
1100	20.786	214.896	199.744	16.667	1059.938	994.333	−47.217
1200	20.786	216.705	201.083	18.746	1062.016	988.277	−43.019
1300	20.786	218.369	202.350	20.824	1064.095	982.048	−39.459
1400	20.786	219.909	203.550	22.903	1066.173	975.659	−36.402
1500	20.786	221.343	204.689	24.982	1068.252	969.121	−33.748
1600	20.786	222.685	205.772	27.060	1070.331	962.445	−31.421
1700	20.786	223.945	206.804	29.139	1072.409	955.638	−29.363
1800	20.786	225.133	207.790	31.217	1074.488	948.709	−27.531
1900	20.786	226.257	208.733	33.296	1076.566	941.665	−25.888
2000	20.786	227.323	209.636	35.375	1078.645	934.511	−24.407
2100	20.786	228.337	210.502	37.453	1080.724	927.253	−23.064
2200	20.786	229.304	211.335	39.532	1082.802	919.896	−21.841
2300	20.786	230.228	212.137	41.610	1084.881	912.445	−20.722
2400	20.786	231.113	212.909	43.689	1086.959	904.903	−19.695
2500	20.786	231.961	213.654	45.768	1089.038	897.275	−18.748
2600	20.786	232.777	214.374	47.846	1091.117	889.563	−17.872
2700	20.786	233.561	215.070	49.925	1093.195	881.772	−17.059
2800	20.786	234.317	215.744	52.004	1095.274	873.903	−16.303
2900	20.786	235.046	216.397	54.082	1097.352	865.961	−15.598
3000	20.786	235.751	217.031	56.161	1099.431	857.946	−14.938
3100	20.787	236.433	217.646	58.239	1101.510	849.862	−14.320
3200	20.787	237.093	218.243	60.318	1103.588	841.711	−13.740
3300	20.787	237.732	218.824	62.397	1105.667	833.496	−13.193
3400	20.788	238.353	219.389	64.476	1107.746	825.217	−12.678
3500	20.788	238.955	219.940	66.554	1109.825	816.877	−12.191
3600	20.789	239.541	220.476	68.633	1111.903	808.478	−11.731
3700	20.790	240.111	220.999	70.712	1113.982	800.020	−11.294
3800	20.791	240.665	221.510	72.791	1116.061	791.507	−10.880
3900	20.792	241.205	222.008	74.870	1118.140	782.939	−10.486
4000	20.794	241.732	222.494	76.949	1120.220	774.318	−10.112
4100	20.796	242.245	222.970	79.029	1122.299	765.644	−9.754
4200	20.798	242.746	223.435	81.109	1124.379	756.920	−9.414
4300	20.800	243.236	223.889	83.189	1126.459	748.147	−9.088
4400	20.803	243.714	224.335	85.269	1128.539	739.325	−8.777
4500	20.807	244.181	224.770	87.349	1130.619	730.456	−8.479
4600	20.811	244.639	225.197	89.430	1132.700	721.540	−8.193
4700	20.815	245.086	225.616	91.511	1134.782	712.579	−7.919
4800	20.820	245.525	226.026	93.593	1136.863	703.574	−7.656
4900	20.825	245.954	226.428	95.675	1138.946	694.526	−7.404
5000	20.831	246.375	226.823	97.758	1141.028	685.435	−7.161
5100	20.838	246.787	227.211	99.842	1143.112	676.303	−6.927
5200	20.845	247.192	227.591	101.926	1145.196	667.129	−6.701
5300	20.853	247.589	227.964	104.011	1147.281	657.916	−6.484
5400	20.861	247.979	228.332	106.096	1149.367	648.663	−6.275
5500	20.870	248.362	228.692	108.183	1151.453	639.371	−6.072
5600	20.879	248.738	229.047	110.270	1153.541	630.042	−5.877
5700	20.890	249.108	229.396	112.359	1155.629	620.675	−5.688
5800	20.901	249.471	229.739	114.448	1157.719	611.272	−5.505
5900	20.912	249.828	230.076	116.539	1159.809	601.832	−5.328
6000	20.924	250.180	230.408	118.631	1161.901	592.357	−5.157

PREVIOUS: CURRENT: March 1982 (1 bar)

0	to	368.3 K	crystal, alpha
368.3	to	388.36 K	crystal, beta
388.36	to	882.117 K	liquid
above		882.117 K	ideal diatomic gas (see below)

The normal boiling point of sulfur at 1 atm, 717.824 K, is a secondary standard on the International Practical Temperature Scale of 1968. The vapor composition at this temperature is a mixture of several sulfur species, the predominant species being S_8(g), S_7(g), and S_6(g). In our reference state for sulfur, we have **arbitrarily** chosen 0.5 S_2(g) to be the gas phase species.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.412	0.	0.	0.
100	12.770	12.522	49.744	−3.722	0.	0.	0.
200	19.368	23.637	34.038	−2.080	0.	0.	0.
298.15	22.698	32.056	32.056	0.	0.	0.	0.
300	22.744	32.196	32.056	0.042	0.	0.	0.
368.300	24.246	37.015	32.540	1.648	ALPHA <--> BETA TRANSITION		
368.300	24.773	38.103	32.540	2.049			
388.360	25.167	39.427	32.861	2.550	BETA <--> LIQUID TRANSITION		
388.360	31.058	43.859	32.861	4.271			
400	32.162	44.793	33.195	4.639	0.	0.	0.
432.020	53.808	47.431	34.151	5.737	C_p LAMBDA MAXIMUM TRANSITION		
432.020	53.806	47.431	34.151	5.737			
500	37.986	53.532	36.398	8.567	0.	0.	0.
600	34.308	60.078	39.825	12.152	0.	0.	0.
700	32.681	65.241	43.099	15.499	0.	0.	0.
800	31.699	69.530	46.143	18.710	0.	0.	0.
882.117	31.665	72.624	48.467	21.310	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
882.117	18.454	133.077	48.467	74.636			
900	18.483	133.448	50.152	74.967	0.	0.	0.
1000	18.638	135.403	58.581	76.823	0.	0.	0.
1100	18.792	137.187	65.647	78.694	0.	0.	0.
1200	18.947	138.829	71.678	80.581	0.	0.	0.
1300	19.103	140.352	76.903	82.484	0.	0.	0.
1400	19.257	141.773	81.486	84.402	0.	0.	0.
1500	19.409	143.107	85.550	86.335	0.	0.	0.
1600	19.556	144.364	89.187	88.283	0.	0.	0.
1700	19.697	145.554	92.468	90.246	0.	0.	0.
1800	19.830	146.684	95.449	92.223	0.	0.	0.
1900	19.956	147.759	98.174	94.212	0.	0.	0.
2000	20.072	148.786	100.679	96.213	0.	0.	0.
2100	20.176	149.768	102.993	98.226	0.	0.	0.
2200	20.274	150.708	105.141	100.248	0.	0.	0.
2300	20.364	151.612	107.142	102.280	0.	0.	0.
2400	20.448	152.480	109.013	104.321	0.	0.	0.
2500	20.526	153.316	110.769	106.370	0.	0.	0.
2600	20.589	154.123	112.421	108.426	0.	0.	0.
2700	20.650	154.901	113.980	110.488	0.	0.	0.
2800	20.707	155.653	115.455	112.555	0.	0.	0.
2900	20.762	156.381	116.853	114.629	0.	0.	0.
3000	20.813	157.085	118.183	116.708	0.	0.	0.
3100	20.855	157.768	119.449	118.791	0.	0.	0.
3200	20.898	158.431	120.657	120.879	0.	0.	0.
3300	20.940	159.075	121.811	122.971	0.	0.	0.
3400	20.983	159.701	122.916	125.067	0.	0.	0.
3500	21.025	160.310	123.976	127.167	0.	0.	0.
3600	21.065	160.902	124.994	129.272	0.	0.	0.
3700	21.106	161.480	125.972	131.380	0.	0.	0.
3800	21.149	162.044	126.914	133.493	0.	0.	0.
3900	21.194	162.594	127.822	135.610	0.	0.	0.
4000	21.240	163.131	128.698	137.732	0.	0.	0.
4200	21.337	164.169	130.362	141.989	0.	0.	0.
4400	21.443	165.164	131.922	146.267	0.	0.	0.
4600	21.558	166.120	133.388	150.567	0.	0.	0.
4800	21.680	167.040	134.771	154.891	0.	0.	0.
5000	21.810	167.928	136.080	159.240	0.	0.	0.
5200	21.948	168.786	137.321	163.615	0.	0.	0.
5400	22.090	169.617	138.502	168.019	0.	0.	0.
5600	22.236	170.423	139.628	172.452	0.	0.	0.
5800	22.385	171.206	140.703	176.914	0.	0.	0.
6000	22.538	171.967	141.733	181.406	0.	0.	0.

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 33.028 \pm 0.050\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 368.3 \pm 0.3\ K\ (\alpha-\beta)$
$T_{fus} = 388.36 \pm 0.1\ K\ (\beta\text{-}l)$

$\Delta_f H°(0\ K) = 0.247\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0.360\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.4004 \pm 0.0029\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 1.721 \pm 0.008\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy formation of monoclinic sulfus at 298.15 K is calculated from that of orthorhombic sulfur by adding $\Delta_{trs}H°$ and the difference is enthalpy, $H°(368.3)-H°(298.15\ K)$, between orthorhombic and monoclinic sulfur.

Heat Capacity and Entropy

Experimentally determined heat capacity vlaues for monoclinic (β) sulfur have been reported by Eastman and McGavock (64.83–376.16 K),[1] West (368–388 K),[2] and Montgomery (12.41–386.83 K).[3] The thermochemical functions tabulated by Hultgren *et al.*[4] are based on work of Eastman and McGavock[1] and West.[2]

We adopt the heat capacity values tabulated (in 10 K increments) by Montgomery.[3] The heat capacity values above T_{fus} = 388.36 K are obtained by linear extrapolation of the tabulated heat capacity values[3] above 360 K. Using $S°(10\ K) = 0.063\ cal \cdot K^{-1} \cdot mol^{-1}$ and integrating the heat capacity values, we calculate $S°(298.15\ K) = 7.893\ cal \cdot K^{-1} \cdot mol^{-1}$. The $S°(10)$ value contains a contribution of $0.007\ cal \cdot K^{-1} \cdot mol^{-1}$ which is needed to make $S°(S, cr, \beta, T) = S°(S, cr, \alpha, T) + \Delta_{trs}H°/T_{trs}$. Since both forms of sulfur are perfectly ordered crystals at 0 K,[3] the $S°(0\ K)$ value should be zero, by definition. The contribution of $0.007\ cal \cdot K^{-1} \cdot mol^{-1}$ is arbitrarily added at10 K although it could appear in any temperature region at or below 368.3 K. Part of this entropy may be in the region of the lambda anomaly at 198.3 K. This contribution is comparable to the uncertainty expected from this adiabatic calorimeter.

Phase Data

The α–β transition at 368.3 K is discussed on the orthorhombic sulfur table.[5] The heat capacity data of Montgomery[3] did not support the transition at 374 K reported by West.[2]

Montgomery[3] reported a λ anomaly in the heat capacity of monoclinic sulfur with a peak at 198.3 K. The entropy change in the lambda anomaly was $0.052 \pm 0.005\ cal \cdot K^{-1} \cdot mol^{-1}$, this was interpreted as due to the disordering of the structure of monoclinic sulfur on heating.[7]

Fusion Data

The melting of sulfur has been studied by many workers. An excellent review by Meyer[6] summarizes these studies. In addition, Hultgren *et al.*[4] tabulated numerous enthalpy of melting determinations. We adopt the results obtained by Montgomery[3] via adiabatic calorimetry: $T_{fus} = 388.36 \pm 0.02$ K and $\Delta_{fus}H° = 0.4128 \pm 0.0006\ kcal \cdot mol^{-1}$. The only other precise study reported in the literature is that of West[2] who obtained $\Delta_{fus}H° = 0.41051 \pm 0.0005\ kcal \cdot mol^{-1}$ by adiabatic calorimetry.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−4.525	0.247	0.247	INFINITE
100	12.874	12.964	51.217	−3.825	0.257	0.213	−0.111
198.300	21.966	24.242	35.146	−2.162	____ C_p LAMBDA MAXIMUM ____		
198.300	21.966	24.242	35.146	−2.162	TRANSITION		
200	20.154	24.421	35.054	−2.127	0.313	0.157	−0.041
250	21.736	29.066	33.402	−1.084	0.336	0.115	−0.024
298.15	23.225	33.028	33.028	0.	0.360	0.070	−0.012
300	23.276	33.172	33.028	0.043	0.361	0.068	−0.012
350	24.414	36.849	33.316	1.237	0.388	0.017	−0.003
368.300	24.773	38.103	33.523	1.687	---- ALPHA <--> BETA ----		
388.360	25.167	39.427	33.794	2.188	---- BETA <--> LIQUID ----		
400	25.397	40.173	33.969	2.482	−1.797	0.050	−0.007
450	26.380	43.222	34.830	3.776	−2.428	0.310	−0.036
500	27.363	46.052	35.812	5.120	−3.087	0.653	−0.068
600	29.330	51.215	37.957	7.955	−3.838	1.481	−0.129
700	31.296	55.884	40.189	10.986	−4.153	2.397	−0.179
800	33.263	60.191	42.424	14.214	−4.136	3.335	−0.218

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 32.056 \pm 0.050\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 368.3 \pm 0.3\ K\ (\alpha-\beta)$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.4004 \pm 0.0029\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Experimentally determined heat capacity vlaues for orthorhombic (α) sulfur have been reported by Nernst,[1] 23–202 K), Eastman and McGavock,[2] 12.68–365.60 K), West,[3] 298l–368 K), Mal'tsev and Demidenko,[4] 53–305 K), Finke,[5] 12–432 K), Montgomery,[6] 12.34–360.99 K), and Paukov.[7] The thermochemical functions tabulated by Hultgren *et al.*[8] are based primarily on the work of Eastman and McGavock[2] and unpublished work of Finke,[5] the latter presumably being the preliminary results of Montgomery.[6] The tentative values reported by CODATA[9] for $S°(298.15\ K)$ and $H°(298.15\ K)-H°(0\ K)$ are based on Eastman and McGavock,[2] Montgomery,[6] and Paukov.[7]

We adopt the heat capacity values tabulated (in 10 K increments) by Montgomery.[6] Using $S°(10) = 0.036\ cal \cdot K^{-1} \cdot mol^{-1}$ and integrating the heat capacity values, we calculate $S°(298.15\ K) = 7.661\ cal \cdot K^{-1} \cdot mol^{-1}$, in agreement with CODATA[9]. The heat capacity values above $T_{trs} = 368.3$ K are obtained by linear extrapolation of the tabulated values[6] above 340 K.

The various heat capacity studies are in reasonably good agreement. The values recommended by Eastman and McGavock,[2] West,[3] and Mal'tsev and Demidenko[4] agree with Montgomery[6] to within 0.5% except for the ranges 15–50 K[2] and 53–80 K.[3] The smoothed value at 190 K reported by Mal'tsev and Demidenko[4] is undoubtedly a typographical error. The selected values of Hultgren *et al.*[8] agree within 0.5% with the data of Montgomery[6] except below 35 K.

Fusion Data

The orthorhomic–monoclinic (α–β) phase change has been studied by many workers. An excellent review by Meyer[10] summarizes these studies. We adopt the results obtained by Montgomery[6] via adiabatic calorimetry: $T_{trs} = 368.3 \pm 0.3$ K and $\Delta_{trs} H° = 0.0957 \pm 0.0007\ kcal \cdot mol^{-1}$. The only other precise study reported in the literature is that of West[3] who obtained $\Delta_{trs} H° = 0.0960 \pm 0.0005\ kcal \cdot mol^{-1}$ by adiabatic calorimetry. Other drop calorimetric[11,12] and vapor pressure[13,14] studies are much less precise with an uncertainty of $\pm 5\ cal \cdot mol^{-1}$ or greater.

Sublimation Data

Since the reference state of sulfur involves 0.5 S_2(g) rather than S(g), we define the enthalpy of sublimation (at 298.15 K) of orthorhombic sulfur as the process S(cr, α) = 0.5 S_2(g). Thus the enthalpy of sublimation of orthorhombic sulfur is one–half the enthalpy of formation of S_2(g). Since the dominant gaseous sulfur species at room temperature is actually S_8(g), the enthalpy of sublimation to the equilibrium gas is significantly smaller.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.412	0.	0.	0.
100	12.770	12.522	49.744	−3.722	0.	0.	0.
200	19.368	23.637	34.038	−2.080	0.	0.	0.
250	21.297	28.179	32.422	−1.061	0.	0.	0.
298.15	22.698	32.056	32.056	0.	0.	0.	0.
300	22.744	32.196	32.056	0.042	0.	0.	0.
350	23.870	35.789	32.337	1.208	0.	0.	0.
368.300	24.246	37.015	32.540	1.648	---- ALPHA <--> BETA ----		
400	24.895	39.044	32.975	2.427	−2.212	0.088	−0.011
450	25.920	42.035	33.818	3.698	−2.867	0.406	−0.047
500	26.945	44.819	34.780	5.019	−3.548	0.809	−0.084
600	28.995	49.913	36.886	7.816	−4.336	1.764	−0.154
700	31.045	54.537	39.082	10.818	−4.680	2.812	−0.210
800	33.095	58.816	41.284	14.025	−4.685	3.887	−0.254

PREVIOUS: December 1965 CURRENT: September 1977

$S°(298.15\ K) = [36.825]\ J·K^{-1}·mol^{-1}$
$T_{trs} = 432.02 \pm 0.2\ K$
$T_{fus} = 388.36 \pm 0.2\ K$

$\Delta_f H°(298.15\ K) = [1.854]\ kJ·mol^{-1}$
$\Delta_{trs} H° = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 1.7272 \pm 0.0025\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of liquid sulfur at 298.15 K is calculated from that of monoclinic sulfur by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(388.6\ K)–H°(298.15\ K)$, between the monoclinic crystal and the liquid.

Heat Capacity and Entropy

The adopted heat capacity values are based on the studies by Montgomery,[4] 05.79–433.31 K) and West (373–678 K).[2] Liquid sulfur undergoes a second order transition with a maximum reported at 432.02 ± 0.20 K[1] and 432.25 ± 0.30 K;[2] this has been attributed to the depolymerization of S_8 molecules.[3] We adopt the tabulated heat capacity values of Montgomery[1] up to 434 K and those of West[2] above 434 K. The heat capacity is assumed to be constant at 7.568 $cal·K^{-1}·mol^{-1}$ above 810 K. Below T_m = 388.36 K, the heat capacity values are obtained by linear extrapolation using the slope of the values in the region Tm to 420 K. The entropy at 298.15 K is calculated in a manner analogous to that used for the enthalpy of formation.

Vaporization Data

The normal boiling point of sulfur, T_{vap}(1 atm) = 717.834 K is a secondary reference on the International Practical Temperature Scale of 1968. At this temperature, equilibrium sulfur vapor contains monomeric and several polymeric sulfur species: S_2(g) and S(g) predominate above 1000 K while S_6(g), S_7(g) and S_8(g) dominate at T_{vap}.

Since our reference state for sulfur is arbitrarily defined to involve 0.5 S_2(g) as the vapor species, we calculate the arbitrary normal boiling point, T_{vap}(1 bar), for the process S(l) = 0.5 S_2(g). The brackets are used to indicate the arbitrary nature of this value. Since we only consider S_2(g) in this vaporization, note that the boiling point is considerably different from the secondary reference IPTS value. If **all** n–mers of sulfur are considered in the vaporization process, then a normal boiling point (1 atm) is closely reproduced.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	22.531	36.825	36.825	0.	1.854	0.432	−0.076
300	22.707	36.965	36.826	0.042	1.854	0.423	−0.074
350	27.434	40.821	37.120	1.295	1.941	0.180	−0.027
388.360	31.058	43.859	37.635	2.417	---- BETA <--> LIQUID ----		
400	32.162	44.793	37.829	2.785	0.	0.	0.
432.020	53.829	47.431	38.442	3.884	___ C_p LAMBDA MAXIMUM ___		
432.020	53.808	47.431	38.442	3.884	TRANSITION		
450	43.046	49.308	38.840	4.711	0.	0.	0.
500	37.986	53.532	40.106	6.713	0.	0.	0.
600	34.308	60.078	42.915	10.298	0.	0.	0.
700	32.681	65.241	45.748	13.645	0.	0.	0.
800	31.699	69.530	48.460	16.856	0.	0.	0.
882.117	31.665	72.624	50.568	19.456	----- FUGACITY = 1 bar -----		
900	31.665	73.260	51.012	20.023	−53.090	1.079	−0.063
1000	31.665	76.596	53.407	23.189	−51.780	7.028	−0.367
1100	31.665	79.614	55.654	26.356	−50.485	12.846	−0.610
1200	31.665	82.369	57.767	29.522	−49.205	18.546	−0.807
1300	31.665	84.904	59.758	32.689	−47.941	24.141	−0.970
1400	31.665	87.250	61.639	35.855	−46.693	29.639	−1.106
1500	31.665	89.435	63.420	39.021	−45.460	35.048	−1.220

PREVIOUS: December 1965 CURRENT: September 1977

0	to	368.3	K crystal, alpha
368.3	to	388.36	K crystal, beta
above		388.36	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.412	0.	0.	0.
100	12.770	12.522	49.744	−3.722	0.	0.	0.
200	19.368	23.637	34.038	−2.080	0.	0.	0.
250	21.297	28.179	32.422	−1.061	0.	0.	0.
298.15	22.698	32.056	32.056	0.	0.	0.	0.
300	22.744	32.196	32.056	0.042	0.	0.	0.
350	23.870	35.789	32.337	1.208	0.	0.	0.
368.300	24.246	37.015	32.540	1.648	ALPHA <--> BETA TRANSITION		
368.300	24.773	38.103	32.540	2.049			
388.360	25.167	39.427	32.861	2.550	BETA <--> LIQUID TRANSITION		
388.360	31.062	43.859	32.861	4.271			
400	32.162	44.793	33.195	4.639	0.	0.	0.
432.020	53.808	47.431	34.151	5.737	C_p LAMBDA MAXIMUM TRANSITION		
432.020	53.806	47.431	34.151	5.737			
450	43.046	49.308	34.720	6.564	0.	0.	0.
500	37.986	53.532	36.398	8.567	0.	0.	0.
600	34.308	60.078	39.825	12.152	0.	0.	0.
700	32.681	65.241	43.099	15.499	0.	0.	0.
800	31.699	69.530	46.143	18.710	0.	0.	0.
882.117	31.665	72.624	48.467	21.310	FUGACITY = 1 bar		
900	31.665	73.260	48.952	21.877	−53.090	1.079	−0.063
1000	31.665	76.596	51.553	25.043	−51.780	7.028	−0.367
1100	31.665	79.614	53.969	28.209	−50.485	12.846	−0.610
1200	31.665	82.369	56.222	31.376	−49.205	18.546	−0.807
1300	31.665	84.904	58.332	34.542	−47.941	24.141	−0.970
1400	31.665	87.250	60.315	37.709	−46.693	29.639	−1.106
1500	31.665	89.435	62.185	40.875	−45.460	35.048	−1.220

PREVIOUS: CURRENT: September 1977

IP(S, g) = 83558.0 ± 1 cm^{-1}
$S°(298.15\ K)$ = 167.828 ± 0.035 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 274.73 ± 0.25 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 276.98 ± 0.25 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.00	5
$^3P_1$	396.09	3
$^3P_0$	573.65	1
$^1D_2$	9238.58	5
$^1S_0$	22179.99	1

Enthalpy of Formation

The enthalpy of formation is based on the dissociation energy for S_2(g) as recommended by CODATA.[1] The adopted value for $\Delta_f H°$(S, g, 298.15 K) is calculated using $D_0°(S_2)$ = 35216.4 ± 2.5 cm^{-1}(421.282 ± 0.03 $kJ·mol^{-1}$) from the study of Ricks and Barrow.[2]

The selected dissociation energy, obtained from precise spectrospcopic measurements,[2] is supported by additional studies on thermochemical cycles,[3] photoionization[4,5] and torsion–effusion measurements.[6] Earlier measurements have been reviewed by Herzberg,[7] Gaydon,[8] Brewer,[9] and Drowart and Goldfinger.[3]

Heat Capacity and Entropy

The electronic levels for S(g) are given in the compilation by Moore.[10,11] Our calculations indicate that, except for the five levels lying below 23000 cm^{-1}, the inclusion of levels up to n = 10 has no effect on the termodynamic function to 6000 K. This is a result of the high energy of these levels; the fifthe excited state lies at 52623.88 cm^{-1} above the ground state. Since the inclusion of these upper levels has no effect on the thermodynamic function (to 6000 K) we list only the lowest lying states (ϵ_i < 23000 cm^{-1}). The reported uncertainty is $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and utilization of proper fill and cutoff procedures.[12] In fact, the inclusion of these higher excited states and consideration of various cutoff procedures leads to calculational differences in the Gibbs energy function of ~0.4 $J·K^{-1}·mol^{-1}$ or greater at temperatures in excess of 11500 K.The thermal functions at 298.15 K agree with CODATA recommendation[1] except for two minor differences. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard state presssure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, an entropy difference of 0.004 $J·K^{-1}·mol^{-1}$ arises due to the use of slightly different values for the fundamental constants.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.657	274.735	274.735	INFINITE
100	21.356	142.891	188.580	−4.569	276.133	263.096	−137.427
200	23.388	158.392	169.994	−2.320	276.740	249.789	−65.238
250	23.696	163.653	168.218	−1.141	276.899	243.031	−50.779
298.15	23.673	167.828	167.828	0.	276.980	236.500	−41.434
300	23.669	167.974	167.828	0.044	276.982	236.248	−41.135
350	23.480	171.610	168.116	1.223	276.995	229.458	−34.245
400	23.233	174.729	168.752	2.391	274.732	222.757	−29.089
450	22.979	177.451	169.571	3.546	273.962	216.297	−25.107
500	22.741	179.859	170.481	4.689	273.102	209.938	−21.932
600	22.338	183.968	172.398	6.942	271.770	197.436	−17.188
700	22.031	187.388	174.302	9.160	270.641	185.138	−13.815
800	21.800	190.314	176.125	11.351	269.621	172.994	−11.295
900	21.624	192.871	177.847	13.522	215.535	162.055	−9.405
1000	21.489	195.142	179.465	15.677	215.834	156.096	−8.154
1100	21.386	197.185	180.984	17.821	216.106	150.109	−7.128
1200	21.307	199.042	182.413	19.955	216.354	144.098	−6.272
1300	21.249	200.745	183.758	22.083	216.579	138.067	−5.548
1400	21.209	202.318	185.029	24.205	216.784	132.020	−4.926
1500	21.186	203.781	186.231	26.325	216.970	125.959	−4.386
1600	21.178	205.148	187.371	28.443	217.140	119.886	−3.914
1700	21.184	206.432	188.455	30.561	217.295	113.803	−3.497
1800	21.203	207.643	189.487	32.680	217.438	107.711	−3.126
1900	21.234	208.790	190.473	34.802	217.570	101.611	−2.793
2000	21.276	209.880	191.417	36.927	217.694	95.505	−2.494
2100	21.327	210.920	192.321	39.058	217.812	89.392	−2.224
2200	21.386	211.913	193.189	41.193	217.925	83.275	−1.977
2300	21.452	212.865	194.024	43.335	218.035	77.152	−1.752
2400	21.523	213.780	194.828	45.484	218.143	71.024	−1.546
2500	21.598	214.660	195.604	47.640	218.250	64.892	−1.356
2600	21.676	215.508	196.353	49.803	218.358	58.755	−1.180
2700	21.756	216.328	197.078	51.975	218.467	52.615	−1.018
2800	21.837	217.121	197.780	54.155	218.579	46.470	−0.867
2900	21.919	217.888	198.460	56.343	218.694	40.321	−0.726
3000	21.999	218.633	199.120	58.538	218.811	34.169	−0.595
3100	22.078	219.355	199.761	60.742	218.931	28.012	−0.472
3200	22.155	220.058	200.384	62.954	219.055	21.851	−0.357
3300	22.230	220.740	200.991	65.173	219.183	15.687	−0.248
3400	22.303	221.405	201.582	67.400	219.313	9.518	−0.146
3500	22.372	222.053	202.157	69.634	219.447	3.346	−0.050
3600	22.439	222.684	202.719	71.874	219.583	−2.830	0.041
3700	22.502	223.300	203.267	74.121	219.721	−9.011	0.127
3800	22.561	223.900	203.802	76.375	219.862	−15.194	0.209
3900	22.618	224.487	204.325	78.634	220.003	−21.382	0.286
4000	22.670	225.061	204.836	80.898	220.146	−27.573	0.360
4100	22.720	225.621	205.336	83.167	220.289	−33.768	0.430
4200	22.766	226.169	205.826	85.442	220.432	−39.966	0.497
4300	22.808	226.705	206.305	87.720	220.575	−46.168	0.561
4400	22.847	227.230	206.775	90.003	220.716	−52.373	0.622
4500	22.884	227.744	207.235	92.290	220.856	−58.581	0.680
4600	22.917	228.247	207.686	94.580	220.993	−64.792	0.736
4700	22.947	228.740	208.129	96.873	221.127	−71.006	0.789
4800	22.974	229.224	208.563	99.169	221.258	−77.223	0.840
4900	22.999	229.698	208.990	101.468	221.386	−83.443	0.890
5000	23.021	230.163	209.409	103.769	221.509	−89.665	0.937
5100	23.040	230.619	209.820	106.072	221.628	−95.890	0.982
5200	23.057	231.066	210.224	108.377	221.741	−102.117	1.026
5300	23.072	231.505	210.622	110.683	221.849	−108.346	1.068
5400	23.085	231.937	211.013	112.991	221.952	−114.577	1.108
5500	23.096	232.361	211.397	115.300	222.048	−120.810	1.147
5600	23.105	232.777	211.775	117.610	222.138	−127.044	1.185
5700	23.112	233.186	212.147	119.921	222.222	−133.281	1.221
5800	23.117	233.588	212.513	122.232	222.299	−139.518	1.256
5900	23.121	233.983	212.874	124.544	222.368	−145.757	1.290
6000	23.124	234.372	213.229	126.857	222.431	−151.997	1.323

PREVIOUS: September 1977 (1 atm) CURRENT: September 1982 (1 bar)

IP(S^+, g) = 188200 ± 100 cm^{-1}
$S°$(298.15 K) = 163.627 ± 0.03 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1274.311 ± 0.4 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1282.293] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4S_{3/2}$	0.0	4
$^2D_{3/2}$	14853.0	4
$^2D_{5/2}$	14884.8	6
$^2P_{1/2}$	24524.9	2
$^2P_{3/2}$	24571.6	4

Enthalpy of Formation

$\Delta_f H°(S^+, g, 0 K)$ is calculated from $\Delta_f H°(S, g, 0 K)$[1] using the spectroscopic value of IP(S) = 83558.0 ± 1 cm^{-1} (238.904 ± 0.01 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(S^+, g, 298.15 K)$ is calculated from $\Delta_f H°(S, g, 0 K)$ by using IP(S) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for S(g), $S^+(g)$, and e^-(ref). $\Delta_f H°(S \rightarrow S^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is approximately 79000 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	1274.311		
100	20.786	140.920	182.108	−4.119			
200	20.786	155.328	165.529	−2.040			
250	20.786	159.966	163.970	−1.001			
298.15	20.786	163.627	163.627	0.	1282.293	1236.811	−216.684
300	20.786	163.756	163.628	0.038	1282.328	1236.528	−215.299
350	20.786	166.960	163.881	1.078	1283.241	1228.822	−183.392
400	20.786	169.736	164.443	2.117	1281.888	1221.076	−159.456
450	20.786	172.184	165.170	3.156	1282.042	1213.457	−140.854
500	20.786	174.374	165.983	4.196	1282.118	1205.834	−125.973
600	20.786	178.164	167.707	6.274	1282.690	1190.530	−103.645
700	20.786	181.368	169.435	8.353	1283.500	1175.108	−87.688
800	20.786	184.143	171.104	10.431	1284.446	1159.560	−75.711
900	20.786	186.592	172.692	12.510	1232.347	1144.969	−66.452
1000	20.786	188.782	174.193	14.589	1234.648	1135.137	−59.293
1100	20.786	190.763	175.611	16.667	1236.934	1125.075	−53.425
1200	20.786	192.571	176.950	18.746	1239.204	1114.805	−48.526
1300	20.786	194.235	178.216	20.825	1241.459	1104.347	−44.373
1400	20.787	195.776	179.416	22.903	1243.698	1093.716	−40.807
1500	20.789	197.210	180.555	24.982	1245.922	1082.926	−37.711
1600	20.792	198.552	181.639	27.061	1248.131	1071.987	−34.997
1700	20.797	199.812	182.671	29.140	1250.326	1060.911	−32.598
1800	20.806	201.001	183.656	31.221	1252.509	1049.706	−30.462
1900	20.820	202.127	184.599	33.302	1254.679	1038.380	−28.547
2000	20.840	203.195	185.503	35.385	1256.839	1026.939	−26.821
2100	20.867	204.212	186.369	37.470	1258.991	1015.391	−25.256
2200	20.904	205.184	187.203	39.558	1261.135	1003.741	−23.832
2300	20.951	206.114	188.005	41.651	1263.275	991.994	−22.529
2400	21.009	207.007	188.778	43.749	1265.410	980.153	−21.332
2500	21.080	207.866	189.525	45.853	1267.545	968.223	−20.230
2600	21.164	208.694	190.246	47.965	1269.679	956.208	−19.210
2700	21.262	209.495	190.944	50.086	1271.817	944.111	−18.265
2800	21.374	210.270	191.621	52.218	1273.960	931.935	−17.385
2900	21.500	211.022	192.277	54.362	1276.108	919.682	−16.565
3000	21.640	211.753	192.914	56.519	1278.265	907.354	−15.798
3100	21.795	212.465	193.533	58.690	1280.432	894.955	−15.080
3200	21.962	213.160	194.136	60.878	1282.611	882.486	−14.405
3300	22.142	213.839	194.722	63.083	1284.802	869.948	−13.770
3400	22.335	214.502	195.295	65.307	1287.009	857.343	−13.171
3500	22.538	215.153	195.853	67.550	1289.230	844.674	−12.606
3600	22.751	215.791	196.398	69.815	1291.469	831.941	−12.071
3700	22.973	216.417	196.930	72.101	1293.725	819.145	−11.564
3800	23.204	217.033	197.451	74.410	1296.000	806.288	−11.083
3900	23.441	217.638	197.961	76.742	1298.293	793.371	−10.626
4000	23.684	218.235	198.460	79.098	1300.606	780.395	−10.191
4100	23.931	218.823	198.950	81.479	1302.939	767.361	−9.776
4200	24.182	219.403	199.430	83.884	1305.292	754.269	−9.381
4300	24.436	219.975	199.901	86.315	1307.665	741.122	−9.003
4400	24.691	220.539	200.364	88.772	1310.059	727.919	−8.641
4500	24.946	221.097	200.818	91.253	1312.472	714.661	−8.296
4600	25.201	221.648	201.265	93.761	1314.905	701.350	−7.964
4700	25.454	222.193	201.705	96.294	1317.358	687.985	−7.646
4800	25.705	222.731	202.137	98.852	1319.830	674.568	−7.341
4900	25.953	223.264	202.563	101.434	1322.320	661.099	−7.047
5000	26.197	223.791	202.982	104.042	1324.828	647.580	−6.765
5100	26.436	224.312	203.395	106.674	1327.354	634.010	−6.494
5200	26.671	224.827	203.803	109.329	1329.897	620.390	−6.232
5300	26.899	225.338	204.204	112.008	1332.456	606.721	−5.980
5400	27.121	225.842	204.600	114.709	1335.030	593.004	−5.736
5500	27.337	226.342	204.991	117.432	1337.619	579.239	−5.501
5600	27.545	226.837	205.377	120.176	1340.222	565.427	−5.274
5700	27.746	227.326	205.757	122.940	1342.838	551.568	−5.055
5800	27.940	227.810	206.133	125.725	1345.466	537.663	−4.842
5900	28.125	228.289	206.505	128.528	1348.106	523.713	−4.637
6000	28.302	228.763	206.872	131.350	1350.756	509.718	−4.437

PREVIOUS: September 1977 (1 atm) CURRENT: September 1982 (1 bar)

EA(S, g) = 2.077120 ± 0.000001 eV
$S°(298.15\ K) = 164.918 \pm 0.001\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 74.325 \pm 0.25\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = [70.180]\ kJ \cdot mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_3$	0.0	4
$^2P_1$	483.54	2

Enthalpy of Formation

$\Delta_f H°(S^-, g, 0\ K)$ is calculated from $\Delta_f H°(S, g, 0\ K)$[1] using the adopted electron affinity of EA(S) = 2.077120 ± 0.000001 eV (200.4100 ± 0.0001 $kJ \cdot mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a tunable laser photodetachment threshold study.[3] Additional information on $S^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(S^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(S, g, 0\ K)$ by using EA(S) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for $S^-(g)$, S(g), and e^-(ref). $\Delta_r H°(S^- \rightarrow S + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ \cdot mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state and the fine-structure separation (483.54 ± 0.01 cm^{-1}) for $S^-(g)$ has been experimentally determined;[3] a discussion of the relevant work is given by Hotop and Lineberger[2] and Massey.[6] Lacking any experimental evidence as to the stability of any excited states, we assume no stable excited states exist.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.465	74.325		
100	20.977	140.952	184.787	−4.383			
200	22.291	155.895	166.994	−2.220			
250	22.660	160.914	165.293	−1.095			
298.15	22.783	164.918	164.918	0.	70.180	36.822	−6.451
300	22.784	165.059	164.919	0.042	70.142	36.615	−6.375
350	22.757	168.571	165.196	1.181	69.075	31.111	−4.643
400	22.653	171.603	165.812	2.317	65.741	25.851	−3.376
450	22.515	174.264	166.606	3.446	63.905	20.966	−2.434
500	22.370	176.628	167.493	4.568	61.985	16.300	−1.703
600	22.096	180.682	169.364	6.791	58.545	7.492	−0.652
700	21.868	184.071	171.229	8.989	55.317	−0.760	0.057
800	21.687	186.978	173.021	11.166	52.205	−8.558	0.559
900	21.543	189.524	174.716	13.327	−3.969	−14.889	0.864
1000	21.429	191.788	176.312	15.476	−5.756	−16.007	0.836
1100	21.338	193.826	177.813	17.614	−7.568	−16.944	0.805
1200	21.264	195.679	179.226	19.744	−9.403	−17.716	0.771
1300	21.203	197.378	180.558	21.867	−11.261	−18.334	0.737
1400	21.153	198.948	181.816	23.985	−13.140	−18.807	0.702
1500	21.112	200.406	183.007	26.098	−15.039	−19.146	0.667
1600	21.076	201.767	184.138	28.207	−16.956	−19.357	0.632
1700	21.047	203.044	185.213	30.313	−18.891	−19.448	0.598
1800	21.021	204.246	186.237	32.417	−20.843	−19.425	0.564
1900	20.999	205.382	187.215	34.518	−22.810	−19.292	0.530
2000	20.980	206.459	188.151	36.617	−24.791	−19.056	0.498
2100	20.963	207.482	189.047	38.714	−26.785	−18.720	0.466
2200	20.949	208.457	189.907	40.809	−28.791	−18.289	0.434
2300	20.936	209.388	190.734	42.904	−30.807	−17.767	0.403
2400	20.924	210.279	191.530	44.997	−32.833	−17.156	0.373
2500	20.914	211.133	192.297	47.089	−34.869	−16.461	0.344
2600	20.905	211.953	193.037	49.180	−36.912	−15.685	0.315
2700	20.897	212.742	193.753	51.270	−38.963	−14.829	0.287
2800	20.890	213.501	194.445	53.359	−41.020	−13.898	0.259
2900	20.883	214.234	195.114	55.448	−43.083	−12.893	0.232
3000	20.877	214.942	195.764	57.536	−45.153	−11.817	0.206
3100	20.871	215.627	196.393	59.623	−47.227	−10.671	0.180
3200	20.866	216.289	197.005	61.710	−49.307	−9.459	0.154
3300	20.862	216.931	197.599	63.796	−51.391	−8.181	0.130
3400	20.858	217.554	198.177	65.882	−53.479	−6.841	0.105
3500	20.854	218.158	198.739	67.968	−55.573	−5.439	0.081
3600	20.850	218.746	199.287	70.053	−57.671	−3.976	0.058
3700	20.847	219.317	199.820	72.138	−59.773	−2.456	0.035
3800	20.844	219.873	200.341	74.222	−61.880	−0.879	0.012
3900	20.841	220.414	200.849	76.307	−63.991	0.754	−0.010
4000	20.838	220.942	201.344	78.391	−66.108	2.441	−0.032
4100	20.836	221.457	201.829	80.474	−68.229	4.181	−0.053
4200	20.834	221.959	202.302	82.558	−70.355	5.973	−0.074
4300	20.832	222.449	202.765	84.641	−72.487	7.816	−0.095
4400	20.830	222.928	203.218	86.724	−74.624	9.708	−0.115
4500	20.828	223.396	203.661	88.807	−76.767	11.648	−0.135
4600	20.826	223.854	204.095	90.890	−78.916	13.637	−0.155
4700	20.824	224.301	204.520	92.972	−81.070	15.672	−0.174
4800	20.823	224.740	204.937	95.055	−83.232	17.753	−0.193
4900	20.821	225.169	205.345	97.137	−85.399	19.880	−0.212
5000	20.820	225.590	205.746	99.219	−87.573	22.050	−0.230
5100	20.819	226.002	206.139	101.301	−89.754	24.264	−0.249
5200	20.818	226.406	206.525	103.383	−91.943	26.521	−0.266
5300	20.816	226.803	206.904	105.464	−94.138	28.820	−0.284
5400	20.815	227.192	207.276	107.546	−96.340	31.161	−0.301
5500	20.814	227.574	207.642	109.627	−98.550	33.542	−0.319
5600	20.813	227.949	208.001	111.709	−100.767	35.964	−0.335
5700	20.812	228.317	208.354	113.790	−102.992	38.425	−0.352
5800	20.811	228.679	208.701	115.871	−105.224	40.926	−0.369
5900	20.811	229.035	209.043	117.952	−107.464	43.465	−0.385
6000	20.810	229.385	209.379	120.033	−109.711	46.042	−0.401

PREVIOUS: September 1977 (1 atm) CURRENT: September 1982 (1 bar)

$S°(298.15\ K) = 223.80 \pm 2.0\ J\cdot K^{-1}\cdot mol^{-1}$

$\Delta_f H°(0\ K) = 104.6 \pm 12.6\ kJ\cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 106.0 \pm 12.6\ kJ\cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$X^1\Sigma^+$	0	1
$[a^3\Pi]$	[24700]	6
$D^1\Pi$	35029	2
$[e^3\Sigma^-]$	[35140]	3
F	37114	2
$I^1\Sigma^-$	[37290]	1
$\Sigma^1\Sigma^+$	41924	1

$\omega_e = 740.34\ cm^{-1}$ $\omega_e x_e = 2.544\ cm^{-1}$ $\sigma = 1$
$B_e = 0.29930\ cm^{-1}$ $\alpha_e = 0.00145\ cm^{-1}$ $r_e = 1.92932$

Enthalpy of Formation

Herzberg[2] suggests a dissociation energy for SiS(g) of 6.6 eV. This result was derived from a spectroscopic analysis of the D–X and E–X band systems by Barrow and Jevons,[4] Vago and Barrow,[5] and Barrow.[6] Robinson and Barrow[8] extended the work of Vago and Barrow[5] and arrived at a value of 147.4 ± 3.0 kcal·mol^{-1} (6.39 eV). In this latter work, a graphical Birge–Sponer extrapolation was made using 28 vibrational levels of the E state. The highest level is quite near the convergence limit and thus only a short extrapolation is necessary. The extrapolation graphically indicates the absolute minimum and maximum to be 6.28 eV and 6.57 eV, respectively. This amounts to a range of maximum uncertainty of approximately 7 kcal·mol^{-1}. The products of the dissociation must be Si(^{3}p) and S(^{3}p) but it is not certain as to which of the sublevels of the ^{3}p states are involved. This leads to an uncertainty of ±1.2 kcal·mol^{-1}.[8] The result is in agreement with a rotational analysis of the $D^1\Pi$–$X^1\Sigma^+$ system by Lagerqvist, Nilheden, and Barrow[7] which led to a value of 6.47 eV (149.2 kcal·mol^{-1}).

The value of the dissociation energy chosen is 147.4 ± 3.0 kcal·mol^{-1}, based on the work by Robinson and Barrow.[8] Gaydon[1] and Vedeneyev *et al.*[3] suggest a similar value, based on the work by Robinson and Barrow[8] and others. This value is also consistent with the tabulated dissociation energies of Gaydon[1] as far as trends which might be expected in the oxides, sulfides, and selenides of C, Si, Ge, Sn, and Pb. The resulting enthalpy of formation is $\Delta_f H°(0\ K) = 25.01 \pm 3.00$ kcal·mol^{-1}.

Rosenqvist and Tungesvik[13] studied two reaction systems by a transportation method. By combining these two systems, the standard free energy of the reaction 2 Si(s) + S_2(g) = 2 SiS(g) was calculated. Using JANAF values[14] for Si(s) and S_2(g), $\Delta_f G°$ (1 atm) values for SiS(g) at 0 K and 300 K are 27.652 kcal·mol^{-1} and 15.933 kcal·mol^{-1}, respectively. These values are within the error range of the values in this tabulation.

Heat Capacity and Entropy

The spectroscopic constants, corrected for the natural abundances of Si and S, are from Hoeft,[9] and Lagerqvist, Nilheden, and Barrow.[7]

Herzberg[2] tabulates the $X^1\Sigma^+$, $D^1\Pi$, and E states and comments on unresolved bands at 16000–29000 cm^{-1}. The $a^3\Pi$ state is predicted by an interpolation of similar $a^3\Pi$ $X^1\Sigma^+$ splittings in the sulfides and oxides of C, Ge, Sn.[10,11] The remaining states are deduced by a rotational analysis of the E–X system of SiS.[7, 12] It is not known conclusively whether the F state is $^1\Pi$ or $^1\Delta$. The energy of the e and I states are upper bound estimates.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J\cdot K^{-1}\cdot mol^{-1}$			$kJ\cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−8.940	104.650	104.650	INFINITE
100	29.129	190.877	251.180	−6.030	106.603	89.151	−46.568
200	30.303	211.317	226.691	−3.075	106.738	71.535	−18.683
250	31.355	218.191	224.325	−1.534	106.410	62.769	−13.115
298.15	32.332	223.799	223.799	0.	105.960	54.403	−9.531
300	32.368	223.999	223.799	0.060	105.941	54.083	−9.417
350	33.239	229.056	224.197	1.701	105.380	45.483	−6.788
400	33.953	233.542	225.090	3.381	102.543	37.056	−4.839
450	34.531	237.576	226.257	5.094	101.206	28.942	−3.359
500	34.996	241.239	227.575	6.832	99.789	20.990	−2.193
600	35.681	247.684	230.404	10.368	97.364	5.464	−0.476
700	36.148	253.222	233.277	13.961	95.162	−9.676	0.722
800	36.478	258.072	236.080	17.594	93.074	−24.510	1.600
900	36.722	262.383	238.767	21.254	37.916	−38.005	2.206
1000	36.908	266.262	241.326	24.936	37.131	−46.399	2.424
1100	37.054	269.787	243.755	28.634	36.302	−54.712	2.598
1200	37.173	273.016	246.061	32.346	35.428	−62.947	2.740
1300	37.271	275.995	248.251	36.068	34.507	−71.108	2.857
1400	37.355	278.761	250.332	39.800	33.538	−79.197	2.955
1500	37.427	281.340	252.315	43.539	32.519	−87.214	3.037
1600	37.491	283.758	254.205	47.285	31.451	−95.161	3.107
1700	37.548	286.033	256.011	51.037	−19.845	−102.594	3.152
1800	37.600	288.180	257.739	54.794	−20.783	−107.435	3.118
1900	37.647	290.214	259.395	58.556	−21.730	−112.223	3.085
2000	37.692	292.147	260.985	62.323	−22.684	−116.961	3.055
2100	37.733	293.987	262.513	66.095	−23.645	−121.651	3.026
2200	37.773	295.743	263.984	69.870	−24.612	−126.295	2.999
2300	37.811	297.423	265.401	73.649	−25.584	−130.896	2.973
2400	37.848	299.033	266.769	77.432	−26.561	−135.453	2.948
2500	37.885	300.579	268.091	81.219	−27.543	−139.971	2.925
2600	37.922	302.065	269.369	85.009	−28.528	−144.448	2.902
2700	37.959	303.497	270.607	88.803	−29.516	−148.888	2.880
2800	37.998	304.878	271.806	92.601	−30.505	−153.291	2.860
2900	38.040	306.212	272.970	96.403	−31.496	−157.659	2.840
3000	38.084	307.503	274.100	100.209	−32.489	−161.992	2.821
3100	38.132	308.752	275.197	104.020	−33.481	−166.293	2.802
3200	38.185	309.964	276.265	107.836	−34.472	−170.561	2.784
3300	38.243	311.140	277.304	111.657	−35.462	−174.799	2.767
3400	38.308	312.282	278.316	115.484	−36.451	−179.006	2.750
3500	38.380	313.394	279.303	119.319	−37.436	−183.185	2.734
3600	38.460	314.476	280.265	123.161	−422.570	−176.874	2.566
3700	38.549	315.531	281.204	127.011	−423.134	−170.041	2.401
3800	38.648	316.560	282.121	130.871	−423.694	−163.194	2.243
3900	38.758	317.566	283.017	134.741	−424.250	−156.331	2.094
4000	38.880	318.548	283.893	138.623	−424.800	−149.454	1.952
4100	39.013	319.510	284.750	142.517	−425.342	−142.564	1.816
4200	39.160	320.452	285.589	146.426	−425.876	−135.660	1.687
4300	39.320	321.375	286.410	150.350	−426.399	−128.744	1.564
4400	39.493	322.281	287.215	154.290	−426.912	−121.816	1.446
4500	39.681	323.171	288.004	158.249	−427.411	−114.876	1.333
4600	39.884	324.045	288.778	162.227	−427.897	−107.926	1.226
4700	40.101	324.905	289.538	166.226	−428.367	−100.965	1.122
4800	40.334	325.752	290.283	170.248	−428.821	−93.994	1.023
4900	40.582	326.586	291.016	174.294	−429.256	−87.014	0.928
5000	40.844	327.408	291.735	178.365	−429.672	−80.025	0.836
5100	41.122	328.220	292.443	182.463	−430.067	−73.028	0.748
5200	41.415	329.021	293.139	186.590	−430.440	−66.024	0.663
5300	41.723	329.813	293.823	190.746	−430.791	−59.012	0.582
5400	42.045	330.596	294.497	194.935	−431.116	−51.995	0.503
5500	42.381	331.370	295.160	199.156	−431.416	−44.971	0.427
5600	42.730	332.137	295.814	203.411	−431.689	−37.942	0.354
5700	43.092	332.897	296.458	207.702	−431.935	−30.909	0.283
5800	43.467	333.649	297.092	212.030	−432.152	−23.871	0.215
5900	43.853	334.396	297.718	216.396	−432.340	−16.830	0.149
6000	44.251	335.136	298.336	220.801	−432.496	−9.787	0.085

PREVIOUS: December 1971 (1 atm) CURRENT: December 1971 (1 bar)

$S°(298.15\ K) = 68.41 \pm 0.8\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = -467.4 \pm 17\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = -468.6 \pm 17\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Sabatier[1] measured the enthalpy of solution of SrS in hydrochloric acid solution as $\Delta_r H(283.6\ K) = -26.9 \pm 1.0\ kcal \cdot mol^{-1}$ for SrS(cr) + 2 HCl(aq, 100 H_2O) → $SrCl_2$(aq, 100 H_2O) + H_2S(aq). We derive $\Delta_f H°$(SrS, cr, 298.15 K) = $-113.1 \pm 2.0\ kcal \cdot mol^{-1}$ based on the following auxiliary data: $\Delta_f H°$(HCl·aq, 100 H_2O, 298.15 K) = $-39.657\ kcal \cdot mol^{-1}$ (3), $\Delta_f H°$(H_2S, aq, 298.15 K) = $-9.5\ kcal \cdot mol^{-1}$,[2] and $\Delta_f H°$($SrCl_2$·aq, 200 H_2O, 298.15 K) = $-209.78\ kcal \cdot mol^{-1}$.[3] The uncertainty reflects the correction to 298.15 K and the ambiguity of the exact solution composition. Mourlot[4] also measured the enthalpy of solution of SrS in hydrochloric acid solution as $\Delta_r H° = -27.1 \pm 1.0\ kcal \cdot mol^{-1}$ from which we calculate $\Delta_f H°$(SrS, cr, 298.15 K) = $-112.8 \pm 2.0\ kcal \cdot mol^{-1}$, using the same auxiliary data.

Cater and Johnson[5] determined that SrS sublimes congruently and derived partial pressures of the various gaseous species Sr(g), S(g), and SrS(g) in an effusion and mass-spectrometric study. We analyze their data and the equilibrium study of Schenck and Hammerschmidt[6] below. Other mass-spectrometric studies of Berkowitz and Marquart[7] and Colin *et al.*[8] are also listed. The calculated 3rd law $\Delta_r H°$(298.15 K) may have an uncertainty of 0.5 $kcal \cdot mol^{-1}$ since the JANAF Gibbs energy functions are partially based on the estimated $C_p°$ data (above 300 K).

The enthalpy of solution studies[1,4] show wide disagreement from the mass spectrometric studies.[5,7,8] Our experience tends to indicate that mass spectrometric experiments provide very good data on gas phase species for homogeneous reactions, but are not as reliable for condensed phases in heterogeneous reactions. A weighted average of the equilibrium and enthalpy of solution studies, $\Delta_f H°$(SrS, cr, 298.15 K) = $-112.0 \pm 4\ kcal \cdot mol^{-1}$ is adopted in the tabulation.

Source	Method	Reaction*	T/K	Data Points	δS cal·K⁻¹·mol⁻¹	Δ$_f$H°(298.15 K), kcal·mol⁻¹ 2nd law	3rd law	Δ$_f$H°(298.15 K) kcal·mol⁻¹
[5]	Knudsen mass spec.	A	1825–2181	Equation	1.26	212.70	210.18 ± 0.38	−104.70 ± 2
[5]	Knudsen mass spec.	B	1825–2181	Equation	0.23	131.75	131.29 ± 0.08	−105.43 ± 2
[6]	Equilibrium	C	1237–1383	3	8.8 ± 1.8	−53.0 ± 2.4	−64.55 ± 1.3	−110.02 ± 4
[7]	Mass spec.	B	1809	1			210.18 ± 1.0	−104.7 ± 2
[8]	Mass spec.	D	1857–2170	9	−12.6 ± 2.8	−3.3 ± 5.5	21.8 ± 2.4	−119.8 ± 16
[9]	Vaporization	B	1400–1700	Equation	−3.3	102.6	107.7 ± 0.9	82 ± 30

A) SrS(cr) = Sr(g) + S(g)
B) SrS(cr) = SrS(g)
C) SrS(cr) + 2 SO_2(g) = $SrSO_4$(cr) + S_2(g)
D) SrS(cr) + 3 S(g) = Sr(g) + 2 S_2(g)

Heat Capacity and Entropy

King and Weller[10] measured the low temperature heat capacities from 53–296 K. Their smooth values are adopted in the tabulation. The entropy, S°(298.15 K) = 16.3 ± 0.2 $cal \cdot K^{-1} \cdot mol^{-1}$, is based on S°(51 K) = 1.59 $cal \cdot K^{-1} \cdot mol^{-1}$ as extrapolated by King and Weller using Debye and Einstein functions (θ_D = 208, θ_E = 311). The $C_p°$ values above 300 K are estimated by graphical extrapolation combined with method B of Kubaschewski *et al.*[11]

Fusion Data

Literature melting data for SrS(cr) are not available. The value quoted by Mills[12] for the melting point, 2275 K, seems too low when compared to the alkaline earth oxide melting points.[13]

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[13]JANAF Thermochemical Tables: BaO(cr), 6–30–74; CaO(cr), 6–30–73; SrO(cr), 12–31–72.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K⁻¹·mol⁻¹)	$S° - [G° - H°(T_r)]/T$ (J·K⁻¹·mol⁻¹)	$H° - H°(T_r)$ (kJ·mol⁻¹)	Δ$_f$H° (kJ·mol⁻¹)	Δ$_f$G° (kJ·mol⁻¹)	log K$_f$
0	0.	0.	INFINITE	−9.811	−467.438	−467.438	INFINITE
100	32.008	22.471	108.640	−8.617	−468.434	−466.624	243.739
200	44.936	49.669	72.763	−4.619	−468.566	−464.731	121.375
298.15	48.702	68.410	68.410	0.	−468.608	−462.842	81.088
300	48.727	68.711	68.411	0.090	−468.609	−462.806	80.582
400	50.208	82.927	70.339	5.035	−470.990	−460.763	60.169
500	51.882	94.318	74.032	10.143	−472.639	−458.026	47.850
600	53.179	103.897	78.232	15.399	−473.897	−454.979	39.609
700	54.099	112.165	82.503	20.764	−474.913	−451.744	33.710
800	54.894	119.443	86.674	26.215	−475.813	−448.372	29.276
900	55.522	125.944	90.683	31.735	−530.424	−443.737	25.754
1000	56.233	131.832	94.508	37.324	−529.724	−434.143	22.677
1100	56.777	137.217	98.149	42.974	−536.882	−424.255	20.146
1200	57.321	142.180	101.614	48.679	−537.010	−414.010	18.021
1300	57.870	146.790	104.914	54.439	−537.099	−403.756	16.223
1400	58.409	151.099	108.061	60.253	−537.150	−393.496	14.682
1500	58.937	155.146	111.066	66.120	−537.162	−383.235	13.345
1600	59.455	158.967	113.942	72.040	−537.137	−372.974	12.176
1700	59.951	162.586	116.698	78.010	−673.990	−361.536	11.109
1800	60.459	166.027	119.343	84.030	−672.032	−343.212	9.960
1900	60.982	169.310	121.887	90.103	−670.040	−324.999	8.935
2000	61.505	172.451	124.338	96.227	−668.017	−306.891	8.015
2100	62.028	175.465	126.701	102.403	−665.965	−288.885	7.186
2200	62.551	178.362	128.984	108.632	−663.886	−270.977	6.434
2300	63.074	181.154	131.192	114.914	−661.788	−253.165	5.750
2400	63.597	183.850	133.330	121.247	−659.674	−235.444	5.124
2500	64.120	186.456	135.403	127.633	−657.552	−217.811	4.551
2600	64.643	188.981	137.416	134.071	−655.430	−200.263	4.023
2700	65.166	191.431	139.371	140.562	−653.314	−182.797	3.536
2800	65.689	193.810	141.273	147.104	−651.216	−165.409	3.086
2900	66.212	196.124	143.125	153.699	−649.143	−148.095	2.667
3000	66.735	198.378	144.929	160.347	−647.107	−130.853	2.278

PREVIOUS: CURRENT: September 1977

$S°(298.15\ K) = 243.107 \pm 0.42\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 109.6 \pm 8.4\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 108.2 \pm 8.4\ kJ·mol^{-1}$

Electronic States and Molecular Constants

State	ϵ_i, cm^{-1}	g_i	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	r_e, Å	Source
$X^1\Sigma^+$	0.0	1	388.38	1.310	0.12072	0.00044	2.4405	7
$^3\pi$	[7800.]	6	[270]	[1.1]	[0.0943]	[0.0005]	[2.76]	6
$^3\Sigma^+$	[8000.]	3	[330]	[1.2]	[0.114]	[0.0005]	[2.51]	6
$^1\pi$	[8100.]	2	[270]	[1.1]	[0.0943]	[0.0005]	[2.76]	6
$^1\Sigma^+$	[11000.]	1	[330]	[1.2]	[0.114]	[0.0005]	[2.51]	6
$B^1\Sigma^+$	26531.2	1	286.8	0.84	0.10566	0.00032	2.609	7,8

Enthalpy of Formation

The adopted value for the enthalpy of formation, $\Delta_f H°$(SrS, g, 298.15 K) = 25.86 ± 2 kcal·mol^{-1}, is based on the Knudsen mass spectrometric studies analyzed below. The three independent studies are in very good agreement and we have chosen the average of the measurements. Our value is in very good agreement with $\Delta_f H°(298.15\ K) = 25.0$ kcal·mol^{-1} adopted by NBS[4] and is slightly greater than $\Delta_f H°(298.15\ K) = 24.1 \pm 4$ kcal·mol^{-1} obtained by Mills[5] (using different Gibbs energy functions) in a recent critical compilation. Using auxiliary JANAF data[6] and a recommended value for $D_0°(S_2, g,) = 100.69 \pm 0.01$ kcal·mol^{-1},[6] we calculate $D_0°$(SrS, g) = 78.8 ± 2.0 kcal·mol^{-1}.

Source	Method	Reaction*	T/K	Data Points	δS cal·K^{-1}·mol^{-1}	$\Delta_f H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	$\Delta_f H°$(298.15 K) kcal·mol^{-1}	$D_0°$ kcal·mol^{-1}
1	Mass spec	A	2010–2170	4	−1.86 ± 8.5	17.42 ± 17.9	21.310 ± 1.60	25.06 ± 1.66	79.63 ± 2.0
2	Mass spec	A	1809–1934	2	6.85	34.19	21.375 ± 1.21	25.12 ± 1.3	79.56 ± 1.5
3	Mass spec	A	1825–2181	Equation	−1.16	20.85	23.07 ± 0.34	26.82 ± 0.6	77.87 ± 1.0
3	Mass spec	B	1825–2181	Equation	−1.03	−80.95	−78.89 ± 0.31	26.60 ± 0.6	78.09 ± 0.3

*A) Sr(g) + S_2(g) = SrS(g) + S(g) B) Sr(g) + S(g) = SrS(g)

Heat Capacity and Entropy

Electronic levels (T_e) and vibrational–rotational constants for the observed states are from the optical study of Barrow.[7,8] Other low–lying electronic states and their vibrational–rotational constants are estimated in isoconfigurational groups by analogy with SrO[6] and from trends observed in the known states of the other alkaline–earth oxides and sulfides.[6] Uncertainty in the energy and constants for the estimated states may contribute as much as 2–3 cal·K^{-1}·mol^{-1} to $S°$ at 3000 K. The molecular constants have been corrected to the natural isotopic abundances. The thermodynamic functions are calculated using first–order anharmonic corrections to Q_r^i and Q_v^i in the partition function $Q = Q_{ii}\Sigma Q_r^i Q_v^i g_i \exp(-c_2\epsilon_i/T)$.

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[5] K. C. Mills, "Thermodynamic Data for Inorganic Sulphies, Selenides, and Tellurides," Butterworths, London, (1974).
[6] JANAF Thermochemical Tables: Sr(g), 12–31–70; S(g), 6–30–71; S_2(g), 12–31–65; BaO(g), SrO(g), 6–30–74; BeO(g), CaO(g), MgO(g), 12–31–74; BeS(g), MgS(g), CaS(g), BaS(g), 9–30–77.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ J·K^{-1}·mol^{-1}	$S°$ J·K^{-1}·mol^{-1}	$-[G°-H°(T_r)]/T$ J·K^{-1}·mol^{-1}	$H°-H°(T_r)$ kJ·mol^{-1}	$\Delta_f H°$ kJ·mol^{-1}	$\Delta_f G°$ kJ·mol^{-1}	log K_f
0	0.	0.	INFINITE	−9.536	109.642	109.642	INFINITE
100	30.117	207.226	273.308	−6.608	110.381	93.716	−48.952
200	33.694	229.274	246.305	−3.406	109.453	77.367	−20.206
250	34.778	236.918	243.688	−1.692	108.845	69.410	−14.502
298.15	35.477	243.107	243.107	0.	108.198	61.878	−10.841
300	35.499	243.327	243.108	0.066	108.172	61.591	−10.724
350	35.993	248.838	243.542	1.854	107.441	53.884	−8.042
400	36.343	253.669	244.512	3.663	104.443	46.374	−6.056
450	36.601	257.965	245.773	5.486	102.940	39.197	−4.550
500	36.796	261.832	247.188	7.322	101.346	32.202	−3.364
600	37.072	268.567	250.207	11.016	98.526	18.642	−1.623
700	37.262	274.296	253.249	14.733	95.863	5.540	−0.413
800	37.414	279.282	256.198	18.467	93.246	−7.185	0.469
900	37.578	283.698	259.013	22.216	36.864	−18.428	1.070
1000	37.811	287.668	261.683	25.985	35.743	−24.512	1.280
1100	38.185	291.288	264.212	29.783	26.734	−30.118	1.430
1200	38.773	294.634	266.610	33.629	24.746	−35.198	1.532
1300	39.639	297.770	268.887	37.547	22.816	−40.115	1.612
1400	40.828	300.749	271.057	41.568	20.972	−44.886	1.675
1500	42.357	303.616	273.133	45.724	19.249	−49.529	1.725
1600	44.211	306.407	275.126	50.050	17.680	−54.062	1.765
1700	46.345	309.150	277.047	54.576	−120.618	−57.323	1.761
1800	48.689	311.865	278.906	59.326	−119.930	−53.618	1.556
1900	51.155	314.563	280.711	64.318	−119.019	−49.958	1.373
2000	53.642	317.250	282.471	69.558	−117.880	−46.352	1.211
2100	56.053	319.926	284.191	75.044	−116.518	−42.808	1.065
2200	58.297	322.586	285.876	80.763	−114.950	−39.334	0.934
2300	60.298	325.223	287.530	86.695	−113.200	−35.935	0.816
2400	62.001	327.826	289.154	92.813	−111.302	−32.616	0.710
2500	63.372	330.386	290.753	99.084	−109.295	−29.378	0.614
2600	64.398	332.893	292.325	105.475	−107.219	−26.223	0.527
2700	65.086	335.337	293.873	111.952	−105.117	−23.147	0.448
2800	65.456	337.712	295.397	118.482	−103.032	−20.150	0.376
2900	65.538	340.011	296.896	125.034	−101.002	−17.226	0.310
3000	65.370	342.231	298.370	131.581	−99.066	−14.370	0.250
3100	64.991	344.369	299.820	138.101	−97.255	−11.577	0.195
3200	64.443	346.424	301.244	144.574	−95.598	−8.840	0.144
3300	63.762	348.397	302.643	150.985	−94.120	−6.152	0.097
3400	62.983	350.289	304.017	157.323	−92.841	−3.506	0.054
3500	62.136	352.102	305.365	163.580	−91.778	−0.895	0.013
3600	61.248	353.840	306.688	169.749	−90.945	1.689	−0.025
3700	60.339	355.506	307.985	175.828	−90.349	4.254	−0.060
3800	59.427	357.103	309.257	181.817	−89.998	6.805	−0.094
3900	58.526	358.635	310.503	187.714	−89.896	9.351	−0.125
4000	57.645	360.106	311.725	193.523	−90.045	11.897	−0.155
4100	56.793	361.519	312.922	199.244	−90.443	14.450	−0.184
4200	55.975	362.877	314.096	204.882	−91.085	17.016	−0.212
4300	55.195	364.185	315.246	210.440	−91.972	19.599	−0.238
4400	54.455	365.446	316.372	215.923	−93.097	22.207	−0.264
4500	53.756	366.661	317.476	221.333	−94.451	24.842	−0.288
4600	53.098	367.836	318.558	226.675	−95.962	27.505	−0.312
4700	52.481	368.971	319.619	231.954	−97.733	30.208	−0.336
4800	51.903	370.070	320.659	237.172	−99.702	32.950	−0.359
4900	51.364	371.134	321.678	242.336	−101.861	35.736	−0.381
5000	50.861	372.167	322.677	247.446	−104.191	38.567	−0.403
5100	50.394	373.169	323.658	252.509	−106.669	41.444	−0.424
5200	49.960	374.144	324.619	257.526	−109.320	44.374	−0.446
5300	49.557	375.091	325.563	262.502	−112.113	47.356	−0.467
5400	49.183	376.014	326.488	267.439	−115.037	50.392	−0.487
5500	48.837	376.913	327.397	272.339	−118.080	53.484	−0.508
5600	48.517	377.790	328.289	277.207	−121.231	56.631	−0.528
5700	48.221	378.647	329.165	282.044	−124.479	59.836	−0.548
5800	47.948	379.483	330.026	286.852	−127.814	63.099	−0.568
5900	47.696	380.300	330.871	291.634	−131.016	66.395	−0.588
6000	47.464	381.100	331.701	296.392	−134.465	69.770	−0.607

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 228.165 \pm 0.05\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 128.30 \pm 0.30\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 128.60 \pm 0.30\ kJ \cdot mol^{-1}$

Electronic and Molecular Constants								
State	g_i	ϵ_i, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	B_e, cm^{-1}	α_e, cm^{-1}	D_e, cm^{-1}	r_e, Å
$X^3\Sigma_g^-$	3	0	724.67	2.836	0.2946	0.00157	2.134×10^{-7}	1.889
$a^1\Delta_g$	2	4700	702.35	3.09	0.2923	0.0017	2.040×10^{-7}	1.889
$b^1\Delta_g$	1	8500	700.87	3.47	[0.29]	[0.0016]	$[2.0 \times 10^{-7}]$	—
$A^3\Delta$	6	21855	488.6	2.63	0.2284	0.0014	1.996×10^{-7}	2.148

Enthalpy of Formation

The adopted enthalpy of formation is that selected by CODATA.[1] The value was calculated from measurments of the equilibrium $H_2S(g) = H_2(g) \pm 0.05\ S_2(g)$ reported by Randall and Bichowsky,[2] Preuner,[3] and Preuner and Schupp,[4] and from measurements of the partial pressure of S_2(g) over sulfur reported by Drowart *et al.*[5]

The dissociation energy, $D_0° = 35216.4 \pm 2.5\ cm^{-1}$ (100.689 ± 0.021 kcal·mol^{-1}) is from the spectroscopic study by Ricks and Barrow.[12]

Heat Capacity and Entropy

The thermal functions above 600 K are calculated using the program of McBride and Gordon.[6] The contribution of vibrational anharmonicity, rotation–vibration interaction, and centrifugal stretching are calculated via the procedures given by Pennington and Kobe.[7] The electronic and molecular constant data in the above table are that summarized by Rosen[8] and Suchard[9] with the exception that the position of the $a^1\Delta_g$ state at 4700 ± 800 cm^{-1} is from the more recent absorption study by Carleer and Colin.[10] The thermal functions below 600 K are calculated by direct summation over vibrational–rotational energy levels of the ground state (including the proper treatment of the splitting of this level, i.e. $\alpha = -0.0066\ cm^{-1}$ and = 11.84 cm^{-1} and three excited states. We performed the direct summation with a program written by W. H. Evans of the U. S. Bureau of Standards. The direct summation results are not extended to temperatures above 600 K since the enrgy levels derived from the reported vibrational– rotational constants do not converge to the dissociation energy. For these higher temperatures, the program of McBride and Gordon is used, as in the case of gaseous O_2.[11]

The value of $S°(298.15\ K)$ agrees exactly with the CODATA recommended value.[1] The uncertainty in $S°(298.15\ K)$ is due to uncertainties in fundamental constants, the atomic weight, and the ground state molecular constants. The contributions of the excited states above 22000 cm^{-1} do not affect the thermal functions below 2000 K but do become significant at higher temperatures. However, these states are not included for two reasons. First, the electronic and molecular constants are not all well–defined. Second, many of these levels have a sufficiently shallow potential energy well, which would lead to unreasonably large heat capacity values at high temperatures.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−9.124	128.300	128.300	INFINITE
100	29.367	195.067	255.684	−6.062	129.983	112.980	−59.015
200	30.452	215.621	231.072	−3.090	129.670	96.001	−25.073
250	31.513	222.529	228.695	−1.541	129.180	87.637	−18.311
298.15	32.490	228.165	228.165	0.	128.600	79.687	−13.961
300	32.525	228.366	228.166	0.060	128.576	79.384	−13.822
350	33.387	233.447	228.565	1.709	127.892	71.238	−10.632
400	34.090	237.953	229.462	3.396	122.718	63.371	−8.275
450	34.656	242.002	230.634	5.115	120.586	56.063	−6.508
500	35.111	245.678	231.958	6.860	118.326	49.019	−5.121
600	35.781	252.142	234.798	10.407	114.703	35.511	−3.092
700	36.260	257.695	237.681	14.009	111.612	22.562	−1.684
800	36.637	262.562	240.493	17.655	108.835	10.033	−0.655
882.117	36.908	266.155	242.717	20.674	----- FUGACITY = 1 bar -----		
900	36.966	266.896	243.191	21.335	0.	0.	0.
1000	37.277	270.807	245.760	25.047	0.	0.	0.
1100	37.584	274.374	248.201	28.790	0.	0.	0.
1200	37.894	277.658	250.521	32.564	0.	0.	0.
1300	38.205	280.703	252.727	36.369	0.	0.	0.
1400	38.514	283.546	254.828	40.205	0.	0.	0.
1500	38.818	286.213	256.832	44.072	0.	0.	0.
1600	39.112	288.728	258.748	47.968	0.	0.	0.
1700	39.394	291.108	260.582	51.894	0.	0.	0.
1800	39.661	293.367	262.341	55.847	0.	0.	0.
1900	39.911	295.518	264.031	59.825	0.	0.	0.
2000	40.144	297.571	265.657	63.828	0.	0.	0.
2100	40.352	299.535	267.224	67.853	0.	0.	0.
2200	40.547	301.417	268.736	71.898	0.	0.	0.
2300	40.729	303.223	270.196	75.962	0.	0.	0.
2400	40.897	304.960	271.609	80.044	0.	0.	0.
2500	41.052	306.633	272.977	84.141	0.	0.	0.
2600	41.179	308.246	274.302	88.253	0.	0.	0.
2700	41.299	309.802	275.588	92.377	0.	0.	0.
2800	41.414	311.306	276.837	96.512	0.	0.	0.
2900	41.523	312.761	278.051	100.659	0.	0.	0.
3000	41.626	314.171	279.232	104.817	0.	0.	0.
3100	41.711	315.537	280.381	108.984	0.	0.	0.
3200	41.795	316.863	281.500	113.159	0.	0.	0.
3300	41.880	318.150	282.592	117.343	0.	0.	0.
3400	41.966	319.402	283.656	121.535	0.	0.	0.
3500	42.051	320.619	284.695	125.736	0.	0.	0.
3600	42.130	321.805	285.709	129.945	0.	0.	0.
3700	42.212	322.960	286.700	134.162	0.	0.	0.
3800	42.298	324.087	287.669	138.387	0.	0.	0.
3900	42.388	325.187	288.617	142.622	0.	0.	0.
4000	42.481	326.261	289.545	146.865	0.	0.	0.
4100	42.575	327.312	290.454	151.118	0.	0.	0.
4200	42.675	328.339	291.343	155.380	0.	0.	0.
4300	42.778	329.344	292.215	159.653	0.	0.	0.
4400	42.886	330.329	293.070	163.936	0.	0.	0.
4500	42.997	331.294	293.909	168.230	0.	0.	0.
4600	43.115	332.240	294.732	172.536	0.	0.	0.
4700	43.236	333.169	295.540	176.853	0.	0.	0.
4800	43.361	334.080	296.334	181.183	0.	0.	0.
4900	43.488	334.975	297.113	185.525	0.	0.	0.
5000	43.619	335.855	297.879	189.881	0.	0.	0.
5100	43.757	336.721	298.632	194.250	0.	0.	0.
5200	43.897	337.572	299.373	198.632	0.	0.	0.
5300	44.038	338.409	300.102	203.029	0.	0.	0.
5400	44.181	339.234	300.819	207.440	0.	0.	0.
5500	44.325	340.046	301.525	211.865	0.	0.	0.
5600	44.472	340.845	302.220	216.305	0.	0.	0.
5700	44.620	341.634	302.904	220.760	0.	0.	0.
5800	44.770	342.411	303.579	225.229	0.	0.	0.
5900	44.922	343.178	304.243	229.714	0.	0.	0.
6000	45.075	343.934	304.899	234.213	0.	0.	0.

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = [80.333 \pm 4.2]\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1363\ K$

$\Delta_f H°(0\ K)$ = Unknown
$\Delta_f H°(298.15\ K) = -213.384 \pm 20.9\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = [8.4 \pm 4.2]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Rocquet and Ancey–Haret[1] determined the enthalpy of reaction for the following:

$$SiS_2(cr) + 6\ HF(20\%) \rightarrow H_2SiF_6(<20\%HF) + 2\ H_2S(g),\ \Delta_r H°(298.15\ K) = -72.8 \pm 2.2\ kcal \cdot mol^{-1}.$$

A related system was examined by Kilday and Prosen:[2]

$$SiO_2\ (\alpha\text{–quartz}) + 6\ HF(20.0\%) \rightarrow H_2SiF_6(<20.0\%\ HF) + 2\ H_2O(l),\ \Delta_r H°(298.15\ K) = -32.65 \pm 0.02\ kcal \cdot mol^{-1}.$$

Combining these two systems mathematically yields approximately the following:

$$SiO_2\ (\alpha\text{–quartz}) + 2\ H_2S(g) \rightarrow SiS_2(cr) + 2\ H_2O(l),\ \Delta_r H°(298.15\ K) = 40.2 \pm 3.0\ kcal \cdot mol^{-1}.$$

Using JANAF[4] and NBS[6] auxiliary data, $\Delta_f H°(SiS_2, cr, 298.15\ K)$ is equal to $-51.1 \pm 3.0\ kcal \cdot mol^{-1}$. In addition to the normal experimental error in each study, another source of error arises from the saturated solution of H_2S in the former work but not the latter.

Emmons and Theisen[3] measured the equilibrium vapor pressures for the system $1/2\ SiS_2(cr) + 1/2\ Si(cr) \rightarrow SiS(g)$ and presented graphically log P(SiS) vs 1/T data. Using these data, a 3rd law analysis yields $\Delta_r H°(298.15\ K) = 55.27\ kcal \cdot mol^{-1}$ with a drift of $5.1 \pm 1.2\ cal\ K^{-1} \cdot mol^{-1}$. A 2nd law analysis yields $\Delta_r H°(298.15\ K) = 50.09\ kcal \cdot mol^{-1}$. These results lead, respectively, to $\Delta_f H°(SiS_2, cr, 298.15\ K) = -59.84\ kcal \cdot mol^{-1}$ and $\Delta_f H°(SiS_2, cr, 298.15\ K) = -49.53\ kcal \cdot mol^{-1}$, with JANAF[4] auxiliary data.

Fruehan and Turkdogan[5] studied the same reaction by means of a silica Knudsen cell–mass specrometer combination. A 2nd law analysis of their graphical data for two different orifice sizes yields values of $\Delta_r H°(298.15\ K) = 53.74\ kcal \cdot mol^{-1}$ and $46.9\ kcal \cdot mol^{-1}$. Again, using JANAF auxiliary data,[4] $\Delta_f H°(SiS_2, cr, 298.15\ K) = -56.83\ kcal \cdot mol^{-1}$ and $-42.33\ kcal \cdot mol^{-1}$respectively, or an average value of $-49.58\ kcal \cdot mol^{-1}$.

The value chosen for the enthalpy of formation is $\Delta_f H°(SiS_2, cr, 298.15\ K) = -51.0 \pm 5.0\ kcal \cdot mol^{-1}$. This value is a rounded value of the work of Rocquet and Ancey–Maret[1]. Berezknoi[7] references five reported values for the enthalpy of formation (through 1954) and recommended the work of Rocquet and Ancey–Maret[1] as the most accurate. Kubaschewski *et al.*[8] in their compilation of enthlpies of formation (through 1965) also rely on the data from Rocquet and Ancey–Maret.[1]

Heat Capacity and Entropy

The heat capacity is assumed to be given by the relation $C_p°/cal \cdot K^{-1} \cdot mol^{-1} = 17.72 \pm 2.96 \times 10^{-3}\ T$ for $298 < T < 1363$ K. This relation was suggested by Rasch[9] following procedures described by Kubaschewski *et al.*[8] This equation was linearly extrapolated to yield $C_p°$ values up to 2000 K. Kubaschewski *et al.*[8] suggested $S°(298.15\ K) = 19.2\ cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

The melting point of SiS_2(cr) was determined to be $T_{fus} = 1363$ K by Tiede and Thimann.[10] $\Delta_{fus} H°$ was estimated, based on the entropy of melting for SiO_2 (quartz and cristobolite).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
0							
100							
200							
250							
298.15	77.488	80.333	80.333	0.	−213.384	−212.609	37.248
300	77.508	80.812	80.334	0.143	−213.362	−212.605	37.018
400	78.617	103.260	83.387	7.949	−216.872	−212.329	27.727
500	79.789	120.915	89.189	15.863	−219.092	−210.962	22.039
600	81.714	135.657	95.737	23.952	−220.548	−209.185	18.211
700	82.006	148.265	102.363	32.131	−221.511	−207.211	15.462
800	83.136	159.289	108.804	40.388	−222.185	−205.119	13.393
900	84.266	169.146	114.970	48.758	−328.891	−200.795	11.654
1000	85.395	178.083	120.842	57.241	−326.731	−186.677	9.751
1100	86.525	186.275	126.423	65.837	−324.534	−172.778	8.205
1200	87.655	193.852	131.730	74.546	−322.297	−159.081	6.925
1300	88.784	200.913	136.783	83.368	−320.021	−145.571	5.849
1363.000	89.496	205.131	139.846	88.984	--- CRYSTAL <--> LIQUID ---		
1400	89.915	207.534	141.603	92.303	−317.704	−132.239	4.934
1500	91.044	213.776	146.208	101.351	−315.347	−119.073	4.146
1600	92.154	219.687	150.618	110.511	−312.950	−106.066	3.463
1700	93.270	225.307	154.847	119.782	−360.689	−92.764	2.850
1800	94.391	230.670	158.912	129.165	−357.979	−77.081	2.237
1900	95.518	235.804	162.824	138.660	−355.182	−61.552	1.692
2000	96.650	240.732	166.597	148.269	−352.296	−46.172	1.206

PREVIOUS: December 1960 CURRENT: June 1972

$S°(298.15\ K) = [84.687]\ J\ K^{-1}\cdot mol^{-1}$
$T_{fus} = 1363\ K$

$\Delta_f H°(298.15\ K) = [-206.924]\ kJ\cdot mol^{-1}$
$\Delta_{fus} H° = [8.4 \pm 4.2]\ kJ\cdot mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(cr, 298.15 K) is calculated from $\Delta_f H°$(cr, 298.15 K) by adding $\Delta_{fus} H°$ and the difference in enthalpy, $H°(1363\ K)-H°(298.15\ K)$, between the crystal and the liquid.

Heat Capacity and Entropy

Using methods suggested by Kubaschewski *et al.*,[1] the heat capacity of the liquid is assumed to be a constant 21.75 $cal\cdot K^{-1}\cdot mol^{-1}$ from 1363 K to 1403 K. $S°$(l, 298.15 K) is calculated in a manner similar to that used for the enthalpy of formation. A glass transition is assumed at 900 K.

Fusion Data

Refer to the crystal table for details.

References

[1]O. Kubaschewski, E. Ll. Evans, and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press, New York, (1967).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		J·K⁻¹mol⁻¹			kJ·mol⁻¹		
0							
100							
200							
250							
298.15	77.488	84.687	84.687	0.	−206.924	−207.448	36.344
300	77.508	85.166	84.688	0.143	−206.902	−207.451	36.120
400	78.617	107.614	87.742	7.949	−210.412	−207.610	27.111
500	79.789	125.269	93.543	15.863	−212.632	−206.679	21.592
600	81.714	140.011	100.091	23.952	−214.089	−205.337	17.876
700	82.006	152.619	106.717	32.131	−215.051	−203.799	15.208
800	83.136	163.643	113.158	40.388	−215.725	−202.142	13.199
900	84.266	173.500	119.324	48.758	−322.431	−198.254	11.506
900.000	84.266	173.500	119.324	48.758	____ GLASS <---> LIQUID ____		
900.000	91.002	173.500	119.324	48.758	TRANSITION		
1000	91.002	183.088	125.230	57.858	−319.654	−184.606	9.643
1100	91.002	191.762	130.890	66.958	−316.952	−171.232	8.131
1200	91.002	199.680	136.297	76.059	−314.325	−158.102	6.882
1300	91.002	206.964	141.457	85.159	−311.770	−145.187	5.834
1363.000	91.002	211.270	144.585	90.892	--- CRYSTAL <---> LIQUID ---		
1400	91.002	213.708	146.380	94.259	−309.288	−132.467	4.942
1500	91.002	219.986	151.080	103.359	−306.879	−119.921	4.176
1600	91.002	225.859	155.572	112.459	−304.541	−107.534	3.511
1700	91.002	231.376	159.871	121.560	−352.452	−94.844	2.914
1800	91.002	236.578	163.989	130.660	−350.024	−79.760	2.315
1900	91.002	241.498	167.940	139.760	−347.622	−64.811	1.782
2000	91.002	246.166	171.736	148.860	−345.244	−49.988	1.306

PREVIOUS: December 1960 CURRENT: June 1972

0	to	1363 K	crystal
above		1363 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	77.488	80.333	80.333	0.	−213.384	−212.609	37.248
300	77.508	80.812	80.334	0.143	−213.362	−212.605	37.018
400	78.617	103.260	83.387	7.949	−216.872	−212.329	27.727
500	79.789	120.915	89.189	15.863	−219.092	−210.962	22.039
600	81.714	135.657	95.737	23.952	−220.548	−209.185	18.211
700	82.006	148.265	102.363	32.131	−221.511	−207.211	15.462
800	83.136	159.289	108.804	40.388	−222.185	−205.119	13.393
900	84.266	169.146	114.970	48.758	−328.891	−200.795	11.654
1000	85.395	178.083	120.842	57.241	−326.731	−186.677	9.751
1100	86.525	186.275	126.423	65.837	−324.534	−172.778	8.205
1200	87.655	193.852	131.730	74.546	−322.297	−159.081	6.925
1300	88.784	200.913	136.783	83.368	−320.021	−145.571	5.849
1363.000	89.496	205.131	139.846	88.984	CRYSTAL <--> LIQUID TRANSITION		
1363.000	91.002	211.270	139.846	97.352			
1400	91.002	213.708	141.766	100.719	−309.288	−132.467	4.942
1500	91.002	219.986	146.773	109.819	−306.879	−119.921	4.176
1600	91.002	225.859	151.535	118.919	−304.541	−107.534	3.511
1700	91.002	231.376	156.071	128.020	−352.452	−94.844	2.914
1800	91.002	236.578	160.400	137.120	−350.024	−79.761	2.315
1900	91.002	241.498	164.540	146.220	−347.622	−64.811	1.782
2000	91.002	246.166	168.506	155.320	−345.244	−49.988	1.306

PREVIOUS: CURRENT: June 1972

$S°(298.15\ K) = [269.5 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [141.5 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation for each vapor phase sulfur species S_3 to S_7 is calculated by a third law calculation using the thermal functions described below and assuming that the vapor pressure data given by Hultgren *et al.*[1] and Rau *et al.*[2] are correct. These values for the enthalpy of formation are dependent on the somewhat arbitrary thermal functions adopted for the polyatomic sulfur gases.

Heat Capacity and Entropy

The thermal functions for the polyatomic species, S_3 to S_7, are estimated following the suggestion of *et al.*[2] Using thermal functions calculated for S(g), S_2(g), and S_8(g), the heat capacity values for the remaining species were calculated by Rau *et al.*[2] assuming that the vibrational heat capacity per degree of freedom is the same for all sulfur polyatomic species. The resulting heat capacity equations are given by Rau *et al.*[2]

The use of the procedure of Rau *et al.*[2] leads to a set of thermal functions and associated enthalpies of formation which reproduce the observed sulfur vapor pressure data. That is, the sum of the calculated partial pressures of all eight sulfur vapor species, S_1(g) to S_8(g), does closely reproduce the observed vapor pressure. [A difference between the calculated boiling point (at 1 atm) and the secondary reference temperature boiling point is due to the difference between the ideal gas calculation and the real observed value.]

The thermal fuctions for S_8(g) were calculated[3] by adjusting the low valued vibrational frequencies such that S(298.15 K) and $\Delta_f H°$(298.15 K) values could be found which reproduced the partial pressure of the octamer. The entropy of S_2(g) is well–known,[3] being based on reliable data and sound statistical mechanical calculations.

The thermal functions which would result from the use of the available structural and vibrational inbformation for the remaining polyatomic species, are biased in the same way as for S_8(g). Some of the necessary information is derived from condensed phase spectra (rather than gas phase spectra). as with the octamer, the low–valued vibrational frequencies (and possibly the structure) may need to be adjusted. In any event, the use of the existing spectroscopic data (unaltered) leads to calculated entropies which are unreasonable when used in a 3rd law analysis to mesh in the vapor pressure with these thermal functions.

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements", American Society for Metals, Metals Park, Ohio, (1973).

[2]H. Rau, R. N. Kutty and J. R. F. Guedes de Carvalho, J. Chem. Thermodyn. **5**, 833 (1973).

[3]JANAF Thermochemical Tables: S_2(g), 9–30–77.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	47.764	269.517	304.899	0.	141.461	89.777	−15.729
300	47.862	269.813	269.518	.088	141.423	89.456	−15.576
350	49.996	277.363	270.109	2.539	140.375	80.877	−12.070
400	51.458	284.140	271.447	5.077	132.621	72.716	−9.496
450	52.528	290.265	273.203	7.678	129.446	65.392	−7.590
500	53.356	295.844	275.192	10.326	126.086	58.462	−6.107
600	54.586	305.687	279.477	15.727	120.732	45.460	−3.958
700	55.500	314.173	283.841	21.233	116.198	33.281	−2.483
800	56.246	321.635	288.108	26.821	112.152	21.717	−1.418
900	56.895	328.298	292.210	32.479	−50.960	13.882	−.806
1000	57.482	334.323	296.125	38.198	−50.809	21.078	−1.101
1100	58.030	339.827	299.851	43.974	−50.648	28.259	−1.342
1200	58.551	344.899	303.397	49.803	−50.480	35.425	−1.542
1300	59.053	349.606	306.772	55.684	−50.307	42.577	−1.711
1400	59.541	354.000	309.990	61.613	−50.131	49.715	−1.855
1500	60.019	358.124	313.063	67.591	−49.953	56.841	−1.979
1600	60.489	362.013	316.002	73.617	−49.772	63.955	−2.088
1700	60.953	365.694	318.818	79.689	−49.588	71.057	−2.183
1800	61.413	369.191	321.520	85.807	−49.399	78.148	−2.268
1900	61.869	372.524	324.118	91.972	−49.203	85.229	−2.343
2000	62.321	375.709	326.618	98.181	−48.998	92.299	−2.411
2100	62.772	378.760	329.029	104.436	−48.781	99.359	−2.471
2200	63.220	381.691	331.356	110.735	−48.549	106.407	−2.526
2300	63.666	384.511	333.607	117.080	−48.300	113.445	−2.576
2400	64.112	387.230	335.785	123.469	−48.033	120.472	−2.622
2500	64.556	389.856	337.895	129.902	−47.746	127.487	−2.664
2600	64.998	392.397	339.943	136.380	−47.436	134.491	−2.702
2700	65.441	394.858	341.931	142.902	−47.100	141.482	−2.737
2800	65.882	397.246	343.864	149.468	−46.738	148.460	−2.770
2900	66.323	399.565	345.745	156.078	−46.348	155.424	−2.799
3000	66.763	401.821	347.577	162.732	−45.930	162.375	−2.827
3100	67.203	404.018	349.363	169.431	−45.482	169.311	−2.853
3200	67.642	406.158	351.104	176.173	−45.002	176.232	−2.877
3300	68.081	408.246	352.804	182.959	−44.492	183.138	−2.899
3400	68.520	410.285	354.465	189.789	−43.950	190.028	−2.919
3500	68.958	412.278	356.088	196.663	−43.378	196.901	−2.939
3600	69.396	414.226	357.676	203.581	−42.773	203.758	−2.956
3700	69.834	416.134	359.231	210.542	−42.138	210.597	−2.973
3800	70.271	418.002	360.753	217.547	−41.471	217.419	−2.989
3900	70.709	419.833	362.244	224.596	−40.773	224.223	−3.003
4000	71.146	421.629	363.706	231.689	−40.045	231.008	−3.017
4100	71.583	423.391	365.141	238.825	−39.288	237.776	−3.029
4200	72.020	425.121	366.548	246.006	−38.502	244.524	−3.041
4300	72.457	426.821	367.930	253.229	−37.687	251.253	−3.052
4400	72.894	428.492	369.288	260.497	−36.844	257.963	−3.062
4500	73.330	430.135	370.622	267.808	−35.974	264.653	−3.072
4600	73.767	431.751	371.933	275.163	−35.077	271.324	−3.081
4700	74.203	433.342	373.223	282.561	−34.155	277.975	−3.089
4800	74.639	434.909	374.492	290.004	−33.208	284.606	−3.097
4900	75.076	436.452	375.740	297.489	−32.236	291.217	−3.104
5000	75.512	437.974	376.970	305.019	−31.239	297.808	−3.111
5100	75.948	439.473	378.181	312.592	−30.219	304.379	−3.117
5200	76.384	440.952	379.374	320.208	−29.177	310.930	−3.123
5300	76.820	442.411	380.549	327.869	−28.112	317.460	−3.129
5400	77.256	443.851	381.708	335.572	−27.024	323.970	−3.134
5500	77.692	445.273	382.851	343.320	−25.915	330.460	−3.138
5600	78.128	446.677	383.978	351.111	−24.784	336.929	−3.143
5700	78.564	448.063	385.091	358.945	−23.631	343.378	−3.147
5800	79.000	449.434	386.188	366.824	−22.457	349.806	−3.150
5900	79.435	450.788	387.272	374.745	−21.262	356.215	−3.154
6000	79.871	452.126	388.341	382.711	−20.046	362.602	−3.157

PREVIOUS: December 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = [310.6 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [145.8 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation for each vapor phase sulfur species S_3 to S_7 is calculated by a third law using the thermal functions described below and assuming that the vapor pressure data given by Hultgren *et al.*[1] and Rau *et al.*[2] are correct. These values for the enthalpy of formation are dependent on the somewhat arbitrary thermal functions adopted for the polyatomic sulfur gases.

Heat Capacity and Entropy

The thermal functions for the polyatomic species, S_3 to S_7, are estimated following the suggestion of Rau *et al.*[2] Using thermal functions calculated for S(g), S_2(g), and S_8(g), the heat capacity values for the remaining species were calculated by Rau *et al.*[2] assuming that the vibrational heat capacity per degree of freedom is the same for all sulfur polyatomic species. The resulting heat capacity equations are given by Rau *et al.*[2]

The use of the procedure of Rau *et al.*[2] leads to a set of thermal functions and associated enthalpies of formation which reproduce the observed sulfur vapor pressure data. That is, the sum of the calculated partial pressures of all eight sulfur vapor species, S_1(g) to S_8(g), does closely reproduce the observed vapor pressure. [A difference between the calculated boiling point (at 1 atm) and the secondary reference temperature boiling point is due to the difference between the ideal gas calculation and the real observed value.]

The thermal fuctions for S_8(g) were calculated[3] by adjusting the low valued vibrational frequencies such that S(298.15 K) and $\Delta_f H°$(298.15 K) values could be found which reproduced the partial pressure of the octamer. The entropy of S_2(g) is well–known,[3] being based on reliable data and sound statistical mechanical calculations.

The thermal functions which would result from the use of the available structural and vibrational inbformation for the remaining polyatomic species, are biased in the same way as for S_8(g). Some of the necessary information is derived from condensed phase spectra (rather than gas phase spectra). As with the octamer, the low–valued vibrational frequencies (and possibly the structure) may need to be adjusted. In any event, the use of the existing spectroscopic data (unaltered) leads to calculated entropies which are unreasonable when used in a 3rd law analysis to mesh in the vapor pressure with these thermal functions.

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements," American Society for Metals, Metals Park, Ohio, (1973).
[2]H. Rau, R. N. Kutty and J. R. F. Guedes de Carvalho, J. Chem. Thermodyn. **5**, 833 (1973).
[3]JANAF Thermochemical Tables: S_2(g), 9–30–77.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	67.585	310.646	388.341	0.	145.771	91.381	−16.010
300	67.754	311.065	310.647	.125	145.728	91.044	−15.852
350	71.396	321.803	311.487	3.611	144.548	82.023	−12.241
400	73.817	331.505	313.393	7.245	134.459	73.525	−9.601
450	75.529	340.303	315.902	10.981	130.493	66.111	−7.674
500	76.799	348.330	318.749	14.790	126.292	59.192	−6.184
600	78.569	362.500	324.892	22.565	119.728	46.416	−4.041
700	79.766	374.707	331.156	30.485	114.261	34.640	−2.585
800	80.658	385.419	337.283	38.508	109.439	23.600	−1.541
900	81.373	394.962	343.172	46.611	−107.485	17.462	−1.013
1000	81.977	403.567	348.788	54.779	−106.741	31.305	−1.635
1100	82.509	411.406	354.129	63.004	−106.002	45.074	−2.140
1200	82.993	418.606	359.206	71.280	−105.275	58.776	−2.558
1300	83.442	425.267	364.035	79.602	−104.563	72.418	−2.910
1400	83.865	431.466	368.633	87.967	−103.869	86.006	−3.209
1500	84.271	437.266	373.017	96.374	−103.196	99.545	−3.466
1600	84.662	442.718	377.205	104.821	−102.542	113.039	−3.690
1700	85.042	447.862	381.211	113.306	−101.908	126.494	−3.887
1800	85.414	452.733	385.050	121.829	−101.291	139.911	−4.060
1900	85.779	457.361	388.735	130.389	−100.688	153.295	−4.214
2000	86.138	461.770	392.278	138.984	−100.098	166.647	−4.352
2100	86.493	465.981	395.688	147.616	−99.517	179.970	−4.477
2200	86.845	470.013	398.975	156.283	−98.940	193.265	−4.589
2300	87.193	473.881	402.149	164.985	−98.366	206.535	−4.691
2400	87.539	477.599	405.216	173.721	−97.792	219.779	−4.783
2500	87.882	481.180	408.183	182.493	−97.216	232.999	−4.868
2600	88.224	484.633	411.057	191.298	−96.634	246.196	−4.946
2700	88.564	487.969	413.844	200.137	−96.042	259.371	−5.018
2800	88.903	491.196	416.550	209.011	−95.440	272.523	−5.084
2900	89.241	494.322	419.178	217.918	−94.827	285.654	−5.145
3000	89.578	497.353	421.734	226.859	−94.201	298.764	−5.202
3100	89.914	500.296	424.221	235.834	−93.560	311.852	−5.255
3200	90.249	503.156	426.643	244.842	−92.903	324.919	−5.304
3300	90.584	505.938	429.004	253.883	−92.229	337.966	−5.350
3400	90.918	508.647	431.306	262.958	−91.538	350.992	−5.392
3500	91.251	511.287	433.554	272.067	−90.831	363.997	−5.432
3600	91.584	513.863	435.749	281.209	−90.108	376.982	−5.470
3700	91.916	516.377	437.895	290.384	−89.367	389.946	−5.505
3800	92.248	518.832	439.992	299.592	−88.610	402.891	−5.538
3900	92.580	521.233	442.045	308.833	−87.837	415.815	−5.569
4000	92.911	523.581	444.054	318.108	−87.049	428.719	−5.598
4100	93.243	525.879	446.022	327.415	−86.247	441.603	−5.626
4200	93.574	528.130	447.950	336.756	−85.431	454.468	−5.652
4300	93.904	530.336	449.840	346.130	−84.602	467.313	−5.677
4400	94.235	532.498	451.694	355.537	−83.761	480.138	−5.700
4500	94.565	534.620	453.514	364.977	−82.910	492.945	−5.722
4600	94.895	536.702	455.300	374.450	−82.048	505.732	−5.743
4700	95.225	538.746	457.053	383.956	−81.177	518.500	−5.762
4800	95.555	540.754	458.776	393.495	−80.297	531.250	−5.781
4900	95.885	542.728	460.470	403.067	−79.410	543.982	−5.799
5000	96.214	544.669	462.134	412.672	−78.516	556.695	−5.816
5100	96.544	546.577	463.771	422.310	−77.616	569.390	−5.832
5200	96.873	548.455	465.382	431.981	−76.710	582.068	−5.847
5300	97.202	550.303	466.967	441.684	−75.800	594.728	−5.861
5400	97.531	552.123	468.527	451.421	−74.885	607.371	−5.875
5500	97.860	553.916	470.063	461.191	−73.966	619.997	−5.888
5600	98.189	555.682	471.576	470.993	−73.043	632.606	−5.901
5700	98.518	557.423	473.067	480.829	−72.117	645.199	−5.913
5800	98.847	559.139	474.536	490.697	−71.188	657.775	−5.924
5900	99.176	560.832	475.985	500.598	−70.256	670.335	−5.935
6000	99.505	562.501	477.413	510.532	−69.321	682.880	−5.945

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = [308.6 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [109.4 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation for each vapor phase sulfur species S_3 to S_7 is calculated by a third law using the thermal functions described below and assuming that the vapor pressure data given by Hultgren *et al.*[1] and Rau *et al.*[2] are correct. These values for the enthalpy of formation are dependent on the somewhat arbitrary thermal functions adopted for the polyatomic sulfur gases.

Heat Capacity and Entropy

The thermal functions for the polyatomic species, S_3 to S_7, are estimated following the suggestion of Rau *et al.*[2] Using thermal functions calculated for S(g), S_2(g), and S_8(g), the heat capacity values for the remaining species were calculated by Rau *et al.*[2] assuming that the vibrational heat capacity per degree of freedom is the same for all sulfur polyatomic species. The resulting heat capacity equations are given by Rau *et al.*[2]

The use of the procedure of Rau *et al.*[2] leads to a set of thermal functions and associated enthalpies of formation which reproduce the observed sulfur vapor pressure data. That is, the sum of the calculated partial pressures of all eight sulfur vapor species, S_1(g) to S_8(g), does closely reproduce the observed vapor pressure. [A difference between the calculated boiling point (at 1 atm) and the secondary reference temperature boiling point is due to the difference between the ideal gas calculation and the real observed value.]

The thermal fuctions for S_8(g) were calculated[3] by adjusting the low valued vibrational frequencies such that S(298.15 K) and $\Delta_f H°$(298.15 K) values could be found which reproduced the partial pressure of the octamer. The entropy of S_2(g) is well–known[3] being based on reliable data and sound statistical mechanical calculations.

The thermal functions which would result from the use of the available structural and vibrational inbformation for the remaining polyatomic species, are biased in the same way as for S_8(g). Some of the necessary information is derived from condensed phase spectra (rather than gas phase spectra). As with the octamer, the low–valued vibrational frequencies (and possibly the structure) may need to be adjusted. In any event, the use of the existing spectroscopic data (unaltered) leads to calculated entropies which are unreasonable when used in a 3rd law analysis to mesh in the vapor pressure with these thermal functions.

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements", American Society for Metals, Metals Park, Ohio, (1973).
[2]H. Rau, R. N. Kutty and J. R. F. Guedes de Carvalho, J. Chem. Thermodyn. **5**, 833 (1973).
[3]JANAF Thermochemical Tables: S_2(g), 9–30–77.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0							
100							
200							
250							
298.15	89.501	308.638	477.413	0.	109.370	65.137	−11.412
300	89.721	309.192	308.639	.166	109.325	64.862	−11.294
350	94.425	323.403	309.751	4.778	108.107	57.548	−8.588
400	97.497	336.226	312.272	9.581	95.756	50.851	−6.640
450	99.619	347.839	315.589	14.512	91.060	45.475	−5.279
500	101.153	358.419	319.351	19.534	86.068	40.689	−4.251
600	103.187	377.057	327.458	29.759	78.370	32.370	−2.818
700	104.456	393.065	335.714	40.146	72.022	25.218	−1.882
800	105.316	407.073	343.777	50.637	66.457	18.919	−1.235
900	105.939	419.515	351.514	61.201	−204.262	18.690	−1.085
1000	106.415	430.703	358.883	71.820	−202.924	43.391	−2.266
1100	106.795	440.864	365.881	82.481	−201.620	67.959	−3.227
1200	107.109	450.170	372.522	93.177	−200.359	92.410	−4.022
1300	107.377	458.754	378.830	103.902	−199.147	116.758	−4.691
1400	107.612	466.720	384.826	114.651	−197.988	141.014	−5.261
1500	107.821	474.152	390.537	125.423	−196.883	165.190	−5.752
1600	108.012	481.117	395.982	136.215	−195.832	189.293	−6.180
1700	108.188	487.670	401.185	147.025	−194.836	213.333	−6.555
1800	108.353	493.859	406.163	157.852	−193.891	237.315	−6.887
1900	108.509	499.722	410.934	168.695	−192.994	261.247	−7.182
2000	108.657	505.291	415.514	179.554	−192.143	285.132	−7.447
2100	108.800	510.596	419.917	190.427	−191.333	308.975	−7.685
2200	108.937	515.661	424.154	201.314	−190.558	332.781	−7.901
2300	109.071	520.506	428.239	212.214	−189.818	356.553	−8.098
2400	109.201	525.151	432.181	223.128	−189.108	380.293	−8.277
2500	109.329	529.611	435.989	234.054	−188.425	404.003	−8.441
2600	109.453	533.902	439.673	244.993	−187.765	427.688	−8.592
2700	109.576	538.035	443.240	255.945	−187.123	451.347	−8.732
2800	109.697	542.022	446.697	266.909	−186.499	474.982	−8.861
2900	109.817	545.873	450.051	277.884	−185.890	498.596	−8.981
3000	109.935	549.598	453.308	288.872	−185.297	522.188	−9.092
3100	110.052	553.205	456.472	299.871	−184.714	545.762	−9.196
3200	110.168	556.701	459.550	310.882	−184.142	569.316	−9.293
3300	110.283	560.093	462.546	321.905	−183.579	592.853	−9.384
3400	110.397	563.387	465.463	332.939	−183.025	616.373	−9.469
3500	110.511	566.588	468.307	343.984	−182.482	639.877	−9.550
3600	110.624	569.703	471.081	355.041	−181.948	663.365	−9.625
3700	110.736	572.736	473.787	366.109	−181.422	686.839	−9.696
3800	110.848	575.690	476.430	377.188	−180.907	710.298	−9.764
3900	110.959	578.571	479.013	388.279	−180.402	733.745	−9.827
4000	111.070	581.382	481.537	399.380	−179.909	757.178	−9.888
4100	111.181	584.126	484.006	410.493	−179.429	780.599	−9.945
4200	111.291	586.806	486.421	421.616	−178.961	804.009	−9.999
4300	111.401	589.426	488.787	432.751	−178.508	827.407	−10.051
4400	111.511	591.989	491.103	443.896	−178.070	850.796	−10.100
4500	111.620	594.496	493.373	455.053	−177.649	874.174	−10.147
4600	111.729	596.950	495.598	466.220	−177.245	897.543	−10.192
4700	111.838	599.354	497.780	477.399	−176.861	920.904	−10.235
4800	111.947	601.710	499.921	488.588	−176.496	944.257	−10.276
4900	112.056	604.019	502.022	499.788	−176.152	967.603	−10.315
5000	112.164	606.284	504.084	510.999	−175.829	990.941	−10.352
5100	112.273	608.507	506.110	522.221	−175.530	1014.274	−10.388
5200	112.381	610.688	508.100	533.454	−175.254	1037.600	−10.423
5300	112.489	612.829	510.056	544.697	−175.002	1060.922	−10.456
5400	112.597	614.933	511.979	555.952	−174.775	1084.239	−10.488
5500	112.705	617.000	513.870	567.217	−174.573	1107.552	−10.519
5600	112.812	619.032	515.730	578.492	−174.397	1130.862	−10.548
5700	112.920	621.030	517.559	589.779	−174.247	1154.169	−10.577
5800	113.027	622.994	519.360	601.076	−174.123	1177.473	−10.604
5900	113.135	624.927	521.133	612.385	−174.026	1200.776	−10.631
6000	113.242	626.830	522.879	623.703	−173.957	1224.077	−10.657

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = [354.1 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [101.9 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation for each vapor phase sulfur species S_3 to S_7 is calculated by a third law using the thermal functions described below and assuming that the vapor pressure data given by Hultgren *et al.*[1] and Rau *et al.*[2] are correct. These values for the enthalpy of formation are dependent on the somewhat arbitrary thermal functions adopted for the polyatomic sulfur gases.

Heat Capacity and Entropy

The thermal functions for the polyatomic species, S_3 to S_7, are estimated following the suggestion of Rau *et al.*[2] Using thermal functions calculated for S(g), S_2(g), and S_8(g), the heat capacity values for the remaining species were calculated by Rau *et al.*[2] assuming that the vibrational heat capacity per degree of freedom is the same for all sulfur polyatomic species. The resulting heat capacity equations are given by Rau *et al.*[2]

The use of the procedure of Rau *et al.*[2] leads to a set of thermal functions and associated enthalpies of formation which reproduce the observed sulfur vapor pressure data. That is, the sum of the calculated partial pressures of all eight sulfur vapor species, S_1(g) to S_8(g), does closely reproduce the observed vapor pressure. [A difference between the calculated boiling point (at 1 atm) and the secondary reference temperature boiling point is due to the difference between the ideal gas calculation and the real observed value.]

The thermal fuctions for S_8(g) were calculated[3] by adjusting the low valued vibrational frequencies such that S(298.15 K) and $\Delta_f H°$(298.15 K) values could be found which reproduced the partial pressure of the octamer. The entropy of S_2(g) is well-known,[3] being based on reliable data and sound statistical mechanical calculations.

The thermal functions which would result from the use of the available structural and vibrational inbformation for the remaining polyatomic species, are biased in the same way as for S_8(g). Some of the necessary information is derived from condensed phase spectra (rather than gas phase spectra). As with the octamer, the low-valued vibrational frequencies (and possibly the structure) may need to be adjusted. In any event, the use of the existing spectroscopic data (unaltered) leads to calculated entropies which are unreasonable when used in a 3rd law analysis to mesh in the vapor pressure with these thermal functions.

References

[1]R. Hultgren, P. D. Desai, *et al.*, "Selected Values of the Thermodynamic Properties of the Elements", American Society for Metals, Metals Park, Ohio, (1973).
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[3]JANAF Thermochemical Tables: S_2(g), 9–30–77.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	111.571	354.076	522.879	0.	101.922	53.699	−9.408
300	111.826	354.767	354.078	.207	101.877	53.400	−9.298
350	117.278	372.446	355.462	5.945	100.618	45.419	−6.778
400	120.826	388.354	358.596	11.903	85.991	38.152	−4.982
450	123.265	402.735	362.715	18.009	80.544	32.445	−3.766
500	125.018	415.817	367.381	24.218	74.738	27.426	−2.865
600	127.318	438.833	377.424	36.845	65.856	18.838	−1.640
700	128.725	458.573	387.640	49.653	58.583	11.592	−.865
800	129.656	475.826	397.608	62.575	52.237	5.320	−.347
900	130.310	491.137	407.165	75.575	−272.303	6.293	−.365
1000	130.792	504.893	416.262	88.631	−270.383	37.144	−1.940
1100	131.162	517.377	424.895	101.729	−268.514	67.806	−3.220
1200	131.455	528.802	433.085	114.861	−266.705	98.300	−4.279
1300	131.694	539.334	440.858	128.019	−264.962	128.646	−5.169
1400	131.894	549.101	448.245	141.198	−263.290	158.861	−5.927
1500	132.066	558.207	455.276	154.397	−261.692	188.958	−6.580
1600	132.215	566.735	461.979	167.611	−260.167	218.951	−7.148
1700	132.347	574.755	468.379	180.839	−258.715	248.851	−7.646
1800	132.466	582.323	474.501	194.080	−257.333	278.668	−8.087
1900	132.575	589.488	480.366	207.332	−256.017	308.410	−8.479
2000	132.675	596.291	485.994	220.594	−254.763	338.084	−8.830
2100	132.768	602.766	491.401	233.867	−253.566	367.696	−9.146
2200	132.855	608.945	496.605	247.148	−252.420	397.253	−9.432
2300	132.938	614.852	501.618	260.437	−251.322	426.759	−9.692
2400	133.016	620.512	506.455	273.735	−250.269	456.218	−9.929
2500	133.091	625.943	511.127	287.040	−249.256	485.634	−10.147
2600	133.164	631.164	515.644	300.353	−248.278	515.010	−10.347
2700	133.234	636.191	520.016	313.673	−247.330	544.349	−10.531
2800	133.302	641.038	524.252	327.000	−246.410	573.654	−10.702
2900	133.368	645.717	528.361	340.333	−245.518	602.926	−10.860
3000	133.432	650.239	532.348	353.673	−244.650	632.168	−11.007
3100	133.496	654.616	536.222	367.020	−243.804	661.381	−11.144
3200	133.558	658.855	539.988	380.373	−242.978	690.567	−11.272
3300	133.619	662.966	543.653	393.731	−242.170	719.728	−11.392
3400	133.679	666.955	547.221	407.096	−241.382	748.865	−11.505
3500	133.738	670.831	550.698	420.467	−240.614	777.978	−11.611
3600	133.796	674.600	554.087	433.844	−239.864	807.070	−11.710
3700	133.854	678.266	557.394	447.226	−239.133	836.142	−11.804
3800	133.911	681.837	560.622	460.615	−238.421	865.194	−11.893
3900	133.968	685.316	563.775	474.008	−237.730	894.227	−11.977
4000	134.024	688.708	566.856	487.408	−237.060	923.243	−12.056
4100	134.080	692.018	569.869	500.813	−236.414	952.243	−12.132
4200	134.135	695.250	572.816	514.224	−235.790	981.227	−12.203
4300	134.190	698.407	575.700	527.640	−235.192	1010.196	−12.271
4400	134.245	701.493	578.524	541.062	−234.619	1039.152	−12.336
4500	134.299	704.510	581.290	554.489	−234.075	1068.095	−12.398
4600	134.353	707.462	584.001	567.922	−233.559	1097.026	−12.457
4700	134.407	710.352	586.659	581.360	−233.073	1125.947	−12.513
4800	134.461	713.183	589.265	594.803	−232.619	1154.857	−12.567
4900	134.514	715.956	591.823	608.252	−232.198	1183.759	−12.619
5000	134.567	718.674	594.333	621.706	−231.810	1212.652	−12.668
5100	134.621	721.339	596.797	635.165	−231.457	1241.538	−12.716
5200	134.673	723.954	599.217	648.630	−231.140	1270.417	−12.761
5300	134.726	726.519	601.595	662.100	−230.860	1299.290	−12.805
5400	134.779	729.038	603.932	675.575	−230.618	1328.159	−12.847
5500	134.831	731.512	606.229	689.056	−230.413	1357.023	−12.888
5600	134.884	733.942	608.488	702.542	−230.247	1385.884	−12.927
5700	134.936	736.330	610.710	716.033	−230.119	1414.742	−12.965
5800	134.988	738.677	612.896	729.529	−230.032	1443.598	−13.001
5900	135.040	740.985	615.048	743.030	−229.984	1472.454	−13.036
6000	135.092	743.255	617.165	756.537	−229.977	1501.308	−13.070

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = [407.7 \pm 4]\ J \cdot K^{-1} \cdot mol^{-1}$ $\Delta_f H°(298.15\ K) = [113.7 \pm 8]\ kJ \cdot mol^{-1}$

Enthalpy of Formation

The enthalpy of formation for each vapor phase sulfur species S_3 to S_7 is calculated by a third law using the thermal functions described below and assuming that the vapor pressure data given by Hultgren *et al.*[1] and Rau *et al.*[2] are correct. These values for the enthalpy of formation are dependent on the somewhat arbitrary thermal functions adopted for the polyatomic sulfur gases.

Heat Capacity and Entropy

The thermal functions for the polyatomic species, S_3 to S_7, are estimated following the suggestion of Rau *et al.*[2] Using thermal functions calculated for S(g), S_2(g), and S_8(g), the heat capacity values for the remaining species were calculated by Rau *et al.*[2] assuming that the vibrational heat capacity per degree of freedom is the same for all sulfur polyatomic species. The resulting heat capacity equations are given by Rau *et al.*[2]

The use of the procedure of Rau *et al.*[2] leads to a set of thermal functions and associated enthalpies of formation which reproduce the observed sulfur vapor pressure data. That is, the sum of the calculated partial pressures of all eight sulfur vapor species, S_1(g) to S_8(g), does closely reproduce the observed vapor pressure. [A difference between the calculated boiling point (at 1 atm) and the secondary reference temperature boiling point is due to the difference between the ideal gas calculation and the real observed value.]

The thermal fuctions for S_8(g) were calculated[3] by adjusting the low valued vibrational frequencies such that S(298.15 K) and $\Delta_f H°$(298.15 K) values could be found which reproduced the partial pressure of the octamer. The entropy of S_2(g) is well–known,[3] being based on reliable data and sound statistical mechanical calculations.

The thermal functions which would result from the use of the available structural and vibrational inbformation for the remaining polyatomic species, are biased in the same way as for S_8(g). Some of the necessary information is derived from condensed phase spectra (rather than gas phase spectra). As with the octamer, the low–valued vibrational frequencies (and possibly the structure) may need to be adjusted. In any event, the use of the existing spectroscopic data (unaltered) leads to calculated entropies which are unreasonable when used in a 3rd law analysis to mesh in the vapor pressure with these thermal functions.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	133.502	407.673	617.165	0.	113.679	59.034	−10.342
300	133.780	408.500	407.675	.247	113.632	58.695	−10.220
350	139.733	429.603	409.328	7.096	112.318	49.641	−7.409
400	143.642	448.534	413.067	14.187	95.393	41.399	−5.406
450	146.363	465.619	417.972	21.441	89.169	34.960	−4.058
500	148.345	481.147	423.525	28.811	82.520	29.310	−3.062
600	151.017	508.450	435.467	43.790	72.406	19.665	−1.712
700	152.729	531.867	447.605	58.983	64.171	11.543	−.861
800	153.931	552.344	459.445	74.319	57.029	4.522	−.295
900	154.836	570.529	470.796	89.759	−321.328	5.919	−.344
1000	155.556	586.881	481.600	105.280	−318.800	42.144	−2.201
1100	156.155	601.736	491.857	120.867	−316.314	78.117	−3.709
1200	156.672	615.346	501.588	136.508	−313.881	113.867	−4.956
1300	157.132	627.904	510.828	152.199	−311.508	149.416	−6.004
1400	157.549	639.565	519.612	167.934	−309.200	184.784	−6.894
1500	157.936	650.448	527.976	183.708	−306.958	219.990	−7.661
1600	158.299	660.652	535.953	199.520	−304.785	255.049	−8.326
1700	158.643	670.260	543.573	215.367	−302.676	289.974	−8.910
1800	158.974	679.337	550.866	231.248	−300.630	324.776	−9.425
1900	159.293	687.941	557.856	247.161	−298.642	359.466	−9.882
2000	159.603	696.119	564.566	263.106	−296.708	394.053	−10.292
2100	159.905	703.914	571.018	279.082	−294.820	428.545	−10.659
2200	160.201	711.359	577.229	295.087	−292.972	462.947	−10.992
2300	160.492	718.487	583.217	311.122	−291.161	497.267	−11.293
2400	160.779	725.324	588.996	327.185	−289.382	531.508	−11.568
2500	161.063	731.893	594.582	343.278	−287.632	565.675	−11.819
2600	161.343	738.215	599.985	359.398	−285.902	599.774	−12.050
2700	161.621	744.310	605.218	375.546	−284.187	633.805	−12.262
2800	161.896	750.192	610.292	391.722	−282.487	667.774	−12.457
2900	162.170	755.878	615.214	407.925	−280.798	701.682	−12.639
3000	162.442	761.381	619.995	424.156	−279.118	735.532	−12.807
3100	162.712	766.711	624.643	440.414	−277.445	769.326	−12.963
3200	162.981	771.882	629.163	456.698	−275.773	803.066	−13.109
3300	163.249	776.901	633.565	473.010	−274.105	836.754	−13.245
3400	163.516	781.778	637.852	489.348	−272.440	870.392	−13.372
3500	163.782	786.522	642.033	505.713	−270.778	903.980	−13.491
3600	164.048	791.140	646.111	522.105	−269.118	937.521	−13.603
3700	164.312	795.638	650.091	538.523	−267.460	971.016	−13.708
3800	164.576	800.024	653.980	554.967	−265.804	1004.466	−13.807
3900	164.840	804.302	657.779	571.438	−264.154	1037.873	−13.901
4000	165.103	808.479	661.495	587.935	−262.508	1071.237	−13.989
4100	165.365	812.559	665.130	604.458	−260.870	1104.560	−14.072
4200	165.627	816.547	668.688	621.008	−259.239	1137.844	−14.151
4300	165.889	820.447	672.172	637.584	−257.617	1171.088	−14.226
4400	166.150	824.264	675.585	654.186	−256.006	1204.296	−14.297
4500	166.411	828.000	678.931	670.814	−254.407	1237.466	−14.364
4600	166.672	831.661	682.211	687.468	−252.823	1270.601	−14.428
4700	166.932	835.248	685.429	704.148	−251.254	1303.702	−14.489
4800	167.192	838.765	688.587	720.854	−249.702	1336.770	−14.547
4900	167.452	842.215	691.688	737.587	−248.168	1369.806	−14.602
5000	167.712	845.601	694.732	754.345	−246.654	1402.810	−14.655
5100	167.971	848.925	697.723	771.129	−245.160	1435.785	−14.705
5200	168.231	852.189	700.662	787.939	−243.690	1468.730	−14.754
5300	168.490	855.396	703.552	804.775	−242.242	1501.647	−14.800
5400	168.749	858.548	706.393	821.637	−240.818	1534.538	−14.844
5500	169.008	861.646	709.187	838.525	−239.419	1567.401	−14.886
5600	169.267	864.694	711.937	855.439	−238.045	1600.240	−14.926
5700	169.525	867.692	714.644	872.378	−236.696	1633.055	−14.965
5800	169.784	870.643	717.308	889.344	−235.374	1665.846	−15.003
5900	170.042	873.547	719.931	906.335	−234.078	1698.615	−15.038
6000	170.301	876.408	722.516	923.352	−232.810	1731.361	−15.073

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

$S°(298.15\ K) = 430.31 \pm 0.05\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 104.39 \pm 0.63\ kJ \cdot mol^{-1}$

$\Delta_f H°(298.15\ K) = 100.42 \pm 0.63\ kJ \cdot mol^{-1}$

Vibrational Frequencies and Degeneracies		
ν, cm^{-1}	ν, cm^{-1}	ν, cm^{-1}
475(1)	475(2)	243(1)
218(1)	152(2)	437(2)
471(2)	56(2)	248(2)
191(2)	411(1)	

Ground State Quantum Weight: [1] $\sigma = 8$

Point Group: D_{4d}

Bond Distance: S–S = 2.059 ± 0.002 Å

Bond Angle: S–S–S = 107.9 ± 0.6°

Product of the Moments of Inertia: $I_A I_B I_C = 3.90326 \times 10^{-111}\ g^3 \cdot cm^6$

Enthalpy of Formation

The vapor pressure of S(cr) has been measured by many investigators. Using the seven more recent vapor pressure data, the respective enthalpy of sublimation was calculated by both the 2nd and 3rd law methods. The values obtained are tabulated as follows:

Source	T/K	$\Delta_{sub}H°(298.15)$, $kcal \cdot mol^{-1}$ 3rd law	2nd law
West–Menzies[1]	376.6 – 448.8	24.29	21.29
Neumann[2]	332.6 – 362.1	24.35	26.47
Fouretier[3]	304.1 – 351.6	24.36	24.10
Taillade[4]	303.6 – 352.5	24.29	24.87
Bradley[5]	288.3 – 305.7	24.29	23.80
Magee[6]	331.9 – 368.0	24.11	24.44
	332.7 – 367.4	24.12	23.88
Briske[7]	273.2 – 313.2	24.28	24.00

Due to the presence of S_6(g) in S_8(g), the measured total pressures were corrected to give the parttial pressures of S_8(g) for the first five sets of vapor pressure data, according to Scott.[8] However, the magnitude of the correction is only 0.1–0.2 $kcal \cdot mol^{-1}$. The adopted value is the weighted average of both the 2nd and 3rd law values.

Heat Capacity and Entropy

The vibrational frequencies were taken from Scott *et al.*[9] Four of the eighteen frequencies, i.e. 86(2) and 218(2) cm^{-1}, were changed to 56(2) and 248 (2) cm^{-1}, respectively, as suggested by Scott.[10] The molecular structure and bond distance and angle were reported by Donohur *et al.*[11] The principle moments of inertia are: $I_A = I_B = 1.28594 \times 10^{-37}$, and $I_C = 2.36042 \times 10^{-37}\ g \cdot cm^2$.

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Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	722.516	−31.324	104.388	104.388	0.
100	87.155	295.550	552.531	−25.698	104.495	84.958	−44.377
200	134.162	372.097	444.003	−14.381	102.677	66.077	−17.258
250	147.427	403.559	432.835	−7.319	101.582	57.051	−11.920
298.15	156.043	430.311	430.311	0.	100.416	48.578	−8.511
300	156.314	431.277	430.314	.289	100.369	48.257	−8.402
350	162.400	455.858	432.241	8.266	99.016	39.677	−5.921
400	166.689	477.839	436.591	16.499	79.803	32.003	−4.179
450	169.799	497.662	442.294	24.915	72.816	26.376	−3.062
500	172.113	515.677	448.745	33.466	65.345	21.636	−2.260
600	175.248	547.358	462.613	50.847	54.048	14.009	−1.220
700	177.206	574.531	476.707	68.477	44.903	8.078	−.603
800	178.506	598.284	490.450	86.267	37.003	3.368	−.220
900	179.411	619.364	503.625	104.165	−395.153	8.246	−.479
1000	180.064	638.302	516.162	122.140	−392.026	52.900	−2.763
1100	180.552	655.488	528.059	140.172	−388.966	97.243	−4.618
1200	180.925	671.215	539.342	158.247	−385.987	141.312	−6.151
1300	181.216	685.709	550.051	176.355	−383.099	185.136	−7.439
1400	181.448	699.147	560.227	194.488	−380.310	228.741	−8.534
1500	181.636	711.672	569.910	212.643	−377.622	272.150	−9.477
1600	181.790	723.400	579.141	230.814	−375.037	315.383	−10.296
1700	181.918	734.425	587.954	249.000	−372.553	358.458	−11.014
1800	182.025	744.826	596.383	267.197	−370.167	401.389	−11.648
1900	182.116	754.670	604.457	285.404	−367.875	444.191	−12.212
2000	182.194	764.013	612.203	303.620	−365.671	486.874	−12.716
2100	182.261	772.904	619.646	321.843	−363.548	529.448	−13.169
2200	182.319	781.384	626.806	340.072	−361.499	571.924	−13.579
2300	182.370	789.490	633.705	358.306	−359.520	614.307	−13.951
2400	182.414	797.253	640.359	376.546	−357.607	656.607	−14.291
2500	182.453	804.700	646.784	394.789	−355.753	698.827	−14.601
2600	182.488	811.857	652.996	413.036	−353.952	740.975	−14.886
2700	182.519	818.744	659.009	431.287	−352.198	783.054	−15.149
2800	182.547	825.383	664.833	449.540	−350.488	825.069	−15.392
2900	182.572	831.789	670.480	467.796	−348.819	867.023	−15.617
3000	182.595	837.979	675.961	486.054	−347.191	908.921	−15.826
3100	182.615	843.966	681.284	504.315	−345.598	950.765	−16.020
3200	182.634	849.764	686.459	522.577	−344.037	992.558	−16.202
3300	182.651	855.385	691.493	540.841	−342.508	1034.303	−16.372
3400	182.666	860.838	696.394	559.107	−341.011	1076.002	−16.531
3500	182.680	866.133	701.169	577.375	−339.547	1117.657	−16.680
3600	182.693	871.279	705.823	595.643	−338.114	1159.272	−16.821
3700	182.705	876.285	710.362	613.913	−336.713	1200.846	−16.953
3800	182.716	881.158	714.793	632.184	−335.344	1242.384	−17.078
3900	182.726	885.904	719.120	650.456	−334.008	1283.885	−17.196
4000	182.736	890.530	723.348	668.729	−332.709	1325.353	−17.307
4100	182.744	895.042	727.481	687.003	−331.446	1366.789	−17.413
4200	182.752	899.446	731.523	705.278	−330.221	1408.194	−17.513
4300	182.760	903.747	735.478	723.554	−329.036	1449.571	−17.609
4400	182.767	907.948	739.350	741.830	−327.892	1490.921	−17.699
4500	182.774	912.056	743.143	760.107	−326.791	1532.245	−17.786
4600	182.780	916.073	746.859	778.385	−325.736	1573.545	−17.868
4700	182.786	920.004	750.501	796.663	−324.728	1614.823	−17.947
4800	182.791	923.852	754.073	814.942	−323.768	1656.079	−18.022
4900	182.796	927.621	757.576	833.221	−322.859	1697.317	−18.094
5000	182.801	931.314	761.014	851.501	−322.000	1738.536	−18.162
5100	182.805	934.934	764.389	869.782	−321.195	1779.739	−18.228
5200	182.810	938.484	767.703	888.062	−320.445	1820.926	−18.291
5300	182.814	941.966	770.958	906.343	−319.751	1862.100	−18.352
5400	182.817	945.383	774.157	924.625	−319.113	1903.261	−18.410
5500	182.821	948.738	777.300	942.907	−318.532	1944.410	−18.466
5600	182.824	952.032	780.391	961.189	−318.009	1985.550	−18.520
5700	182.828	955.268	783.431	979.472	−317.545	2026.681	−18.572
5800	182.831	958.448	786.421	997.755	−317.140	2067.804	−18.623
5900	182.834	961.573	789.363	1016.038	−316.795	2108.921	−18.671
6000	182.836	964.646	792.259	1034.321	−316.510	2150.032	−18.718

PREVIOUS: September 1977 (1 atm) CURRENT: September 1977 (1 bar)

REFERENCE STATE

0	to 1685	K	crystal
1685	to 3504.616	K	liquid
above	3504.616	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−3.218	0.	0.	0.
100	7.268	3.833	33.351	−2.952	0.	0.	0.
200	15.636	11.665	20.531	−1.773	0.	0.	0.
298.15	20.000	18.820	18.820	0.	0.	0.	0.
300	20.050	18.943	18.820	0.037	0.	0.	0.
400	22.142	25.032	19.636	2.159	0.	0.	0.
500	23.330	30.110	21.237	4.436	0.	0.	0.
600	24.154	34.440	23.086	6.812	0.	0.	0.
700	24.803	38.212	24.983	9.260	0.	0.	0.
800	25.359	41.562	26.850	11.769	0.	0.	0.
900	25.874	44.579	28.655	14.331	0.	0.	0.
1000	26.338	47.329	30.387	16.942	0.	0.	0.
1100	26.778	49.860	32.044	19.598	0.	0.	0.
1200	27.196	52.208	33.627	22.297	0.	0.	0.
1300	27.614	54.401	35.142	25.037	0.	0.	0.
1400	28.033	56.463	36.592	27.820	0.	0.	0.
1500	28.451	58.411	37.982	30.644	0.	0.	0.
1600	28.870	60.261	39.317	33.510	0.	0.	0.
1685.000	29.225	61.765	40.412	35.979	CRYSTAL <--> LIQUID		
1685.000	27.196	91.562	40.412	86.187	TRANSITION		
1700	27.196	91.803	40.864	86.595	0.	0.	0.
1800	27.196	93.357	43.738	89.315	0.	0.	0.
1900	27.196	94.827	46.388	92.034	0.	0.	0.
2000	27.196	96.222	48.846	94.754	0.	0.	0.
2100	27.196	97.549	51.133	97.473	0.	0.	0.
2200	27.196	98.815	53.272	100.193	0.	0.	0.
2300	27.196	100.023	55.279	102.913	0.	0.	0.
2400	27.196	101.181	57.167	105.632	0.	0.	0.
2500	27.196	102.291	58.950	108.352	0.	0.	0.
2600	27.196	103.358	60.638	111.071	0.	0.	0.
2700	27.196	104.384	62.239	113.791	0.	0.	0.
2800	27.196	105.373	63.762	116.511	0.	0.	0.
2900	27.196	106.327	65.214	119.230	0.	0.	0.
3000	27.196	107.249	66.600	121.950	0.	0.	0.
3100	27.196	108.141	67.925	124.669	0.	0.	0.
3200	27.196	109.005	69.196	127.389	0.	0.	0.
3300	27.196	109.842	70.415	130.109	0.	0.	0.
3400	27.196	110.653	71.586	132.828	0.	0.	0.
3500	27.196	111.442	72.714	135.548	0.	0.	0.
3504.616	27.196	111.478	72.765	135.673	LIQUID <--> IDEAL GAS		
3504.616	23.023	221.204	72.765	520.221	FUGACITY = 1 bar		
3600	23.046	221.822	76.706	522.419	0.	0.	0.
3700	23.066	222.454	80.637	524.725	0.	0.	0.
3800	23.081	223.070	84.377	527.032	0.	0.	0.
3900	23.093	223.669	87.941	529.341	0.	0.	0.
4000	23.102	224.254	91.341	531.651	0.	0.	0.
4100	23.108	224.825	94.590	533.961	0.	0.	0.
4200	23.111	225.381	97.698	536.272	0.	0.	0.
4300	23.113	225.925	100.673	538.583	0.	0.	0.
4400	23.112	226.457	103.526	540.895	0.	0.	0.
4500	23.111	226.976	106.264	543.206	0.	0.	0.
4600	23.108	227.484	108.893	545.517	0.	0.	0.
4700	23.104	227.981	111.422	547.827	0.	0.	0.
4800	23.100	228.467	113.855	550.138	0.	0.	0.
4900	23.096	228.943	116.199	552.447	0.	0.	0.
5000	23.092	229.410	118.459	554.757	0.	0.	0.
5100	23.089	229.867	120.639	557.066	0.	0.	0.
5200	23.087	230.316	122.744	559.374	0.	0.	0.
5300	23.086	230.755	124.777	561.683	0.	0.	0.
5400	23.086	231.187	126.744	563.992	0.	0.	0.
5500	23.087	231.610	128.647	566.300	0.	0.	0.
5600	23.091	232.026	130.489	568.609	0.	0.	0.
5700	23.098	232.435	132.274	570.918	0.	0.	0.
5800	23.108	232.837	134.005	573.228	0.	0.	0.
5900	23.121	233.232	135.683	575.539	0.	0.	0.
6000	23.135	233.621	137.312	577.851	0.	0.	0.

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 18.820 \pm 0.04\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 1685 \pm 3\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 50.2 \pm 0.4\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Low temperature heat capacities are based on the precise data of Flubacher *et al.* (8–300 K).[1] The entropy is obtained from the heat capacity using $S°(8\ K) = 0.0003\ cal \cdot K^{-1} \cdot mol^{-1}$. The selected values are consistent with recent data of Keesom and Seidel (1.2–4.2 K),[2] and Kalishevich *et al.* (60–300 K).[3] Earlier data have been reviewed by Hultgren *et al.*[10]

High temperature studies are summarized below along with the pertinent low temperatures studies. The selected heat capacities above 300 K are obtained from a Shomate plot of the adopted low temperature heat capacities and the enthalpies reported or derived from the work of Dennison,[5] Kantor *et al.*,[6] Olette,[7] Serebrennikov and Gel'd[8] and Magnus.[9] Discrepancies are apparent in the enthalpy data, particularly in the range of 370–1100 K where only the recent study of Dennison[5] made use of a high purity sample. Enthalpies from Dennison[5] join most smoothly with the low temperature heat capacity but deviate increasingly at higher temperatures, being 1–2% lower than the other measurements above 1000 K. The selected functions agree with Dennison[5] below 600 K, with Magnus[1] from 600 to 1200 K, and with Kantor *et al.*[6] above 1200 K. The resulting heat capacities are slightly different from those selected by Hultgren, *et al.*;[10] the latter are 0.07 $cal \cdot K^{-1} \cdot mol^{-1}$ higher at 800 K and 0.21 $cal \cdot K^{-1} \cdot mol^{-1}$ lower at the melting point.

Source	Method	Quantity Reported	T/K	Sample
1	Calorimetry	$C_p°$	7.7–300	Single crystal, 3mm pieces, Resistance (300 K) = 100 ohm cm, Carrier Concentration $\leq 10^{15}$ cm^{-3}
2	Calorimetry	Specific Heat	1.2–4.2	
3	Calorimetry	$C_p°$	60–300	99.999%
4	Temperature Modulation	$C_p°$	300–900	Resistance (300 K) = 0.027 ohm cm, Carrier Concentration = 10^{19} cm^{-3}
5	Drop Calorimetry	Specific Heat	273–1373	Resistance (300 K) = 107 ohm cm
6	Drop Calorimetry	Enthalpy Equation	1148–1685	"Highly purified"
7	Drop Calorimetry	Specific Enthalpy	1467–1685	99.99%
8	Drop Calorimetry	Specific Enthalpy	302 – 1556	99.3%
9	Drop Calorimetry	Specific Enthalpy	372 – 1175	99.2%

Fusion Data

Refer to the liquid table for details.

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−3.218	0.	0.	0.
100	7.268	3.833	33.351	−2.952	0.	0.	0.
200	15.636	11.665	20.531	−1.773	0.	0.	0.
250	18.221	15.446	19.138	−0.923	0.	0.	0.
298.15	20.000	18.820	18.820	0.	0.	0.	0.
300	20.050	18.943	18.820	0.037	0.	0.	0.
350	21.276	22.132	19.069	1.072	0.	0.	0.
400	22.142	25.032	19.636	2.159	0.	0.	0.
450	22.803	27.680	20.385	3.283	0.	0.	0.
500	23.330	30.110	21.237	4.436	0.	0.	0.
600	24.154	34.440	23.086	6.812	0.	0.	0.
700	24.803	38.212	24.983	9.260	0.	0.	0.
800	25.359	41.562	26.850	11.769	0.	0.	0.
900	25.874	44.579	28.655	14.331	0.	0.	0.
1000	26.338	47.329	30.387	16.942	0.	0.	0.
1100	26.778	49.860	32.044	19.598	0.	0.	0.
1200	27.196	52.208	33.627	22.297	0.	0.	0.
1300	27.614	54.401	35.142	25.037	0.	0.	0.
1400	28.033	56.463	36.592	27.820	0.	0.	0.
1500	28.451	58.411	37.982	30.644	0.	0.	0.
1600	28.870	60.261	39.317	33.510	0.	0.	0.
1685.000	29.225	61.765	40.412	35.979	--- CRYSTAL <---> LIQUID ---		
1700	29.288	62.024	40.602	36.418	−50.177	0.447	−0.014
1800	29.706	63.710	41.839	39.368	−49.947	3.418	−0.099
1900	30.125	65.327	43.033	42.359	−49.675	6.376	−0.175
2000	30.543	66.883	44.187	45.393	−49.361	9.318	−0.243
2100	30.962	68.383	45.303	48.468	−49.006	12.243	−0.305
2200	31.380	69.833	46.386	51.585	−48.608	15.151	−0.360
2300	31.798	71.237	47.436	54.744	−48.169	18.039	−0.410
2400	32.217	72.600	48.456	57.945	−47.688	20.908	−0.455
2500	32.635	73.923	49.448	61.187	−47.165	23.755	−0.496

PREVIOUS: December 1962 CURRENT: December 1966

$S°(298.15\ K)$ = [44.460] $J·K^{-1}·mol^{-1}$
T_{fus} = 1685 ± 3 K

$\Delta_f H°(298.15\ K)$ = [48.470] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 50.2 ± 0.4 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation, $\Delta_f H°$(Si, l, 298.15 K) is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°$(1685 K)–$H°$(298.15 K), between the crystal and liquid.

Heat Capacity and Entropy

Enthalpy data for high purity samples in quartz or vitreous silica capsules have been reported for the range 1698–1915 K by Kantor *et al.*[1] and for the range 1686–1825 K by Olette.[2] Due to the limited temperature range and the experimental uncertainty, the data do not appear to justify more than a constant heat capacity. A value of 6.5 $cal·K^{-1}·mol^{-1}$ is selected, intermediate between the values of 6.75 and 6.15 obtained from separate experiments.

The entropy is calculated in a manner analogous to that used for the enthalpy of formation.

Fusion Data

Modern determinations of the melting point range from 1683 ± 1 to 1690 ± 4 K, the former from the specific volume study of Lucas and Urbain[3] and the later from the enthalpy study of Kantor *et al.*[1] The selected value, T_{fus} = 1685 K, is taken from Hultgren *et al.*,[4] who have reviewed the melting data.

The enthalpy of melting is calculated from the selected enthalpy of the crystal and the liquid enthalpy measurements of Kantor *et al.*[1] and Olette,[2] who reported comparable values of $\Delta_{fus}H°$ = 11.95 ± 0.18 and 12.095 ± 0.1 $kcal·mol^{-1}$, respectively.

Vaporization Data

T_{vap} is calculated as the temperature for which $\Delta_r G°$ = 0 for Si(l) = Si(g). $\Delta_{vap}H°$ is calculated as the difference between $\Delta_f H°$(g) and $\Delta_f H°$(l) at T_{vap}. The normal boiling for the equilibrium vapor is calculated as the temperature at which Si, Si_2, and Si_3 attain a total pressure of 1 atm; the vapor containing 92.1%, 7.0% and 0.9% (mole) of monomer, dimer, and trimer, repectively. tetramer and high polymers, which are ignored in this calculation, are probably negligible at this temperature (~3490 K).

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
0							
100							
200							
250							
298.15	27.196	44.460	44.460	0.	48.470	40.826	−7.152
300	27.196	44.628	44.461	0.050	48.483	40.778	−7.100
350	27.196	48.821	44.792	1.410	48.808	39.467	−5.890
400	27.196	52.452	45.527	2.770	49.082	38.114	−4.977
450	27.196	55.655	46.478	4.130	49.317	36.728	−4.263
500	27.196	58.521	47.542	5.490	49.523	35.318	−3.690
600	27.196	63.479	49.797	8.209	49.867	32.443	−2.824
700	27.196	67.671	52.059	10.929	50.139	29.517	−2.203
800	27.196	71.303	54.243	13.648	50.349	26.556	−1.734
900	27.196	74.506	56.320	16.368	50.507	23.572	−1.368
1000	27.196	77.372	58.284	19.088	50.616	20.573	−1.075
1100	27.196	79.964	60.139	21.807	50.679	17.565	−0.834
1200	27.196	82.330	61.891	24.527	50.700	14.554	−0.634
1300	27.196	84.507	63.548	27.246	50.679	11.542	−0.464
1400	27.196	86.522	65.118	29.966	50.616	8.534	−0.318
1500	27.196	88.399	66.608	32.686	50.512	5.531	−0.193
1600	27.196	90.154	68.026	35.405	50.365	2.537	−0.083
1685.000	27.196	91.562	69.178	37.717	--- CRYSTAL <--> LIQUID ---		
1700	27.196	91.803	69.376	38.125	0.	0.	0.
1800	27.196	93.357	70.666	40.844	0.	0.	0.
1900	27.196	94.827	71.899	43.564	0.	0.	0.
2000	27.196	96.222	73.081	46.284	0.	0.	0.
2100	27.196	97.549	74.215	49.003	0.	0.	0.
2200	27.196	98.814	75.304	51.723	0.	0.	0.
2300	27.196	100.023	76.353	54.442	0.	0.	0.
2400	27.196	101.181	77.363	57.162	0.	0.	0.
2500	27.196	102.291	78.338	59.882	0.	0.	0.
2600	27.196	103.358	79.280	62.601	0.	0.	0.
2700	27.196	104.384	80.191	65.321	0.	0.	0.
2800	27.196	105.373	81.073	68.040	0.	0.	0.
2900	27.196	106.327	81.928	70.760	0.	0.	0.
3000	27.196	107.249	82.756	73.480	0.	0.	0.
3100	27.196	108.141	83.561	76.199	0.	0.	0.
3200	27.196	109.005	84.343	78.919	0.	0.	0.
3300	27.196	109.842	85.103	81.638	0.	0.	0.
3400	27.196	110.653	85.842	84.358	0.	0.	0.
3500	27.196	111.442	86.562	87.078	0.	0.	0.
3504.616	27.196	111.478	86.595	87.203	----- FUGACITY = 1 bar -----		
3600	27.196	112.208	87.264	89.797	−384.152	10.461	−0.152
3700	27.196	112.953	87.949	92.517	−383.738	21.417	−0.302
3800	27.196	113.678	88.616	95.236	−383.326	32.361	−0.445
3900	27.196	114.385	89.268	97.956	−382.915	43.295	−0.580
4000	27.196	115.073	89.904	100.676	−382.505	54.218	−0.708
4100	27.196	115.745	90.526	103.395	−382.096	65.131	−0.830
4200	27.196	116.400	91.135	106.115	−381.687	76.034	−0.946
4300	27.196	117.040	91.730	108.834	−381.279	86.927	−1.056
4400	27.196	117.665	92.312	111.554	−380.871	97.811	−1.161
4500	27.196	118.277	92.882	114.274	−380.462	108.686	−1.262

PREVIOUS: December 1966 CURRENT: March 1967

CRYSTAL-LIQUID

0 to 1685 K crystal
above 1685 K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−3.218	0.	0.	0.
100	7.268	3.833	33.351	−2.952	0.	0.	0.
200	15.636	11.665	20.531	−1.773	0.	0.	0.
250	18.221	15.446	19.138	−0.923	0.	0.	0.
298.15	20.000	18.820	18.820	0.	0.	0.	0.
300	20.050	18.943	18.820	0.037	0.	0.	0.
350	21.276	22.132	19.069	1.072	0.	0.	0.
400	22.142	25.032	19.636	2.159	0.	0.	0.
450	22.803	27.680	20.385	3.283	0.	0.	0.
500	23.330	30.110	21.237	4.436	0.	0.	0.
600	24.154	34.440	23.086	6.812	0.	0.	0.
700	24.803	38.212	24.983	9.260	0.	0.	0.
800	25.359	41.562	26.850	11.769	0.	0.	0.
900	25.874	44.579	28.655	14.331	0.	0.	0.
1000	26.338	47.329	30.387	16.942	0.	0.	0.
1100	26.778	49.860	32.044	19.598	0.	0.	0.
1200	27.196	52.208	33.627	22.297	0.	0.	0.
1300	27.614	54.401	35.142	25.037	0.	0.	0.
1400	28.033	56.463	36.592	27.820	0.	0.	0.
1500	28.451	58.411	37.982	30.644	0.	0.	0.
1600	28.870	60.261	39.317	33.510	0.	0.	0.
1685.000	29.225	61.765	40.412	35.979	___ CRYSTAL <--> LIQUID ___		
1685.000	27.196	91.562	40.412	86.187	TRANSITION		
1700	27.196	91.803	40.864	86.595	0.	0.	0.
1800	27.196	93.357	43.738	89.315	0.	0.	0.
1900	27.196	94.827	46.388	92.034	0.	0.	0.
2000	27.196	96.222	48.846	94.754	0.	0.	0.
2100	27.196	97.549	51.133	97.473	0.	0.	0.
2200	27.196	98.815	53.272	100.193	0.	0.	0.
2300	27.196	100.023	55.279	102.913	0.	0.	0.
2400	27.196	101.181	57.167	105.632	0.	0.	0.
2500	27.196	102.291	58.950	108.352	0.	0.	0.
2600	27.196	103.358	60.638	111.071	0.	0.	0.
2700	27.196	104.384	62.239	113.791	0.	0.	0.
2800	27.196	105.373	63.762	116.511	0.	0.	0.
2900	27.196	106.327	65.214	119.230	0.	0.	0.
3000	27.196	107.249	66.600	121.950	0.	0.	0.
3100	27.196	108.141	67.925	124.669	0.	0.	0.
3200	27.196	109.005	69.196	127.389	0.	0.	0.
3300	27.196	109.842	70.415	130.109	0.	0.	0.
3400	27.196	110.653	71.586	132.828	0.	0.	0.
3500	27.196	111.442	72.714	135.548	0.	0.	0.
3504.616	27.196	111.478	72.765	135.673	----- FUGACITY = 1 bar -----		
3600	27.196	112.208	73.800	138.267	−384.152	10.461	−0.152
3700	27.196	112.953	74.848	140.987	−383.738	21.417	−0.302
3800	27.196	113.678	75.861	143.707	−383.326	32.361	−0.445
3900	27.196	114.385	76.840	146.426	−382.915	43.295	−0.580
4000	27.196	115.073	77.787	149.146	−382.505	54.218	−0.708
4100	27.196	115.745	78.704	151.865	−382.096	65.131	−0.830
4200	27.196	116.400	79.594	154.585	−381.687	76.034	−0.946
4300	27.196	117.040	80.458	157.305	−381.279	86.927	−1.056
4400	27.196	117.665	81.296	160.024	−380.871	97.811	−1.161
4500	27.196	118.277	82.111	162.744	−380.462	108.686	−1.262

PREVIOUS: CURRENT: March 1967

IP(Si, g) = 65747.5 ± 0.6 cm^{-1}
$S°$(298.15 K) = 167.980 ± 0.035 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 446 ± 8 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 450 ± 8 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3P_2$	0.00	5
$^3P_1$	77.115	3
$^3P_0$	223.157	1
$^1D_2$	6298.850	5
$^1S_0$	15394.370	1

Enthalpy of Formation

The enthalpy of formation of silicon gas is chosen to be the value recommended by CODATA.[1] This value was calculated from the sublimation and decomposition measurements of Davis *et al.* (1848–2003 K),[2] Grievison and Alcock (1940–2054 K),[3] Drowart *et al.*,[4] Gulbranson *et al.* (1373–1623 K),[5] Batdorf and Smits (1493–1601 K),[6] and Zenbov *et al.*[7]

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[8,9] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels (for n<11) and cutting off the summation in the partition function[10] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than those listed above; the next excited state is approximately 33326 cm^{-1} above the ground state. Although we list only a few levels, all levels given by Moore[8,9] and estimated levels (for n<11) are considered in the calculation. The reported uncertainty is $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states (for n<10) and use of different fill and cutoff procedures.[10]

The termal functions at 298.15 K closely agree with the recent CODATA recommendations[1] except for two minor changes. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table used a reference pressure of 1 bar, whereas CODATA recommendations are based on 1 atm. Second, the entropy differs by ~0.001 $J·K^{-1}·mol^{-1}$ due to the use of slightly different values for the fundamental constants.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
T/K	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−7.550	445.668	445.668	INFINITE
100	28.022	140.886	188.980	−4.809	448.142	434.437	−226.927
200	23.796	158.817	170.054	−2.247	449.526	420.095	−109.718
250	22.821	164.013	168.349	−1.084	449.839	412.697	−86.228
298.15	22.251	167.980	167.980	0.	450.000	405.528	−71.047
300	22.234	168.117	167.980	0.041	450.004	405.252	−70.561
350	21.861	171.515	168.249	1.143	450.071	397.787	−59.366
400	21.613	174.417	168.843	2.229	450.071	390.317	−50.970
450	21.440	176.952	169.606	3.305	450.023	382.850	−44.440
500	21.316	179.204	170.456	4.374	449.938	375.391	−39.217
600	21.153	183.075	172.246	6.497	449.684	360.504	−31.385
700	21.057	186.328	174.032	8.607	449.347	345.666	−25.794
800	21.000	189.135	175.748	10.710	448.940	330.881	−21.604
900	20.971	191.607	177.376	12.808	448.476	316.151	−18.349
1000	20.968	193.816	178.911	14.905	447.962	301.476	−15.747
1100	20.989	195.815	180.358	17.002	447.404	286.854	−13.622
1200	21.033	197.643	181.724	19.103	446.806	272.284	−11.852
1300	21.099	199.329	183.014	21.210	446.172	257.766	−10.357
1400	21.183	200.896	184.236	23.323	445.504	243.298	−9.078
1500	21.282	202.360	185.396	25.447	444.803	228.879	−7.970
1600	21.394	203.737	186.500	27.580	444.070	214.508	−7.003
1700	21.513	205.038	187.552	29.726	393.131	200.631	−6.165
1800	21.638	206.271	188.558	31.883	392.569	189.323	−5.494
1900	21.764	207.444	189.522	34.053	392.019	178.047	−4.895
2000	21.889	208.564	190.446	36.236	391.482	166.799	−4.356
2100	22.011	209.635	191.334	38.431	390.958	155.578	−3.870
2200	22.129	210.662	192.190	40.638	390.445	144.382	−3.428
2300	22.241	211.648	193.014	42.857	389.944	133.208	−3.025
2400	22.346	212.597	193.811	45.086	389.454	122.056	−2.656
2500	22.444	213.511	194.581	47.326	388.974	110.924	−2.318
2600	22.535	214.393	195.326	49.575	388.503	99.812	−2.005
2700	22.617	215.245	196.048	51.832	388.041	88.717	−1.716
2800	22.692	216.069	196.748	54.098	387.587	77.639	−1.448
2900	22.759	216.866	197.428	56.370	387.140	66.578	−1.199
3000	22.819	217.639	198.089	58.649	386.700	55.531	−0.967
3100	22.872	218.388	198.732	60.934	386.265	44.500	−0.750
3200	22.918	219.115	199.358	63.223	385.835	33.482	−0.547
3300	22.958	219.821	199.967	65.517	385.409	22.477	−0.356
3400	22.993	220.507	200.561	67.815	384.987	11.486	−0.176
3500	23.022	221.174	201.141	70.116	384.568	0.507	−0.008
3504.616	23.023	221.204	201.167	70.222	---- FUGACITY = 1 bar -----		
3600	23.046	221.822	201.706	72.419	0.	0.	0.
3700	23.066	222.454	202.258	74.725	0.	0.	0.
3800	23.081	223.070	202.798	77.032	0.	0.	0.
3900	23.093	223.669	203.325	79.341	0.	0.	0.
4000	23.102	224.254	203.841	81.651	0.	0.	0.
4100	23.108	224.825	204.346	83.961	0.	0.	0.
4200	23.111	225.381	204.840	86.272	0.	0.	0.
4300	23.113	225.925	205.324	88.583	0.	0.	0.
4400	23.112	226.457	205.799	90.895	0.	0.	0.
4500	23.111	226.976	206.264	93.206	0.	0.	0.
4600	23.108	227.484	206.719	95.517	0.	0.	0.
4700	23.104	227.981	207.167	97.827	0.	0.	0.
4800	23.100	228.467	207.605	100.138	0.	0.	0.
4900	23.096	228.943	208.036	102.447	0.	0.	0.
5000	23.092	229.410	208.459	104.757	0.	0.	0.
5100	23.089	229.867	208.874	107.066	0.	0.	0.
5200	23.087	230.316	209.282	109.375	0.	0.	0.
5300	23.086	230.755	209.683	111.683	0.	0.	0.
5400	23.086	231.187	210.077	113.992	0.	0.	0.
5500	23.087	231.610	210.465	116.300	0.	0.	0.
5600	23.091	232.026	210.846	118.609	0.	0.	0.
5700	23.098	232.435	211.221	120.918	0.	0.	0.
5800	23.108	232.837	211.591	123.228	0.	0.	0.
5900	23.121	233.232	211.954	125.539	0.	0.	0.
6000	23.135	233.621	212.312	127.851	0.	0.	0.

PREVIOUS: March 1967 (1 atm) CURRENT: March 1983 (1 bar)

IP(Si^+, g) = 131838.4 ± 0.1 cm^{-1}
$S°$(298.15 K) = 163.426 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1232.2 ± 4 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1242.505] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{1/2}$	0.0	2
$^2P_{3/2}$	287.32	4
$^4P_{1/2}$	42824.35	4
$^4P_{3/2}$	42932.68	6
$^4P_{5/2}$	43107.97	4

Enthalpy of Formation

$\Delta_f H°(Si^+, g, 0 K)$ is calculated from $\Delta_f H°(Si, g, 0 K)$[1] using the spectroscopic value of IP(Si) = 65747.5 ± 0.6 cm^{-1} (786.515 ± 0.001 $kJ·mol^{-1}$) from Moore.[2,6] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Si^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Si, g, 0 K)$ by using IP(Si) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Si(g), $Si^+(g)$, and e^-(ref). $\Delta_f H°(Si \rightarrow Si^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first four excited states; the next excited state is 55309.61 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
0	0.	0.	INFINITE	−7.343	1232.183		
100	25.060	134.836	186.411	−5.158			
200	26.512	153.262	165.719	−2.491			
250	25.337	159.052	163.832	−1.195			
298.15	24.338	163.426	163.426	0.	1242.505	1193.136	−209.032
300	24.304	163.577	163.427	0.045	1242.551	1192.829	−207.690
350	23.520	167.261	163.719	1.240	1243.750	1184.446	−176.769
400	22.943	170.362	164.361	2.400	1244.864	1175.897	−153.556
450	22.518	173.039	165.180	3.536	1245.915	1167.213	−135.487
500	22.201	175.394	166.086	4.654	1246.918	1158.414	−121.019
600	21.773	179.400	167.982	6.851	1248.818	1140.532	−99.292
700	21.509	182.735	169.858	9.014	1250.611	1122.342	−83.750
800	21.337	185.596	171.651	11.156	1252.323	1103.900	−72.077
900	21.219	188.101	173.342	13.283	1253.967	1085.248	−62.986
1000	21.134	190.332	174.932	15.401	1255.552	1066.416	−55.704
1100	21.072	192.344	176.425	17.511	1257.085	1047.427	−49.738
1200	21.025	194.175	177.829	19.615	1258.570	1028.302	−44.761
1300	20.989	195.857	179.152	21.716	1260.008	1009.054	−40.544
1400	20.960	197.411	180.401	23.814	1261.402	989.697	−36.926
1500	20.937	198.856	181.584	25.908	1262.751	970.243	−33.787
1600	20.918	200.207	182.706	28.001	1264.056	950.699	−31.037
1700	20.903	201.475	183.773	30.092	1215.141	931.522	−28.622
1800	20.890	202.669	184.790	32.182	1216.590	914.797	−26.547
1900	20.879	203.798	185.761	34.270	1218.037	897.991	−24.688
2000	20.870	204.869	186.690	36.358	1219.484	881.109	−23.012
2100	20.862	205.887	187.580	38.444	1220.929	864.155	−21.495
2200	20.855	206.857	188.434	40.530	1222.374	847.132	−20.113
2300	20.849	207.784	189.256	42.615	1223.818	830.043	−18.851
2400	20.844	208.671	190.046	44.700	1225.262	812.892	−17.692
2500	20.839	209.522	190.808	46.784	1226.705	795.680	−16.625
2600	20.835	210.339	191.544	48.868	1228.148	778.410	−15.638
2700	20.831	211.126	192.255	50.951	1229.590	761.085	−14.724
2800	20.828	211.883	192.942	53.034	1231.032	743.707	−13.874
2900	20.825	212.614	193.608	55.117	1232.474	726.277	−13.082
3000	20.823	213.320	194.254	57.199	1233.915	708.797	−12.341
3100	20.820	214.003	194.880	59.281	1235.356	691.270	−11.648
3200	20.818	214.664	195.488	61.363	1236.797	673.696	−10.997
3300	20.816	215.304	196.078	63.445	1238.238	656.076	−10.385
3400	20.814	215.926	196.653	65.526	1239.678	638.414	−9.808
3500	20.813	216.529	197.212	67.608	1241.119	620.708	−9.264
3600	20.811	217.115	197.757	69.689	858.407	613.423	−8.901
3700	20.810	217.685	198.288	71.770	860.261	606.592	−8.564
3800	20.809	218.240	198.806	73.851	862.113	599.711	−8.244
3900	20.808	218.781	199.311	75.932	863.964	592.782	−7.939
4000	20.807	219.308	199.805	78.013	865.814	585.805	−7.650
4100	20.807	219.821	200.286	80.093	867.662	578.782	−7.374
4200	20.806	220.323	200.758	82.174	869.511	571.714	−7.110
4300	20.806	220.812	201.218	84.254	871.359	564.601	−6.859
4400	20.806	221.291	201.669	86.335	873.207	557.446	−6.618
4500	20.806	221.758	202.110	88.416	875.055	550.249	−6.387
4600	20.806	222.216	202.542	90.496	876.903	543.011	−6.166
4700	20.807	222.663	202.966	92.577	878.751	535.732	−5.954
4800	20.808	223.101	203.381	94.658	880.601	528.414	−5.750
4900	20.809	223.530	203.788	96.738	882.450	521.058	−5.555
5000	20.811	223.951	204.187	98.819	884.300	513.664	−5.366
5100	20.813	224.363	204.578	100.901	886.151	506.233	−5.185
5200	20.816	224.767	204.963	102.982	888.002	498.765	−5.010
5300	20.819	225.163	205.340	105.064	889.854	491.262	−4.842
5400	20.822	225.553	205.711	107.146	891.706	483.724	−4.679
5500	20.827	225.935	206.075	109.228	893.559	476.152	−4.522
5600	20.832	226.310	206.433	111.311	895.412	468.546	−4.370
5700	20.838	226.679	206.785	113.395	897.265	460.907	−4.224
5800	20.845	227.041	207.131	115.479	899.117	453.236	−4.082
5900	20.852	227.398	207.472	117.564	900.969	445.532	−3.944
6000	20.861	227.748	207.807	119.649	902.822	437.797	−3.811

PREVIOUS: December 1971 (1 atm) CURRENT: March 1983 (1 bar)

EA(Si, g) = 1.385 ± 0.005 eV
$S°$(298.15 K) = 161.977 ± 0.001 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 312.04 ± 3 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [308.819] kJ·mol^{-1}

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4S_3$	0	4
^2D	6952	10
^2P	10937	6

Enthalpy of Formation

$\Delta_f H°(Si^-, g, 0 K)$ is calculated from $\Delta_f H°(Si, g, 0 K)$[1] using the adopted electron affinity of EA(Si) = 1.385 ± 0.005 eV (133.631 ± 0.482 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Si^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Si^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Si, g, 0 K)$ by using EA(Si) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Si^-(g), Si(g), and e^-(ref). $\Delta_f H°(Si^- \rightarrow Si + e^-, 298.15 K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15 K)$ should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

Electronic energy levels are from the laser photodetachment electron spectrometry study of Kasdan *et al.*[3] These workers found that the $Si^-(^2D)$ and $Si^-(^2P)$ states have binding energies of 0.523 ± 0.005 eV and 0.029 ± 0.005 eV, respectively, relative to ground state $Si(^3P_0)$. The electronic energies of 6952 cm^{-1} and 10937 cm^{-1} are the difference in binding energy between ground and excited states. We neglect the spin–orbit splitting of the ^2D and ^2P states; its effect is negligible.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}		
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	312.037		
100	20.786	139.270	180.457	−4.119			
200	20.786	153.678	163.878	−2.040			
250	20.786	158.316	162.319	−1.001			
298.15	20.786	161.977	161.977	0.	308.819	272.391	−47.722
300	20.786	162.106	161.977	0.038	308.782	272.165	−47.388
350	20.786	165.310	162.231	1.078	307.747	266.143	−39.720
400	20.786	168.085	162.793	2.117	306.660	260.274	−33.988
450	20.786	170.534	163.520	3.156	305.536	254.543	−29.547
500	20.786	172.724	164.332	4.196	304.382	248.938	−26.006
600	20.786	176.513	166.056	6.274	302.006	238.071	−20.726
700	20.787	179.718	167.785	8.353	299.558	227.608	−16.984
800	20.791	182.494	169.454	10.432	297.050	217.500	−14.201
900	20.803	184.943	171.041	12.511	294.489	207.709	−12.055
1000	20.831	187.136	172.543	14.593	291.881	198.207	−10.353
1100	20.887	189.124	173.961	16.678	289.232	188.967	−8.973
1200	20.981	190.945	175.302	18.771	286.547	179.971	−7.834
1300	21.122	192.629	176.571	20.876	283.833	171.199	−6.879
1400	21.318	194.202	177.775	22.998	281.094	162.638	−6.068
1500	21.572	195.681	178.920	25.142	278.335	154.273	−5.372
1600	21.884	197.082	180.011	27.314	275.562	146.092	−4.769
1700	22.253	198.420	181.055	29.520	222.605	138.532	−4.257
1800	22.674	199.704	182.056	31.766	220.053	133.661	−3.879
1900	23.140	200.942	183.017	34.057	217.545	128.930	−3.545
2000	23.645	202.141	183.944	36.396	215.086	124.329	−3.247
2100	24.179	203.308	184.838	38.787	212.679	119.851	−2.981
2200	24.735	204.445	185.704	41.232	210.326	115.486	−2.742
2300	25.303	205.558	186.543	43.734	208.030	111.227	−2.526
2400	25.876	206.646	187.358	46.293	205.790	107.066	−2.330
2500	26.444	207.714	188.151	48.909	203.608	102.998	−2.152
2600	27.002	208.762	188.923	51.581	201.483	99.015	−1.989
2700	27.542	209.792	189.677	54.309	199.412	95.114	−1.840
2800	28.058	210.803	190.414	57.089	197.394	91.288	−1.703
2900	28.548	211.796	191.134	59.920	195.426	87.533	−1.577
3000	29.005	212.772	191.839	62.797	193.506	83.846	−1.460
3100	29.428	213.730	192.530	65.719	191.629	80.222	−1.352
3200	29.815	214.670	193.207	68.682	189.794	76.657	−1.251
3300	30.164	215.593	193.871	71.681	187.995	73.150	−1.158
3400	30.475	216.498	194.524	74.714	186.229	69.696	−1.071
3500	30.748	217.386	195.164	77.775	184.492	66.294	−0.989
3600	30.982	218.255	195.794	80.862	−201.371	73.402	−1.065
3700	31.180	219.107	196.412	83.970	−202.647	81.052	−1.144
3800	31.343	219.941	197.020	87.097	−203.906	88.736	−1.220
3900	31.472	220.757	197.619	90.238	−205.153	96.454	−1.292
4000	31.568	221.555	198.207	93.390	−206.389	104.203	−1.361
4100	31.635	222.335	198.786	96.550	−207.617	111.983	−1.427
4200	31.674	223.098	199.356	99.716	−208.841	119.793	−1.490
4300	31.687	223.843	199.917	102.884	−210.063	127.632	−1.550
4400	31.676	224.572	200.469	106.053	−211.284	135.500	−1.609
4500	31.643	225.283	201.012	109.219	−212.508	143.395	−1.664
4600	31.591	225.978	201.548	112.381	−213.736	151.317	−1.718
4700	31.521	226.657	202.075	115.536	−214.969	159.267	−1.770
4800	31.435	227.320	202.594	118.684	−216.210	167.242	−1.820
4900	31.336	227.967	203.105	121.823	−217.460	175.244	−1.868
5000	31.224	228.599	203.609	124.951	−218.720	183.271	−1.915
5100	31.101	229.216	204.105	128.067	−219.991	191.323	−1.960
5200	30.969	229.819	204.593	131.171	−221.275	199.401	−2.003
5300	30.829	230.407	205.075	134.261	−222.572	207.503	−2.045
5400	30.683	230.982	205.549	137.337	−223.884	215.630	−2.086
5500	30.531	231.544	206.017	140.397	−225.209	223.781	−2.125
5600	30.374	232.092	206.478	143.443	−226.552	231.957	−2.164
5700	30.214	232.629	206.932	146.472	−227.910	240.156	−2.201
5800	30.051	233.153	207.379	149.485	−229.286	248.380	−2.237
5900	29.886	233.665	207.821	152.482	−230.679	256.627	−2.272
6000	29.720	234.166	208.255	155.463	−232.089	264.899	−2.306

PREVIOUS: CURRENT: March 1983 (1 bar)

$S°(298.15\ K) = 229.79\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 587.1 \pm 13\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 589.9 \pm 13\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i	State	ϵ_i, cm^{-1}	g_i
$^3\Sigma_g^-$	0	3	$[^1\Delta_g]$	[10000]	[2]	$^3\Pi_g$	[30000]	6
$^3\Pi_u$	[2000]	6	$[^1\Sigma_g^+]$	[13000]	[1]	$^3\Sigma_u^-$	30769	3
$[^1\Sigma_g^+]$	[6000]	[1]	$[^3\Sigma_u^+]$	[20000]	[3]	$[^1\Pi_g]$	[40000]	[2]
$[^1\Pi_u]$	[8000]	[2]	$^3\Sigma_u^-$	24583	3	$[^1\Sigma_u^+]$	[45000]	[1]
						$^3\Sigma_u^-$	46762	3

$\omega_e = 510.98\ cm^{-1}$ $\omega_e x_e = 2.02\ cm^{-1}$ $\sigma = 2$

$B_e = 0.2390\ cm^{-1}$ $\alpha_e = 0.0013\ cm^{-1}$ $r_e = 2.246$ Å

Enthalpy of Formation

The selected value is based on the spectroscopic and equilibrium data summarized below. Verma and Warsop[1] concluded from analysis of the absorption spectra that $D_0° = 70 \pm 4$ kcal·mol^{-1}. Predissociation of the H state suggested the upper limit $D_0° \leq 74.0$, while linear Birgen–Sponer extrapolations of the H and K states gave 78.4 and 68.9 kcal·mol^{-1} for the ground state. By assuming that the true extrapolation would not reduce the linear extrapolation for the H state by more than half, i.e. from 26 to 13 kcal·mol^{-1}, the authors arrived at the lower limit of $D_0° \geq 65.5$ for the ground state.

Drowart and co-workers have used the Knudsen effusion–mass spectrometric technique to determine the vapor equilibria over the systems SiC–graphite,[2] SiC–silicon[3] and boron–carbon–silicon.[4] Third law analysis of the partial pressures of Si_2 and Si over the three systems yields $D_0°$ values of 73.3, 74.3 and 70.4 kcal·mol^{-1}, which are in good agreement with the spectroscopic values. The selected value, $\Delta_f H°(298.15\ K) = 141 \pm 3$ kcal·mol^{-1}, corresponds to $D_0° = 73.0$ kcal·mol^{-1}.

Source	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15\ K)$ kcal·mol^{-1}
1	Prediss. of H state		–	≤75.4		–	≥140.0
	LEX of K state		–	70.3			145.1
	Extrap. of H state		–	≥66.9			≤148.5
2	Mass spec.	2149–2316	7	95.3 ± 7.1	74.68	−9 ± 3	140.7
3	Mass spec.	1703–2160	9	81.0 ± 1.1	75.71	−2.7 ± 0.6	139.7
4	Mass spec.	2166–2344	4	68.0 ± 16	71.76	2 ± 7	143.6

*For the reaction $Si_2(g) = 2\ Si(g)$

Heat Capacity and Entropy

Vibrational and rotational constants are those obtained by Verma and Warsop[1] through combination of their data for the H–X system with those of Douglas.[5] Observation of the same H–X system in matrix isolation by Weltner and McLeod[6] confirms that the lower state is the ground state. Comparison with the isoelectronic molecules C_2, BN, BeO and MgO[7–10] suggest that there are several possible low-lying excited states in Si_2. Tentative estimates for these levels are given above, based on this comparison and on the observed states.[1,5] These estimates are relatively uncertain and probably yield an upper limit for the entropy at temperatures where Si_2 is significant. A probable lower limit may be obtained by increasing the two $^3\Pi$ states by 8000 cm^{-1} and omitting the other estimated levels. This would reduce the entropy by 1.7 cal·K^{-1}·mol^{-1} at 2000 K, corresponding to a change of 3.4 kcal·mol^{-1} in $\Delta_f H°$ values based on equilibrium data.

References

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$		$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−9.263	587.118	587.118	INFINITE
100	29.412	195.317	258.806	−6.349	589.499	570.734	−298.121
200	32.184	216.488	232.879	−3.278	590.212	551.581	−144.058
250	33.463	223.812	230.355	−1.636	590.154	541.924	−113.229
298.15	34.452	229.793	229.793	0.	589.944	532.653	−93.319
300	34.487	230.007	229.794	0.064	589.934	532.298	−92.681
350	35.374	235.390	230.217	1.811	589.611	522.716	−78.011
400	36.227	240.170	231.168	3.601	589.228	513.185	−67.015
450	37.096	244.487	232.412	5.434	588.812	503.705	−58.469
500	37.986	248.441	233.820	7.311	588.382	494.272	−51.636
600	39.743	255.524	236.860	11.198	587.517	475.531	−41.399
700	41.286	261.770	239.981	15.252	586.675	456.933	−34.097
800	42.472	267.365	243.061	19.443	585.848	438.455	−28.628
900	43.274	272.417	246.046	23.734	585.015	420.081	−24.381
1000	43.738	277.003	248.916	28.087	584.146	401.801	−20.988
1100	43.941	281.183	251.663	32.472	583.220	383.611	−18.216
1200	43.963	285.008	254.284	36.869	582.219	365.508	−15.910
1300	43.869	288.524	256.785	41.261	581.130	347.493	−13.962
1400	43.709	291.769	259.169	45.640	579.945	329.564	−12.296
1500	43.520	294.779	261.444	50.002	578.658	311.724	−10.855
1600	43.324	297.581	263.616	54.344	577.268	293.974	−9.597
1700	43.135	300.202	265.692	58.667	475.421	277.207	−8.518
1800	42.962	302.662	267.678	62.972	474.287	265.579	−7.707
1900	42.810	304.981	269.581	67.260	473.136	254.016	−6.983
2000	42.679	307.174	271.406	71.534	471.971	242.513	−6.334
2100	42.569	309.253	273.160	75.797	470.794	231.069	−5.748
2200	42.479	311.231	274.846	80.049	469.607	219.682	−5.216
2300	42.407	313.118	276.469	84.293	468.412	208.348	−4.732
2400	42.352	314.922	278.034	88.531	467.210	197.067	−4.289
2500	42.311	316.650	279.544	92.764	466.004	185.836	−3.883
2600	42.282	318.308	281.003	96.993	464.795	174.653	−3.509
2700	42.264	319.904	282.415	101.221	463.583	163.517	−3.163
2800	42.255	321.441	283.781	105.446	462.369	152.425	−2.844
2900	42.254	322.923	285.106	109.672	461.155	141.377	−2.546
3000	42.259	324.356	286.390	113.897	459.942	130.371	−2.270
3100	42.271	325.742	287.637	118.124	458.729	119.405	−2.012
3200	42.287	327.084	288.849	122.352	457.518	108.479	−1.771
3300	42.307	328.386	290.028	126.581	456.308	97.590	−1.545
3400	42.331	329.649	291.174	130.813	455.101	86.738	−1.333
3500	42.358	330.876	292.291	135.048	453.896	75.921	−1.133
3600	42.388	332.070	293.380	139.285	−315.609	86.060	−1.249
3700	42.420	333.232	294.441	143.525	−315.980	97.223	−1.373
3800	42.455	334.364	295.477	147.769	−316.351	108.396	−1.490
3900	42.492	335.467	296.488	152.016	−316.721	119.578	−1.602
4000	42.531	336.543	297.476	156.267	−317.090	130.770	−1.708
4100	42.571	337.594	298.442	160.523	−317.456	141.971	−1.809
4200	42.614	338.620	299.386	164.782	−317.819	153.181	−1.905
4300	42.658	339.623	300.311	169.045	−318.177	164.399	−1.997
4400	42.704	340.605	301.215	173.313	−318.532	175.626	−2.085
4500	42.751	341.565	302.101	177.586	−318.881	186.861	−2.169
4600	42.800	342.505	302.969	181.864	−319.226	198.103	−2.250
4700	42.850	343.426	303.820	186.146	−319.565	209.353	−2.327
4800	42.902	344.329	304.655	190.434	−319.897	220.610	−2.401
4900	42.955	345.214	305.474	194.726	−320.224	231.874	−2.472
5000	43.010	346.082	306.277	199.025	−320.545	243.145	−2.540
5100	43.066	346.934	307.066	203.328	−320.859	254.422	−2.606
5200	43.123	347.771	307.841	207.638	−321.167	265.705	−2.669
5300	43.181	348.593	308.602	211.953	−321.469	276.994	−2.730
5400	43.241	349.401	309.350	216.274	−321.765	288.288	−2.789
5500	43.302	350.195	310.086	220.601	−322.054	299.588	−2.845
5600	43.364	350.976	310.809	224.935	−322.338	310.893	−2.900
5700	43.427	351.744	311.520	229.274	−322.618	322.204	−2.953
5800	43.492	352.500	312.220	233.620	−322.892	333.519	−3.004
5900	43.557	353.244	312.909	237.973	−323.162	344.838	−3.053
6000	43.623	353.976	313.588	242.332	−323.427	356.163	−3.101

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

$S°(298.15\ K) = 267.90\ J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K) = 632.7 \pm 42\ kJ·mol^{-1}$

$\Delta_f H°(298.15\ K) = 636.0 \pm 42\ kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3\Sigma^-$	0	3
$^3\Pi_u$	[10000]	[6]
$^1\Pi_u$	[18000]	[2]
$^3\Sigma^+$	21460	3

Vibrational Frequencies and Degeneracies
ν, cm^{-1}
[360](1)
[200](2)
[630](1)

Point Group: $[D_{\infty h}]$ σ = [2]
Bond Distance: [2.25] Å
Bond Angle: [180]°
Rotational Constant: B_0 = [0.059282] cm^{-1}

Enthalpy of Formation

The selected value is an average based on the equilibrium data summarized below. Drowart *et al.* have used the Knudsen effusion–mass spectrometric technique to determine the vapor species over the systems SiC–graphite[1] and SiC–silicon.[2] Third law analysis of the partial pressures of Si_3 and Si yields the values 154.0 and 149.9 $kcal·mol^{-1}$. Both drifts suggest that the entropy may be lower than the tabulated values. It is unlikely that the entropy is in error by more than 5 $cal·K^{-1}·mol^{-1}$ so that most of the drift is inherent in the data. The adopted value of $\Delta_f H°(298.15\ K) = 152 \pm 10\ kcal·mol^{-1}$ includes allowance for an error of up to 5 $cal·K^{-1}·mol^{-1}$.

Source	Method	T/K	Data Points	$\Delta_r H°(298.15\ K)$, $kcal·mol^{-1}$* 2nd law	3rd law	$cal·K^{-1}·mol^{-1}$ Drift	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
[1]	Mass Spec.	2230–2316	2	209	169.1	−18	154.0
[2]	Mass Spec.	1703–1890	4	204 ± 3	173.2	−17 ± 2	149.9

*For reaction $Si_3(g) = 3\ Si(g)$

Heat Capacity and Entropy

Weltner and McLeod[3] observed an absorption band near 4660 Å in matrix isolation studies. Their tenative assignment of this band as the $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition of Si_3 is adopted here. A $^1\Pi_u$ state is assumed at 18000 cm^{-1}, which is 7000 and 2000 cm^{-1} below the analogous levels[3] for C_3 and C_2Si. Also a $^3\Pi_u$ level is assumed at 10000 cm^{-1}, presumably arising from the same molecular orbital configuration as the $^1\Pi_u$ state. The molecule is assumed to be linear with a bond distance equal to that in Si_2. Vibrational frequencies are estimated from a valence bond calculation using $k_l = 2.16 \times 10^5$ and $k\sigma/l^2 = 0.11 \times 10^5$ dyn cm^{-1}. The stretching force constant is obtained from Si_2, while the bending force constant is based on C_2Si and the $^1\Pi_u$ excited state[3] of C_3.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−12.919	632.703	632.703	INFINITE
100	39.149	216.004	312.988	−9.698	635.125	614.674	−321.073
200	49.903	246.896	272.794	−5.180	636.108	593.728	−155.066
250	52.965	258.381	268.794	−2.603	636.134	583.123	−121.837
298.15	55.055	267.898	267.898	0.	635.968	572.927	−100.374
300	55.122	268.239	267.899	0.102	635.959	572.536	−99.687
350	56.664	276.859	268.577	2.899	635.651	561.989	−83.872
400	57.787	284.502	270.099	5.761	635.254	551.492	−72.017
450	58.621	291.359	272.087	8.673	634.792	541.048	−62.803
500	59.255	297.570	274.329	11.620	634.279	530.660	−55.438
600	60.129	308.457	279.135	17.593	633.123	510.042	−44.403
700	60.686	317.770	284.005	23.636	631.823	489.629	−36.537
800	61.060	325.900	288.745	29.724	630.384	469.412	−30.649
900	61.323	333.108	293.281	35.844	628.818	449.383	−26.082
1000	61.516	339.579	297.593	41.986	627.128	429.536	−22.437
1100	61.663	345.450	301.681	48.146	625.319	409.863	−19.463
1200	61.781	350.820	305.555	54.318	623.395	390.360	−16.992
1300	61.884	355.769	309.230	60.501	621.357	371.022	−14.908
1400	61.981	360.359	312.720	66.695	619.203	351.846	−13.128
1500	62.081	364.639	316.040	72.898	616.934	332.827	−11.590
1600	62.190	368.649	319.204	79.111	614.549	313.964	−10.250
1700	62.312	372.423	322.225	85.336	461.519	296.594	−9.113
1800	62.451	375.988	325.114	91.574	459.598	286.948	−8.327
1900	62.610	379.369	327.881	97.827	457.692	277.408	−7.626
2000	62.789	382.585	330.536	104.097	455.803	267.969	−6.999
2100	62.989	385.653	333.089	110.385	453.933	258.623	−6.433
2200	63.208	388.588	335.545	116.695	452.084	249.366	−5.921
2300	63.445	391.403	337.913	123.028	450.258	240.192	−5.455
2400	63.699	394.109	340.198	129.385	448.456	231.098	−5.030
2500	63.966	396.714	342.407	135.768	446.681	222.078	−4.640
2600	64.244	399.228	344.545	142.178	444.932	213.128	−4.282
2700	64.531	401.658	346.615	148.617	443.212	204.246	−3.951
2800	64.824	404.011	348.623	155.085	441.521	195.426	−3.646
2900	65.121	406.291	350.573	161.582	439.860	186.666	−3.362
3000	65.420	408.503	352.467	168.109	438.228	177.963	−3.099
3100	65.718	410.653	354.309	174.666	436.626	169.314	−2.853
3200	66.013	412.744	356.103	181.252	435.054	160.717	−2.623
3300	66.304	414.780	357.850	187.868	433.511	152.168	−2.409
3400	66.589	416.764	359.554	194.513	431.997	143.665	−2.207
3500	66.867	418.698	361.216	201.186	430.511	135.206	−2.018
3600	67.136	420.586	362.839	207.886	−723.403	158.172	−2.295
3700	67.396	422.429	364.425	214.613	−723.593	182.663	−2.579
3800	67.646	424.229	365.975	221.365	−723.763	207.158	−2.848
3900	67.886	425.990	367.492	228.142	−723.913	231.658	−3.103
4000	68.114	427.711	368.976	234.942	−724.042	256.162	−3.345
4100	68.330	429.396	370.429	241.764	−724.151	280.668	−3.576
4200	68.535	431.045	371.853	248.607	−724.241	305.177	−3.795
4300	68.727	432.660	373.248	255.471	−724.312	329.688	−4.005
4400	68.908	434.242	374.616	262.353	−724.363	354.200	−4.205
4500	69.077	435.792	375.959	269.252	−724.398	378.713	−4.396
4600	69.233	437.312	377.276	276.167	−724.415	403.227	−4.579
4700	69.379	438.803	378.569	283.098	−724.416	427.741	−4.754
4800	69.512	440.265	379.839	290.043	−724.402	452.255	−4.922
4900	69.635	441.699	381.087	297.000	−724.374	476.769	−5.082
5000	69.747	443.107	382.314	303.969	−724.333	501.281	−5.237
5100	69.848	444.490	383.519	310.949	−724.280	525.793	−5.385
5200	69.939	445.847	384.705	317.939	−724.217	550.304	−5.528
5300	70.020	447.180	385.871	324.937	−724.145	574.813	−5.665
5400	70.091	448.489	387.018	331.942	−724.065	599.321	−5.797
5500	70.154	449.776	388.148	338.955	−723.976	623.827	−5.925
5600	70.208	451.041	389.260	345.973	−723.885	648.332	−6.047
5700	70.254	452.284	390.354	352.996	−723.790	672.835	−6.166
5800	70.291	453.506	391.433	360.023	−723.693	697.336	−6.280
5900	70.322	454.708	392.495	367.054	−723.596	721.836	−6.391
6000	70.345	455.890	393.542	374.087	−723.498	746.334	−6.497

PREVIOUS: March 1967 (1 atm) CURRENT: March 1967 (1 bar)

REFERENCE STATE

0	to	820	K crystal, alpha
820	to	1050	K crystal, beta
1050	to	1685.492	K liquid
above		1685.492	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−6.568	0.	0.	0.
100	23.481	28.050	78.738	−5.069	0.	0.	0.
200	25.757	45.209	58.112	−2.581	0.	0.	0.
298.15	26.791	55.694	55.694	0.	0.	0.	0.
300	26.809	55.859	55.694	0.050	0.	0.	0.
400	27.777	63.704	56.757	2.779	0.	0.	0.
500	28.785	70.010	58.797	5.607	0.	0.	0.
600	29.814	75.349	61.122	8.536	0.	0.	0.
700	30.864	80.023	63.495	11.570	0.	0.	0.
800	31.935	84.214	65.827	14.710	0.	0.	0.
820.000	32.151	85.005	66.285	15.351	ALPHA <--> BETA TRANSITION		
820.000	29.790	86.026	66.285	16.188			
900	30.125	88.814	68.165	18.584	0.	0.	0.
1000	30.543	92.010	70.393	21.618	0.	0.	0.
1050.000	30.752	93.505	71.458	23.150	BETA <--> LIQUID TRANSITION		
1050.000	39.463	100.582	71.458	30.581			
1100	39.463	102.418	72.824	32.554	0.	0.	0.
1200	39.463	105.852	75.435	36.500	0.	0.	0.
1300	39.463	109.010	77.898	40.446	0.	0.	0.
1400	39.463	111.935	80.226	44.393	0.	0.	0.
1500	39.463	114.658	82.432	48.339	0.	0.	0.
1600	39.463	117.204	84.526	52.285	0.	0.	0.
1685.492	39.463	119.259	86.236	55.659	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1685.492	20.834	200.650	86.236	192.844			
1700	20.839	200.829	87.214	193.146	0.	0.	0.
1800	20.882	202.021	93.559	195.232	0.	0.	0.
1900	20.949	203.152	99.297	197.323	0.	0.	0.
2000	21.049	204.229	104.517	199.423	0.	0.	0.
2100	21.191	205.259	109.290	201.534	0.	0.	0.
2200	21.383	206.249	113.675	203.662	0.	0.	0.
2300	21.636	207.205	117.721	205.813	0.	0.	0.
2400	21.959	208.132	121.469	207.992	0.	0.	0.
2500	22.361	209.036	124.953	210.207	0.	0.	0.
2600	22.849	209.923	128.204	212.467	0.	0.	0.
2700	23.430	210.796	131.247	214.780	0.	0.	0.
2800	24.109	211.660	134.104	217.157	0.	0.	0.
2900	24.889	212.519	136.793	219.606	0.	0.	0.
3000	25.770	213.377	139.331	222.138	0.	0.	0.
3100	26.753	214.238	141.734	224.763	0.	0.	0.
3200	27.834	215.104	144.013	227.492	0.	0.	0.
3300	29.008	215.978	146.181	230.333	0.	0.	0.
3400	30.270	216.863	148.246	233.296	0.	0.	0.
3500	31.611	217.759	150.220	236.389	0.	0.	0.
3600	33.022	218.670	152.108	239.620	0.	0.	0.
3700	34.493	219.594	153.920	242.995	0.	0.	0.
3800	36.011	220.534	155.660	246.520	0.	0.	0.
3900	37.565	221.490	157.336	250.199	0.	0.	0.
4000	39.142	222.461	158.952	254.034	0.	0.	0.
4100	40.730	223.447	160.513	258.027	0.	0.	0.
4200	42.304	224.446	162.023	262.176	0.	0.	0.
4300	43.874	225.460	163.487	266.485	0.	0.	0.
4400	45.418	226.486	164.907	270.950	0.	0.	0.
4500	46.927	227.524	166.287	275.568	0.	0.	0.
4600	48.214	228.556	167.628	280.269	0.	0.	0.
4700	49.584	229.608	168.936	285.159	0.	0.	0.
4800	50.884	230.665	170.211	290.182	0.	0.	0.
4900	52.114	231.727	171.455	295.332	0.	0.	0.
5000	53.254	232.791	172.671	300.596	0.	0.	0.
5200	55.250	234.914	175.024	311.429	0.	0.	0.
5400	56.945	237.032	177.282	322.655	0.	0.	0.
5600	58.296	239.129	179.453	334.184	0.	0.	0.
5800	59.317	241.193	181.547	345.951	0.	0.	0.
6000	59.709	243.172	183.564	357.650	0.	0.	0.

PREVIOUS: December 1970 (1 atm) CURRENT: September 1983 (1 bar)

Pearson Notation: CF4
$S°(298.15\ K) = 55.69 \pm 0.1\ J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta) = 820 \pm 8\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{trs} H°(820\ K) = 0.8368 \pm 0.17\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted heat capacities are derived from the heat capacity[1,2] and enthalpy[2] data by fitting the experimental data with orthogonal polynomials over selected overlapping temperature intervals. The temperature region of 1–9 K is described by the equation: $C_p° = 3.281 \times 10^{-3}\ T + 1.89 \times 10^{-4}\ T^3$ cal·K^{-1}·mol^{-1}. The $S°$(298.15 K) value calculated from the polynomials agrees to within 0.002 cal·K^{-1}·mol^{-1} with that given by Boerio and Westrum[1] and adopted by Gurvich *et al.*[3]

Boerio and Westrum[1] used adiabatic–shield calorimetry to measure the low temperature heat capacity, 83 data points in the range 6.28 to 346.42 K. Two other studies have also been made: Kreplovich and Paukov (5–300 K)[4,5] and Roberts (1–20 K).[6] In the temperature region below 20 K, both these studies deviate from the adopted values similarly, from ~44% low at 5 K to ~15% low at 20 K. Since the sample used by Kreplovich and Paukov[4,5] was shown to contain a substantial oxygen impurity, of the order of 6 ± 3 mole %,[1] the sample used by Roberts[6] probably had similar impurities. Roberts reported a purity of 98.25% but only metallic impurities were analyzed.

Stephens and Roth[2] measured enthalpy (350–1191 K) by drop calorimetry and heat capacity (298–785 K) by differential scanning calorimetry. We fit the 14 enthalpy points at 400–812 K with a polynomial, using the adiabatic[1] and DSC[2] data as a guide to the shape of the heat capacity curve. We adopt this fit only above 350 K, although the derived $C_p°$ values agree closely (± 0.3%) with the adiabatic data[1] at 250 to 320 K. Between 320 and 400 K the adopted $C_p°$ values are a compromise between those of Boerio and Westrum and those of Stephens and Roth. This compromise yields an upward inflection point in $C_p°$ versus T near 330 K. The largest deviation of Boerio and Westrum[1] above 320 K is −0.7% at 343.42 K. The DSC data[2] deviate by −0.8 to +2.0% except for +3.8% at 785 K. The enthalpy data[2] deviate by −1.6 to +1.8% (400–812 K) with larger deviations at 350 and 550 K.

Phase Data

According to Pearson,[7] α–strontium has the face–centered–cubic structure, isotypic with Cu, designated as CF4. In the alkaline earth metal series, only α–calcium has the same structure.

Transition Data

Refer to the β–crystal table for details.

Sublimation Data

The enthalpy of sublimation of α–strontium is the enthalpy of formation of the gas. The experimental studies are discussed in the ideal gas table.

References

[1]J. Boerio and E. F. Westrum, J. Chem. Thermodyn. **10**, 1 (1978).
[2]H. J. Stephens and E. P. Roth, Sandia National Laboratories, Albuquerque, New Mexico, personal communication, (May 3, 1982).
[3]L. V. Gurvich, I. V. Veits *et al.*, "Thermodynamic Properties of Individual Substances," 3rd ed., Vol. III, Nauka, Moscow, (1981).
[4]L. M. Khriplovich and I. E. Paukov, Zh. Fiz. Khim. **50**, 567 (1976).
[5]L. M. Khriplovich and I. E. Paukov, VINITI Documentary Deposit No. 3190–75, (November, 11, 1975).
[6]L. M. Roberts, Proc. Phys. Soc. (London) **B70**, 733 (1957).
[7]W. B. Pearson, "A Handbook of Lattice Spacing and Structures of Metals and Alloys," Pergamon Press, London, 1958, (1967).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−6.568	0.	0.	0.
100	23.481	28.050	78.738	−5.069	0.	0.	0.
200	25.757	45.209	58.112	−2.581	0.	0.	0.
298.15	26.791	55.694	55.694	0.	0.	0.	0.
300	26.809	55.859	55.694	0.050	0.	0.	0.
350	27.298	60.029	56.022	1.402	0.	0.	0.
400	27.777	63.704	56.757	2.779	0.	0.	0.
450	28.278	67.005	57.716	4.180	0.	0.	0.
500	28.785	70.010	58.797	5.607	0.	0.	0.
600	29.814	75.349	61.122	8.536	0.	0.	0.
700	30.864	80.023	63.495	11.570	0.	0.	0.
800	31.935	84.214	65.827	14.710	0.	0.	0.
820.000	32.151	85.005	66.285	15.351	--- ALPHA <--> BETA -----		
900	33.027	88.038	68.085	17.958	−0.626	0.072	−0.004
1000	34.139	91.576	70.260	21.316	−0.302	0.133	−0.007
1100	35.273	94.882	72.349	24.786	−7.768	0.522	−0.025
1200	36.428	98.001	74.358	28.371	−8.129	1.292	−0.056
1300	37.604	100.963	76.292	32.073	−8.374	2.088	−0.084
1400	38.801	103.794	78.156	35.893	−8.500	2.898	−0.108
1500	40.019	106.512	79.956	39.834	−8.505	3.713	−0.129

PREVIOUS: December 1970 CURRENT: September 1983

Pearson Notation: cI2
$S°(298.15\ K)$ = [57.175] $J·K^{-1}·mol^{-1}$
$T_{trs}(\alpha \rightarrow \beta)$ = 820 ± 8 K
$T_{fus}(\beta \rightarrow l)$ = 1050 ± 10 K

$\Delta_f H°(298.15\ K)$ = [1.211] $kJ·mol^{-1}$
$\Delta_{trs}H°(820\ K)$ = 0.8368 ± 0.17 $kJ·mol^{-1}$
$\Delta_{fus}H°(1050\ K)$ = 7.4308 ± 0.8 $kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(Sr, cr, β, 298.15 K) is calculated from $\Delta_f H°$(Sr, α, cr, 298.15 K) by adding the enthalpy of transition, $\Delta_{trs}H°$, and the difference in enthalpy, $H°(820\ K)–H°(298.15\ K)$, between α–Sr and β–Sr.

Heat Capacity and Entropy

The drop–calorimetry data of Stephens and Roth[1] contain 9 points (819.6–1048.8 K) that appear to be in the region of stability of β–strontium. Their values of $[H°(T)–H°(298.15\ K)]/(T–298.15)$ show systematic curvature suggestive of the effects of incomplete transition or premelting near the extreme temperatures. Constant $C_p°$ values ranging from ~6.3 to 9.3 $cal·K^{-1}·mol^{-1}$ can be derived by various selections and weightings of the points. We arbitrarily select a $C_p°$ near 7.3 $cal·K^{-1}·mol^{-1}$ with a linear temperature dependence that maintains the proper stability relationships when extrapolated below T_{trs} and above T_{fus}. This curve reproduces the enthalpy data within ±1.2% (819.6–990.5 K) and corresponds to premelting effects of ~140 to 450 $cal·mol^{-1}$ in the region from 1029 to 1049 K. $S°(298.15\ K)$ is calculated from that of α–strontium using entropy increments analogous to the enthalpy increments used to calculate $\Delta_f H°(298.15\ K)$.

Phase Data

According to Pearson,[2] β–strontium has the body–centered–cubic structure, isotypic with W, designated as CI_2. In the alkaline earth metal series, β–calcium, β–beryllium, and barium have the same structure. Note that we now use the name beta[3] for the phase of Sr stable near T_{fus}, unlike Pearson who retains the historical name gamma. The change arose when Peterson and Colburn[3] found that an intermediate hexagonal–close–packed phase does not occur in Sr containing a smaller amount of H_2 impurity.

Transition Data

We select T_{trs} = 820 ± 8 K based on enthalpy data of Stephens and Roth[1] and DTA data of Peterson and Colburn.[3] DTA gave ~813 K on cooling and 828 K (after correction for H impurity) on heating. We adopt an enthalpy of transition of 200 ± 40 $cal·mol^{-1}$ derived from our fits of the enthalpy data[1] for β and α phases; Stephens and Roth selected the same value. Almost 170 out of the 200 cal/mol appeared between 812 and 819.6 K. Another 30 $cal·mol^{-1}$ appeared between 819.6 and 824.9 K, while possibly 40 $cal·mol^{-1}$ appeared between 824.9 and 835.6 K. The latter enthalpy increments are uncertain because of almost equal–sized scatter in the data and because of uncertainty in $C_p°(\beta)$. Our adopted value of T_{trs} = 820 K is in the middle of the DTA hystersis range. The temperature range up to T_{trs} includes most of the transition enthalpy seen in the sample of Stephens and Roth. Their sample was identical with that used by Boerio and Westrum[4] to measure the low temperature $C_p°$ and $S°$ of α phase.

Peterson and Colburn[3] found that T_{trs} increased rapidly with increasing hydrogen content. They also observed the intermediate hexagonal–close–packed phase at hydrogen contents of >3 mole % but not at 0.4 mole %, suggesting that this phase does not occur in pure strontium. The enthalpy and heat capacity data[1] are consistent with this interpretation.

Sublimation Data

The enthaply of sublimation of β–strontium is calculated as the difference in the enthlapies of formation of the gas and β– strontium. The experimental studies are discussed in the Sr(g) table.

References

[1]H. J. Stephens and E. P. Roth, Sandia National Laboratories, Albuquerque, New Mexico, personal communication, (May 3, 1982).
[2]W. B. Pearson, "A Handbook of Lattice Spacing and Structures of Metals and Alloys," Pergamon Press, London, 1958, (1967).
[3]D. T. Peterson and R. P. Colburn, J. Phys. Chem. **70**, 463 (1966).
[4]J. Boerio and E. F. Westrum, J. Chem. Thermodyn. **10**, 1 (1978).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	27.607	57.175	57.175	0.	1.211	0.770	−0.135
300	27.614	57.346	57.175	0.051	1.213	0.767	−0.134
400	28.033	65.347	58.263	2.833	1.266	0.609	−0.080
500	28.451	71.647	60.332	5.658	1.262	0.444	−0.046
600	28.870	76.872	62.665	8.524	1.199	0.285	−0.025
700	29.288	81.353	65.022	11.432	1.073	0.142	−0.011
800	29.706	85.291	67.315	14.381	0.883	0.021	−0.001
820.000	29.790	86.026	67.762	14.976	---- ALPHA <--> BETA ----		
900	30.125	88.814	69.511	17.373	0.	0.	0.
1000	30.543	92.010	71.604	20.406	0.	0.	0.
1050.000	30.752	93.505	72.611	21.939	---- BETA <--> LIQUID ----		
1100	30.962	94.941	73.594	23.481	−7.861	0.364	−0.017
1200	31.380	97.653	75.487	26.599	−8.690	1.149	−0.050
1300	31.798	100.181	77.291	29.757	−9.478	2.001	−0.080
1400	32.217	102.553	79.011	32.958	−10.223	2.912	−0.109
1500	32.635	104.790	80.656	36.201	−10.927	3.875	−0.135

PREVIOUS: CURRENT: September 1983

$S°(298.15\ K) = [50.901]\ J·K^{-1}·mol^{-1}$ $\Delta_f H°(298.15\ K) = [0.911]\ kJ·mol^{-1}$

$T_{fus}(\beta \rightarrow l) \approx 1050 \pm 10\ K$ $\Delta_{fus}H°(1050\ K) \approx 7.4308 \pm 0.8\ kJ·mol^{-1}$

Enthalpy of Formation

$\Delta_f H°$(Sr, l, 298.15 K) is calculated from $\Delta_f H°$(Sr, cr, β, 298.15 K) by adding the enthalpy of fusion, $\Delta_{fus}H°$, and the difference in enthalpy, $H°(1050\ K)-H°(298.15\ K)$, between β–Sr and the liquid.

Heat Capacity and Entropy

$C_p°$ is the constant value derived fron three enthalpy points (1059–1191 K) measured by Stephens and Roth.[1] Their points deviate from the adopted enthalpies by −0.8 to +0.5%. We assume a glass transition with zero enthalpy at 650 K; below 650 K we assume that $C_p°$ (glass) is equal to the $C_p°$ (α) curve derived from the enthalpy data for α strontium (refer to that table). These or similar assumptions are necessary to ensure that $S°$(298.15 K) of the supercooled liquid is larger than that of α–strontium. $S°$(298.15 K) is calculated from that of β–strontium using entropy increments analogous to the enthalpy increments used to calculate $\Delta_f H°$(298.15 K).

Fusion Data

$T_{fus} = 1050 \pm 10$ K is the value selected by Stephens and Roth[1] based on their enthalpy study. Previous studies by thermal analysis[2-3] gave 1042 ± 2 K (IPTS–68) for high–purity strontium. The reason for the difference is not clear; although it probably arises from differences in sample purity or measurement method. The observed enthalpies[1] showed that melting of the sample was complete at 1059.1 K but only ~20 to 30% complete at 1048.8 K. This suggests either that the sample needed a much longer equilibration time at 1048.8 K or that it actually melted at least 7 degrees higher than 1042 K. The enthalpy at 1035.1 K showed a small premelting effect. A melting point of 1048 K (IPTS–68) was found by Kanda and coworkers[4-6] for three samples that, based on their transition behavior, probably contained over 3 mole % of hydrogen. Although hydrogen increases both T_{fus} and T_{trs}, the changes are greatest in the transition region.[2] The sample in the enthalpy study had normal transition behavior without the changes typical of hydrogen impurity. This sample was identical to that used in measurement of $C_p°$ and $S°$ at low temperature; analytical data[7] showed it to be of high purity. We choose to base all properties, including melting point, on the data for this same sample.

The enthalpy of fusion is derived from our fits of the enthalpy data[1] in the liquid and beta regions. Stephens and Roth[1] selected the value 1871 ± 55 cal·mol^{-1} based on a somewhat different fit in the β region.

Vaporization Data

T_{vap} is calculated as the temperature for which $\Delta_{vap}G° = 0$ for the liquid vaporizing to the ideal monatomic gas. T_{vap} corresponds to a fugacity of one bar. The enthalpy of vaporization is calculated from the enthalpy of formation of the liquid and the gas at T_{vap}. Vaporization studies are discussed in the ideal gas table.[8]

References

[1]H. J. Stephens and E. P. Roth, Sandia National Laboratories, Albuquerque, New Mexico, personal communication, (May 3, 1982).
[2]D. T. Peterson and R. P. Colburn, J. Phys. Chem. **70**, 468 (1966).
[3]A. S. Dworkin, H. R. Bronstein and M. A. Bredig, J. Phys. Chem. **72**, 1892 (1968).
[4]W. O. Roberts, Ph.D. Dissertation, Syracuse Univ., 1964; Diss. Abstr. **25**, 6218 (1965).
[5]F. E. Wang, F. A. Kanda and A. J. King, J. Phys. Chem. **66**, 2138 (1962).
[6]J. C. Schottmiller, A. J. King and F. A. Kanda, J. Phys. Chem. **62**, 1446 (1958).
[7]J. Boerio and E. F. Westrum, Jr., J. Chem. Thermodyn. **10**, 1 (1978).
[8]JANAF Thermochemical Tables: Sr(g), 9–30–83.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	39.463	50.901	50.901	0.	0.911	2.340	−0.410
300	39.463	51.145	50.902	0.073	0.934	2.348	−0.409
400	39.463	62.498	52.450	4.019	2.151	2.634	−0.344
500	39.463	71.304	55.373	7.966	3.270	2.623	−0.274
600	39.463	78.498	58.645	11.912	4.286	2.396	−0.209
700	39.463	84.582	61.927	15.858	5.199	2.008	−0.150
800	39.463	89.851	65.096	19.804	6.005	1.496	−0.098
900	39.463	94.499	68.110	23.751	6.077	0.961	−0.056
1000	39.463	98.657	70.960	27.697	6.990	0.343	−0.018
1050.000	39.463	100.582	72.325	29.670	---- BETA <--> LIQUID ----		
1100	39.463	102.418	73.652	31.643	0.	0.	0.
1200	39.463	105.852	76.194	35.589	0.	0.	0.
1300	39.463	109.010	78.598	39.536	0.	0.	0.
1400	39.463	111.935	80.877	43.482	0.	0.	0.
1500	39.463	114.658	83.039	47.428	0.	0.	0.
1600	39.463	117.204	85.095	51.374	0.	0.	0.
1685.492	39.463	119.259	86.777	54.748	----- FUGACITY = 1 bar -----		
1700	39.463	119.597	87.055	55.321	−136.914	1.180	−0.036
1800	39.463	121.853	88.926	59.267	−135.054	9.249	−0.268
1900	39.463	123.986	90.716	63.213	−133.199	17.215	−0.473
2000	39.463	126.010	92.431	67.159	−131.352	25.084	−0.655
2100	39.463	127.936	94.076	71.106	−129.518	32.861	−0.817
2200	39.463	129.771	95.657	75.052	−127.700	40.550	−0.963
2300	39.463	131.526	97.179	78.998	−125.904	48.158	−1.094
2400	39.463	133.205	98.645	82.944	−124.137	55.688	−1.212
2500	39.463	134.816	100.060	86.891	−122.406	63.145	−1.319
2600	39.463	136.364	101.427	90.837	−120.720	70.533	−1.417
2700	39.463	137.853	102.748	94.783	−119.086	77.858	−1.506
2800	39.463	139.288	104.028	98.729	−117.516	85.123	−1.588
2900	39.463	140.673	105.268	102.676	−116.019	92.334	−1.663
3000	39.463	142.011	106.470	106.622	−114.605	99.494	−1.732

PREVIOUS: December 1970 CURRENT: September 1983

0	to	820	K crystal, alpha
820	to	1050	K crystal, beta
above		1050	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.568	0.	0.	0.
100	23.481	28.050	78.738	−5.069	0.	0.	0.
200	25.757	45.209	58.112	−2.581	0.	0.	0.
298.15	26.791	55.694	55.694	0.	0.	0.	0.
300	26.809	55.859	55.694	0.050	0.	0.	0.
350	27.298	60.029	56.022	1.402	0.	0.	0.
400	27.777	63.704	56.757	2.779	0.	0.	0.
450	28.278	67.005	57.716	4.180	0.	0.	0.
500	28.785	70.010	58.797	5.607	0.	0.	0.
600	29.814	75.349	61.122	8.536	0.	0.	0.
700	30.864	80.023	63.495	11.570	0.	0.	0.
800	31.935	84.214	65.827	14.710	0.	0.	0.
820.000	32.151	85.005	66.285	15.351	ALPHA <--> BETA TRANSITION		
820.000	29.790	86.026	66.285	16.188			
900	30.125	88.814	68.165	18.584	0.	0.	0.
1000	30.543	92.010	70.393	21.618	0.	0.	0.
1050.000	30.752	93.505	71.458	23.150	BETA <--> LIQUID TRANSITION		
1050.000	39.463	100.582	71.458	30.581			
1100	39.463	102.418	72.824	32.554	0.	0.	0.
1200	39.463	105.852	75.435	36.500	0.	0.	0.
1300	39.463	109.010	77.898	40.446	0.	0.	0.
1400	39.463	111.935	80.226	44.393	0.	0.	0.
1500	39.463	114.658	82.432	48.339	0.	0.	0.
1600	39.463	117.204	84.526	52.285	0.	0.	0.
1685.492	39.463	119.259	86.236	55.659	----- FUGACITY = 1 bar -----		
1700	39.463	119.597	86.520	56.231	−136.914	1.180	−0.036
1800	39.463	121.853	88.421	60.178	−135.054	9.249	−0.268
1900	39.463	123.986	90.237	64.124	−133.199	17.215	−0.473
2000	39.463	126.010	91.975	68.070	−131.352	25.084	−0.655
2100	39.463	127.936	93.642	72.016	−129.518	32.861	−0.817
2200	39.463	129.771	95.243	75.963	−127.700	40.550	−0.963
2300	39.463	131.526	96.783	79.909	−125.904	48.158	−1.094
2400	39.463	133.205	98.266	83.855	−124.137	55.688	−1.212
2500	39.463	134.816	99.696	87.801	−122.406	63.145	−1.319
2600	39.463	136.364	101.076	91.748	−120.720	70.533	−1.417
2700	39.463	137.853	102.411	95.694	−119.086	77.858	−1.506
2800	39.463	139.288	103.703	99.640	−117.516	85.123	−1.588
2900	39.463	140.673	104.954	103.586	−116.019	92.334	−1.663
3000	39.463	142.011	106.167	107.533	−114.605	99.494	−1.732

PREVIOUS: CURRENT: September 1983

IP(Sr, g) = 45932.0 ± 0.2 cm^{-1}
$S°(298.15\ K)$ = 164.64 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 164.4 ± 1.7 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 164.0 ± 1.7 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5S_0$	0.00	1
$^3P_0$	14317.520	1
$^3P_1$	14504.351	3
$^3P_2$	14898.563	5
$^3D_1$	18159.056	3
$^3D_2$	18218.795	5
$^3D_3$	18319.267	7

Enthalpy of Formation

The enthalpy of formation is the enthalpy of sublimation, 164.0 ± 1.7 $kJ·mol^{-1}$. The adopted value is derived mainly from the boiling point study of Bohdansky and Schins.[1] It is confirmed by the early data of Hartmann and Schneider[2] and by the Knudsen effusion–mass-spectrometric study of Boerboom *et al.*[4] Data of Ruff and Hartmann[3] are readily dismissed due to the large entropy discrepancy.

A complete reanalysis of all the alkaline earth metals is in progress.

Source	Method	T/K	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	δS $cal·K^{-1}·mol^{-1}$
[1]	Boiling Point	1218–1982	40.1 ± 0.4	39.16 ± 0.46	0.6 ± 0.3
[2]	Boiling Point	1200–1380	40.0 ± 0.6	39.46 ± 0.14	0.4 ± 0.4
[3]	Boiling Point	1218–1412	77 ± 4	38.0 ± 5	29 ± 3
[4]	Effusion–Mass Spec.	772–923	36.4	39.04 ± 0.39	−3.1
[5]	Effusion	673–873	35.7 ± 0.5	38.65 ± 0.57	−3.8 ± 0.6

[a]Temperatures are adjusted to IPTS–68 by assuming published values to be IPTS–48.

Heat Capacity and Entropy

Observed energy levels and quantum weights are from Moore[6] as modified by Garton *et al.*[7,8] Energies of unobserved but predicted terms[6] are estimated by comparison of Ca I, Sr I, Ba I and their isolectronic ions. The most important energies are for terms of the 4d5s' configuration which are erstimated at 25000 ± 10000 cm^{-1}. We adopt an energy–level cutoff which is about kT_{max} (T_{max}–6000 K) below each series limit. For Sr I this corresponds to omitting levels above 8s, 7p, 6d and 5f. Levels above 30000 cm^{-1} are averaged. The adopted functions are essentially identical with earlier tables up to 3000 K; however, the entropies at 6000 K differ as follows: Hilsenrath *et al.*,[9] 57.49; Gurvich *et al.*,[10] 58.80 $cal·K^{-1}·mol^{-1}$. These differences arise from different methods of cutoff and different degrees of accounting for the unobserved terms.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	164.371	164.371	INFINITE
100	20.786	141.933	183.121	−4.119	164.950	153.562	−80.212
200	20.786	156.341	166.542	−2.040	164.540	142.314	−37.169
250	20.786	160.979	164.982	−1.001	164.277	136.782	−28.579
298.15	20.786	164.640	164.640	0.	164.000	131.518	−23.041
300	20.786	164.769	164.641	0.038	163.989	131.316	−22.864
350	20.786	167.973	164.894	1.078	163.675	125.895	−18.789
400	20.786	170.749	165.456	2.117	163.338	120.521	−15.738
450	20.786	173.197	166.183	3.156	162.976	115.190	−13.371
500	20.786	175.387	166.996	4.196	162.589	109.901	−11.481
600	20.786	179.177	168.719	6.274	161.738	99.441	−8.657
700	20.786	182.381	170.448	8.353	160.783	89.133	−6.651
800	20.786	185.156	172.117	10.431	159.722	78.968	−5.156
900	20.786	187.605	173.705	12.510	157.926	69.015	−4.006
1000	20.786	189.795	175.206	14.589	156.971	59.187	−3.092
1100	20.786	191.776	176.624	16.667	148.113	49.820	−2.366
1200	20.787	193.584	177.963	18.746	146.246	40.967	−1.783
1300	20.788	195.248	179.229	20.825	144.378	32.269	−1.297
1400	20.791	196.789	180.429	22.904	142.511	23.715	−0.885
1500	20.798	198.224	181.568	24.983	140.644	15.295	−0.533
1600	20.813	199.566	182.652	27.063	138.778	6.999	−0.229
1685.492	20.834	200.650	183.537	28.844	----- FUGACITY = 1 bar -----		
1700	20.839	200.829	183.684	29.146	0.	0.	0.
1800	20.882	202.021	184.670	31.232	0.	0.	0.
1900	20.949	203.152	185.613	33.323	0.	0.	0.
2000	21.049	204.229	186.517	35.423	0.	0.	0.
2100	21.191	205.259	187.385	37.534	0.	0.	0.
2200	21.383	206.249	188.220	39.663	0.	0.	0.
2300	21.636	207.205	189.025	41.813	0.	0.	0.
2400	21.959	208.132	189.802	43.992	0.	0.	0.
2500	22.361	209.036	190.553	46.207	0.	0.	0.
2600	22.849	209.923	191.281	48.467	0.	0.	0.
2700	23.430	210.796	191.988	50.780	0.	0.	0.
2800	24.109	211.660	192.675	53.157	0.	0.	0.
2900	24.889	212.519	193.345	55.606	0.	0.	0.
3000	25.770	213.377	193.998	58.138	0.	0.	0.
3100	26.753	214.238	194.637	60.763	0.	0.	0.
3200	27.834	215.104	195.263	63.492	0.	0.	0.
3300	29.008	215.978	195.878	66.333	0.	0.	0.
3400	30.270	216.863	196.482	69.296	0.	0.	0.
3500	31.611	217.759	197.077	72.389	0.	0.	0.
3600	33.022	218.670	197.664	75.620	0.	0.	0.
3700	34.493	219.594	198.244	78.996	0.	0.	0.
3800	36.011	220.534	198.818	82.520	0.	0.	0.
3900	37.565	221.490	199.387	86.199	0.	0.	0.
4000	39.142	222.461	199.952	90.034	0.	0.	0.
4100	40.730	223.447	200.513	94.028	0.	0.	0.
4200	42.304	224.446	201.071	98.176	0.	0.	0.
4300	43.874	225.460	201.626	102.485	0.	0.	0.
4400	45.418	226.486	202.180	106.950	0.	0.	0.
4500	46.927	227.524	202.731	111.568	0.	0.	0.
4600	48.214	228.556	203.280	116.269	0.	0.	0.
4700	49.584	229.608	203.829	121.159	0.	0.	0.
4800	50.884	230.665	204.377	126.182	0.	0.	0.
4900	52.114	231.727	204.925	131.333	0.	0.	0.
5000	53.254	232.791	205.471	136.597	0.	0.	0.
5100	54.274	233.851	206.017	141.953	0.	0.	0.
5200	55.250	234.914	206.563	147.429	0.	0.	0.
5300	56.141	235.975	207.108	153.000	0.	0.	0.
5400	56.945	237.032	207.652	158.655	0.	0.	0.
5500	57.662	238.084	208.196	164.386	0.	0.	0.
5600	58.296	239.129	208.739	170.184	0.	0.	0.
5700	58.846	240.166	209.281	176.042	0.	0.	0.
5800	59.317	241.193	209.822	181.951	0.	0.	0.
5900	59.417	242.171	210.359	187.693	0.	0.	0.
6000	59.709	243.172	210.897	193.650	0.	0.	0.

PREVIOUS: December 1970 (1 atm) CURRENT: September 1983 (1 bar)

IP(Sr^+, g) = 88964.0 ± 0.5 cm^{-1}
$S°$(298.15 K) = 170.403 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 713.840 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [719.666] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.00	2
$^2D_{3/2}$	14555.90	4
$^2D_{5/2}$	14836.24	6
$^2P_{1/2}$	23715.19	2
$^2P_{3/2}$	24516.65	4
$^2S_{1/2}$	47736.53	2

Enthalpy of Formation

$\Delta_f H°(Sr^+, g, 0 K)$ is calculated from $\Delta_f H°(Sr, g, 0 K)$[1] using the spectroscopic value of IP(Sr) = 45932.0 ± 0.2 cm^{-1} (549.469 ± 0.002 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Sr^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Sr, g, 0 K)$ by using IP(Sr) with JANAF[1] enthalpies, $H°(0 K)–H°(298.15 K)$, for Sr(g), $Sr^+(g)$, and e^-(ref). $\Delta_f H°(Sr \rightarrow Sr^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has as no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the levels listed above; the next excited state is approximately 53286 cm^{-1} above the ground state. Since inclusion of these higher excited states have little effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first four excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	713.840		
100	20.786	147.696	188.884	−4.119			
200	20.786	162.104	172.305	−2.040			
250	20.786	166.742	170.745	−1.001			
298.15	20.786	170.403	170.403	0.	719.666	679.211	−118.995
300	20.786	170.532	170.404	0.038	719.694	678.960	−118.217
350	20.786	173.736	170.657	1.078	720.419	672.113	−100.307
400	20.786	176.512	171.219	2.117	721.122	665.164	−86.861
450	20.786	178.960	171.946	3.156	721.799	658.128	−76.394
500	20.786	181.150	172.759	4.196	722.451	651.018	−68.011
600	20.786	184.940	174.483	6.274	723.678	636.615	−55.422
700	20.786	188.144	176.211	8.353	724.802	622.014	−46.415
800	20.786	190.919	177.880	10.431	725.819	607.259	−39.650
900	20.786	193.368	179.468	12.510	726.102	592.456	−34.385
1000	20.786	195.558	180.969	14.589	727.226	577.546	−30.168
1100	20.786	197.539	182.387	16.667	720.447	562.889	−26.729
1200	20.786	199.347	183.726	18.746	720.658	548.556	−23.878
1300	20.787	201.011	184.992	20.825	720.869	534.206	−21.465
1400	20.789	202.552	186.192	22.903	721.080	519.839	−19.395
1500	20.792	203.986	187.331	24.982	721.291	505.457	−17.602
1600	20.799	205.328	188.415	27.062	721.503	491.061	−16.032
1700	20.811	206.589	189.447	29.142	584.802	477.832	−14.682
1800	20.831	207.780	190.433	31.224	586.876	471.480	−13.682
1900	20.861	208.907	191.376	33.309	588.948	465.012	−12.784
2000	20.904	209.978	192.279	35.397	591.015	458.436	−11.973
2100	20.963	210.999	193.146	37.490	593.075	451.756	−11.237
2200	21.041	211.976	193.980	39.590	595.126	444.978	−10.565
2300	21.140	212.913	194.783	41.699	597.163	438.108	−9.950
2400	21.264	213.815	195.557	43.819	599.182	431.149	−9.384
2500	21.414	214.686	196.305	45.953	601.179	424.107	−8.861
2600	21.590	215.530	197.029	48.103	603.148	416.985	−8.377
2700	21.795	216.348	197.729	50.272	605.082	409.788	−7.928
2800	22.028	217.145	198.408	52.463	606.976	402.520	−7.509
2900	22.290	217.922	199.068	54.678	608.821	395.185	−7.118
3000	22.580	218.683	199.709	56.922	610.611	387.788	−6.752
3100	22.897	219.428	200.333	59.195	612.338	380.332	−6.409
3200	23.239	220.161	200.941	61.502	613.994	372.821	−6.086
3300	23.605	220.881	201.535	63.844	615.574	365.260	−5.782
3400	23.993	221.592	202.114	66.223	617.069	357.652	−5.495
3500	24.400	222.293	202.681	68.643	618.474	350.001	−5.223
3600	24.824	222.986	203.235	71.104	619.782	342.312	−4.967
3700	25.263	223.672	203.778	73.608	620.990	334.587	−4.724
3800	25.714	224.352	204.311	76.157	622.093	326.832	−4.493
3900	26.174	225.026	204.833	78.751	623.087	319.048	−4.273
4000	26.640	225.694	205.346	81.392	623.971	311.241	−4.064
4100	27.110	226.358	205.851	84.079	624.744	303.413	−3.866
4200	27.581	227.017	206.347	86.814	625.408	295.567	−3.676
4300	28.051	227.672	206.835	89.596	625.959	287.707	−3.495
4400	28.517	228.322	207.316	92.424	626.401	279.835	−3.322
4500	28.976	228.968	207.790	95.299	626.737	271.955	−3.157
4600	29.428	229.610	208.258	98.219	627.035	264.063	−2.999
4700	29.869	230.247	208.719	101.184	627.188	256.171	−2.847
4800	30.299	230.881	209.174	104.193	627.252	248.276	−2.702
4900	30.715	231.510	209.623	107.243	627.231	240.380	−2.562
5000	31.115	232.134	210.067	110.335	627.137	232.486	−2.429
5100	31.500	232.754	210.506	113.466	626.991	224.592	−2.300
5200	31.868	233.369	210.940	116.634	626.761	216.704	−2.177
5300	32.217	233.980	211.369	119.839	626.474	208.821	−2.058
5400	32.548	234.585	211.793	123.077	626.136	200.944	−1.944
5500	32.859	235.185	212.213	126.348	625.754	193.074	−1.834
5600	33.151	235.780	212.628	129.648	625.335	185.210	−1.728
5700	33.423	236.369	213.040	132.977	624.884	177.355	−1.625
5800	33.675	236.953	213.447	136.332	624.409	169.508	−1.527
5900	33.908	237.530	213.850	139.712	624.125	161.645	−1.431
6000	34.121	238.102	214.250	143.113	623.649	153.810	−1.339

PREVIOUS: CURRENT: September 1983 (1 bar)

REFERENCE STATE

0	to 3258	K	crystal
3258	to 5778.070	K	liquid
above	5778.070	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.681	0.	0.	0.
100	19.744	16.143	63.003	−4.686	0.	0.	0.
200	24.085	31.586	43.756	−2.434	0.	0.	0.
250	24.861	37.049	41.886	−1.209	0.	0.	0.
298.15	25.295	41.471	41.471	0.	0.	0.	0.
300	25.307	41.628	41.472	0.047	0.	0.	0.
350	25.598	45.552	41.781	1.320	0.	0.	0.
400	25.840	48.986	42.471	2.606	0.	0.	0.
450	26.088	52.044	43.368	3.904	0.	0.	0.
500	26.349	54.806	44.376	5.215	0.	0.	0.
600	26.843	59.655	46.530	7.875	0.	0.	0.
700	27.214	63.822	48.709	10.579	0.	0.	0.
800	27.459	67.473	50.831	13.313	0.	0.	0.
900	27.668	70.718	52.864	16.069	0.	0.	0.
1000	27.933	73.647	54.798	18.848	0.	0.	0.
1100	28.281	76.325	56.635	21.659	0.	0.	0.
1200	28.662	78.802	58.380	24.507	0.	0.	0.
1300	28.989	81.110	60.041	27.390	0.	0.	0.
1400	29.202	83.267	61.624	30.301	0.	0.	0.
1500	29.319	85.286	63.135	33.227	0.	0.	0.
1600	29.439	87.182	64.579	36.164	0.	0.	0.
1700	29.688	88.973	65.962	39.119	0.	0.	0.
1800	30.124	90.682	67.288	42.108	0.	0.	0.
1900	30.665	92.325	68.563	45.148	0.	0.	0.
2000	31.191	93.911	69.791	48.240	0.	0.	0.
2100	31.713	95.445	70.976	51.386	0.	0.	0.
2200	32.252	96.933	72.122	54.584	0.	0.	0.
2300	32.828	98.379	73.233	57.837	0.	0.	0.
2400	33.459	99.789	74.310	61.151	0.	0.	0.
2500	34.167	101.169	75.357	64.532	0.	0.	0.
2600	34.970	102.525	76.376	67.988	0.	0.	0.
2700	35.890	103.861	77.369	71.530	0.	0.	0.
2800	36.946	105.185	78.339	75.170	0.	0.	0.
2900	38.158	106.502	79.287	78.924	0.	0.	0.
3000	39.546	107.819	80.216	82.808	0.	0.	0.
3100	41.130	109.141	81.128	86.840	0.	0.	0.
3200	42.930	110.474	82.024	91.041	0.	0.	0.
3258.000	44.080	111.256	82.538	93.564	____ CRYSTAL <--> LIQUID ____		
3258.000	41.840	122.480	82.538	130.132	TRANSITION		
3300	41.840	123.016	83.049	131.889	0.	0.	0.
3400	41.840	124.265	84.243	136.073	0.	0.	0.
3500	41.840	125.478	85.404	140.257	0.	0.	0.
3600	41.840	126.656	86.534	144.441	0.	0.	0.
3700	41.840	127.803	87.634	148.625	0.	0.	0.
3800	41.840	128.919	88.706	152.809	0.	0.	0.
3900	41.840	130.005	89.751	156.993	0.	0.	0.
4000	41.840	131.065	90.770	161.177	0.	0.	0.
4100	41.840	132.098	91.766	165.361	0.	0.	0.
4200	41.840	133.106	92.738	169.545	0.	0.	0.
4300	41.840	134.091	93.688	173.729	0.	0.	0.
4400	41.840	135.052	94.618	177.913	0.	0.	0.
4500	41.840	135.993	95.527	182.097	0.	0.	0.
4600	41.840	136.912	96.416	186.281	0.	0.	0.
4700	41.840	137.812	97.288	190.465	0.	0.	0.
4800	41.840	138.693	98.141	194.649	0.	0.	0.
4900	41.840	139.556	98.978	198.833	0.	0.	0.
5000	41.840	140.401	99.798	203.017	0.	0.	0.
5200	41.840	142.042	101.391	211.385	0.	0.	0.
5400	41.840	143.621	102.926	219.753	0.	0.	0.
5600	41.840	145.143	104.407	228.121	0.	0.	0.
5778.070	41.840	146.452	105.682	235.572	____ LIQUID <--> IDEAL GAS ____		
5778.070	43.671	274.300	105.682	974.285	FUGACITY = 1 bar		
5800	43.762	274.465	106.320	975.244	0.	0.	0.
6000	44.636	275.963	111.950	984.082	0.	0.	0.

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

$S°(298.15\ K) = 41.47 \pm 0.21\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3258 \pm 10\ K$

$\Delta_f H°(0\ K) = 0\ kJ·mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ·mol^{-1}$
$\Delta_{fus} H° = 36.57 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for $T \leq 10$ K are chosen to be the same as those adopted by Hultgren *et al.*[1] A graphical integration of these $C_p°$ data yields $S°(10\ K) = 0.025\ cal·K^{-1}mol^{-1}$. The adopted $C_p°$ values for the range $10 \leq T \leq T_{fus}$ are based on the following experimental data.

Source	T/K	Method
[2]	53– 295	$C_p°$
[3]	10– 273	$C_p°$
[4]	12– 550	$C_p°$
[5]	300–1554	drop, enthalpy
[6]	533–1383	drop, enthalpy
[7]	1900–3200	$C_p°$, pulse heating

The data of Cezairliyan,[7] reported as smoothed $C_p°$ values and represented by a third–order polynomial, yields $C_p°$ values from 3200 K to T_{fus} by extrapolation. These smooth $C_p°$ values, as reported by Cezirliyan,[7] are adopted for the range 1900–3200 K. Using a polynomial fit for each enthalpy data set,[5, 6] $C_p°$ values are obtained which define the region 298–1500 K. A polynomial, constrained at 10 K, is used to produce smoothed $C_p°$ values in the range 10–298 K based on the three low temperature studies.[3–5]

For $T < 100$ K, the tabulated values do not agree well with the experimental data. In this region the deviations from the tabulated values are ± 5% for Clusius and Losa,[3] −0.3 to +1.9% for Kelley,[2] and −1.7 to 2.8% for Sterrett and Wallace.[4] The deviations are due in part to experimental scatter[3] and a poor match of experimental data at 10 K.

Many other experimental studies have been referenced by Gmelin[8] and Hultgren *et al.*[1] In addition, Cezairliyan[7] has compared graphically many of the investigations. The $C_p°$ data and enthalpy data are all in generally good agreement. The importance of the recent Cezairliyan study[7] is that it gives added evidence to the deviation from a linear C_p–T relationship above 1000 K.

Fusion Data

The melting point of Ta is chosen as 3258 ± 10 K based on the subsecond pulse heating technique of Cezairliyan.[7] This choice is made so as to have a T_{fus} consistent with $C_p°$ data at temperatures near T_{fus} (see heat capacity discussion). Other T_{fus} values covering the range 3053–3273 K are referenced by Charlesworth;[9] while additional references are found in Gmelin.[8] Hultgren *et al.*[1] recommends a T_{fus} value of 3287 K.

The enthalpy of fusion, $\Delta_{fus}H°$, for Ta has been measured by Lebedev *et al.*[10] They reported a $\Delta_{fus}H°$ value of 8.74 ± 0.5 kcal·mol^{-1} based on measurements made during electrical explosion in thin wires. We adopt this value for $\Delta_{fus}H°$. Based on $\Delta_{fus}H° = 8.74\ kcal·mol^{-1}$ and $T_{fus} = 3258$ K, the entropy of melting, $\Delta_{fus}S°$, is calculated to be $2.68\ cal·K^{-1}·mol^{-1}$. This compares with $\Delta_{fus}S° = 2.33\ cal·K^{-1}·mol^{-1}$ for Nb, as reported in these tables.

References

[1] R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Ta table, (August 1971).
[2] K. K. Kelley, J. Chem. Phys. **8**, 316 (1940).
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[9] J. H. Charlesworth, Melting Points of Metallic Elements and Selected Compounds, AFML–TR–70–137, (October 1970).
[10] S. V. Lebedev, A. I. Savvatimskii, and Yu. B. Smirnov, High Temperature USSR **9**, 635 (1971).

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−5.681	0.	0.	
100	19.744	16.143	63.003	−4.686	0.	0.	0.
200	24.085	31.586	43.756	−2.434	0.	0.	0.
250	24.861	37.049	41.886	−1.209	0.	0.	0.
298.15	25.295	41.471	41.471	0.	0.	0.	0.
300	25.307	41.628	41.472	0.047	0.	0.	0.
350	25.598	45.552	41.781	1.320	0.	0.	0.
400	25.840	48.986	42.471	2.606	0.	0.	0.
450	26.088	52.044	43.368	3.904	0.	0.	0.
500	26.349	54.806	44.376	5.215	0.	0.	0.
600	26.843	59.655	46.530	7.875	0.	0.	0.
700	27.214	63.822	48.709	10.579	0.	0.	0.
800	27.459	67.473	50.831	13.313	0.	0.	0.
900	27.668	70.718	52.864	16.069	0.	0.	0.
1000	27.933	73.647	54.798	18.848	0.	0.	0.
1100	28.281	76.325	56.635	21.659	0.	0.	0.
1200	28.662	78.802	58.380	24.507	0.	0.	0.
1300	28.989	81.110	60.041	27.390	0.	0.	0.
1400	29.202	83.267	61.624	30.301	0.	0.	0.
1500	29.319	85.286	63.135	33.227	0.	0.	0.
1600	29.439	87.182	64.579	36.164	0.	0.	0.
1700	29.688	88.973	65.962	39.119	0.	0.	0.
1800	30.124	90.682	67.288	42.108	0.	0.	0.
1900	30.665	92.325	68.563	45.148	0.	0.	0.
2000	31.191	93.911	69.791	48.240	0.	0.	0.
2100	31.713	95.445	70.976	51.386	0.	0.	0.
2200	32.252	96.933	72.122	54.584	0.	0.	0.
2300	32.828	98.379	73.233	57.837	0.	0.	0.
2400	33.459	99.789	74.310	61.151	0.	0.	0.
2500	34.167	101.169	75.357	64.532	0.	0.	0.
2600	34.970	102.525	76.376	67.988	0.	0.	0.
2700	35.890	103.861	77.369	71.530	0.	0.	0.
2800	36.946	105.185	78.339	75.170	0.	0.	0.
2900	38.158	106.502	79.287	78.924	0.	0.	0.
3000	39.546	107.819	80.216	82.808	0.	0.	0.
3100	41.130	109.141	81.128	86.840	0.	0.	0.
3200	42.930	110.474	82.024	91.041	0.	0.	0.
3258.000	44.080	111.256	82.538	93.564	--- CRYSTAL <---> LIQUID ---		
3300	44.965	111.826	82.907	95.433	−36.456	0.471	−0.007
3400	47.256	113.202	83.778	100.042	−36.031	1.584	−0.024
3500	49.823	114.608	84.638	104.894	−35.363	2.681	−0.040
3600	52.685	116.051	85.491	110.017	−34.424	3.756	−0.054
3700	55.864	117.537	86.337	115.441	−33.184	4.800	−0.068
3800	59.377	119.073	87.178	121.201	−31.609	5.806	−0.080

PREVIOUS: CURRENT: December 1972

$S°(298.15\ K) = [50.366]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 3258 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [30.795]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 36.57 \pm 4.2\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Ta(l) at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(3258\ K)–H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity for Ta(l) is estimated as 10.0 $cal·K^{-1}·mol^{-1}$ by analogy with other monatomic metals. The same value was adopted by Hultgren *et al.*[1] and Stull and Sinke.[2] A glass transition is assumed at 2150 K. Below this temperature, the heat capacity values used are those of Ta(cr). The entropy at 298.15 K is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

T_{vap} is the temperature at which the Gibbs energy change for the reaction Ta(l) → Ta(g) is zero. The difference between $\Delta_f H°$(Ta, g) and $\Delta_f H°$(Ta, l) at T_{vap} is $\Delta_{vap}H°$. The uncertainty in the boiling point is probably of the order of ±200 K.

References

[1]R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Ta table, (August 1971).
[2]D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., (1956).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	25.295	50.366	50.366	0.	30.795	28.143	−4.931
300	25.307	50.522	50.366	0.047	30.795	28.127	−4.897
350	25.598	54.447	50.676	1.320	30.795	27.682	−4.131
400	25.840	57.881	51.366	2.606	30.795	27.237	−3.557
450	26.088	60.938	52.263	3.904	30.795	26.793	−3.110
500	26.349	63.701	53.271	5.215	30.795	26.348	−2.753
600	26.843	68.550	55.424	7.875	30.795	25.458	−2.216
700	27.214	72.717	57.604	10.579	30.795	24.569	−1.833
800	27.459	76.367	59.726	13.313	30.795	23.680	−1.546
900	27.668	79.613	61.758	16.069	30.795	22.790	−1.323
1000	27.933	82.541	63.693	18.848	30.795	21.901	−1.144
1100	28.281	85.220	65.530	21.659	30.795	21.011	−0.998
1200	28.662	87.697	67.275	24.507	30.795	20.122	−0.876
1300	28.989	90.005	68.936	27.390	30.795	19.232	−0.773
1400	29.202	92.162	70.518	30.301	30.795	18.343	−0.684
1500	29.319	94.181	72.029	33.227	30.795	17.453	−0.608
1600	29.439	96.076	73.474	36.164	30.795	16.564	−0.541
1700	29.688	97.868	74.856	39.119	30.795	15.674	−0.482
1800	30.124	99.576	76.183	42.108	30.795	14.785	−0.429
1900	30.665	101.219	77.457	45.148	30.795	13.896	−0.382
2000	31.191	102.806	78.685	48.240	30.795	13.006	−0.340
2100	31.713	104.340	79.871	51.386	30.795	12.117	−0.301
2150.000	31.980	105.089	80.448	52.978	GLASS <--> LIQUID TRANSITION		
2150.000	41.840	105.089	80.448	52.978			
2200	41.840	106.051	81.019	55.070	31.281	11.222	−0.266
2300	41.840	107.911	82.148	59.254	32.212	10.289	−0.234
2400	41.840	109.692	83.259	63.438	33.082	9.317	−0.203
2500	41.840	111.400	84.351	67.622	33.885	8.310	−0.174
2600	41.840	113.041	85.423	71.806	34.613	7.272	−0.146
2700	41.840	114.620	86.475	75.990	35.256	6.208	−0.120
2800	41.840	116.141	87.508	80.174	35.799	5.122	−0.096
2900	41.840	117.610	88.521	84.358	36.229	4.018	−0.072
3000	41.840	119.028	89.514	88.542	36.529	2.902	−0.051
3100	41.840	120.400	90.488	92.726	36.681	1.778	−0.030
3200	41.840	121.728	91.444	96.910	36.664	0.652	−0.011
3258.000	41.840	122.480	91.990	99.337	CRYSTAL <--> LIQUID		
3300	41.840	123.016	92.381	101.094	0.	0.	0.
3400	41.840	124.265	93.301	105.278	0.	0.	0.
3500	41.840	125.478	94.203	109.462	0.	0.	0.
3600	41.840	126.656	95.088	113.646	0.	0.	0.
3700	41.840	127.803	95.957	117.830	0.	0.	0.
3800	41.840	128.919	96.810	122.014	0.	0.	0.
3900	41.840	130.005	97.647	126.198	0.	0.	0.
4000	41.840	131.065	98.469	130.382	0.	0.	0.
4100	41.840	132.098	99.277	134.566	0.	0.	0.
4200	41.840	133.106	100.070	138.750	0.	0.	0.
4300	41.840	134.091	100.850	142.934	0.	0.	0.
4400	41.840	135.052	101.617	147.118	0.	0.	0.
4500	41.840	135.993	102.370	151.302	0.	0.	0.
4600	41.840	136.912	103.111	155.486	0.	0.	0.
4700	41.840	137.812	103.840	159.670	0.	0.	0.
4800	41.840	138.693	104.557	163.854	0.	0.	0.
4900	41.840	139.556	105.262	168.038	0.	0.	0.
5000	41.840	140.401	105.957	172.222	0.	0.	0.
5200	41.840	142.042	107.313	180.590	0.	0.	0.
5400	41.840	143.621	108.629	188.958	0.	0.	0.
5600	41.840	145.143	109.906	197.326	0.	0.	0.
5778.070	41.840	146.452	111.012	204.776	FUGACITY = 1 bar		
5800	41.840	146.611	111.146	205.694	−738.755	2.801	−0.025
6000	41.840	148.029	112.352	214.062	−739.225	28.380	−0.247

PREVIOUS: CURRENT: December 1972

0	to	3258	K crystal
above		3258	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−5.681	0.	0.	0.
100	19.744	16.143	63.003	−4.686	0.	0.	0.
200	24.085	31.586	43.756	−2.434	0.	0.	0.
250	24.861	37.049	41.886	−1.209	0.	0.	0.
298.15	25.295	41.471	41.471	0.	0.	0.	0.
300	25.307	41.628	41.472	0.047	0.	0.	0.
350	25.598	45.552	41.781	1.320	0.	0.	0.
400	25.840	48.986	42.471	2.606	0.	0.	0.
450	26.088	52.044	43.368	3.904	0.	0.	0.
500	26.349	54.806	44.376	5.215	0.	0.	0.
600	26.843	59.655	46.530	7.875	0.	0.	0.
700	27.214	63.822	48.709	10.579	0.	0.	0.
800	27.459	67.473	50.831	13.313	0.	0.	0.
900	27.668	70.718	52.864	16.069	0.	0.	0.
1000	27.933	73.647	54.798	18.848	0.	0.	0.
1100	28.281	76.325	56.635	21.659	0.	0.	0.
1200	28.662	78.802	58.380	24.507	0.	0.	0.
1300	28.989	81.110	60.041	27.390	0.	0.	0.
1400	29.202	83.267	61.624	30.301	0.	0.	0.
1500	29.319	85.286	63.135	33.227	0.	0.	0.
1600	29.439	87.182	64.579	36.164	0.	0.	0.
1700	29.688	88.973	65.962	39.119	0.	0.	0.
1800	30.124	90.682	67.288	42.108	0.	0.	0.
1900	30.665	92.325	68.563	45.148	0.	0.	0.
2000	31.191	93.911	69.791	48.240	0.	0.	0.
2100	31.713	95.445	70.976	51.386	0.	0.	0.
2200	32.252	96.933	72.122	54.584	0.	0.	0.
2300	32.828	98.379	73.233	57.837	0.	0.	0.
2400	33.459	99.789	74.310	61.151	0.	0.	0.
2500	34.167	101.169	75.357	64.532	0.	0.	0.
2600	34.970	102.525	76.376	67.988	0.	0.	0.
2700	35.890	103.861	77.369	71.530	0.	0.	0.
2800	36.946	105.185	78.339	75.170	0.	0.	0.
2900	38.158	106.502	79.287	78.924	0.	0.	0.
3000	39.546	107.819	80.216	82.808	0.	0.	0.
3100	41.130	109.141	81.128	86.840	0.	0.	0.
3200	42.930	110.474	82.024	91.041	0.	0.	0.
3258.000	44.080	111.256	82.538	93.564	____ CRYSTAL <-- --> LIQUID ____		
3258.000	41.840	122.480	82.538	130.132	TRANSITION		
3300	41.840	123.016	83.049	131.889	0.	0.	0.
3400	41.840	124.265	84.243	136.073	0.	0.	0.
3500	41.840	125.478	85.404	140.257	0.	0.	0.
3600	41.840	126.656	86.534	144.441	0.	0.	0.
3700	41.840	127.803	87.634	148.625	0.	0.	0.
3800	41.840	128.919	88.706	152.809	0.	0.	0.
3900	41.840	130.005	89.751	156.993	0.	0.	0.
4000	41.840	131.065	90.770	161.177	0.	0.	0.
4100	41.840	132.098	91.766	165.361	0.	0.	0.
4200	41.840	133.106	92.738	169.545	0.	0.	0.
4300	41.840	134.091	93.688	173.729	0.	0.	0.
4400	41.840	135.052	94.618	177.913	0.	0.	0.
4500	41.840	135.993	95.527	182.097	0.	0.	0.
4600	41.840	136.912	96.416	186.281	0.	0.	0.
4700	41.840	137.812	97.288	190.465	0.	0.	0.
4800	41.840	138.693	98.141	194.649	0.	0.	0.
4900	41.840	139.556	98.978	198.833	0.	0.	0.
5000	41.840	140.401	99.798	203.017	0.	0.	0.
5200	41.840	142.042	101.391	211.385	0.	0.	0.
5400	41.840	143.621	102.926	219.753	0.	0.	0.
5600	41.840	145.143	104.407	228.121	0.	0.	0.
5778.070	41.840	146.452	105.682	235.572	----- FUGACITY = 1 bar -----		
5800	41.840	146.611	105.837	236.489	−738.755	2.801	−0.025
6000	41.840	148.029	107.220	244.857	−739.225	28.380	−0.247

PREVIOUS: CURRENT: December 1972

IP(Br, g) = 63600 ± 100 cm^{-1}
$S°(298.15\ K)$ = 185.22 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 781.47 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 781.99 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{3/2}$	0.00	4
$^4F_{5/2}$	2010.10	6
$^4F_{7/2}$	3963.92	8
$^4F_{9/2}$	5621.04	10

Enthalpy of Formation

The enthalpy of sublimation of tantalum has been derived from 2nd and 3rd law analysis of the vapor pressure data of several investigators. These four studies are based on the Langmuir method.

Source	T/K	Data Points	$\Delta_{sub}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
[1]	2628–2952	7	190.0 ± 3.0	186.9	−1.1 ± 1.1
[2]	2004–3269	16*	183.0	186.9	1.5
[3]	2637–2854	7	151.9 ± 10.1	182.6	11.2 ± 3.7
[4]	2904–3155	8**	233.1	190.3	−14.2

*Only smooth data was reported; however, 16 refers to the number of experimental determinations.
**Only smooth data reported.

Babeliowsky[5] reported an enthalpy of sublimation value of 168.4 ± 4.0 $kcal·mol^{-1}$. This value is based on mass spectrometric vaporization studies and is calculated by the 2nd law method. Sasaki *et al.*,[6] also using a mass spectrometer, reported an enthalpy of sublimation value of 185.4 ± 0.3 $kcal·mol^{-1}$ as an average value in the range 2550–2770 K. The value chosen for the enthalpy of sublimation which, in this case, is the enthalpy of formation of Ta(g) is 186.9 ± 0.5 $kcal·mol^{-1}$, based on the work of Edwards *et al.*[1] and Langmuir and Malter.[2]

Heat Capacity and Entropy

The electronic levels and quantum weights are obtained from Moore.[7] Although not all levels are listed, all levels given by Moore are used in the calculation. There are predicted electronic levels which have not been observed.[7] These levels are assumed to lie above 20000 cm^{-1} and thus will not significantly affect the entropy at temperatures below 3000 K. The heat capacity and entropy values are very similar to those adopted by Hultgren *et al.*,[8] being identical at 298.15 K and differing by 0.154 $cal·K^{-1}·mol^{-1}$ in $C_p°$ at 6000 K.

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[7] C. E. Moore, U. S. Natl. Bur. Std. NSRDS–NBS–35, Volume III, (1970) [Reprint of NBS Circular 467, Vol III, 1958].
[8] R. Hultgren, R. L. Orr, and K. K. Kelley, Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Ta table, (August 1971).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.200	781.471	781.471	INFINITE
100	20.786	162.504	203.713	−4.121	782.555	767.919	−401.120
200	20.787	176.912	187.123	−2.042	782.381	753.316	−196.746
250	20.802	181.551	185.562	−1.003	782.196	746.071	−155.883
298.15	20.858	185.219	185.219	0.	781.990	739.131	−129.493
300	20.861	185.348	185.219	0.039	781.981	738.865	−128.648
350	21.006	188.573	185.474	1.085	781.754	731.697	−109.200
400	21.259	191.394	186.041	2.141	781.525	724.562	−94.618
450	21.624	193.918	186.778	3.213	781.298	717.455	−83.280
500	22.082	196.219	187.609	4.305	781.080	710.373	−74.212
600	23.183	200.340	189.395	6.567	780.681	696.270	−60.616
700	24.381	204.003	191.225	8.945	780.355	682.229	−50.909
800	25.562	207.336	193.033	11.442	780.119	668.228	−43.631
900	26.676	210.412	194.796	14.055	779.975	654.251	−37.972
1000	27.701	213.276	196.502	16.774	779.916	640.286	−33.445
1100	28.633	215.961	198.150	19.592	779.923	626.323	−29.742
1200	29.470	218.489	199.741	22.498	779.981	612.357	−26.655
1300	30.212	220.878	201.276	25.483	780.082	598.385	−24.043
1400	30.865	223.141	202.757	28.537	780.226	584.403	−21.804
1500	31.437	225.291	204.189	31.653	780.416	570.409	−19.863
1600	31.937	227.336	205.572	34.822	780.648	556.401	−18.165
1700	32.377	229.286	206.910	38.039	780.909	542.378	−16.665
1800	32.768	231.147	208.205	41.296	781.177	528.339	−15.332
1900	33.119	232.929	209.460	44.591	781.433	514.285	−14.139
2000	33.441	234.636	210.676	47.919	781.668	500.219	−13.064
2100	33.739	236.275	211.856	51.278	781.882	486.141	−12.092
2200	34.021	237.851	213.002	54.666	782.072	472.053	−11.208
2300	34.289	239.369	214.116	58.082	782.234	457.958	−10.401
2400	34.548	240.834	215.199	61.524	782.362	443.856	−9.660
2500	34.799	242.249	216.253	64.991	782.449	429.750	−8.979
2600	35.045	243.619	217.279	68.484	782.486	415.641	−8.350
2700	35.287	244.946	218.279	72.000	782.460	401.532	−7.768
2800	35.525	246.234	219.255	75.541	782.360	387.425	−7.227
2900	35.761	247.484	220.207	79.105	782.171	373.323	−6.724
3000	35.994	248.701	221.136	82.693	781.875	359.229	−6.255
3100	36.226	249.885	222.045	86.304	781.454	345.148	−5.816
3200	36.457	251.039	222.933	89.938	780.887	331.082	−5.404
3300	36.688	252.164	223.802	93.595	743.696	317.507	−5.026
3400	36.918	253.263	224.652	97.276	743.192	304.600	−4.680
3500	37.149	254.336	225.485	100.979	742.712	291.707	−4.353
3600	37.381	255.386	226.301	104.706	742.254	278.828	−4.046
3700	37.614	256.413	227.101	108.455	741.820	265.961	−3.755
3800	37.849	257.419	227.886	112.228	741.409	253.106	−3.479
3900	38.085	258.406	228.656	116.025	741.022	240.261	−3.218
4000	38.324	259.373	229.412	119.846	740.658	227.425	−2.970
4100	38.565	260.322	230.154	123.690	740.319	214.599	−2.734
4200	38.810	261.254	230.883	127.559	740.003	201.780	−2.510
4300	39.057	262.171	231.600	131.452	739.713	188.969	−2.296
4400	39.309	263.071	232.305	135.370	739.447	176.164	−2.091
4500	39.566	263.958	232.999	139.314	739.207	163.365	−1.896
4600	39.827	264.830	233.681	143.284	738.992	150.571	−1.710
4700	40.096	265.689	234.353	147.280	738.804	137.781	−1.531
4800	40.371	266.536	235.015	151.303	738.644	124.995	−1.360
4900	40.655	267.372	235.667	155.354	738.511	112.212	−1.196
5000	40.948	268.196	236.309	159.434	738.407	99.432	−1.039
5100	41.251	269.010	236.942	163.544	738.333	86.653	−0.888
5200	41.566	269.814	237.567	167.685	738.289	73.875	−0.742
5300	41.893	270.609	238.183	171.858	738.278	61.098	−0.602
5400	42.235	271.395	238.791	176.064	738.300	48.321	−0.467
5500	42.592	272.173	239.390	180.305	738.358	35.543	−0.338
5600	42.964	272.944	239.983	184.583	738.451	22.764	−0.212
5700	43.354	273.708	240.568	188.899	738.583	9.983	−0.091
5778.070	43.671	274.300	241.020	192.296	----- FUGACITY = 1 bar -----		
5800	43.762	274.465	241.146	193.254	0.	0.	0.
5900	44.189	275.217	241.717	197.652	0.	0.	0.
6000	44.636	275.963	242.281	202.093	0.	0.	0.

PREVIOUS: December 1972 (1 atm) CURRENT: December 1972 (1 bar)

IP(Ta^+, g) = [130660 ± 4000] cm^{-1}
$S°$(298.15 K) = 183.38 ± 0.2 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1542.3 ± 2 kJ mol^{-1}
$\Delta_f H°$(298.15 K) = [1549.150] kJ mol^{-1}

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5F_1$	0.00	3
$^5F_2$	1031.33	5
$^5F_3$	2642.19	7
$^5F_4$	4415.70	9
$^5F_5$	6186.72	11

Enthalpy of Formation

$\Delta_f H°(Ta^+, g, 0 K)$ is calculated from $\Delta_f H°(Ta, g, 0 K)$[1] using the spectroscopic value of IP(Ta) = 63600 ± 100 cm^{-1} (760.825 ± 1.20 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ta^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Ta, g, 0 K)$ by using IP(Ta) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Ta(g), Ta^+(g), and e^-(ref). $\Delta_r H°(Ta \rightarrow Ta^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have only a few of the atomic energy levels for Ta^+(g), all levels listed by Moore[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for Ta^+(g), the thermodynamic functions are independent of the estimated missing levels (for n=6), and the cut–off procedure up to 6000 K; the Gibbs energy function showing no significant variations at this temperature. The reported uncertainty is $S°$(298.15 K) is due to uncertainties in the relative ionic mass, and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>6), and use of different fill and cut–off procedures.[6]

References

[1]JANAF Thermochemical Tables: Ta(g), 12–31–72; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.338	1542.296		
100	20.787	160.112	202.703	−4.259			
200	21.242	174.589	185.431	−2.168			
250	22.067	179.411	183.759	−1.087			
298.15	23.109	183.385	183.385	0.	1549.150	1500.584	−262.896
300	23.151	183.528	183.385	0.043	1549.185	1500.283	−261.222
350	24.256	187.181	183.671	1.228	1550.136	1492.057	−222.677
400	25.237	190.485	184.320	2.466	1551.128	1483.693	−193.750
450	26.048	193.506	185.175	3.749	1552.152	1475.203	−171.237
500	26.708	196.286	186.149	5.069	1553.200	1466.597	−153.214
600	27.734	201.251	188.262	7.793	1555.342	1449.076	−126.153
700	28.581	205.591	190.434	10.610	1557.534	1431.192	−106.797
800	29.369	209.459	192.575	13.507	1559.776	1412.991	−92.259
900	30.120	212.962	194.648	16.482	1562.074	1394.506	−80.935
1000	30.818	216.172	196.642	19.530	1564.420	1375.762	−71.862
1100	31.441	219.139	198.554	22.643	1566.802	1356.781	−64.428
1200	31.971	221.899	200.386	25.815	1569.205	1337.582	−58.223
1300	32.399	224.475	202.141	29.034	1571.619	1318.182	−52.965
1400	32.725	226.889	203.824	32.291	1574.044	1298.596	−48.451
1500	32.956	229.155	205.438	35.576	1576.481	1278.836	−44.533
1600	33.103	231.287	206.987	38.880	1578.926	1258.914	−41.099
1700	33.181	233.297	208.476	42.194	1581.365	1238.838	−38.065
1800	33.204	235.194	209.908	45.514	1583.774	1218.620	−35.363
1900	33.188	236.989	211.287	48.834	1586.133	1198.269	−32.943
2000	33.145	238.690	212.615	52.151	1588.435	1177.795	−30.761
2100	33.085	240.306	213.895	55.462	1590.680	1157.208	−28.784
2200	33.017	241.844	215.131	58.767	1592.866	1136.515	−26.984
2300	32.947	243.310	216.325	62.066	1594.989	1115.724	−25.339
2400	32.881	244.710	217.478	65.357	1597.045	1094.842	−23.829
2500	32.821	246.051	218.595	68.642	1599.028	1073.876	−22.437
2600	32.768	247.338	219.676	71.921	1600.930	1052.832	−21.152
2700	32.724	248.574	220.723	75.196	1602.742	1031.716	−19.960
2800	32.689	249.763	221.739	78.467	1604.450	1010.535	−18.852
2900	32.660	250.910	222.725	81.734	1606.042	989.296	−17.819
3000	32.639	252.016	223.683	84.999	1607.502	968.003	−16.854
3100	32.623	253.086	224.615	88.262	1608.812	946.665	−15.951
3200	32.610	254.122	225.521	91.524	1609.951	925.286	−15.104
3300	32.601	255.125	226.403	94.784	1574.442	904.346	−14.315
3400	32.594	256.098	227.262	98.044	1575.596	884.023	−13.581
3500	32.586	257.043	228.099	101.303	1576.750	863.666	−12.890
3600	32.579	257.951	228.916	104.561	1577.903	843.276	−12.236
3700	32.569	258.853	229.713	107.818	1579.055	822.853	−11.617
3800	32.558	259.722	230.492	111.075	1580.206	802.400	−11.030
3900	32.544	260.567	231.252	114.330	1581.355	781.917	−10.473
4000	32.527	261.391	231.995	117.584	1582.504	761.404	−9.943
4100	32.506	262.194	232.722	120.835	1583.650	740.862	−9.439
4200	32.482	262.977	233.433	124.085	1584.794	720.292	−8.958
4300	32.453	263.741	234.129	127.331	1585.935	699.695	−8.500
4400	32.421	264.487	234.811	130.575	1587.074	679.072	−8.062
4500	32.386	265.215	235.478	133.816	1588.209	658.423	−7.643
4600	32.347	265.926	236.132	137.052	1589.340	637.748	−7.242
4700	32.305	266.622	236.774	140.285	1590.467	617.049	−6.858
4800	32.260	267.301	237.403	143.513	1591.590	596.327	−6.489
4900	32.212	267.966	238.020	146.737	1592.708	575.580	−6.136
5000	32.163	268.616	238.625	149.955	1593.821	554.811	−5.796
5100	32.112	269.253	239.219	153.169	1594.930	534.020	−5.469
5200	32.060	269.876	239.803	156.378	1596.033	513.207	−5.155
5300	32.008	270.486	240.376	159.581	1597.131	492.373	−4.853
5400	31.955	271.084	240.939	162.779	1598.224	471.518	−4.561
5500	31.904	271.670	241.493	165.972	1599.311	450.644	−4.280
5600	31.853	272.244	242.037	169.160	1600.394	429.749	−4.009
5700	31.805	272.807	242.572	172.343	1601.471	408.835	−3.747
5800	31.758	273.360	243.098	175.521	863.789	390.703	−3.519
5900	31.715	273.903	243.615	178.695	864.644	382.539	−3.387
6000	31.675	274.435	244.125	181.864	865.451	374.361	−3.259

PREVIOUS: CURRENT: March 1984 (1 bar)

EA(Ta, g) = 0.322 ± 0.012 eV
$S°(298.15\ K)$ = 174.560 ± 0.002 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 750.403 ± 1.5 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [744.941] $kJ·mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5D_0$	0	1
$^5D_1$	1070	3
$^5D_2$	2240	5

Enthalpy of Formation

$\Delta_f H°(Ta^-, g, 0\ K)$ is calculated from $\Delta_f H°(Ta, g, 0\ K)$[1] using the adopted electron affinity of EA(Ta) = 0.322 ± 0.012 eV (31.068 ± 1.158 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $Ta^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[6] and Massey.[6]

$\Delta_f H°(Ta^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ta, g, 0\ K)$ by using EA(Ta) with JANAF[1] enthalpies, $H°(0\ K)$–$H°(298.15\ K)$, or $Ta^-(g)$, Ta(g), and e^-(ref). $\Delta_r H°(Ta^- \rightarrow Ta + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $Ta^-(g)$ is given by Hotop and Lineberger,[2,4] Rosenstock *et al.*,[5] and Massey.[6] The fine structure separation has been calculated by an isoelectronic extrapolation of ratios of fine structure separations[3] and is that recommended by Hotop and Lineberger.[2]

References

[1]JANAF Thermochemical Tables: Ta(g), 12–31–72; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K					Standard State Pressure = $p°$ = 0.1 MPa		
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.416	750.403		
100	20.787	150.978	194.351	−4.337			
200	21.456	165.484	176.691	−2.241			
250	22.780	170.401	174.954	−1.138			
298.15	24.558	174.560	174.560	0.	744.941	711.515	−124.654
300	24.632	174.712	174.561	0.045	744.901	711.308	−123.850
350	26.631	178.660	174.868	1.327	743.870	705.791	−105.334
400	28.486	182.340	175.575	2.706	742.924	700.417	−91.465
450	30.041	185.788	176.520	4.171	742.051	695.157	−80.692
500	31.236	189.018	177.610	5.704	741.234	689.991	−72.083
600	32.583	194.852	180.009	8.906	739.697	679.888	−59.189
700	32.816	199.904	182.499	12.184	738.192	670.038	−49.999
800	32.336	204.261	184.954	15.446	736.642	660.407	−43.120
900	31.479	208.022	187.313	18.638	735.000	650.975	−37.782
1000	30.476	211.288	189.551	21.737	733.240	641.732	−33.521
1100	29.464	214.145	191.660	24.733	731.348	632.672	−30.043
1200	28.511	216.667	193.641	27.631	729.320	623.790	−27.153
1300	27.649	218.914	195.500	30.439	727.165	615.082	−24.714
1400	26.885	220.935	197.246	33.164	724.902	606.545	−22.630
1500	26.216	222.766	198.887	35.819	722.551	598.172	−20.830
1600	25.633	224.439	200.432	38.411	720.127	589.959	−19.260
1700	25.127	225.977	201.890	40.948	717.631	581.900	−17.880
1800	24.688	227.401	203.269	43.438	715.053	573.989	−16.657
1900	24.306	228.725	204.574	45.887	712.384	566.225	−15.567
2000	23.972	229.963	205.813	48.301	709.626	558.603	−14.589
2100	23.680	231.126	206.991	50.683	706.785	551.122	−13.708
2200	23.424	232.221	208.113	53.038	703.863	543.777	−12.911
2300	23.199	233.258	209.184	55.369	700.862	536.568	−12.186
2400	23.000	234.241	210.208	57.679	697.779	529.490	−11.524
2500	22.823	235.176	211.188	59.970	694.611	522.543	−10.918
2600	22.666	236.068	212.128	62.244	691.351	515.724	−10.361
2700	22.525	236.921	213.030	64.504	687.990	509.033	−9.848
2800	22.399	237.737	213.898	66.750	684.517	502.468	−9.374
2900	22.286	238.521	214.734	68.984	680.918	496.029	−8.934
3000	22.184	239.275	215.539	71.207	677.180	489.717	−8.527
3100	22.091	240.001	216.317	73.421	673.283	483.532	−8.147
3200	22.008	240.701	217.068	75.626	669.208	477.476	−7.794
3300	21.931	241.377	217.794	77.823	628.478	472.020	−7.471
3400	21.862	242.031	218.498	80.012	624.405	467.340	−7.180
3500	21.799	242.664	219.179	82.195	620.325	462.780	−6.907
3600	21.740	243.277	219.840	84.372	616.239	458.337	−6.650
3700	21.687	243.872	220.482	86.543	612.148	454.007	−6.409
3800	21.638	244.449	221.105	88.710	608.052	449.787	−6.183
3900	21.593	245.011	221.711	90.871	603.951	445.676	−5.969
4000	21.551	245.557	222.300	93.028	599.845	441.670	−5.768
4100	21.512	246.089	222.874	95.182	595.736	437.766	−5.577
4200	21.476	246.607	223.433	97.331	591.623	433.963	−5.397
4300	21.443	247.112	223.977	99.477	587.506	430.258	−5.227
4400	21.412	247.604	224.509	101.620	583.386	426.649	−5.065
4500	21.383	248.085	225.027	103.759	579.263	423.133	−4.912
4600	21.356	248.555	225.534	105.896	575.138	419.709	−4.766
4700	21.331	249.014	226.029	108.031	571.009	416.375	−4.627
4800	21.307	249.463	226.512	110.163	566.879	413.128	−4.496
4900	21.285	249.902	226.985	112.292	562.746	409.968	−4.370
5000	21.264	250.332	227.448	114.420	558.610	406.892	−4.251
5100	21.245	250.752	227.900	116.545	554.473	403.898	−4.137
5200	21.227	251.165	228.344	118.669	550.334	400.986	−4.028
5300	21.209	251.569	228.778	120.790	546.193	398.154	−3.924
5400	21.193	251.965	229.204	122.911	542.051	395.399	−3.825
5500	21.178	252.354	229.621	125.029	537.907	392.722	−3.730
5600	21.163	252.735	230.031	127.146	533.761	390.120	−3.639
5700	21.149	253.110	230.432	129.262	529.614	387.591	−3.552
5800	21.136	253.478	230.827	131.376	−213.289	387.937	−3.494
5900	21.124	253.839	231.214	133.489	−217.652	398.340	−3.527
6000	21.112	254.194	231.594	135.601	−222.060	408.818	−3.559

PREVIOUS: CURRENT: March 1984 (1 bar)

REFERENCE STATE

0	to	1166	K	crystal, alpha
1166	to	1939	K	crystal, beta
1939	to	3630.956	K	liquid
3630.956	to	6000	K	ideal monatomic gas

Refer to the individual tables for details

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.830	0.	0.	0.
100	14.334	8.261	50.955	−4.269	0.	0.	0.
200	22.367	21.227	32.989	−2.352	0.	0.	0.
298.15	25.238	30.759	30.759	0.	0.	0.	0.
300	25.276	30.915	30.760	0.047	0.	0.	0.
400	26.862	38.423	31.772	2.660	0.	0.	0.
500	27.877	44.534	33.733	5.401	0.	0.	0.
600	28.596	49.683	35.973	8.226	0.	0.	0.
700	29.135	54.134	38.257	11.114	0.	0.	0.
800	29.472	58.039	40.490	14.039	0.	0.	0.
900	30.454	61.561	42.639	17.030	0.	0.	0.
1000	32.074	64.848	44.697	20.151	0.	0.	0.
1100	34.334	68.006	46.673	23.466	0.	0.	0.
1166.000	36.175	70.058	47.938	25.791	ALPHA <--> BETA TRANSITION		
1166.000	29.245	73.636	47.938	29.963			
1200	29.459	74.479	48.679	30.961	0.	0.	0.
1300	30.175	76.864	50.756	33.941	0.	0.	0.
1400	31.023	79.131	52.702	37.000	0.	0.	0.
1500	32.003	81.304	54.537	40.150	0.	0.	0.
1600	33.115	83.404	56.276	43.405	0.	0.	0.
1700	34.359	85.448	57.932	46.778	0.	0.	0.
1800	35.736	87.451	59.517	50.281	0.	0.	0.
1900	37.244	89.422	61.039	53.929	0.	0.	0.
1939.000	37.868	90.186	61.617	55.394	BETA <--> LIQUID TRANSITION		
1939.000	47.237	97.481	61.617	69.540			
2000	47.237	98.944	62.734	72.421	0.	0.	0.
2100	47.237	101.249	64.513	77.145	0.	0.	0.
2200	47.237	103.446	66.233	81.869	0.	0.	0.
2300	47.237	105.546	67.897	86.592	0.	0.	0.
2400	47.237	107.557	69.508	91.316	0.	0.	0.
2500	47.237	109.485	71.069	96.040	0.	0.	0.
2600	47.237	111.338	72.582	100.764	0.	0.	0.
2700	47.237	113.120	74.051	105.487	0.	0.	0.
2800	47.237	114.838	75.477	110.211	0.	0.	0.
2900	47.237	116.496	76.863	114.935	0.	0.	0.
3000	47.237	118.097	78.211	119.659	0.	0.	0.
3100	47.237	119.646	79.523	124.382	0.	0.	0.
3200	47.237	121.146	80.800	129.106	0.	0.	0.
3300	47.237	122.600	82.045	133.830	0.	0.	0.
3400	47.237	124.010	83.259	138.554	0.	0.	0.
3500	47.237	125.379	84.443	143.277	0.	0.	0.
3600	47.237	126.710	85.598	148.001	0.	0.	0.
3630.956	47.237	127.114	85.951	149.463	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
3630.956	34.219	240.028	85.951	559.447			
3700	34.613	240.676	88.832	561.823	0.	0.	0.
3800	35.173	241.607	92.840	565.313	0.	0.	0.
3900	35.721	242.527	96.667	568.857	0.	0.	0.
4000	36.254	243.439	100.324	572.456	0.	0.	0.
4100	36.772	244.340	103.826	576.108	0.	0.	0.
4200	37.273	245.232	107.182	579.810	0.	0.	0.
4300	37.757	246.115	110.403	583.562	0.	0.	0.
4400	38.223	246.988	113.497	587.361	0.	0.	0.
4500	38.670	247.852	116.473	591.206	0.	0.	0.
4600	39.097	248.707	119.339	595.094	0.	0.	0.
4700	39.505	249.552	122.100	599.025	0.	0.	0.
4800	39.892	250.388	124.764	602.995	0.	0.	0.
4900	40.259	251.214	127.336	607.002	0.	0.	0.
5000	40.606	252.031	129.822	611.046	0.	0.	0.
5200	41.240	253.637	134.554	619.232	0.	0.	0.
5400	41.796	255.204	138.993	627.537	0.	0.	0.
5600	42.277	256.733	143.171	635.945	0.	0.	0.
5800	42.686	258.224	147.113	644.443	0.	0.	0.
6000	43.029	259.677	150.841	653.015	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

$S°(298.15\ K) = 30.759 \pm 0.2\ J \cdot K \cdot mol^{-1}$
$T_{trs} = 1166 \pm 10\ K\ (\alpha–\beta)$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 0.997 \pm 0.03\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition

Heat Capacity and Entropy

The adopted thermal functions for α–Ti(cr) are derived from the studies of Collings and Ho,[1] Clusius and Franzosini,[2] Stalinski and Bieganski,[3] Scott,[4] Backhurst[5] and Cezairliyan and Miiller.[6] The mathematical and graphical treatment of these four studies yields a continuous and smooth heat capacity curve.

There are ten studies[1,7–15] on the heat capacity of titanium in the range 1–5 K. Wolcott[9] and Aven *et al.*[8] reported the experimental data. In the other studies, an equation (with two constants) was given to describe the entire set of experimental data. The constants given by Collings and Ho[1] agree with the experimental data of Wolcott[9] and of Aven *et al.*[8] The maximum difference in the calculated values for $S°(5\ K)$ is $0.00071\ cal \cdot K^{-1} \cdot mol^{-1}$, with the adopted value being $S°(5\ K) = 0.0043\ cal \cdot K^{-1} \cdot mol^{-1}$. Similarly for $C_p°(5\ K)$ the maximum difference is $0.00211\ cal \cdot K^{-1} \cdot mol^{-1}$, with the adopted value being $C_p°\ (5\ K) = 0.0049\ cal \cdot K^{-1} \cdot mol^{-1}$.

In the region above 5 K and below 360 K, there are seven heat capacity studies.[2,3,8,9–18] The adopted values were based on the work of Clusius and Franzosini[2] and Stalinski and Bieganski.[3] The maximum deviation of all studies from the adopted is 2.5% over this temperature range.

Above 300 K, there are eleven heat capacity studies[4–6,18–25] and seven enthalpy studies.[26–32] The heat capacity studies all have a similar temperature dependence in comparison with the adopted values. However, the studies of Holland,[19] Affortit,[23] Arutyunov,[24] and Rumyantsev *et al.*[25] lie roughly 9–33% higher than the adopted values. There is much scatter in all studies within 50 K of the α–β transition temperature. The adopted values were based on Scott,[4] Backhurst[5], and Cezairliyan and Miller.[6] The enthalpy studies show a large scatter within each study as well as a general lack of agreement between the studies.

Transition Data

Refer to the β–crystal table for details.

Sublimation Data

There are no sublimation studies involving α–Ti(cr). The enthalpy of sublimation is calculated as the difference between the enthalpy of formation of the monatomic gas and the enthalpy of formation of α–Ti(cr).

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Continued on page 1915

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.830	0.	0.	0.
100	14.334	8.261	50.955	−4.269	0.	0.	0.
200	22.367	21.227	32.989	−2.352	0.	0.	0.
250	24.074	26.414	31.169	−1.189	0.	0.	0.
298.15	25.238	30.759	30.759	0.	0.	0.	0.
300	25.276	30.915	30.760	0.047	0.	0.	0.
350	26.169	34.882	31.071	1.334	0.	0.	0.
400	26.862	38.423	31.772	2.660	0.	0.	0.
450	27.418	41.620	32.692	4.018	0.	0.	0.
500	27.877	44.534	33.733	5.401	0.	0.	0.
600	28.596	49.683	35.973	8.226	0.	0.	0.
700	29.135	54.134	38.257	11.114	0.	0.	0.
800	29.472	58.039	40.490	14.039	0.	0.	0.
900	30.454	61.561	42.639	17.030	0.	0.	0.
1000	32.074	64.848	44.697	20.151	0.	0.	0.
1100	34.334	68.006	46.673	23.466	0.	0.	0.
1166.000	36.175	70.058	47.938	25.791	---- ALPHA <--> BETA ----		
1200	37.233	71.113	48.580	27.039	−3.922	0.118	−0.005
1300	40.771	74.228	50.433	30.934	−3.007	0.420	−0.017
1400	44.948	77.399	52.245	35.214	−1.786	0.640	−0.024
1500	49.764	80.660	54.030	39.945	−0.205	0.760	−0.026
1600	55.220	84.043	55.800	45.189	1.784	0.762	−0.025
1700	61.314	87.570	57.564	51.010	4.232	0.625	−0.019

PREVIOUS: September 1966 CURRENT: June 1979

$S°(298.15\ K) = [38.122]\ J·K^{-1}·mol^{-1}$
$T_{trs} = 1166 \pm 10$ K (α–β)
$T_{fus} = 1939 \pm 10$ K (β–l)

$\Delta_f H°(298.15\ K) = [6.860]\ kJ·mol^{-1}$
$\Delta_{trs}H° = 4.172 \pm 0.13\ kJ·mol^{-1}$
$\Delta_{fus}H° = 14.146 \pm 5.0\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the α–crystal by addition of $\Delta_{trs}H°$ and the difference in enthalpy, $H°(1166\ K)-H°(298.15\ K)$, between the α–crystal and the β–crystal.

Heat Capacity and Entropy

For the β–crystal there are ten heat capacity studies and six enthalpy studies. The discussion on heat capacity and enthalpy on the α–Ti(cr) table also applies to the β–Ti(cr).

The entropy at 298.15 K is calculated in a manner similar to that for the enthalpy of formation.

Phase Data

Titanium, at ambient pressures, exists in two crystal modifications. The low temperature form, α–Ti, is hexagonal close packed, an hcp (A3) structure isotypic with Mg. The high temperature form, β–Ti, is body centered cubic, a bcc (A2) structure isotypic with W.

Transition Data

The following table indicates the values of transition temperatures and enthalpies of transition reported by various investigators. The value of T_{trs} adoped is 1166 ± 10 K, and the value of $\Delta_{trs}H°$ is selected as 0.997 ± 0.03 kcal·mol^{-1}, based on the work of Cezairliyan and Miller.[1]

Source	T_{trs}/K	$\Delta_{trs}H°$, kcal·mol^{-1}	Purity, %	Method
Fast[2]	1158 ± 10		Iodide	electrical resistance
Greiner and Ellis[3]	1158 ± 2		99.9	electrical resitance
McQuillan[4]	1155.7 ± 1	0.67	99.93	hydrogen solubility
Worner[5]	1158 ± 2		99.93	thermoelectric power
Duwez[6]	1155 ± 4		Iodide	cooling curve
Kothen[7]	1154	0.943	99.96	drop calorimetry
Edwards *et al.*[8]	1157 ± 3.5		99.88	cooling curve
Schofield[9]	1158	0.814	—	rate of heating
Scott[10]	1156 ± 2	0.978 ± 0.025	Iodide	adiabatic calorimetry
Backhurst[11]	1165–1179	0.88	Commercial	adiabatic calorimetry
Golutvin[12]	1155	0.82 ± .020	Iodide	drop calorimetry
Kohlhaas *et al.*[13]	1167	0.992	99.8	adiabatic calorimetry
Gel'd and Putintsev[14]		0.998		
Martynyuk and Tsapkov[15]		1.028	99.74	pulsed heating
Harmelin and Lehr[16]		1.007		DTA
Etchessahar and Debuiqne[17]	1154			dilatometric
Cezairliyan and Miller[1]	1166	0.997	99.9+	electrical resistance

Fusion Data

Refer to the liquid table for details.

Sublimation Data

There are three sublimation studies involving β–Ti(cr). They are summarized on the ideal gas table. The enthalpy of sublimation for β–Ti(cr) is calculated as the difference in the enthalpies of formation at 298.15 K of Ti(g) and β–Ti(cr).

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Continued on page 1915

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	23.995	38.122	38.122	0.	6.860	4.665	−0.817
300	24.006	38.271	38.123	0.044	6.858	4.652	−0.810
350	24.309	41.994	38.416	1.252	6.779	4.290	−0.640
400	24.611	45.260	39.071	2.475	6.675	3.941	−0.515
450	24.914	48.176	39.924	3.713	6.556	3.606	−0.419
500	25.216	50.816	40.883	4.967	6.427	3.285	−0.343
600	25.821	55.467	42.937	7.519	6.153	2.682	−0.234
700	26.426	59.493	45.020	10.131	5.877	2.126	−0.159
800	27.031	63.061	47.057	12.804	5.625	1.607	−0.105
900	27.636	66.280	49.017	15.537	5.368	1.120	−0.065
1000	28.241	69.223	50.892	18.331	5.040	0.665	−0.035
1100	28.846	71.943	52.684	21.185	4.580	0.248	−0.012
1166.000	29.245	73.636	53.822	23.102	---- ALPHA <--> BETA ----		
1200	29.459	74.479	54.396	24.100	0.	0.	0.
1300	30.175	76.864	56.033	27.081	0.	0.	0.
1400	31.023	79.131	57.603	30.140	0.	0.	0.
1500	32.003	81.304	59.111	33.290	0.	0.	0.
1600	33.115	83.404	60.564	36.544	0.	0.	0.
1700	34.359	85.448	61.968	39.917	0.	0.	0.
1800	35.736	87.451	63.328	43.421	0.	0.	0.
1900	37.244	89.422	64.650	47.069	0.	0.	0.
1939.000	37.868	90.186	65.155	48.533	---- BETA <--> LIQUID ----		
2000	38.885	91.374	65.937	50.874	−14.687	0.454	−0.012
2100	40.657	93.314	67.195	54.850	−15.435	1.230	−0.031
2200	42.562	95.248	68.426	59.010	−15.998	2.037	−0.048
2300	44.599	97.185	69.634	63.367	−16.365	2.866	−0.065
2400	46.768	99.128	70.822	67.934	−16.522	3.706	−0.081
2500	49.069	101.084	71.994	72.725	−16.455	4.549	−0.095

PREVIOUS: September 1966 CURRENT: June 1979

$S°(298.15\ K) = [39.181]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 1936 \pm 10\ K$

$\Delta_f H°(298.15\ K) = [13.652]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 14.146 \pm 5.0\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the β–crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(1936\ K)-H°(198.15\ K)$, between the β–crystal and the liquid.

Heat Capacity and Entropy

There are two enthalpy studies[1,2] covering the liquid region of titanium. The work of Treverton and Margrave[1] was adopted. A glass transition is assumed at 1300 K below which extrapolated β–Ti heat capacity values are used. The entropy is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The investigators reporting melting temperatures and heats of melting are listed below. The value of T_{fus} adopted is 1939 ± 10 K, and the value of $\Delta_{fus}H°$ is selected as 3.381 ± 0.03 kcal·mol^{-1}, based on the work of Berezin *et al.*[2,13]

Source	T_{fus}/K	$\Delta_{fus}H°$ kcal·mol^{-1}
Burgess and Waltenburg[3]	2068	
Fast[4]	1993	
Adenstedt *et al.*[5]	1973	
Hansen *et al.*[6]	1993	
Maykuth *et al.*[7]	1953	
Schofield and Bacon[8]	1933	
Oriani and Jones[9]	1945	
Deardorff and Hayes[10]	1941	
Westrum and Feick[11]	1933	
Elyutin *et al.*[12]	1941	4.1 ± 0.1
Treverton and Margrave[1]	1943	3.161 ± 0.12
Berezin *et al.*[13]	1939	3.381 ± 0.115

Vaporization Data

The two vaporization studies are summarized on the ideal gas table. The boiling point is calculated as that temperature for which $\Delta G° = 0$ for Ti(l) = Ti(g). $\Delta_{vap}H°$ is the corresponding enthalpy change. T_{vap} is the temperature at which fugacity is one bar. The normal boiling point (p=1 bar) would be a slightly lower temperature.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	27.638	39.181	39.181	0.	13.652	11.141	−1.952
300	27.639	39.352	39.181	0.051	13.657	11.126	−1.937
350	27.667	43.614	39.518	1.434	13.752	10.696	−1.596
400	27.694	47.310	40.266	2.818	13.810	10.255	−1.339
450	27.722	50.574	41.234	4.203	13.838	9.809	−1.139
500	27.750	53.496	42.316	5.590	13.842	9.360	−0.978
600	27.805	58.560	44.614	8.368	13.794	8.468	−0.737
700	27.860	62.851	46.921	11.151	13.689	7.587	−0.566
800	27.916	66.573	49.150	13.939	13.552	6.725	−0.439
900	28.104	69.871	51.272	16.739	13.361	5.882	−0.341
1000	28.423	72.847	53.283	19.564	13.065	5.066	−0.265
1100	28.875	75.576	55.188	22.428	12.614	4.286	−0.204
1200	29.459	78.113	56.993	25.343	8.035	3.674	−0.160
1300	30.175	80.498	58.711	28.324	8.035	3.311	−0.133
1400	31.023	82.765	60.348	31.383	8.035	2.948	−0.110
1460.000	31.595	84.078	61.297	33.261	GLASS <--> LIQUID		
1460.000	47.237	84.078	61.297	33.261	TRANSITION		
1500	47.237	85.355	61.921	35.150	8.652	2.576	−0.090
1600	47.237	88.404	63.482	39.874	10.121	2.122	−0.069
1700	47.237	91.267	65.033	44.598	11.473	1.580	−0.049
1800	47.237	93.967	66.566	49.321	12.693	0.962	−0.028
1900	47.237	96.521	68.076	54.045	13.768	0.281	−0.008
1939.000	47.237	97.481	68.658	55.887	BETA <--> LIQUID		
2000	47.237	98.944	69.560	58.769	0.	0.	0.
2100	47.237	101.249	71.014	63.493	0.	0.	0.
2200	47.237	103.446	72.439	68.216	0.	0.	0.
2300	47.237	105.546	73.833	72.940	0.	0.	0.
2400	47.237	107.557	75.197	77.664	0.	0.	0.
2500	47.237	109.485	76.530	82.388	0.	0.	0.
2600	47.237	111.338	77.833	87.111	0.	0.	0.
2700	47.237	113.120	79.107	91.835	0.	0.	0.
2800	47.237	114.838	80.353	96.559	0.	0.	0.
2900	47.237	116.496	81.571	101.283	0.	0.	0.
3000	47.237	118.097	82.762	106.006	0.	0.	0.
3100	47.237	119.646	83.927	110.730	0.	0.	0.
3200	47.237	121.146	85.067	115.454	0.	0.	0.
3300	47.237	122.600	86.182	120.178	0.	0.	0.
3400	47.237	124.010	87.274	124.901	0.	0.	0.
3500	47.237	125.379	88.343	129.625	0.	0.	0.
3600	47.237	126.710	89.391	134.349	0.	0.	0.
3630.956	47.237	127.114	89.711	135.811	FUGACITY = 1 bar		
3700	47.237	128.004	90.417	139.072	−409.098	7.788	−0.110
3800	47.237	129.264	91.423	143.796	−407.864	19.039	−0.262
3900	47.237	130.491	92.409	148.520	−406.685	30.258	−0.405
4000	47.237	131.687	93.376	153.244	−405.560	41.447	−0.541
4100	47.237	132.853	94.324	157.967	−404.488	52.609	−0.670
4200	47.237	133.991	95.255	162.691	−403.467	63.745	−0.793
4300	47.237	135.103	96.169	167.415	−402.495	74.858	−0.909
4400	47.237	136.189	97.066	172.139	−401.570	85.948	−1.020
4500	47.237	137.250	97.948	176.862	−400.691	97.018	−1.126

PREVIOUS: September 1966 CURRENT: June 1979

0	to	1166	K crystal, alpha
1166	to	1936	K crystal, beta
above		1936	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.830	0.	0.	0.
100	14.334	8.261	50.955	−4.269	0.	0.	0.
200	22.367	21.227	32.989	−2.352	0.	0.	0.
250	24.074	26.414	31.169	−1.189	0.	0.	0.
298.15	25.238	30.759	30.759	0.	0.	0.	0.
300	25.276	30.915	30.760	0.047	0.	0.	0.
350	26.169	34.882	31.071	1.334	0.	0.	0.
400	26.862	38.423	31.772	2.660	0.	0.	0.
450	27.418	41.620	32.692	4.018	0.	0.	0.
500	27.877	44.534	33.733	5.401	0.	0.	0.
600	28.596	49.683	35.973	8.226	0.	0.	0.
700	29.135	54.134	38.257	11.114	0.	0.	0.
800	29.472	58.039	40.490	14.039	0.	0.	0.
900	30.454	61.561	42.639	17.030	0.	0.	0.
1000	32.074	64.848	44.697	20.151	0.	0.	0.
1100	34.334	68.006	46.673	23.466	0.	0.	0.
1166.000	36.175	70.058	47.938	25.791	ALPHA <--> BETA TRANSITION		
1166.000	29.245	73.636	47.938	29.963			
1200	29.459	74.479	48.679	30.961	0.	0.	0.
1300	30.175	76.864	50.756	33.941	0.	0.	0.
1400	31.023	79.131	52.702	37.000	0.	0.	0.
1500	32.003	81.304	54.537	40.150	0.	0.	0.
1600	33.115	83.404	56.276	43.405	0.	0.	0.
1700	34.359	85.448	57.932	46.778	0.	0.	0.
1800	35.736	87.451	59.517	50.281	0.	0.	0.
1900	37.244	89.422	61.039	53.929	0.	0.	0.
1939.000	37.868	90.186	61.617	55.394	BETA <--> LIQUID TRANSITION		
1939.000	47.237	97.481	61.617	69.540			
2000	47.237	98.944	62.734	72.421	0.	0.	0.
2100	47.237	101.249	64.513	77.145	0.	0.	0.
2200	47.237	103.446	66.233	81.869	0.	0.	0.
2300	47.237	105.546	67.897	86.592	0.	0.	0.
2400	47.237	107.557	69.508	91.316	0.	0.	0.
2500	47.237	109.485	71.069	96.040	0.	0.	0.
2600	47.237	111.338	72.582	100.764	0.	0.	0.
2700	47.237	113.120	74.051	105.487	0.	0.	0.
2800	47.237	114.838	75.477	110.211	0.	0.	0.
2900	47.237	116.496	76.863	114.935	0.	0.	0.
3000	47.237	118.097	78.211	119.659	0.	0.	0.
3100	47.237	119.646	79.523	124.382	0.	0.	0.
3200	47.237	121.146	80.800	129.106	0.	0.	0.
3300	47.237	122.600	82.045	133.830	0.	0.	0.
3400	47.237	124.010	83.259	138.554	0.	0.	0.
3500	47.237	125.379	84.443	143.277	0.	0.	0.
3600	47.237	126.710	85.598	148.001	0.	0.	0.
3630.956	47.237	127.114	85.951	149.463	FUGACITY = 1 bar		
3700	47.237	128.004	86.727	152.725	−409.098	7.788	−0.110
3800	47.237	129.264	87.830	157.449	−407.864	19.039	−0.262
3900	47.237	130.491	88.908	162.172	−406.685	30.258	−0.405
4000	47.237	131.687	89.963	166.896	−405.560	41.447	−0.541
4100	47.237	132.853	90.995	171.620	−404.488	52.609	−0.670
4200	47.237	133.991	92.005	176.343	−403.467	63.745	−0.793
4300	47.237	135.103	92.994	181.067	−402.495	74.857	−0.909
4400	47.237	136.189	93.964	185.791	−401.570	85.948	−1.020
4500	47.237	137.250	94.914	190.515	−400.691	97.018	−1.126

PREVIOUS: CURRENT: June 1979

IP(Ti, g) = 55010 ± 100 cm^{-1}
$S°(298.15K)$ = 180.297 ± 0.03 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 470.92 ± 16.7 $kJ·mol^{-1}$
$\Delta_f H°(298.15K)$ = 473.63 ± 16.7 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_2$	0.00	5
$^3F_3$	170.132	7
$^3F_4$	386.874	9
.	.	.
.	.	.
.	.	.
.	.	.
.	.	.
$^1P_1$	53663.32	3
IP	55010	

Enthalpy of Formation

The value adopted for the enthalpy of formation of Ti(g) is that recommended by CODATA.[1] It is obtained from a 2nd and 3rd law evaluation of the vapor pressure data of Wu and Wahlbeck,[2] Berstein and Kaufman,[3] Koch *et al.*,[4] Strassmair and Stark,[5] and Edwards *et al.*[6]

Source	Reaction	T/K	Data Points	$\Delta_r H°(298.15K)$, kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}	$\Delta_f H°(298.15K)$ kcal·mol^{-1}
Edwards *et al.*[6]	a	1587–1764	8	112.0 ± 1.1	111.5 ± 0.2	−0.3 ± 0.6	113.1
Strassmair and Stark[5]	a	1554–1772	8	111.4 ± 3.5	109.8 ± 0.8	−1.0 ± 2.1	111.4
Wu and Wahlbeck[2]	a	1830–1923	16	112.2 ± 9.3	111.6 ± 1.0	−0.3 ± 4.9	113.2
Koch *et al.*[4]	b	1955–2379	21*	110.9 ± 2.4	109.2 ± 1.3	−0.8 ± 1.1	112.46
Bernstein and Kaufman[3]	b	2000–3000	Smooth	110.6	109.0	−0.6	112.3

*Two points deleted due to a statistical test Reaction: a) Ti(β) = Ti(g) b) Ti(l) = Ti(g)

Heat Capacity and Entropy

The electronic energy levels are given in the recent compilation by Corliss and Sugar.[7] Although we have listed only the ground state, first two excited states, the highest observed excited state, and the ionization potential for Ti(g), all levels listed by Corliss and Sugar,[7] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. In our calculations, the missing levels for n = 4, n = 5, and n = 6 have been arbitrarily added near the ionization limit. Our calculations indicate that for Ti(g) the thermochemical functions are independent of the estimated missing levels (for n = 4,5,6) and the cut–off procedure up to 3000 K. The Gibbs energy function is essentially unaffected (<0.002 cal·K^{-1}·mol^{-1}) at 6000 K. The reported uncertainty in $S°(298.15K)$ is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n > 6), more precise estimation of missing states (all n), and utilization of proper fill and cut–off procedures.[8] In fact, the inclusion of some higher states (n = 4,5,6) and consideration of various cut–off procedures leads to calculational differences in the Gibbs energy function of rougly 0.1 cal·K^{-1}·mol^{-1}) or greater at temperatures near 10000 K.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−7.539	470.920	470.920	INFINITE
100	26.974	151.246	203.383	−5.214	472.684	458.386	−239.436
200	26.487	170.126	182.593	−2.493	473.488	443.708	−115.885
250	25.355	175.913	180.704	−1.198	473.620	436.245	−91.148
298.15	24.430	180.297	180.297	0.	473.629	429.044	−75.167
300	24.399	180.448	180.297	0.045	473.627	428.768	−74.655
350	23.661	184.151	180.591	1.246	473.541	421.297	−62.875
400	23.104	187.272	181.236	2.414	473.383	413.843	−54.042
450	22.683	189.968	182.060	3.558	473.169	406.413	−47.175
500	22.360	192.340	182.972	4.684	472.912	399.009	−41.684
600	21.913	196.374	184.881	6.896	472.299	384.284	−33.455
700	21.632	199.729	186.769	9.072	471.587	369.670	−27.585
800	21.454	202.605	188.573	11.226	470.816	355.163	−23.190
900	21.353	205.126	190.275	13.366	469.965	340.756	−19.777
1000	21.323	207.373	191.875	15.499	468.977	326.451	−17.052
1100	21.362	209.407	193.377	17.633	467.795	312.254	−14.828
1200	21.474	211.270	194.792	19.774	462.442	298.293	−12.984
1300	21.657	212.996	196.127	21.930	461.617	284.647	−11.437
1400	21.910	214.609	197.390	24.107	460.736	271.066	−10.114
1500	22.228	216.132	198.589	26.314	459.793	257.551	−8.969
1600	22.604	217.578	199.731	28.555	458.779	244.101	−7.969
1700	23.029	218.961	200.822	30.836	457.688	230.717	−7.089
1800	23.497	220.290	201.867	33.162	456.510	217.399	−6.309
1900	23.999	221.574	202.870	35.537	455.237	204.149	−5.612
2000	24.529	222.818	203.837	37.963	439.171	191.423	−4.999
2100	25.080	224.028	204.769	40.443	436.927	179.091	−4.455
2200	25.648	225.208	205.672	42.979	434.740	166.864	−3.962
2300	26.228	226.361	206.546	45.573	432.610	154.736	−3.514
2400	26.819	227.489	207.396	48.225	430.538	142.699	−3.106
2500	27.416	228.596	208.221	50.937	428.526	130.748	−2.732
2600	28.019	229.683	209.026	53.709	426.574	118.875	−2.388
2700	28.626	230.752	209.811	56.541	424.683	107.077	−2.072
2800	29.235	231.804	210.578	59.434	422.852	95.347	−1.779
2900	29.846	232.841	211.328	62.388	421.082	83.682	−1.507
3000	30.456	233.863	212.062	65.403	419.374	72.077	−1.255
3100	31.065	234.871	212.781	68.479	417.726	60.528	−1.020
3200	31.671	235.867	213.487	71.616	416.139	49.031	−0.800
3300	32.273	236.851	214.180	74.813	414.612	37.582	−0.595
3400	32.870	237.823	214.861	78.071	413.146	26.179	−0.402
3500	33.460	238.785	215.531	81.387	411.739	14.818	−0.221
3600	34.042	239.736	216.190	84.762	410.390	3.497	−0.051
3630.956	34.219	240.028	216.392	85.819	----- FUGACITY = 1 bar -----		
3700	34.613	240.676	216.840	88.195	0.	0.	0.
3800	35.173	241.607	217.479	91.685	0.	0.	0.
3900	35.721	242.527	218.110	95.229	0.	0.	0.
4000	36.254	243.439	218.731	98.828	0.	0.	0.
4100	36.772	244.340	219.345	102.480	0.	0.	0.
4200	37.273	245.232	219.951	106.182	0.	0.	0.
4300	37.757	246.115	220.549	109.934	0.	0.	0.
4400	38.223	246.988	221.140	113.733	0.	0.	0.
4500	38.670	247.852	221.724	117.578	0.	0.	0.
4600	39.097	248.707	222.301	121.466	0.	0.	0.
4700	39.505	249.552	222.872	125.397	0.	0.	0.
4800	39.892	250.388	223.437	129.367	0.	0.	0.
4900	40.259	251.214	223.995	133.374	0.	0.	0.
5000	40.606	252.031	224.548	137.418	0.	0.	0.
5100	40.933	252.839	225.095	141.495	0.	0.	0.
5200	41.240	253.637	225.636	145.604	0.	0.	0.
5300	41.528	254.425	226.172	149.742	0.	0.	0.
5400	41.796	255.204	226.702	153.909	0.	0.	0.
5500	42.046	255.973	227.227	158.101	0.	0.	0.
5600	42.277	256.733	227.747	162.317	0.	0.	0.
5700	42.490	257.483	228.263	166.556	0.	0.	0.
5800	42.686	258.224	228.773	170.815	0.	0.	0.
5900	42.866	258.955	229.278	175.092	0.	0.	0.
6000	43.029	259.677	229.779	179.387	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

IP(Ti^+, g) = 109500 ± 1000 cm^{-1}
$S°$(298.15K) = 183.594 ± 0.04 $J·K^{-1}mol^{-1}$

$\Delta_f H°$(0 K) = 1128.985 ± 6.3 $kJ·mol^{-1}$
$\Delta_f H°$(298.15K) = [1138.252] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{3/2}$	0.00	4
$^4F_{5/2}$	93.94	6
$^4F_{7/2}$	225.47	8
$^4F_{9/2}$	393.22	10
.	.	.
.	.	.
.	.	.
$^2F_{7/2}$	70893.00	8
IP	109500	

Enthalpy of Formation

$\Delta_f H°(Ti^+, g, 0 K)$ is calaculated from $\Delta_f H°(Ti, g, 0 K)$[1] using the spectroscopic value of IP(Ti) = 55010 ± 100 cm^{-1} (658.07 ± 0.4 $kJ·mol^{-1}$) from Corliss and Sugar.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 kJ cm^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levine amd Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Ti^+, g, 298.15K)$ is calculated from $\Delta_f H°(Ti, g, 0 K)$ by using IP(Ti) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15K)$, for Ti(g), $Ti^+(g)$, and $e^-(g)$. $\Delta_f H°(Ti \rightarrow Ti^+ + e^-, 298.15K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in this ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic energy levels are given in the recent compilation by Corliss and Sugar.[2] Although we have listed only the ground state, the first three excited states, the highest observed excited state, and the ionization potential for $Ti^+(g)$, all levels listed by Corliss and Sugar,[2] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. In our calculations the missing levels for n = 4,5 have been arbitrarily added near the ionization limit. The calculations indicate that for $Ti^+(g)$, the thermochemical functions are independent of the estimated missing levels for n = 4,5, the cut–off procedure, and the inclusion of n = 6 levels up to 6000 K. The Gibbs energy function is essentially unaffected (by less than 0.2%) up to 20000 K. The reported uncertainty in $S°$(298.15K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states (n>6), and use of proper fill and cut–off procedures.[6]

References

[1]JANAF Thermochemical Tables: Ti(g), 6–30–79; e^-(g), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.899	1128.985		
100	28.375	153.817	207.355	−5.354			
200	26.772	173.059	185.998	−2.588			
250	26.305	178.974	184.025	−1.263			
298.15	26.181	183.594	183.594	0.	1138.252	1086.429	−190.338
300	26.180	183.756	183.595	0.048	1138.292	1086.108	−189.108
350	26.166	187.790	183.913	1.357	1139.353	1077.326	−160.782
400	26.128	191.282	184.621	2.665	1140.373	1068.395	−139.518
450	26.021	194.354	185.535	3.969	1141.359	1059.338	−122.965
500	25.843	197.087	186.556	5.265	1142.312	1050.173	−109.711
600	25.356	201.758	188.714	7.826	1144.126	1031.573	−89.806
700	24.817	205.626	190.862	10.335	1145.826	1012.678	−75.567
800	24.320	208.907	192.917	12.791	1147.436	993.546	−64.872
900	23.903	211.746	194.855	15.202	1148.934	974.218	−56.542
1000	23.572	214.247	196.672	17.575	1150.264	954.732	−49.870
1100	23.322	216.481	198.373	19.919	1151.372	935.123	−44.405
1200	23.145	218.502	199.968	22.242	1148.279	915.543	−39.853
1300	23.030	220.350	201.465	24.550	1149.685	896.091	−36.005
1400	22.970	222.054	202.876	26.850	1151.004	876.534	−32.704
1500	22.959	223.638	204.208	29.146	1152.229	856.886	−29.839
1600	22.992	225.121	205.469	31.443	1153.350	837.159	−27.330
1700	23.065	226.517	206.667	33.745	1154.358	817.365	−25.115
1800	23.173	227.838	207.806	36.057	1155.245	797.516	−23.143
1900	23.313	229.095	208.894	38.381	1156.000	777.621	−21.378
2000	23.480	230.295	209.934	40.721	1141.926	758.144	−19.801
2100	23.670	231.445	210.931	43.078	1141.638	738.962	−18.381
2200	23.879	232.551	211.889	45.455	1141.370	719.793	−17.090
2300	24.104	233.617	212.811	47.854	1141.124	700.636	−15.912
2400	24.340	234.648	213.699	50.276	1140.901	681.489	−14.832
2500	24.583	235.646	214.557	52.722	1140.702	662.351	−13.839
2600	24.832	236.615	215.387	55.193	1140.527	643.221	−12.922
2700	25.082	237.557	216.191	57.689	1140.378	624.096	−12.074
2800	25.331	238.474	216.970	60.209	1140.254	604.977	−11.286
2900	25.576	239.367	217.727	62.755	1140.154	585.862	−10.553
3000	25.816	240.238	218.463	65.324	1140.078	566.750	−9.868
3100	26.048	241.088	219.179	67.918	1140.026	547.640	−9.228
3200	26.272	241.919	219.877	70.534	1139.997	528.531	−8.627
3300	26.486	242.731	220.557	73.172	1139.990	509.423	−8.063
3400	26.689	243.524	221.221	75.831	1140.004	490.315	−7.533
3500	26.881	244.301	221.870	78.509	1140.037	471.206	−7.032
3600	27.060	245.061	222.503	81.206	1140.089	452.096	−6.560
3700	27.228	245.804	223.123	83.921	731.060	440.772	−6.223
3800	27.384	246.533	223.730	86.652	732.380	432.909	−5.951
3900	27.528	247.246	224.323	89.397	733.660	425.011	−5.692
4000	27.660	247.944	224.905	92.157	734.899	417.081	−5.447
4100	27.781	248.629	225.476	94.929	736.098	409.121	−5.212
4200	27.890	249.300	226.035	97.712	737.258	401.132	−4.989
4300	27.989	249.957	226.584	100.507	738.379	393.115	−4.775
4400	28.078	250.602	227.122	103.310	739.462	385.073	−4.571
4500	28.157	251.234	227.651	106.122	740.507	377.007	−4.376
4600	28.227	251.853	228.170	108.941	741.517	368.918	−4.189
4700	28.289	252.461	228.681	111.767	742.491	360.808	−4.010
4800	28.343	253.057	229.182	114.599	743.431	352.677	−3.838
4900	28.390	253.642	229.676	117.435	744.339	344.527	−3.673
5000	28.430	254.216	230.161	120.276	745.215	336.358	−3.514
5100	28.464	254.779	230.638	123.121	746.061	328.173	−3.361
5200	28.493	255.332	231.107	125.969	746.879	319.971	−3.214
5300	28.516	255.875	231.570	128.819	747.669	311.753	−3.073
5400	28.535	256.408	232.025	131.672	748.434	303.521	−2.936
5500	28.550	256.932	232.473	134.526	749.175	295.275	−2.804
5600	28.561	257.447	232.914	137.382	749.893	287.016	−2.677
5700	28.569	257.952	233.349	140.238	750.589	278.744	−2.554
5800	28.575	258.449	233.778	143.096	751.266	270.460	−2.436
5900	28.578	258.938	234.200	145.953	751.925	262.165	−2.321
6000	28.579	259.418	234.616	148.811	752.566	253.858	−2.210

PREVIOUS: June 1979 (1 atm) CURRENT: March 1984 (1 bar)

EA(Ti, g) = 0.079 ± 0.014 eV
$S°(298.15\ K)$ = 183.715 ± 0.001 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 463.3 ± 4 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [459.833] $kJ·mol^{-1}$

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_3$	0	4
$^4F_{5/2}$	72	6
$^4F_{7/2}$	171	8
$^4F_{9/2}$	295	10

Enthalpy of Formation

$\Delta_f H°(Ti^-, g, 0\ K)$ is calculated from $\Delta_f H°(Ti, g, 0\ K)$[1] using the adopted electron affinity of EA(Ti) = 0.079 ± 0.014 eV (7.622 ± 1.351 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Ti^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Ti^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(Ti, g, 0\ K)$ by using EA(Ti) with JANAF[1] enthalpies, $H°(0\ K) - H°(298.15\ K)$, for Ti^-(g), Ti(g), and e^-(ref). $\Delta_r H°(Ti^- \rightarrow Ti + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by +6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Ti^-(g) is given by Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6] The fine structure has been calculated via an isoelectronic extrapolation from a logarithmic plot[3] and is that recommended by Hotop and Lineberger.[2]

References

[1]JANAF Thermochemical Tables: Ti(g), 6–30–79; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−7.563	463.297		
100	28.077	155.897	205.362	−4.947			
200	24.629	174.264	185.851	−2.317			
250	23.533	179.634	184.094	−1.115			
298.15	22.835	183.715	183.715	0.	459.833	420.484	−73.667
300	22.813	183.856	183.715	0.042	459.790	420.240	−73.170
350	22.330	187.334	183.991	1.170	458.591	413.742	−61.748
400	21.995	190.293	184.598	2.278	457.333	407.420	−53.204
450	21.756	192.869	185.377	3.371	456.030	401.259	−46.577
500	21.580	195.151	186.243	4.454	454.691	395.245	−41.291
600	21.344	199.063	188.064	6.600	451.932	383.613	−33.396
700	21.199	202.342	189.876	8.726	449.092	372.450	−27.793
800	21.103	205.166	191.615	10.841	446.203	361.698	−23.616
900	21.037	207.647	193.261	12.948	443.241	351.311	−20.390
1000	20.990	209.861	194.812	15.049	440.142	341.261	−17.826
1100	20.955	211.860	196.273	17.146	436.846	331.531	−15.743
1200	20.928	213.682	197.649	19.240	429.366	322.230	−14.026
1300	20.907	215.356	198.947	21.332	426.399	313.422	−12.593
1400	20.890	216.905	200.175	23.422	423.351	304.845	−11.374
1500	20.877	218.346	201.339	25.510	420.211	296.489	−10.325
1600	20.866	219.693	202.445	27.597	416.965	288.346	−9.414
1700	20.857	220.958	203.497	29.683	413.600	280.410	−8.616
1800	20.849	222.150	204.500	31.769	410.103	272.676	−7.913
1900	20.843	223.277	205.459	33.853	406.461	265.139	−7.289
2000	20.837	224.346	206.377	35.937	387.974	258.253	−6.745
2100	20.832	225.362	207.257	38.021	383.255	251.883	−6.265
2200	20.828	226.331	208.102	40.104	378.536	245.737	−5.835
2300	20.825	227.257	208.915	42.186	373.816	239.807	−5.446
2400	20.821	228.143	209.698	44.269	369.096	234.082	−5.095
2500	20.819	228.993	210.453	46.351	364.376	228.553	−4.775
2600	20.816	229.810	211.182	48.432	359.655	223.213	−4.484
2700	20.814	230.595	211.886	50.514	354.934	218.055	−4.219
2800	20.812	231.352	212.568	52.595	350.213	213.072	−3.975
2900	20.810	232.082	213.228	54.676	345.492	208.257	−3.751
3000	20.809	232.788	213.869	56.757	340.770	203.605	−3.545
3100	20.807	233.470	214.490	58.838	336.049	199.111	−3.355
3200	20.806	234.131	215.094	60.919	331.327	194.769	−3.179
3300	20.805	234.771	215.680	62.999	326.605	190.575	−3.017
3400	20.804	235.392	216.251	65.080	321.884	186.523	−2.866
3500	20.803	235.995	216.806	67.160	317.162	182.611	−2.725
3600	20.802	236.581	217.348	69.240	312.439	178.834	−2.595
3700	20.801	237.151	217.875	71.320	−101.381	182.976	−2.583
3800	20.800	237.706	218.390	73.400	−104.869	190.708	−2.621
3900	20.799	238.246	218.892	75.480	−108.413	198.532	−2.659
4000	20.799	238.773	219.382	77.560	−112.010	206.448	−2.696
4100	20.798	239.286	219.862	79.640	−115.660	214.455	−2.732
4200	20.798	239.787	220.330	81.720	−119.362	222.551	−2.768
4300	20.797	240.277	220.788	83.800	−123.112	230.736	−2.803
4400	20.797	240.755	221.237	85.879	−126.910	239.009	−2.837
4500	20.796	241.222	221.676	87.959	−130.754	247.368	−2.871
4600	20.796	241.679	222.106	90.038	−134.642	255.814	−2.905
4700	20.795	242.126	222.527	92.118	−138.571	264.344	−2.938
4800	20.795	242.564	222.940	94.197	−142.540	272.959	−2.970
4900	20.794	242.993	223.345	96.277	−146.547	281.656	−3.002
5000	20.794	243.413	223.742	98.356	−150.590	290.436	−3.034
5100	20.794	243.825	224.132	100.436	−154.666	299.297	−3.065
5200	20.794	244.229	224.514	102.515	−158.774	308.238	−3.096
5300	20.793	244.625	224.890	104.594	−162.912	317.259	−3.127
5400	20.793	245.013	225.259	106.674	−167.077	326.357	−3.157
5500	20.793	245.395	225.622	108.753	−171.269	335.534	−3.187
5600	20.792	245.770	225.978	110.832	−175.485	344.786	−3.216
5700	20.792	246.138	226.329	112.912	−179.722	354.114	−3.245
5800	20.792	246.499	226.673	114.991	−183.981	363.517	−3.274
5900	20.792	246.855	227.012	117.070	−188.258	372.993	−3.302
6000	20.792	247.204	227.346	119.149	−192.552	382.542	−3.330

PREVIOUS: June 1979 (1 atm) CURRENT: March 1984 (1 bar)

Continued from page 1908

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REFERENCE STATE

0	to 2190	K	crystal
2190	to 3690.080	K	liquid
above	3690.080	K	ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹·mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.640	0.	0.	0.
100	13.119	7.185	48.695	−4.151	0.	0.	0.
200	21.876	19.558	31.133	−2.315	0.	0.	0.
298.15	24.896	28.936	28.936	0.	0.	0.	0.
300	24.928	29.090	28.936	0.046	0.	0.	0.
400	26.234	36.459	29.932	2.611	0.	0.	0.
500	26.945	42.392	31.850	5.271	0.	0.	0.
600	27.489	47.353	34.032	7.993	0.	0.	0.
700	28.033	51.630	36.247	10.768	0.	0.	0.
800	28.660	55.413	38.411	13.602	0.	0.	0.
900	29.372	58.830	40.493	16.504	0.	0.	0.
1000	30.083	61.961	42.485	19.476	0.	0.	0.
1100	30.878	64.864	44.389	22.523	0.	0.	0.
1200	31.798	67.590	46.210	25.656	0.	0.	0.
1300	32.740	70.172	47.955	28.882	0.	0.	0.
1400	33.807	72.638	49.630	32.210	0.	0.	0.
1500	34.811	75.004	51.244	35.640	0.	0.	0.
1600	35.857	77.283	52.800	39.173	0.	0.	0.
1700	37.028	79.492	54.306	42.817	0.	0.	0.
1800	38.200	81.641	55.765	46.577	0.	0.	0.
1900	39.539	83.742	57.182	50.464	0.	0.	0.
2000	40.920	85.805	58.562	54.485	0.	0.	0.
2100	42.468	87.837	59.908	58.652	0.	0.	0.
2190.000	44.141	89.653	61.093	62.547	CRYSTAL <--> LIQUID TRANSITION		
2190.000	46.204	100.085	61.093	85.392			
2200	46.204	100.295	61.271	85.854	0.	0.	0.
2300	46.204	102.349	63.012	90.474	0.	0.	0.
2400	46.204	104.315	64.693	95.095	0.	0.	0.
2500	46.204	106.202	66.316	99.715	0.	0.	0.
2600	46.204	108.014	67.885	104.335	0.	0.	0.
2700	46.204	109.757	69.403	108.956	0.	0.	0.
2800	46.204	111.438	70.875	113.576	0.	0.	0.
2900	46.204	113.059	72.302	118.197	0.	0.	0.
3000	46.204	114.626	73.687	122.817	0.	0.	0.
3100	46.204	116.141	75.032	127.437	0.	0.	0.
3200	46.204	117.607	76.339	132.058	0.	0.	0.
3300	46.204	119.029	77.612	136.678	0.	0.	0.
3400	46.204	120.409	78.850	141.299	0.	0.	0.
3500	46.204	121.748	80.057	145.919	0.	0.	0.
3600	46.204	123.049	81.233	150.539	0.	0.	0.
3690.080	46.204	124.191	82.268	154.701	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
3690.080	29.042	245.321	82.268	601.678			
3700	29.090	245.399	82.705	601.967	0.	0.	0.
3800	29.591	246.181	86.997	604.901	0.	0.	0.
3900	30.105	246.956	91.088	607.885	0.	0.	0.
4000	30.631	247.725	94.995	610.922	0.	0.	0.
4100	31.166	248.488	98.729	614.012	0.	0.	0.
4200	31.710	249.246	102.304	617.156	0.	0.	0.
4300	32.260	249.998	105.730	620.354	0.	0.	0.
4400	32.817	250.746	109.017	623.608	0.	0.	0.
4500	33.379	251.490	112.175	626.918	0.	0.	0.
4600	33.946	252.230	115.211	630.284	0.	0.	0.
4700	34.517	252.966	118.135	633.707	0.	0.	0.
4800	35.093	253.699	120.951	637.187	0.	0.	0.
4900	35.672	254.428	123.668	640.726	0.	0.	0.
5000	36.255	255.155	126.290	644.322	0.	0.	0.
5100	36.843	255.878	128.824	647.977	0.	0.	0.
5200	37.435	256.600	131.274	651.691	0.	0.	0.
5300	38.031	257.318	133.646	655.464	0.	0.	0.
5400	38.632	258.035	135.943	659.297	0.	0.	0.
5500	39.238	258.749	138.169	663.190	0.	0.	0.
5600	39.849	259.462	140.329	667.144	0.	0.	0.
5700	40.465	260.172	142.425	671.160	0.	0.	0.
5800	41.087	260.881	144.461	675.237	0.	0.	0.
5900	41.712	261.589	146.440	679.376	0.	0.	0.
6000	42.343	262.295	148.365	683.579	0.	0.	0.

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

$S°(298.15\ K) = 28.936 \pm 0.42\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 2190 \pm 20\ K$

$\Delta_f H° = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 22.84 \pm 6.28\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The heat capacity values for temperatures below 10 K are those chosen by Hultgren *et al.*[1] A graphical integration yeilds $S°(10\ K) = 0.0253\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(10\ K) - H°(0\ K) = 0.147\ cal \cdot mol^{-1}$. The adopted heat capacity values for $10 \leq T \leq 320$ K are obtained graphically, based on the following three works.

Source	Year	T/K	Purity of Vanadium
[2]	1936	54–297	reported ≥ 99.5%
[3]	1960	10–274	99.5%; remainder oxygen
[4]	1961	25–340	99.8%; metallic impurities <0.08%

The low temperature ($T < 50$ K) results of Clusius *et al.*[3] do not join smoothly with the values adopted for $T < 10$ K. This mismatch is in part due to the oxygen impurity in the vanadium sample used by Clusius *et al.*[3] In order to effect a smooth joining of the C_{pd} values, a graphical representation of C_p(lattice)/T^3 versus T for the Hultgren *et al.*[1] data and the Clusius *et al.*[3] data was used to derive adjusted $C_p°$ values. The three data sets[2–4] are in reasonably good agreement; two sets[2,4] lie predominantly above the adopted values while the remaining set[3] lies below. Above 100 K, the three data sets differ from the adopted $C_p°$ values by roughly 1%, with the difference decreasing as T increases.

For the region $320 \leq T \leq 2190$, there are four works upon which the adopted $C_p°$ values are based.

Source	Year	Method	T/K	Purity of Vandadium
[5]	1965	$C_p°$	320–1800	99.74%
[6]	1934	drop	565–1928	reported as "purest"
[7]	1962	drop	488–1486	0.1%C, 0.07, 0.03%N
[8]	1971	levitation	1989–2284	0.06% total impurities

The heat capacity values reported by Kohlhaas *et al.*[5] are 1–2% lower than the adopted values below 950 K; 0.3% higher in the region 950–1300 K; and 7% lower above 1600 K. The results of Golutvin and Kozlowskaya[7] show considerable scatter and lie roughly 2–10% above the tabulated enthalpy values. The enthalpy data of Jaeger and Veenstra[6] do not join smoothly with that of Berezin *et al.*[8] In the region 1500–2000 K the adopted enthalpy values are a compromise between the latter two sets of data. Below roughly 1100 K the adopted enthalpy and that reported by Jaeger and Veenstra[6] differ at most by ±15 $cal \cdot mol^{-1}$. From 1300–1800 K the difference increases from 70 $cal \cdot mol^{-1}$ to 308 $cal \cdot mol^{-1}$ or from 1.0% to 2.6%. The enthalpy at 2190 K (T_{fus}) is very close to that which is obtained from a linear fit of the Berezin *et al.*[8] data. Whereas the two sets of data[6,8] separately indicate a $C_p°$ value near T_{fus} to be at least 11 $cal \cdot K^{-1} \cdot mol^{-1}$, the compromise yields 10.5 $cal \cdot K^{-1} \cdot mol^{-1}$.

Fusion Data

Refer to the liquid for details.

Tansition Data

The literature indicates differences in opinion as to the possibility of a transition in the region 175–325 K and near 1825 K. Although there are no detailed enthalpy measurements in the 1825 K region, Barnes[9] used field–electron emission techniques to show that an allotropic trnsformation does not occur in vanadium in this region if the samples are of high purity. Earlier work concerning a possible transition in this regilon was referenced by Barnes.[9]

Documentation exists in the literature as to the observation of anomalies in the temperature dependence of some physical properties of vanadium in the range 175–325 K. Although the anomaly was attributed by different workers to an antiferromagnetic transition, a small distortion of the body–centered cubic crystal structure, and impurities, Kinkel' *et al.*[10] recently ascribed the anomaly to a second order phase transition at 230 K. Using low temperature x–ray diffraction techniques in the study of a single crystal of vanadium, Kinkel' *et al.*[10] observed a decrease in crystal lattice symmetry form body–centered cubic ($T > 230$ K) to tetragonal ($T < 230$ K). Nevertheless, Crangle and Smith[11] measured the specific heat of polycrystalline vanadium and confirmed the results of Clusius *et al.*[3] that no appreciable anomaly in $C_p°$ exists in vanadium between 175 and 265 K. We do not adopt a ΔC_p or $\Delta_t H$ value in the two previously mentioned regions.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$ (J·K⁻¹·mol⁻¹)	$S° - [G° - H°(T_r)]/T$ (J·K⁻¹·mol⁻¹)	$H° - H°(T_r)$ (kJ·mol⁻¹)	$\Delta_f H°$ (kJ·mol⁻¹)	$\Delta_f G°$ (kJ·mol⁻¹)	log K_f
0	0.	0.	INFINITE	−4.640	0.	0.	0.
100	13.119	7.185	48.695	−4.151	0.	0.	0.
200	21.876	19.558	31.133	−2.315	0.	0.	0.
250	23.703	24.655	29.340	−1.171	0.	0.	0.
298.15	24.896	28.936	28.936	0.	0.	0.	0.
300	24.928	29.090	28.936	0.046	0.	0.	0.
350	25.681	32.992	29.243	1.312	0.	0.	0.
400	26.234	36.459	29.932	2.611	0.	0.	0.
450	26.610	39.571	30.833	3.932	0.	0.	0.
500	26.945	42.392	31.850	5.271	0.	0.	0.
600	27.489	47.353	34.032	7.993	0.	0.	0.
700	28.033	51.630	36.247	10.768	0.	0.	0.
800	28.660	55.413	38.411	13.602	0.	0.	0.
900	29.372	58.830	40.493	16.504	0.	0.	0.
1000	30.083	61.961	42.485	19.476	0.	0.	0.
1100	30.878	64.864	44.389	22.523	0.	0.	0.
1200	31.798	67.590	46.210	25.656	0.	0.	0.
1300	32.740	70.172	47.955	28.882	0.	0.	0.
1400	33.807	72.638	49.630	32.210	0.	0.	0.
1500	34.811	75.004	51.244	35.640	0.	0.	0.
1600	35.857	77.283	52.800	39.173	0.	0.	0.
1700	37.028	79.492	54.306	42.817	0.	0.	0.
1800	38.200	81.641	55.765	46.577	0.	0.	0.
1900	39.539	83.742	57.182	50.464	0.	0.	0.
2000	40.920	85.805	58.562	54.485	0.	0.	0.
2100	42.468	87.837	59.908	58.652	0.	0.	0.
2190.000	44.141	89.653	61.093	62.547	--- CRYSTAL <--> LIQUID ---		
2200	44.329	89.856	61.223	62.991	−22.863	0.104	−0.002
2300	46.254	91.869	62.512	67.520	−22.954	1.151	−0.026
2400	48.179	93.878	63.777	72.242	−22.853	2.198	−0.048
2500	50.103	95.884	65.021	77.156	−22.559	3.236	−0.068
2600	52.028	97.886	66.247	82.263	−22.073	4.259	−0.086
2700	53.932	99.886	67.456	87.561	−21.395	5.259	−0.102

PREVIOUS: CURRENT: June 1973

Continued on page 1924

$S°(298.15\ K)$ = [36.136] $J·K^{-1}·mol^{-1}$
T_{fus} = 2190 ± 20 K

$\Delta_f H°(298.15\ K)$ = [17.288] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 22.84 ± 6.28 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of V(l) at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy $H°(2190)–H°(298.15\ K)$, between the crystal and liquid. Refer to V(g) table for an additional $\Delta_f H°(298.15\ K)$ value as derived from effusion–mass spectrometric work.[10]

Heat Capacity and Entropy

Enthalpy data in the liquid phase have been reported by Treverton and Margrave[1] and Berezin *et al.*[2] Using levitation calorimetry, Treverton and Margrave[1] determined the enthalpy of V(l) in the range 2205–2638 K. They reported a least squares analysis of the enthalpy data in the form $H°(T)–H°(298.15\ K)$ = 11.6527T – 5837.7 where T is in Kelvins and the enthalpy difference is in $cal·mol^{-1}$. The standard deviation of the experimental points from the calculated values was ± 167 $cal·mol^{-1}$. Berezin *et al.*[2] also used a form of levitation calorimetry and measured enthalpies in the region 1990–2325 K. For the liquid region their data were represented by $H°(T)–H°(298.15\ K)$ = 11.043T − 3776, with a standard deviation of ±90 $cal·mol^{-1}$. These two works agree remarkably well for the $C_p°$ value of V(l). In the measured enthalpy region, the Treverton and Margrave data[1] lie lower than the Berezin *et al.* data[2] by roughly 600–700 $cal·mol^{-1}$. The two linear representations of the data intersect at 3380 K. We adopt the enthalpy values of Berezin *et al.*[2] since this work contains enthalpy data surrounding the melting point and a T_{fus} value which is our adopted value.

Fusion Data

The adopted value of the enthalpy of fusion, $\Delta_{fus}H°$ = 5.46 ± 1.50 $kcal·mol^{-1}$ is based on the work by Berezin *et al.*[2] The actual value is calculated by taking the difference in the adopted value of $H°(2190) – H°(298.15\ K)$ for V(l) and V(cr). Refer to the heat capacity discussion in the tables for V(cr) and V(l).

Preliminary results of experiments by Berezin *et al.*[2] indicated that T_{fus} for 99.96% pure vanadium was close to 2190 K. Representative values of T_{fus} reported in the literature are tabulated below.

Source	Purity of V	T_{fus}, K
[3]	0.33% O, 0.078% N 0.15% of 7 other impurities	2161 ± 10
[4]	99.8–99.9%	2192 ± 2
[5]	purity not given	2223
[6]	purified by electron zone fusion 99.8%	2173 ± 25
[7]	purity not given	2193

We adopt T_{fus} = 2190 ± 20 K principally since it is consistent with the work upon which $\Delta_{fus}H°$ is based. The adopted T_{fus} value is also suggested by Charlesworth[8] in his compilation of elemental melting points.

Vaporization Data

The vaporization of V(l) was studied by Farber and Srivastava.[10] Refer to V(g) table for details. Kant and Lin,[9] using a combination of effusion and mass-spectrometric techniques, reported the ratio of observed ion intensities relating to V_2(g) and V(g) and corresponding to the vaporization of vanadium in the range 2060–2316 K. This ratio is of the order of 10^{-6} which suggests that at least in this region the contribution of V_2(g) in the vapor phase may be neglected. Linearly extrapolating these data to T_{vap}, the V_2 partial pressure is of the order of 10^5 smaller than the V partial pressure.

T_{vap} is calculated as the temperature at which the Gibbs energy change for the reaction V(l) → V(g) is zero. The difference between $\Delta_f H°$(V, g) and $\Delta_f H°$(V, l) at T_{vap} is $\Delta_{vap}H°$. The uncertainty in T_{vap} is probably of the order of ±50 K.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
		$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$		
0							
100							
200							
250							
298.15	24.896	36.136	36.136	0.	17.288	15.141	−2.653
300	24.928	36.290	36.137	0.046	17.288	15.128	−2.634
350	25.681	40.192	36.443	1.312	17.288	14.768	−2.204
400	26.234	43.659	37.132	2.611	17.288	14.408	−1.881
450	26.610	46.771	38.033	3.932	17.288	14.048	−1.631
500	26.945	49.592	39.050	5.271	17.288	13.688	−1.430
600	27.489	54.553	41.232	7.993	17.288	12.968	−1.129
700	28.033	58.830	43.447	10.768	17.288	12.248	−0.914
800	28.660	62.613	45.611	13.602	17.288	11.528	−0.753
900	29.372	66.030	47.693	16.504	17.288	10.808	−0.627
1000	30.083	69.161	49.685	19.476	17.288	10.088	−0.527
1100	30.878	72.064	51.589	22.523	17.288	9.368	−0.445
1200	31.798	74.790	53.410	25.656	17.288	8.648	−0.376
1300	32.740	77.372	55.155	28.882	17.288	7.928	−0.319
1400	33.807	79.838	56.831	32.210	17.288	7.208	−0.269
1450.000	34.304	81.033	57.645	33.913	GLASS <--> LIQUID TRANSITION		
1450.000	46.204	81.033	57.645	33.913			
1500	46.204	82.599	58.451	36.223	17.871	6.478	−0.226
1600	46.204	85.581	60.054	40.844	18.959	5.682	−0.185
1700	46.204	88.382	61.639	45.464	19.935	4.822	−0.148
1800	46.204	91.023	63.199	50.084	20.795	3.907	−0.113
1900	46.204	93.521	64.729	54.705	21.529	2.948	−0.081
2000	46.204	95.891	66.229	59.325	22.128	1.954	−0.051
2100	46.204	98.146	67.695	63.946	22.582	0.934	−0.023
2190.000	46.204	100.085	68.987	68.104	--- CRYSTAL <--> LIQUID ---		
2200	46.204	100.295	69.129	68.566	0.	0.	0.
2300	46.204	102.349	70.529	73.186	0.	0.	0.
2400	46.204	104.315	71.896	77.807	0.	0.	0.
2500	46.204	106.202	73.231	82.427	0.	0.	0.
2600	46.204	108.014	74.534	87.048	0.	0.	0.
2700	46.204	109.757	75.806	91.668	0.	0.	0.
2800	46.204	111.438	77.049	96.288	0.	0.	0.
2900	46.204	113.059	78.263	100.909	0.	0.	0.
3000	46.204	114.626	79.449	105.529	0.	0.	0.
3100	46.204	116.141	80.608	110.150	0.	0.	0.
3200	46.204	117.607	81.742	114.770	0.	0.	0.
3300	46.204	119.029	82.850	119.390	0.	0.	0.
3400	46.204	120.409	83.935	124.011	0.	0.	0.
3500	46.204	121.748	84.996	128.631	0.	0.	0.
3600	46.204	123.049	86.035	133.251	0.	0.	0.
3690.080	46.204	124.191	86.953	137.414	----- FUGACITY = 1 bar -----		
3700	46.204	124.315	87.053	137.872	−446.807	1.201	−0.017
3800	46.204	125.548	88.050	142.492	−445.120	13.286	−0.183
3900	46.204	126.748	89.027	147.113	−443.485	25.328	−0.339
4000	46.204	127.918	89.984	151.733	−441.901	37.329	−0.487
4100	46.204	129.058	90.923	156.353	−440.370	49.290	−0.628
4200	46.204	130.172	91.845	160.974	−438.894	61.216	−0.761
4300	46.204	131.259	92.749	165.594	−437.472	73.106	−0.888
4400	46.204	132.321	93.636	170.215	−436.105	84.964	−1.009
4500	46.204	133.360	94.507	174.835	−434.795	96.792	−1.124

PREVIOUS: CURRENT: June 1973

CRYSTAL-LIQUID

0	to	2190	K crystal
above		2190	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = p° = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	C_p°	S°	$-[G^\circ-H^\circ(T_r)]/T$	$H^\circ-H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−4.640	0.	0.	0.
100	13.119	7.185	48.695	−4.151	0.	0.	0.
200	21.876	19.558	31.133	−2.315	0.	0.	0.
250	23.703	24.655	29.340	−1.171	0.	0.	0.
298.15	24.896	28.936	28.936	0.	0.	0.	0.
300	24.928	29.090	28.936	0.046	0.	0.	0.
350	25.681	32.992	29.243	1.312	0.	0.	0.
400	26.234	36.459	29.932	2.611	0.	0.	0.
450	26.610	39.571	30.833	3.932	0.	0.	0.
500	26.945	42.392	31.850	5.271	0.	0.	0.
600	27.489	47.353	34.032	7.993	0.	0.	0.
700	28.033	51.630	36.247	10.768	0.	0.	0.
800	28.660	55.413	38.411	13.602	0.	0.	0.
900	29.372	58.830	40.493	16.504	0.	0.	0.
1000	30.083	61.961	42.485	19.476	0.	0.	0.
1100	30.878	64.864	44.389	22.523	0.	0.	0.
1200	31.798	67.590	46.210	25.656	0.	0.	0.
1300	32.740	70.172	47.955	28.882	0.	0.	0.
1400	33.807	72.638	49.630	32.210	0.	0.	0.
1500	34.811	75.004	51.244	35.640	0.	0.	0.
1600	35.857	77.283	52.800	39.173	0.	0.	0.
1700	37.028	79.492	54.306	42.817	0.	0.	0.
1800	38.200	81.641	55.765	46.577	0.	0.	0.
1900	39.539	83.742	57.182	50.464	0.	0.	0.
2000	40.920	85.805	58.562	54.485	0.	0.	0.
2100	42.468	87.837	59.908	58.652	0.	0.	0.
2190.000	44.141	89.653	61.093	62.547	CRYSTAL <--> LIQUID TRANSITION		
2190.000	46.204	100.085	61.093	85.392			
2200	46.204	100.295	61.271	85.854	0.	0.	0.
2300	46.204	102.349	63.012	90.474	0.	0.	0.
2400	46.204	104.315	64.693	95.095	0.	0.	0.
2500	46.204	106.202	66.316	99.715	0.	0.	0.
2600	46.204	108.014	67.885	104.335	0.	0.	0.
2700	46.204	109.757	69.403	108.956	0.	0.	0.
2800	46.204	111.438	70.875	113.576	0.	0.	0.
2900	46.204	113.059	72.302	118.197	0.	0.	0.
3000	46.204	114.626	73.687	122.817	0.	0.	0.
3100	46.204	116.141	75.032	127.437	0.	0.	0.
3200	46.204	117.607	76.339	132.058	0.	0.	0.
3300	46.204	119.029	77.612	136.678	0.	0.	0.
3400	46.204	120.409	78.850	141.299	0.	0.	0.
3500	46.204	121.748	80.057	145.919	0.	0.	0.
3600	46.204	123.049	81.233	150.539	0.	0.	0.
3690.080	46.204	124.191	82.268	154.701	FUGACITY = 1 bar		
3700	46.204	124.315	82.380	155.160	−446.807	1.201	−0.017
3800	46.204	125.548	83.500	159.780	−445.120	13.286	−0.183
3900	46.204	126.748	84.594	164.401	−443.485	25.328	−0.339
4000	46.204	127.918	85.662	169.021	−441.901	37.329	−0.487
4100	46.204	129.058	86.707	173.641	−440.370	49.291	−0.628
4200	46.204	130.172	87.729	178.262	−438.894	61.216	−0.761
4300	46.204	131.259	88.728	182.882	−437.472	73.106	−0.888
4400	46.204	132.321	89.707	187.503	−436.105	84.964	−1.009
4500	46.204	133.360	90.666	192.123	−434.795	96.792	−1.124

PREVIOUS: CURRENT: June 1973

IP(V, g) = 54360 ± 16 cm^{-1}
$S°$(298.15 K) = 182.30 ± 0.8 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 512.2 ± 8 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = 515.5 ± 8 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{3/2}$	0	4
$^4F_{5/2}$	137.38	6
$^4F_{7/2}$	323.42	8
$^4F_{9/2}$	553.02	10
.	.	.
.	.	.
.	.	.
$^2H_{11/2}$	54251.26	12
IP	54360	

Enthalpy of Formation

The vapor pressure over vanadium was measured by Edwards *et al.*[1] using the Knudsen method and by Farber and Srivastava[6] using effusion–mass spectrometric techniques. Our 2nd and 3rd law analysis is tabulated below, where reaction (A) refers to the sublimation V(cr) = V(g) and reaction (B), the vaporization V(l) = V(g).

Source	Reaction	Data Points	T/K	$\Delta_r H°$(298.15 K), kcal·mol^{-1} 2nd law	3rd law	Drift cal·K^{-1}·mol^{-1}
1	A	12+	1666–1882	121.67 ± 0.99	122.95	0.72 ± 0.55
6	A	7	1900–2155	121.60 ± 1.48	123.45	0.91 ± 0.73
6	B	6	2198–2412	113.04 ± 5.34	119.18	2.65 ± 2.30

*A statistical test discounted the 1766 K data point.

We adopt $\Delta_f H°$(298.15 K) = 123.2 kcal·mol^{-1} for V(g). This value, which is identical to $\Delta_{sub} H°$(298.15 K), is a median of the two sublimation studies. Hultgren *et al.*[2] reported a 3rd law value of 123.089 ± 0.250 kcal·mol^{-1} based on a Knudsen vapor pressure study in the range 1771–1880 K by Saxer.[3] This result is consistent with our adopted value.

The results of Kant and Lin[5] indicated that the partial pressure of V_2(g) is negligible in the temperature ranges studied above.

Heat Capacity and Entropy

The electronic energy levels and quantum weights are obtained from Moore.[4] Only a few of the levels are listed above. All levels reported by Moore[4] are considered in the calculation. The heat capacity and entropy values are very similar to those adopted by Hultgren *et al.*,[2] being identical at 298.15 K and differing by 0.045 cal·K^{-1}·mol^{-1} in $C_p°$ at 3800 K. There are predicted levels which have not been observed and/or classified. It is not expected that $S°$(298.15 K) would be affected by the missing states, but that in the range 3000–6000 K, an error of 0.2–0.3 cal·K^{-1}·mol^{-1} might result.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$ (J·K^{-1}·mol^{-1})	$S°$ (J·K^{-1}·mol^{-1})	$-[G°-H°(T_r)]/T$ (J·K^{-1}·mol^{-1})	$H°-H°(T_r)$ (kJ·mol^{-1})	$\Delta_f H°$ (kJ·mol^{-1})	$\Delta_f G°$ (kJ·mol^{-1})	log K_f
0	0.	0.	INFINITE	−7.907	512.201	512.201	INFINITE
100	28.040	151.831	206.684	−5.485	514.134	499.670	−261.001
200	27.960	171.498	184.740	−2.649	515.135	484.747	−126.603
250	26.963	177.633	182.732	−1.275	515.365	477.121	−99.689
298.15	26.012	182.298	182.298	0.	515.469	469.744	−82.297
300	25.978	182.459	182.299	0.048	515.471	469.460	−81.740
350	25.191	186.402	182.612	1.326	515.483	461.790	−68.918
400	24.647	189.727	183.299	2.571	515.430	454.122	−59.302
450	24.330	192.610	184.177	3.795	515.332	446.464	−51.824
500	24.196	195.165	185.150	5.007	515.205	438.819	−45.843
600	24.283	199.579	187.198	7.428	514.905	423.569	−36.875
700	24.582	203.343	189.242	9.871	514.572	408.372	−30.473
800	24.890	206.647	191.215	12.345	514.212	393.225	−25.675
900	25.117	209.592	193.097	14.846	513.811	378.125	−21.946
1000	25.237	212.246	194.881	17.365	513.358	363.073	−18.965
1100	25.262	214.653	196.571	19.890	512.837	348.069	−16.528
1200	25.214	216.849	198.171	22.415	512.227	333.116	−14.500
1300	25.117	218.864	199.686	24.931	511.518	318.218	−12.786
1400	24.994	220.721	201.123	27.437	510.696	303.379	−11.319
1500	24.864	222.441	202.488	29.930	509.758	288.603	−10.050
1600	24.739	224.042	203.785	32.410	508.706	273.893	−8.942
1700	24.630	225.538	205.021	34.878	507.530	259.252	−7.966
1800	24.545	226.943	206.201	37.337	506.229	244.685	−7.101
1900	24.487	228.269	207.327	39.788	504.793	230.193	−6.328
2000	24.460	229.524	208.406	42.235	503.219	215.781	−5.636
2100	24.467	230.717	209.440	44.682	501.498	201.450	−5.011
2200	24.510	231.856	210.434	47.130	476.745	187.310	−4.447
2300	24.588	232.948	211.389	49.585	474.579	174.203	−3.956
2400	24.702	233.996	212.309	52.049	472.423	161.189	−3.508
2500	24.853	235.008	213.197	54.526	470.280	148.265	−3.098
2600	25.040	235.986	214.055	57.021	468.154	135.426	−2.721
2700	25.261	236.935	214.885	59.535	466.048	122.669	−2.373
2800	25.517	237.858	215.689	62.074	463.967	109.990	−2.052
2900	25.806	238.758	216.469	64.640	461.912	97.384	−1.754
3000	26.127	239.639	217.227	67.236	459.888	84.849	−1.477
3100	26.477	240.501	217.963	69.866	457.898	72.380	−1.220
3200	26.855	241.348	218.681	72.533	455.944	59.975	−0.979
3300	27.259	242.180	219.381	75.238	454.029	47.631	−0.754
3400	27.687	243.000	220.063	77.985	452.156	35.344	−0.543
3500	28.136	243.809	220.730	80.776	450.326	23.112	−0.345
3600	28.605	244.608	221.382	83.613	448.543	10.931	−0.159
3690.080	29.042	245.321	221.958	86.210	----- FUGACITY = 1 bar -----		
3700	29.090	245.399	222.021	86.498	0.	0.	0.
3800	29.591	246.181	222.646	89.432	0.	0.	0.
3900	30.105	246.956	223.260	92.417	0.	0.	0.
4000	30.631	247.725	223.862	95.453	0.	0.	0.
4100	31.166	248.488	224.453	98.543	0.	0.	0.
4200	31.710	249.246	225.034	101.687	0.	0.	0.
4300	32.260	249.998	225.606	104.885	0.	0.	0.
4400	32.817	250.746	226.169	108.139	0.	0.	0.
4500	33.379	251.490	226.723	111.449	0.	0.	0.
4600	33.946	252.230	227.270	114.815	0.	0.	0.
4700	34.517	252.966	227.809	118.238	0.	0.	0.
4800	35.093	253.699	228.341	121.719	0.	0.	0.
4900	35.672	254.428	228.866	125.257	0.	0.	0.
5000	36.255	255.155	229.384	128.853	0.	0.	0.
5100	36.843	255.878	229.896	132.508	0.	0.	0.
5200	37.435	256.600	230.403	136.222	0.	0.	0.
5300	38.031	257.318	230.904	139.995	0.	0.	0.
5400	38.632	258.035	231.400	143.828	0.	0.	0.
5500	39.238	258.749	231.891	147.721	0.	0.	0.
5600	39.849	259.462	232.377	151.675	0.	0.	0.
5700	40.465	260.172	232.858	155.691	0.	0.	0.
5800	41.087	260.881	233.335	159.768	0.	0.	0.
5900	41.712	261.589	233.808	163.908	0.	0.	0.
6000	42.343	262.295	234.277	168.110	0.	0.	0.

PREVIOUS: June 1973 (1 atm) CURRENT: June 1973 (1 bar)

Continued from Page 1918

Sublimation Data

Refer to the ideal gas table for details.

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REFERENCE STATE

0 to 3680 K crystal
3680 to 6000 K liquid

Refer to the individual tables for details.

T_{vap}(1 bar) ~ 5924 K
(not included in the reference state)

Enthalpy Reference Temperature = T_r = 298.15 K — Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.973	0.	0.	0.
100	16.033	9.612	52.820	−4.321	0.	0.	0.
200	22.489	23.273	34.839	−2.313	0.	0.	0.
250	23.686	28.431	33.056	−1.156	0.	0.	0.
298.15	24.295	32.660	32.660	0.	0.	0.	0.
300	24.313	32.810	32.660	0.045	0.	0.	0.
350	24.644	36.583	32.957	1.269	0.	0.	0.
400	24.928	39.893	33.622	2.509	0.	0.	0.
450	25.144	42.842	34.485	3.760	0.	0.	0.
500	25.359	45.502	35.456	5.023	0.	0.	0.
600	25.790	50.163	37.529	7.580	0.	0.	0.
700	26.229	54.172	39.627	10.181	0.	0.	0.
800	26.669	57.703	41.670	12.826	0.	0.	0.
900	27.112	60.870	43.631	15.515	0.	0.	0.
1000	27.564	63.750	45.501	18.249	0.	0.	0.
1100	28.017	66.398	47.282	21.028	0.	0.	0.
1200	28.472	68.855	48.978	23.852	0.	0.	0.
1300	28.930	71.152	50.596	26.722	0.	0.	0.
1400	29.393	73.313	52.143	29.639	0.	0.	0.
1500	29.862	75.357	53.623	32.601	0.	0.	0.
1600	30.334	77.299	55.042	35.611	0.	0.	0.
1700	30.807	79.152	56.407	38.668	0.	0.	0.
1800	31.284	80.927	57.720	41.773	0.	0.	0.
1900	31.765	82.631	58.986	44.925	0.	0.	0.
2000	32.254	84.273	60.210	48.126	0.	0.	0.
2100	32.744	85.858	61.394	51.376	0.	0.	0.
2200	33.238	87.393	62.541	54.675	0.	0.	0.
2300	33.736	88.881	63.654	58.024	0.	0.	0.
2400	34.233	90.328	64.735	61.422	0.	0.	0.
2500	34.736	91.735	65.787	64.870	0.	0.	0.
2600	35.246	93.106	66.812	68.366	0.	0.	0.
2700	36.192	94.453	67.811	71.935	0.	0.	0.
2800	37.447	95.791	68.786	75.613	0.	0.	0.
2900	39.120	97.133	69.740	79.440	0.	0.	0.
3000	41.003	98.490	70.676	83.442	0.	0.	0.
3100	43.430	99.873	71.595	87.662	0.	0.	0.
3200	46.024	101.292	72.501	92.132	0.	0.	0.
3300	48.953	102.752	73.396	96.877	0.	0.	0.
3400	52.300	104.261	74.281	101.933	0.	0.	0.
3500	56.484	105.835	75.160	107.363	0.	0.	0.
3600	61.714	107.499	76.035	113.270	0.	0.	0.
3680.000	66.149	108.904	76.734	118.383	CRYSTAL <--> LIQUID TRANSITION		
3680.000	35.564	118.522	76.734	153.780			
3700	35.564	118.715	76.961	154.491	0.	0.	0.
3800	35.564	119.663	78.072	158.048	0.	0.	0.
3900	35.564	120.587	79.150	161.604	0.	0.	0.
4000	35.564	121.488	80.197	165.161	0.	0.	0.
4100	35.564	122.366	81.215	168.717	0.	0.	0.
4200	35.564	123.223	82.205	172.273	0.	0.	0.
4300	35.564	124.060	83.169	175.830	0.	0.	0.
4400	35.564	124.877	84.108	179.386	0.	0.	0.
4500	35.564	125.676	85.023	182.943	0.	0.	0.
4600	35.564	126.458	85.915	186.499	0.	0.	0.
4700	35.564	127.223	86.786	190.055	0.	0.	0.
4800	35.564	127.972	87.636	193.612	0.	0.	0.
4900	35.564	128.705	88.467	197.168	0.	0.	0.
5000	35.564	129.423	89.279	200.725	0.	0.	0.
5100	35.564	130.128	90.073	204.281	0.	0.	0.
5200	35.564	130.818	90.850	207.837	0.	0.	0.
5300	35.564	131.496	91.610	211.394	0.	0.	0.
5400	35.564	132.161	92.355	214.950	0.	0.	0.
5500	35.564	132.813	93.085	218.507	0.	0.	0.
5600	35.564	133.454	93.800	222.063	0.	0.	0.
5700	35.564	134.083	94.501	225.619	0.	0.	0.
5800	35.564	134.702	95.189	229.176	0.	0.	0.
5900	35.564	135.310	95.864	232.732	0.	0.	0.
6000	35.564	135.908	96.526	236.289	0.	0.	0.

PREVIOUS: June 1966 (1 atm) — CURRENT: June 1966 (1 bar)

$S°(298.15\ K) = 32.660 \pm 0.10\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 3680 \pm 20\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 35.40 \pm 10.5\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

There have been several investigations of the low temperature heat capacity of tungsten; Lange[1] covered the range 26–91 K. Horowitz and Daunt[2] reported values in the range 1–77 K, while Waite *et al.*[3] worked from 4–15° and DeSorbo[4] from 15–90 K. Zwikker and Schmidt[5] covered the range from 90 to 2521 K. Clusius *et al.*[6] made a thorough study of the heat capacity in the range 12–274 K, and their measurements were adopted leading to $S°(298.15\ K) = 7.806\ cal \cdot K^{-1} \cdot mol^{-1}$ based on $S°(12.5) = 0.0088\ cal \cdot K^{-1} \cdot mol^{-1}$. This value is in disagreement with the quoted value of $7.83\ cal \cdot K^{-1} \cdot mol^{-1}$ but agrees exactly with a separate integration by Kirillin *et al.*[7] In the intermediate temperature range the adiabatic heat capacity measurements of Bronson *et al.*[8] from 253 to 773 K joined well with the low temperature measurements and were adopted. The high temperature enthalpies have been measured by several investigators from which were selected the values of Jaeger and Rosenbohm[9] from 273–1800 K; Magnus and Holzmann[10] who covered the range 373 to 1173 K; Hoch and Johnston,[11] who made measurements between 1382 and 2900 K; Kirillin *et al.*[7] who have made several determinations over the range 600 to 3100 K, and have also analysed the above data and have presented smooth functions from 0 to 3500 K. The present table agreess with that of Kirillin *et al.*[7] up to 2700 K, above this temperature the values of C_p adopted follow those reported by Novikov *et al.*[12] measured by an electric modulation method, up to the melting point. These values rise rapidly above 2700 K and are not inconsistent with the individual measurements of Kirillin *et al.*[7] at their highest temperatures.

Fusion Data

Langmuir[13] determined the melting point as 3540 K from intrinsic brilliance measurements; this was later corrected to 3655 ± 30 K by Jones *et al.*,[14] and Pirani and Alterthum[15] from pyrometer measurements on a black body hole found 3660 ± 60 K. Using the same technique Zalabak[16] reports 3680 K on a low carbon specimen. He reports a decrease of the melting point with increasing carbon content. Rudy and Windisch[17] report a melting point of 3696 ± 20 K. The value adopted is 3680 K ± 20 K. The enthalpy of melting is obtained by assuming an entropy of melting of $2.3\ cal \cdot K^{-1} \cdot mol^{-1}$ obtained from a comparison of several high melting metals (Fe, Cu, Co, Mg, Al).

Sublimation Data

Refer to the ideal gas table for details.

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Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.973	0.	0.	0.
100	16.033	9.612	52.820	−4.321	0.	0.	0.
200	22.489	23.273	34.839	−2.313	0.	0.	0.
250	23.686	28.431	33.056	−1.156	0.	0.	0.
298.15	24.295	32.660	32.660	0.	0.	0.	0.
300	24.313	32.810	32.660	0.045	0.	0.	0.
350	24.644	36.583	32.957	1.269	0.	0.	0.
400	24.928	39.893	33.622	2.509	0.	0.	0.
450	25.144	42.842	34.485	3.760	0.	0.	0.
500	25.359	45.502	35.456	5.023	0.	0.	0.
600	25.790	50.163	37.529	7.580	0.	0.	0.
700	26.229	54.172	39.627	10.181	0.	0.	0.
800	26.669	57.703	41.670	12.826	0.	0.	0.
900	27.112	60.870	43.631	15.515	0.	0.	0.
1000	27.564	63.750	45.501	18.249	0.	0.	0.
1100	28.017	66.398	47.282	21.028	0.	0.	0.
1200	28.472	68.855	48.978	23.852	0.	0.	0.
1300	28.930	71.152	50.596	26.722	0.	0.	0.
1400	29.393	73.313	52.143	29.639	0.	0.	0.
1500	29.862	75.357	53.623	32.601	0.	0.	0.
1600	30.334	77.299	55.042	35.611	0.	0.	0.
1700	30.807	79.152	56.407	38.668	0.	0.	0.
1800	31.284	80.927	57.720	41.773	0.	0.	0.
1900	31.765	82.631	58.986	44.925	0.	0.	0.
2000	32.254	84.273	60.210	48.126	0.	0.	0.
2100	32.744	85.858	61.394	51.376	0.	0.	0.
2200	33.238	87.393	62.541	54.675	0.	0.	0.
2300	33.736	88.881	63.654	58.024	0.	0.	0.
2400	34.233	90.328	64.735	61.422	0.	0.	0.
2500	34.736	91.735	65.787	64.870	0.	0.	0.
2600	35.246	93.106	66.812	68.366	0.	0.	0.
2700	36.192	94.453	67.811	71.935	0.	0.	0.
2800	37.447	95.791	68.786	75.613	0.	0.	0.
2900	39.120	97.133	69.740	79.440	0.	0.	0.
3000	41.003	98.490	70.676	83.442	0.	0.	0.
3100	43.430	99.873	71.595	87.662	0.	0.	0.
3200	46.024	101.292	72.501	92.132	0.	0.	0.
3300	48.953	102.752	73.396	96.877	0.	0.	0.
3400	52.300	104.261	74.281	101.933	0.	0.	0.
3500	56.484	105.835	75.160	107.363	0.	0.	0.
3600	61.714	107.499	76.035	113.270	0.	0.	0.
3680.000	66.149	108.904	76.734	118.383	--- CRYSTAL <--> LIQUID ---		
3700	67.205	109.265	76.909	119.716	−34.775	0.191	−0.003
3800	72.697	111.130	77.785	126.712	−31.336	1.091	−0.015
3900	78.188	113.089	78.665	134.256	−27.348	1.893	−0.025
4000	83.680	115.138	79.551	142.349	−22.811	2.587	−0.034
4100	89.171	117.272	80.445	150.992	−17.725	3.160	−0.040
4200	94.663	119.487	81.348	160.184	−12.090	3.602	−0.045
4300	100.154	121.778	82.261	169.924	−5.905	3.904	−0.047
4400	105.646	124.144	83.186	180.214	0.828	4.055	−0.048
4500	111.137	126.579	84.123	191.054	8.111	4.047	−0.047
4600	116.629	129.082	85.073	202.442	15.943	3.872	−0.044
4700	122.120	131.649	86.037	214.379	24.324	3.520	−0.039
4800	127.612	134.278	87.014	226.866	33.254	2.984	−0.032

PREVIOUS: December 1961 CURRENT: June 1966

$S°(298.15\ K)$ = [45.678] $J·K^{-1}·mol^{-1}$
T_{fus} = 3680 ± 20 K

$\Delta_f H°(298.15\ K)$ = [46.896] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 35.40 ± 10.5 $kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation at 298.15 K was calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in nthalpy, $H°(3680\ K)-H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The heat capacity was estimated as 8.5 $cal·mol^{-1}\ K^{-1}$ by analogy with other monatomic metals. The entropy at 298.15 K was calculated in manner analogous to that used for the enthalpy of formation. At 2450 K a glass transition is assumed below which the heat capacity was that of the crystal.

Fusion Data

Refer to the crystal table for details.

Vaporization Data

The boiling point and enthalpy of vaporization are calculated from the adopted functions and enthalpy of sublimation in order to maintain proper thermodynamic consistency.

Enthalpy Reference Temperature = T_r = 298.15 K						Standard State Pressure = $p°$ = 0.1 MPa	
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0							
100							
200							
250							
298.15	24.296	45.678	45.678	0.	46.896	43.015	−7.536
300	24.310	45.828	45.678	0.045	46.896	42.991	−7.485
350	24.642	49.601	45.975	1.269	46.896	42.340	−6.319
400	24.928	52.911	46.640	2.508	46.896	41.689	−5.444
450	25.144	55.859	47.503	3.760	46.896	41.038	−4.764
500	25.359	58.519	48.474	5.023	46.896	40.388	−4.219
600	25.790	63.181	50.547	7.580	46.896	39.086	−3.403
700	26.229	67.190	52.645	10.181	46.896	37.784	−2.819
800	26.669	70.721	54.688	12.826	46.896	36.482	−2.382
900	27.112	73.887	56.648	15.515	46.896	35.180	−2.042
1000	27.564	76.767	58.518	18.249	46.896	33.879	−1.770
1100	28.017	79.416	60.299	21.028	46.896	32.577	−1.547
1200	28.472	81.873	61.996	23.852	46.896	31.275	−1.361
1300	28.930	84.170	63.614	26.722	46.896	29.973	−1.204
1400	29.393	86.331	65.160	29.638	46.896	28.672	−1.070
1500	29.862	88.375	66.640	32.601	46.896	27.370	−0.953
1600	30.334	90.317	68.060	35.611	46.896	26.068	−0.851
1700	30.806	92.170	69.424	38.668	46.896	24.766	−0.761
1800	31.284	93.944	70.737	41.772	46.896	23.465	−0.681
1900	31.768	95.649	72.004	44.925	46.896	22.163	−0.609
2000	32.254	97.291	73.228	48.126	46.897	20.861	−0.545
2100	32.745	98.876	74.411	51.376	46.897	19.559	−0.487
2200	33.238	100.411	75.558	54.675	46.897	18.258	−0.433
2300	33.735	101.899	76.672	58.024	46.897	16.956	−0.385
2400	34.233	103.345	77.753	61.422	46.897	15.654	−0.341
2450.000	34.483	104.054	78.283	63.140	GLASS <--> LIQ TRANSITION		
2450.000	35.564	104.054	78.283	63.140			
2500	35.564	104.772	78.805	64.918	46.944	14.352	−0.300
2600	35.564	106.167	79.831	68.475	47.005	13.047	−0.262
2700	35.564	107.509	80.831	72.031	46.992	11.740	−0.227
2800	35.564	108.803	81.807	75.587	46.870	10.437	−0.195
2900	35.564	110.051	82.760	79.144	46.600	9.140	−0.165
3000	35.564	111.256	83.690	82.700	46.155	7.855	−0.137
3100	35.564	112.423	84.598	86.257	45.491	6.589	−0.111
3200	35.564	113.552	85.485	89.813	44.577	5.348	−0.087
3300	35.564	114.646	86.352	93.369	43.388	4.139	−0.066
3400	35.564	115.708	87.200	96.926	41.889	2.972	−0.046
3500	35.564	116.739	88.030	100.482	40.015	1.853	−0.028
3600	35.564	117.741	88.841	104.039	37.665	0.795	−0.012
3680.000	35.564	118.522	89.478	106.884	CRYSTAL <--> LIQUID		
3700	35.564	118.715	89.635	107.595	0.	0.	0.
3800	35.564	119.663	90.413	111.151	0.	0.	0.
3900	35.564	120.587	91.175	114.708	0.	0.	0.
4000	35.564	121.488	91.922	118.264	0.	0.	0.
4100	35.564	122.366	92.653	121.821	0.	0.	0.
4200	35.564	123.223	93.371	125.377	0.	0.	0.
4300	35.564	124.060	94.075	128.933	0.	0.	0.
4400	35.564	124.877	94.766	132.490	0.	0.	0.
4500	35.564	125.676	95.444	136.046	0.	0.	0.
4600	35.564	126.458	96.110	139.603	0.	0.	0.
4700	35.564	127.223	96.764	143.159	0.	0.	0.
4800	35.564	127.972	97.406	146.715	0.	0.	0.
4900	35.564	128.705	98.037	150.272	0.	0.	0.
5000	35.564	129.423	98.658	153.828	0.	0.	0.
5200	35.564	130.818	99.868	160.941	0.	0.	0.
5400	35.564	132.161	101.039	168.054	0.	0.	0.
5600	35.564	133.454	102.174	175.167	0.	0.	0.
5800	35.564	134.702	103.274	182.279	0.	0.	0.
6000	35.564	135.908	104.342	189.392	0.	0.	0.

PREVIOUS: December 1961 CURRENT: June 1966

0	to	3680	K crystal
above		3680	K liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−4.973	0.	0.	0.
100	16.033	9.612	52.820	−4.321	0.	0.	0.
200	22.489	23.273	34.839	−2.313	0.	0.	0.
250	23.686	28.431	33.056	−1.156	0.	0.	0.
298.15	24.295	32.660	32.660	0.	0.	0.	0.
300	24.313	32.810	32.660	0.045	0.	0.	0.
350	24.644	36.583	32.957	1.269	0.	0.	0.
400	24.928	39.893	33.622	2.509	0.	0.	0.
450	25.144	42.842	34.485	3.760	0.	0.	0.
500	25.359	45.502	35.456	5.023	0.	0.	0.
600	25.790	50.163	37.529	7.580	0.	0.	0.
700	26.229	54.172	39.627	10.181	0.	0.	0.
800	26.669	57.703	41.670	12.826	0.	0.	0.
900	27.112	60.870	43.631	15.515	0.	0.	0.
1000	27.564	63.750	45.501	18.249	0.	0.	0.
1100	28.017	66.398	47.282	21.028	0.	0.	0.
1200	28.472	68.855	48.978	23.852	0.	0.	0.
1300	28.930	71.152	50.596	26.722	0.	0.	0.
1400	29.393	73.313	52.143	29.639	0.	0.	0.
1500	29.862	75.357	53.623	32.601	0.	0.	0.
1600	30.334	77.299	55.042	35.611	0.	0.	0.
1700	30.807	79.152	56.407	38.668	0.	0.	0.
1800	31.284	80.927	57.720	41.773	0.	0.	0.
1900	31.765	82.631	58.986	44.925	0.	0.	0.
2000	32.254	84.273	60.210	48.126	0.	0.	0.
2100	32.744	85.858	61.394	51.376	0.	0.	0.
2200	33.238	87.393	62.541	54.675	0.	0.	0.
2300	33.736	88.881	63.654	58.024	0.	0.	0.
2400	34.233	90.328	64.735	61.422	0.	0.	0.
2500	34.736	91.735	65.787	64.870	0.	0.	0.
2600	35.246	93.106	66.812	68.366	0.	0.	0.
2700	36.192	94.453	67.811	71.935	0.	0.	0.
2800	37.447	95.791	68.786	75.613	0.	0.	0.
2900	39.120	97.133	69.740	79.440	0.	0.	0.
3000	41.003	98.490	70.676	83.442	0.	0.	0.
3100	43.430	99.873	71.595	87.662	0.	0.	0.
3200	46.024	101.292	72.501	92.132	0.	0.	0.
3300	48.953	102.752	73.396	96.877	0.	0.	0.
3400	52.300	104.261	74.281	101.933	0.	0.	0.
3500	56.484	105.835	75.160	107.363	0.	0.	0.
3600	61.714	107.499	76.035	113.270	0.	0.	0.
3680.000	66.149	108.904	76.734	118.383	CRYSTAL <--> LIQUID		
3680.000	35.564	118.522	76.734	153.780	TRANSITION		
3700	35.564	118.715	76.961	154.491	0.	0.	0.
3800	35.564	119.663	78.072	158.048	0.	0.	0.
3900	35.564	120.587	79.150	161.604	0.	0.	0.
4000	35.564	121.488	80.197	165.161	0.	0.	0.
4100	35.564	122.366	81.215	168.717	0.	0.	0.
4200	35.564	123.223	82.205	172.273	0.	0.	0.
4300	35.564	124.060	83.169	175.830	0.	0.	0.
4400	35.564	124.877	84.108	179.386	0.	0.	0.
4500	35.564	125.676	85.023	182.943	0.	0.	0.
4600	35.564	126.458	85.915	186.499	0.	0.	0.
4700	35.564	127.223	86.786	190.055	0.	0.	0.
4800	35.564	127.972	87.636	193.612	0.	0.	0.
4900	35.564	128.705	88.467	197.168	0.	0.	0.
5000	35.564	129.423	89.279	200.725	0.	0.	0.
5100	35.564	130.128	90.073	204.281	0.	0.	0.
5200	35.564	130.818	90.850	207.837	0.	0.	0.
5300	35.564	131.496	91.610	211.394	0.	0.	0.
5400	35.564	132.161	92.355	214.950	0.	0.	0.
5500	35.564	132.813	93.085	218.507	0.	0.	0.
5600	35.564	133.454	93.800	222.063	0.	0.	0.
5700	35.564	134.083	94.501	225.619	0.	0.	0.
5800	35.564	134.702	95.189	229.176	0.	0.	0.
5900	35.564	135.310	95.864	232.732	0.	0.	0.
6000	35.564	135.908	96.526	236.289	0.	0.	0.

PREVIOUS: CURRENT: June 1966

IP(W,g) = 64400 ± 100 cm^{-1}
$S°(298.15\ K)$ = 173.95 ± 0.08 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 849.8 ± 6.3 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 851.0 ± 6.3 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^5D_0$	0.00	1
$^5D_1$	1670.29	3
$^5D_2$	3325.53	5
$^5D_3$	4830.00	7
$^5D_4$	6219.33	9
.	.	
.	.	
.	.	
–	62154.50	11
IP	66400.00	

Enthalpy of Formation

The enthalpy of formation is the enthalpy of sublimation at 298.15 K; this has been obtained by a 2nd and 3rd law analysis of the vapor pressure data of three investigators.

Source	T/K**	Data Points	$\Delta_{sub}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$
[1]	2511–3053	12*	200.9 ± 3.6	201.57 ± 1.6	0.1 ± 1.4
[2]	2383–3123	14	214.8 ± 1.4	202.17 ± 2.5	−4.7 ± 0.5
[3]	2574–3183	10	202.4 ± 2.7	203.35 ± 1.2	0.4 ± 1.0

* 1 point rejected due to failure of a statistical test.
** All temperatures are taken from Szwarc[3] who has corrected the earlier measurements.

The values are remarkably good since even at the highest temperature the pressures are less than 10^{-6} atm; all workers used the Langmuir technique. Since the data of references 1 and 3 do not drift, it may be assumed that the accommodation coefficient is unity or close to unity. The drift in the second set cannot be eliminated by assuming a non–unity coefficient, nor does there appear to be a constant pressure error. Most probably the drift is due to slight errors in temperature, for example if the readings were 24 K high at the low end and 10 K low at the high end the drift would be eliminated; errors of this magnitude are quite possible. The value adopted for $\Delta_{sub}H°(298.15\ K)$ is 203.4 ± 1.5 $kcal·mol^{-1}$.

Heat Capacity and Entropy

The electronic energy levels are taken from those listed by Moore.[4] Levels above 25000 cm^{-1} were averaged.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	.000	.000	INFINITE	−6.216	849.782	849.782	INFINITE
100	20.786	151.176	192.554	−4.138	851.209	837.052	−437.231
200	20.808	165.586	175.880	−2.059	851.280	822.817	−214.898
250	20.941	170.240	174.303	−1.016	851.166	815.714	−170.434
298.15	21.306	173.955	173.955	.000	851.026	808.898	−141.716
300	21.326	174.087	173.955	.039	851.020	808.637	−140.796
350	22.059	177.425	174.217	1.123	850.879	801.585	−119.630
400	23.163	180.438	174.809	2.252	850.769	794.550	−103.758
450	24.611	183.247	175.592	3.445	850.710	787.527	−91.414
500	26.344	185.927	176.493	4.717	850.720	780.507	−81.539
600	30.337	191.077	178.497	7.548	850.993	766.445	−66.725
700	34.381	196.061	180.652	10.786	851.631	752.308	−56.138
800	37.765	200.883	182.881	14.402	852.601	738.057	−48.190
900	40.071	205.476	185.139	18.303	853.814	723.668	−42.001
1000	41.235	209.768	187.390	22.377	855.154	709.136	−37.041
1100	41.438	213.714	189.607	26.518	856.516	694.468	−32.978
1200	40.951	217.303	191.768	30.642	857.815	679.678	−29.586
1300	40.037	220.547	193.859	34.694	858.997	664.785	−26.711
1400	38.900	223.473	195.871	38.642	860.029	649.806	−24.245
1500	37.687	226.115	197.801	42.472	860.896	634.758	−22.104
1600	36.488	228.509	199.647	46.180	861.595	619.659	−20.230
1700	35.360	230.687	201.409	49.772	862.129	604.521	−18.575
1800	34.331	232.678	203.092	53.255	862.508	589.355	−17.103
1900	33.417	234.510	204.698	56.642	862.742	574.173	−15.785
2000	32.621	236.203	206.232	59.943	862.842	558.982	−14.599
2100	31.943	237.778	207.697	63.170	862.820	543.789	−13.526
2200	31.379	239.250	209.098	66.335	862.686	528.600	−12.551
2300	30.922	240.635	210.439	69.449	862.451	513.419	−11.660
2400	30.566	241.943	211.725	72.523	862.126	498.251	−10.844
2500	30.304	243.185	212.959	75.566	861.721	483.097	−10.094
2600	30.129	244.370	214.144	78.586	861.246	467.961	−9.401
2700	30.035	245.505	215.285	81.594	860.685	452.845	−8.761
2800	30.013	246.596	216.384	84.596	860.008	437.752	−8.166
2900	30.060	247.650	217.444	87.599	859.184	422.686	−7.613
3000	30.167	248.671	218.468	90.610	858.194	407.650	−7.098
3100	30.331	249.663	219.458	93.634	856.998	392.651	−6.616
3200	30.545	250.629	220.417	96.678	855.571	377.695	−6.165
3300	30.805	251.573	221.347	99.745	853.893	362.786	−5.742
3400	31.106	252.497	222.250	102.840	851.933	347.933	−5.345
3500	31.446	253.403	223.127	105.967	849.630	333.142	−4.972
3600	31.822	254.294	223.980	109.130	846.886	318.423	−4.620
3700	32.230	255.172	224.811	112.333	808.867	303.977	−4.291
3800	32.670	256.037	225.622	115.578	808.555	290.336	−3.991
3900	33.141	256.892	226.413	118.868	808.289	276.702	−3.706
4000	33.642	257.737	227.185	122.207	808.072	263.075	−3.435
4100	34.174	258.574	227.941	125.597	807.906	249.452	−3.178
4200	34.738	259.404	228.680	129.043	807.795	235.833	−2.933
4300	35.335	260.229	229.404	132.546	807.742	222.215	−2.699
4400	35.968	261.048	230.114	136.111	807.750	208.598	−2.476
4500	36.638	261.864	230.810	139.741	807.824	194.980	−2.263
4600	37.348	262.677	231.494	143.440	807.966	181.360	−2.059
4700	38.102	263.488	232.166	147.212	808.182	167.736	−1.864
4800	38.900	264.298	232.827	151.061	808.475	154.107	−1.677
4900	39.746	265.109	233.478	154.993	808.851	140.470	−1.497
5000	40.642	265.921	234.119	159.012	809.313	126.825	−1.325
5100	41.590	266.735	234.750	163.124	809.868	113.170	−1.159
5200	42.591	267.552	235.373	167.332	810.520	99.503	−1.000
5300	43.646	268.374	235.988	171.644	811.275	85.823	−.846
5400	44.755	269.200	236.595	176.063	812.139	72.127	−.698
5500	45.916	270.031	237.196	180.596	813.115	58.414	−.555
5600	47.129	270.870	237.790	185.248	814.211	44.683	−.417
5700	48.391	271.715	238.377	190.024	815.430	30.931	−.283
5800	49.698	272.568	238.959	194.928	816.778	17.156	−.155
5900	51.046	273.429	239.536	199.965	818.258	3.357	−.030
6000	52.431	274.298	240.108	205.138	819.875	−10.468	.091

PREVIOUS: June 1966 (1 atm) CURRENT: June 1966 (1 bar)

IP(W^+, g) = 142800 ± 4000 cm^{-1}
$S°$(298.15 K) = 179.74 ± 0.08 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1620.2 ± 7 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1627.623] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^6D_{1/2}$	0.00	2
$^6D_{3/2}$	1518.78	4
$^6D_{5/2}$	3172.52	6
$^6D_{7/2}$	4716.32	8
$^6D_{9/2}$	6147.16	10
.	.	.
.	.	.
.	.	.
$^4H_{9/2}$	64516.37	10
IP	[142800]	

Enthalpy of Formation

$\Delta_f H°(W^+, g, 0 K)$ is calculated from $\Delta_f H°(W, g, 0 K)$[1] using the spectroscopic value of IP(W) = 64400 ± 100 cm^{-1} (770.40 ± 1.20 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(W^+, g, 298.15 K)$ is calculated from $\Delta_f H°(W, g, 0 K)$ by using IP(W) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for W(g), $W^+(g)$, and e^-(ref). $\Delta_f H°(W \rightarrow W^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°(298.15 K)$ should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2] is incomplete because many theoretically predicted levels have not been observed. Although we have listed only the ground, the first four excited states, the highest observed excited state, and the ionization potential for $W^+(g)$, all levels listed by Moore[6] as well as estimated levels, are used in the calculation. The observed levels are too numerous to list completely. The calculations indicate that for $W^+(g)$, the thermodynamic functions are independent of the estimated missing levels (for $n = 6$) and the cut–off procedure; the Gibbs energy function showing variations of 0.8% at this temperature. The reported uncertainty is $S°$(298.15 K) is due to uncertainties in the relative ionic mass, the fundamental constants, and the low lying atomic energy levels. Extension of these calculations above 6000 K may require consideration of the higher excited states (n > 6), and use of different fill and cut–off procedures.[7]

References

[1]JANAF Thermochemical Tables: W(g), 6–30–66; e^-(ref), 3–31–82.
[2]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–34, 8 pp. (1970).
[3]E. R. Cohen and B. N. Taylor, J. Phys. Chem. Ref. Data **2**, 663 (1973).
[4]H. M. Rosenstock, K. Draxl *et al.*, J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[5]R. D. Levin and S. G. Lias, U. S. Natl. Bur. Stand. NSRDS–NBS–71, 634 pp. (1982).
[6]C. E. Moore, U. S. Nat. Bur. Stand., NSRDS–NBS–35, Volume III, (1970) [Reprint of NBS Circular 467, Volume III, 1958].
[7]J. R. Downey, Jr., The Dow Chemical Company, AFOSR–TR–78–0960, Contract No. F44620–75–1–0048, (1978).

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−6.221	1620.178		
100	20.786	156.939	198.365	−4.143			
200	20.822	171.350	181.667	−2.063			
250	20.989	176.011	180.086	−1.019			
298.15	21.372	179.737	179.737	.000	1627.623	1577.517	−276.374
300	21.391	179.869	179.737	.040	1627.656	1577.206	−274.616
350	22.045	183.213	180.000	1.125	1628.556	1568.727	−234.120
400	22.891	186.210	180.592	2.247	1629.479	1560.117	−203.730
450	23.844	188.961	181.371	3.415	1630.434	1551.390	−180.081
500	24.828	191.524	182.260	4.632	1631.428	1542.554	−161.150
600	26.695	196.219	184.202	7.210	1633.527	1524.585	−132.727
700	28.294	200.458	186.226	9.962	1635.757	1506.253	−112.398
800	29.616	204.325	188.250	12.860	1638.088	1487.595	−97.130
900	30.703	207.878	190.237	15.877	1640.495	1468.639	−85.238
1000	31.603	211.161	192.167	18.994	1642.957	1449.412	−75.710
1100	32.347	214.209	194.034	22.193	1645.455	1429.937	−67.902
1200	32.956	217.051	195.835	25.459	1647.975	1410.233	−61.386
1300	33.441	219.709	197.570	28.780	1650.505	1390.319	−55.864
1400	33.813	222.201	199.242	32.143	1653.031	1370.210	−51.123
1500	34.082	224.544	200.851	35.539	1655.542	1349.921	−47.008
1600	34.261	226.750	202.401	38.957	1658.029	1329.465	−43.403
1700	34.362	228.830	203.896	42.389	1660.482	1308.854	−40.216
1800	34.401	230.795	205.336	45.827	1662.895	1288.100	−37.380
1900	34.393	232.655	206.725	49.267	1665.261	1267.214	−34.838
2000	34.351	234.419	208.066	52.705	1667.576	1246.204	−32.547
2100	34.288	236.093	209.361	56.137	1669.837	1225.079	−30.472
2200	34.218	237.687	210.613	59.562	1672.042	1203.848	−28.583
2300	34.148	239.206	211.823	62.980	1674.190	1182.518	−26.856
2400	34.087	240.658	212.995	66.392	1676.282	1161.096	−25.271
2500	34.041	242.048	214.129	69.798	1678.319	1139.588	−23.810
2600	34.013	243.383	215.229	73.201	1680.304	1118.000	−22.461
2700	34.008	244.666	216.296	76.602	1682.214	1096.336	−21.210
2800	34.026	245.904	217.331	80.003	1684.016	1074.603	−20.047
2900	34.067	247.098	218.337	83.407	1685.672	1052.809	−18.963
3000	34.130	248.254	219.315	86.817	1687.159	1030.960	−17.951
3100	34.216	249.375	220.267	90.234	1688.435	1009.065	−17.003
3200	34.320	250.462	221.193	93.661	1689.470	987.133	−16.113
3300	34.442	251.520	222.096	97.099	1690.241	965.172	−15.277
3400	34.578	252.551	222.977	100.550	1690.715	943.192	−14.490
3500	34.725	253.555	223.836	104.015	1690.828	921.204	−13.748
3600	34.882	254.535	224.676	107.495	1690.480	899.218	−13.047
3700	35.044	255.493	225.496	110.991	1654.834	877.440	−12.387
3800	35.209	256.430	226.297	114.504	1656.869	856.402	−11.772
3900	35.375	257.347	227.082	118.033	1658.920	835.311	−11.188
4000	35.538	258.244	227.850	121.579	1660.988	814.166	−10.632
4100	35.698	259.124	228.602	125.141	1663.072	792.970	−10.103
4200	35.851	259.986	229.339	128.718	1665.172	771.723	−9.598
4300	35.996	260.831	230.061	132.311	1667.286	750.425	−9.116
4400	36.132	261.660	230.770	135.917	1669.415	729.078	−8.655
4500	36.257	262.474	231.466	139.537	1671.557	707.683	−8.215
4600	36.370	263.272	232.149	143.168	1673.710	686.240	−7.792
4700	36.471	264.055	232.819	146.810	1675.875	664.750	−7.388
4800	36.559	264.824	233.478	150.462	1678.049	643.213	−7.000
4900	36.634	265.579	234.125	154.122	1680.231	621.632	−6.627
5000	36.695	266.319	234.762	157.788	1682.419	600.005	−6.268
5100	36.743	267.047	235.388	161.460	1684.614	578.335	−5.923
5200	36.778	267.760	236.003	165.136	1686.812	556.622	−5.591
5300	36.800	268.461	236.609	168.815	1689.013	534.867	−5.271
5400	36.811	269.149	237.206	172.496	1691.216	513.070	−4.963
5500	36.810	269.825	237.792	176.177	1693.419	491.232	−4.665
5600	36.799	270.488	238.370	179.858	1695.622	469.354	−4.378
5700	36.779	271.139	238.940	183.537	1697.823	447.437	−4.100
5800	36.749	271.778	239.500	187.213	1700.022	425.481	−3.832
5900	36.713	272.406	240.053	190.886	1702.217	403.488	−3.572
6000	36.669	273.023	240.597	194.555	1704.409	381.457	−3.321

PREVIOUS: CURRENT: March 1984 (1 bar)

EA(W, g) = 0.815 ± 0.008 eV
$S°(298.15\ K)$ = 188.781 ± 0.08 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 771.147 ± 2.0 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = [766.174] $kJ·mol^{-1}$

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^6S_{5/2}$	0.0	6

Enthalpy of Formation

$\Delta_f H°(W^-, g, 0\ K)$ is calculated from $\Delta_f H°(W, g, 0\ K)$[1] using the adopted electron affinity of EA(W) = 0.815 ± 0.008 eV (78.635 ± 0.772 $kJ·mol^{-1}$). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on $W^-(g)$ may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(W^-, g, 298.15\ K)$ is obtained from $\Delta_f H°(W, g, 0\ K)$ by using EA(W) with JANAF[1] enthalpies, $H°(0\ K)-H°(298.15\ K)$, for $W^-(g)$, W(g), and e^-(ref). $\Delta_r H°(W^- \rightarrow W + e^-, 298.15\ K)$ differs from a room-temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15\ K)$ should be changed by + 6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for $W^-(g)$ is given by Hotop and Lineberger[2,4] and Rosenstock *et al.*[5] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable excited states exist.

References

[1]JANAF Thermochemical Tables: W(g), 6–30–66; e^-(ref), 3–31–82.
[2]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data, **14**, 731 (1985).
[3]C. S. Feigerle, R. R. Corderman, S. V. Bobashev and W. C. Lineberger, J. Chem. Phys. **74**, 1580 (1981).
[4]H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
[5]H. M. Rosenstock, K. Draxl *et al.* J. Phys. Chem. Ref. Data **6**, Supp. 1, 783 pp. (1977).
[6]H. S. W. Massey, "Negative Ions", 3rd ed., Cambridge University Press, Cambridge, 741 pp. (1976).

Enthalpy Reference Temperature = T_r = 298.15 K — **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	771.147		
100	20.786	166.073	207.261	−4.119			
200	20.786	180.481	190.682	−2.040			
250	20.786	185.119	189.123	−1.001			
298.15	20.786	188.781	188.781	0.	766.174	725.882	−127.171
300	20.786	188.909	188.781	0.038	766.129	725.632	−126.344
350	20.786	192.113	189.034	1.078	764.905	718.979	−107.302
400	20.786	194.889	189.596	2.117	763.666	712.502	−93.043
450	20.786	197.337	190.323	3.156	762.414	706.182	−81.971
500	20.786	199.527	191.136	4.196	761.151	700.001	−73.129
600	20.786	203.317	192.860	6.274	758.594	688.011	−59.897
700	20.786	206.521	194.588	8.353	755.993	676.452	−50.477
800	20.786	209.297	196.257	10.431	753.348	665.269	−43.438
900	20.786	211.745	197.845	12.510	750.659	654.420	−37.982
1000	20.786	213.935	199.346	14.589	747.925	643.873	−33.632
1100	20.786	215.916	200.764	16.667	745.146	633.602	−30.087
1200	20.786	217.725	202.103	18.746	742.322	623.586	−27.144
1300	20.786	219.388	203.370	20.824	739.452	613.807	−24.663
1400	20.786	220.929	204.569	22.903	736.536	604.251	−22.545
1500	20.786	222.363	205.708	24.982	733.573	594.906	−20.716
1600	20.786	223.704	206.792	27.060	730.563	585.759	−19.123
1700	20.786	224.965	207.824	29.139	727.506	576.802	−17.723
1800	20.786	226.153	208.810	31.217	724.402	568.027	−16.484
1900	20.786	227.277	209.752	33.296	721.249	559.425	−15.380
2000	20.786	228.343	210.655	35.375	718.049	550.990	−14.390
2100	20.786	229.357	211.522	37.453	714.799	542.717	−13.499
2200	20.786	230.324	212.355	39.532	711.500	534.600	−12.693
2300	20.786	231.248	213.156	41.610	708.151	526.634	−11.960
2400	20.786	232.132	213.929	43.689	704.752	518.814	−11.292
2500	20.786	232.981	214.674	45.768	701.304	511.138	−10.680
2600	20.786	233.796	215.394	47.846	697.809	503.600	−10.117
2700	20.786	234.581	216.090	49.925	694.239	496.198	−9.600
2800	20.786	235.337	216.764	52.004	690.561	488.930	−9.121
2900	20.786	236.066	217.417	54.082	686.734	481.796	−8.678
3000	20.786	236.771	218.050	56.161	682.733	474.797	−8.267
3100	20.786	237.452	218.665	58.239	678.512	467.934	−7.885
3200	20.786	238.112	219.263	60.318	674.042	461.212	−7.529
3300	20.786	238.752	219.844	62.397	669.297	454.634	−7.196
3400	20.786	239.372	220.409	64.475	664.241	448.204	−6.886
3500	20.786	239.975	220.960	66.554	658.811	441.928	−6.595
3600	20.786	240.560	221.496	68.632	652.904	435.813	−6.323
3700	20.786	241.130	222.019	70.711	611.683	430.061	−6.071
3800	20.786	241.684	222.529	72.790	608.127	425.200	−5.845
3900	20.786	242.224	223.027	74.868	604.570	420.433	−5.631
4000	20.786	242.750	223.514	76.947	601.014	415.757	−5.429
4100	20.786	243.264	223.989	79.025	597.457	411.169	−5.238
4200	20.786	243.765	224.454	81.104	593.901	406.669	−5.058
4300	20.786	244.254	224.909	83.183	590.345	402.253	−4.886
4400	20.786	244.732	225.354	85.261	586.788	397.920	−4.724
4500	20.786	245.199	225.790	87.340	583.232	393.667	−4.570
4600	20.786	245.656	226.217	89.418	579.675	389.494	−4.423
4700	20.786	246.103	226.635	91.497	576.119	385.398	−4.283
4800	20.786	246.540	227.045	93.576	572.563	381.377	−4.150
4900	20.786	246.969	227.448	95.654	569.006	377.431	−4.023
5000	20.786	247.389	227.842	97.733	565.450	373.558	−3.903
5100	20.786	247.800	228.229	99.811	561.893	369.755	−3.787
5200	20.786	248.204	228.610	101.890	558.337	366.022	−3.677
5300	20.786	248.600	228.983	103.969	554.781	362.358	−3.571
5400	20.786	248.988	229.350	106.047	551.224	358.761	−3.470
5500	20.786	249.370	229.711	108.126	547.668	355.229	−3.374
5600	20.786	249.744	230.065	110.204	544.111	351.762	−3.281
5700	20.786	250.112	230.414	112.283	540.555	348.359	−3.192
5800	20.786	250.474	230.756	114.362	536.999	345.018	−3.107
5900	20.786	250.829	231.093	116.440	533.442	341.739	−3.026
6000	20.786	251.178	231.425	118.519	529.886	338.520	−2.947

PREVIOUS: CURRENT: March 1984 (1 bar)

0 to 6000 K Ideal Monatomic Gas

IP(Xe, g) = 97834.0 ± 0.1 cm^{-1}
$S°(298.15\ K) = 169.684 \pm 0.003\ J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights

State	ϵ_i, cm^{-1}	g_i
$^1S_0$	0	1

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

Information on the electronic energy levels and quantum weights is taken from Moore.[1,9] Many of the theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[2] has no effect on the thermodynamic properties to 6000 K. This is undoubtedly a result of the high energy of these levels; the first excited level is over 67000 cm^{-1} above the ground state. Therefore, we list the ground state only. Extension to higher temperatures may require consideration of excited states and utilization of different fill and cutoff procedures.[2]

The thermodynamic functions at 298.15 K agree exactly with recent CODATA recommendations[3] except for two minor changes. First, the entropy differs by $0.1094\ J \cdot K^{-1} \cdot mol^{-1}$ because this table uses a reference pressure of 1 bar, whereas the CODATA recommendations are based on 1 atm. Second, entropy differences of the order of $0.001–0.004\ J \cdot K^{-1} \cdot mol^{-1}$ for the rare gases arise due to the use of slightly different values for R and the relative atomic mass; this table uses $R = 8.31441\ J \cdot K^{-1} \cdot mol^{-1}$. Within these same minor changes, the tables agree within the estimated uncertainty with those by Hultgren *et al.*,[4] Hilsenrath *et al.*,[5] Gurvich *et al.*,[8] and Wagman *et al.*[12] The estimated uncertainty is due to uncertainties in the relative atomic mass and fundamental constants which are based on the 1981 scale[6] and the 1973 values[7], respectively.

Phase Data

The triple point, 161.388 K, and boiling point, 165.060 K, are secondary fixed points of IPTS–68.[10,11] Hultgren *et al.*[4] had recommended a triple point of 161.36 K (0.8059 atm) and a boiling point of 165.060 K (1 atm). These values are provided for the convenience of the reader and have not been evaluated by the present authors. As a result of the low values, the reference state for xenon is chosen to be the ideal gas at all temperatures. This may differ from the choice of other authors.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.197	0.	0.	0.
100	20.786	146.977	188.164	−4.119	0.	0.	0.
200	20.786	161.384	171.585	−2.040	0.	0.	0.
250	20.786	166.023	170.026	−1.001	0.	0.	0.
298.15	20.786	169.684	169.684	0.	0.	0.	0.
300	20.786	169.812	169.684	0.038	0.	0.	0.
350	20.786	173.017	169.937	1.078	0.	0.	0.
400	20.786	175.792	170.499	2.117	0.	0.	0.
450	20.786	178.240	171.226	3.156	0.	0.	0.
500	20.786	180.430	172.039	4.196	0.	0.	0.
600	20.786	184.220	173.763	6.274	0.	0.	0.
700	20.786	187.424	175.492	8.353	0.	0.	0.
800	20.786	190.200	177.161	10.431	0.	0.	0.
900	20.786	192.648	178.748	12.510	0.	0.	0.
1000	20.786	194.838	180.249	14.589	0.	0.	0.
1100	20.786	196.819	181.667	16.667	0.	0.	0.
1200	20.786	198.628	183.006	18.746	0.	0.	0.
1300	20.786	200.292	184.273	20.824	0.	0.	0.
1400	20.786	201.832	185.473	22.903	0.	0.	0.
1500	20.786	203.266	186.612	24.982	0.	0.	0.
1600	20.786	204.608	187.695	27.060	0.	0.	0.
1700	20.786	205.868	188.727	29.139	0.	0.	0.
1800	20.786	207.056	189.713	31.217	0.	0.	0.
1900	20.786	208.180	190.655	33.296	0.	0.	0.
2000	20.786	209.246	191.559	35.375	0.	0.	0.
2100	20.786	210.260	192.425	37.453	0.	0.	0.
2200	20.786	211.227	193.258	39.532	0.	0.	0.
2300	20.786	212.151	194.059	41.610	0.	0.	0.
2400	20.786	213.036	194.832	43.689	0.	0.	0.
2500	20.786	213.884	195.577	45.768	0.	0.	0.
2600	20.786	214.699	196.297	47.846	0.	0.	0.
2700	20.786	215.484	196.993	49.925	0.	0.	0.
2800	20.786	216.240	197.667	52.004	0.	0.	0.
2900	20.786	216.969	198.320	54.082	0.	0.	0.
3000	20.786	217.674	198.954	56.161	0.	0.	0.
3100	20.786	218.355	199.569	58.239	0.	0.	0.
3200	20.786	219.015	200.166	60.318	0.	0.	0.
3300	20.786	219.655	200.747	62.397	0.	0.	0.
3400	20.786	220.276	201.312	64.475	0.	0.	0.
3500	20.786	220.878	201.863	66.554	0.	0.	0.
3600	20.786	221.464	202.399	68.632	0.	0.	0.
3700	20.786	222.033	202.922	70.711	0.	0.	0.
3800	20.786	222.587	203.432	72.790	0.	0.	0.
3900	20.786	223.127	203.930	74.868	0.	0.	0.
4000	20.786	223.654	204.417	76.947	0.	0.	0.
4100	20.786	224.167	204.892	79.025	0.	0.	0.
4200	20.786	224.668	205.357	81.104	0.	0.	0.
4300	20.786	225.157	205.812	83.183	0.	0.	0.
4400	20.786	225.635	206.257	85.261	0.	0.	0.
4500	20.786	226.102	206.693	87.340	0.	0.	0.
4600	20.786	226.559	207.120	89.418	0.	0.	0.
4700	20.786	227.006	207.538	91.497	0.	0.	0.
4800	20.786	227.443	207.949	93.576	0.	0.	0.
4900	20.786	227.872	208.351	95.654	0.	0.	0.
5000	20.786	228.292	208.745	97.733	0.	0.	0.
5100	20.786	228.704	209.133	99.811	0.	0.	0.
5200	20.786	229.107	209.513	101.890	0.	0.	0.
5300	20.786	229.503	209.886	103.969	0.	0.	0.
5400	20.786	229.892	210.253	106.047	0.	0.	0.
5500	20.786	230.273	210.614	108.126	0.	0.	0.
5600	20.786	230.648	210.968	110.204	0.	0.	0.
5700	20.786	231.015	211.317	112.283	0.	0.	0.
5800	20.786	231.377	211.659	114.362	0.	0.	0.
5900	20.786	231.732	211.997	116.440	0.	0.	0.
6000	20.786	232.082	212.329	118.519	0.	0.	0.

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

IP(Xe^+, g) = 171068.4 ± 0.2 cm^{-1}
$S°$(298.15 K) = 181.210 ± 0.003 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1170.355 ± 0.001 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1176.552] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2P_{3/2}$	0	4
$^2P_{1/2}$	10537.01	2

Enthalpy of Formation

The ionization limit of neutral xenon (97834.0 ± 0.1 cm^{-1}) reported by Moore[1] is adopted as $\Delta_f H°$(0 K) for Xe^+(g). The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the latest CODATA fundamental constants.[2] The uncertainty in the ionization limit is estimated to be ±0.1 cm^{-1} which corresponds to an uncertainty of ±0.001 $kJ·mol^{-1}$ in the heat of formation. Rosenstock *et al.*[9] and Levine and Lias[11] have summarized additional ionization potential and appearance potential data. Gurvich *et al.*[8] and Wagman *et al.*[10] adopted the same ionization potential, but the use of slightly different fundamental constants by Wagman *et al.*[10] results in a heat of formation difference of 0.011 $kJ·mol^{-1}$.

$\Delta_f H°$(Xe^+, g, 298.15 K) is obtained from $\Delta_f H°$(Xe, g, 0 K) by using IP(Xe) with JANAF[3] enthalpies $H°$(0 K)–$H°$(298.15 K) for Xe^+(g), Xe(r), and e^-(r). $\Delta_f H°$(Xe → $Xe^+ + e^-$, 298.15 K) differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[9] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights of Moore[4] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[5] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the $^2P_{1/2}$ level; the next lowest level is over 90000 cm^{-1} above the ground state. Since inclusion of these upper levels has no effect on the thermodynamic functions (to 6000 K) we list only the ground state and the $^2P_{1/2}$ state, with the energy of the latter state taken from a more recent study by Moore.[1] The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and fundamental constants. Extension of these calculations above 6000 K may require consideration of the higher excited states and use of different fill and cutoff procedures.[5]

The thermodynamic functions reported here agree with those of Green *et al.*,[6] Hilsenrath *et al.*,[7] and Gurvich *et al.*[8] except for two minor changes. First, the entropy differs by 0.1094 $J·K^{-1}·mol^{-1}$ because this table uses a standard state pressure of 1 bar, whereas the cited references used a pressure of 1 atm. Second, smaller differences arise from the use of different values for the fundamental constants, the relative ionic mass, and the position of the $^2P_{1/2}$ electronic level.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	1170.355		
100	20.786	158.503	199.690	−4.119			
200	20.786	172.910	183.111	−2.040			
250	20.786	177.549	181.552	−1.001			
298.15	20.786	181.210	181.210	0.	1176.552	1166.861	−204.429
300	20.786	181.338	181.210	0.038	1176.591	1166.801	−203.158
350	20.786	184.543	181.463	1.078	1177.630	1165.087	−173.880
400	20.786	187.318	182.026	2.117	1178.669	1163.224	−151.902
450	20.786	189.766	182.752	3.156	1179.709	1161.231	−134.792
500	20.786	191.957	183.565	4.196	1180.748	1159.123	−121.093
600	20.786	195.746	185.289	6.274	1182.826	1154.602	−100.517
700	20.786	198.950	187.018	8.353	1184.905	1149.734	−85.794
800	20.786	201.726	188.687	10.431	1186.984	1144.568	−74.733
900	20.786	204.174	190.274	12.510	1189.062	1139.141	−66.114
1000	20.786	206.364	191.776	14.589	1191.141	1133.483	−59.207
1100	20.787	208.345	193.193	16.667	1193.220	1127.616	−53.546
1200	20.788	210.154	194.532	18.746	1195.298	1121.561	−48.820
1300	20.791	211.818	195.799	20.825	1197.377	1115.331	−44.815
1400	20.796	213.359	196.999	22.904	1199.457	1108.942	−41.375
1500	20.803	214.794	198.138	24.984	1201.536	1102.404	−38.389
1600	20.815	216.137	199.221	27.065	1203.617	1095.728	−35.772
1700	20.830	217.399	200.254	29.147	1205.700	1088.921	−33.458
1800	20.851	218.591	201.240	31.231	1207.784	1081.991	−31.399
1900	20.877	219.719	202.183	33.318	1209.870	1074.946	−29.552
2000	20.908	220.790	203.087	35.407	1211.959	1067.791	−27.888
2100	20.945	221.811	203.954	37.499	1214.052	1060.531	−26.379
2200	20.987	222.787	204.788	39.596	1216.148	1053.171	−25.005
2300	21.033	223.720	205.591	41.697	1218.249	1045.716	−23.749
2400	21.085	224.617	206.366	43.803	1220.355	1038.170	−22.595
2500	21.141	225.479	207.113	45.914	1222.466	1030.535	−21.532
2600	21.200	226.309	207.835	48.031	1224.583	1022.816	−20.549
2700	21.262	227.110	208.534	50.154	1226.706	1015.016	−19.637
2800	21.326	227.884	209.212	52.283	1228.836	1007.136	−18.788
2900	21.392	228.634	209.869	54.419	1230.972	999.181	−17.997
3000	21.460	229.360	210.506	56.562	1233.114	991.152	−17.257
3100	21.528	230.065	211.126	58.711	1235.264	983.051	−16.564
3200	21.596	230.750	211.729	60.868	1237.420	974.880	−15.913
3300	21.664	231.415	212.315	63.031	1239.583	966.643	−15.301
3400	21.732	232.063	212.886	65.200	1241.753	958.339	−14.723
3500	21.798	232.694	213.443	67.377	1243.929	949.972	−14.178
3600	21.863	233.309	213.987	69.560	1246.112	941.542	−13.661
3700	21.927	233.909	214.517	71.749	1248.302	933.052	−13.172
3800	21.988	234.494	215.035	73.945	1250.497	924.502	−12.708
3900	22.048	235.066	215.541	76.147	1252.699	915.895	−12.267
4000	22.105	235.625	216.037	78.355	1254.907	907.230	−11.847
4100	22.160	236.172	216.521	80.568	1257.120	898.511	−11.447
4200	22.213	236.706	216.995	82.787	1259.339	889.738	−11.066
4300	22.263	237.230	217.460	85.011	1261.563	880.911	−10.701
4400	22.311	237.742	217.915	87.239	1263.791	872.033	−10.352
4500	22.356	238.244	218.361	89.473	1266.025	863.105	−10.019
4600	22.398	238.736	218.799	91.710	1268.263	854.126	−9.699
4700	22.438	239.218	219.228	93.952	1270.504	845.099	−9.392
4800	22.476	239.691	219.649	96.198	1272.750	836.024	−9.098
4900	22.511	240.154	220.063	98.447	1274.999	826.902	−8.815
5000	22.543	240.610	220.470	100.700	1277.252	817.735	−8.543
5100	22.573	241.056	220.869	102.956	1279.508	808.522	−8.281
5200	22.601	241.495	221.261	105.214	1281.767	799.265	−8.029
5300	22.626	241.926	221.647	107.476	1284.028	789.964	−7.786
5400	22.650	242.349	222.027	109.740	1286.292	780.621	−7.551
5500	22.671	242.765	222.400	112.006	1288.558	771.236	−7.325
5600	22.690	243.173	222.767	114.274	1290.826	761.810	−7.106
5700	22.707	243.575	223.129	116.544	1293.096	752.343	−6.894
5800	22.722	243.970	223.485	118.815	1295.367	742.836	−6.690
5900	22.736	244.359	223.835	121.088	1297.640	733.290	−6.492
6000	22.747	244.741	224.180	123.362	1299.914	723.706	−6.300

PREVIOUS: March 1977 (1 atm) CURRENT: March 1982 (1 bar)

REFERENCE STATE

0	to	692.73	K crystal
692.73	to	1180.173	K liquid
above		1180.173	K ideal monatomic gas

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.669	0.	0.	0.
100	19.455	16.523	63.224	−4.670	0.	0.	0.
200	24.050	31.820	44.005	−2.437	0.	0.	0.
298.15	25.387	41.717	41.717	0.	0.	0.	0.
300	25.406	41.874	41.717	0.047	0.	0.	0.
400	26.346	49.314	42.725	2.636	0.	0.	0.
500	27.386	55.301	44.660	5.321	0.	0.	0.
600	28.588	60.399	46.868	8.118	0.	0.	0.
692.730	29.802	64.591	48.965	10.825	CRYSTAL <--> LIQUID TRANSITION		
692.730	31.380	75.161	48.965	18.147			
700	31.380	75.489	49.239	18.375	0.	0.	0.
800	31.380	79.679	52.788	21.513	0.	0.	0.
900	31.380	83.375	55.985	24.651	0.	0.	0.
1000	31.380	86.681	58.892	27.789	0.	0.	0.
1100	31.380	89.672	61.557	30.927	0.	0.	0.
1180.173	31.380	91.880	63.542	33.443	LIQUID <--> IDEAL GAS FUGACITY = 1 bar		
1180.173	20.786	189.586	63.542	148.754			
1200	20.786	189.933	65.628	149.166	0.	0.	0.
1300	20.786	191.597	75.255	151.244	0.	0.	0.
1400	20.786	193.137	83.620	153.323	0.	0.	0.
1500	20.786	194.571	90.970	155.402	0.	0.	0.
1600	20.786	195.913	97.487	157.480	0.	0.	0.
1700	20.786	197.173	103.315	159.559	0.	0.	0.
1800	20.786	198.361	108.562	161.637	0.	0.	0.
1900	20.786	199.485	113.318	163.716	0.	0.	0.
2000	20.786	200.551	117.653	165.795	0.	0.	0.
2100	20.786	201.565	121.625	167.873	0.	0.	0.
2200	20.786	202.532	125.281	169.952	0.	0.	0.
2300	20.786	203.456	128.660	172.030	0.	0.	0.
2400	20.786	204.341	131.795	174.109	0.	0.	0.
2500	20.786	205.189	134.714	176.188	0.	0.	0.
2600	20.786	206.004	137.440	178.266	0.	0.	0.
2700	20.787	206.789	139.994	180.345	0.	0.	0.
2800	20.787	207.545	142.393	182.424	0.	0.	0.
2900	20.788	208.274	144.653	184.502	0.	0.	0.
3000	20.789	208.979	146.785	186.581	0.	0.	0.
3100	20.791	209.661	148.803	188.660	0.	0.	0.
3200	20.793	210.321	150.715	190.739	0.	0.	0.
3300	20.796	210.961	152.531	192.819	0.	0.	0.
3400	20.800	211.582	154.258	194.899	0.	0.	0.
3500	20.806	212.185	155.905	196.979	0.	0.	0.
3600	20.814	212.771	157.476	199.060	0.	0.	0.
3700	20.824	213.341	158.979	201.142	0.	0.	0.
3800	20.836	213.897	160.417	203.225	0.	0.	0.
3900	20.852	214.438	161.795	205.309	0.	0.	0.
4000	20.871	214.966	163.117	207.395	0.	0.	0.
4100	20.894	215.482	164.388	209.483	0.	0.	0.
4200	20.922	215.986	165.611	211.574	0.	0.	0.
4300	20.955	216.478	166.788	213.668	0.	0.	0.
4400	20.994	216.961	167.923	215.765	0.	0.	0.
4500	21.039	217.433	169.018	217.867	0.	0.	0.
4600	21.091	217.896	170.076	219.973	0.	0.	0.
4700	21.150	218.350	171.098	222.085	0.	0.	0.
4800	21.218	218.796	172.087	224.204	0.	0.	0.
4900	21.295	219.234	173.045	226.329	0.	0.	0.
5000	21.381	219.665	173.973	228.463	0.	0.	0.
5100	21.478	220.090	174.873	230.606	0.	0.	0.
5200	21.585	220.508	175.746	232.759	0.	0.	0.
5300	21.703	220.920	176.595	234.923	0.	0.	0.
5400	21.833	221.327	177.420	237.100	0.	0.	0.
5500	21.976	221.729	178.222	239.290	0.	0.	0.
5600	22.131	222.126	179.002	241.496	0.	0.	0.
5700	22.300	222.519	179.762	243.717	0.	0.	0.
5800	22.482	222.909	180.503	245.956	0.	0.	0.
5900	22.680	223.295	181.225	248.214	0.	0.	0.
6000	22.892	223.678	181.929	250.492	0.	0.	0.

PREVIOUS: December 1978 (1 atm) CURRENT: December 1978 (1 bar)

Pearson Notation: hP2
$S°(298.15\ K) = 41.717 \pm 0.17\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{fus} = 692.73\ K$

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{fus} H° = 7.322 \pm 0.105\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted heat capacity values are derived from the low temperature heat capacity studies of Martin[1] and Zabetakis[2] and four high temperature enthalpy studies.[3, 4, 5, 6] The heat capacity values at the temperature where these two different types of study join are forced to be smooth and continuous.

The results of Martin[1] differ from the adopted values by less than 1% in the range 14–30 K. The results of Zabetakis[2] also agree within 0.4% in the region 23–195 K. In the region 200–260 K, the data of Zabetakis[2] indicated a slight depression of 0.2 $cal \cdot K^{-1} \cdot mol^{-1}$ at the mid–point of this region. Other low temperature studies did not support this result, so that the adopted heat capacity values are smoothed in this region to be in better agreement with the studies of Behrens and Drucker,[7] Bronson and Wilson,[8] and Eichenauer and Schulze.[9] The enthalpy data of Jaeger and Poppema,[6] Eastman *et al.*,[4] Ruer and Kremers,[5] and Schubel[3] all agree within 1% of the adopted enthalpy vlaues.

The thermodynamic functions are based on $S°(12\ K) = 0.0230\ cal \cdot K^{-1} \cdot mol^{-1}$ and $H°(12\ K) - H°(0\ K) = 0.20\ cal \cdot mol^{-1}$. These values are obtained by integration of smoothed low temperature data and are in agreement with the values used by Martin[1] and Zabetakis.[2] Below 0.850 ± 0.01 K, zinc is a superconductive element; this behavior is summarized in a recent review by Roberts.[10] The literature survey for Zn was done in part by Hultgren,[11] his help is greatly appreciated.

Fusion Data

We adopt $\Delta_{fus} H° = 1.750 \pm 0.025\ kcal \cdot mol^{-1}$. This value is derived primarily from the adiabatic calorimetric study of Chiotti *et al.*[12] Numerous other studies (over 20) reported values in the range 1.504–1.850 $kcal \cdot mol^{-1}$ with a mean of 1.735 $kcal \cdot mol^{-1}$.

The adopted value for $T_{fus} = 692.73$ K is a primary reference point on the IPTS–68.[13]

Sublimation Data

The sublimation studies are summarized on the Zn(g) table.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−5.669	0.	0.	0.
100	19.455	16.523	63.224	−4.670	0.	0.	0.
200	24.050	31.820	44.005	−2.437	0.	0.	0.
250	25.039	37.290	42.132	−1.211	0.	0.	0.
298.15	25.387	41.717	41.717	0.	0.	0.	0.
300	25.406	41.874	41.717	0.047	0.	0.	0.
350	25.889	45.828	42.028	1.330	0.	0.	0.
400	26.346	49.314	42.725	2.636	0.	0.	0.
450	26.843	52.446	43.634	3.965	0.	0.	0.
500	27.386	55.301	44.660	5.321	0.	0.	0.
600	28.588	60.399	46.868	8.118	0.	0.	0.
692.730	29.802	64.591	48.965	10.825	--- CRYSTAL <--> LIQUID ---		
700	29.900	64.903	49.129	11.042	−7.333	0.077	−0.006
800	31.284	68.985	51.360	14.101	−7.412	1.143	−0.075
900	32.716	72.752	53.530	17.300	−7.351	2.210	−0.128
1000	34.178	76.275	55.630	20.645	−7.144	3.262	−0.170

PREVIOUS: CURRENT: December 1978

$S°(298.15\ K) = [50.792]\ J·K^{-1}·mol^{-1}$
$T_{fus} = 692.73\ K$

$\Delta_f H°(298.15\ K) = [6.519]\ kJ·mol^{-1}$
$\Delta_{fus}H° = 7.322 \pm 0.105\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation of Zn(l) at 298.15 K is calculated from that of the crystal by adding $\Delta_{fus}H°$ and the difference in enthalpy, $H°(692.73\ K) - H°(298.15\ K)$, between the crystal and liquid.

Heat Capacity and Entropy

The adopted heat capacity for Zn(l) is 7.5 $cal·K^{-1}·mol^{-1}$. It is taken as a constant for the real liquid region. There are five enthalpy and two heat capacity studies on liquid zinc. The enthalpy studies are summarized in the following table. The $C_p°$ value given is that derived from the enthalpy data assuming a linear temperature dependence.

Source	Reference Year	Temperature	No. of Observations Liquid	Total	T/K	$C_p°$ (l) $cal·K^{-1}·mol^{-1}$
1	1919	293	28	47	469–992	8.14
2	1920	293	15	18	675–1140	7.24
3	1926	273	6	14	323–1123	8.20
4	1926	291	4	9	483–914	6.69
5	1960	471	2	13	481–723	7.0

Forster and Tschentke[6] reported heat capacity data graphically in the region 723–973 K. Their study showed a heat capacity of approximately 8.2 $cal·K^{-1}·mol^{-1}$ at the melting point with a steadily decreasing trend to 7.0 $cal·K^{-1}·mol^{-1}$ at 973 K. Cordoba[7] measured heat capacities in the crystal and liquid region, including 22 experimental points in the liquid region up to 798.2 K. This study resulted in a parabolic temperature dependence, with a minimum at 730 K of $C_p° = 6.8\ cal·K^{-1}·mol^{-1}$ and rapidly increasing values on either side of this minimum.

All these heat capacity and enthalpy studies do not conclusively define the temperature dependence of the heat capacity of liquid zinc. In addition, some of these heat capacity and enthalpy studies[3,4,7] do not show good agreement with the adopted values in the crystal region. However, the adopted constant value is consistent with the experimental data (within the uncertainty of the data) and with the vaporization data. The literature survey for Zn was done in part by Hultgren.[8]

Fusion Data

Refer to the crystal table for details.

Vaporization Data

There are numerous studies on the vaporization of liquid zinc.[2,9–22] These studies, when depicted graphically in a log p vs 1/T plot, show remarkably good agreement in the region T_{fus} to 1666 K (approximately 0.2 to 23000 mmHg) with the exception of the studies by Ruff and Bergdahl[10] and Piacente *et al.*[22] A 2nd and 3rd law analysis of all zinc vaporization studies up to 400 mmHg is summarized in the following table.

Source	Year	Number Observations	Method	Vaporization Studies T/K	Drift $cal·mol^{-1}·K^{-1}$	$\Delta_{vap}H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law
9	1919	7	boiling point	926–1198	−1.3 ± 1.0	31.91 ± 1.02	30.58 ± 0.40
10	1920	5	transport	761–995	−0.1 ± 0.1	29.67 ± 0.10	29.62 ± 0.04
11	1925	30	boiling point	857–960	−0.4 ± 0.1	29.94 ± 0.07	29.61 ± 0.04
12	1926	21	static	903–1259	−0.6 ± 0.1	30.22 ± 0.14	29.58 ± 0.10
14	1934	1	transport	954			29.68
15	1934	6	static	955–1089	0.6 ± 0.7	28.90 ± 0.66	29.52 ± 0.16
16	1955	eqn	torsion effusion	700–900	0.0	29.60	29.60
17	1957	3	transport	862–1020	−0.2 ± 0.1	29.76 ± 0.05	29.62 ± 0.02
18	1959	3	transport	823–923	0.6 ± 0.1	29.08 ± 0.04	29.62 ± 0.06
22	1973	10	transpiration	826–1041	−0.1 ± 0.3	29.94 ± 0.25	29.86 ± 0.11

Not including the results of Ruff and Bergdahl[10] and Piacente *et al.*,[22] the mean of the tabulated 3rd law values is $\Delta_{vap}H°(298.15\ K) = 29.59 \pm 0.1\ kcal·mol^{-1}$. This may be compared with our adopted value of 29.531 derived from $\Delta_{fus}H°$ and $\Delta_f r$(Zn, g 298.15 K) = 31.1 ± 0.2 $kcal·mol^{-1}$. This difference of 0.059 $kcal·mol^{-1}$ is within the uncertainty of the vapor pressure studies.

The boiling point is calculated as that temperature for which $\Delta G° = 0$ for Zn(l) = Zn(g). T_{vap} is the temperature for which the fugacity is one bar.

References

References are listed on the Zn(cr, l) table.

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S° - [G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$		
0						
100						
200						
250						
298.15	25.387	50.792	0.	6.519	3.813	−0.668
300	25.406	50.949	0.047	6.519	3.796	−0.661
350	25.889	54.903	1.330	6.519	3.343	−0.499
400	26.346	58.390	2.636	6.519	2.889	−0.377
440.000	26.740	60.919	3.697	GLASS <--> LIQUID TRANSITION		
440.000	31.380	60.919	3.697			
450	31.380	61.624	4.011	6.565	2.435	−0.283
500	31.380	64.930	5.580	6.778	1.964	−0.205
600	31.380	70.652	8.718	7.119	0.967	−0.084
692.730	31.380	75.161	11.628	CRYSTAL <--> LIQUID		
700	31.380	75.489	11.856	0.	0.	0.
800	31.380	79.679	14.994	0.	0.	0.
900	31.380	83.375	18.132	0.	0.	0.
1000	31.380	86.681	21.270	0.	0.	0.
1100	31.380	89.672	24.408	0.	0.	0.
1180.173	31.380	91.880	26.924	FUGACITY = 1 bar		
1200	31.380	92.402	27.546	−115.101	1.935	−0.084
1300	31.380	94.914	30.684	−114.041	11.646	−0.468
1400	31.380	97.240	33.822	−112.982	21.274	−0.794
1500	31.380	99.405	36.960	−111.923	30.827	−1.073
1600	31.380	101.430	40.098	−110.863	40.309	−1.316
1700	31.380	103.332	43.236	−109.804	49.725	−1.528
1800	31.380	105.126	46.374	−108.744	59.078	−1.714
1900	31.380	106.823	49.512	−107.685	68.373	−1.880
2000	31.380	108.432	52.650	−106.626	77.612	−2.027

PREVIOUS: CURRENT: December 1978

0	to	692.73	K crystal
above		692.73	K liquid

Refer to the individual tables for details.

References for Zn(l) table

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.669	0.	0.	0.
100	19.455	16.523	63.224	−4.670	0.	0.	0.
200	24.050	31.820	44.005	−2.437	0.	0.	0.
250	25.039	37.290	42.132	−1.211	0.	0.	0.
298.15	25.387	41.717	41.717	0.	0.	0.	0.
300	25.406	41.874	41.717	0.047	0.	0.	0.
350	25.889	45.828	42.028	1.330	0.	0.	0.
400	26.346	49.314	42.725	2.636	0.	0.	0.
450	26.843	52.446	43.634	3.965	0.	0.	0.
500	27.386	55.301	44.660	5.321	0.	0.	0.
600	28.588	60.399	46.868	8.118	0.	0.	0.
692.730	29.802	64.591	48.965	10.825	____ CRYSTAL <--> LIQUID ____		
692.730	31.380	75.161	48.965	18.147	TRANSITION		
700	31.380	75.489	49.239	18.375	0.	0.	0.
800	31.380	79.679	52.788	21.513	0.	0.	0.
900	31.380	83.375	55.985	24.651	0.	0.	0.
1000	31.380	86.681	58.892	27.789	0.	0.	0.
1100	31.380	89.672	61.557	30.927	0.	0.	0.
1180.173	31.380	91.880	63.542	33.443	----- FUGACITY = 1 bar -----		
1200	31.380	92.402	64.015	34.065	−115.101	1.936	−0.084
1300	31.380	94.914	66.297	37.203	−114.041	11.646	−0.468
1400	31.380	97.240	68.425	40.341	−112.982	21.274	−0.794
1500	31.380	99.405	70.419	43.479	−111.923	30.827	−1.073
1600	31.380	101.430	72.294	46.617	−110.863	40.309	−1.316
1700	31.380	103.332	74.065	49.755	−109.804	49.725	−1.528
1800	31.380	105.126	75.741	52.893	−108.744	59.078	−1.714
1900	31.380	106.823	77.333	56.031	−107.685	68.373	−1.880
2000	31.380	108.432	78.848	59.169	−106.626	77.612	−2.027

PREVIOUS: CURRENT: December 1978

IP(Zn, g) = 75768.10 ± 0.5 cm^{-1}
S(298.15 K) = 160.989 ± 0.025 $J \cdot K^{-1} \cdot mol^{-1}$

$\Delta_f H°(0\ K)$ = 129.89 ± 0.2 $kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 130.42 ± 0.2 $kJ \cdot mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
^1S_o	0	1
^3P_o	32311.308	1
$^3P_1$	32501.390	3
$^3P_2$	32890.317	5

Enthalpy of Formation

The adopted value for the enthalpy of formation is that recommended by CODATA.[1] This value is based on the reanalysis of the vapor pressure data cited by Hultgren *et al.*,[2] and Gurvich *et al.*[3] The studies by Mar and Searcy (512–666 K)[4] and McCreary and Thorn (610–690 K)[5] are also considered. There are twelve sublimation and eleven vaporization studies which lead to enthalpy of formation values showing excellent agreement, which the exception of two studies.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels (for n<10) and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the levels listed above; the next excited state is at approximately 46745 cm^{-1} above the ground state.

Although we list only a few electronic levels, all levels reported by Moore[6] are considered in the calculation. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in he relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states (n>10) and use of different fill and cutoff procedures.[7]

The thermal functions at 298.15 K differ from the CODATA recommendations[1] for two reasons. First, the entropy differs by 0.1094 $J \cdot K^{-1} \cdot mol^{-1}$ because this table uses a reference pressure of 1 bar, wheras CODATA recommendations are based on 1 atm. Second, small changes, ~0.004 $J \cdot K^{-1} \cdot mol^{-1}$, arise presumably due to the use of slightly different values for the fundamental constants.

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−6.197	129.892	129.892	INFINITE
100	20.786	138.281	179.469	−4.119	130.971	118.795	−62.052
200	20.786	152.689	162.890	−2.040	130.817	106.643	−27.852
250	20.786	157.327	161.331	−1.001	130.630	100.620	−21.023
298.15	20.786	160.989	160.989	0.	130.420	94.859	−16.619
300	20.786	161.117	160.989	0.038	130.411	94.638	−16.478
350	20.786	164.321	161.242	1.078	130.168	88.695	−13.237
400	20.786	167.097	161.804	2.117	129.902	82.788	−10.811
450	20.786	169.545	162.531	3.156	129.611	76.916	−8.928
500	20.786	171.735	163.344	4.196	129.295	71.078	−7.425
600	20.786	175.525	165.068	6.274	128.576	59.500	−5.180
700	20.786	178.729	166.797	8.353	120.398	48.130	−3.591
800	20.786	181.505	168.465	10.431	119.339	37.878	−2.473
900	20.786	183.953	170.053	12.510	118.279	27.759	−1.611
1000	20.786	186.143	171.554	14.589	117.220	17.758	−0.928
1100	20.786	188.124	172.972	16.667	116.160	7.863	−0.373
1180.173	20.786	189.586	174.052	18.334	----- FUGACITY = 1 bar -----		
1200	20.786	189.933	174.311	18.746	0.	0.	0.
1300	20.786	191.597	175.578	20.824	0.	0.	0.
1400	20.786	193.137	176.778	22.903	0.	0.	0.
1500	20.786	194.571	177.917	24.982	0.	0.	0.
1600	20.786	195.913	179.000	27.060	0.	0.	0.
1700	20.786	197.173	180.032	29.139	0.	0.	0.
1800	20.786	198.361	181.018	31.217	0.	0.	0.
1900	20.786	199.485	181.960	33.296	0.	0.	0.
2000	20.786	200.551	182.863	35.375	0.	0.	0.
2100	20.786	201.565	183.730	37.453	0.	0.	0.
2200	20.786	202.532	184.563	39.532	0.	0.	0.
2300	20.786	203.456	185.364	41.610	0.	0.	0.
2400	20.786	204.341	186.137	43.689	0.	0.	0.
2500	20.786	205.189	186.882	45.768	0.	0.	0.
2600	20.786	206.004	187.602	47.846	0.	0.	0.
2700	20.787	206.789	188.298	49.925	0.	0.	0.
2800	20.787	207.545	188.972	52.004	0.	0.	0.
2900	20.788	208.274	189.625	54.082	0.	0.	0.
3000	20.789	208.979	190.259	56.161	0.	0.	0.
3100	20.791	209.661	190.874	58.240	0.	0.	0.
3200	20.793	210.321	191.471	60.319	0.	0.	0.
3300	20.796	210.961	192.052	62.399	0.	0.	0.
3400	20.800	211.582	192.617	64.479	0.	0.	0.
3500	20.806	212.185	193.168	66.559	0.	0.	0.
3600	20.814	212.771	193.704	68.640	0.	0.	0.
3700	20.824	213.341	194.227	70.722	0.	0.	0.
3800	20.836	213.897	194.738	72.805	0.	0.	0.
3900	20.852	214.438	195.236	74.889	0.	0.	0.
4000	20.871	214.966	195.722	76.975	0.	0.	0.
4100	20.894	215.482	196.198	79.064	0.	0.	0.
4200	20.922	215.986	196.663	81.154	0.	0.	0.
4300	20.955	216.478	197.118	83.248	0.	0.	0.
4400	20.994	216.961	197.564	85.345	0.	0.	0.
4500	21.039	217.433	198.000	87.447	0.	0.	0.
4600	21.091	217.896	198.428	89.553	0.	0.	0.
4700	21.150	218.350	198.847	91.665	0.	0.	0.
4800	21.218	218.796	199.258	93.784	0.	0.	0.
4900	21.295	219.234	199.661	95.909	0.	0.	0.
5000	21.381	219.665	200.057	98.043	0.	0.	0.
5100	21.478	220.090	200.445	100.186	0.	0.	0.
5200	21.585	220.508	200.827	102.339	0.	0.	0.
5300	21.703	220.920	201.202	104.503	0.	0.	0.
5400	21.833	221.327	201.571	106.680	0.	0.	0.
5500	21.976	221.729	201.934	108.870	0.	0.	0.
5600	22.131	222.126	202.291	111.076	0.	0.	0.
5700	22.300	222.519	202.643	113.297	0.	0.	0.
5800	22.482	222.909	202.989	115.536	0.	0.	0.
5900	22.680	223.295	203.330	117.794	0.	0.	0.
6000	22.892	223.678	203.666	120.072	0.	0.	0.

PREVIOUS: December 1978 (1 atm) CURRENT: September 1984 (1 bar)

IP(Zn^+, g) = 144892.6 ± 2 cm^{-1}
$S°$(298.15 K) = 166.751 ± 0.02 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1030.6 ± 0.84 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1037.336] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0.0	2
$^2P_{1/2}$	48480.6	2
$^2P_{1/2}$	49354.4	4

Enthalpy of Formation

$\Delta_f H°(Zn^+, g, 0 K)$ is calculated from $\Delta_f H°(Zn, g, 0 K)$[1] using the spectroscopic value of IP(Zn) = 75768.10 ± 0.5 cm^{-1}(906.388 ± 0.006 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 $kJ·mol^{-1}$, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Zn^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Zn, g, 0 K)$ by using IP(Zn) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Zn(g), Zn^+(g), and e^-(ref). $\Delta_f H°(Zn \rightarrow Zn^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The information on electronic energy levels and quantum weights, given by Moore,[2,6] is incomplete because many theoretically predicted levels have not been observed. Our calculations indicate that any reasonable method of filling in these missing levels and cutting off the summation in the partition function[7] has no effect on the thermodynamic functions to 6000 K. This is a result of the high energy of all levels other than the ground state and the first two excited states; the next excited state is 62721.9 cm^{-1} above the ground state. Since inclusion of these excited states has no effect on the thermodynamic functions (to 6000 K), we list only the ground state and the first two excited states. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative ionic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the excited states and use of different fill and cutoff procedures.[7]

References

[1]JANAF Thermochemical Tables: Zn(g), 9–30–84; e^-(ref), 3–31–82.
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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
T/K	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0	0.	0.	INFINITE	−6.197	1030.611		
100	20.786	144.043	185.231	−4.119			
200	20.786	158.451	168.652	−2.040			
250	20.786	163.090	167.093	−1.001			
298.15	20.786	166.751	166.751	0.	1037.336	993.803	−174.110
300	20.786	166.879	166.751	0.038	1037.366	993.532	−172.989
350	20.786	170.083	167.004	1.078	1038.162	986.164	−147.177
400	20.786	172.859	167.566	2.117	1038.935	978.682	−127.803
450	20.786	175.307	168.293	3.156	1039.684	971.105	−112.723
500	20.786	177.497	169.106	4.196	1040.407	963.446	−100.651
600	20.786	181.287	170.830	6.274	1041.767	947.925	−82.524
700	20.786	184.491	172.559	8.353	1035.667	932.262	−69.566
800	20.786	187.267	174.227	10.431	1036.686	917.420	−59.901
900	20.786	189.715	175.815	12.510	1037.705	902.451	−52.377
1000	20.786	191.905	177.316	14.589	1038.725	887.368	−46.351
1100	20.786	193.886	178.734	16.667	1039.744	872.183	−41.417
1200	20.786	195.695	180.073	18.746	925.662	858.840	−37.384
1300	20.786	197.359	181.340	20.824	927.741	853.188	−34.282
1400	20.786	198.899	182.540	22.903	929.819	847.375	−31.616
1500	20.786	200.333	183.679	24.982	931.898	841.413	−29.301
1600	20.786	201.675	184.762	27.060	933.977	835.313	−27.270
1700	20.786	202.935	185.794	29.139	936.055	829.083	−25.475
1800	20.786	204.123	186.780	31.217	938.134	822.731	−23.875
1900	20.786	205.247	187.722	33.296	940.212	816.263	−22.441
2000	20.786	206.313	188.626	35.375	942.291	809.685	−21.147
2100	20.786	207.327	189.492	37.453	944.370	803.004	−19.974
2200	20.786	208.294	190.325	39.532	946.448	796.224	−18.905
2300	20.786	209.218	191.126	41.610	948.527	789.349	−17.927
2400	20.786	210.103	191.899	43.689	950.605	782.383	−17.028
2500	20.786	210.951	192.644	45.768	952.684	775.331	−16.200
2600	20.786	211.766	193.364	47.846	954.763	768.196	−15.433
2700	20.786	212.551	194.060	49.925	956.841	760.981	−14.722
2800	20.786	213.307	194.734	52.004	958.920	753.689	−14.060
2900	20.786	214.036	195.387	54.082	960.998	746.323	−13.443
3000	20.786	214.741	196.021	56.161	963.077	738.885	−12.865
3100	20.786	215.422	196.636	58.239	965.155	731.377	−12.324
3200	20.786	216.082	197.233	60.318	967.233	723.803	−11.815
3300	20.786	216.722	197.814	62.397	969.311	716.164	−11.336
3400	20.786	217.343	198.379	64.475	971.388	708.461	−10.884
3500	20.786	217.945	198.930	66.554	973.465	700.698	−10.457
3600	20.786	218.531	199.466	68.632	975.541	692.875	−10.053
3700	20.786	219.100	199.989	70.711	977.616	684.995	−9.670
3800	20.786	219.654	200.499	72.790	979.691	677.058	−9.307
3900	20.786	220.194	200.997	74.868	981.763	669.067	−8.961
4000	20.786	220.721	201.484	76.947	983.835	661.023	−8.632
4100	20.786	221.234	201.959	79.025	985.904	652.927	−8.318
4200	20.786	221.735	202.424	81.104	987.970	644.781	−8.019
4300	20.787	222.224	202.879	83.183	990.033	636.585	−7.733
4400	20.787	222.702	203.324	85.261	992.093	628.342	−7.459
4500	20.787	223.169	203.760	87.340	994.149	620.051	−7.197
4600	20.787	223.626	204.187	89.419	996.200	611.716	−6.946
4700	20.788	224.073	204.605	91.497	998.245	603.335	−6.705
4800	20.788	224.511	205.015	93.576	1000.284	594.911	−6.474
4900	20.789	224.939	205.418	95.655	1002.316	586.445	−6.252
5000	20.790	225.359	205.812	97.734	1004.340	577.937	−6.038
5100	20.791	225.771	206.200	99.813	1006.355	569.389	−5.832
5200	20.792	226.175	206.580	101.892	1008.360	560.802	−5.633
5300	20.794	226.571	206.953	103.972	1010.353	552.176	−5.442
5400	20.796	226.959	207.320	106.051	1012.334	543.512	−5.257
5500	20.798	227.341	207.681	108.131	1014.302	534.812	−5.079
5600	20.800	227.716	208.035	110.211	1016.256	526.076	−4.907
5700	20.803	228.084	208.384	112.291	1018.193	517.306	−4.741
5800	20.807	228.446	208.727	114.371	1020.113	508.502	−4.580
5900	20.811	228.801	209.064	116.452	1022.015	499.665	−4.424
6000	20.815	229.151	209.396	118.533	1023.896	490.795	−4.273

PREVIOUS: December 1978 (1 atm) CURRENT: September 1984 (1 bar)

EA(Zn, g) = 0.9 ± 0.20 eV
$S°$(298.15 K) = 160.99 ± 0.03 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 115.5 ± 20 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [109.870] kJ·mol^{-1}

Electonic Level and Quantum Weight		
State	ϵ_i, cm^{-1}	g_i
$^2S_{1/2}$	0	2

Enthalpy of Formation

$\Delta_f H°(Zn^-, g, 0 K)$ is calculated from $\Delta_f H°(Zn, g, 0 K)$[1] using the adopted electron affinity of EA(Zn) = 0.09 ± 0.20 eV − 0.67 ± 19.3 kJ·mol^{-1}). This value is calculated by Zollwig[2] using a horizontal analysis technique for the ground state $3d^{10}4s^25s(^2S_{1/2})$. There is a possibility that the ground state may be $3d^{10}4s^24p$ (^2P_o) in which case Zollwig[2] calculated an electron affinity EA = −0.67 eV. Hotop and Lineberger,[3] in a recent review, recommends that Zn^-(g) has a metastable state, $4s4p^24p$, with EA>0.[2,4] Additional information on Zn^- may be obtained in the critical discussions of Hotop and Lineberger,[3,4] Rosenstock *et al.*,[6] and Massey;[7] and in the articles by Gohel *et al.*[8] and Kaiser *et al.*[9]

$\Delta_f H°(Zn^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Zn, g, 0 K)$ by using EA(Zn) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Zn^-(g), Zn(g), and e^-(ref). $\Delta_r H°(Zn^- \rightarrow Zn + e^-, 298.15 K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[6] $\Delta_f H°(298.15 K)$ should be changed by + 6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Zn^-(g) is that given by Zollwig.[2] Lacking any experimental evidence as to the stability of any excited states, we assume that no stable states exist.

References

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Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−6.197	115.539		
100	20.786	138.282	179.469	−4.119			
200	20.786	152.689	162.890	−2.040			
250	20.786	157.328	161.331	−1.001			
298.15	20.786	160.989	160.989	0.	109.870	80.564	−14.114
300	20.786	161.117	160.989	0.038	109.823	80.382	−13.996
350	20.786	164.321	161.242	1.078	108.540	75.576	−11.279
400	20.786	167.097	161.804	2.117	107.234	70.956	−9.266
450	20.786	169.545	162.531	3.156	105.905	66.501	−7.719
500	20.786	171.735	163.344	4.196	104.549	62.195	−6.497
600	20.786	175.525	165.068	6.274	101.752	53.985	−4.700
700	20.786	178.729	166.797	8.353	91.495	46.330	−3.457
800	20.786	181.505	168.466	10.431	88.357	40.092	−2.618
900	20.786	183.953	170.053	12.510	85.219	34.247	−1.988
1000	20.786	186.143	171.554	14.589	82.081	28.752	−1.502
1100	20.786	188.124	172.972	16.667	78.943	23.571	−1.119
1200	20.786	189.933	174.311	18.746	−39.296	20.611	−0.897
1300	20.786	191.597	175.578	20.824	−41.374	25.688	−1.032
1400	20.786	193.137	176.778	22.903	−43.453	30.924	−1.154
1500	20.786	194.571	177.917	24.982	−45.532	36.310	−1.264
1600	20.786	195.913	179.000	27.060	−47.610	41.834	−1.366
1700	20.786	197.173	180.032	29.139	−49.689	47.487	−1.459
1800	20.786	198.361	181.018	31.217	−51.767	53.264	−1.546
1900	20.786	199.485	181.960	33.296	−53.846	59.155	−1.626
2000	20.786	200.551	182.864	35.375	−55.925	65.157	−1.702
2100	20.786	201.565	183.730	37.453	−58.003	71.262	−1.773
2200	20.786	202.532	184.563	39.532	−60.082	77.466	−1.839
2300	20.786	203.456	185.364	41.610	−62.160	83.765	−1.902
2400	20.786	204.341	186.137	43.689	−64.239	90.154	−1.962
2500	20.786	205.189	186.882	45.768	−66.318	96.630	−2.019
2600	20.786	206.004	187.602	47.846	−68.396	103.189	−2.073
2700	20.786	206.789	188.298	49.925	−70.475	109.827	−2.125
2800	20.786	207.545	188.972	52.004	−72.554	116.543	−2.174
2900	20.786	208.274	189.625	54.082	−74.632	123.334	−2.221
3000	20.786	208.979	190.259	56.161	−76.711	130.195	−2.267
3100	20.786	209.660	190.874	58.239	−78.790	137.127	−2.311
3200	20.786	210.320	191.471	60.318	−80.869	144.125	−2.353
3300	20.786	210.960	192.052	62.397	−82.949	151.188	−2.393
3400	20.786	211.581	192.617	64.475	−85.029	158.314	−2.432
3500	20.786	212.183	193.168	66.554	−87.109	165.502	−2.470
3600	20.786	212.769	193.704	68.632	−89.190	172.749	−2.507
3700	20.786	213.338	194.227	70.711	−91.272	180.053	−2.542
3800	20.786	213.892	194.737	72.790	−93.355	187.414	−2.576
3900	20.786	214.432	195.235	74.868	−95.439	194.830	−2.609
4000	20.786	214.959	195.722	76.947	−97.525	202.299	−2.642
4100	20.786	215.472	196.197	79.025	−99.614	209.821	−2.673
4200	20.786	215.973	196.662	81.104	−101.704	217.393	−2.704
4300	20.786	216.462	197.117	83.183	−103.798	225.016	−2.733
4400	20.786	216.940	197.562	85.261	−105.895	232.687	−2.762
4500	20.786	217.407	197.998	87.340	−107.997	240.406	−2.791
4600	20.786	217.864	198.425	89.418	−110.103	248.171	−2.818
4700	20.786	218.311	198.843	91.497	−112.215	255.982	−2.845
4800	20.786	218.748	199.253	93.576	−114.334	263.839	−2.871
4900	20.786	219.177	199.656	95.654	−116.459	271.739	−2.897
5000	20.786	219.597	200.050	97.733	−118.593	279.683	−2.922
5100	20.786	220.009	200.438	99.811	−120.736	287.670	−2.946
5200	20.786	220.412	200.818	101.890	−122.889	295.699	−2.970
5300	20.786	220.808	201.191	103.969	−125.053	303.770	−2.994
5400	20.786	221.197	201.558	106.047	−127.230	311.881	−3.017
5500	20.786	221.578	201.919	108.126	−129.420	320.033	−3.039
5600	20.786	221.953	202.273	110.204	−131.626	328.224	−3.062
5700	20.786	222.320	202.622	112.283	−133.847	336.456	−3.083
5800	20.786	222.682	202.964	114.362	−136.086	344.726	−3.105
5900	20.786	223.037	203.302	116.440	−138.344	353.035	−3.126
6000	20.786	223.387	203.634	118.519	−140.622	361.383	−3.146

PREVIOUS: December 1978 (1 atm) CURRENT: September 1984 (1 bar)

REFERENCE STATE

0	to	1135	K	crystal, alpha
1135	to	2125	K	crystal, beta
2125	to	4702.633	K	liquid
4702.633	to	6000	K	ideal monatomic gas

Refer to the individual tables for details

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = p° = 0.1 MPa**

	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.	0.	INFINITE	−5.497	0.	0.	0.
100	18.617	14.055	60.166	−4.611	0.	0.	0.
200	23.873	29.050	41.140	−2.418	0.	0.	0.
298.15	25.202	38.869	38.869	0.	0.	0.	0.
300	25.218	39.025	38.870	0.047	0.	0.	0.
400	25.935	46.384	39.868	2.606	0.	0.	0.
500	26.564	52.238	41.776	5.231	0.	0.	0.
600	27.281	57.143	43.939	7.922	0.	0.	0.
700	28.053	61.406	46.136	10.689	0.	0.	0.
800	28.966	65.210	48.287	13.538	0.	0.	0.
900	30.003	68.680	50.363	16.486	0.	0.	0.
1000	31.128	71.899	52.357	19.542	0.	0.	0.
1100	32.306	74.921	54.272	22.713	0.	0.	0.
1135.000	32.724	75.939	54.925	23.851	ALPHA <--> BETA		
1135.000	28.329	79.478	54.925	27.868	TRANSITION		
1200	28.511	81.060	56.298	29.715	0.	0.	0.
1300	28.879	83.356	58.292	32.584	0.	0.	0.
1400	29.353	85.513	60.160	35.494	0.	0.	0.
1500	29.934	87.558	61.919	38.458	0.	0.	0.
1600	30.621	89.511	63.583	41.485	0.	0.	0.
1700	31.414	91.390	65.164	44.585	0.	0.	0.
1800	32.314	93.211	66.672	47.771	0.	0.	0.
1900	33.320	94.985	68.115	51.052	0.	0.	0.
2000	34.433	96.722	69.502	54.439	0.	0.	0.
2100	35.652	98.431	70.839	57.942	0.	0.	0.
2125.000	35.973	98.854	71.166	58.837	BETA <--> LIQUID		
2125.000	41.840	108.699	71.166	79.757	TRANSITION		
2200	41.840	110.150	72.471	82.895	0.	0.	0.
2300	41.840	112.010	74.150	87.079	0.	0.	0.
2400	41.840	113.791	75.765	91.263	0.	0.	0.
2500	41.840	115.499	77.320	95.447	0.	0.	0.
2600	41.840	117.140	78.820	99.631	0.	0.	0.
2700	41.840	118.719	80.269	103.815	0.	0.	0.
2800	41.840	120.241	81.669	107.999	0.	0.	0.
2900	41.840	121.709	83.025	112.183	0.	0.	0.
3000	41.840	123.127	84.338	116.367	0.	0.	0.
3100	41.840	124.499	85.612	120.551	0.	0.	0.
3200	41.840	125.827	86.848	124.735	0.	0.	0.
3300	41.840	127.115	88.049	128.919	0.	0.	0.
3400	41.840	128.364	89.216	133.103	0.	0.	0.
3500	41.840	129.577	90.352	137.287	0.	0.	0.
3600	41.840	130.756	91.458	141.471	0.	0.	0.
3700	41.840	131.902	92.536	145.655	0.	0.	0.
3800	41.840	133.018	93.586	149.839	0.	0.	0.
3900	41.840	134.105	94.611	154.023	0.	0.	0.
4000	41.840	135.164	95.612	158.207	0.	0.	0.
4100	41.840	136.197	96.589	162.391	0.	0.	0.
4200	41.840	137.205	97.544	166.575	0.	0.	0.
4300	41.840	138.190	98.478	170.759	0.	0.	0.
4400	41.840	139.152	99.392	174.943	0.	0.	0.
4500	41.840	140.092	100.286	179.127	0.	0.	0.
4600	41.840	141.011	101.161	183.311	0.	0.	0.
4700	41.840	141.911	102.019	187.495	0.	0.	0.
4702.633	41.840	141.935	102.041	187.605	LIQUID <--> IDEAL GAS		
4702.633	38.083	261.292	102.041	748.899	FUGACITY = 1 bar		
4800	38.268	262.074	105.279	752.616	0.	0.	0.
4900	38.445	262.865	108.487	756.451	0.	0.	0.
5000	38.608	263.643	111.583	760.304	0.	0.	0.
5200	38.894	265.163	117.460	768.055	0.	0.	0.
5400	39.126	266.636	122.958	775.858	0.	0.	0.
5600	39.306	268.062	128.115	783.702	0.	0.	0.
5800	39.437	269.444	132.965	791.577	0.	0.	0.
6000	39.522	270.782	137.537	799.474	0.	0.	0.

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

$S°(298.15\ K) = 38.87 \pm 0.2\ J \cdot K^{-1} \cdot mol^{-1}$
$T_{trs} = 1135 \pm 10\ K$ (α–β)

$\Delta_f H°(0\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_f H°(298.15\ K) = 0\ kJ \cdot mol^{-1}$
$\Delta_{trs} H° = 4.017 \pm 0.3\ kJ \cdot mol^{-1}$

Enthalpy of Formation

Zero by definition.

Heat Capacity and Entropy

The adopted thermal functions for α–Zr(cr) are derived from the studies of Collings and Ho,[1] Wolcott,[2] Burk *et al.*,[3] Skinner and Johnston,[4] Todd,[5] and Scott.[6] The mathematical and graphical treatment of these four studies yields a continuous and smooth heat capacity curve.

There are six studies[1, 2, 7–10] on the heat capacity of zirconium in the region 1–5 K. Only Wolcott[2] reported the experimental data (60 data points). In the other studies, an equation (with two constants) was given to describe the entire set of experimental data. The constants given by Collings and Ho[1] and the data of Wolcott[2] were used in this region. The maximum difference in the calculated values for $S°$(5 K) is 0.00029 $cal \cdot mol^{-1} \cdot K^{-1}$, with the adopted value being $S°(5\ K) = 0.0043\ cal \cdot mol^{-1} \cdot K^{-1}$. Similarly for $C_p°$(5 K) the maximum difference is 0.00073 $cal \cdot mol^{-1} \cdot K^{-1}$, with the adopted value being $C_p°(5\ K) = 0.00610\ cal \cdot mol^{-1} \cdot K^{-1}$.

In the region above 5 K and below 300 K, there are four heat capacity studies.[2–5] There is much scatter among the different studies, between 150 and 300 K. From 150–200 K, we adopt graphically smoothed C_p values intermediate between Burk *et al.*,[2] Skinner and Johnston,[4] and Todd.[5] From 200–300 K, we adopt the data of Skinner and Johnston,[4] because it meshes better with the high temperature data. Burk's data is 1.4% higher than the adopted at 170 K, Todd's data is 0.7% higher and Skinner's data ia 1% lower. Todd's data is 3% higher than the adopted at 300 K.

Between 300 K and 1135 K there are three heat capacity studies[6, 11, 12] and seven enthalpy studies.[13–19] The three heat capacity studies show much scatter and disagreement. The data of Scott[6] was adopted, although only the data from runs 17 and 64, out of a total of nine runs, was actually used in the fit. None of Scott's data below 540 K were used in the fit, becuase the data had a hump in this region and appeared to be high. The region between the low temperature data (300 K) and 540 K was graphically smoothed to assure continuity in the C_p curve. The data of Scott[6] is about 5% higher than the adopted between 300 and 540 K. Between 540 and 960 K it is within ±3% of the adopted. From 960 K to the transition temperature, there is much scatter; some of the data are as much as 20% higher than the adopted. The data of Vollmer *et al.*[12] are about 3% lower than the adopted at 300 K. Between 540 and 580 it agrees with the adopted. From 580–1000 K it is about 1.5% higher than the adopted. The data of Klein and Danielson[11] was given only as a graph. It is considerably lower than the adopted values.

The enthalpy studies show an unusually large scatter within each study, as well as a lack of agreement between the studies. When plotted as mean heat capacity, the seven studies are all higher than the adopted values, by 2 to 40%.

Transition Data

Refer to the β–Zr(cr) table for details.

Sublimation Data

There are no experimental sublimation studies involving α–Zr(cr). The enthalpy of sublimation is calculated as the difference between the enthalpy of formation of the monatomic gas and the enthalpy of formation of α–Zr(cr).

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J \cdot K^{-1} \cdot mol^{-1}$			$kJ \cdot mol^{-1}$			
0	0.	0.	INFINITE	−5.497	0.	0.	0.
100	18.617	14.055	60.166	−4.611	0.	0.	0.
200	23.873	29.050	41.140	−2.418	0.	0.	0.
250	24.693	34.474	39.281	−1.202	0.	0.	0.
298.15	25.202	38.869	38.869	0.	0.	0.	0.
300	25.218	39.025	38.870	0.047	0.	0.	0.
350	25.606	42.943	39.178	1.318	0.	0.	0.
400	25.935	46.384	39.868	2.606	0.	0.	0.
450	26.246	49.457	40.766	3.911	0.	0.	0.
500	26.564	52.238	41.776	5.231	0.	0.	0.
600	27.281	57.143	43.939	7.922	0.	0.	0.
700	28.053	61.406	46.136	10.689	0.	0.	0.
800	28.966	65.210	48.287	13.538	0.	0.	0.
900	30.003	68.680	50.363	16.486	0.	0.	0.
1000	31.128	71.899	52.357	19.542	0.	0.	0.
1100	32.306	74.921	54.272	22.713	0.	0.	0.
1135.000	32.724	75.939	54.925	23.851	----- ALPHA <---> BETA -----		
1200	33.502	77.783	56.113	26.004	−3.711	0.222	−0.010
1300	34.681	80.511	57.886	29.413	−3.170	0.528	−0.021
1400	35.807	83.123	59.596	32.938	−2.556	0.790	−0.029
1500	36.846	85.630	61.249	36.572	−1.886	1.006	−0.035
1600	37.762	88.038	62.848	40.304	−1.181	1.176	−0.038
1700	38.520	90.351	64.398	44.119	−0.466	1.301	−0.040

PREVIOUS: December 1967 CURRENT: June 1979

$S°(298.15\ K) = [43.192]\ J·K^{-1}·mol^{-1}$
$T_{trs} = 1135 \pm 10\ K$ (α–β)
$T_{fus} = 2125 \pm 15\ K$ (β–l)

$\Delta_f H°(298.15\ K) = [4.810]\ kJ·mol^{-1}$
$\Delta_{trs}H° = 4.017 \pm 0.3\ kJ·mol^{-1}$
$\Delta_{fus}H° = 20.92 \pm 6.3\ kJ·mol^{-1}$

Enthalpy of Formation

The enthalpy of formation is calculated from that of the α–crystal by addition of $\Delta_{trs}H°$ and the difference in enthalpy, $H°(1135\ K)–H°(298.15\ K)$, between the α–crystal and the β–crystal.

Heat Capacity and Entropy

There are five heat capacity studies[1-5] and five enthalpy studies[6-10] over the temperature range 1135–2125 K. The adopted values were based on the heat capcity study of Cezairliyan and Righini.[4] The data of Scott[1] showed much scatter with a maximum deviation of 7% from the adopted. The data of Rumyantsu *et al.*[5] were largely scattered and about 15% high. The data of Vollmer *et al.*[3] and of Klein and Danielson[2] were 5–10% lower than the adopted. The enthalpy studies show an unusually large scatter within each study, as well as lack of agreement between the studies. Like the α–Zr(cr), the mean heat capacities are all higher than the adopted values, by 3 to 10%. The entropy at 298.15 K is calculated in a manner similar to that for the enthalpy of formation.

Phase Data

Zirconium, at ambient pressures, exists in two crystal modifications. The low temperature form, α–Zr, is hexagonal close packed, an hcp (A3) structure isotypic with Mg. The high temperature form, β–Zr, is body centered cubic, a bcc (A2) structure.

Transition Data

The transition temperature and enthalpies of transition are summarized in the table below. The adopted value of T_{trs} is 1135 ± 10 K. The adopted $\Delta_{trs}H°$ is 4.017 kJ·mol^{-1}.

Source	T_{trs}/K	$\Delta_{trs}H°$, kcal·mol^{-1}	Purity	Method
Vogel and Tonn[11]	1135 ± 5	–	–	cooling and dilatometric curves
Jaeger and Veenstra[12]	<1150	–	–	drop calorimetry
Coughlin and King[6]	1135	0.920	97.85	drop calorimetry
Dewey[13]	1138 ± 10	–	–	cooling curve
Skinner[7]	1143 ± 5	1.042	99.05	drop calorimetry
Komar and Shrednik[14]	1135	–	–	electron microscope
Scott[1]	1143 ± 2	0.993 ± 0.025	–	adiabatic calorimetry
Douglas and Victor[9]	1136	0.894	99.91	drop calorimetry
Gertzricken and Slyusar[15]	1135	0.712 ± 0.060	–	differential calorimetry
Klein and Danielson[2]	1138	–	–	resistivity
Rudy *et al.*[16]	1145 ± 15	–	99.81	differential thermal analysis
Vollmer *et al.*[3]	1155	0.950	99.8	adiabatic calorimetry
Peletskii *et al.*[17]	1148 ± 5	–	–	resistivity
Martynyuk and Tsapkov[18]	–	1.076	99.76	resistivity

Fusion Data

Refer to the liquid table for details.

Sublimation Data

The sublimation studies involving β–Zr(cr) are summarized on the Zr(g) table. The enthalpy of sublimation for β–Zr(cr) is calculated as the difference in the enthalpies of formation at 298.15 K of Zr(g) and β–Zr(cr).

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Continued on page 1951

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}mol^{-1}			kJ·mol^{-1}			
0							
100							
200							
250							
298.15	25.202	43.192	43.192	0.	4.810	3.521	−0.617
300	25.218	43.348	43.193	0.047	4.810	3.513	−0.612
350	25.587	47.264	43.501	1.317	4.809	3.297	−0.492
400	25.935	50.703	44.191	2.605	4.809	3.081	−0.402
450	26.238	53.775	45.088	3.909	4.808	2.865	−0.333
500	26.564	56.557	46.098	5.229	4.808	2.649	−0.277
600	27.281	61.462	48.261	7.921	4.809	2.217	−0.193
700	28.053	65.724	50.457	10.687	4.808	1.785	−0.133
800	28.966	69.535	52.608	13.542	4.813	1.353	−0.088
900	28.473	72.916	54.681	16.412	4.736	0.923	−0.054
1000	28.238	75.902	56.656	19.245	4.513	0.511	−0.027
1100	28.260	78.592	58.530	22.068	4.164	0.126	−0.006
1135.000	28.329	79.478	59.163	23.058	---- ALPHA <--> BETA ----		
1200	28.511	81.060	60.306	24.905	0.	0.	0.
1300	28.879	83.356	61.992	27.774	0.	0.	0.
1400	29.353	85.513	63.596	30.684	0.	0.	0.
1500	29.934	87.558	65.126	33.648	0.	0.	0.
1600	30.621	89.511	66.589	36.675	0.	0.	0.
1700	31.414	91.390	67.993	39.776	0.	0.	0.
1800	32.314	93.211	69.344	42.961	0.	0.	0.
1900	33.320	94.985	70.647	46.242	0.	0.	0.
2000	34.433	96.722	71.907	49.629	0.	0.	0.
2100	35.652	98.431	73.130	53.132	0.	0.	0.
2125.000	35.973	98.854	73.430	54.027	---- BETA <--> LIQUID ----		
2200	36.977	100.119	74.318	56.763	−21.323	0.746	−0.018
2300	38.409	101.794	75.476	60.531	−21.738	1.759	−0.040
2400	39.947	103.461	76.608	64.448	−22.005	2.786	−0.061
2500	41.591	105.125	77.715	68.524	−22.113	3.822	−0.080
2600	43.342	106.790	78.801	72.770	−22.052	4.859	−0.098

PREVIOUS: December 1967 CURRENT: June 1979

$S°(298.15\ K)$ = [47.605] $J·K^{-1}·mol^{-1}$
T_{fus} = 2125 ± 15 K

$\Delta_f H°(298.15\ K)$ = [17.404] $kJ·mol^{-1}$
$\Delta_{fus}H°$ = 20.92 ± 6.3 $kJ·mol^{-1}$

Enthalpyof Formation

The enthalpy of formation is calculated from that of the β–crystal by addition of $\Delta_{fus}H°$ and the difference in enthalpy, $H°(2125\ K)–H°(298.15\ K)$, between the β–crystal and the liquid.

Heat Capacity and Entropy

There are no heat capacity or enthalpy studies covering the liquid region of zirconium. A constant value of $C_p°$ = 41.84 $J·K^{-1}·mol^{-1}$ is assumed for the region 2125–5500 K. A glass transition is assumed at 1580 K below which extrapolated β–Zr heat capacity values are used. The entropy is calculated in a manner similar to that used for the enthalpy of formation.

Fusion Data

The available fusion temperature and enthalpy of fusion data are summarized in the table below. We adopt T_{fus} = 2125 ± 15 K and $\Delta_{fus}H°$ = 20.92 ± 6.3 $kJ·mol^{-1}$.

Source	T_{fus}/k	$\Delta_{fus}H°$, $kcal·mol^{-1}$
deBoer and Fast[1]	2130	
Adenstedt [2]	2113	
Oriani and Jones [3]	2125 ± 2	
Deardorff and Hayes [4]	2128	
Scott [5]	2118	
Klein and Danielson [6]	2118	
Rudy et al [7]	2150 ± 20	
Sara [8]	2133 ± 15	
Rudy and Windisch [9]	2149 ± 4	
Elyutin et al [10]		5.0 ± 0.3
Ackerman and Rauk [11]	2134	
Martynyuk and Tsapkov [12]		5.139

Vaporization Data

The vaporization studies are summarized on the Zr(g) table. The boiling point is calculated as that temperature for which $\Delta_r G° = 0$ for Zr(l) = Zr(g). $\Delta_{vap}H°$ is the corresponding enthalpy change. T_{vap} is the temperature at which the fugacity is one bar.

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
0							
100							
200							
250							
298.15	25.202	47.605	47.605	0.	17.404	14.799	−2.593
300	25.218	47.761	47.605	0.047	17.404	14.783	−2.574
350	25.606	51.678	47.914	1.318	17.404	14.346	−2.141
400	25.935	55.120	48.604	2.606	17.404	13.910	−1.816
450	26.246	58.192	49.502	3.911	17.404	13.473	−1.564
500	26.564	60.974	50.512	5.231	17.404	13.036	−1.362
600	27.281	65.878	52.675	7.922	17.404	12.162	−1.059
700	28.053	70.141	54.872	10.689	17.404	11.289	−0.842
800	28.966	73.945	57.022	13.538	17.404	10.415	−0.680
900	30.003	77.416	59.098	16.486	17.404	9.542	−0.554
1000	31.128	80.635	61.093	19.542	17.404	8.668	−0.453
1100	32.306	83.656	63.008	22.713	17.404	7.795	−0.370
1200	33.502	86.519	64.849	26.004	13.693	7.143	−0.311
1300	34.681	89.247	66.622	29.413	14.234	6.575	−0.264
1400	35.807	91.859	68.332	32.938	14.848	5.964	−0.223
1500	36.846	94.365	69.984	36.572	15.518	5.306	−0.185
1580.000	37.614	96.300	71.268	39.551	GLASS <-- -> LIQUID		
1580.000	41.840	96.300	71.268	39.551	TRANSITION		
1600	41.840	96.826	71.584	40.387	16.307	4.602	−0.150
1700	41.840	99.363	73.144	44.571	17.390	3.837	−0.118
1800	41.840	101.754	74.668	48.755	18.388	3.010	−0.087
1900	41.840	104.016	76.154	52.939	19.291	2.131	−0.059
2000	41.840	106.163	77.601	57.123	20.089	1.207	−0.032
2100	41.840	108.204	79.010	61.307	20.769	0.245	−0.006
2125.000	41.840	108.699	79.356	62.353	---- BETA <--> LIQUID		----
2200	41.840	110.150	80.382	65.491	0.	0.	0.
2300	41.840	112.010	81.717	69.675	0.	0.	0.
2400	41.840	113.791	83.016	73.859	0.	0.	0.
2500	41.840	115.499	84.282	78.043	0.	0.	0.
2600	41.840	117.140	85.514	82.227	0.	0.	0.
2700	41.840	118.719	86.715	86.411	0.	0.	0.
2800	41.840	120.241	87.885	90.595	0.	0.	0.
2900	41.840	121.709	89.026	94.779	0.	0.	0.
3000	41.840	123.127	90.139	98.963	0.	0.	0.
3100	41.840	124.499	91.226	103.147	0.	0.	0.
3200	41.840	125.828	92.286	107.331	0.	0.	0.
3300	41.840	127.115	93.322	111.515	0.	0.	0.
3400	41.840	128.364	94.335	115.699	0.	0.	0.
3500	41.840	129.577	95.324	119.883	0.	0.	0.
3600	41.840	130.756	96.292	124.067	0.	0.	0.
3700	41.840	131.902	97.239	128.251	0.	0.	0.
3800	41.840	133.018	98.166	132.435	0.	0.	0.
3900	41.840	134.105	99.074	136.619	0.	0.	0.
4000	41.840	135.164	99.963	140.803	0.	0.	0.
4100	41.840	136.197	100.834	144.987	0.	0.	0.
4200	41.840	137.205	101.688	149.171	0.	0.	0.
4300	41.840	138.190	102.526	153.355	0.	0.	0.
4400	41.840	139.152	103.347	157.539	0.	0.	0.
4500	41.840	140.092	104.153	161.723	0.	0.	0.
4600	41.840	141.011	104.945	165.907	0.	0.	0.
4700	41.840	141.911	105.722	170.091	0.	0.	0.
4702.633	41.840	141.935	105.742	170.201	----- FUGACITY = 1 bar		-----
4800	41.840	142.792	106.485	174.275	−560.936	11.617	−0.126
4900	41.840	143.655	107.235	178.459	−560.588	23.542	−0.251
5000	41.840	144.500	107.971	182.643	−560.257	35.459	−0.370
5100	41.840	145.329	108.696	186.827	−559.941	47.371	−0.485
5200	41.840	146.141	109.408	191.011	−559.640	59.276	−0.595
5300	41.840	146.938	110.109	195.195	−559.352	71.175	−0.701
5400	41.840	147.720	110.798	199.379	−559.075	83.069	−0.804
5500	41.840	148.488	111.476	203.563	−558.809	94.958	−0.902

PREVIOUS: December 1967 CURRENT: June 1979

0	to	1135 K	crystal, alpha
1135	to	2125 K	crystal, beta
above		2125 K	liquid

Refer to the individual tables for details.

Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

	J·K⁻¹mol⁻¹			kJ·mol⁻¹			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	0.	0.	INFINITE	−5.497	0.	0.	0.
100	18.617	14.055	60.166	−4.611	0.	0.	0.
200	23.873	29.050	41.140	−2.418	0.	0.	0.
250	24.693	34.474	39.281	−1.202	0.	0.	0.
298.15	25.202	38.869	38.869	0.	0.	0.	0.
300	25.218	39.025	38.870	0.047	0.	0.	0.
350	25.606	42.943	39.178	1.318	0.	0.	0.
400	25.935	46.384	39.868	2.606	0.	0.	0.
450	26.246	49.457	40.766	3.911	0.	0.	0.
500	26.564	52.238	41.776	5.231	0.	0.	0.
600	27.281	57.143	43.939	7.922	0.	0.	0.
700	28.053	61.406	46.136	10.689	0.	0.	0.
800	28.966	65.210	48.287	13.538	0.	0.	0.
900	30.003	68.680	50.363	16.486	0.	0.	0.
1000	31.128	71.899	52.357	19.542	0.	0.	0.
1100	32.306	74.921	54.272	22.713	0.	0.	0.
1135.000	32.724	75.939	54.925	23.851	ALPHA <--> BETA TRANSITION		
1135.000	28.329	79.478	54.925	27.868			
1200	28.511	81.060	56.298	29.715	0.	0.	0.
1300	28.879	83.356	58.292	32.584	0.	0.	0.
1400	29.353	85.513	60.160	35.494	0.	0.	0.
1500	29.934	87.558	61.919	38.458	0.	0.	0.
1600	30.621	89.511	63.583	41.485	0.	0.	0.
1700	31.414	91.390	65.164	44.585	0.	0.	0.
1800	32.314	93.211	66.672	47.771	0.	0.	0.
1900	33.320	94.985	68.115	51.052	0.	0.	0.
2000	34.433	96.722	69.502	54.439	0.	0.	0.
2100	35.652	98.431	70.839	57.942	0.	0.	0.
2125.000	35.973	98.854	71.166	58.837	BETA <--> LIQUID TRANSITION		
2125.000	41.840	108.699	71.166	79.757			
2200	41.840	110.150	72.471	82.895	0.	0.	0.
2300	41.840	112.010	74.150	87.079	0.	0.	0.
2400	41.840	113.791	75.765	91.263	0.	0.	0.
2500	41.840	115.499	77.320	95.447	0.	0.	0.
2600	41.840	117.140	78.820	99.631	0.	0.	0.
2700	41.840	118.719	80.269	103.815	0.	0.	0.
2800	41.840	120.241	81.669	107.999	0.	0.	0.
2900	41.840	121.709	83.025	112.183	0.	0.	0.
3000	41.840	123.127	84.338	116.367	0.	0.	0.
3100	41.840	124.499	85.612	120.551	0.	0.	0.
3200	41.840	125.827	86.848	124.735	0.	0.	0.
3300	41.840	127.115	88.049	128.919	0.	0.	0.
3400	41.840	128.364	89.216	133.103	0.	0.	0.
3500	41.840	129.577	90.352	137.287	0.	0.	0.
3600	41.840	130.756	91.458	141.471	0.	0.	0.
3700	41.840	131.902	92.536	145.655	0.	0.	0.
3800	41.840	133.018	93.586	149.839	0.	0.	0.
3900	41.840	134.105	94.611	154.023	0.	0.	0.
4000	41.840	135.164	95.612	158.207	0.	0.	0.
4100	41.840	136.197	96.589	162.391	0.	0.	0.
4200	41.840	137.205	97.544	166.575	0.	0.	0.
4300	41.840	138.190	98.478	170.759	0.	0.	0.
4400	41.840	139.152	99.392	174.943	0.	0.	0.
4500	41.840	140.092	100.286	179.127	0.	0.	0.
4600	41.840	141.011	101.161	183.311	0.	0.	0.
4700	41.840	141.911	102.019	187.495	0.	0.	0.
4702.633	41.840	141.935	102.041	187.605	FUGACITY = 1 bar		
4800	41.840	142.792	102.859	191.679	−560.936	11.617	−0.126
4900	41.840	143.655	103.683	195.863	−560.588	23.542	−0.251
5000	41.840	144.500	104.491	200.047	−560.257	35.459	−0.370
5100	41.840	145.329	105.283	204.231	−559.941	47.371	−0.485
5200	41.840	146.141	106.061	208.415	−559.640	59.276	−0.595
5300	41.840	146.938	106.825	212.599	−559.352	71.175	−0.701
5400	41.840	147.720	107.575	216.783	−559.075	83.069	−0.804
5500	41.840	148.488	108.312	220.967	−558.809	94.958	−0.902

PREVIOUS: CURRENT: June 1979

IP(Zr, g) = 55145 ± 500 cm^{-1}
$S°(298.15\ K)$ = 181.343 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°(0\ K)$ = 608.7 ± 8.4 $kJ·mol^{-1}$
$\Delta_f H°(298.15\ K)$ = 610.0 ± 8.4 $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^3F_2$	0.00	5
$^3F_3$	570.41	7
$^3F_4$	1240.84	9
–	–	–
–	–	–
–	–	–
IP_0^1	51899.40	3
IP	55145	

Enthalpy of Formatiom

Vapor pressures over Zr(β) and Zr(l) were measured, using the Langmuir free–vaporization method, by Zwikker,[1] Skinner *et al.*,[2] Fidorov and Smirnov[3,4] and Koch and Anable.[5] Trulson and Goldstein[6] used a mass spectrometric method with a high temperature Knudson effusion source to obtain the vapor pressure for Zr(β) and Zr(l). Similarly, Ackermann and Rauh[7] determined the vapor pressure for Zr(l) by a combination of mass effusion and mass spectrometric techniques. In this latter study the reported values (equation only) were obtained from vapor pressure measurements over Zr(l) saturated with tungsten. These values were then corrected for the dissolved tungsten by the corresponding mole fraction.

A plot of log p vs. 1/T for the above mentioned studies reveals considerable discrepancy. The results of Fredorov and Smirnov[3,4] are an order of magnitude higher than those of Zwikker;[1] however, both studies appear inconsistent with the other studies involving Zr(β).[2,6,7] The sublimation studies of Golubtsov *et al.*[9] and Sumin and Peizularz[10] reported $\Delta_f H°(0\ K)$ values of 143.1 ± 0.22 and 145.6 ± 0.4 $kcal·mol^{-1}$, respectively. The experimental data is not given in either study.

A second and third law evaluation of seven studies yields an adopted enthalpy of formation value, $\Delta_f H°(298.15\ K, Zr, g)$ = 145.8 ± 2.0 $kcal·mol^{-1}$. This adopted value is a weighted average of four vapor pressure studies.[2,5,6,7] Hultgren,[8] using different thermodynamic functions and data available through 1967, recommended a enthalpy of foramtion (at 298.15 K) of 145.5 ± 1.0 $kcal·mol^{-1}$, based primarily on the data of Skinner *et al.*[2]

Investigator	Reaction	T/K	Points	$\Delta_f H°(298.15\ K)$, $kcal·mol^{-1}$ 2nd law	3rd law	Drift $cal·K^{-1}·mol^{-1}$	$\Delta_f H°(298.15\ K)$ $kcal·mol^{-1}$
Zwikker[1]	a	1600–2100	Eqn	62.9	139.6	41.5	140.8
Skinner *et al.*[2]	a	1949–2054	12	144.2 ± 3.0	146.5 ± 0.3	1.2 ± 1.0	147.7
Trulson and Goldstein[6]	a	1968–2112	14	143.0 ± 3.6	142.8 ± 0.5	−0.1 ± 1.8	144.0
Federov *et al.*[3,4]	a	1498–1723	6	59.9 ± 0.1	122.4 ± 6.8	39.0 ± 0.1	123.6
Ackermann and Rauh[7]	a	1975–2100	Eqn	148.5	144.4	−2.0	145.6
Trulson and Goldstein[6]	b	2148–2274	8	129.7 ± 4.9	137.7 ± 0.6	3.6 ± 2.2	142.7
Koch and Anable[5]	b	2229–2795	16	144.5 ± 4.2	144.1 ± 2.4	−0.2 ± 1.7	149.1
Ackermann and Rauh[7]	b	2150–2500	Eqn	139.6	139.3	−0.1	144.3

Reactions: a. Zr(β) = Zr(g) b. Zr(l) = Zr(g)

Heat Capacity and Entropy

The electronic energy levels are given in the compilation by Moore.[11,12] Although we have only listed the ground state, first two excited states, the highest observed excited state, and the ionization limit for Zr(g), all levels listed by Moore,[11,12] as well as estimated missing levels for n = 5 and 6, are used in our calculations. The observed levels are too numerous to list completely. Our calculations indicate that for Zr(g) the thermochemical functions are independent of the estimated missing levels for n = 5 and 6 (levels estimated and included above 52000 cm^{-1}) and the cut–off procedure up to 4000 K. The Gibbs energy function is essentially unaffected (<0.001 $kcal·mol^{-1}$) up to 6000 K. The reported uncertainty in $S°(298.15\ K)$ is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the more exact estimation of excited states for n = 5 and 6, the consideration of states for n > 6, and the utilization of proper fill and cut–off procedures.[13]

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Continued on page 1951

Enthalpy Reference Temperature = T_r = 298.15 K **Standard State Pressure = $p°$ = 0.1 MPa**

	$J·K^{-1}·mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−6.816	608.709	608.709	INFINITE
100	21.000	155.846	203.189	−4.734	609.904	595.725	−311.175
150	22.249	164.561	188.944	−3.657	609.946	588.621	−204.976
200	24.029	171.205	183.708	−2.501	609.944	581.514	−151.876
250	25.576	176.740	181.776	−1.259	609.970	574.404	−120.015
298.15	26.641	181.343	181.343	.000	610.027	567.549	−99.432
300	26.674	181.507	181.343	.049	610.030	567.285	−98.773
350	27.344	185.675	181.671	1.401	610.111	560.155	−83.599
400	27.664	189.350	182.406	2.778	610.199	553.012	−72.216
450	27.718	192.614	183.362	4.163	610.280	545.859	−63.362
500	27.589	195.529	184.436	5.547	610.343	538.697	−56.277
600	27.045	200.514	186.714	8.280	610.385	524.362	−45.650
700	26.424	204.636	188.989	10.953	610.292	510.031	−38.059
800	25.934	208.130	191.168	13.570	610.058	495.722	−32.367
900	25.660	211.167	193.225	16.147	609.689	481.451	−27.943
1000	25.610	213.866	195.157	18.709	609.194	467.227	−24.405
1100	25.754	216.312	196.971	21.276	608.590	453.059	−21.514
1200	26.048	218.565	198.677	23.865	604.177	439.172	−19.117
1300	26.442	220.665	200.289	26.489	603.932	425.431	−17.094
1400	26.895	222.641	201.816	29.155	603.688	411.710	−15.361
1500	27.371	224.513	203.267	31.869	603.438	398.006	−13.860
1600	27.844	226.294	204.651	34.629	603.172	384.319	−12.547
1700	28.298	227.996	205.974	37.437	602.878	370.649	−11.389
1800	28.724	229.626	207.243	40.288	602.544	356.998	−10.360
1900	29.118	231.189	208.463	43.180	602.156	343.367	−9.440
2000	29.482	232.692	209.637	46.111	601.699	329.758	−8.612
2100	29.819	234.139	210.770	49.076	601.161	316.174	−7.864
2200	30.134	235.534	211.864	52.074	579.206	303.363	−7.203
2300	30.432	236.880	212.922	55.102	578.050	290.850	−6.605
2400	30.719	238.181	213.948	58.160	576.924	278.388	−6.059
2500	31.000	239.441	214.942	61.246	575.826	265.971	−5.557
2600	31.279	240.662	215.908	64.360	574.756	253.598	−5.095
2700	31.559	241.848	216.847	67.501	573.713	241.266	−4.668
2800	31.843	243.000	217.761	70.671	572.699	228.972	−4.272
2900	32.132	244.123	218.650	73.870	571.714	216.713	−3.903
3000	32.428	245.217	219.518	77.098	570.758	204.488	−3.560
3100	32.729	246.285	220.364	80.356	569.832	192.295	−3.240
3200	33.037	247.329	221.190	83.644	568.936	180.130	−2.940
3300	33.350	248.351	221.998	86.963	568.071	167.994	−2.659
3400	33.666	249.351	222.788	90.314	567.238	155.883	−2.395
3500	33.985	250.331	223.561	93.697	566.437	143.796	−2.146
3600	34.306	251.293	224.318	97.111	565.667	131.731	−1.911
3700	34.626	252.238	225.060	100.558	564.930	119.688	−1.690
3800	34.944	253.165	225.787	104.036	564.224	107.664	−1.480
3900	35.258	254.077	226.501	107.547	563.551	95.658	−1.281
4000	35.568	254.974	227.202	111.088	562.908	83.669	−1.093
4100	35.871	255.856	227.890	114.660	562.296	71.695	−.913
4200	36.167	256.724	228.566	118.262	561.714	59.737	−.743
4300	36.455	257.578	229.231	121.893	561.161	47.791	−.581
4400	36.733	258.419	229.885	125.552	560.636	35.859	−.426
4500	37.001	259.248	230.528	129.239	560.139	23.938	−.278
4600	37.258	260.064	231.161	132.952	559.668	12.027	−.137
4700	37.488	260.867	231.785	136.685	559.217	.127	−.001
4800	37.717	261.658	232.399	140.446	0.000	.000	.000
4900	37.934	262.438	233.004	144.228	0.000	.000	.000
5000	38.137	263.207	233.600	148.032	0.000	.000	.000
5100	38.327	263.964	234.188	151.855	0.000	.000	.000
5200	38.503	264.710	234.768	155.697	0.000	.000	.000
5300	38.666	265.445	235.340	159.556	0.000	.000	
5400	38.816	266.169	235.904	163.430	0.000	.000	.000
5500	38.952	266.882	236.461	167.318	0.000	.000	.000
5600	39.074	267.585	237.010	171.220	0.000	.000	.000
5700	39.184	268.278	237.553	175.133	0.000	.000	.000
5800	39.281	268.960	238.089	179.056	0.000	.000	.000
5900	39.366	269.633	238.618	182.989	0.000	.000	.000
6000	39.438	270.295	239.140	186.929	0.000	.000	.000

PREVIOUS: June 1979 (1 atm) CURRENT: June 1979 (1 bar)

IP(Zr^+, g) = 105900 ± 100 cm^{-1}
$S°$(298..15 K) = 183.639 ± 0.04 $J·K^{-1}·mol^{-1}$

$\Delta_f H°$(0 K) = 1268.4 ± 25.1 $kJ·mol^{-1}$
$\Delta_f H°$(298.15 K) = [1276.563] $kJ·mol^{-1}$

Electronic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{3/2}$	0.00	4
$^4F_{5/2}$	314.67	6
$^4F_{7/2}$	763.44	8
$^4F_{9/2}$	1322.91	10
–	–	–
–	–	–
–	–	–
$^2H_{11/12}$	91737.40	12
IP	105900	

Enthalpy of Formation

$\Delta_f H°(Zr^+, g, 0 K)$ is calculated from $\Delta_f H°(Zr, g, 0 K)$[1] using the spectroscopic value of IP(Zr) = 55145 ± 5 cm^{-1} (659.68 ± 0.06 $kJ·mol^{-1}$) from Moore.[2] The ionization limit is converted from cm^{-1} to $kJ·mol^{-1}$ using the factor, 1 cm^{-1} = 0.01196266 kJ cm^{-1}, which is derived from the 1973 CODATA fundamental constants.[3] Rosenstock *et al.*[4] and Levin and Lias[5] have summarized additional ionization and appearance potential data.

$\Delta_f H°(Zr^+, g, 298.15 K)$ is calculated from $\Delta_f H°(Zr, g, 0 K)$ by using IP(Zr) with JANAF[1] enthalpies, $H°(0 K)–H°(298.15 K)$, for Zr(g), Zr^+(g), and e^-(g). $\Delta_f H°(Zr \rightarrow Zr^+ + e^-, 298.15 K)$ differs from a room temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[4] $\Delta_f H°$(298.15 K) should be changed by −6.197 $kJ·mol^{-1}$ if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The electronic energy levels are given in the compilations by Moore.[2,6] Although we have only listed the ground state, first three excited states, the highest observed excited state, and the ionization limit for Zr^+(g), all levels listed by Moore,[2,6] as well as estimated missing levels for n = 5 and 6, are used in our calculations. The observed levels are too numerous to list completely. Our calculations indicate that for Zr^+(g) the thermochemical functions are independent of the estimated missing levels for n = 5 and 6 (levels estimated and included above 90000 cm^{-1}) and the cut–off procedure up to 6000 K. The Gibbs energy function is essentially unaffected (<0.001 $cal·mol^{-1}·K^{-1}$) up to 12000 K. The reported uncertainty in $S°$(298.15 K) is due to uncertainties in the relative atomic mass and the fundamental constants. Extension of these calculations above 6000 K may require consideration of the more exact estimation of excited states for n = 5 and 6, the consideration of states for n>6, and the utilization of proper fill and cut–off procedures.[7]

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Enthalpy Reference Temperature = T_r = 298.15 K				Standard State Pressure = $p°$ = 0.1 MPa			
	$J·K^{-1}mol^{-1}$			$kJ·mol^{-1}$			
T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
0	.000	.000	INFINITE	−7.472	1268.391		
100	23.495	154.699	208.027	−5.333			
150	26.127	164.776	192.014	−4.086			
200	27.404	172.491	186.207	−2.743			
250	28.010	178.679	184.104	−1.356			
298.15	28.282	183.639	183.639	.000	1276.563	1227.145	−214.991
300	28.288	183.814	183.640	.052	1276.607	1226.838	−213.612
350	28.358	188.182	183.985	1.469	1277.792	1218.450	−181.844
400	28.280	191.965	184.751	2.886	1278.959	1209.892	−157.996
450	28.112	195.287	185.741	4.296	1280.104	1201.190	−139.430
500	27.905	198.238	186.846	5.696	1281.224	1192.361	−124.565
600	27.513	203.290	189.179	8.466	1283.381	1174.384	−102.239
700	27.268	207.510	191.505	11.204	1285.431	1156.054	−86.266
800	27.188	211.145	193.738	13.925	1287.381	1137.438	−74.267
900	27.232	214.348	195.853	16.646	1289.233	1118.583	−64.921
1000	27.351	217.223	197.849	19.374	1290.984	1099.527	−57.433
1100	27.502	219.837	199.731	22.117	1292.634	1080.300	−51.299
1200	27.658	222.237	201.508	24.875	1290.469	1061.150	−46.191
1300	27.803	224.456	203.189	27.648	1292.452	1041.959	−41.866
1400	27.928	226.522	204.782	30.435	1294.407	1022.617	−38.154
1500	28.031	228.452	206.297	33.233	1296.320	1003.137	−34.932
1600	28.110	230.264	207.739	36.040	1298.179	983.530	−32.109
1700	28.169	231.970	209.114	38.854	1299.971	963.809	−29.614
1800	28.208	233.581	210.429	41.673	1301.683	943.985	−27.394
1900	28.233	235.107	211.688	44.495	1303.303	924.069	−25.404
2000	28.244	236.555	212.896	47.319	1304.818	904.069	−23.612
2100	28.245	237.933	214.055	50.144	1306.218	883.997	−21.988
2200	28.238	239.247	215.171	52.968	1286.168	864.606	−20.528
2300	28.225	240.502	216.245	55.791	1286.886	845.428	−19.200
2400	28.208	241.703	217.281	58.613	1287.602	826.219	−17.982
2500	28.187	242.854	218.281	61.433	1288.316	806.980	−16.861
2600	28.164	243.959	219.248	64.250	1289.028	787.713	−15.825
2700	28.139	245.022	220.183	67.066	1289.738	768.418	−14.866
2800	28.114	246.045	221.088	69.878	1290.445	749.097	−13.975
2900	28.087	247.031	221.966	72.688	1291.150	729.750	−13.144
3000	28.060	247.983	222.817	75.496	1291.852	710.380	−12.369
3100	28.033	248.902	223.644	78.300	1292.551	690.986	−11.643
3200	28.006	249.792	224.447	81.102	1293.248	671.569	−10.962
3300	27.979	250.653	225.228	83.902	1293.942	652.131	−10.322
3400	27.951	251.488	225.989	86.698	1294.633	632.672	−9.720
3500	27.924	252.298	226.729	89.492	1295.321	613.192	−9.151
3600	27.897	253.084	227.450	92.283	1296.007	593.693	−8.614
3700	27.869	253.848	228.153	95.071	1296.690	574.175	−8.106
3800	27.842	254.591	228.839	97.857	1297.370	554.639	−7.624
3900	27.816	255.314	229.509	100.640	1298.048	535.084	−7.167
4000	27.789	256.018	230.163	103.420	1298.722	515.513	−6.732
4100	27.763	256.704	230.802	106.197	1299.395	495.924	−6.318
4200	27.737	257.372	231.426	108.972	1300.064	476.319	−5.924
4300	27.712	258.025	232.038	111.745	1300.731	456.698	−5.548
4400	27.687	258.661	232.635	114.515	1301.396	437.062	−5.189
4500	27.664	259.283	233.221	117.282	1302.058	417.410	−4.845
4600	27.641	259.891	233.794	120.048	1302.718	397.744	−4.517
4700	27.619	260.485	234.356	122.811	1303.375	378.064	−4.202
4800	27.599	261.067	234.906	125.571	743.094	369.987	−4.026
4900	27.579	261.636	235.446	128.330	744.096	362.203	−3.861
5000	27.561	262.193	235.975	131.087	745.079	354.399	−3.702
5100	27.545	262.738	236.494	133.843	746.044	346.576	−3.550
5200	27.530	263.273	237.004	136.596	746.994	338.734	−3.403
5300	27.517	263.797	237.505	139.349	747.929	330.874	−3.261
5400	27.505	264.311	237.997	142.100	748.852	322.997	−3.124
5500	27.495	264.816	238.480	144.850	749.763	315.102	−2.993
5600	27.488	265.311	238.954	147.599	750.664	307.191	−2.865
5700	27.481	265.798	239.421	150.347	751.557	299.264	−2.742
5800	27.477	266.276	239.880	153.095	752.442	291.321	−2.624
5900	27.475	266.745	240.331	155.843	753.322	283.363	−2.509

PREVIOUS: June 1979 (1 atm) CURRENT: March 1984 (1 bar)

EA(Zr, g) = 0.426 ± 0.014 eV
$S°$(298.15 K) = 185.762 ± 0.001 J·K^{-1}·mol^{-1}

$\Delta_f H°$(0 K) = 568.92 ± 1.5 kJ·mol^{-1}
$\Delta_f H°$(298.15 K) = [564.979] kJ·mol^{-1}

Electonic Levels and Quantum Weights		
State	ϵ_i, cm^{-1}	g_i
$^4F_{3/2}$	0	4
$^4F_{5/2}$	250	6
$^4F_{7/2}$	580	8
$^4F_{9/2}$	950	10

Enthalpy of Formation

$\Delta_f H°(Zr^-, g, 0 K)$ is calculated from $\Delta_f H°(Zr, g, 0 K)$[1] using the adopted electron affinity of EA(Zr) = 0.426 ± 0.014 eV (41.102 ± 1.351 kJ·mol^{-1}). This value, recommended by Hotop and Lineberger,[2] is based on a laser photodetachment electron spectrometry study.[3] Additional information on Zr^-(g) may be obtained in the critical discussions of Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6]

$\Delta_f H°(Zr^-, g, 298.15 K)$ is obtained from $\Delta_f H°(Zr, g, 0 K)$ by using EA(Zr) with JANAF[1] enthalpies, $H°(0 K)-H°(298.15 K)$, for Zr^-(g), Zr(g), and e^-(ref). $\Delta_r H°(Zr^- \rightarrow Zr + e^-, 298.15 K)$ differs from a room–temperature threshold energy due to inclusion of these enthalpies and to threshold effects discussed by Rosenstock *et al.*[5] $\Delta_f H°(298.15 K)$ should be changed by +6.197 kJ·mol^{-1} if it is to be used in the ion convention that excludes the enthalpy of the electron.

Heat Capacity and Entropy

The ground state electronic configuration for Zr^-(g) is given by Hotop and Lineberger,[2,4] Rosenstock *et al.*[5] and Massey.[6] The fine structure separation has been calculated by an isoelectronic extrapolation of ratios of fine struture separations and is that recommended by Hotop and Lineberger.[2]

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Enthalpy Reference Temperature = T_r = 298.15 K Standard State Pressure = $p°$ = 0.1 MPa

T/K	$C_p°$	$S°$	$-[G°-H°(T_r)]/T$	$H°-H°(T_r)$	$\Delta_f H°$	$\Delta_f G°$	log K_f
	J·K^{-1}·mol^{-1}			kJ·mol^{-1}			
0	0.	0.	INFINITE	−7.749	568.925		
100	25.123	155.513	211.008	−5.550			
200	28.509	174.284	188.395	−2.822			
250	28.830	180.691	186.236	−1.386			
298.15	28.693	185.762	185.762	0.	564.979	527.438	−92.405
300	28.681	185.940	185.763	0.053	564.947	527.205	−91.795
350	28.231	190.330	186.110	1.477	564.061	520.984	−77.753
400	27.627	194.061	186.877	2.874	563.130	514.894	−67.238
450	26.976	197.278	187.858	4.239	562.151	508.922	−59.074
500	26.339	200.087	188.944	5.571	561.124	503.063	−52.555
600	25.216	204.786	191.207	8.147	558.930	491.653	−42.802
700	24.332	208.604	193.428	10.623	556.561	480.626	−35.865
800	23.656	211.807	195.531	13.021	554.030	469.948	−30.684
900	23.139	214.562	197.496	15.359	551.343	459.598	−26.674
1000	22.742	216.978	199.326	17.652	548.501	449.555	−23.482
1100	22.433	219.131	201.030	19.911	545.509	439.804	−20.885
1200	22.188	221.072	202.621	22.141	538.660	430.554	−18.742
1300	21.993	222.840	204.109	24.350	535.921	421.655	−16.942
1400	21.834	224.464	205.506	26.541	533.123	412.970	−15.408
1500	21.704	225.965	206.820	28.718	530.258	404.487	−14.086
1600	21.597	227.363	208.061	30.883	527.317	396.198	−12.935
1700	21.507	228.669	209.235	33.038	524.293	388.095	−11.925
1800	21.430	229.896	210.349	35.184	521.175	380.173	−11.032
1900	21.365	231.053	211.409	37.324	517.956	372.427	−10.239
2000	21.310	232.148	212.419	39.458	514.624	364.853	−9.529
2100	21.262	233.186	213.383	41.586	511.171	357.449	−8.891
2200	21.220	234.174	214.306	43.710	486.263	350.958	−8.333
2300	21.183	235.117	215.190	45.830	482.120	344.901	−7.833
2400	21.151	236.017	216.039	47.947	477.974	339.024	−7.379
2500	21.122	236.880	216.856	50.061	473.825	333.319	−6.964
2600	21.097	237.708	217.642	52.172	469.674	327.781	−6.585
2700	21.075	238.504	218.400	54.280	465.520	322.403	−6.237
2800	21.054	239.270	219.132	56.387	461.363	317.178	−5.917
2900	21.036	240.009	219.839	58.491	457.205	312.102	−5.622
3000	21.020	240.721	220.523	60.594	453.046	307.169	−5.348
3100	21.005	241.410	221.186	62.695	448.884	302.375	−5.095
3200	20.991	242.077	221.829	64.795	444.721	297.716	−4.860
3300	20.979	242.723	222.452	66.894	440.557	293.186	−4.641
3400	20.968	243.349	223.058	68.991	436.392	288.783	−4.437
3500	20.958	243.957	223.646	71.087	432.226	284.502	−4.246
3600	20.948	244.547	224.218	73.183	428.058	280.340	−4.068
3700	20.940	245.121	224.776	75.277	423.890	276.294	−3.901
3800	20.932	245.679	225.318	77.370	419.721	272.361	−3.744
3900	20.924	246.223	225.847	79.463	415.551	268.537	−3.597
4000	20.917	246.752	226.364	81.555	411.381	264.821	−3.458
4100	20.911	247.269	226.867	83.647	407.210	261.209	−3.328
4200	20.905	247.773	227.359	85.738	403.038	257.698	−3.205
4300	20.900	248.264	227.839	87.828	398.865	254.287	−3.089
4400	20.894	248.745	228.309	89.917	394.693	250.973	−2.979
4500	20.890	249.214	228.768	92.007	390.519	247.753	−2.876
4600	20.885	249.673	229.218	94.095	386.345	244.627	−2.778
4700	20.881	250.123	229.658	96.184	382.171	241.591	−2.685
4800	20.877	250.562	230.089	98.272	−182.940	250.261	−2.723
4900	20.873	250.993	230.511	100.359	−186.767	259.326	−2.764
5000	20.870	251.414	230.925	102.446	−190.611	268.469	−2.805
5100	20.867	251.827	231.331	104.533	−194.471	277.689	−2.844
5200	20.864	252.233	231.729	106.620	−198.346	286.985	−2.883
5300	20.861	252.630	232.119	108.706	−202.234	296.355	−2.921
5400	20.858	253.020	232.503	110.792	−206.134	305.799	−2.958
5500	20.855	253.403	232.879	112.877	−210.045	315.315	−2.995
5600	20.853	253.778	233.249	114.963	−213.964	324.903	−3.031
5700	20.850	254.147	233.613	117.048	−217.892	334.560	−3.066
5800	20.848	254.510	233.970	119.133	−221.827	344.286	−3.101
5900	20.846	254.866	234.321	121.218	−225.767	354.081	−3.135
6000	20.844	255.217	234.666	123.302	−229.711	363.942	−3.168

PREVIOUS: June 1979 (1 atm) CURRENT: March 1984 (1 bar)

Continued from page 1945

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